In contemporary organic synthesis, substances that access strongly oxidizing and/or reducing states upon irradiation have been exploited to facilitate powerful and unprecedented transformations. However, the implementation of light-driven reactions in large-scale processes remains uncommon, limited by the lack of general technologies for the immobilization, separation, and reuse of these diverse catalysts. Here, we report a new class of photoactive organic polymers that combine the flexibility of small-molecule dyes with the operational advantages and recyclability of solid-phase catalysts. The solubility of these polymers in select non-polar organic solvents supports their facile processing into a wide range of heterogeneous modalities. The active sites, embedded within porous microstructures, display elevated reactivity, further enhanced by the mobility of excited states and charged species within the polymers. The independent tunability of the physical and photochemical properties of these materials affords a convenient, generalizable platform for the metamorphosis of modern photoredox catalysts into active heterogeneous equivalents.
Photoredox catalysis refers to an energy-conversion process in which the absorption of photons by a substance triggers electron transfer. In the past decade, the application of this phenomenon to organic synthesis has evolved from an academic curiosity to an enabling technology widely adopted in pharmaceutical synthesis. By coupling photoexcitation with other molecular processes, including cooperative catalytic schemes, hundreds of powerful and previously inconceivable organic transformations have now been realized. However, compared to the rapid discovery of new photon-dependent reactions, the implementation of these processes on large scale has seen only limited progress due to the high cost of many photocatalysts, challenges in catalyst removal, and restricted light penetration in traditional batch reactors. Thus, the conception of new technologies that generally enhance photoredox catalysis on scale is a pressing goal that has attracted immense research effort.

Photoredox catalysts can be divided into two major groups (Fig. 1a): homogeneous materials, which are soluble in the solvents typically used for photoredox catalysis, and heterogeneous, which operate as insoluble solids. Due to ease of synthesis and tunability, the vast majority of newly developed catalysts belong to the former group, which includes small-molecule organic dyes, such as perylene diimides (PDIs), and organometallic complexes, such as Ir(ppy)$_3$. Meanwhile, heterogeneous catalysts have the advantages of facile removal from reaction mixtures and recyclability, which are important from both cost and sustainability perspectives. Well-known examples include two-dimensional (2-D) surface photocatalysts, especially semiconductors, such as mesoporous graphitic carbon nitride (mpg-CN), and porous three-dimensional (3-D) constructs, such as metal-organic/covalent organic frameworks (MOFs/COFs). The appealing characteristics of these materials arrive at the expense of diversity and tunability: there is often no rational technique to finely alter their photochemical properties while retaining the bulk physical properties. Importantly, the inability of most heterogeneous catalysts to be cast into films or coatings from liquid or solution phase is a considerable practical limitation, particularly towards their synergistic application with emerging technologies such as continuous-flow synthesis.

A strategy that allows synthetic chemists to simultaneously take advantage of the respective desirable properties of homogeneous and heterogeneous catalysts would be exceptionally empowering. We proposed that one solution might involve a general method for converting any member of the vast toolbox of soluble photocatalysts into equivalent insoluble materials, while maintaining the original photochemical attributes and activity. However, to our knowledge, no heterogenization approach exists with broad scope both in the kinds of dyes incorporated and in the types of catalytic materials accessible. Although several examples of photocatalyst immobilization on insoluble solids have been demonstrated, each strategy addresses only a small subset of chromophore structures, and the vast majority of supported catalysts lack solution-processability, severely limiting the operational modes that are available (typically only particles or dispersions).

Herein, by extending our recently reported Pd-catalyzed polycondensation reaction, we present a method that, in principle, allows for any organic or organometallic photocatalyst to be heterogenized through copolymerization with porosity-promoting bulky organic monomers (tritycenes and spirobifluorenes). We note that while 2D and 3D extended materials are well represented among heterogeneous photocatalysts, examples of

![Fig. 1 Overview of photoredox catalyst design.](https://example.com/fig1.png)

**Fig. 1 Overview of photoredox catalyst design.** a Classification of photoredox catalysts according to solubility and geometric dimension of active surface. b Transforming a broad scope of small-molecule photocatalysts into diverse heterogeneous materials through solution-processable polymers.
one-dimensional (1D) photocatalysts, in which the active components form chains, are relatively rare.26,27 Importantly, our linear-polymer structures, while insoluble in the solvents typically employed for photoredox catalysis, remain highly soluble in a few, select handling solvents (DCM and THF). As a result of this processability, our immobilization technique is not restricted to any particular target mode of heterogeneous catalysis but can conveniently access a wide range of known morphologies, including dispersions, films, coatings, textiles, and magnetic nanoparticles.

