

Supplementary Information for

## **Visible light-initiated living cationic dark polymerization**

Lei Wang, Pei Huang, Lei Huang, Chuanshuang Chen, Meiwei Qi, Wenfeng Jiang, Chunyang Yu, Shaodong Zhang and Yongfeng Zhou\*

School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, State Key Laboratory of Metal Matrix Composites, Shanghai Key Laboratory of Electrical Insulation and Thermal Ageing, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

E-mail: yfzhou@sjtu.edu.cn

Table of Contents

**1. Experimental Section**

**2. Supplementary Figures S1-S23**

**3. References**

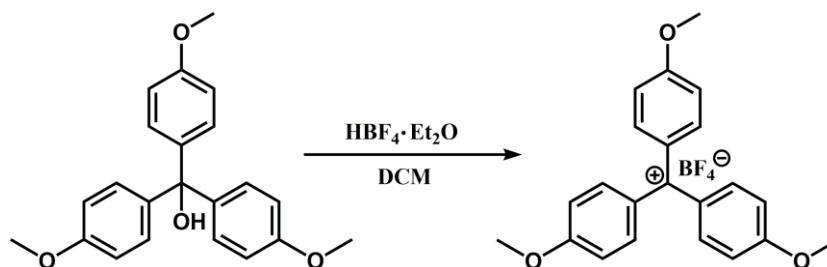
### General Reagent Information

Tris(4-methoxyphenyl) methanol (98%), tetrafluoroboric acid-diethyl ether complex (50-55%), tetra-*n*-butylammonium hexafluorophosphate (99%) were purchased from Adamas-beta. 4-Methoxystyrene (*p*-MOS, 96%) and 4-*tert*-butoxystyrene (*p*-*t*BOS, 98%) was purchased from Aladdin and distilled twice over calcium hydride (CaH<sub>2</sub>) under reduced pressure and stored under argon atmosphere at -20 °C before use. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, HPLC), acetonitrile (ACN, HPLC), methanol (MeOH, HPLC), ethanol (EtOH, HPLC), 2-propanol (*i*-PrOH, 99.9%), and 2,2,2-trifluoroethanol (TFE, 99.8%) were purchased from Adamas and stored in Schlenk bar under argon atmosphere followed by being transferred into the glovebox.

### General Analytical Information

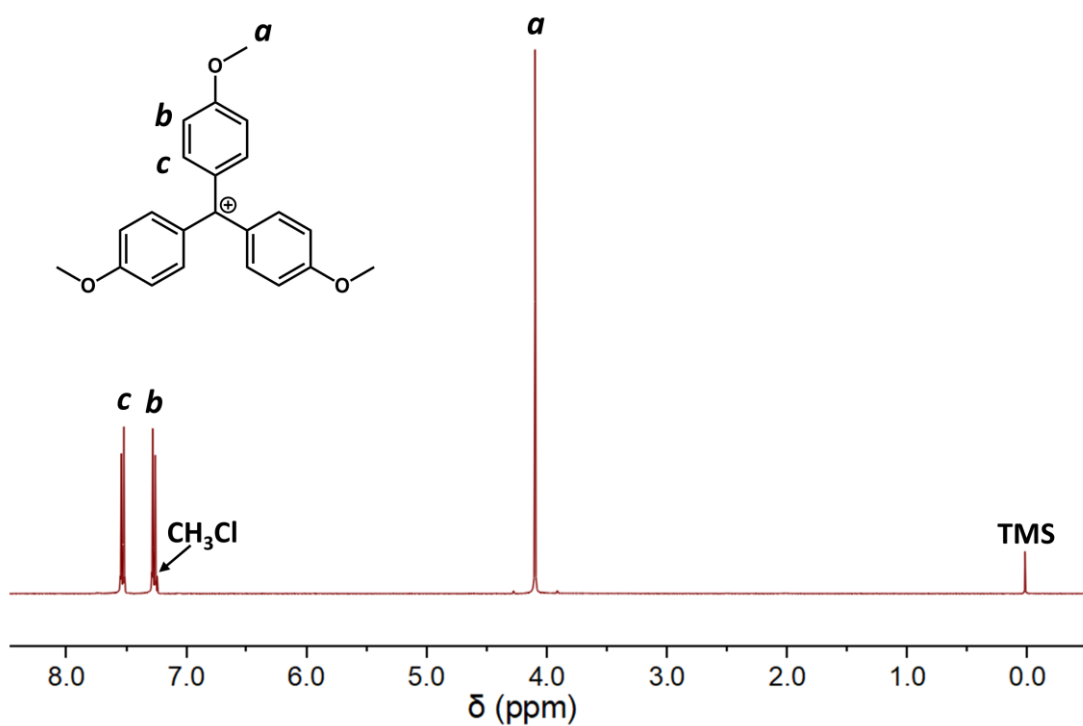
<sup>1</sup>H NMR spectra was recorded using Bruker AVANCEIII HD 400 MHz spectrometer with CDCl<sub>3</sub> as solvents at 298K. Tetramethylsilane (TMS) was used as an internal standard. GPC measurements were carried out using an HLC-8320GPC (TOSOH, EcoSEC GPC System) system at 40 °C with THF as mobile phase at a flow rate of 1.0 mL/min. All number-average molecular weights ( $M_n$ ), weight-average molecular weights ( $M_w$ ), and dispersities ( $D$ ) were determined relative to polystyrene standards. The UV-vis absorption spectra of samples were recorded at 298K in the range of 200-800 nm on a Shimadzu UV 3600 spectrometer. The fluorescence quenching spectra were recorded on a PTI QM/TM/IM steady-state & time-resolved fluorescence spectro-fluorometer (USA/CAN Photon Technology International Int.). ESR spectra were recorded on a Bruker EMX plus-9.5/12 ESR spectrometer. The results of MALDI-TOF-MS were performed on a solariX XR 7.0 T hybrid quadrupole-FTICR mass spectrometer equipped with an ESI/APCI/MALDI ion source (Bruker Daltonics, Bremen, Germany).

### Synthesis of tris(4-methoxyphenyl)methylium tetrafluoroborate (1)

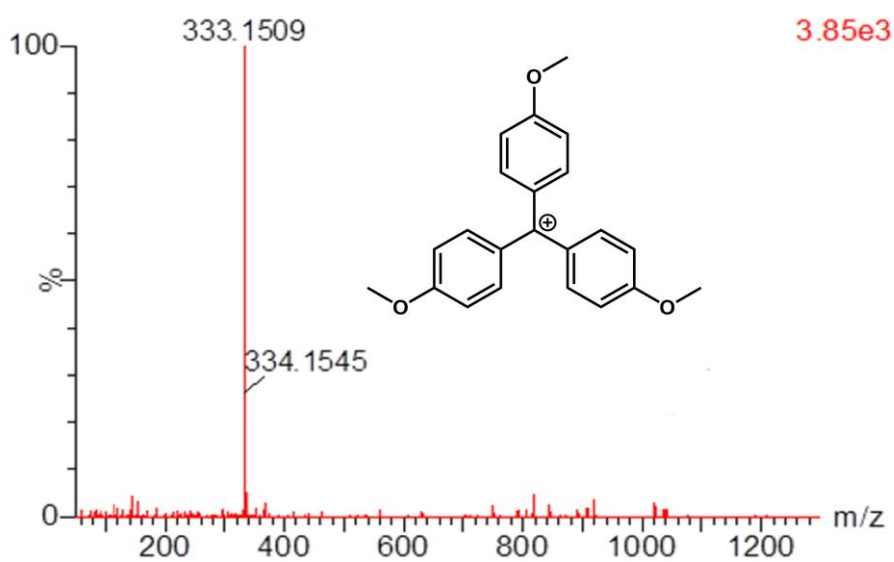


In a flame dried flask, a solution of HBF<sub>4</sub> in Et<sub>2</sub>O (0.52 mL, 2.0 M, 1.0 mmol, 1.2 equiv) was added dropwise to a solution of tris(4-methoxyphenyl)methanol (308 mg, 0.88 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) over 5 minutes at 0 °C and stirred for 1.5 hours under nitrogen. This solution was then added dropwise in Et<sub>2</sub>O (50 mL) over 5 min at 0 °C, followed by filtration and washing with Et<sub>2</sub>O, and finally drying under vacuum at room temperature. To purify the product further, it was dissolved in a small volume of CH<sub>2</sub>Cl<sub>2</sub> and reprecipitated in excess dry cold Et<sub>2</sub>O, filtered and dried under vacuum to yield an orange powder (404 mg, 96% yield).

