Organopolymer with dual chromophores and fast charge-transfer properties for sustainable photocatalysis

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Photocatalytic polymers offer an alternative to prevailing organometallics and nanomaterials, and they may benefit from polymer-mediated catalytic and material enhancements. **MPC-1**, a polymer photoredox catalyst reported herein, exhibits enhanced catalytic activity arising from charge transfer states (CTSs) between its two chromophores. Oligomeric and polymeric **MPC-1** preparations both promote efficient hydride dehalogenation of α-halocarbonyl compounds while exhibiting different solubility properties. The polymer is readily recovered by filtration. **MPC-1**-coated vessels enable batch and flow photocatalysis, even with opaque reaction mixtures, via “backside irradiation.” Ultrafast transient absorption spectroscopy indicates a fast charge-transfer process within 20 ps of photoexcitation. Time-resolved photoluminescence measurements reveal an approximate 10 ns lifetime for bright valence states. Ultrafast measurements suggest a long CTS lifetime. Empirical catalytic activities of small-molecule models of **MPC-1** subunits support the CTS hypothesis. Density functional theory (DFT) and time-dependent DFT calculations are in good agreement with experimental spectra, spectral peak assignment, and proposed underlying energetics.
In spite of their comparative unsustainability, heterogeneous photocatalysts containing transition metal-based organometallic complexes and nanomaterials are well-precedented, yet reports on heterogeneous organophotocatalysts are comparatively sparse. Recently documented implementations include immobilization of dyes on various resin, silica, and polymer supports, dye entrapment in polyethylene pellets, soft gel dye entrapment, immobilization of dyes onto metal-oxide films, and incorporation into polymers as un conjugated pendant groups. Although π-conjugated polymers are well-recognized with the 2000 Nobel Prize in Chemistry, their direct application as macromolecular photocatalysts (MPCs) for organic synthesis is still nascent. Carbon nitride systems have received substantial attention as inherently photocatalytic organopolymers, but their two-dimensional networks suffer from a lack of solution-processability. The archetypal polymer of intrinsic micro porosity, PIM-1, was first reported in 2004 by Budd et al. as a fluorescent yellow double-strand polymer prepared from a reaction of tetrafluoroterephthalonitrile (1) and a tetra hydropyridine (2), yet to the best of our knowledge, its photocatalytic catalytic properties have not been reported. The precedent for the terephthalonitrile motif of PIM-1 in organophotoredox catalysis suggests that PIM-1 and its analogs could be competent MPCs. Beyond the typical advantages of heterogenization (i.e., improved catalyst recyclability and product purity), organopolymer MPCs offer the possibility of leveraging a tunable macromolecular structure to enhance catalytic and material properties. A variety of reports have appeared documenting the modular tunability of PIM-1 properties through nitride derivatization or co-incorporation of different monomers, especially for the purpose of changing the gas permeability of the resultant analog. A PIM-1 analog, which proximally incorporates two distinct chromophores, separated by a flexible, conjugation-breaking spirocyclic comonomer, might be expected to provide catalytic enhancements in a manner analogous to organometallic systems. It is well-known that triplet metal-to-ligand charge-transfer (3MLCT) states play a critical role in the photocatalysis of transition metal complexes. Photoexcitation of electronic transitions from the ground-state to the singlet metal-to-ligand charge-transfer (1MLCT) states is followed by the 1MLCT→3MLCT intersystem crossing (ISC) process. Transition metal complexes in the long-lived 3MLCT states may act as either a reducing or an oxidizing agent. For organometallic photocatalysts, electron transfer takes place via an outer sphere process that involves electron tunneling between the catalyst and another molecule. In a dual-chromophore PIM-1 analog, the charge-transfer states (CTSs) would instead arise from intramolecular transfer between separate chromophores, but these CTSs would likewise be associated with half-filled molecular orbitals and exhibit long lifetimes. Aside from potential enhancement of excited-state lifetime and catalyst–substrate redox processes, macromolecular structure provides additional means by which to adjust the overall catalytic process. In particular, catalyst solubility is tunable by monomer choice, feed ratio, and extent of polymerization. With appropriate solubility properties, organopolymer MPCs have the potential to be readily solution-processed into macroscopic structures such as thin-films, and it may be possible for the charge-transfer process to enable photoactivation when irradiating the film on the face not in contact with the reaction mixture (i.e., the face in contact with the wall of the vessel). Such a “backside irradiation” process could enable efficient photoactivation of systems suffering from poor light transmittance such as large-scale batch reactions and opaque reaction mixtures.

Hydrodehalogenation is a mechanistically straightforward model reaction suitable for demonstration of photoredox catalyst efficacy and is also of general interest to the chemistry community. Thousands of halogenated natural products have been discovered in organisms ranging from bacteria to humans, including chloramphenicol, one of the first three broad-spectrum antibiotics. Conversely, halogens also feature in many persistent organic contaminants, which are not readily degraded by microbial systems. Control of hydrohalog enation allows for modulation of the biological activity of chemical scaffolds, whether drug compounds or environmental contaminants, and appreciation of the role of halogen binding in drug-target binding affinity increasingly influences drug discovery, development, and lead optimization. Hydrodehalogenations have also long been utilized in synthetic strategy to remove halides that have served their purpose, e.g., for alkene protection, iodocyclization, or as a blocking group, and similar opportunities for the beneficial application of this approach continue to appear. Traditional hydrodehalogenation methods, however, suffer from a number of problems with respect to toxicity, selectivity, recyclability, functional group tolerance, product purification, and operational simplicity. With recent advances in the scope of the three prevailing alternatives—ground-state organometallic catalysis, metallophotoredox catalysis, and organophotoredox catalysis—the older methods should now be deprecated. Of these modern approaches, organophotoredox catalysis exhibits the best sustainability profile and is therefore an appropriate basis for a sustainability-oriented MPC system.

We report herein the development of a dual-chromophore PIM-1 analog and its application as an organopolymer MPC to the mild hydrodehalogenation of α-halocarbonyl compounds. Benchmarking against common organophotoredox catalysts indicates that the MPC is more than five times as effective as its nearest competitor. The MPC can be efficiently recovered and reused, and it is effective when employed as a wall-coating in flow and batch reaction modes with backside irradiation, even with opaque reaction mixtures. The significance of the dual-chromophore system is supported by the catalytic activities of oligomeric compounds synthesized to model polymer substructures, as well as by ultrafast spectroscopic and computational studies.

