Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Ligand regulated strategy of COF-based photocatalyst for ROS-mediated RAFT polymerization

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Materials

2,5-dimethoxy-terephthalaldehyde (DMTA), 4-aminobenzonirile (>99%), 2,5-dihydroxyterephthalaldehyde (DHTA), 2-hydroxypropyl methacrylate (HPMA, 97%, stabilized with 4-methoxyphenol), poly(ethleneglycol) dimethacrylate (PEGMA, M=475 g/mol), 2-Hydroxypropyl methacrylate (HPMA), 2-iodo-2-methylpropionitrile (CP-I) were purchased from Aldrich, all monomer solution were passed through a neutral alumina column before used.

Light-emitting diode flex strip (15 mW cm^{-2}) was purchased from Philips company and used as light source.

Methods

^{1}H NMR and solid ^{13}C NMR of materials were detected on Bruker Advance III. Ultraviolet-visible spectrum (UV-vis DRS) was recorded on Varian Cary 300 UV-vis spectrophotometer. Fourier transform infrared (FT-IR) spectra was collected on Thermo Scientific Nicolet i5. Powder X-ray diffraction (P-XRD) was measured by EmpyreanDY1602 with Cu Kα radiation. The surface areas and pore size distribution of samples were calculated by Autosorb-iQ analyzer (Quantachrome). Solid state photoluminescence spectra were recorded by Hitachi F-7600 spectrofluorometer, and the fluorescence lifetime was performed under DeltaProTM fluorescence lifetime system (Horiba JobinYvon IBH Ltd. Scotland). The field-emission scanning electron microscope (Nova Nano SEM 230) equipped with an energy dispersive detector and high-resolution transmission electron microscopy (HR-TEM) were used to record the morphology and lattice structure of sample. Edinburgh fls980 was used to record fluorescence spectra at different temperature.

Gel permeation chromatography (GPC) with refractive index detector (Waters, 2414) was employed to record number average molecular weight (M_n) and molecular weight dispersity (M_w/M_n) of polymer. PMMA was served as standard to calibrate GPC and use THF as elution at a flow rate of 1.00 mL/min (30 ℃).

Photoelectronchemical measurements

Photoelectrochemical was recorded by CHI 760 electrochemical workstation, using sodium sulfate solution (0.2M) as electrolyte. Platinum plate, saturated Ag/AgCl electrode were served as

counter electrode and reference electrode, and working electrode were combined to construct three-electrode eletrochemical cell.

Working electrode: COF (5 mg), Nafio solution (2 μL) were added into ethanol (1 mL) to form a mixture solution after sonicating. The solution was dropped onto the surface of FTO glass plate (1 × 1 cm^2) and dried under room temperature before texting.

Mott-Schottky plots (MS) and electrochemical impedance spectroscopy (EIS) were measured in a three-electrode cell at the frequencies of 500 Hz, 1000 Hz and 2000 Hz. The transient photocurrent response was recorded by switching on/off the light (300 W Xe-lamp, λ≥420 nm).

Experiments section

1. Preparation of COFs.

TAPT-DMTA-COF: TAPT (28.3 mg, 0.08 mmol) and DMTA (23.3, 0.12 mmol) were mixed in Schlenk tube (10 mL), then 1,4-dioxane (0.2 mL) and mesitylene (0.8 mL) were added into the tube. Acetic acid solution (0.1 mL, 6M) was served as catalyst. After gone through freeze-pump-threw in liquid nitrogen for three times, the tube was sealed under vacuum and put into oven for 3 days at 120 ºC to afford yellow precipitate. The product was washed with THF and subjected to soxhlet extraction with THF overnight. After dried under vacuum, the final product was obtained as a yellow powder (yield ~83%).

TAPT-DMTA/TP-COF: TAPT (28.3 mg, 0.08 mmol), DMTA (11.7, 0.06 mmol), and 1,4-phthalaldehyde (8.1, 0.06 mmol) were mixed in Schlenk tube (10 mL), then 1,4-dioxane (0.25 mL) and mesitylene (0.75 mL) were added into the tube. Acetic acid solution (0.1 mL, 6M) was served as catalyst. After gone through freeze-pump-threw in liquid nitrogen for three times, the tube was sealed under vacuum and put into oven for 3 days at 120 ºC to afford yellow precipitate. The product was washed with THF and subjected to soxhlet extraction with THF overnight. After dried under vacuum, the final product was obtained as a yellow powder (yield ~80%).

TAPT-TP-COF: TAPT (28.3 mg, 0.08 mmol) and 1,4-phthalaldehyde (16.1, 0.12 mmol) were mixed in Schlenk tube (10 mL), then 1,4-dioxane (0.5 mL) and *n*-BuOH (0.5 mL) were added into the tube. Acetic acid solution (0.1 mL, 6M) was served as catalyst. After gone through freeze-pump-threw in liquid nitrogen for three times, the tube was sealed under vacuum and put into oven for 3 days at

120 ºC to afford yellow precipitate. The product was washed with THF and subjected to soxhlet extraction with THF overnight. After dried under vacuum, the final product was obtained as a yellow powder (yield ~78%).

TAPT-DHTA-COF: TAPT (28.3 mg, 0.08 mmol) and DHTA (19.9, 0.12 mmol) were mixed in Schlenk tube (10 mL), then 1,4-dioxane (0.2 mL) and mesitylene (0.8 mL) were added into the tube. Acetic acid solution (0.1 mL, 6M) was served as catalyst. After gone through freeze-pump-threw in liquid nitrogen for three times, the tube was sealed under vacuum and put into oven for 3 days at 120 ºC to afford yellow precipitate. The product was washed with THF and subjected to soxhlet extraction with THF overnight. After dried under vacuum, the final product was obtained as a dark red powder (yield ~88%).

2. Electron paramagnetic resonance (EPR) study

Using 2,2,6,6-tetramethylpiperidine (TEMP) as free radical scavenger to detect $^1O_2$ generated by COFs in 1 mL mixture solvent (CH_3CN:H_2O=4:1) mixed with 1mg of COF. The EPR experiments were carried out under light irradiation (500 W xenon lamp, $\lambda > 420$ nm).

5,5-dimethyl-1-pyrroline N-oxide (DMPO) was chosen as scavenger to detect the generation of $O_2^{\bullet-}$ radicals in 1 mL methanol mixed with 1mg of COF. The EPR experiments were carried out under light irradiation (500 W xenon lamp, $\lambda > 420$ nm).

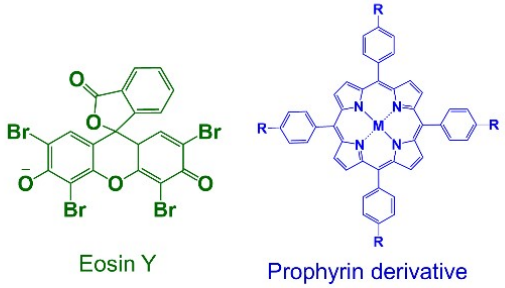
3. General methods of polymerization

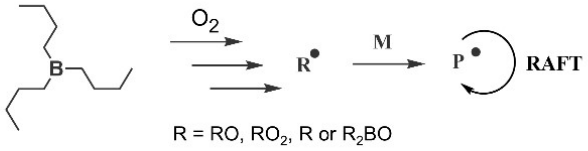
Typically, COF (10 mg), PEGMA (475 g/mol, 1 mL, 2.3 mmol), CPADB (6.3 mg, 0.023 mmol), H_2O (1 mL) and TEA were added into glass vial (3 mL) under open-to-air condition. The reaction was conducted under magnetic stirring under room temperature by white light irradiation (15 mW, cm^{-2}). A trace amount of mixture was taken with needle at a predetermined time and measured by GPC to obtain the polymeric molecular weight (M_n) and molecular weight dispersity (M_w/M_n). The monomer conversion was analyzed by ^1H NMR.

Chain extension polymerization by in-suit synthetic processes: PPEGMA-I was synthesized in aqueous solution with a molar ration of [PEGMA]:[CP-I] =100:1 under aqueous condition (H_2O=1mL, PEGMA=1mL, TAPT-DMTA/TP-COF=10mg). When the monomer conversion exceeds 90%, the

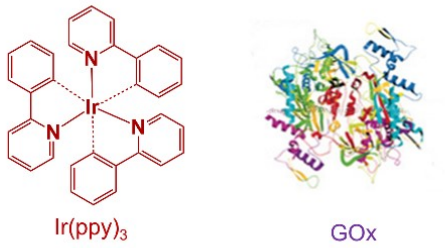
second monomers HPMA (1 mL) was added for further polymerization. The sample was taken at predetermined time and characterized by GPC to give the value of M_n and M_w/M_n of product.

Cycling experiments: COF (10 mg), PEGMA (475 g/mol, 1 mL, 2.3 mmol), CPADB (6.3 mg, 0.023 mmol), H_2O (1 mL) and TEA (32 μL, 0.23 mmol, 10 eq.) were added into glass vial (3 mL) under open-to-air condition. After reaction, the solid and liquid phases were separated by centrifugation, and a trace amount of polymer was collected and then analyzed by ^1H NMR and GPC to obtain the monomer conversion. The COF was recovered and washed with THF, and reused after dried.

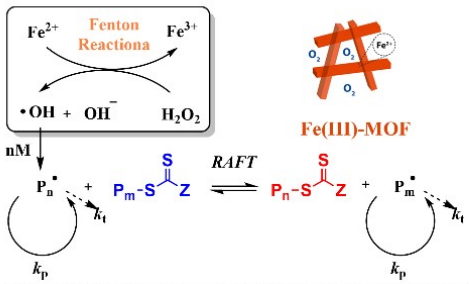




(b) Alkylborane catalyze RAFT polymerization by reacting with oxygen to form initiator



(a) Photocatalysts for RAFT polymerization by converting oxygen into inactivate speices



(c) Fenton reaction mediated RAFT polymerization by using H_2O_2 as co-initiator under open-to-air condition

Scheme S1. Several structures of previous reports photocatalysts for mediating RAFT polymerization under aerobic condition.[1] (a) Oxygen consuming photocatalysts, (b) oxygen-mediated photocatalyst and (c) Fenton-reaction for initiating RAFT polymerization using H_2O_2 as co-initiator under open-to-air condition.