Tris(4-methoxyphenyl)methylium tetrafluoroborate (OPC 1): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.52-7.58 (dt, 4H), 7.27-7.32 (dt, 4H), 4.10 (s, 9 H). HRMS (m/z): [M]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>27</sub>O<sub>6</sub>, 333.15; found, 333.1509.



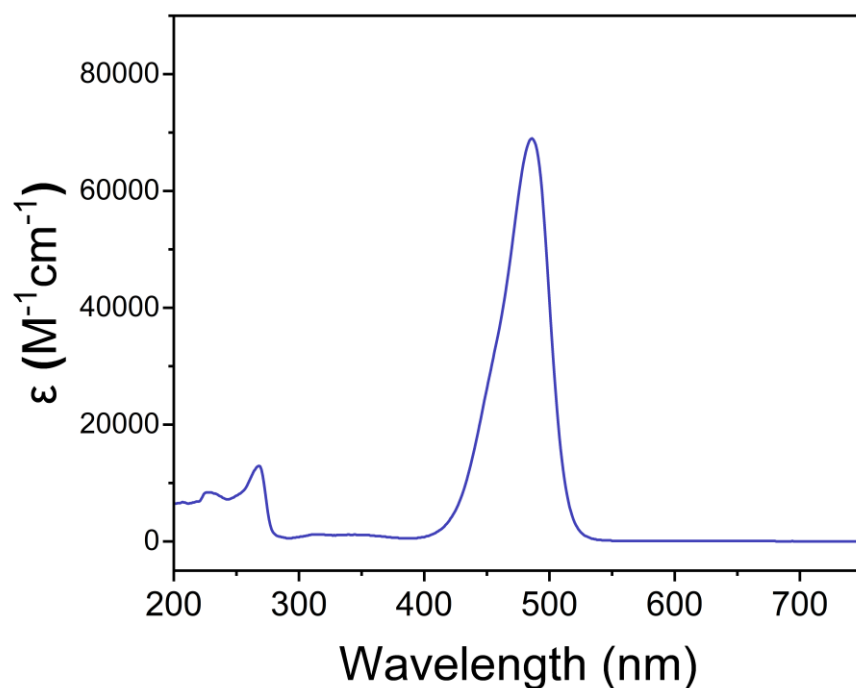
**Fig. S1.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 298K) of tris(4-methoxyphenyl)methyl tetrafluoroborate (OPC 1).



**Fig. S2.** The Mass spectra of tris(4-methoxyphenyl)methyl tetrafluoroborate (OPC 1).

### Procedure for Ultraviolet-visible Absorption Spectroscopy

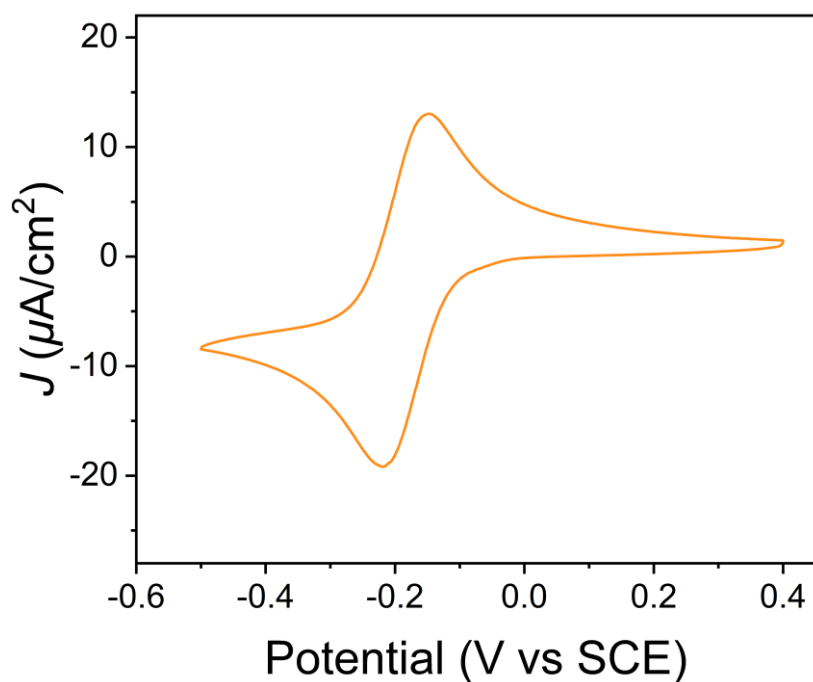
The UV-vis absorption spectra of sample were recorded at 298K in the range of 200-800 nm on a Shimadzu UV 3600 spectrometer. The solutions of the samples were added to a 1 cm quartz cuvette with sealed plug in an argon-filled glove box for the measurements under argon atmosphere.



**Fig. S3.** UV- visible spectra of OPC 1 in dichloromethane.

### Procedure for Cyclic Voltammetry (CV)

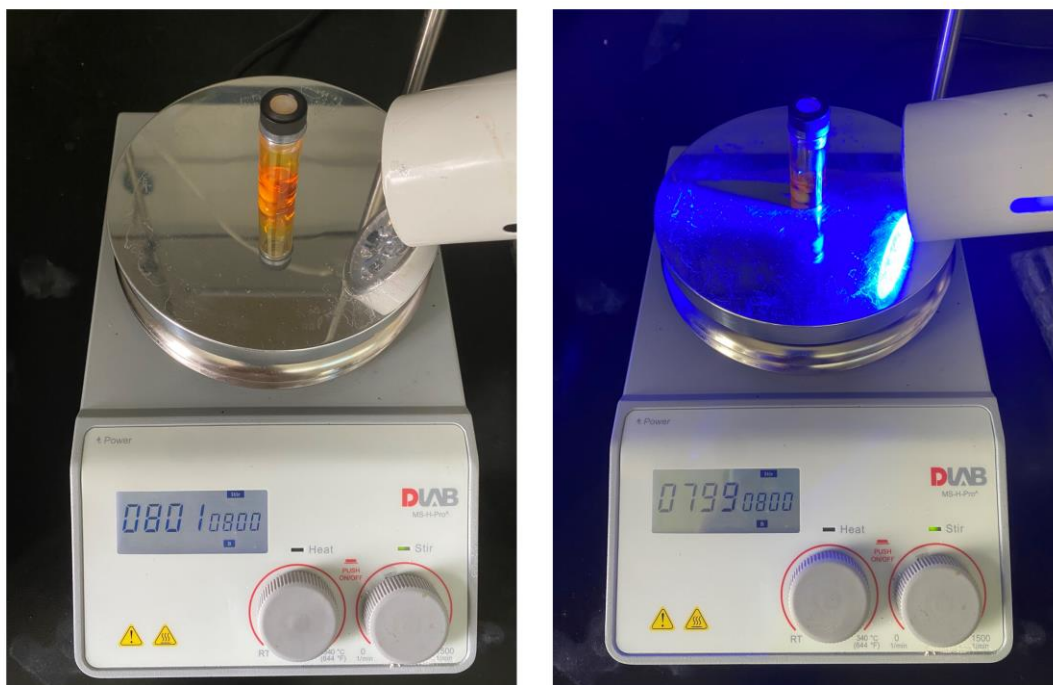
All electrochemical measurements were performed on a CHI 760E electrochemistry workstation in a three-electrode system with platinum sheet, calomel electrode (Hg/Hg<sub>2</sub>Cl<sub>2</sub>), a glassy carbon (0.22 cm<sup>2</sup>) as counter electrode, reference electrode, and working electrode, respectively. Using acetonitrile containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte, electrodes were immersed in glass flasks under argon at 298 K. The scan rate was set at 50 mV s<sup>-1</sup>.



**Fig. S4.** Cyclic voltammogram of OPC 1.<sup>2</sup>

## General Reaction Setup

All manipulations for the photo-initiated living cationic polymerization were set up in an Argon atmosphere glove-box. The reactions were conducted under a 5 W blue diode led® SEEWEE lights, and the distance between the vial and LED beads is ca. 4 cm. The light intensity at the place of vessel was recorded at 30 mW/cm<sup>2</sup>. The emission spectra of the green LEDs were recorded on a Perfect Light PL-MW 2000 photoradiometer.

