

# Electronic Supplementary Material(ESI)

## **Covalent organic frameworks as photocatalyst for atom transfer radical polymerization under white light irradiation**

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## 1. Materials

Most of the chemicals were purchased from commercial sources. Methyl methacrylate (99%, stabilized with MEHO) was purchased from Aldrich (solution was passed through a column of basic alumina before used). Ethyl  $\alpha$ -bromophenylacetate (EBPA, 98%; Aldrich), anhydrous acetonitrile (99.8%, Aldrich), triethylamine (TEA, 99.8%), copper bromide ( $\text{CuBr}_2$ , 99%, Aldrich), Tris(2-dimethylaminoethyl)amine ( $\text{Me}_6\text{TREN}$ , 99%; Aldrich), *n*-Butanol (99.8%, Aldrich), 1,2-dichlorobenzene (99.8%, Aldrich), acetic acid (98%, Aldrich) were used without further purification. 4-Benzoylphenylboronic acid, 1,3,6,8-tetrabromopyrene, 4-Aminophenylboronic acid pinacol ester, 4,7-Dibromo-2,1,3-benzothiadiazole were purchased from Aldrich and used as received.

White light-emitting diode flex strip ( $13 \text{ W m}^{-1}$ ,  $15 \text{ mW cm}^{-2}$ ) was used as an LED white source.

## 2. Characterization

$^1\text{H}$  NMR (500 MHz) spectra were recorded on Bruker Advance III. The UV-vis spectra were recorded on Genesys 10S Uv-vis spectrophotometer (Thermal Fisher Scientific). Solid state emission spectra were performed with Hitachi F-4600 spectrofluorometer. Powder X-ray diffraction (PXRD) studies were performed on EmpyreanDY1602. The specific surface areas and pore size distributions of product were investigated on an Autosorb-iQ analyzer (Quantachrome).

## 3. Gel Permeation Chromatography (GPC)

Number-average molecular weight ( $M_n$ ) and polydispersities ( $M_w/M_n$ ) of obtained polymers were measured by GPC with refractive index detector (Waters, 2414), using THF as eluent at a flow rate of 1.00 mL/min ( $40^\circ\text{C}$ ). The GPC system was calibrated with PMMA standards.

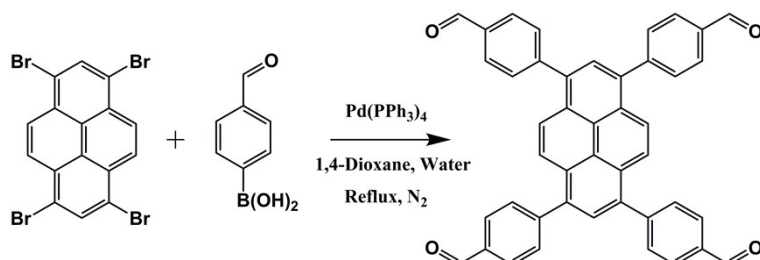
## 4. Photoelectrochemical measurements

Photoelectrochemical measurements were performed on CHI 660e electrochemical workstation with standard three-electrode electrochemical cell with a working electrode, a platinum plate as counter electrode, a saturated Ag/AgCl electrode as reference electrode and using sodium sulfate solution (0.2 M) as the electrolyte.

Working electrode prepared: 2 mg TFPPy-Td-COFs powder was mixed with 1.0 mL ethanol and 20  $\mu\text{L}$

Nafio solution and sonicated for 0.5 h. Subsequently, 10  $\mu$ L of the mixture was dropped onto the surface of a FTO glass plate with  $1 \times 1$  cm<sup>2</sup> area and left it in the air to dry.

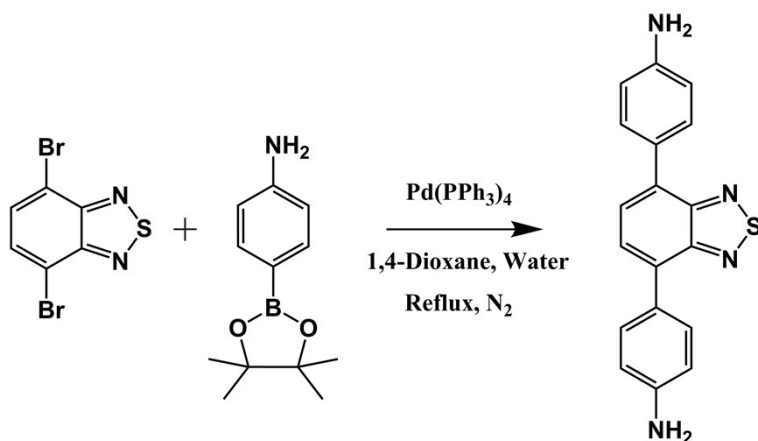
## 5. Synthesis procedure



### 5.1. Synthesis of 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzaldehyde [TFPPy]:<sup>1</sup>

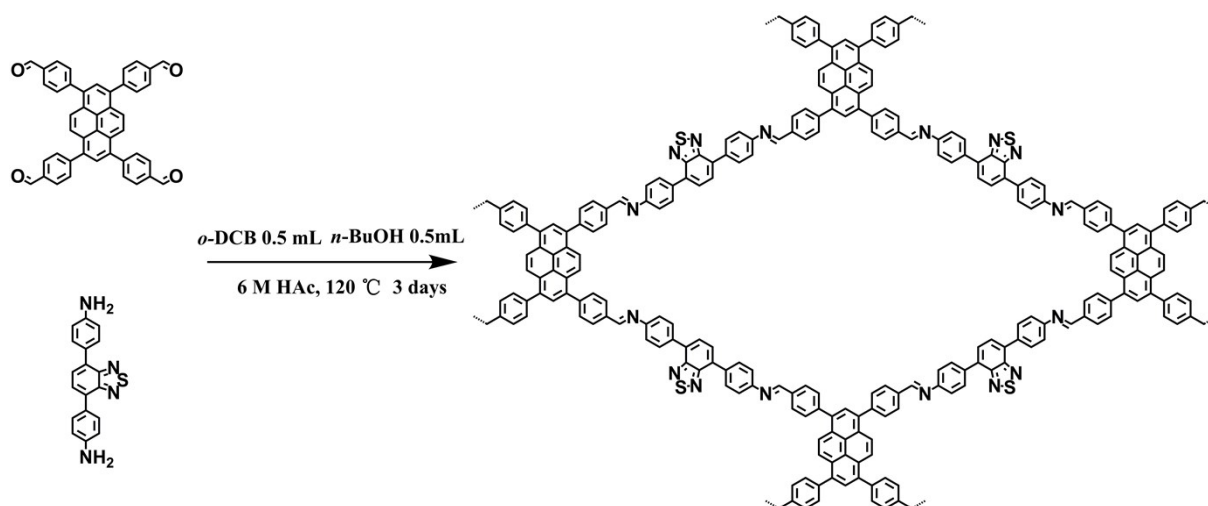
1,3,6,8-tetrabromopyrene (2 g, 3.86 mmol), 4-Benzoylphenylboronic acid (3.78 g, 23.2 mmol), K<sub>2</sub>CO<sub>3</sub> (4.32 g, 31.2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.35 g, 0.3 mmol) were added into the mixture of 1,4-dioxane (100 mL) and water (10 mL). The mixture was degassed for 30 min and then refluxed under N<sub>2</sub> atmosphere for 3 days. The formed precipitate was filtered off to get crude product and washed with water and acetone. Finally, CHCl<sub>3</sub> was used to extract the obtained product and then removed under reduced pressure. The title product was obtained as yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  10.19 (s, 4 H), 8.20 (s, 4H), 8.12 (d,  $J$  = 8.1 Hz, 8H), 8.07 (s, 2H), 7.88 (d,  $J$  = 8.0 Hz, 8H).