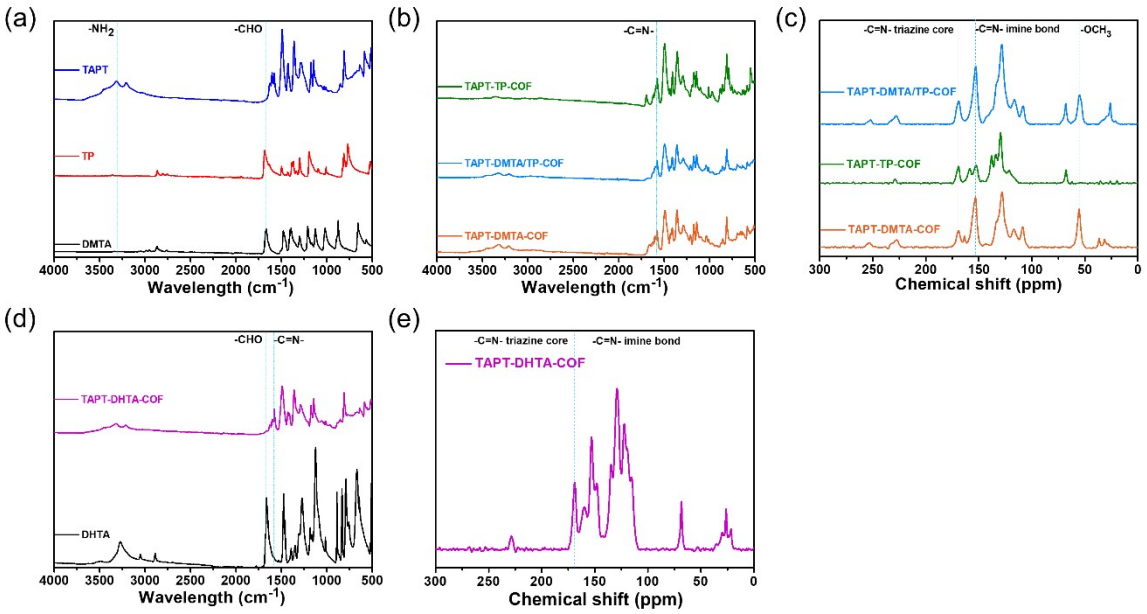


Figure S1. FT-IR spectra of monomers and COFs (a, b, d) and ^{13}C NMR spectra of synthetic COFs (c, e).

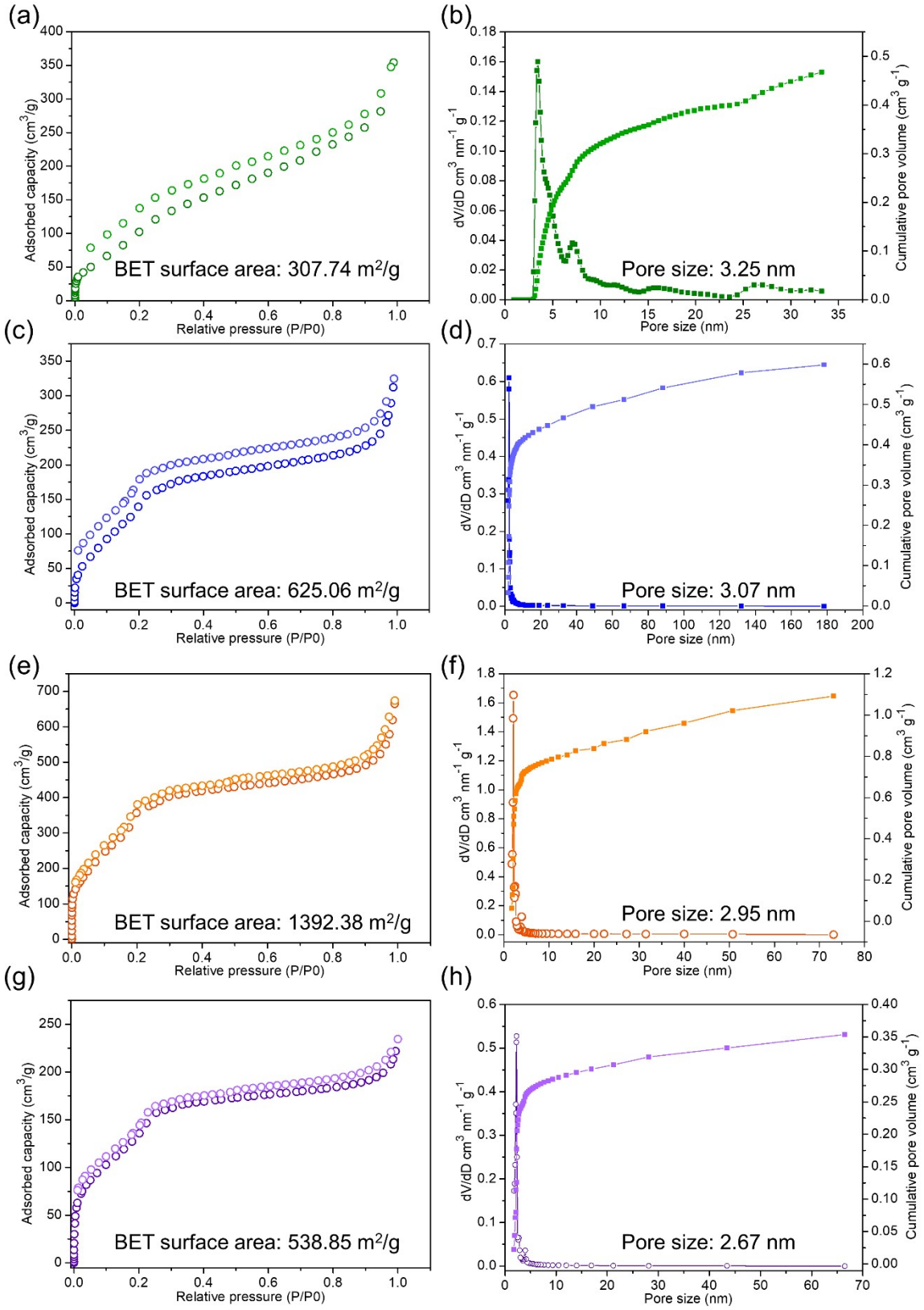


Figure S2. The nitrogen adsorption-desorption isothermal and pore distribution and pore volume of (a, b) TAPT-TP-COF, (c, d) TAPT-DMTA/TP-COF, (e, f) TAPT-DMTA-COF and (g, h) TAPT-DHTA-COF.

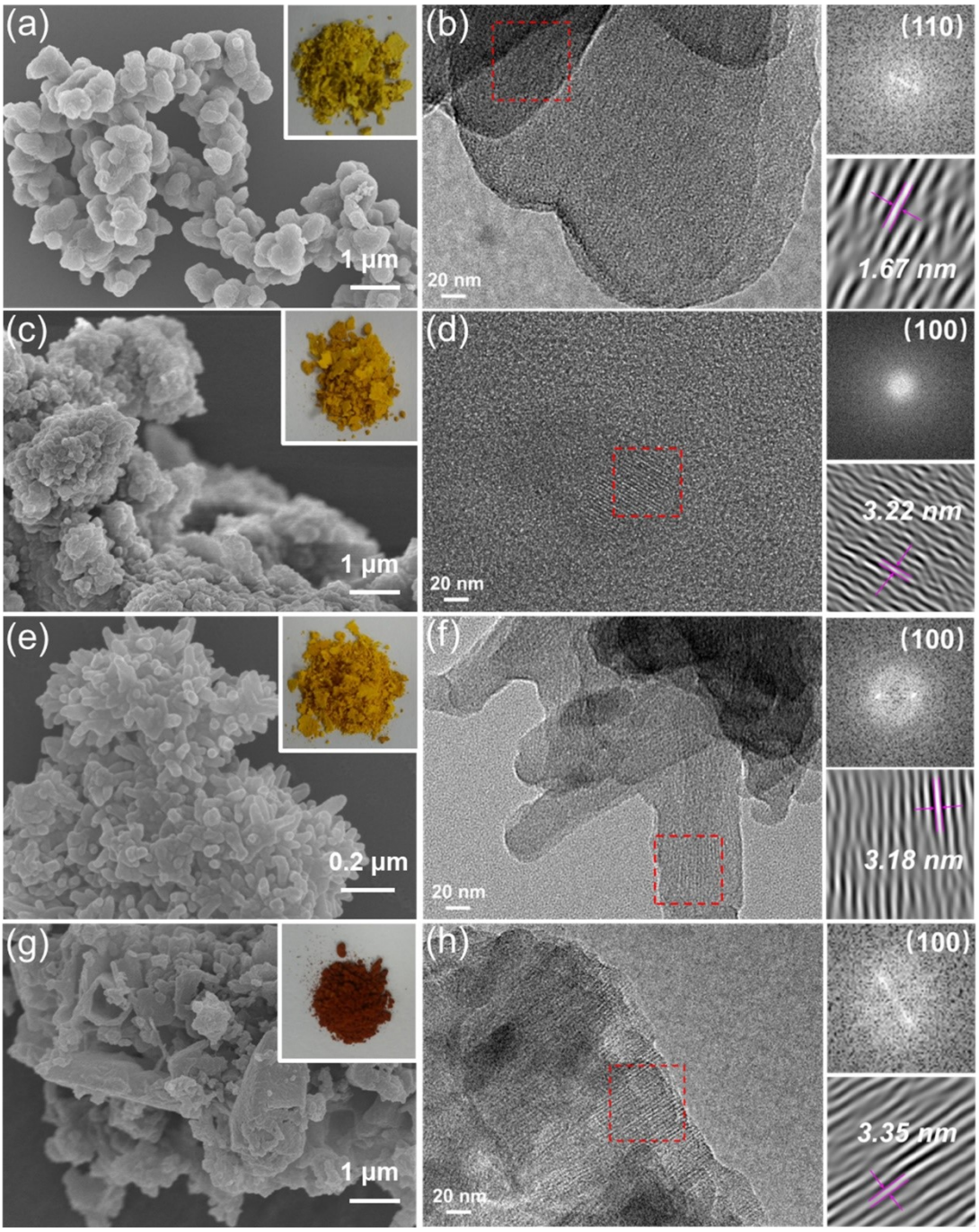


Figure S3. SEM and TEM images of (a, b) TAPT-TP -COF, (c, d) TAPT-DMTA/TP-COF, (e, f) TAPT- DMTA-COF and (g, h) TAPT-DHTA-COF.

