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**Electro-Photoredox Catalysis under Red Light: From Challenging C-X Bond
Cleavage to Controlled Radical Polymerizations under Mild Conditions**

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Glossary of acronyms

4CzIPN	2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile
4DPAIPN	2,4,5,6-Tetrakis(diphenylamino)isophthalonitrile
ATRP	Atom Transfer Radical Polymerization
BET	Back Electron Transfer
BzMA	Benzyl methacrilate
CDET	Concerted DET
CDTPA	4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid
CE	Counter Electrode
CRP	Controlled Radical Polymerization
CTA	Chain Transfer Agent
CV	Cyclic Voltammetry
$\bar{D}$	Dispersity
DCA	9,10-dicyanoanthracene
DET	Dissociative Electron Transfer
DMF	<i>N,N</i> -Dimethylformamide
DMSO	Dimethylsulfoxide
DPA	9,10-diphenylanthracene
DTRP	Degenerative Chain-Transfer Radical Polymerization
eATRP	Electrochemically-mediated ATRP
ePC	Electrophotocatalysis
ePRC	Electrochemically mediated photoredox catalysis
eRAFT	Electrochemically-mediated RAFT
ESA	Excited State Absorption
ET	Electron Transfer
FRP	Free Radical Polymerization
GC	Glassy Carbon

GPC	Gel Permeation Chromatography
GSB	Ground State Bleaching
HAT	Hydrogen Atom Abstraction
HOMO	Highest Occupied Molecular Orbital
IC	Internal Conversion
iPEC	Interfacial Photoelectrochemistry
ISC	Intersystem Crossing
LAM	Less-Activated Monomer
LRP	Living Radical Polymerization
LUMO	Lowest Unoccupied Molecular Orbital
MAM	More-Activated Monomer
MeCN	Acetonitrile
MeOH	Methanol
Mes-Acr	3,6-di-tert-butyl-9-mesityl-10-phenylacridin-10-ium
MMA	Methyl Methacrylate
M_n	Number Average Molecular Weight
M_w	Mass Average Molecular Weight
NDI	Naphthalene Diimide
NHE	Normal Hydrogen Electrode
NIR	Near-infrared
NMI	Naphthalene Monoimide
NMP	Nitroxide Mediated Polymerization
NMR	Nuclear Magnetic Resonance
OSET	Outer Sphere Electron Transfer
PC	Photocatalyst
PDI	N,N'-Bis(2,6-diisopropylphenyl)-3,4,9,10-perylenetetracarboxylic Diimide
PET	Photoinduced Electron Transfer
PET-eRAFT	Photoinduced Electron Transfer eRAFT
PET-RAFT	Photoinduced Electron Transfer RAFT

PI-RAFT	Photoiniferter RAFT
PMI	Perylene Monoimide
P(BzMA)	Poly(benzyl methacrylate)
PMMA	Poly(methyl methacrylate)
PRC	Photoredox Catalysis
PRE	Persistent Radical Effect
RAFT	Reversible Addition-Fragmentation Chain Transfer
RDE	Rotating Disk Electrode
RDRP	Reversible-Deactivation Radical Polymerization
RE	Reference Electrode
RVC	Reticulated Vitreous Carbon
RX	Organic halide
SCE	Saturated Calomel Electrode
SDET	Stepwise DET
SE	Stimulated Emission
SET	Single Electron Transfer
SOMO	Singly Occupied Molecular Orbital
SRMP	Stable Radical-Mediated Polymerization
TADF	Thermally-Activated Delayed Fluorescence
TAS	Transient Absorption Spectroscopy
TBAI	Tetrabutylammonium Iodide
TEATFB	Tetraethylammonium Tetrafluoroborate
THF	Tetrahydrofuran
UV-Vis	Ultraviolet-Visible
WE	Working electrode

1. Introduction

The challenge of running chemical transformations is inherently linked to the requirement for energy. Among the various forms of energy, heat has always been the most straightforward solution for overcoming the kinetic barriers associated with bonds breaking and formation. Most of the industrial processes developed throughout the decades, including the petrochemical-based productions established after WWII, relied on massive amounts of thermal energy. Owing to their economic competitiveness, these conventional synthetic routes are still exploited nowadays to produce almost all commodity chemicals, which represent the building blocks for countless consumer goods. In the last few years, however, the rising cost of fossil energy – driven by geopolitical tensions – along with the growing interest in public opinion for the transition to more sustainable energy sources, is starting to compromise the economic and social feasibility of energy-demanding industrial processes. Moreover, the harsh reaction conditions associated with high temperatures impose significant constraints, particularly regarding the lack of selectivity, thus pushing the search toward alternative energy forms, capable of providing fine control over reaction products.

Electrochemistry represented the first alternative approach to thermal activation for chemical synthesis. Since the late nineteenth century, the development of electrochemical industrial processes – such as chlor-alkali process – demonstrated that electrons could drive large-scale chemical reactions with high efficiency¹. In more recent years, this technique has progressively evolved into a powerful tool for conducting also redox transformations for fine organic synthesis, mainly thanks to its selectivity and the tunability of its driving force.

Parallel to this, the study of the ability of natural pigments – such as chlorophyll – in solar energy harvesting, gave the inspiration for the birth of photochemistry, which relies on photons to promote molecules to high-energy excited-states, opening the way for reaction pathways inaccessible by heat. Already in the early XX century, Giacomo Ciamician gave a lecture in which he envisioned a future where solar energy would power industrial processes, highlighting the remarkable potential of light for overcoming the kinetic barriers of chemical reactions².

Despite their promising achievements in catalysis, both electrochemistry and photochemistry still face significant hurdles when addressing challenging reactions, mainly because of the limited energy attainable by electrons or photons alone. Therefore, in the last few years, the opportunity to integrate photochemical and electrochemical processes in homogeneous catalysis is emerging as an effective solution for merging the advantages of these two so far distinct branches of chemistry, while

mitigating their individual weaknesses. Within this framework, electrochemically mediated photoredox catalysis (ePRC), which resides at the intersection of traditional electrosynthesis and photoredox catalysis, effectively combines the power of electricity and light in the same catalytic cycle to provide high-energy reaction pathways, as exemplified by the cleavage of strong C-Cl and even C-F bonds to forge new C-C, C-N, or C-P bonds³.

1.1. Electrocatalysis and organic electrosynthesis

The roots of organic electrosynthesis can be dated back to the nineteenth century, particularly in the pioneering works of Michael Faraday on electrolysis laws⁴ and, shortly after, Hermann Kolbe on anodic decarboxylations⁵. For a long time, however, the mainstream practice in organic synthesis has been dominated by chemical redox reagents, primarily due to the technical complexity associated with electron transfer kinetics in large-scale reactors. It was not until 1960s that Monsanto developed the first electrosynthesis industrial process for acrylonitrile hydrodimerization⁶. Nowadays, the research in this field is stimulated by the need for sustainable and energy-efficient synthetic routes, as well as the advancements in analytical technique for mechanistic investigations^{7,8}.

In a typical undivided two-electrode electrosynthetic setup, a cathode and an anode are positioned in a solution containing the organic substrate and a supporting electrolyte. In most cases, only one of the two electrodes – the working electrode (WE) – produces the desired product, while at the other one – the counter electrode (CE) – a nonproductive reaction occurs. In the case of a divided cell, a membrane physically separates the anodic and cathodic compartments, allowing for an improved selectivity and suppression of side-reactions (Figure 1, left). For both cell architectures, applying a proper potential difference between the electrodes with an external power source results in the oxidation or reduction of the substrate. This working modality is usually referred to as *direct electrolysis*, because the substrate gains or loses electrons directly at the electrode, leading to a heterogeneous electron transfer. Conversely, *indirect electrolysis* involves a redox mediator (electrocatalyst), which is a soluble species more readily oxidized or reduced than the substrate itself (Figure 1, right). The mediator acts as the electron transfer shuttle from the heterogeneous electrode surface to the dissolved substrate or vice-versa; therefore, this second scenario is also termed homogeneous electrocatalysis. It is worth noting that indirect electrolysis is generally preferred for organic synthesis, since it offers several advantages over direct one, such as ability to operate at lower overpotentials, the better chemoselectivity and the suppression of side-reactions⁹.

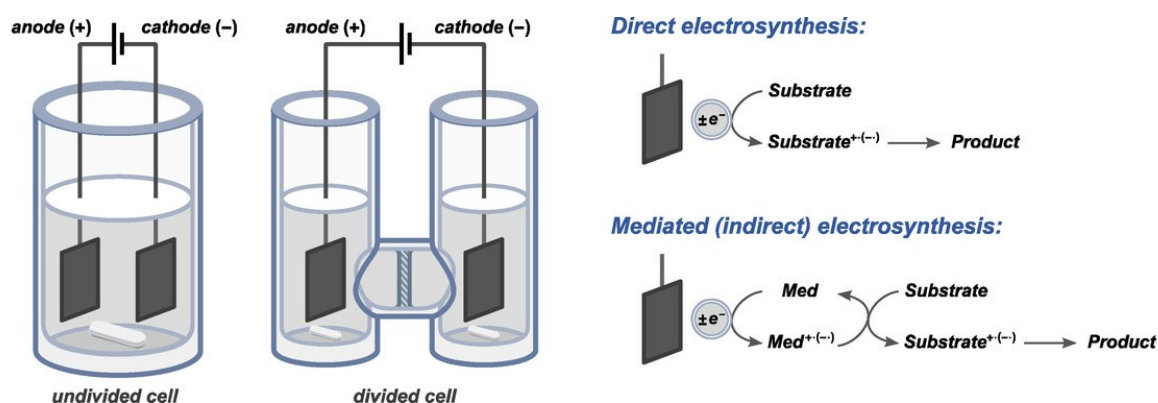


Figure 1. Schematic representation of undivided and divided electrochemical cells (left). General scheme for direct and indirect electrocatalysis (right). Taken from ref. ¹⁰.

In principle, electrocatalysis in the context of organic chemistry offers multiple appealing features when compared to more conventional procedures. To cite the most relevant ones, it enables the use of renewable energy sources and mild operating conditions (i.e., room temperature, atmospheric pressure), it minimizes the reliance on often highly toxic stoichiometric chemical oxidants or reductants, and it allows for the prediction of reaction pathways on the basis of electroanalytical techniques. Finally, electrosynthesis enables the fine-tuning of driving force and reaction rate simply by modulating the external potential and the current density, gaining precise control over reaction progress and selectivity^{6,11}. Nevertheless, this approach still faces significant technical issues, most notably mass transfer constraints and limited redox window imposed by the stability of the solvent-electrolyte system. The inherent complexity of electrode-solution interfaces is also a major drawback of electrochemically driven syntheses, particularly when high potentials are needed. In such conditions, in fact, reaction control is easily lost as a result of unwanted side reactions, which cause massive accumulation of reactive intermediates near the electrode surface, leading to passivation and adsorption phenomena¹².

1.2. Photochemistry and photocatalysis

Light-induced reactions occur on our planet since its formation and are intimately related to the evolution of life, since a sophisticated series of photochemical and photophysical processes – known as photosynthesis – made it possible for simple cells to become autotrophic, providing energy for biological activity and eventually leading to the storage of solar energy into fossil fuels, that still supply our lives today.

The basic mechanism of organic photochemistry lies in the absorption by a molecule of a photon with energy equal to the gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), which results in the promotion of an electron to a higher energy level. A similar electronic reorganization alters the redox properties of the molecule compared to the starting configuration. Upon photoexcitation of a stable, closed-shell organic molecule, an electron is promoted to a singlet excited state. Electronically excited states possess high energy content and therefore must rapidly undergo deactivation. This can occur through vibrational relaxation followed by non-radiative decay, so that the energy of the photon is entirely dissipated as thermal energy transferred to the surrounding medium. Alternatively, radiative deactivation can proceed through fluorescence, with the emission of a photon from the first excited singlet, or phosphorescence, which involves intersystem crossing (ISC) to a lower-energy triplet state and the subsequent emission of the photon¹³. All the photophysical events briefly described above can be summarized in the *Jablonski diagram* (Figure 2), where the electronic and vibrational states are horizontal lines and states of different multiplicity are separated horizontally.

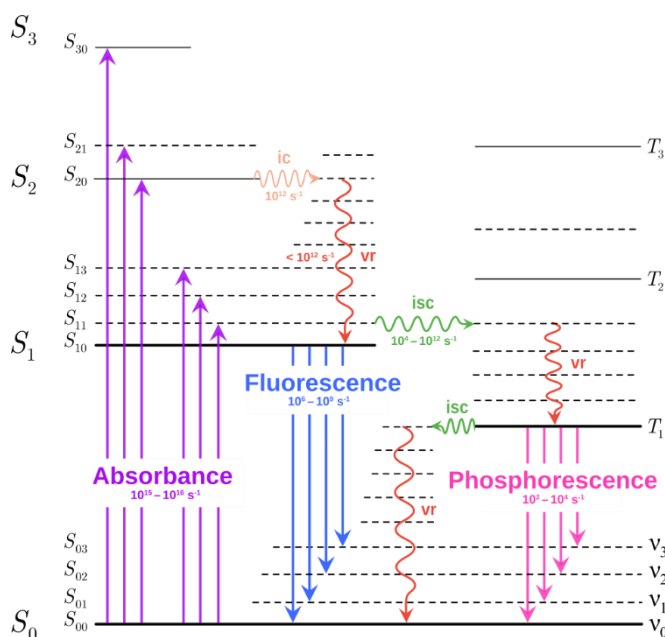


Figure 2. General Jablonski diagram used to depict the ground and excited states of a molecule and the photophysical processes allowed by selection rules.

Excited states can also achieve deactivation by a variety of chemical processes, given that the energy gain from the incident photon makes them much more reactive than the corresponding ground states.

The three main mechanisms by which photocatalysis effectively converts light into chemical energy are (i) energy transfer, (ii) atom transfer – particularly HAT (hydrogen atom abstraction) – and (iii) electron transfer, also referred to as *photoredox catalysis* (PRC)¹⁴. Therefore, photonic energy can be selectively targeted to a specifically designed light absorbing catalyst (photocatalyst, PC), which, upon excitation, promotes reaction pathways toward a target substrate otherwise inaccessible through thermal activation.

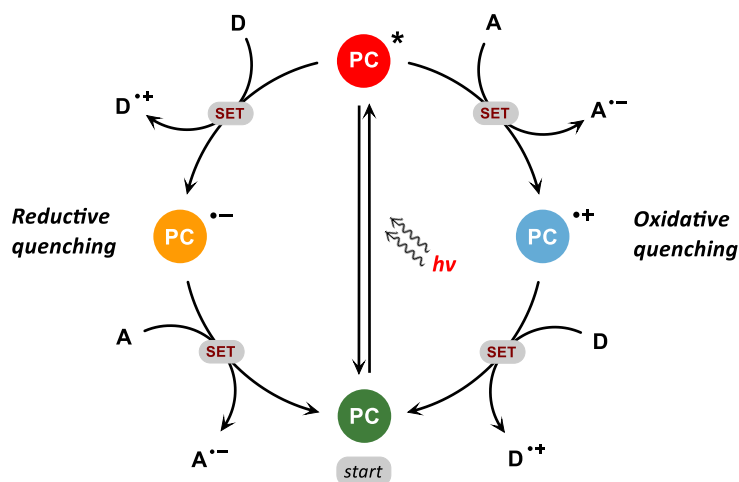
Historically, the field of photoredox catalysis has been dominated by transition metal complexes, primarily those based on Ruthenium (II) and Iridium (II), owing to their excellent stability and long-lived triplet excited states^{15–17}. However, the need for more sustainable and cheaper photocatalyst has spurred the development of organic PCs, where photoinduced electron transfer (PET) is provided by organic chromophores^{18–20}. Despite their quite common photostability issues, organic photocatalysts – ranging from dyes like Eosin Y²¹ or Rhodamin²² to more modern cyanoarenes^{23–25} and acridinium salts^{25–27} – exhibit noteworthy advantages over metal complexes, as they enable to tune photophysical and redox properties through substituent effect, thus attaining very high excited state reduction potentials.

Photoredox catalysis has widely expanded the scope of organic synthesis^{14,19,28–30}, introducing a paradigm shift from the classical two electron polar mechanism – involving the interaction between a nucleophile and an electrophile – to single electron transfer (SET) pathways. This transition enables the activation of molecules that lack the traditional nucleophilic or electrophilic character, thereby granting access to unconventional chemical disconnections³¹.

1.2.1. Single-photon excitation

Since the excited state of the photocatalyst (PC*) possesses both a high energy electron in the LUMO and a hole in the HOMO, it can effectively operate as either a single-electron reductant or oxidant toward a substrate. Photoinduced electron transfer with the substrate can be accessed by PC* participating in either a *reductive quenching* or an *oxidative quenching* process (Scheme 1). In the first case, PC* is firstly reduced by an electron donor (D) to generate the ground-state radical anion (PC^{•-}), which subsequently transfers an electron to an electron acceptor (A) to close the catalytic cycle. Conversely, in the latter case, *PC is firstly oxidized by A to yield a ground-state radical cation (PC^{•+}), which then extracts an electron from the D to regenerate PC (Scheme 1). Several synthetic pathways are possible, where A and D can be any combination of a substrate, an intermediate or a

sacrificial oxidant/reductant. The process is redox neutral if both A and D are used productively, or net oxidative/reductive when a sacrificial redox reagent is needed³¹.

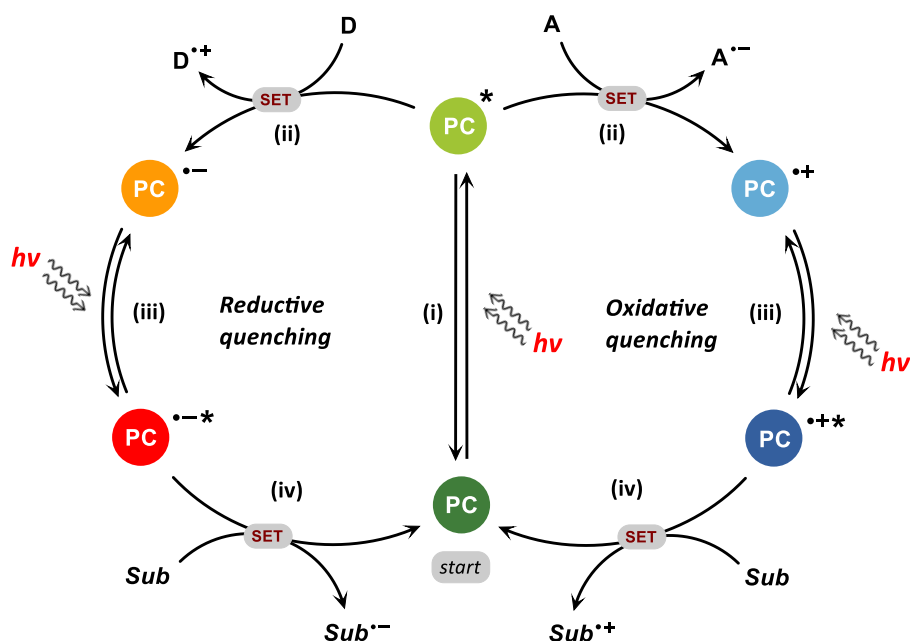


Scheme 1. General PRC mechanism for reductive quenching (left) and for oxidative quenching (right).

The thermodynamic hurdles of such single-photon excitation pathways are governed by two key factors, namely the limited energy attainable through visible light (up to 3 eV) and the energy loss by means of non-radiative decay or ISC on the way from light harvesting to substrate activation via PET (as a rule of thumb, at least 25% of the incident light)³². Hence, the range of chemical transformations that can be carried out in such manifold is rather narrow in terms of reduction potentials.

1.2.2. Two-photon excitation

Since increasing the photon energy (i.e., using UV light) is not an option for many applications due to the risk of photodamage and undesired side reactions, a series of more viable alternatives, which rely on multiple excitation events, has been developed in recent years in order to engage challenging moieties. These strategies take inspiration from Nature's solution to the "3 eV limitation", which consists in the accumulation of the energy of multiple photons in photosynthetic pigments to drive ATP formation. Among the various approaches, *consecutive photoinduced electron transfer* (conPET), firstly disclosed in 2014³³, is probably the most facile and promising one. The general concept of conPET (Scheme 2) involves: (i) a first excitation of PC; (ii) the subsequent SET from or to a sacrificial donor or acceptor; (iii) a second excitation event followed by (iv) substrate activation from the open-shell intermediate in its excited state.



Scheme 2. General conPET mechanism for reductive quenching (left) and for oxidative quenching (right).

Owing to the energy gain provided by the harvesting of two photons per catalytic turnover, $PC^{\bullet-*}$ and $PC^{\bullet+*}$ are usually referred to as “*super-reductant*” and “*super-oxidant*” species respectively, since, as will be discussed later, they display superior redox properties, expanding the thermodynamic window of the accessible reactivity with respect to traditional photoredox catalysis.

Nevertheless, the introduction of a second excitation event introduces further complexity, as the transient nature of $PC^{\bullet-*}$ (or $PC^{\bullet+*}$) may hamper the overall efficiency of the catalytic cycle. Another major kinetic bottleneck is represented by the typically limited lifetime of PC^* (in the range of ns to few μ s), since this intermediate must live long enough to react with the sacrificial electron donor or acceptor before decay to the ground state occurs. For this reason, high excitation density or specifically designed PCs with long-living excited states are mandatory. While remarkable advancements have been made in designing photocatalysts with persistent excited states, they all must reach a compromise between lifetimes and the amount of energy attainable, since longer-lived excited states are usually lower in energy.

It is however worth noting that, despite the constraints linked to the ephemeral nature of the species involved, conPET has been successfully employed in many synthetic applications, mainly exploiting blue or green light irradiation^{20,32,34–36}.

1.3. Photoelectrochemistry

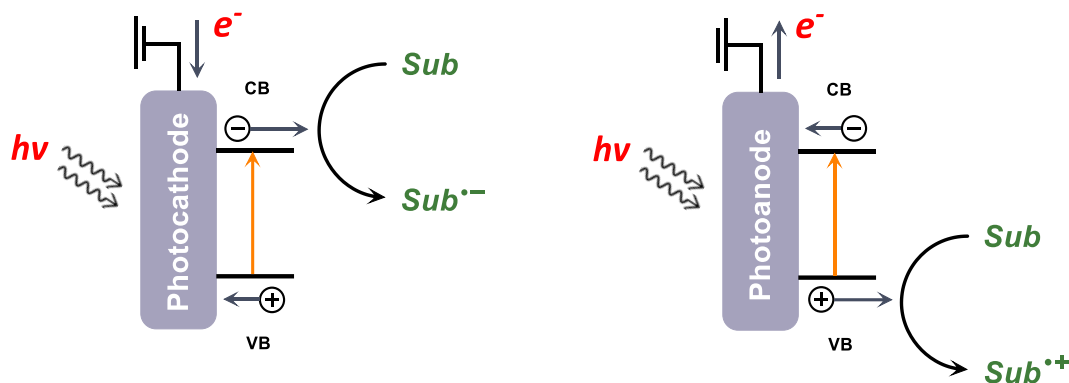
Although photoredox catalysis and electrochemistry share the common feature of open-shell intermediates generation and therefore are often mentioned together or compared alongside one another, they historically developed as distinct disciplines, each governed by unique operational principles and occupying a specific domain within the synthetic landscape. Hence, it was not until recent years that attention has been paid to the concept of merging these two fields of green chemistry for synthetic purposes. The evolution toward hybrid systems involving the synergistic combination of both electrons and photons as energy input in catalysis represents a significant advancement over single-activation manifolds in order to access increasingly challenging chemical transformations.

According to IUPAC, all the techniques which combine photochemical and electrochemical methods for the study of redox chemistry are encompassed under the general term *photoelectrochemistry*³⁷. Thus, a generic classification into two main classes is useful to avoid terminology ambiguity³⁸:

- 1) *Photoelectrocatalysis* (PEC), also known as *interfacial photoelectrochemistry* (iPEC);
- 2) *Electrophotocatalysis* (ePC).

Traditional photoelectrocatalysis typically refers to heterogeneous systems involving photo-active electrodes – most commonly semiconductors – extensively studied since the 1970s for solar-to-fuel applications (i.e., water splitting and CO₂ reduction)^{39,40}, and, lately, also for organic synthesis⁴¹. In this manifold, the semiconductor electrode itself, upon light irradiation, absorbs photons with energy corresponding to or larger than its bandgap. This triggers the promotion of an electron from the valence band to the conduction band, leaving a hole in the valence band. Electrons and holes, which are the required species to perform respectively substrate reduction and oxidation, must remain separated long enough to migrate toward the electrode-solution interface. Therefore, to suppress recombination of charge carrier pairs, an external bias (i.e., a constant potential) is applied. For net oxidative reactions, a n-type semiconductor (photoanode) is used, while net reductive reactions involve a p-type semiconductor (photocathode).

Analogously to electrocatalytic processes, iPEC processes can be distinguished into direct ones, if the reaction of interest occurs on the photoelectrode surface, and indirect ones, when a mediator promotes a homogeneous electron transfer and is continuously regenerated at the photoelectrode. The direct iPEC mechanism is summarized in Scheme 3.



Scheme 3. Schematic representation of reductive (left) and oxidative (right) direct iPEC.

By contrast, electrophotocatalysis operates in a homogeneous environment, with a molecular photocatalyst dissolved in solution. Here, the photocatalyst itself is the light-harvesting species, while the electrode only acts as the external reservoir of electrons or holes, to drive reduction or oxidation of the photocatalyst. This methodology decouples the external potential bias from the light absorption event, allowing for superior operational versatility and higher redox potentials over iPEC, where the same material covers both functions. Moreover, most semiconductors exhibit low ability to harvest visible photons due to their wide bandgaps, while being much more effective under UV or near-UV irradiation⁴¹. Molecular photocatalysts, instead, can work also with the low energy part of the visible spectrum, since their photophysical properties can be fine-tuned through rational molecular engineering. Nevertheless, ePC faces inherent limitations regarding photodegradation and catalyst separation, in contrast to iPEC, which usually provides a more robust, albeit rigid, setup.

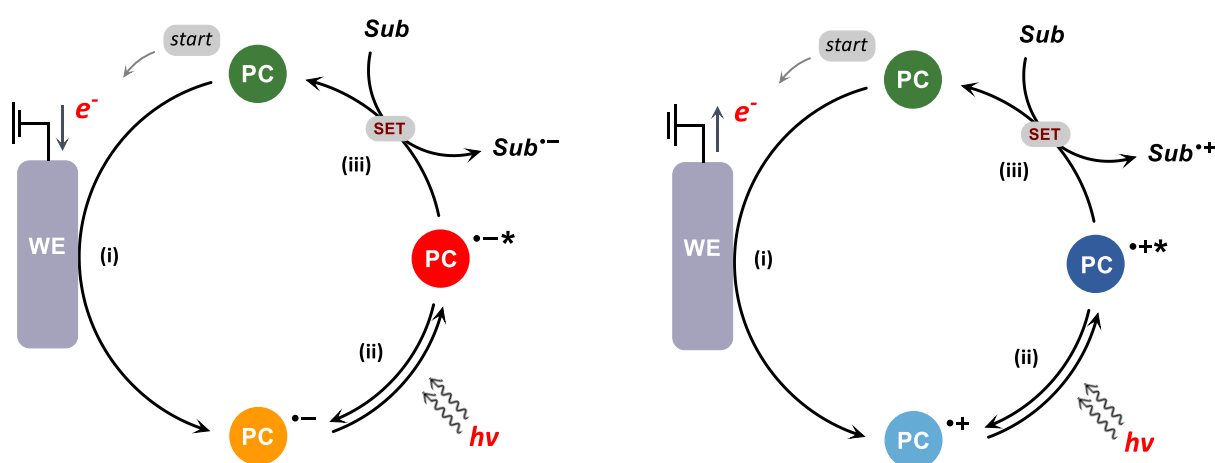
Electrophotocatalysis admits a broad array of mechanistic and operational possibilities, but it is usually useful to distinguish between two main subcategories⁴². In the first one – known as *electrochemical recycling photoredox catalysis* – the excited state photocatalyst (PC*) – which is both a better oxidant and reductant than ground state PC – provides SET with the substrate, while the electrochemical potential simply allows to regenerate the neutral form of PC. Although this strategy is relatively inefficient due to short PC* lifetimes and the limited accessible redox potentials, it avoids the use of the stoichiometric sacrificial redox reagents typically required in conventional photoredox catalysis. These sacrificial reagents can promote undesired side reactions, thereby decreasing selectivity toward the target products and increasing the complexity of the reaction system³⁸.

An alternative approach to electrophotocatalysis consists in the use of an electrochemical potential to convert a nonadsorbing precursor into a reduced (or oxidised) open-shell photocatalyst, which can then promote SET to or from a substrate. In such manifold, very high excited-state redox potentials can be reached compared to the previously mentioned approach, while still avoiding sacrificial redox reagents. This strategy – named *electrochemically mediated photoredox catalysis* (ePRC) and often abbreviated to *electro-photoredox catalysis* – is the main focus of this thesis and will be detailed in the following section.

1.3.1. Electrochemically mediated photoredox catalysis

With the exception of few seminal works in the 1980s^{43,44}, ePRC has been firstly reported in 2019^{45–47}. Since then, this research area has experienced a flourishing interest, spurred by the opportunity to accomplish demanding reactions for organic synthesis^{12,42,48–52}.

The general mechanism of ePRC requires (i) the electrochemical activation of a pre-catalyst (PC), to access the corresponding radical anion ($PC^{\bullet-}$) or cation ($PC^{\bullet+}$), followed by (ii) excitation of this open shell intermediate through an incident photon and (iii) single electron transfer with a substrate in the turnover step. It should be noted that this reaction pathway is reminiscent of that of conPET, except for the replacement of a chemical redox event with direct electrochemical reduction/oxidation for the generation of the ground state radical species. Scheme 4 illustrates the generic catalytic cycle for net reductive and oxidative ePRC quenching.



Scheme 4. Schematic representation of reductive (left) and oxidative (right) ePRC quenching.

Analogously to conPET, electrochemically mediated photoredox catalysis takes advantage of the extreme redox potential attained by the active form of the catalyst, which eventually arises from the peculiar photophysical behaviour of radical ions⁵³. Generally speaking, the electronic transition that occurs after photon absorption from open-shell species involves the promotion of an electron from a subfrontier orbital to the SOMO (singly occupied molecular orbital), resulting in SOMO-HOMO level inversion⁵⁴ (Figure 3).

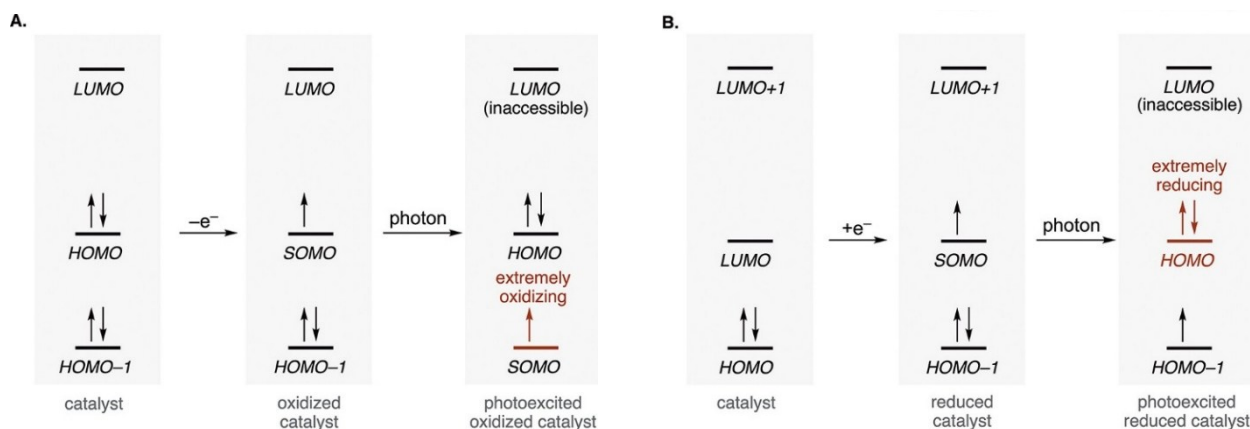


Figure 3. Orbital scheme for “super oxidants” (a) and “super-reductants” (b) species. Taken from ref. ⁵⁰.

In the case of PC^{+*} , the presence of an electron vacancy in a lower-lying, relatively stable orbital results in a greater oxidizing power than if this vacancy were created in the original HOMO. Conversely, for PC^{-*} , the level inversion can be conceptualized as the double population of the original LUMO of the pre-catalyst, so that a high energy electron is favourably transferred to the substrate^{42,50,55}. In contrast, neither traditional photoredox catalysis – relying on SET directly via the frontier SOMO – nor electrocatalysis – based on SET via the Fermi level of the electrode material – can achieve the potent driving force for electron transfer inherent to systems involving SOMO-HOMO level inversion³¹.

While conPET and ePRC methods are analogous in the nature of the active catalyst and in the scope of SET reactions, the latter offers distinct features derived from the decoupling of light harvesting and redox-state management. Firstly, as mentioned above, net oxidative or reductive quenching can be performed without stoichiometric oxidants or reductants; secondly, ground state radical ions are generated more efficiently, since diffusion-controlled electron transfer (ET) involving a transient PC^* intermediate affected by fast unproductive decay is replaced with the more straightforward ET at the

electrode surface. Finally, radical ions absorption spectra are typically red-shifted compared to those of the parent closed-shell pre-catalysts, enabling the use of lower energy photons, up to the red or near-infrared (NIR) regions.

Every ePRC catalytic cycle must satisfy three major requirements in order to work efficiently⁵⁶:

- (i) PC has to undergo a facile SET at the electrode to yield a ground state open-shell intermediate sufficiently stable for light harvesting to be efficient;
- (ii) $PC^{\bullet-}$ (or $PC^{\bullet+}$) must absorb light at a different (typically, longer) wavelength than PC;
- (iii) $PC^{\bullet-*}$ (or $PC^{\bullet+*}$) should be long-lived enough to interact with the substrate.

It should be stressed that, in principle, condition (iii) is met only if excited state lifetimes are in the order of magnitude of nanoseconds, since in slower timescales electron transfer cannot occur effectively for bimolecular diffusion-controlled reactions²⁰. Nevertheless, while early proposals suggested that excited organic radicals directly engage in PET to the substrate molecules, this has been experimentally substantiated only in few cases, as such excited states are typically extremely short-lived⁵⁷. Instead, it is likely that some of these radical catalysts transform into different species, which possess significantly longer lifetimes and are thus expected to be responsible for much of the observed reactivity⁵⁸.

Generally speaking, SET from $PC^{\bullet-*}$ always yields a radical intermediate, which can then undergo different downstream transformations with a wide variety of radical trapping agents, providing numerous opportunities for further functionalization of the cleaved moiety. Reductive ePRC, which is the key mechanism investigated throughout this thesis, has been implemented to date in many synthetic transformations. Of particular interest within this context are carbon-halogen (C-X) bond cleavage of alkyl and aryl halides^{3,59}, which will be treated extensively in Chapter 1.5, reductive functionalization of C-N or C-O bonds⁶⁰⁻⁶² and olefin functionalization^{63,64}. Oxidative ePRC is not further treated here; however, it should be mentioned that many noteworthy results have been achieved in alcohol oxidations, olefin functionalization, N-H arylation, oxidative decarboxylation and C-H bond functionalization^{42,50}.

Moreover, several asymmetric syntheses via both oxidative and reductive ePRC have been recently disclosed⁶⁵⁻⁶⁹. Finally, ePRC is progressively expanding beyond fundamental organic transformations, as in the fields of CO₂ valorisation, bio-hybrid catalysis and living radical polymerizations, where it could offer unique precision control over complex kinetic landscapes.

1.4. Carbon-halogen bond cleavage via ePRC

The single-electron reductive cleavage of carbon-halogen (C-X) bonds of alkyl and aryl halides represents a relevant strategy for generating carbon-centred radicals in modern synthetic chemistry. Indeed, while C-X bonds can be manipulated via different ionic pathways – such as nucleophilic substitution or transition-metal catalysed cross-coupling reactions⁷⁰ – the SET-driven reductive cleavage offers a route for forming new C-C and C-heteroatom bonds that bypass traditional steric and electronic constraints of polar mechanisms, while working under milder environments (i.e., ambient temperature and absence of strong bases or reactive organometallic species). Hence, this approach is particularly relevant for late-stage functionalization of complex molecular architectures, where the C-X bond represents a latent, site-specific handle to execute precise structural modifications on complex molecular scaffolds without disrupting sensitive motifs elsewhere in the molecule⁵².

Furthermore, C-X cleavage via SET unlocks access to a diverse array of chemical modifications, as the radical intermediate can engage in several downstream processes – namely (i) hydrogen atom abstraction, (ii) addition to a heteroatom trapping agent, (iii) addition to an unsaturated partner in a C-C coupling reaction and (iv) reduction to a carbanion. In the latter case, further reactions can occur, such as protonation, elimination of an α -leaving group or electrophilic trapping⁴⁹.

Beyond organic synthesis, this reaction pathway holds significant potential for environmental remediation, particularly regarding the degradation of persistent halogenated organic pollutants, including poly- and perfluoroalkyl substances (PFAS). In this context, the injection of an electron directly into the σ^* antibonding orbital of the C-F bond represents an efficient strategy to cleave these notably stable bonds, typically refractory to conventional degradation methods^{71,72}.

Historically, the cleavage of strong, recalcitrant C-Cl and C-F bonds in unactivated aryl halides under benign conditions remained largely inaccessible: even though strongly reducing, visible light active photoredox catalysts have been developed, the extremely negative reduction potentials of such substrates (up to -3 V vs SCE) places them beyond the energetic limit^{23,73}. Similarly, while traditional electrocatalysis could theoretically achieve such reductions at sufficiently negative cathodic potentials, the harsh operating conditions required preclude its application in complex syntheses. As a consequence, methods that exploit single photonic or electrical inputs for inducing SET to C-X bonds were long limited to aryl bromides and iodides – significantly easier to reduce – or to aryl chlorides and fluorides bearing electron-withdrawing groups.

A pivotal milestone in the transition toward super-reducing photocatalysts occurred in 2014, when the König group pioneered conPET for the activation of aryl chlorides under blue light³³. This breakthrough spurred the development of several ePRC methodologies for analogous transformations, which proved particularly effective in terms of dehalogenation yields^{3,59}.

1.4.1. Typical catalysts for ePRC

Typical organic catalysts for carbon-halogen bond activation via ePRC are usually selected among well-known conPET photocatalysts, and they consist of a highly conjugated aromatic structure, that favours light harvesting in the visible region (Figure 4). In order to be implemented in ePRC protocols, these catalysts must possess PC^{•+} reduction potential more negative than that of the target C-X bond (i.e., $\Delta G_{\text{SET}} < 0$), while providing sufficiently long-lived super-reducing species to permit diffusion-controlled ET. Furthermore, electrochemical and photochemical stability are essential. Good solubility and compatibility with electrochemical media – specifically regarding solvents and supporting electrolytes – are also crucial to maintain a homogeneous reaction environment.

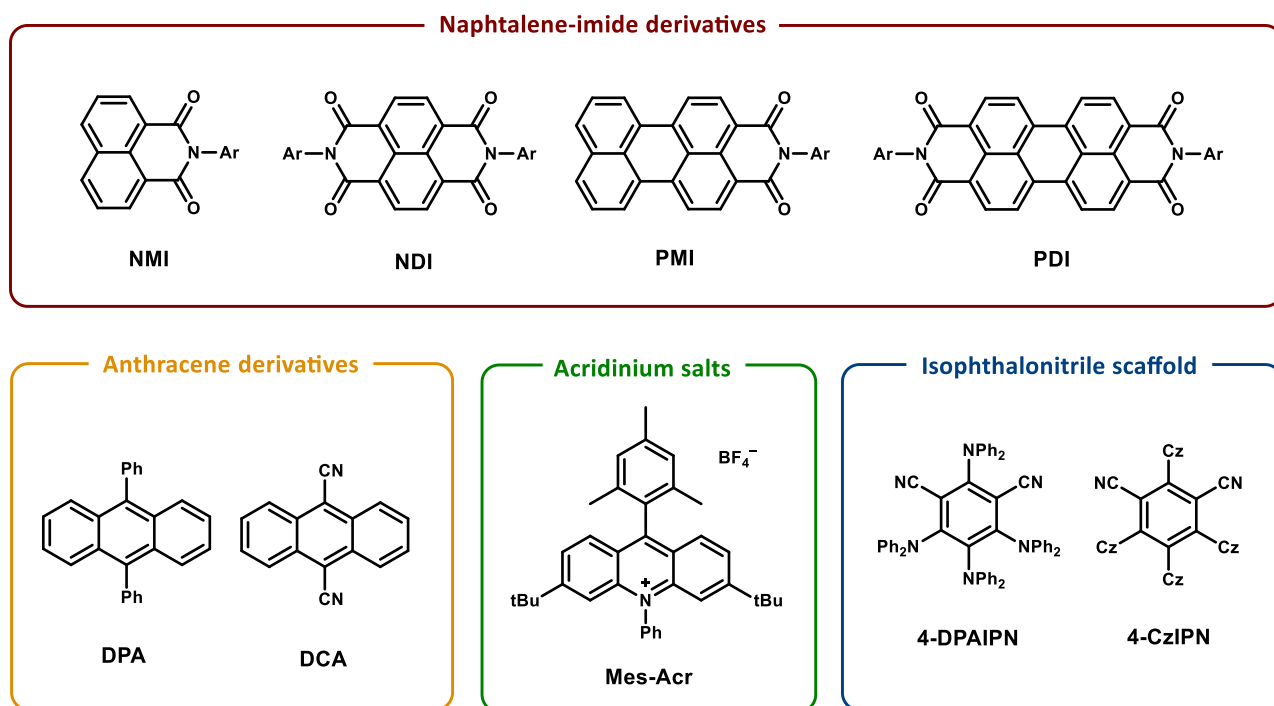


Figure 4. Structures of typical ePRC organic photocatalysts, grouped by common molecular architectures (Ar = 2,6-diisopropylphenyl; Cz = carbazole).

Naphtalene-based analogues such as naphthalene monoimide (NMI) and naphthalene diimide (NDI) are well-known potent reductants in their open-shell excited state, generated under blue-light irradiation⁷⁴ (e.g., $E^{\circ}_{NMI/NMI^{\cdot-}} = -4.05\text{ V vs SCE}$ under 440 nm light)⁷⁵. The extension to the perylene core – such as in perylene monomide (PMI) and perylene diimide (PDI) – significantly enhances light-harvesting capabilities by shifting the radical anion absorption profile toward the visible and infrared regions; however, this also results in lower reducing power, precluding the activation of recalcitrant halides⁷⁶. Nevertheless, PDI exhibit also a stable closed-shell reduced form (PDI^{2-}), whose excited state demonstrates higher reactivity toward dehalogenation⁷⁷.

9,10-diphenylanthracene (DPA), despite its modest reduction potential, represents the first catalyst reported for ePRC-mediated C-X reductive cleavage⁷⁸. Its structural analogue – 9,10-dicyanoanthracene (DCA) – provides significantly higher reduction power ($E^{\circ}_{DCA/DCA^{\cdot-}} = -3.20\text{ V vs SCE}$ under blue light)⁵⁹, but suffers from high oxygen and moisture sensitivity.

3,6-di-tert-butyl-9-mesityl-10-phenylacridin-10-ium (Mes-Acr) radical and its derivatives are also potent reducing agents ($E^{\circ}_{Mes-Acr/Mes-Acr^{\cdot-}} = -3.36\text{ V vs SCE}$ under 390 nm light)⁷⁹. However, their use for C-X activation is currently restricted to conPET methodologies, as the partial spectral overlap between their cationic and radical forms complicates the selective excitation of the latter.

Cyanoarene chromophores derived from isophthalonitrile are ubiquitous photocatalysts in organic synthesis. Among these, 2,4,5,6-Tetrakis(diphenylamino)isophthalonitrile (4DPAIPN) and 2,4,5,6-Tetrakis(9*H*-carbazol-9-yl) isophthalonitrile (4CzIPN) represent the most prominent examples. Such molecules embody the “donor-acceptor” design principle, as the general structure features an electron-withdrawing core (isophthalonitrile), surrounded by electron-donor moieties, such as carbazolyl or diphenylamine units. As a consequence, upon photoexcitation, the charge migrates from the peripherally located HOMO onto the core-centred LUMO, effectively mimicking metal-to-ligand charge transfer (MLCT) of transitions-metal complexes. However, due to the large torsion angles between the π -systems of the core and appended groups, the overlap between HOMO and LUMO is negligible, resulting in a small energy difference between singlet (S_1) and triplet (T_1) excited state. As a consequence, after efficient intersystem crossing and population of T_1 , thermally-induced reverse intersystem crossing occurs, driven by the small S_1 - T_1 energy gap^{80–82}. This photophysical behaviour – known as thermally-activated delayed fluorescence (TADF) – significantly extends PC* lifetime, leading to more efficient conPET catalytic cycles^{23,24}. Nonetheless, cyanoarene chromophores have not yet been implemented in ePRC-driven C-X bond cleavage reactions.

1.4.2. Analytical tools for ePRC systems: Transient absorption spectroscopy (TAS)

The operational efficiency of photocatalyst involved in electrophotocatalytic processes is determined by the dynamics of short-lived doublet excited states generated after light absorption. *Transient absorption spectroscopy* (TAS) – also referred to as ultrafast spectroscopy or flash photolysis – serves as the primary tool for studying these phenomena with ultrafast temporal resolution (up to few femtoseconds), in order to measure photophysical parameters and to elucidate reaction mechanisms.

TAS measurements rely on the pump-probe principle: a high intensity laser pulse (pump) excites the radical anion from the ground state (D_0) to a doublet excited state (D_n); after that, a lower-intensity, broadband light pulse (probe) is focused on the sample at variable time delays (Δt) relative to the pump (Figure 5a). By comparing the absorbance of the probe pulse through the excited sample versus the absorbance of the ground state sample in the full spectral range, the change in optical density induced by the pump pulse (ΔA) can be derived as a function of the wavelength (λ). The resulting TAS spectrum (ΔA vs λ) is characterized by three distinct signals (Figure 5b)^{83–86}:

- (i) *Ground state bleaching* (GSB): a negative signal appears in the spectral region where the ground-state radical anion absorbs light, as a result of the depletion in ground-state population after the pump pulse.
- (ii) *Excited state absorption* (ESA): a positive signal originates from the light absorption by excited species during their transition to even higher excited states. This band provides crucial information on the electronic structure of the excited state itself, while its decrease in intensity as a function of Δt allows to calculate its lifetime.
- (iii) *Stimulated emission* (SE): a negative signal results from the excited state being “forced” to relax to the ground state by the probe pulse, with the emission of a photon.

