Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Organocatalytic PET-RAFT Polymerization with ppm of Organic Photocatalyst under Visible Light

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1. General information

Materials

Methyl methacrylate (MMA), Benzyl methacrylate (BnMA) and Styrene (St) were purchased from TCI chemicals. *N,N*-dimethylacrylamide (DMA) and *n*-butyl acrylate (BA) were purchased from J&K chemicals. 1,1'-bi-2- naphthol, potassium carbonate (K_2CO_3), cuprous chloride [CuCl(I)], m-xylene, *N*-methylimidazole and other reagents were purchased from Energy Chemicals or Adamas chemicals and were used as received without further purification. Solvents [Toluene (J&K chemical), Dimethyl sulfoxide (DMSO, J&K chemical)] were redistilled before use. MMA and BnMA were degassed and dried over CaH_2 overnight, followed by vacuum distillation; The monomer was deoxygenized by freeze–pump–thaw cycle three times, stored under a nitrogen atmosphere and sealed up. St, DMA and BA were purified by passing it through a plug of aluminum oxide (activated, basic) to remove the inhibitor, deoxygenized by freeze–pump–thaw cycle three times, backfilled with argon and sealed up. Subsequently, all of the purified monomers were stored under inert atmosphere at -20°C. Thiocarbonylthiol compounds: 4-cyanopentanoic acid dithiobenzoate (CPADB) and 2-(*n*-butyltrithiocarbonate)- propionic acid (BTPA) were synthesized according to literature procedures.[1, 2]

Instruments

^{1}H NMR, ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer or AVANCE NEO 600 spectrometer. Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane (TMS), chloroform or dichloromethane as internal standard, and coupling constants (J) in Hertz. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray ionization in Positive/Negative ion detection (ESI^+/ESI^-) mode. Significant fragments are reported in the following fashion: m/z (relative intensity).

The number-average molecular weight ($M_{n,\ GPC}$) and molecular weight distribution (M_w/M_n) values of the obtained polymers determined by a Waters 1515 gel permeation chromatograph (GPC-THF) equipped with a Waters 2414 refractive-index detector, using a Styragel HR 3 THF (7.8 × 300 mm) Column and a Styragel HR 4 THF (7.8 × 300 mm) column with measurable molecular weights ranging from 10^2 to 10^6 $g \cdot mol^{-1}$. THF was used as eluent at a flow rate of 1.0 mL/min at 35 °C. GPC samples were injected manually and PSS poly(methyl methacrylate) standards were used for calibration. Another gel permeation chromatography (GPC-water) measurements were performed in 8.5g/L sodium chloride and sodium azide (two parts in ten thousand) aqueous solution at 35 °C with an elution rate of 1.0 mL/min, equipped with a Waters 2695 refractive-index detector. Three columns were employed, including one Ultrahydrogel 250 (7.8 × 300 mm) column, Ultrahydrogel 500 (7.8 × 300 mm) column and Ultrahydrogel 1000 (7.8 × 300 mm) column (molecular weight range $10^3 \sim 6*10^5$ g mol^{-1}) and calibrated by PEG standards. Analysis of some polymer samples' absolute molecular weights was performed via gel permeation chromatography (GPC) coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column and two Shodex GPC KD-806M gel permeation columns, a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology DAWN EOS light scattering detector, using THF as the eluent at a flow rate of 1.0 mL/min.

The ultraviolet−visible (UV−vis) spectra were obtained using a Perkins Elmer Lambda 900 spectrometer equipped with a PTP-1 Peltier temperature controller and the photoluminescence (PL) spectra were recorded at room temperature on an Edinburgh Instruments, FLS980 spectrometer equipped with a 450 W Xe lamp for excitation and detected by a photomultiplier (PMT R928P). UV−vis measurements were carried out using anhydrous DCM solution at sample concentration of 0.04, 0.08, 0.12 mM respectively. (Transparent cuvette on four sides: 1×1×5 cm^3); PL measurements were carried out using anhydrous DCM solution at sample concentration of 0.08 mM. Fluorescence decay measurements were carried out by the time-correlated single photon counting (TCSPC) technique. TCSPC event timer with 1 ns time resolution was used to measure the PL decay. The excitation source was a 340nm pulsed light emitting diode (EP-LED Edinburgh Instruments) of pule width (FWHM) 835.5 ps. The decay time fitting procedure was carried out by using the F980 software (Edinburgh Instruments). Smallest residual values were obtained in the fitting procedure.

Cyclic voltammetry experiments were carried out with a CHI660 D electrochemical workstation (Shanghai Chenhua Instrument Plant, China) using a one compartment electrolysis cell consisting of a typical glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and a Ag/AgCl reference electrode. Before performing electrochemical cleaning, the electrode should be sonicated in ethanol and deionized water for 1~3mins respectively to obtain a clean electrode. The measurements were done in 1.0 mM DCM solution with 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6, TCI chemicals) as supporting electrolyte at a scan rate of 50 mV/s. The redox potential was calibrated after each experiment against the ferrocenium/ferrocenecouple (Fc^+/Fc), which allowed conversion of all potentials to the aqueous saturated calomel electrode (SCE) scale by using $E^0\ (Fc^+/Fc)$ = 0.42 V vs. SCE in CH_3CN.

Photo reaction setups

6 W blue LEDs reactors and 12 W blue bulbs were purchased from GeAo Chemical (see: www.geaochem.com/) and were used as shown below (**Figure S1**). At this distance, we estimate the dosage of 6 W blue LEDs and 12 W blue bulbs to be ~30 mW/cm^2 and ~ 3 mW/cm^2 respectively.

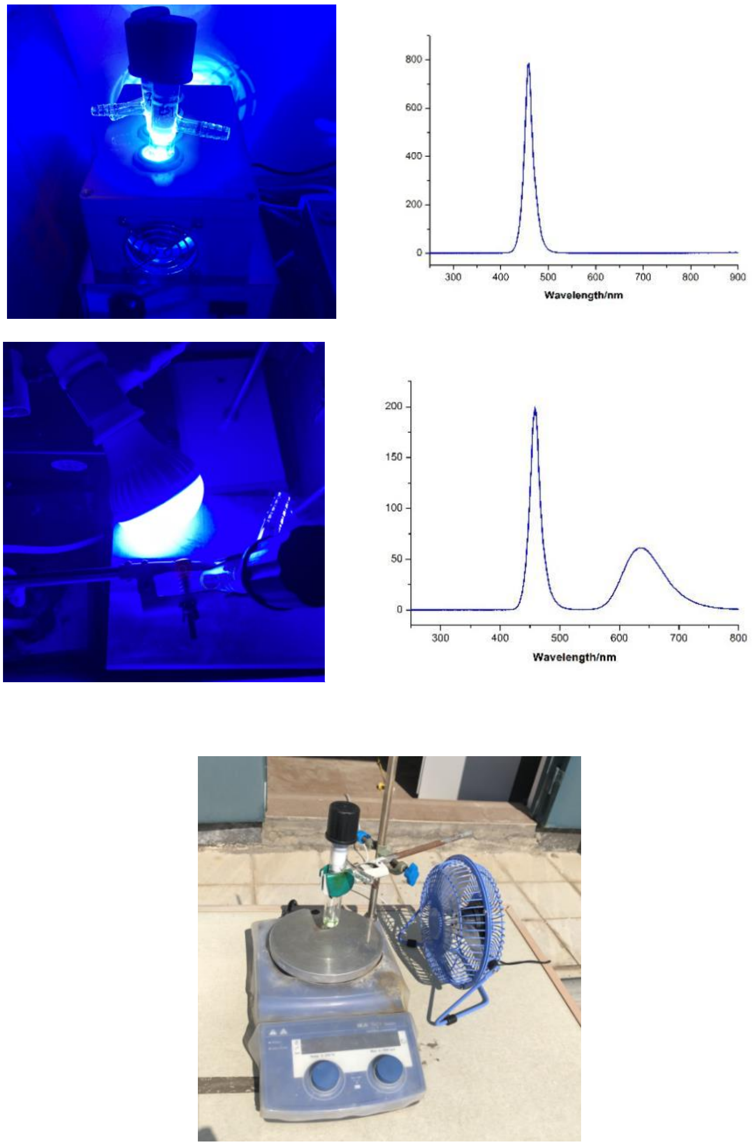
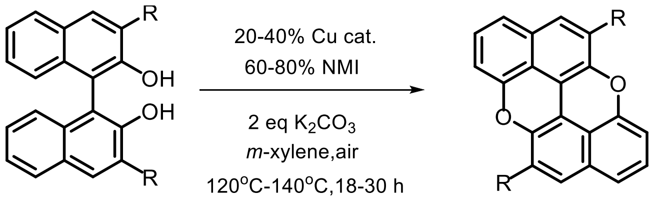


Figure S1. Reactors with blue LEDs (λ_{max} = 460 nm) and blue bulb (λ_{max} = 455 nm)

2. Synthesis and characterization of photocatalysts

Synthesis of organic photocatalyst ODA 1&2[3]

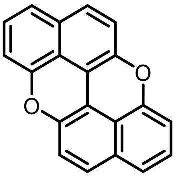


BINOL **ODA**

ODA 1: R = H
ODA 2: R = 4-*t*-BuC_6H_4

Under ambient air, 1,1'-bi-2-naphthol (143 mg, 0.5 mmol), K_2CO_3 (138 mg, 1 mmol), CuCl(I) (15.0 mg, 0.15 mmol). m-xylene was added (3 mL), followed by N-methylimidazole (24 μL, 0.30 mmol). The vessel was heated at 120 °C for 30 h. After removal of solvent under reduced pressure, the residue was filtered through silica gel short pad with $CHCl_3$ as the eluent and recrystallized from toluene to afford oxygen-dopant of antratherene product ODA **5a** in 75% yield (106 mg) as yellow solid.

xantheno[2,1,9,8-*klmna*]xanthene



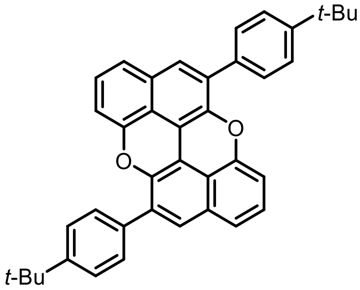
NMR and HRMS data for the catalyst **ODA 1**:

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm):7.31 (d, J = 8.8 Hz, 2H), 7.09 (m, 4H), 6.90 (d, J = 8.8 Hz, 2H), 6.63 (m, 2H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm): 153.0, 144.6 131.7, 127.6, 126.8, 121.9, 120.5, 117.7, 111.8, 109.0.

HRMS (ESI): *m/z* calculated for $C_{20}H_{10}O_2$: 282.0675, found 282.0674.

5,11-bis(4-(*tert*-butyl)phenyl)xantheno[2,1,9,8-*klmna*]xanthene



NMR and HRMS data for the catalyst **ODA 2**:

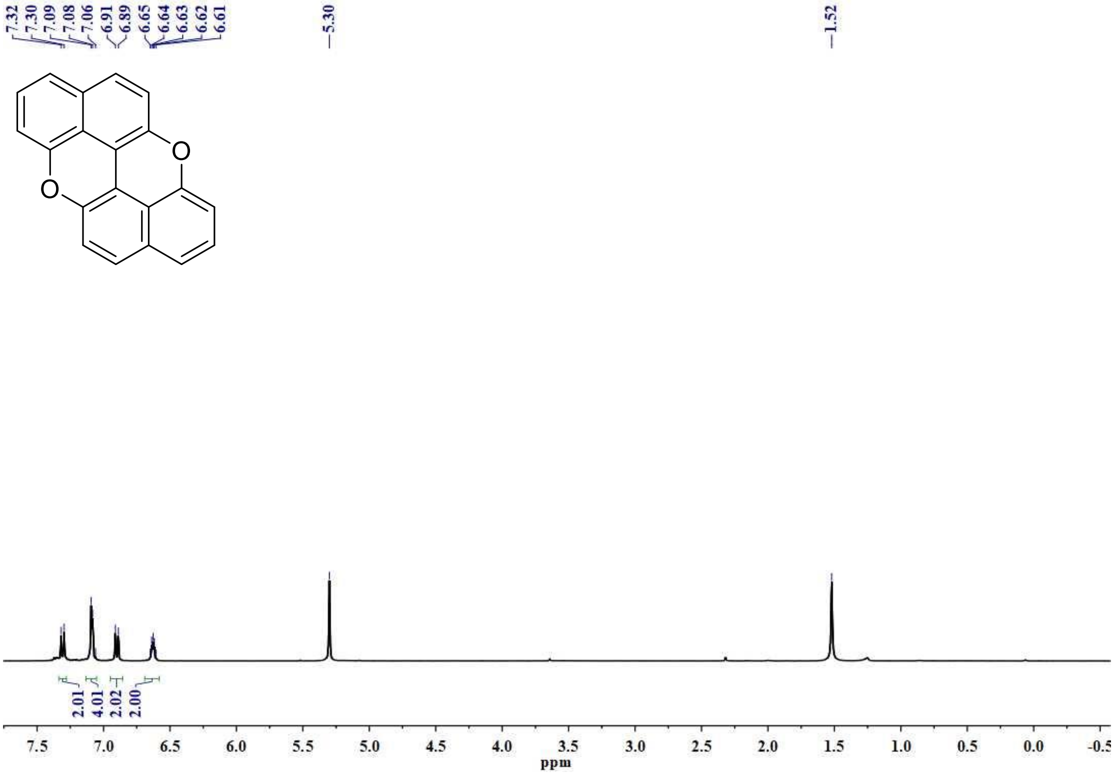
^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm):7.62 (d, J = 7.8 Hz, 4H), 7.51 (d, J = 8.4 Hz, 4H), 7.37 (s, 2H), 7.07 - 7.11 (m, 4H), 6.62 (dd, J = 6.8, 1.5 Hz, 2H), 1.41 (s, 18H).

