Supporting Information

Visible light-triggered non-deoxygenated PET-RAFT polymerization by heterogeneous conjugated microporous polymer photocatalysts

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1. Materials

Most of the chemicals were purchased from commercial sources. Methyl methacrylate (MMA) (> 99.8%), Glycidyl methacrylate (GMA) (>95.0%), Benzyl methacrylate (BZMA) (> 98.0%), 2-methoxyethyl methacrylate (MEMA) (> 98.0%), Butyl methacrylate (BMA) (> 99.0%). 4-Cyano-4-(thiobenzoylthio)pentanoic acid (CPADB) was purchased from Aladdin (China) and was used as received. N-N-Dimethylacetamide (DMAc, AR), triethylamine (TEA, 99.8%), n-Butanol (99.8%), 1,2-dichlorobenzene (99.8%), acetic acid (98%), methol (MeOH, AR), tetrahydrofuran (THF, AR). 1,3,6,8-tetra-(p-aminophenyl)-pyrene (TAPPY) and 2',5'-dimethyl-[1,1':4',1"-terphenyl]-4,4"-dicarbaldehyde (DTDD) was synthesized using published procedures. All other reagents were used as received unless otherwise specified. Light emitting diode (LED) strips (13 W m⁻¹, 15 mW cm⁻²) were used as the external light source for the experiments, white LED: (420-750nm), blue LED: (460nm), green LED: (530nm).

2. Experimental sections

Gel permeation chromatography (GPC). The GPC monitoring system is fitted with a Waters 717 plus autosampler, a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector and Shodex K-805, K-804 and K-802.5 columns in tandem. GPC operating parameters: test flow rate 1.0 mL/min (with THF as eluent), test temperature: 40 °C (both column and detector), calibration protocol: a range of molecular weight polymethylmethacrylate (PMMA) standards. Samples are drawn from the reaction mass at expected time intervals using a 2 mL disposable syringe and filtered through a filter to obtain a clarified sample, and the parameters (average molecular weight (M_n) and polydispersity (M_w/M_n)) of the polymer samples are determined by a GPC detection system. The monomer conversion (α) of the samples can be calculated from the corresponding peak areas of the ¹H NMR spectra.

Characterization. ¹H NMR (600 MHz) and ¹³C NMR spectra were documented on

a Bruker Advance III. Powder X-ray diffraction (PXRD) investigations were made on Empyrean DY1602. Fourier transform infrared (FT-IR) spectra were recorded by Thermo Scientific Nicolet i5. Solid diffuse reflectance ultraviolet-visible spectra (UVvis DRS) were gathered by a Varian Cary 300 UV-Vis spectrophotometer. Analyze thermogravimetry (TGA) on the LS00-HS-TGA-101 (at the heating rate of 10 °C/min under N₂ flow rate = 100 mL/min). The specific surface area and pore size distribution of the products were surveyed on an Autosorb-iQ analyzer (Quantachrome). The synthesized photocatalysts were characterized morphologically using a Hitachi S-5500 field emission scanning electron microscope (FE-SEM). CHI 660e electrochemical workstation equipped with a standard three-electrode electrochemical cell with the working electrode, platinum plate as a counter electrode, and saturated Ag/AgCl electrode as a reference electrode is applied for photoelectrochemical detection of TAPPY-DTDT-CMP with sodium sulfate solution (0.2 M) as electrolyte for testing. Determination of time-of-flight mass spectrometry using Bruker ultra-fine MALDI-TOF/TOF spectrometer.

Measurement of superoxide anion (O2[•]).

Single oxygen (${}^{1}O_{2}$) **measurements.** A 1 mL reaction solvent (H₂O) charged with 0.5 mg/mL PCs (${}^{1}O_{2}$ generator) and 2mM 2,2'-(anthracene-9,10-diylbis(methylene))dimalonic acid (ABDA) (${}^{1}O_{2}$ trapper), which was added into a glass cuvette (1 mm pathlength) and sealed with a rubber septum. The mixture was irradiated under LED light (13 W m⁻¹, 15 mW cm⁻²), and the absorbance was recorded by UV-vis spectrophotometer at the indicated times.

Superoxide anion radical (O_2 ⁻) measurements. A 1 mL reaction mixture consisting of 0.5 mg/mL PCs (O_2 ⁻ generator) and 2 mM p-benzoquinone (p-BQ) (O_2 ⁻ trapper) in DMAc were added into a glass cuvette (1 mm pathlength) and sealed with a rubber septum. The mixture was irradiated under LED light (13W m⁻¹, 15 mW cm⁻²) and the absorbance was recorded by UV-vis spectrophotometer at the indicated times.

