

Photocatalytic Polymerization

Better Together: Photoredox/Copper Dual Catalysis in Atom Transfer Radical Polymerization

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Dedicated to Professor Violetta Patroniak on the occasion of her 60th birthday

Abstract: Photomediated Atom Transfer Radical Polymerization (photoATRP) is an activator regeneration method, which allows for the controlled synthesis of well-defined polymers via light irradiation. Traditional photoATRP is often limited by the need for high-energy ultraviolet or violet light. These could negatively affect the control and selectivity of the polymerization, promote side reactions, and may not be applicable to biologically relevant systems. This drawback can be circumvented by an introduction of the catalytic amount of photocatalysts, which absorb visible and/or NIR light and, therefore, controlled, regenerative ATRP can be performed with the dual-catalytic cycle. Herein, a critical summary of recent developments in the field of dual-catalysis concerning Cu-catalyzed ATRP is provided. Contributions of involved species are examined mechanistically, followed by challenges and future directions towards the next generation of advanced functional macromolecular materials.

1. Introduction

This review presents the principles and progress in dual catalytic systems in atom transfer radical polymerization (ATRP). Conventional radical polymerization (RP) is used to produce about 1/3 of synthetic polymers worldwide but cannot provide tailor-made polymers such as block copoly-

mers, due to the very short lifetime (ca. 1 second) of growing chains. On the other hand, ATRP is one of the most efficient reversible deactivation radical polymerization (RDRP) methods which enables long lifetimes of growing chains. This facilitates the preparation of well-defined polymers with controlled composition, topology, and functionality, as well as many hybrid materials and bioconjugates.^[1]

In ATRP, the lifetime of growing chains is extended to > 1h via intermittent activation of dormant species with Cu-based catalysts. Lower oxidation state transition metal complexes (activators) react with dormant alkyl halides to intermittently form growing radicals which are rapidly deactivated by higher oxidation state deactivators. This provides concurrent growth of all chains, enabling the synthesis of uniform polymers with low dispersity. ATRP catalysis has recently made tremendous progress by employing Cu-based catalysts up to a billion times more active than originally used catalysts.^[2] This enabled the decrease in the concentration of Cu-catalysts to ppm level to simplify the purification of the obtained polymeric products, thus diminishing the metal content and environmental impact of ATRP. However, ATRP carried out at low-ppm levels of activators stops at limited conversion because activators are irreversibly converted to deactivators through unavoidable radical termination. Thus, the concept of activator regeneration was developed. It employs various chemical reagents, such as ascorbic acid, inorganic sulfites, thermal radical initiators (e.g., AIBN), or external stimuli, such as electrical current, sonication, mechanical forces, and light. In this review, light is emphasized through photocatalysts.

Originally, stoichiometric or even excess amounts of Cu-catalysts were used with respect to the initiator, which similarly required higher equivalents of regeneration additives. However, by decreasing Cu-catalyst loading, additive concentrations were also significantly diminished for the task of regenerating low-ppm levels of activators. Within a concurrent catalytic cycle, photocatalysts (PCs) regenerate Cu-ATRP activator complexes (cationic complex denoted as Cu^IL⁺) and undergo regeneration themselves to function at low, truly catalytic concentrations. In traditional photo-ATRP, activator regeneration typically requires high energy irradiation (< 400 nm) based on the absorption of cationic X–Cu^{II}L⁺ deactivator complexes (higher oxidation state). New dual-catalytic systems combining Cu-ATRP complexes and PCs can be used at much longer wavelengths, including

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red and even near-infrared light, which are more benign, especially in the synthesis of bioconjugates. They also have much longer penetration in opaque, scattering media, provide enhanced oxygen tolerance, and offer good temporal control. The mechanism and role of various components of such dual catalytic systems will be explained.

Figure 1 shows a photoredox/copper dual-catalytic ATRP (PC/Cu-ATRP) system involving PC, Cu-ATRP catalyst, and light for the regeneration of $\text{Cu}^{\text{I}}\text{L}^+$ activators. After PC is photoexcited, its corresponding excited PC^* state reduces $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ deactivators to $\text{Cu}^{\text{I}}\text{L}^+$ activators, thereby regenerating the ATRP activator. An oxidative quenching proceeds by forming $\text{PC}^{\bullet+}\text{X}^-$. Then, the oxidized $\text{PC}^{\bullet+}\text{X}^-$ returns to the ground state by reacting with an amine electron donor (ED). Alternatively, the excited PC^*

species can be converted into a radical anion $\text{PC}^{\bullet-}$ by reacting with an ED in a reductive quenching process and then react with $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ to regenerate PC and $\text{Cu}^{\text{I}}\text{L}^+$. This dual catalytic system provides several advantages, illustrated in Figure 1. Similar catalytic systems were reported in organic reactions in photoinduced electron, energy or hydrogen atom transfer^[3] as well as in some polymerization systems.^[4] For PC, both transition metal complexes and organic dyes/photosensitizers were used.^[5,6] The mechanism and role of each component within such dual catalytic systems will be explained.

Current Cu-ATRP catalysts can efficiently control ATRP by rapidly equilibrating active and dormant species, providing concurrent growth of all polymer chains. However, due to unavoidable radical termination and loss of



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Adam Gorczyński received his Ph.D. in 2017 from the Faculty of Chemistry, Adam Mickiewicz University and is currently working towards his habilitation at the same institution. He completed a postdoctoral fellowship at the Matyjaszewski Polymer Group at Carnegie Mellon, with a focus on RDRP techniques, mostly ATRP. His research centers on designing advanced multifunctional materials for applications in materials science, electrochemistry, biology, and catalysis, with the goal of discovering novel materials with unique properties.



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Kris Matyjaszewski is J.C. Warner University Professor of Natural Sciences at Carnegie Mellon University. In 1994, he discovered Cu-mediated atom transfer radical polymerization, commercialized in 2004 in the US, Japan, and Europe. He synthesized many advanced materials for biomedical, environmental, and energy-related applications. He has co-authored >1,300 publications, (>200,000 citations, h-index 213) and 72 US patents. He is a member of NAS, NAE, and European, Australian, Polish Academies of Sciences. He received 2023 NAS Award in Chemical Sciences, 2021 Grand Prix de la Maison de la Chimie, France, 2017 Franklin Medal in Chemistry, 2015 Dreyfus Prize in Chemical Sciences, 2011 Wolf Prize in Chemistry, 2009 Presidential Green Chemistry Challenge Award, >10 awards from ACS and thirteen doctorates honoris causa.

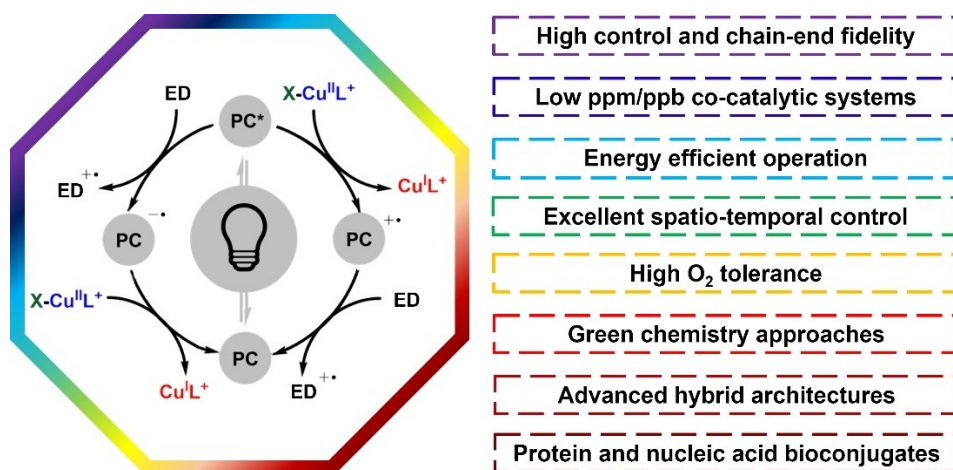


Figure 1. Overview of $\text{Cu}^{\text{I}}\text{L}^+$ activator regeneration in dual-catalysis PC/Cu-ATRP with their advantages (ED - electron donor, PC - photocatalyst).

activators, they cannot be applied at ppm concentrations alone and require some reducing agents. On the other hand, newly designed PCs can absorb visible light and can act as activators of dormant alkyl halides but generate only uncontrolled, very high molecular weight polymers. When Cu-catalysts and PCs are synergistically applied at ppm levels, they produce very well-defined polymers with rates depending on the concentration and quantum efficiency of PC and control defined by Cu-catalysts. Thus, they can act much better together, providing control, oxygen tolerance, and access to new materials, as discussed in this review.

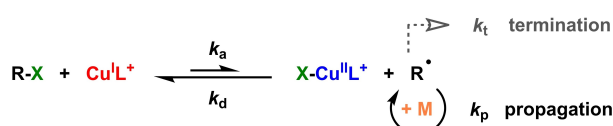
2. Mechanistic Principles of ATRP

2.1. Normal ATRP

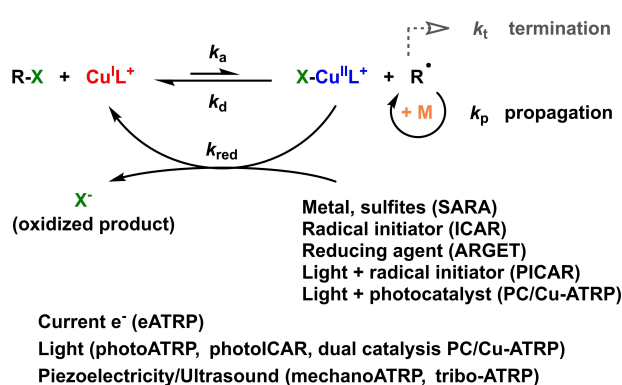
ATRP is one of the most robust and well-established methods to form well-defined, functional macromolecules.^[7] At its core is the fate of short-lived radicals, which can be reversibly deactivated to form dormant species, hence the IUPAC term Reversible Deactivation Radical Polymerization (RDRP).^[8] This ATRP equilibrium between the active monomer-derived alkyl radicals $\text{R}^\bullet$ and R-X dormant species (initiators and polymers with carbon-halogen bond) is governed by redox-active transition metal complexes $\text{Mt}^{\text{I}}\text{L}$; $\text{X-Mt}^{\text{n}+1}\text{L}$ (Mt: $\text{Cu}^{\text{I/II}}$, $\text{Ru}^{\text{II/III}}$, $\text{Fe}^{\text{II/III}}$), with seminal example using Cu halides and L: 2,2'-bipyridine^[9] (Scheme 1a).

The activation step (k_a) proceeds via a concerted inner-sphere electron transfer (ISET) by transferring X between R-X and $\text{Cu}^{\text{I}}\text{L}^+$ activator to form $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator and propagating radical (chain).^[10] The radical may undergo addition to monomer units or be deactivated by $\text{X-Cu}^{\text{II}}\text{L}^+$ to restore the halogen-capped dormant species alongside $\text{Cu}^{\text{I}}\text{L}^+$ activator.^[11] Rate constants of the processes reflect a shift towards the dormant species ($k_a \ll k_d$; $K_{\text{ATRP}} = k_a/k_d$), and they depend significantly on the nature of the radical, i.e., the bond dissociation free energy (BDFE), the catalyst and reaction conditions (solvent, temperature, pressure).

a) Atom Transfer Radical Polymerization (ATRP)



b) ATRP with (re)generation of activator



Scheme 1. Comparison of normal and regenerative ATRP mechanisms. For $\text{Cu}^{\text{I}}\text{L}^+$ activators and $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivators, acceptable notations include $[\text{Cu}^{\text{I}}/\text{L}]^+$ and $[\text{X-Cu}^{\text{II}}/\text{L}]^+$, while even the shorthand $\text{Cu}^{\text{I}}/\text{L}$ and $\text{X-Cu}^{\text{II}}/\text{L}$ forms have been used.

Recently, data-driven techniques for reactivity prediction of the atom transfer process were demonstrated, which account for all of the above parameters in the multivariate linear regression model for k_a that spans over 13 orders of magnitude.^[12] The intermittent activation/deactivation of the propagating radical chain allows for precise control over polymer structural features, specifically molecular weight, molecular weight distribution, and chain-end fidelity.^[13] Those are altogether influenced by unavoidable radical termination reactions, which result in the accumulation of the $\text{X-Cu}^{\text{II}}\text{L}^+$ (persistent radical effect)^[14] and slowing/

halting polymerization. Therefore, the first “normal ATRP” conditions necessitated high $[\text{Cu}^{\text{I}}\text{L}^+]$ catalyst concentration (1,000–10,000 ppm vs. $[\text{M}]$, solubility limited), strictly oxygen-free conditions and generally elevated temperatures, which limited some applications.^[7a,15]

2.2. Regenerative ATRP Methods

The important breakthrough was the development of the activator regeneration methods, which share an elementary reduction step of $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ deactivators via different internal reducing agents or external (light, electricity, ultrasound) stimuli and/or their combination (Scheme 1b). As a result, catalyst concentration was reduced down to ppm levels,^[16] and oxygen tolerance was improved^[17] while maintaining proper control and chain-end fidelity over the polymerization.^[18] This was further improved by developing new ligand classes and up to a billion times more active Cu-catalysts.^[2] With strongly reducing Cu-catalytic systems, activation of less-active initiators was achieved,^[19] lower catalyst concentration was needed for controlled polymerization, and near-total temporal control in photomediated Cu-ATRP was reached.^[20] More active catalysts are not compatible with normal ATRP conditions, as the initiation efficiency is compromised through the enhanced termination with the increased number of radicals generated at the beginning of the polymerization.

One of the most advantageous features of regenerative ATRP is that the rates of polymerization are proportional to the square root of the ratio of the rate of total Cu^{I} -regeneration to the termination rate coefficient k_t (Figure 2). While a small value of K_{ATRP} (10^{-4} – 10^{-9}) is desirable for well-controlled normal ATRP,^[21] regenerative ATRP techniques rely upon catalysts with intermediate or high K_{ATRP} to maximize in situ deactivator concentration (i.e. $[\text{X}-\text{Cu}^{\text{II}}\text{L}^+] \approx [\text{X}-\text{Cu}^{\text{II}}\text{L}^+]_0$) during ATRP. This is because the control (dispersity equation) in ATRP bears a term inversely dependent on the in situ concentration of deactivators during ATRP (i.e., the steady-state concentration of

$[\text{X}-\text{Cu}^{\text{II}}\text{L}^+]$) (Figure 2).^[13] In turn, the elementary reduction step is fastest at maximum in situ deactivator concentration, since $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ is a reactant in the reduction step. The number of monomer units added in each activation-deactivation cycle, represented as the ratio of polymerization and deactivation rates (R_p/R_d), dictates the final width of the molecular weight distribution.

Catalyst regeneration in Cu-ATRP allows for precise control over the polymerization kinetics, followed by previously impossible-to-achieve features such as spatio-temporal control of the polymerization process. Notably, precise temporal control is a function of the ligand activity, since the polymerization rate in regenerative ATRP methods is determined by K_{ATRP} and the in situ established $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ ratio, not the total amount of Cu-catalyst.^[20b] However, this useful relationship only applies when termination proceeds (nearly) exclusively via conventional radical termination, which can be selectively engineered by employing highly active Cu-ATRP catalysts^[19,22] at low-ppm concentrations or by manipulating activator regeneration through stimuli. This review presents dual PC/Cu-ATRP as an advancement in the tunability and control of ATRP through a mechanistic perspective, rather than by ligand design.

Zerovalent Cu was used for the first time to achieve the regeneration of the activator through the comproportionation between Cu^0 and $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ deactivator, requiring one equivalent of free-ligand.^[23] This was termed as supplemental activator and reducing agent (SARA) ATRP, because the zerovalent metal could also activate the dormant chain-ends, thus acting as an activator supplemental to $\text{Cu}^{\text{I}}\text{L}^+$. Alternative mechanisms encountered in the literature denoted as single electron transfer living radical polymerization (SET-LRP) should be disregarded.^[24] Other metal ions were also employed for SARA ATRP, such as Fe, Zn, or Mg.^[25] Micro/nanodroplets of eutectic gallium-indium alloy (EGaIn) can also function in SARA ATRP, without typical ultrasonication for liquid metals.^[26] Environmentally friendly inorganic sulfites allow SARA ATRP in alcohol/aqueous mixtures or solely aqueous conditions, leading to

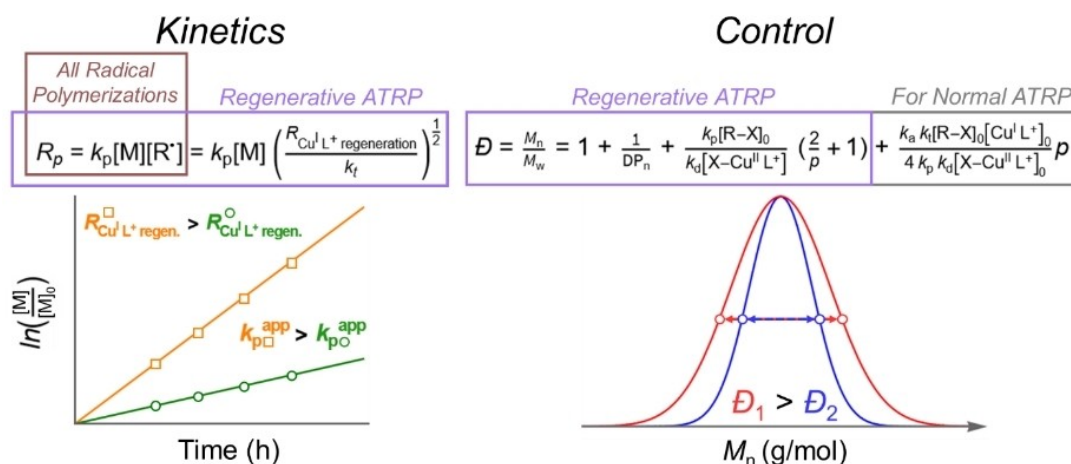


Figure 2. Kinetic and control parameters of normal and regenerative ATRP processes.

well-defined macromolecules and protein-polymer hybrids.^[27]

Other commonly used reducing agents are FDA-approved Sn^{II} 2-ethylhexanoate ($\text{Sn}(\text{EH})_2$),^[16b,c] glucose^[16c] or ascorbic acid,^[28] which facilitate Activators ReGenerated by Electron Transfer (ARGET) ATRP. These systems do not generate radicals and cannot activate R-X , and their role is limited to $\text{Cu}^{\text{I}}\text{L}^+$ activator regeneration. Slow feeding of appropriate reducing agent can account for the activity of the monomer. However, such systems allow ATRP to follow the green chemistry principles.^[29] Heterogeneous conditions can be achieved with Ag^0 , which facilitates the purification of the final products,^[30] whereas ATRP components such as excess ligands^[31] or nitrogen-containing monomers^[32] can also act as reducing agents.