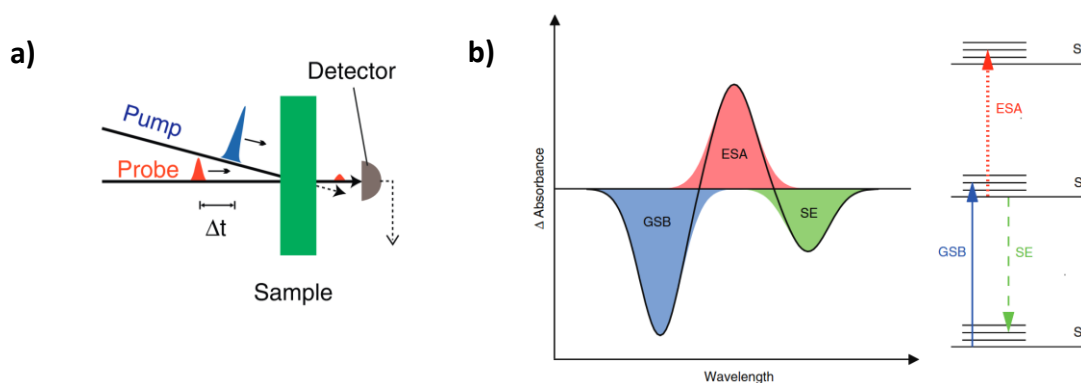


Figure 5. Operating principle of TAS (a) and characteristic signals in the spectrum (b). Taken from ref.⁸³.

1.4.3. Analytical tools for ePRC systems: Cyclic voltammetry (CV)

The widespread adoption of TAS in daily laboratory practice is significantly constrained by its requirement for sophisticated instrumentation, highly specialized personnel and substantial capital investments. Therefore, in recent years, electrochemical techniques were proposed as a complementary analytical tool for studying ePRC systems. In this context, the theoretical framework for quantitative cyclic voltammetry (CV) investigations has been established by Costentin in 2020,⁵⁶ followed by the first experimental investigation of excited state dynamics by CV conducted by our group⁷⁷. In a typical CV experiment under visible light irradiation, a pre-catalyst (PC) diffuses in solution and can be reduced to $PC^{\bullet-}$ at the WE surface. This radical anion is the only species which absorbs light to generate the excited state ($PC^{\bullet-*}$). While diffusing, the excited state can evolve in three ways: i) nonradiative deactivation; ii) reaction with a substrate, regenerating PC; and iii) reoxidation at the electrode surface, also regenerating PC (i.e, back electron transfer, BET).

A peculiar aspect of CV under irradiation is that alters the mass-transport regime during the voltammetric scan. If no incident light is present, and provided that the scan rate is not too slow (i.e., > 20 mV/s), mass transport can be assumed to occur under semi-infinite linear diffusion, meaning that it is not significantly perturbed by natural convection (Figure 6a). The *diffusion layer thickness* (δ) defines the maximum region of solution in which the photocatalytic process can occur, because $PC^{\bullet-}$ concentration is negligible beyond this layer. Under dark conditions, δ continuously increases over time. Upon irradiation, however, this behaviour no longer holds. Light absorption by $PC^{\bullet-}$, followed by non-radiative decay, generates a local increase in temperature near the electrode surface, thus causing convective motions⁸⁷. As a consequence, δ rapidly reaches a stationary value, which is a function of the photon flux passing through the diffusion-reaction layer, and the mass transport regime shifts from semi-infinite to finite diffusion (Figure 6b)^{56,77}.

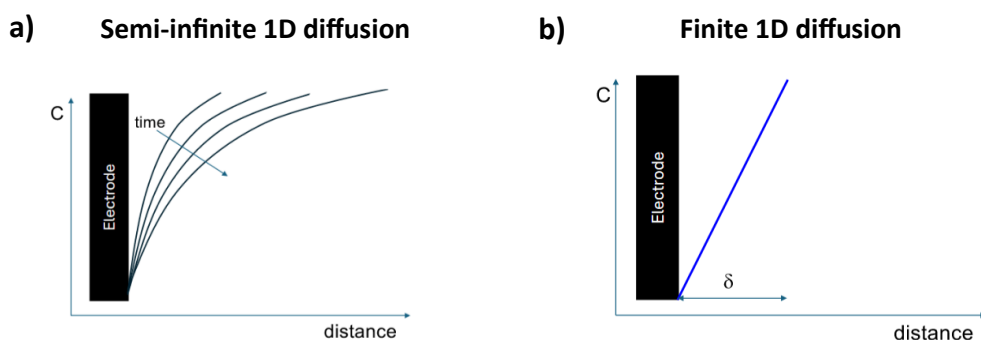


Figure 6. Semi-infinite diffusion condition (a) and finite diffusion condition due to local heating (b).

Overall, the effect of light irradiation alone on the CV trace of PC is an increase in the cathodic current and a decrease in the anodic one. When a substrate that is readily reduced by $\text{PC}^{\bullet-}$ – but not by $\text{PC}^{\bullet-}$ – is added in solution, the CV response shows a dramatic change: the cathodic current increases significantly, with the wave becoming irreversible (i.e., the anodic peak decreases) (Figure 7). This response clearly indicates electrophotocatalysis occurring under irradiation at the electrode surface⁷⁷.

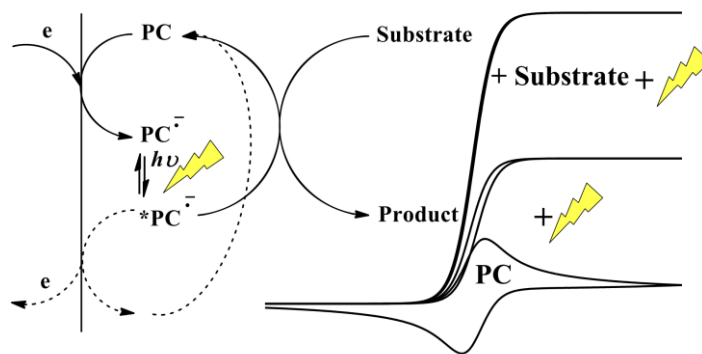


Figure 7. Effect of light and of substrate addition on the CV trace for ePRC systems. Taken from ref. ⁵⁶. (Note that here the applied potential becomes more negative from left to right).

Given that the magnitude of the cathodic current enhancement directly relates to the kinetics of the homogeneous electron transfer step to the substrate, CV can provide fundamental quantitative parameters – such as the SET rate constant – that are complementary or independent from that extracted from TAS. In turn, these kinetic measurements allow to gain fundamental mechanistic insights on the reaction taking place, eventually helping in rationalizing the design of ePRC processes.

1.4.4. Mechanistic debate in excited state quenching dynamics

One of the most fundamental principles in photophysics – known as Kasha’s rule – states that “the emitting electronic level of a given spin multiplicity is the lowest excited level of that multiplicity”⁸⁸. In contrast, higher excited states rapidly undergo internal conversion (IC) to the lowest excited state before photon emission can occur. By analogy, photochemical reactions are generally observed to proceed from the lowest singlet or triplet excited state, which is typically longer-lived. Nevertheless, to account for unexpected high-energy reactivity, some transformations are thought to occur before internal conversion to the lowest excited level is complete (i.e., directly from higher excited states), a behaviour referred to as “Anti-Kasha” (Figure 8)⁸⁹.

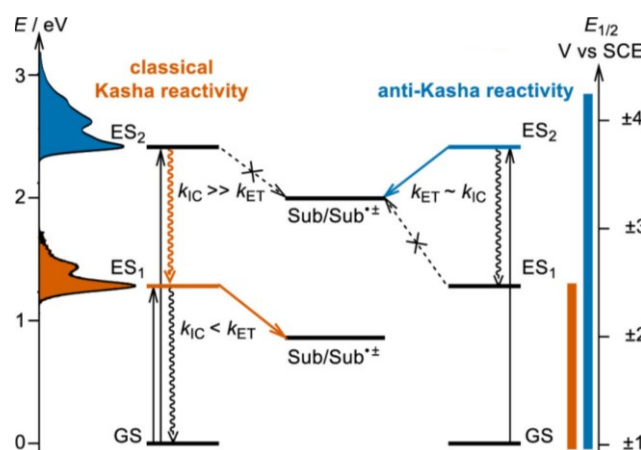
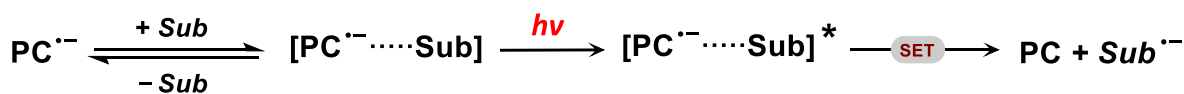


Figure 8. Energy diagram of Kasha reactivity (left) and Anti-Kasha reactivity (right). Adapted from ref. ⁹⁰.

Given that the maximum reaction rate for diffusion-controlled bimolecular reactions in solution is approximately 10^9 s^{-1} at typical substrate concentrations, $\text{PC}^{\bullet-}$ lifetime (τ_0) must extend into the nanosecond regime for ET (rate constant k_{ET}) to effectively compete against IC (rate constant $k_{\text{IC}} = 1/\tau_0$)⁹⁰. However, as previously hinted, recent investigations into doublet excited states higher than D_1 involved in ConPET and ePRC catalytic protocols have uncovered a central kinetic paradox: many of these upper-lying energy levels are extremely short-lived – usually, on the picosecond or femtosecond timescale – yet they manage to drive efficient SET processes with recalcitrant substrates. As a result, Anti-Kasha bimolecular quenching cannot be invoked to justify the observed super-reducing properties. Eventually, it appears clear that the level of complexity of ePRC and conPET systems transcends the traditional photocatalytic framework, requiring further understanding of the fundamental photophysical principles underlying SET from high-energy, elusive species^{58,91,92}.

In this context, four different hypotheses have been advanced to date to account for reactivity beyond the thermodynamic limit dictated by Kasha's rule (i.e, at energies higher than that of D_1):

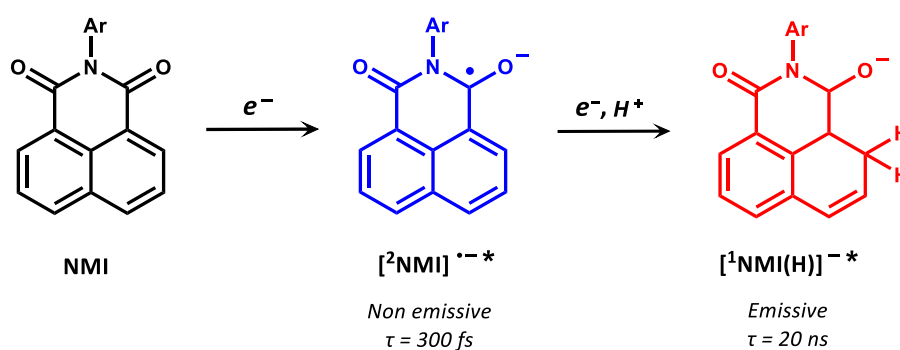
- 1) *Preassociation*: rather than relying on a diffusion-controlled encounter in solution, the catalyst and the substrate may reversibly form aggregates, ion-pairs or charge transfer complexes in the ground state (Scheme 5).



Scheme 5. General scheme of preassociation phenomena prior to excitation and SET.

When the radical anion of the catalyst is promoted to the excited state, the electron donor and acceptor are already in contact, allowing SET to occur on a timescale that can compete with rapid non-radiative decay. In principle, many of the catalyst involved in C-X bond cleavage reactions (Figure 4) could form weak π -stacking interactions with aryl halides. If this is the case, one should expect that increasing the substrate concentration leads to diminishing improvement in reaction performance once these concentrations become high enough, due to saturation of the preassembly equilibrium⁹³. In contrary, preassociation contribution should become negligible at very low substrate concentrations, eventually leading to no catalysis under very diluted conditions. Overall, experimental evidence supporting preassociation remain heavily debated, as weak interactions have been observed only for specific catalysts and with sophisticated TAS measurements^{57,90–94}.

- 2) *Solvent reduction*: in extremely reductive regimes, the thermodynamic driving force of PC^{*-} is theoretically sufficient to directly reduce the solvent or components of the supporting electrolyte. Although this reaction pathway could rationalize SET rate constants exceeding the diffusion limit, experimental evidence of solvent-derived radical anions are scarce – having been documented only for some neutral quinolinoacridine radicals⁹⁵ – thereby precluding solvent reduction as the primary pathway for productive C-X activation.
- 3) *In-situ generation of photoactive decomposition products*: for some systems, SET to the substrate is suspected to proceed via closed-shell degradation products, which result from rapid structural rearrangement or decomposition of radical anion intermediates. Prominent examples of this reaction pathway in the literature include the abovementioned DCA and NMI. In the case of NMI, Nocera et al. suggested that the radical anion reacts by an ECE (electrochemical-chemical-electrochemical) process, where the chemical step involves the reaction with an H^+ ion, to generate the closed-shell Meisenheimer product $[NMI(H)]^-$ (Scheme 6)⁹⁶.



Scheme 6. Two-electron reduction of NMI to form the closed-shell Meisenheimer complex.

The singlet excited state of $[\text{NMI}(\text{H})]^-$ is proposed as the true photoactive catalyst, as it is significantly longer-lived compared to the NMI radical anion. Similarly, DCA is thought to react with trace oxygen gas to form the doubly reduced 10-cyanoanthrolate $[\text{DCA}(\text{H})]^-$, which excited state lifetime also extends to the nanosecond regime, allowing for SET to occur⁹⁷. However, the involvement of closed-shell species cannot fully explain the successful activation of many inert aryl halides – proved both for NMI and DCA – as the reduction potential of such degradation products is rather less negative than that of the parent radical anions⁹⁸.

- 4) *Photo-detachment of solvated electrons*: in the last two years, an increasing number of ultrafast spectroscopy studies revealed that long-lived solvated electrons are generated upon excitation of several radical anions in acetonitrile, suggesting them as the active reducing species. A solvated electron is the smallest possible anion that can be stabilized through electrostatic interactions with the solvent. Historically, the concept of solvated electrons traces back in 1808, when Sir Humphry Davy firstly described the deep metallic blue colour formed when potassium crystals were heated in the presence of ammonia vapours⁹⁹. It was only a century after that it became clear that the intense colour of alkali metals dissolved in liquid ammonia stems from electrons stabilized within a solvent shell¹⁰⁰. In classical synthetic chemistry, solvated electrons have been exploited since the 1940s in the well-known Birch reduction, as well as in other reductions involving the dissolution of metals in solution¹⁰¹. In recent years, spurred by mechanistic studies on electron ejection from organic dyes in the excited state, metal-free, visible-light driven Birch-type reactions have been developed in alcoholic solvents¹⁰². While in protic media – typically, water and alcohols – solvated electrons have been extensively characterized and successfully harnessed to drive chemical reactions, their generation and dynamics in the aprotic organic solvents used in ePRC protocols, such as acetonitrile (MeCN) and dimethylformamide (DMF), have been exclusively investigated from a mechanistic point of view by means of pulsed radiolysis^{103–106}.

Building upon these spectroscopic foundations, in 2024 Ceroni et al. provided the first experimental evidence of the photo-ejection of solvated electrons in MeCN from the higher-lying excited levels of 4DPAIPN and 4CzIPN radical anions¹⁰⁷. Shortly thereafter, Nocera et al. demonstrated the generality of this phenomenon by observing the same behaviour across other established photoactive catalysts for C-X reductive cleavage, such as NMI, DCA and Mes-Acr⁹⁸. In both studies, the solvated electron was detected using extremely sensitive (temporal resolution up to hundreds of femtoseconds) flash photolysis equipment, upon excitation with a laser pulse wavelength tailored to the specific radical anion.

Consistent with the previously reported pulse radiolysis experiments in MeCN¹⁰⁶, the characteristic signal of the solvated electron in the TAS spectrum appears as a broad, featureless ESA band peaking at *ca.* 1440 nm (Figure 9a). For all the mentioned catalysts, the decay of this signal is multiexponential, with lifetimes ranging from hundreds of picoseconds to few nanoseconds (Figure 9b).

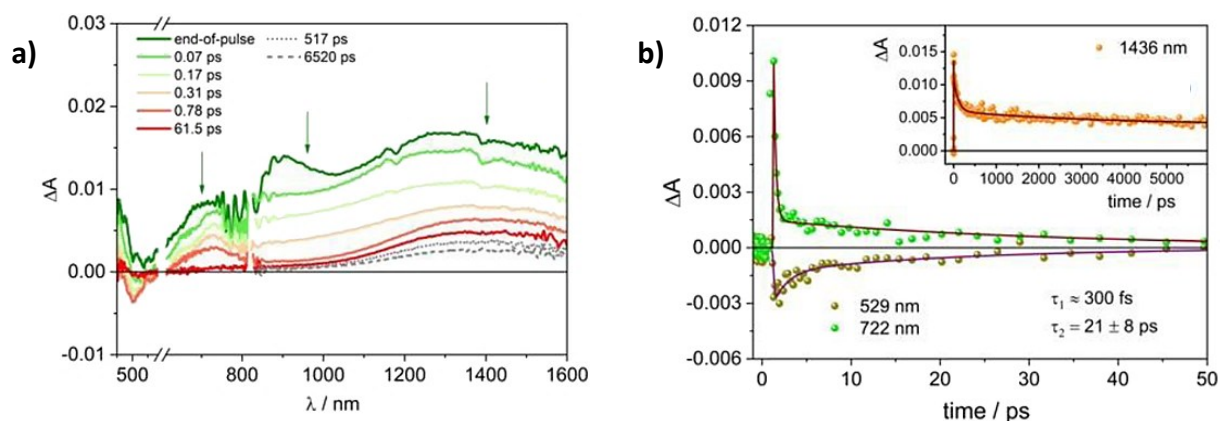


Figure 9. TAS spectra at different delays of a degassed acetonitrile solution of 4DPAIPN^{•-} (a) and the corresponding ΔA temporal evolution at significant wavelengths (b). Excitation wavelength: 600 nm; solution absorbance = 0.22; 0.2 cm optical path; 8 μ J laser pulse. Taken from ref.¹⁰⁷.

Remarkably, this level of accuracy was not accessible until recent years, due to the modest lifetime of the solvated electron in aprotic media and to the previously too low signal-to-noise ratio in the NIR region of the TAS spectrum. Conversely, in protic solvents, a more efficient cavity stabilization leads to longer lifetimes and to absorption bands in the visible region, thus facilitating the characterization of solvated electrons. Overall, these experimental data suggest the photogeneration of solvated electrons as a highly efficient pathway for circumventing the inherent kinetic bottleneck of the excited state lifetime, as the electron ejection process provides significantly longer-lived reducing agents.

Ultimately, although the photoejection of solvated electrons is currently the most compelling explanation for the mechanisms of high-energy ePRC and conPET reactions, the idea that these processes proceed through a single, uniform pathway appears overly simplistic. Instead, multiple pathways may operate in parallel, with their relative contributions depending on the nature of the catalyst and the operating conditions. One of the aims of this thesis is to investigate the mechanism of electron ejection from excited-state organic dyes, and the role of solvated electrons in the reduction of strong carbon–halogen bonds.

1.4.5. Dissociative electron transfer (DET) and fundamentals of Marcus-Hush theory

The process consisting of a single-electron injection to a carbon-halogen σ bond (R-X) and resulting in its cleavage into a carbon radical and a halide anion is generally known as dissociative electron transfer (DET)¹⁰⁸. Savéant and co-workers proposed two alternative mechanisms for DET: concerted DET (CDET) and stepwise DET (SDET). In the former, the SET step and the bond breaking occur simultaneously, while the latter proceeds in two steps via a radical anion intermediate (RX^{•-}) (Figure 10a). Accordingly, these mechanisms correspond to two different reaction energy profiles (Figure 10b). For CDET, Savéant also developed an additional variation, named sticky model, in which R[•] and X⁻ fragments interact within the solvent cage via ion-dipole forces, leading to a reduction of the activation energy compared with traditional CDET^{109,110}.

For alkyl halides, CDET is generally favoured, since the accommodation of the incoming electron in the LUMO – an antibonding σ^* orbital – would form a high-energy intermediate, which cannot be stabilized. Conversely, for aryl halides, the direct attachment of the halogen atom to the aromatic ring allows the accommodation of the incoming electron on a lower-energy π^* orbital, rendering RX^{•-} stable enough to live at least longer than a molecular vibration. The following discussion will specifically focus on SDET pathway, as only aryl halides have been investigated in the present work.

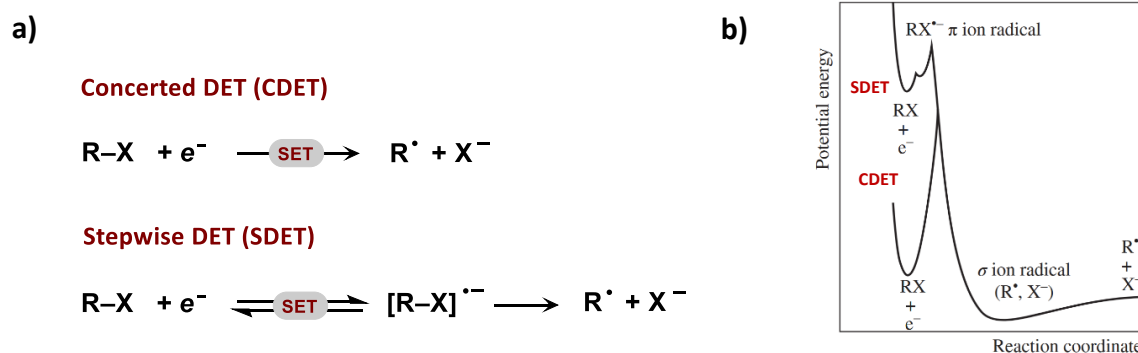


Figure 10. Mechanisms for DET processes (a) and relative energy profiles (b), adapted from ref.¹¹⁰.

In general, bimolecular ET processes such as DET are governed by the following relationships^{111,112}:

$$k_{\text{SET}} = K_A \kappa v_n \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (1.4.1)$$

$$\Delta G^\ddagger = \frac{(\Delta G^\circ + \lambda)^2}{4\lambda} \quad (1.4.2)$$

Equation 1.4.1 is the Marcus-Sutin adaption of Eyring equation, where K_A is the equilibrium constant for the formation of the precursor complex, κ ($0 \leq \kappa \leq 1$) is the electronic transmission coefficient (further described in the next paragraph), ν_n is the nuclear frequency factor for motion along the reaction coordinate, and $\Delta G^\ddagger$ is the activation energy. Equation 1.4.2 is the classical Marcus relationship between $\Delta G^\ddagger$ and the driving force (ΔG°), in which λ is the total reorganization energy.

The complex reality of electron transfer is generally simplified with two free energy surfaces, one representing the reagents and the other one representing the products. The electronic transmission coefficient κ is defined as the probability that the system, having reached the transition-state nuclear configuration, actually crosses from the reactant to the product electronic surface, rather than remaining on the reactant surface. The value of κ distinguishes two limiting regimes of ET. In the *nonadiabatic* regime (Figure 11a), electron transfer is constrained by the Born-Oppenheimer approximation: the energy barrier is overcome by thermal activation, and the electron crossing occurs via tunnel effect, according to Frank-Condon's principle. As a consequence, the reaction probability is less than unity ($\kappa \ll 1$): even when the nuclear configuration reaches the optimal transition-state geometry, the system may remain on the reactant surface. This happens when the electronic coupling matrix element between the HOMO wavefunction of the electron donor and the LUMO wavefunction of the acceptor (H_{DA}) is weak; in such a case, k_{SET} is proportional to H_{DA}^2 . In the *adiabatic* regime (Figure 11b), ET proceeds via continuous motion along the nuclear reaction coordinate, with $\kappa \approx 1$. This regime is reached as H_{DA} increases to the point that the electronic frequency associated with the coupling approaches or exceeds the nuclear frequency; here, the Born-Oppenheimer approximation is instead violated, as nuclear and electronic motion become correlated. In practice, once this adiabatic limit is reached, the maximal rate constant is dictated by ν_n rather than by H_{DA} ¹¹³.

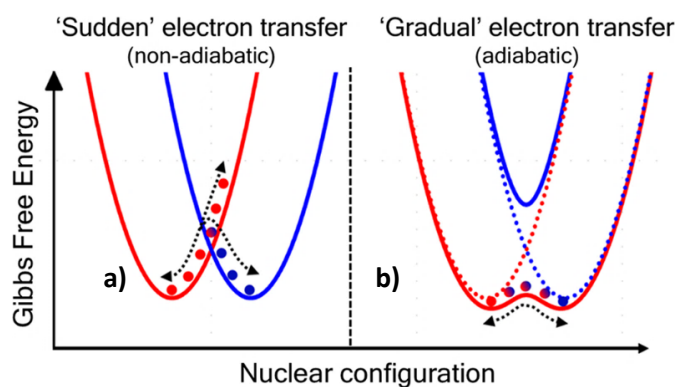


Figure 11. Nonadiabatic (a) and adiabatic (b) ET represented by free energy surfaces. Taken from ref.¹¹³.

1.5. Reversible-Deactivation Radical Polymerizations (RDRPs)

The 1950s marked the foundation of the modern polymer industry, as novel polymerization techniques rapidly scaled to meet the increasing global demand for commodity materials, promoting a fundamental shift in consumer patterns and permanently embedding synthetic plastics into everyone's daily lives^{114,115}. At the core of this revolution stood *free radical polymerization* (FRP), which established itself as the industrial gold standard for the polymerization of vinyl monomers. FRP relies on a radical chain mechanism characterized by rapid initiation and propagation, where growth and termination of propagating chains occur through random, unselective radical collisions. For commodity plastics, rubbers and fibres, where bulk properties are prioritized over precise molecular architecture, this stochastic nature of FRP mechanism was, and still remains, an advantage more than a drawback, since it enables robust, cost-effective and high-throughput productions. However, FRP suffers severe limitations when precise control over polymer composition, topology, architecture and chain length distribution is sought. Indeed, the occurrence of undesirable chain transfer and termination reactions results in a broad chain length distribution, as a consequence of “dead” chain formation throughout the process, which are inactive in further monomer addition.

To further expand the boundaries of macromolecular chemistry into high-performance, highly-specialized polymers, characterized by well-defined morphological and compositional features (Figure 12), new polymerization techniques that suppress or control irreversible termination and chain transfer reactions have been developed.

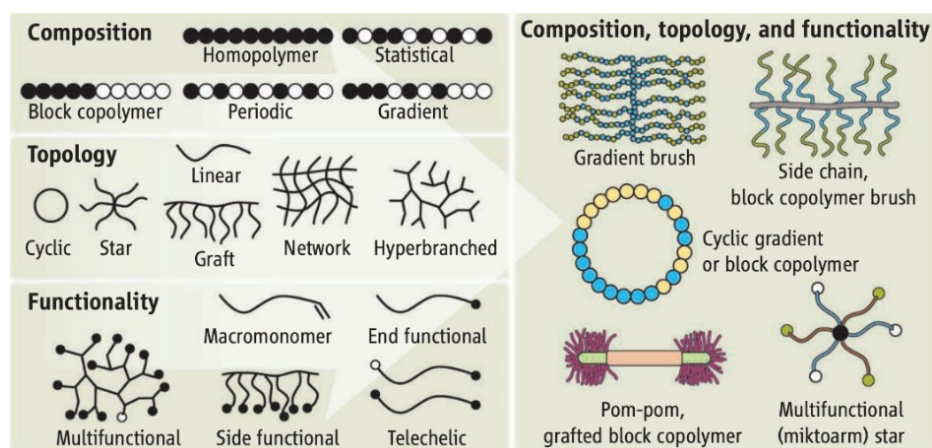


Figure 12. Examples of different polymer composition, topology and functionality provided by RDRP.

While “living” anionic polymerization of styrene – pioneered in 1956 – represented the first example in this regard for the manufacturing of block copolymers^{116,117}, it was not until the 1990s that similar levels of precision became finally accessible also via radical chemistry, marking the advent of *reversible-deactivation radical polymerizations* (RDRPs)¹¹⁸. The term RDRP has been designated by IUPAC in 2010 as comprehensive of all chain polymerizations propagated by radicals that are deactivated reversibly, bringing them into active-dormant equilibria¹¹⁹. Importantly, these equilibria must be shifted toward the dormant form of the propagating chain, so that the concentration of propagating radicals remains constantly low, thus minimizing unwanted chain transfer and bimolecular terminations by radical coupling or disproportion. Additionally, the interconversion between the active and dormant species must be rapid compared to monomer addition, in order to achieve simultaneous growth of all polymer chains.

The recent IUPAC definition encompasses the rather confusing array of terms formerly introduced by different authors, such as controlled radical polymerization (CRP) and living radical polymerization (LRP). Unlike “living” polymerization, which strictly implies the absence of bimolecular radical terminations, RDRP acknowledges that while termination is suppressed by keeping low the radical concentration, it is never entirely eliminated¹²⁰.

All RDRPs share common peculiar aspects, arising from the coupling of the usual radical initiation, propagation and termination steps to the simultaneous reversible deactivation of active radicals¹²¹:

- 1) *Chain end fidelity*. Because of the predominance of dormant chains over propagating ones – typically, less than one propagating radical every 10^5 dormant species¹²² – the probability of bimolecular interactions between active radicals drastically diminishes compared to FRP. Consequently, the “dead chain” fraction remains virtually close to zero throughout the polymerization process, with most of the propagating chain retaining their chain end functionality at the end of the reaction. This distinctive feature allows the polymer chains to be extended in the presence of additional monomers, leading to topologically complex macromolecules.
- 2) *Narrow distribution of molecular weights*. For RDRPs, initiation rate and active/dormant chain equilibration are significantly higher than propagation rate. A fast initiation guarantees that all the propagating radicals start growing simultaneously, while a fast deactivation allows limited monomer addition before the dormant state is established. As a result, all polymer chains incorporate nearly the same number of monomer units and ultimately reach very similar molecular weights. The distribution of molecular weights is typically quantified through dispersity ($\bar{D}$),

which is defined as the ratio between mass average molecular weight (M_w) and number average molecular weight (M_n). By convention, a polymerization process is considered “controlled” when $\bar{D} < 1.5$; while for FRP this value typically approaches 2 or more, for RDRPs it is possible to obtain polymers very close to be defined monodisperse, especially at high monomer conversions.

3) *First-order kinetic behaviour*. The polymerization rate (R_p) can be written as:

$$R_p = -\frac{d[M]}{dt} = k_p[P^\bullet][M] \quad (1.5.1)$$

where k_p is the propagation kinetic constant, $[P^\bullet]$ is the propagating species concentration and $[M]$ is monomer concentration. Given that the negligible contribution of irreversible termination makes the concentration of the active propagating species approximately constant, Equation 1.5.1 can be linearized as follows:

$$\ln \frac{[M]_0}{[M]} = k_p[P^\bullet] t = k_{p,app} \cdot t \quad (1.5.2)$$

resulting in a first-order kinetic law ruled by an apparent polymerization constant ($k_{p,app}$).

4) *Pre-determinable degree of polymerization (DP)*. Since under the conditions mentioned above the number of growing chains should be equal to the number of initiator (I) molecules present at the beginning, the reagent stoichiometry determines the average number of monomer units per chain (i.e., the predicted DP at full conversion). Therefore, polymers with predetermined M_n can be easily achieved just by choosing the initial concentrations and running the reaction until a specific conversion is reached. The relationship linking DP with conversion is the following (where MW is the molecular weight):

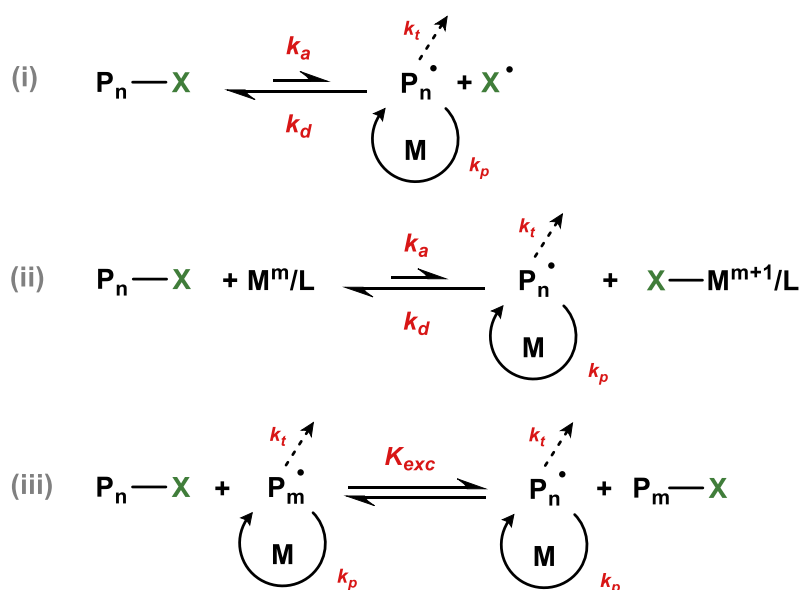
$$DP = \frac{MW_{(polymer)}}{MW_{(monomer)}} = \frac{[M]_0}{[I]_0} \cdot \frac{[M]_0 - [M]_t}{[M]_0} = \frac{[M]_0}{[I]_0} \cdot \text{Conversion} \quad (1.5.3)$$

Three classes of RDRPs can be distinguished according to the type of activation mechanism¹²⁰:

- (i) *Stable radical-mediated polymerization (SRMP)*, where a stable radical couples with the active radical and reversibly forms dormant covalent species (activation-deactivation equilibrium). Within this class, *nitroxide-mediated radical polymerization (NMP)*, in which the deactivation step involves coupling with stable nitroxide (more properly, aminoxyl) radicals^{123,124}, is historically the most studied and developed methodology.

- (ii) *Atom-transfer radical polymerization* (ATRP), in which deactivation occurs through reversible halogen atom transfer from a higher oxidation state metal complex to the propagating radical. ATRP, independently presented in 1994-1995 by Matyjaszewski's¹²⁵ and Sawamoto's¹²⁶ teams, has progressively evolved into numerous specialized variants throughout last two decades¹²⁷.
- (iii) *Degenerative chain-transfer radical polymerization* (DTRP), based on the reversible exchange of a labile end-group between a dormant chain and an active macroradical. The seminal DTRP technique – *reversible addition-fragmentation chain transfer* (RAFT), developed in 1988 by Rizzardo et al.¹²⁸, is currently the most relevant and widespread one.

These three general approaches to the RDRP concept are summarised in Scheme 7. Mechanisms (i) and (ii) are controlled by a process called persistent radical effect (PRE): propagating radicals are trapped by stable radical captor species, thereby maintaining low the instantaneous active radical concentration¹²⁹. In contrast, DTRP functions independently of the PRE, since activation-deactivation equilibrium is achieved through rapid transfer of radical functionality between chains.

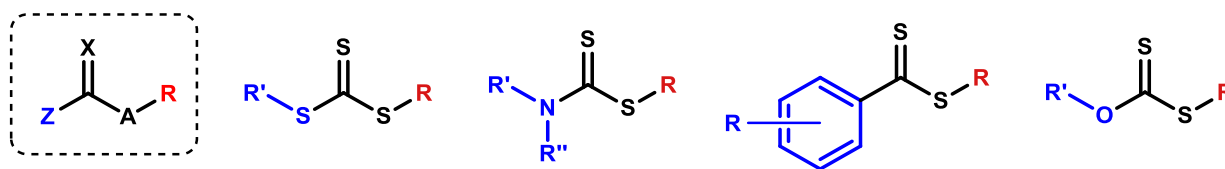


Scheme 7. General mechanisms of (i) SRMP, (ii) ATRP, (iii) DTRP, where k_a = activation kinetic constant; k_d = deactivation kinetic constant; k_p = propagation kinetic constant; k_t = termination kinetic constant; K_{exc} = exchange equilibrium constant.

1.5.1. Overview of traditional RAFT polymerizations

The RAFT process is now a widely recognized polymerization technique, and it has been extensively adopted beyond polymer synthesis laboratories as a tool to generate materials with a broad range of applications, spanning from materials science to medicine. These include block, star, branched, hyperbranched, network, stimuli-responsive and surface-grafted copolymers, as well as nanoparticles and nanocomposites^{130–133}.

In RAFT polymerizations, the radical exchange equilibrium is established using a chain transfer agent (CTA), also referred to as RAFT agent. The general structure of the most representative CTAs – thiocarbonylthio compounds – is depicted in Scheme 8, where X and A are both sulphur atoms, Z is a varying substituent and R is an alkyl chain. Different CTA families, such as trithiocarbonates, dithiocarbamates, dithiobenzoates and xanthates, are identified on the basis of the Z group.

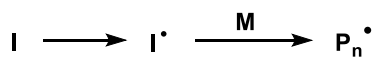


Scheme 8. Typical CTA structures. From left to right: generic CTA structure, trithiocarbonates, dithiocarbamates, dithiobenzoates, xanthates.

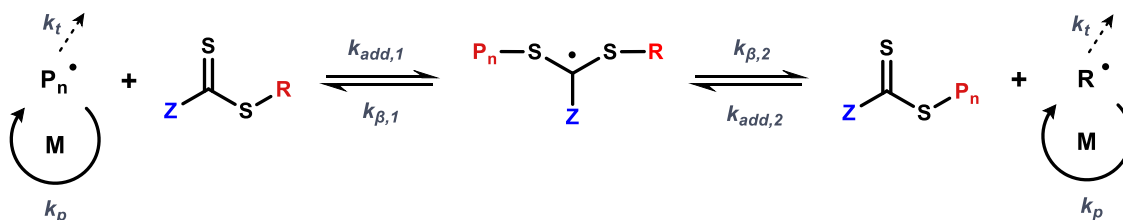
One of the major features of RAFT polymerization is its ability to polymerize an extensive range of both “more-activated” monomers (MAMs), which possess a carbonyl group conjugated to a double bond, and “less-activated” monomers (LAMs), which exhibit a double bond adjacent to oxygen, nitrogen, halogen, sulphur lone pairs or to a saturated carbon¹³⁴. The versatility in monomer compatibility arises from the reactivity of the CTA, which depends on the choice of Z and R groups¹³⁵. The role of Z is to modulate the reactivity with respect to the target monomer and to provide stability to the radical intermediate formed after radical addition, while the nature of R mainly affects the fragmentation step, as R[•] should be a better homolytic leaving group than the propagating radical.

The RAFT kinetic scheme encompasses the well-known steps of free radical polymerization (i.e., initiation, propagation, termination and transfer processes), onto which the reactions associated with the RAFT equilibrium are superimposed. A generic RAFT polymerization mechanism involving a thiocarbonylthio CTA is presented in Scheme 9.

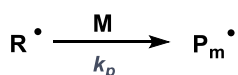
1) Initiation and propagation



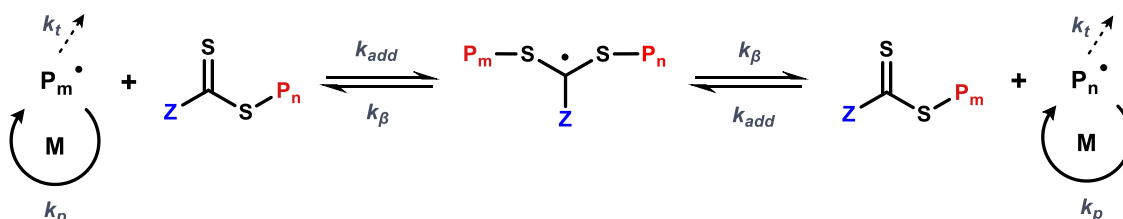
2) RAFT pre-equilibrium



3) Reinitiation and propagation



4) Main RAFT equilibrium



5) Termination



Scheme 9. Conventional RAFT mechanism.

In conventional RAFT methods, a thermal radical initiator, typically 2,2-azobisisobutyronitrile (AIBN), benzoyl peroxide or potassium peroxydisulfate, provides the initiating radicals ($I^\bullet$), which can add monomer units to form propagating chains ($P_n^\bullet$). After initiation and propagation, two subsequent RAFT equilibria may be distinguished¹³⁶. One refers to the pre-equilibrium period, where $P_n^\bullet$ adds to the C-S double bond of the starting CTA, yielding a radical intermediate. In turn, such intermediate rapidly fragments either backwards to the reactants or forwards, to produce a macroCTA

and a new propagating radical ($R^\bullet$), derived from the R group, which also adds monomer units to form $P_m^\bullet$. After consumption of the small-molecule CTA, rapid exchange of $P_n^\bullet$ and $P_m^\bullet$ occurs via a polymeric radical intermediate in the so-called main RAFT equilibrium. The copresence of a vast majority of dormant polymeric RAFT agents and a tiny fraction of propagating radicals throughout the process ensures an equal probability for chain growth, while suppressing dead chains formation. Retention of the thiocarbonylthio groups in the final polymer chain end is responsible for the living character of RAFT polymerization.

In order for the process to be controlled, the rate of the addition-fragmentation equilibrium must be higher than that of propagation, so that less than one monomer unit is added per activation cycle¹³⁴.

In a RAFT process, the theoretical number average molecular weight of the polymer is given by:

$$M_{n,th} = \text{Conversion} \cdot MW_{(\text{monomer})} \cdot DP_0 + MW_{(CTA)} \quad (1.5.4)$$

where DP_0 is the DP at full conversion (target DP), calculated according to Equation 1.5.3 as follows:

$$DP_0 = \frac{[M]_0}{[CTA]_0} \quad (1.5.4)$$

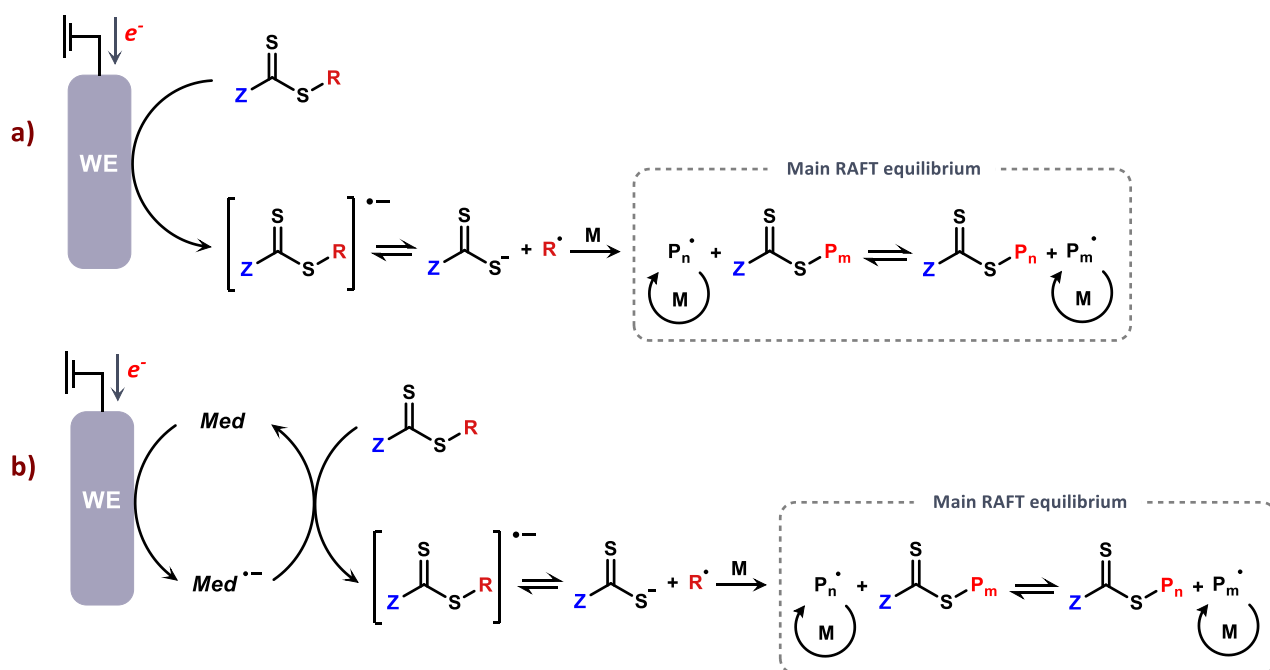
1.5.2. Electrochemically-mediated RAFT polymerizations (eRAFT)

A continuous supply of radicals is essential in RAFT due to the unavoidable termination processes. The classical initiation route – thermal decomposition of radical sources – typically requires temperatures between 50 and 70°C. However, such temperatures may not be suitable for some functional monomers or for biological or thermoresponsive systems. For this reason, alternative radical generation methods, such as electrical current or light irradiation have been proposed.

Electrochemically-mediated ATRP (eATRP) pioneered the use of electricity in RDRPs and has now evolved into a well-established technique, which benefits from spatiotemporal reaction control, in addition to the “green” character inherent to electricity-driven organic synthesis¹³⁷. In contrast, only few electrochemically-mediated RAFT polymerizations (eRAFT) have been developed until now, due to the challenging and largely unexplored electrochemical reactivity of RAFT agents¹³⁸.

In direct eRAFT, the CTA is reduced to the corresponding radical anion directly on the electrode surface (Scheme 10a). Conversely, mediated eRAFT exploits a mediator species that carries out the CTA reduction in solution and is regenerated at the electrode, thus converting a heterogeneous ET to

a homogeneous one (Scheme 10b). Importantly, the reduction of the mediator must occur at more positive potentials than the reduction of all the other species involved in the process. Small unconjugated molecules proved to be inefficient mediators, likely because of side-reactions such as radical-radical coupling, while mediators with highly conjugated structures effectively minimize these unwanted processes¹³⁹.



Scheme 10. Direct e-RAFT (a) and mediated eRAFT (b) mechanisms.

