Organocatalytic atom transfer radical polymerization (O-ATRP) is recently emerging as an appealing method for the synthesis of metal-free polymer materials with well-defined microstructures and architectures. However, the development of highly effective catalysts that can be employed at a practical low loading are still a challenging task. Herein, we introduce a catalyst design logic based on heteroatom-doping of polycyclic arenes, which leads to the discovery of oxygen-doped anthanthrene (ODA) as highly effective organic photoredox catalysts for O-ATRP. In comparison with known organocatalysts, ODAs feature strong visible-light absorption together with high molar extinction coefficient ($\varepsilon_{455\text{nm}}$ up to 23,950 M$^{-1}$ cm$^{-1}$), which allow for the establishment of a controlled polymerization under sunlight at low ppm levels of catalyst loading.
Since the discovery in the 1990s, atom transfer radical polymerization (ATRP) has evolved into one of the most versatile and utilized polymerization methods for the synthesis of polymer materials with well-defined structures and architectures, and widely employed in a variety of industrial applications including coatings, adhesives, cosmetics, inkjet printings, etc.\textsuperscript{1-3} However, conventional ATRPs rely on transition metal catalysts [i.e., Cu(I), Ru(II)],\textsuperscript{3} which will result in transition metal contaminations in the final products, and thus raise concerns when applied to fields sensitive to metal contaminants.\textsuperscript{4-6} Therefore, considerable efforts have been dedicated to lowering catalyst loadings or removing residual metals since the initial discovery of ATRP.\textsuperscript{5-8} Whereas, the recent emerging organocatalytic atom transfer radical polymerization (O-ATRP) using organic photoredox catalysts, undoubtedly, represents an ideal solution to this challenging issue.\textsuperscript{9-15}

Since the conceptual work first demonstrated O-ATRP in 2014 by using organic molecules such as \textit{N}-phenyl phenothiazine or perylene as a catalyst,\textsuperscript{16-18} it has immediately attracted wide research interests in the past 5 years.\textsuperscript{19-22} Until now, several frameworks/core structures\textsuperscript{22} including phenothiazine (1),\textsuperscript{16,23,24} dihydrophenazine (2),\textsuperscript{25-28} phenoxazine (3),\textsuperscript{29,30} etc.\textsuperscript{31-37} have been successfully identified as efficient photocatalysts (PC) for O-ATRP (Fig. 1a). However, a 1000-ppm level of catalyst loading was typically required to reach a satisfactory control over the polymerization. Controlled polymerization at a practical low catalyst loading (<10 ppm) could not only eliminate the need of further product purification or residual catalyst removal, but...
could also decrease the cost of commercial production.\textsuperscript{14,28} Therefore, the development of highly effective photocatalysts for O-ATRP has thus become a focus of extensive studies in recent years.\textsuperscript{20–22,24,28} Whereas, many mechanistic aspects in O-ATRP remain unclear so far, and there is still a lack of general guidelines for the catalyst design.\textsuperscript{22,38}

Phenothiazine,\textsuperscript{16} dihydrophenazine,\textsuperscript{25} and phenoxazine\textsuperscript{29} are among the most efficient and widely used catalyst frameworks that could achieve a well-controlled O-ATRP polymerization with low dispersity.\textsuperscript{22} To further increase the catalyst efficiency, much effort has been dedicated to the modifications of the catalyst structures such as introducing aryl groups, which could enhance the visible-light absorption, but the red shift of absorption maximum ($\lambda_{\text{max}}$) was often quite limited.\textsuperscript{21,22} Interestingly, an analysis on the UV-visible-light absorption of these photocatalysts unveiled a uniformly decreased light absorption profile from its absorption maximum (<400 nm) to visible light.\textsuperscript{16,22,25,29} Therefore, we questioned whether there is a possibility to find a suitable and tunable O-ATRP catalyst framework with its absorption maximum located in the visible-light region, and a stronger light absorption could probably lower the catalyst loading. The three photocatalysts (1–3) can be recognized as derivatives obtained by modifying the corresponding core chromophoric structures: phenothiazine, dihydrophenazine, and phenoxazine, respectively (Fig. 1a). Recently, we were thinking that heteroatom-doping\textsuperscript{39,40} of small polycyclic arenes might be a feasible catalyst design logic for the O-ATRP photocatalyst development (Fig. 1b).

