

Red-Light-Induced, Copper-Catalyzed Atom Transfer Radical Polymerization

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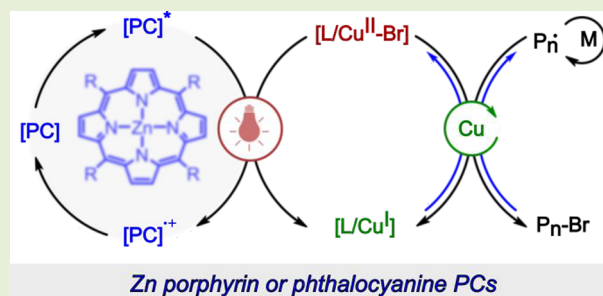


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Supporting Information

ABSTRACT: Despite advances in photochemical atom transfer radical polymerization (photoATRP), these systems often rely on the use of UV light for the activation/generation of the copper-based catalytic species. To circumvent the problems associated with the UV light, we developed a dual photoredox catalytic system to mediate photoinduced ATRP under red-light irradiation. The catalytic system is comprised of a Cu catalyst to control the polymerization via ATRP equilibrium and a photocatalyst, such as zinc(II) tetraphenylporphine or zinc(II) phthalocyanine, to generate the activator Cu^{I} species under red-light irradiation. In addition, this system showed oxygen tolerance due to the consumption of oxygen in the photoredox reactions, yielding well-controlled polymerizations without the need for deoxygenation processes.



Integration of photochemical processes in controlled polymerizations have provided new opportunities for the synthesis of well-defined polymeric materials.^{1–8} The efficiency of photoinduced controlled polymerizations depends on the efficient transfer of photon energy to activate/drive polymerization processes. This can be achieved by either direct excitation and photolysis of polymer chain ends or by using various photocatalytic/photosensitizer systems to promote the activation of the dormant polymer chains. In particular, the advances in light-mediated atom transfer radical polymerization (ATRP) or reversible addition–fragmentation chain-transfer (RAFT) polymerization by use of various photocatalytic/photosensitizer systems have provided new mechanisms and possibilities for synthesis of well-defined polymers.^{9–13}

Photochemical ATRP encompasses various modes of activation, including ground state metal-catalyzed or excited state photoredox-catalyzed processes. In photoredox- or organo-catalyzed ATRP, the photocatalysts in the excited state are capable of activating the C–X chain ends to form initiating/propagating radicals. The oxidized form of the photocatalyst can mediate the deactivation of growing radicals in conjunction with halide anions.^{13,14} In metal-catalyzed ATRP, the activators (typically Cu^{I} species) are generated by photochemical reduction of deactivators (Cu^{II} species) in the presence of electron donors and can then start the ATRP catalysis in the ground state.

Direct excitation of copper^{15–20} or iron-based²¹ catalysts can lead to the generation of the corresponding activators and thus initiate and control polymerization. Although Fe-catalyzed photoinduced ATRP can be activated under visible light

irradiation,^{22,23} direct photoactivation of Cu-catalyzed ATRP requires the use of UV or violet lights. However, because of the high energy of the UV light and its limited depth of penetration, it can pose adverse effects in some delicate applications. Therefore, developing dual photoredox catalytic systems would be beneficial to take advantage of the long wavelengths of the visible or near-infrared light in ATRP.^{24–30}

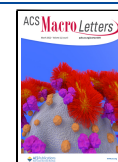
In this paper, we present the development of a dual photoredox catalytic system that enabled performing ATRP under red-light irradiation. Inspired by the development of porphyrin- or phthalocyanine-based photocatalysts in RAFT polymerization,^{31–35} we used zinc(II) tetraphenylporphine (ZnPor) and zinc(II) phthalocyanine (ZnPc)³⁶ as photocatalysts for promoting Cu-catalyzed ATRP. The ATRP activator, $\text{L}/\text{Cu}^{\text{I}}$, was generated in situ in the presence of the photocatalysts irradiated under red light, whereby control over the polymerization was achieved via ATRP equilibrium.