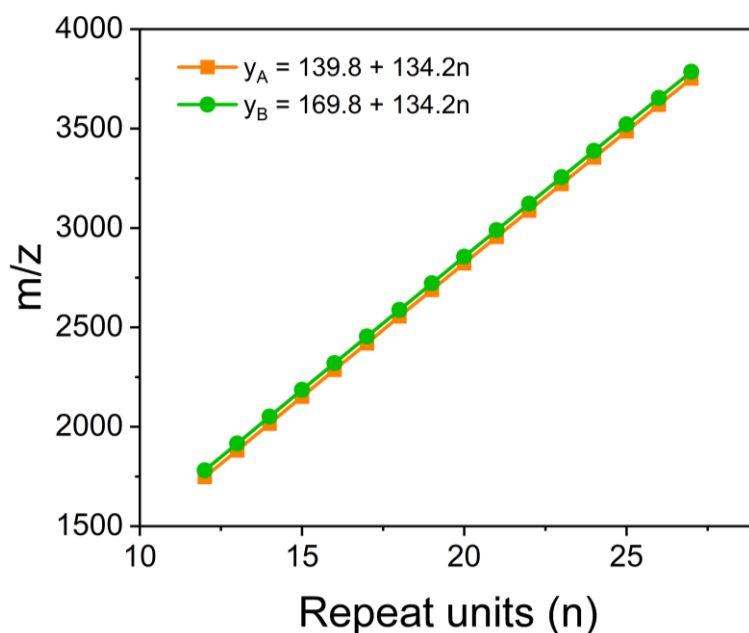


**Fig. S5.** Photo-polymerization reaction setup.



## Matrix-assisted Laser Desorption and Ionization Time-of-flight Mass Spectrometry (MALDI-TOF-MS)

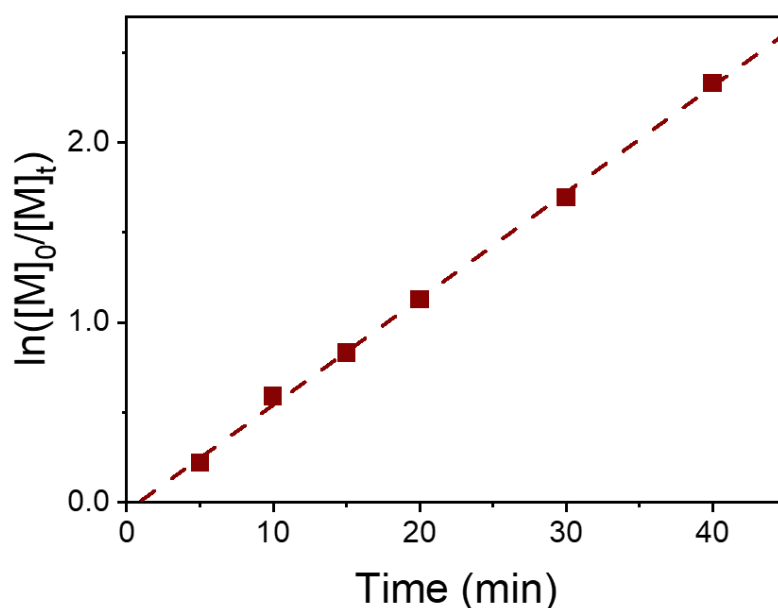
MALDI-TOF-MS was performed on a solariX XR 7.0 T hybrid quadrupole-FTICR mass spectrometer equipped with an ESI/APCI/MALDI ion source (Bruker Daltonics, Bremen, Germany). The MS instrument was tuned and calibrated with ESI-L low concentration tuning mix (Agilent Technologies, Santa Clara, CA, USA) and sodium formate. The analytical sample was prepared by mixing the polymer solution (5.0 mg/mL in  $\text{CH}_2\text{Cl}_2$ ) with the matrix solution (10 mg/mL DCTB in  $\text{CH}_2\text{Cl}_2$ ) and silver nitrate (0.01 M in  $\text{H}_2\text{O}$ ) in a volume ratio of 5/25/1, and then loaded onto the MALDI plate. The sample on the plate was thoroughly dried prior to analysis. The mass spectra were analyzed using Compass Data Analysis 5.0 (Bruker).



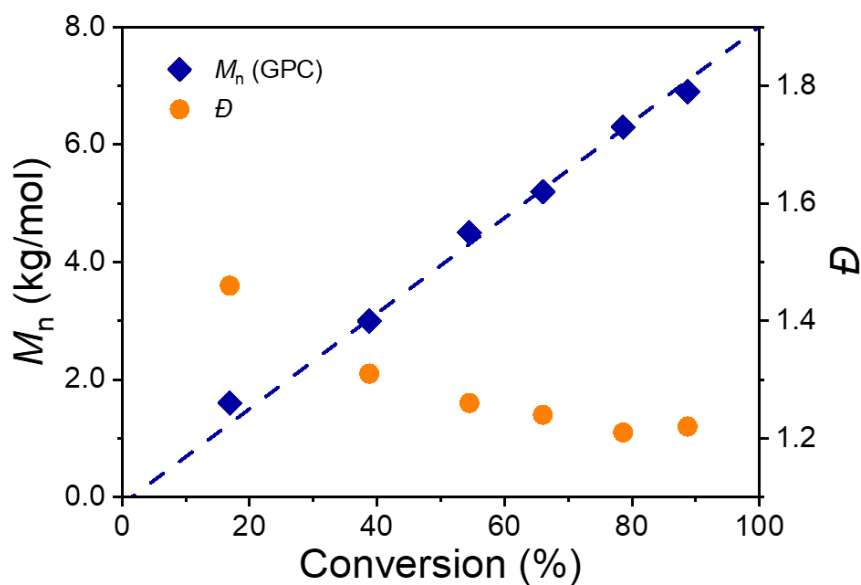
**Fig. S6.** Plot of mass-to-charge ratio ( $m/z$ ) vs. number of monomer repeat units from the results of MALDI-TOF MS analysis of a poly( $p$ -MOS) using methanol as CTA. The orange points are corresponding to poly( $p$ -MOS) cationized by silver and bearing  $\alpha$ -methyl terminal group and  $\omega$ -methoxy terminal group. Green points correspond to poly( $p$ -MOS) cationized by silver and bearing two methoxy terminal groups.

### Kinetic Investigation of Photo-initiated Living Cationic Polymerization of *p*-MOS and *p*-*t*BOS with OPC 1 as the Photocatalyst and methanol as the CTA

Polymerization kinetic investigation of *p*-MOS: In an argon-filled glovebox, *p*-MOS (0.33 mL, 2.5 mmol, 50.0 equiv), 0.2 mL of a stock solution of methanol in CH<sub>2</sub>Cl<sub>2</sub> (0.25 mM, 0.05 mmol, 1.0 equiv), 0.2 mL of a stock solution of OPC 1 in CH<sub>2</sub>Cl<sub>2</sub> (0.05 mM, 0.01 mmol, 0.2 equiv), and 3.5 mL CH<sub>2</sub>Cl<sub>2</sub> were charged in an oven-dried vial with a stir bar. A septum cover was then applied to the vial, which was then put outside the glove box in front of a blue LED spot lamp (5 W,  $\lambda_{\max} = 480$  nm, 30 mW/cm<sup>2</sup>). Aliquots were taken after 5 min, 10 min, 15 min, 20 min, 30 min, and 40 min. The samples were subjected to <sup>1</sup>H NMR and GPC analysis.



