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Metal-free atom transfer radical polymerization: reaching ppm catalyst loading under sunlight

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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 led to the discovery of oxygen-doped antratherene (ODA) as a new class of organic photoredox catalysts for O-ATRP. In comparison with known organocatalysts, ODAs feature strong visible-light absorption together with high molar extinction coefficient ($\epsilon_{455\text{nm}}$ up to $23950 \text{ M}^{-1}\text{cm}^{-1}$), 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.¹⁻³ However, conventional ATRPs rely on transition metal catalysts [i.e., Cu(I), Ru(II)],³ which will result in transition metal contaminations in the final products, and thus raise concerns when applied to fields sensitive to metal contaminants. In particular, for the biomedical and electronic applications, a complete removal of metal is often required.⁴⁻⁶ Therefore, extensive research efforts have been

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dedicated to lowering catalyst loadings or removing residual metals since the initial discovery of ATRP.⁵⁻⁷ Whereas, the recent emerging organocatalyzed atom transfer radical polymerization (O-ATRP) using organic photoredox catalysts, undoubtedly, represents an ideal solution to this challenging issue.⁸⁻¹⁴

Since the conceptual work first demonstrated in 2014 by using organic molecules such as *N*-phenyl phenothiazine or perylene as a catalyst,¹⁵⁻¹⁷ O-ATRP has immediately attracted wide research interests in the past five years.¹⁸⁻²¹ Until now, several frameworks/core structures²¹ including phenothiazine (**1**),^{15,22,23} dihydrophenazine (**2**),²⁴⁻²⁶ phenoxazine (**3**),^{27,28} etc.²⁹⁻³⁵ have been successfully identified as efficient photocatalysts for O-ATRP (Figure 1a). However, a 1000-ppm level of catalyst loading was typically required to reach a satisfactory control over the polymerization. Controlled polymerization with narrow dispersity at a practical low catalyst loading (<10 ppm) could not only eliminate the need of residual catalyst removal or further product purification, but could also decrease the cost of commercial production.^{13,26} Therefore, the development of highly effective photocatalysts for O-ATRP has thus become a focus of extensive studies in recent years.^{19-21,23,26} According to the oxidative quenching mechanism (Figure 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.³⁶ 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 living polymerization with narrow dispersities.³⁶⁻³⁹ Whereas, many mechanistic aspects in O-ATRP remain unclear so far, and there is still a lack of general guidelines for the catalyst design.^{21,39}

Phenothiazine,¹⁵ dihydrophenazine,²⁴ and phenoxazine²⁷ are among the most efficient and widely used catalyst frameworks that could achieve a well-controlled O-ATRP polymerization

a O-ATRP catalyst development via core structure modification (previous studies)

b O-ATRP catalyst design based on the heteroatom-doping logic (this work)

c Catalytic cycle for O-ATRP

d Polymerization under sunlight and product color

Figure 1 | The development of catalysts for O-ATRP. **a**, Catalyst development via core structure modification. **b**, O-ATRP photocatalyst design based on a heteroatom-doping logic (this work). **c**, Catalytic cycle for a light-mediated O-ATRP. **d**, Polymerization under sunlight and the product color (PMMA).

with low dispersity.²¹ 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 ($\lambda_{\max}$) was often quite limited.^{20,21} 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.^{15,21,24,27} Therefore, we questioned whether there is a possibility to find a suitable and tuneable O-ATRP catalyst framework with their absorption maximum locating 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 (Figure 1a). Recently, we were thinking heteroatom doping^{40,41} of small polycyclic arenes might be a feasible catalyst design logic for the O-ATRP photocatalyst development (Figure 1b).

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^{36,40} and thus probably lead to an improvement in their catalytic performance on polymerization and suppress underside catalyst decomposition or catalyst-initiation.^{16,29,30} With this idea in mind, we thus decided to practice this heteroatom-doping strategy on graphene, and narrowed down the parental pi system to antratherene (Figure 1b, left), which possesses the desired strong absorption in visible light region.⁴² 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,²³⁻²⁸ and all contains a triaryl amine moiety, which is typically required to impose a twisted donor-acceptor structure to favor the charge-transfer process.^{23-26,43} Therefore, the development of a completely new photocatalyst framework lacking this moiety that could achieve the same level or better performance can be of fundamental significance, which, to the best of our known, remains unknown so far; ii) O-doping can regulate the photophysical and redox properties of antratherene, probably leading to a more oxidizing OPC⁺⁺ in comparison with the typical amine-containing catalyst **1-3**, which may thus afford a better deactivation control.²⁴⁻²⁶ Herein, we wish to report our efforts toward this goal, and the discovery of oxygen-doped antratherene (ODA) as a new organocatalyst framework for O-ATRP, which exhibits strong absorption at the visible light region ($\epsilon_{450\text{ nm}} > 20000\text{ M}^{-1}\text{cm}^{-1}$), and allows for a ppm/sub-ppm level of catalyst loading only to deliver a metal-free, controlled polymerization under visible light or even sunlight (Figure 1d).