For direct eRAFT, the selection of the applied potential at the WE should be finely regulated for the specific CTA-monomer couple, in order to avoid direct reduction of the propagating radicals and of the monomer. Moreover, the presence of electron-withdrawing moieties in the R group of the CTA makes the macroCTA more difficult to be reduced, thus progressively decreasing the efficiency of the electrochemical stimulus during the process. Finally, direct eRAFT is severely hampered by the irreversible consumption of the CTA, as shown by CVs after several hours of electrolysis, leading to low conversions and polymers with a broad distribution of MWs¹³⁹. On the other hand, results of mediated eRAFT have been much more promising, despite still suffering from modest CTA degradation phenomena and slow kinetics^{139–141}.

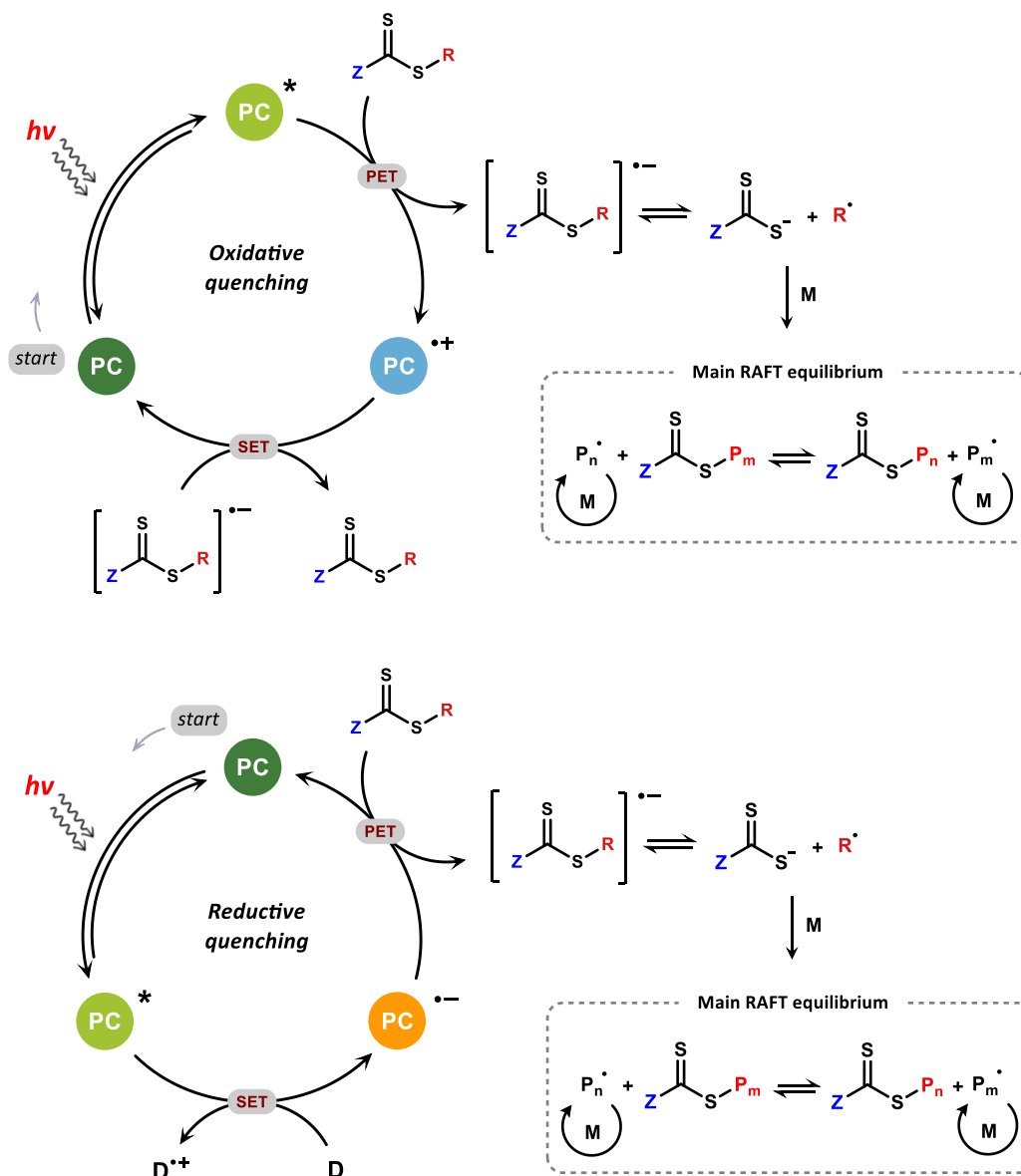
1.5.3. Photoinduced electron transfer RAFT polymerizations (PET-RAFT)

Parallel to electrochemistry, the low cost and ubiquity of light, along with the selectivity and spatiotemporal control it can provide, position light activation among the most attractive non-thermal modes of activation. Hence, the photo-induced RDRPs literature is witnessing a rapid expansion, driven by continuous breakthroughs in photocatalyst design and the pursuit of increasingly mild, sustainable, and precisely tuned macromolecular syntheses^{142–144}.

Light-triggered RAFT methodologies are generally divided into three main categories^{145,146}:

- 1) *Photomediated RAFT polymerization* is analogous to conventional thermal RAFT in which the thermal initiator has been replaced with a photoinitiator that decomposes and generates radicals upon irradiation with a specific wavelength. Since most commercially-available photoinitiators are activated by UV light, which usually excites also the CTA, photodegradation of the polymer end group is possible¹⁴⁶. As a consequence, this activation pathway is more frequently used in FRPs, and its application to RAFT is marginal.
- 2) *Photoiniferter RAFT polymerization (PI-RAFT)* is a variant of the traditional *iniferter* process. Iniferter polymerization, developed before the advent of RAFT, employs a compound – typically, a dithiocarbamate – which acts simultaneously as initiator, transfer agent and terminator¹⁴⁷. Upon decomposition, the iniferter fragments can initiate the polymerization and reversibly combine with the growing chains, effectively establishing the active-dormant equilibrium. CTAs involved in RAFT can act as photoiniferters: excitation with either UV or blue light triggers the homolysis of the C-S bond, releasing an active alkyl radical and a persistent thiyl radical. The first engages in degenerative chain transfer entering the RAFT equilibrium, while the latter can reversibly deactivate active radical species^{148–150}. Photoiniferter RAFT guarantees extraordinarily high livingness, as termination is suppressed by the persistent radical effect. Nevertheless, it often suffers from sluggish initiation rates due to inefficient direct photolysis and propensity for UV-induced side-reactions.
- 3) *Photoinduced electron transfer polymerization (PET-RAFT)*, firstly disclosed by Boyer and co-workers¹⁵¹, relies on light harvesting by photocatalyst (PC) that, in the excited state, can interact with a CTA to generate initiating alkyl radicals. Contrary to photomediated RAFT, the catalyst is not incorporated into the polymer chains, as the R group of the CTA is the exclusive initiating species. In a PET-RAFT process, PC* undergoes an oxidative or reductive quenching by the CTA itself or an electron donor to reduce the thiocarbonylthio compound to a radical anion, which then

fragments to generate a propagating radical (Scheme 11)^{145,152}. The resulting radical can enter the degenerative chain transfer equilibrium and form a dormant polymer chain. Regeneration of the catalyst via electron transfer closes the catalytic cycle.



Scheme 11. PET-RAFT via oxidative quenching (top) and reductive quenching (bottom).

It should be specified that PC^* can also transfer its energy to the CTA, facilitating homolysis of the C-S bond in a manner analogous to the photoiniferter mechanism. This different pathway – named photoinduced energy transfer RAFT – can be thought of as a photocatalyzed photoiniferter process. Often, a complex interplay of photoinduced electron and energy transfer takes place¹⁵³.

1.6. Aim of the thesis

Despite the demonstrated utility of ePRC, the mechanisms underlying these processes remain highly speculative and are still the subject of considerable debate. This limited mechanistic understanding has significantly hindered the rational development and broader application of these powerful methodologies. The first objective of this thesis is to elucidate the mechanism of photoelectrochemical activation of recalcitrant C–X bonds. By combining synthetic studies with fundamental mechanistic investigations – including the role of electrons ejected from organocatalysts – this work provides new insights into the elementary steps governing ePRC transformations.

A second limitation of current ePRC methodologies is their reliance on high-energy blue light, which can promote undesired side reactions and is incompatible with certain functional groups. Therefore, the second objective of this thesis is to develop ePRC methodologies driven by lower-energy red and near-infrared light. These wavelengths are exploited both for the activation of strong C–X bonds in organic synthesis and for the controlled synthesis of well-defined polymeric materials via photoelectrochemically mediated RAFT polymerization under mild conditions.

Overall, this work establishes ePRC as a versatile and energy-efficient platform that spans applications ranging from advanced organic synthesis at extreme redox potentials to low-energy, spatiotemporally controlled polymerization, while simultaneously advancing the fundamental mechanistic understanding required for the rational design of the next-generation electrophotocatalytic systems.

2. Experimental section

This section lists the chemicals and instrumentation used for this work, along with a brief description of the main experimental procedures.

2.1. Chemicals

Solvents

N,N-Dimethylformamide (DMF, VWR, HPLC grade 99.9%). Dimethylsulfoxide (DMSO, Carlo Erba, ACS grade). Acetonitrile (MeCN, VWR, HPLC grade). Tetrahydrofuran (THF, Sigma-Aldrich, HPLC grade $\geq$ 99.9%). Methanol (MeOH, VWR, HPLC grade). Chloroform-*d* (CDCl₃, Sigma-Aldrich, 99.8% atom %D).

Photocatalysts

N,N'-Bis(2,6-diisopropylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (PDI, TCI America, > 98,0%). 2,4,5,6-Tetrakis(diphenylamino)isophthalonitrile (4DPAIPN, Ossila, > 98%). 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN, synthesized). *N*-(2,6-diisopropylphenyl)-1,8-naphthalimide (NMI, synthesized).

Substrates (aryl halides)

4-fluoroanisole (4MeOPhF, Sigma-Aldrich, 99%). Fluorobenzene (PhF, Sigma-Aldrich, 99%). 4-chloroanisole (4MeOPhCl, Sigma-Aldrich, 99%). 4-chlorotoluene (4MePhCl, Sigma-Aldrich, 98%). Chlorobenzene (PhCl, Sigma-Aldrich, 99.5%). 4-bromoanisole (4MeOPhBr, TCI, > 97%). Bromobenzene (PhBr, Sigma-Aldrich, 99%). 2-chloropyridine (2ClPy, EGA-Chemie, 99%). 3-chloropyridine (3ClPy, Sigma-Aldrich, 99%). 2-bromopyridine (2BrPy, FluoroChem). 1-bromonaphthalene (1BrNaph, Sigma-Aldrich, 98%). 4-bromobenzonitrile (4CNPhBr, Sigma-Aldrich, 95%). Iodobenzene (PhI, Sigma-Aldrich, 98%).

Monomers

Methyl methacrylate (MMA, Thermo Fisher, 99%, stabilized). Benzyl methacrylate (BzMA, Thermo Fisher, 98%, stabilized).

Chain transfer agent (CTA)

4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA, Boron Molecular, 97%).

Supporting electrolytes

Tetraethylammonium tetrafluoroborate (TEATFB, Thermo Fisher, 99%; BLD pharm, 97%), recrystallized in ethanol, dried under vacuum at 70°C for 48 hours and stored under P₂O₅. Tetrabutylammonium iodide (TBAI, Sigma-Aldrich, ≥ 99.0%).

Other chemicals

Ferrocene (Fc, Acros Organics, 98%). 2-propanol (iPrOH, Sigma-Aldrich, 99.9%).

2.2. Instrumentation

2.2.1. Electrodes

Working electrode (WE): four different working electrodes were used.

- (i) Rotating disk electrode (RDE) with a glassy carbon (GC) tip (3 mm diameter, homemade). The RDE is connected to a Metrohm AG engine which controls the stirring. The GC tip geometrical surface area was estimated as $7.07 \cdot 10^{-2} \text{ cm}^2$.
- (ii) Small GC electrode (3 mm diameter, homemade).
- (iii) Platinum gauze (homemade).
- (iv) Reticulated vitreous carbon (RVC) foam.

To ensure reproducibility, the GC electrode surface was polished with a 0.25 µm diamond paste and ultrasonically rinsed in absolute ethanol for 10 minutes prior to each electrochemical measurement. Before inserting the electrode in the cell, it was carefully washed with HPLC grade acetone. The same procedure was followed for the RVC electrode, except for the polishing step.

Platinum electrode cleaning requires electrochemical activation. The Pt gauze was burned with a blow torch and activated via CV scans between -0,67 V and +0,91 V vs Hg/HgSO₄ in a 0.5 M H₂SO₄ solution, until reproducible CVs were obtained.

Counter electrode (CE): two different counter electrodes were used.

- (i) Platinum wire fused in a glass tube.
- (ii) Graphite rod or aluminium wire inserted in a glass tube filled with a 0.1 M solution of TEATFB in DMF. The liquid junction with the reaction solution is guaranteed by a porous tip (G2), which is partially stuffed with Agar gel.

Reference electrode (RE): silver (Ag) wire covered in AgI and inserted in a glass tube filled with a 0.1 M solution of TBAI in DMF. The liquid junction with the reaction solution is guaranteed by a porous tip (G3), which is partially stuffed with Agar gel. AgI was deposited onto the metallic wire in galvanostatic mode (0.4 mA/cm², KI 0.1 M + HNO₃ 0.1 M). The RE was calibrated against the ferrocene/ferrocenium (Fc⁺/Fc) redox couple used as internal standard: at the end of each cyclic voltammetry experiment, a small amount of Fc was added to the reaction mixture, and its oxidation potential was measured via CV.

The measured potentials (V vs Ag/AgI) were converted to the saturated calomel electrode (SCE) scale. Therefore, potentials were scaled versus Fc⁺/Fc according to Equation 2.2.1, and versus the SCE according to Equation 2.2.2:

$$E_{\text{ox/red}} (\text{vs } \text{Fc}^+/\text{Fc}) = E_{\text{ox/red}} (\text{vs } \text{Ag}/\text{AgI}) - E_{\text{Fc}^+/\text{Fc}} (\text{vs } \text{Ag}/\text{AgI}) \quad (2.2.1)$$

$$E^{\circ}_{\text{Fc}^+/\text{Fc}} = 0.436 \text{ V vs SCE in DMF} + 0.1 \text{ M TEATFB}^{154} \quad (2.2.2)$$

After approximately two weeks of usage, both reference and type (ii) counter electrodes were prepared anew, prior to cleaning of glass tubes and their sintered glass septum with Piranha solution (3:1 mixture in volume of concentrated sulfuric acid and hydrogen peroxide, a highly corrosive and oxidizing solution). This allows to remove all the organic residues of the gel and reaction products.

2.2.2. Potentiostat and simulation software

An Autolab PGSTAT204 potentiostat/galvanostat (Eco-Chemie, Utrecht, Netherlands), connected to a computer with the Nova 2.1 software was used for all the experiments.

CV simulations were performed with the DigiElch8FD software.

2.2.3. Light sources

The following light sources were used: Kessil P160L lamp of 525 nm; homemade 13 W LED systems of 595 nm, 630 nm, 850 nm (CHANZON); homemade 45 W LED system of 850 nm (CHANZON).

Lamps emission spectra and photon flux were measured with the AvaSpec-Mini2048CL spectrometer (Avantes), coupled with the software AvaSoft. The optical fiber sensor was placed in the exact position of the GC electrode during CV measurements under irradiation.

Glassy carbon electrode reflectivity was measured using an 8.7mW commercial Class IIIa red laser and a Glassy Carbon Sheet (Tokai Carbon), polished in the same way as GC electrodes. A Thorlabs PM100USB Power and Energy Meter, with a S120VC sensor was used to measure the power reflected by the GC sheet surface.

2.2.4. UV-vis spectrophotometer

UV-Vis measurements were registered on an Agilent Cary 60 UV-Vis spectrophotometer (Xenon flash lamp, 80 Hz), connected with a computer with Cary WinUV software.

2.2.5. Spectroelectrochemistry equipment

Spectroelectrochemistry experiments were carried out with a kit by BAS Inc, composed of a thin layer quartz glass cell (0.5 mm light optical pathway), a Pt gauze WE (80 mesh), a Pt CE, and a non-aqueous Ag/Ag⁺ RE.

2.2.6. Nuclear magnetic resonance (NMR) spectrometer

All ¹H-NMR analyses were performed on a Bruker 400 Advance III HD spectrometer (400 MHz), coupled with Topspin 3.8.0 software and equipped with a BBFO SmartProbe probehead.

2.2.7. Gel permeation chromatography (GPC) equipment

For polymer molecular weight and dispersity measurements, an Agilent Infinity 1260 gel permeation chromatograph was used. The instrument is equipped with two columns (Agilent PLgel 5 µm MIXED-C 300 x 7.5 mm), connected in series and heated at 60°C. The solid phase consists of polystyrene cross-linked with divinylbenzene. The mobile phase is DMF + 10 mM LiBr.

The operative flow rate is of 1 mL/min. A refractive index detector (RID) is set at 50°C. The calibration curve was constructed based on the elution times of PMMA standards (Agilent EasiVial) fitted with a third-degree polynomial.

2.3. Experimental setup and procedures

2.3.1. Spectroelectrochemical analysis

Spectroelectrochemistry experiments were conducted with the specific kit, coupled with the UV-Vis spectrophotometer and the potentiostat. Cuvette, electrodes and degassing system (2 L gas balloon filled with argon) were arranged as shown in Figure 13.

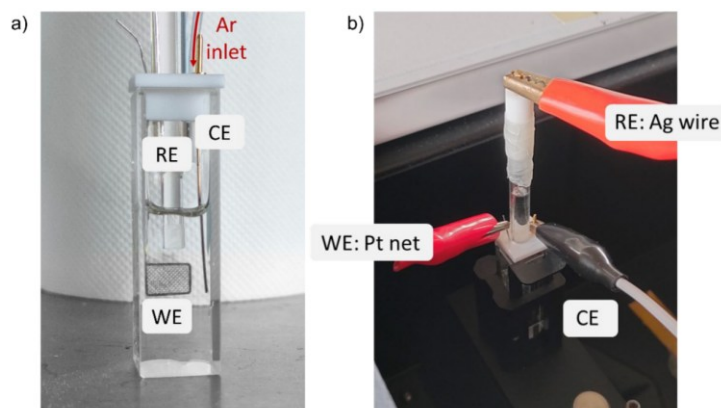


Figure 13. Spectroelectrochemical setup: side view (a) and top view, when inserted in the spectrometer (b).

The Pt net was activated before running the electrolysis. Baseline measurements (absorption spectra of DMF + 0.1 M TEATFB) were firstly recorded, followed by the spectrum of the neutral photocatalyst. Then, the system was degassed under a continuous flow of argon and a potentiostatic electrolysis was carried out, while simultaneously registering UV-Vis spectra every 30 seconds.

2.3.2. Photoelectrochemical cyclic voltammetry

Cyclic voltammetry measurements were performed into a jacketed electrochemical cell with 5 necks. The central neck is occupied by the RDE with GC tip, which acts both as WE and as solution stirrer in between CVs acquisitions. Of the remaining 4 necks, two are occupied by RE and CE respectively, one is used as inlet/outlet for the degassing system and the last one is used to add reagents during the experiments. The cell jacket is connected to a Thermo Scientific SC100 thermostat set at 25.00°C, in order to keep the temperature of the cell walls constant, thus ensuring reproducibility. When irradiation was needed, the light source was placed beneath the cell, which has a flat glass bottom without a jacket (Figure 14).

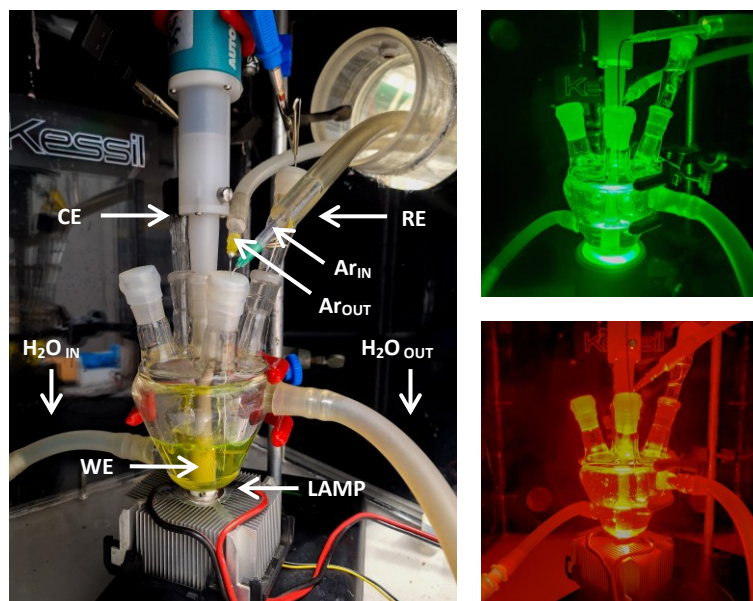


Figure 14. Cell setup with no irradiation (left) and under irradiation (right, 630 nm bottom 525 nm top).

The electrochemical cell was loaded with 18 mL of DMF + 0.1 M TEATFB and purged with argon under stirring for 30 minutes. The argon flux was kept low and constant throughout the experiment. Firstly, before adding reactants, background CVs were recorded both in dark conditions and under irradiation at operational scan rates. Solution resistance compensation was applied during the measurements. After that, 4DPAIPN was added at 1 mM concentration (except for when otherwise indicated), and CVs were collected under dark and irradiation conditions. Finally, a substrate was introduced and CVs under irradiation were registered for increasing substrate concentrations. After each experiment, the cell was carefully rinsed with HPLC grade acetone and stored in oven at 60°C.

2.3.3. *C-X cleavage bulk electrolysis*

Electrolysis experiments for electrophotocatalytic reductive cleavage of aryl halides were conducted in an electrochemical H-cell (Figure 15). Cathodic and anodic chambers are kept separated by a G3 sintered glass septum, which was partially stuffed with agar gel. The cell is equipped with two necks for the cathodic chamber; one was occupied by the RE, and the other one by the WE – alternatively the small GC electrode for preliminary and final CVs acquisitions and the RVC foam for running the electrolysis. The anodic chamber – graphite rod dipped into a DMF + 0.1 M TEATFB solution – represents the CE itself.

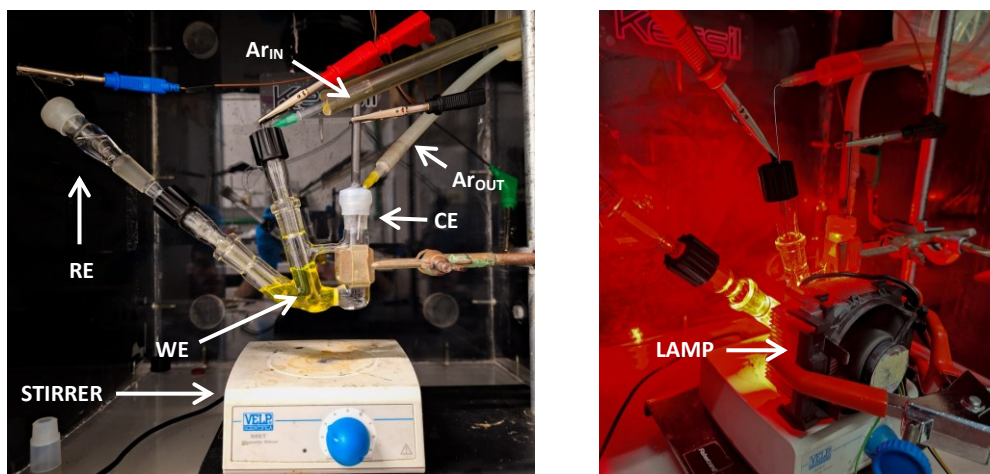


Figure 15. Electrolysis setup before starting the electrolysis (left) and under 630 nm light (right).

The cathodic chamber was filled with 7 mL of a DMF + 0.1 M TEATFB solution, containing 50 mM of substrate (4-bromoanisole), 5 mM of photocatalyst (4DPAIPN) and 0.5 M of 2-propanol, which acts both as proton and hydrogen atom donor. The anodic meniscus height was then adjusted at the same level of the cathodic one, in order to prevent osmotic pressure effects. The reaction mixture was degassed for 30 minutes, placing the argon flow inlet in the WE neck and the outlet in the CE neck. Firstly, CVs of the photocatalyst were collected, in order to identify the working potential. Then, the GC electrode was replaced with the RVC foam and the system was further degassed for 15 minutes. After that, a constant potential – equal to the half-wave potential of the initial 4DPAIPN CV – was applied, and the electrolysis was run for 7 hours under 630 nm light irradiation and continuous argon flow. No solution resistance compensation was applied. At the end of the reaction, the GC electrode was newly inserted into the WE neck, to register a post-electrolysis CV. Samples for NMR analysis were collected during the electrolysis using a degassed needle.

2.3.4. PET-eRAFT polymerizations

PET-eRAFT polymerizations were performed in two different electrochemical cells. For most the reactions, a 5-neck jacketed cell (Figure 16, left) was used. Of the five necks, one was occupied by the Pt gauze WE, used to run the electrolysis. A neck accommodated the small GC electrode, which served as WE to record preliminary and post-reaction CVs. A RE and a type (ii) CE were placed in other two necks, while the remaining one was used as inlet/outlet for degassing. The temperature of the cell walls was maintained constant at 35°C with a Thermo Scientific SC100 thermostat.

For final setup optimization under NIR irradiation, a 6-neck non-jacketed electrochemical cell was chosen (Figure 16, right). Similarly to the previous setup, four necks accommodated the WE Pt gauze, the WE small GC, RE and CE, respectively. Of the two remaining necks, one was used as inlet/outlet for the degassing system and the other one was used to take reaction mixture samples. Since the cell is not jacketed, a small cooling fan was placed on one side, in order to dissipate excess heat.

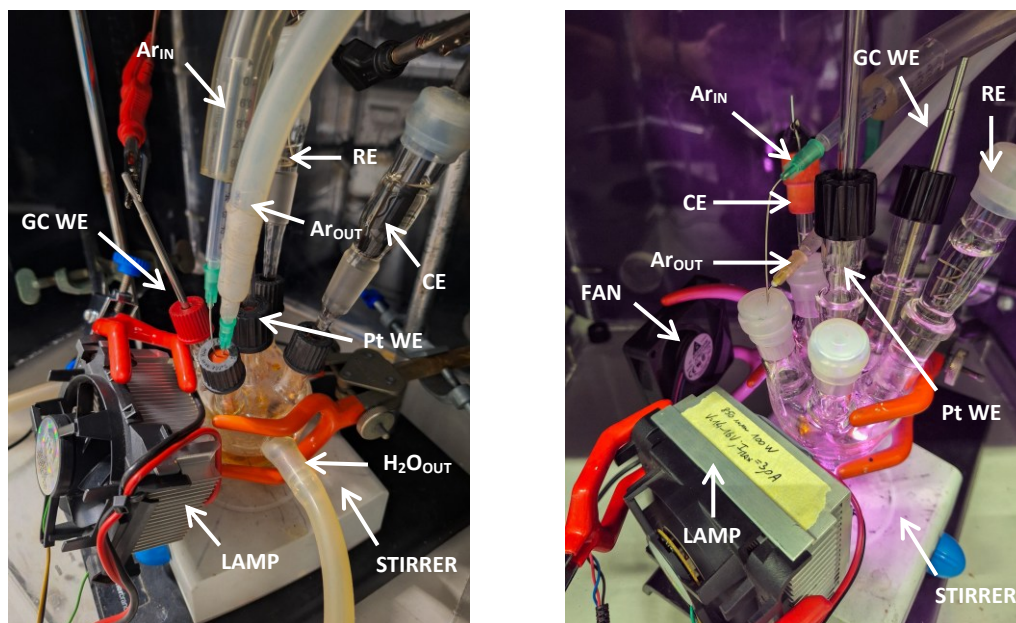


Figure 16. PET-eRAFT polymerization thermostated setup with 630 nm light off (left) and non-thermostated setup with 850 nm light on (right). The violet colour is a digital camera artifact typical of NIR irradiation.

All experiments were carried out under inert atmosphere: the reaction mixture was degassed for 30 minutes, while the argon flow was kept constant and low throughout the polymerization. The saturation of the inlet argon flow with monomer vapours in a prebubbler allowed to minimize monomer loss due to slow stripping phenomena.

The cell was filled with 10 mL solution (12 mL for the non-jacketed setup) of DMF + 0.1 M TEATFB + catalyst (PDI) + CTA (CDTPA) + monomer (methyl methacrylate, MMA or benzyl methacrylate, BzMA). For all experiments, a 1:3 monomer to solvent ratio was chosen, while PDI and CDTPA concentration varied based on the specific experiment carried out. Before adding the monomer, it was passed through basic alumina to remove the polymerization inhibitor.

The chronoamperometry (potentiostatic electrolysis process) was then set to start, selecting an applied potential based on the preliminary CV of PDI. Light was turned on simultaneously with the beginning of the electrolysis. After each experiment, the cell was washed with HPLC grade acetone and dried in oven at 60°C.

Before starting the reaction, a sample was drawn from the reaction mixture with a degassed needle, to have a “time zero” reference. Additional samples were then periodically taken; an aliquot was put in a NMR tube for the NMR analysis, while the remaining part was used for the GPC run.

NMR analysis and determination of monomer conversion: each NMR tube was filled with CDCl₃ to have a 1-2 mg/mL concentration. To determine the conversion of monomer into the corresponding polymer, the ratio between monomer and polymer signals, normalized by the number of protons generating them, was evaluated. For MMA, the methoxy group of MMA appears as a sharp singlet at 3.78 ppm, while the methoxy group of PPMA is a broad singlet at 3.58 ppm (Figure 17).

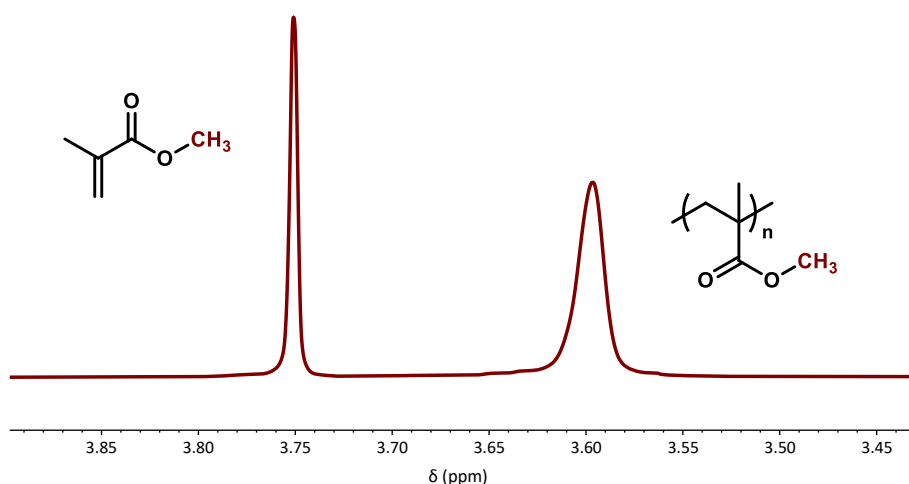


Figure 17. ¹H-NMR spectrum of the polymerization solution of MMA at a given conversion.

Therefore, monomer conversion can be calculated as follows, where A_m and A_p are the areas of the monomer and polymer signal respectively:

$$\text{Conversion \%} = \frac{A_p}{A_m + A_p} \cdot 100 \quad (2.3.1)$$

Equation 2.3.1 applies also to the polymerization of BzMA, when the areas of the benzyl CH₂ group of BzMA (5.18 ppm) and P(BzMA) (4.87 ppm) are considered.

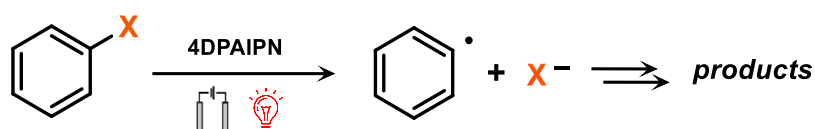
GPC analysis: prior to injection in the GPC columns, polymeric samples underwent a specific procedure to remove the supporting electrolyte. This operation ensures more accurate results by suppressing the TEATFB signal in the RID chromatogram, which would otherwise partially overlap with polymer peaks, especially at low molecular weights. Each aliquot taken from the reaction mixture was first diluted in 1.5 mL of THF, where the polymer is soluble, while the electrolyte precipitates. After that, the solution was filtrated with neutral alumina and the THF solvent was removed at the rotary evaporator. The sample was then diluted in DMF to a theoretical concentration of 1-2 mg/mL of polymer), filtered again with neutral alumina and finally injected into the instrument (typical injection volume of 50-100 μ L). The eluted chromatograms were integrated with the dedicated software to obtain M_n , M_w and D .

To synthesize the methacrylate block copolymers, the first block was precipitated into a 9:1 (v/v) water/methanol mixture and recovered by vacuum filtration. The precipitate was then redissolved in a minimal volume of THF and precipitated a second time under the same conditions, before being filtered and dried under vacuum for 48 h. NMR analysis was performed to confirm that no significant amounts of catalyst, monomer, or electrolyte co-precipitated with the polymer.

3. Results and discussion

3.1. The mechanism of reductive C-X cleavage via e-PRC

This section aims to elucidate the mechanism underlying the electrophotocatalytic activation of recalcitrant C-X bonds of aryl halides mediated by the organic electrophotocatalyst 4DPAIPN (Scheme 12), as well as to prove the synthetic utility of such reactivity under low-energy red light.



Scheme 12. General reaction scheme for the ePRC transformation investigated in this section.

The mechanistic study presented here is articulated in a few steps. First, the electrochemical and photophysical properties of 4DPAIPN are studied through combined CV and UV-Vis analyses. Next, the catalytic activity of 4DPAIPN towards a library of substrates – ranging from inert aryl fluorides to labile aryl bromides and iodides (Figure 18) – is evaluated via CV coupled with digital simulations. Finally, a comprehensive reaction mechanism is proposed based on these experimental insights.

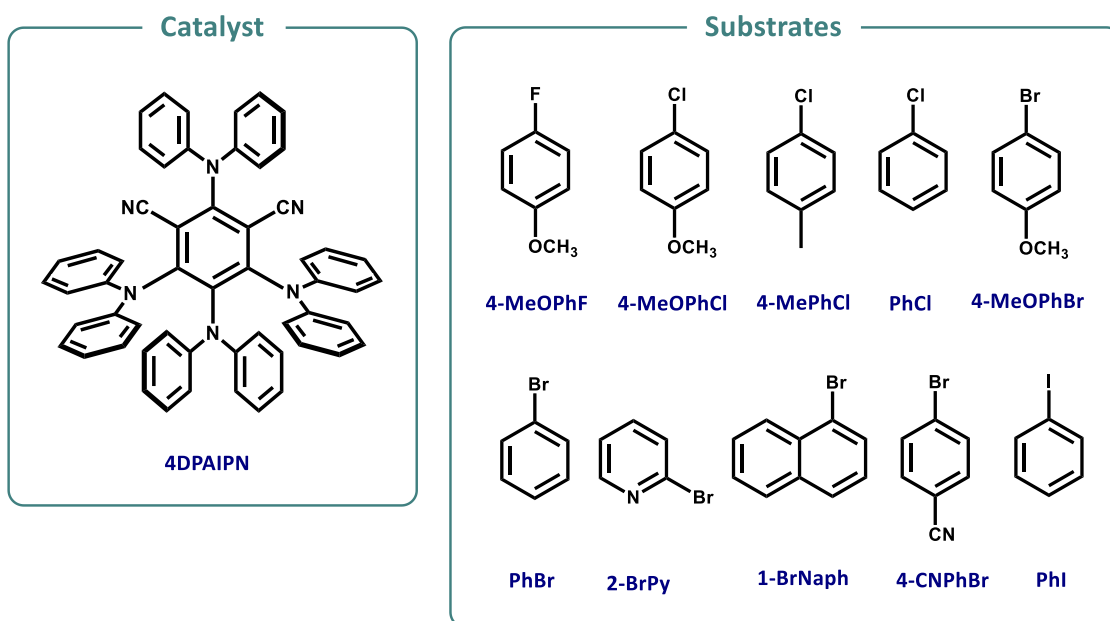


Figure 18. Structures of the catalyst and of the different aryl halides employed as substrates.

3.1.1. Electrochemical and photochemical characterization of 4DPAIPN

Cyanoarene-based donor-acceptor fluorophores are a well-established class of cost-effective, metal-free and easily accessible photoredox catalysts for organic synthesis, whose redox properties can be systematically modulated by altering the substitution pattern on the central benzene ring¹⁵⁵. Among commercial options, 4DPAIPN was selected for this study as it exhibits one of the most negative ground-state reduction potentials in this family. Since this catalyst has been predominantly applied in pure photochemical catalytic protocols, reports on its electrochemical activation in the literature are relatively scarce. Therefore, to establish the thermodynamic framework governing the investigated ePRC process, a rigorous electrochemical characterization of 4DPAIPN was first undertaken.

For this purpose, a series of CVs of 4DPAIPN were collected in dark conditions at different scan rates (Figure 19, solid lines). The DigiElch simulation software was then used to fit the experimental CV traces, providing superimposable simulated curves (Figure 19, hollow dots).

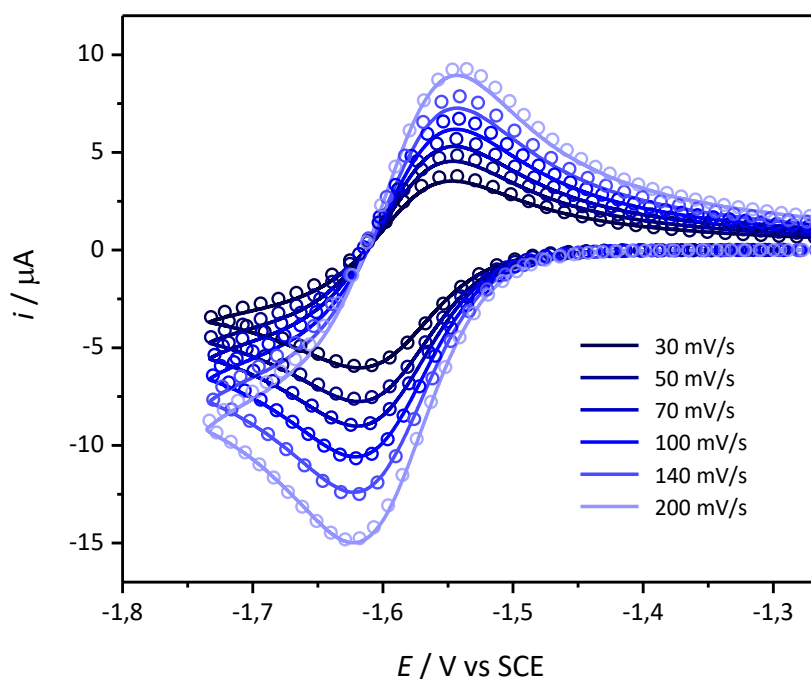


Figure 19. Experimental (solid lines) and fitted (hollow dots) CVs of 4DPAIPN at different scan rates.

The catalyst shows a single quasi-reversible wave, associated with the following heterogeneous electron transfer reaction:



By means of the simulation software, it was possible to obtain the standard reduction potential of the catalyst ($E^\circ_{4\text{DPAIPN}/4\text{DPAIPN}^{\bullet-}$), its diffusion coefficient (D) and the heterogeneous electron transfer constant between the WE and 4DPAIPN (k^0) (Table 1). The fitting procedure starts with the loading of experimental CV traces, followed by the input of a reaction scheme and known experimental parameters, such as concentrations, electrode surface area, scan rates and the electron transfer coefficient (α), here assumed to be 0.5. The software runs a global non-linear least-squares fitting routine, adjusting target variables until the simulated current-voltage curves match the experimental ones. The global fitting of more than one experimental CV aims to minimize random errors, thus yielding statistically more robust data.

Table 1. Relevant electrochemical constants for 4DPAIPN at 25°C.^a

Redox couple	E° (V vs SCE)	D (cm ² s ⁻¹)	k^0 (cm s ⁻¹)
4DPAIPN / 4DPAIPN ^{•-}	-1.57	$(3.46 \pm 0.11) \cdot 10^{-6}$	0.007

^a These constants can also be derived through traditional methods (i.e., the measurement of the half wave potential for E° , the Randles-Ševčík equation for D and the Nicholson method¹⁵⁶ for k^0). Digital simulations were employed for continuity with subsequent analyses.

As previously mentioned, a good electrophotocatalyst must be characterized by a significantly red-shifted UV-Vis absorption spectrum of its radical anion compared to that of the parent neutral species. Therefore, a photophysical characterization of both catalyst forms is required. 4DPAIPN^{•-} was generated by spectroelectrochemistry (see setup in the Experimental section) and several UV-Vis absorption spectra were collected over time under potentiostatic bulk electrolysis. The exact concentration of the reduced form in the cuvette is not known, as the reduction is not quantitative. Therefore, the radical anion spectrum (i.e., molar absorption coefficient (ϵ) as a function of the incident wavelength) was calculated through global fitting of the absorbance vs time data (see details in Appendix A). The UV-Vis spectra of the neutral and reduced forms are shown in Figure 20.

4DPAIPN^{•-} exhibits a pronounced red shift compared to its parent molecule, featuring a broad absorption band that peaks at 550 nm and spans from the green to the red regions. Hence, a 13 W 630 nm LED was chosen as the irradiation source, as its emission spectrum promotes the selective excitation of the radical anion. This setup allows the electrochemical and photochemical processes to operate independently, as required for efficient ePRC catalytic cycles.

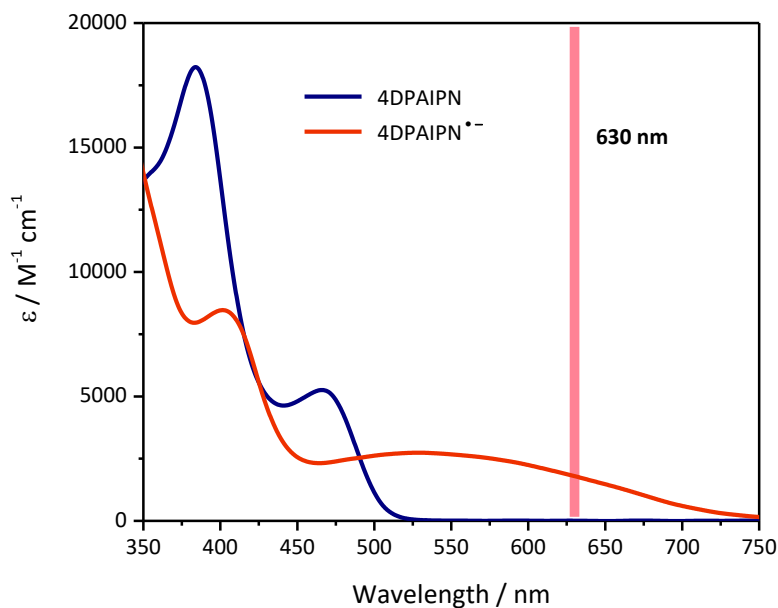


Figure 20. Experimental absorption spectrum of 4DPAIPN (blue trace) and calculated absorption spectrum of its radical anion (red trace) in DMF + 0.1 M TEATFB. The vertical straight line indicates the chosen incident light wavelength for all the following experiments, when not differently specified.

According to the computational absorption spectrum of 4DPAIPN^{•-} from the literature¹⁰⁷, the D₀ → D₁ transition can be associated with a quasi-dark state (i.e., too weak to be detected) in the infrared region, while the experimental broad absorption peak at 550 nm, corresponding well to the computed 533 nm peak¹⁰⁷, is attributed to the combined transitions from the D₀ state to the D₂-D₅ states.

Having established the standard reduction potential of 4DPAIPN and the absorption profile of the corresponding radical anion, the energetics of its excited state (4DPAIPN^{•-}*) can be quantified. The total energy gain of a general ePRC process can be calculated as the sum of the energies of the electron and of the photon injected into the catalyst. Accordingly, the standard reduction potential of 4DPAIPN^{•-} was computed through the following relationship:

$$E^{\circ}_{4\text{DPAIPN}/4\text{DPAIPN}^{\bullet-}} = E^{\circ}_{4\text{DPAIPN}/4\text{DPAIPN}^{\bullet-}} - E_{00} = E^{\circ}_{4\text{DPAIPN}/4\text{DPAIPN}^{\bullet-}} - \frac{\hbar c}{\lambda e_0} \quad (3.1.2)$$

where E_{00} is the electronic excitation energy (in eV), namely the energy associated to the electronic transition from the ground state to the specific excited state involved.

In turn, E_{00} is proportional to the wavelength at which the absorption and emission spectra intersect (λ), the proportionality constant depending on the reduced Planck constant ($\hbar$), the speed of light (c) and the elementary charge (e_0). Since 4DPAIPN^{•-} is not emissive, λ was estimated from the onset of the absorption peak, which was determined to be 730 nm (Figure 21a).

Using the onset wavelength in Equation 3.1.2 yielded $E_{00} = 1.70$ eV, corresponding to an open-shell excited state reduction potential of -3.27 V vs SCE (Figure 21b), comparable to that of Mes-Acr or DCA and slightly lower to that of NMI under blue-light irradiation (see Section 1.4.1).

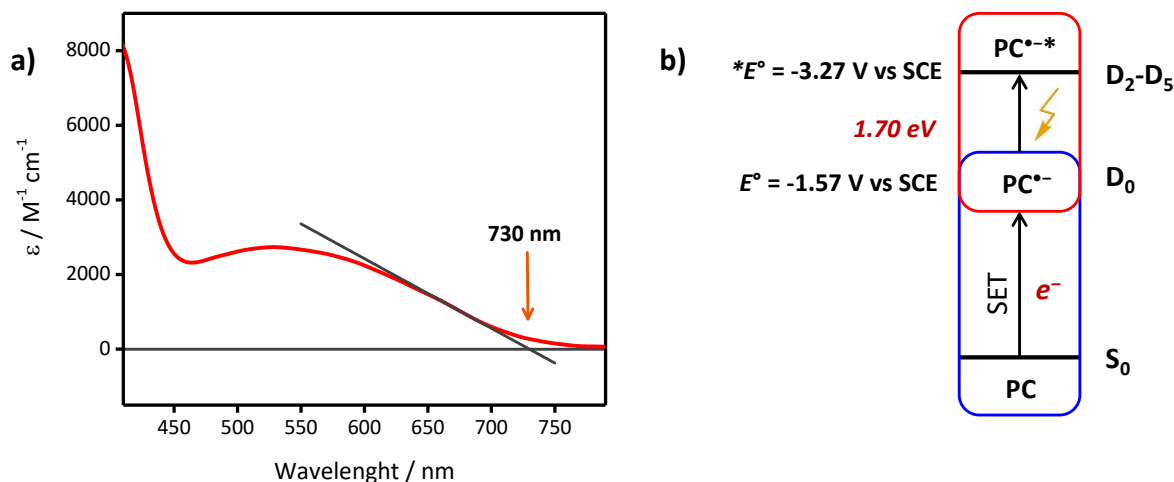


Figure 21. Estimation of the onset wavelength (a) and general energy scheme for the ePRC process (b).