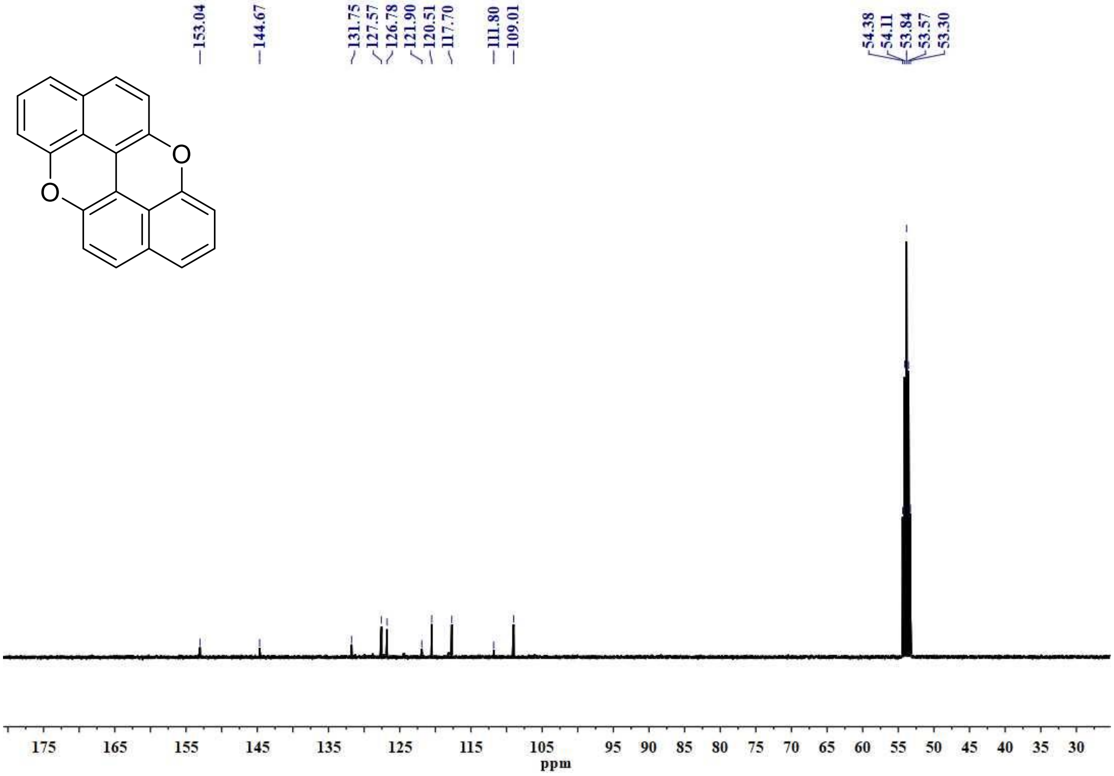
^{13}C NMR (150 MHz, $CDCl_3$):δ (ppm): 152.5, 150.9, 142.3, 133.7, 131.4, 131.1, 129.2, 127.5, 127.0, 125.4, 121.0, 120.1, 112.4, 108.7, 34.8, 31.5.

HRMS (ESI): *m/z* calculated for $C_{40}H_{34}O_2$: 546.2559, found 546.2565.

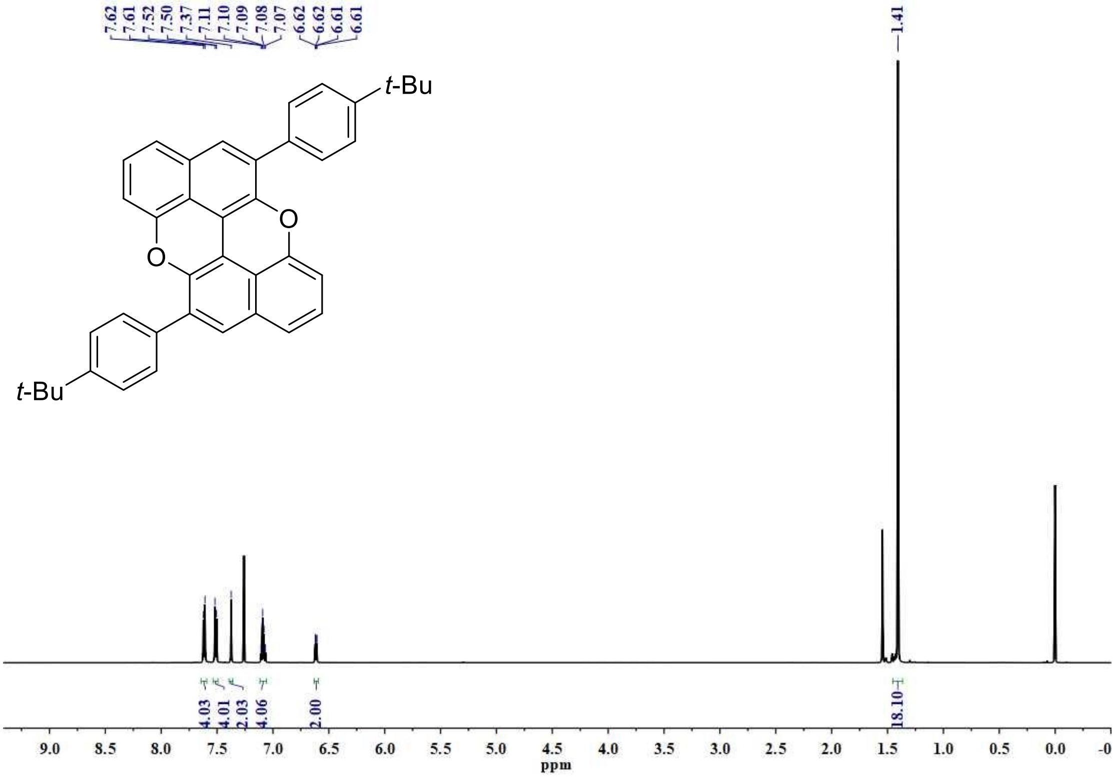
NMR spectra of photocatalysts

ODA 1:





ODA 2


7.62
7.61
7.52
7.50
7.37
7.11
7.10
7.09
7.08
7.07
6.62
6.62
6.61
6.61
1.41
t-Bu
O
O
t-Bu
4.03
4.01
2.03
4.06
2.00
18.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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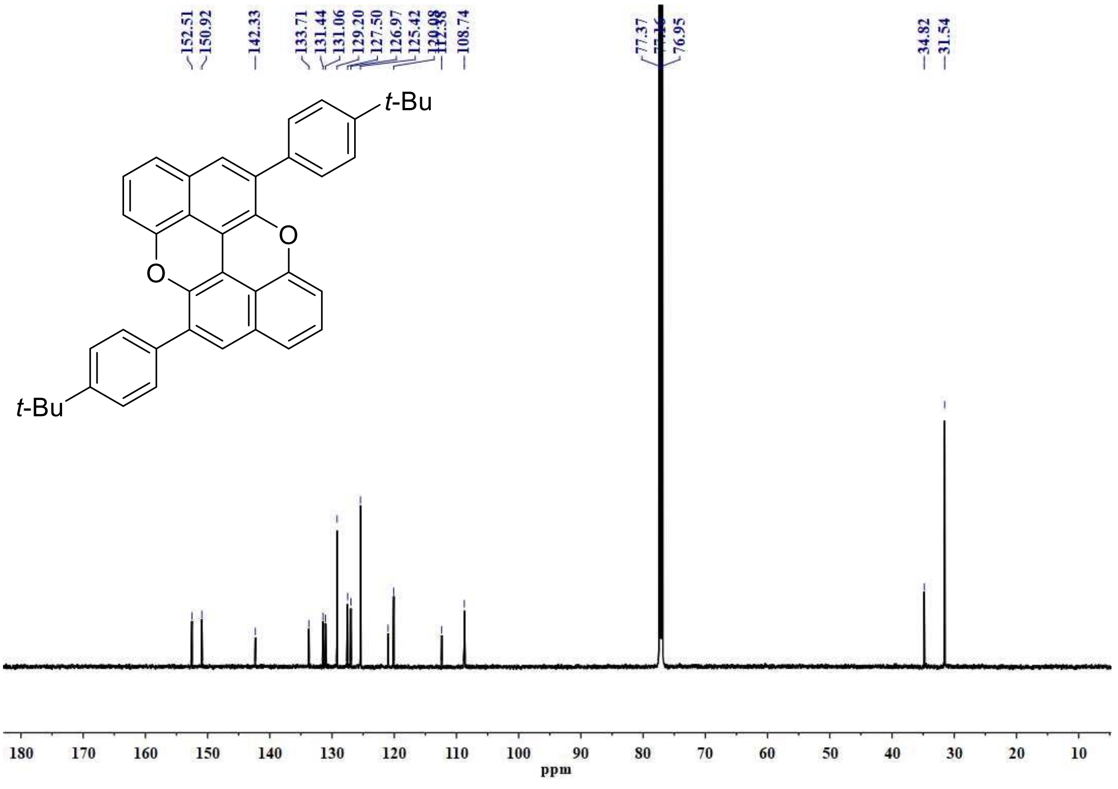
0.5
0.0
-0
ppm


152.51
150.92
142.33
133.71
131.44
131.06
129.20
127.50
126.97
125.42
120.98
112.38
108.74
77.37
77.16
76.95
34.82
31.54
t-Bu
O
O
t-Bu
180
170
160
150
140
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110
100
90
80
70
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50
40
30
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10
ppm

UV-Vis absorption spectra

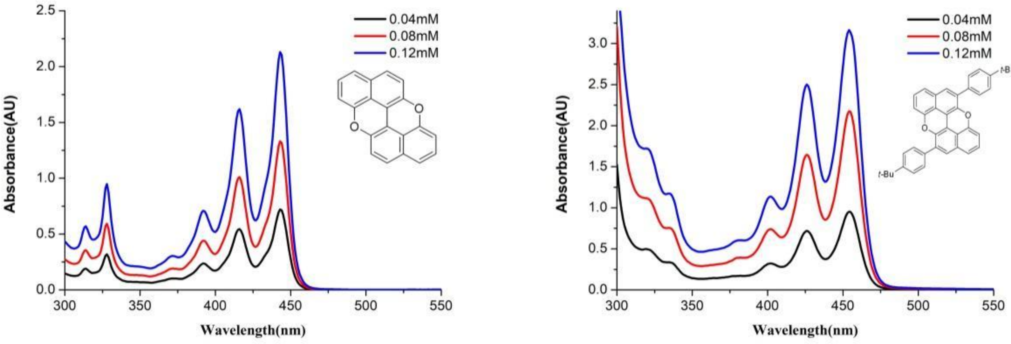


Figure S2. UV-Vis spectra of catalysts ODA **1** and ODA **2** at different concentration in DCM.

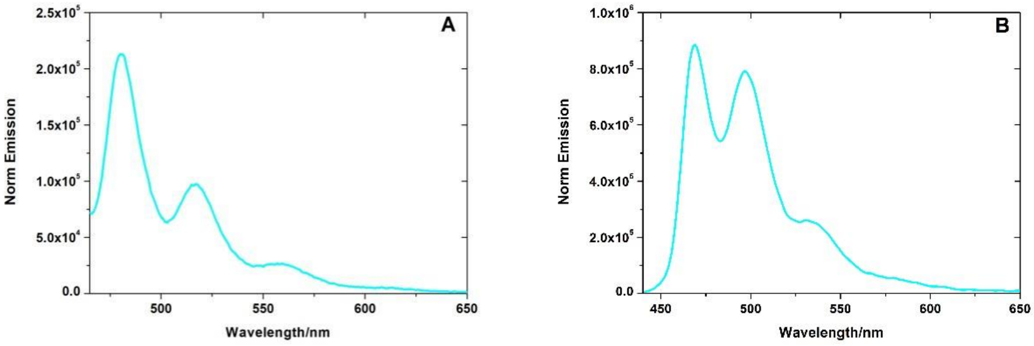


Figure S3. Fluorescence emission spectra of catalyst ODA **1** (A) and ODA **2** (B) in DCM.

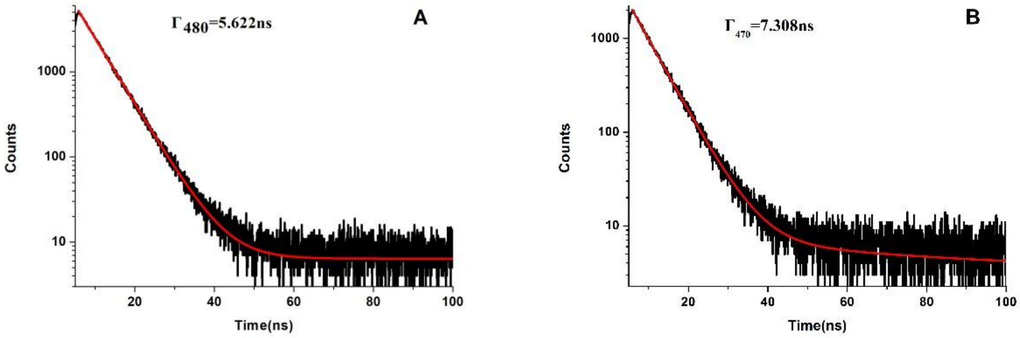


Figure S4. Time-resolved emission decay curves of catalyst ODA **1** (A) and ODA **2** (B) in DCM.

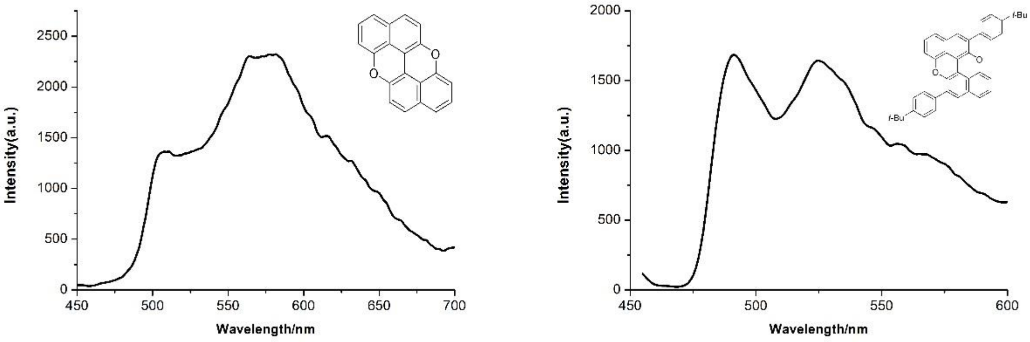


Figure S5. Gated photoluminescence (PL, 77K) spectra of ODA **1** and ODA **2** in DMA.