3. Synthesis procedure

3.1 Synthesis of 1,3,6,8-tetra-(p-aminophenyl)-pyrene (TAPPY):



A reaction mixture containing 1,3,6,8-tetrabromopyrene (1.50 g, 2.86 mmol, 1.0 eq.), 4-aminophenylboronic acid pinacol ester (3.10 g, 13.7 mmol, 4.8 eq.), K₂CO₃ (2.20 g, 15.7 mmol, 5.5 eq.) and Pd(PPh₃)₄ (0.33 g, 0.29 mmol, 10 mol%) in 32 mL 1,4-dioxane and 8 mL H₂O. The reaction mixture was purged with nitrogen and heated to reflux (115 °C) for 3 d. After cooling to room temperature, H₂O was added. The resulting precipitate was collected via filtration and was washed with H₂O and MeOH. Recrystallization from 1,4-dioxane, followed by drying under high vacuum furnished the title compound, co-crystallized with approximately 1.5 dioxane molecules per formula unit, as a bright yellow powder (1.8 g, 2.56 mmol, 90%). ¹H NMR (400 MHz, DMSO-d6): 8.12 (s, 4 H), 7.78 (s, 2 H), 7.34 (d, J = 8.4 Hz, 8 H), 6.77 (d, J = 8.5 Hz, 8 H), 5.33 (s, 8 H), 3.56 (s, 12 H, dioxane).



Figure S1. ¹H NMR spectrum of TAPPY in DMSO-*d*₆.

3.2 Synthesis of 2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (DTDD):



7.58 1,4-Dibromo-2,5-dimethylbenzene (2.00)mmol) and 4g, formylphenylboronic acid (2.39 g, 15.9 mmol, 2.1 eq) were dissolved in 200 mL of tetrahydrofuran. An aqueous solution of potassium carbonate (8 mL, 2.0 M) was added to the solution under a nitrogen atmosphere. The resulting suspension was cycles. subjected to three freeze pump-thaw After the addition of bis(triphenylphosphine)palladium (II) dichloride (0.266 g, 0.379 mmol, 0.05 eq), the mixture was refluxed for 24 h. After cooling to room temperature, the mixture was extracted twice with dichloromethane (2×100 mL). The obtained organic layer was collected and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel (hexane/ $CH_2Cl_2 = 1/1$) to give the expected product in a S-6 75% yield (1.80 g, 5.73 mmol) as a white solid. ¹H NMR (500 MHz,

CDCl3, 300 K): δ 10.11 (s, 2H), 7.99 (d, 4H), 7.57 (d, 4H), 7.21 (s, 2H), 2.32 (s, 6H).



Figure S2. ¹H NMR spectrum of DTDD in CDCl₃.

3.3 Synthesis of TAPPY-DTDD-CMP

TAPPY (11.3 mg, 0.02 mmol), DTDD (12.6 mg, 0.04 mmol), 0.143 mL of nbutanol, 0.857 mL of 1,2-dichlorobenzene, and HAc (0.1 mL, 6 M) were added into Schlenk tube. After freeze-pump-thawing three times and sealing under vacuum, the tubes were placed in an oven at 120 °C for 5 days. The mixture was cooled to room temperature, and the yellow precipitate was collected and washed several times with THF. Subsequently, the tubes were soxhlet extracted with THF as solvent for 12 h and dried under vacuum at 120 °C for 2 h. The final product, TAPPY-DTDD-CMP, was afforded as a yellow powder with 87% yield.



Figure S3. (a) FT-IR spectra of TAPPY, DTDD building blocks, and photocatalyst TAPPY-DTDD-CMP. (b) Solid-state ¹³C NMR spectrum of TAPPY-DTDD-CMP.



Figure S4. P-XRD pattern of TAPPY-DTDD-CMP.



Figure S5. SEM image of TAPPY-DTDD-CMP.



Figure S6. (a) N_2 adsorption and desorption curves of TAPPY-DTDD-CMP. (b) Pore size distribution of TAPPY-DTDD-CMP.

Figure S7. The TGA curve of TAPPY-DTDD-CMP. (W_{loss} denotes the weightloss)

Figure S8. GPC elution time curves of the PET-RAFT process mediated by TAPPY-DTDD-CMP correspond to different variable factors. (a) Different catalyst loadings. (b) Different TEA concentrations. (c) Irradiated by blue LED. (d) Irradiated by green LED.