**Fig. S7.** Plots of  $\ln([M]_0/[M]_t)$  vs. reaction time of *p*-MOS under the irradiation of blue LED.

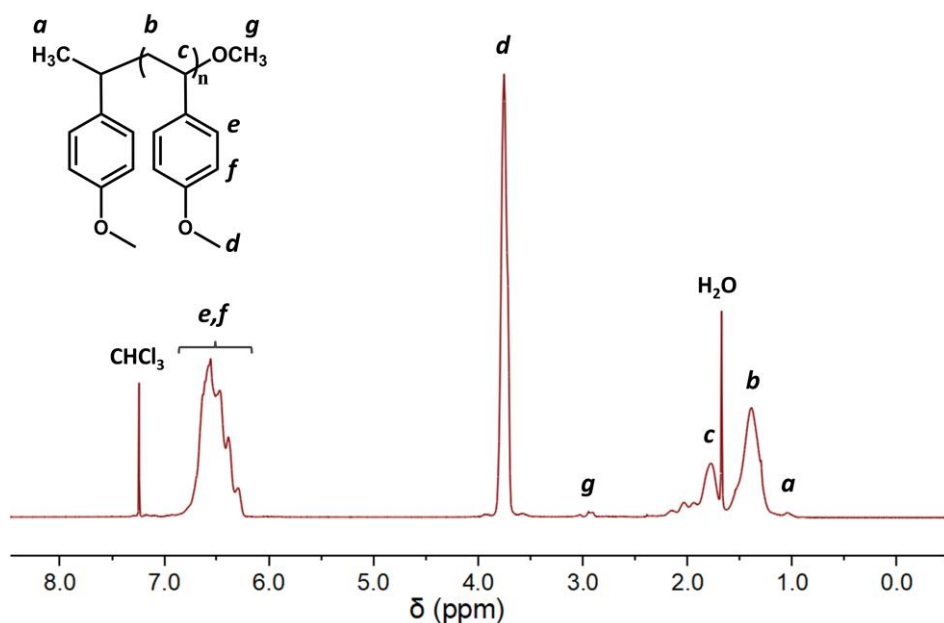


**Fig. S8.**  $M_n$  (■) and  $\bar{D}$  (●) against conversion of *p*-MOS under the irradiation of blue LED.

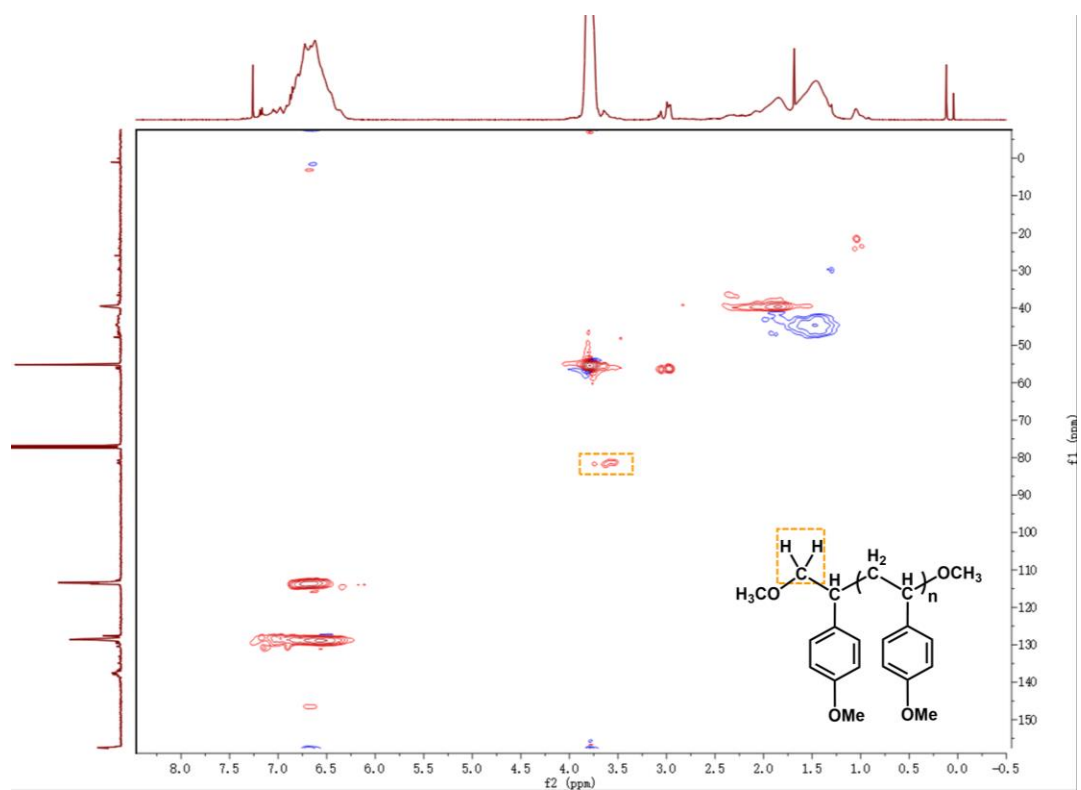
Polymerization kinetic investigation of *p*-*t*BOS: In an argon-filled glovebox, *p*-*t*BOS (0.34 mL, 2.5 mmol, 50.0 equiv), 0.2 mL of a stock solution of methanol in  $\text{CH}_2\text{Cl}_2$  (0.25 mM, 0.05 mmol, 1.0 equiv), 0.2 mL of a stock solution of OPC **1** in  $\text{CH}_2\text{Cl}_2$  (0.05 mM, 0.01 mmol, 0.2 equiv), and 3.5 mL  $\text{CH}_2\text{Cl}_2$  were charged in an oven-dried vial with a stir bar. A septum cover was then applied to the vial, which was then put outside the glove box in front of a blue LED spot lamp (5 W,  $\lambda_{\text{max}} = 480$  nm, 30  $\text{mW}/\text{cm}^2$ ). After 20 min of irradiation, the light source was switched off, and the aliquots were taken after 30 min, 60 min, 90 min, 120 min, 180 min, and 240 min. The samples were subjected to  $^1\text{H}$  NMR and GPC analysis.

## Structure Investigation of poly(*p*-MOS)

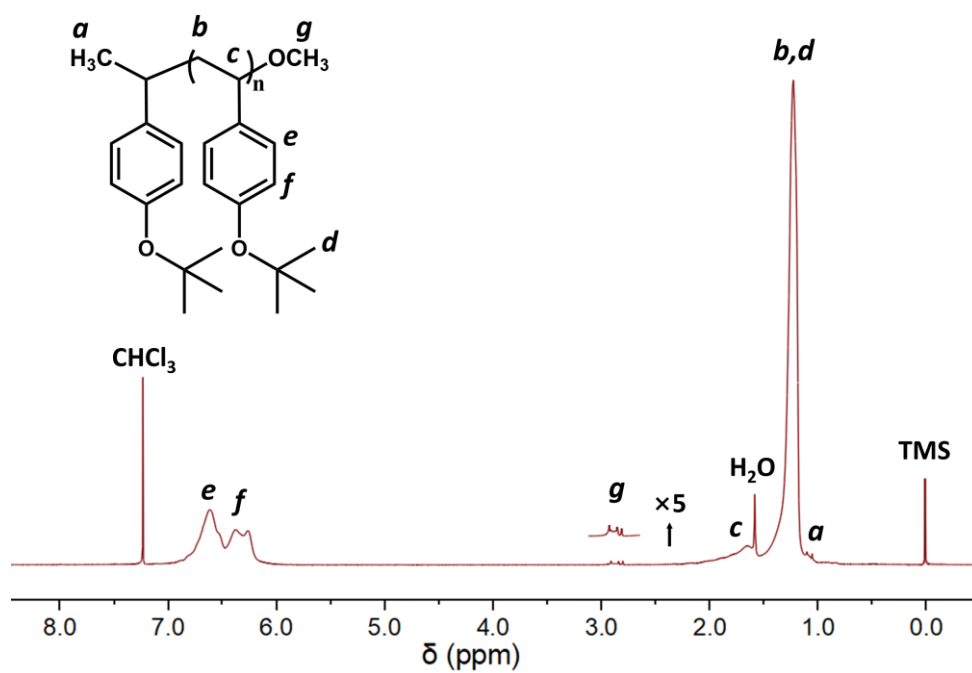
The  $^1\text{H}$  NMR spectrum for poly(*p*-MOS) using methanol as CTA is shown in Figure S9. The HSQC 2D NMR spectrum of Poly(*p*-MOS) using methanol as CTA is shown in Figure S10. The  $^1\text{H}$  NMR spectrum for poly(*p*-*t*BOS) using methanol as CTA is shown in Figure S11.