Results
Preliminary investigation and optimization of conditions. Our previous report on the synthesis of polyfluoro(hetero)aryl sul fones via micellar catalysis provided a wide variety of possible monomers for inclusion with 1 and 2 in the preparation of a PIM-1 analog; sulfone 3 was selected and the resultant MPC system was designated as MPC-1 (Fig. 1a). We envisioned (and ultimately found) that sulfone 3 could imbue MPC-1 with suitable photophysical and solubility properties to function as an efficient and readily recoverable catalyst for hydrodehalogenation reactions (Fig. 1b). In particular, we suspected that incorporation of 3 as a second chromophore unit in the polymer would support the formation of long-lived CTSs during photoexcitation. We also anticipated that the solution-processability of MPC-1 would allow it to be applied as a coating to flow and batch reactors (Fig. 1c). An initial preparation of the MPC-1 system (designated as MPC-1–0) was expeditiously synthesized in a one-pot adaptation of a previously reported polymerization procedure starting from the precursors of 3; the targeted ratio of monomeric units of 1, 2, and 3 was 2:3:1. MPC-1–0 was encouragedly obtained as a bright yellow solid with a strong absorbance near 2.85 eV (435 nm), suggesting the possibility of visible-light catalysis with blue light-emitting diode (LED) irradiation (Supplementary Fig. 1). Although adequate for preliminary investigation, this preparation exhibited incomplete solubility in chloroform and under- incorporation of the sulfone.
monomeric units; these deficiencies were attributed to incomplete sulfonylation and concomitant branching/cross-linking defects (see Supplementary Note 1). For initial reactivity screening, N-methyl-2-pyrrolidone (NMP) was selected as the reaction solvent given its aptitude for solubilization of structurally similar polymers. To our delight, NMP fully dissolved the polymer, and α-keto bromide 4a underwent hydrodehalogenation in the presence of i-Pr₃NMe sacrificial reductant, 1 mol% MPC-1–0 (based on the molecular weight of the constitutional unit of an ideal regular polymer), and blue LED irradiation (Table 1, entry 1). Control experiments confirm that the MPC-1 system catalyzed the transformation and that sacrificial reductant, blue LED irradiation, and oxygen-free atmosphere are all essential to catalysis (Supplementary Table 1). Screening catalyst loading confirmed that 1 mol% MPC-1–0 was suitable for preliminary optimization (Supplementary Table 2). Solvent screening revealed a clear correlation between reaction efficiency and solvent polarity index (Table 1, entries 1–6), suggesting the reaction pathway involves excited-state charge separation, which is more effectively stabilized by more polar solvents. NMP was the only solvent capable of fully dissolving the polymer, but the ability of the solvent to dissolve MPC-1–0 (which was used as a finely ground powder) was of limited importance, indicating that the catalyst worked well in both homogenous and heterogeneous states. Indeed, although NMP was the most effective solvent, dimethyl sulfoxide (DMSO) was nearly as competent and is a far greener choice. Water is the greenest solvent, has the highest polarity through the facile termination of chain growth by hydroxide replacement of fluoride; the micelles assisted in protecting the aromatic fluorides until polymer size was sufficient to precipitate out of the solution. MPC-1–1 successfully obtained as an opaque yellow solid that was readily soluble in acetone. Nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) measurements suggested that the average permitted partial reaction progress, but the reaction mixture eventually developed clumping and opacity that prevented reaction completion. Isolated yields of reactions run with i-Pr₃NMe were consistently poor (ca. 40%) due to side reactions, but switching the reductant to Hantzsch ester (HE) dramatically increased reaction rate and yield (entry 9). Following optimization of HE loading, acetone was deemed sufficiently competent and was selected as a green and easily distillable reaction medium. With the final optimized conditions, dehalogenated product 5a was successfully obtained in 92% isolated yield after 3 h in acetone with 1.5 equiv HE and 1 mol% MPC-1–0 (entry 10). Full optimization results are provided in Supplementary Tables 2–9. Reaction scope and scalability with oligomeric MPC-1–1. A new procedure was developed to produce oligomeric MPC-1, designated as MPC-1–1, while avoiding the defects associated with the one-pot procedure used for MPC-1–0. Polymerization was conducted in 3 wt% aqueous PS-750-M surfactant using separately synthesized sulfone 3; the feed ratio of monomers 1, 2, and 3 was 2:3:1. PS-750-M was designed to mimic toxic polar aprotic solvents such as DMF, which had been employed in the synthesis of MPC-1–0. Typically, PIM-1 analogs are synthesized under anhydrous conditions. By intentionally using an aqueous system, it was possible to severely restrict polymer chain length through the facile termination of chain growth by hydroxide replacement of fluoride; the micelles assisted in protecting the aromatic fluorides until polymer size was sufficiently large to precipitate out of the solution. MPC-1–1 was successfully obtained as an opaque yellow solid that was readily soluble in acetone. Nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) measurements suggested that the average.
chain length of MPC-1–1 was sufficiently long to incorporate 4–7 chromophore subunits (i.e., monomer units of 1 or 3); although successful in producing oligomeric chains, this method was still susceptible to branching defects and appeared to under-incorporate the terephthalonitrile monomeric unit (see Supplementary Note 1). Using MPC-1–1 under the optimized reaction conditions afforded 5a in 86% isolated yield after 3 h, indicating that the activity of the oligomeric preparation was slightly inferior to MPC-1–0.

It was initially suspected that the catalytic activity of MPC-1 preparations would improve with higher degrees of polymerization; because MPC-1–1 represents a non-arbitrary lower limit in this regard, it was used to establish well-defined baseline substrate scope results. Longer-chain MPC-1 preparations indeed performed better, but the origin of this improvement turned out to be more complicated (vide infra). A wide-range of α-halocarbonyl compounds were amenable to hydrodehalogenation under the established conditions. As suggested by the chemoselectivity in the reaction used for optimization, aryl halides (which exhibit a larger reduction potential) were unaffected by the reaction conditions (Table 2, 4a–h). Aside from ketones (4a–n), alkyl aryl ethers (4e), aryl nitro groups (4l), amides (4o), and esters (4p) were also well tolerated. α-Keto chlorides, bromides, and iodides were reduced with rates that increased with decreasing magnitude of substrate reduction potential (4b–d). With a sufficient quantity of reductant, geminal bromides were both reduced (4m); when only 1 equiv reductant was used, a roughly equal mixture of acetophenone and 2-bromoacetoephone products was observed. Greater steric bulk around the halide did not prevent reduction, but rate was affected in accordance with the effect of the geminal alkyl substituents on the stabilization of a radical intermediate (4h–j). In addition to α-aryl keto carbonyl systems (4a–m), reduction was successful with strained aliphatic (4n) and heteroaromatic (4q) ketones, as well as for α-amide (4o) and α-ester (4p) systems. The reactions were generally clean, affording only oxidized HE and the desired product.