After assessing the electrochemical system in the dark and selecting the excitation wavelength, CVs at different scan rates were collected under 630 nm light irradiation. The effect of local heating on CV traces is to cause an increase of the cathodic peak and a decrease of the anodic one (Figure 22).

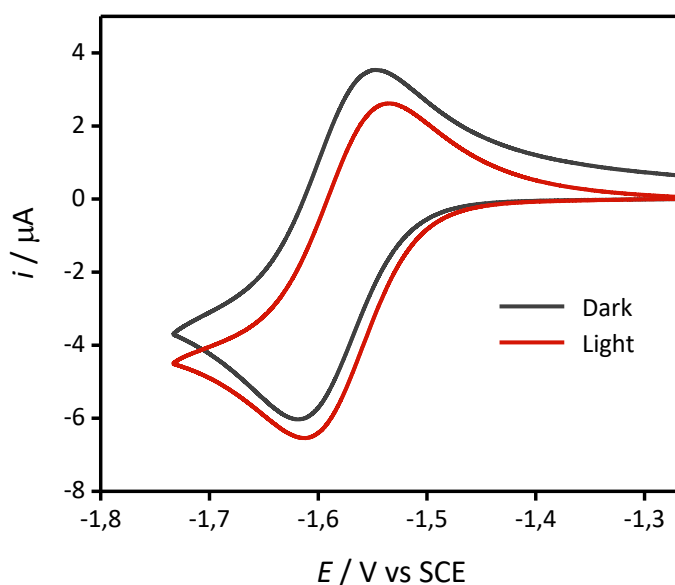


Figure 22. Effect of full power 630 nm light irradiation on the CV of 4DPAIPN (scan rate: 30 mV/s).

As discussed in Chapter 1.4.3, irradiating the WE surface causes local heating of the solution, giving rise to a convective contribution to mass transport. The effective temperature at the electrode surface, determined through calibration (see Appendix B for the detailed calibration procedure) was found to be of approximately 31°C. As a consequence of the convective contribution, a finite diffusion profile was assumed, where the maximum diffusion layer thickness (δ) is fixed.

Given the mathematical complexity of mixed diffusion/convection-controlled mass-transport regimes, the effect of light irradiation on CVs was modelled using the DigiElch simulation software (the complete fitting procedure under light irradiation is summarised in Appendix C). As shown in Figure 23, the best fit demonstrates excellent congruence with experimental data, proving the validity of the simulation procedure.

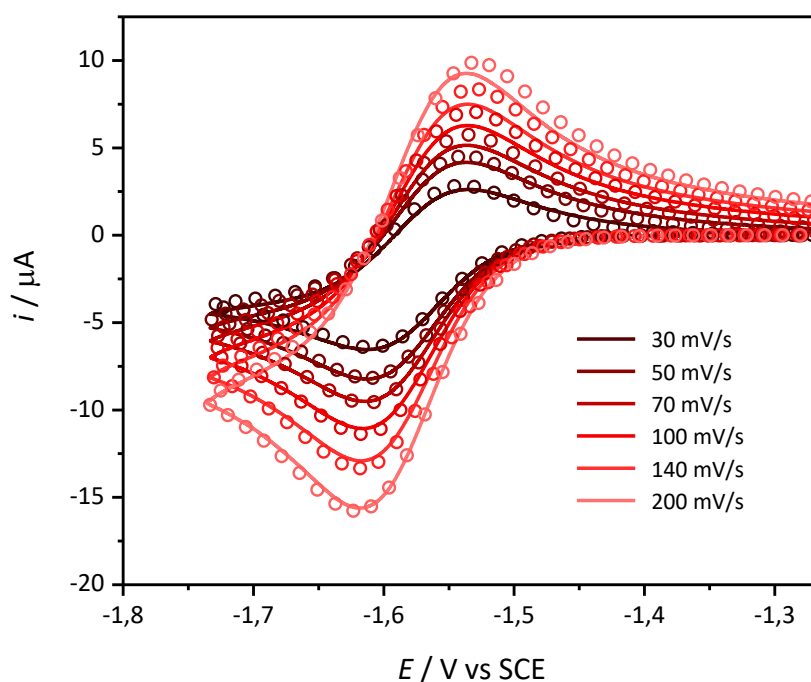


Figure 23. Experimental (solid lines) and fitted (hollow dots) CVs of 4DPAIPN under 630 nm light.

DigiElch returned an average diffusion coefficient under irradiation of $(4.00 \pm 0.13) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is approximately 16% higher than that measured in dark at 25°C. According to the Stokes-Einstein equation, this percentage shift in D aligns with a 6°C thermal increase in DMF, thereby confirming the reliability of the calibration-derived local temperature data.

3.1.2. Qualitative assessment of 4DPAIPN electrophotocatalytic activity

Once the electrochemical and photochemical properties of the catalyst were known, cyclic voltammetry was used as the primary analytical tool to evaluate the catalytic activity of 4DPAIPN toward various RX substrates. Introducing RX in the presence of light irradiation alters the CV profile, leading to a further increase in the cathodic current and decrease in the anodic one compared to the effect of light alone, thus indicating the occurrence of electrophotocatalysis (Figure 24).

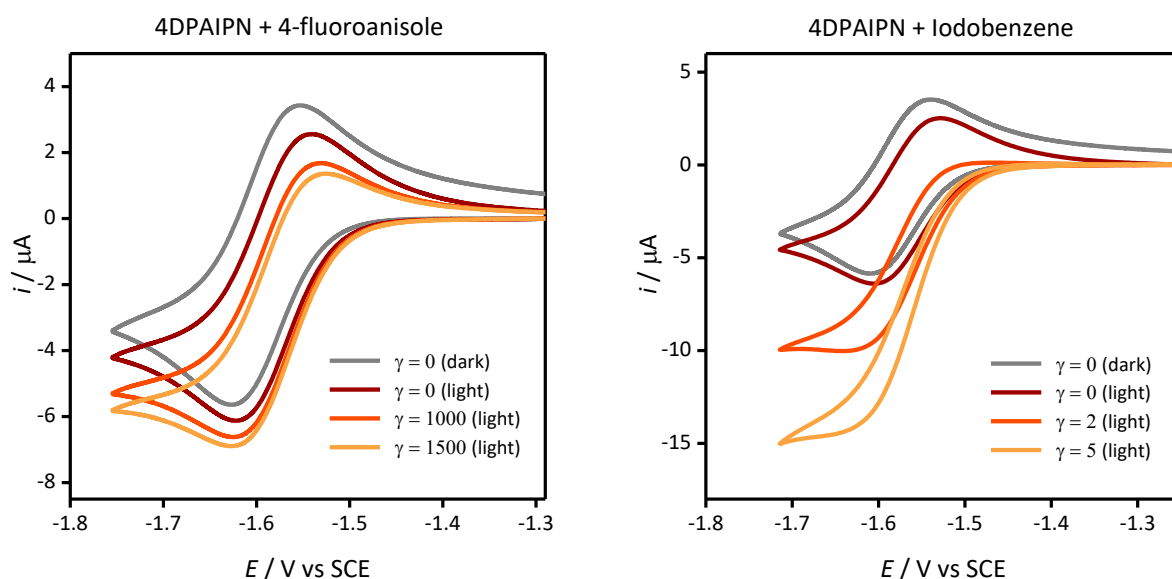


Figure 24. CVs of 4DPAIPN in dark, under 630 nm light without substrate and under 630 nm light in the presence of 4-fluoroanisole (left) and iodobenzene (right), at different substrate-to-catalyst ratios (γ). All the CVs were registered at a scan rate of 30 mV/s.

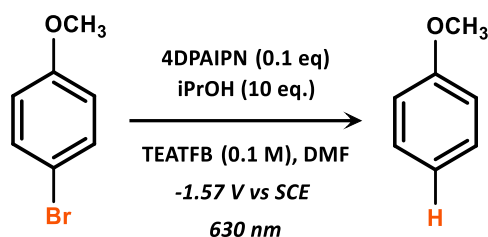
This current enhancement in the presence of substrate – commonly referred to as catalytic current – stems from a photochemical reaction following the electrochemical step: in this case, neutral DPAIPN is continually regenerated at the electrode, amplifying the cathodic wave (the detailed mechanism and the nature of the active catalyst species will be addressed in the following section).

The magnitude of the catalytic current depends primarily on the duration of the experiment, dictated by the scan rate (ν). At low scan rates, the chemical reaction has sufficient time to regenerate the electroactive species, resulting in a well-defined current response; conversely, at high scan rates, changes in the CV profile become negligible. Another key parameter is substrate excess (γ , defined as the ratio between the substrate and the catalyst concentrations). Higher γ values promote a greater number of catalytic cycles, yielding larger current enhancements at any given scan rate.

Furthermore, because the catalytic current extent at a given scan rate and RX excess is governed by the nature of the substrate itself – particularly, how readily it undergoes reductive cleavage – a qualitative evaluation of the substrate reactivity can be achieved by monitoring the γ needed to reach a specific current increase. For instance, Figure 24 compares the CVs of the most recalcitrant halide tested (4-fluoroanisole, left panel) with those of the most labile one (iodobenzene, right panel). While 4-fluoroanisole requires very high concentrations to display discernible catalytic currents, iodobenzene exhibits significant changes at near-stoichiometric amounts. It must be specified that iodobenzene, as well as other labile substrates, can also be slowly reduced by the ground state 4DPAIPN^{•-}. Such “dark” reactivity provides a minority, albeit non-negligible, background contribution to the total catalytic current, which is quantified in detail in Appendix D.

Overall, cyclic voltammetry experiments demonstrate that the active 4DPAIPN species – generated via electrochemical reduction followed by red-light photoexcitation – manages to reduce even unactivated aryl fluorides, such as 4-fluoroanisole, which features an extreme reduction potential, exceeding -3 V vs SCE¹⁵⁷. While this serves as a powerful and efficient proof of principle for the investigated ePRC protocol, CV provides only a transient and small-scale electrochemical assessment of the system. Because cyclic voltammetry experiments typically span a timescale of 10 to 60 seconds, they fail to capture preparative-scale challenges like long-term catalyst degradation or cumulative side reactions. Moreover, since CV is inherently limited to probing the rate determining step of the process (i.e., the DET reaction step), it cannot provide information on the reaction products or determine isolated chemical yields. Therefore, to bridge the gap between voltammetric studies and synthetic utility, preparative scale bulk electrolysis experiments were performed.

For this purpose, the reductive hydrogenation of 4-bromoanisole was chosen as the model reaction. This substrate features an intermediate standard reduction potential within the investigated RX scope ($E^\circ = -2.57$ V vs SCE). The reaction was performed in DMF (see Experimental section) to ensure consistency with CVs experimental conditions. The catalyst loading which provided the highest RX conversion was 10 mol% relative to the substrate, comparable to the typical loadings employed in similar ePRC protocols¹⁵⁸. A large excess of 2-propanol, which is both a good proton donor and hydrogen atom donor, was used to quench the resulting intermediate aryl radical or carbanion (depending on whether the radical is readily reduced by 4DPAIPN^{•-} or not). The electrolysis was conducted on RVC WE at constant potential ($E_{1/2}$ of 4DPAIPN); more negative potentials (e.g., $E_{1/2} - 60$ mV) resulted in lower conversions, likely due to excessive accumulation of the ground state radical anion. The optimized operating conditions are summarized in Scheme 13.



Scheme 13. Operative conditions for the ePRC-driven RX dehalogenation under red light.

The conversion of 4-bromoanisole into anisole was monitored over time via ^1H -NMR, based on the characteristic signals of the methoxy protons for both species (Figure 25).

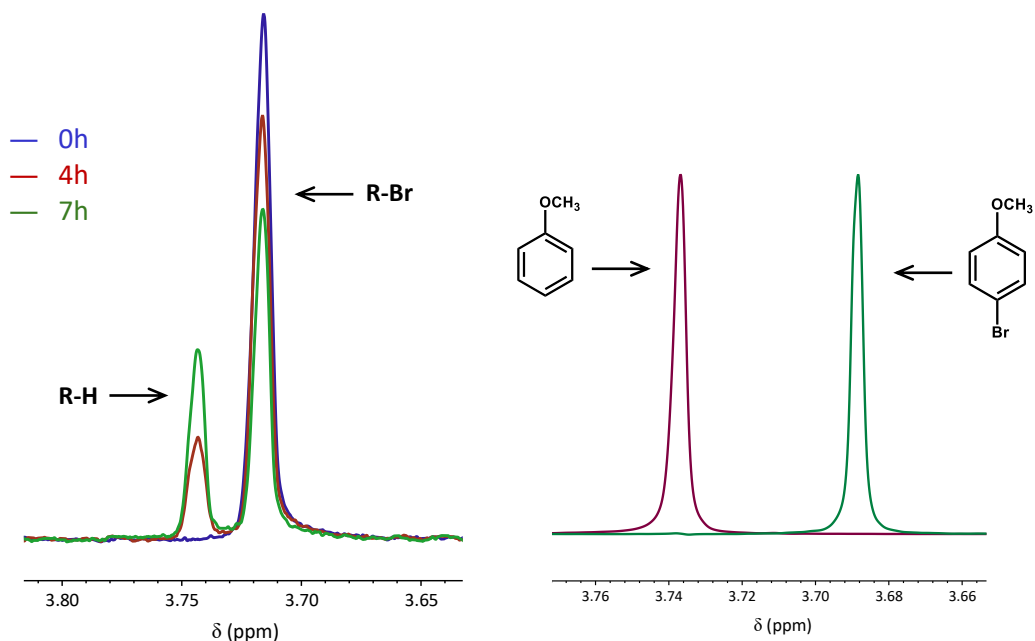
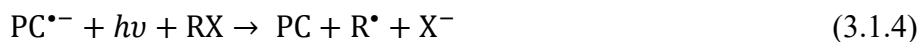


Figure 25. Zoom in the methoxy protons region of the ^1H -NMR spectrum of the reaction mixture as a function of time (left) and of pure 4-bromoanisole + pure anisole (right).

Taking advantages of the downfield shift of the methoxy signal upon converting the brominated substrate into the product, it was possible to monitor the depletion of the starting material and the concurrent formation of the product over time. After 7 hours of electrolysis, the 4-bromoanisole conversion – calculated as the ratio between the area of the anisole signal and the sum of the two areas of both species – reached 36.5%. Given that the conversion increased approximately linearly over time, no major catalyst deactivation pathways occurred over 7 hours.

The reaction proceeds according to the following simplified mechanism:



The first step is catalyst reduction, followed by light-assisted activation of the RX. Generally speaking, the downstream processes competing at expenses of the aryl radical ($\text{R}^\bullet$) resulting from DET are (i) its subsequent reduction by the ground-state reduced catalyst (Equation 3.1.5) and (ii) the coupling between the two open-shell species, leading to catalyst arylation (Equation 3.1.6)¹⁵⁹. The predominance of the former or the latter process dictates whether multiple catalyst turnover can occur.

From the potentiometry curve, it was calculated that the reaction required 2.1 F/mol, consistent with a bielectronic reduction of the RX. Therefore, $\text{R}^\bullet$ appears to be further reduced by ground-state $4\text{DPAIPN}^{\bullet-}$, consuming overall two electrons per RX molecule before final protonation by $i\text{PrOH}$. This preference for a bielectronic pathway with 4DPAIPN aligns with literature data, which place the standard reduction potential of the phenyl radical at approximately -1.25 V vs SCE in DMF¹⁶⁰, ca. 300 mV more positive than that of $4\text{DPAIPN}/4\text{DPAIPN}^{\bullet-}$.

Conversely, catalysts with lower ground-state reducing power (e.g., 4CzIPN or NMI) favour radical coupling, a trend consistent with CV data discussed below. This coupling is inherently detrimental, as it gradually degrades the catalyst's structural integrity and triggers deactivation pathways that hinder preparative-scale application. Ultimately, 4DPAIPN succeeds precisely because its strongly negative reduction potential effectively suppresses catalyst arylation in favour of cleaner downstream reductive turnover.

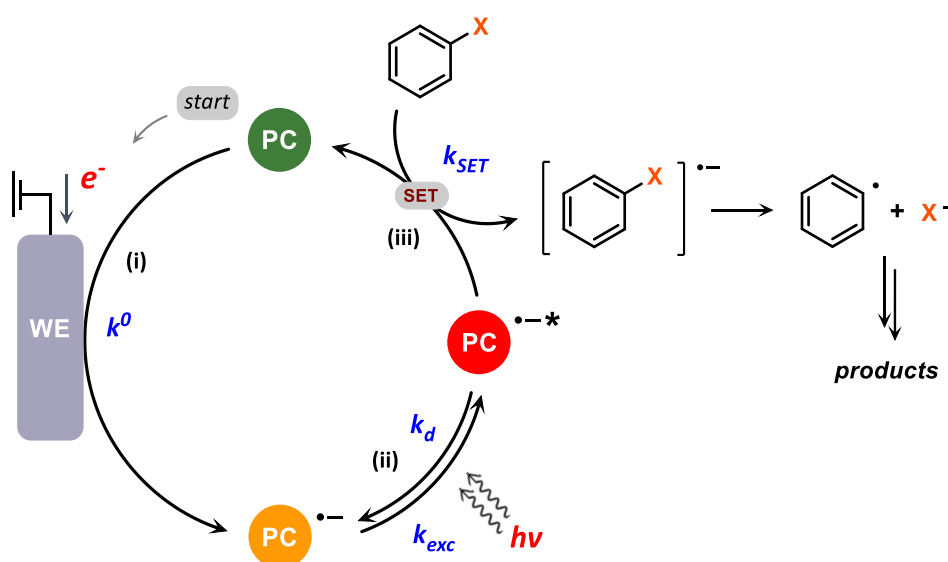
Despite these encouraging preliminary results, further studies are required to optimize the reaction setup and conditions, as well as to evaluate catalyst stability over longer timescales (i.e., the 24-48 hours typical of reductive cleavage protocols for challenging RX).

3.1.3. Quantitative insights into the electron transfer mechanism

Digital fitting of experimental CV profiles under electrophotocatalytic conditions is a powerful tool to extract quantitative kinetic information and mechanistic insights regarding the DET process. For quantitative CV analysis, first a large series of experimental CVs (ca. 30 individual traces) was recorded for different values of RX concentration and at different scan rates. This data collection procedure was repeated for all the investigated substrates reported in Figure 18. Second, a plausible reaction mechanism and the related known parameters were defined and used as input for the simulation software. Third, a global digital fitting of the entire CV set was performed for each substrate, in order to obtain optimized kinetic constants. The viability of a proposed mechanism can be evaluated from the degree of agreement between experimental and fitted CV traces, as well as from the physical significance of the obtained results.

Direct quenching of the open-shell excited state

First, the classical ePRC mechanism, involving the direct quenching of the excited state, was considered (Scheme 14). In this case, (i) 4DPAIPN is electrochemically reduced to the radical anion, (ii) 4DPAIPN^{•-} is excited under red light and (iii) the open-shell excited state species transfers the electron to the aryl halide in the turnover step, regenerating the neutral catalyst. The full mechanism and the kinetic constants implemented into the simulation software are listed in Table 2.



Scheme 14. Reaction scheme for the ePRC-driven RX cleavage via direct excited state quenching.

Table 2. Mechanism and fitting parameters for the direct bimolecular excited state quenching.

Reaction	Kinetic constant	Value
$\text{PC} + \text{e}^- \rightleftharpoons \text{PC}^{\bullet-}$	k^0	0.007 cm s^{-1}
$\text{PC}^{\bullet-} + h\nu \rightarrow \text{PC}^{\bullet--*}$	k_{exc}	14.07 s^{-1}
$\text{PC}^{\bullet--*} \rightarrow \text{PC}^{\bullet-}$	k_{d}	$3.333 \cdot 10^{12} \text{ s}^{-1}$
$\text{PC}^{\bullet--*} + \text{RX} \rightarrow \text{PC} + \text{R}^\bullet + \text{X}^-$	k_{SET}	<i>Fitted</i> ($\text{M}^{-1} \text{ s}^{-1}$)
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow \text{PC} + \text{R}^-$	k_{red}	$1.33 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$

For this and all next fitting routines, the following parameters were calculated or estimated as follows:

- (i) The RX diffusion coefficient was set to $(1.12 \pm 0.07) \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, representing the average across the investigated RX derivatives; individual diffusion coefficients were derived from empirical correlations on the basis of the molecular weight¹⁶¹.
- (ii) The excitation kinetic constant (k_{exc}) was calculated based on the LED photon flux and the molar absorption coefficient of the catalyst, as described in Appendix E.
- (iii) The sum of the kinetic constants for all excited-state decay processes equals the reciprocal of the excited state lifetime. For the excited states involved in the red-light transition (D₂-D₅), a lifetime of $\approx 300 \text{ fs}$ was used (i.e. $k_{\text{d}} = 3.33 \cdot 10^{12} \text{ s}^{-1}$), corresponding to the value measured via TAS for 4DPAIPN. Conversely, the D₁ level is longer-lived, (21 ps lifetime), but this is not relevant as it has insufficient energy to trigger any photochemical reactivity¹⁰⁷.
- (iv) The reduction rate (k_{red}) of the generated aryl radical ($\text{R}^\bullet$) by 4DPAIPN^{•-} (see Equation 3.1.3) was fixed at the diffusion limit in solution (k_{diff}), calculated as explained in Appendix F. Instead, radical-radical coupling (Equation 3.1.4) was neglected, as fitting sensitivity tests indicated that for 4DPAIPN this pathway accounts for less than 10% of the total $\text{R}^\bullet$ reactivity.
- (v) For the most labile RX – namely 1-bromonaphthalene, 4-bromobenzonitrile and iodobenzene – the background catalytic current arising from dark reactions and direct RX reduction at the WE was directly incorporated into the input mechanism (details in Appendix D).

Although the simulated CVs display an excellent fit with the experimental data (Figure 26), this mechanism is not physically plausible, since the k_{SET} values exceed the diffusion-controlled limit for a bimolecular reaction across nearly the entire substrate library ($1.2 \cdot 10^{10} - 1.3 \cdot 10^{13} \text{ M}^{-1} \text{ s}^{-1}$). Hence, direct electron transfer from 4DPAIPN^{•-} to RX cannot account for the observed catalytic current.

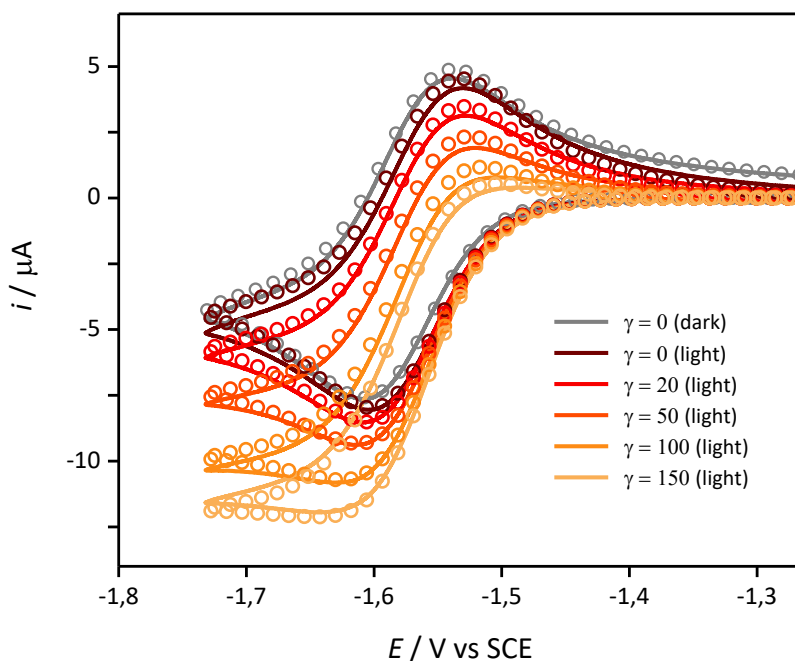


Figure 26. Solid lines: CVs of 4DPAIPN in dark, under 630 nm light, and under 630 nm light + 4-bromoanisole at different γ values. Hollow dots: fitted curves returned by the software for the model involving the direct bimolecular excited state quenching. Scan rate: 50 mV/s.

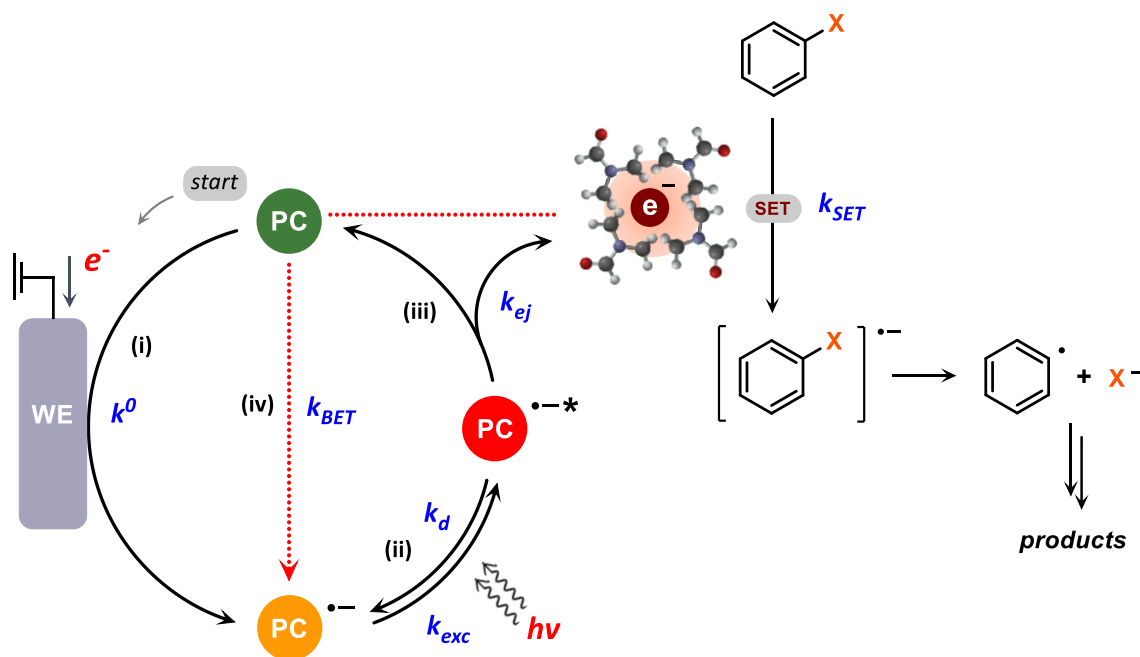
The infeasibility of anti-Kasha bimolecular reactivity from D₂-D₅ is not surprising, given the exceptionally short lifetimes involved, consistent with literature precedents concerning the general behaviour of excited open-shell species⁵⁸.

As highlighted in Chapter 1.4.4, various alternative mechanisms have been invoked to explain the catalytic activity of extremely short-lived super-reducing species. In the case of 4DPAIPN, catalyst-substrate preassembly can be ruled out, given that (i) no cathodic peak anticipation or complex voltametric signals have been observed and (ii) the catalytic activity persists even at remarkably low substrate concentrations (e.g. iodobenzene, Figure 24). Similarly, catalysis mediated by solvent reduction is highly unlikely, as no alteration in the CV profile occur upon light irradiation in the absence of substrate. Furthermore, no closed-shell or decomposition species of the catalyst were detected, even during slow CV scans or long spectroelectrochemistry measurements.

Altogether, these observations strongly support the mechanism proposed in 2024 by Ceroni and co-workers – namely, RX reductive cleavage mediated by solvated electrons ejected from 4DPAIPN^{•-}*, which currently stands as the most plausible reaction pathway.

Photo-ejection of long-lived free solvated electrons

Although CV paired with digital simulation cannot detect solvated electrons, it can indirectly probe the proposed reaction pathway (Scheme 15) based on the fit quality and on the physical significance of the extracted kinetic parameters. Table 3 summarizes the full mechanism for the free solvated electron model and the kinetic parameters chosen to fit experimental data.



Scheme 15. Reaction scheme for the ePRC-driven RX cleavage via photo-ejection of free solvated electrons.

Table 3. Mechanism and fitting parameters for the reactivity via free solvated electrons.

Reaction	Kinetic constant	Value
$\text{PC} + \text{e}^- \rightleftharpoons \text{PC}^{\bullet-}$	k^0	0.007 cm s^{-1}
$\text{PC}^{\bullet-} + h\nu \rightarrow \text{PC}^{\bullet-*}$	k_{exc}	14.07 s^{-1}
$\text{PC}^{\bullet-*} \rightarrow \text{PC}^{\bullet-}$	k_{d}	$2.67 \cdot 10^{12} \text{ s}^{-1}$
$\text{PC}^{\bullet-*} \rightarrow \text{PC} + \text{e}_{\text{solv.}}^-$	k_{ej}	$6.67 \cdot 10^{11} \text{ s}^{-1}$
$\text{e}_{\text{solv.}}^- + \text{RX} \rightarrow \text{R}^\bullet + \text{X}^-$	k_{SET}	<i>Fitted</i> ($\text{M}^{-1} \text{ s}^{-1}$)
$\text{e}_{\text{solv.}}^- + \text{PC} \rightarrow \text{PC}^{\bullet-}$	k_{BET}	$7.7 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow \text{PC} + \text{R}^-$	k_{red}	$1.33 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$

The proposed mechanism involves catalyst reduction (with rate constant k^0), excitation (k_{exc}), and ejection of a solvated electron (k_{ej}). Such electron, after solvation by DMF, can react either with a RX molecule (k_{SET}) or with a neutral 4DPAIPN molecule to regenerate the ground state radical anion (k_{BET}). The latter case – referred to as bimolecular back electron transfer (BET) – represents an unproductive pathway, leading to the wastage of an incident photon.

The quantum yield of electron photo-ejection (ϕ_{ej}), which represents the fraction of photoexcited catalyst molecules that undergo electron ejection relative to all deactivation pathways, is defined as:

$$\phi_{\text{ej}} = \frac{k_{\text{ej}}}{k_{\text{ej}} + k_{\text{d}}} \quad (3.1.7)$$

Hence, k_{d} and k_{ej} were estimated based on a 300 fs excited state lifetime and a 20% quantum yield of electron photo-ejection, as reported by Ceroni and co-workers¹⁰⁷. Given the large thermodynamic driving force for the bimolecular ET between the solvated electron and the neutral catalyst, the back electron transfer rate constant was set equal to the diffusion limit in solution (see Appendix F). Contrary to expectations, digital simulations incorporating solvated electrons as the actual reducing agents failed to match experimental CV profiles (Figure 27).

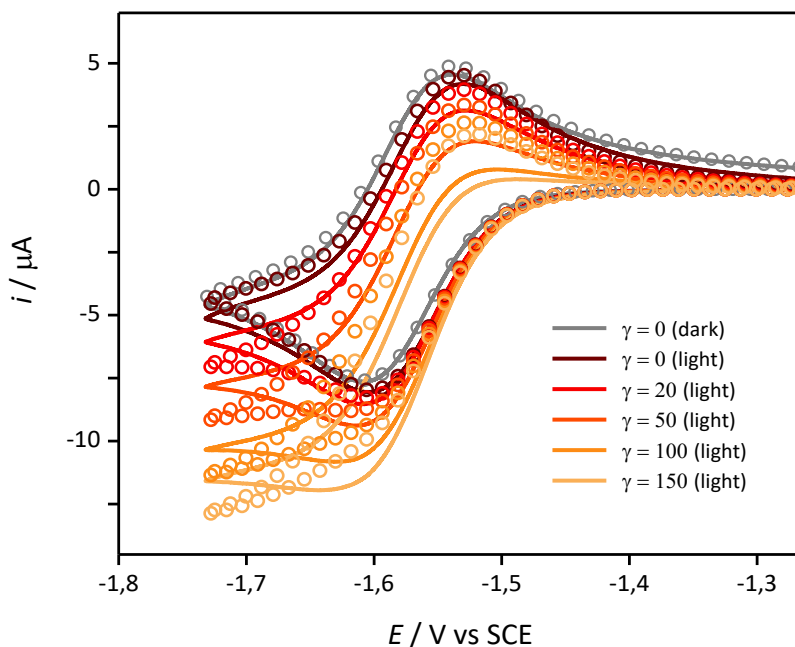
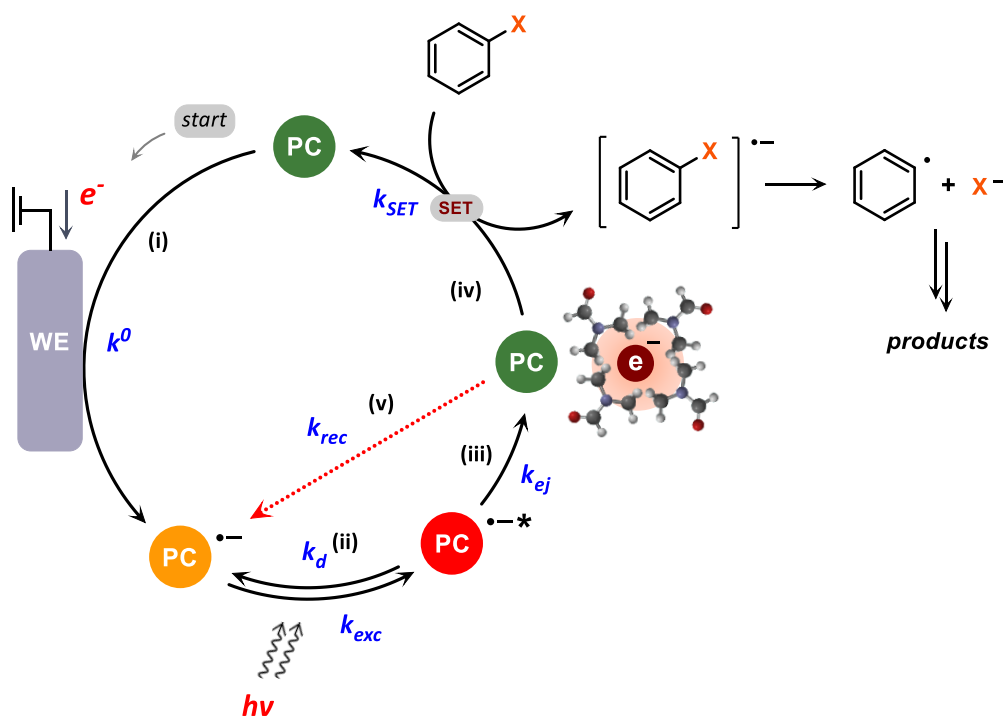


Figure 27. Solid lines: CVs of 4DPAIPN in dark, under 630 nm light, and under 630 nm light + 4-bromoanisole at different γ values. Hollow dots: fitted curves returned by the software for the model involving the photo-ejection of free solvated electrons (Table 3). Scan rate: 50 mV/s.

Furthermore, the optimization process forced k_{SET} values down to an unrealistically sluggish regime for a potent reductant such as the solvated electron ($10^5 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Therefore, the mechanism of electrophotocatalysis with electron ejection was revised as proposed in the next paragraph.

Revisited mechanism for the photo-ejection of “localized” solvated electrons

TAS data unequivocally demonstrate that cyanoarene-based radical anions eject solvated electrons through photoexcitation, and that such species are quenched upon substrate addition. To reconcile this apparent discrepancy between two complementary analytical techniques – ultrafast spectroscopy and cyclic voltammetry – a novel variant of the ePRC mechanism operating via “localized” solvated electrons is proposed here (Scheme 16).



Scheme 16. Reaction scheme for the ePRC-driven RX cleavage via localized solvated electrons.

Unlike the mechanism depicted in Scheme 15, the ejected electron was considered as remaining spatially confined in the immediate vicinity of the parent catalyst, rather than freely diffusing into the bulk solution. This spatial restriction does not stem from electrostatic forces holding neutral 4DPAIPN and the electron together; instead, it arises from kinetic constraints, because the solvated electron promptly either reacts with a proximal RX molecule or recombines with the parent catalyst before appreciable diffusion into the bulk can occur.

As a consequence, another key distinction between the proposed model and previous representations lies in the nature of the unproductive electron annihilation pathway: rather than relying on a diffusion-controlled, bimolecular BET, the recombination process is localized, and thus unimolecular in character, occurring via geminate recombination (rate constant k_{rec}). All reactions and rate constants implemented in the simulation software are listed in Table 4. To prevent a physically impossible continuous replenishment of the neutral catalyst following electron ejection, the two species are defined as a bound pair within the mechanism, despite the absence of physical attractive interactions.

Table 4. Mechanism and fitting parameters for the reactivity via localized solvated electrons.

Reaction	Kinetic constant	Value
$\text{PC} + \text{e}^- \rightleftharpoons \text{PC}^{\bullet-}$	k^0	0.007 cm s^{-1}
$\text{PC}^{\bullet-} + h\nu \rightarrow \text{PC}^{\bullet--*}$	k_{exc}	14.07 s^{-1}
$\text{PC}^{\bullet--*} \rightarrow \text{PC}^{\bullet-}$	k_{d}	$2.00 \cdot 10^{12} \text{ s}^{-1}$
$\text{PC}^{\bullet--*} \rightarrow \text{PC}^{\bullet\cdots}\text{e}_{\text{solv.}}^-$	k_{ej}	$1.33 \cdot 10^{12} \text{ s}^{-1}$
$\text{PC}^{\bullet\cdots}\text{e}_{\text{solv.}}^- + \text{RX} \rightarrow \text{PC} + \text{R}^\bullet + \text{X}^-$	k_{SET}	<i>Fitted</i> ($\text{M}^{-1} \text{ s}^{-1}$)
$\text{PC}^{\bullet\cdots}\text{e}_{\text{solv.}}^- \rightarrow \text{PC}^{\bullet-}$	k_{rec}	$9.174 \cdot 10^9 \text{ s}^{-1}$
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow \text{PC} + \text{R}^-$	k_{red}	$1.33 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$

When incorporated into the digital simulation software, this refined localized solvated electron model – which entails bimolecular catalyst turnover (rate constant k_{SET}) – accurately simulates the CV profiles experimentally observed (Figure 28, right). Simultaneously, it aligns with spectroscopic evidence and provides physically reasonable rate constants (i.e., close but below the diffusion limit) for all tested RX (see below).

By contrast, the reaction pathway initially tested (Table 3) entails unimolecular catalyst turnover – limited by the rate of electron ejection (rate constant k_{ej}) – which leaves a distinctive signature on the CV shape. The discrepancy between the two mechanisms rules out the free solvated electron pathway. In simulations, ejection of a free electron continuously recycles 4DPAIPN, suppressing the diffusion-controlled depletion layer at the electrode. This rapid turnover manifests as a steady-state cathodic plateau rather than a diffusional peak, accompanied by a large anodic reverse peak from accumulated reduced species (Figure 28, left). The total absence of these voltammetric signatures experimentally proves that this idealized free solvated electron pathway does not operate in the actual mechanism.

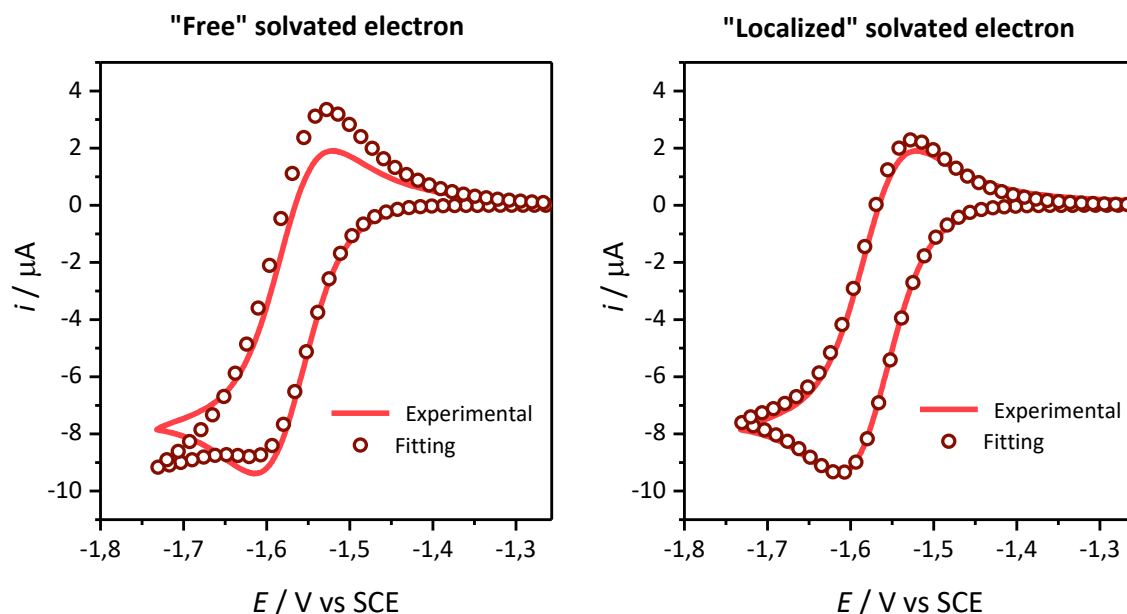


Figure 28. Comparison of the fitting results for the free solvated electron (left) and the localized solvated electron (right) models. Conditions: 4-bromoanisole, $\gamma = 50$, scan rate = 50 mV/s.

The assumption of the “spatial confinement”, proposed here to explain experimental CV profiles, aligns with Ceroni and co-workers’ finding that the ESA signal decay of the solvated electron follows a multiexponential function. More precisely, they state that the decay fitting features a rapid component (109 ps lifetime), which accounts for 55% of the total signal, and two longer-lived components, expanding into the nanosecond regime¹⁰⁷. Since no explicit explanation for such multiexponential decay was advanced, we propose to assign these components to two distinct “populations” of solvated electrons. The rapid component represents the solvated electron fraction that undergoes geminate (i.e., unimolecular) recombination with the parent 4DPAIPN molecule, whereas the long-lived component corresponds to electrons escaping into the bulk. In the highly dilute solutions ($[4\text{DPAIPN}] \approx 0$ M) characteristic of TAS experiments, these free electrons persist for nanoseconds until scavenged by unfavourable bimolecular BET or trace impurities (such as oxygen or moisture). Adding a substrate shortens the lifetime of both components, indicating that both species react with RX. Importantly, under our CV conditions, which better reflect preparative-scale parameters (higher PC and RX concentrations, non-anhydrous solvents), free solvated electrons are entirely suppressed, preventing their bulk accumulation in agreement with our proposed mechanism.

Building on this interpretation, the geminate recombination rate for the 4DPAIPN–electron pair (k_{rec}) was set to the inverse of the unimolecular decay time (109 ps), while the photo-ejection quantum yield (ϕ_{ej}) was set to 40%, as the prior 20% estimate considered only the long-lived component¹⁰⁷.

Evaluation of ET rate constants through simulations with the localized solvated electron model

Having established a robust mechanism and a suitable simulation protocol, the CV datasets for each tested RX substrate were fitted according to the parameters listed in Table 4. Table 5 presents a comprehensive overview of the performed electrophotocatalytic experiments and fitted k_{SET} values, which span 3 orders of magnitude.

Table 5. Experimental CV conditions and fitted k_{SET} values for the various tested substrates according to the localized solvated electron model. All E° data are taken from ref. ¹⁶², except when otherwise indicated.

SUBSTRATE	$E^\circ_{\text{RX/R}^\bullet+\text{X}^-}$ (V vs SCE)	Scan rates (mV/s)	γ	$\log(k_{\text{SET}})$ [M ⁻¹ s ⁻¹]
4-MeOPhF	< -3.00 ¹⁵⁷	20, 30, 50, 70, 100, 140	500, 1000, 1500, 2000	7.57
4-MeOPhCl	-2.90 ⁵⁹	30, 50, 70, 100, 140, 200	20, 50, 100, 200, 400	7.87
4-MePhCl	-2.85 ⁷⁵	30, 50, 70, 100, 140, 200	20, 50, 100, 200, 400	8.42
PhCl	-2.76	30, 50, 70, 100, 140, 200, 300	100, 200, 400, 600, 1000, 1400, 1800, 2600	8.60
4-MeOPhBr	-2.57 ^a	30, 50, 70, 100, 140, 200	5, 10, 20, 50, 100, 150	9.29
PhBr	-2.43	30, 50, 70, 100, 140, 200	2, 5, 10, 20, 50	9.48
		30, 50, 70, 100, 140, 200	5, 10, 20	9.41
2-BrPy	-2.26	30, 50, 70, 100, 140, 200	2, 5, 10, 15	10.05
1-BrNaph ^b	-2.17	30, 50, 70, 100, 140, 200	1, 2, 5, 10, 15	10.15
4-CNPhBr ^b	-1.94	30, 50, 70, 100, 140, 200	0.5, 1, 2	10.44
PhI ^b	-1.91	30, 50, 70, 100, 140, 200	2, 5	10.61
		30, 50, 70, 100, 140, 200	2, 4	10.57

^a Estimated as follows: a β parameter, defined as the shift in E° due to the methoxy moiety in para position, is determined using the E° data of 4-MeOPhCl and PhCl. Given the structural similarities between aryl chlorides and bromides, the same β value has been used to calculate the E° of 4-MeOPhBr knowing that of PhBr.

^b Dark reactivity subtracted as explained in Appendix D.

The high quality of the fit achieved with the localized solvated electron model is exemplified in Figure 29, which demonstrates that a single k_{SET} value successfully reproduces the entire set of experimental CVs for a given substrate.