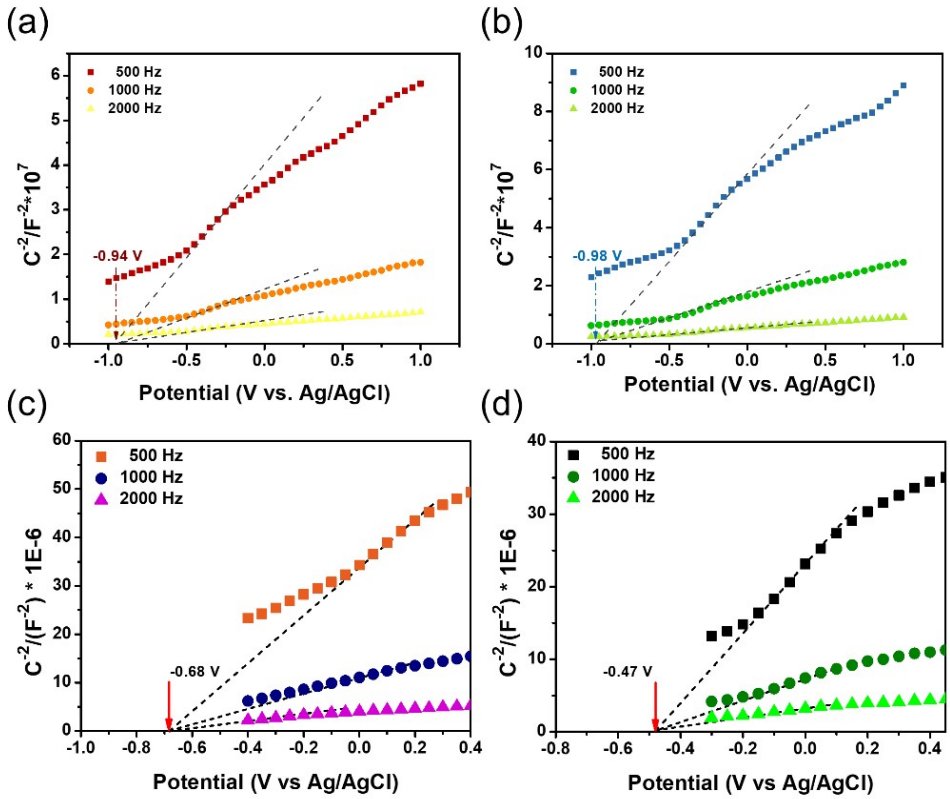
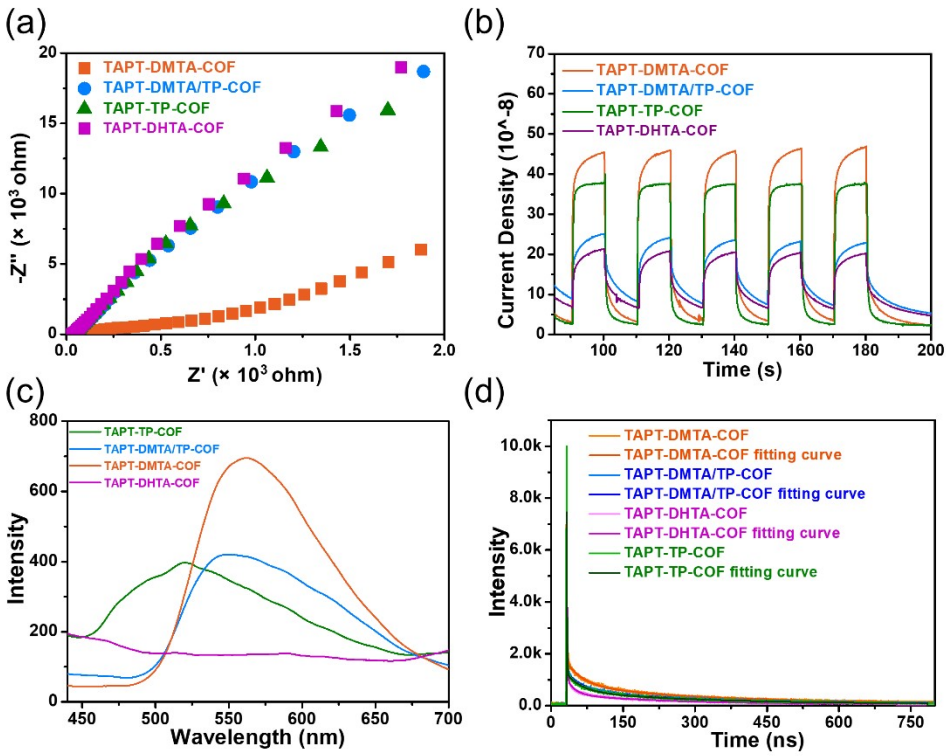


Figure S4. Mott-Schottky plots of (a) TAPT-DMTA-COF, (b) TAPT-DMTA/TP-COF, (c) TAPT-TP-COF and (d) TAPT-DHTA-COF.



#	τ1 (ns)	τ2 (ns)	τ3 (ns)	Average lifetime (ns)
TAPT-DMTA-COF	35.03	259.56	0.77	23.08
TAPT-DMTA/TP-COF	30.01	232.35	0.66	14.10
TAPT-DHTA-COF	17.58	201.11	0.90	9.66
TAPT-TP-COF	30.91	239.14	0.81	16.17

Figure S5. (a) Nyquist plots and (b) photocurrent response of COFs. (c) Photoluminescence spectra of materials with the excitation wavelength of 365 nm and (d) time-resolved photoluminescence spectra of COFs.

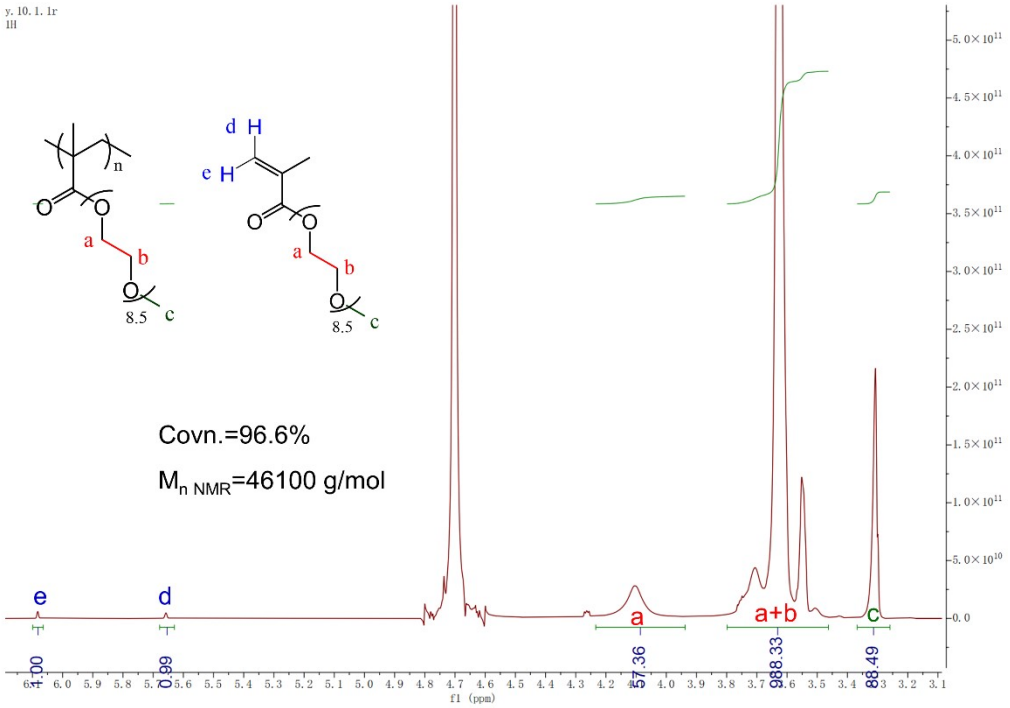


Figure S6. [1] H NMR spectrum of obtained crude product in D_2O for calculating monomer conversion by using TAPT-DMTA/TP-COF as photocatalyst ([PEGMA]:[CPADB]=100:1 in aqueous system under open-to-air condition).

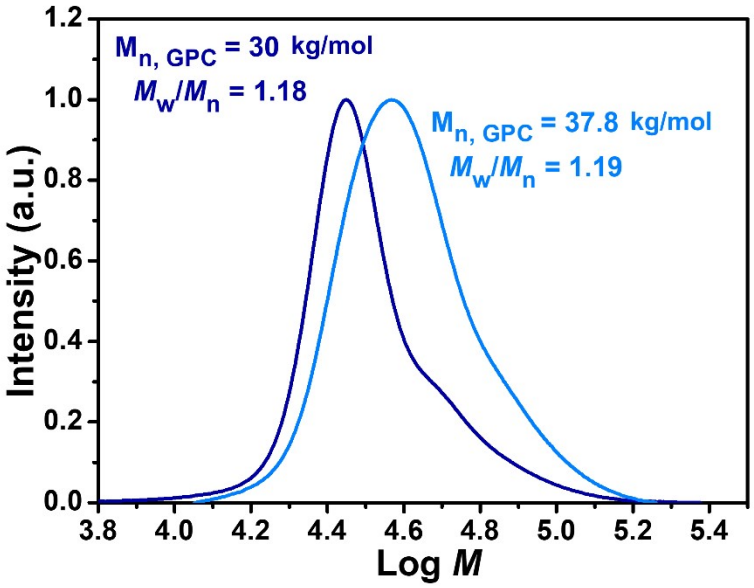


Figure S7. Chain-extension reaction by using $PPEGMA_{475}$ as macroinitiator, HPMA as monomers and TAPT-DMTA/TP-COF as photocatalyst.