Besides the chemical reducing agents that directly reduce $\text{X-Cu}^{\text{II}}\text{L}^+$ to $\text{Cu}^{\text{I}}\text{L}^+$, thermally unstable peroxides and organic-diazo compounds like azobisisobutyronitrile (AIBN) can indirectly fulfill the same function. When employing small quantities of the exogenous radical initiator relative to loaded alkyl halide initiators, the process is termed Initiators for Continuous Activator Regeneration (ICAR) ATRP and can be tuned by the structure of the radical initiator, temperature and also through varying the feeding rate.^[16a] Temperature control is crucial since uncontrolled thermal runaway can occur due to the exothermic nature of the polymerization process. This was circumvented in Ultimate ATRP[®], which allowed the industrial scale-up to 750-gallon capacity and good control under low ppm conditions via a slow feeding approach.^[29,33]

Electricity, ultrasound, and light can also (re)generate the $\text{Cu}^{\text{I}}\text{L}^+$ activator, which can be described as non-chemical methods since those are mediated by external stimuli.^[18] In eATRP, electrolysis of the $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator in the 3-electrode setup provided clean regeneration of the $\text{Cu}^{\text{I}}\text{L}^+$ species through the readily dissociating $\text{X-Cu}^{\text{I}}\text{L}$ intermediate and controlled polymerization as a function of the applied voltage.^[34] The galvanostatic simplified eATRP under aqueous conditions without deoxygenation was also demonstrated, with the scale-up to 15 liters indicating the

potential for the industry.^[35] Removing and recycling the catalyst is feasible since the catalyst can be electrodeposited on the working electrode.^[36] A combination of BaTiO_3 or ZnO piezoelectric nanomaterials and ultrasound is another means to form the $\text{Cu}^{\text{I}}\text{L}^+$ activator, referred to as mechano/sonoATRP.^[37] Interestingly, no piezoelectric inorganics are needed in aqueous media, where ultrasound-generated hydroxyl radicals allow for the controlled formation of water-soluble polymers, including DNA-polymer biohybrids.^[38] Much lower energetic output is also feasible, as demonstrated for ATRP via tribochemistry.^[39] Controlled polymerization of various (meth)acrylates was mediated by low-frequency ultrasonic scission from TiO_2 , resulting in an electron transfer (ET) to the $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator and regeneration of $\text{Cu}^{\text{I}}\text{L}^+$. ATRP under solid-state conditions was also performed in an efficient manner via the ball-milling approach, providing an alternative method where control of polymerization is difficult to achieve in the solution.^[40] Finally, the regenerative ATRP methods offer improved oxygen tolerance,^[17] either based on enzymatic degassing,^[41] organoboron compounds,^[42] ball-milling, or irradiation of α -oxo carboxylates such as sodium pyruvate via photoinduced ICAR ATRP mechanism (PICAR ATRP).^[43]

PhotoATRP typically uses high-energy UV or violet light to (re)generate the $\text{Cu}^{\text{I}}\text{L}^+$ activator. It opened a number of previously unattainable opportunities,^[4a] but promotes side reactions and is incompatible with some biomolecules (DNA, proteins). A way to overcome this limitation is to introduce a PC compatible with Cu-based ATRP that can efficiently absorb visible or near-infrared light and induce activator regeneration via a pathway involving photoexcited PC^* . To differentiate, this approach is termed photoredox dual-catalysis (PC/Cu-ATRP), though sometimes it is referred to broadly as photomediated ATRP or photoATRP (Figure 3, photoredox dual catalysis). Herein, the mechanisms of dual PC/Cu-ATRP as a robust and versatile regenerative ATRP will be discussed, with implications for controlled polymeric-material design.

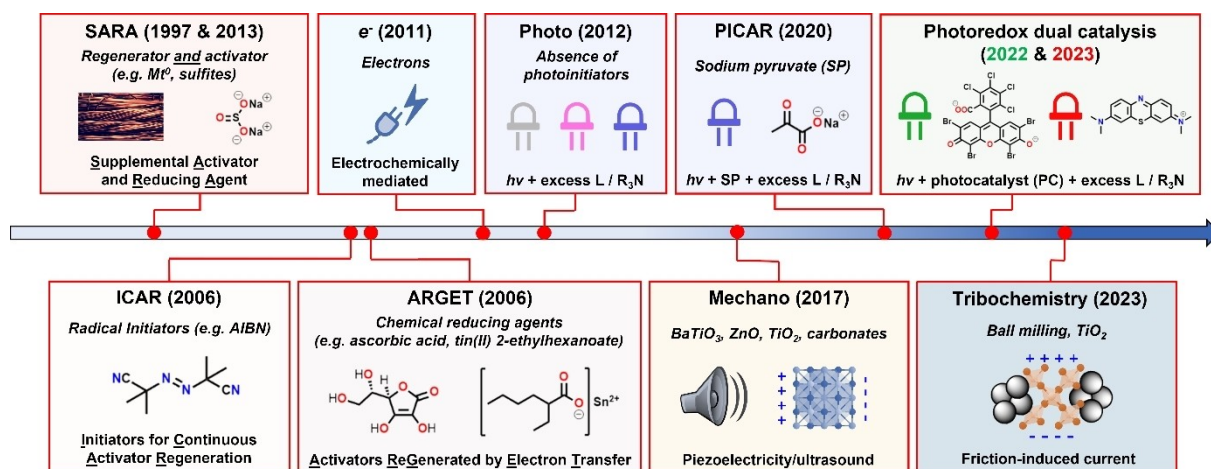


Figure 3. Timeline and summary of ATRP-regenerative methods.

3. Principles of Photomediated ATRP

Normal ATRP was accelerated using high energy light starting with $\text{Cu}^{\text{I}}\text{L}^+$.^[44] However, ATRP can also be started with an air-stable higher oxidation state Cu-ATRP catalyst (the deactivator, $\text{X-Cu}^{\text{II}}\text{L}^+$) while (re)generating the air-sensitive $\text{Cu}^{\text{I}}\text{L}^+$ activators in situ. With light irradiation, the $\text{X-Cu}^{\text{II}}\text{L}^+$ complex can be reduced directly through its photoexcitation, or indirectly through a photosensitive additive. The direct (near-) UV irradiation of $\text{X-Cu}^{\text{II}}\text{L}^+$ generates strongly oxidizing excited $\text{X-Cu}^{\text{II}}\text{L}^{+*}$ species that react with sacrificial EDs (i.e., excess ligands) to (re)generate $\text{Cu}^{\text{I}}\text{L}^+$ activators. Alternatively, in the dual catalytic process, the excited photocatalysts (photosensitizers) can stimulate the reduction of the $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator to $\text{Cu}^{\text{I}}\text{L}^+$ activator.

3.1. Reduction Mechanisms

3.1.1. Direct Irradiation: Photoexcitation of $\text{X-Cu}^{\text{II}}\text{L}^+$ by UV Light

The simplest photomediated Cu-ATRP method is through photoexciting the Cu-ATRP catalyst itself, which requires no additives other than the main components of an ATRP system.^[45] Referred to herein as classical photoATRP, excess amines (typically ligand) relative to Cu-catalyst serve as sacrificial EDs for reducing photoexcited $\text{X-Cu}^{\text{II}}\text{L}^{+*}$ (photoARGET). The photoARGET step is rapid due to the highly positive redox potential of $\text{X-Cu}^{\text{II}}\text{L}^{+*}$ relative to the ground state.^[46] Thus, the rate-determining step for the regeneration of $\text{Cu}^{\text{I}}\text{L}^+$ activators in the photoARGET pathway could be either a reaction with ED or photoexcitation of $\text{X-Cu}^{\text{II}}\text{L}^+$.^[47] Classical photoATRP is the simplest photomediated regenerative ATRP system and can thereby operate at intermediate ppm-levels of Cu-ATRP catalyst (cf. Scheme 3a).

Though lacking full oxygen tolerance and rapid photo-reduction by visible light, classical photoATRP was employed in different studies due to its advantages over normal ATRP. Low Cu-catalyst concentrations were used to carry out photoinduced ATRP of (meth)acrylic monomers through tail-absorption of $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivators under visible light and sunlight without any photoinitiators.^[48] It was applied to polymerize oligo(ethylene oxide) methyl ether methacrylate with a very small amount of copper catalyst (22 ppm) in aqueous media.^[49] Excess (tris[2-(dimethylamino)ethyl]amine) (Me_6TREN) acted as an ED and accelerated photoATRP with excited $\text{X-Cu}^{\text{II}}\text{L}^{+*}$ under UV-light irradiation to form polyacrylates with low dispersity and preserved chain-end fidelity.^[50] Recently, photoATRP was regulated by a photoswitchable hexaarylbiimidazole mediator in which periods of photoirradiation reversibly quenched propagating radicals while regenerating $\text{Cu}^{\text{I}}\text{L}^+$ activators, allowing polymerization to proceed in dark periods as a normal ATRP.^[51]

Photoexcited $\text{X-Cu}^{\text{II}}\text{L}^{+*}$ complexes are strongly oxidizing (ca. +2 V vs saturated calomel electrode (SCE)).^[46] Thus, they can rapidly accept an electron from many amine-

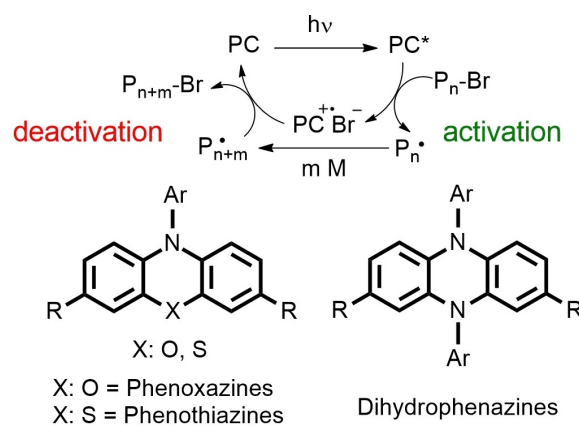
based EDs (ca. +0.7 V vs SCE, excess ligand, organic base or amine-bearing monomer) via a reductive quenching mechanism. The actual efficiency depends also on the lifetime of excited states and any potential side reactions as discussed later. An analogous outer sphere electron transfer (OSET) process in the dark is very slow because the redox potential of $\text{Br-Cu}^{\text{II}}\text{L}^+$ (L: Me_6TREN or tris(2-pyridylmethyl)amine (TPMA)) is ca. -0.3 V vs. SCE (Section 6.4). In electrochemistry, a difference in redox potentials $\Delta E_{1/2} = 0.059$ V corresponds to a 10-fold equilibrium or rate constants ratio.^[2,11,22b] These redox potentials indicate that $\text{Cu}^{\text{I}}\text{L}^+$ activators cannot react directly with alkyl halides (redox potential around -1.0 V vs SCE) via an OSET process. Instead, ATRP proceeds by ISET via a concerted atom transfer process (ISET-AT, Section 6.2).^[10b]

3.1.2. Photoredox Alone: O-ATRP and its Limitations

In regenerative ATRP systems, the concentration of $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator plays a crucial role in both control and kinetics (through K_{ATRP} at steady-state).^[11,13,52] The $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivators provide superior control over molecular weight distribution and chain-end functionality via rapid, reversible deactivation of propagating radicals and concurrent growth of all polymer chains. However, residual copper is typically an undesirable impurity in the final polymer. Residual copper can be limited by decreasing the loading of Cu catalyst.^[53] The alternative strategy is completely removing transition metals from ATRP and replacing them with organic catalysts. Organocatalyzed ATRP (O-ATRP) was accomplished as a photocatalytic systems in this manner.^[54]

In O-ATRP, the photocatalytic system employs the excited PC^* that can directly activate R-X by OSET, generating propagating radicals and $\text{PC}^{\bullet+}$ radical cations via oxidative quenching (Scheme 2).

In this mechanism, the activation or radical generation proceeds through an ET from a very strongly reducing excited state PC^* to R-X . Very negative potentials of excited PC^* are needed ($E_{\text{red}}(\text{PC}^{\bullet+}/\text{PC}^*) \sim -2.0$ V vs SCE)



Scheme 2. Examples of PCs used in O-ATRP and their corresponding photochemical mechanisms.

since the reduction potentials of R–X are low ($[E^\circ(\text{C–Br}/\text{C–Br}^\bullet)] \sim -0.6 \text{ V vs SCE}$, and $E^\circ(\text{C–Cl}/\text{C–Cl}^\bullet) \sim -0.7 \text{ V vs SCE}$) or even more negative due to the large reduction overpotential.^[10a,55] PCs include organic dyes such as hetero-aromatic compounds, perylene, pyrene, and transition-metal complexes such as Ir complexes (e.g. *fac*-Ir^{III}(ppy)₃ where ppy = 2-pyridylphenyl^[56] or Cu^I(phen)₂⁺ where phen = phenanthroline^[57]), which have very negative redox potentials up to -2 V vs SCE in the excited state.

One of the most challenging steps in O-ATRP is deactivation. In Cu-ATRP, deactivation proceeds rapidly through the $\text{X–Cu}^{\text{II}}\text{L}^+$ deactivator, transferring halogen to the radical, thereby forming $\text{Cu}^{\text{I}}\text{L}^+$ activator again. Deactivation in O-ATRP proceeds by the reaction of $\text{PC}^{\bullet+}\text{Br}^-$ ion pairs with propagating radicals to form the ground-state photocatalyst and the dormant chain ends again. Alternatively, the termolecular process was also considered.^[58]

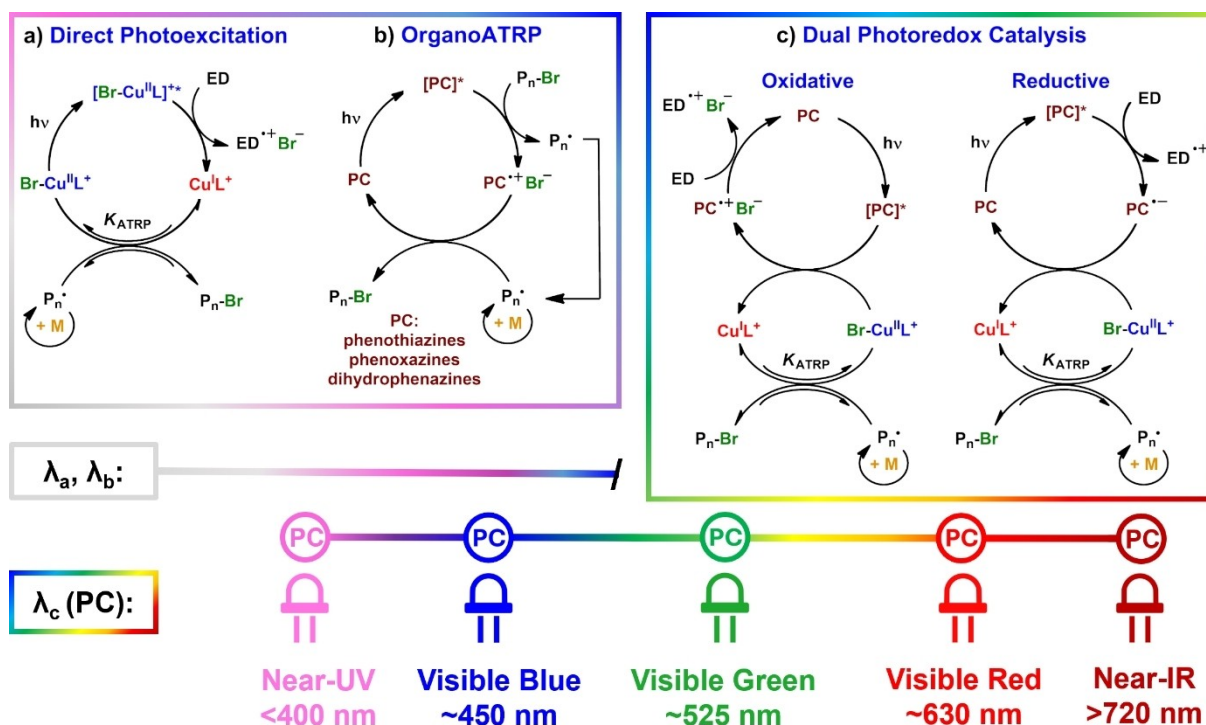
A PC should have convenient redox properties both in its ground and excited states, a long-excited state lifetime, and high photostability. In addition, the corresponding $\text{PC}^{\bullet+}\text{X}^-$ ion pair should be stable and have appropriate reduction potential to deactivate the growing radicals. The range of chain-ends for O-ATRP is limited to alkyl bromides, as alkyl chlorides are less efficiently formed in deactivation. The most efficient photocatalysts for O-ATRP include phenothiazines,^[59] phenoxazines,^[60] dihydrophenazines,^[61] dihydroacridines,^[62] and oxygen-doped anthanthrene.^[63] Others include commercially available polynuclear aromatic compounds such as perylene,^[64] pyrene,^[65] though they lead

to lower initiation efficiencies and broader molecular weight distributions due to slower deactivation.

O-ATRP could also proceed via reductive quenching in which PC^* is first reduced by an ED to a radical anion, which then transfers an electron to alkyl halides producing radicals. This process is much less efficient as it has no clear deactivation step. It generally produces uncontrolled polymers with very high molecular weight and broad molecular weight distribution.^[66] Despite some advantages, O-ATRP also has limitations associated with limited commercial availability of PCs, their high cost and potential toxicity, generally high loading required, and inferior molecular weight control compared to systems relying on $\text{Cu}^{\text{I}}\text{L}^+/\text{X–Cu}^{\text{II}}\text{L}^+$ for activation/deactivation redox events at the chain ends.