According to the oxidative quenching mechanism (Fig. 1c), organic photoredox catalysts possessing a highly reducing excited state are required to reduce the alkyl bromides via a single electron transfer (SET) to initiate the polymerization.\textsuperscript{41} Besides, redox potential, photophysical property, stability, etc. of the related catalytic species are also critical to establish a fast and effective switching between propagating and dormant states of the macro-initiators, thus achieving a controlled polymerization with narrow dispersities.\textsuperscript{38,41–43} The integration of heteroatoms such as N, O, S, etc. into aromatic hydrocarbons could regulate...
the photophysical and photoredox properties of these polycyclic arene catalysts, and thus probably lead to an improvement in their catalytic performance on polymerization and suppress undesired catalyst decomposition or catalyst-initiation.

With this idea in mind, we thus decided to practice this heteroatom-doping strategy on graphene, and narrowed down the parental aromatic (extended π) system to anthanthrene (Fig. 1b, left), which possesses the desired strong absorption in the visible-light region. Oxygen-doping was chosen for the current research, as: (i) the known high-performance photocatalysts for O-ATRP were developed based on the charge-transfer (CT) principle, and typically contain a triaryl amine part, which is required to impose a twisted donor–acceptor structure to favor the CT process. Therefore, the development of a completely new photocatalyst framework lacking this moiety and that could also achieve the same level or even better performance can be of fundamental significance, which, to the best of our knowledge, remains unknown so far; (ii) O-doping can regulate the photophysical and redox properties of anthanthrene, probably leading to a more oxidizing OPC moiety and that could also achieve the same level or even better photocatalyst performance 

### Results

#### Catalyst synthesis and characterization

The ODA can be readily constructed via dual oxidative cyclization from the commercially available 1,1′-bisnaphthol (BINOL) (Fig. 2a). Further, by virtue of its high modifiability, ODAs with different substituents can be readily synthesized via a 3,3′-modification of BINOL/oxidative cyclization sequence (see Supplementary Methods). To improve the catalyst solubility, we synthesized the n-buty substituted catalyst 5b, while 5a and 5d were prepared to examine the influence of aryl substituents (for synthetic procedures and spectra, see Supplementary Information). As anticipated, 5a did show a strong absorption in the visible-light region (Fig. 2b), with a red shift of the absorption maximum from 437 to 443 nm (comparing with the parental anthanthrene). This absorption profile is in sharp contrast to that of the known photocatalysts such as 1–3, which possess a smaller conjugation in the core structure and absorption maximum appearing in the ultra-violet region (<400 nm). Both the absorption maximums (λmax = 454 and 455 nm) of 5c and 5d have shown a further red shift (ca. 12 nm) as well as enhanced light absorption (εmax = 22,580 and 23,950 vs 17,450 M⁻¹ cm⁻¹). In addition, a notable feature of the ODA catalysts substantially different from the known high-performance O-ATRP photocatalysts is the lack of a charge-separation in their excited states (Fig. 2c). Based on the fluorescence emission and the cyclic voltammetry (CV) data, we could assess the reducing capability of the excited singlet states (E0(PCS/PC)) of these catalysts, ranging from −1.76 to −1.84 V vs SCE (saturated calomel electrode) (Fig. 2d). Density functional theory (DFT) was used to estimate the reduction ability of the triplet excited-states (E0(PCS/PC)), which are in the range of −1.58 to −1.71 V vs SCE (Fig. 2c, for details, see Supplementary Information and Computational details). Although the excited states of ODA 5a–5d are less reductive than that of N-phenyl phenothiazine (1, Ar = Ph, R = H, E0 = −2.1 V vs SCE), all are more negative than −0.7 V that is required to reduce ethyl α-bromophenylacetate (EBP, a common initiator, E0(EBP/EBP*) = −0.74 V SCE). Notably, the radical cations (PC⁺) of ODA catalysts are much more oxidizing (up to +0.82 V vs SCE), in comparison with the most efficient dihydrophenazine-based photocatalyst (+0.38 V vs SCE).