### 5.2. Synthesis of 4,4'-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)dianiline [Td]:<sup>2</sup>



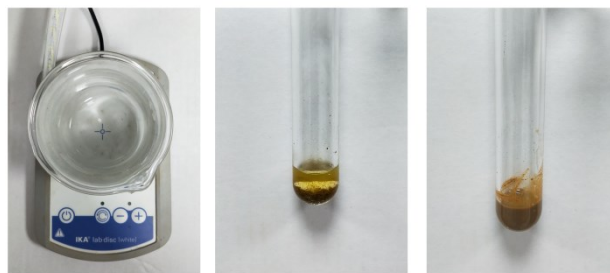
4,7-Dibromo-2,1,3-benzothiadiazole (2 g, 6.82 mmol), 4-Aminophenylboronic acid pinacol ester (3.59 g, 16.39 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.28 g, 0.24 mmol) and K<sub>2</sub>CO<sub>3</sub> (4.5 g, 32.45 mmol) were added into the mixture of 1,4-dioxane (100 mL) and water (20 mL), and the mixture was refluxed under N<sub>2</sub> atmosphere for 3 days. After cooling down to the room temperature, the residue was extracted by ethyl acetate, then washed with brine. The organic layer was combined and the solvent was removed under reduced pressure to give the crude product. The crude product was purified with silica-gel column chromatography with eluent (hexane/ethyl acetate = 1:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.86-7.82 (m, 4 H), 7.70 (s, 2H), 6.87 (d, *J* = 8.2 Hz, 4H), 3.92-3.81 (s, 4H).

### 5.3. Synthesis of TFPPy-Td-COFs



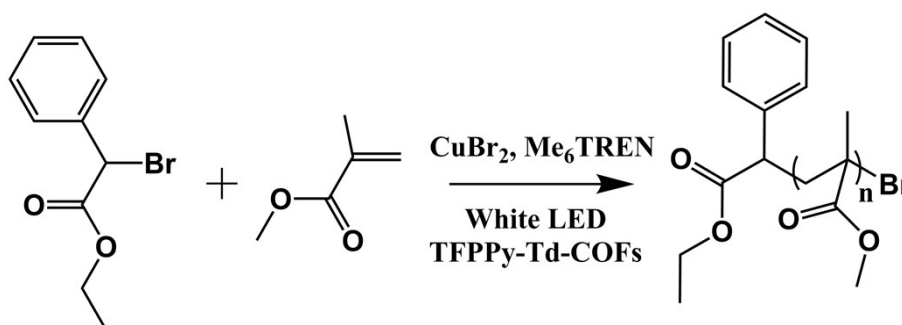
To mixture of TFPPy (20.6 mg, 0.03 mmol), and Td (21.2 mg, 0.06 mmol) in a Schlenk tube (5 mL), *o*-DCB (0.5 mL), *n*-BuOH (0.5 mL) and acetic acid (6M aq., 0.1 mL) were added. After being treated with ultrasoundwave for 3 minutes, the tube was flash frozen using liquid nitrogen and then gone through freeze-pump-thaw for three times. The tube was heated at 120 °C for 3 days to afford a red precipitate. The product was washed with THF and then Soxhlet extracted with THF for 1 day. And then the obtained solid was dried under vacuum to give the final product TFPPy-Td-COF (yield ~ 80 %).

## 6. Installation for photo-induced radical polymerization of Methyl methacrylate (MMA)



**Fig. S1** Installation for photo-induced atom transfer radical polymerization of MMA (left one). The middle image suggests the reaction mixture at the start of polymerization, and the right one shows the mixture after 8 hours.

## 7. General polymerization procedure



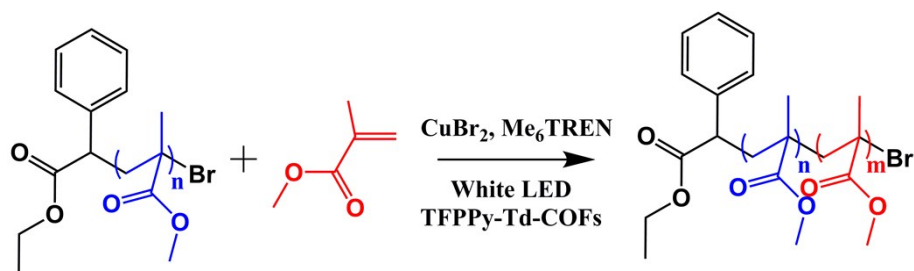
TFPPy-Td-COFs (10 mg), MMA (2 mL, 18.6 mmol), EPBA (17  $\mu\text{L}$ , 0.093 mmol),  $\text{CuBr}_2$  (4.2 mg, 0.018 mmol),  $\text{Me}_6\text{TREN}$  (12  $\mu\text{L}$ , 0.08 mmol) and anhydrous acetonitrile (0.5 mL) were introduced into a 25 mL Schlenk tube, and the mixture was deoxygenized by freeze-pump-thaw for three times and irradiated under white LED ( $13 \text{ W m}^{-1}$ ,  $15 \text{ mW cm}^{-2}$ ). Trace amounts of mixture was taken at predesigned time and measured by GPC. The monomer conversions, the number-average molecular weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) of obtained polymers were acquired by GPC.