The oxygen-doped antratherene (ODA) can be readily constructed via dual oxidative cyclization⁴⁴ from the commercially available 1,1'-bisanthol (BINOL) (Figure 2a). Further, by

virtue of its easy modifiability,⁴⁵ BINOLs 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*-butyl substituted catalyst **5b**, while **5c** and **5d** were prepared to examine the influence of aryl substituents (for synthetic procedures and spectra, please see the Supplementary Information). As anticipated, **5a** did show a strong absorption in the visible light region (Figure 2b), with a red shift of the absorption maximum from 437 nm to 443 nm (comparing with the parental antratherene⁴²). 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 maximums appearing below 400 nm. Both the absorption maximums ($\lambda_{\text{max}} = 454$ and 455 nm) of **5c** and **5d** shown a further red shift (ca. 12 nm) as well as enhanced light absorption ($\epsilon_{\text{max}} = 22580$ and 23950 vs 17450 M⁻¹cm⁻¹). In addition, a notable feature of the ODA catalysts substantially different from the known high performance O-ATRP photocatalysts^{23,26} is the lack of a charge-separation in their excited states (Figure 2c). Based on the fluorescence emission and the cyclic voltammetry (CV) data, we could assess the reducing capability of the excited singlet states ($E^{0*}(\text{PC}^{\cdot+}/^1\text{PC}^*)$ vs SCE) of these catalysts, ranging from -1.76 V to -1.84 V vs SCE (Figure 2d). Density functional theory (DFT) was used to estimate the reduction potentials of the triplet excited-states ($E^0(\text{PC}^{\cdot+}/^3\text{PC}^*)$), which are in the range of -1.58 to -1.71 V vs SCE (Fig 2c, for details, see Supplementary Information & Computational details). Although the excited states of ODA **5a-5d** are less reductive than that of *N*-phenyl phenothiazine (**1**, Ar = Ph, R = H, $E^{0*} = -2.1$ V vs SCE),¹⁵ but all are more negative than -0.7 V that is required to reduce the initiator EBP (ethyl α -bromophenylacetate, $E^0(\text{EBP}/\text{EBP}^{\cdot-}) = -0.74$ V SCE).²⁴ Notably, the radical cations ($\text{PC}^{\cdot+}$) 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).²⁶

Figure 2 | Synthesis and characterization of photocatalysts. **a**, Synthesis of oxygen-dopants of antratherene **5a-d**. **b**, UV-Vis absorption profiles. **c**, SOMO orbitals and triplet reduction potentials of **5a** and **5d**. **d**, Characterization data of photocatalyst **5a-5d** by UV-Vis, fluorescence emission, CV, and calculated reduction potentials.

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, $\lambda_{\max}$ 400 nm). To our delight, **5a** could afford a controlled polymerization with a moderate dispersity (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 M_n (entry 3). Remarkably, ODA **5a** is also effective with other initiators such as ethylbromopropanoate (EBrP), ethyl-2-bromoisobutanoate (EBiB), diethyl 2-bromomalonate (DBM)

and diethyl 2-bromo-2-methylmalonate (DBMM) ($\bar{D}$ 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 8-10), and ODA **5b** could achieve a dispersity ($\bar{D}$) lower than 1.20 (entry 8). Catalysts **5b** and **5d** were further examined with DBMM (entry 12 & 13), and a remarkable narrow dispersity ($\bar{D}$ = 1.12, entry 12) was obtained with **5d**. Irradiation with lower energy blue LEDs was also effective (entry 13 & 14).