Aside from solution-processability and broad generality, our 1D polyether platform offers additional valuable benefits compared to existing heterogeneous photoredox catalysts. First, the solubility of organic polymers enables simple characterization of structure, molecular weight distribution, photocatalyst loading, defect concentration, and batch-to-batch quality variations, all of which are often impractical to analyze for conventional insoluble catalysts. Second, traditional materials relying on non-covalent interactions for dye attachment, or labile covalent bonds such as catalysts. Second, traditional materials relying on non-covalent interactions for dye attachment, or labile covalent bonds such as Si–O or Al–O bonds, can exhibit poor chemical stability.21 In contrast, the polymers developed in this work exhibit exceptional thermal stability and inertness toward a variety of chemical conditions. Third, the immobilization of small-molecule catalysts on heterogeneous supports often leads to drastically decreased turnover frequencies; however, with our polymer materials, due to a combination of reduced aggregation-induced quenching, highly porous-polymer structure, and energy- and charge-transport processes, very efficient catalysis can be achieved, in some cases with rates exceeding than with the corresponding monomers. Finally, the design of our polymers enables independent control of the physical and photochemical properties without alteration to the synthetic procedure.

### Results and discussion

Our recent systematic study22 showed that the foundational building blocks of our proposed material, t-Bu-triptycene hydroquinone 1-A and spirobifluorene dibromide 1-B, could be cross-coupled to form polymer 1 with excellent molecular weight, polydispersity, porosity, and film properties (Fig. 2a). Through slight alteration of these prior conditions, we were able to introduce chromophore-containing comonomers to generate materials with similar physical attributes as 1, but with added photocatalytic capabilities. As a model, we selected the classic dye perylene diimide (PDI) as synthetically versatile redox-active photocatalytic capabilities. As a model, we selected the classic dye perylene diimide (PDI) as synthetically versatile redox-active photocatalyst (Fig. 2c). With the addition of 10% of PDI dibromide (1-C) in the polycondensation process, we obtained a near-quantitative yield of a deep-red solid (1-PDI) with high molecular weight and moderate polydispersity. The porosity was evaluated through the Brunauer–Emmett–Teller (BET) gas adsorption method, revealing a considerable specific surface area (SSA) of 338 m²/g. The essential role of the triptycene units in endowing the polymer with this exceptional porosity is evident from the very low SSA of related polymer 1-PDI-HQ, in which para-phenylenes are present instead. Based on the N₂ adsorption isotherm, the estimated pore size distribution was concentrated in the microporous range (<2 nm, Supplementary Fig. 3–1). Furthermore, the polymer showed excellent thermal and chemical stability under controlled conditions (Supplementary Fig. 4–2). The extent of incorporation of the PDI was determined by ¹H NMR analysis to be 10%, in agreement with the fraction of monomer employed during the synthesis.

The absorption and steady-state photoluminescence spectra of 1-PDI contained distinctive features (λₘ₉₃₇ = 523 nm, λₑₙ = 528 nm in THF solution) characteristic of PDI units (Fig. 2b). The solid-state photophysical properties of 1-PDI showed notable differences when compared to monomeric (PDI-Mono) and non-porous (1-PDI-HQ) analogues. Although the molecular dye displayed a very low fluorescence quantum yield in the solid state (ϕ = 0.02), the chromophores covalently hosted within triptycene-containing frameworks were bright emitters (ϕ = 0.29 for 1-PDI), indicating a reduction in aggregation-based quenching. Monomeric PDIs are known to exhibit a substantial emission red-shift upon aggregation, and we found that the difference in emission maxima between solid and solid states was substantially smaller for the polymers than for monomers and, in particular, smallest for the porous 1-PDI.