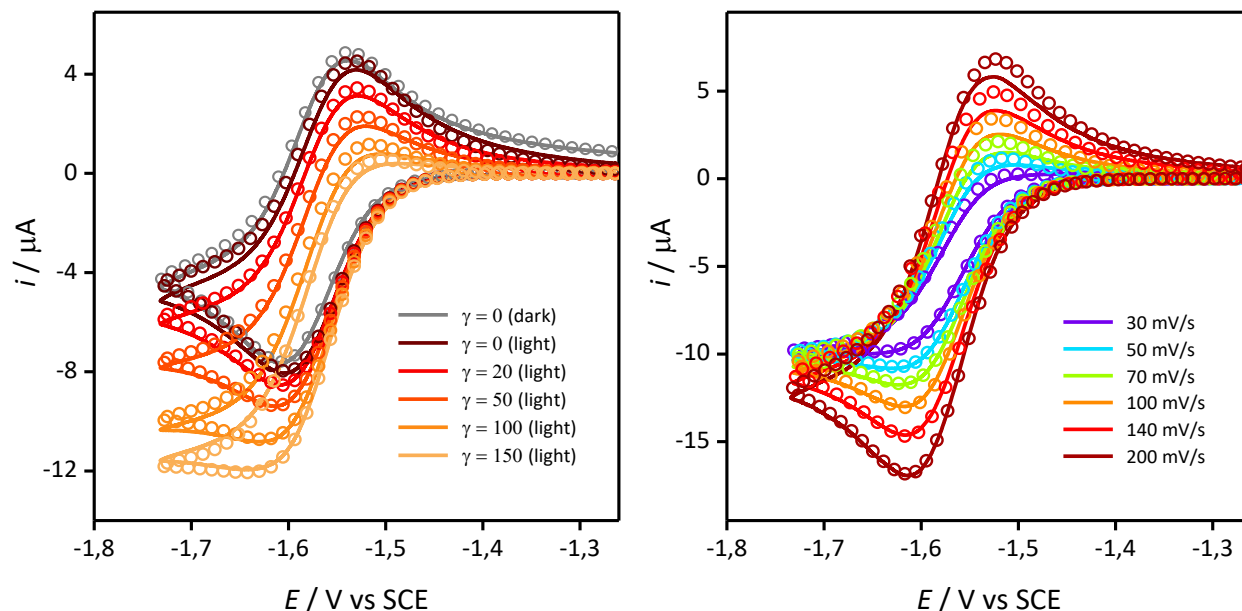


Figure 29. Global fitting of 4DPAIPN CVs using the localized solvated electron model. Substrate: 4-bromoanisole. Left: increasing substrate excess and fixed scan rate (50 mV/s); Right: different scan rates and fixed substrate excess ($\gamma = 100$). Solid lines: experimental voltammograms. Hollow dots: fitted curves.

For PhBr and PhI substrates, duplicate experiments were performed to verify experimental repeatability. The extracted k_{SET} data remained within a narrow range of ca. 0.1 log units, indicating that the electrophotocatalytic CV analysis is highly reliable and reproducible.

To further validate the proposed model, a series of control experiments were conducted (Table 6).

Table 6. Control experiments: effect of catalyst concentration, irradiation wavelength and solvent.

Substrate	Variations	$\log(k_{\text{SET}})$ ($\text{M}^{-1} \text{s}^{-1}$)
4-MeOPhBr	None	9.29
4-MeOPhBr	0.5 mM 4DPAIPN	9.09
4-MeOPhBr	1.5 mM 4DPAIPN	9.11
4-MeOPhBr	595 nm light	9.38
PhCl	None	8.60
PhCl	MeCN as solvent	8.49

If a free solvated electron were assumed, the catalytic activity would diminish when rising 4DPAIPN concentration, due to increasingly favourable unproductive BET. Conversely, in the case of a true geminate recombination model (i.e. localized solvated electron), the rate constant should remain invariant with respect to 4DPAIPN concentration. The results in Table 4 validate this second scenario: $\log(k_{\text{SET}})$ shows no significant concentration dependence, remaining virtually unchanged when moving from 0.5 mM to 1.5 mM 4DPAIPN, instead of showing a clear descending trend. A slight increase in the incident light energy (595 nm instead of 630 nm), which potentially leads to more energetic electrons, reproduced both the wave shape and the ET rate constant within the experimental error (mainly associated with the estimation of k_{exc}). This suggests that the reaction mechanism remains unchanged. Furthermore, a control experiment replacing DMF with MeCN (thus matching TAS solvent conditions) yielded nearly identical CV profiles, as well as a similar k_{SET} value, confirming that even in MeCN, ejected electrons are scavenged prior to bulk diffusion.

Finally, experimental 4DPAIPN CVs recorded with extremely high RX (chlorobenzene) concentrations revealed that the catalytic current increases indefinitely without reaching a plateau (Figure 30). Typically, a plateau arises when homogeneous electron transfer to RX is fast enough to immediately scavenge every ejected electron. In the system investigated here, this condition would require $k_{\text{SET}}[\text{RX}] \gg k_{\text{rec}}$. The absence of such a plateau is fully consistent with a picosecond lifetime of the localized solvated electron: even when k_{SET} is close to the diffusion limit, the ET rate cannot surpass the geminate recombination rate at realistic [RX] values, consistent with the proposed model.

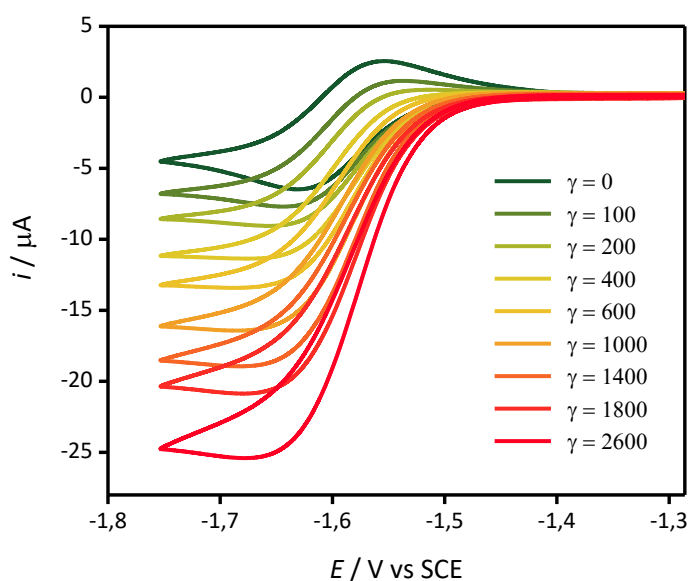


Figure 30. CVs of 4DPAIPN + PhCl at extremely high substrate concentrations. Scan rate: 30 mV/s.

3.1.4. Thermodynamic and kinetic correlation: a Marcus theory approach

Digital fitting of experimental voltammograms reveals a clear signature of Marcus-type behaviour: the extracted ET rate constants (Table 5) increase predictably with the thermodynamic driving force (i.e., the less negative substrate's standard reduction potential). Notably, such Marcus-type activation control is not universal for solvated electrons: reactions of the hydrated electron in water have been reported to exhibit anomalously similar activation energies across a range of substrates, a behaviour incompatible with Marcus theory¹⁶³. We can clearly conclude that the activation of RX substrates by 4DPAIPN^{•-} is an activated process and not a diffusion limited process.

Extending in a quantitative way Marcus' formalism to an unconventional reducing agent such as the solvated electron is not straightforward, and requires addressing some fundamental assumptions originally raised by Marcus himself^{164,165}. First, the electronic wavefunction of a solvated electron is spread over several solvent molecules and is very sensitive to orientation fluctuation of those molecules. As a consequence, the electronic coupling matrix element (H_{DA}) is large, resulting in adiabatic ET regime. Second, the solvated electron “vanishes” into the acceptor molecule, so that there is a change in the number of reacting particles. Nevertheless, a semi-classical treatment remains valid, provided that the peculiar features of the solvated electron are properly taken into account. The DET reactions investigated in this thesis are treated within the framework Savéant developed by extending Marcus-Hush theory, originally formulated for outer-sphere electron transfer (OSET), to the case of electron transfer accompanied by bond cleavage.

The activation energy ($\Delta G^\ddagger$) for a reaction between a generic electron donor and an aryl halide substrate is related to the driving force by the Marcus-Agmon-Levine equation¹⁶⁶:

$$\Delta G^\ddagger = \Delta G^\circ_{ET} + \frac{\Delta G_0^\ddagger}{\ln(2)} \cdot \ln \left[1 + \exp \left(-\ln(2) \cdot \frac{\Delta G^\circ_{ET}}{\Delta G_0^\ddagger} \right) \right] \quad (3.1.7)$$

where ΔG°_{ET} is the Gibbs free energy of the reaction and $\Delta G_0^\ddagger$ is the intrinsic kinetic barrier to electron transfer, defined as the activation free energy in isoergonic conditions (i.e., $\Delta G^\circ_{ET} = 0$).

In turn, $\Delta G_0^\ddagger$ is a function of solvent reorganization energy (λ_o) and inner reorganization energy (λ_i):

$$\Delta G_0^\ddagger = \frac{\lambda_i + \lambda_o}{4} \quad (3.1.8)$$

Unlike many conventional electron transfers, typical reactions involving the solvated electron are diffusion controlled, precluding access to the Marcus inverted region predicted by Equation 1.4.2.

Experimentally, this manifests as a rate constant that plateaus at the diffusion limit for large driving forces, a classic behaviour famously described by Rehm and Weller¹⁶⁷. Implementing the diffusion limitation into the general rate expression (Equation 1.4.1) and explicating $\Delta G^\ddagger$ according to Equation 3.1.7 leads to the following composite relationship⁷⁷:

$$k_{\text{SET}} = \frac{k_{\text{diff}}}{1 + \frac{k_{\text{diff}}}{K_A \kappa v_n} \exp \left(\frac{\Delta G^\circ_{\text{ET}} + \frac{\Delta G_0^\ddagger}{\ln(2)} \ln \left[1 + \exp \left(-\ln(2) \frac{\Delta G^\circ_{\text{ET}}}{\Delta G_0^\ddagger} \right) \right]}{RT} \right) + \exp \left(\frac{\Delta G^\circ_{\text{ET}}}{RT} \right)} \quad (3.1.9)$$

in which k_{diff} is the diffusion-limited reaction rate, calculated as described in Appendix F.

The equilibrium constant for the formation of the encounter complex (K_A), is given by (r in m):

$$K_A = 4/3 \pi N_A \cdot (r_{e^-} + r_{\text{RX}})^3 \cdot 1000 \quad (3.1.10)$$

Given the adiabatic character established above – which implies $\kappa \approx 1$ – the nuclear frequency factor (v_n) cannot be taken as a kinetic bimolecular collision frequency. Instead, because barrier crossing in the adiabatic limit requires the collective reorientation of the surrounding solvent dipoles around the transferring charge, v_n is dictated by the dynamics of solvent polarization relaxation itself^{168–170}:

$$v_n \approx \tau_L^{-1} = [\tau_D \cdot (\varepsilon_\infty / \varepsilon_0)]^{-1} \quad (3.1.11)$$

where τ_L is the longitudinal dielectric relaxation time of DMF, τ_D is the Debye relaxation time of DMF, ε_0 is the static dielectric constant and ε_∞ is the optical (high-frequency) dielectric constant. Equation 3.1.11 must be considered just a rough estimate of v_n , as a more precise calculation would require knowing the specific geometry of the energy barrier.

The solvent reorganization energy (λ_i) can be determined from the following semi-empirical law¹⁷¹:

$$\lambda_0 = 414 \text{ [kJ mol}^{-1} \text{ \AA]} \cdot \left(\frac{1}{2r_{e^-}} + \frac{1}{2r} - \frac{1}{r_{e^-} + r} \right) \quad (3.1.12)$$

$$r = \frac{(2r_{\text{RX}} - r_{\text{X}})r_{\text{X}}}{r_{\text{RX}}} \quad (3.1.13)$$

Finally, $\Delta G^\circ_{\text{ET}}$ can be expressed as a function of the standard reduction potential of the substrate:

$$\Delta G^\circ_{\text{ET}} = F(E^\circ_{e^-} - E^\circ_{\text{RX/R}^\bullet + \text{X}^-}) \quad (3.1.14)$$

The known parameters entering Equation 3.1.9 are listed in Table 7. Two remain unknown: the standard reduction potential of the solvated electron in DMF (E°_{e-}) and the inner reorganization energy λ_i . Since λ_i cannot be estimated a priori, neither can the intrinsic barrier $\Delta G_0^\ddagger$.

Table 7. Calculated values for relevant parameters used in Marcus analysis.

k_{diff} ($\text{M}^{-1} \text{s}^{-1}$) ^a	K_A ($\text{M}^{-1} \text{s}^{-1}$) ^a	τ_D (ps)	τ_L (ps) ^b	v_n (s^{-1})	r ($\text{\AA}$) ^c	λ_0 (kJ/mol) ^a
$5.03 \cdot 10^{10}$	0.783	13.2	1.5	$6.67 \cdot 10^{11}$	2.82	69.4

^a The solvated electron radius was estimated as in Appendix F.

^b Calculated via Equation 3.1.11 using $\epsilon_0 = 38.37$; $\epsilon_\infty = 4.36$; $\tau_D = 13.2 \text{ ps}$ ^{172,173}.

^c Calculated via Equation 3.1.13 using $r_{\text{Cl}} = 1.81 \text{ \AA}$; $r_{\text{Br}} = 1.96 \text{ \AA}$ and $r_{\text{I}} = 2.20 \text{ \AA}$ ¹⁷⁴.

With experimental k_{SET} data available for all substrates tested, $\log(k_{\text{SET}})$ values were plotted against the thermodynamic driving force of the reaction, here expressed as the standard reduction potential of each RX (see Equation 3.1.14), yielding the experimental “Marcus plot” (Figure 31). Fitting these experimental points, which span over 1 V in driving force and 3 orders of magnitude in k_{SET} , with the Savéant-modified Marcus-Hush model developed in this section – Equation 3.1.9, populated with the parameters of Table 7 – allowed the two remaining unknowns (i.e., $\Delta G_0^\ddagger$ and E°_{e-}) to be extracted as $\Delta G_0^\ddagger = 41 \pm 5 \text{ kJ/mol}$ and $E^\circ_{e-} = -3.37 \pm 0.17 \text{ V vs SCE}$.

This values of $\Delta G_0^\ddagger$ is fairly large, which is consistent with this electron transfer process, as both the internal and external reorganization energies are expected to be substantial. The external reorganization energy depends explicitly on the donor radius (Eq. 3.1.12). Specifically, a smaller donor generates a stronger local electric field, thus demanding greater energy to reorganize the surrounding solvent dipoles. Consequently, the comparatively small size of the solvated electron relative to conventional organic mediators suggests a higher value here. Similarly, the internal reorganization energy is also expected to be quite large due to substantial stretching and weakening of the R–X bond upon electron transfer¹⁶².

The extracted E°_{e-} is of the same order of magnitude as the well-established value for the hydrated electron (-2.88 V vs. NHE ¹⁷⁵, i.e., $\approx -3.12 \text{ V vs SCE}$), though somewhat more negative, consistent with weaker stabilization of the electron in aprotic DMF relative to water, where hydrogen bonding provides additional stabilization and thus lowers the reducing power. However, E°_{e-} is even more negative than the standard reduction potential of 4DPAIPN^{•*} (-3.27 V vs SCE); this apparent physical inconsistency will be addressed in the following section.

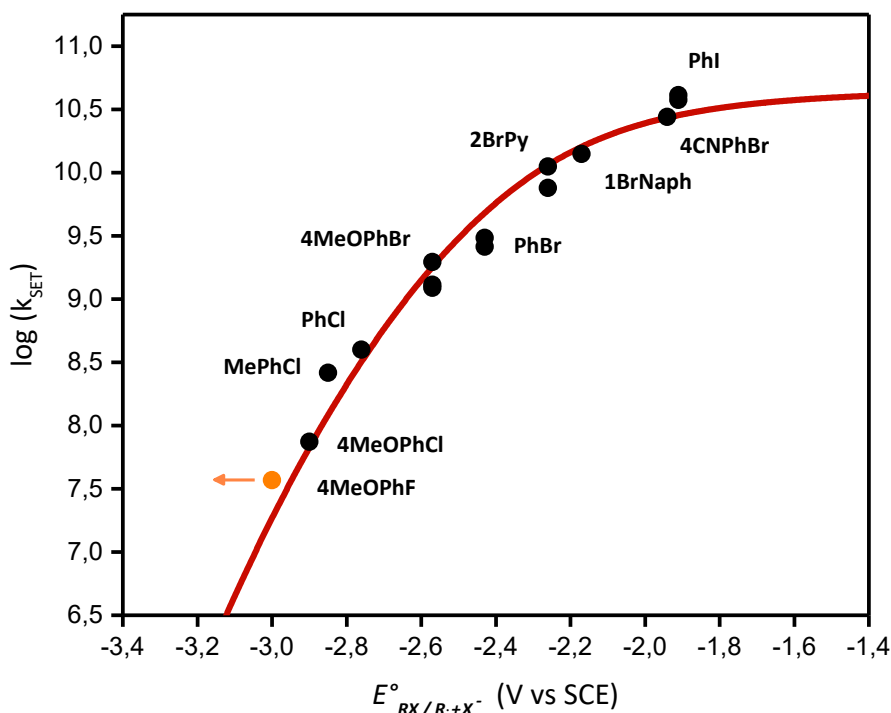


Figure 31. Marcus plot correlating $\log(k_{\text{SET}})$ values with the standard reduction potential of various RX . Black dots: experimental points (taken from Table 5); solid line: fitting curve obtained for $\Delta G_0^\ddagger$ fixed at 41 kJ/mol, corresponding to the central value of the optimal fitting quality range. 4-fluoroanisole (yellow dot) was not included in the fitting due to the uncertainty in its redox potential.

It should be stressed that the extracted E°_{e-} is necessarily approximate, resting on several simplifying assumptions as well as uncertainties in the photophysical parameters of 4DPAIPN, particularly the quantum yield of electron photo-detachment and the lifetime of the solvated electron itself.

Further approximations affect the fitting parameters of Equation 3.1.9, such as ν_n and k_{diff} . The latter, in particular, is likely underestimated if calculated following the classical hard-sphere formalism (Equation F.1), since the electronic wavefunction of the solvated electron extends beyond its cavity boundary, allowing SET to proceed via tunnelling before physical contact is reached^{176,177}.

3.1.5. Towards a comprehensive model for electron ejection dynamics

Building on the mechanistic insights drawn from digital CV simulations and Marcus analysis, a broader rationale is now proposed for the dynamics of solvated electron generation by organic super-reductant photocatalysts. Promotion of 4DPAIPN^{•-} to the D₂–D₅ excited states by red light absorption populates excited vibrational levels according to the Franck-Condon progression, which governs the

vertical nature of the electronic transition. Because electron photo-detachment is fast enough to compete with ultrafast (femtosecond) internal conversion, it may occur before vibrational relaxation can take place, meaning the electron is ejected from a vibrationally excited state. The resulting species is termed a "*hot photoelectron*": an electron ejected with excess vibrational energy, prior to any equilibration with the solvent^{178,179}. Its reduction potential (E°) corresponds to the vertical transition energy and thus can be estimated by combining the ground state E° (−1.57 V vs SCE) with the energy of a 630 nm photon (1.99 eV), yielding $E^\circ \approx -3.54$ V vs SCE. This value exceeds that of the adiabatic excited state ($E^\circ_{4\text{DPAIPN}/4\text{DPAIPN}^{*-}} = -3.27$ V vs SCE, calculated from Equation 3.1.2), as it also accounts for this additional vibrational energy.

Upon ejection into the bulk solution, the hot electron undergoes a sequence of inelastic collisions with the surrounding solvent molecules, progressively losing its kinetic energy to the medium's translational, rotational, and vibrational degrees of freedom. This process – usually referred to as thermalization – continues until the electron reaches thermal equilibrium with the solvent and becomes trapped in a transient, “pre-solvated” state. Full solvation then follows, as the surrounding solvent dipoles reorganize around the trapped charge, on a timescale comparable to the longitudinal relaxation time of the solvent (τ_L). This sequence of events is consistent with the TAS spectrum of Figure 9a, where the earliest ESA traces, distinct from those recorded at longer delay times, likely identify this pre-solvated state.

Because thermalization proceeds stochastically via a random-walk rather than with a ballistic trajectory, the thermalization length – i.e., the spatial separation between the sites of electron ejection and thermalization – is best described as a statistical distribution of distances. Nonetheless, the average value is expected to increase, to a first approximation, with the electron's initial kinetic energy, as more energetic electrons undergo more scattering events before reaching thermal equilibrium with the solvent.

Given that the fully solvated electron in DMF always relaxes to the same final energy, regardless of the nature of the photocatalyst, the energy gap between the hot electron and this common endpoint – i.e., the excess energy to be dissipated during thermalization – depends directly on the catalyst's reducing power: electrons generated from stronger reducing excited states carry more excess kinetic energy, and are thus expected to thermalize farther from their parent catalyst. This separation distance is mechanistically significant, as longer thermalization lengths are expected to suppress geminate recombination, favouring the escape into the bulk of free solvated electrons^{180,181}.

As discussed extensively in Section 3.1.3, experimental CV data and digital simulations show that the 4DPAIPN-derived solvated electron is consumed almost immediately after generation, either by reaction with a nearby substrate molecule or by geminate recombination with the neutral 4DPAIPN formed upon its ejection, well before it can diffuse appreciably into the bulk.

This behaviour aligns with the solvation dynamics discussed above: for 4DPAIPN under 630 nm irradiation, the hot electron's excess energy relative to E° of the solvated electron is expected to be small, so that thermalization occurs, on average, close to the parent species. As a result, the catalytic activity is inherently limited, since SET to the substrate must compete with unimolecular, geminate recombination occurring on a picosecond timescale.

As a further test of the proposed picture, the same CV fitting routine in the presence of RX substrate was extended to two additional catalysts capable of electron photo-detachment: 4CzIPN under green light and NMI under blue light, chosen to probe opposite ends of the excess kinetic energy range.

4CzIPN, despite being structurally similar to 4DPAIPN, is characterized by a less reducing ground state E° (-1.20 V vs SCE, calculated as the half-wave potential). However, excitation at a more energetic wavelength (525 nm vs 630 nm) perfectly compensates for this difference, generating a hot photoelectron with an essentially identical reduction potential ($E^\circ \approx -3.56$ V vs SCE) to that ejected from 4DPAIPN $^{*-}$. Indeed, experimental CVs of 4CzIPN with increasing RX excess are very similar to those of 4DPAIPN, and remain best described by a bimolecular mechanism (see Appendix G), whereas the free solvated electron model again fails to reproduce the experimental data.

NMI, by contrast, possesses a comparable ground state reduction potential to that of 4CzIPN (-1.23 V vs SCE), but 440 nm light excitation generates a considerably more energetic hot photoelectron ($E^\circ \approx -4.05$ V vs SCE). This larger excess energy is expected to result in a longer thermalization length and, consequently, a higher quantum yield of true free solvated electrons. Electrons that escape geminate recombination decay only through bimolecular back electron transfer, a comparatively slow, diffusion-controlled process at the low photocatalyst concentrations employed here ($\leq 10^{-3}$ M), and should therefore remain available for substrate reduction over a much longer timeframe, enhancing catalytic activity.

This perfectly aligns with experimental data (Figure 32): NMI generates a substantially higher catalytic current compared to 4DPAIPN for CVs recorded under the same conditions (comparable excitation rate constants, 4-chlorotoluene $\gamma = 50$ as substrate, 30 mV/s scan rate).

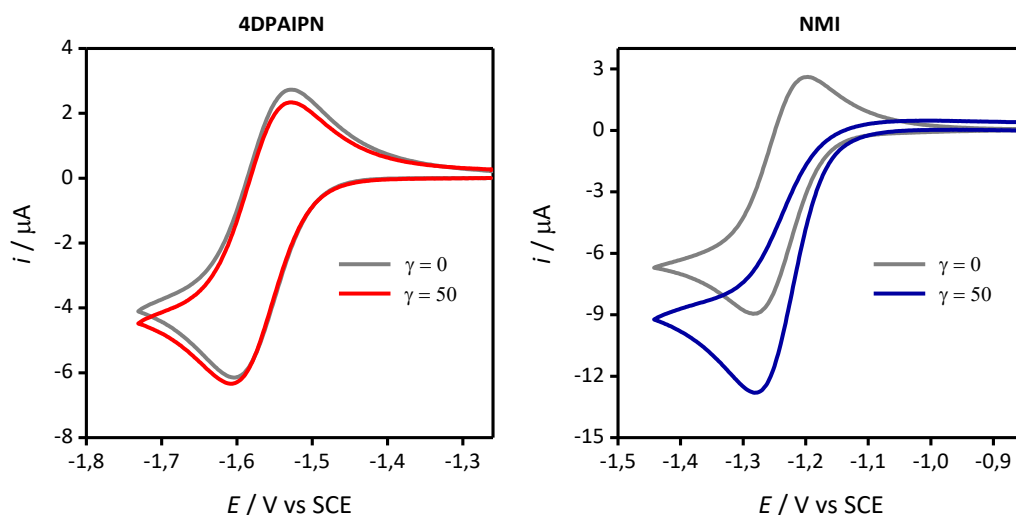


Figure 32. Left panel: CVs of 4DPAIPN under 630 nm light without substrate and in the presence of 4-chlorotoluene ($\gamma = 50$). Right panel: CVs of NMI under 440 nm light without substrate and in the presence of 4-chlorotoluene ($\gamma = 50$). Scan rate: 30 mV/s. k_{exc} of NMI under 440 nm light is approximately double compared to that of 4DPAIPN under 630 nm light, but the effect on the catalytic current is negligible.

In addition to the significantly enhanced electrophotocatalytic performance promoted by NMI, the underlying mechanism is fundamentally different. This distinction arises from the disparity in excess kinetic energy between NMI and the cyanoarene PCs, which leads to different thermalization lengths. Consequently, a bimolecular turnover mechanism – such as the localized solvated electron model that successfully accounts for the reactivity of 4DPAIPN and 4CzIPN – failed to fit the CVs of NMI. Instead, the competing free solvated electron model (involving bimolecular BET, Table 3) reproduced the experimental CVs far more faithfully. Comparing the fit quality of these mechanisms confirms that NMI, unlike 4DPAIPN and 4CzIPN, is best described by a unimolecular mechanism, consistent with a substantially higher yield of free solvated electrons (see Appendix G).

In summary, cyanoarene photocatalysts ejected electrons via electrophotocatalysis with very low excess kinetic energy. Consequently, these electrons thermalized in close proximity to the parent photocatalyst, undergoing rapid geminate recombination or only infrequent reactions with nearby substrates. In contrast, NMI photo-ejected electrons with substantially higher excess kinetic energy; these electrons thermalized far from the parent molecule, effectively suppressing geminate recombination. This generated a significantly higher yield of true free solvated electrons, which ultimately could drive much higher electrophotocatalytic currents. Despite its lower current, 4DPAIPN remains synthetically valuable, as it can effectively cleave R-X bonds in just a few hours.

3.2. Application of e-PRC in RAFT polymerizations

So far, interest in ePRC protocols has largely focused on challenging, high-energy reactions, whereas their application to transition well-known processes into mild, renewable energy conditions has never been explored. Having previously established that red light drives demanding transformations via DET, this same fundamental pathway is now leveraged under milder potentials to expand the scope of electrophotocatalysis into the domain of polymer science.

As outlined in Section 1.5, both electrochemistry and photochemistry have been independently employed as alternatives to thermal radical initiators for triggering RAFT polymerizations. While eRAFT has seen restricted adoption due to modest performance, PET-RAFT represent a flourishing research field, spurred by the ongoing development of increasingly efficient light harvesting materials¹⁸², which can operate under both low-energy wavelengths (e.g., NIR light)¹⁸³ and low-intensity conditions (e.g., microwatt irradiation)¹⁸⁴. Herein, we introduce electrophotocatalytic RAFT polymerization – termed PET-eRAFT – as a hybrid, dual-stimuli strategy that effectively translates the ePRC concept into RAFT chemistry, thereby complementing PET-RAFT features with orthogonal electrochemical control over the reaction progress.

To accomplish PET-eRAFT polymerizations of methacrylate monomers under red/NIR light, a perylene diimide photocatalyst (PDI) and a trithiocarbonate CTA (CDTPA) were used (Figure 33).

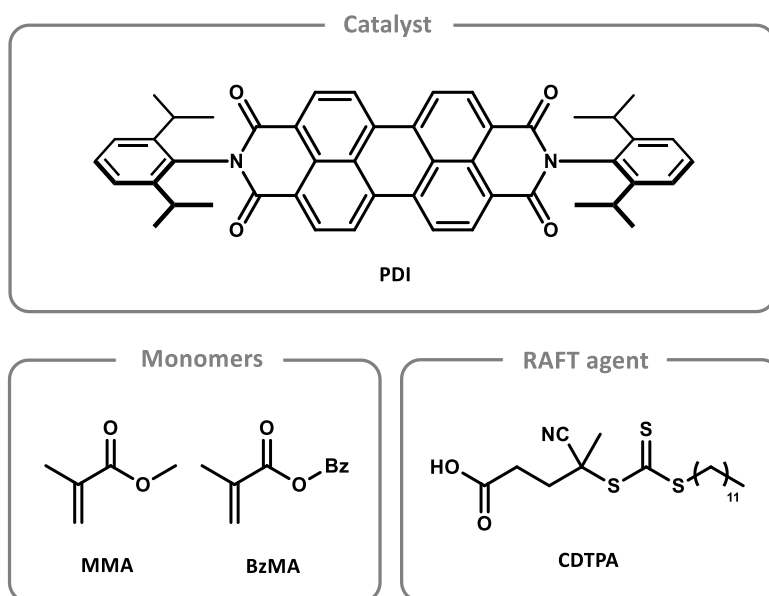


Figure 33. Structures of catalyst, monomers and RAFT agents used for PET-eRAFT polymerizations.

Catalysts of the perylene diimide family are widely employed in photoredox catalysis, primarily because they offer a powerful combination of strong visible light absorption, exceptional fluorescence, facile functionalization, remarkable thermal and photochemical stability and cost-effectiveness^{185,186}. Since these organic chromophores generally offer a more moderate reducing power compared to that of the high-energy photocatalysts discussed so far, they are better suited for mild reaction conditions, such as those required in controlled polymerizations^{187,188}.

Recalling the procedure followed for the electrochemical and photophysical characterization of 4DPAIPN (see Section 3.1.1), the same experimental routine was adopted for PDI. As shown in Figure 34a, the CV profile of PDI exhibits two consecutive and reversible waves, which can be associated with the following electron transfer processes:



The standard reduction potentials of the two redox couples, calculated from their half-wave potentials, are $E^\circ_{\text{PDI}/\text{PDI}^{\bullet-}} = -0.410 \text{ V vs SCE}$ and $E^\circ_{\text{PDI}^{\bullet-}/\text{PDI}^{2-}} = -0.703 \text{ V vs SCE}$.

Spectroelectrochemistry (Figure 34b) revealed that the absorption spectrum of $\text{PDI}^{\bullet-}$ is significantly red-shifted compared to that of neutral PDI, allowing for selective excitation of the former species under both 630 nm red light and 850 nm NIR light.

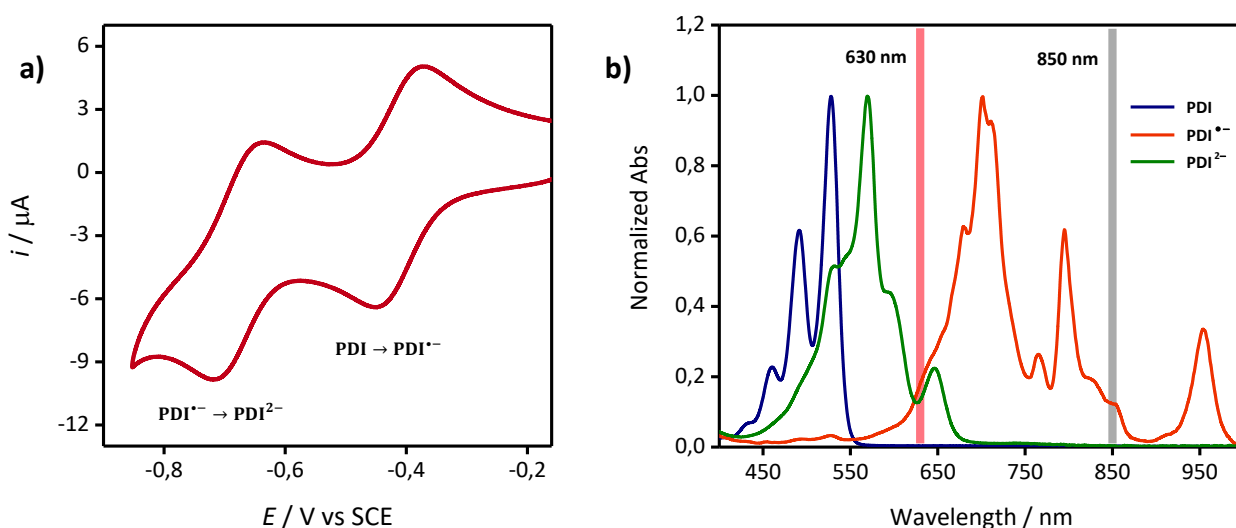
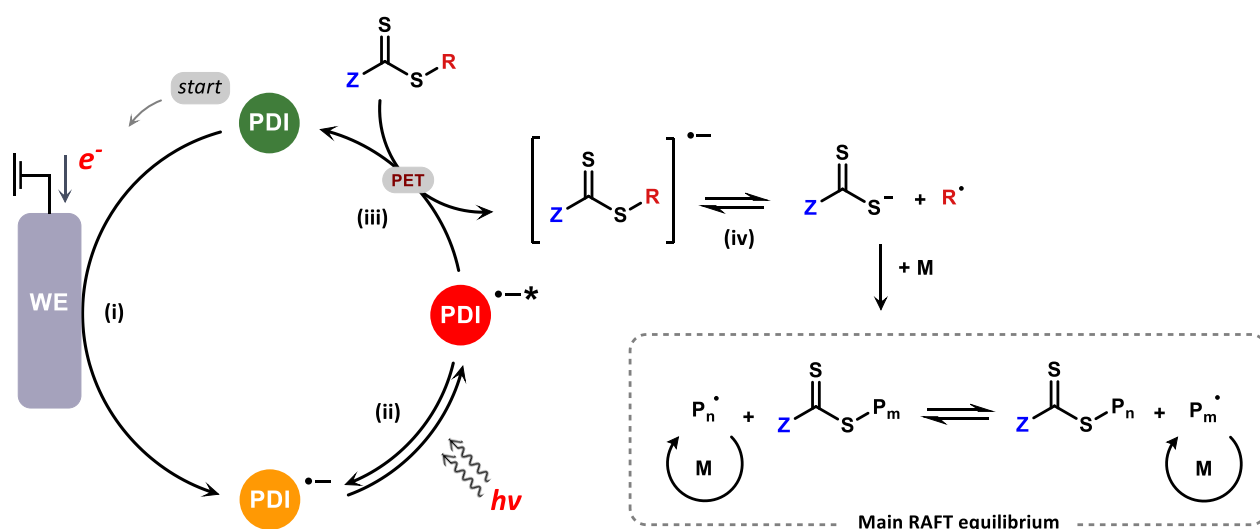


Figure 34. a) CV of PDI in DMSO + 0.1 M TEATFB, scan rate: 200 mV/s. b) UV-Vis absorption spectra of neutral PDI and its two reduced forms in DMF + 0.1 M TEATFB. The radical anion and dianion were obtained via electrolysis at -0.55 V vs SCE and -1.2 V vs SCE, respectively.

Following the classical ePRC mechanism, $\text{PDI}^{\bullet-*$ is generated via sequential one-electron electrochemical reduction of PDI to $\text{PDI}^{\bullet-}$ and photoexcitation of the latter species. Literature reports that $\text{PDI}^{\bullet-*$ features a standard reduction potential ($E^\circ_{\text{PDI}/\text{PDI}^{\bullet-}}$) of -1.87 V vs SCE and a lifetime of 160 ps¹⁸⁹. Unlike 4DPAIPN, this mild reduction potential excludes any ejection of solvated electrons, while this relatively long lifetime allows dissociative electron transfer (DET) towards labile bonds to compete against non-radiative decay to the ground state. In the context of RAFT polymerizations, DET targets the C-S bond of the CTA, prompting its rapid fragmentation. This process yields propagating radicals, which can add monomer units and eventually enter the main RAFT equilibrium. Overall, PET to the RAFT agent, and thus polymerization initiation step, is achieved via the combined electrochemical-photochemical approach depicted in Scheme 17.



Scheme 17. Proposed mechanism for PET-eRAFT polymerization.

Successful initiation and good control over the PET-eRAFT process rely primarily on a precisely tuned thermodynamic compatibility among catalyst, CTA and monomer. Specifically, $\text{PDI}^{\bullet-*$ must be sufficiently reducing to activate the CTA, yet mild enough to leave the monomer intact. Furthermore, the CTA must possess a sufficiently negative cathodic peak potential (E_{pc}), to avoid direct reduction but ensuring selective activation by the open shell excited state catalyst. In the specific case of the system presented here, all requirements are satisfied: $\text{PDI}^{\bullet-*$ provides sufficient driving force to activate the CTA ($E_{\text{pc,CDTPA}} = -1.05$ V vs SCE) without affecting the monomer ($E_{\text{onset,MMA}} = -1.97$ V vs SCE), whereas the CTA itself is inert toward reduction from ground state $\text{PDI}^{\bullet-}$ or directly at the electrode surface.

Building on these thermodynamic and mechanistic premises, bulk electrolyses in DMSO + 0.1 M TEATFB solutions containing MMA, CDTA and PDI were performed under continuous 630 nm or 850 nm light irradiation (see Experimental section). Overall, satisfactory polymer growth was achieved within a few hours (Figure 35), validating the ePRC-driven initiation strategy. Additionally, consistent with classical RDRP criteria – outlined in Section 1.5 – the polymerizations proceeded with linear first order kinetics and low dispersities, while providing high chain-end fidelity, thus reflecting good control over the reaction progress.

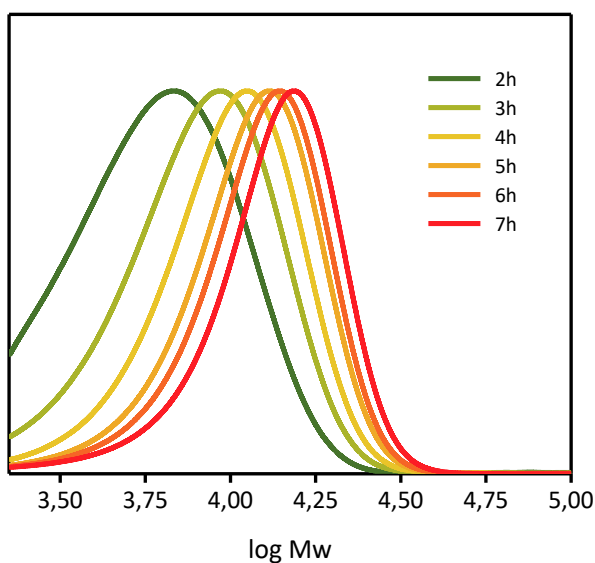


Figure 35. Evolution of GPC traces over time for a general PET-eRAFT polymerization.

Despite these highly encouraging preliminary outcomes, the PET-eRAFT process was consistently characterized by a distinct induction period (see for example Figure 36), during which no detectable monomer consumption occurred. Notably, this initiation delay proved to be correlated with experimental molecular weights slightly higher than theoretical predictions, suggesting that fewer chains were initially activated. In traditional PET-RAFT systems, extended induction phases are well-documented only for oxygen-tolerant or oxygen-accelerated protocols, where they correspond to the time required to scavenge dissolved molecular oxygen into reactive oxygen species, like singlet oxygen or superoxide radicals¹⁹⁰. Conversely, in rigorously degassed environments – such as the system investigated here – induction times are expected to be negligible or restricted to a few minutes, typically stemming from slow primary radical generation rates or trace inhibitors/impurities. Therefore, encountering an extended induction phase under rigorous anaerobic conditions pointed toward a more complex underlying mechanism, unique to the electrophotocatalytic setup.

Accordingly, elucidating the origin of this unexpected behaviour is paramount to mitigating its impact, thus optimizing the overall PET-eRAFT protocol and electrophotochemical reactions in general. To achieve this, a systematic parametric study was conducted, mapping the individual influence of various reaction variables on both induction times and overall polymerization kinetics. All experiments were conducted under constant 13 W 630 nm irradiation within the thermostated setup (see Experimental section) to guarantee full reproducibility. This work provided the rational basis required for the subsequent translation and optimization of the process from red to low-energy 850 nm NIR irradiation, illustrating how rigorous mechanistic understanding dictates the design of efficient catalytic systems.

3.2.1. Effect of catalyst loading

First, the role of PDI loading was investigated. Catalyst loading is herein defined as the ratio between catalyst and monomer concentrations and it is expressed in ppm units. Four different electrolyses were conducted under 630 nm light with varying PDI loadings (50, 100, 200 and 300 ppm, respectively), while keeping fixed the applied potential ($E'_{1/2}$ -60 mV, i.e., 60 mV more negative than the half wave potential of the PDI/PDI⁻ couple) and the target DP (DP200).

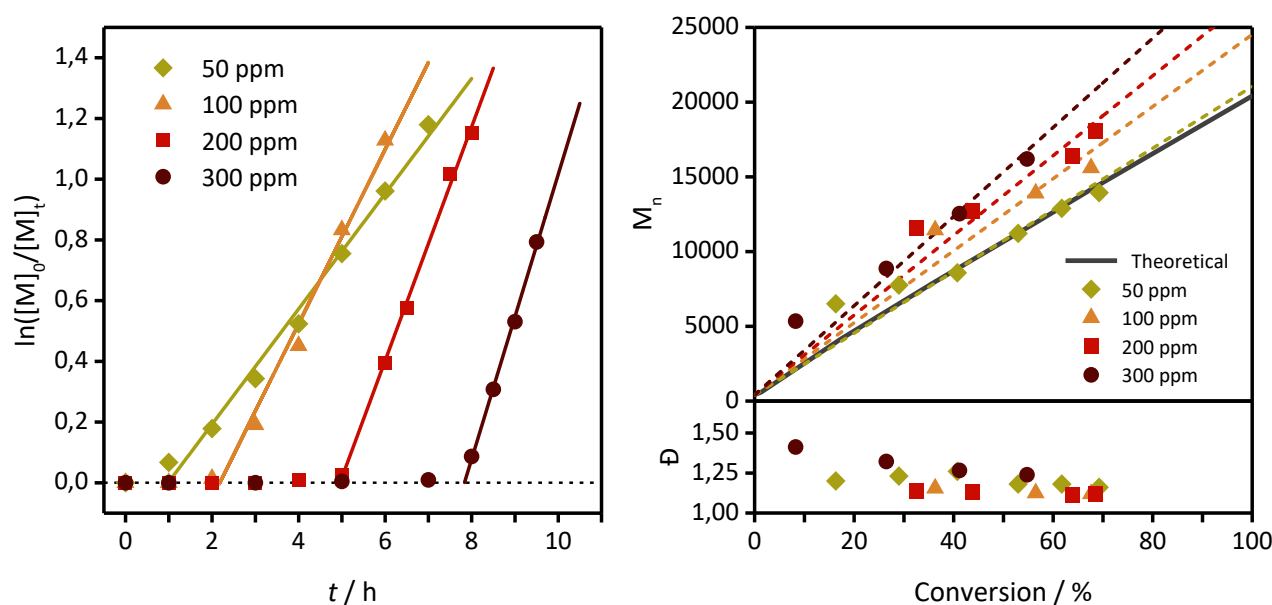


Figure 36. Left panel: semilogarithmic plot for PET-eRAFT of MMA at different PDI loadings (solid lines represent the best fit of the dataset, excluding the induction period). Right panel: M_n (top) and dispersity (bottom) as vs monomer conversion. The solid line represents the theoretical M_n ; dashed lines represent the best fit of the experimental M_n datasets. Conditions: 630 nm light, $E'_{1/2}$ -60 mV applied potential, DP200.

The kinetics of monomer consumption were followed by plotting $\ln[M]_0/[M]_t$ against reaction time (Figure 36, left). According to Equation 1.5.2, a polymerization that is first order in monomer concentration should give a linear correlation, whose slope corresponds to the apparent rate constant of polymerization ($k_{p,app}$). This semilogarithmic plot revealed two distinct, opposing effects of catalyst loading: increasing PDI concentration progressively lengthens the induction period, but once polymerization is underway, the trend reverses, with higher loadings producing steeper slopes and thus faster propagation. Catalyst concentration therefore does not simply scale the overall polymerization rate up or down; instead, it shifts the balance between how long the system takes to initiate and how fast it proceeds afterward.

Concurrently, the molecular weight data obtained by GPC (Figure 36, right) provided a complementary observation. At every catalyst loading investigated, the experimental molecular weights exceed the theoretical values calculated via Equation 1.5.4, and the extent of this positive deviation increases progressively with PDI loading. Nevertheless, dispersities remain narrow across all conditions, indicating that excellent control over chain growth was retained.

Taken together, direct visual observation of the reaction mixture and the chronoamperometric traces recorded during electrolysis (Figure 37, left) indicate that the induction period is characterized by the progressive accumulation of $PDI^{\bullet-}$. The behaviour of current as a function of time can be rationalized by considering three distinct phases, each associated with a corresponding colour change in solution. In the first phase, immediately following application of the potential and illumination of the WE, the current drops sharply as neutral PDI is reduced to its radical anion; this phase is characterized by a progressive transition from the original orange colour, typical of the neutral PDI, to the green typical of $PDI^{\bullet-}$. In the second phase, the current stabilizes at a low, near-constant value, indicating that $PDI^{\bullet-}$ remains accumulated in the bulk solution while neutral PDI remains depleted (i.e., no or very slow catalyst turnover occurs). The duration of this phase increases with catalyst loading, and so does the intensity of the green coloration, consistent with a larger pool of accumulated radical anion. The third phase begins when the cathodic current starts rising again, signalling the onset of catalytic turnover: as neutral PDI becomes increasingly available at the electrode, the solution gradually turns back to orange, marking the effective start of polymerization (highlighted in Figure 37 left by the vertical bars). Finally, once $PDI^{\bullet-}$ has been almost entirely consumed – reflected in the current approaching its initial value – the system follows the classical hydrodynamic chronoamperometric behaviour, with the current decaying exponentially as expected.