Scalability and catalyst recovery were demonstrated with the gram-scale hydrodehalogenation of 4b (Table 2). With a lowered catalyst loading, i.e., 0.2 mol%, product 5b was afforded in 99% isolated yield after 24 h. In addition to the lower catalyst loading, the longer reaction time is partly attributable to the change in reaction vessel and the resultant decrease in flux of irradiation. The reaction was worked up by removing acetone under reduced pressure and extracting the product with 1:16 ethyl acetate/hexanes, a solvent system in which MPC-1–1 was insoluble. To liberate product entrapped in the polymeric phase, ethyl acetate was admixed before precipitating the polymer back out with the addition of hexanes. A preliminary recycle study using this extraction technique confirmed that the catalyst remained active in subsequent cycles, but buildup of residual Hantzsch pyridine caused the reaction rate to decrease (see Supplementary Method 1). This limitation to recyclability was overcome with the development of a longer-chain MPC-1 preparation, MPC-1–2, which was fully recyclable and retained its catalytic efficiency over multiple recycles (vide infra).

Synthesis and evaluation of polymeric MPC-1–2. Rigorous polymerization conditions were devised to yield long chains with limited cross-linking defects. Monomer 1 was purified by sublimation, monomer 2 was recrystallized from methanol/water, monomer 3 was purified by column chromatography, and potassium carbonate was dried in a vacuum oven at 200 °C overnight prior to use. The polymerization was conducted in a thick-walled Schlenk tube under argon atmosphere at 90 °C in dry N,N-dimethylacetamide (DMAc). Activated 3 Å molecular sieves were included in the reaction mixture to scavenge moisture. Upon reaction completion, the reaction mixture was extracted with chloroform and the product was precipitated out with the addition of methanol. Thus, resultant polymer preparation MPC-1–2 was obtained as a translucent yellow solid. To assess the significance of different polymer chain lengths within MPC-1–2, which had a moderate polydispersity index, a portion of the material was further processed by thrice reprecipitating from chloroform with methanol such that the polymer mass in the precipitate was approximately equal to the polymer mass in the combined supernatant layers; the higher molecular weight fractionation from the precipitate is designated as MPC-1–2LMW, and the lower molecular weight fractionation from the supernatant layers is designated as MPC-1–2HMW.

MPC-1–2 1H NMR integrations were in good agreement with the 2:3:1 feed ratio of 1, 2, and 3 (Fig. 2a): the alkyl methyl signals from 2 (labeled as i) integrated to 36; the methylene signals of 2 (ii) and the overlapping aryl methyl signals of 3 (iii and iv) integrated to 18; the N-methyl signals of 3 (v) integrated to 3; and the aromatic signals of 2 (labeled as vi and vii) integrated to 12. Sulfone 3 was moderately over-incorporated in fractionation MPC-1–2LMW (3:1.14 ratio of 2 and 3) and under-incorporated in MPC-1–2HMW (3:0.88 ratio of 2 and 3); this variation suggests either that the fractionation method is partly affected by the solubility of randomly incorporated constituent monomers, or that shorter chains tend to incorporate greater amounts of 3.

Table 1 Optimization of reaction conditions.

| Entry | Reductant | Solvent | Yield (%) |
|-------|-----------|---------|-----------|
| 1     | i-Pr₂NNet | NMP     | 47        |
| 2     | i-Pr₂NNet | 2-MeTHF | 5         |
| 3     | i-Pr₂NNet | Chloroform | 14   |
| 4     | i-Pr₂NNet | Acetone | 15        |
| 5     | i-Pr₂NNet | Acetonitrile | 23   |
| 6     | i-Pr₂NNet | DMSO    | 45        |
| 7     | i-Pr₂NNet | Water   | 41        |
| 8     | i-Pr₂NNet | 3 w/1%aq.SDS | 32 |
| 9     | HE        | NMP     | 100       |
| 10    | 1.5 equiv HE | Acetone | 92        |

HE Hantzsch ester, 2-MeTHF 2-methyltetrahydrofuran
*Conditions: 4a (0.25 mmol), MPC-1-0 (1 mol%) approximating the molecular weight as 1529 g mol⁻¹ for the ideal constitutional unit; reductant (0.25 mmol), solvent (0.5 mL, argon-sparged), argon atmosphere, 10 × 75 mm borosilicate test tube (spin-vane-equipped, septum/PDTE-tape-sealed), blue LED irradiation, 37 °C, 1 h, unless otherwise noted
*Determinated by 1H NMR
*Average of two runs (44 and 49%)
*Purely aqueous and surfactant reaction media suffered from solution turbidity and/or clumping of solids, which prevented reactions from going to completion and led to aliquots being unrepresentative of progress in the overall mixture
*81% at 5 min
*Isolated yield after 3 h
Table 2 α-Halocarbonyl compound hydrodehalogenation scope and scalability with MPC-1-1a

| α-Halocarbonyl compound hydrodehalogenation scope with MPC-1-1 |
|------------------|------------------|
| hν (blue LED),  | MPC-1-1 (1 mol%), HE (1.5 equiv), acetone (0.5 M, Ar-sparged), Ar atm, 37 °C |
| 4 | 1 | 5 |
| Br | 3 h, 86% | |
| Cl | 6 h, 96% | |
| Br | 3 h, 83% | |
| Cl | 4 h, 96% | |
| Br | 3 h, 87% | |
| Cl | 1 | 4 | |
| Br | 5 h, 94% | |
| Cl | 6 h, 92%a | |
| Br | 4 h, 96% | |
| Cl | 5 h, 97% | |
| Br | 3 h, 92%a | |
| Cl | 3 h, 92%a | |
| Br | 4 h, 98% | |
| Cl | 4 h, 99%b | |

Scalability

| hν (blue LED), | MPC-1-1 (0.2 mol%), HE (2 equiv), acetone (0.5 M, Ar-sparged), Ar atm, 37 °C |
|---------------|------------------|
| | 5.0 mmol (1.12 g) |
| 5b | 5.0 mmol (1.12 g) |
| 6b | 5.0 mmol (1.12 g) |
| 7b | 5.0 mmol (1.12 g) |

*Conditions (unless otherwise noted): halide 4 (0.25 mmol), MPC-1-1 (1 mol%), approximated as 1529 g mol⁻¹, HE (0.375 mmol), acetone (0.5 mL, Ar-sparged), argon atmosphere, 10 × 75-mm borosilicate test tube (spin-vane-equipped, septum/PTFE-tape-sealed), blue LED irradiation, 37 °C. Gram-scale reaction conditions: 4a (5.0 mmol), MPC-1-1 (0.2 mol%), HE (10.0 mmol), acetone (10.0 mL, Ar-sparged), argon atmosphere, 25 mL round-bottom flask (stir-bar-equipped, septum/PTFE-tape-sealed), blue LED irradiation, 37 °C, 24 h. Reported yields are isolated.

10 mL acetone and 2 mol% of MPC-1-1 were used
20 equiv of HE was used, and both bromides were reduced
(see Supplementary Note 1). Acetone admixed with MPC-1-2LMW developed coloration but did not completely dissolve the solid, whereas acetone admixed with MPC-1-2HMW remained colorless, suggesting that an acetone-soluble component in MPC-1-2 had been at least mostly confined to the MPC-1-2LMW fractionation.