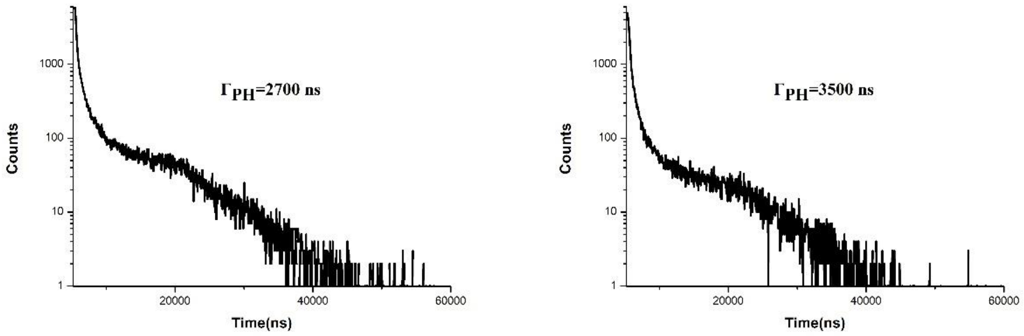


Figure S6. Time resolved phosphorescence decay transients of catalysts ODA **1** (right) and ODA **2** (left) in DMA.

Cyclic voltammetry

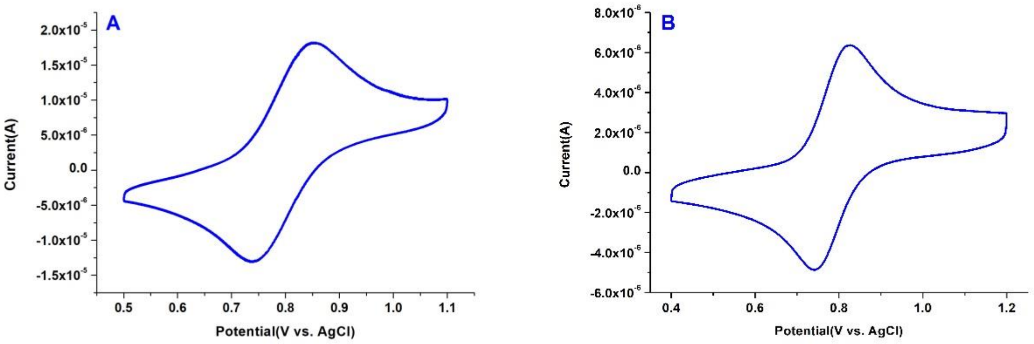


Figure S7. Cyclic voltammograms (vs. Ag/AgCl) of catalyst ODA 1 (A) and ODA 2 (B) in DCM.

Experimental determination of excited state reduction potentials

Using photoluminescence maximum and E^{ox}, the excited state reduction potential was estimated for OPCs ($\boldsymbol{E_{red}}$ **(OPC$^{\bullet+}$/ OPC*)**) according to the following equations[3]

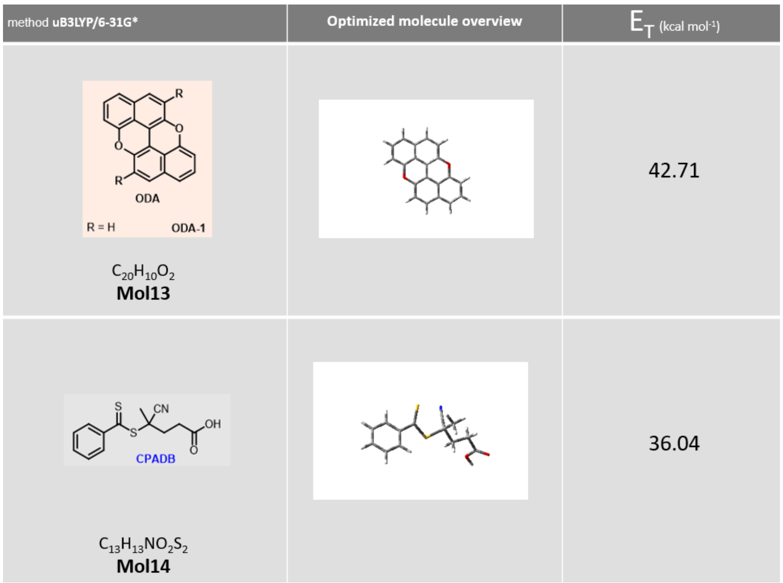
$$\boldsymbol{E_{red}\ (\mathrm{OPC}^{\bullet+}/\ \mathrm{OPC}^*) = \mathrm{E}^{ox} - \mathrm{E}_{0,0}}$$

$$\textbf{where } \boldsymbol{\mathrm{E}_{0,0} = hc / \lambda_{max} = 1240\ \mathrm{nm} / \lambda_{max}}$$

Table S1. Experimentally measured excited state reduction potentials of ODA 1 & 2.

Photocatalyst	Abs λ_{max}(nm)	ε λmax (M^{-1} cm^{-1})	em λ_{max}(nm)	E_{ox} vs. SCE	E_{red}($PC^{\cdot+}$/PC*) vs. SCE
ODA 1	**443**	**17450**	**481**	**+0.82 V**	**-1.76V**
ODA 2	**455**	**23950**	**469**	**+0.80 V**	**-1.84V**

By DFT molecular calculation performed at uB3LYP/6-31G* level of theory.



method **uB3LYP/6-31G***	**Optimized molecule overview**	E_T (kcal mol^{-1})
$C_{20}H_{10}O_2$ **Mol13**		42.71
$C_{13}H_{13}NO_2S_2$ **Mol14**		36.04

The triplet state energy of ODA is slightly higher than CPADB therefore a triplet-triplet energy transfer can not be completely ruled out. However, as we observe singlet state quenching by fluorescence spectroscopy (below Figure S21-23: **7.** Fluorescence quenching study, a significant fluorescence quenching by addition of two CTA was observed.), the electron transfer probably predominates as a singlet state quenching of ODA which could also decrease the chance of intersystem crossing to the triplet state and the subsequent energy transfer activation.

3. Genaral preocedures for polymerizations

Typical PET-RAFT polymerization procedures with the molar ratio of [monomer]$_0$: [CTA]$_0$: [catalyst]$_0$ = 2000: 10: 0.01 were showed as follows. The polymerization was conducted with MMA (1.0 mL, 9.35 mmol, 2000 eq.) as the model monomer, CTA (46.75 μmol, 10 eq.), organic photocatalyst (0.04675 μmol, 0.01 eq., 5 ppm) and DMSO (1.0 mL) as the solvent in a 10mL 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 light irradiation at room temperature. Aliquots were withdrawn by Argon-purged syringes from the reaction mixture at predetermined interval times and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to measure the conversions, number average molecular weights (M_n), and polydispersities (M_n/M_w).

Stock solution of OPCs in DMSO was used for a better reproducibility. (Take ODA **1** as an example: stock solution of ODA **1**: 1.88 μmol/mL in DMSO, weigh 5.27 mg ODA 1 (18.8 μmol) accurately, dissolve in 10 mL dry DMSO, and dilute again if it's necessary. High Mn's polymer product repeated the same steps to prepare solution of chain transfer agent (CTA).

General procedures for negative control experiments of PET-RAFT polymerization

A typical PET-RAFT polymerization procedure with the molar ratio of [monomer]$_0$: [CTA]$_0$: [catalyst]$_0$ = 2000: 10: 0 was showed as follows. The polymerization was conducted with MMA (1.0 mL, 9.35 mmol, 2000 eq.) as the model monomer, CTA (46.75 μmol, 10 eq.) and DMSO (1.0 mL) as the solvent in a 10mL 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 light irradiation at room temperature. Aliquots were withdrawn by Argon-purged syringes from the reaction mixture at predetermined interval times and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to measure the conversions, number average molecular weights (M_n), and polydispersities (M_n/M_w), detailed data see Table S2.

General procedure for light ON-OFF experiment of PET-RAFT polymerization

Light ON-OFF experiments were performed in glovebox using a [MMA]: [CPADB] ratio of 200:1 with 5 ppm of OPC and 1 mL:1.5 mL of MMA: DMSO. The samples were irradiated for predetermined time at which point an aliquot was taken for ^{1}H NMR and GPC analysis. The lights were turned off and the reaction vial was wrapped entirely in aluminum foil. After certain dark period, another aliquot was taken for ^{1}H NMR and GPC analysis. This light on–off cycle was repeated several times until over 80% conversion of the monomer was achieved.

General procedures for kinetic studies of PET-RAFT polymerization

In a typical experiment of kinetic study of MMA polymerization, In a glove box, a 10mL Schlenk tube with a PTFE stirring bar and charged with DMSO (2 mL), MMA (2ml, 18.7 mmol), CPADB (26 mg, 93.5 μmol), and OPC (9.35×10^{-2} μmol). The mixture was then irradiated by a blue bulb at room temperature. Aliquots were withdrawn by Argon-purged syringes from the reaction mixture at predetermined interval times and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to measure the conversions, number average molecular weights (M_n), and polydispersities (M_n/M_w).

For the kinetic study of BA polymerization, In a glove box, a 10mL Schlenk tube with a PTFE stirring bar and charged with DMSO (2 mL), BA (2.0 mL, 13.9 mmol), BTPA (16.5 mg, 69.4 μmol), and OPC (6.94×10^{-2} μmol). The mixture was then irradiated by a blue bulb at room temperature. Aliquots were withdrawn by Argon-purged syringes from the reaction mixture at predetermined interval times and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to measure the conversions, number average molecular weights (M_n), and polydispersities (M_n/M_w).

General procedure for the preparation of diblock copolymers by PET-RAFT polymerization

In a typical experiment synthesizing the diblock copolymer poly(methyl methacrylate)-b-poly(methyl methacrylate) (PMMA-b-PMMA), a 10mL Schlenk tube with a PTFE stirring bar and charged with DMSO (0.5 mL), MMA (0.5 mL, 4.7 mmol), CPADB (6.5 mg, 23.4 μmol), ODA **2** (1.28×10^{-2} mg, 2.34×10^{-2} μmol). The mixture was deoxygenized by freeze–pump–thaw cycle three times, backfilled argon and sealed up subsequently. The mixture was then irradiated by a blue bulb as light source at room temperature for 14 h. The final solution was precipitated in mixture of methanol/petroleum spirit (1/1, v/v) with stirring. The pink precipitate was collected, re-dissolved in a minimal amount of dichloromethane, and precipitated a second time. The pink precipitate was collected and dried to give desired products: $M_n = 15.1$ kg/mol, $M_n/M_w = 1.06$.

For the chain extension, a 10mL Schlenk tube with a PTFE stirring bar and charged with DMSO (0.8 mL), MMA (0.42mL, 3.97 mmol, 1 eq.), PMMA macro-initiator (200 mg, $M_n = 15100$ g/mol, 0.0132 mmol, 300 eq.), and ODA **2** (1.08×10^{-2} mg, 0.01985 μmol). The mixture was deoxygenized by freeze–pump–thaw cycle three times, backfilled argon and sealed up subsequently. The mixture was then irradiated by a blue bulb as light source at room temperature for 22 h. The final solution was precipitated in methanol with stirring. The pink precipitate was then collected and dried to give desired products: M_n = 39.6 kg/mol, M_n/M_w = 1.19.

Preparation of decablock copolymer of BA by photoinduced PET-RAFT polymerization without purification.

In a glove box, butyl acrylate (BA, 0.25 mL, 1.74 mmol, 100 eq.), DMSO (0.3 mL), BTPA (4.14 mg, 0.0174 mmol, 1 eq.), and ODA **2** (9.2 μmol, 0.0047 mg, 0.0087 μmol, 5 ppm) were charged to a pear-shaped flask fitted with a rubber septum. The mixture was then irradiated by a blue bulb as light source at room temperature for 4 h. After 4h, an aliquot of the reaction mixture was withdrawn for ^{1}H NMR and GPC (THF) analysis. The sample for ^{1}H NMR was simply diluted with CDCl3 and the sample for GPC (THF) analysis was diluted with THF and filtered through a Teflon filter. For the iterative chain extensions, a further 0.25 mL or 0.3 mL g of a degassed monomer (in 45 v-% DMSO for 2-5 blocks, and 25 v-% DMSO for 6-10 blocks) solution was added via a argon-purged syringe, and again the solution was allowed to polymerize at room temperature for 4 h. The above polymerization-sampling-extension procedure was repeated as required.

General procedures for kinetic studies of PET-RAFT polymerization under air.

In a typical experiment of kinetic study of MMA polymerization, a 10mL Schlenk tube with a PTFE stirring bar and charged with DMSO (2 mL), MMA (2 ml, 18.7 mmol), CPADB (26 mg, 93.5 μmol), and OPC (9.35×10^{-2} μmol). The mixture was then irradiated by a blue bulb at room temperature. Aliquots were withdrawn by argon-purged syringes from the reaction mixture at predetermined interval times and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to measure the conversions, number average molecular weights (M_n), and polydispersities (M_n/M_w).

4. **Additional data of PET-RAFT polymerization**

Table S2. Background reaction results of PET-RAFT polymerization of monomer families.[a]

Entry	[M]:[CTA]:[OPC]	Monomer	CTA	time	Conv.	M_n (kg/mol)	Đ
1	200:1:0	MMA	CPADB	18 h	<1%	/	/
2	200:1:0	BnMA	CPADB	10 h	<1%	/	/
3	200:1:0	BA	BTPA	5 h	<1%	/	/
4	200:1:0	St	BTPA	30 h	<1%	/	/
5	200:1:0	DMA	BTPA	5 h	<1%	/	/

[a]Polymerizations of various monomer families were performed at [M]:[CTA]:[OPC] = [200]:[1]:[0] with blue bulb irradiation and the same volume of solvent as that of the monomer added. (M_n = number-average molecular weight). Conv. measured by ^{1}H NMR, M_n and $Đ$ were determined using GPC with PMMA standards. Please see Figure **S24-S28** for the spectra of ^{1}H NMR, which indicated no background reaction under this photo reaction setup after light irradiation of the predetermined time duration.