4. Mechanism of Dual PC/Cu-ATRP

While photoirradiation has a dramatic effect that enables photomediated ATRP, the involved photoexcited species define the process. In a classical photoATRP, it is the photoexcitation of $\text{X–Cu}^{\text{II}}\text{L}^+$ (Scheme 3a). In O-ATRP which has no Cu-ATRP catalyst, the photoexcited species are strongly reducing excited organic dyes (Scheme 3b). They rely on one catalyst to perform both photoexcitation and activation/deactivation at chain ends, and generally require higher energy UV or violet light. Certain systems, e.g., perylene dyes, can also function under visible light



Scheme 3. Three modes for photomediated ATRP as (a) direct photoreduction of the photoexcited Cu-ATRP catalyst, (b) photoredox in O-ATRP, and (c) dual photoredox catalysis through oxidative or reductive quenching pathways, with a spectrum of photoirradiation wavelengths given as approximations to typical light intensity maxima.

conditions,^[67] and their performance can be improved via the two-photon excitation process.^[68] Cyanoarenes,^[69] substituted phenazines^[69,70] or *O*-doped anthanthrenes^[63] allow O-ATRP under blue light with low ppm/sub-ppm loading. Scheme 3c presents dual photoredox catalysis (PC/Cu-ATRP) as a third mode of photomediated ATRP. It limits the participation of the photoactive species in the regeneration of $\text{Cu}^{\text{I}}\text{L}^+$ activators, while redox events at chain ends are performed by Cu-ATRP catalyst in lower and higher oxidation states that stay at the ground states.

In a dual PC/Cu-ATRP catalysis, PCs can be less reducing and cannot efficiently directly reduce polymeric alkyl halides (i.e., -1 V vs SCE).^[10a] Alkyl halides are activated by $\text{Cu}^{\text{I}}\text{L}^+$ activators, unlike by the excited organo-catalysts used in O-ATRP. However, PC in dual PC/Cu-ATRP can efficiently react with $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ deactivators (-0.3 V vs SCE) to enable $\text{Cu}^{\text{I}}\text{L}^+$ activator regeneration. The employed PCs for PC/Cu-ATRP can be excited by lower energy light (visible to NIR) to avoid direct excitation of $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ deactivators. They can be used at even less than 1 ppm concentrations to be catalytic with respect to the monomer.^[71] They are typically organic dyes with highly conjugated aromatic species and adequate redox properties in the excited states.

Two mechanisms are possible for $\text{Cu}^{\text{I}}\text{L}^+$ activator regeneration in dual PC/Cu-ATRP. In the oxidative quenching mechanism, the excited state PC (PC^*) is oxidized by $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ to form radical cation $\text{PC}^{\bullet+}$ and $\text{Cu}^{\text{I}}\text{L}^+$ (Scheme 3c, oxidative). The $\text{PC}^{\bullet+}$ then accepts an electron from the ED and returns to the ground state, completing its catalytic cycle. In the reductive quenching pathway, PC^* is first reduced by the ED (i.e., amines) to form radical anion $\text{PC}^{\bullet-}$, which then donates an electron to $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ to (re)generate $\text{Cu}^{\text{I}}\text{L}^+$ activator (Scheme 3c, reductive). Depending on their electrochemical properties, a PC can undergo one of these mechanisms to (re)generate the activators for ATRP. The major pathway in the reduction of $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ is determined by the photophysical properties of the PC, which are summarized in Section 6.1.

5. Dual Catalytic Systems in Organic Synthesis and Other RDRP Methods

Dual PC/Cu-catalysis was used for several organic transformations to increase their selectivity and rate. Some examples include atom transfer radical addition (Cu^{I} species with either PPh_3 ^[72] or *fac*- $\text{Ir}(\text{ppy})_3$),^[73] fluoroalkylative alkene difunctionalization (with $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ and *fac*- $\text{Ir}(\text{ppy})_3$),^[73a] C–N bond forming cross-coupling reaction (with $\text{Cu}(\text{OAc})_2$ and *fac*- $[\text{Ir}(\text{ppy})_3]$),^[74] three-component defluorinative alkylboration of alkenes (with CuCN and phenoxazine),^[75] decarboxylative thiolation of esters to thioesters (with CuBr and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$),^[76] and three-component decarboxysulfonylative cross-coupling to arylsulfones (with CuOTf and acridine).^[77]

There are three general mechanisms for photomediated polymerization techniques involving RAFT chain-transfer

agent (CTA): 1) photo-iniferter (PI) RAFT, 2) photo radical-initiators (PRI) RAFT, and 3) photoinduced electron/energy transfer (PET–)RAFT.^[78] Of the three, only PET-RAFT could be considered a dual-catalytic system for equivalent comparison to dual PC/Cu-ATRP (Section 6.8). PI RAFT polymerization relies on the direct photoactivation of dithioesters or trithiocarbonates RAFT agents using UV light through the excitation of $\pi-\pi^*$ or visible light by excitation of $n-\pi^*$.^[79] This process combines reversible deactivation (like in nitroxide-mediated polymerization) and degenerative transfer mechanisms, thus operating in the absence of photoactive additives. PRI RAFT is reminiscent of classical RAFT polymerization, but radicals are photo-generated from radical photoinitiators (e.g., lithium phenyl-2,4,6-trimethylbenzoylphosphinate, sodium pyruvate, or redox initiating systems). By using non-catalytic, photoactive additives, PRI RAFT could be most closely compared to PICAR ATRP (Section 6.5). Lastly, PET-RAFT polymerization proceeds by excitation of PC which subsequently transfers energy or an electron to the RAFT agent.^[4b,80] Similarly to dual PC/Cu-ATRP, the PC does not initiate radicals itself and remains surrogate to the RAFT CTA regarding their control.

6. Dual Catalytic Systems in ATRP: the Roles and Requirements of Components

A significant limitation of the photoATRP discussed above is the need to use short-wavelength UV light, which could promote side reactions and is incompatible with biomolecules such as proteins or DNA. This limitation is circumvented by introducing a PC or photosensitizer that efficiently absorbs visible or near-infrared light and is compatible with Cu-based ATRP. Polymerizations performed in the UV range do not require a PC, since the sacrificial EDs can reduce the $\text{X}-\text{Cu}^{\text{II}}\text{L}^{+*}$ excited state formed upon UV irradiation. Due to the tail absorption in the blue LED region, classical photoATRP (i.e., without PC) can be conducted, albeit more slowly.

In a dual PC/Cu-ATRP system, the PC predominantly undergoes photoexcitation. Since $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ is transparent in that region, it can be reduced either by the PC^* excited state or by a radical anion form of PC ($\text{PC}^{\bullet-}$). The former case involves a single ET from PC^* to $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$, oxidizing PC to the $\text{PC}^{\bullet+}(\text{X}^-)$ radical cation while regenerating a $\text{Cu}^{\text{I}}\text{L}^+$ activator. In the latter path, PC^* first accepts an electron from ED, forming radical anion ($\text{PC}^{\bullet-}$) which then reduces $\text{X}-\text{Cu}^{\text{II}}\text{L}^+$ to $\text{Cu}^{\text{I}}\text{L}^+$ (residual halide forms an ion pair, $\text{ED}^{\bullet+}\text{X}^-$). In both cases, the Cu-based deactivator and activator control the polymerization process.

Dual PC/Cu-ATRP depends on the synergistic action of its components. The dominant roles discussed below of each component in dual PC/Cu-ATRP are as follows: (1) PC loading and light intensity define kinetics through $\text{Cu}^{\text{I}}\text{L}^+$ activator regeneration (Section 6.1); (2) Cu-catalyst performs reversible deactivation and controls dispersity and molecular weights while following kinetics through K_{ATRP}

(Section 6.2); (3) alkyl halide and monomer define molecular weights and initiation efficiency (Section 6.3); (4) sacrificial EDs primarily serve for closing the photosensitizing cycle involving PC and can also effect overall rate (Section 6.4). As with any regenerative ATRP technique, higher K_{ATRP} activity Cu-ATRP catalyst maintains control at lower loadings and decreases the inhibition period.

6.1. PC Catalytic Component: Requirements and Quantification of Mechanistic Pathways

In RDRP, the terms “photocatalyst” and “photosensitizer” are often used interchangeably, and the exact role of the photochemically active species should be related to the pertinent mechanism.^[81] Energy transfer usually follows “photosensitization”, whereas electron or atom transfer processes are associated with “photocatalysis”.^[82]

There is a weak correlation between the absorption coefficients of a photoactive species at a particular wavelength and the catalyst activity.^[83] Therefore, time-resolved spectroscopic methods should be used to explain the interactions between the PC, the Cu catalyst, and the ED in a photoATRP system. Electronic structures, photoredox properties, and kinetics play a key role in the final contributions of quenching mechanisms. In addition, it is important to determine the structure of the excited state of a PC, since the excited singlet or triplet states display different reactivities and lifetimes due to thermodynamic and kinetic reasons. The excited state properties of various PCs used in ATRP are shown in Table 1.

PCs reported in Table 1 can be excited with blue, green, red, and even NIR light. Depending on the reduction potential, PC* can also contribute to the direct supplemental activation of halide chain-ends.^[92]

Table 1 lists PCs used under homogeneous conditions, whereas Table 3 presents heterogeneous PCs (Section 7). PCs shown in Table 1 were divided into four groups. The most in-depth studied family are tricyclic heteroatom dyes such as commercially available xanthene dyes: fluorescein (FL),^[84] EY,^[85] rose bengal (RB),^[71a] rhodamine-6G (RD-6G),^[71a] or phenothiazine derivative methylene blue (MB).^[86] Thermodynamic and kinetic parameters of the possible quenching processes are listed in Table 2. PCs can be designed via fine-tuned engineering of redox states by means of classical organic chemistry approaches. Polymethine (PM)^[87] dyes with barbitol moiety, diarylamine-substituted terephthalates (DAST 1–3)^[88] and dicyanoaryls (CyAr 1–5)^[71b] are examples of how electron donating/withdrawing groups can significantly modify band gap and electronic properties. They can be used at ppm/ppb concentrations (e.g., DAST 2: 1 ppm, CyAr 1: 50 ppb). However, they are not commercially available. Perylene-3,4,9,10-bis(dicarboximide) dyes were structurally modified, either at the peripheral N-terminus (PDI)^[89] or at the PDI core bay region (PDII^H/PDII[−]; PDII^H/PDII^F).^[90] The former acted not only as a PC but also as an initiator. Metal-containing PCs, such as ZnPor (Por - tetraphenylporphine) and ZnPc

(Pc - phthalocyanine),^[91] were employed for polymerization by red light.

Both thermodynamic and kinetic parameters affect the nature of a photoinduced ET process. Calculations were performed to predict the thermodynamic feasibility of an ET reaction, but kinetics determined the predominant mechanism. The thermodynamics of a photoinduced redox process can be calculated according to the following equations:

$$\Delta E = E_{\text{ox}} - E_{\text{red}} - E^* \quad (1)$$

$$\Delta G = -n \cdot F \cdot \Delta E \quad (2)$$

E_{ox} and E_{red} represent the oxidation and reduction potentials of the reactants in the ground state, respectively. ΔE is the difference in the redox potentials in the excited state, ΔG is the Gibbs free energy of the redox reaction, n is the number of electrons transferred, and F is the Faraday constant (96.485 kJ·V^{−1}·mol^{−1}). E^* is the excited state energy of the PC*.

Some PCs which were studied in depth for Cu-ATRP include methylene blue (MB⁺)^[86a] (Figure 4a) and eosin Y (EY).^[85a] Both operate through their excited triplet states (Figure 4a and Figure 4b). The reduction and oxidation potentials of ³[MB⁺]* are ($E_{1/2}(\text{³MB⁺*/MB[•])} = +1.60$ V vs SCE) and ($E_{1/2}(\text{³MB⁺*/MB²⁺)} = −0.68$ V vs SCE), respectively. The reduction potential of Br-Cu^{II}TPMA⁺ and oxidation potential of TPMA are $E_{1/2}(\text{Br-Cu^{II}TPMA⁺/Cu^ITPMA⁺)} = −0.23$ V vs. SCE and $E_{1/2}(\text{TPMA/TPMA^{•+}}) = +0.96$ V vs. SCE. Using these values, the free energies of the reductive and oxidative quenching were calculated as $\Delta G_{\text{red}} = −0.64$ eV and $\Delta G_{\text{ox}} = −0.45$ eV, which implies both mechanisms are thermodynamically feasible. However, time-resolved emission experiments and nanosecond flash photolysis pointed towards reductive quenching as the dominant quenching mechanism for MB⁺. The transient absorption decay profile of ³[MB⁺]* remained unchanged in the presence Br-Cu^{II}TPMA⁺, excluding the oxidative pathway. The reductive quenching pathway was confirmed by an indirect approach due to a significant overlap between ³[MB⁺]* and the semi-reduced product, MB[•]. The triplet state oxygen ³(O₂)* was monitored for ³[MB⁺]* with and without TPMA. The latter showed a 7 % decrease in the intensity of O₂ phosphorescence. The rate constant of reductive quenching was $k_{\text{q,red}} = 4.5 \times 10^6$ M^{−1}s^{−1}. Similar experiments in the emulsion phase showed that the water-soluble triethanolamine was a more suitable ED than TPMA.^[86b] Regeneration of the PC was achieved by subsequent ET to X-Cu^{II}L⁺ deactivator, thereby regenerating Cu^IL⁺ activator (see Section 6.4 for downstream reactions of amine radical cations). Steady-state irradiation of argon-saturated MB⁺ in the presence of TPMA was monitored by UV-Vis, which further confirmed the reductive quenching process for MB⁺. The process is accompanied by a clear visual transformation of the ground-state MB⁺ with blue color to the colorless semi-reduced MB[•] under light irradiation (Figure 5a).

Table 1: Structures, photophysical and photochemical properties of PCs used in dual PC/Cu-ATRP.

Tricyclic heteroatom dyes

FL

EY

RB

RD-6G

MB

Structurally bandgap-engineered organic dyes

PM

DAST 1 DAST 2 DAST 3
R - H R - *t*-Bu R - Ph

CyAr 1 CyAr 2 CyAr 3
R - CN R - H R - OMe

CyAr 4 CyAr 5
R - *t*-Bu R - H

Perylenediimide-based dyes

PDI

PDII PDIIIF
R = H R = CF₃

Zn-chelated polyazamacrocycles

ZnPor

ZnPc

PC	λ_{max} (nm)	Φ_{ISC}	E_{red}^* (V vs SCE) ^a	E_{ox}^* (V vs SCE) ^b	E^* (eV)	Mechanism	Ref.
Tricyclic heteroatom dyes							
FL	491	0.03	1.25 (S ₁)	−1.55 (S ₁)	2.42 (S ₁)	oxidative	[84]
EY	570	0.32	1.23 (S ₁)	−1.58 (S ₁)	2.31 (S ₁)	oxidative	[85]
			0.83 (T ₁)	−1.15 (T ₁)	1.91 (T ₁)		
RB	565	0.77	0.81 (T ₁)	−0.96 (T ₁)	1.8 (T ₁)	mixed, solvent dependent	[71a]
RD-6G	540	0.002	1.18 (S ₁)	−1.09 (S ₁)	2.32 (S ₁)	mixed	[71a]
MB	610, 670	0.52	1.60 (T ₁)	−0.68 (T ₁)	1.85 (T ₁)	reductive	[86]
Structurally band gap-engineered organic dyes							
PM	791	− (T ₁)	0.48	−0.97	−	oxidative	[87]
DAST 1 (R-H)	414	− (T ₁)	−	−1.48 (T ₁)	2.33 (T ₁)	oxidative	[88]
DAST 2 (R- <i>t</i> -Bu)	422	− (T ₁)	−	−1.50 (T ₁)	2.23 (T ₁)	oxidative	[88]
DAST 3 (R-Ph)	420	− (T ₁)	−	−	2.16 (T ₁)	oxidative	[88]
CyAr 1 (R-CN)	458	0.61*	1.45 (S ₁)	−0.92 (S ₁)	2.58 (S ₁)	oxidative	[71b]
			1.28 (T ₁)	−0.75 (T ₁)	2.41 (T ₁)		
CyAr 2 (R-H)	469	0.84	0.79 (S ₁)	−1.44 (S ₁)	2.45 (S ₁)	−	[71b]
			0.63 (T ₁)	−1.48 (T ₁)	2.29 (T ₁)		
CyAr 3 (R-OMe)	493	0.01*	0.68 (S ₁)	−1.62 (S ₁)	2.38 (S ₁)	−	[71b]
			0.54 (T ₁)	1.28 (T ₁)	2.24 (T ₁)		
CyAr 4 (R- <i>t</i> -Bu)	440	0.05*	1.30 (S ₁)	−1.31 (S ₁)	2.61 (S ₁)	−	[71b]
			1.30 (T ₁)	−1.31 (T ₁)	2.61 (T ₁)		
CyAr 5 (R-H)	420	0.041	1.44 (S ₁)	−1.13 (S ₁)	2.65 (S ₁)	−	[71b]
			1.40 (T ₁)	−1.09 (T ₁)	2.61 (T ₁)		

Table 1: (Continued)

Perylenediimide-based dyes							
PDI	521	- (S ₁)	1.92 (S ₁)	-0.72 (S ₁)	2.35 (S ₁)	oxidative	[89]
PDII ^H (R-H)	592	0.38	0.99 (S ₁)	-	2.02 (S ₁)	reductive	[90]
Protonated form							
PDII ⁻ (R-H)	689	0.06	-	-1.77 (S ₁)	1.68 (S ₁)	oxidative	[90]
Deprotonated form							
PDII ^H (R-CF ₃)	588	0.48	0.77 (S ₁)	-	2.03 (S ₁)	reductive	[90]
Protonated form							
PDII ⁻ (R-CF ₃)	683	0.07	-	-1.84 (S ₁)	1.69 (S ₁)	oxidative	[90]
Deprotonated form							
Zn-chelated polyazamacrocycles							
ZnPP	560, 600	0.9	-	-0.95 (S ₁) -0.45 (T ₁)	1.81 (S ₁) 1.31 (T ₁)	oxidative	[91]
ZnPC	680	-	-	-1.19 (S ₁)	1.83 (S ₁)	oxidative	[91]

* Quantum Fluorescence Yields (Φ_f) were given since Φ_{isc} were not reported. ^a $E_{red}^*(S_1 \text{ or } T_1)$ (V vs SCE) = E_{red} (V vs SCE) + E^* (S₁ or T₁) (eV), E_{red} : ground state reduction potential ^b $E_{ox}^*(S_1 \text{ or } T_1)$ (V vs SCE) = E_{ox} (V vs SCE) - E^* (S₁ or T₁) (eV), E_{ox} : ground state oxidation potential

Table 2: The thermodynamic and kinetic parameters of the possible quenching processes of MB⁺, RB, RD-6G.