GPC results were obtained using an Omnisec GPC from Malvern, which was equipped with four on-line detectors: a dual-angle light scattering detector, an ultraviolet (UV) detector, a refractive index detector, and a viscosity detector (Fig. 2b). In the chromatogram (Fig. 2c), the refractive index peak of MPC-1-2 is situated between MPC-1-2LMW and MPC-1-2HMW while its distribution covered the range of both components, which was consistent with the tabulated results. Minor peaks indicating the existence of oligomers were observed at retention volume >19 mL for MPC-1-2 and its fractionations. All four samples were fully soluble in the tetrahydrofuran eluent, and Mark–Houwink plots were also constructed to assess their structures (Fig. 2d). The curves of MPC-1-2 and its fractionations overlapped with each other at a wide-range, which implied a similar Mark–Houwink exponent (M–H α) and the same branching degree with the different polymer compositions.

Fourier-transform infrared spectroscopy showed that all monomers were incorporated into the derivative polymers, and MPC-1-2 lacked the hydroxyl stretches present in MPC-1-1 (Supplementary Fig. 2). Both MPC-1-1 and MPC-1-2 exhibited high thermal stability when subjected to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), which showed very little change up to 200 °C, followed by a gradual loss of mass until 450 °C (Supplementary Fig. 3). A sheet of MPC-1-2 was subjected to scanning electron microscopy (SEM); the sheet was observed to be regular and smooth (Fig. 2e). High-resolution transmission electron microscopy (HRTEM) imaging of MPC-1-1 and MPC-1-2 showed that MPC-1-2 had a more regular macrostructure consisting of large layers of stacked sheets while MPC-1-1 had smaller planes of sheets with smaller and rounder edges (Fig. 2f). At high magnification, both samples were seen to exhibit a similar porous structure. Inductively coupled plasma mass spectrometry (ICP-MS) confirmed the absence of iridium and ruthenium traces, which might otherwise be responsible for observed photocatalytic activity.

Having made and characterized a variety of MPC-1 preparations, we sought to assess their catalytic activities and generalize the results by benchmarking against well-known organophotoredox catalysts (Fig. 2g). Higher isolated yields for hydrodehalogenation of bromide 4a and chloride 4b were obtained in less time with MPC-1-2 compared to MPC-1-1. Unsurprisingly, MPC-1-2 exhibited improved catalytic activity in acetone when used as a fine powder instead of larger pieces, which would be expected to remain undissolved and thereby exclude interior active units from participating in catalysis. Accordingly, to better exclude influence of active unit entrapment in the interior of undissolved solid, the catalytic activities of MPC-1-2 and its fractionations were compared with the hydrodehalogenation of 4b in chloroform, a reaction medium in which all were fully soluble; observed activities were nearly the same. MPC-1-2 was benchmarked against six common organophotoredox catalysts using the same model reaction in acetone. MPC-1-2 proved to be the best by far, catalyzing more than five times as much product formation as its nearest competitor in the timeframe of the experiment. Leveraging the improved catalytic activity of MPC-1-2, difficult substrate 4o was hydrodehalogenated with significant improvements to reaction rate and yield, and a vicinal dibromide was efficiently converted into the corresponding alkene (Fig. 2h).

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Recyclability of MPC-1-2. The altered solubility properties of MPC-1-2 appeared promising for improved recycling techniques. A batch reaction recycle study was conducted using MPC-1-2LMW for the hydrodehalogenation of 4b under standard conditions (Fig. 3a). The partial solubility of MPC-1-2LMW in the reaction medium was readily overcome upon reaction completion with the addition of methanol, whereupon the suspension was passed through a fritted glass funnel to separate the catalyst from the rest of the reaction mixture. The catalyst could then be returned to the reaction vessel as a solid or through solution processing to pass it through the frit; these two approaches worked equally well. Six reaction cycles were conducted in this manner without appreciable decrease in catalyst activity. The complete acetone wash of the reaction mixture. The catalyst could then be returned to the reaction vessel as a solid or through solution processing to pass it through the frit; these two approaches worked equally well.

To further demonstrate the unique possibilities afforded by an innately photocatalytic solution-processable polymer, a new approach to catalyst recycling under flow conditions was envisioned wherein the photocatalytic polymer would be coated on the walls of a flow cell. The reaction solvent would be selected so as not to dissolve the coating. Following a post-reaction rinse, the flow cell could then be reused in subsequent reactions. Although a precedent exists for flow cells containing heterogenized photoredox catalyst immobilized by polymer support or sol–gel techniques, to the best of our knowledge the wall-coating of a transparent and inherently photocatalytic polymer on the walls of a flow cell has not yet been reported. We fashioned a prototype large-volume flow cell to accommodate the poorly soluble reductant and coated its walls by dissolving MPC-1-2HMW in dichloromethane, which was allowed to evaporate as
the cell was rotated. The flow cell was loaded with HE and an acetonitrile solution of 4b was peristaltically circulated from a reservoir through the cell, which was subjected to blue LED irradiation (Fig. 3b). The polymer coating was retained on the walls of the flow cell throughout the course of the reaction, and after 26 h the reactor loop was drained into the reservoir and the product was isolated in 83% yield, confirming the viability of the concept. It is noteworthy that MPC-1–2LMW was required for retention of the coating; unfractionated MPC-1–2 was gradually stripped from the walls under reaction conditions.

Mechanistic studies and assessment of backside irradiation. A series of control studies were conducted with halide 4b, which confirmed that hydrodehalogenation product 5b only formed in the simultaneous presence of MPC-1, HE, and blue LED irradiation; no conversion was observed when one or more of these components was omitted (Supplementary Table 1). Subsequently, the ground-state redox potentials of the control reaction components were determined experimentally by cyclic voltammetry, and the excited-state redox potentials of the catalyst were estimated using the polymer emission wavelength. On the basis of this information, a plausible mechanism is proposed (Fig. 4a).

The need for the sacrificial reductant indicates that, as is often the case with the monomeric analog p-dicyanobenzene, MPC-1 is operating as an excited-state oxidant\(^2\), and the reactivity-determining potential is that of the reduced form, MPC-1\(^+\) (\(E_{\text{ox}} = 1.42\) V vs. SCE). Thus, following photoexcitation, MPC-1\(^+\) (\(E_{\text{red}} = 1.01\) V vs. SCE) is reductively quenched through single electron transfer (SET) from reductant HE (\(E_{\text{ox}} = 0.89\) V vs. SCE). Subsequently, SET from MPC-1\(^+\) to halide 4b (\(E_{\text{red}} = 1.24\) V vs. SCE) leads to homolytic cleavage of the carbon–halogen bond. The resultant alkyl radical is then converted to the product by forming a bond with a methylene hydrogen from HE\(^+\) as it establishes aromaticity to form Hantzsch pyridine.