Considering the absorption profile of ZnPor and ZnPc photocatalysts in the red-light region (Figure S2), their utility as photocatalysts was examined in Cu-catalyzed ATRP (Scheme 1). We began our studies with the spectroscopic analysis of the photocatalytic system, which revealed that $\text{L}/\text{Cu}^{\text{I}}$ as the ATRP activator was generated in the presence of

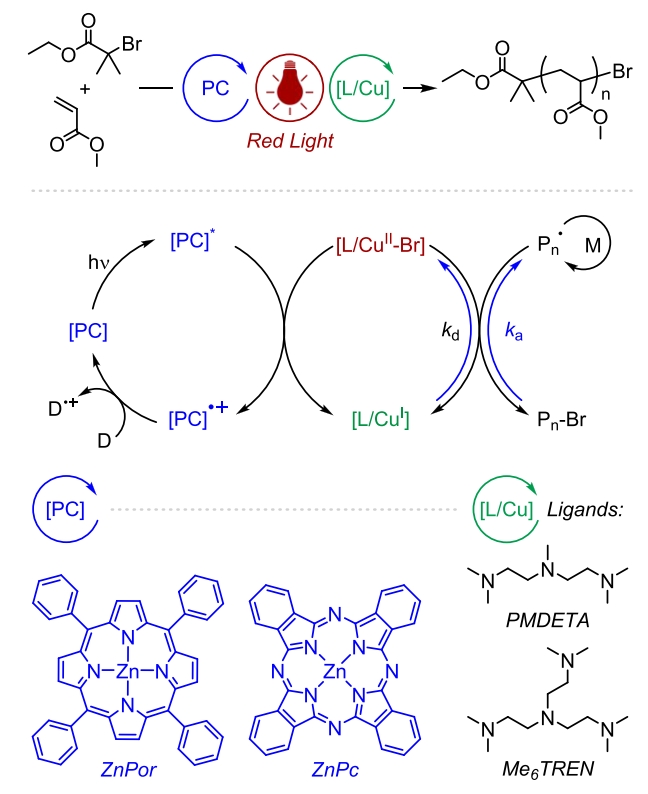
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Scheme 1. Photoinduced ATRP under Red-Light Irradiation Using Zinc(II) Tetraphenylporphyrine (ZnPor) or Zinc(II) Phthalocyanine (ZnPc) as Photocatalysts (PCs) to Generate ATRP Activator Species



ZnPor under red-light irradiation. The evolution of the UV–vis spectra of a solution of copper(II) bromide (CuBr_2) and N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA) ligand in dimethyl sulfoxide (DMSO) was monitored in the presence of ZnPor under red-light irradiation. A decrease of the absorbance of the L/Cu^{II} species at ~ 714 nm indicated photoreduction to L/Cu^{I} (Figure 1A). No significant change was observed in the absorbance of ZnPor ~ 600 nm.

As demonstrated in Scheme 1, excitation of the photocatalyst (PC) under red-light irradiation generates an excited state species (PC^*), which is capable of reducing L/Cu^{II} and

generating L/Cu^{I} as the ATRP activator by a photoinduced electron transfer process. The oxidized form of the photocatalyst ($\text{PC}^{\bullet+}$) could be reduced back to the initial ground state by amine electron donors (D), thus, completing the photocatalytic cycle. Therefore, ZnPor could be used in catalytic amounts with respect to CuBr_2 ($[\text{ZnPor}]/[\text{CuBr}_2] = 1/40$).

Furthermore, fluorescence quenching experiments of ZnPor showed that the excited state of the photocatalyst was quenched upon addition of $\text{CuBr}_2/\text{PMDETA}$. A decrease in the emission intensity of ZnPor (excitation at 630 nm and emission maximum at 680 nm) was observed upon addition of $\text{CuBr}_2/\text{PMDETA}$, as shown in the Stern–Volmer plot in Figure 1C and Figure S3. These results confirm the interaction of ZnPor^* with $\text{CuBr}_2/\text{PMDETA}$ to generate the activator L/Cu^{I} and therefore initiate ATRP. In contrast, only negligible quenching of the excited state of ZnPor was observed in the presence of the ATRP initiator, ethyl α -bromoisobutyrate (EBiB). According to the fluorescence measurements, the singlet excited state reduction potential of ZnPor was estimated to be -0.95 V versus SCE (see Supporting Information). Additionally, intersystem crossing (ISC, with a triplet yield of ~ 0.9 for ZnPor)³⁷ can generate triplet excited states, which have lower reduction potentials (~ 0.5 V lower than the singlet states for ZnPor).³⁸ Despite the lower reduction potential, the longer lifetime of the triplet excited states can afford efficient electron transfer and reaction with the quencher (i.e., CuBr_2/L). The reduction potential of the triplet excited state ZnPor should be sufficiently strong to enable photoreduction of the $\text{CuBr}_2/\text{PMDETA}$ catalyst, which has a reduction potential of ~ -0.2 V versus SCE (Figure S4), as opposed to the EBiB initiator with a more negative reduction potential (-0.58 V vs SCE).³⁹ The singlet excited state reduction potential of ZnPc photocatalyst can also be estimated ~ -1.1 V versus SCE, according to the literature reports.^{40,41}