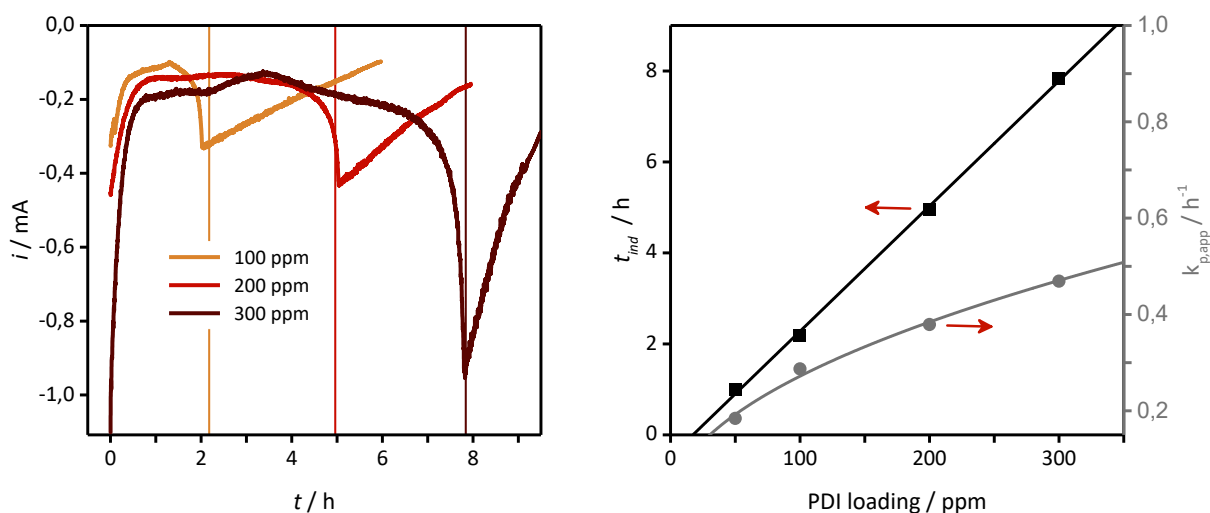


Figure 37. Left panel: chronoamperometries at different PDI loadings (vertical solid lines represent induction times from NMR measurements). Right panel: induction periods and apparent polymerization kinetic constants as a function of PDI loading. Induction periods are calculated as the x axis intercept of the linear fitting in the semilogarithmic plot; $k_{p,app}$ are calculated as the slope of the linear fitting in the semilogarithmic plot.

Two clear trends can be derived from the experimental data: (i) induction time scales linearly with PDI loading, and (ii) $k_{p,app}$ scales with the square root of PDI loading (Figure 37, right). While the origin of the linear scaling of the induction time is not immediately obvious, the square root dependence on catalyst loading, is the classic signature of a regime in which the concentration of propagating radicals is set by a steady-state balance between radical generation and bimolecular termination (the full derivation is provided in Appendix H). This behaviour is analogous to the well-known square root dependence of the polymerization rate on initiator concentration in free radical polymerization¹⁹¹, with PDI here playing the role of the radical initiator though the electrophotocatalytic cycle.

The systematic positive deviation of experimental molecular weights compared to theoretical ones is consistent with a lower-than-expected number of polymer chains: when the same amount of monomer is distributed among fewer chains, each chain necessarily grows longer than predicted. Since every CTA molecule is nominally expected to initiate one propagating chain, GPC results indicate that a fraction of the CTA population fails in doing so. We propose that this loss of active CTA reflects a competition, at the level of the primary radical, between two possible reaction pathways. Upon reduction and fragmentation of the CTA, the resulting primary radical can either add a monomer unit and initiate a propagating chain or terminate rapidly by combining with another radical species before monomer addition can occur.

We attribute the observed CTA loss to the latter pathway: a fraction of the primary radicals generated during the induction period undergo premature radical-radical termination rather than initiating the propagation cycle, effectively removing active chain carriers.

Two independent approaches were used to estimate the fraction of loss, or “dead”, CTA as a function of PDI loading (Table 8). The first one relies on charge balance considerations: the reduction of PDI during the induction period can be considered quantitative, consistent with the massive accumulation of PDI^{•-} observed over this stage; any charge passed in excess of that required for this reduction can be attributed to unproductive CTA activation. Based on this, the dead CTA fraction is given by:

$$\% \text{ CTA}_{\text{dead}} = \frac{Q_{\text{ind}} - Q_{\text{ind th.}}}{F \cdot n_{\text{CTA},0}} \cdot 100 \quad (3.2.3)$$

where $Q_{\text{ind th.}}$ is the charge required for quantitative PDI reduction, calculated from Faraday’s law.

The second approach estimates the alive CTA fraction indirectly from GPC M_n data. For each PDI loading, the experimental M_n values were linearly fitted and extrapolated to full conversion. Expressing M_n as the total polymer mass at a given conversion divided by the number of chains gives:

$$M_{n(\text{GPC})} = \frac{n_{\text{M},0} \cdot MW_{\text{M}} \cdot \text{conversion} + n_{\text{CTA alive}} \cdot MW_{\text{CTA}}}{n_{\text{CTA alive}}} \quad (3.2.4)$$

Rearranging Equation 3.2.4 to explicitly express the dead fraction yields:

$$\% \text{ CTA}_{\text{dead}} = \left[1 - \frac{n_{\text{M},0} \cdot MW_{\text{M}} \cdot \text{conversion}}{n_{\text{CTA},0} \cdot (M_{n(\text{GPC})} - MW_{\text{CTA}})} \right] \cdot 100 \quad (3.2.5)$$

Results from both methods, across all PDI loadings tested, are summarized in Table 8.

Table 8. Effect of PDI loading on key reaction parameters and CTA degradation.

Loading (ppm)	50	100	200	300
t_{ind} (h)	1.00	2.18	4.96	7.84
$k_{\text{p,app}}$ (h ⁻¹)	0.18	0.29	0.38	0.47
Q_{ind} (C)	0.67	1.27	3.05	6.57
$Q_{\text{ind th.}}$ (C)	0.14	0.29	0.59	0.89
% CTA _{dead} from Q_{ind}	3.55	6.35	16.36	38.13
% CTA _{dead} from final M_n	2.81	17.05	25.00	32.90

Overall, the two methods yield comparable estimates, suggesting that the relationship between CTA loss and PDI loading is mediated by charge consumption. Both methods independently confirm the same order of magnitude for dead CTA, indicating that at the highest loading tested (300 ppm) roughly one third of the total CTA is lost before polymerization effectively begins. Therefore, it appears that during the induction phase the CTA is unproductively lost without generating new chains. The best balance between short induction period, fast polymerization rate, and reasonably catalyst loading was found at 100 ppm PDI.

3.2.2. Effect of applied potential

The effect of applied potential on PET-eRAFT kinetics was investigated by comparing four electrolyses, all carried out under 630 nm irradiation, with a 200 ppm PDI loading and a target DP of 200. The potential imposed at the WE was varied across the different runs: the standard $E'_{1/2} - 60$ mV, a milder $E'_{1/2} + 30$ mV, and two potential-step sequences. The milder potential ($E'_{1/2} + 30$ mV) sits on the rising portion of the catalyst's first CV wave, where the equilibrium at the electrode surface no longer strongly favours the reduced form, rather than immediately after the cathodic peak, where the reduction of PDI reaching the WE is essentially quantitative (Figure 38, left). This is reflected in both a roughly halved CV current compared to the $E'_{1/2} - 60$ mV condition and a correspondingly lower starting current in chronoamperometry (Figure 38, right), despite the constant catalyst loading.

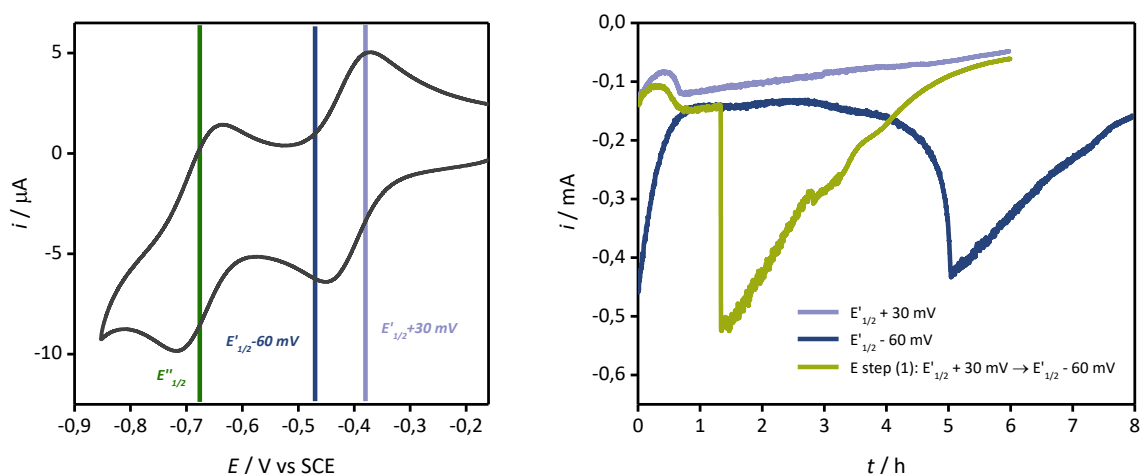


Figure 38. Left panel: The three different WE potentials employed, visualized as superimposed to the CV trace of PDI. Right panel: electrolysis curves (chronoamperometries) for different applied potential protocols.

The resulting slower and less extensive generation of $\text{PDI}^{\bullet-}$ produced the same effect as a lower catalyst loading: the induction period collapsed from nearly five hours (at $E'_{1/2} -60$ mV) to only 40 minutes at $E'_{1/2} +30$ mV; additionally, experimental M_n values moved closer to theoretical predictions. The more negative potential resulted in faster polymerization once initiated (Figure 39).

As no single applied potential appeared capable of delivering both a short induction period and a fast propagation rate, two potential-step protocols were designed specifically to reconcile these two requirements: both started at $E'_{1/2} +30$ mV for 80 minutes before switching to a more negative value: $E'_{1/2} -60$ mV in “E step (1)”, or $E''_{1/2}$ (i.e., half wave potential of the second wave) in “E step (2)”. Beginning the electrolysis at the milder potential minimizes the induction period; switching to a more negative potential once the reaction is underway then accelerates propagation, without resetting the system into a new induction phase. Achieving this, however, requires precise timing: the shift must be performed only once the RAFT equilibrium has already been set, herein approximately 40 minutes after the end of induction. Consistent with this, chronoamperometric data show that upon sharply shifting to the more negative potential, the current rises, but immediately follows the expected hydrodynamic decay, rather than exhibiting the plateau characteristic of renewed $\text{PDI}^{\bullet-}$ accumulation (see the “E step (1)” trace in Figure 38, right).

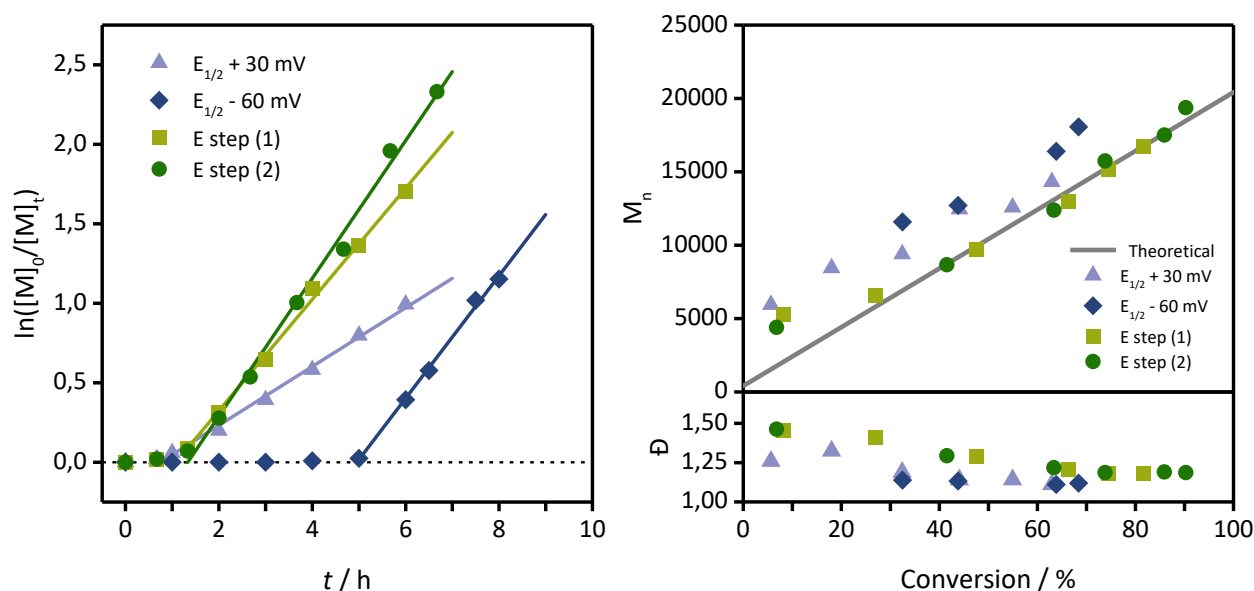


Figure 39. Left panel: semilogarithmic kinetic plot for different applied potentials (solid line represent the best fit of the dataset, excluding the induction period). Right panel: M_n (top) and dispersity (bottom) as a function of monomer conversion. The solid line represents the theoretical M_n . Conditions: 630 nm light, 200 ppm PDI loading, DP200. E step (1): 80 minutes $E'_{1/2} +30$ mV, then $E'_{1/2} -60$ mV till the end. E step (2): 80 minutes $E'_{1/2} +30$ mV, then $E''_{1/2}$ till the end.

This sequential design proved highly effective: kinetic data (Figure 39, left) confirm simultaneously reduced induction times and accelerated polymerization, while GPC data (Figure 39, right) reveal excellent agreement between experimental and theoretical M_n , together with low dispersities. Monomer conversion after 6 hours of electrolysis reached 82% under "E step (1)", and 87% under "E step (2)", while keeping a fixed $E'_{1/2} +30$ mV applied potential only yields a 62% conversion within the same timeframe.

When switching to $E''_{1/2}$, a certain amount of PDI^{2-} is also generated at the electrode; this species most likely comproportionates with neutral PDI to yield additional $\text{PDI}^{\bullet-}$, thus further boosting the propagation relative to the standard $E'_{1/2} -60$ mV condition.

3.2.3. Other variables governing PET-eRAFT kinetics

To isolate the effect of CTA loading on the reaction kinetics, an electrolysis at a lower target DP of 100 was carried out, with all other conditions kept at their standard values (630 nm light, 200 ppm PDI loading and $E'_{1/2} -60$ mV potential). Shifting from DP200 to DP100 (i.e., doubling the CTA-to-monomer ratio) reduced the induction time from approximately 5 hours to 3 hours (Figure 40, left), while $k_{p,app}$ remained essentially unchanged within the experimental error (0.370 vs 0.380 h^{-1}).

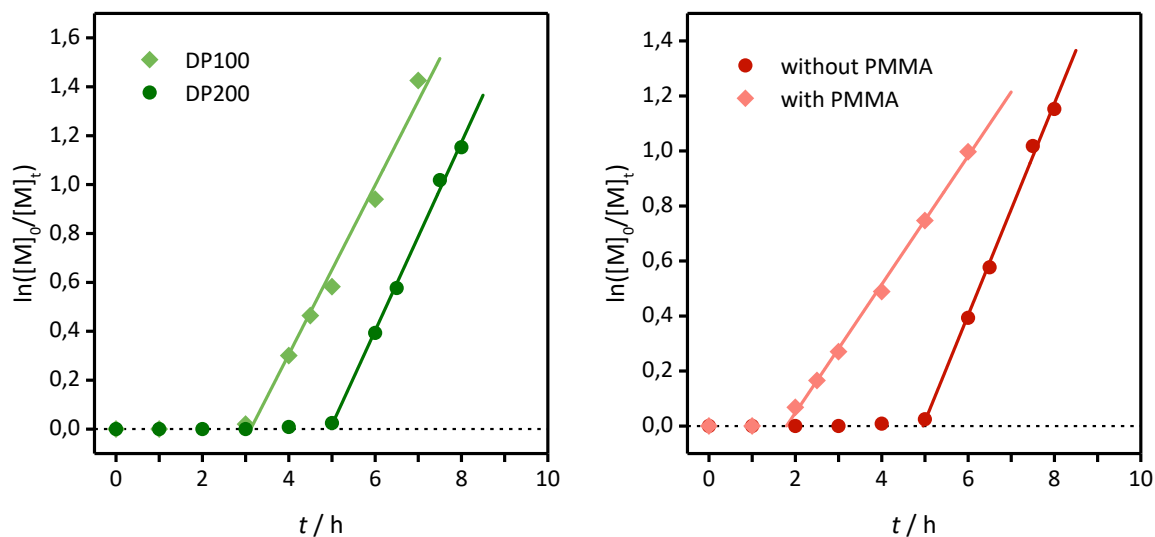


Figure 40. Semilogarithmic kinetic plot for different target DP (left panel) and for different solution viscosities (right panel). Solid line represent the best fit of the dataset, excluding the induction period. Conditions: 630 nm light, 200 ppm PDI loading, $E'_{1/2} -60$ mV applied potential.

The independence of $k_{p,app}$ from CTA concentration is consistent with the nature of the RAFT equilibrium: degenerative transfer redistributes which chain is growing at any given moment, but does not change the total number of active radicals in solution. Since $k_{p,app}$ depends only on this total radical population (see Appendix H), it is unaffected by how much CTA is present. The shorter induction period is consistent with a faster consumption of $PDI^{\bullet-}$ with higher CTA concentrations.

Finally, to determine whether mass transport dynamics also play a role in the induction period, a polymerization was carried out under the standard conditions (630 nm light, 200 ppm PDI loading, $E'_{1/2} = 60$ mV and DP200), but with increased solution viscosity. To increase viscosity without significantly altering the solvent – and thus avoid concurrently changing polarity and other solution properties – commercial PMMA obtained by free-radical polymerization ($M_w = 93300$; $M_n = 46400$) was dissolved in the reaction mixture at 8 wt%. Two opposite effects were observed: (i) the propagation rate decreased markedly ($k_{p,app}$ drops from 0.380 to 0.233 h⁻¹); and (ii) the induction time more than halved, dropping from approximately 5 hours to 2 hours (Figure 40, right). Under the standard operating potential, the reduction current is governed by the rate of PDI diffusion toward the electrode surface. Since the mass transport scales inversely with solution viscosity, the increased viscosity is expected to reduce the effective rate of $PDI^{\bullet-}$ generation, an effect analogous to that produced by shifting to a milder applied potential (see above). This could explain both the shorter induction period and the slower subsequent propagation rate.

3.2.4. A mechanistic proposal for the induction period

As previously discussed, GPC and NMR data clearly indicate that, during the induction period, most of the radicals generated via PET from $PDI^{\bullet-}$ to the CTA preferentially undergo bimolecular termination rather than adding monomer and entering the main RAFT equilibrium. What remains to be established is why this unproductive pathway dominates at first, and what causes it to eventually give way to productive propagation, marking the end of the induction period. A preliminary picture can be assembled by combining the insights obtained by varying PDI loading, applied potential, target DP, and medium viscosity. Across all four variables, the induction period reflects the progressive build-up of a steady state $PDI^{\bullet-}$ concentration in solution: its duration increases whenever this concentration is raised, either by increasing the amount of neutral PDI available for reduction, or by increasing the rate at which $PDI^{\bullet-}$ is generated at the WE. Conversely, this duration is shorter when a larger number of chains must be started, i.e., at higher CTA concentrations.

In the electrophotochemical setup, the two external stimuli act at essentially different locations within the cell: electrochemical reduction occurs at the center, where the Pt gauze WE is placed, while photoexcitation occurs predominantly near the cell wall, where light intensity is highest (see Experimental section). Crucially, however, $\text{PDI}^{\bullet-}$ is not merely an innocent intermediate of the ePRC cycle: it is itself a strongly absorbing species at 630 nm, and its accumulation therefore directly affects how much light is available within the cell. Once the optical density of $\text{PDI}^{\bullet-}$ rises sufficiently, it effectively shields the bulk of the cell from incoming light, confining photoexcitation to a thin layer near the cell wall. This behaviour follows directly from the Lambert-Beer law, which relates the lamp irradiance attenuation (I/I_0) to the thickness of the solution crossed (x):

$$I/I_0 = \exp(-\ln(10) \cdot \varepsilon \cdot [\text{PDI}^{\bullet-}] \cdot x) \quad (3.2.6)$$

where ε is the molar absorption coefficient of $\text{PDI}^{\bullet-}$ ($16620 \text{ M}^{-1} \text{ cm}^{-1}$ at 630 nm) and $[\text{PDI}^{\bullet-}]$ is approximated as equal to the neutral PDI loading, assuming quantitative reduction.

At high PDI loadings – where the intense green coloration and the chronoamperometric traces both indicate near-quantitative PDI reduction sustained over a prolonged steady state – more than 90% of the incident light is absorbed in less than 1 mm of the wall (Figure 41), thereby confining photoexcitation to a vanishingly small fraction of the total solution volume. We refer to this self-limiting phenomenon as an *inner filter effect*, borrowing a term typically used in fluorescence spectroscopy, where it describes light attenuation by absorbing species within the sample itself.¹⁹².

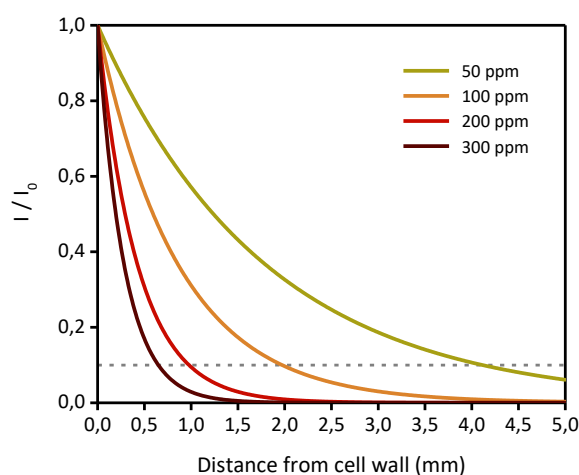


Figure 41. Lamp irradiance attenuation due to absorption from PDI radical anion as a function of the distance from the cell wall for different PDI loadings. Calculated from Equation 3.2.6, assuming quantitative reduction. Intersections with the horizontal dashed line indicate the solution thickness at which the incoming light loses 90% of its original irradiance.

Since photoexcitation is confined to a small volume near the cell wall, all primary radicals are generated within that same region, resulting in a locally high radical concentration. Because bimolecular termination scales with the square of the radical concentration ($v_t \propto [R^\bullet]^2$), while propagation scales only linearly with it ($v_p \propto [R^\bullet][M]$), this local excess of radicals inherently favours termination: once the inner filter effect is established, most primary radicals are lost before adding monomer, yielding fewer propagating chains than expected.

However, this regime is not entirely unproductive. NMR analysis of samples collected during the induction period showed that a small, slowly growing polymeric population is already present at this stage (e.g., ~0.90% conversion after 7 hours at 300 ppm loading – one hour before the end of induction, while the solution is still dark green), indicating that a minor fraction of the generated radicals manages to enter the main RAFT equilibrium. We propose that this minor productive fraction is ultimately responsible for ending the induction period, through a “self-reinforcing” sequence of events. Even under efficient stirring, hydrodynamic theory predicts the persistence of a tens of μm thick diffusion boundary layer next to the cell wall, in which fluid velocity drops sharply and mass transport occurs primarily by diffusion rather than convection¹⁹³. Within this boundary layer, a local increase in viscosity, driven by slow macroCTA accumulation, would be expected to further hinder diffusive transport, progressively limiting the extent to which PDI^- can reach the cell wall from the solution bulk. As a consequence, a depletion layer could form, in which PDI^- consumed in CTA activation is no longer efficiently replenished. As PDI^- becomes locally depleted, light would penetrate more deeply into the cell, expanding the photoactive volume. In turn, radical generation would then become distributed in a larger volume, lowering the local radical concentration until propagation once again prevails over termination. This self-reinforcing loop is consistent with the observed return of the solution to its original orange colour and with the current increase in the chronoamperometric trace, reflecting catalytic turnover.

Further experiments to validate this proposed mechanism are planned, including visualizing the surface depletion layer and monitoring the conversion of CTA to macroCTA in real time.

3.2.5. PET-eRAFT process optimization under NIR light irradiation

The pronounced red-shift of the PDI^- absorption spectrum relative to that of the parent neutral catalyst (Figure 34b) opens the way to extending the scope of PET-eRAFT toward much lower excitation energies – namely, into the NIR region. Electrolyses conducted under 13W 850 nm light

confirmed that PET to the CTA remains feasible even at such low photon energies. As in the 630 nm system, if electrochemical PDI reduction outpaces photoexcitation, $\text{PDI}^{\bullet-}$ accumulates in the bulk, giving rise to an induction period driven by the inner filter effect. Under NIR irradiation, however, this induction phase is accompanied by non-negligible conversion and is therefore better described as a "sluggish regime" rather than a true induction period. This difference likely stems from the lower molar absorption coefficient of $\text{PDI}^{\bullet-}$ at 850 nm, roughly 1/3 below the value measured at 630 nm.

NIR-triggered PET-eRAFT retains excellent control, as shown by the successful synthesis of a block copolymer. A macroCTA (target DP of 50) was first prepared using the same setup as the red light experiments – except for the excitation wavelength – and the electrolysis was stopped before full MMA conversion, to yield a macroCTA of $M_n = 3488$ Da. As expected from the low catalyst loading (50 ppm) and target DP, no induction period was observed. This macroCTA was purified (see Experimental section) and used as the RAFT agent in a second electrolysis with benzyl methacrylate (BzMA) as the monomer. Despite the higher target DP (DP100), no induction period was observed here either, likely as a consequence of the high viscosity induced by the presence of the macroCTA. The reaction reached 97% conversion after 30 hours, affording a narrowly dispersed PMMA-b-PBzMA block copolymer, as confirmed by the GPC trace shift (Figure 42, left) and following a first-order kinetics (Figure 42, right). These data confirm the high chain-end fidelity of the NIR-triggered process, establishing PET-eRAFT as a viable strategy for accessing complex polymer architectures.

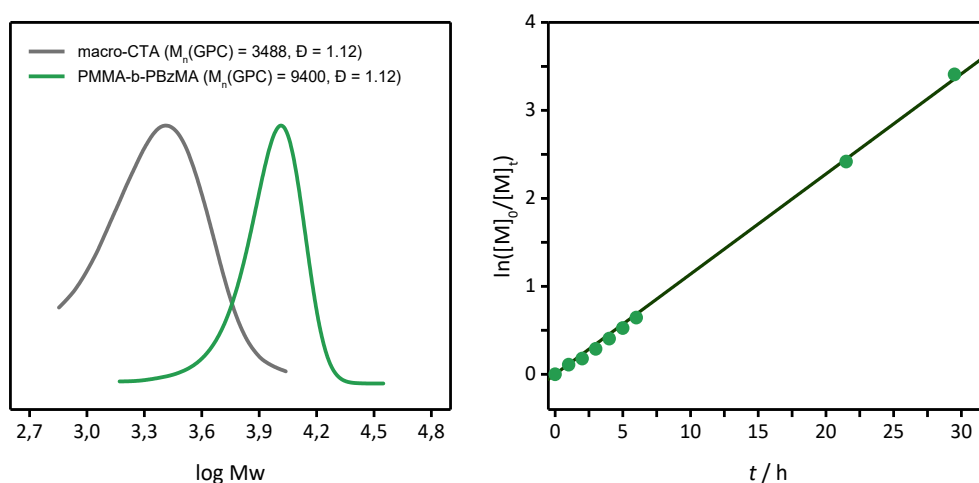


Figure 42. Left panel: GPC traces of PMMA macroCTA (grey) and PMMA-b-PBzMA block copolymer resulting from chain extension (green). Right panel: chain extension semilogarithmic kinetic plot (the solid line represents the linear fit of the experimental points). Conditions for macroCTA synthesis: 850 nm light, 50 ppm PDI loading, $E'_{1/2} - 60$ mV applied potential, DP50. Conditions for chain extension with BzMA: 850 nm light, 50 ppm PDI loading, $E'_{1/2} - 60$ mV applied potential, DP100.

Building on the mechanistic insights gained above, two main changes were introduced to optimize the experimental setup relative to the conditions used so far. First, a more powerful light source (45 W at 850 nm, versus the 13 W sources previously used at both 630 and 850 nm) was employed. Second, the thermostated cell was replaced with a non-thermostated one, allowing the lamp to be positioned closer to the reaction mixture (see Experimental section). Together, these changes were aimed at improving light penetration into the bulk solution, thereby suppressing the buildup of $\text{PDI}^{\cdot-}$ responsible for the inner filter effect. In turn, this was expected to eliminate the induction period altogether without affecting the subsequent polymerization rate.

Two experiments were designed to directly test this setup. The first was conducted under the new 45 W, 850 nm setup, at 200 ppm PDI loading, $E'_{1/2}$ -60 mV applied potential and target DP of 200; the second replicated these same conditions, but with the lamp intensity reduced to one third. Semilogarithmic plots and GPC data for both experiments are reported in Figure 43.

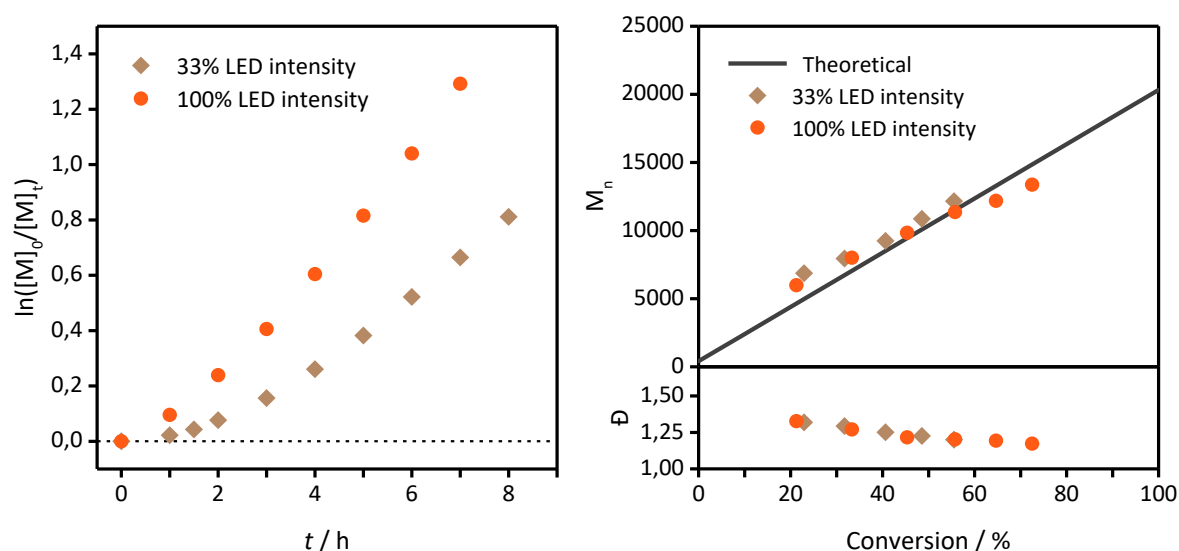


Figure 43. Left panel: semilogarithmic kinetic plot for different light intensities. Right panel: M_n (top) and dispersity (bottom) as a function of monomer conversion. The solid line represents the theoretical M_n . Conditions: 850 nm light, 200 ppm PDI loading, $E'_{1/2}$ -60 mV applied potential, DP200.

At full light intensity, no induction phase was observed at all, in sharp contrast to the nearly 5 hour induction period recorded under the previous setup (13 W, 630 nm lamp, jacketed cell). Beyond eliminating the induction period, full light intensity also boosted the propagation rate, reaching 72% conversion after 7 hours of electrolysis, while still preserving excellent control over molecular weights and dispersities. Without the cooling jacket, however, heat rising from the LED itself and

from non-radiative decay raised the solution temperature to nearly 40 °C, causing modest monomer evaporation – reflected by a slight kinetic acceleration and by final molecular weights below theoretical predictions. Addressing this unwanted heating will require further setup optimization.

Reducing the lamp intensity to one third of the maximum power avoided this heating issue entirely, but was on its own sufficient to cause $\text{PDI}^{\bullet-}$ accumulation, restoring an induction period lasting approximately two hours. The semilogarithmic plot highlights that this phase is better described as a sluggish regime than a true induction period, with the polymerization rate rising sharply once the solution reverts to the colour of neutral PDI. Consistent with this partial re-establishment of the inner filter effect, conversion after 7 hours reached only 49% and the experimental molecular weights were slightly higher than predicted, due to modest CTA loss occurred during induction.

Ultimately, the results of these two electrolyses confirmed that the induction period stems from a kinetic mismatch between two coupled processes – electrochemical generation and photochemical activation of $\text{PDI}^{\bullet-}$ – which can be deliberately corrected by proper reactor and light source design.

4. Conclusions and perspectives

Coupling light and electricity as two independently tunable energy inputs allows electro-photoredox catalysis to access demanding redox transformations under remarkably mild conditions – with clear implications for sustainability of chemical reactions – while simultaneously offering a degree of control over reactivity and selectivity that neither electrochemistry nor photochemistry can achieve alone. This same combination, however, adds mechanistic and operational complexity, making the resulting processes difficult to rationalize, predict, and scale. This work addressed this gap through a multi-scale perspective, spanning from the molecular-level processes governing ePRC reaction mechanisms to synthetic applicability and, ultimately, to practical aspects of cell configuration and light/electricity balance.

Two objectives were pursued in parallel: i) addressing the mechanism of high-energy ePRC reactions driven by a super-reducing catalyst, and its successful transposition to low-energy red light irradiation; and ii) expanding ePRC to polymer science, showing that RAFT polymerization under red and near-infrared light can be independently controlled through applied potential and light.

i) CV analysis of electron ejection dynamics from organic super-reductants

This work disclosed for the first time that recalcitrant aryl halides can be reduced under red light irradiation using 4DPAIPN, a readily available and comparatively inexpensive organocatalyst, marking a substantial shift toward milder reaction conditions relative to the blue light typically required by conventional photoredox catalysis. This reactivity – first observed through the catalytic current in CV – was subsequently validated at the preparative scale via bulk electrolysis, confirming that it holds over longer reaction timescales. Nonetheless, further optimization of reaction conditions and cell design, as well as a more detailed characterization of reaction products and possible catalyst deactivation pathways remain necessary.

Two additional features reinforce the practical appeal of this system. First, the combined photochemical-electrochemical strategy sidesteps a well-documented degradation pathway in conPET systems, where the cyano groups on the catalyst core are progressively replaced by methyl or hydrogen substituents derived from sacrificial amines, limiting catalytic turnover²⁴. Second, both CV and bulk electrolyses showed that, unlike 4CzIPN or NMI, the strongly negative ground state potential of 4DPAIPN favours aryl radical reduction over coupling with the reduced catalyst, suppressing another common deactivation pathway.

Rationalizing the actual reaction mechanism meant confronting a process largely inaccessible to conventional characterization: the extremely rapid generation and quenching of a solvated electron born from an excited state that decays on a femtosecond timescale. The voltammetric method employed here provided an indirect but efficient qualitative probe of this process, as it effectively distinguished the nature of catalytic turnover, thereby affording complementary mechanistic insights to those provided by ultrafast spectroscopy with far simpler instrumentation (a common potentiostat and inexpensive lights). Digital simulations of a large pool of experimental voltammograms, interpreted within the Marcus-Hush framework, then translated this study into quantitative terms, yielding key kinetic and thermodynamic parameters. In particular, this analysis returned a standard reduction potential of -3.37 ± 0.17 V vs SCE for the solvated electron in DMF, together with an intrinsic kinetic barrier of 41 ± 5 kJ/mol for its reaction with aryl halides. Finally, extending the voltammetric approach across different catalysts revealed that electron ejection dynamics depend sensitively on the excess kinetic energy imparted upon excitation: more reducing catalyst can impart excess kinetic energy to the ejected electron, increasing the yield of true free solvated electrons.

Going forward, this mechanistic picture establishes a clear design principle for future super-reducing photocatalysts: pairing a highly reducing ground state with an excited state energetic enough to eject catalytically productive, free solvated electrons. Achieving this combination could extend high-energy ePRC protocols to a broader range of transformations, while bringing them closer to authentic competitiveness with traditional synthesis.

ii) Development and optimization ePRC-driven RAFT polymerizations under red/NIR light

The PET-eRAFT polymerization developed here is, to our knowledge, the first NIR-light-triggered RAFT process to operate without a metal based catalyst, as organocatalytic PET-RAFT has so far been limited to far-red irradiation^{194,195}, while purely NIR-triggered variants have only been achieved with metal based catalysts, principally zinc porphyrins or phthalocyanines¹⁹⁶. Two compounding constraints explain this limitation. First, organic chromophores that absorb in the NIR region tend to undergo ultrafast non radiative decay, limiting the efficiency of PET to the CTA. Second, and more important, NIR photons frequently carry insufficient energy to activate the C–S bond. The ePRC-initiated process introduced here particularly circumvents this latter thermodynamic constraint, by supplementing the limited energy of NIR photons with an electrochemical reduction. This combination of a metal free catalyst and NIR activation carries clear practical implications,

particularly for applications requiring biocompatibility or the synthesis of well-defined, specialized polymeric materials through thick, opaque barriers¹⁹⁶.

Beyond extending PET-RAFT into the NIR, this work also revealed a further advantage inherent to the dual-stimuli design, namely the orthogonal control over the polymerization process, whereby the reaction can be accelerated, slowed, or halted and restarted simply by independently adjusting light intensity or applied potential. This flexibility, however, comes at the cost of increased practical complexity, as demonstrated by the unwanted induction periods and unproductive reaction pathways emerging whenever the reaction setup is not carefully optimized. The systematic investigation of the variables governing this behaviour allowed us to conclude that a fast, well-controlled PET-eRAFT polymerization hinges on matching the rate of photochemical activation to that of electrochemical PDI reduction. This balance was readily achieved by progressively varying the applied potential over the course of the reaction and by improving the cell configuration.

Looking ahead, the principles underlying this balance are unlikely to be specific to PET-eRAFT. A more quantitative assessment of inner filter effects and mass transport limitations could offer a template for reactor design applicable to ePRC techniques more broadly. Flow architectures, already developed for conventional PET-RAFT¹⁹⁷, appear particularly well suited to this task, offering a route to overcome the poor light penetration identified here as a key setup limitation, while also enabling scale-up beyond the laboratory framework. Building on such advances, NIR-driven ePRC might extend beyond polymer chemistry – and beyond synthesis altogether – to fields such as pollutant degradation or chemical waste upcycling, where its comparatively mild operating conditions could offer a meaningful advantage over current approaches.

References

- (1) Stock, J. T. Electrochemistry in Retrospect. *Electrochem. Past Present* **1989**, *390*, 1–17. <https://doi.org/10.1021/bk-1989-0390.ch001>.
- (2) Roth, H. D. The Beginnings of Organic Photochemistry. *Angew. Chem. Int. Ed. Engl.* **1989**. <https://doi.org/10.1002/anie.198911931>.
- (3) Cowper, N. G. W.; Chernowsky, C. P.; Williams, O. P.; Wickens, Z. K. Potent Reductants via Electron-Primed Photoredox Catalysis: Unlocking Aryl Chlorides for Radical Coupling. *J. Am. Chem. Soc.* **2020**, *142* (5), 2093–2099. <https://doi.org/10.1021/jacs.9b12328>.
- (4) Faraday, M. VI. Experimental Researches in Electricity.-Seventh Series. *Philos. Trans. R. Soc. Lond.* **1834**, No. 124, 77–122. <https://doi.org/10.1098/rstl.1834.0008>.
- (5) Kolbe, H. Untersuchungen Über Die Elektrolyse Organischer Verbindungen. *Justus Liebigs Ann. Chem.* **1849**, *69* (3), 257–294. <https://doi.org/10.1002/jlac.18490690302>.
- (6) Frontana-Urbe, B. A.; Little, R. D.; Ibanez, J. G.; Palma, A.; Vasquez-Medrano, R. Organic Electrosynthesis: A Promising Green Methodology in Organic Chemistry. *Green Chem.* **2010**, *12* (12), 2099–2119. <https://doi.org/10.1039/C0GC00382D>.
- (7) Yan, M.; Kawamata, Y.; Baran, P. S. Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. *Chem. Rev.* **2017**, *117* (21), 13230–13319. <https://doi.org/10.1021/acs.chemrev.7b00397>.
- (8) Novaes, L. F. T.; Liu, J.; Shen, Y.; Lu, L.; Meinhardt, J. M.; Lin, S. Electrocatalysis as an Enabling Technology for Organic Synthesis. *Chem. Soc. Rev.* **2021**, *50* (14), 7941–8002. <https://doi.org/10.1039/d1cs00223f>.
- (9) Zhu, C.; Ang, N. W. J.; Meyer, T. H.; Qiu, Y.; Ackermann, L. Organic Electrochemistry: Molecular Syntheses with Potential. *ACS Cent. Sci.* **2021**, *7* (3), 415–431. <https://doi.org/10.1021/acscentsci.0c01532>.
- (10) Shatskiy, A.; Lundberg, H.; Kärkäs, M. D. Organic Electrosynthesis: Applications in Complex Molecule Synthesis. *ChemElectroChem* **2019**, *6* (16), 4067–4092. <https://doi.org/10.1002/celec.201900435>.
- (11) Wiebe, A.; Gieshoff, T.; Möhle, S.; Rodrigo, E.; Zirbes, M.; Waldvogel, S. R. Electrifying Organic Synthesis. *Angew. Chem. Int. Ed.* **2018**, *57* (20), 5594–5619. <https://doi.org/10.1002/anie.201711060>.
- (12) Qian, L.; Shi, M. Contemporary Photoelectrochemical Strategies and Reactions in Organic Synthesis. *Chem. Commun.* **2023**, *59* (24), 3487–3506. <https://doi.org/10.1039/D3CC00437F>.
- (13) Balzani, V.; Ceroni, P.; Juris, A. *Photochemistry and Photophysics: Concepts, Research, Applications*; Wiley, 2014.
- (14) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.* **2016**, *81* (16), 6898–6926. <https://doi.org/10.1021/acs.joc.6b01449>.
- (15) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113* (7), 5322–5363. <https://doi.org/10.1021/cr300503r>.
- (16) Cheung, K. P. S.; Sarkar, S.; Gevorgyan, V. Visible Light-Induced Transition Metal Catalysis. *Chem. Rev.* **2022**, *122* (2), 1543–1625. <https://doi.org/10.1021/acs.chemrev.1c00403>.
- (17) Kumar, N.; Sharma, T.; Thakur, N.; Jain, R.; Sinha, N. Abundant Transition Metal Based Photocatalysts for Red Light-Driven Photocatalysis. *Chem. – Eur. J.* **2025**, *31* (26), e202500365. <https://doi.org/10.1002/chem.202500365>.
- (18) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116* (17), 10075–10166. <https://doi.org/10.1021/acs.chemrev.6b00057>.
- (19) Lee, Y.; Kwon, M. S. Emerging Organic Photoredox Catalysts for Organic Transformations. *Eur. J. Org. Chem.* **2020**, *2020* (38), 6028–6043. <https://doi.org/10.1002/ejoc.202000720>.
- (20) Bortolato, T.; Cuadros, S.; Simionato, G.; Dell’Amico, L. The Advent and Development of Organophotoredox Catalysis. *Chem. Commun.* **2022**, *58* (9), 1263–1283. <https://doi.org/10.1039/D1CC05850A>.