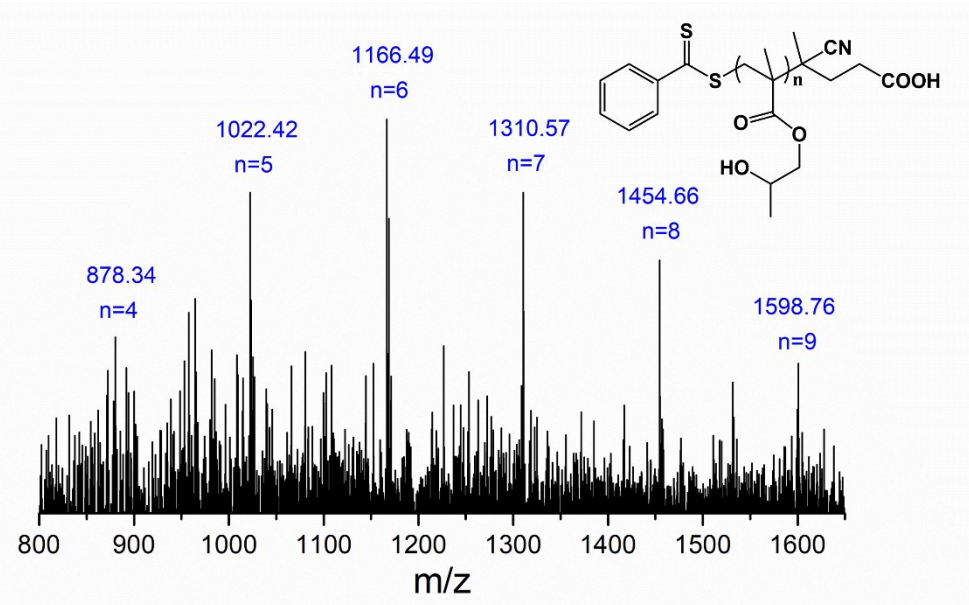


Figure S8. LC-QTOF-MS spectrometry with HPMA (using TAPT-DMTA-COF as photocatalyst, DP = 30, [CPADB] : [TEA] = 100 : 10).

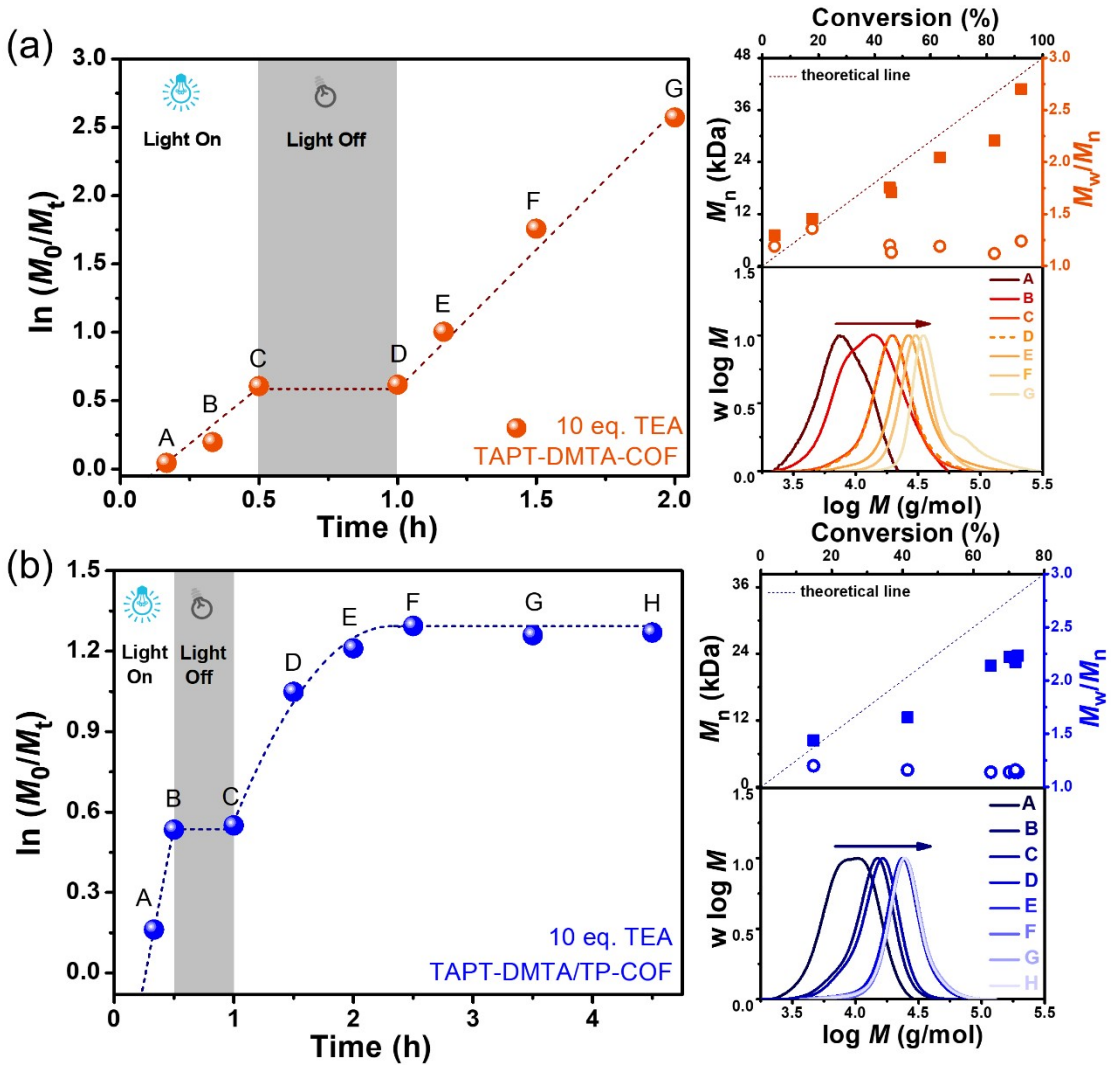


Figure S9. (a) Kinetic plots and temporal control in RAFT polymerization by using (a) TAPT-DMTA-COF and (b) TAPT-DMTA/TP-COF as photocatalysts with the molar ration of [$PEGMA_{475}$]:[CPADB]:[TEA]=100:1:10 in aqueous solution.

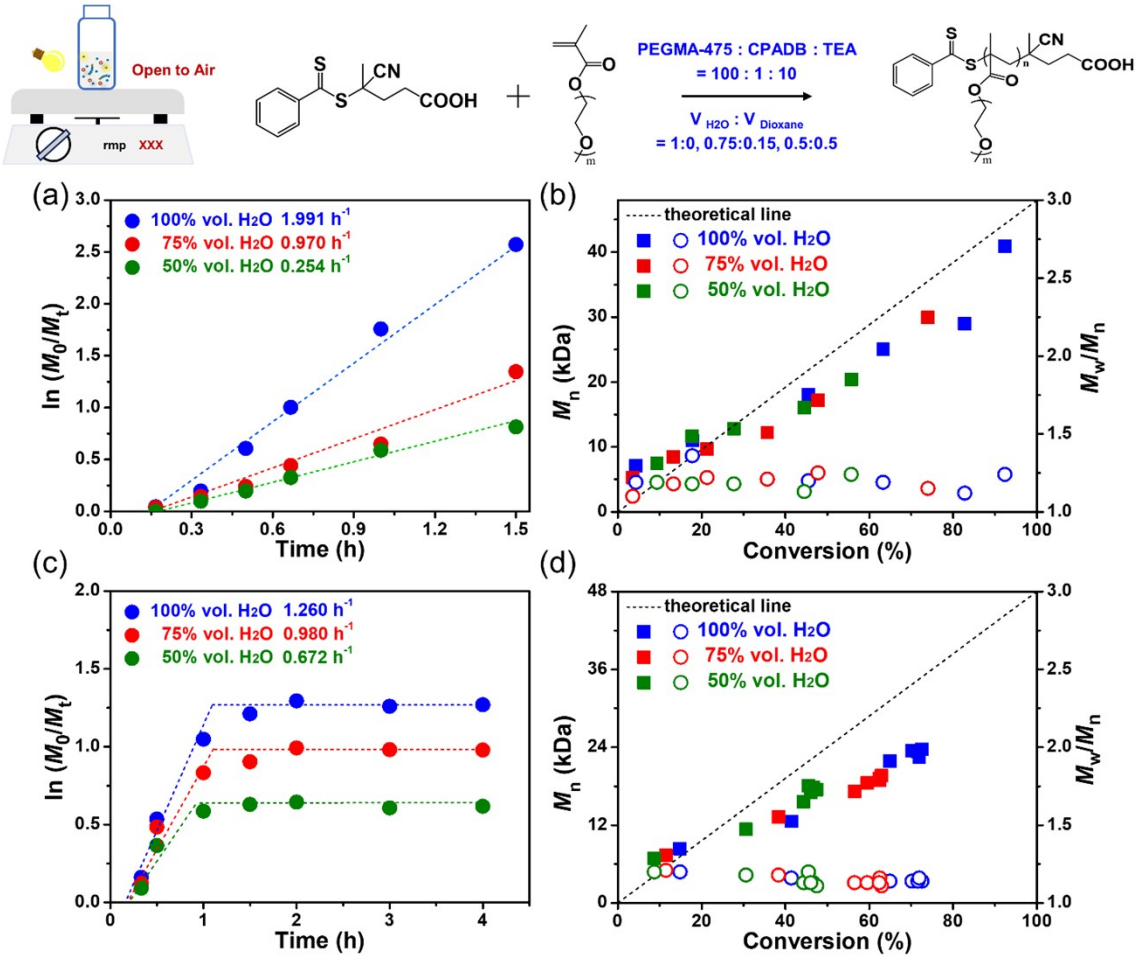


Figure S10. Kinetic plots and M_n vs conversion at different volume of H_2O and dioxane by using (a, b) TAPT-DMTA-COF and (c, d) TAPT-DMTA/TP-COF as photocatalysts under white light irradiation, using molar ration of [PEGMA] : [CPADB] : [TEA] = 100 : 1 : 10.