Having shown the capability for the ATRP activator generation by ZnPor under red light irradiation, polymerization of methyl acrylate (MA) was attempted to study the effect of the photocatalysts and other polymerization components (Scheme 1). Polymerization of MA was well-controlled using $\text{CuBr}_2/\text{PMDETA}$ and ZnPor as a photocatalyst under red light irradiation (630 nm). No polymer-

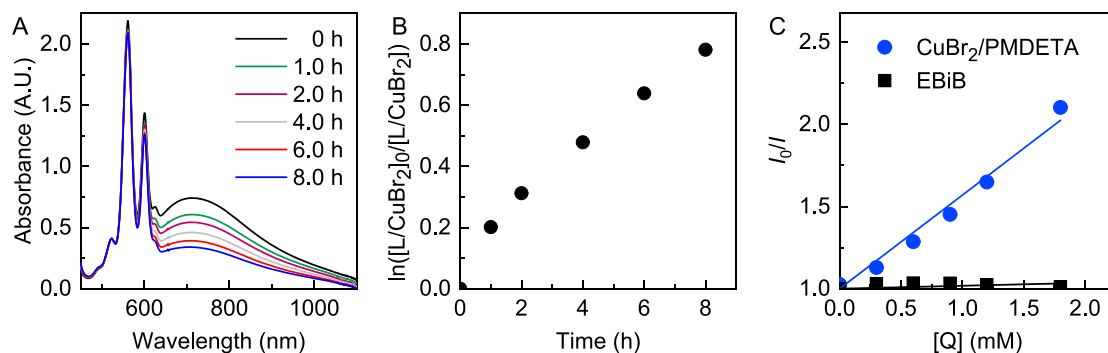


Figure 1. Photoreduction of CuBr_2 using ZnPor as a photocatalyst under red-light irradiation (630 nm, ~ 4 mW/cm²). (A) Evolution of the UV–vis spectra and (B) kinetics of the reduction of L/CuBr_2 . Reaction conditions: $[\text{CuBr}_2] = 5$ mM, $[\text{PMDETA}] = 50$ mM, and $[\text{ZnPor}] = 0.125$ mM in DMSO. Absorption peaks at ~ 560 and 600 nm correspond to ZnPor and the broad peak at ~ 710 nm corresponds to the absorption of $\text{CuBr}_2/\text{PMDETA}$. (C) The Stern–Volmer plot for ZnPor in the presence of $\text{CuBr}_2/\text{PMDETA}$ or EBiB as quenchers (Q) in DMSO (nondeoxygenated) showing fluorescence quenching mainly by the Cu catalyst. Excitation at 630 nm and emission intensity recorded at 680 nm. The fluorescence spectra are shown in Figure S3.

Table 1. Results of ATRP of MA Using Zinc(II) Tetraphenylporphyrine (ZnPor) under Red-Light Irradiation^a

entry	ligand (L)	CuBr ₂ /L	ZnPor (ppm)	conversion (%)	<i>M</i> _{n,th}	<i>M</i> _n	<i>Đ</i>
1	PMDETA	1/10	0	0			
2	PMDETA	1/5	5	52	8900	8400	1.08
3	PMDETA	1/10	5	73	12800	13900	1.06
4	PMDETA	1/5	10	62	10700	10200	1.07
5	PMDETA	1/10	10	80	13800	13100	1.08
6	PMDETA	1/10	100	90	15500	15100	1.07
7	Me ₆ TREN	1/10	0	0			
8	Me ₆ TREN	1/5	10	81	14100	12600	1.09
9	Me ₆ TREN	1/10	10	91	15800	14600	1.09
10			10	76	13200	213000	2.30