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

Reaction scheme: $R-Br$ (initiator) + MMA $\xrightarrow[\text{solvent, rt, 10 h}]{\text{ODA photocatalyst, purple or blue LEDs}}$ $PMMA-Br$

Entry	PC	Initiator	Solvent	Conv	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{GPC}}$ (kDa)	$\bar{D}$
1	5a	EBP	DMA	88.5%	9.10	19.9	1.34
2	5a	EBP	DMF	83.4%	8.59	18.3	1.33
3	5a	EBP	DCM	73.3%	7.58	12.8	1.25
4	5a	EBrP	DCM	72.7%	7.46	13.3	1.27
5	5a	EBiB	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	EBP	DCM	88.2%	9.07	13.5	1.23
11	5b	DBMM	DCM	69.1%	7.17	13.5	1.15
12	5d	DBMM	DCM	84.8%	8.75	12.0	1.12
13 ^a	5a	EBP	DCM	82.7%	8.52	15.7	1.25
14 ^a	5d	DBMM	DCM	71.8%	7.44	10.9	1.15

Reaction conditions: $[MMA]_0:[\text{initiator}]_0:[\text{PC}]_0 = 100:1:0.05$, solvent (9.4 M of MMA), at room temperature, under the irradiation of purple LEDs (400 nm), 10 h. Conv. were determined by ^1H NMR. M_n and $\bar{D}$ (M_w/M_n) were determined by GPC with PMMA standards. ^aIrradiated by blue LEDs (460nm), 8 h.

A prominent feature of the O-ATRP is that the polymerization can be regulated by light.⁴⁶ 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 Figure 3a, the polymerization only preceded in the presence of light irradiation, while no polymerization was observed in dark. This strict control by light over the whole process indicates an efficient 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 (Figure 3b). The

Figure 3 | Temporal control and kinetic study on ODA 5d-catalyzed ATRP of MMA. **a**, Light on/off experiments and the plot of monomer conversion versus time. **b**, Kinetic plot for the metal-free ATRP. **c**, Plot of M_n and PDI versus monomer conversion for the polymerization of MMA under continuous irradiation. **d**, GPC traces of each polymer depicted in **c** (color coded). All polymerization were performed at a $[\text{MMA}]_0/[\text{DBMM}]_0/[\text{5d}]_0$ ratio of 200/1/0.05 under purple light irradiation.

$M_{n,\text{GPC}}$ values were plotted against the monomer conversion, as shown in Figure 3c, and a linear increase of molecular mass and narrow dispersity throughout the polymerization process were observed. Notably, the y-intercept of the number average molecular weight (M_n) versus conversion plot was 870 Da, suggesting the control of the polymerization was achieved after the initial

addition of ~6 MMA (Figure 3c).²⁴ This strict control may benefit from a more efficient deactivation process^{25,35,43} due to the radical cations of ODA photocatalysts possessing a better oxidizing ability.

Regarding the chain-end fidelity, a PMMA sample obtained via **5d**-mediated metal-free ATRP was subjected to MALDI-TOF analysis (Supplementary Figure 10), which shows a consistence of observed molecular weight with the expected values for the individual PMMA polymers, based on the presence of the initiating unit at one chain end and a bromine atom at the propagating chain end with each peak separated by the mass of one monomer unit (100 Da). An advantage of high chain-end fidelity is it enables the synthesis of block polymers. As shown in Figure 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 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 macroinitiators (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, triblock synthesis is also viable with this system as demonstrated with the preparation of PMMA-*b*-PBnMA-*b*-PBA (see Supplementary Figure 13).

The high molar extinction coefficient (ϵ_{max} upto 23950 M⁻¹cm⁻¹) of ODA catalysts at the visible light region encouraged us to examine their performance at extremely low catalyst loadings. As shown in Table 2, decreasing the catalyst loading from 500 ppm to 10 ppm, both photocatalyst **5a** and **5d** could maintain their catalytic efficiency, giving a controlled polymerization with low dispersity (entries 1-3). To our delight, in the present system, very narrow dispersity can be achieved with 10 ppm **5d** only (entry 3). Remarkably, the catalyst loading of **5d** can be further

Figure 4 | Block polymer preparation. Left: chain-extension from a PMMA macro-initiator (black) to produce block copolymers after a further polymerization with MMA (green), BnMA (red), and BA (blue). Right: GPC traces of the corresponding polymers depicted in left by using the same color coded.