PC	Excited State	ΔG_{ox} (eV)	ΔG_{red} (eV)	$k_{q,ox}$ (M ⁻¹ s ⁻¹)	$k_{q,red}$ (M ⁻¹ s ⁻¹)	Major Path	Ref
MB ⁺ ^a	triplet	-0.45	-0.64	-	4.5×10^6	reductive	[86a]
RB ^b	triplet	-0.63	-0.30	1.04×10^{10}	4.3×10^8	oxidative (92.3 %)	[71a]
RD-6G ^a	singlet	-1.00	-0.67	5.4×10^9	2.03×10^9	comparable oxidative: 57 %	[71a]

^a DMSO, ^b water

The reduction and oxidation potentials of ³EY* are ($E_{1/2}$ (³EY*/EY^{•-}) = +0.83 V vs. SCE) and ($E_{1/2}$ (EY^{•+}/³EY*) = -1.15 V vs. SCE). Combining the corresponding oxidation potential of EY*, and the reduction potential of X-Cu^{II}L⁺ yields ΔG_{ox} = -0.92 eV. Similarly, for a reductive quenching mechanism, the reductive quenching potential of EY* and the oxidation potential of TPMA provide ΔG_{red} = +0.13 eV (Figure 4b). Based on these values, the oxidative quenching pathway should be favored. Indeed, detailed excited state quenching kinetics indicated no significant reductive quenching pathway (Figure 5b).

Other xanthene dyes resembling EY, such as rose bengal (RB) and rhodamine 6G (RD-6G), were employed as PCs for a dual ATRP of methyl acrylate in DMSO.^[71a] The ligand used in this system was Me₆TREN, with the redox potentials: ($E_{1/2}$ ([Br-Cu^{II}Me₆TREN⁺]/Cu^IMe₆TREN⁺) = -0.33 V vs. SCE)^[93] and ($E_{1/2}$ (Me₆TREN/Me₆TREN^{•+}) = +0.51 V vs. SCE). RB acts via an excited triplet state due to efficient ISC, whereas RD-6G acts via a singlet excited state. Based on the excited state redox potentials of the PCs (Table 1), the thermodynamic feasibility of the photo-induced ETs was calculated for ³RB*: ΔG_{ox} = -0.63 eV vs ΔG_{red} = -0.30 eV, and for ¹RD-6G*: ΔG_{ox} = -1.0 eV vs ΔG_{red} = -0.67 eV.

Ground state and quenching analyses in DMSO showed that a non-fluorescent ion pair was formed between RB and Br-Cu^{II}Me₆TREN⁺ that exhibited rapid static quenching.

Fluorescence quenching experiments of RD-6G with either Br-Cu^{II}Me₆TREN⁺ or Me₆TREN gave the comparable rate constants for the oxidative ($k_{q,ox}$ = $5.4 \pm 0.09 \times 10^9$) and reductive quenching ($k_{q,red}$ = $2.03 \pm 0.09 \times 10^9$) in DMSO. Thus, the rates (*R*) of each quenching mechanism could be compared based on the initial concentrations (*C*) of the cocatalyst components ([CuBr₂]/[Me₆TREN] = 1/3, resulting in [Br-Cu^{II}Me₆TREN⁺]/[Me₆TREN] = *C*/[2 *C*] = 1/2 molar ratio). Consequently, the contributions of each quenching mechanism of RD-6G for activator regeneration were similar according to Equation 3: 57 % oxidative and 43 % reductive quenching pathways.

$$\frac{R_{ox}}{(R_{ox} + R_{red})} = \frac{k_{ox}[\text{Br-Cu}^{\text{II}}\text{Me}_6\text{TREN}^+]/(k_{ox}[\text{Br-Cu}^{\text{II}}\text{Me}_6\text{TREN}^+] + k_{red}[\text{Me}_6\text{TREN}])}{(3)} \quad (3)$$

$$\frac{R_{ox}}{(R_{ox} + R_{red})} = 5.4 \times 10^9 [C]/(5.4 \times 10^9 [C] + 2.03 \times 10^9 [2C]) = 5.4/9.46 (\times 100\%) = 57\%$$

These PCs were also used in an aqueous medium for the polymerization of oligo(ethylene oxide) methyl ether methacrylate. Therefore, spectral analyses were also performed in water. Ground state analyses showed that RB did not form an ion pair with Br-Cu^{II}Me₆TREN in water (dissocia-

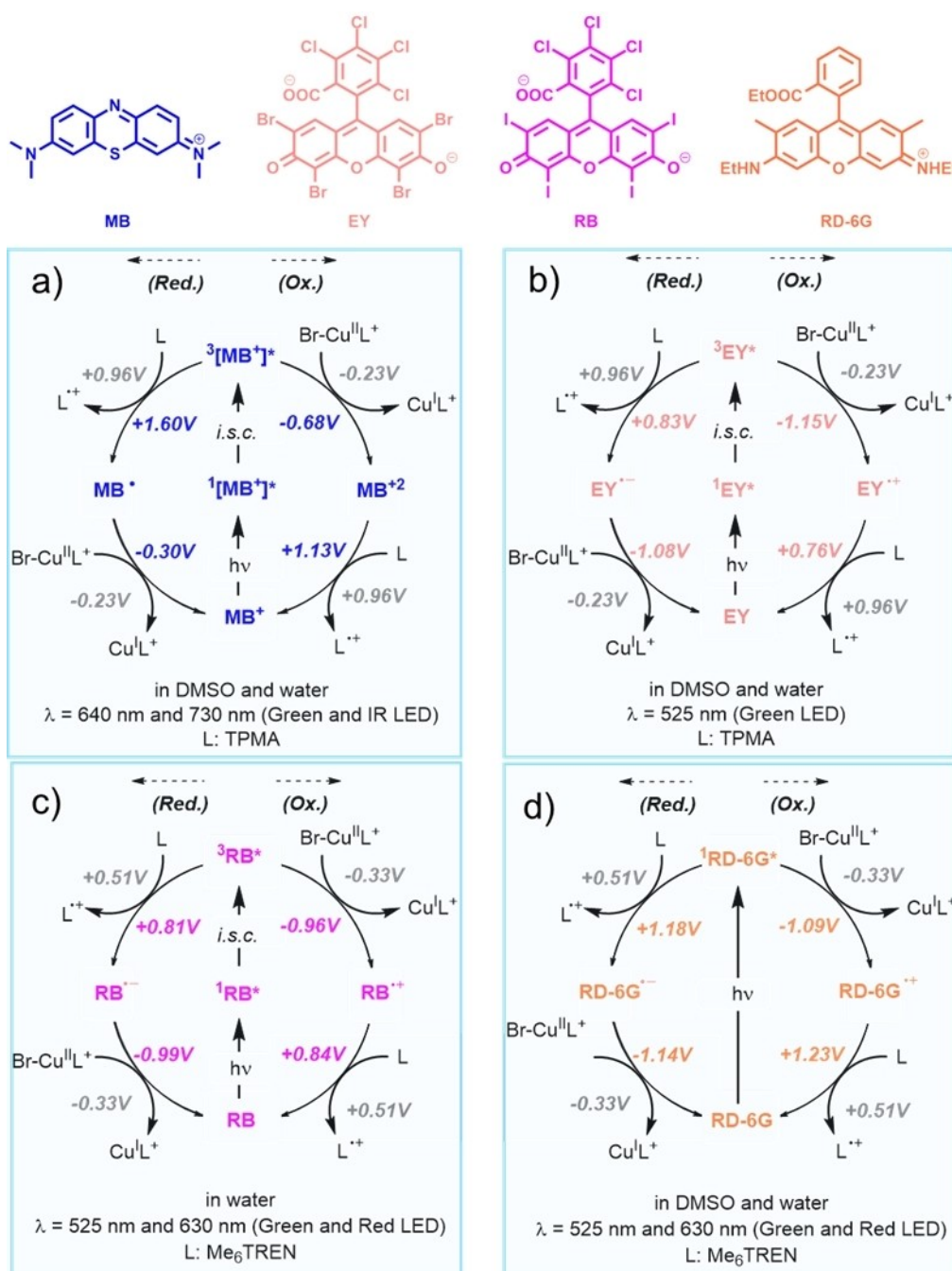


Figure 4. Quenching cycles with redox potentials shown for Br-Cu^{II}L⁺, with L=TPMA, Me₆TREN as ligands and EDs, for a) eosin Y (EY), b) methylene blue (MB), c) rose bengal (RB), and d) rhodamine-6G (RD-6G) as PCs.

tion). Excited state analyses (Figure 5) revealed that for the investigated excited state PCs, the oxidative pathway was more dominant than the reductive pathway (³RB^{*}: 92.3 % oxidative, ¹RD-6G^{*}: 67.1 % oxidative). The thermodynamic and kinetic parameters of the possible quenching mechanisms of these PCs are listed in Table 2.

Dual PC/Cu-ATRP featuring a rapid ET to X-Cu^{II}L⁺ from PC^{*} and/or PC^{•+} enables the instantaneous (re)generation of Cu^IL⁺ activators and therefore rapid polymerization. Fast polymerization is best achieved using a

PC with a high reduction potential in the excited state and low fluorescence quantum yield, resulting in higher selectivity and efficiency for (re)generating Cu^IL⁺ activators. For example, comparing FL and EY suggested that polymerization in the presence of FL is significantly slower despite its higher excited reduction potential, which was explained by its high fluorescence yield.^[84] Silicon-doped carbon dots also showed improved photoinduced Cu^IL⁺ activator regeneration, which decreased with improved luminescence quantum yield.^[94]

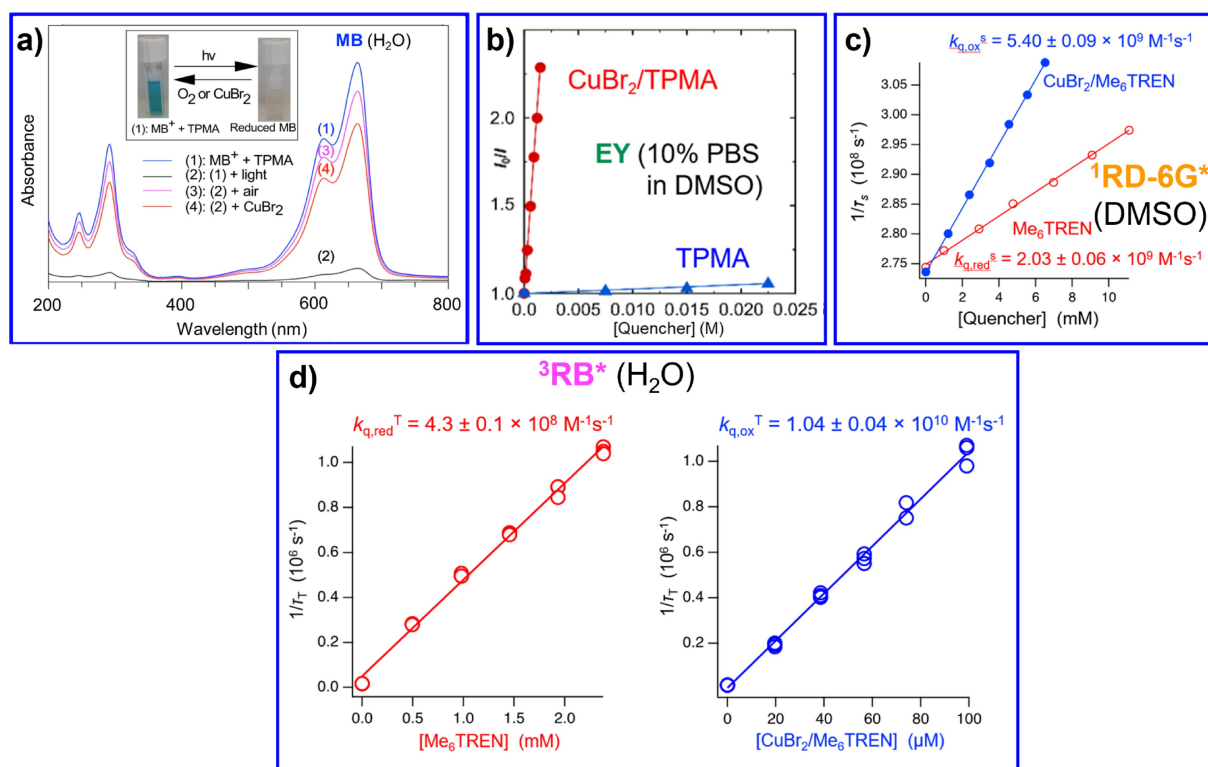


Figure 5. a) UV/Vis absorption of MB⁺ (23 μM) in the presence of TPMA (11 mM) before irradiation (blue), after steady-state irradiation with 640 nm LED (black), after purging with air (pink) or addition of air-free CuBr₂ (red). Reprinted with permission.^[86a] Copyright 2023, American Chemical Society; b) The Stern-Volmer plot for EY (15 μM) in the presence of CuBr₂/TPMA or TPMA as quenchers (Q) in PBS with DMSO (10% v/v) (non-deoxygenated) showing fluorescence quenching mainly by the Cu catalyst. Reprinted with permission.^[85a] Copyright 2022, The Royal Society of Chemistry; c) Determination of the bimolecular rate constants k_q^s of quenching of RD-6G singlet excited states by Me₆TREN (red) and Br-Cu^{II}/Me₆TREN (1:1) (blue) in DMSO fluorescence lifetime measurements (λ_{ex} = 496 nm, pulsed LED). The inverse fluorescence lifetime of RD-6G (λ_{em} = 568 nm) was determined by time-correlated single photon counting vs. varying concentration of quencher. Reprinted with permission.^[71a] Copyright 2024, American Chemical Society; d) Determination of the bimolecular rate constants k_q^T of the quenching of RB triplet states by Me₆TREN (left) and Br-Cu^{II}/Me₆TREN (1:1) (right) in H₂O using laser flash photolysis (λ_{ex} = 532 nm, 7 ns pulse width, [RB] = 6.3 μM). The inverse triplet lifetime of RB was determined from the decay of the transient absorption at 620 nm vs. varying concentrations of Me₆TREN (red) or Br-Cu^{II}/Me₆TREN (1:1) (blue). Reprinted with permission.^[71a] Copyright 2024, American Chemical Society.

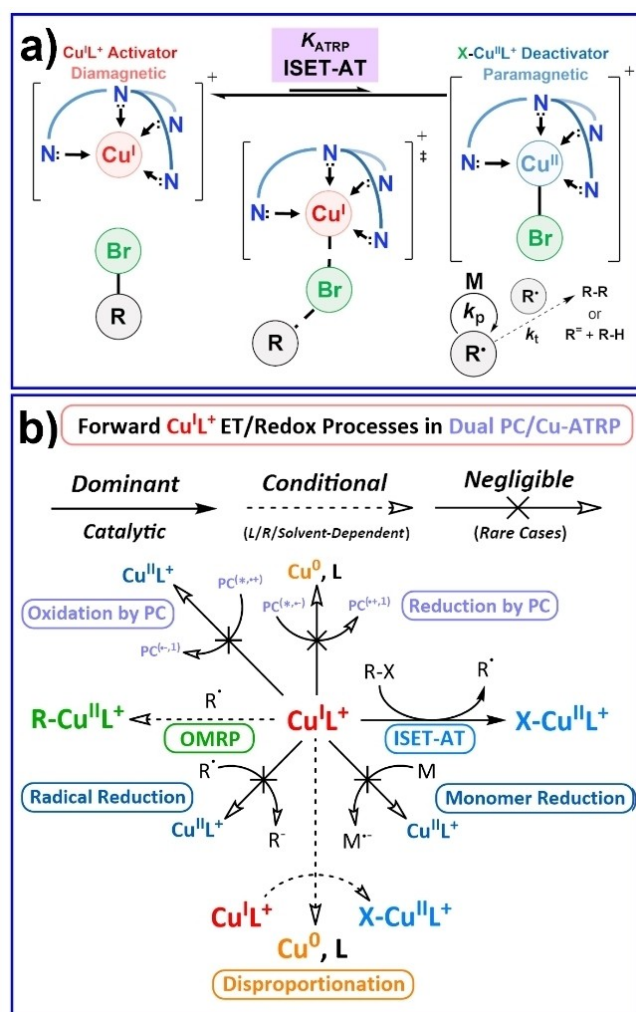
Parameters such as fluorescence lifetime, quantum yield, and intersystem crossing rates are crucial in determining polymerization rates and yields. Generally, a high efficiency of triplet state formation of a PC is desirable. Since the transition from a triplet state to the corresponding ground state is spin-forbidden, the excited triplet states have longer lifetimes, allowing for higher efficiency of ET processes and likelihood of activator regeneration. This phenomenon increases the yield of the activator generation, thereby increasing the polymerization rate. Heavy atoms in the chromophore provide higher quantum yields of triplet state formation, as shown for RB. Triplet states are advantageous for oxygen tolerance as they can readily react with triplet-state oxygen (annihilation) and thus prevent inhibition in open air.