^aReaction conditions: [MA]/[EBiB]/[CuBr₂]/[L] = 200/1/0.04/*x* (L = PMDETA or Me₆TREN; *x* = 0, 0.2, or 0.4) in 50 vol % solvent (DMSO with PMDETA or DMF with Me₆TREN), under red-light irradiation (630 nm, ~4 mW/cm²) for 24 h, ZnPor = 0, 5, 10, or 100 ppm (corresponding to 0, 0.001, 0.002, or 0.02 equiv with respect to the initiator).

ization of MA was observed by irradiating a solution of CuBr₂/PMDETA under red light in the absence of the photocatalyst (Table 1, entry 1), indicating no productive excitation of the Cu^{II}/L and no formation of the activator species. However, using 5–10 ppm (relative to monomer) of the ZnPor photocatalyst started the polymerization and yielded polymers with well-controlled properties. Excess PMDETA was needed as the electron donor for promoting photocatalysis and starting the polymerization. Increasing the concentration of PMDETA from 0.2 to 0.4 equiv with respect to the initiator led to an increase in the monomer conversion from 52 to 73%, respectively (Table 1, entries 2 and 3). In addition, increasing the concentration of ZnPor from 5 to 10 and 100 ppm resulted in increasing the monomer conversion (Table 1, entries 3, 5, and 6).

In addition to PMDETA, tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was also used as a suitable ligand in conjunction with CuBr₂ to successfully control polymerization of MA under red-light irradiation (Table 1, entries 7–9 and Figure S6). No monomer conversion was observed in the absence of the photocatalyst. However, using 10 ppm of ZnPor in the presence of CuBr₂/Me₆TREN yielded well-controlled polymers with high monomer conversion, controlled molecular weights, and low dispersity values. Polymerizations using Me₆TREN were conducted in *N,N*-dimethylformamide (DMF) to rule out the possibility of background initiation in DMSO in the dark.^{42,43} A control experiment carried out in the presence of only ZnPor and EBiB (no added CuBr₂ and ligand) showed uncontrolled polymerization of MA with a high dispersity of 2.30 and molecular weight much higher than the theoretical value (initiator efficiency ~6%, Table 1, entry 10). These results further confirm the negligible activation of EBiB by the excited state ZnPor and poor deactivation of the growing radicals by the oxidized form of the photocatalyst, ZnPor^{•+}/Br[−].

Additionally, ZnPc was also used as an efficient photocatalyst for promoting Cu-catalyzed ATRP. Phthalocyanines possess a red-shifted absorption profile (up to 700 nm) compared to the analog porphyrins (Figure S2). The use of ZnPc enabled carrying out ATRP under red-light irradiation (630 nm). Polymerization of MA was initiated in the presence of ZnPc and was well-controlled, with molecular weights close to theoretical values and low dispersity values (Table S1). Increasing the concentration of ZnPc from 5 to 100 ppm resulted in an increase in monomer conversion from 66 to 93% (Table S1, entries 2–4 and Figure S7).

Temporal control experiments showed the growth of polymer chains could be mediated by switching the red light between on and off states. Polymerization of MA was observed only in the presence of red-light irradiation, whereas during the light-off periods no/negligible monomer conversion was observed (Figure 2A). Control over polymerization was

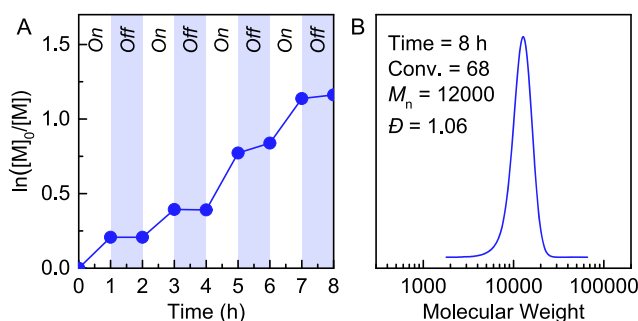


Figure 2. (A) Temporal control in red-light-induced ATRP of MA by switching light between the on/off states in the presence of the ZnPor photocatalyst. (B) GPC analysis of the resulting polymer after 8 h (four cycles of light on/off periods). Reaction conditions: [MA]/[EBiB]/[CuBr₂]/[Me₆TREN]/[ZnPor] = 200/1/0.04/0.2/0.002 in DMF (50 vol %).

maintained throughout multiple light on/off cycles, as proved by the agreement between the theoretical and experimental molecular weights ($M_n = 12000$, $M_{n,th} = 11950$) and low dispersity ($\bar{D} = 1.06$) of the resulting polymers (Figure 2B).