Table S3. Synthesis of decablock PBA polymers by an iterative approach. via PET-RAFT polymerization.

Entry	Experimental Conditions[a] [M]:[BTPA]	Conv. [b]	$M_{n,\text{theo}}$ (kg/mol)	$M_{n,\text{exp}}$ (kg/mol)	M_w/M_n [d]
1	100:1	94 %	12.23	12.4	1.04
2	120:1	99 %	27.5	28.6	1.06
3	120:1	98 %	42.6	42.4	1.08
4	100:1	99 %	55.4	54.2	1.10
5	120:1	98 %	70.5	69.8	1.14
6	120:1	96 %	85.2	84.9	1.17
7	120:1	96 %	99.9	107.0	1.18
8	120:1	98 %	115.0	118.3	1.21
9	100:1	96 %	127.3	127.7	1.25
10	120:1	97 %	142.2	143.2	1.31

a) The reactions were performed in DMSO at room temperature for 4 h under blue bulb as light source with an initial [ODA **2**]/[BA] molar ratio of 5 ppm. We did not add photocatalyst during the chain extension process. After 5 chain extensions, the polymerization was diluted by addition of DMSO due to viscosity and carried out using BA/DMSO mixture of 25/75 (v/v); b) Monomer conversion determined by ^{1}H NMR spectroscopy was calculated by the following equation: α = (1 & [($I^{5.5\text{-}6.5ppm}$/3)/($I^{3.6ppm}$/3)]) × 100; c) Theoretical molecular weight calculated using the following equation: $M_{n,\,th} = [BA]_0/[BTPA]_0 \times MW_{BA} \times \alpha + MW_{BTPA}$, where $[BA]_0$, $[BTPA]_0$, MW_{BA}, α and MW_{BTPA} correspond to BA and BTPA concentration, molar mass of BA, monomer conversion and molar mass of BTPA; d) Molecular weight and dispersity determined by GPC analysis (THF used as eluent).

Table S4. The synthesis of high Mn PMMA and additional investigation of oxygen tolerance.[a]

Entry	PC	ratio	loading	Atmosphere	Conv.	$M_{n,exp}$ kg/mol	$M_{n,theo}$ kg/mol	Đ	I%
1	ODA **1**	4000:1:0.02	5 ppm	Ar	44.8%	201.8	179.7	1.28	89.1
2	ODA **2**	4000:1:0.02	5 ppm	Ar	51.2%	226.6	205.3	1.26	90.6
3	ODA **1**	8000:1:0.04	5 ppm	Ar	40.5%	405.1	324.6	1.39	80.2
4	ODA **2**	8000:1:0.04	5 ppm	Ar	48.5%	411.3	388.7	1.59	94.5
5	ODA **1**	200:1:0.001	5 ppm	Blow air	82.3%	41.9	16.7	1.21	39.9
6	ODA **2**	200:1:0.001	5 ppm	Blow air	83.8%	44.7	17.0	1.35	38.2
7	ODA **1**	200:1:0.001	5 ppm	No degassing	50.8%	13.2	10.4	1.12	79.1
8	ODA **2**	200:1:0.001	5 ppm	No degassing	41.4%	10.6	8.6	1.13	80.7

a) The reactions were performed at [MMA]: [CPADB]: [OPC]=X: 1: 5 ppm in DMSO at room temperature for 20 h under blue bulb (3 mw/cm^2) as light source with 5 ppm catalyst loading.

Table S5. Comparison with other photocatalysts (metal and organic photocatalysts) in PET-RAFT.

Entry	Monomer	Catalyst/Initiator System	Catalyst Residue	Reaction Temp	Reference
1	MMA/BnMA	ODAs/CPADB	1-10 ppm	25, Blue Light	This work
	BA/DMA/St	ODAs/BTPA	0.1-10/1-5/5 ppm		
2	Fuorinated (Meth)acrylates	PTZ-biP/PTF1/CTA	2000 ppm	25, White Light	*Angew. Chem. Int. Ed.* **2020**, *59*, 919–927
3	MMA	4DP-IPN/CPADB	5 ppm	25, Blue Light	*Macromolecules* **2019**, *52*, 5538−5545
4	DMA	Halogenated Xanthene Dyes/BTPA	20 ppm	25, Yellow or green Light	*Macromolecules* **2019**, *52*, 236−248
5	Semifluorinated (Meth)acrylates	sub-PTH/TTC	500 ppm	25, White Light	*Angew. Chem., Int. Ed.* **2018**, *57*, 333−337
6	MA	*N,N*-diaryl dihydrophenazines /BTPA	50 ppm	25, Blue Light	*ACS Macro Lett.* **2018**, *7*, 662−666
7	MMA	Benzaldehyde Derivatives /CPADB	200000 ppm	25, White CFL Bulb	*J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 229−236
8	AN	4CZ-IPN/CPDN	25-100 ppm	25, Blue Light	*Polymers* **2017**, *9*, 4
9	MMA/MA	Pheo A & Zn-TPP/CPADB BTPA	1-100 ppm	25, Blue or red Light	*J. Am. Chem. Soc.* **2016**, *138*, 3094−3106
10	MMA	eosin Y & fluorescein /CPADB/TEA	10-100 ppm	25, Blue or green Light	*Polym. Chem.* **2015**, *6*, 5615−5624
11	NiPAAm/t-BA	PTH 1a/TTC	200 ppm	25, White CFL Bulb	*ACS Macro Lett.* **2015**, *4*, 566−569
12	MMA	$Ru(bpy)_3Cl_2$/CPADB	5 ppm	25, Blue Light	*Macromolecules* **2014**, *47*, 4217−4229
	MA/DMA/St	$Ru(bpy)_3Cl_2$/BTPA	1/1/20 ppm		
13	MMA/HPMA	*fac*-$Ir(ppy)_3$/CPADB	1-5 ppm	25, Blue Light	*J. Am. Chem. Soc.* **2014**, *136*, 5508−5519
	MA/DMA/St	*fac*-$Ir(ppy)_3$/BTPA	0.1-5/1/10-100		

5. NMR spectra of precipitated polymer products

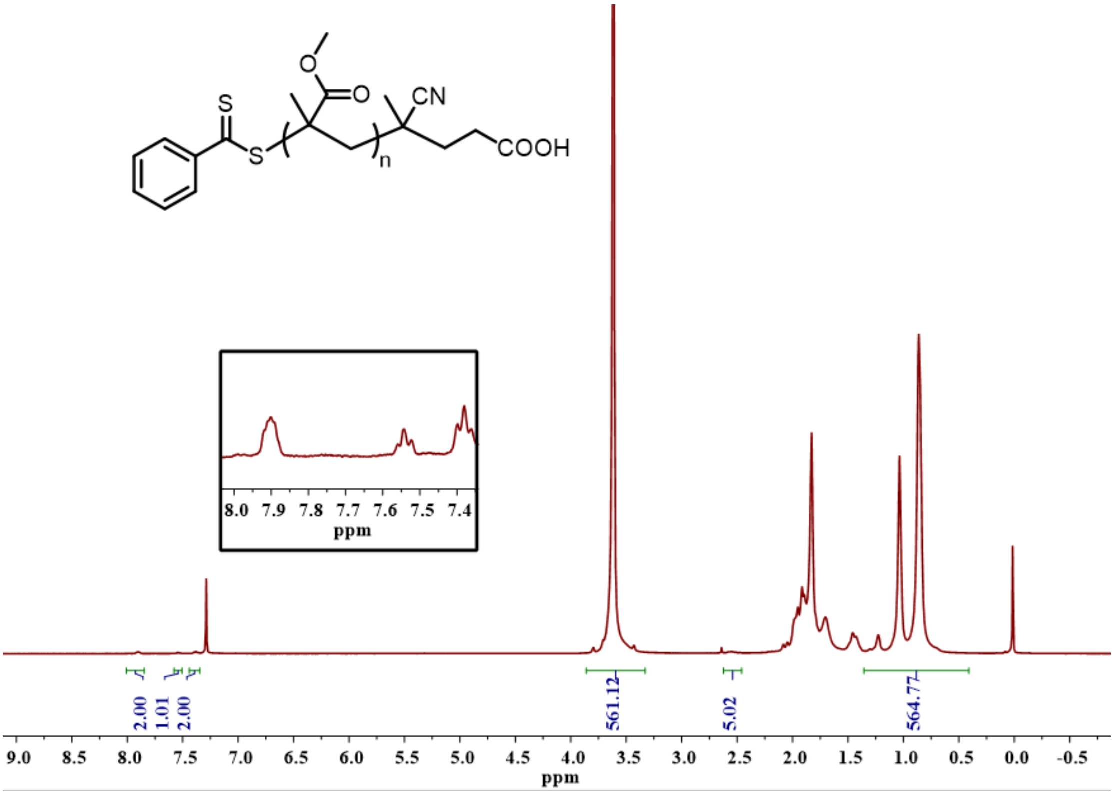


Figure S8. ^{1}H NMR spectra for purified PMMA polymer synthesized by photoinduced living polymerization ($M_{n,NMR,PMMA}$ = 19000 g/mol, $M_{n,exp,PMMA}$ = 18600 g/mol, monomer conversion 91%)

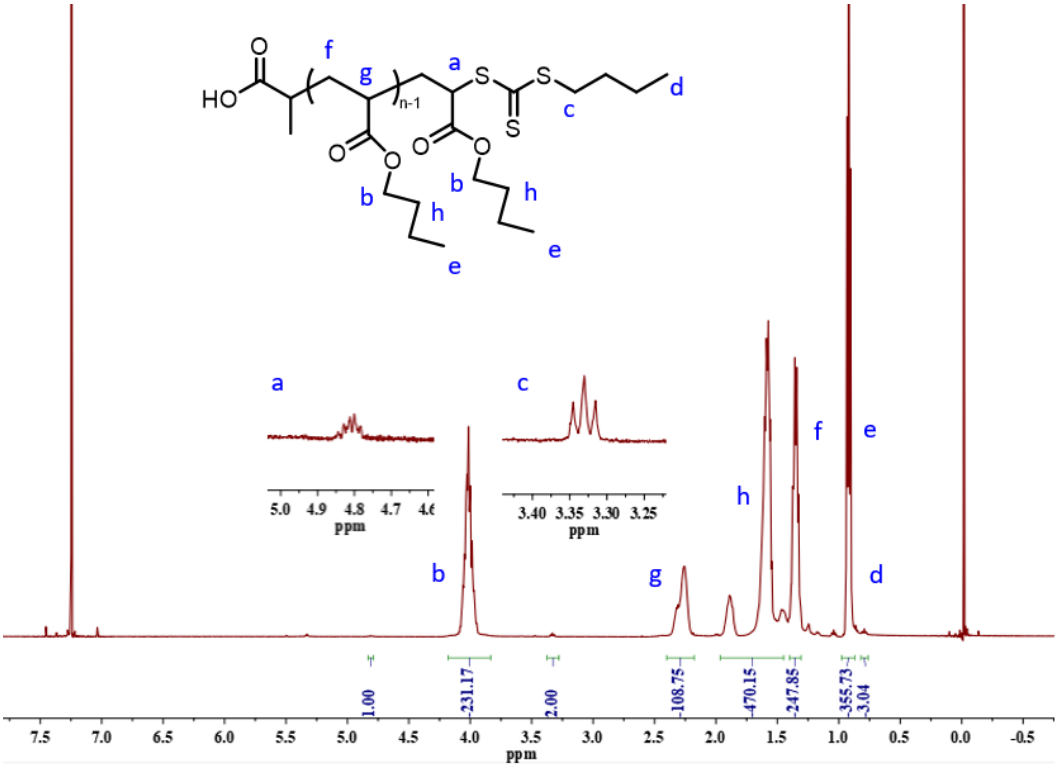


Figure S9. ^{1}H NMR spectra for purified PBA polymer synthesized by photoinduced living polymerization ($M_{n,NMR,PMMA}$ = 15200 g/mol, $M_{n,exp,PMMA}$ = 15600 g/mol, monomer conversion 61%)

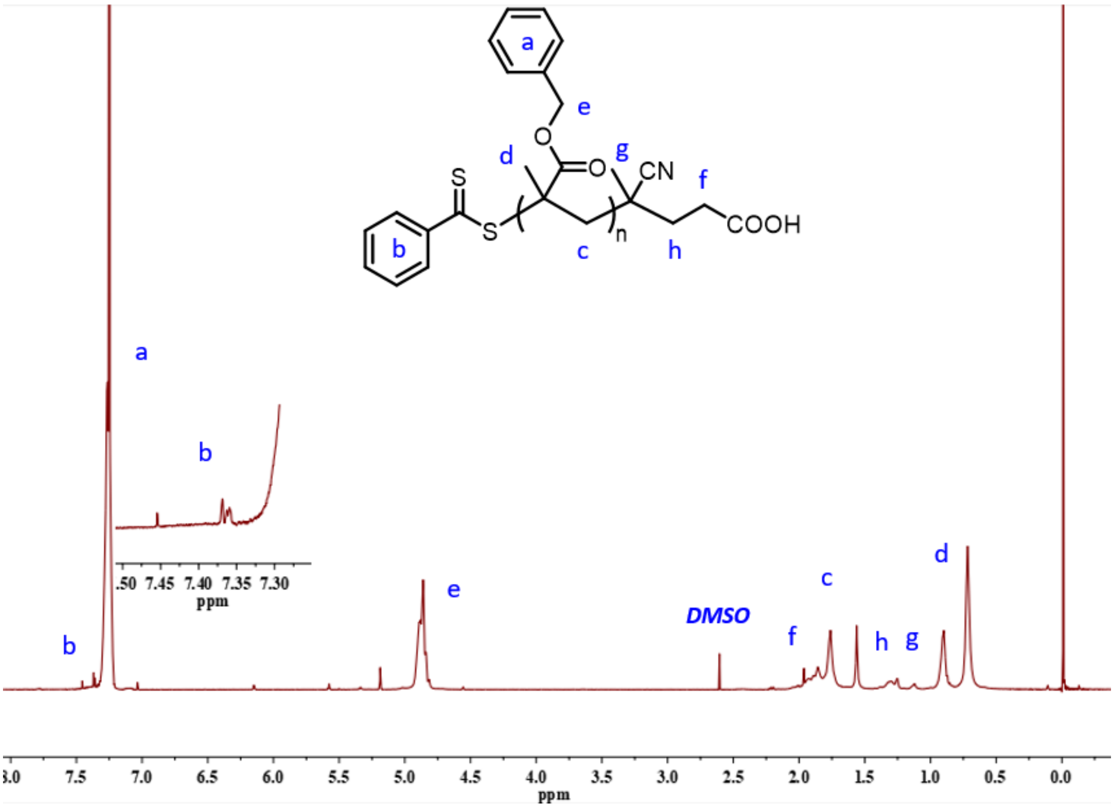


Figure S10. ^{1}H NMR spectrum of isolated poly(benzyl methacrylate) made using **ODA 2** (5 ppm PC loading) as the catalyst. (CDCl$_3$)