decreased from 10 ppm to 0.1 ppm (entry 3-6), and even to 50 ppb by more than two orders of magnitude (entry 7), which is among the lowest catalyst loadings so far in O-ATRP.²⁶ It is worth mentioning that a catalyst loading less than 10 ppm could be very meaningful, which may eliminate the need of the catalyst removal process for industrial and biomedical applications. Importantly, white polymer products can be obtained at the catalyst loading less than 50 ppm, even though the photocatalysts are normally colored compounds (Figure 1d). The high catalytic performance may benefit from their strong visible-light absorption (**5d**, $\epsilon_{455\text{nm}} = 23950 \text{ M}^{-1}\text{cm}^{-1}$). In fact, the visible light absorption is approximately one order of magnitude stronger than that of *fac*-Ir(ppy)₃ ($\epsilon_{458\text{nm}} = 2450 \text{ M}^{-1}\text{cm}^{-1}$), which is a commonly used organometallic photoredox catalyst.⁴⁷ Remarkably, sunlight is also suitable to drive the polymerization with 10 ppm catalyst only (entry 8 & 9). To the best of our known, 10 ppm represents the lowest catalyst loading achieved so far in controlled O-ATRP under sunlight.

Furthermore, other methacrylate monomers such as 2,2,2-trifluoroethyl methacrylate (TFEMA) and benzyl methacrylate (BnMA) can also be polymerized with low dispersity at 10 or 50 ppm

Table 2. Polymerization with extremely low catalyst loadings.

Entry	PC loading	Monomer	PC	Initiator	Light Source	Time	Conv	$M_{n,GPC}$	$\bar{D}$
1	100 ppm	MMA	EBP	5a	Purple LEDs	10 h	71.4%	14.3	1.19
2	10 ppm	MMA	DBMM	5a	Blue LEDs	10 h	88.1%	14.8	1.20 (1.09)
3	10 ppm	MMA	DBMM	5d	Blue LEDs	12 h	90.4%	14.5	1.17 (1.08)
4	5 ppm	MMA	DBMM	5d	Blue LEDs	12 h	83.2%	14.3	1.25
5	0.5 ppm	MMA	DBMM	5d	Blue LEDs	14 h	77.4%	19.2	1.34 (1.26)
6	0.1 ppm	MMA	DBMM	5d	Blue LEDs	14 h	70.3%	25.6	1.39
7	0.05 ppm	MMA	DBMM	5d	Blue LEDs	14 h	62.5%	30.8	1.51
8 ^c	10 ppm	MMA	DBMM	5d	Sunlight [‡]	7 h	50.7%	11.4	1.31
9 ^c	50 ppm	MMA	DBMM	5d	Sunlight [‡]	7 h	49.2%	9.40	1.22
10	10 ppm	TFEMA	DBMM	5d	Blue LEDs	12h	87.5%	13.6	1.22
11	50 ppm	TFEMA	DBMM	5d	Blue LEDs	12h	81.6%	11.5	1.09
12	50 ppm	BnMA	DBMM	5d	Blue LEDs	12h	93.5%	11.5	1.29
13	10 ppm	BA	DBMM	5d	Blue LEDs	7h	78.2%	22.3	1.49 (1.37)
14	50 ppm	BA	DBMM	5d	Blue LEDs	7h	91.6%	30.8	1.41 (1.29)
15 ^d	10 ppm	MMA	CPADB	5a	Sunlight [‡]	18h	60.3%	15.4	1.08
16 ^d	10 ppm	MMA	CPADB	5d	Sunlight [‡]	18h	67.1%	14.0	1.07
17 ^d	1 ppm	MMA	CPADB	5d	Sunlight [‡]	18h	34.5%	10.8	1.08

The polymerizations were performed under standard conditions. Conversions were measured by ¹H NMR. M_n and $\bar{D}$ were determined using GPC with PMMA standards. $\bar{D}$ in parentheses were determined using GPC coupled with MALS. Purple LEDs ($\lambda_{\max}$ 400 nm); Blue LEDs ($\lambda_{\max}$ 460 nm). Sunlight experiments were performed outside in a sunny winter day at Fuzhou University (26 °N, 119 °E, 25 °C).

catalyst loading (entries 10-12). Surprisingly, ODA catalysts could also deliver a controlled polymerization with low dispersity in the polymerization of *n*-butyl acrylate (entry 13 & 14, also see Supplementary Table 6). It is worth mentioning that acrylate monomers proved to be very challenging to achieve a controlled polymerization with low dispersity by O-ATRP methods due to their high polymerization rate.^{24,26,43} To our delight, this control on low dispersity is even better than that with dihydroacridine photocatalysts which were developed especially for this type of monomers very recently.⁴³ In addition, ODA photocatalysts could also mediate the reversible addition-fragmentation chain transfer (RAFT) polymerization⁴⁸⁻⁵⁰ of MMA at low ppm catalyst loading (1–10 ppm) under sunlight, with excellent control and narrow dispersity ($\bar{D} < 1.10$, entries