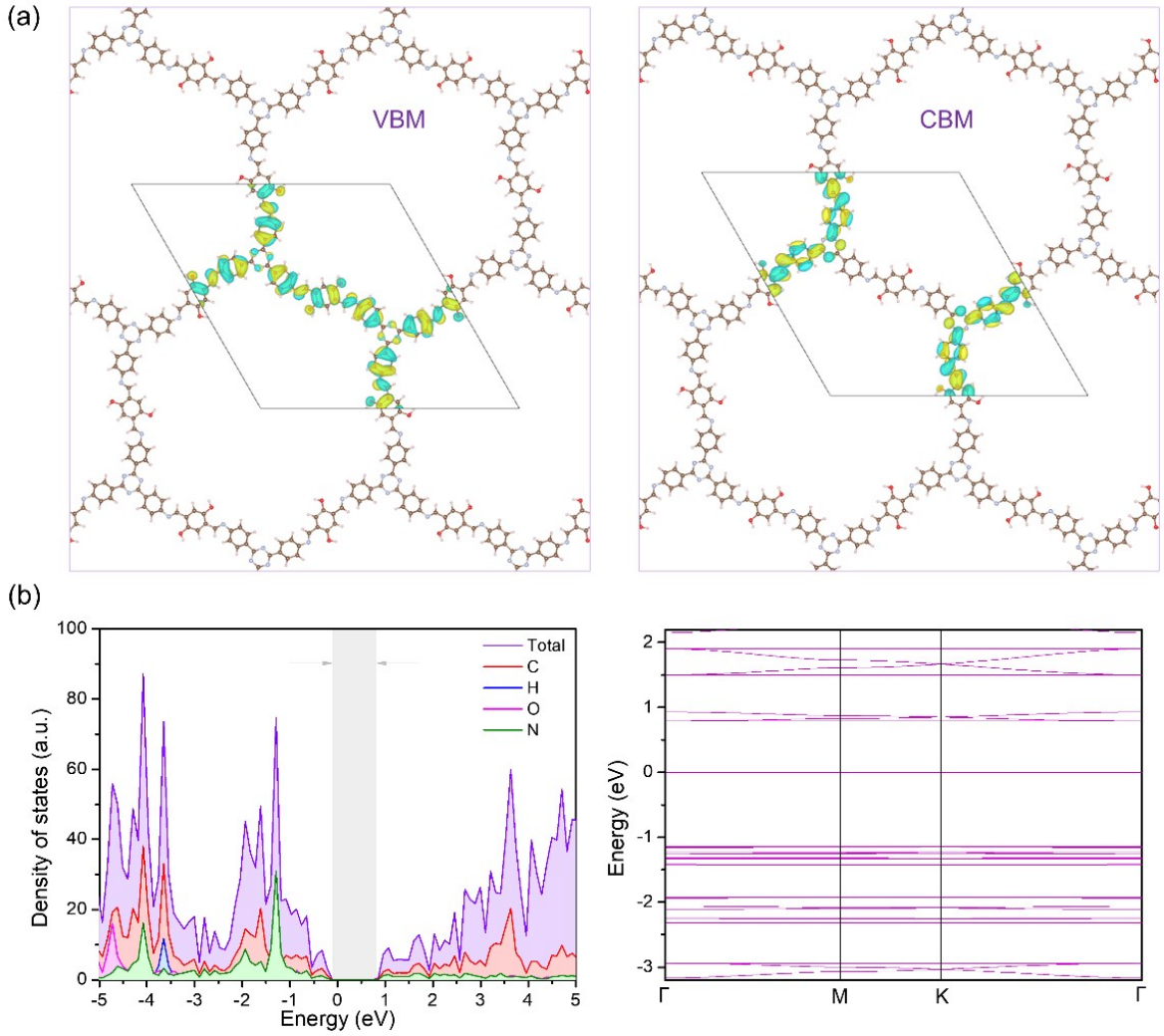


Figure S11. The charges spatial distribution of (a) VBM and CBM, (b) electron density of states and energy band gap structure of TAPT-DHTA-COF.

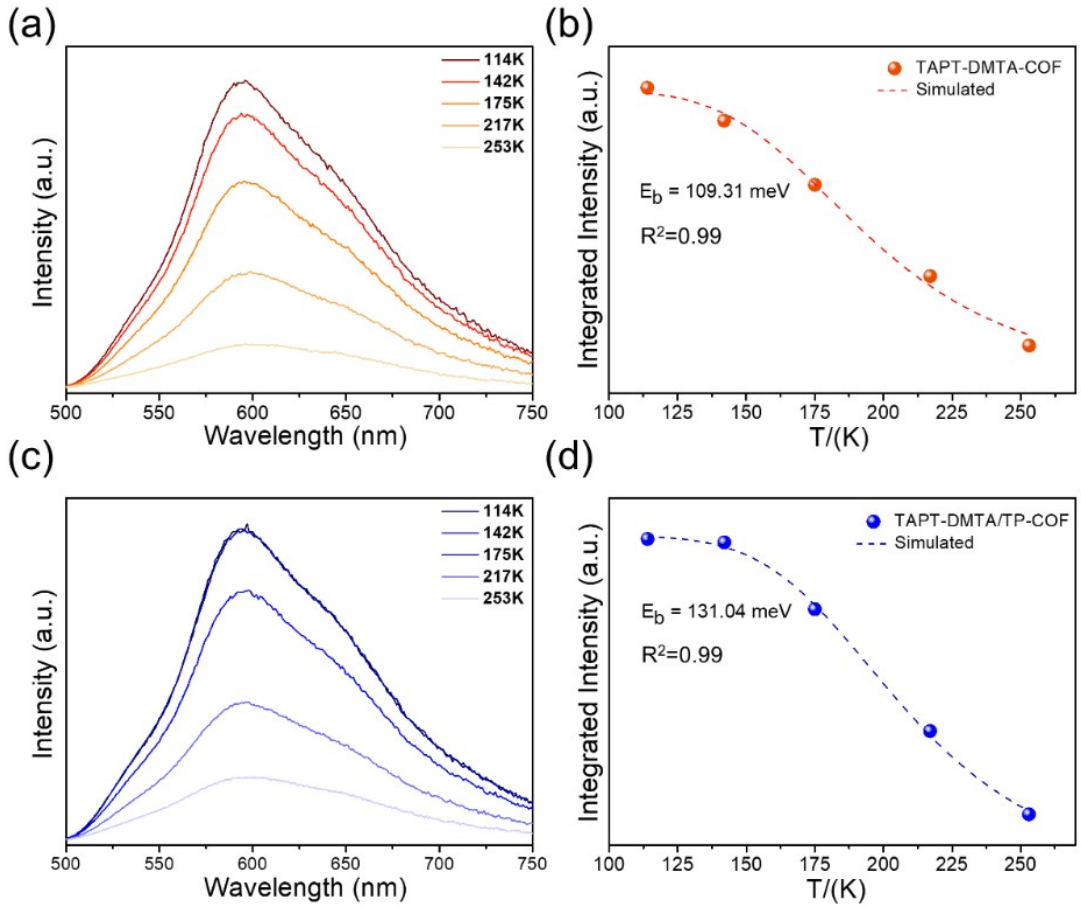


Figure S12. Temperature-dependent of photoluminescence spectra with excitation wavelength at 360 nm and exciton binding energy of (a, b) TAPT-DMTA-COF and (c, d) TAPT-DMTA/TP-COF.

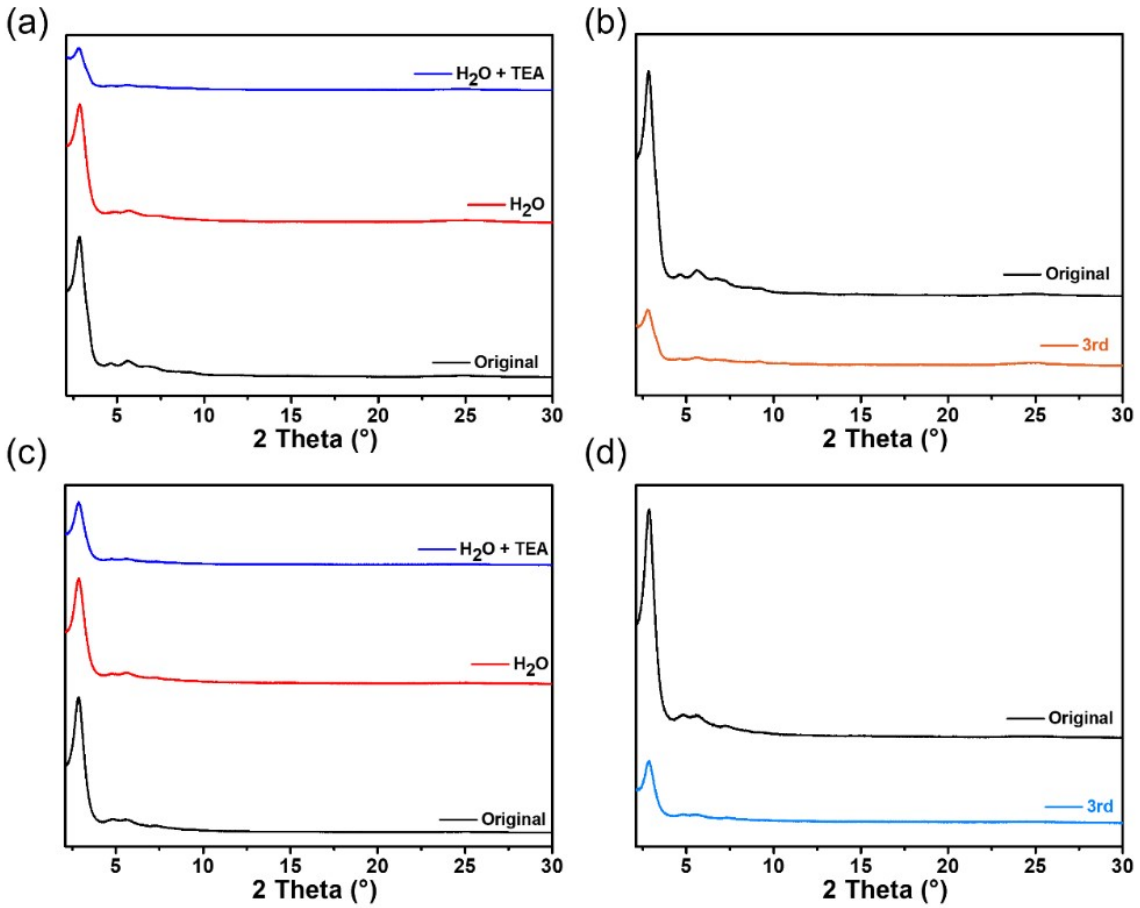


Figure S13. PXRD data of COFs immersed in water for overnight and after catalyzed (a, b) TAPT-DMTA-COF, (c, d) TAPT-DMTA/TP-COF.