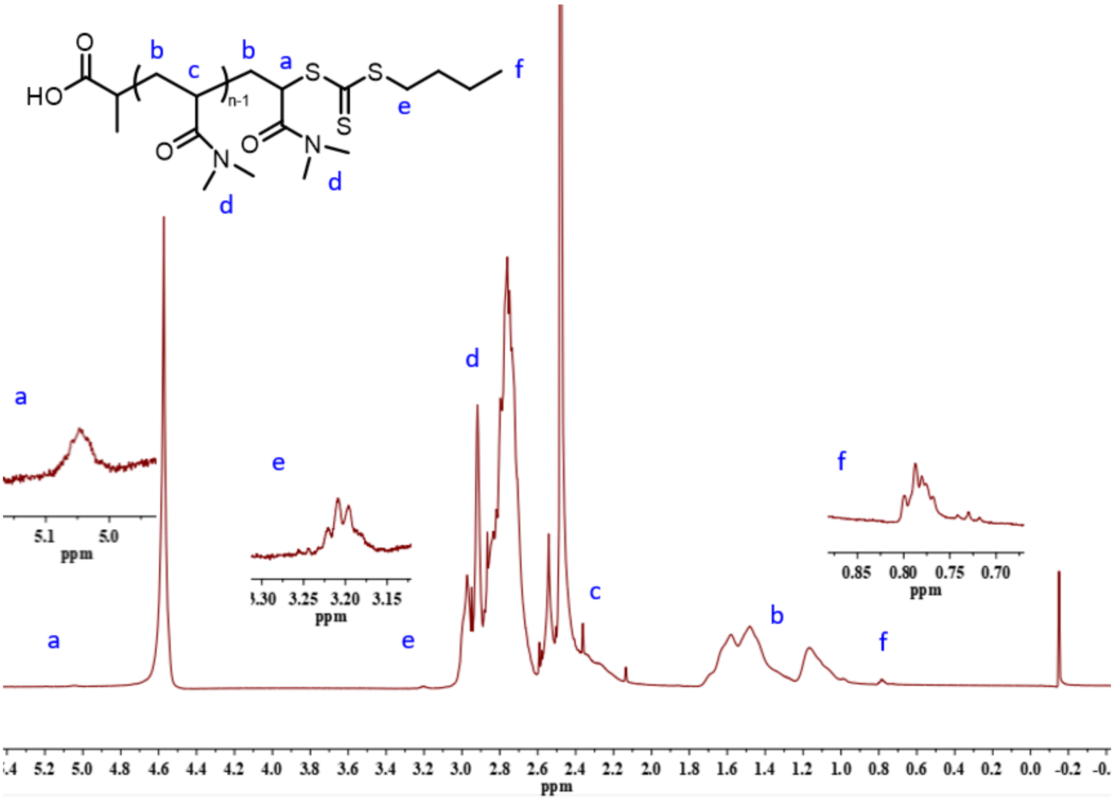


Figure S11. ^{1}H NMR spectrum of isolated poly(*N*,*N*-dimethylacrylamide) made using **ODA 2** (5 ppm PC loading) as the catalyst. (CDCl$_3$)

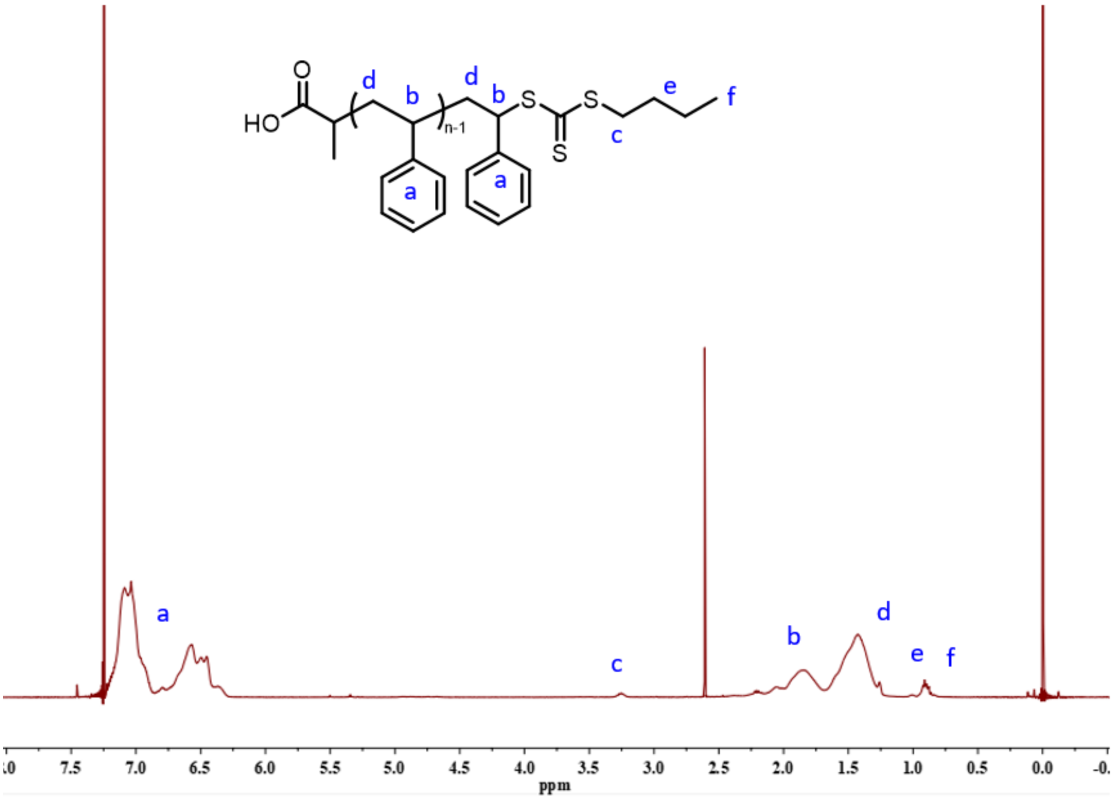


Figure S12. ^{1}H NMR spectrum of isolated poly(styrene) made using **ODA 2** (5 ppm PC loading) as the catalyst. ($CDCl_3$)

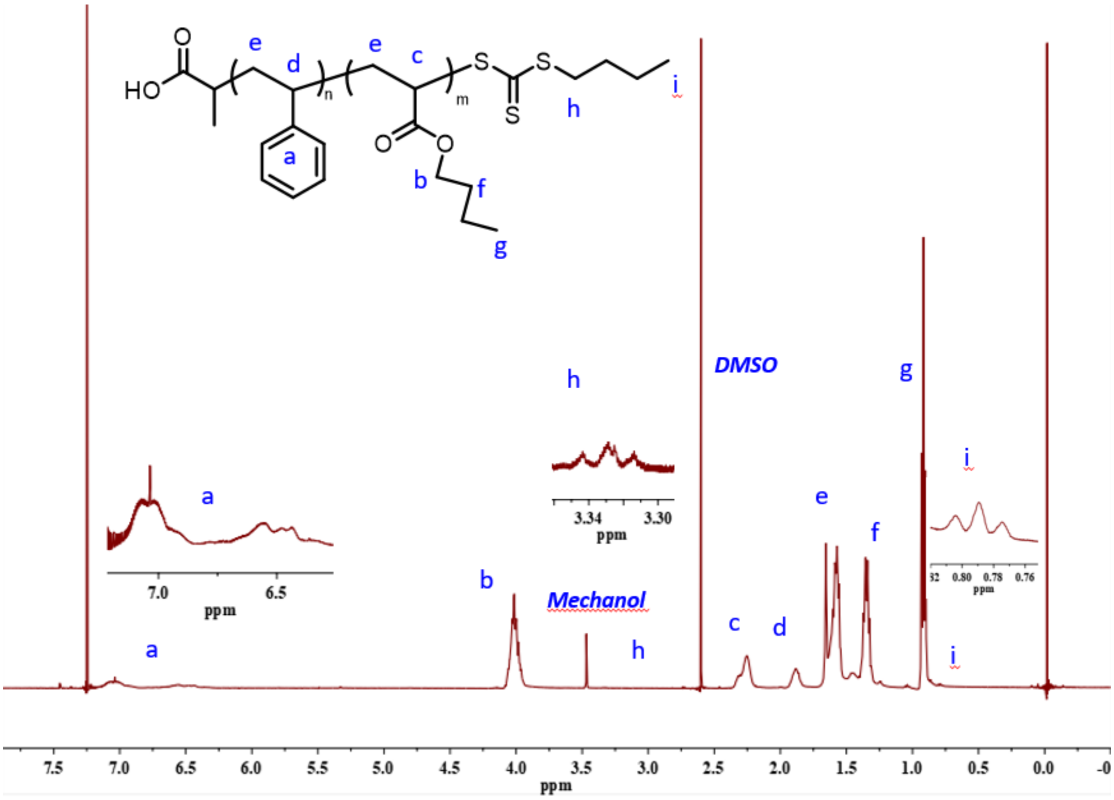


Figure S13. ^{1}H NMR spectrum of isolated poly(styrene)-*b*-poly(butyl acrylate) made using **ODA 2** (5 ppm PC loading) as the catalyst. ($CDCl_3$)

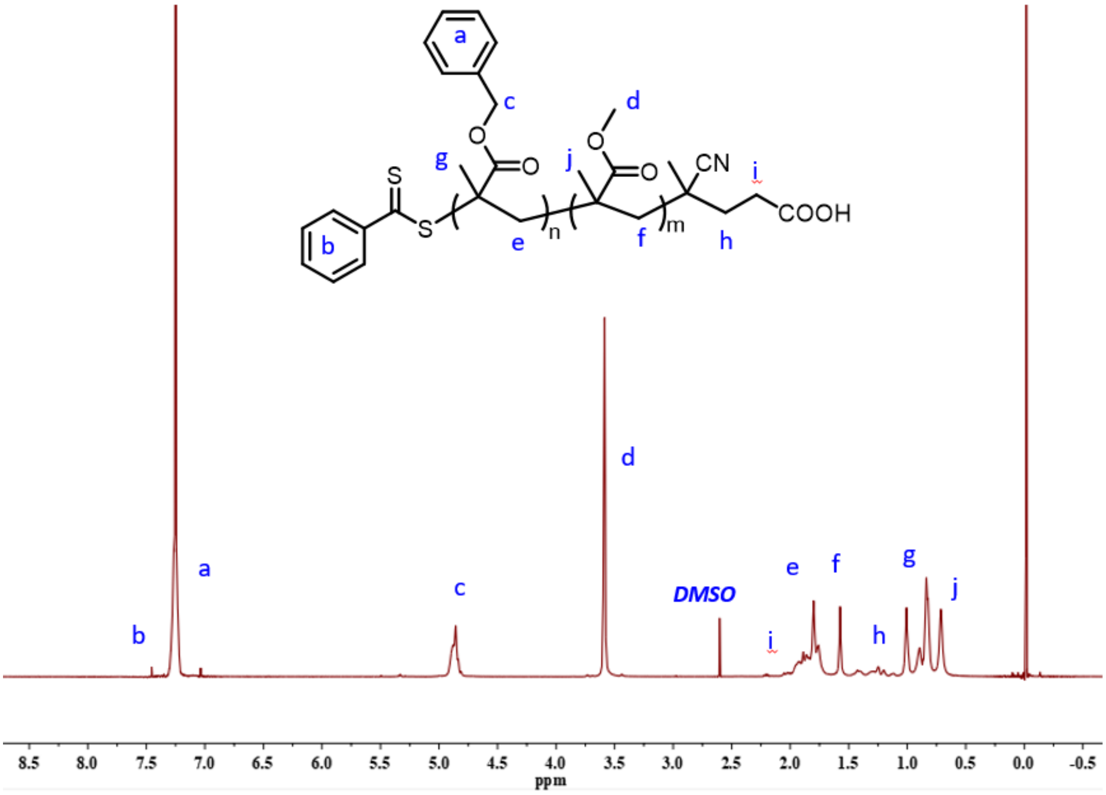


Figure S14. ^{1}H NMR spectrum of isolated poly(benzyl methacrylate)-b-poly(methyl methacrylate) made using **ODA 2** (5 ppm PC loading) as the catalyst. (CDCl$_3$)

6. Additional copolymer GPC traces

Synthesis of PBnMA Macroinitiator

BnMA (1.00 mL, 5.90 mmol, 100 eq.), CPADB (16.5 mg, 0.059 mmol, 1 eq.), and ODA **2** (0.017 mg, 0.0295 μmol, 0.0005 eq., 5 ppm) were dissolved in 1.5 mL DMSO and reacted according to the above general polymerization procedure for 12 hours. After predetermined time, the reaction was removed from the light, poured into 50 mL of methanol, stirred for approximately 1 hour, and the product polymer was then isolated by vacuum filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of THF and the process repeated two times to ensure complete removal of any unreacted monomer, CTA, or catalyst. (Conv =81%, M_n = 14.5 kg/mol, $Đ$ = 1.10) (GPC trace in **Figure S15**, Black line).