Recent developments in controlled radical polymerization techniques have enabled conducting polymerizations under mild conditions, without the need for performing extensive oxygen removal processes.^{44,45} Oxygen-tolerant polymerizations further simplify the synthetic procedures and offer new opportunities for performing polymerizations where removal of oxygen may not be possible by conventional deoxygenation means. To study the potential of ZnPor or ZnPc as photocatalysts in providing oxygen tolerance in ATRP, polymerization of MA was then conducted with no deoxygenation processes. Initially, the rate of oxygen consumption was monitored under red-light irradiation to study the effect of polymerization components. Irradiating a solution of ZnPor in DMSO (in 1 dram vial with no headspace) under red light resulted in a fast reduction in the concentration of oxygen (Figure 3). The rate of oxygen consumption was increased by increasing the concentration of

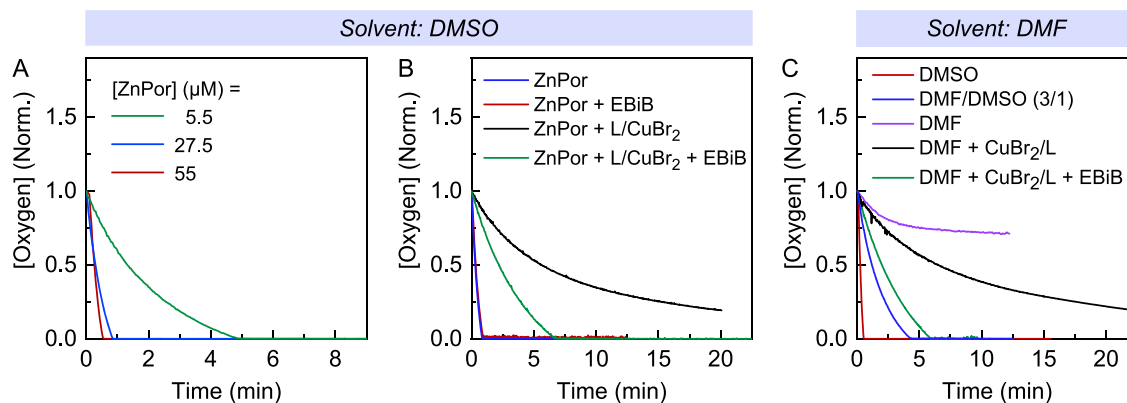


Figure 3. Rate of oxygen consumption in the presence of ZnPor photocatalyst in DMSO or DMF under red-light irradiation (630 nm, ~ 4 mW/cm²). (A) Effect of the concentration of ZnPor in DMSO ([ZnPor] = 5.5, 27.5, and 55 μ M). (B) Effect of polymerization components in the rate of oxygen consumption ([ZnPor] = 27.5 μ M, CuBr₂ = 1.1 mM, CuBr₂/PMDETA = 1/10, and [EBiB] = 27.5 mM, in DMSO). (C) Rate of oxygen consumption in DMF ([ZnPor] = 55 μ M, CuBr₂ = 1.1 mM, CuBr₂/Me₆TREN = 1/10, and [EBiB] = 27.5 mM, in DMF). Measurements were performed in closed vials with no deoxygenation and free headspace (total volume = 4 mL).

Table 2. Results of Copper-Catalyzed Photoinduced ATRP without Deoxygenation^a

entry	PC	ligand	solvent	conversion (%)	$M_{n,th}$	M_n	$\bar{D}$
1	ZnPor	PMDETA	DMSO	94	16400	17200	1.08
2	ZnPc	PMDETA	DMSO	75	13100	12600	1.10
3	ZnPor	Me ₆ TREN	DMF	93	16300	15700	1.07
4	ZnPc	Me ₆ TREN	DMF	86	15000	14000	1.08

^aReaction conditions: [MA]/[EBiB]/[CuBr₂]/[L] = 200/1/0.04/0.4 (L = PMDETA or Me₆TREN) in 50 vol% solvent under red light irradiation (630 nm, ~ 4 mW/cm²) for 24 h, PC = 10 ppm (corresponding to 0.002 equiv with respect to the initiator). Reactions were run in 4 mL vials without deoxygenation and no headspace.

the photocatalyst from 5.5 to 27.5 and 55 μ M (corresponding to 1, 5, and 10 ppm with respect to monomer under polymerization conditions), showing a complete reduction in <1 min (Figure 3A).