As a test of the photo-activated reactivity of these polymers, irradiation of a DCM solution of 1-PDI with excess Et₃N resulted in isosbestic conversion to a new species, with spectral features indicative of PDI radical anions (Fig. 2c)30. Exposure of the resulting solution to atmospheric oxygen regenerated the original polymer over the course of 2 h. Given its promising reversibly stoichiometric reactivity, a dispersion of the catalyst in methanol was evaluated in a simple aerobic photo-oxidation reaction31 of methyl phenyl sulfoxide (2a, Fig. 2d). At remarkably low loading of catalyst (0.018 mol%), full consumption of starting material could be observed after 6 h. Parallel experiments with equivalent optical densities of a non-porous analogue (1-PDI-HQ) and a monomeric PDI (PDI-Mono) proceeded at a significantly lower rate and only preceded to 80 and 76% conversion over the same time period. An additional control using a combination of PDI-Mono with dye-free polyether 1 (premixed in dichloromethane solution, then dried and dispersed in methanol) showed a reaction rate similar to using PDI-Mono alone. The reactions did not progress during a 30 min interval with no LED irradiation, confirming that the chosen transformation requires continuous photoirradiation. We hypothesized that, in addition to the steric insulation from aggregation-based quenching, the elevated activity of 1-PDI is partially the result of the photoexcited state “hopping” between different dye centers, thereby enhancing the probability of encounter with a substrate or cocatalyst. Indeed, using fluorescence polarization spectroscopy, we observed quencher-dependent behavior consistent with considerable excited-state energy transfer between dye units (for extended discussion, see the Supplementary Information, Section 10.2, Figs. S7-2–S7-4). The mobility of charged states throughout the porous polymer can similarly contribute to an enhanced efficiency. In bulk conductivity measurements, we showed that irradiation of a film of 1-PDI in the presence of triethylamine results in an instantaneous and reversible increase in conductivity (Supplementary Fig. 7-5), suggesting facile transport of negative charges between PDI units.

To illustrate the synthetic versatility of porous linear-polymer catalysts, we applied 1-PDI to a representative range of modern photoredox transformations (Fig. 3a). On a 1.0 mmol scale, the aerobic oxidation of thioether 2a to sulfoxide 3a was accomplished in 95% yield using an alcoholic dispersion of 1-PDI and irradiation with a 450 nm LED. Photoreduction reactions could be performed through the in situ generation of PDI radical anion under inert atmosphere. Using triethylamine as the terminal reductant, aryl bromide 2b was successfully hydrodehalogenated. The same catalyst could induce atom-transfer radical addition reactions to alkenes: fluorinated alkyl bromide 3c was prepared in high yield from 5-bromo-1-pentene (2c) and perfluorooctyl iodide. Since 3c is a non-commercial fluorosurfactant essential to other research in our laboratory, we pursued a scaled-up synthesis enabled by catalyst 1-PDI. Over 12 g of product could be obtained in a single run, demonstrating the applicability of these porous materials in a preparative setting. Heterogeneous photoredox conditions were also applicable in polar addition to alkenes, as shown by the anti-Markovnikov hydrodeoethirification of 2d. In another activation mode, the oxidative C–H functionalization of electron-rich arene 2e was conducted using potassium...
bromide as the bromine-atom source.\(^{17}\) Both oxidative and reductive modes of radical generation were successful using 1-PDI as a photocatalyst, and regioselective addition of these radicals to heteroarenes was accomplished (3f and 3g).\(^{34,35}\)

Many valuable modes of heterogeneous catalysis are accessible due to the solubility profile of poly(arylene ether). Using a standard rotary evaporator, a thin film layer could be deposited on the bottom portion of a glass reaction vial, which has maximal exposure to the light source (Fig. 3b). The coated vessel could be conveniently reused to perform the photo-oxidation of 2a, with negligible change in reaction yield over five cycles.

Textile-supported organocatalysts have recently been advanced as convenient promoters for acid- and base-dependent reactions.\(^{36}\) We showed that 1-PDI can be robustly deposited onto cotton, and that the resulting fluorescent fabric is also a reusable photo-oxidation catalyst (Fig. 3c). The polymer coating could adhere strongly to silica nanoparticles bearing a superparamagnetic iron oxide core (Fig. 3d), which facilitates separation from reaction mixtures for which filtration is impractical. The resulting red powder was an effective agent in photoredox reactions, and the application of a handheld permanent magnet allowed for rapid and complete separation of the catalyst from the methanol.