### 7.1. Synthesis of macro-initiator PMMA-Br

TFPPy-Td-COFs (10 mg), MMA (2 mL, 18.6 mmol), EPBA (17  $\mu\text{L}$ , 0.093 mmol),  $\text{CuBr}_2$  (2.1 mg, 0.009 mmol),  $\text{Me}_6\text{TREN}$  (6  $\mu\text{L}$ , 0.04 mmol) and anhydrous acetonitrile (0.5 mL) were introduced into a 25 mL Schlenk tube. The mixture was deoxygenized by freeze-pump-thaw for three times and irradiated under

white LED ( $13 \text{ W m}^{-1}$ ,  $15 \text{ mW cm}^{-2}$ ) for 8 hours. Trace amount of the mixture was collected to examine the monomer conversion by GPC (Conv. = 47 %). The residue was dissolved in a minimal amount of THF and reprecipitated with diethyl ether for three times. The macro-initiator was afforded by filtration as white powder. Then, its molecular weight and dispersity were collected by GPC analysis.

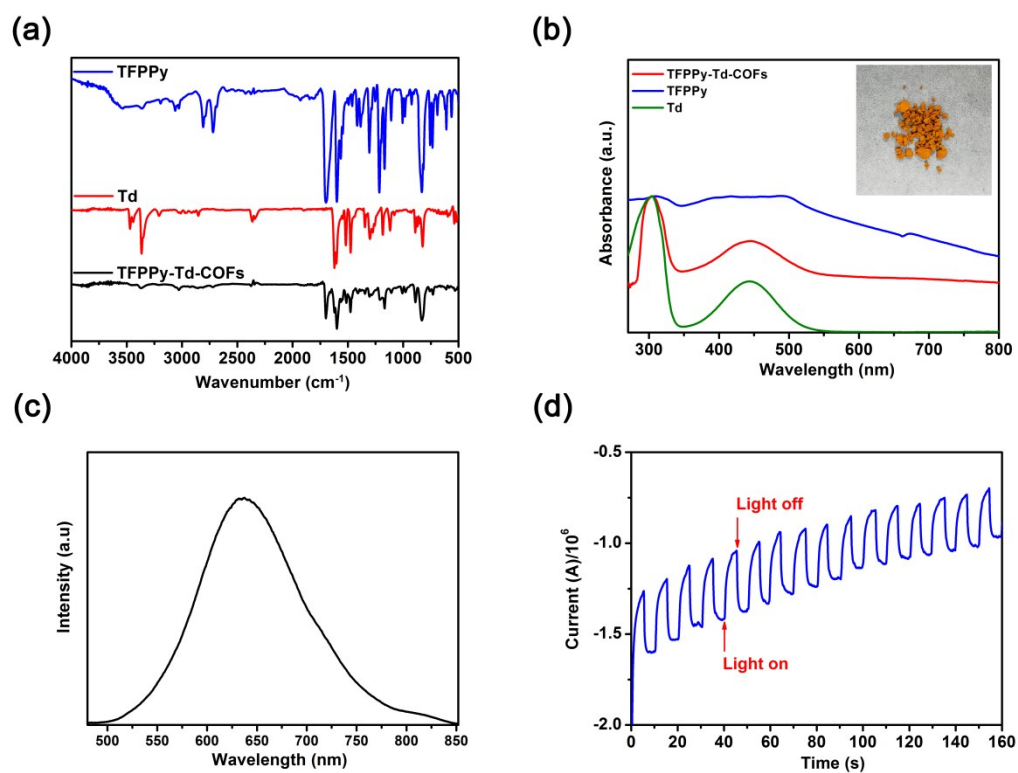
## 7.2. Typical procedures for the synthesis of block copolymer



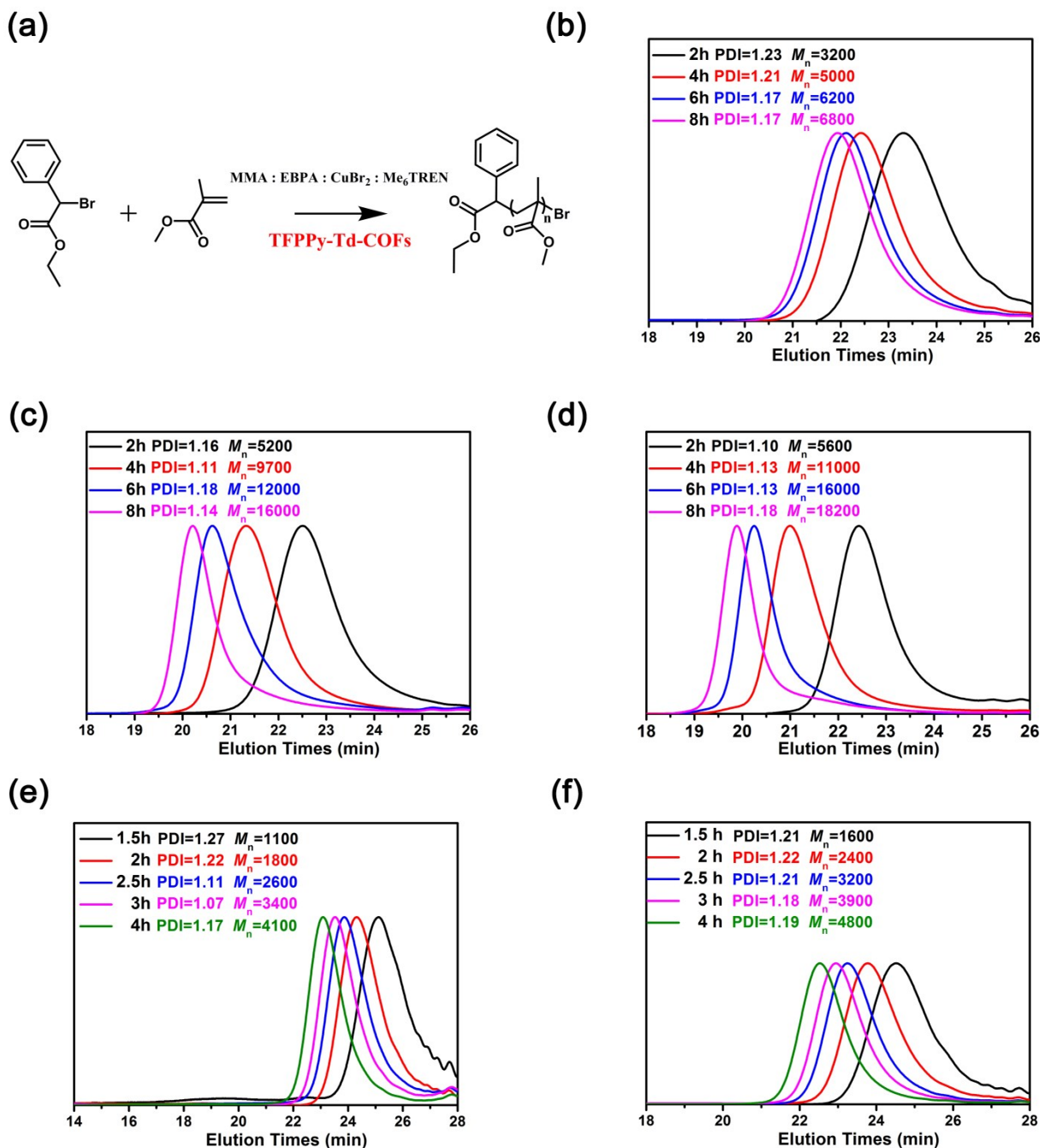
A general process for the synthesis of **PMMA-*b*-PMMA** is shown as follow: TFPPy-Td-COFs (10 mg), MMA (2 mL, 18.6 mmol), macro-initiator **PMMA-Br** (870mg, 0.093 mmol),  $\text{CuBr}_2$  (2.1 mg, 0.009 mmol),  $\text{Me}_6\text{TREN}$  (6  $\mu\text{L}$ , 0.04 mmol) and anhydrous acetonitrile (0.5 mL) were added into Schlenk tube, and the mixture was deoxygenized by freeze-pump-thaw for three times and irradiated with white light LED ( $13 \text{ W m}^{-1}$ ,  $15 \text{ mW cm}^{-2}$ ). After 4 hours, small amount of the polymer was taken and measured by GPC to determine its molecular weight and polydispersity.