**Initial evaluation of the photocatalysts.** We conducted the initial evaluation of these oxygen-doped catalysts in the polymerization of methyl methacrylate (MMA) by using EBP as initiator, dimethylacetamide (DMA) as solvent under the irradiation of purple light-emitting diodes (LEDs, λmax 400 nm). To our delight, 5a could afford a controlled polymerization with a moderate dispersity (Table 1, entry 1). The polymerization can also be conducted with control in other solvents, such as dimethylformamide (DMF, entry 2), dichloromethane (DCM), toluene, tetrahydrofuran, etc. (Supplementary Table 2). DCM gave the lowest dispersity (D = 1.25) together with a good agreement between the experimental and theoretical Mn (entry 3). Remarkably, ODA 5a is also effective with other initiators such as ethyl bromoacetate (EBP), ethyl 2-bromo-2-methylmalonate (DBMM), diethyl 2-bromoisobutyrate (EBIB), diethyl 2-bromomalonate (DBM), and diethyl 2-bromo-2-methylmalonate (DBMM) (D 1.19–1.27, entries 4–7). 5b–5d with different substituents were then compared under the standard conditions by using EBP as the initiator. Pleasingly, all the three new catalysts are effective for the polymerization (entries

| Entry | PC | Initiator | Solvent | Conv. (%) | Mn, theo (kDa) | Mn, gPC (kDa) | D |
|-------|----|-----------|---------|-----------|---------------|---------------|---|
| 1     | 5a | EBP       | DMA     | 88.5      | 9.10          | 19.9          | 1.34 |
| 2     | 5a | EBP       | DFM     | 83.4      | 8.59          | 18.3          | 1.33 |
| 3     | 5a | EBP       | DCM     | 73.3      | 7.58          | 12.8          | 1.25 |
| 4     | 5a | EBP       | DCM     | 72.7      | 7.46          | 13.3          | 1.27 |
| 5     | 5a | EBI       | DCM     | 78.2      | 8.02          | 14.9          | 1.23 |
| 6     | 5a | DBM       | DCM     | 80.8      | 8.33          | 13.7          | 1.22 |
| 7     | 5a | DBMM      | DCM     | 81.2      | 8.38          | 12.8          | 1.19 |
| 8     | 5b | EBP       | DCM     | 66.5      | 6.90          | 12.3          | 1.19 |
| 9     | 5c | EBP       | DCM     | 79.2      | 8.17          | 13.8          | 1.22 |
| 10    | 5d | EBI       | DCM     | 88.2      | 9.07          | 13.5          | 1.23 |
| 11    | 5b | DBM       | DCM     | 69.1      | 7.17          | 13.5          | 1.15 |
| 12    | 5b | DBMM      | DCM     | 84.8      | 8.75          | 12.0          | 1.12 |
| 13a   | 5a | EBP       | DMA     | 82.7      | 8.52          | 12.5          | 1.25 |
| 14a   | 5d | EBP       | DMF     | 71.8      | 7.44          | 10.9          | 1.15 |

Table 1: Catalyst evaluation in the atom-transfer radical polymerization of MMA.

Reaction conditions: [MMA]0/[ Initiator]0/[PC]0 = 100:1:0.05, solvent (9.4 M of MMA), at room temperature, under the irradiation of purple LEDs (400 nm, 25 mW cm⁻²), 10 h. Conversions were determined by 'H NMR, Mw, and D were determined by gPC with poly(methyl methacrylate) (PMMA) standards. Abbreviations: MMA methyl methacrylate, PC photocatalyst, Conv. conversion, gPC gel permeation chromatography, D = Mw/Mn, EBP ethyl α-bromophenylacetate, EBP ethyl-bromomopropionate, EBIB ethyl-2-bromoisobutyrate, DBM diethyl 2-bromomalonate, DBMM diethyl 2-bromo-2-methylmalonate, DMA dimethylacetamide, DMF dimethylformamide, DCM dichloromethane. + irradiated by blue LEDs (440 nm, 30 mW cm⁻²), 8 h.
8–10), and ODA 5b could achieve a dispersity (Đ) lower than 1.20 (entry 8). Catalysts 5b and 5d were further examined with DBMM (entries 12 & 13), and a remarkable narrow dispersity (Đ = 1.12, entry 12) was obtained with 5d. Irradiation with lower energy blue LEDs was also effective (entries 13 & 14).

**Light regulation, kinetics, and block polymer synthesis.** A prominent feature of the O-ATRP is that the polymerization can be regulated by light.48,49 To examine the temporal control ability of the current system, a light on–off experiment was performed with light on–off cycle repeating for several times until over 90% conversion was achieved. As depicted in Fig. 3a, the polymerization only preceded in the presence of light irradiation, while no polymerization was observed in dark. Further, light on–off experiments have shown no conversion even over a long dark period up to 12 h. This strict control by light over the whole process suggests an effective activation and deactivation mechanism of the polymerization. The polymerization was then followed by 1H NMR to gain some insights about the polymerization kinetics, which unveiled a first-order kinetics through the course of the reaction (Fig. 3b). The $M_n$ vs conversion plot was observed. Notably, the y-intercept of the $M_n$ vs conversion plot was 870 Da, indicating that the control of the polymerization was achieved after the initial addition of ~6 MMA (Fig. 3c).25 This strict control may benefit from a more efficient deactivation process26,37,45 due to the radical cations of ODA photocatalysts possessing a better oxidizing ability, when compared with the dihydrophenazine-derived photocatalysts.25,28