| Compound | \(\lambda_{\text{max}}\) [nm] | \(\lambda_{\text{em}}\) [nm] | \(\Phi_{\text{abs}}\) | \(\Phi_{\text{em}}\) |
|----------|-----------------|-----------------|-----------------|-----------------|
| PDI-Mono | 521 | 538 | 0.95 | 643 | 0.02 |
| 1-PDI-HQ | 524 | 528 | 0.16 | 605 | 0.14 |
| 1-PDI | 523 | 528 | 0.43 | 599 | 0.29 |

Fig. 2 Perylene diimide porous-polymer catalyst. a Synthesis of 1, 1-PDI, and 1-PDI-HQ. See the Supplementary Information for detailed conditions. b Photophysical properties. c Light-driven reversible redox process with an amine partner. d Kinetics of catalytic photo-oxidation model reaction. BET = Brunauer–Emmett–Teller method. a Too low to be reliably determined from N\(_2\) adsorption isotherm. b Dilute THF solution (1.0 × 10\(^{-5}\)–5.0 × 10\(^{-7}\) M). c Solid state (powder).
solution (Supplementary Movie 1). The catalytic layer could be instantly desorbed from the surface by immersion in tetrahydrofuran and thus recovered from the silica (Supplementary Movie 2).

Continuous-flow synthesis, referring to processes performed within narrow tubing under constant material input and output, has attracted significant attention as an alternative to traditional batch chemical processes. Flow systems are associated with superior heat exchange, mixing, reproducibility, and safety profiles. The narrow-channel configuration of the reactors has proved particularly promising in large-scale photocatalysis applications, as enhanced light exposure is afforded with decreased risk of over-irradiation that can induce unwanted side-reactions. A solution-processable material for the immobilization of diverse photocatalysts along the interior surface of the reactor tubing would provide two main advantages. First, no separation of the dyes from the mobile phase would be required after the reaction. Second, by concentrating the chromophores close to the exterior of the reaction mixture, light exposure could be enhanced. Taking advantage of the excellent film-forming characteristics of our porous polyethers, we showed that flow chemistry could be conducted using a photoredox-active coating as a stationary phase (Fig. 3e). To the coolant coil of a spiral reflux condenser, a standard piece of equipment in laboratories

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**Fig. 3 Synthetic applications of porous-polymer photocatalyst.**

**a** Performance of 1-PDI across various reaction classes. **b** Recyclable usage of 1-PDI as a coating on a glass vial in the photo-oxidation of 2a. **c** Recyclable usage of 1-PDI deposited on cotton in the photo-oxidation of 2a. **d** Coated superparamagnetic silica nanoparticles. **e** Continuous-flow synthesis using a film of 1-PDI in glass tubing.

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| Reaction Type | Chemicals | Conditions | Product Yield |
|--------------|-----------|------------|--------------|
| Oxidation | 1-PDI (0.018 mol%) | Air, 450 nm light, 6 h | 3a, 95% yield |
| Reduction | 1-PDI (0.31 mol%) | EtOH, 450 nm light, 8 h | 3b, 99% yield |
| Radical Addition | 1-PDI (0.05 mol%) | sodium ascorbate, H₂O, MeCN, N₂, 450 nm light, 8 h | 3c, 68% yield (12.3 g) |
| Hydroetherification | 1-PDI (1.0 mol%) | PhSH, CH₂Cl₂, N₂, 450 nm light, 3 h, rt | 3d, 75% yield |
| C–H Bromination | 1-PDI (0.31 mol%) | KBr, H₂O, DMSO, 450 nm light, 36 h, rt | 3e, 90% yield |
| Oxidative Fluoroalkylation | 1-PDI (1.0 mol%) | NaO₂SCF₃, DMSO, 450 nm light, 24 h, rt | 3f, 71% yield |

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In the context of flow synthesis, it is crucial to consider the specific requirements of each reaction, ensuring optimal light exposure and minimizing the risk of over-irradiation. The use of photoredox-active coatings as stationary phases within the reactor tubing offers several advantages, including improved light absorption and enhanced reaction efficiency. These advancements in continuous-flow photocatalysis have the potential to revolutionize the field, offering more controlled and efficient synthetic processes.
that perform microscale organic synthesis, was applied a thin layer of 1-PDI as a solution in THF, drying with gentle heating and air flow. With the system under constant irradiation with blue LEDs, reactants for the C–H bromination of 2e were pumped into the coil using a syringe pump (approximate residence time of 60 min). At steady state, a good yield of 3e was measured in the output stream.