## 7.3. Study of the reusability of TFPPy-Td-COFs in photo-induced ATRP

Typically reaction cycle: TFPPy-Td-COFs (20 mg), MMA (2 mL, 18.6 mmol), EPBA (17  $\mu\text{L}$ , 0.093 mmol),  $\text{CuBr}_2$  (2.1 mg, 0.009 mmol),  $\text{Me}_6\text{TREN}$  (6  $\mu\text{L}$ , 0.04 mmol) and anhydrous acetonitrile (0.5 mL) were introduced into a 25 mL Schlenk tube. The tube was degassed with nitrogen for three times. The mixture was irradiated under white LED ( $13 \text{ W m}^{-1}$ ,  $15 \text{ mW cm}^{-2}$ ) at room temperature for 8 hours. A trace amount of sample was collected and analyzed with GPC after each 2 hours reaction, by which the monomer conversion, molecular weight and polydispersity were determined. After 8 hours reaction, large amount of THF was used to wash the tube and then the catalyst was collected by centrifugation. The catalyst was washed by acetonitrile and Soxhlet extraction with THF solvent overnight before next run.

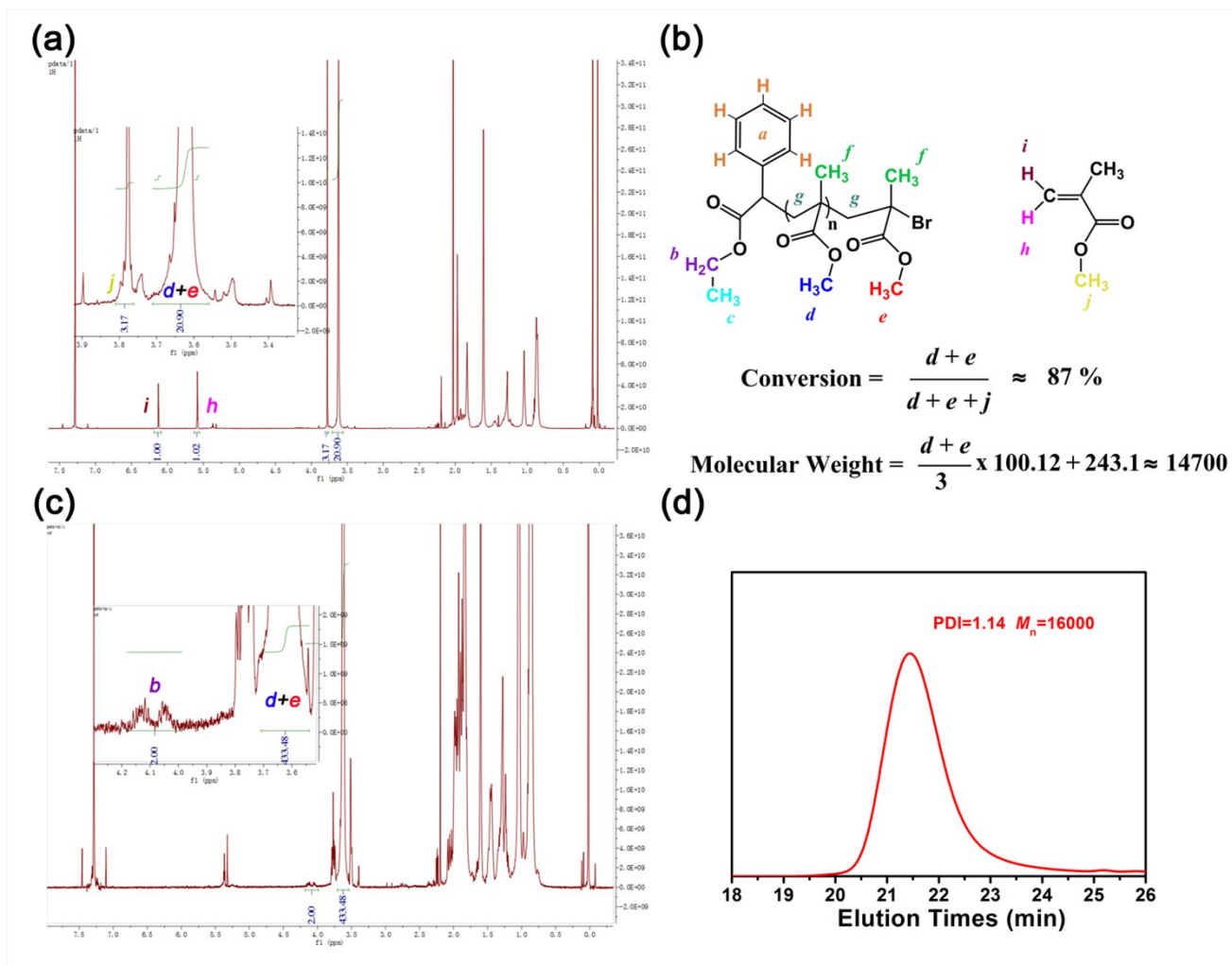


**Fig. S2** (a) FT-IR spectra for TFPPy, Td and **TFPPy-Td-COFs**, (b) the absorption spectra of TFPPy, Td and **TFPPy-Td-COFs** (inset image shows the powder state of COFs), (c) the emission spectrum of **TFPPy-Td-COFs** in acetonitrile, (d) the transient photocurrent response of **TFPPy-Td-COFs**.