Synthesis of PBnMA-*b*-PBnMA from isolated macroinitiator

PBnMA macroinitiator (vide supra) (100 mg, 6.89 μmol, 10 eq.), BnMA (350 μL, 2.07mmol, 3000 eq.), and ODA **2** (0.0059 mg, $10.3 * 10^{-3}$ μmol, 5 ppm) were dissolved in 1.40 mL DMSO and reacted according to the above general polymerization procedure for 9 h. The resulting polymer was isolated according to the above general polymerization procedure and analyzed (isol. yield = 50%, M_n = 42.4 kg/mol, $Đ$ = 1.18) (GPC trace in **Figure S15**, Blue line).

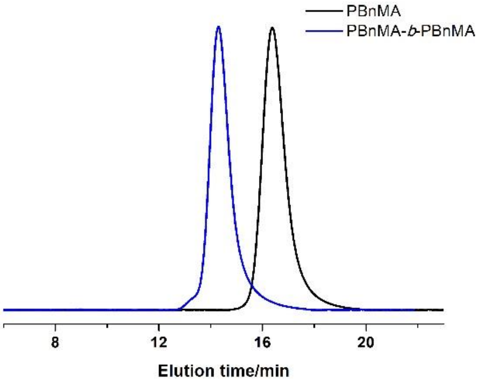


Figure S15. GPC trace showing the results of the synthesis of PBnMA-*b*-PBnMA (M_n =42.4 kg/mol, $Đ$ =1.18) from macro-initiator (black line, PBnMA, M_n =14.5 kg/mol, $Đ$ =1.10).

Synthesis of PSt macroinitiator

PSt (1.00 mL, 8.72 mmol, 200 eq.), BTPA (10.4 mg, 0.0436 mmol, 1 eq.), and ODA **2** (0.046 μmol, 5 ppm) were dissolved in 2.0 mL DMSO and reacted according to the above general polymerization procedure (under air) for 24 hours. At this time, the reaction was removed from the light, poured into 50 mL of methanol, stirred for approximately 1 hour, and the product polymer was then isolated by vacuum filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of THF and the process repeated two times to ensure complete removal of any unreacted monomer, CTA, or catalyst. (Conv =15%, M_n = 3.50 kg/mol, $Đ$ = 1.12) (GPC trace in **Figure S16**, Black line).

Synthesis of PSt-*b*-PSt from isolated macroinitiator

PSt macroinitiator (vide supra) (100 mg, 28.6 µmol, 10 eq.), St (982 µL, 8.57 mmol, 3000 eq.), and ODA **2** (0.025 mg, 0.042 µmol, 5 ppm) were dissolved in 2.0 mL DMSO and reacted according to the above general polymerization procedure for 36 h. The resulting polymer was isolated according to the above general polymerization procedure and analyzed (isol. yield = 29%, M_n = 12.9 kg/mol, $Đ$ = 1.20) (GPC trace in **Figure S16**, Blue line).

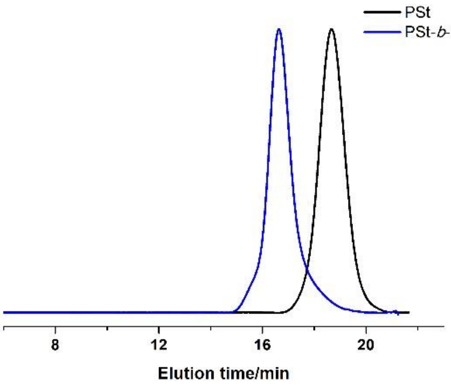


Figure S16. GPC trace showing the results of the synthesis of PSt-*b*-PSt (M_n =12.9 kg/mol, $Đ$ =1.20) from macroinitiator (black line, PSt, M_n =3.5 kg/mol, $Đ$ =1.12).

Synthesis of PMMA Macroinitiator

MMA (2.00 mL, 18.8 mmol, 200 eq.), CPADB (26.3 mg, 0.094 mmol, 1 eq.), and ODA **2** (0.054 mg, 0.094 µmol, 0.001 eq., 5 ppm) were dissolved in 2.5 mL DMSO and reacted according to the above general polymerization procedure for 18 hours. After predetermined time, the reaction was removed from the light, poured into 100 mL of methanol, stirred for approximately 1 hour, and the product polymer was then isolated by vacuum filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of THF and the process repeated two times to ensure complete removal of any unreacted monomer, CTA, or catalyst. (Conv =80%, M_n = 16.2 kg/mol, $Đ$ = 1.08) (GPC trace in **Figure S17**, Black line).

Synthesis of PMMA-*b*-PBnMA from isolated macroinitiator

PMMA macroinitiator (vide supra) (200 mg, 12.3 µmol, 10 eq.), BnMA (625 µL, 3.70 mmol, 3000 eq.), and ODA **2** (0.0106 mg, $18.5 * 10^{-3}$ µmol, 5 ppm) were dissolved in 2.0 mL DMSO and reacted according to the above general polymerization procedure for 9 h. The resulting polymer was isolated according to the above general polymerization procedure and analyzed (isol. yield = 56%, M_n = 46.5 kg/mol, $Đ$ = 1.29) (GPC trace in **Figure S17**, Blue line).

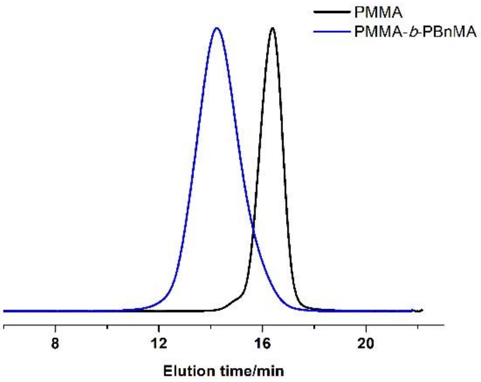


Figure S17. GPC trace showing the results of the synthesis of PMMA-*b*-PBnMA (M_n =46.5 kg/mol, $Đ$ =1.29) from macro-initiator (black line, PMMA, M_n =16.2 kg/mol, $Đ$ =1.08).

Synthesis of PBnMA Macroinitiator without degassing

BnMA (2.00 mL, 11.8 mmol, 200 eq.), CPADB (16.5 mg, 0.059 mmol, 1 eq.), and ODA **2** (0.034 mg, 0.059 µmol, 0.001 eq., 5 ppm) were dissolved in 2.5 mL DMSO and reacted according to the above general polymerization procedure for 16 hours. At this time, the reaction was removed from the light, poured into 100 mL of methanol, stirred for approximately 1 hour, and the product polymer was then isolated by vacuum filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of THF and the process repeated two times to ensure complete removal of any unreacted monomer, CTA, or catalyst. (Conv =78%, M_n = 31.0 kg/mol, $Đ$ = 1.11) (GPC trace in **Figure S18 & 19**, Black line).

Synthesis of PBnMA-*b*-PBnMA from isolated macroinitiator

PBnMA macroinitiator (vide supra) (200 mg, 6.45 µmol, 10 eq.), BnMA (325 µL, 1.93 mmol, 3000 eq.), and ODA **2** (0.0055 mg, 9.65 $*$ 10^{-3} µmol, 5 ppm) were dissolved in 1.00 mL DMSO and reacted according to the above general polymerization procedure with no degassing and irradiated for 18 h. The resulting polymer was isolated according to the above general polymerization procedure and analyzed (isol. yield = 81%, M_n = 75.1 kg/mol, $Đ$ = 1.33) (GPC trace in **Figure S18**, Red line).

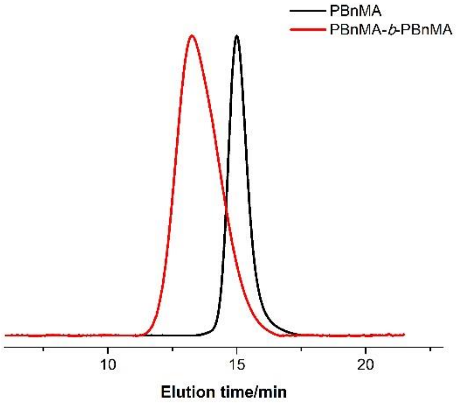


Figure S18. GPC trace showing the results of the synthesis of PBnMA-*b*-PBnMA (M_n =75.1 kg/mol, $Đ$ =1.33) from macro-initiator (black line, PBnMA, M_n =31.0 kg/mol, $Đ$ =1.11).

Synthesis of PBnMA-*b*-PMMA from isolated macroinitiator

PBnMA macroinitiator (vide supra) (200 mg, 6.45 μmol, 10 eq.), MMA (205 μL, 1.93 mmol, 3000 eq.), and ODA **2** (0.0055 mg, $9.65 * 10^{-3}$ μmol, 5 ppm) were dissolved in 1.00 mL DMSO and reacted according to the above general polymerization procedure with no degassing and irradiated for 21 h. The resulting polymer was isolated according to the above general polymerization procedure and analyzed (isol. yield = 86%, M_n = 57.2 kg/mol, $Đ$ = 1.35) (GPC trace in **Figure S19**, Red line).

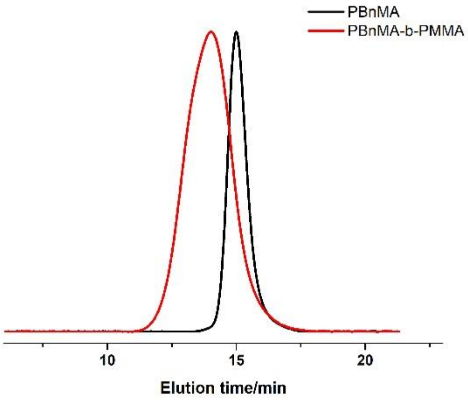


Figure S19. GPC trace showing the results of the synthesis of PBnMA-*b*-PMMA (M_n =57.2 kg/mol, $Đ$ =1.35) from macro-initiator (black line, PBnMA, M_n =31.0 kg/mol, $Đ$ =1.11).

Synthesis of PSt macroinitiator without degassing

PSt (1.00 mL, 8.72 mmol, 200 eq.), BTPA (10.4 mg, 0.0436 mmol, 1 eq.), and ODA **2** (0.043 μmol, 5 ppm) were dissolved in 2.0 mL DMSO and reacted according to the above general polymerization procedure for 32 hours. At this time, the reaction was removed from the light, poured into 50 mL of methanol, stirred for approximately 1 hour, and the product polymer was then isolated by vacuum filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of THF and the process repeated two times to ensure complete removal of any unreacted monomer, CTA, or catalyst. (Conv =21%, M_n = 5.07 kg/mol, $Đ$ = 1.09) (GPC trace in **Figure S20**, Black line).

Synthesis of PSt-*b*-PSt from isolated macroinitiator

PSt macroinitiator (vide supra) (100 mg, 19.7 μmol, 10 eq.), St (677 μL, 5.91 mmol, 3000 eq.), and ODA **2** (0.016 mg, 0.029 μmol, 5 ppm) were dissolved in 1.50 mL DMSO and reacted according to the above general polymerization procedure with no degassing and irradiated for 36 h. The resulting polymer was isolated according to the above general polymerization procedure and analyzed (isol. yield = 19%, M_n = 10.8 kg/mol, $Đ$ = 1.14) (GPC trace in **Figure S20**, Red line).

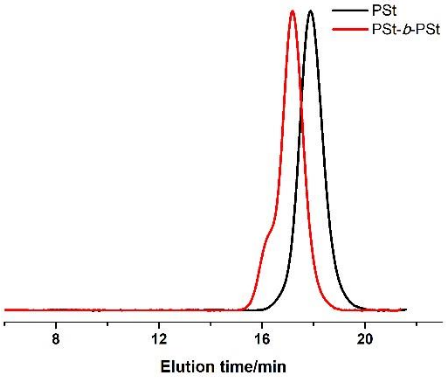


Figure S20. GPC trace showing the results of the synthesis of PSt-*b*-PSt (M_n =10.8 kg/mol, $Đ$ =1.14) from macroinitiator (black line, PBnMA, M_n =5.1 kg/mol, $Đ$ =1.09).

7. Fluorescence quenching study

The solutions of ODA **1** were excited at 418 nm and the fluorescence spectra were recorded between 430 and 650 nm. The emission of a 0.20 mM solution of ODA **1** in DMSO was measured at varying volumes of CPADB or BTPA (500 mM). As shown in **Figures S21 & S22** a significant fluorescence quenching by addition of CTA was observed. The emission of a 0.20 mM solution of ODA **1** in DMSO was also measured at varying volume of methyl methacrylate (MMA) (1 M). As shown in **Figure S23** no significant quenching of the emission of ODA **1** was observed.