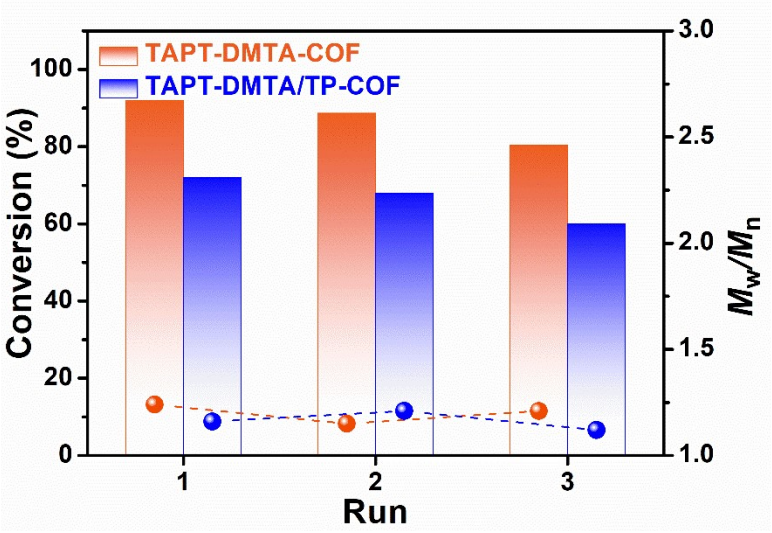


Figure S14. Polymerization results of COFs recycled experiments. Polymerization condition: COF (10 mg), [$PEGMA_{475}$]:[CPADB]:[TEA]=100:1:10, H_2O=1mL under white light irradiation.

Polymerization setup was shown as below

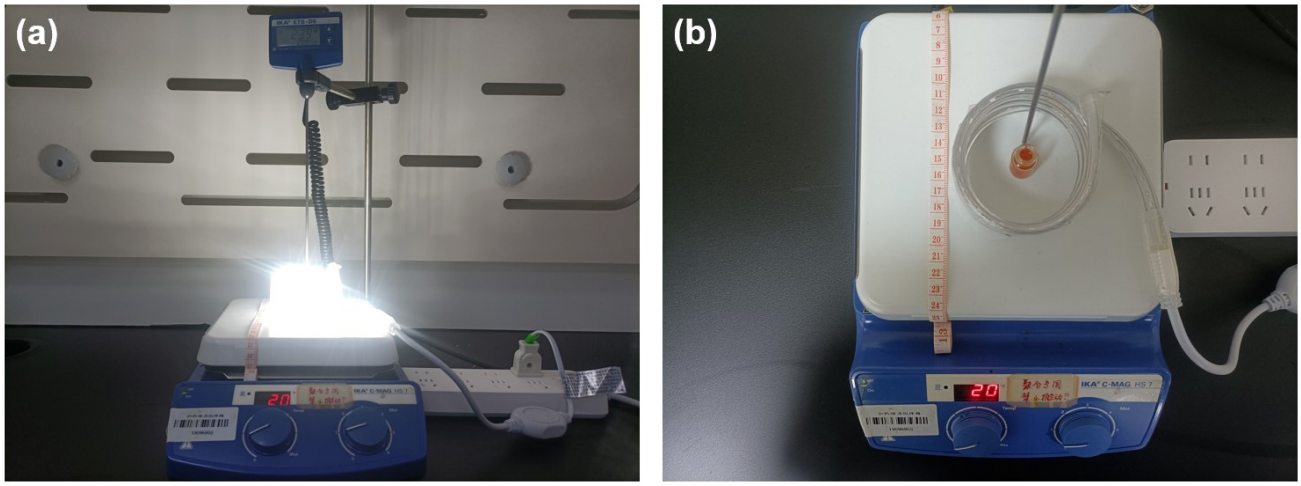


Figure S15. Photo of the polymerization setup (V_{vessel}=3 mL).

Table S1. Controlled experiments for COF-mediated RAFT polymerization[a]

#	[M]:[CPADB]:[TEA]	COF	T (h)	$M_{n,GPC}$[b] (kDa)	$M_{n,th}$[c] (kDa)	α[d] (%)	M_w/M_n[b]
1	100:1:0	-	15	-	-	-	-
2	100:1:10	-	15	-	-	-	-
3	100:1:0	TAPT-DMTA-COF	8	26.1	40.1	75.1	1.14
4	100:1:10	TAPT-DMTA-COF	1.5	40.9	44.2	92.4	1.24
5[e]	100:1:0	TAPT-DMTA-COF	8	-	-	-	-
6	100:1:0	TAPT-DMTA/TP-COF	10	35.3	41.9	87.7	1.19
7	100:1:10	TAPT-DMTA/TP -COF	4	22.5	34.4	71.9	1.16
8[e]	100:1:0	TAPT-DMTA/TP -COF	10	-	-	-	-
9	100:1:10	TAPT-TP-COF	15	-	-	-	-
10[e]	100:1:10	TAPT-TP-COF	15	-	-	-	-
11	100:1:10	TAPT-DHTA-COF	15	-	-	-	-
12[e]	100:1:10	TAPT-DHTA-COF	15	-	-	-	-

a) The polymerization was conducted under white light irradiation (15 mW cm^{-2}); b) $M_{n,GPC}$ and M_w/M_n were calculated by GPC analysis using PMMA as standard; c) $M_{n,th}$ = M_W (initiator)+M_W (monomer)×α×([monomer]/[initiator]); d) monomer conversion α was detected by ^{1}H NMR; e) polymerization in the dark.

Table S2. Results of RAFT polymerization of $PEGMA_{475}$ using COF (10 mg) as photocatalyst under air condition[a]

#	[M]:[CPADB]:[TEA]	Solvent	COFs	T (h)	$M_{n,GPC}$[b] (kDa)	$M_{n,th}$[c] (kDa)	α[d] (%)	M_w/M_n[b]
1	100:1:10	DMAc	TAPT-DMTA-COF	16	-	-	-	-
2	100:1:10	EtOH	TAPT-DMTA-COF	16	-	-	-	-
3	100:1:10	MeCN	TAPT-DMTA-COF	16	-	-	-	-
4	100:1:10	Dioxane	TAPT-DMTA-COF	16	-	-	-	-
5	100:1:10	H_2O/Dioxane (v/v=75/25)	TAPT-DMTA-COF	1.5	29.9	35.4	74.0	1.15
6	100:1:10	H_2O/Dioxane (v/v=50/50)	TAPT-DMTA-COF	1.5	20.4	26.7	55.7	1.24
4	100:1:10	DMAc	TAPT- DMTA/TP-COF	20	-	-	-	-
5	100:1:10	EtOH	TAPT- DMTA/TP-COF	20	-	-	-	-
6	100:1:10	MeCN	TAPT- DMTA/TP-COF	20	-	-	-	-
7	100:1:10	Dioxane	TAPT- DMTA/TP-COF	20	-	-	-	-
8	100:1:10	H_2O/Dioxane (v/v=75/25)	TAPT- DMTA/TP-COF	4	19.2	29.9	62.4	1.13
9	100:1:10	H_2O/Dioxane (v/v=50/50)	TAPT- DMTA/TP-COF	4	17.0	22.2	46.1	1.13

a) The polymerization was conducted under white light irradiation (15 mW cm^{-2}); b) $M_{n,GPC}$ and M_w/M_n were calculated by GPC analysis using PMMA as standard; c) $M_{n,th} = M_W$ (initiator)+M_W (monomer)×α×([monomer]/[initiator]); d) monomer conversion α was detected by ^1H NMR.

Table S3. Radical scavenging RAFT polymerization experiments using TAPT-DMTA-COF (#1-8) and TAPT-DMTA/TP-COF (#9-14) as a photocatalyst under air condition[a]

#	Quencher	Role	[$PEGMA_{475}$]:[CPADB]:[TEA]:[Quencher]	T (h)	$M_{n,GPC}$[b] (kDa)	α[c] (%)	M_w/M_n[b]
1	BQ	$O_2^{\bullet-}$ scavenger	100:1:10:0.5	1.5	-	-	-
2	MB	$OH^{\bullet}$ scavenger	100:1:10:0.5	1.5	-	-	-
3	BQ	$O_2^{\bullet-}$ scavenger	100:1:10:0.05	1.5	11.2	28.2	1.17
4	MB	$OH^{\bullet}$ scavenger	100:1:10:0.05	1.5	20.4	55.8	1.36
5	BQ	$O_2^{\bullet-}$ scavenger	100:1:10:0.01	1.5	29.0	82.8	1.12
6	MB	$OH^{\bullet}$ scavenger	100:1:10:0.01	1.5	37.5	86.5	1.52
7	BQ	$O_2^{\bullet-}$ scavenger	100:1:0:0.01	8	15.8	50.2	1.21
8	MB	$OH^{\bullet}$ scavenger	100:1:0:0.01	8	6.3	3.3	1.16
9	BQ	$O_2^{\bullet-}$ scavenger	100:1:10:0.5	8	-	-	-
10	MB	$OH^{\bullet}$ scavenger	100:1:10:0.5	8	-	-	-
11	BQ	$O_2^{\bullet-}$ scavenger	100:1:10:0.05	8	6.8	9.1	1.14
12	MB	$OH^{\bullet}$ scavenger	100:1:10:0.05	8	6.5	16.9	1.16
13	BQ	$O_2^{\bullet-}$ scavenger	100:1:0:0.05	8	-	-	-
14	MB	$OH^{\bullet}$ scavenger	100:1:0:0.05	8	-	-	-

a) The polymerization was conducted under white light irradiation (15 mW cm^{-2}), BQ=1,4-benzoquinone, MB= methylene blue; b) $M_{n,GPC}$ and M_w/M_n were calculated by GPC analysis using PMMA as standard; c) monomer conversion α was detected by ^1H NMR.

DFT calculations

COFs periodic density functional theory (DFT) simulations were performed to obtain electronic properties using the Vienna Ab initio Simulation Package (VASP)[2].