Figure S9. The ¹H NMR spectrum of crude product (RAFT process catalyzed by TAPPY-DTDD-CMP at ratio [MMA]: [CPADB]: [TEA] = 200: 1: 10 for 48 h with 5 mg catalyst loading).

Figure S10. GPC traces for different polymers obtained by the PET-RAFT polymerization of functional methacrylates.

Figure S11. (a) FT-IR spectra of TAPPY-DTDD-CMP before the first cycle and after the third cycle, (b) 13^C NMR spectra of TAPPY-DTDD-CMP before the first cycle and after the third cycle.

Figure S12. Plot of monomer conversion versus molecular weight (Mn) and dispersity (Mw/Mn) in TAPPY-DTDD-CMP -mediated PET-RAFT polymerization ([MMA]/[CPADB] = 200) under air and nitrogen.

Figure S13. Monitoring spectra of TAPPY-DTDD-CMP as ROS producer while 2,2'-(anthracene-9,10-diylbis(methylene))dimalonic acid (ABDA) and p-benzoquinone (p-BQ) as ROS trapper with white LED light irradiation under aerobic conditions. UV-Vis absorption spectrum of p-BQ at 247 nm (a) 0 eq. TEA; (b) 10 eq. TEA; UV-vis

absorption spectrum of ABDA at 251 nm. (c) 0 eq. TEA; (e) 10 eq. TEA.

Orbital 371 is HOMO, energy: -0.174119 a.u. -4.738031 eV Orbital 372 is LUMO, energy: -0.073223 a.u. -1.992507 eV LUMO/HOMO gap: 0.100896 a.u. 2.745525 eV 264.902926 kJ/mol

Figure S14. HOMO, LUMO and band gap of TAPPY-DTDD-CMP structure segment unit.

Table S1. Results of TAPPY-DTDD-CMP -mediated oxygen-containing PET-

RAFT polymerization	under white LED	irradiation for	r monomer	compatibility ^a
1 2				1 2

Entry	Monomer	T(h)	Conv. ^b (%	$M_{n,GPC}^{c}(g/mol)$	$M_{\rm n,th}^{\rm d}({\rm g/mol})$	$M_{ m w}/M_{ m n}^{ m c}$
)		·	
1	MEMA	12	33.1	5600	5100	1.17
2	BMA	12	39.5	6700	5900	1.10
3	BzMA	14	40.1	7500	7300	1.16
4	GMA	9	36.3	7200	5500	1.12

^a Polymerization was conducted using 7 mg TAPPY-DTDD-CMP with the ratio [Monomer]: [CPADB]: [TEA] = 100: 1: 10 under white LED irradiation.

^b Conversions were obtained based on the peak areas corresponding to ¹H NMR.

^c $M_{n, GPC}$ and M_w/M_n were detected by GPC (mobile phase: THF, calibration system: PMMA).

^d $M_{n,th} = MW$ (initiator) + MW (monomer) × Conv. × ([monomer]/[initiator]].

 Table S2. Results of TAPPY-DTDD-CMP -mediated oxygen-containing RAFT

 chain extension polymerization under white LED irradiation

Entry	Monomer	DP	T(h)	Conv. ^a (%)	$M_{n,GPC}^{b}(g/mol)$	$M_{\rm n,th}^{\rm c}({\rm g/mol})$	$M_{\rm w}/M_{\rm n}^{\rm b}$
1	MMA	200	6	22.6	11000	11400	1.12
2	GMA	400	8	15.8	10600	13100	1.16

^a Conversions were obtained based on the peak areas corresponding to ¹H NMR.

^b $M_{n, GPC}$ and M_w/M_n were detected by GPC (mobile phase: THF, calibration system: PMMA).

^c $M_{n,th} = MW$ (initiator) + MW (monomer) × Conv. × ([monomer]/[initiator].

References:

1. A.D. Becke, J. Chem. Phys. 1993, 98, 1372.

2. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B, 1988, 37, 785.

3. Benjamin P. Pritchard, Doaa Altarawy, Brett Didier, Tara D. Gibson, Theresa L. Windus. J. Chem. Inf. Model. 2019, 59(11), 4814-4820.

4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 09, revision D.01; Gaussian, Inc., Wallingford, CT, 2010.

5. T. Lu, F. Chen, J. Comput. Chem., 2012, 33, 580-592.