The stoichiometry of PC vs. Cu-catalyst is an important parameter. Increasing the PC/Cu-catalyst ratio may result in an overabundance of generated Cu^IL⁺, excessive activation, and dead polymer chains from radical-radical termination events. Decreasing PC/Cu-catalyst ratio excessively may reduce the polymerization rate, induce inhibition periods,

and lower the oxygen tolerance. Generally, long reaction times are undesirable as side reactions may become pertinent. Photobleaching is a detrimental side reaction specific to the PC within PC/Cu-ATRP, depending on the energy of used light and the PC's structure. Usually, [PC] is 10-fold lower than [Cu]-catalyst, although lower amounts were used at the expense of polymerization rate. Homogeneous, blue-light irradiated dual PC/Cu-ATRP systems were reported with concentrations of 1 ppm of PC and 5 ppm of Cu-catalyst,^[88] and even < 50 ppb concentration of PC and 10–50 ppm of Cu-catalyst.^[71]

6.2. Cu-ATRP Catalyst

In dual PC/Cu-ATRP, the Cu-ATRP catalyst is responsible for all redox reactions involving alkyl halide initiator and chain ends. Activation should proceed (nearly) exclusively by Cu^IL⁺ activator complexes through an inner-sphere electron transfer (Scheme 4, ISET-AT for atom transfer) reaction to form corresponding alkyl radicals and higher



Scheme 4. a) Simplified schematic of ISET-AT involving a Cu-ATRP catalyst and an initiating alkyl halide (R–X), with arrows representing dative bonds from N donors of the neutral ligand to the Cu-center; b) Possible forward ET processes involving $\text{Cu}^{\text{I}}\text{L}^+$ in a dual PC/Cu-ATRP system, with corresponding contributions listed as dominant (i.e. high turnover), conditional (dependent on solvent, ligand, and/or alkyl radical structure), and negligible (only occurring under incompatible or otherwise problematic circumstances). Redox states of PC are paired respectively within parentheses, where a/a' and b/b' are pairs of states for $\text{PC}^{(a,b)}$ going to $\text{PC}^{(a',b')}$.

oxidation-state $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator complexes. The Cu^{I} -center is oxidized through direct contact and transfer with the halogen. ISET-AT proceeds through a bridged bent transition-state intermediate (i.e. $[\text{R-X-Cu/L}]^{+\ddagger}$) for $\text{L} = \text{TPMA}$ and $\text{R-X} = \text{methyl } \alpha\text{-bromoisobutyrate}$.^[10,95] (Scheme 4a). Likewise, deactivation proceeds through an ISET-AT involving alkyl radicals in proximity to the inner-sphere halide in $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator.

Other possible ET processes involving $\text{Cu}^{\text{I}}\text{L}^+$ activators as reactants are summarized below (Scheme 4b). Disproportionation involves the reaction of two $\text{Cu}^{\text{I}}\text{L}^+$ activators to generate a $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivator, a zerovalent Cu^0 atom, and a free ligand, which should be avoided (disproportionation: conditional) Depending on alkyl radical and ligand

structure, $\text{Cu}^{\text{I}}\text{L}^+$ activators may associate with alkyl radicals (solvent-influenced) to form Cu^{II} -alkyl complexes in organo-metallic-mediated radical polymerization (OMRP: conditional). However, $\text{Cu}^{\text{I}}\text{L}^+$ activator complexes do not appreciably reduce alkyl radicals or monomers (monomer/radical reduction: negligible). For a proper dual PC/Cu-ATRP, $\text{Cu}^{\text{I}}\text{L}^+$ activators should not react with PC in any state (oxidation/reduction by PC should be negligible).

The “true” deactivators in a Cu-ATRP system are ternary $\text{X-Cu}^{\text{II}}\text{L}^+$ halide complexes, where the “X-“ counterion remains strongly ligated to the Cu-center in organic solvents and impacts the $E_{1/2}$ of the $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ redox couple.^[93] In this manner, ternary $\text{X-Cu}^{\text{II}}\text{L}^+$ halide complexes exhibit more negative $E_{1/2}$ values than non-coordinating anions, e.g., triflates, tetrafluoroborates, and hexafluorophosphates. However, this difference could be used advantageously; regenerative ATRP could be induced more rapidly by starting from binary $\text{Cu}^{\text{II}}\text{L}^+$ complexes. The implicated mechanism generates activators and subsequently ternary $\text{X-Cu}^{\text{II}}\text{L}^+$ species at the cost of an alkyl halide functionality, but this can bear a negligible impact on chain-end functionality at low-ppm Cu-catalyst loadings.^[93]

To maximize the catalytic efficiency of the Cu-ATRP system for the ISET-AT pathway, the following criteria should be employed: 1) Employing chain-end/catalyst pairs with high K_{ATRP} ; 2) Relative stabilities should maintain most Cu^{I} species in the form of binary $\text{Cu}^{\text{I}}\text{L}^+$ complexes, while Cu^{II} species should be in the form of ternary $\text{X-Cu}^{\text{II}}\text{L}^+$ species; 3) No disproportionation of $\text{Cu}^{\text{I}}\text{L}^+$ activators to allow activation (also solvent-dependent); 4) High reversibility of the $\text{Cu}^{\text{I}}\text{L}^+/\text{X-Cu}^{\text{II}}\text{L}^+$ redox couple.

The typical Cu-ATRP catalysts employed for dual catalysis PC/Cu-ATRP include commercially available $\text{X-Cu}^{\text{II}}\text{TPMA}^+/\text{Cu}^{\text{I}}\text{TPMA}^+$ or $\text{X-Cu}^{\text{II}}\text{Me}_6\text{TREN}^+/\text{Cu}^{\text{I}}\text{Me}_6\text{TREN}^+$ redox pairs, which fulfill the above criteria for common monomers in ATRP. The $\text{X-Cu}^{\text{II}}\text{L}^+$ deactivators rapidly deactivate radicals and readily react with various PCs in oxidative or reductive quenching pathways. It is recommended that the Cu-ATRP catalyst for proper activator regeneration, control and polymerization rate should be at least equivalent in activity to pairing $\text{L} = \text{N,N,N',N',N''-pentamethyldiethylenetriamine}$ (PMDETA) with methacrylates in MeCN. Equivalently, acrylates can be matched by switching PMDETA to Me_6TREN or at least TPMA, or by switching solvent from MeCN to DMF or DMSO.

Efficient, high-yielding Cu complexes with intrinsic photochemical activity above 400 nm wavelengths are desirable but remain rare. One case is bis(1,10-phenanthroline)copper(I) ($\text{Cu}^{\text{I}}(\text{phen})_2^+$) which enabled a variation of photomediated ATRP where the activator complex, $\text{Cu}^{\text{I}}(\text{phen})_2^+$, was directly photoexcited under blue photoirradiation.^[57a] The excited activator complex directly activated alkyl halides through the oxidative quenching pathway. Sacrificial ED (i.e. triethylamine) was used to perform a (photo)ARGET step to regenerate $\text{Cu}^{\text{I}}(\text{phen})_2^+$ activators, closing the cycle.

6.3. Monomer and Initiator

Various monomers were successfully polymerized via ATRP, including (meth)acrylates, (meth)acrylamides, styrenes, acrylonitrile. Low activity monomers (LAMs) such as vinyl esters or *N*-vinylamides have yet to be efficiently polymerized due to the corresponding dormant species' high BDFE and degradative side reactions such as OMRP-CRT. Structure-activity correlations of alkyl halide initiators are important for gaining insight into the kinetics and performance of ATRP. Proper pairing of alkyl halide initiators with corresponding monomer structures enables quantitative initiation and narrow molecular weight distributions.^[96] Fast polymerizations could cause a loss of non-negligible chain-end functionality (CEF).^[97] Therefore, fast ATRP is the most suitable for monomers with high k_p (e.g., acrylates and acrylamides) and low k_t .

The combination of Cu-catalysts and PCs can result in fast polymerization. For example, aqueous-ATRP of hydroxyethyl acrylate with carbon quantum dots, CuBr₂/TPMA catalyst, and ethylenediaminetetraacetic acid disodium salt (Na₂EDTA) as ED, reached high conversion (> 85 %) after only 1 minute of irradiation with blue light.^[98] This system's oxygen-tolerance and fast polymerization allowed its application in 3D printing (Section 7).

The activity of R–X is defined by the degree of substitution and the nature of the substituents.^[12,21,99] Analogous R–Br structures have approximately 1–2 orders of magnitude larger values of K_{ATRP} than R–Cl structures. Due to the high BDFE, R–F can be more than ten million times less active than analogous R–Cl, as reported in the diethyl halomalonate family.^[12,100] Alkyl halide initiators and polymeric end-groups should be stable to hydrolysis (stability 3° > 2° > 1°) to avoid loss of CEF. Besides small molecule forms, initiators can be tethered to various functional materials such as silica nanoparticles, carbon nanodots, or biomacromolecules like proteins and nucleic acids to form polymeric hybrid materials (Section 7).

Alkyl and polymeric halide/radicals should selectively undergo activation/deactivation to avoid OMRP (Scheme 4) and catalytic radical termination (CRT) to preserve high CEF. Under typical Cu^IL⁺ activator species used in dual PC/Cu-ATRP (L = TPMA, Me₆TREN), the propensity towards OMRP obeys the following order: less-activated vinyl monomers (vinyl esters, amides) > secondary acrylates > styrenes > tertiary methacrylates.^[22a,101] While the loss of chain-end fidelity is generally detrimental, CRT-promoting conditions have been used to prevent the coupling/gelation of polymeric brushes.^[52,102] Dual PC/Cu-ATRP offers control over the contribution of OMRP-CRT by tuning the regeneration rate and concentration of Cu^IL⁺ activator species through PC loading, Cu-catalyst loading, and light intensity.

6.4. Excess Amines and Their Role in PhotoATRP and Dual PC/Cu-ATRP

Amines are essential components of all photomediated ATRP processes as not only ligands but also as sacrificial

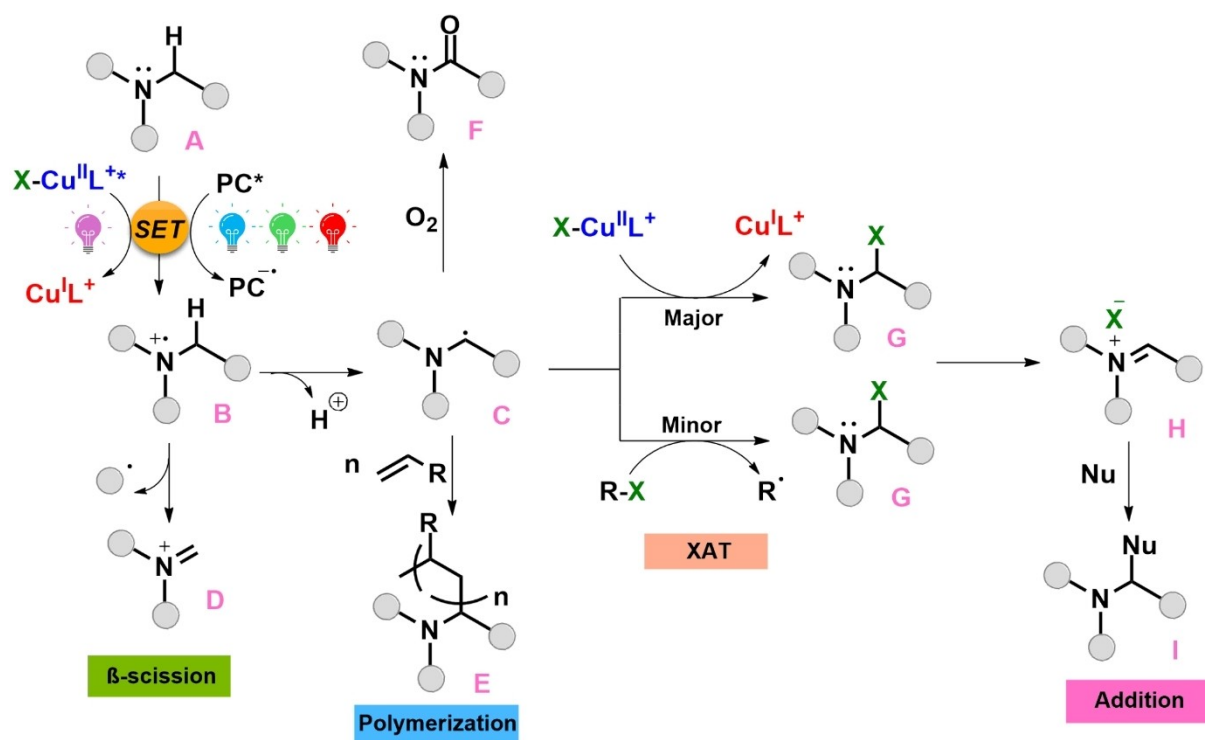
EDs. In dual PC/Cu-ATRP, sacrificial amine ED regenerates ground state PC from PC^{•+} (oxidative quenching pathway) or reduces PC^{*} to form redox-active PC^{•-} (reductive quenching pathway). In classical photoATRP, amines perform photoARGET (Section 3.1.1). Nevertheless, the involved amines and downstream products of oxidation by single ET processes are discussed below (Scheme 5).

Tertiary alkyl amines (A) undergo single ET to form amine radical cations (B) by reacting with either PC^{•+} or PC^{*}.^[103] One undesired reaction of amine radical cations is the reverse reaction as a back electron transfer from Cu^I and the formation of the starting materials.^[104] To irreversibly decompose, amine radical cations can undergo a proton transfer to form α -amino-alkyl radical (C) or cleave C–C bond at α position to form a corresponding radical and an iminium ion (D). The former can be realized due to the α -amino C–H bond of amine radical cations being more acidic and thus having significantly lower bond dissociation energy ($pK_a \approx 14.7$; BDFE ≈ 176 kJ/mol) compared to tertiary alkyl amine ($pK_a = \geq 40$; BDFE ≈ 379 kJ/mol).^[105]

The α -amino radical can participate in downstream reactions^[106] due to its reactive nature: 1) initiation of polymerization (E) analogous to type II photoinitiating radicals;^[107] 2) deactivation by X–Cu^{II}L⁺ deactivator and generation of Cu^IL⁺ or halogen atom transfer (XAT) and activation of R–X.^[108] While XAT could be relevant in O-ATRP, it is more likely that α -amino radicals reduce X–Cu^{II}L⁺ in dual PC/Cu-ATRP. XAT is independent of R–X's redox potential and relates to the BDFE, polarization of carbon-halogen bond, and stability of corresponding radicals and halogenated products. The deactivated amine (G) decomposes into iminium cation (H), an excellent electrophile that reacts with nucleophiles to form (I).^[109] 3) reaction with oxygen and formation of amides (F).^[110] In addition, in the presence of water, iminium cations may hydrolyze and form aldehydes and ketones.^[111]

Without light, amines can act as reducing agents with ground-state X–Cu^{II}L⁺, referred to herein as amine-ARGET.^[22b,85a,86a] However, compared to photoARGET, it is significantly slower (Br–Cu^{II}TPMA⁺ $E_{1/2}(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}) = -0.23$ V vs. SCE). The scope of ED includes sp^3 -hybridized amine-bearing ligands,^[31,112] monomers^[32] or other compounds, such as guanidine, that enable good control and chain-end fidelity for polymerizing MMA.^[113] Low loadings of Cu^IMe₆TREN⁺ provided controlled polymerizations with excess Me₆TREN by generating Br–Cu^{II}Me₆TREN⁺ in situ and proceeding through an amine-ARGET ATRP without light.^[112b]

The downstream reactions of amines have not yet been comprehensively assessed in dual PC–Cu ATRP. The final role of amines should depend on their structure and the photocatalytic system. However, the efficiency of forming exogenous chains is generally low, given synthesis of polymers with targeted molecular weight, chain extensions, and advanced architectures.

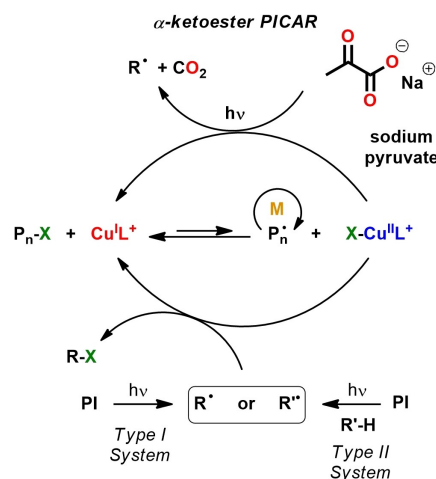


Scheme 5. Possible chemical events involving amines in photoATRP and PC/Cu-ATRP (SET – single ET; XAT – halogen atom transfer).

6.5. Non-Catalytic PhotoATRP Additives

While dual PC/Cu-ATRP relies on a PC as a photoactive additive that can catalytically perform the regeneration of $\text{Cu}^{\text{I}}\text{L}^+$ activators, other photoactive additives can perform a similar role but stoichiometrically. These additives usually undergo photodecomposition into initiating radicals that can undertake deactivation, thereby regenerating $\text{Cu}^{\text{I}}\text{L}^+$ activators and forming new chains. Such systems resemble a photoinduced ICAR process (PICAR). A radical photo-initiator may be involved in an α -cleavage photodecomposition (Scheme 6, *Type I*) or a hydrogen abstraction type (*Type II*). Unfortunately, only a few photoinitiators absorb light above the UV region where $\text{X-Cu}^{\text{II}}\text{L}^+$ is transparent. Examples include bisacylphosphine oxide, titanocene (*Type I*), and camphorquinone (*Type II*).

One example of such an additive is sodium pyruvate, which facilitated PICAR ATRP of acrylamides by significantly accelerating the polymerization rate and providing oxygen tolerance.^[43a] The proposed mechanism proceeded through a pyruvate- $\text{Cu}^{\text{II}}\text{L}^+$ complex formed via bromide anion dissociation and pyruvate anion association. Subsequent UV light irradiation reduced Cu^{II} to Cu^{I} and decarboxylation of pyruvate radical. This system was extended to dual catalysis by adding $\text{FeCl}_3/\text{TPMA}$ for polymerizing OEOMA in water by lower energy blue light (Fe/Cu -ATRP).^[43c] PICAR ATRP combines full oxygen tolerance, a high degree of control, and rapid polymerization. However, the reduction step in PICAR ATRP is not catalytic as sodium pyruvate irreversibly decomposes, form-



Scheme 6. Photochemical ATRP in the presence of photoinitiators (*Type I*), photosensitizers (*Type II*) or α -ketocarboxylates (PICAR). For the latter, Cu-speciation is omitted.

ing CO_2 and radicals, limiting the initiation efficiency and molecular weight control.