Addition of EBiB to a solution of ZnPor in DMSO gave a similar rate of oxygen consumption in the presence of only ZnPor (Figure 3B). This observation indicates that oxygen reduction by the photocatalyst in its excited state is not impeded by possible interactions with the initiator. However, when CuBr₂/PMDETA was added to a solution of ZnPor in DMSO, the rate of oxygen consumption was significantly diminished compared to when only ZnPor was used. This observation suggests that the reduction of L/Cu^{II} by the excited state ZnPor potentially competes with oxygen reduction, thus, inhibiting the complete and fast removal of oxygen. Interestingly, when both the EBiB initiator and CuBr₂/PMDETA catalyst were used in the presence of ZnPor, the rate of oxygen consumption increased and showed a complete removal of oxygen in ~ 5 min. Although in the presence of L/Cu^{II} the rate of oxygen removal was diminished, the reduction of L/Cu^{II} generates L/Cu^I, which can further activate the EBiB initiator and generate isobutyryl radicals. Therefore, in addition to the singlet oxygen scavenging by DMSO⁴⁶ or tertiary amines³⁵ that form dimethyl sulfone or superoxide (O₂^{•-}), respectively, the radicals also increased the rate of oxygen trapping in accordance with previous literature reports.⁴⁷ Moreover, use of photocatalysts can provide faster oxygen removal compared to previous works, which relied on consumption of oxygen by radicals and Cu^I species.^{48,49}

By changing the solvent from DMSO to DMF, a significant decrease in the rate of oxygen reduction was observed (Figure 3C). In contrast to DMF, DMSO is known to act as a

scavenger of singlet oxygen species, which can be generated by the excited state ZnPor under red light irradiation.⁴⁶ Therefore, changing the solvent to DMF diminished the rate of oxygen removal. Reduction of oxygen to O₂^{•-} by the photocatalyst can be responsible for the observed decrease in the concentration of oxygen in DMF. In the presence of additional DMSO (33 vol %), oxygen consumption in DMF was complete in <5 min, confirming the role of DMSO as the scavenger of the singlet oxygen generated in the presence of the excited state ZnPor, hence facilitating the consumption of oxygen. The addition of CuBr₂/Me₆TREN to the solution of ZnPor in DMF resulted in a slow consumption of oxygen, presumably consumed by the in situ generated L/Cu^I. In the presence of both CuBr₂/Me₆TREN and EBiB, consumption of oxygen reached completion in ~ 5 min, confirming the fast reaction of oxygen with isobutyryl radicals. The excited state ZnPor generated L/Cu^I species, which could also further react with EBiB and generate radicals capable of reacting with oxygen. Therefore, under polymerization conditions in DMF, both the Cu catalyst and the initiator can participate in removal of oxygen.

To demonstrate the oxygen tolerance of ATRP in the presence of ZnPor or ZnPc photocatalysts, polymerization of MA was performed without prior deoxygenation of polymerization solutions. Both the photocatalysts provided excellent oxygen tolerance and yielded well-controlled polymers in the presence of CuBr₂/L catalysts (Table 2). High monomer conversions were achieved using CuBr₂ with either PMDETA or Me₆TREN ligands, yielding polymers with molecular weights close to theoretical values and low dispersity ($\bar{D}$ < 1.1, Figure S8).

In summary, we demonstrated the development of dual photoredox catalysis to carry out ATRP under low-energy, red-light irradiation. Zinc porphyrin or zinc phthalocyanine were used as efficient red-light photocatalysts to generate the L/Cu^I activator species. Use of Cu catalysts at ppm levels ensured control over polymerization via ATRP process yielding polymers with controlled molecular weights and low dispersity values. This system further provided excellent oxygen tolerance to enable performing ATRP in a controlled manner without the need for extensive deoxygenation processes. Future studies will expand the range and efficiency of suitable photoredox catalysts, as well as a focus on the facile synthesis of hybrid, complex polymer materials, via ATRP under mild conditions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00080>.

Details of experimental procedures and additional supplementary results and characterization (PDF)

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Notes

The authors declare no competing financial interest.

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