15-17), which are comparable to the precious iridium photocatalyst⁵¹ (Supplementary Table 7).
Notably, ODA **5d** also represent a rare example of organic photocatalysts that could promote the
polymerization of both MMA and BA, as well as RAFT polymerization of MMA with good
controls.^{43,49}

In summary, a catalyst design logic based on heteroatom-doping of polycyclic arenes has been
successfully introduced into the development of new photocatalysts for organocatalyzed atom
transfer radical polymerization (O-ATRP). Oxygen-doped antratherene (ODA) has been identified
as a novel catalyst framework with unprecedented high efficiency, featuring its strong visible light
absorption and excellent performance at extremely low catalyst loadings in both organocatalyzed
ATRP and RAFT polymerization. This framework also represents the first example of non-N-
heterocyclic organocatalysts lacking a CT character that could mediate the atom transfer radical
polymerization with good control and low dispersity ($\bar{D} < 1.20$) at a ppm level of catalyst loading.
We anticipate that this new 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. A typical metal-free organocatalyzed ATRP
procedures with the molar ratio of $[MMA]_0: [initiator]_0: [catalyst]_0 = 100: 1: 0.05$ were showed as follows.
The polymerization was conducted with MMA (1.0 mL, 9.35 mmol, 100 eq.) as the model monomer,
DBMM (18 μ L, 93.5 μ mol, 1.0 eq.) as the ATRP initiator, organic photocatalyst (4.70 μ mol, 0.5 eq.) and
DCM (1.0 mL) as the solvent in a Schlenk tube with a PTFE stirring bar. The mixture was deoxygenized
by freeze–pump–thaw cycle three times, backfilled argon and sealed up subsequently. And then the
polymerization was 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 μ L of mixture were syringed out and
quenched into $CDCl_3$ containing 250 ppm BHT to determine the monomer 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 hours. The precipitates was then collected by suction filtration with a Buchner funnel and dried in vacuum oven until a constant weight at 30 °C to give the purified polymers. For details, additional data and experiments, please see the Supplementary Information (Supplementary Methods, Data, Supplementary Figure 1-18, Supplementary Table 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, and characterization etc.; J.S. performed the computational study; X.Z., Y. J. & L.J. participated in the catalyst

1 synthesis and polymerization development; S.L. conceived this concept and prepared this manuscript with
2 feedback from Q.M. & J.S.

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7 **Supplementary information** is available in the online version of the paper. Correspondence and requests
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Figures

a O-ATRP catalyst development via core structure modification (previous studies)

b O-ATRP catalyst design based on the heteroatom-doping logic (this work)

c Catalytic cycle for O-ATRP

d Polymerization under sunlight and product color

Figure 1

The development of catalysts for O-ATRP. a, Catalyst development via core structure modification. b, O-ATRP photocatalyst design based on a heteroatom-doping logic (this work). c, Catalytic cycle for a light-mediated O-ATRP. d, Polymerization under sunlight and the product color (PMMA).

Figure 2

Synthesis and characterization of photocatalysts. a, Synthesis of oxygen-dopants of antratherene 5a-d. b, UV-Vis absorption profiles. c, SOMO orbitals and triplet reduction potentials of 5a and 5d. d, Characterization data of photocatalyst 5a-5d by UV-Vis, fluorescence emission, CV, and calculated reduction potentials.

Figure 3

Temporal control and kinetic study on ODA 5d-catalyzed ATRP of MMA. a, Light on/off experiments and the plot of monomer conversion versus time. b, Kinetic plot for the metal-free ATRP. c, Plot of M_n and PDI versus monomer conversion for the polymerization of MMA under continuous irradiation. d, GPC traces of each polymer depicted in c (color coded). All polymerization were performed at a $[MMA]_0/[DBMM]_0/[5d]_0$ ratio of 200/1/0.05 under purple light irradiation.

Figure 4

Block polymer preparation. Left: chain-extension from a PMMA macro-initiator (black) to produce block copolymers after a further polymerization with MMA (green), BnMA (red), and BA (blue). Right: GPC traces of the corresponding polymers depicted in left by using the same color coded.

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