Well-defined models of MPC-1 substructures 7–11 were synthesized to better elucidate the effects of chain formation and dual chromophores (Fig. 4b). The activity of the models was assessed with the same reaction conditions used for the benchmarking studies (Fig. 2g); the catalyst loading was adjusted to maintain a constant amount of active chromophore units across experiments. Catalyst model 7, which contained one sulfone chromophore, was inferior to all other models with only 27% yield after 2 h. The other single chromophore model, 8, which contained the terephthalonitrile motif, was highly active, providing 99% product in the same timeframe. As the chain length was increased with models 9 and 10, the yield decreased (97% and 84%, respectively); this observation was in agreement with the expectation that yield would decrease with decreasing molecular concentration of catalyst even though active unit loading was held constant. However, when using catalyst model...
Fig. 4 Investigation of mechanism and viability of backside irradiation. a Proposed mechanism. b Activity screening of polymer subunit models; all models were prepared as mixtures of isomers. c Illustration of backside irradiation. d Results of charcoal occlusion study for coatings and suspensions of MPC-1-2HMW. Source data are provided as a Source Data file.

11, which replaced the middle terephthalonitrile unit in 10 with the less active sulfone chromophore, the activity was superior to even single terephthalonitrile model 8; this improved activity in spite of lower molecular catalyst concentration and partial use of the less effective sulfone chromophore is in agreement with the charge-transfer state hypothesis. An additional experiment using a 1:2 ratio of models 7 and 8 afforded only 93% yield, indicating that the dual-chromophore activity enhancements are only present when the two-chromophore types are incorporated into the same molecule.

To further demonstrate the impact of this catalyst, backside irradiation technology was explored as a proof-of-concept (Fig. 4c). This technology could prove useful for reaction mixtures with low light transmittance. Four reactions were set up in parallel; two vessels contained a wall-coating of MPC-1–2HMW, and two contained the catalyst as a suspension; in one of each of the vessel sets, the reaction mixture was made opaque with the inclusion of charcoal (Fig. 1c, Fig. 4d). The hydrodehalogenation of 4b was more efficient with a wall-coating than with a suspension, even with the inclusion of charcoal, supporting that the backside irradiation process played a role (Fig. 4c).

Likewise, coated vessels are not affected by the occlusion of light caused by undissolved HE: the trend in conversion over time for coated reaction vessels lacks the inflection point observed for vessels with catalyst suspension; this inflection point is attributable to opaque, poorly soluble HE being sufficiently converted to Hantzsch pyridine to allow for improved light transmittance.

Quantum chemical calculations. To aid in understanding the energetics and electronic structure of the MPCs, density functional theory (DFT) and time-dependent (TD-)DFT calculations were performed at the B3LYP/6–31G(d) level of theory, utilizing the Frenkel-Davydov exciton model to interpret the results (see Supplementary Note 2 and Supplementary Fig. 4). The investigations were carried out on a hypothetical heterodimer subunit, DXY, as well as the isolated chromophores, X and Y, present in MPC-1 chains (Fig. 5a). All DFT/TD-DFT calculations were performed using Gaussian 16 Rev. A.03. The polarizable continuum model (PCM) was employed to simulate the solvent effect of chloroform. Figure 5b depicts frontier molecular orbitals of the DXY heterodimer model and their energies predicted by DFT.
TD-DFT calculations were carried out to predict the transition energies of the first few excited states of X, Y, and DXY at ground-state equilibrium geometry (cartesian coordinates are listed in Supplementary Note 3). After characterizing the states of interest, geometry optimization of the first excited states (S1) of both X- and Y-chromophores and the first valence state (VS1) of the DXY heterodimer were performed. Geometry optimization of the second valence state (VS2) and the second charge-transfer states (CTS2) of DXY converged to the VS1 and CTS1 state, respectively. Frontier molecular orbitals and transition energies resulting from these calculations are briefly summarized in Fig. 5b, c, respectively (further details are provided in Supplementary Note 4, Supplementary Figs. 5 and 6, and Supplementary Table 10). The observation that the vertical excitation energy of VS1 is smaller than that of CTS1 at the ground-state geometry (Eg,v(VS1) < Eg,v(CTS1)), while the adiabatic excitation energy of VS1 is larger than that of CTS1 (Ead(VS1) > Ead(CTS1)), suggests the existence of a conical intersection (CI) between these two states. However, due to the size of the heterodimer model, no multiconfiguration calculations were attempted to locate the CI.
Steady-state absorption and photoluminescence spectra. The UV–visible (Vis) absorption and photoluminescence (PL) spectra of MPC-1–1 and MPC-1–2 are presented in Fig. 6a. Both absorption spectra consist of a relatively broad peak approximately centered at 2.9 eV (428 nm) and a stronger peak located around 4.3 eV (288 nm). The PL spectra are dominated by a peak centered at 2.54 eV (488 nm) with a long tail extending into the red region (~ 2.0 eV, ~ 620 nm).

Figure 6b shows the predicted absorption spectra of X and Y chromophores and the heterodimer DXY. The simulated spectrum of the heterodimer is in good agreement with the experimental spectra of both MPC-1–1 and MPC-1–2. The lowest-energy peak at ~ 2.9 eV (428 nm) is assigned to the VS1 ← GS and VS2 ← GS transitions, predicted by TD-DFT calculations for the heterodimer to be at 2.72 eV (456 nm) and 2.91 eV (426 nm), respectively. The higher-energy peak is also predicted by TD-DFT calculations. Figure 6b also demonstrates that most bright states of the heterodimer are closely associated with those of the isolated chromophores X and Y. This observation implies a possibility of decomposing the experimental absorption and PL spectra of both MPC-1–1 and MPC-1–2. Decomposition was carried out using two Gaussian lineshapes, corresponding to contributions from X and Y chromophores. Assignment of the decomposed electronic transitions is aided by the TD-DFT-predicted transition energies (Fig. 5c). Briefly, the higher-energy absorption band, and the lower-energy emission band are assigned to electronic transitions localized at the Y chromophore, while the lower-energy absorption band and the higher-energy emission band are assigned to transitions localized at the X chromophore. The resulting central transitions and Stokes shifts from the decomposition of absorption and PL spectra are in good agreement with the energetics of X and Y chromophores predicted by TD-DFT (results are summarized in Supplementary Note 5, Supplementary Fig. 7, and Supplementary Table 11). The slight blue shift of the MPC-1–1 absorption peak from that of MPC-1–2 is likely due to the difference in their chromophoric composition as discussed in Supplementary Note 1.