6.6. Medium

Polymerization medium affects the rate constants of activation and deactivation, and thus the ATRP equilibrium.^[114] More polar medium increases K_{ATRP} , culminating in water. Most ATRP monomers can be considered non-polar,

especially relative to such ATRP solvents as DMF, DMSO, and water. In water, the halidophilicity of $X-Cu^{II}L^+$ decreases appreciably, so excess halide salt is routinely used to shift the equilibrium to the ternary deactivator complex.^[49] Aqueous Cu-ATRP systems require excess halide anions to suppress the dissociation of $X-Cu^{II}L^+$ deactivators into non-deactivating binary $Cu^{II}L^+$ species. The polymerization in dual PC/Cu-ATRP is often slower in organic than in aqueous media.^[115]

The overall polymerization rate is based on Cu^IL^+ regeneration and K_{ATRP} , which inevitably change with the solvent to complicate its study merely by polymerization kinetics. Nevertheless, these dye studies in different solvents reveal different rates of reduction for Cu alongside different speciation in the case of RB and RD (rhodamine B) and their contribution to pathways.^[71a] For example, xanthene-based dyes can exist in quinoid and lactone equilibrium, the latter being photochemically inactive. Therefore, only the quinoid form is responsible for the photoinduced redox processes. Interestingly, the equilibrium concentrations of these two forms were different in DMSO and water in the presence of the cocatalyst components. While RB is stable in DMSO, the lactone form exists in 15 % of the total RB concentration in reaction stoichiometry ($[RB]/[CuBr_2]/[Me_6TREN] = 1/10/30$). On the contrary, RD predominantly exists in its lactone form in DMSO under reaction stoichiometry conditions. This resulted in higher concentrations of RD (5 ppm) compared to RB (100 ppb) needed for MA polymerization in DMSO. Notably, no lactonization was observed for RD in aqueous medium under a broad range of conditions.^[71a] This highlights the effect of medium when dealing with the photocatalytic efficiency of PCs under polymerization conditions.

Dual MB/Cu-ATRP was also carried out in aqueous dispersed media, i.e., emulsions, mini-emulsions, and micro-emulsions.^[116] Successful ATRP was possible, since the proper PC catalyst's design circumvented the limited penetration depth of short wavelengths. MB^+ worked efficiently under red and near-infrared light, even in a large-scale 250 ml volume.^[86b]

6.7. Oxygen Tolerance

The presence of oxygen is detrimental to radical polymerization, including ATRP. Triplet oxygen reacts with radicals to form unreactive peroxy radicals. Therefore, polymerization in the presence of oxygen is accompanied by a long induction period or complete inhibition of the polymerization if oxygen concentration is high or radical concentration is low.^[17,117] Oxygen further complicates Cu-ATRP because it readily scavenges Cu^IL^+ activators. Hence, starting ATRP from Cu^IL^+ with no regeneration requires stringent oxygen removal. Oxidized $O_2-Cu^{II}L^+$ complexes serve as neither activators nor deactivators and, thus, do not contribute to catalytic performance. Thus, ATRP is conventionally performed with degassing/deoxygenation procedures (i.e., freeze-pump-thaw and/or sparging with inert gas)

or using specialized equipment (i.e., glove box or Schlenk line).

PhotoATRP without PC has some oxygen tolerance without introducing additional reagents, but only reliably if the headspace in the polymerization flask is removed and the reaction vessel is air-tight.^[118] Cu-catalyst, photoirradiated by (near-)UV, converts O_2 to other reactive oxygen species (ROS, i.e., superoxide anion, hydrogen peroxide (H_2O_2), and hydroxy radicals ($\cdot OH$)) or completely inert H_2O via two electrons/two protons transfer.^[119] The ROS generated in photoATRP are mostly scavenged by DMSO, used as a solvent or additive, which reacts with ROS and forms dimethyl sulfone ($DMSO_2$).^[120] The measurement of oxygen concentration by IR probe in photoATRP demonstrated the increasing trend in oxygen consumption in the presence of more active ATRP ligands (i.e., $Me_6TREN > PMDETA$) and initiator (i.e., benzylic $>$ tertiary $>$ secondary $>$ primary $R-X$).^[121] Indeed, ATRP performed in the presence of oxygen was reported to have lower initiation efficiency than deoxygenated conditions, suggesting decreased initiation efficiency by reaction with oxygen.

Oxygen tolerance in ATRP was advanced by introducing additional components and/or stimuli that scavenge O_2 in situ to convert O_2 into chemically inactive species (Figure 6b). Three common strategies are 1) chemical by using an excess of reducing agents or radical initiators,^[122] 2) biological by using oxygen scavenger enzymes (i.e., glucose oxidase),^[41,123] and 3) photochemical by using photocatalysts (Figure 6b).^[85c,124]

Dual catalytic ATRP has high oxygen tolerance, enabling ATRP in completely open-cap vessels with stirring or well-plates without degassing. Both PC and Cu-catalyst contribute to oxygen tolerance (Figure 6, photocatalyst). The Cu^IL^+ activators can act as a catalytic platform for oxygen removal by associating with oxygen to form $O_2-Cu^{II}L^+$ complexes. Normally, this would impede polymerization, but $O_2-Cu^{II}L^+$ can be readily reduced to Cu^IL^+ again and decompose the ligated oxygen onto oxidized byproducts in the presence of light, PC, and ED.^[86a,106a,112c,120] On the other end, excited PC^* can also directly react with triplet oxygen to form ROS, such as singlet O_2 through triplet-triplet annihilation (e.g., with $^3MB^+$). In total, both co-catalytic cycles can interact with oxygen and regenerate Cu^IL^+ (via ET from PC) and ground-state PC (via ET from amines) to rapidly deplete oxygen from polymerization media. Thus, the combination of PCs and Cu-catalyst has promoted oxygen tolerance. The exception would be the addition of Cu-ATRP catalyst in the presence of zinc(II) tetraphenylporphine (ZnPor) which diminished oxygen scavenging ability, as attributed to the competition between the reduction of $X-Cu^{II}L^+$ and O_2 by excited ZnPor.^[91] Nevertheless, robust oxygen tolerance provided by dual PC/Cu-ATRP at large has facilitated 3D printing, high-throughput polymer synthesis, and biomolecule-polymer hybrids, i.e., protein- or DNA/RNA-polymer hybrids^[17,85c,98,125] (Section 7).

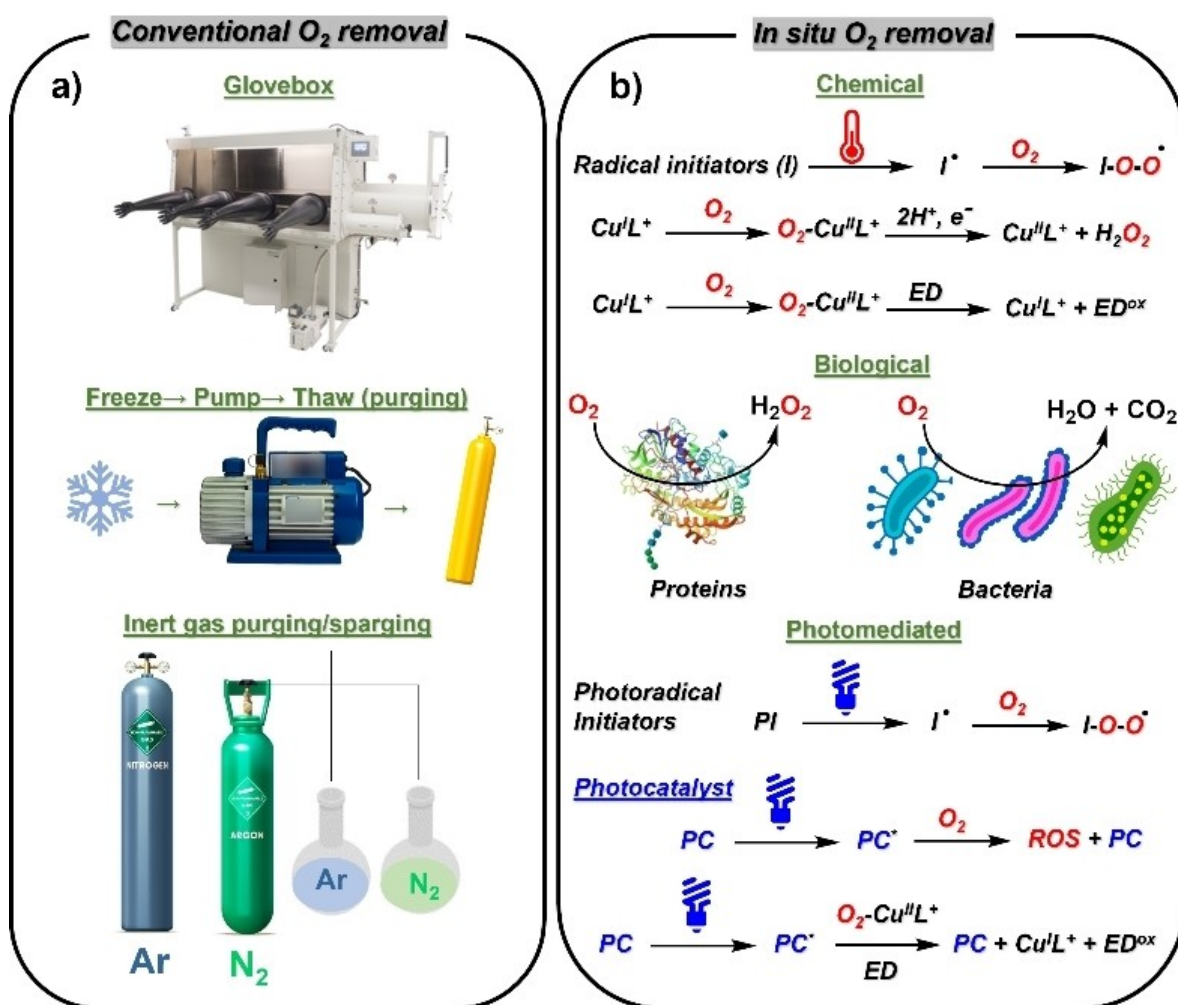


Figure 6. Oxygen removal in ATRP by involving (a) conventional and (b) in situ routes.

6.8. Comparison of Dual PC/Cu-ATRP and PET-RAFT

Some organic PCs used in dual PC/Cu ATRP were inspired by their efficient operation in PET-RAFT polymerization. EY sees widespread use for different organic transformations through its broad absorption in the visible region, high reduction potential of the excited state, and low fluorescence quantum yield. For instance, EY/Cu-ATRP readily polymerized hydrophilic methacrylates and acrylates in aqueous^[85c,d,126] and organic medium, initially reported under PET-RAFT polymerization. The direct comparison of PET-RAFT and ATRP polymerization of oligo(ethylene oxide) methyl ether methacrylate (OEOMA) in water revealed that EY photobleaching was more prevalent in PET-RAFT polymerization than in dual EY/Cu-ATRP.^[85a] Consequently, polymers with significantly lower dispersity values were obtained in photoATRP ($\bar{D}$ =1.16) compared to PET-RAFT ($\bar{D}$ =1.45). Also, polymerization at higher DP was more successful by dual EY/Cu-ATRP than PET-RAFT, which formed controlled polymers up to DP=100 (Figure 7).

Even though PET-RAFT polymerization can proceed via energy transfer catalysis, which does not rely on the reducing ability of PCs,^[4b] an important advantage of Cu-ATRP over RAFT polymerization is the lower oxidation potential of $\text{Br-Cu}^{\text{II}}\text{L}^+$ ($E_{1/2}(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}) = -0.23 \text{ V vs SCE}$ with $\text{L} = \text{TPMA}$) versus typical RAFT CTAs (ca. $-1.2 \text{ V} - 0.9 \text{ V vs SCE}$ for dithiobenzoates and ca. $-1.6 \text{ V} - -1.0 \text{ V vs SCE}$ for trithiocarbonates).^[127] This advantage enables activator generation by a broader range of (reducing) PCs compared to the range of CTAs in PET-RAFT. For example, while photogenerated $\text{MB}^{\bullet}$ provided $\text{Cu}^{\text{I}}\text{L}^+$ activator regeneration, $\text{MB}^{\bullet}$ could not directly activate dithioester RAFT CTA.^[86a,128] Instead, MB co-catalytically enabled RAFT polymerization by reducing H_2O_2 to $\bullet\text{OH}$ via a Fenton-like reaction, which initiated RAFT polymerization.^[128] In MB/Cu-ATRP, polymers are selectively formed from the R-X initiator. In MB/RAFT, an exogenous $\bullet\text{OH}$ source forms some additional polymer chains. Thus, dual MB/Cu-ATRP defines chain population more precisely. Furthermore, the interaction of O_2 with xanthate-based CTAs in aerated PI-RAFT polymerization is unfavorable; for example, such conditions formed poly(butyl

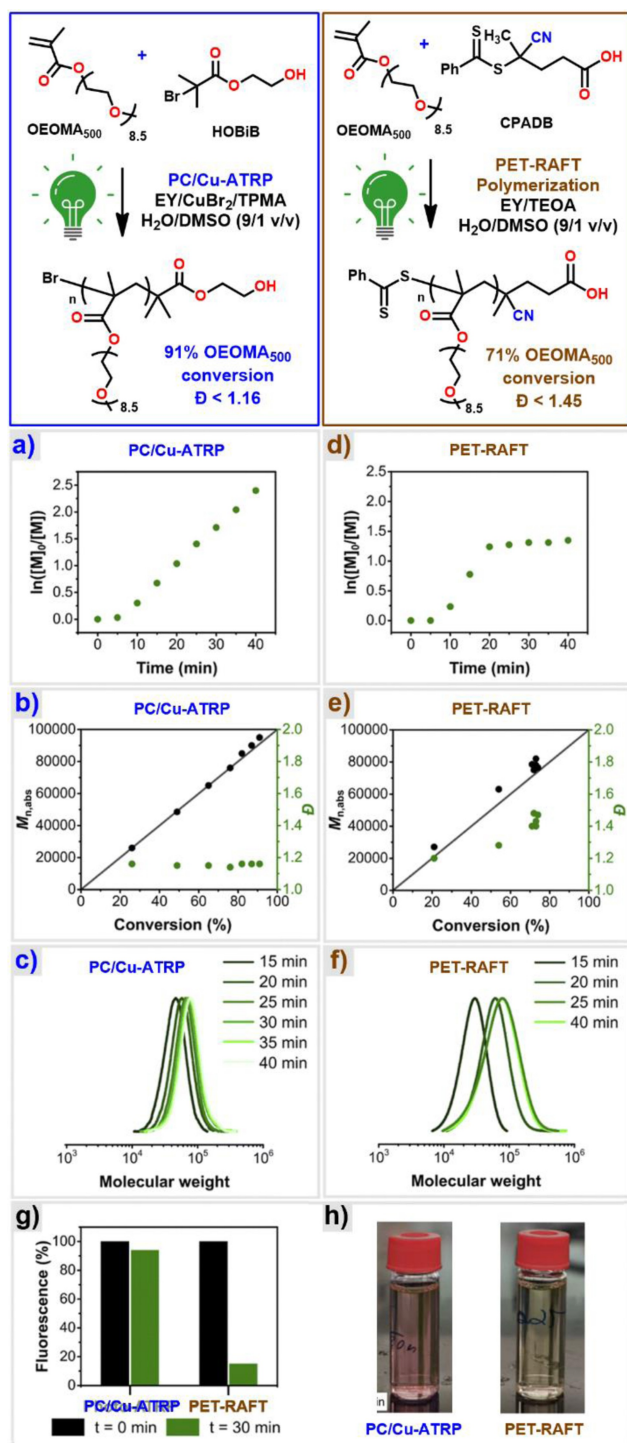


Figure 7. Comparison of dual catalysis ATRP and PET-RAFT polymerization with EY. Under their respective Schemes are the semi-logarithmic plots monomer vs time (a, d), evolution of absolute number average molecular weight ($M_{n,abs}$) and dispersity ($\bar{D}$) and their associated molecular weight traces (c, f). The fluorescence (g) was monitored at 30 minutes of photoirradiation of the respective methods to observe the extent of photobleaching. Digital image (h) of dual PC/Cu ATRP and PET-RAFT polymerization solution after irradiation. Reprinted with permission.^[85a] Copyright 2022, The Royal Society of Chemistry.

acrylates) with higher molecular weight, i.e., diminished initiation efficiency and chain-end fidelity, than identical polymerization carried out with deoxygenation.^[129]

While the benefits of dual-PC/Cu-ATRP have only recently become evident, PET-RAFT polymerization has been widely investigated in the past 10 years,^[4b,80,130] resulting in comprehensive insight into the polymerization mechanism and PC discovery. In addition, PET-RAFT can offer wavelength-dependent activation of CTAs. The interaction of ZnPor and trithiocarbonates resulted in photoinduced radical generation for the polymerization of styrene, (meth)acrylates, and (meth)acrylamide, while Ni, Co and Fe-containing porphine catalysts did not yield polymers.^[131]

7. Applications and Materials by Dual PC-Cu-ATRP

ATRP has been recognized as a robust technique that offers precise macromolecular engineering and preparation of both specialty and commodity materials. With the advent of dual PC/Cu-ATRP techniques, some ATRP limitations can be circumvented (Figure 8).

To make dual catalysis PC/Cu-ATRP systems more appealing to the industry, extension to large-scale emulsion polymerizations is desirable.^[116] Indeed, miniemulsion with longer wavelength light (MB/Cu-ATRP) improved light penetration, demonstrating up to 250 ml scale as a starting point for further upscaling studies and probing other emulsion techniques (Figure 8a).^[86b] Dual MB/Cu-ATRP processes were also performed in a 96-well plate,^[86a] demonstrating excellent oxygen tolerance. The combination of high pressure ($p \leq 250$ MPa) and EY/Cu-ATRP resulted in linear ultrahigh molecular weight polymers reaching up to ca. 10 million, which would not be possible for a system with side reactions or exogenously-dosed radicals (Figure 8b).^[85b]

Grafting from poly(vinylidene fluoride), PVDF, and related fluorocarbon elastomers was achieved with EY under green light irradiation (Figure 8c).^[132] The grafting density was tuned by light intensity and/or solvent composition and proceeded without the formation of unattached homopolymers or unwanted amine-mediated dehydrohalogenation side processes. Formed materials exhibited improved mechanical properties and lower crystallinity.