Table S4. Atomic coordinates of COFs

Eclipsed mode --- TAPT-TP-COF			
Atom	x	y	z
C1	0.967115402	19.77421761	2.094314098
C2	2.050683975	18.80335045	1.949317455
C3	3.256928444	19.26242065	1.392290235
C4	4.30710125	18.38175583	1.218297005
C5	4.181774139	17.04196167	1.649602771
C6	2.947608948	16.56392288	2.129673958
C7	1.88222599	17.44551468	2.279963255
C8	6.418521881	16.7667675	1.913576365
C9	7.698339462	16.09670067	1.892210126
C10	8.860954285	16.89859963	1.905111313
C11	10.11312008	16.30692291	1.875748158
C12	0.287737846	21.94774628	2.094314098
C13	0.586766243	23.37154388	1.949317455
C14	-0.413921356	24.18664742	1.392290235
C15	-0.17633152	25.53645515	1.218297005
C16	1.046611786	26.09784699	1.649602771
C17	2.077707291	25.26801872	2.129673958
C18	1.846934319	23.90454102	2.279963255
C19	0.1665802	28.17249489	1.913576365
C20	0.106967926	29.61588287	1.892210126
C21	-1.168804169	30.2217865	1.905111313
C22	16.61380386	0.604756832	1.875748158
C23	-1.254903793	20.27262116	2.094314098
C24	-2.637446404	19.81965828	1.949317455
C25	-2.84300375	18.54548454	1.392290235
C26	-4.130766392	18.07634163	1.218297005
C27	-5.228435516	18.85477638	1.649602771
C28	-5.025312901	20.16261292	2.129673958
C29	-3.729102135	20.64446449	2.279963255
C30	-6.585098267	17.05529022	1.913576365
C31	-7.80530405	16.28197098	1.892210126
C32	-7.692145824	14.87416649	1.905111313

C33	26.96194077	14.08559704	1.875748158
C34	16.92917252	11.22305965	2.094314098
C35	15.8456068	12.1939249	1.949317455
C36	14.63936234	11.73485565	1.392290235
C37	13.58919144	12.61551952	1.218297005
C38	13.71451664	13.95531464	1.649602771
C39	14.94868088	14.43335533	2.129673958
C40	16.01406479	13.55176067	2.279963255
C41	11.47776794	14.2305088	1.913576365
C42	10.19795036	14.90057659	1.892210126
C43	9.035335541	14.09867764	1.905111313
C44	7.783168793	14.69035339	1.875748158
C45	17.60855293	9.049530983	2.094314098
C46	17.30952072	7.625732899	1.949317455
C47	18.31021309	6.810628414	1.392290235
C48	18.07261848	5.460821152	1.218297005
C49	16.84967804	4.899429321	1.649602771
C50	15.81858254	5.729257584	2.129673958
C51	16.04935646	7.092734814	2.279963255
C52	17.72971153	2.824781895	1.913576365
C53	17.7893219	1.381393552	1.892210126
C54	19.06509399	0.775489807	1.905111313
C55	1.282485962	30.39252091	1.875748158
C56	19.15119553	10.7246542	2.094314098
C57	20.53373718	11.17761803	1.949317455
C58	20.73929215	12.45179176	1.392290235
C59	22.02705574	12.92093563	1.218297005
C60	23.12472343	12.14250183	1.649602771
C61	22.92160225	10.83466435	2.129673958
C62	21.62539291	10.35281086	2.279963255
C63	24.48138619	13.94198608	1.913576365
C64	25.7015934	14.71530628	1.892210126
C65	25.58843613	16.12310982	1.905111313
C66	-9.065649986	16.91168022	1.875748158
N1	1.327727318	21.08533859	2.11009717
N2	5.293525696	16.17837906	1.642393589
N3	-1.028014183	21.60445023	2.11009717
N4	1.238639832	27.49241447	1.642393589
N5	-0.299708366	19.30476379	2.11009717
N6	-6.532161713	18.32376099	1.642393589
N7	16.56856346	9.911937714	2.11009717
N8	12.60276318	14.81889916	1.642393589
N9	18.92430496	9.39282608	2.11009717

N10	16.6576519	3.50486207	1.642393589
N11	18.19599533	11.69251347	2.11009717
N12	24.42844963	12.67351627	1.642393589
H1	8.75531292	17.99295807	1.930357814
H2	3.328818321	20.30823708	1.080353379
H3	5.229905128	18.71435738	0.730287015
H4	2.871353149	15.51252461	2.434840918
H5	0.922340393	17.10876083	2.682936668
H6	6.451219559	17.84742546	2.185630322
H7	-2.063727379	29.58311844	1.930357814
H8	-1.355570793	23.72599602	1.080353379
H9	-0.925756454	26.16929627	0.730287015
H10	3.026371002	25.7276783	2.434840918
H11	2.618515968	23.24163246	2.682936668
H12	-0.785627365	27.66044998	2.185630322
H13	-6.69158268	14.41847611	1.930357814
H14	-1.973243713	17.96031761	1.080353379
H15	-4.304092884	17.11086845	0.730287015
H16	-5.897720337	20.75435066	2.434840918
H17	-3.540797234	21.64412689	2.682936668
H18	-5.665534019	16.48664475	2.185630322
H19	9.140977859	13.00431824	1.930357814
H20	14.56747055	10.68903828	1.080353379
H21	12.66638565	12.28291893	0.730287015
H22	15.02493763	15.4847517	2.434840918
H23	16.97394943	13.88851643	2.682936668
H24	11.44507027	13.14984989	2.185630322
H25	19.96001816	1.414157748	1.930357814
H26	19.25185967	7.271278858	1.080353379
H27	18.82204628	4.827980518	0.730287015
H28	14.86991882	5.269598961	2.434840918
H29	15.27777672	7.755642414	2.682936668
H30	18.68191719	3.336825848	2.185630322
H31	24.58787346	16.5788002	1.930357814
H32	19.86953354	13.03695869	1.080353379
H33	22.20038223	13.88640785	0.730287015
H34	23.79401016	10.24292564	2.434840918
H35	21.43708611	9.353149414	2.682936668
H36	23.56182098	14.51063061	2.185630322
H37	11.04050732	16.89258575	1.868604183
H38	15.64291191	1.115065098	1.868604183
H39	27.00544357	12.98962593	1.868604183
H40	6.855783463	14.10469055	1.868604183

H41	2.253376007	29.88221169	1.868604183
H42	-9.109155655	18.00765038	1.868604183

Eclipsed mode --- TAPT-DHTA-COF			
Atom	x	y	z
C1	0.943060875	19.75136185	2.021702051
C2	2.004306793	18.75020599	1.899740815
C3	3.231724739	19.16475678	1.353739738
C4	4.260090828	18.25086594	1.210954905
C5	4.094885826	16.92084694	1.661845803
C6	2.840568542	16.48735428	2.137203693
C7	1.797935486	17.40239143	2.253024817
C8	6.31075573	16.58277702	1.955345035
C9	7.616603851	15.96591282	1.905917287
C10	8.709261894	16.85822296	1.917523026
C11	10.03148842	16.42969322	1.869673967
C12	0.321925163	21.94238281	2.021702051
C13	0.658348083	23.3619976	1.899740815
C14	-0.314372063	24.21769714	1.353739738
C15	-0.037121773	25.56526375	1.210954905
C16	1.197311401	26.08720207	1.661845803
C17	2.199903488	25.21764565	2.137203693
C18	1.928756714	23.85721397	2.253024817
C19	0.382154465	28.17523575	1.955345035
C20	0.263450623	29.6145668	1.905917287
C21	-1.055644989	30.11468124	1.917523026
C22	16.5530014	0.472677588	1.869673967
C23	-1.264985085	20.30895233	2.021702051
C24	-2.662602425	19.89046669	1.899740815
C25	-2.917299271	18.62021637	1.353739738
C26	-4.222969055	18.18656921	1.210954905
C27	-5.292198181	18.99464989	1.661845803
C28	-5.040418148	20.29767036	2.137203693
C29	-3.726693153	20.74309731	2.253024817
C30	-6.692909241	17.24468613	1.955345035
C31	-7.880055428	16.42222214	1.905917287
C32	-7.653618813	15.02979565	1.917523026
C33	27.11142731	14.09897995	1.869673967
C34	16.95557404	11.24998665	2.021702051
C35	15.89433098	12.25114441	1.899740815
C36	14.66691399	11.83659458	1.353739738

C37	13.63854694	12.75048351	1.210954905
C38	13.80375195	14.08050251	1.661845803
C39	15.05807209	14.51399517	2.137203693
C40	16.10070229	13.59895897	2.253024817
C41	11.58788204	14.41857338	1.955345035
C42	10.28203487	15.03543854	1.905917287
C43	9.189376831	14.14312553	1.917523026
C44	7.867149353	14.57165718	1.869673967
C45	17.57671356	9.058966637	2.021702051
C46	17.2402916	7.639352798	1.899740815
C47	18.21300888	6.783653259	1.353739738
C48	17.9357605	5.436086655	1.210954905
C49	16.70132637	4.914147854	1.661845803
C50	15.69873238	5.783704758	2.137203693
C51	15.96988106	7.144136906	2.253024817
C52	17.51648331	2.826113939	1.955345035
C53	17.63518906	1.386783361	1.905917287
C54	18.95428085	0.886669636	1.917523026
C55	1.345636368	30.52867317	1.869673967
C56	19.16362381	10.69239616	2.021702051
C57	20.56123924	11.11088371	1.899740815
C58	20.81593704	12.38113403	1.353739738
C59	22.12160683	12.81478024	1.210954905
C60	23.19083405	12.00669861	1.661845803
C61	22.93905449	10.70368099	2.137203693
C62	21.62533188	10.25825405	2.253024817
C63	24.59154511	13.75666332	1.955345035
C64	25.77869415	14.57912922	1.905917287
C65	25.55225754	15.97155476	1.917523026
C66	-9.212786674	16.90237045	1.869673967
N1	1.338799477	21.05149651	2.034480095
N2	5.179184914	16.02466011	1.653328419
N3	-1.001876831	21.63500595	2.034480095
N4	1.431282997	27.47432709	1.653328419
N5	-0.336870193	19.31616592	2.034480095
N6	-6.610467434	18.50371361	1.653328419
N7	16.55983734	9.94985199	2.034480095
N8	12.71945095	14.97669029	1.653328419
N9	18.9005146	9.366345406	2.034480095
N10	16.46735764	3.527023554	1.653328419
N11	18.23550797	11.68518353	2.034480095
N12	24.50910568	12.49763584	1.653328419
H1	8.489609718	17.93669891	1.948562145