Femtosecond transient absorption spectroscopy. Transient absorption (TA) spectra of both MPC-1–1 and MPC-1–2 shared similar main features (Fig. 7a and Supplementary Fig. 8). Following photoexcitation with a 3.2 eV (388 nm) laser pulse, four main spectral features were observed within the probe detection range. The photobleach (PB) negative signal centered around 2.86 eV (434 nm) was consistent with the lowest-energy feature observed in the steady-state absorption spectrum (Fig. 7b). The second negative feature centered around 2.31 eV (537 nm) was also in good agreement with the central transition and lineshape of the measured PL spectrum (Fig. 7b). Therefore, it was attributed to a stimulated emission (SE) process. Two positive signals associated with photoinduced absorption (PIA) processes were observed. The tail of the first one (PIA1) was observed at the edge of the detection range, around 1.80 eV (689 nm); it was assigned to singlet-singlet transitions from VSs to higher-lying electronic states. The second positive signal (PIA2) centered around 2.55 eV (486 nm) was assigned to transitions from CTS1 to higher-lying states. Fig. 7a depicts the TA spectrum of MPC-1–2, while Fig. 7b, c highlight the correlation between the main spectral features in the TA spectrum and their steady-state spectral counterparts.
Briefly, a sum of bi-exponential growth ($\tau_1$, $\tau_2$) and a single exponential decay ($\tau_3$) was utilized to simulate the PIA2 kinetics, while a bi-exponential decay ($\tau_2$, $\tau_3$) was used to simulate both the PIA1 and SE kinetics, which shared identical time constants. The slower time constant in PIA2’s growth function ($\tau_2$) was shared with the fast decay component of PIA1/SE, while PB kinetic trace was simulated with a single exponential decay ($\tau_4$). Slow decay constants of PB and PIA4 were also shared.

Summary of relevant time constants are presented in Fig. 7d. The PIA2 growth components ($\tau_1$, $\tau_2$) were assigned to relaxation to CTS1; the faster component ($\tau_1 \leq 5$ ps) was assigned to the charge-transfer from VS2 to CTS1 (CT$_{VS2}$→CTS1), while the slower component ($\tau_2 \leq 20$ ps) was assigned to the charge-transfer from VS1 to CTS1 (CT$_{VS1}$→CTS1). This difference in observed time constants can be rationalized by the fact that the latter CT process is hindered by a barrier formed via the crossing of the VS1 and CTS1 potential energy surfaces (see Fig. 7e). Furthermore, the slower growth component of PIA1 ($\tau_2$) matches a detectable decay in SE and PIA1 kinetics, both of which originate from the low-lying valance states, VS1 and VS2. It is worth noting that the fast growth component ($\tau_1$) was not resolvable in either PIA1 or SE signals in the TA measurement, likely due to their low signal-to-noise ratio.

The slow decay component in PIA1 and SE ($\tau_3$) was assigned to (radiative and non-radiative) decay processes originating from VS2 (PL$_{VS2}$). Time constant of the decay component of PIA2 and PB ($\tau_4$) was deemed unreliable because its value is comparable with the time window of the TA apparatus (1.6 ns). Nevertheless, the estimated value of the time constant suggests a long lifetime of CTS1. Time-resolved photoluminescence (TRPL) measurements were carried out to deduce the lifetime of VS1 (PL$_{VS1}$), which was found to be about 10 ns for both MPC-1-1 and MPC-1-2, consistent with the previously reported lifetimes of homopolymer PIM-1 and its isolated chromophore.$^{34}$ Further details and results of the TRPL data acquisition and analysis are presented in Supplementary Note 7 and Supplementary Figs. 10 and 11.

Combining experimental and computational results, the proposed photoinduced processes are described in Fig. 7e. The 3.2 eV (388 nm) pump laser excites the polymer to VS1 and VS2. Facilitated by CIs, the charge-transfer process from VSs to CTS1 occurs on a timescale of $\leq 20$ ps. Relaxation of the bright VSs takes place in approximately 10 ns, while that of the dark CTS1 is expected to be significantly longer.

**Discussion**

A photocatalytically active double-strand polymer system, MPC-1, was developed and successfully employed in the hydrodehalogenation of $\alpha$-halocarbyl compounds in mostly excellent yields. Variation of the polymerization technique demonstrated the robustness of the substituent chromophores and led to the...
development of MPC-1–2, an optimal preparation with improved catalytic activity and solubility properties. The recyclability of the photocatalyst was demonstrated in batch reactions, and a proof-of-concept flow cell reactor demonstrated the efficacy of the polymer when used as a transparent wall-coating. The backside irradiation approach employed in the flow reaction was found to be superior to use of the catalyst as a suspension and was effective even when the reaction mixture was made opaque with the addition of charcoal. Well-defined compounds were synthesized to clearly model the polymer substructure, and their catalytic activities supported the formation of beneficial CTSs within the model two-chromophore system. Steady-state absorption and PL spectra, as well as DFT calculations verified the Frenkel–Davydov exciton model in predicting the electronic structure of the polymer; features in the TA spectra can be well explained using this model. The recorded ultrafast kinetics supported the presence of long-lived CTS, which enable the polymer to act as an effective photocatalyst.

**Methods**

**General experimental details.** All manipulations were carried out under air unless otherwise noted. Solvent molarity listed in reaction schemes is relative to the limiting reagent. The molecular weight for all MPC–1 preparations (MPC–1–0, MPC–1–1, MPC–1–2, MPC–1–2LMW, and MPC–1–32LMW) was approximated as 1529 g mol−1, which corresponds to the constitutional unit of an ideal regular polymer. The molar mass at the molar ratio used for all preparations: the one polymer preparation, MPC–1–2, was in very close agreement with this approximation based on NMR and GPC measurements. An analysis of the divergence of other preparations from this approximation is provided (see Supplementary Note 1 and Supplementary Figs. 12–17). All flash chromatography was conducted using a Teledyne Isco CombiFlash Rf 150. NMR spectra were recorded at 23 °C on Varian MR-400, Varian Unity INOVA 500, and Varian VNMRS 700 spectrometers (400, 500, and 700 MHz, respectively). Reported chemical shifts are referenced to residual solvent peaks. GCMS data was obtained using a Thermo Scientific Trace 1300 Gas Chromatograph coupled with a Thermo Scientific ISQ-QD Single Quadrupole Mass Spectrometer. Infrared absorbance spectra were acquired on a PerkinElmer Spectrum Two spectrometer using 1 cm−1 resolution unless stated otherwise. High-resolution mass analyses were obtained either using a 5975C Mass Selective Detector coupled with a 7890 A Gas Chromatograph (Agilent Technologies) or orbit-trap. Matrix-assisted laser desorption/ionization time-of-flight analyses were obtained using a Bruker Autoflex III.