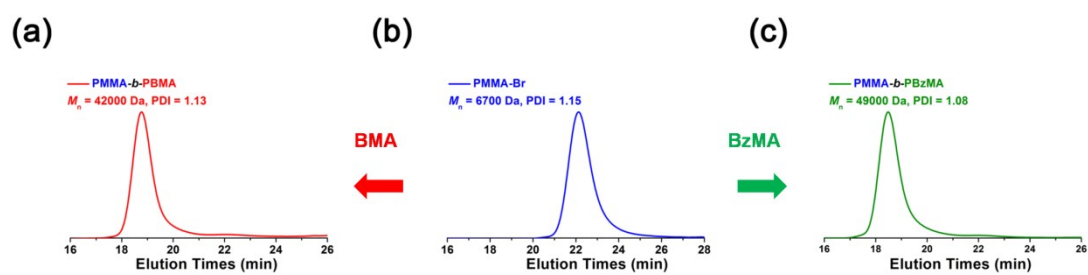


**Fig. S3** (a) Photo-ATRP protocol mediated by **TFPPy-Td-COFs**, (b), (c) and (d) GPC traces of polymers obtained by using 5 mg, 10 mg and 20 mg of **TFPPy-Td-COFs** ( $[MMA]/[EBPA]/[CuBr_2]/[Me_6TREN] = 200/1/0.2/0.9$ ) under white LED irradiation, (e), (f) GPC traces of polymers obtained by using 10 mg and 20 mg of **TFPPy-Td-COFs** ( $[MMA]/[EBPA]/[CuBr_2]/[Me_6TREN] = 200/1/0.1/0.45$ ) under white LED irradiation, respectively.

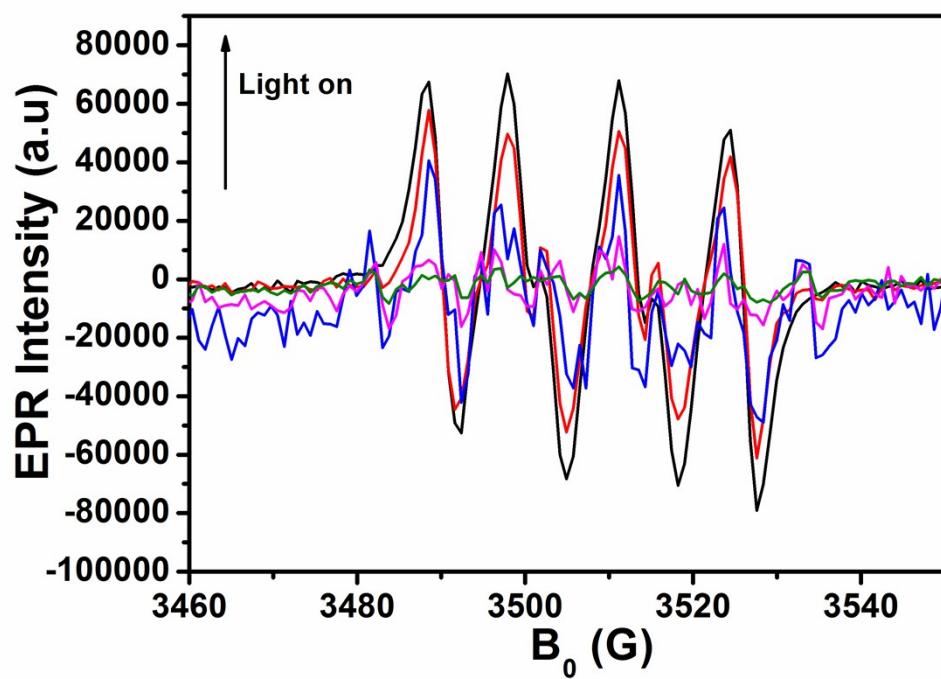




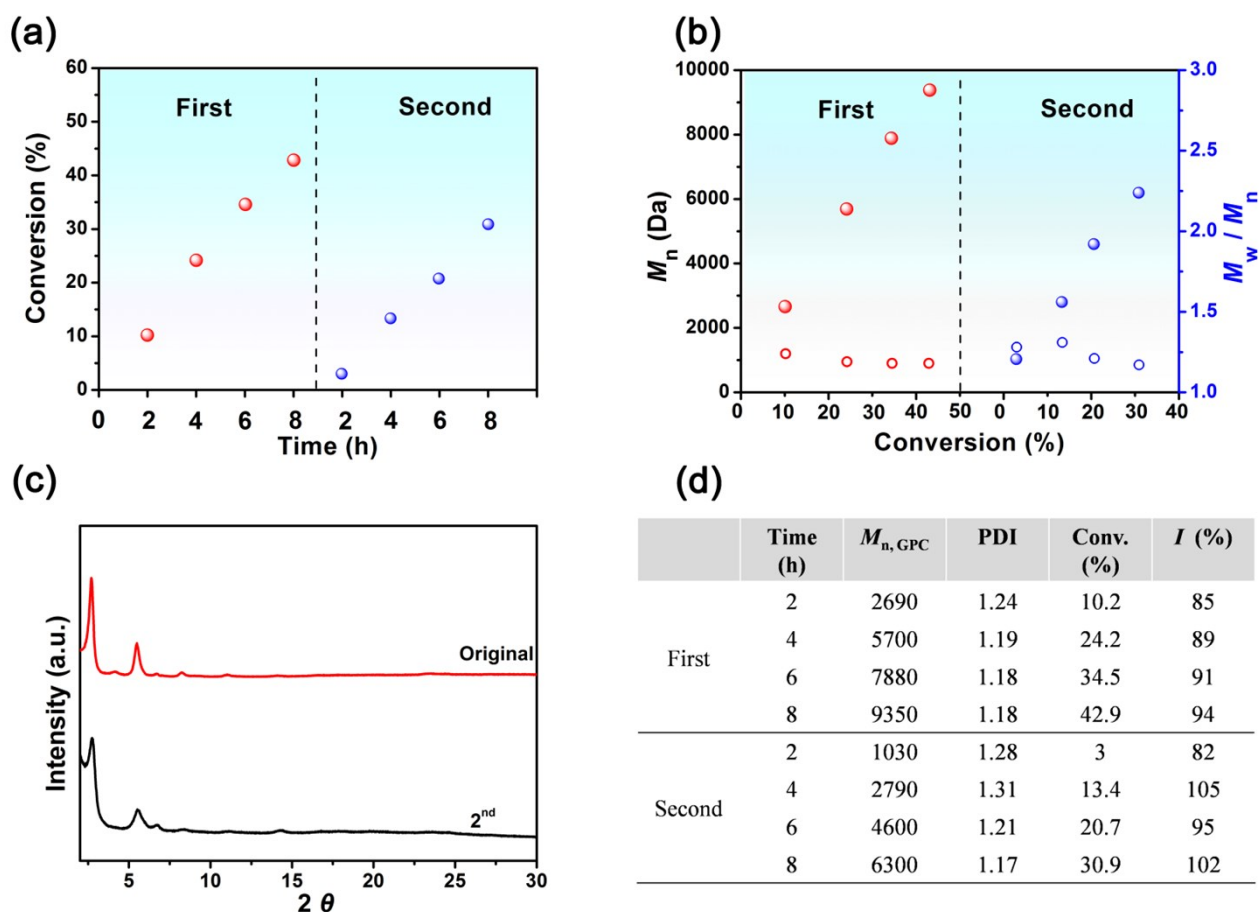
**Fig. S4** (a) The  $^1\text{H}$  NMR spectra of crude product ( $[\text{MMA}]/[\text{EBPA}]/[\text{CuBr}_2]/[\text{Me}_6\text{TREN}] = 200/1/0.2/0.9$  with 10 mg **TFPPy-Td-COFs** for 8 hours), (b) the conversion calculation formula, (c) the calculation of  $M_n$  of the obtained PMMA by  $^1\text{H}$  NMR, (d) GPC trace of the obtained polymer.