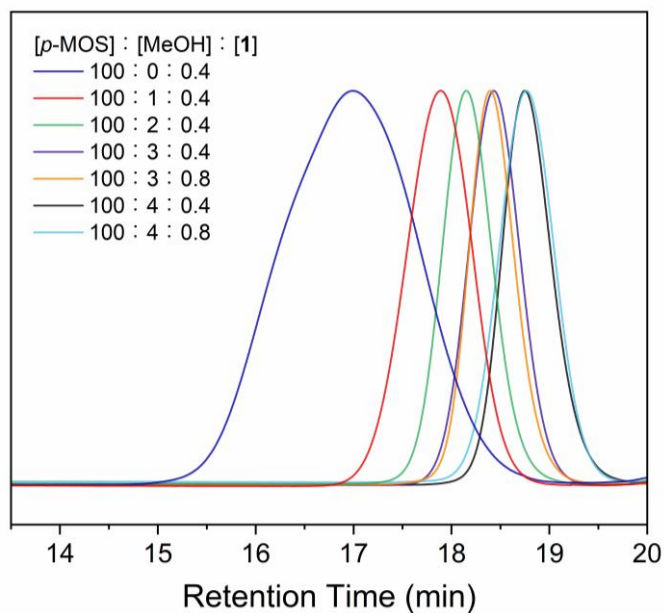
**Fig. S9.** The  $^1\text{H}$  NMR spectrum (CDCl<sub>3</sub>, 298K) of poly(*p*-MOS) using methanol as CTA;  $M_n = 8.5$  kg/mol,  $D = 1.18$ .



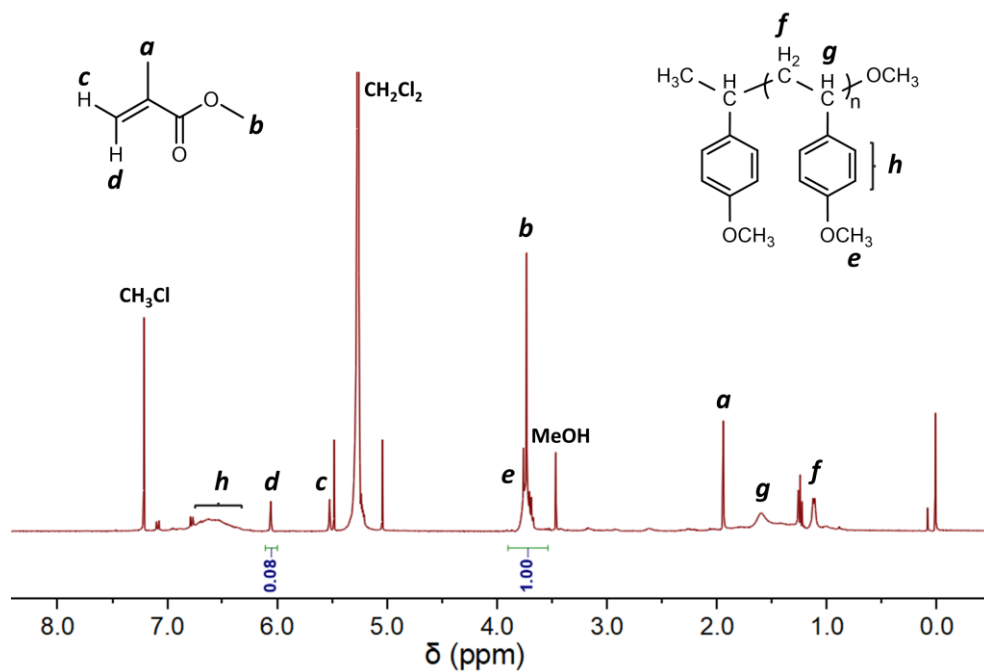
**Fig. S10.** The HSQC 2D NMR spectrum ( $\text{CDCl}_3$ , 298K) of poly(*p*-MOS),  $M_n = 2.5$  kg/mol,  $D = 1.16$ . The cross peak shown by the orange dotted rectangle is within the expected chemical shift range for a methylene group connected to a methoxy end group.<sup>1</sup>



**Fig. S11.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 298K) of poly(*p*-*t*BOS) using methanol as CTA;  $M_n = 9.2$  kg/mol,  $D = 1.16$ .



**Fig. S12.** GPC traces of poly(*p*-MOS) visible light-initiated with different ratio of MeOH.

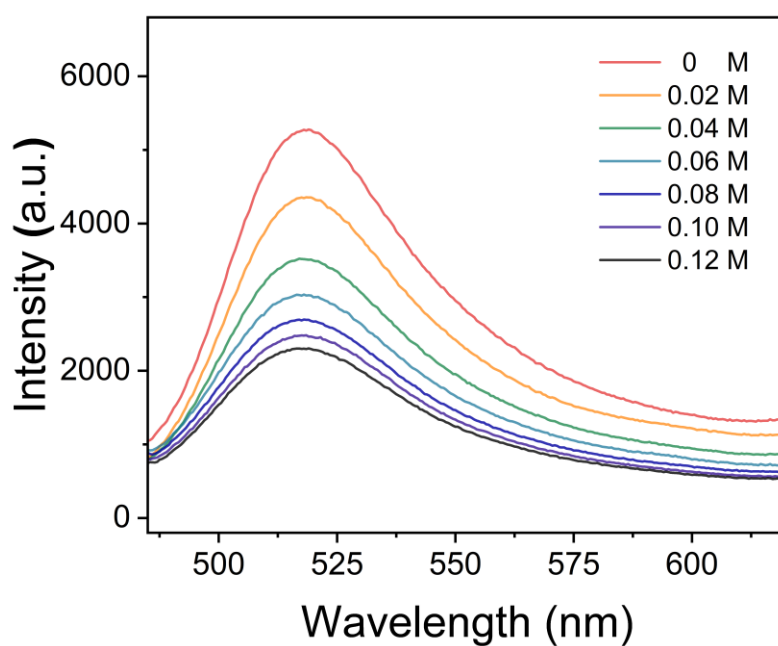


**Fig. S13.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 298K) of photo-polymerization of a mixture of methyl methacrylate (MMA) and *p*-MOS using OPC **1** as photocatalyst and methanol as CTA.

## Fluorescence Quenching Studies

The fluorescence quenching spectra were recorded on a PTI QM/TM/IM steady-state & time-resolved fluorescence spectro-fluorometer (USA/CAN Photon Technology International Int.) spectrometer. Step increment was set as 1 nm, and scan speed was set as 600 nm/min.

The solutions of OPC **1** (0.02 mM) in CH<sub>2</sub>Cl<sub>2</sub> were prepared in an argon-filled glove box and sealed before being taken out of the box. The fluorescence spectra were excited at 480 nm and recorded between 485 and 620 nm at various concentrations of *p*-MOS (0 – 0.12 M).

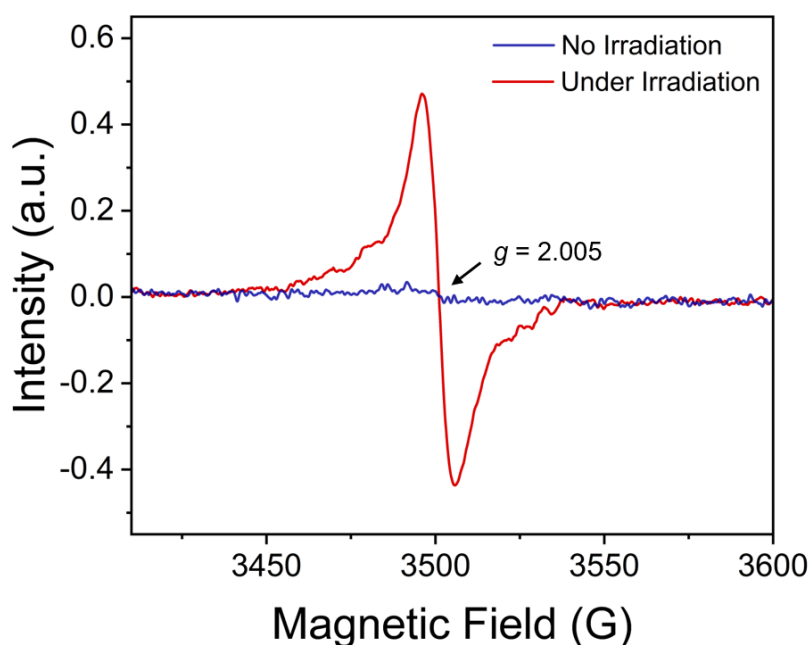


**Fig. S14.** Spectral changes of the photocatalyst **1** fluorescence with the addition of *p*-MOS.



## Electron Spin Resonance Spectroscopy

ESR spectra were recorded on a Bruker EMX plus-9.5/12 ESR spectrometer. The acquisition parameters were fixed to 10 mW microwave power, 30 dB receiver gain, and 100 kHz modulation frequency. All samples were prepared in an argon-filled glove box and sealed before being taken out of the box. Samples in MeCN (20  $\mu$ l) were transferred into quartz capillaries of 1.0 mm i.d. and 2.0 mm o.d. capillaries were then centered in standard 4 mm o.d. ESR quartz tubes. A mixture solution of **1** (0.1 M) and *p*-MOS (0.1 M) shows no signal in the absence of irradiation. While an ESR signal that can be assigned to  $1\bullet$  generated under steady-state irradiation (480 nm, 60 W luminous power) after a 60 scans accumulation (Figure).