Regarding the chain-end fidelity, a polymethyl methacrylate (PMMA) sample obtained via 5d-mediated metal-free ATRP was subjected to MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight mass-spectrometer) analysis (Supplementary Fig. 10), which shows a consistency observed molecular weight with the expected values with each peak separated by the mass of one MMA (100 Da), and individual PMMA polymers having the initiating unit at one chain end and a bromine atom at the propagating chain end. An advantage of high chain-end fidelity is it enables the synthesis of block polymers. As shown in Fig. 4, chain extension (PMMA-b-PMMA) and block copolymerization products (PMMA-b-PBnMA and PMMA-b-PBA) can all be prepared with this catalytic system. Notably, the gel permeation chromatography (GPC) traces, all clearly show an obvious shift to higher molecular weight species with little tailing in the homo-polymer regime, giving further support to the high alkyl bromide chain-end fidelity in the PMMA macro-initiators (purified via re-precipitation from methanol) and also a high re-initiation efficiency. Of note, this result is also in consistence with the high initiator efficiency observed in the polymerizations with freshly distilled DBMM (Supplementary Table 8). Moreover,
dispersity can be achieved with 10 ppm catalyst loadings. Remarkably, sunlight is also suitable to drive the polymerization process. Importantly, white polymer products can be obtained at the catalyst loading less than 50 ppm, even though the photocatalysts are normally colored compounds (Fig. 1d). The high catalytic performance may benefit from their strong visible-light absorption ($\varepsilon_{\text{abs}}$), which is a commonly used organometallic photoredox catalyst.50 The polymerizations were performed under standard conditions. Conversions were measured by $^1$H NMR. $M_n$ and $\theta$ were determined using GPC with PMMA standards. $\theta$ in parentheses were determined using GPC coupled with multi-angle light scattering (MALS). Purple LEDs ($\lambda_{\text{max}}$, 400 nm, 25 mW cm$^{-2}$), Blue LEDs ($\lambda_{\text{max}}$, 460 nm, 30 mW cm$^{-2}$). Abbreviations: PC, photocatalyst, Conv., conversion, GPC gel permeation chromatography, $\text{D} = M_w / M_n$, MMA methyl methacrylate, TFEMA 2,2,2-trifluoroethyl methacrylate, BnMA benzyl methacrylate, BA butyl acrylate, EBP ethyl a-bromophenylacetate, DBMM diethyl 2-bromo-2-methylmalonate. *Sunlight experiments were performed outside on a sunny winter day at Fuzhou University. (26 °N, 119 °E, 25 °C).

**Table 2** Polymerization with low catalyst loadings.

| Entry | PC loading (ppm) | Monomer | Initiator | PC | Light source | Time (h) | Conv. (%) | $M_n$,GPC | D |
|-------|------------------|---------|-----------|----|--------------|----------|-----------|------------|---|
| 1     | 100              | MMA     | EBP       | 5a | Purple LEDs  | 10       | 71.4      | 14.3       | 1.19 |
| 2     | 10               | MMA     | DBMM      | 5a | Blue LEDs    | 10       | 88.1      | 1.48       | 1.20 (1.09) |
| 3     | 10               | MMA     | DBMM      | 5d | Blue LEDs    | 12       | 90.4      | 1.45       | 1.17 (1.08) |
| 4     | 5                | MMA     | DBMM      | 5d | Blue LEDs    | 12       | 83.2      | 1.43       | 1.25 |
| 5     | 0.5              | MMA     | DBMM      | 5d | Blue LEDs    | 14       | 77.4      | 1.92       | 1.34 (1.26) |
| 6     | 0.1              | MMA     | DBMM      | 5d | Blue LEDs    | 14       | 70.3      | 2.56       | 1.39 |
| 7     | 0.05             | MMA     | DBMM      | 5d | Blue LEDs    | 14       | 62.5      | 30.8       | 1.51 |
| 8\*   | 10               | MMA     | DBMM      | 5d | Sunlight\*   | 7        | 50.7      | 11.4       | 1.31 |
| 9\*   | 50               | MMA     | DBMM      | 5d | Sunlight\*   | 7        | 49.2      | 9.40       | 1.22 |
| 10    | 10               | TFEMA   | DBMM      | 5d | Blue LEDs    | 12       | 87.5      | 13.6       | 1.22 |
| 11    | 10               | TFEMA   | DBMM      | 5d | Blue LEDs    | 12       | 81.6      | 11.5       | 1.09 |
| 12    | 50               | BnMA    | DBMM      | 5d | Blue LEDs    | 12       | 93.5      | 11.5       | 1.29 |
| 13    | 10               | BA      | DBMM      | 5d | Blue LEDs    | 7        | 78.2      | 22.3       | 1.49 (1.37) |
| 14    | 50               | BA      | DBMM      | 5d | Blue LEDs    | 7        | 91.6      | 30.8       | 1.41 (1.29) |