To prepare hyperbranched polymers by dual PC/Cu-ATRP, inibramers (IBs) were employed as branching junction sites.^[133] EY/Cu-ATRP provided well-defined branched polymethacrylates under aqueous conditions with sodium 2-bromoacrylate (SBA) to induce branching (Figure 8d).^[85d] The method was extended to the synthesis of DNA and protein bioconjugates and exhibited high oxygen tolerance. Water soluble oligo(ethylene oxide) methyl ether 2-bromoacrylate IB was used to synthesize hyperbranched block copolymers and protein hybrids, but only with polyacrylate backbone.^[126] With polymethacrylates, degradation via β -carbon C–C bond scission was observed, as corroborated by computational studies. EY/Cu-ATRP was also applied for the synthesis of bottlebrushes and hydrogels based on short synthetic oligoRNA and RNA extracted from natural biomass, which acted as ATRP macroinitiators

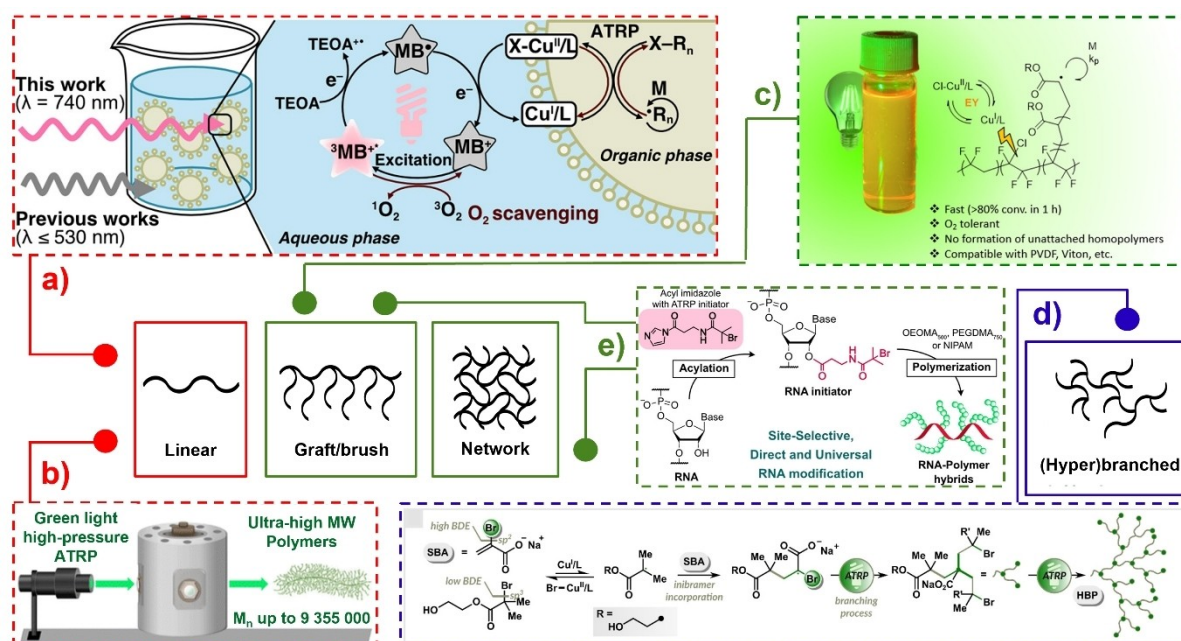


Figure 8. Examples of controlled polymers by ATRP. Singled-out examples represent advancements with dual PC–Cu-ATRP. Detailed discussion in the text, based on^[86b,85b,132,85d,e]. Reproduced with permissions from Refs.^[86b] Copyright 2024,^[132] Copyright 2024,^[83e] Copyright 2023, American Chemical Society. Reproduced with permission from Ref.^[85b] Copyright 2024, The Royal Society of Chemistry. Reproduced with permission from Ref.^[85b] Copyright 2022, Wiley.

(Figure 8e).^[85e] Dual PC/Cu-ATRP with PC=EY or MB were benign to living cells under photoirradiation conditions.^[85a,86a] In addition, ATRP-derived polymeric dyes acted as sensors for bacteria, with potential in biosensors and bioimaging.^[134]

Advanced bio-cargo and drug delivery systems and enhanced stability of bioconjugate-polymer hybrids are expected, alongside new possibilities in bio-sensing or probes. For example, dual PC/Cu-ATRP was applied in nucleic acid photocatalysis using nucleic acid binding dyes (NuABDs, Figure 9).^[135] NuABDs such as GelGreen (GG), GelRed (GR), and SYBR Gold fulfilled PC role in dual PC/Cu-ATRP mechanism only upon binding to a variety of nucleic acids. The dominant mechanisms involved oxidative quenching for nucleic acid-bound GelGreen and GelRed as PCs.

Oxygen tolerance and fast polymerization enabled 3D printing of hydrogel through digital light processing to form objects with high resolution (Figure 10a).^[98] The hydrogels prepared by ATRP with carbon quantum dots as PC maintained their functional end groups, further used to functionalize 3D-printed objects. However, residual PC imparted yellow color to the final objects. With silicon-doped carbon dots, the least emissive PCs were the most desirable for dual ATRP 3D printing.^[94] The advantage of ATRP in forming a more homogeneous 3D printed network compared to FRP is widely reported, which is an exciting area for further development with dual-catalytic ATRP.^[136]

Green light-driven dual PC/Cu surface-initiated ATRP (SI-ATRP) was used to graft several brush polymers from polypropylene (PP) 384-well plate (Figure 10b).^[125] Glycidyl

methacrylate-functionalized PP was then used for enzyme immobilization, enabling rapid and combinatorial high-throughput screening for the optimal brush composition for enzyme support under thermally and chemically denaturing conditions.

Designing structural patterns that result in good efficiency of triplet state formation can be a key challenge. An alternative way to provide a longer lifetime of the excited states was realized by the confinement of photoactive species into a rigid matrix such as silica to give photocatalysts that operate in the heterogeneous phase. For example, carbon dots supported on such matrices were applicable to photoATRP systems with highly oxygen-tolerant properties under blue light irradiation (Figure 11a).^[137]

Other examples of photocatalysts that can function in the heterogeneous phase include mesoporous carbon nitride (Figure 11b, mpg-C₃N₄),^[138] zinc oxide,^[140] titanium dioxide.^[141] Upon light irradiation at appropriate wavelengths, they form electron holes and transfer a single electron for Cu^IL⁺ activator regeneration. Chromophore groups with strongly reducing properties in the excited state were confined in a crosslinked material that exhibited high photocatalytic activity.^[106a] Reacting phenothiazine as the photoactive core with dimethoxybenzene via a Friedel–Crafts reaction gave a network with a red-shifted absorbance due to extended conjugation. Dual PC/Cu-ATRP employed this material as the photocatalyst in the presence of X–Cu^{II}L⁺ with green or red-light irradiation (Figure 11c). A similar phosphine-based conjugated crosslinked structure (PPh₃-CHCP) was used as a photocatalyst for large-scale

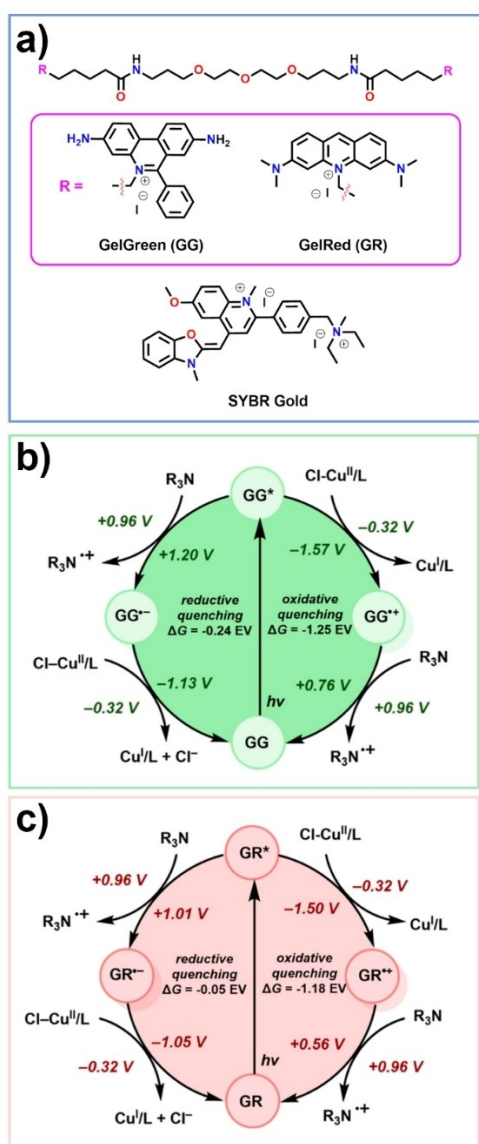


Figure 9. a) Structures of GelGreen (GG), GelRed (GR), and SYBR Gold nucleic-acid binding dyes used in dual PC/Cu-ATRP with the associated quenching pathways of GG and GR (b and c, respectively) by Cl-Cu^{II}/TPMA⁺. Both GelGreen and GelRed are dimeric species linked by 27 atom long water soluble linkers to efficiently intercalate with DNA and only then become emissive and act as photocatalysts for ATRP. Reproduced with permission.^[135] Copyright 2024, American Chemical Society.

photoATRP.^[139] Acrylates and methacrylates were polymerized to high conversions under a wide range (450–940 nm) of radiation or sunlight. Polymerization proceeded with the oxidative quenching of the photocatalyst not only by the deactivator, X–Cu^I/L⁺, but also by the alkyl halide initiator (Figure 11d). NIR-absorbing inorganic nanoparticles sensitized the Cu-catalyst through the up-conversion mechanism.^[142] Interestingly, dual PC/Cu-ATRP systems offered selective polymerization based on the photochemical properties of the PC, e.g., in the presence of DNA^[135] or as a function of pH-controlled pyrene dyes.^[90]

A compilation of various polymeric materials made by dual PC/Cu-ATRP is presented in Table 3 (cf. PCs listed in Table 1). Metal-based and organic PCs, carbon-based materials, conjugated polymeric materials (including covalent organic frameworks (COFs) and metal–organic frameworks (MOFs)), combined with various Cu catalysts were used for a successful controlled polymerization of various monomers, e.g., acrylates, methacrylates, acrylamides or styrene. The future design of new photocatalytic systems deserves detailed structure/relationship studies, corroborated by computational chemistry.^[143]

8. Why Better Together?

The rapid development of dual-catalysis PC/Cu-ATRP as a regenerative ATRP technique originates in the synergy between PCs and Cu-ATRP complexes used as co-catalysts. Herein, the benefits are summarized below (Scheme 7). These advantages include:

1. Low energy light with deeper penetration in opaque and scattering media,
2. Using co-catalysts at concentrations lower than required separately,
3. Tunable kinetics and spatio-temporal control,
4. Selective co-catalytic cycles with high turnover numbers,
5. Oxygen tolerance enhanced synergistically by PC* and Cu-complexes,
6. Synthesis of well-defined (co)polymers (i.e., negligible generation of exogenous radicals) with high CEF and narrow/tunable molecular weight distributions,
7. Access to advanced macromolecular architectures and hybrid materials,
8. Precise synthesis of bioconjugates with proteins and nucleic acids.

With longer wavelength light, dual PC/Cu-ATRP offers an avenue for ATRP to improve energy efficiency with benign stimuli into a wider scope of media (1) and substrates (7, 8), even at low-ppm levels of co-catalysts (2). The distinct co-catalyst roles imply that PC photophysical properties, light intensity, and loading are responsible for kinetics, where PC is generally not involved in chain-end deactivation/activation (2, 3, 4). Likewise, the Cu-catalyst separately controls chain ends and molecular weight distributions through intermediate activation/deactivation.

Precision-tailored macromolecular materials take advantage of the following instances: (1, 6, 7, 8) high-value polymers defined by specialty monomers, physical properties, and CEF through controlled initiation and molecular weight distribution; (2) less impurities in final polymeric material; (4, 5, 8) facile operation at conventional or ambient conditions. Environmental impact is mitigated by implementing the features of (1) energy-efficient and benign stimuli, particularly at higher wavelengths; (2, 4, 5) enhanced and tunable atom economy; (5, 8) control at ambient conditions without energy-intensive/costly oxygen removal.

The advancement of dual PC/Cu-ATRP can be related to the mechanistic and photophysical understanding of the

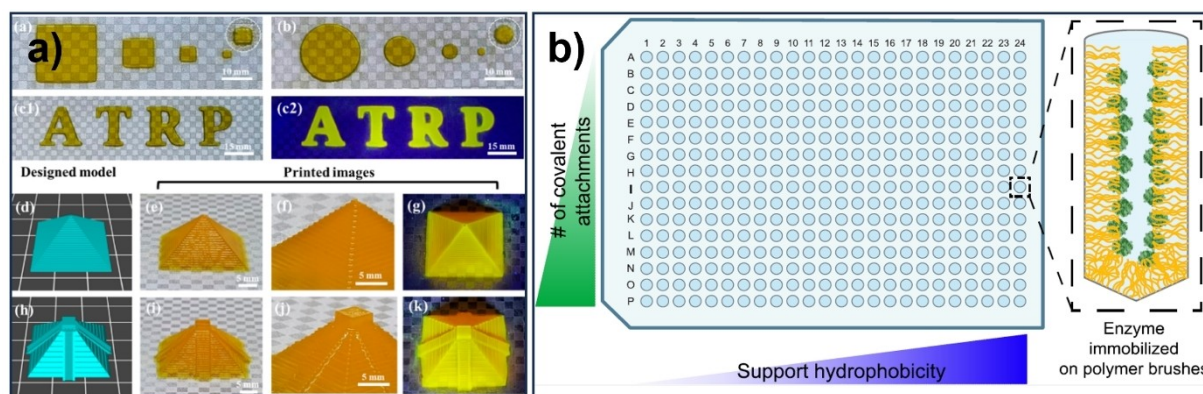


Figure 10. a) The use of fast and oxygen-tolerant dual catalytic $\text{CuBr}_2/\text{TPMA}$ and carbon dots system for 3D-printing of prism with digital light processing. Reprinted with permission.^[98] Copyright 2022, American Chemical Society; b) The use of green light driven CuBr_2/EY ATRP to synthesize polymer brushes from PP for high-throughput screening of immobilized enzymes (right). Reprinted with permission.^[125] Copyright 2024, American Chemical Society.

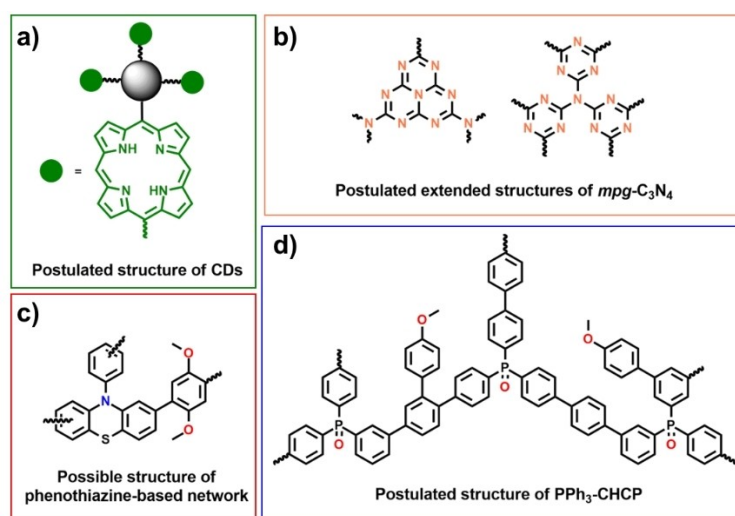


Figure 11. a) Postulated structures of heterogeneous-phase PCs for ATRP: a) carbon dots,^[137] b) $\text{g-C}_3\text{N}_4$,^[138] c) crosslinked phenothiazine,^[106a] d) $\text{PPh}_3\text{-CHCP}$ conjugated crosslinked polymer.^[139]

co-catalytic system. The light employed in dual PC/Cu-ATRP does not need to coincide fully with the maxima of the PC absorption spectra, which should offer additional wavelength tunability.^[71a] The fundamental mismatch between photochemical activity and absorption was demonstrated in RAFT and other processes.^[79a,83b] This highlights the necessity for more in-depth mechanistic studies of ET from excited states using transient absorption spectroscopy. Specialized setups like wavelength-tunable nanosecond pulsed laser polymerization method and photochemical action plots.^[83b,151] This would also help better understand and match the PC/Cu-catalyst pair, specifically their redox potentials and electronic structures.

The loading limit for PC depends on its photophysical properties and behavior in the employed medium.^[71a] Meanwhile, the minimal loading for the Cu catalysts depends on the desired control of the molecular weight distribution of the final polymer. This control relies on properly matching

the alkyl halide initiator and monomer and can be improved by employing higher-activity Cu catalysts (Section 6.2).^[11]

Design principles of dual PC/Cu-ATRP obey general guidelines for nearly all regenerative ATRPs (Sections 2 & 6.2). The catalyst should possess a sufficiently high K_{ATRP} to offer control at ppm levels under a regenerative kinetic regime. K_{ATRP} typically increases for higher polarity/polarizability solvents, which modifies ATRP kinetics and control. The solvent-ligand pair should be selected to prevent the disproportionation of $\text{Cu}^{\text{II}}\text{L}^+$, which acts as the primary activator. Furthermore, the deactivator complexes should fully exist in the ternary $\text{X-Cu}^{\text{II}}\text{L}^+$ state (organic media or aqueous media with chloride/bromide salts).

Spatio-temporal control is inherent to dual PC/Cu-ATRP through the light source as an external stimulus. Activator regeneration halts when the light is off. Design considerations for improved spatio-temporal control include tuning of light source wavelength and intensity (higher

Table 3: Examples of polymers made by dual PC/Cu-ATRP.