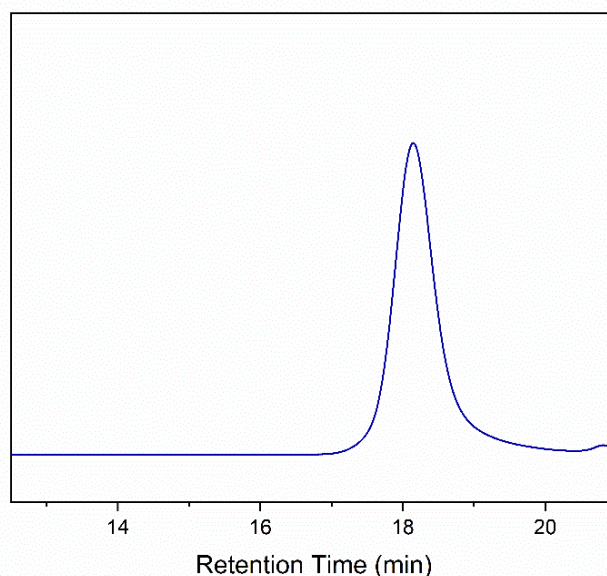
**Fig. S15.** Electron spin resonance spectrum of 0.1 M OPC **1** with 0.1 M *p*-MOS in acetonitrile under steady-state 60 W 480 nm irradiation.

## Chain Extension Experiments

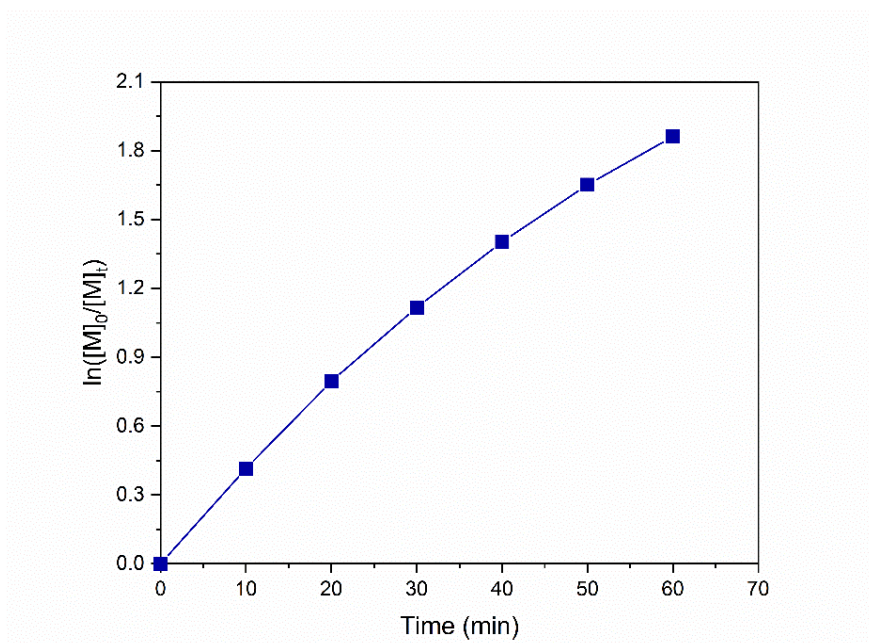
In an argon-filled glovebox, *p*-MOS (0.33 mL, 2.5 mmol, 50.0 equiv), 0.2 mL of a stock solution of methanol in CH<sub>2</sub>Cl<sub>2</sub> (0.25 mM, 0.05 mmol, 1.0 equiv), 0.2 mL of a stock solution of OPC 1 in CH<sub>2</sub>Cl<sub>2</sub> (0.05 mM, 0.01 mmol, 0.2 equiv), and 8.0 mL CH<sub>2</sub>Cl<sub>2</sub> were charged in an oven-dried vial with a stir bar. A septum cover was then applied to the vial, which was then put outside the glove box in front of a blue LED spot lamp (5 W,  $\lambda_{\text{max}} = 480 \text{ nm}$ , 30 mW/cm<sup>2</sup>). After 10 min irradiation, light source was switched off, and the reaction was conducted to full conversion in the dark for 1 hour. Then the vial was brought back in the glove box and a sample for <sup>1</sup>H NMR and GPC analysis (Conv. = 99 %,  $M_n = 7.2 \text{ kg/mol}$ ,  $D = 1.19$ ) was taken prior to the addition of *p*-*t*BOS (0.34 mL, 2.5 mmol, 50.0 equiv). Then the vial was stirred in the dark until the reaction reached full conversion (4 hour). The <sup>1</sup>H NMR and GPC analysis (Conv. = 93 %,  $M_n = 15.7 \text{ kg/mol}$ ,  $D = 1.31$ ) for chain extension experiment were conducted.

## Studies in Catalyst Generality

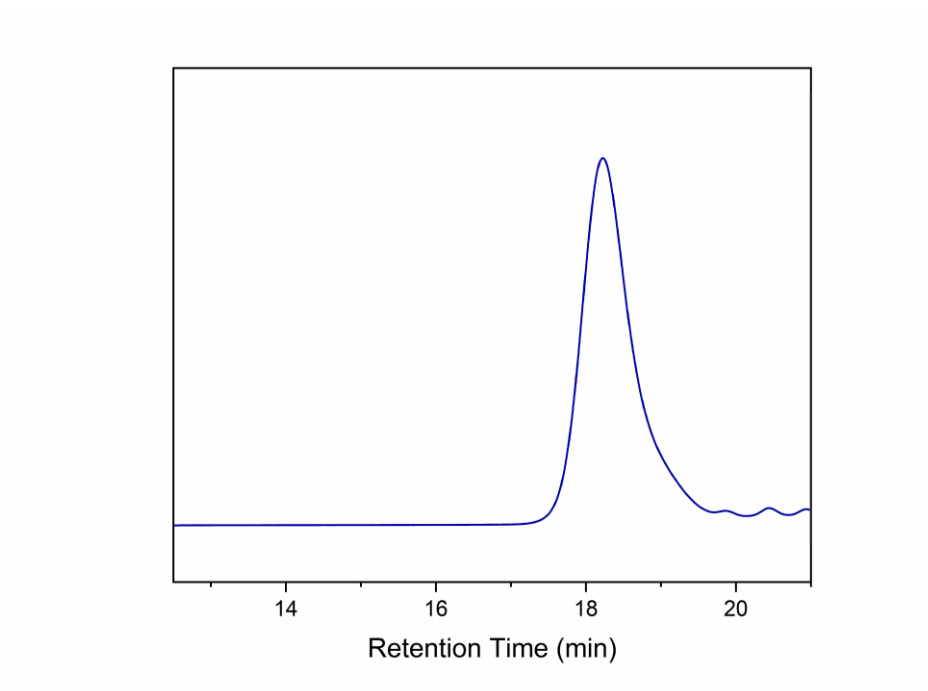
Under the protection of nitrogen, *p*-MOS (0.33 mL, 2.5 mmol, 50.0 equiv), 0.2 mL of a stock solution of methanol in CH<sub>2</sub>Cl<sub>2</sub> (0.25 mM, 0.05 mmol, 1.0 equiv), 0.2 mL of a stock solution of catalyst in CH<sub>2</sub>Cl<sub>2</sub> (0.05 mM, 0.01 mmol, 0.2 equiv), and 3.5 mL CH<sub>2</sub>Cl<sub>2</sub> were charged in an oven-dried vial with a stir bar. A septum cover was applied to the vial, which was put in the dark stirred for 3 h to determine whether or not polymerization occurred before irradiation. We took the sample from the reaction mixture, which was subjected to <sup>1</sup>H NMR analysis after quenching by triethylamine to investigate the monomer conversion. After that, the reaction vial was placed in front of a 5 W green LED spot lamp for 10 mins. Then the reaction vial was stirred in the dark for 60 minutes. The samples were taken at 10-min intervals for <sup>1</sup>H NMR analysis after quenching with trimethylamine.