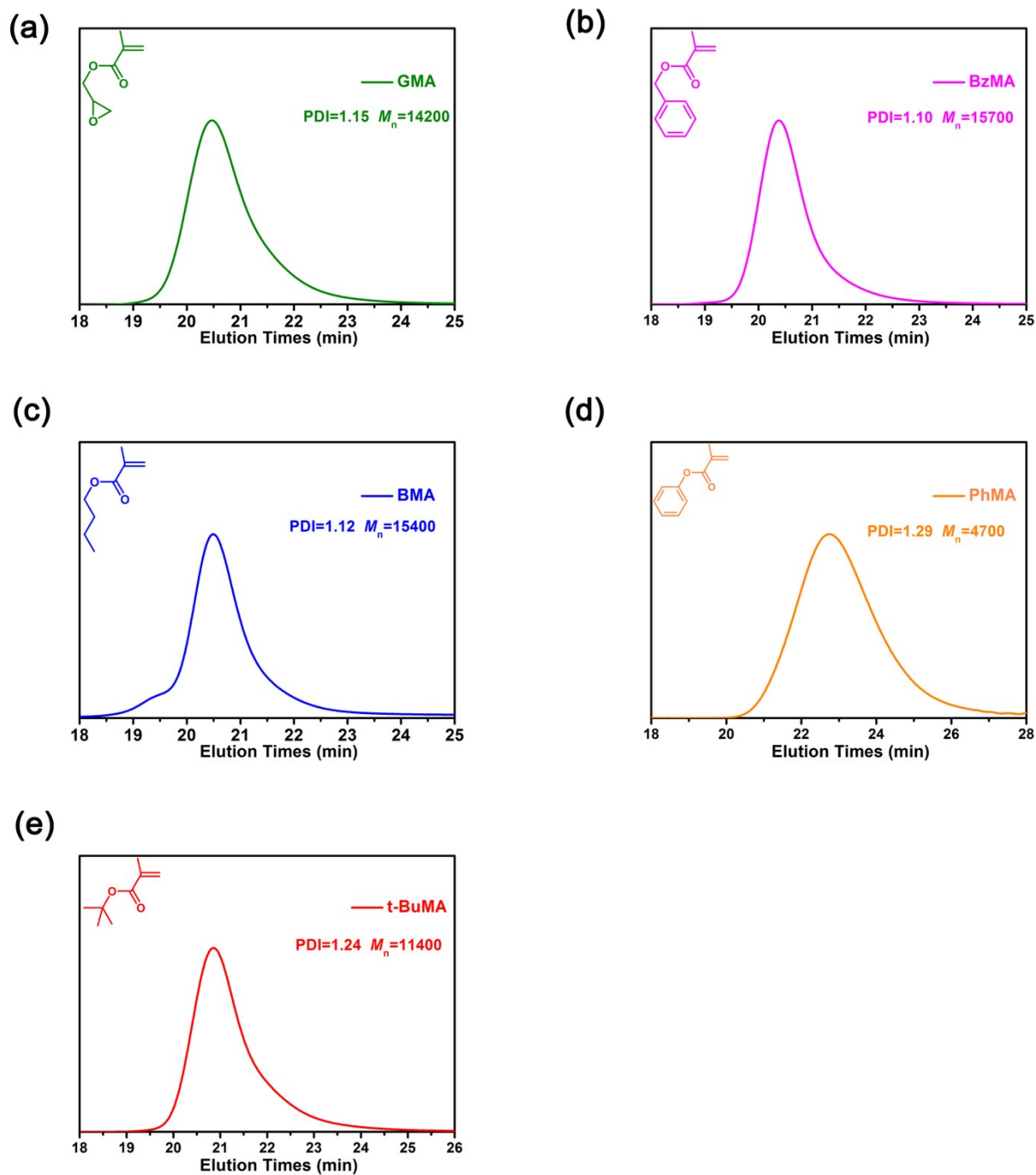
**Fig. S5** GPC traces of chain-extension experiments using PMMA-Br as macro-initiator ( $[\text{Monomer}]/[\text{PMMA-Br}]/[\text{CuBr}_2]/[\text{Me}_6\text{TREN}] = 800/1/0.2/0.9$ ) with 10 mg **TFPPy-Td-COFs** under white LED irradiation for 8 hours.



**Fig. S6** EPR spectra of TFPPy-Td-COFs measured during white light irradiation.



**Fig. S7** The results of the polymerization of MMA by using re-collected **TFPPy-Td-COFs** ( $[MMA]/[EBPA]/[CuBr_2]/[Me_6TREN] = 200/1/0.1/0.45$ ) under white LED irradiation. (a) the plot of reaction time and monomer conversion (red circle: first catalytic results; blue circle: second catalytic results), (b) the plots of monomer conversion with number average molecule weight and polydispersity of the obtained polymer, respectively (red circle: first catalytic results; blue circle: second catalytic results), (c) The XRD curves of **TFPPy-Td-COFs** before used and after 2 time used, (d) the detail data of the polymerization of MMA.