- (21) Hari, D. P.; König, B. Synthetic Applications of Eosin Y in Photoredox Catalysis. *Chem. Commun.* **2014**, 50 (51), 6688–6699. <https://doi.org/10.1039/C4CC00751D>.
- (22) Yoshioka, E.; Kohtani, S.; Jichu, T.; Fukazawa, T.; Nagai, T.; Kawashima, A.; Takemoto, Y.; Miyabe, H. Aqueous-Medium Carbon–Carbon Bond-Forming Radical Reactions Catalyzed by Excited Rhodamine B as a Metal-Free Organic Dye under Visible Light Irradiation. *J. Org. Chem.* **2016**, 81 (16), 7217–7229. <https://doi.org/10.1021/acs.joc.6b01102>.
- (23) Xu, J.; Cao, J.; Wu, X.; Wang, H.; Yang, X.; Tang, X.; Toh, R. W.; Zhou, R.; Yeow, E. K. L.; Wu, J. Unveiling Extreme Photoreduction Potentials of Donor–Acceptor Cyanoarenes to Access Aryl Radicals from Aryl Chlorides. *J. Am. Chem. Soc.* **2021**, 143 (33), 13266–13273. <https://doi.org/10.1021/jacs.1c05994>.
- (24) Kwon, Y.; Lee, J.; Noh, Y.; Kim, D.; Lee, Y.; Yu, C.; Roldao, J. C.; Feng, S.; Gierschner, J.; Wannemacher, R.; Kwon, M. S. Formation and Degradation of Strongly Reducing Cyanoarene-Based Radical Anions towards Efficient Radical Anion-Mediated Photoredox Catalysis. *Nat. Commun.* **2023**, 14 (1), 92. <https://doi.org/10.1038/s41467-022-35774-5>.
- (25) Tlili, A.; Lakhdar, S. Acridinium Salts and Cyanoarenes as Powerful Photocatalysts: Opportunities in Organic Synthesis. *Angew. Chem.* **2021**, 133 (36), 19678–19701. <https://doi.org/10.1002/ange.202102262>.
- (26) Fukuzumi, S.; Lee, Y.-M.; Nam, W. Photoredox Catalysis of Acridinium and Quinolinium Ion Derivatives. *Bull. Korean Chem. Soc.* **2025**, 46 (1), 4–23. <https://doi.org/10.1002/bkcs.12922>.
- (27) Singh, P. P.; Singh, J.; Srivastava, V. Visible-Light Acridinium-Based Organophotoredox Catalysis in Late-Stage Synthetic Applications. *RSC Adv.* **2023**, 13 (16), 10958–10986. <https://doi.org/10.1039/D3RA01364B>.
- (28) Pitre, S. P.; Overman, L. E. Strategic Use of Visible-Light Photoredox Catalysis in Natural Product Synthesis. *Chem. Rev.* **2022**, 122 (2), 1717–1751. <https://doi.org/10.1021/acs.chemrev.1c00247>.
- (29) Goti, G.; Manal, K.; Sivaguru, J.; Dell’Amico, L. The Impact of UV Light on Synthetic Photochemistry and Photocatalysis. *Nat. Chem.* **2024**, 16 (5), 684–692. <https://doi.org/10.1038/s41557-024-01472-6>.
- (30) Schade, A. H.; Mei, L. Applications of Red Light Photoredox Catalysis in Organic Synthesis. *Org. Biomol. Chem.* **2023**, 21 (12), 2472–2485. <https://doi.org/10.1039/D3OB00107E>.
- (31) Tay, N. E. S.; Lehnher, D.; Rovis, T. Photons or Electrons? A Critical Comparison of Electrochemistry and Photoredox Catalysis for Organic Synthesis. *Chem. Rev.* **2022**, 122 (2), 2487–2649. <https://doi.org/10.1021/acs.chemrev.1c00384>.
- (32) Glaser, F.; Kerzig, C.; Wenger, O. S. Multi-Photon Excitation in Photoredox Catalysis: Concepts, Applications, Methods. *Angew. Chem. Int. Ed.* **2020**, 59 (26), 10266–10284. <https://doi.org/10.1002/anie.201915762>.
- (33) Ghosh, I.; Ghosh, T.; Bardagi, J. I.; König, B. Reduction of Aryl Halides by Consecutive Visible Light-Induced Electron Transfer Processes. *Science* **2014**, 346 (6210), 725–728. <https://doi.org/10.1126/science.1258232>.
- (34) Castellanos-Soriano, J.; Herrera-Luna, J. C.; Díaz Díaz, D.; Jiménez, M. C.; Pérez-Ruiz, R. Recent Applications of Biphotonic Processes in Organic Synthesis. *Org. Chem. Front.* **2020**, 7 (13), 1709–1716. <https://doi.org/10.1039/d0qo00466a>.
- (35) Markushyna, Y.; Savateev, A. Light as a Tool in Organic Photocatalysis: Multi-Photon Excitation and Chromoselective Reactions. *Eur. J. Org. Chem.* **2022**, 2022 (24), e202200026. <https://doi.org/10.1002/ejoc.202200026>.
- (36) Lepori, M.; Schmid, S.; Barham, J. P. Photoredox Catalysis Harvesting Multiple Photon or Electrochemical Energies. *Beilstein J. Org. Chem.* **2023**, 19, 1055–1145. <https://doi.org/10.3762/bjoc.19.81>.
- (37) *The IUPAC Compendium of Chemical Terminology: The Gold Book*, 5th ed.; Gold, V., McNaught, A., The International Union of Pure and Applied Chemistry (IUPAC), Eds.; International Union of Pure and Applied Chemistry (IUPAC): Research Triangle Park, NC, 2025. <https://doi.org/10.1351/goldbook>.
- (38) Barham, J. P.; König, B. Synthetic Photoelectrochemistry. *Angew. Chem. Int. Ed.* **2020**, 59 (29), 11732–11747. <https://doi.org/10.1002/anie.201913767>.

- (39) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238 (5358), 37–38. <https://doi.org/10.1038/238037a0>.
- (40) Bard, A. J. Photoelectrochemistry. *Science* **1980**. <https://doi.org/10.1126/science.207.4427.139>.
- (41) Chan, G.; Corsi, D.; Savateev, O.; Giusto, P.; Barham, J. P. Interfacial Photoelectrochemistry in Organic Synthesis. *Angew. Chem. Int. Ed.* **2025**, 64 (42), e202424300. <https://doi.org/10.1002/anie.202424300>.
- (42) Huang, H.; Steiniger, K. A.; Lambert, T. H. Electrophotocatalysis: Combining Light and Electricity to Catalyze Reactions. *J. Am. Chem. Soc.* **2022**, 144 (28), 12567–12583. <https://doi.org/10.1021/jacs.2c01914>.
- (43) Moutet, J.-C.; Reverdy, G. Photochemistry of Cation Radicals in Solution; Photoinduced Electron-Transfer Reactions between Alcohols and the N,N,N',N'-Tetraphenyl-p-Phenylenediamine Cation Radical. *J. Chem. Soc. Chem. Commun.* **1982**, 18 (12), 654–655. <https://doi.org/10.1039/C39820000654>.
- (44) Scheffold, R.; Orlinski, R. Synthesis and Reactions of Porphine-Type Metal Complexes. 15. Carbon-Carbon Bond Formation by Light Assisted B12-Catalysis. Nucleophilic Acylation of Michael Olefins. *J. Am. Chem. Soc.* **1983**, 105 (24), 7200–7202. <https://doi.org/10.1021/ja00362a047>.
- (45) Yan, H.; Hou, Z.-W.; Xu, H.-C. Photoelectrochemical C–H Alkylation of Heteroarenes with Organotrifluoroborates. *Angew. Chem. Int. Ed.* **2019**, 58 (14), 4592–4595. <https://doi.org/10.1002/anie.201814488>.
- (46) Wang, F.; Stahl, S. S. Merging Photochemistry with Electrochemistry: Functional-Group Tolerant Electrochemical Amination of C(Sp³)–H Bonds. *Angew. Chem. Int. Ed.* **2019**, 58 (19), 6385–6390. <https://doi.org/10.1002/anie.201813960>.
- (47) Huang, H.; Strater, Z. M.; Rauch, M.; Shee, J.; Sisto, T. J.; Nuckolls, C.; Lambert, T. H. Electrophotocatalysis with a Trisaminocyclopropenium Radical Dication. *Angew. Chem. Int. Ed.* **2019**, 58 (38), 13318–13322. <https://doi.org/10.1002/anie.201906381>.
- (48) Liu, J.; Lu, L.; Wood, D.; Lin, S. New Redox Strategies in Organic Synthesis by Means of Electrochemistry and Photochemistry. *ACS Cent. Sci.* **2020**, 6 (8), 1317–1340. <https://doi.org/10.1021/acscentsci.0c00549>.
- (49) Wu, S.; Kaur, J.; Karl, T. A.; Tian, X.; Barham, J. P. Synthetic Molecular Photoelectrochemistry: New Frontiers in Synthetic Applications, Mechanistic Insights and Scalability. *Angew. Chem. Int. Ed.* **2022**, 61 (12), e202107811. <https://doi.org/10.1002/anie.202107811>.
- (50) Lamb, M. C.; Steiniger, K. A.; Trigoura, L. K.; Wu, J.; Kundu, G.; Huang, H.; Lambert, T. H. Electrophotocatalysis for Organic Synthesis. *Chem. Rev.* **2024**, 124 (21), 12264–12304. <https://doi.org/10.1021/acs.chemrev.4c00464>.
- (51) Medici, F.; Chioli, V.; Raimondi, L.; Benaglia, M. Latest Updates in ElectroPhotoChemical Reactions. *Tetrahedron Chem* **2024**, 9, 100061. <https://doi.org/10.1016/j.tchem.2023.100061>.
- (52) Sun, C.-Y.; Lin, T.-J.; Chen, Y.-Y.; Li, H.-L.; Chiang, C.-W. Synergistic Photoredox and Electrochemical Catalysis in Organic Synthesis and Late-Stage Functionalizations. *ChemCatChem* **2024**, 16 (14), e202301537. <https://doi.org/10.1002/cctc.202301537>.
- (53) Fox, M. A. The Photoexcited States of Organic Anions. *Chem. Rev.* **1979**, 79 (3), 253–273. <https://doi.org/10.1021/cr60319a002>.
- (54) Kumar, A.; Sevilla, M. D. SOMO–HOMO Level Inversion in Biologically Important Radicals. *J. Phys. Chem. B* **2018**, 122 (1), 98–105. <https://doi.org/10.1021/acs.jpcc.7b10002>.
- (55) Grimaud, L.; Lakhdar, S.; Vitale, M. R. Electrophotocatalysis: Taking the Best from the Two Worlds. *Curr. Opin. Electrochem.* **2023**, 40, 101307. <https://doi.org/10.1016/j.coelec.2023.101307>.
- (56) Costentin, C.; Fortage, J.; Collomb, M.-N. Electrophotocatalysis: Cyclic Voltammetry as an Analytical Tool. *J. Phys. Chem. Lett.* **2020**, 11 (15), 6097–6104. <https://doi.org/10.1021/acs.jpcclett.0c01662>.
- (57) Horsewill, S. J.; Hierlmeier, G.; Farasat, Z.; Barham, J. P.; Scott, D. J. Shining Fresh Light on Complex Photoredox Mechanisms through Isolation of Intermediate Radical Anions. *ACS Catal.* **2023**, 13 (14), 9392–9403. <https://doi.org/10.1021/acscatal.3c02515>.
- (58) Wagner, D. S.; Spierling, L.; Wenger, O. S. Expanding Thermodynamic and Kinetic Frontiers in Molecular Photocatalysis. *ACS Cent. Sci.* **2026**, 12 (2), 144–156. <https://doi.org/10.1021/acscentsci.5c02047>.

- (59) Kim, H.; Kim, H.; Lambert, T. H.; Lin, S. Reductive Electrophotocatalysis: Merging Electricity and Light To Achieve Extreme Reduction Potentials. *J. Am. Chem. Soc.* **2020**, *142* (5), 2087–2092. <https://doi.org/10.1021/jacs.9b10678>.
- (60) Chernowsky, C. P.; Chmiel, A. F.; Wickens, Z. K. Electrochemical Activation of Diverse Conventional Photoredox Catalysts Induces Potent Photoreductant Activity. *Angew. Chem. Int. Ed.* **2021**, *60* (39), 21418–21425. <https://doi.org/10.1002/anie.202107169>.
- (61) Tian, X.; Karl, T. A.; Reiter, S.; Yakubov, S.; de Vivie-Riedle, R.; König, B.; Barham, J. P. Electro-Mediated PhotoRedox Catalysis for Selective C(Sp³)-O Cleavages of Phosphinated Alcohols to Carbanions. *Angew. Chem. Int. Ed.* **2021**, *60* (38), 20817–20825. <https://doi.org/10.1002/anie.202105895>.
- (62) Kang, W.-J.; Zhang, Y.; Li, B.; Guo, H. Electrophotocatalytic Hydrogenation of Imines and Reductive Functionalization of Aryl Halides. *Nat. Commun.* **2024**, *15* (1), 655. <https://doi.org/10.1038/s41467-024-45015-6>.
- (63) Edgecomb, J. M.; Alektiar, S. N.; Cowper, N. G. W.; Sowin, J. A.; Wickens, Z. K. Ketyl Radical Coupling Enabled by Polycyclic Aromatic Hydrocarbon Electrophotocatalysts. *J. Am. Chem. Soc.* **2023**, *145* (37), 20169–20175. <https://doi.org/10.1021/jacs.3c06347>.
- (64) Zeng, L.; Qin, J.-H.; Lv, G.-F.; Hu, M.; Sun, Q.; Ouyang, X.-H.; He, D.-L.; Li, J.-H. Electrophotocatalytic Reductive 1,2-Diarylation of Alkenes with Aryl Halides and Cyanoaromatics. *Chin. J. Chem.* **2023**, *41* (16), 1921–1930. <https://doi.org/10.1002/cjoc.202300174>.
- (65) Cai, C.-Y.; Lai, X.-L.; Wang, Y.; Hu, H.-H.; Et., A. Photoelectrochemical Asymmetric Catalysis Enables Site- and Enantioselective Cyanation of Benzylic C–H Bonds. *Nat. Catal.* **2022**. <https://doi.org/10.1038/s41929-022-00855-7>.
- (66) Lai, X.-L.; Chen, M.; Wang, Y.; Song, J.; Xu, H.-C. Photoelectrochemical Asymmetric Catalysis Enables Direct and Enantioselective Decarboxylative Cyanation. *J. Am. Chem. Soc.* **2022**, *144* (44), 20201–20206. <https://doi.org/10.1021/jacs.2c09050>.
- (67) Yuan, Y.; Yang, J.; Zhang, J. Cu-Catalyzed Enantioselective Decarboxylative Cyanation via the Synergistic Merger of Photocatalysis and Electrochemistry. *Chem. Sci.* **2023**, *14* (3), 705–710. <https://doi.org/10.1039/d2sc05428k>.
- (68) Lai, X.-L.; Xu, H.-C. Photoelectrochemical Asymmetric Catalysis Enables Enantioselective Heteroarylcyanation of Alkenes via C–H Functionalization. *J. Am. Chem. Soc.* **2023**, *145* (34), 18753–18759. <https://doi.org/10.1021/jacs.3c07146>.
- (69) Xiong, P.; Xu, H.-C. Molecular Photoelectrocatalysis for Radical Reactions. *Acc. Chem. Res.* **2025**, *58* (2), 299–311. <https://doi.org/10.1021/acs.accounts.4c00739>.
- (70) Miyaura, Norio.; Suzuki, Akira. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95* (7), 2457–2483. <https://doi.org/10.1021/cr00039a007>.
- (71) Calvillo Solís, J. J.; Sandoval-Pauker, C.; Bai, D.; Yin, S.; Senftle, T. P.; Villagrán, D. Electrochemical Reduction of Perfluorooctanoic Acid (PFOA): An Experimental and Theoretical Approach. *J. Am. Chem. Soc.* **2024**, *146* (15), 10687–10698. <https://doi.org/10.1021/jacs.4c00443>.
- (72) Doyle, M. G. J.; Jespersen, M. E.; Noureen, S.; Chen, Z.; Jefferson, T. L.; Baptista, C. A.; Houot, M.; Struijs, J. J. C.; Goult, C. A.; Bakulin, A. A.; Paton, R. S.; Avestro, A.-J.; Gouverneur, V. Photocatalytic Controlled Halodefluorination of Perfluoroalkyl Compounds Using N-Arylphenothiazines. *J. Am. Chem. Soc.* **2026**, *148* (27), 29084–29093. <https://doi.org/10.1021/jacs.6c07703>.
- (73) Cybularczyk-Cecotka, M.; Szczepanik, J.; Giedyk, M. Photocatalytic Strategies for the Activation of Organic Chlorides. *Nat. Catal.* **2020**. <https://doi.org/10.1038/s41929-020-00515-8>.
- (74) Fujitsuka, M.; Kim, S. S.; Lu, C.; Tojo, S.; Majima, T. Intermolecular and Intramolecular Electron Transfer Processes from Excited Naphthalene Diimide Radical Anions. *J. Phys. Chem. B* **2015**, *119* (24), 7275–7282. <https://doi.org/10.1021/jp510850z>.
- (75) Cortese, E. Electrochemical Investigation Of Catalytic Cycles That Combine Light Absorption And Electron Transfer: Naphtalene Monoimide And C-X Bond Cleavage Via Electrophotocatalysis.
- (76) Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. Excited Doublet States of Electrochemically Generated Aromatic Imide and Diimide Radical Anions. *J. Phys. Chem. A* **2000**, *104* (28), 6545–6551. <https://doi.org/10.1021/jp000706f>.

- (77) Casadei, T.; Piccoli, A.; Zeppilli, D.; Orian, L.; Isse, A. A.; Fantin, M. Rapid Electrochemical Assessment of Excited-State Quenching Dynamics. *ACS Catal.* **2025**, *15* (19), 16938–16952. <https://doi.org/10.1021/acscatal.5c02778>.
- (78) Shukla, S. S.; Rusling, J. F. Photoelectrocatalytic Reduction of 4-Chlorobiphenyl Using Anion Radicals and Visible Light. *J. Phys. Chem.* **1985**, *89* (15), 3353–3358. <https://doi.org/10.1021/j100261a039>.
- (79) MacKenzie, I. A.; Wang, L.; Onuska, N. P. R.; Williams, O. F.; Begam, K.; Moran, A. M.; Dunietz, B. D.; Nicewicz, D. A. Discovery and Characterization of an Acridine Radical Photoreductant. *Nature* **2020**, *580* (7801), 76–80. <https://doi.org/10.1038/s41586-020-2131-1>.
- (80) Speckmeier, E.; Fischer, T. G.; Zeitler, K. A Toolbox Approach To Construct Broadly Applicable Metal-Free Catalysts for Photoredox Chemistry: Deliberate Tuning of Redox Potentials and Importance of Halogens in Donor–Acceptor Cyanoarenes. *J. Am. Chem. Soc.* **2018**, *140* (45), 15353–15365. <https://doi.org/10.1021/jacs.8b08933>.
- (81) Fina, F.; Bellatreccia, C.; Wu, X.; Cozzi, P. G.; Troisi, A.; Vinogradov, S.; Ceroni, P. Reactivity of Organic Photocatalysts Displaying Thermally Activated Delayed Fluorescence (TADF): Rationalizing Unexpected Differences between Rates of Quenching of the Lowest Singlet and Triplet States. *Chem. Sci.* **2025**, *16* (43), 20536–20543. <https://doi.org/10.1039/d5sc04948b>.
- (82) Medrano-Urbe, K.; Dell’Amico, L. Thermally Activated Delayed Fluorescence (TADF) Compounds in Energy Transfer Processes. A General Alternative to Metal-Based Complexes. *Green Chem.* **2026**, *28* (22), 9168–9180. <https://doi.org/10.1039/d6gc01789d>.
- (83) Chergui, M. 1.19 Ultrafast Structural Dynamics of Biological Systems. *Compr. Biophys.* **2012**. <https://doi.org/10.1016/B978-0-12-374920-8.00123-5>.
- (84) Cruz Neto, D. H.; Pino, T.; Ha-Thi, M.-H. Mechanistic Investigations of Photocatalytic Systems by Pump-Pump-Probe Spectroscopy. *ChemPhotoChem* **2025**, *9* (9), e202500113. <https://doi.org/10.1002/cptc.202500113>.
- (85) Lahm, M. T.; Unterreiner, A.-N. Femtosecond Absorption Spectroscopy to Elucidate Elementary Mechanisms of Molecules in Complex Environments. *Top. Catal.* **2026**. <https://doi.org/10.1007/s11244-026-02286-1>.
- (86) Chou, K.-C.; Zeitz, D. C.; Khvichia, M.; Zhang, J. Z. Tutorial: Transient Absorption Spectroscopy for Probing Ultrafast Dynamics. *ACS Phys. Chem. Au* **2026**. <https://doi.org/10.1021/acspyschemau.6c00027>.
- (87) Carlsson, H. S.; Lund, H.; Heby, O.; Von Bahr, C.; Glaumann, H. Photochemistry of Radical Ions. II. Influence of Thermal Convection and Photoexcitation on Voltammetric Curves. *Acta Chem. Scand.* **1980**, *34b*, 409–412. <https://doi.org/10.3891/acta.chem.scand.34b-0409>.
- (88) Kasha, M. Characterization of Electronic Transitions in Complex Molecules. *Discuss. Faraday Soc.* **1950**. <https://doi.org/10.1039/DF9500900014>.
- (89) Demchenko, A. P.; Tomin, V. I.; Chou, P.-T. Breaking the Kasha Rule for More Efficient Photochemistry. *Chem. Rev.* **2017**, *117* (21), 13353–13381. <https://doi.org/10.1021/acs.chemrev.7b00110>.
- (90) Pfund, B.; Wenger, O. S. Breaking Kasha’s Rule to Enable Higher Reactivity in Photoredox Catalysis. *J. Am. Chem. Soc.* **2025**, *147* (30), 26477–26485. <https://doi.org/10.1021/jacs.5c06115>.
- (91) Pfund, B.; Wenger, O. S. Excited Organic Radicals in Photoredox Catalysis. *JACS Au* **2025**, *5* (2), 426–447. <https://doi.org/10.1021/jacsau.4c00974>.
- (92) Hardegger, R.; Wenger, O. S. Mechanistic Design in Photocatalysis. *Acc. Chem. Res.* **2026**, *59* (6), 849–860. <https://doi.org/10.1021/acs.accounts.5c00842>.
- (93) Horsewill, S. J.; Sharrock, K. M. M.; Fehér, P. P.; Woolley, J. M.; Pápai, I.; Scott, D. J. Counterintuitive Photochemistry of an Isolated Acridinyl Radical: ConPET via Preassembly, Solvated Electrons or a Long-Lived Excited State? *Angew. Chem. Int. Ed.* **2025**, *64* (34), e202506701. <https://doi.org/10.1002/anie.202506701>.
- (94) Pfund, B.; Gejsnæs-Schaad, D.; Lazarevski, B.; Wenger, O. S. Picosecond Reactions of Excited Radical Ion Super-Reductants. *Nat. Commun.* **2024**, *15* (1), 4738. <https://doi.org/10.1038/s41467-024-49006-5>.

- (95) Shaikh, A. C.; Hossain, M. M.; Moutet, J.; Kumar, A.; Thompson, B.; Huxter, V. M.; Gianetti, T. L. Isolated Neutral Organic Radical Unveiled Solvent-Radical Interaction in Highly Reducing Photocatalysis. *Angew. Chem. Int. Ed.* **2025**, *64* (9), e202420483. <https://doi.org/10.1002/anie.202420483>.
- (96) Rieth, A. J.; Gonzalez, M. I.; Kudisch, B.; Nava, M.; Nocera, D. G. How Radical Are “Radical” Photocatalysts? A Closed-Shell Meisenheimer Complex Is Identified as a Super-Reducing Photoreagent. *J. Am. Chem. Soc.* **2021**, *143* (35), 14352–14359. <https://doi.org/10.1021/jacs.1c06844>.
- (97) Mandigma, M. J. P.; Kaur, J.; Barham, J. P. Organophotocatalytic Mechanisms: Simplicity or Naïvety? Diverting Reactive Pathways by Modifications of Catalyst Structure, Redox States and Substrate Preassemblies. *ChemCatChem* **2023**, *15* (11), e202201542. <https://doi.org/10.1002/cctc.202201542>.
- (98) Johnston, B.; Reynolds, K. G.; Campbell, B. M.; Li, A.; Nocera, D. G. A Unified Picture of Radical Anion Photoredox Chemistry. *J. Am. Chem. Soc.* **2025**, *147* (34), 31025–31033. <https://doi.org/10.1021/jacs.5c09029>.
- (99) Thomas, S. J. M.; Edwards, P. P.; Kuznetsov, V. L. Sir Humphry Davy: Boundless Chemist, Physicist, Poet and Man of Action. *ChemPhysChem* **2008**, *9* (1), 59–66. <https://doi.org/10.1002/cphc.200700686>.
- (100) Dye, J. L. The Solvated Electron. *Sci. Am.* **1967**, *216* (2), 76–85.
- (101) Birch, A. J.; Mukherji, S. M. 532. Reduction by Dissolving Metals. Part VI. Some Applications in Synthesis. *J. Chem. Soc. Resumed* **1949**, *152*, 2531–2536. <https://doi.org/10.1039/JR9490002531>.
- (102) Cole, J. P.; Chen, D.-F.; Kudisch, M.; Pearson, R. M.; Lim, C.-H.; Miyake, G. M. Organocatalyzed Birch Reduction Driven by Visible Light. *J. Am. Chem. Soc.* **2020**, *142* (31), 13573–13581. <https://doi.org/10.1021/jacs.0c05899>.
- (103) Singh, A.; Gesser, H. D.; Scott, A. R. Solvated Electron in Acetonitrile. *Chem. Phys. Lett.* **1968**. [https://doi.org/10.1016/0009-2614\(68\)80071-5](https://doi.org/10.1016/0009-2614(68)80071-5).
- (104) Tran-Thi, T. H.; Koulekès-Pujo, A. M.; Sutton, J.; Anitoff, O. Pulse Radiolysis of Amides and Their Aqueous Organic Mixtures. *Radiat. Phys. Chem.* **1977** **1984**. [https://doi.org/10.1016/0146-5724\(84\)90096-7](https://doi.org/10.1016/0146-5724(84)90096-7).
- (105) Hayon, E.; Hayashi, N.; Ibata, T.; Lichtin, N. N.; Matsumoto, A. Pulse Radiolysis of Liquid Amides. *J. Phys. Chem.* **2002**, *75* (15), 2267–2272. <https://doi.org/10.1021/j100684a007>.
- (106) Grills, D. C.; Lyman, S. V. Solvated Electron in Acetonitrile: Radiation Yield, Absorption Spectrum, and Equilibrium between Cavity- and Solvent-Localized States. *J. Phys. Chem. B* **2022**, *126* (1), 262–269. <https://doi.org/10.1021/acs.jpcc.1c08946>.
- (107) Villa, M.; Fermi, A.; Calogero, F.; Wu, X.; Gualandi, A.; Cozzi, P. G.; Troisi, A.; Ventura, B.; Ceroni, P. Organic Super-Reducing Photocatalysts Generate Solvated Electrons via Two Consecutive Photon Induced Processes. *Chem. Sci.* **2024**, *15* (36), 14739–14745. <https://doi.org/10.1039/D4SC04518A>.
- (108) Mazzucato, M.; Isse, A. A.; Durante, C. Dissociative Electron Transfer Mechanism and Application in the Electrocatalytic Activation of Organic Halides. *Curr. Opin. Electrochem.* **2023**, *39*, 101254. <https://doi.org/10.1016/j.coelec.2023.101254>.
- (109) Costentin, C.; Robert, M.; Savéant, J.-M. Electron Transfer and Bond Breaking: Recent Advances. *Chem. Phys.* **2006**, *324* (1), 40–56. <https://doi.org/10.1016/j.chemphys.2005.09.029>.
- (110) Savéant, J. M.; Costentin, C. *Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry*, Second edition.; Wiley: Hoboken, NJ, 2019.
- (111) Saveant, J. M. Dissociative Electron Transfer. New Tests of the Theory in the Electrochemical and Homogeneous Reduction of Alkyl Halides. *J. Am. Chem. Soc.* **2002**, *114* (26), 10595–10602. <https://doi.org/10.1021/ja00052a065>.
- (112) Marcus, R. A.; Sutin, N. Electron Transfers in Chemistry and Biology. *Biochim. Biophys. Acta BBA - Rev. Bioenerg.* **1985**. [https://doi.org/10.1016/0304-4173\(85\)90014-X](https://doi.org/10.1016/0304-4173(85)90014-X).
- (113) Piechota, E. J.; Meyer, G. J. Introduction to Electron Transfer: Theoretical Foundations and Pedagogical Examples. *J. Chem. Educ.* **2019**, *96* (11), 2450–2466. <https://doi.org/10.1021/acs.jchemed.9b00489>.
- (114) Feldman, D. Polymer History. *Des. Monomers Polym.* **2008**, *11* (1), 1–15. <https://doi.org/10.1163/156855508X292383>.

- (115) Morris, P. J. T. *The Polymer Revolution: A Journey Through Polymer Science*; Royal Society of Chemistry, 2025. <https://doi.org/10.1039/9781837673025>.
- (116) Szwarc, M. 'Living' Polymers. *Nature* **1956**, *178* (4543), 1168–1169. <https://doi.org/10.1038/1781168a0>.
- (117) Szwarc, M.; Levy, M.; Milkovich, R. POLYMERIZATION INITIATED BY ELECTRON TRANSFER TO MONOMER. A NEW METHOD OF FORMATION OF BLOCK POLYMERS1. *J. Am. Chem. Soc.* **1956**, *78* (11), 2656–2657. <https://doi.org/10.1021/ja01592a101>.
- (118) Corrigan, N.; Jung, K.; Moad, G.; Hawker, C. J.; Matyjaszewski, K.; Boyer, C. Reversible-Deactivation Radical Polymerization (Controlled/Living Radical Polymerization): From Discovery to Materials Design and Applications. *Prog. Polym. Sci.* **2020**, *111*, 101311. <https://doi.org/10.1016/j.progpolymsci.2020.101311>.
- (119) Fellows, C. M.; Jones, R. G.; Keddie, D. J.; Luscombe, C. K.; Matson, J. B.; Matyjaszewski, K.; Merna, J.; Moad, G.; Nakano, T.; Penczek, S.; Russell, G. T.; Topham, P. D. Terminology for Chain Polymerization (IUPAC Recommendations 2021). *Pure Appl. Chem.* **2022**, *94* (9), 1093–1147. <https://doi.org/10.1515/pac-2020-1211>.
- (120) *Polymer Science, Engineering, and Sustainability*, 1st ed.; Saldívar-Guerra, E., Vivaldo-Lima, E., Eds.; Wiley, 2025; Vol. 1. <https://doi.org/10.1002/9781119820123>.
- (121) Qiu, J.; Charleux, B.; Matyjaszewski, K. Controlled/Living Radical Polymerization in Aqueous Media: Homogeneous and Heterogeneous Systems. *Prog. Polym. Sci.* **2001**, *26* (10), 2083–2134. [https://doi.org/10.1016/S0079-6700\(01\)00033-8](https://doi.org/10.1016/S0079-6700(01)00033-8).
- (122) Goto, A.; Fukuda, T. Kinetics of Living Radical Polymerization. *Prog. Polym. Sci.* **2004**, *29* (4), 329–385. <https://doi.org/10.1016/j.progpolymsci.2004.01.002>.
- (123) Solomon, D. H.; Rizzardo, E.; Cacioli, P. Polymerization Process and Polymers Produced Thereby. US4581429A, April 8, 1986. <https://patents.google.com/patent/US4581429A/en> (accessed 2026-07-15).
- (124) Moad, G.; Rizzardo, E. The History of Nitroxide-Mediated Polymerization. **2015**. <https://doi.org/10.1039/9781782622635-00001>.
- (125) Wang, J.-S.; Matyjaszewski, K. Controlled/"living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. *J. Am. Chem. Soc.* **1995**, *117* (20), 5614–5615. <https://doi.org/10.1021/ja00125a035>.
- (126) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris- (Triphenylphosphine)Ruthenium(II)/Methylaluminum Bis(2,6-Di-Tert-Butylphenoxide) Initiating System: Possibility of Living Radical Polymerization. *Macromolecules* **1995**, *28* (5), 1721–1723. <https://doi.org/10.1021/ma00109a056>.
- (127) Harrisson, S.; Whitfield, R.; Anastasaki, A.; Matyjaszewski, K. Atom Transfer Radical Polymerization. *Nat. Rev. Methods Primer* **2025**, *5* (1), 2. <https://doi.org/10.1038/s43586-024-00370-y>.
- (128) Chiefari, J.; Chong, Y. K. (Bill); Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living Free-Radical Polymerization by Reversible Addition–Fragmentation Chain Transfer: The RAFT Process. *Macromolecules* **1998**, *31* (16), 5559–5562. <https://doi.org/10.1021/ma9804951>.
- (129) Fischer, H. The Persistent Radical Effect In "Living" Radical Polymerization. *Macromolecules* **1997**, *30* (19), 5666–5672. <https://doi.org/10.1021/ma970535l>.
- (130) Boyer, C.; Bulmus, V.; Davis, T. P.; Ladmiral, V.; Liu, J.; Perrier, S. Bioapplications of RAFT Polymerization: *Chem. Rev.* **2009**, *109* (11), 5402–5436. <https://doi.org/10.1021/cr9001403>.
- (131) Gregory, A.; Stenzel, M. H. Complex Polymer Architectures via RAFT Polymerization: From Fundamental Process to Extending the Scope Using Click Chemistry and Nature's Building Blocks. *Prog. Polym. Sci.* **2012**, *37* (1), 38–105. <https://doi.org/10.1016/j.progpolymsci.2011.08.004>.
- (132) Keddie, D. J. A Guide to the Synthesis of Block Copolymers Using Reversible-Addition Fragmentation Chain Transfer (RAFT) Polymerization. *Chem. Soc. Rev.* **2014**, *43* (2), 496–505. <https://doi.org/10.1039/c3cs60290g>.

- (133) Moad, G. RAFT Polymerization to Form Stimuli-Responsive Polymers. *Polym. Chem.* **2017**, *8* (1), 177–219. <https://doi.org/10.1039/c6py01849a>.
- (134) Perrier, S. 50th Anniversary Perspective: RAFT Polymerization—A User Guide. *Macromolecules* **2017**, *50* (19), 7433–7447. <https://doi.org/10.1021/acs.macromol.7b00767>.
- (135) *Handbook of RAFT Polymerization*, 1st ed.; John Wiley & Sons, Ltd, 2008. <https://doi.org/10.1002/9783527622757>.
- (136) *RAFT Polymerization*, 1st ed.; Moad, G., Rizzardo, E., Eds.; Wiley, 2021. <https://doi.org/10.1002/9783527821358.fmatter>.
- (137) Chmielarz, P.; Fantin, M.; Park, S.; Isse, A. A.; Gennaro, A.; Magenau, A. J. D.; Sobkowiak, A.; Matyjaszewski, K. Electrochemically Mediated Atom Transfer Radical Polymerization (eATRP). *Prog. Polym. Sci.* **2017**, *69*, 47–78. <https://doi.org/10.1016/j.progpolymsci.2017.02.005>.
- (138) Strover, L. T.; Cantalice, A.; Lam, J. Y. L.; Postma, A.; Hutt, O. E.; Horne, M. D.; Moad, G. Electrochemical Behavior of Thiocarbonylthio Chain Transfer Agents for RAFT Polymerization. *ACS Macro Lett.* **2019**, *8* (10), 1316–1322. <https://doi.org/10.1021/acsmacrolett.9b00598>.
- (139) Lorandi, F.; Fantin, M.; Shanmugam, S.; Wang, Y.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. Toward Electrochemically Mediated Reversible Addition–Fragmentation Chain-Transfer (eRAFT) Polymerization: Can Propagating Radicals Be Efficiently Electrogenerated from RAFT Agents? *Macromolecules* **2019**, *52* (4), 1479–1488. <https://doi.org/10.1021/acs.macromol.9b00112>.
- (140) Wang, Y.; Fantin, M.; Park, S.; Gottlieb, E.; Fu, L.; Matyjaszewski, K. Electrochemically Mediated Reversible Addition–Fragmentation Chain-Transfer Polymerization. *Macromolecules* **2017**, *50* (20), 7872–7879. <https://doi.org/10.1021/acs.macromol.7b02005>.
- (141) Strover, L. T.; Postma, A.; Horne, M. D.; Moad, G. Anthraquinone-Mediated Reduction of a Trithiocarbonate Chain-Transfer Agent to Initiate Electrochemical Reversible Addition–Fragmentation Chain Transfer Polymerization. *Macromolecules* **2020**, *53* (23), 10315–10322. <https://doi.org/10.1021/acs.macromol.0c02392>.
- (142) Chen, M.; Zhong, M.; Johnson, J. A. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. *Chem. Rev.* **2016**, *116* (17), 10167–10211. <https://doi.org/10.1021/acs.chemrev.5b00671>.
- (143) Corbin, D. A.; Miyake, G. M. Photoinduced Organocatalyzed Atom Transfer Radical Polymerization (O-ATRP): Precision Polymer Synthesis Using Organic Photoredox Catalysis. *Chem. Rev.* **2021**, *122* (2), 1830–1874. <https://doi.org/10.1021/acs.chemrev.1c00603>.
- (144) Aydogan, C.; Yilmaz, G.; Shegiwal, A.; Haddleton, D. M.; Yagci, Y. Photoinduced Controlled/Living Polymerizations. *Angew. Chem.* **2022**, *134* (23), e202117377. <https://doi.org/10.1002/ange.202117377>.
- (145) Lee, Y.; Boyer, C.; Kwon, M. S. Photocontrolled RAFT Polymerization: Past, Present, and Future. *Chem. Soc. Rev.* **2023**, *52* (9), 3035–3097. <https://doi.org/10.1039/d1cs00069a>.
- (146) Beres, M. A.; Boyer, C.; Hartlieb, M.; Konkolewicz, D.; Qiao, G. G.; Sumerlin, B. S.; Perrier, S. RAFT with Light: A User Guide to Using Thiocarbonylthio Compounds in Photopolymerizations. *ACS Polym. Au* **2025**, *5* (3), 184–213. <https://doi.org/10.1021/acspolymersau.4c00101>.
- (147) Otsu, T.; Yoshida, M. Role of Initiator-transfer Agent-terminator (Iniferter) in Radical Polymerizations: Polymer Design by Organic Disulfides as Iniferters. *Makromol. Chem. Rapid Commun.* **1982**. <https://doi.org/10.1002/marc.1982.030030208>.
- (148) Lehnen, A.-C.; Kurki, J. A. M.; Hartlieb, M. The Difference between Photo-Iniferter and Conventional RAFT Polymerization: High Livingness Enables the Straightforward Synthesis of Multiblock Copolymers. *Polym. Chem.* **2022**, *13* (11), 1537–1546. <https://doi.org/10.1039/d1py01530c>.
- (149) Hartlieb, M. Photo-Iniferter RAFT Polymerization. *Macromol. Rapid Commun.* **2022**, *43* (1), 2100514. <https://doi.org/10.1002/marc.202100514>.
- (150) Hughes, R. W.; Lott, M. E.; Olson, S. R. A.; Sumerlin, B. S. Photoiniferter Polymerization: Illuminating the History, Ascendancy, and Renaissance. *Prog. Polym. Sci.* **2024**, *156*, 101871. <https://doi.org/10.1016/j.progpolymsci.2024.101871>.

- (151) Xu, J.; Jung, K.; Atme, A.; Shanmugam, S.; Boyer, C. A Robust and Versatile Photoinduced Living Polymerization of Conjugated and Unconjugated Monomers and Its Oxygen Tolerance. *J. Am. Chem. Soc.* **2014**, *136* (14), 5508–5519. <https://doi.org/10.1021/ja501745g>.
- (152) Zhu, J.; Wang, R.; Ma, Z.; Zuo, W.; Zhu, M. Unleashing the Power of PET-RAFT Polymerization: Journey from Porphyrin-Based Photocatalysts to Combinatorial Technologies and Advanced Bioapplications. *Biomacromolecules* **2024**, *25* (3), 1371–1390. <https://doi.org/10.1021/acs.biomac.3c01356>.
- (153) Allegrezza, M. L.; Konkolewicz, D. PET-RAFT Polymerization: Mechanistic Perspectives for Future Materials. *ACS Macro Lett.* **2021**, *10* (4), 433–446. <https://doi.org/10.1021/acsmacrolett.1c00046>.
- (154) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001.
- (155) Luo, J.; Zhang, J. Donor–Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic C(Sp³)–C(Sp²) Cross-Coupling. *ACS Catal.* **2016**, *6* (2), 873–877. <https://doi.org/10.1021/acscatal.5b02204>.
- (156) Nicholson, R. S. Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics. *Anal. Chem.* **2002**, *37* (11), 1351–1355. <https://doi.org/10.1021/ac60230a016>.
- (157) Wu, S.; Schiel, F.; Melchiorre, P. A General Light-Driven Organocatalytic Platform for the Activation of Inert Substrates. *Angew. Chem.* **2023**, *135* (32), e202306364. <https://doi.org/10.1002/ange.202306364>.
- (158) Chernowsky, C. P.; Chmiel, A. F.; Wickens, Z. K. Electrochemical Activation of Diverse Conventional Photoredox Catalysts Induces Potent Photoreductant Activity. *Angew. Chem. Int. Ed.* **2021**, *60* (39), 21418–21425. <https://doi.org/10.1002/anie.202107169>.
- (159) Bortolamei, N.; Isse, A. A.; Gennaro, A. Estimation of Standard Reduction Potentials of Alkyl Radicals Involved in Atom Transfer Radical Polymerization. *Electrochimica Acta* **2010**, *55* (27), 8312–8318. <https://doi.org/10.1016/j.electacta.2010.02.099>.
- (160) Romańczyk, P. P.; Rotko, G.; Kurek, S. S. The Redox Potential of the Phenyl Radical/Anion Couple and the Effect Thereon of the Lithium Cation: A Computational Study. *Electrochem. Commun.* **2014**, *48*, 21–23. <https://doi.org/10.1016/j.elecom.2014.08.003>.
- (161) Valencia, D. P.; González, F. J. Estimation of Diffusion Coefficients by Using a Linear Correlation between the Diffusion Coefficient and Molecular Weight. *J. Electroanal. Chem.* **2012**, *681*, 121–126. <https://doi.org/10.1016/j.jelechem.2012.06.013>.
- (162) Enemærke, R. J.; Christensen, T. B.; Jensen, H.; Daasbjerg, K. Application of a New Kinetic Method in the Investigation of Cleavage Reactions of Haloaromatic Radical Anions†. *J. Chem. Soc. Perkin Trans. 2* **2001**, No. 9, 1620–1630. <https://doi.org/10.1039/b102835a>.
- (163) Neupane, P.; Katiyar, A.; Bartels, D. M.; Thompson, W. H. Investigation of the Failure of Marcus Theory for Hydrated Electron Reactions. *J. Phys. Chem. Lett.* **2022**, *13* (39), 8971–8977. <https://doi.org/10.1021/acs.jpclett.2c02168>.
- (164) Marcus, R. A. Theoretical Study of Electron Transfer Reactions of Solvated Electrons. *Adv. Chem.* **1965**. <https://doi.org/10.1021/ba-1965-0050.ch011>.
- (165) Marcus, R. A. Theory of Electron-Transfer Reaction Rates of Solvated Electrons. *J. Chem. Phys.* **1965**, *43* (10), 3477–3489. <https://doi.org/10.1063/1.1696504>.
- (166) Ebersson, L. Theories of Electron Transfer in Organic Chemistry. *React. Struct. Concepts Org. Chem.* **1987**. https://doi.org/10.1007/978-3-642-72544-9_3.
- (167) Rehm, D.; Weller, A. Kinetics of Fluorescence Quenching by Electron and H-Atom Transfer. *Isr. J. Chem.* **1970**. <https://doi.org/10.1002/ijch.197000029>.
- (168) Zusman, L. D. Outer-Sphere Electron Transfer in Polar Solvents. *Chem. Phys.* **1980**. [https://doi.org/10.1016/0301-0104\(80\)85267-0](https://doi.org/10.1016/0301-0104(80)85267-0).
- (169) Calef, D. F.; Wolynes, P. G. Classical Solvent Dynamics and Electron Transfer. 1. Continuum Theory. *J. Phys. Chem.* **1983**, *87* (18), 3387–3400. <https://doi.org/10.1021/j100241a008>.
- (170) Sumi, H.; Marcus, R. A. Dynamical Effects in Electron Transfer Reactions. *J. Chem. Phys.* **1986**. <https://doi.org/10.1063/1.449978>.

- (171) Lin, C. Y.; Coote, M. L.; Gennaro, A.; Matyjaszewski, K. Ab Initio Evaluation of the Thermodynamic and Electrochemical Properties of Alkyl Halides and Radicals and Their Mechanistic Implications for Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2008**, *130* (38), 12762–12774. <https://doi.org/10.1021/ja8038823>.
- (172) Tabassum, S.; Pawar, V. P.; Shinde, G. N. Structural Properties Of Polar Liquids Using Microwave Technique. **2017**, *4* (9).
- (173) Chalaris, M.; Samios, J. Systematic Molecular Dynamics Studies of Liquid N,N-Dimethylformamide Using Optimized Rigid Force Fields: Investigation of the Thermodynamic, Structural, Transport and Dynamic Properties. *J. Chem. Phys.* **2000**, *112* (19), 8581–8594. <https://doi.org/10.1063/1.481460>.
- (174) Pan, X.; Fang, C.; Fantin, M.; Malhotra, N.; So, W. Y.; Peteanu, L. A.; Isse, A. A.; Gennaro, A.; Liu, P.; Matyjaszewski, K. Mechanism of Photoinduced Metal-Free Atom Transfer Radical Polymerization: Experimental and Computational Studies. *J. Am. Chem. Soc.* **2016**, *138* (7), 2411–2425. <https://doi.org/10.1021/jacs.5b13455>.
- (175) Armstrong, D. A.; Huie, R. E.; Koppenol, W. H.; Lymar, S. V.; Merényi, G.; Neta, P.; Ruscic, B.; Stanbury, D. M.; Steenken, S.; Wardman, P. Standard Electrode Potentials Involving Radicals in Aqueous Solution: Inorganic Radicals (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87* (11–12), 1139–1150. <https://doi.org/10.1515/pac-2014-0502>.
- (176) Buxton, G. V.; Cattell, F. C. R.; Dainton, F. S. Application of Time-Dependent Rate Constant Theory to Reactions of Solvated Electrons. Reaction Distances, Rate Constants and Diffusion Coefficients in Concentrated Aqueous Solutions. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1975**. <https://doi.org/10.1039/F19757100115>.
- (177) Kuznetsov, A. M.; Ulstrup, J. Quantum Theory of Chemical Reactions of the Solvated Electron. *Faraday Discuss. Chem. Soc.* **1982**. <https://doi.org/10.1039/DC9827400031>.
- (178) Vilchiz, V. H.; Klopfer, J. A.; Germaine, A. C.; Lenchenkov, V. A.; Bradforth, S. E. Map for the Relaxation Dynamics of Hot Photoelectrons Injected into Liquid Water via Anion Threshold Photodetachment and above Threshold Solvent Ionization. *J. Phys. Chem. A* **2001**, *105* (10), 1711–1723. <https://doi.org/10.1021/jp003974m>.
- (179) Myahkostupov, M.; Pagba, C. V.; Gundlach, L.; Piotrowiak, P. Vibrational State Dependence of Interfacial Electron Transfer: Hot Electron Injection from the S1 State of Azulene into TiO2 Nanoparticles. *J. Phys. Chem. C* **2013**, *117* (40), 20485–20493. <https://doi.org/10.1021/jp406662n>.
- (180) Kawakami, T.; Koga, M.; Sotome, H.; Miyasaka, H. Ultrafast Capture of Electrons Ejected by Photoionization Leading to the Formation of a Charge-Separated State at a High Energy Level. *Phys. Chem. Chem. Phys.* **2020**, *22* (31), 17472–17481. <https://doi.org/10.1039/d0cp02029j>.
- (181) Kajita, M.; Takaya, T.; Iwata, K. Dynamics of Electron Ejection on Photoionization of *Trans*-Stilbene and Biphenyl in Acetonitrile as Observed with Femtosecond Time-Resolved near-IR Absorption Spectroscopy. *Phys. Chem. Chem. Phys.* **2022**, *24* (9), 5411–5418. <https://doi.org/10.1039/D1CP05533J>.
- (182) Wu, C.; Corrigan, N.; Lim, C.-H.; Liu, W.; Miyake, G.; Boyer, C. Rational Design of Photocatalysts for Controlled Polymerization: Effect of Structures on Photocatalytic Activities. *Chem. Rev.* **2022**, *122* (6), 5476–5518. <https://doi.org/10.1021/acs.chemrev.1c00409>.
- (183) Wu, Z.; Boyer, C. Near-Infrared Light-Induced Reversible Deactivation Radical Polymerization: Expanding Frontiers in Photopolymerization. *Adv. Sci.* **2023**, *10* (33), 2304942. <https://doi.org/10.1002/advs.202304942>.
- (184) Lissandrini, G.; Zeppilli, D.; Lorandi, F.; Matyjaszewski, K.; Isse, A. A.; Orian, L.; Fantin, M. Photo-RAFT Polymerization Under Microwatt Irradiation via Unimolecular Photoinduced Electron Transfer. *Angew. Chem. Int. Ed.* **2025**, *64* (19), e202424225. <https://doi.org/10.1002/anie.202424225>.
- (185) Rosso, C.; Filippini, G.; Prato, M. Use of Perylene Diimides in Synthetic Photochemistry. *Eur. J. Org. Chem.* **2021**, *2021* (8), 1193–1200. <https://doi.org/10.1002/ejoc.202001616>.
- (186) Shang, T.; Qiu, G.; Li, Y.; Lv, Q.; Liu, Y.; Yu, B. Emerging Perylene Diimide-Based Photocatalysts: Status and Trends in Organic Synthesis. *Chem. Commun.* **2025**, *61* (93), 18208–18219. <https://doi.org/10.1039/d5cc05653e>.