Entry	PC	Metal-based photocatalysts	CuBr ₂ /L	Monomers	Solvent	M _n × 1000	Đ	Ref.
1	FeCl ₃ , FeBr ₃		TPMA	OEOMA	H ₂ O/DMSO (9/1 v/v)	32.0–195.0	1.13–1.21	[43c]
2	ZnO nanocrystals		TPMA	MA, EA, HEA, MMA	DMSO	2.9–41.6	1.10–1.41	[120]
3	TiO ₂ nanoparticles		bpy	DMAEMA, NIPAM, OEOMA, SPMA	H ₂ O/MeOH (2/1 v/v)	N.D.	N.D.	[141]
4	Zinc(II) Tetraphenylporphine (ZnPc), Zinc(II) Phthalocyanine (ZnPc)		Me ₆ TREN, PMDETA	MA	DMSO, DMF	8.4–17.2	1.06–1.10	[91]
Organic photocatalysts								
5	EY		TPMA Me ₆ TREN	OEOMA, OEOMA, MSEA, HEA, CBA, GMA, SBMA, MA, BA, t-BA, n-BMA, LA, CEA	H ₂ O/DMSO (9/1 v/v), DMSO, DMF	16.5–607.0 10.9–75.4	1.14–1.21 1.14–1.27	[85]
6	EY, FL, Riboflavin		TPMA	OEOMA, HEMA, CBMA	H ₂ O/DMSO (9/1 v/v)	42.2–120.3	1.16–1.35	[84]
7	RD, RD-6G, RB		Me ₆ TREN	MA, OEOMA	DMSO, H ₂ O	8–142.2	1.12–1.19	[71a]
8	MB		TPMA	OEOMA, NIPAM, OEOMA, CBMA, QAMA, MAPS, HEA, MA, HEMA, BMA	H ₂ O/DMSO (9/1 v/v), DMSO (mini-emulsion)	9.0–321.2	1.09–1.39	[86a]
9	Polymethine dye PM		TPMA	MMA	DMF	13.1–43.4	1.09–1.71	[86]
10	Diaryl substituted terephthalates DAST 1–3		TPMA Me ₆ TREN (ineffective)	MMA, BZMA, MEMA, NFHMA	DMF	22.0	1.17–1.27	[87]
11	Cyanoaryl's CyAr 1–5		TPMA	MMA, BMA, t-BMA, BZMA, GMA	DMF	11.2–77.3	1.13–1.26	[88]
12	Bay-modified perylene dyes PDII [−] /PDIIF [−]		TPMA	MMA, DMA, AM, BZMA, MEMA, NFHMA, YRMA	DMF	16.7–20.3 15.7–104.2	1.20–1.35 1.13–1.31	[71b] [90]
13	TPMA impurities (i.e., dipyrindine imine, nitroene dipyrindine)		TPMA	OEOMA	H ₂ O/DMSO (9/1 v/v)	20.4–54.3	1.18–1.25	[144]
Carbon-based materials								
14	Furfuraldehyde CD		TPMA	MMA, ST	DMSO	1.85–55.8	1.10–1.97	[913]
15	Pyridine nitrogen doped CD		TPMA, PMDETA	HEA, MMA	H ₂ O, DMSO, DMF, MeCN	18.0–42.6	1.20–1.47	[98] [145]
16	Silicon-doped CD		TPMA	HEA	H ₂ O	28.9–35.8	1.23–1.39	[94]
17	Graphitic carbon nitride mpg-C ₃ N ₄		PMDETA	MMA, MA, ST	MeCN	6.6–55.2	1.11–1.28	[146]
Conjugated polymers, covalent organic frameworks (COFs) and metal–organic frameworks (MOFs)								
18	Cross-linked phenothiazine PTZ		TPMA, Me ₆ TREN, PMDETA	MA, BA, MEA,	DMSO, DMF, MeCN	8.3–29.7	1.07–2.06	[901]
19	Crosslinked triarylphosphine PPh ₃ -CHCP		TPMA, Me ₆ TREN, PMDETA	MA, MMA, BMA, CHMA, BA, MEA, TFEA, BZA, t-BA	DMSO, DMF, MeCN	15.5–43.6	1.09–1.29	[139]

Table 3: (Continued)

Entry	PC	CuBr ₂ /L	Monomers	Solvent	M _n × 1000	Đ	Ref.
Metal-based photocatalysts							
20	PyTTA-DMTA-COF-1 TFPPY-Td-COF-2 TCPB-DMTA-COF-3	TPMA, Me ₆ TREN	OEOMA, MMA, BZMA, BMA, GMA, t-BMA, HPMA, DEAMA, PhMA 4VP, 2VP, DMAEMA, MMA	H ₂ O, MeCN	11.8–41.1 4.1–18.0 1.6–77.0	1.05–1.32 1.11–1.17 1.13–1.39	[147] [148] [147,149]
21	MOF-1 Cu ₂ (bdc) ₂ (dabco)	PMDETA		MeOH, DMF	3.2–33.6	1.20–1.30	[150]
Monomers: AM: acrylamide, BA: butyl acrylate, t-BA: tert-butyl acrylate, BMA: butyl methacrylate, BZA: benzyl methacrylate, CBA: carboxy betaine acrylate, CEA: 2-cyanoethyl acrylate, CHMA: cyclohexyl methacrylate, DMA: N,N'-dimethylacrylamide, DMAEMA: dimethylaminoethyl methacrylate, GMA: glycidyl methacrylate, HEA: 2-hydroxyethyl methacrylate, HEMA: 2-hydroxyethyl methacrylate, HPMA: hydroxypropyl methacrylate, LMA: lauryl methacrylate, MAPS: 3-sulfopropyl methacrylate potassium salt, MEA: methoxyethyl methacrylate, MEMA: methoxyethyl methacrylate, MA: methyl acrylate, MMA: methyl methacrylate, MSEA: 2-(methylsulfonyl)ethyl methacrylate, NFHMA: nonafluorohexyl methacrylate, PhMA: phenyl methacrylate, QAMA: quaternary amine methacrylate, SPMA: 3-sulfopropyl methacrylate potassium salt, SYRMA: syringyl methacrylate, ST: styrene, TFEA: 2,2,2-trifluoroethyl methacrylate, 2VP: 2-vinylpyridine, 4VP: 4-vinylpyridine; Other: H ₂ bdc: terephthalic acid, dabco: 1,4-diazabicyclo[2.2.2]octane, PyTTA: 4,4',4'',4'''-(1,8-dihydropyrene-1,3,6,8-tetrayl)tetraaniline, DMTA: 2,5-dimethoxy-terephthalaldehyde, TFPPY: 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaldehyde, Td: 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dianiline, TCPB: 1,3,5-tris(4-cyanomethylphenyl)benzene.							

intensity will regenerate more Cu^IL⁺ activators) alongside higher K_{ATRP} values.^[106a,152] The principle depends on the feature of regenerative ATRP in which a lower ratio of activators to deactivators (Cu^I/Cu^{II}) at the steady state of polymerization allows for nearly instantaneous quenching of residual activators in the dark periods.

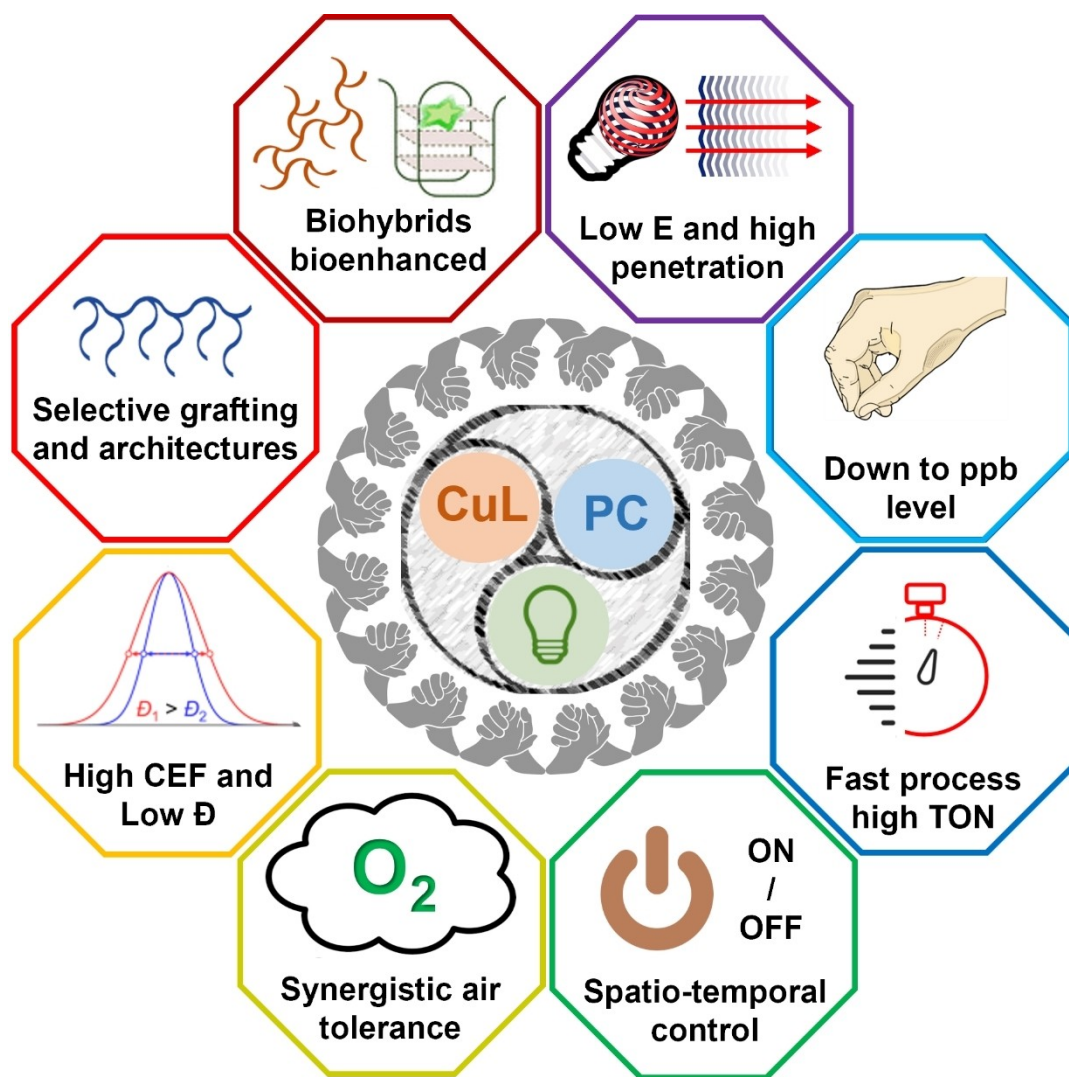
Dual PC/Cu-ATRP demonstrates unique oxygen tolerance (Section 6.5) for scale-up, 3D printing, or biological applications. O-ATRP and classical photoATRP exhibit some degree of oxygen tolerance on their own. Still, dual PC/Cu-ATRP combines these corresponding features for facile reaction setup. Without appropriate photochemical properties in its intermediates, the PC may not appreciably remove oxygen alone. Downstream ED intermediates can scavenge oxygen and decompose into innocent byproducts (Section 6.4, Scheme 5). Thus, dual PC/Cu-ATRP offers multiple avenues of oxygen scrubbing that would not be fully available to the separate techniques of O-ATRP and Cu-ATRP.

Dual PC/Cu-ATRP has exhibited high biocompatibility and even bio-synergy by relating PC photophysical properties with the biological system, e.g., nucleic acid-binding dyes. Nevertheless, each dye should be investigated within its assigned bio-related system for compatibility. For example, photoirradiation of MB⁺ resulted in diminished cytotoxicity in the presence of Cu-ATRP catalyst and ED, caused by rapid quenching.^[86a] Thus, dual PC/Cu-ATRP is *better together*, where toxicity can be limited through low loadings of co-catalysts and PC quenching selectivity.

9. “Dream” Systems and Outlook

In summary, dual PC/Cu-ATRP provides access to advanced functional materials by combining the control of Cu-ATRP with the photochemical action of a PC for activator regeneration. The high co-catalytic efficiency, oxygen tolerance, commercial availability of dyes, and facile setup of dual PC/Cu-ATRP can extend ATRP to non-specialists, adjacent materials-focused communities, and resource-limited settings. It is desirable to develop bulk polymerization and high-throughput approaches using dual PC/Cu-ATRP in industrial settings.

The scope of dual PC/Cu-ATRP (Sections 6.1 & 7) is expanding with pre-existing and new PCs and their response to different media and light. The engineering of PC and Cu-catalyst electronic states should emphasize activator regeneration through efficient photoexcitation by PC and rapid ET to X–Cu^{II}L⁺. Ground and excited states of PCs should be precisely characterized by absorption/emission spectroscopy, cyclic voltammetry, and Density Functional Theory, to determine the possible reductive/oxidative quenching pathways. An abundance of data related to properties of PCs studied in other fields of materials science, such as OLEDs or perovskite materials, encourages the creative use of quantum chemistry, artificial intelligence, and machine learning models.^[153] It is envisaged that PCs for dual/Cu-ATRP should be appropriately designed instead of using a trial-and-error approach.



Better Together: Photoredox/Copper Dual Catalytic ATRP

Scheme 7. Overview of advantages and scope of the PC/Cu-ATRP. Inset reproduced with permission.^[135] Copyright 2024, American Chemical Society.

Immobilization of dual PC/Cu-ATRP components is promising for purification and recyclability to align with green chemistry principles.^[29] Immobilization has already been successfully applied for PCs, particularly as heterogeneous PCs^[106a,134,137–138,154] in RDRP (Section 6.3). Immobilization of PC is feasible because $X-Cu^{II}L^+$ deactivators are small molecules that can readily diffuse to and from a PC-hosting network for reduction. Furthermore, it would be interesting to define PC-embedded networks with controlled periodicity for investigating PC^*-Cu and potential PC^*-PC interactions (for example, aggregation-induced emission (AIE)). Immobilization of Cu-ATRP catalyst, while theoretically beneficial for facile removal of Cu ions post-polymerization, would require polymeric radicals to diffuse there, slowing down deactivation and resulting in strongly reducing control. Lastly, immobilization of the ED is feasible or could be offloaded electrochemically because the corresponding

PC^{*+} (oxidative quenching system) or PC^* (reductive quenching system) can readily diffuse as small molecules. Overall, dual PC/Cu-ATRP fully relies on diffusion-controlled interactions of PC, Cu, and ED, so immobilization of more than one component at once could prevent proper kinetic participation. Nevertheless, PC immobilization as a heterogeneous network for easier post-polymerization removal and recyclability as a proof of concept has been validated (Section 7).

Current characterization of heterogeneous PCs is mostly derivative of equivalent “monomeric-like” PC structures, e.g., phenothiazine or PPh_3 , with limited control of the material properties like porosity, morphology on photochemical activity. As a result, heterogeneous PCs may not necessarily be kinetically equivalent to their homogeneous analogs, which have already exhibited high conversions with good control as low as 50 ppb.^[71] Such low co-catalyst

loading under homogeneous conditions renders the polymers pristine and uncolored. Dual PC/Cu-ATRP could benefit from well-defined, periodic MOF^[155] or COF-based^[156] photocatalysts. To these ends, both homogeneous and heterogeneous conditions for dual PC/Cu-ATRP conditions are worth pursuing.

PCs linked to acrylates^{[134][157]} or norbornenes^[158] were copolymerized for biological and theranostic applications. While immobilized PC networks would be diffusion-limited, PC-linked polymers could overcome this limitation and efficiently regenerate activators. Linear polymers hosting PC could better diffuse (molecular weight- and architecture-dependent) and synergistically combine the photochemical PC properties with the physical properties and processibility associated with polymers. If linked to polymers with LCST properties like poly(*N*-isopropyl acrylamide), they can be separated from solution at elevated temperatures.^[157] Covalent immobilization of EY on highly swellable crosslinked poly(ethylene oxide) matrix resulted in highly efficient non-leachable dual catalytic systems.^[159]

The scope of sacrificial ED additives in dual PC/Cu-ATRP has yet to extend beyond excess amines/ligands. While the redox properties of amines have robustly matched the needs of dual PC/Cu-ATRP and provided mechanistic insight, their remaining decomposition products can be undesirable from the standpoint of materials and industry. However, this is currently offset by the low overall amount of Cu-ATRP catalyst which must be regenerated and can already operate at low ppm levels. The atom economy further improves by employing higher K_{ATRP} catalysts, which require less overall turnover and regeneration.

The simple process of $\text{Cu}^{\text{I}}\text{L}^+$ activator regeneration can be achieved through a variety of stimuli. Dual PC/Cu-ATRP system may be enhanced by additional stimuli beyond photoirradiation, such as electrochemistry and mechano/sonochemistry (sonication, ball-milling, or tribochemistry) for alternative control and benefits within Cu-ATRP catalysis. ZnO nanocrystals served as co-catalysts that could utilize both sono- and photostimuli.^[120] UV photoirradiation efficiently scrubbed the reaction of oxygen in 3 minutes, which was followed by sonication for mechanoATRP.

ATRP has been recognized as a highly robust technique for macromolecular engineering and preparing both commodity and specialty materials (Section 7).^[7b] Dual PC/Cu-ATRP represents a selective regenerative ATRP option for avoiding side reactions or exogenously dosed radicals. This becomes especially important for high molecular weight polymers, biocompatibility, chain extensions, branching, and other advanced architectures. Dual PC/Cu-ATRP systems for depolymerization have yet to be realized, but small-scale photoATRP depolymerization with $\text{FeCl}_2/\text{FeCl}_3$ salts has been demonstrated.^[160] Extending photoredox dual-catalysis into abundant Fe-catalysts will require development in ligands and PC/Fe-catalyst combinations. Meanwhile, dual PC/Cu-ATRP developments can also be extended retrospectively to small molecule synthesis. Finally, dual-catalysis has been recognized for the preparation of hybrid materials, such as surface-initiated (SI) PVDF by selective EY/Cu-SI-ATRP,^[132] and preparation of complex bioconjugates or bio-

enhanced systems that combine synergy with biologically relevant substrates.^[135] To these ends, we envision rapid progress of dual catalysis PC/Cu-ATRP and resultant applications, with increased interest from academic and industrial perspectives over their individual photoATRP processes.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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