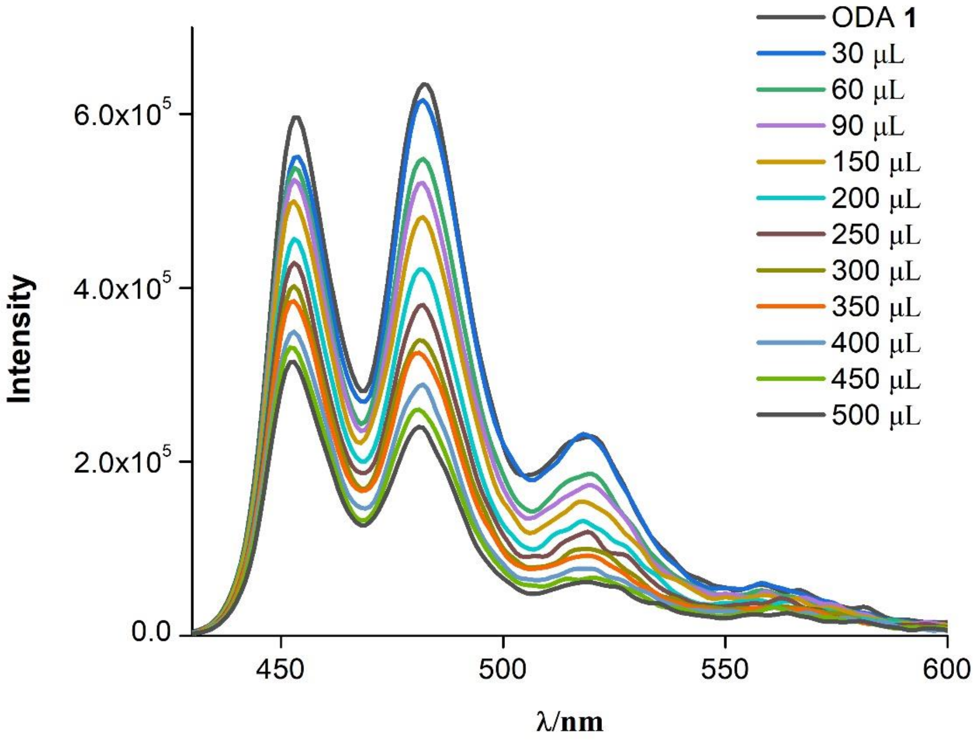


Figure S21. **Fluorescence quenching of ODA 1 by CPADB.**

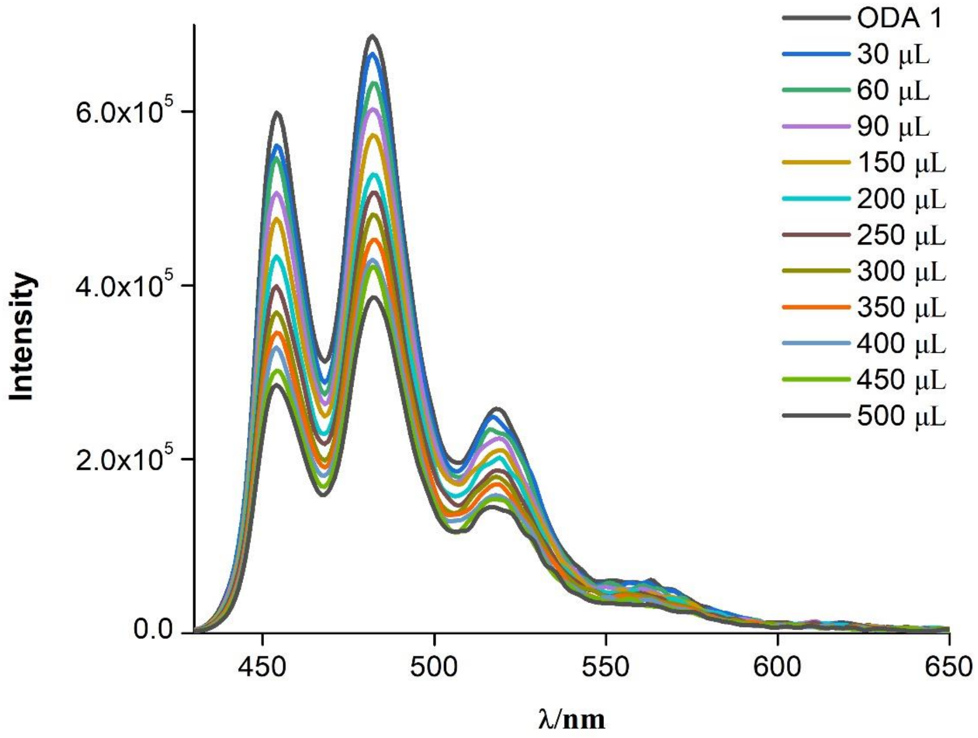


Figure S22. **Fluorescence quenching of ODA 1 by BTPA.**

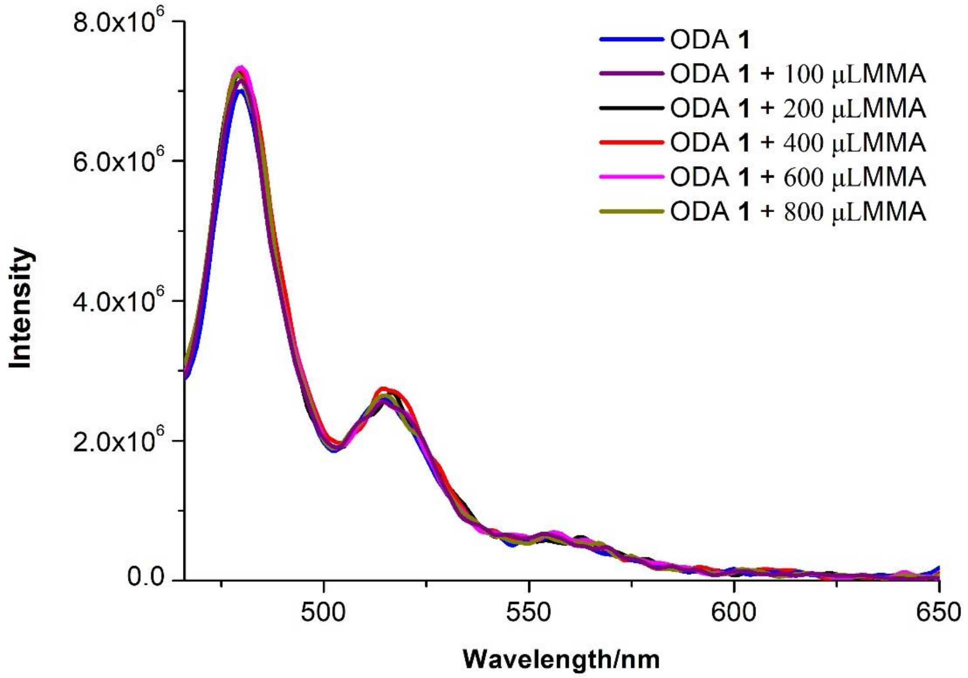


Figure S23. **Fluorescence quenching of ODA 1 by MMA.**

8. Additional Plots and Spectra

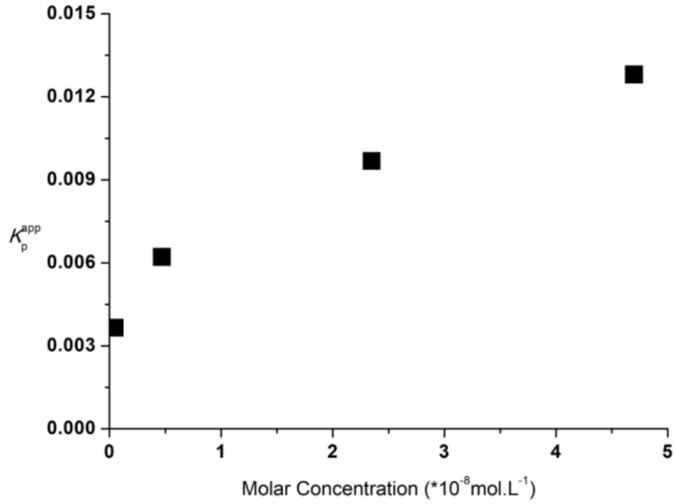


Figure S24. **The Plot of K_p^{app} vs PC molar concentration for Figure 4A.**

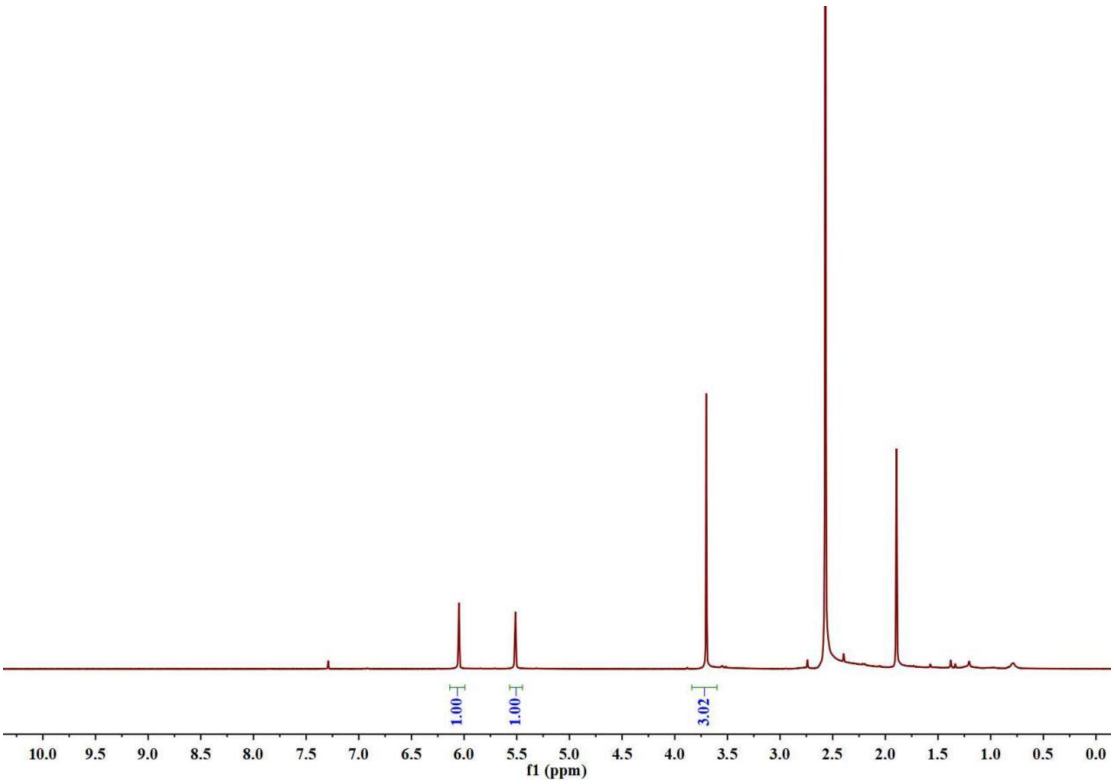


Figure S25. ^{1}H NMR spectrum of MMA reaction system in the absence of OPC after 18 h light irradiation. ($CDCl_3$)

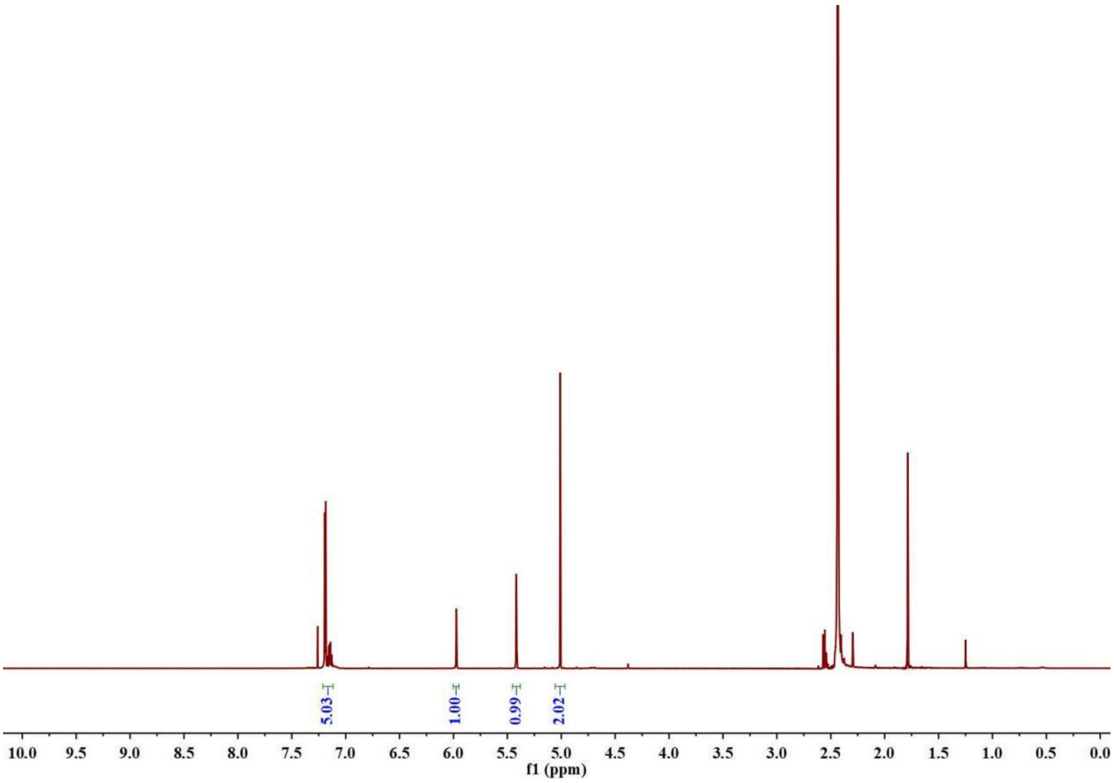


Figure S26. ^{1}H NMR spectrum of BnMA reaction system in the absence of OPC after 10 h light irradiation. ($CDCl_3$)