**Supplies and chemicals.** **Supplies:** Thin-layer chromatography (TLC) plates (UV 254 indicator, aluminum backed, 175–225 μm thickness, standard grade silica gel, 230–400 mesh) were purchased from Merck. Silica gel (60 Å pore size, 230–400 mesh) was purchased from Silicycle. Sand was purchased from Fisher Chemical. Celite 545 was purchased from Acros Organics. **Solvents:** Acetone, ethyl acetate, hexanes, methanol, ethanol, N,N-dimethylformamide, diethyl sulfoxide, dichloromethane, tetrahydrofuran, and high performance liquid chromatography (HPLC)-grade water were purchased from Fisher Chemical. Pentane, chloroform and 2-methyltetrahydrofuran were purchased from Sigma-Aldrich. N,N-Dimethylacetamide was purchased from Acros Organics. N-Methyl-2-pyrrolidone was purchased from Antec Inc. Acetonitrile was purchased from Pharmco Products Inc. 1,4-Dioxane was purchased from EMD Chemicals. NMR solvents were purchased from Cambridge Isotope Laboratories. Dry solvents were prepared using standard procedures. Surfactant solutions were prepared in HPLC-grade water. PS-750-M (also known as FL-750-M) was prepared as previously reported. TPGS-750-M and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. **Substrates and reagents:** 1,3,5-Trimethyl-1H-pyrazole-4-sulfonic acid supplied by Maybridge was received as a gift from Novartis Pharmaceutical Chemicals. N,N-Diisopropylamine, sodium bicarbonate, and anhydrous potassium carbonate were purchased from Fisher Chemical. Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantzsch ester) was purchased from Combi-Blocks Inc. and Oakwood Chemicals, and both sources were confirmed to work equally well. 2-Chloro-1,3-dipropylpropane-1,3-dihydroxypropane was purchased from ChemImpex. (1R,3S,4S)-3-Bromo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one was purchased from TCI. Sodium sulfinate, 2-bromo-1-(4-bromomethyl)propan-1-one, benzyl 2-bromocetate and 1,2-dibromoethane were purchased from Acror Organics. 2-Chloro-1-(4-fluorophenyl)ethan-1-one, 2-bromo-2-methyl-1-(4-fluorophenyl)ethan-1-one, and tert-butyl (2-chloro-1-methylvinylidene)stannane was purchased from Oakwood Chemicals. 2,3,4,5,6-Pentafluorobenzonitrile was purchased from Matrix Scientific. 3-Bromo-1,3,4,5-tetrahydro-2H-benzof[b]azepin-2-one was purchased from Ark Pharm. 2-Bromo-1-(2,4-dichlorophenyl)ethan-1-one and 1-(2,4-dichlorophenyl)2-iodoethan-1-one were prepared by heating a 0.2 M dry acetone solution of 2-chloro-1-(2,4-dichlorophenyl)ethan-1-one at 70 °C in a thick-walled sealed reaction vessel with 1.5 equiv of sodium bromide and sodium iodide, respectively, and spectral data was in agreement with the literature. 2,2-Dibromo-1-phenylethanol-1-one was prepared as previously described. 2-Chloro-1-(3,3-dipropylprop-2-enyl)phenol was recrystallized from 2-bromo-3-methyl-3-propenylphenol through the dropwise addition of 2 M bromine in dichloromethane (DCM) to a 0.2 M substrate in DCM solution at 0 °C followed by room temperature stirring and quenching with aqueous sodium sulfite, and spectral data was in agreement with the literature.

**Preparation of polymer photocatalysts.** Polymer syntheses were partly adapted from published procedures. **MPC–1–0:** Silafone monomer 3 was prepared as described in Supplementary Method 3. NMR spectra are presented in Supplementary Figs. 12–17. **MPC–1–1:** Monomers 1 (equiv. 0.115 mmol), 1 (equiv. 0.23 mmol), and 2 (equiv. 0.345 mmol), and potassium carbonate (10 equiv, 1.15 mmol) were stirred in dimethoxyethane (400, 500, and 700 MHz, respectively). Reported chemical shifts are referenced to residual solvent peaks. GCMS data was obtained using a Thermo Scientific Trace 1300 Gas Chromatograph coupled with a Thermo Scientific ISQ-QD Single Quadrupole Mass Spectrometer. Infrared absorbance spectra were acquired on a PerkinElmer Spectrum Two spectrometer using 1 cm−1 resolution unless stated otherwise. High-resolution mass analyses were obtained either using a 5975C Mass Selective Detector coupled with a 7890 A Gas Chromatograph (Agilent Technologies) or orbit-trap. Matrix-assisted laser desorption/ionization time-of-flight analyses were obtained using a Bruker Autoflex III.

**Optimization of hydrodehalogenation.** Detailed results from the optimization of the hydrodehalogenation reaction are provided in Supplementary Tables 2–9. Except where otherwise noted, optimization reactions were conducted as follows. Solid reaction components were added to a spin-vane-equipped 10 × 75-mm flow cell reactor demonstrated the efficacy of the polymer when used as a transparent wall-coating. The backside irradiation approach employed in the flow reaction was found to be superior to use of the catalyst as a suspension and was effective even when the reaction mixture was made opaque with the addition of charcoal. Well-defined compounds were synthesized to clearly model the polymer substructure, and their catalytic activities supported the formation of beneficial CTSs within the model two-chromophore system. Steady-state absorption and PL spectra, as well as DFT calculations verified the Frenkel–Davydov exciton model in predicting the electronic structure of the polymer; features in the TA spectra can be well explained using this model. The recorded ultrafast kinetics supported the presence of long-lived CTS, which enable the polymer to act as an effective photocatalyst.
blue LED irradiation at 37 °C (see Supplementary Fig. 1). Samples for 1H NMR monitoring of reaction progress were prepared by transferring a 20 µL reaction mixture into an NMR tube, quickly followed by the addition of 400 µL chloroform-d and capping of the tube.

**Dehalogenation procedure** Characterization of dehalogenation products is presented in Supplementary Note 8, and NMR spectra are presented in Supplementary Figs. 27–46. The photoreactor set-up is presented in Supplementary Fig. 1. Solvents were not dried prior to use.

Procedure A: The halide (1 equiv, 0.25 mmol) was added according to its phase at room temperature. Solid reaction components—MPC-1—(1 mol%), HE—(1 equiv, 0.75 mmol), and halide (if solid)—were added to a spin-vane-equipped 10 × 75-mm borosilicate test tube that was then inserted into the narrow opening of a 1/20 rubber septum. The septum was wrapped with PTFE tape, and the vessel was thrice evacuated/argon back-filled. Halide (if liquid) and then 0.5 mL acetonitrile (which had been sparged with argon for at least 10 min) were added by syringe. The septum punctures were covered with electrical tape, and the reaction vessel was placed in the photoreactor to stir under blue LED irradiation at 37 °C. Following reaction completion (as monitored by TLC or GCMS), the solvent was removed under reduced pressure, 0.5 mL deionized water was added, and the mixture was extracted with ethyl acetate (3 × 0.5 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The resultant crude residue was purified by flash chromatography.