- (187) Dumur, F. Recent Advances on Perylene-Based Photoinitiators of Polymerization. *Eur. Polym. J.* **2021**, *159*, 110734. <https://doi.org/10.1016/j.eurpolymj.2021.110734>.
- (188) Yang, Y.-Y.; Zhang, P.; Hadjichristidis, N. Two-Photon Excitation Photoredox Catalysis Enabled Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2023**, *145* (23), 12737–12744. <https://doi.org/10.1021/jacs.3c02832>.
- (189) Zeman, C. J., IV; Kim, S.; Zhang, F.; Schanze, K. S. Direct Observation of the Reduction of Aryl Halides by a Photoexcited Perylene Diimide Radical Anion. *J. Am. Chem. Soc.* **2020**, *142* (5), 2204–2207. <https://doi.org/10.1021/jacs.9b13027>.
- (190) Wylie, R. A. L.; Grace, J. L.; Jafari, V. F.; Jameson, G. N. L.; Connal, L. A.; Qiao, G. G. Oxygen Initiated and Accelerated PET-RAFT in Ionic Liquid Solutions. *Macromolecules* **2026**, *59* (13), 7525–7540. <https://doi.org/10.1021/acs.macromol.6c01311>.
- (191) Matyjaszewski, K.; Davis, T. P. *HANDBOOK OF RADICAL POLYMERIZATION*; Wiely, 2002. <https://doi.org/10.1002/0471220450>.
- (192) Kumar Panigrahi, S.; Kumar Mishra, A. Inner Filter Effect in Fluorescence Spectroscopy: As a Problem and as a Solution. *J. Photochem. Photobiol. C Photochem. Rev.* **2019**, *41*, 100318. <https://doi.org/10.1016/j.jphotochemrev.2019.100318>.
- (193) Schlichting, H.; Gersten, K. Fundamentals of Boundary–Layer Theory. *Bound.-Layer Theory* **2016**. https://doi.org/10.1007/978-3-662-52919-5_2.
- (194) Cao, H.; Wang, G.; Xue, Y.; Yang, G.; Tian, J.; Liu, F.; Zhang, W. Far-Red Light-Induced Reversible Addition–Fragmentation Chain Transfer Polymerization Using a Man-Made Bacteriochlorin. *ACS Macro Lett.* **2019**, *8* (5), 616–622. <https://doi.org/10.1021/acsmacrolett.9b00320>.
- (195) Shanmugam, S.; Xu, J.; Boyer, C. Light-Regulated Polymerization under Near-Infrared/Far-Red Irradiation Catalyzed by Bacteriochlorophyll a. *Angew. Chem. Int. Ed.* **2016**, *55* (3), 1036–1040. <https://doi.org/10.1002/anie.201510037>.
- (196) Wu, Z.; Fang, W.; Wu, C.; Corrigan, N.; Zhang, T.; Xu, S.; Boyer, C. An Aqueous Photo-Controlled Polymerization under NIR Wavelengths: Synthesis of Polymeric Nanoparticles through Thick Barriers. *Chem. Sci.* **2022**, *13* (39), 11519–11532. <https://doi.org/10.1039/d2sc03952d>.
- (197) Corrigan, N.; Zhernakov, L.; Hashim, M. H.; Xu, J.; Boyer, C. Flow Mediated Metal-Free PET-RAFT Polymerisation for Upscaled and Consistent Polymer Production. *React. Chem. Eng.* **2019**, *4* (7), 1216–1228. <https://doi.org/10.1039/c9re00014c>.
- (198) Borrego-Sánchez, A.; Zemmouche, M.; Carmona-García, J.; Francés-Monerris, A.; Mulet, P.; Navizet, I.; Roca-Sanjuán, D. Multiconfigurational Quantum Chemistry Determinations of Absorption Cross Sections (σ) in the Gas Phase and Molar Extinction Coefficients (ϵ) in Aqueous Solution and Air–Water Interface. *J. Chem. Theory Comput.* **2021**, *17* (6), 3571–3582. <https://doi.org/10.1021/acs.jctc.0c01083>.
- (199) Brouwer, A. C.; Kirsch, J. F. Investigation of Diffusion-Limited Rates of Chymotrypsin Reactions by Viscosity Variation. *Biochemistry* **1982**, *21* (6), 1302–1307. <https://doi.org/10.1021/bi00535a030>.
- (200) Handbook of Chemistry and Physics 95th Edition.
- (201) Schindewolf, U. *Pressure effects in metal-ammonia solutions*. <https://doi.org/10.5445/IR/270003160>.
- (202) Schindewolf, U.; Wünschel, P. Comparison of Solvated Electron Reaction Rates in Water and Ammonia. *Can. J. Chem.* **1977**, *55* (11), 2159–2164. <https://doi.org/10.1139/v77-299>.
- (203) Gavlas, J. F.; Jou, F. Y.; Dorfman, L. M. Optical Absorption Spectrum of the Solvated Electron in Some Liquid Amides and Amines. *J. Phys. Chem.* **1974**, *78* (25), 2631–2635. <https://doi.org/10.1021/j100618a020>.

Appendix

A. Iterative calculation of 4DPAIPN radical anion absorption spectrum

In our spectroelectrochemistry setup, 4DPAIPN could not be quantitatively reduced to 4DPAIPN^{•-}. Therefore, the absorption spectrum of 4DPAIPN^{•-} was reconstructed as follows. The UV-Vis spectrum of a 2 mM 4DPAIPN solution was first collected to obtain the molar absorption coefficient ($\varepsilon(\lambda)$) of the neutral catalyst. This solution was then electrolyzed under constant applied potential of -1.5 V vs. Ag/AgI, and twelve UV-Vis spectra were recorded during electrolysis at 30 s intervals, during which 4DPAIPN progressively, but not quantitatively converted to 4DPAIPN^{•-}. For each collected spectrum at any given wavelength, the total absorbance is the sum of the contributions from neutral and reduced catalyst forms, which is related to their concentrations by the Lambert-Beer law (where b is the optical path length (cm) of the cell) and the following mass balance:

$$A_{\text{tot}} = b \cdot \{\varepsilon(\lambda)_{4\text{DPAIPN}} \cdot [4\text{DPAIPN}] + \varepsilon(\lambda)_{4\text{DPAIPN}^{\bullet-}} \cdot [4\text{DPAIPN}^{\bullet-}]\} \quad (\text{A.1})$$

$$[4\text{DPAIPN}] + [4\text{DPAIPN}^{\bullet-}] = 2 \text{ mM} \quad (\text{A.2})$$

$\varepsilon(\lambda)_{4\text{DPAIPN}^{\bullet-}}$ was obtained by a global fitting procedure (Figure 44): trial $[4\text{DPAIPN}^{\bullet-}]$ values for each absorption spectrum and trial $\varepsilon(\lambda)_{4\text{DPAIPN}^{\bullet-}}$ values at each wavelength were used to compute theoretical absorbances via Equations A.1 and A.2. Clear isosbestic points highlighted the smooth conversion between neutral and reduced photocatalyst.

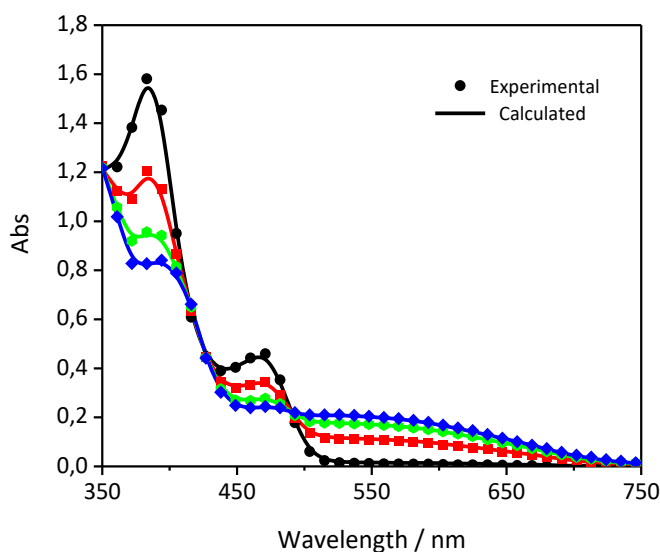


Figure 44. Solid lines: representative absorption spectra collected during electrolysis. Dots: absorbances calculated by the global fitting procedure, showing excellent agreement with experimental ones.

Then, the Excel Solver tool was used to minimize the sum of squared residuals between calculated and experimental absorbances across all spectra and wavelengths, returning optimized concentrations and absorption coefficients which perfectly reproduced the experimental dataset. The resulting $\varepsilon(\lambda)_{4\text{DPAIPN}^{\bullet-}}$ values define the calculated radical anion absorption spectrum.

B. Estimation of the effective temperature at the WE under irradiation

The effective temperature near the WE surface under 630 nm light irradiation was estimated from a calibration curve relating the diffusion coefficient (D) of 4DPAIPN to temperature. CVs of 4DPAIPN at different scan rates (20, 30, 50, 70, 100, 140, 200 mV/s) were recorded under dark conditions, with the cell thermostated at six different temperatures (25–50 °C, 5 °C increments).

At each temperature, the experimental voltammograms were fitted using DigiElch software to extract the corresponding diffusion coefficient. These values were then plotted against the reciprocal of solution temperature (Arrhenius plot) and linearly fitted, since diffusion is an activated process. Interpolation of the average diffusion coefficient under irradiation – $(4.0 \pm 0.1) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, see Section 3.1.1 – on the calibration curve yielded an effective temperature of 31°C (Figure 45).

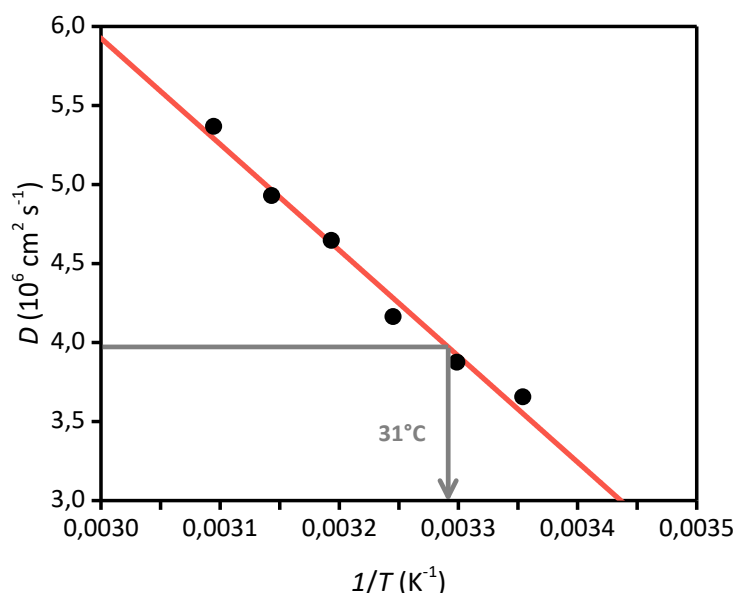


Figure 45. Calibration curve relating the diffusion coefficient of 4DPAIPN to $1/T$, used to determine the effective temperature in the diffusion layer under irradiation. Experimental points: diffusion coefficients extracted from digital simulations of 4DPAIPN CVs; solid line: linear fitting of the dataset.

C. Accounting for light-induced convection in the digital fitting of CVs

To capture light-induced convection in the digital fitting of CVs recorded under illumination, simulations were performed using the "Finite 1D" diffusion mode in the DigiElch software, which allows the diffusion layer thickness (δ) to be treated as a finite, adjustable parameter rather than assuming semi-infinite diffusion. Since neither δ nor the diffusion coefficient (D) under these conditions are known, both had to be extracted from the fit. First, δ was calculated through an iterative optimization. For a series of δ values, spanning a reasonable range in increments of 0.001 cm, the CV dataset was fitted and the corresponding standard deviation (S) between experimental and simulated curves was recorded. Plotting S as a function of δ identifies the δ value that minimizes the fitting error, and thus that is most consistent with experimental data. For the light source and catalyst used in this work, this optimal δ was typically around 70 μm . With δ fixed at this value, D remained the only unknown parameter, and its best fit value was obtained directly from the simulation.

D. Assessing of background dark reactivity for labile aryl halides

4DPAIPN is a fairly strong reductant even in its ground state. As a result, when the standard reduction potential of the aryl halide is sufficiently accessible, DET can proceed via the ground state radical anion without photoexcitation, following a classical EC' mechanism (Table 9).

Table 9. Mechanism and fitting parameters for the dark reactivity toward labile aryl halides.

Reaction	Kinetic constant	Value
$\text{PC} + \text{e}^- \rightleftharpoons \text{PC}^{\bullet-}$	k^0	0.007 cm s^{-1}
$\text{PC}^{\bullet-} + \text{RX} \rightarrow \text{PC} + \text{R}^\bullet + \text{X}^-$	k_{dark}	<i>Fitted</i>
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow \text{PC} + \text{R}^-$	k_{red}	$1.28 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow [\text{R} - \text{PC}]^-$	k_{c}	0

As elsewhere in this work, RX is assumed to be reduced to the carbanion (rate constant at the diffusion limit), neglecting radical coupling pathways. Under dark conditions, non-negligible catalytic activity was observed only for three substrates – namely, 1-bromonaphthalene, 4-bromobenzonitrile, and iodobenzene. As shown in Figure 46 for iodobenzene, the catalytic current observed in the dark (left) is significant compared to that recorded under irradiation (right). This dark contribution must therefore be quantified and subtracted from the total catalytic current, to avoid overestimating k_{SET} .

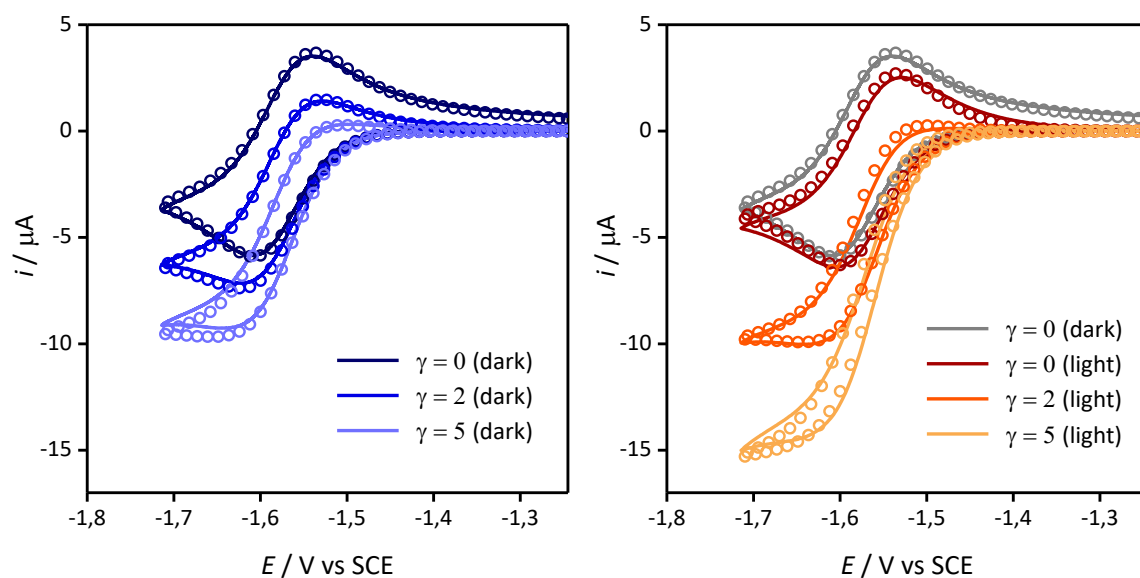


Figure 46. CVs of 4DPAIPN in dark (left panel) and under 630 nm light (right panel), in the presence of iodobenzene at different substrate-to-catalyst ratios (γ). Solid lines: experimental voltammograms. Hollow dots: fitted curves. Scan rate: 30 mV/s. CVs in dark were fitted according to the mechanism reported in Table 9; CVs under irradiation were fitted according to the mechanism reported in Table 4.

For this purpose, a CV in dark conditions was recorded in addition to that under irradiation at each substrate addition and scan rate. The full set of dark CVs was then fitted globally using the EC' mechanism above, yielding $k_{\text{dark}} = 60.92 \text{ M}^{-1} \text{ s}^{-1}$ for iodobenzene.

This value, however, underestimates the actual reaction rate under irradiation, since the increase in catalytic activity observed under light is not solely due to the solvated electron generated upon photoexcitation, but also, to a smaller extent, to a higher dark background resulting from local heating nearby the WE. To correct for this, a separate series of dark CVs with increasing iodobenzene excess was recorded at 31 °C, thus matching the local temperature estimated under irradiation. The digital fitting of this new CV dataset returned $k_{\text{dark}} = 88.54 \text{ M}^{-1} \text{ s}^{-1}$, meaning that the reaction rate increases of 45.3% for a 6°C rise in temperature. This 45.3% correction factor was applied to the 25 °C k_{dark} values obtained for the other two labile substrates, allowing the dark contribution to the overall catalytic current to be quantified without additional dedicated experiments.

The resulting 31°C k_{dark} values were incorporated as an additional chemical step in the localized solvated electron mechanism (see Table 4), enabling the software to decouple the background dark contribution from the reactivity provided by the solvated electron itself. The results of the background dark reactivity quantitative assessment are listed in Table 10.

Table 10. SET kinetic constants in dark used in the CV fitting for labile aryl halides and the corresponding values under irradiation upon subtraction of the background dark contribution.

Substrate	k_{dark} (25°C) [$\text{M}^{-1} \text{s}^{-1}$]	k_{dark} (31°C) [$\text{M}^{-1} \text{s}^{-1}$]	$\log(k_{\text{SET}})$ [$\text{M}^{-1} \text{s}^{-1}$]
1-BrNaph	3.59	5.21	10.15
4CNPhBr	154.2	223.66	10.44
PhI	60.92	88.54	10.57; 10.61

All three substrates (particularly 1-bromonaphthalene) additionally showed the onset of a second wave, arising from direct reduction of the aryl halide at the WE surface. This contribution was isolated by including an additional electrochemical step in the simulation:



with $E^\circ_{\text{RX}/\text{R}^\bullet + \text{X}^-}$ and the k^0 manually adjusted to best fit the experimental CV traces.

E. Estimation of the excitation rate constant from the LED photon flux

The formation of 4DPAIPN^{•-}* proceeds through a first order reaction driven by light absorption, whose rate constant (k_{exc}) is given by¹⁹⁸:

$$k_{\text{exc}} = \int I_{\text{ph}}(\lambda) \cdot \sigma(\lambda) d\lambda \quad (\text{E.1})$$

where $I_{\text{ph}}(\lambda)$ [photons $\text{s}^{-1} \text{cm}^{-2}$] is the incident photon flux at the electrode surface and $\sigma(\lambda)$ [cm^2] is the molecular absorption cross section.

Since $\sigma(\lambda)$ is a per-molecule parameter, it is convenient to define its molar counterpart, the molar Napierian absorption coefficient $\kappa(\lambda)$ [$\text{cm}^2 \text{mol}^{-1}$], such that:

$$\kappa(\lambda) = \sigma(\lambda) \cdot N_A \quad (\text{E.2})$$

Substituting Equation E.2 into E.1 and expressing the incident photon flux on a molar basis ($I_{\text{mol}}(\lambda)$ [$\text{mol s}^{-1} \text{cm}^{-2}$]) by dividing $I_{\text{ph}}(\lambda)$ for N_A , yields:

$$k_{\text{exc}} = \int I_{\text{mol}}(\lambda) \cdot \kappa(\lambda) d\lambda \quad (\text{E.3})$$

In turn, $\kappa(\lambda)$ is obtained from the molar decadic absorption coefficient $\varepsilon(\lambda)$ [$\text{M}^{-1} \text{cm}^{-1}$] – the quantity measured in this work by UV-Vis spectroscopy – through:

$$\kappa(\lambda) = 1000 \cdot \ln(10) \cdot \varepsilon(\lambda) \quad (\text{E.4})$$

Here, the factor 1000 converts the volume unit from L to cm^3 , while the factor $\ln(10)$ converts the absorption coefficient from the decadic convention to the Napierian one, required to describe photon absorption as a probabilistic event.

Based on Equation E.3, for the two light sources used in digital fittings the $I_{\text{mol}}(\lambda) \cdot \kappa(\lambda)$ product was plotted against wavelength and the area under the curve was calculated (Figure 47).

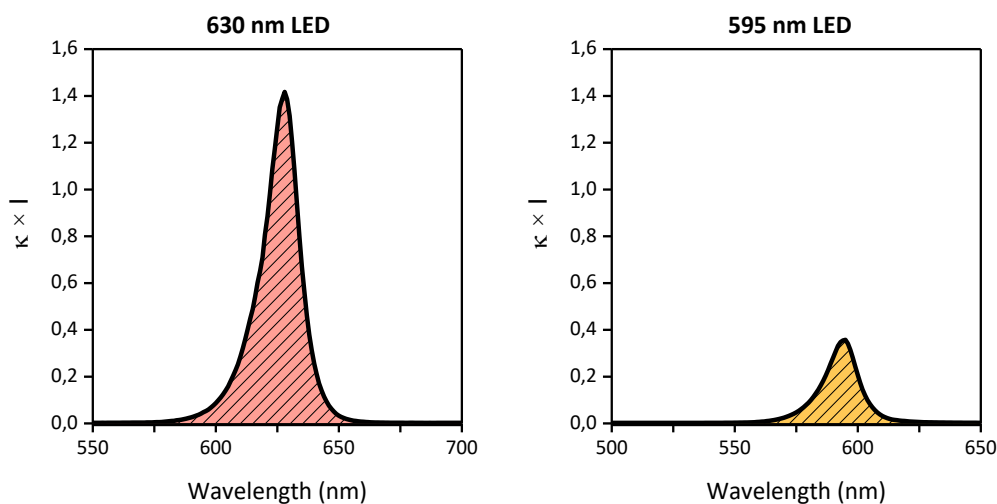


Figure 47. Plots of $\kappa \cdot I$ vs λ for the two different light sources used in quantitative kinetic analysis. The area under the curve represents the rate constant for the formation of the excited state.

Two correction factors were considered for the k_{exc} value obtained from Equation E.3. The first arises from incident light reflection at the electrode surface, which enhances excitation efficiency: for the GC surface of the WE used, a reflectivity of 16% was measured, and the k_{exc} value was corrected accordingly by a factor of 1.16. The second relates to light attenuation within the diffusion layer, where 4DPAIPN^- itself absorbs light, potentially lowering the intensity reaching the electrode compared to that recorded by the optical fiber sensor (see Experimental section). However, applying the Lambert-Beer equation to typical experimental conditions ($[4\text{DPAIPN}] = 1\text{mM}$, $\delta = 70 \mu\text{m}$) indicated that only less than 1% of the incident light was absorbed. This second contribution was therefore neglected. The correction for light reflection at the GC surface yielded $k_{\text{exc}} = 32.39 \text{ s}^{-1}$ for the 630 nm light source and $k_{\text{exc}} = 7.77 \text{ s}^{-1}$ for the 595 nm light source.

F. Determination of diffusion-limited reaction rates

The diffusion limit (k_{diff}) for a second-order reaction between two generic species A and B in a given solvent and at a given temperature is given by¹⁹⁹:

$$k_{\text{diff}} = 4\pi N_A(r_A + r_B)(D_A + D_B) \quad (\text{F.1})$$

where r [m] and D [$\text{m}^2 \text{s}^{-1}$] are, respectively, the radius and diffusion coefficient of each species.

Evaluating k_{diff} for the relevant reactions involved in this work therefore requires the radius and diffusion coefficient of aryl halides, 4DPAIPN^{•-} and solvated electron.

For the aryl halides, the average r value was estimated using the hard-sphere approximation:

$$r_{RX} = \frac{3}{4} \left(\frac{MW_{RX}}{N_A \rho \pi} \right)^{1/3} \quad (\text{F.2})$$

based on the molecular weight (MW_{RX}) and density (ρ) of each substrate, while the average diffusion coefficient was derived as described in Section 3.1.1.

For 4DPAIPN^{•-}, conversely, the diffusion coefficient was determined through digital simulations (Section 3.1.1) and used to calculate the radius via the Stokes–Einstein equation:

$$r = \frac{k_B T}{6\pi\eta D} \quad (\text{F.3})$$

where η is the solvent viscosity (for DMF, $7.94 \cdot 10^{-4} \text{ Pa s}$ at 25°C ²⁰⁰).

The effective cavity radius of the solvated electron in DMF was estimated through a calibration approach based on liquid ammonia. In a simple spherical *particle in the box* model, the radius of the cavity calculated in NH_3 from the absorption maximum ($\lambda_{\text{max}} \approx 1700 \text{ nm}$ ²⁰¹) is $r_{\text{calc}} \approx 7.3 \text{ \AA}$. Comparing this value with the “real” cavity radius derived from experimental and simulation data ($r_{\text{real}} \approx 3.2 \text{ \AA}$ ²⁰²) yields a correction factor $f = r_{\text{real}}/r_{\text{calc}} \approx 0.44$. Applying this factor to the radius calculated within the same model in DMF ($\lambda_{\text{max}} \approx 1680 \text{ nm}$ ²⁰³), which again results $r_{\text{calc}} \approx 7.3 \text{ \AA}$, leads to $r \approx 3.2 \text{ \AA}$ also in DMF. While this approach neglects solvent-specific effects, it provides a physically grounded rough estimate of the cavity radius in DMF, anchored to a well-characterized reference system. Sensitivity analysis indicated that limited variations in this value do not appreciably affect the outcome of the Marcus plot fitting. The diffusion coefficient for the solvated electron was then determined according to Equation F.3.

All radii and diffusion coefficients used to estimate diffusion limits are summarized in Table 11.

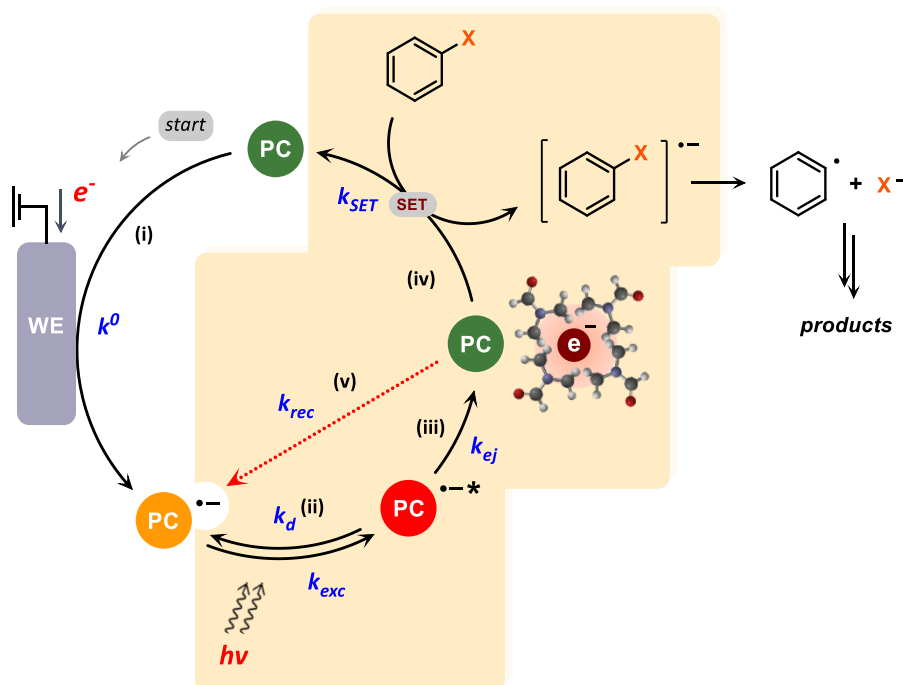
Table 11. Parameters used to calculate diffusion-limited reaction rates.

Reactant	RX (average)	4DPAIPN ^{•-}	Solvated electron
D (cm ² s ⁻¹)	$(1.12 \pm 0.07) \cdot 10^{-5}$	$(3.46 \pm 0.11) \cdot 10^{-6}$ (dark) $(4.00 \pm 0.13) \cdot 10^{-6}$ (light)	$1.11 \cdot 10^{-4}$
r (Å)	3.57 ± 0.11	8.01	3.2

G. Digital fitting of 4CzIPN and NMI CVs with simplified EC' mechanisms

To rapidly and qualitatively assess whether electrons ejected from non-4DPAIPN catalysts remain localized near the parent catalyst (i.e., localized solvated electron model) or are projected far into the bulk solution (i.e., free solvated electron model), simplified EC' electrocatalytic mechanisms were implemented in DigiElch. This approach allowed us to probe the overarching mechanism without prior knowledge of the photophysical parameters of the newly investigated photocatalysts.

The complete mechanism for the localized solvated electron ejection is represented in Scheme 18.



Scheme 18. Reaction scheme for the ePRC-driven RX cleavage via localized solvated electrons, where the shadowed region represents all processes encompassed in k_{obs} .

Applying the steady state approximation to the PC/solvated electron couple (encompassing all processes in the orange box of the scheme) yields the following expression for its concentration:

$$[\text{PC}/\text{e}^-] = \frac{k_{\text{ej}} k_{\text{exc}} [\text{PC}^{\bullet-}]}{(k_{\text{d}} + k_{\text{ej}})(k_{\text{rec}} + k_{\text{SET}} [\text{RX}])} \quad (\text{G.1})$$

From this, the rate of RX consumption is expressed as:

$$\frac{d[\text{RX}]}{dt} = k_{\text{SET}} [\text{PC}/\text{e}^-] [\text{RX}] = \frac{k_{\text{SET}} k_{\text{ej}} k_{\text{exc}} [\text{PC}^{\bullet-}] [\text{RX}]}{(k_{\text{d}} + k_{\text{ej}})(k_{\text{rec}} + k_{\text{SET}} [\text{RX}])} \quad (\text{G.2})$$

Alternatively, all steps within the orange box were lumped into a single observed rate constant (k_{obs}), yielding a simplified bimolecular EC' mechanism (Table 12). Consistent with the model applied to 4DPAIPN, the two possible downstream fates of the aryl radical – reduction (k_{red}) and coupling (k_{c}) – were explicitly accounted for.

Table 12. Mechanism and fitting parameters for the simplified bimolecular EC' mechanism.

Reaction	Kinetic constant	Value
$\text{PC} + \text{e}^- \rightleftharpoons \text{PC}^{\bullet-}$	k^0	0.0075 cm s ⁻¹ (4CzIPN); 0.03 cm s ⁻¹ (NMI)
$\text{PC}^{\bullet-} + \text{RX} \rightarrow \text{PC} + \text{R}^\bullet + \text{X}^-$	k_{obs}	<i>Fitted</i> (M ⁻¹ s ⁻¹)
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow \text{PC} + \text{R}^-$	k_{red}	<i>Fitted</i> (M ⁻¹ s ⁻¹)
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow [\text{R} - \text{PC}]^-$	k_{c}	<i>Fitted</i> (M ⁻¹ s ⁻¹)

Within this simplified mechanism, the rate of RX consumption is instead expressed as:

$$\frac{d[\text{RX}]}{dt} = k_{\text{obs}} [\text{PC}^{\bullet-}] [\text{RX}] \quad (\text{G.3})$$

Equating G.2 and G.3 yields the expression for k_{obs} :

$$k_{\text{obs}} = \frac{k_{\text{SET}} k_{\text{ej}} k_{\text{exc}}}{(k_{\text{d}} + k_{\text{ej}})(k_{\text{rec}} + k_{\text{SET}} [\text{RX}])} \quad (\text{G.4})$$

Therefore, by folding all photophysical and chemical processes downstream of electrochemical reduction (highlighted in Scheme 18) into a single observed rate constant (k_{obs}), the bimolecular EC' turnover faithfully reproduces the electrophotocatalytic behaviour of a localized solvated electron.

Fitting the mechanism of Table 12 to experimental CVs of 4CzIPN under 525 nm light, recorded with increasing iodobenzene concentrations, gave excellent agreement with the data (Figure 48). Unlike 4DPAIPN, the fit indicates that coupling between the aryl radical and the reduced catalyst dominates over reduction, as also evident from the marked loss of reversibility even at low catalytic currents. This is most likely due to the less negative ground state reduction potential of 4CzIPN, which provides a lower driving force for aryl radical reduction.

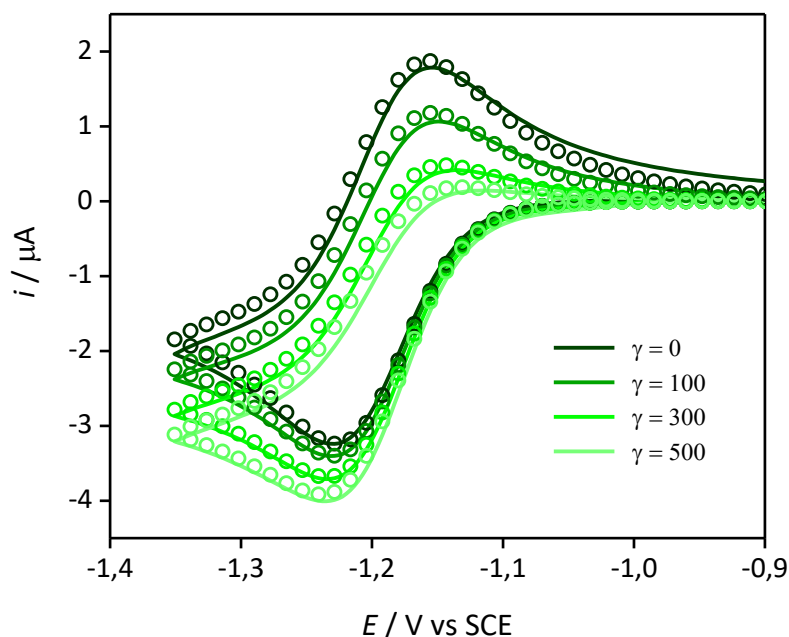


Figure 48. Solid lines: CVs of 4CzIPN under 525 nm light in the presence of iodobenzene at different substrate-to-catalyst ratios (γ). Hollow dots: fitted curves using the bimolecular EC' mechanism. Scan rate: 30 mV/s.

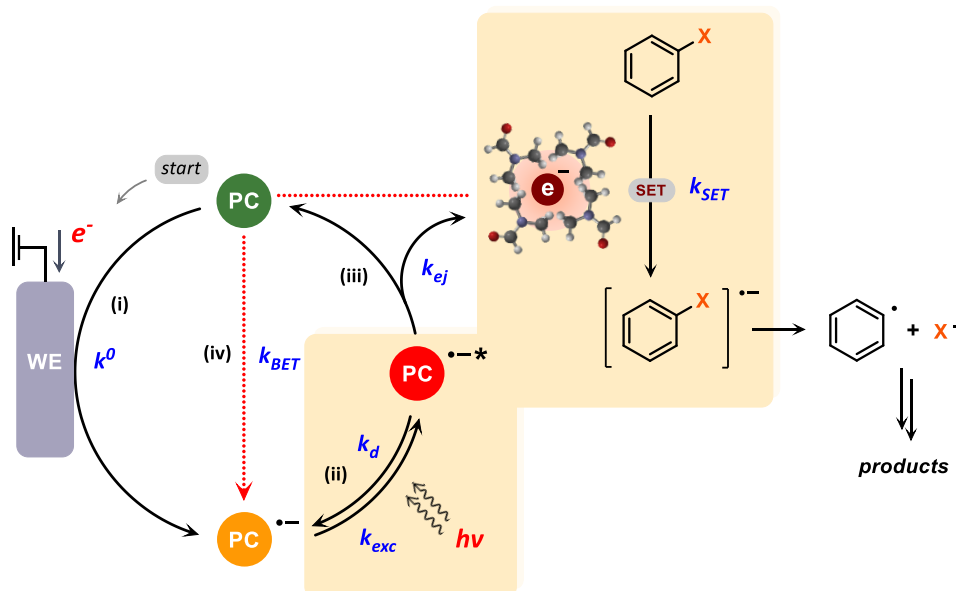
A second, unimolecular variant of the simplified EC' mechanism was then considered (Table 13).

Table 13. Mechanism and fitting parameters for the simplified unimolecular EC' mechanism.

Reaction	Kinetic constant	Value
$\text{PC} + \text{e}^- \rightleftharpoons \text{PC}^{\bullet-}$	k^0	0.03 cm s ⁻¹ (NMI)
$\text{PC}^{\bullet-} \rightarrow \text{PC} + \text{D}^{\bullet-}$	k_{sep}	Fitted (s ⁻¹)
$\text{D}^{\bullet-} + \text{RX} \rightarrow \text{D} + \text{R}^\bullet + \text{X}^-$	k_{obs}	Fitted (M ⁻¹ s ⁻¹)
$\text{D}^{\bullet-} + \text{PC} \rightarrow \text{D} + \text{PC}^{\bullet-}$	k_{BET}	Fitted (M ⁻¹ s ⁻¹)
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow \text{PC} + \text{R}^-$	k_{red}	Fitted (M ⁻¹ s ⁻¹)
$\text{PC}^{\bullet-} + \text{R}^\bullet \rightarrow [\text{R} - \text{PC}]^-$	k_{c}	Fitted (M ⁻¹ s ⁻¹)

Herein, the reduced catalyst is assumed to eject a donor species – effectively mimicking the ejection of a solvated electron – while itself immediately reverting to the neutral, re-reducible form. The ejected donor species can subsequently either reduce the substrate or recombine with the neutral catalyst. This simplified unimolecular EC' turnover effectively reproduces the electrophotocatalytic behaviour of a free solvated electron.

The complete mechanism for free solvated electron ejection is represented in Scheme 19. The mechanism of Table 13 result from the encompassing of photoexcitation, non-radiative decay and SET to the substrate (orange box) into a single rate constant (k_{obs}). However, a closed-form expression for k_{obs} , analogous to Equation G.4, could not be derived in this case, as the additional donor ejection step (k_{sep}) introduces further complexity that the steady-state treatment cannot resolve into a single explicit relationship.



Scheme 19. Reaction scheme for the ePRC-driven RX cleavage via free solvated electrons, where the shadowed region represents all processes encompassed in k_{obs} .

Experimental NMI voltammograms – recorded under 440 nm light with increasing 4-chlorotoluene concentrations – were fitted using both bimolecular and unimolecular EC' mechanisms, with the latter showing markedly improved fit quality (Figure 49). Nevertheless, it is likely that experimental CVs are affected also by a minor bimolecular contribution, so that a mixed unimolecular-bimolecular fitting would provide the best results. As with 4CzIPN, radical coupling dominates over reduction as the downstream fate of the aryl radical.

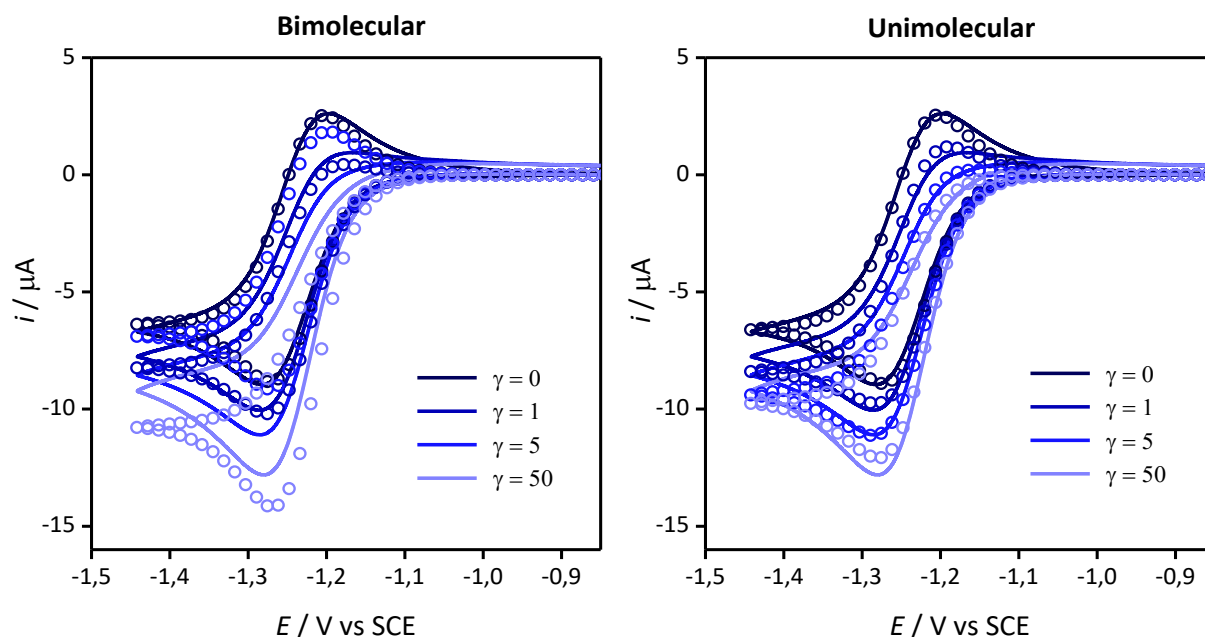


Figure 49. Solid lines: CVs of NMI under 440 nm light in the presence of 4-chlorotoluene at different substrate-to-catalyst ratios (γ). Hollow dots: fitted curves using the bimolecular EC' mechanism (left panel) and the unimolecular EC' mechanism (right panel). Scan rate: 30 mV/s.

H. Derivation of the apparent polymerization rate dependence on PDI loading

The simplified reaction mechanism for PET-eRAFT polymerization is summarized in Table 14.

Table 14. Mechanism steps and their relative rate constants for PET-eRAFT polymerization.

Reaction	Kinetic constant
$\text{PDI} + \text{e}^- \rightleftharpoons \text{PDI}^{\bullet-}$	k^0
$\text{PDI}^{\bullet-} + h\nu \rightarrow \text{PDI}^{\bullet--*}$	k_{exc}
$\text{PDI}^{\bullet--*} \rightarrow \text{PDI}^{\bullet-}$	k_{d}
$\text{PDI}^{\bullet--*} + \text{CTA} \rightarrow \text{PDI} + \text{R}^\bullet$	k_{PET}
$\text{R}^\bullet + \text{M} \rightarrow \text{P}^\bullet$	k_{p}
$\text{R}^\bullet + \text{R}^\bullet \rightarrow \text{dead chain}$	k_{t}

Applying the steady-state approximation to $\text{PDI}^{\bullet-}$ and $\text{PDI}^{\bullet--*}$, together with the general mass balance on all PDI species, yields the Equations H.1–H.3, where $[\text{PDI}]_0$ is the initial PDI concentration:

$$[\text{PDI}^{\bullet-}] = \frac{k^0 [\text{PDI}]_0}{k^0 + k_{\text{exc}} \cdot \phi_{\text{PET}}} \quad (\text{H.1})$$

$$[\text{PDI}^{\bullet-*}] = \frac{k_{\text{exc}} \cdot [\text{PDI}^{\bullet-}]}{k_{\text{d}} + k_{\text{PET}} \cdot [\text{CTA}]} \quad (\text{H.2})$$

$$\phi_{\text{PET}} = \frac{k_{\text{PET}} \cdot [\text{CTA}]}{k_{\text{d}} + k_{\text{PET}} \cdot [\text{CTA}]} \quad (\text{H.3})$$

Given that the polymerization follows pseudo first order kinetics, radical concentration is constant, and the initiation rate must be equal to the termination rate:

$$k_{\text{PET}} \cdot [\text{CTA}] \cdot [\text{PDI}^{\bullet-*}] = 2k_{\text{t}} \cdot [\text{R}^{\bullet}]^2 \quad (\text{H.4})$$

Solving Equation G.4 for $[\text{R}^{\bullet}]$ and substituting Equation H.2 gives:

$$[\text{R}^{\bullet}] = \sqrt{\frac{k_{\text{PET}} \cdot [\text{CTA}] \cdot [\text{PDI}^{\bullet-*}]}{2k_{\text{t}}}} = \sqrt{\frac{k_{\text{PET}} \cdot k_{\text{exc}} \cdot [\text{CTA}] \cdot [\text{PDI}^{\bullet-}]}{2k_{\text{t}} \cdot (k_{\text{d}} + k_{\text{PET}} \cdot [\text{CTA}])}} \quad (\text{H.5})$$

Finally, since $k_{\text{p,app}}$ is directly proportional to $[\text{R}^{\bullet}]$, it follows from Equation H.5 that $k_{\text{p,app}}$ depends on the square root of $[\text{PDI}^{\bullet-}]$ and hence, through Equation H.1, this translates into an analogous square root dependence on $[\text{PDI}]_0$.