**Fig. S8** GPC traces of different polymers obtained from different monomers.

**Table S1** The polymerization results of MMA by **TFPPy-Td-COFs** mediated ATRP under white LED irradiation.<sup>a</sup>

No.	[MMA]/[EPBA]/[Cu <sup>II</sup> ] /[Me <sub>6</sub> TREN]/[Solv.]	Cat. (mg)	Time (h)	$M_{n, \text{GPC}}$ (Da)	$M_{n, \text{th}}^{\text{b}}$ (Da)	PDI	Conv. <sup>c</sup> (%)	$I^{\text{d}}$ (%)
1	200/1/0.2/0.9/103	20	2	5600	4050	1.10	19	72.3
			4	11000	8850	1.13	43	80.5
			6	16000	13260	1.13	65	82.9
			8	18200	15060	1.18	74	82.7
2	200/1/0.2/0.9/103	10	2	5200	3650	1.16	17	70.2
			4	9700	8250	1.11	40	85.1
			6	12000	11060	1.18	54	92.2
			8	16000	14660	1.14	72	91.6
3	200/1/0.2/0.9/103	5	2	3200	2280	1.23	10	71.4
			4	5060	4100	1.21	19	81.1
			6	6250	4580	1.17	22	73.3
			8	6800	5100	1.17	24	74.9
4	200/1/0.1/0.45/103	20	1.5	1650	1240	1.21	5	75.2
			2	2400	2240	1.22	10	93.3
			2.5	3200	3350	1.21	16	104.7
			3	3900	3700	1.18	17	94.8
			4	4820	5150	1.19	25	106.9
5	200/1/0.1/0.45/103	10	1.5	1120	890	1.27	3	79.4
			2	1790	1490	1.22	6	83.2
			2.5	2620	1950	1.11	8	74.4
			3	3380	2640	1.07	12	78.1
			4	4100	3950	1.17	19	95.3
6	200/1/0.1/0.45/103	10 mg TFPPy	8	1200	350	1.16	2	30
7	200/1/0.1/0.45/103	10 mg Td	8	1100	250	1.04	0.1	22
8 <sup>e</sup>	200/1/0.2/0.9/103	10 mg	10	16700	15060	1.16	74	90

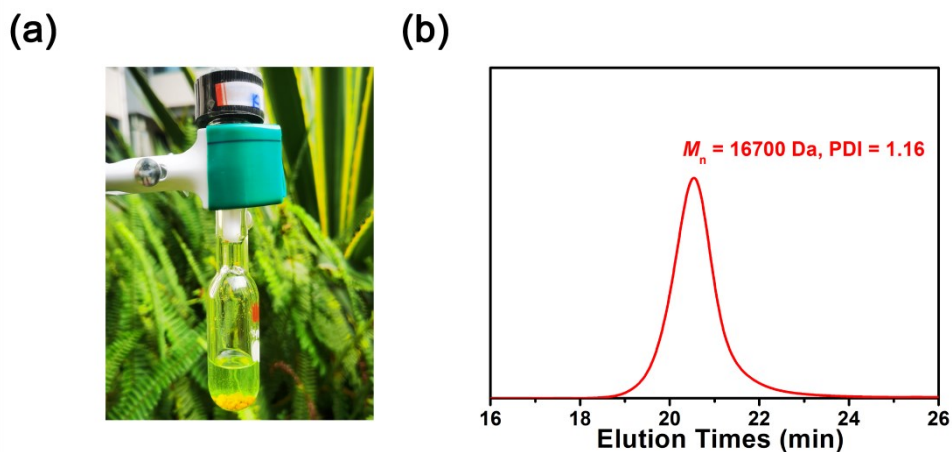
<sup>a</sup>All experiments were conducted at room temperature and protected with nitrogen using acetonitrile as solvent under white LED irradiation (13 W m<sup>-1</sup>, 15 mW cm<sup>-2</sup>);

<sup>b</sup> $M_{n, \text{th.}} = M_{\text{W}}(\text{initiator}) + M_{\text{W}}(\text{monomer}) \times \text{Conv.} \times ([\text{monomer}]/[\text{initiator}]);$

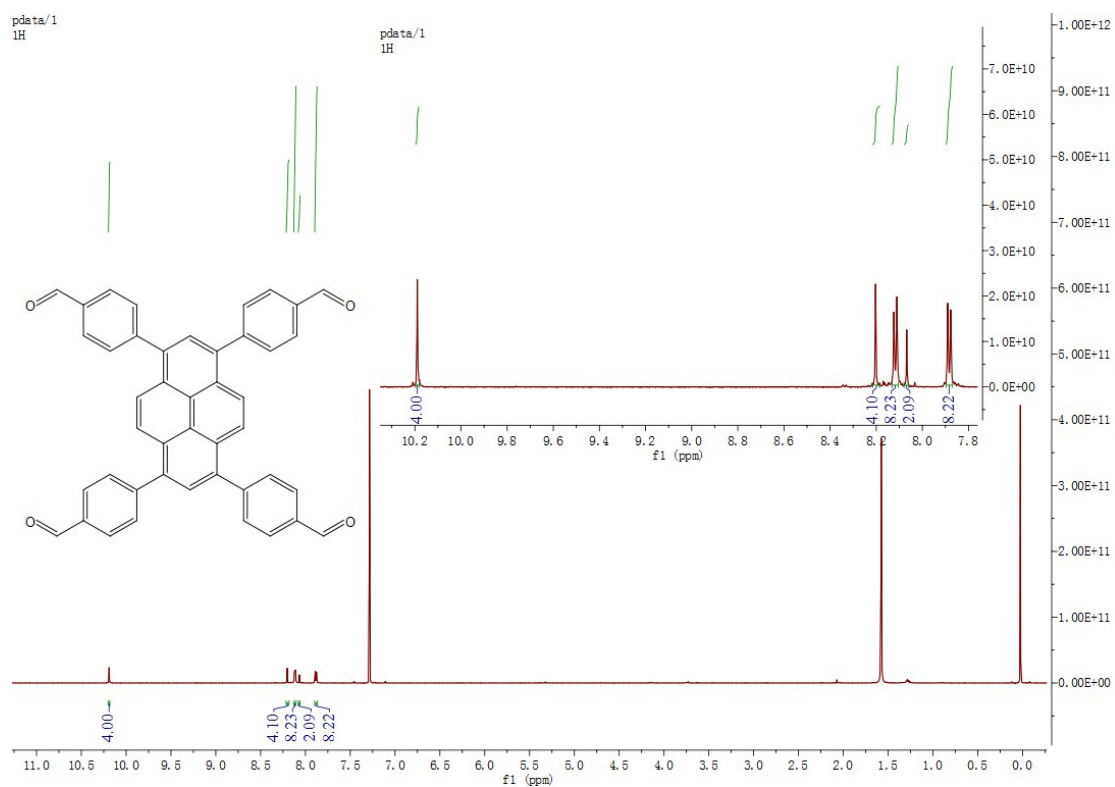
<sup>c</sup>Conv. (%) was calculated from GPC data;