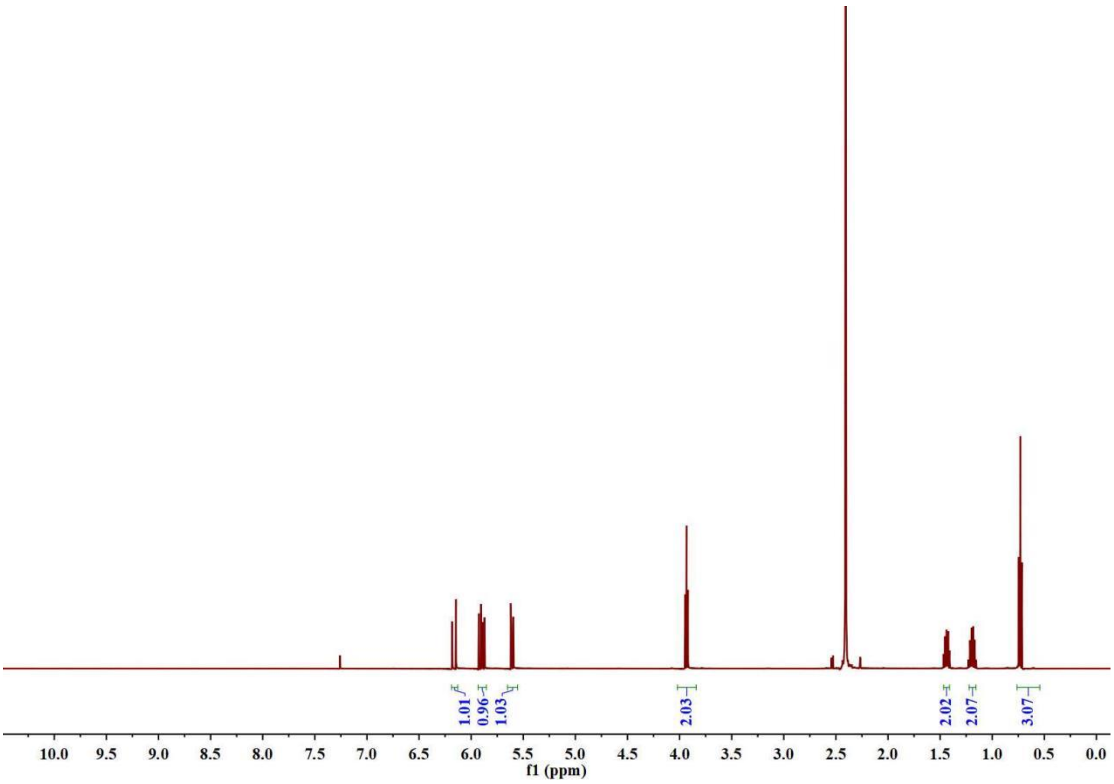


Figure S27. ^{1}H NMR spectrum of BA reaction system in the absence of OPC after 5 h light irradiation. ($CDCl_3$)

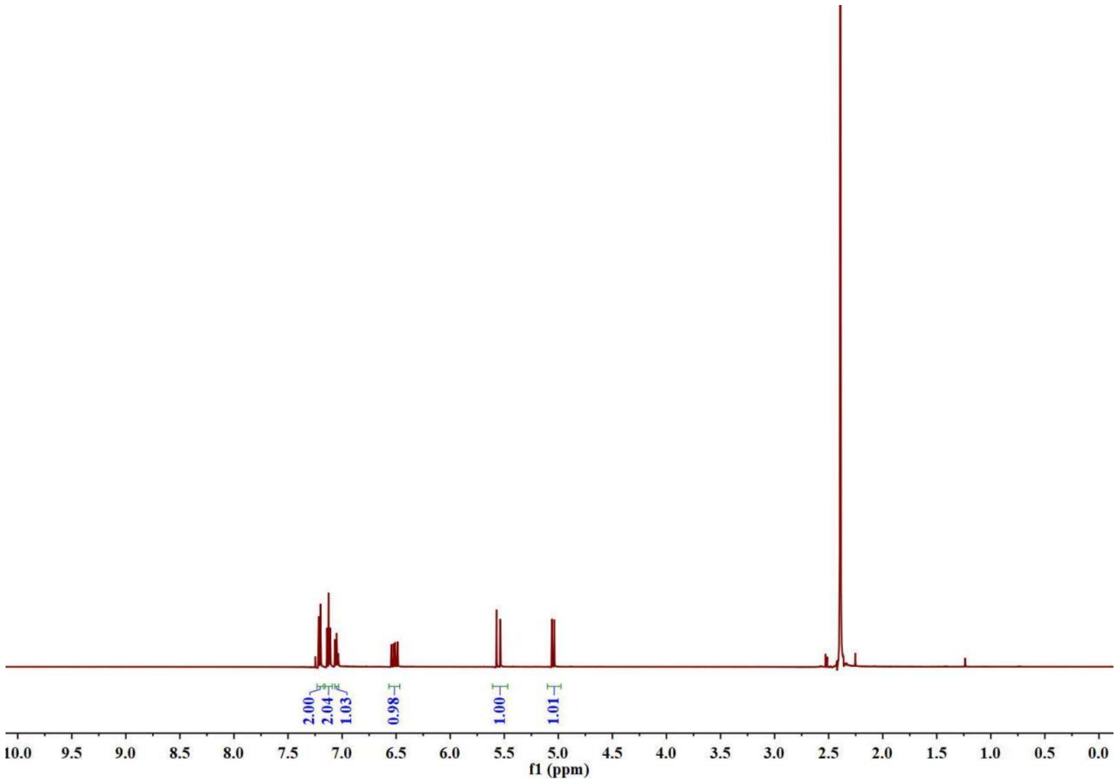


Figure S28. ^{1}H NMR spectrum of St reaction system in the absence of OPC after 30 h light irradiation. ($CDCl_3$)

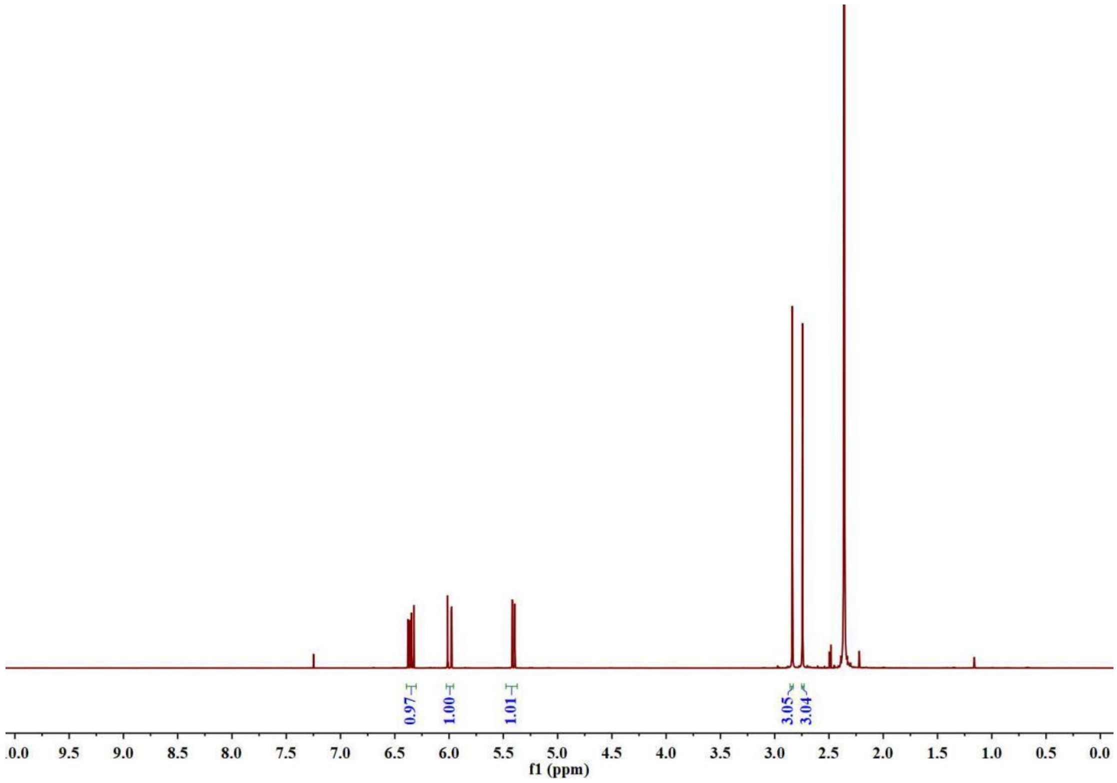


Figure S29. ^{1}H NMR spectrum of DMA reaction system in the absence of OPC after 5 h light irradiation. ($CDCl_3$)

9. Computational detail

All of the theoretical calculations were performed in Gaussian09 package. Geometries optimization calculations were carried out by a meta-GGA hybrid functional PBE0 with 6-31G* basis set for all atoms. Vibrational frequencies were calculated analytically at the same level to obtain the thermodynamic corrections. The CPCM solvation model using the self-consistent reaction field (SCRF) method with the solvents of acetonitrile was employed to account the solvent effect. The changes in Gibbs free energy are reported in the content.[5]

Computational geometries and energies

ODA 1

```
Ground state
C    4.476932   0.833126   0.000072
C    3.424481   1.776056   0.000072
C    2.123351   1.329281   0.000039
C    1.851718  -0.061276   0.000008
C    2.908173  -1.007974   0.000010
C    4.240474  -0.523602   0.000042
C    0.513032  -0.497476  -0.000023
C    0.197993  -1.835708  -0.000048
C    1.228814  -2.795014  -0.000047
C    2.545802  -2.384587  -0.000019
C   -0.513032   0.497476  -0.000011
C   -0.197993   1.835708   0.000023
C   -1.228814   2.795014   0.000046
C   -2.545802   2.384587   0.000035
C   -2.908173   1.007974   0.000003
C   -1.851718   0.061276  -0.000020
C   -4.240474   0.523602  -0.000008
C   -4.476932  -0.833126  -0.000037
C   -3.424481  -1.776056  -0.000058
C   -2.123351  -1.329281  -0.000050
O   -1.107937  -2.259388  -0.000076
O    1.107937   2.259388   0.000034
H    5.499135   1.200697   0.000098
H    3.629380   2.841772   0.000096
H    5.066337  -1.229361   0.000044
H    3.335423  -3.130967  -0.000019
H   -3.335423   3.130967   0.000053
H   -5.066337   1.229361   0.000008
H   -5.499135  -1.200697  -0.000044
H   -3.629380  -2.841772  -0.000081
H   -0.972377   3.849928   0.000072
H    0.972377  -3.849928  -0.000068
Energies (0K) = -917.604574681
Energies (0K) + ZPE = -917.361437
Enthalpies (298K) = -917.346988
Free Energies (298K) = -917.400918

Triplet state
C    4.483797   0.819009   0.000070
```

```
C    3.455153   1.763519   0.000067
C    2.139009   1.307462   0.000036
C    1.860155  -0.060942   0.000008
C    2.898960  -1.025245   0.000011
C    4.224193  -0.549531   0.000042
C    0.491951  -0.474209  -0.000020
C    0.174951  -1.869239  -0.000046
C    1.181256  -2.812707  -0.000043
C    2.530149  -2.407227  -0.000015
C   -0.491951   0.474209  -0.000009
C   -0.174951   1.869239   0.000026
C   -1.181256   2.812707   0.000050
C   -2.530149   2.407227   0.000039
C   -2.898960   1.025245   0.000004
C   -1.860155   0.060942  -0.000021
C   -4.224193   0.549531  -0.000007
C   -4.483797  -0.819009  -0.000040
C   -3.455153  -1.763519  -0.000063
C   -2.139009  -1.307462  -0.000052
O   -1.140376  -2.249391  -0.000079
O    1.140376   2.249391   0.000031
H    5.513127   1.165651   0.000094
H    3.659424   2.828974   0.000089
H    5.048071  -1.257892   0.000046
H    3.312626  -3.159299  -0.000012
H   -3.312626   3.159299   0.000059
H   -5.048071   1.257892   0.000010
H   -5.513127  -1.165651  -0.000048
H   -3.659424  -2.828974  -0.000089
H   -0.924528   3.867538   0.000078
H    0.924528  -3.867538  -0.000062
Energies (0K) = -917.536315066
Energies (0K) + ZPE = -917.296855
Enthalpies (298K) = -917.282005
Free Energies (298K) = -917.337599

Cation radical
C    4.463950   0.831372   0.000057
C    3.428068   1.773552   0.000065
C    2.119218   1.320037   0.000043
C    1.845551  -0.061125   0.000012
C    2.892884  -1.012296   0.000004
C    4.216736  -0.536493   0.000026
C    0.506808  -0.486142  -0.000008
C    0.182833  -1.846278  -0.000037
C    1.207502  -2.808473  -0.000047
C    2.522259  -2.392449  -0.000027
C   -0.506808   0.486142   0.000004
C   -0.182833   1.846278   0.000035
C   -1.207502   2.808473   0.000047
C   -2.522259   2.392449   0.000029
C   -2.892884   1.012296  -0.000002
C   -1.845551   0.061125  -0.000014
C   -4.216736   0.536493  -0.000023
C   -4.463950  -0.831372  -0.000053
C   -3.428068  -1.773552  -0.000064
```

```
C   -2.119218  -1.320037  -0.000045
O   -1.107481  -2.239405  -0.000056
O    1.107481   2.239405   0.000052
H    5.489171   1.187012   0.000074
H    3.632702   2.838583   0.000089
H    5.042832  -1.240560   0.000021
H    3.310725  -3.139168  -0.000034
H   -3.310725   3.139168   0.000038
H   -5.042832   1.240560  -0.000015
H   -5.489171  -1.187012  -0.000068
H   -3.632702  -2.838583  -0.000088
H   -0.950796   3.861995   0.000071
H    0.950796  -3.861995  -0.000069
Energies (0K) = -917.428082074
Energies (0K) + ZPE = -917.183970
Enthalpies (298K) = -917.169601
Free Energies (298K) = -917.223952
```

10. Reference

(1) Hakobyan, K.; Gegenhuber, T.; McErlean, C. S. P.; Müllner, M. Visible-Light-Driven MADIX Polymerisation via a Reusable, Low-Cost, and Non-Toxic Bismuth Oxide Photocatalyst. *Angew. Chem. Int. Ed.* **2019,** *58*, 1828-1832.

(2) Niu, J.; Lunn, D. J.; Pusuluri, A.; Yoo, J. I.; O'Malley, M. A.; Mitragotri, S.; Soh, H. T.; Hawker, C. J. Engineering live cell surfaces with functional polymers via cytocompatible controlled radical polymerization. *Nat. Chem.* **2017,** *9*, 537-545.

(3) Kamei, T.; Uryu, M.; Shimada, T. Cu-Catalyzed Aerobic Oxidative C–H/C–O Cyclization of 2,2′-Binaphthols: Practical Synthesis of PXX Derivatives. *Org. Lett.* **2017,** *19*, 2714-2717.

(4) Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. Single-ion solvation free energies and the normal hydrogen electrode potential in methanol, acetonitrile, and dimethyl sulfoxide. *J. Phys. Chem. B* **2007**, *111*, 408−422.

(5) Ma, Q.; Song, J.; Zhang, X.; Jiang, Y.; Ji, L.; Liao, S. Metal-free atom transfer radical polymerization with ppm catalyst loading under sunlight. *Nat. Commun.* **2021**, *12*:429.