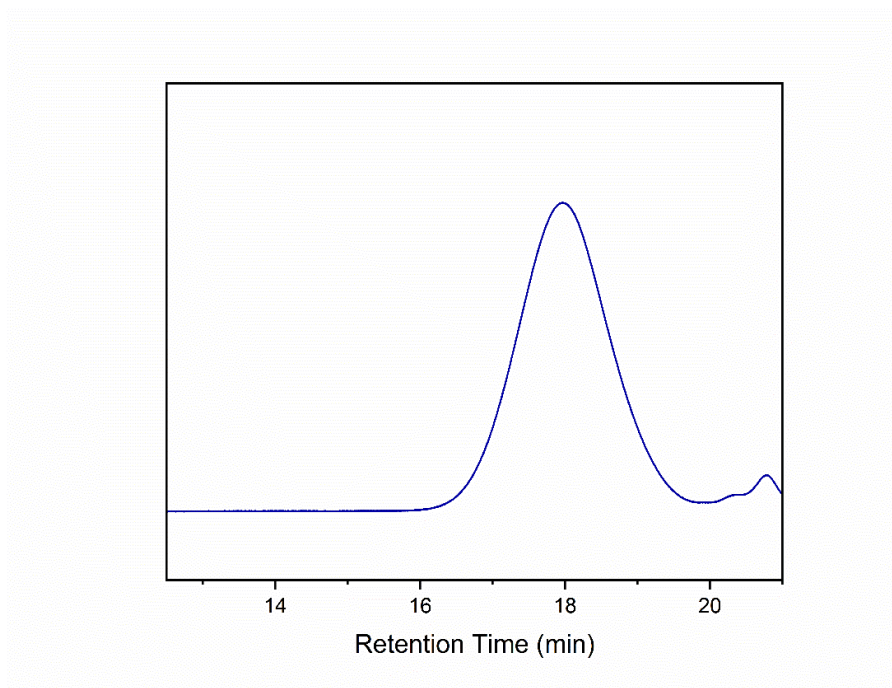
**Fig. S16.** GPC trace of poly(*p*-MOS) using tris(2,4-dimethoxyphenyl) methylum tetrafluoroborate as photocatalyst and methanol as CTA initiated by green LED ([monomer]/[methanol]/[catalyst] = 50/1/0.2);  $M_n = 8.7$  kg/mol,  $D = 1.27$ .



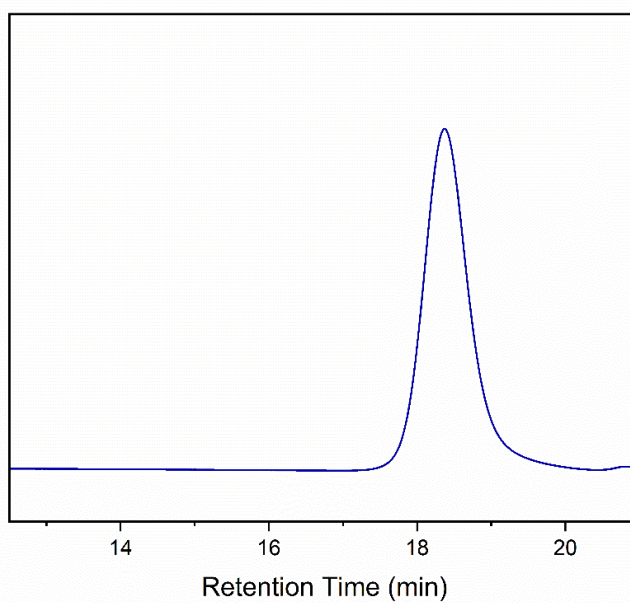
**Fig. S17.** Kinetic study of the visible light-initiated cationic polymerization of *p*-MOS using tris(2,4-dimethoxyphenyl)methylm tetrafluoroborate as photocatalyst and methanol as CTA triggered by 10-min irradiation of green LED.



**Fig. S18.** GPC trace of dark polymerization of *p*-MOS using tris(2,4-dimethoxyphenyl)methylm tetrafluoroborate as photocatalyst and methanol as CTA initiated by green LED ( $[monomer]/[methanol]/[catalyst] = 50/1/0.2$ );  $M_n = 7.7$  kg/mol,  $D = 1.41$ .



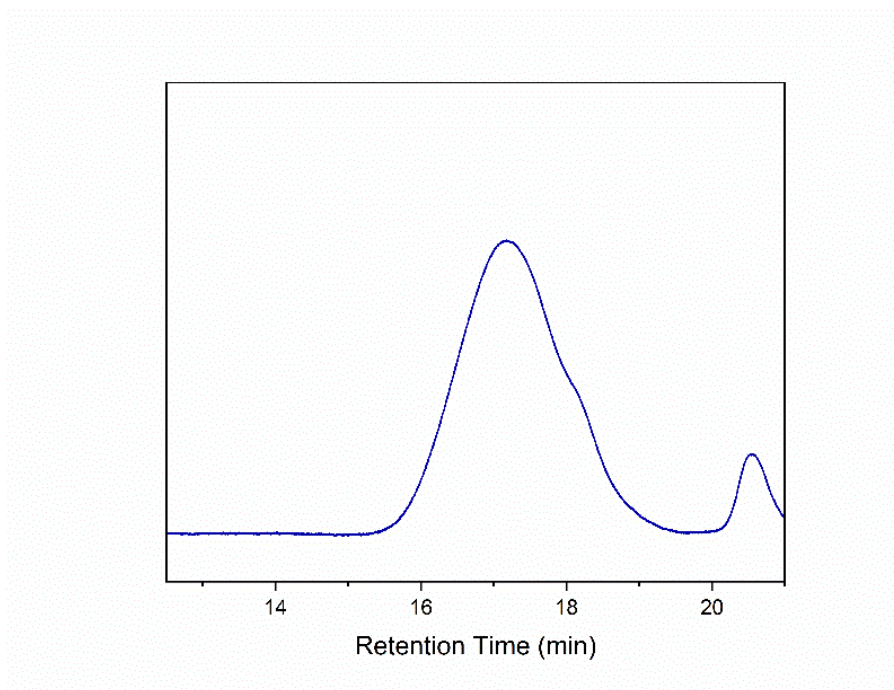
**Fig. S19.** GPC trace of poly(*p*-MOS) using triphenylmethyl tetrafluoroborate as catalyst and methanol as CTA ([monomer]/[methanol]/[catalyst] = 50/1/0.2);  $M_n = 12.8$  kg/mol,  $D = 1.73$ .



**Fig. S20.** GPC trace of poly(*p*-MOS) using 4-methoxytrityl tetrafluoroborate as catalyst and methanol as CTA ([monomer]/[methanol]/[catalyst] = 50/1/0.2);  $M_n = 7.3$  kg/mol,  $D = 1.32$ .