A unique advantage of linear polymers as an immobilization platform is the ability to independently adjust the backbone-derived physical characteristics and the chromophore-derived photochemical attributes (Fig. 4a). Achieving adhesion to fluoropolymer surfaces was desirable since inert, flexible substances such as perfluorooalkoxy (PFA) plastics are the most common tubing materials for modern continuous-flow synthesis. Since most poly(arylene ether) polymers such as 1-PDI adsorb poorly to fluorinated surfaces, and therefore do not form high-quality films, we wondered if we could enhance the attractive interaction through post-polymerization functionalization of the backbone. We subjected the polymer to C–H fluoroalkylation conditions with photogenerated perfluoroalkyl (n-C17F35) radicals to obtain 1-PDI-C17F35 with relatively high fluorine content (F/C ratio = 1:4 by XPS). This new polymer was successfully deposited...
on narrow inner diameter (1/16 in) PFA tubing and effectively employed as a catalytic stationary phase in the flow synthesis of 3e (Fig. 4b).

The identity of the covalently-included dye and its doping concentration could be adjusted arbitrarily with little effect on the porosity, solution-processability, and film-forming properties of the polymer. The substitution of other groups in lieu of PDI is synthetically straightforward and requires essentially no procedural modifications (Fig. 4c). Perylenes are highly reducing photocatalysts that have been used in applications such as light-activated atom-transfer radical polymerization (photo-ATRP) reactions31. Using perylene-containing 1-Per as a catalyst, the polymerization of methyl methacrylate could be performed using sunlight as the energy source. With minimal optimization, the poly(methyl methacrylate) (PMMA, 4a) product could be obtained with good molecular weight and polydispersity. Furthermore, the catalytic polymer was easily separated from the product polymer, as the former is strictly insoluble in acetone. The outcome of photo-ATRP could be greatly improved by changing the chromophore and adding the catalytic framework of In particular, we anticipate that these porous-polymer materials for efficient and economical organic synthesis. In particular, we anticipate that these porous-polymer films, in

the role of photocatalytic stationary phases in continuous flow, could represent an enabling technology for large-scale chemical manufacturing.

Methods

Example photocatalytic reaction: synthesis of methyl phenyl sulfide (3a). A dry 20 mL scintillation vial, equipped with a magnetic stir bar, was charged sequentially with 1-PDI (1.34 mg, 0.18 μmol, 0.018 mol% PDI), methanol (4.0 mL), and methyl phenyl sulfide (124.2 mg, 1.0 mmol, 1.0 equiv). The vial was submerged into an ultrasonic bath for 1 min to disperse the catalyst. The vial was capped with a screw cap containing a rubber septum, which was punctured with two 18-gauge needles to vent the reaction mixture to the atmosphere. The cloudy red suspension was stirred vigorously at rt under illumination from a 450 nm blue LED lamp for 6 h. At this point, both the irradiation and the stirring were stopped, and the catalyst allowed to settle for 30 min. Additional methanol (1.0 mL) was added, and the mixture was filtered through a short plug of Celite, washing with methanol (5.0 mL). The filtrate was concentrated with the aid of a rotary evaporator, and the title compound was obtained as a clear oil (133.1 mg, 95% yield) after column chromatography on silica gel, using DCM as the eluent. The catalytic polymer 1-PDI could be recovered from the Celite by washing with THF (10 mL). 1H NMR (500 MHz, CDCl3) δ 7.67–7.61 (m, 2H), 7.55–7.47 (m, 3H), 2.72 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 145.9, 131.1, 129.5, 123.6, 44.1. The spectral data agreed closely with those reported in the literature46.

Data availability

Additional experimental methods and data are available in the Supplementary Information of this paper.

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Author contributions

R.Y.L., S.G., and T.M.S. designed and planned the main experiments. S.G. synthesized and characterized the polymers. S.-X.L.L. carried out XPS studies and assisted with photoconductivity measurements. R.Y.L. performed photophysical characterization, catalytic studies, and other experiments. R.Y.L., S.G., and T.M.S. wrote the manuscript.

Competing interests

The authors (R.Y.L., S.G., and T.M.S.) declare the following competing interests: a patent has been filed covering the materials and methods reported herein. All of the authors declare no other competing interests.

Additional information

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