H2	3.338006973	20.20410729	1.025517941
H3	5.196117401	18.548666	0.725635231
H4	2.732460022	15.4458952	2.461974621
H5	0.82188797	17.10223579	2.650525331
H6	6.343832016	17.65195084	2.268310308
H7	10.73404694	18.20923233	1.923866749
H8	-1.879805565	29.38521957	1.948562145
H9	-1.267635345	23.79009438	1.025517941
H10	-0.763019562	26.22695541	0.725635231
H11	3.155869484	25.64478302	2.461974621
H12	2.676722527	23.16200829	2.650525331
H13	-0.560317039	27.66929436	2.268310308
H14	14.66059494	0.191340327	1.923866749
H15	-6.609806061	14.68078232	1.948562145
H16	-2.070370674	18.00849915	1.025517941
H17	-4.43304491	17.22704697	0.725635231
H18	-5.88833046	20.91202354	2.461974621
H19	-3.498610497	21.73845673	2.650525331
H20	-5.783515453	16.68145561	2.268310308
H21	28.30127335	12.60077763	1.923866749
H22	9.409029007	13.06465149	1.948562145
H23	14.5606308	10.79724312	1.025517941
H24	12.70252037	12.4526844	0.725635231
H25	15.16617966	15.55545425	2.461974621
H26	17.07675171	13.89911366	2.650525331
H27	11.55480576	13.34939861	2.268310308
H28	7.164592266	12.79211807	1.923866749
H29	19.77844238	1.616131425	1.948562145
H30	19.16627312	7.211255074	1.025517941
H31	18.66165543	4.774394035	0.725635231
H32	14.74276829	5.356568336	2.461974621
H33	15.22191429	7.839342594	2.650525331
H34	18.45895386	3.332056284	2.268310308
H35	3.238042831	30.81001091	1.923866749
H36	24.50844574	16.32056809	1.948562145
H37	19.9690094	12.99285221	1.025517941
H38	22.33168411	13.77430248	0.725635231
H39	23.78696823	10.08932781	2.461974621
H40	21.39724922	9.262893677	2.650525331
H41	23.6821537	14.31989574	2.268310308
H42	-10.40263557	18.40057373	1.923866749
O1	11.08971024	17.30823898	1.827961802
O2	15.26304531	0.94985038	1.827961802

O3	27.34315682	12.74326038	1.827961802
O4	6.80892849	13.69311047	1.827961802
O5	2.635591507	30.05150032	1.827961802
O6	-9.44452095	18.25808907	1.827961802

Eclipsed mode --- TAPT-DMTA-COF			
Atom	x	y	z
C1	1.117768288	19.84981537	1.926617384
C2	2.300260544	19.06910324	1.921570659
C3	3.433720589	19.54314995	1.366328359
C4	4.539008141	18.82204056	1.375763416
C5	4.535620689	17.59383774	1.917986751
C6	3.410006523	17.10434914	2.438304901
C7	2.312027931	17.83564949	2.464159966
C8	6.797904968	17.17321587	1.78395772
C9	7.861289978	16.26341248	1.785786271
C10	9.095132828	16.74580193	1.781361222
C11	10.14889336	15.940382	1.78209269
C12	11.39129448	17.40607071	1.764429331
C13	0.080770493	21.92574501	1.926617384
C14	0.165641785	23.34017181	1.921570659
C15	-0.811626434	24.08475113	1.366328359
C16	-0.739770889	25.4025135	1.375763416
C17	0.325577736	26.0136795	1.917986751
C18	1.31229496	25.28361511	2.438304901
C19	1.227958679	23.9670887	2.464159966
C20	-0.441295624	28.18318749	1.78395772
C21	-0.18507576	29.55900765	1.785786271
C22	-1.21975708	30.38635254	1.781361222
C23	16.78097534	0.819007576	1.78209269
C24	14.89045143	1.162113667	1.764429331
C25	-1.19853878	19.98971176	1.926617384
C26	-2.465902328	19.3560009	1.921570659
C27	-2.622095108	18.13737297	1.366328359
C28	-3.799236774	17.54071999	1.375763416
C29	-4.861198425	18.1577549	1.917986751
C30	-4.722301483	19.3773098	2.438304901
C31	-3.539987087	19.96253586	2.464159966
C32	-6.356608391	16.4088707	1.78395772
C33	-7.676214695	15.94285297	1.785786271
C34	-7.875376225	14.63312054	1.781361222

C35	26.56042862	14.1232481	1.78209269
C36	27.20855331	12.31445217	1.764429331
C37	16.71232987	11.03282261	1.926617384
C38	15.52983761	11.81353569	1.921570659
C39	14.39637947	11.33948612	1.366328359
C40	13.29109001	12.06059551	1.375763416
C41	13.29447842	13.28879833	1.917986751
C42	14.42009163	13.77828884	2.438304901
C43	15.51806831	13.04698753	2.464159966
C44	11.03219509	13.7094202	1.78395772
C45	9.968809128	14.61922264	1.785786271
C46	8.734965324	14.13683605	1.781361222
C47	7.681207657	14.94225502	1.78209269
C48	6.43880558	13.47656536	1.764429331
C49	17.74932861	8.95689106	1.926617384
C50	17.66445923	7.54246664	1.921570659
C51	18.64172554	6.797885895	1.366328359
C52	18.56987	5.480123997	1.375763416
C53	17.50452042	4.868956089	1.917986751
C54	16.51780319	5.599021912	2.438304901
C55	16.60214043	6.915548801	2.464159966
C56	18.27139282	2.699451447	1.78395772
C57	18.01517487	1.323629856	1.785786271
C58	19.04985809	0.496284008	1.781361222
C59	1.049123764	30.06362915	1.78209269
C60	2.939647675	29.72052193	1.764429331
C61	19.02863884	10.89292336	1.926617384
C62	20.29600143	11.52663517	1.921570659
C63	20.45219231	12.74526405	1.366328359
C64	21.62933731	13.34191704	1.375763416
C65	22.69129753	12.72488117	1.917986751
C66	22.5524025	11.50532723	2.438304901
C67	21.37008667	10.92010021	2.464159966
C68	24.18670654	14.47376537	1.78395772
C69	25.50631332	14.93978405	1.785786271
C70	25.70547485	16.24951744	1.781361222
C71	-8.730330467	16.75938988	1.78209269
C72	-9.378454208	18.56818581	1.764429331
N1	1.179282188	21.17745972	1.927312136
N2	5.636094093	16.79953766	1.919449568
N3	-1.099759102	21.31519508	1.927312136
N4	0.463225365	27.36386871	1.919449568
N5	-0.079522133	19.27261734	1.927312136

N6	-6.099319935	17.60186768	1.919449568
N7	16.65081596	9.705177307	1.927312136
N8	12.19400501	14.08310032	1.919449568
N9	18.92985916	9.567440987	1.927312136
N10	17.3668747	3.518767595	1.919449568
N11	17.90962029	11.61001873	1.927312136
N12	23.92941856	13.28076935	1.919449568
H1	9.241341591	17.75875092	1.77839911
H2	3.469559669	20.45635033	0.877387464
H3	5.374526024	19.21486855	0.908545077
H4	3.392533302	16.15995789	2.86010313
H5	1.48738575	17.43510056	2.946189165
H6	7.016324043	18.16918182	1.710086346
H7	11.44513989	17.77975273	0.688722789
H8	12.30740547	17.76739883	2.338614941
H9	10.44790459	17.8109436	2.260318756
H10	-2.170101166	30.00649643	1.77839911
H11	-1.620398521	23.65918732	0.877387464
H12	-1.497728348	25.92967987	0.908545077
H13	2.138897896	25.74067879	2.86010313
H14	1.987164497	23.45320129	2.946189165
H15	-1.413035393	27.87435913	1.710086346
H16	14.53973198	1.022215366	0.688722789
H17	14.11947632	1.774825215	2.338614941
H18	15.01151657	0.142677784	2.260318756
H19	-7.071239471	14.00002575	1.77839911
H20	-1.849160194	17.6497364	0.877387464
H21	-3.87679863	16.62072754	0.908545077
H22	-5.531431675	19.86463928	2.86010313
H23	-3.474552155	20.8769722	2.946189165
H24	-5.603286266	15.72173309	1.710086346
H25	27.50489044	12.08097839	0.688722789
H26	27.06341553	11.34041309	2.338614941
H27	28.03087807	12.92901611	2.260318756
H28	8.588759422	13.12388516	1.77839911
H29	14.36054134	10.42628765	0.877387464
H30	12.45557404	11.66776943	0.908545077
H31	14.43756676	14.72267914	2.86010313
H32	16.3427124	13.44753552	2.946189165
H33	10.81377602	12.7134552	1.710086346
H34	6.384958744	13.10288525	0.688722789
H35	5.522695541	13.11523819	2.338614941
H36	7.38219595	13.07169342	2.260318756

H37	20.00020027	0.876140416	1.77839911
H38	19.45049858	7.223448753	0.877387464
H39	19.32782745	4.95295763	0.908545077
H40	15.69120026	5.14195919	2.86010313
H41	15.84293556	7.42943573	2.946189165
H42	19.24313355	3.008277655	1.710086346
H43	3.290367126	29.86042213	0.688722789
H44	3.710622787	29.10781097	2.338614941
H45	2.818582535	30.73995781	2.260318756
H46	24.90133667	16.88261223	1.77839911
H47	19.67925644	13.23290157	0.877387464
H48	21.70689774	14.26191044	0.908545077
H49	23.36153221	11.0179987	2.86010313
H50	21.30465126	10.00566483	2.946189165
H51	23.43338585	15.16090393	1.710086346
H52	-9.674790382	18.80165863	0.688722789
H53	-9.233317375	19.54222488	2.338614941
H54	-10.20077896	17.95362282	2.260318756
O1	11.36864948	16.44902039	1.769146919
O2	15.73060608	1.621029615	1.769146919
O3	26.39104271	12.81258869	1.769146919
O4	6.461449623	14.43361855	1.769146919
O5	2.099494934	29.26160812	1.769146919
O6	-8.560943604	18.07004929	1.769146919

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