### Studies in Solvent Generality

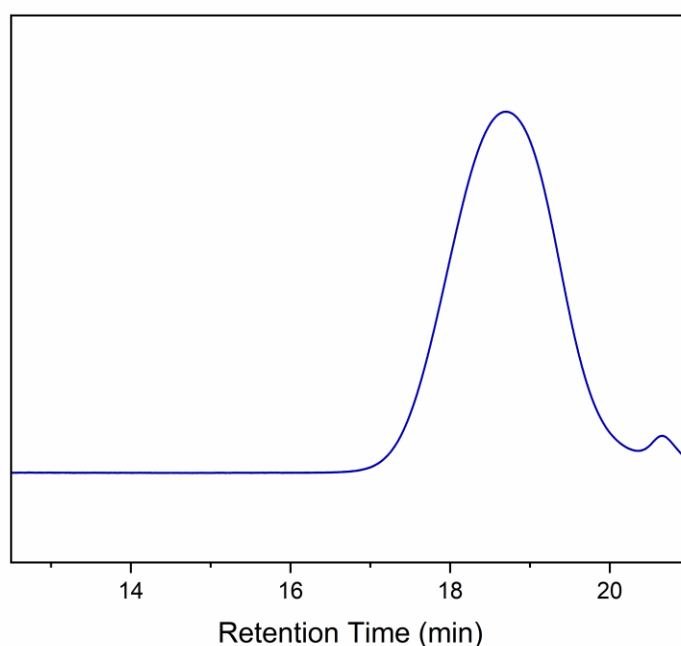
Under the protection of nitrogen, *p*-MOS (0.33 mL, 2.5 mmol, 50.0 equiv), 1.6 mg of methanol (0.25 mM, 0.05 mmol, 1.0 equiv), 4.2 mg of OPC **1** (0.05 mM, 0.01 mmol, 0.2 equiv), and 4.0 mL solvent were charged in an oven-dried vial with a stir bar. A septum cover was applied to the vial, which was put in the dark stirred for 3 h to determine whether or not polymerization occurs before irradiation. The sample was taken from the reaction mixture, which was subjected to  $^1\text{H}$  NMR analysis after quenching by triethylamine to investigate the monomer conversion. After that, the reaction vial was placed in front of a 5 W blue LED spot lamp for 3 h. The sample was taken for  $^1\text{H}$  NMR and GPC analysis after quenching with trimethylamine.



**Fig. S21.** GPC trace of poly(*p*-MOS) using tris(4-methoxyphenyl)methyl tetrafluoroborate as catalyst and methanol as CTA in acetonitrile ([monomer]/[methanol]/[catalyst] = 50/1/0.2);  $M_n = 14.9$  kg/mol,  $D = 1.87$ .

### Studies in Monomer Generality

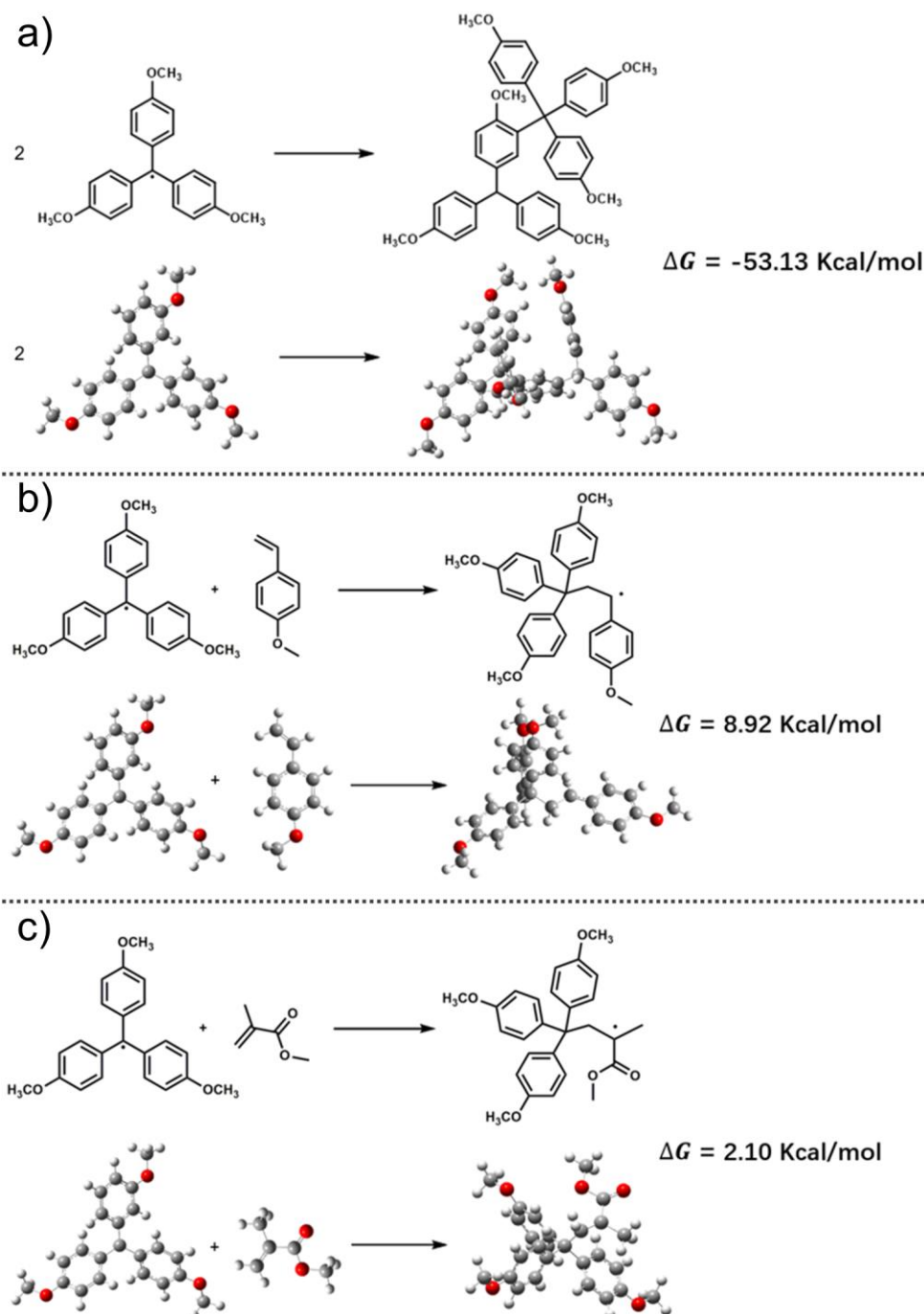
Under the protection of nitrogen, *n*-butyl vinyl ether (0.32 mL, 2.5 mmol, 50.0 equiv), 0.2 mL of a stock solution of methanol in CH<sub>2</sub>Cl<sub>2</sub> (0.25 mM, 0.05 mmol, 1.0 equiv), 0.2 mL of a stock solution of OPC **1** in CH<sub>2</sub>Cl<sub>2</sub> (0.05 mM, 0.01 mmol, 0.2 equiv), and 3.5 mL CH<sub>2</sub>Cl<sub>2</sub> were charged in an oven-dried vial with a stir bar. A septum cover was applied to the vial, which was put in the dark stirred for 3 h to determine whether or not polymerization occurs before irradiation. The sample was taken from the reaction mixture, which was subjected to <sup>1</sup>H NMR analysis after quenching by triethylamine to investigate the monomer conversion. After that, the reaction vial was placed in front of a 5 W blue LED spot lamp for 3 h. The sample was taken for <sup>1</sup>H NMR and GPC analysis after quenching with trimethylamine.



**Fig. S22.** GPC trace of poly(*n*-butyl vinyl ether) using tris(4-methoxyphenyl)methyl tetrafluoroborate as catalyst and methanol as CTA;  $M_n = 4.3$  kg/mol,  $D = 1.69$ .

## DFT calculations

The ground state geometry was optimized using DFT calculations. All calculations are performed with the Gaussian 16 package<sup>3</sup> using the hybrid B3LYP functionals<sup>4-5</sup> and the 6-311++G\*\* basis set. Grimme's D3BJ dispersion correction<sup>6-7</sup> was used to improve calculation accuracy.



**Fig. S23.** Models computed to simulate change in Gibbs free energy for a) dimerization of OPC 1, b) radical polymerization of *p*-MOS and c) MMA.



### 3. References

- [1] A. J. Perkowski, W. You, D. A. Nicewicz, *J. Am. Chem. Soc.*, 2015, 137, 7580-7583.
- [2] S. Fukuzumi, K. Ohkubo, J. Otera, *J. Org. Chem.*, 2001, 66, 1450-1454.
- [3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16, Revision A.03: Gaussian, Inc., Wallingford CT*, 2016.
- [4] C. Jean- Louis, *Int J Quantum Chem*, 1993, 47: 101.
- [5] K. Burke, *J Chem Phys*, 2012, 136: 150901.
- [6] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J Chem Phys*, 2010, 132: 154104.
- [7] S. Grimme, S. Ehrlich, L. Goerigk, *J Comput Chem*, 2011, 32: 1456–1465.