<sup>d</sup> $I (\%) = M_{n, \text{th.}}/M_{n, \text{GPC}} \times 100;$

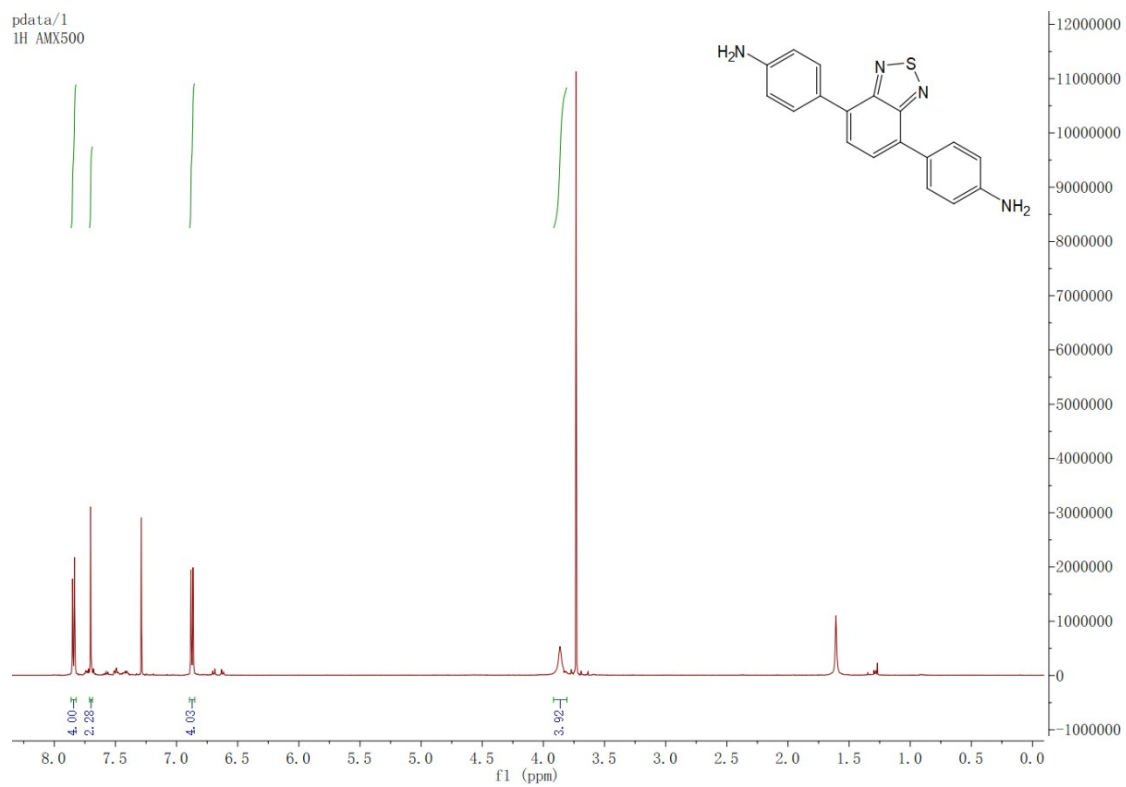
<sup>e</sup>No. 8 was used natural sunlight as light source.



**Fig. S9** (a) Photograph of ATRP polymerization of MMA under natural sunlight, (b) GPC trace of the obtained PMMA after 10 hours irradiation.

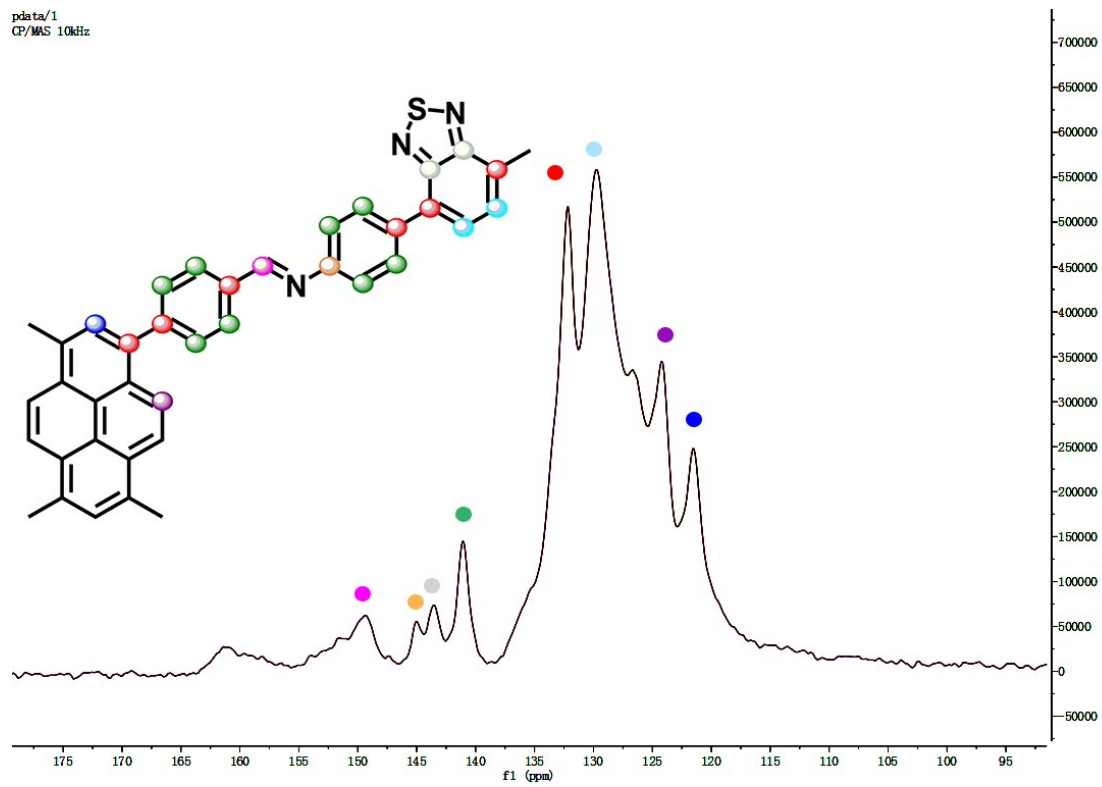


**Fig. S10**  $^1\text{H}$  NMR spectra of TFPPy.



**Fig. S11**  $^1\text{H}$  NMR spectra of Td.





**Fig. S12**  $^{13}\text{C}$  NMR spectrum of TFPPy-Td-COFs.

**Reference:**

1. E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen and D. Jiang, *Science*, 2017, **357**, 673-676.
2. S. Wang, Q. Sun, W. Chen, Y. Tang, B. Aguila, Y. Pan, A. Zheng, Z. Yang, L. Wojtas, S. Ma and F.-S. Xiao, *Matter*, 2020, **2**, 416-427.