The polymerizations were performed under standard conditions. Conversions were measured by $^1$H NMR. $M_n$ and $\theta$ were determined using GPC with PMMA standards. $\theta$ in parentheses were determined using GPC coupled with multi-angle light scattering (MALS). Purple LEDs ($\lambda_{\text{max}}$, 400 nm, 25 mW cm$^{-2}$), Blue LEDs ($\lambda_{\text{max}}$, 460 nm, 30 mW cm$^{-2}$). Abbreviations: PC, photocatalyst, Conv., conversion, GPC gel permeation chromatography, $\text{D} = M_w / M_n$, MMA methyl methacrylate, TFEMA 2,2,2-trifluoroethyl methacrylate, BnMA benzyl methacrylate, BA butyl acrylate, EBP ethyl a-bromophenylacetate, DBMM diethyl 2-bromo-2-methylmalonate. *Sunlight experiments were performed outside on a sunny winter day at Fuzhou University. (26 °N, 119 °E, 25 °C).
Methods

polymer synthesis and other photocatalysis-related correspondences

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Discussion

In this work, a catalyst design logic based on heteroatom-doping of polycyclic arenes has been successfully introduced into the development of photocatalysts for O-ATRP. ODA has been identified as a catalyst framework with high efficiency, featuring its strong visible-light absorption and excellent performance at very low catalyst loadings (50 ppb to 10 ppm) in organocatalytic ATRP. This framework also represents a rare example of non-N-heterocyclic organocatalysts lacking a CT character that could mediate the ATRP with good control and low dispersity (D < 1.20) at a ppm level of catalyst loading. We anticipate that this class of photoredox catalysts will find further applications in polymer synthesis and other photocatalysis-related fields.

Methods

Typical procedure for O-ATRP of MMA under light. Typical metal-free organocatalytic ATRP procedures with the molar ratio of [MMA]0: initiator: cata-

yst= 100:1:0.2 were shown. The polymerization was conducted with MMA (1.0 mL, 9.35 mmol, 100 eq.) as the model monomer, DBMM (18 μL, 93.5 μmol, 1.0 eq.) as the ATRP initiator, organic photocatalyst (4.70 μmol, 0.5 eq.), and DCM (1.0 mL) as the solvent in a Schlenk tube with a PTFE stirring bar. The mixture was degassed by freeze–pump–thaw cycle three times, backfilled with argon, and sealed up subsequently. And then the polymerization occurred under purple LED or blue LED or sunlight irradiation at room temperature. After the desired time, the tube was opened under argon and 20.0 μL of mixture was syringed out and quenched into CDCl3 containing 250 ppm BHT to determine the mono-
er conversion by 1H NMR. The reaction mixture was then diluted with 0.5 mL dichloromethane and dissolved completely, then dripped into 75 mL methanol and stirred for 2 h. The precipitate was then collected by suction filtration with a Buchner funnel and dried in vacuum oven until a constant weight was achieved, at 30 °C to give the puri
dy polymer. For details, additional data, and experiments, please see the Supplementary Information (Supplementary Methods, Supplementary Figs. 1–18, Supplementary Tables 1–8, etc.).

Data availability

The authors declare that all data supporting the findings of this study are available within the article and Supplementary Information files, and are also available from the corresponding author upon reasonable request.

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**Author contributions**

Q.M. conducted the research on the catalyst synthesis, polymerization evaluation, kinetic study, characterization, etc.; J.S. performed the computational study; X.Z., Y. J., and I.J. participated in the catalyst synthesis and polymerization development; S.L. conceived this concept and prepared this manuscript with feedback from Q.M. and J.S.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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