Procedure B: This method was employed for substrates that did not approach full conversion after 96 h with Procedure A. The halide (1 equiv, 0.25 mmol) was added according to its phase at room temperature. Solid reaction components—MPC-1—(1 mol%), HE—(1 equiv, 0.75 mmol), and halide (if solid)—were added to a spin-vane-equipped 10 × 75-mm borosilicate test tube that was then inserted into the narrow opening of a 1/20 rubber septum. The septum was wrapped with PTFE tape, and the vessel was thrice evacuated/argon back-filled. Halide (if liquid) and then 1 mL acetonitrile (which had been sparged with argon for at least 10 min) were added by syringe. The septum punctures were covered with electrical tape, the solvent level was marked on the outside of the vessel, and the vessel was placed in the photoreactor to stir under blue LED irradiation at 37 °C. Every 24 h, the reaction was monitored by TLC and GCMS, the solvent was replenished with sparged argon, and then 1 mL acetonitrile (which had been sparged with argon for at least 10 min) was added by syringe. The septum punctures were covered with electrical tape, and the reaction vessel was placed in the photoreactor to stir under blue LED irradiation at 37 °C. For each cycle: after 3 h in the photoreactor, the vessel was removed from irradiation and its contents were diluted with 0.5 mL methanol; the resultant suspension was then passed through a fritted glass frit, rinsing with additional methanol; the recovered catalyst was returned to the reaction vessel; the filtrate solvent was removed under reduced pressure, and the resultant crude residue was purified by flash chromatography (ethyl acetate/hexanes) to provide product 4b as a clear slightly yellow oil. Product purity was confirmed by 1H NMR. The catalyst was typically returned to the reaction vessel by passing through the frit with DCM, which was subsequently removed under reduced pressure, but after the third recycle the catalyst was returned to the reaction vessel as a solid using a spatula, and no deterioration in activity was observed.

**Recycle studies.** Details for the recycle study with MPC-1—(1 mol%) are provided in Supplementary Method 1. The recycle study with polymeric MPC-1—2LMW (HE—(1.5 equiv, 0.375 mmol) was conducted using Procedure B, and Procedures A and C (catalyst and workup were changed) for the zeroth cycle (Fig. 3a). Each recycle: additional halide 4b (1 equiv, 0.25 mmol) and HE (1.5 equiv, 0.375 mmol) were added to the recovered MPC-1—2LMW catalyst (1 mol%, 3.8 mg) originating from the zeroth cycle; the reaction vessel was septum/PTFE-tape-sealed, the mixture evacuated/argon back-filled, and then filled with 0.5 mL argon-sparged acetonitrile; the punctures were sealed with electrical tape, and the reaction vessel was placed in the photoreactor to stir under blue LED irradiation at 37 °C. For each cycle: after 3 h in the photoreactor, the vessel was removed from irradiation and its contents were diluted with 0.5 mL methanol; the resultant suspension was then passed through a fritted glass frit, rinsing with additional methanol; the recovered catalyst was returned to the reaction vessel; the filtrate solvent was removed under reduced pressure, and the resultant crude residue was purified by flash chromatography (ethyl acetate/hexanes) to provide product 5b as a clear slightly yellow oil. Product purity was confirmed by 1H NMR. The catalyst was typically returned to the reaction vessel by passing through the frit with DCM, which was subsequently removed under reduced pressure, but after the third recycle the catalyst was returned to the reaction vessel as a solid using a spatula, and no deterioration in activity was observed.

**Flow reactor study.** The set-up for the flow reactor is pictured in Fig. 3b and Supplementary Fig. 55. MPC-1—2LMW (25 mol%, 26.5 mg) was dissolved in a minimal volume of DCM and transferred into a glass flow cell. Keeping the path through the reactor parallel to the floor, the cell was then inserted into the walls as the DCM evaporated. Small portions of DCM were added to the cell to reapply any portions of the film, which formed without adhering to the glass. Once the catalyst was evenly coated on the flow cell walls, the vessel was subjected to rotary evaporation and then high vacuum for 3 h.

**Gel-permeation chromatography.**GPC was conducted on an Omnisec GPC from Malvern equipped with four on-line detectors: a dual-angle light scattering detector, a refractive index detector, a UV detector, and a viscosity detector. Samples were fully dissolved in THF and eluted through two columns (Viscotoc, LT500L and LT 3000L) at a rate of 1 mL min⁻¹. MPC-1—0 was not fully soluble in THF and was not analyzed. More detailed results are provided in Supplementary Figs. 49–54. Estimation of the average number of chromophores in different MPC-1 preparations is presented in Supplementary Note 9 and Supplementary Tables 13–16.

**Electron microscopy.** SEM was conducted with a TESCAN Vega3 SEM. HRTEM was conducted with a 200-kV FEI Tecnai F20 FEG-TEM/STEM. Additional SEM and HRTEM images are provided in Supplementary Figs. 47 and 48.

**Cyclic voltammetry.**Cyclic voltammetry measurements were conducted with a Gamry Interface 1000 potentiostat using a glassy carbon working electrode (0.071 cm² surface area), a platinum wire counter electrode, and a silver wire
pseudo-reference electrode. Prior to use, the working electrode was polished with aqueous alumina slurry, and both the working and counter electrodes were cleaned by washing sequentially with water, ethanol, acetone, and dichloromethane and then sonicating in dichloromethane for 15 min. A three-electrode electrochemical cell was washed and oven-dried prior to use. Measurements were taken at a scan rate of 200 mV s \(^{-1}\) under a nitrogen atmosphere using a 25 μL volume of 0.1 M (rBu)4NPF6 in dichloromethane. Potentials were referenced to ferrocene and adjusted so that the approximate concentration of chromophore units per unit volume was 1–10, 20 μL steps, and logarithmically after 1 ps such that each order of magnitude contained 100 steps.

### Reporting summary
Further information on experimental design is available in the Nature Research Reporting Summary linked to this article.

### Data availability
The authors declare that the data supporting the findings of this study are available within the paper, its Supplementary Information, and its Source Data files, including source data for Figs. 2–7.

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Author contributions
S.H. directed the overall project, wrote the manuscript with J.D.S and A.M.J., and analyzed all data. I.D.S. performed all synthetic work including project development, TGA, and cyclic voltammetry. J.D.S. designed and developed the coated flow cell, charcoal occlusion, and model polymer subunit studies. A.M.J. performed DFT calculations, acquired spectroscopy data, and analyzed both. J.B.I. performed HRTEM imaging. F.G. verified reaction reproducibility and provided insight on industrial applicability. J.G. conducted GPC and EGA measurements and interpreted the results under the guidance of R.A. J.L. analyzed the photophysics data and advised A.M.J. D.S and A.M.J. contributed equally.
Additional information
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Competing interests: The authors declare that a patent is pending for double-strand organic polymer photoredox catalysts and their applications (Justin D. Smith and Sachin Handa). The remaining authors declare no competing interests.

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