

Electronic Supplementary Information (ESI)

Tetraphenylethene-based caged compound: synthesis, properties and applications

Chris Y. Y. Yu,^a Ryan T. K. Kwok,^a Ju Mei,^a Yuning Hong,^a Sijie Chen,^a Jacky W. Y.

*Lam^a and Ben Zhong Tang^{*abc}*

^a Department of Chemistry, HKUST Jockey Club Institute for Advanced Study, Division of Biomedical Engineering, Division of Life Science, State Key Laboratory of Molecular Neuroscience and Institute of Molecular Functional Materials, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

^b Guangdong Innovative Research Team, SCUT-HKUST joint Research Laboratory, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

^c HKUST Shenzhen Research Institute, No. 9 Yuexing First RD, South Area, Hi-tech Park, Nanshan, Shenzhen 518057, China

Table of Contents

| | |
|---|-----|
| Experimental section | S3 |
| Fig. S1. Absorption spectra of TPE-P and TPE-C in THF solution. Concentration: 10 μ M. | S5 |
| Fig. S2. Particle size analysis of TPE-P (A) and TPE-C (B) in the mixture of THF/water with $f_w = 95$ vol% | S5 |
| Scheme. S1. Proposed uncaging mechanism of TPE-C. | S6 |
| Fig. S3 PL spectra of TPE-C in THF/water mixtures with $f_w = 85$ vol% at different irradiation time. Concentration: 10 μ M; excitation wavelength: 320 nm | S6 |
| Fig. S4 Fluorescent photographs of TPE-C in the mixture of THF/water with $f_w = 95$ vol% taken at different irradiation time. | S7 |
| Fig. S5 HPLC spectra of TPE-P (A) and TPE-C before (B), and after being irradiated under UV light for 3 (C) and 8 (D) min respectively. All samples were eluted with acetonitrile at a flow rate of 1 mL/min. | S7 |
| Fig. S6 Change in the integrated area of the specific peaks in HPLC spectra <i>versus</i> irradiation time. | S8 |
| Fig. S7 High resolution mass spectrum (MALDI-TOF) of the peak at 1.5 min in HPLC spectrum | S8 |
| Fig. S8 Photographs of filter paper at ambient conditions taken under UV irradiation at 365 nm with different irradiation time. Letters “A” and “E” were written by TPE-P and letter “I” was written by TPE-C using capillary tubes. | S9 |
| Fig. S9 Photographs of the process of photo-pattern by a mask with HKSAR logo under UV irradiation and pattern erasing process after removing the mask under further UV irradiation. | S9 |
| Fig. S10 ^1H NMR spectrum of TPE-P in CDCl_3 . | S10 |
| Fig. S11 ^{13}C NMR spectrum of TPE-P in CDCl_3 . | S10 |

| | |
|--|-----|
| Fig. S12 ¹ H NMR spectrum of TPE-P in CD ₂ Cl ₂ . | S11 |
| Fig. S13 ¹³ C NMR spectrum of TPE-P in CD ₂ Cl ₂ . | S11 |
| Fig. S14 High resolution mass spectrum (MALDI-TOF) of TPE-P. | S12 |
| Fig. S15 ¹ H NMR spectrum of TPE-C in CD ₂ Cl ₂ . | S12 |
| Fig. S16 ¹³ C NMR spectrum of TPE-C in CD ₂ Cl ₂ . | S13 |
| Fig. S17 High resolution mass spectrum (MALDI-TOF) of TPE-C. | S13 |
| Reference | S14 |

Experimental Section

Materials and Instruments

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Other chemicals were purchased from Aldrich or Alfa Aesar and used as received without further purification. ¹H NMR spectra were measured on a Bruker AV 400 spectrometer in CDCl₃ and CD₂Cl₂ using tetramethylsilane (TMS; δ = 0) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. HPLC measurements were conducted on an Agilent Technologies HPLC using acetonitrile as solvent and the flow rate is 1 mL/min.

Synthesis of TPE-P.

4-Bromotetraphenylethylene (**1**) is synthesized as previous report.¹ Into a 250 mL two-necked round bottom flask equipped a condenser. **1** (2.00 g, 4.86 mmol), (4-hydroxyphenyl)boronic acid (**2**, 0.74 g, 5.35 mmol), sodium bicarbonate (5.14 g, 48.62 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) were dissolved in to 90 mL distilled THF and 30 mL water under nitrogen. The mixture was heated to reflux overnight. After being cooled to room temperature, the mixture was extracted with dichloromethane for three times. The organic phase was combined and washed with water and dried over anhydrous sodium sulfate. After the evaporation of solvents, the crude product was purified by silica gel column chromatography using DCM/hexane in the volume ratio of 1:3 as eluent. The white solid was obtained in the yield of 78%. ¹H NMR (400 MHz, CDCl₃): 7.42 (dd, 2H, *J* = 8.8 Hz), 7.28 (dd, 2H, *J* = 6.8 Hz), 7.13-7.02 (m, 17H), 6.84 (dd, 2H, *J* = 8.8 Hz). ¹³C NMR (100 MHz, CDCl₃): 154.3, 143.2, 141.5, 140.3, 139.9, 137.7, 132.8, 131.1, 130.8, 130.7, 127.5, 127.1, 127.1,

127.0, 125.8, 125.8, 125.1. ¹H NMR (400 MHz, CD₂Cl₂): 7.46 (dd, 2H, *J* = 8.8 Hz), 7.33 (dd, 2H, *J* = 8.4 Hz), 7.16-7.05 (m, 17H), 6.88 (dd, 2H, *J* = 8.4 Hz). ¹³C NMR (100 MHz, CD₂Cl₂): 154.7, 143.2, 141.5, 140.4, 140.0, 137.7, 132.4, 131.0, 130.6, 130.5, 127.3, 127.1, 127.0, 125.8, 125.7, 124.9. HRMS (MALDI-TOF) *m/z* 424.1821 (M⁺, calcd. 424.5324).

Synthesis of TPE-C.

Into a two-necked round bottom flask, TPE-P (0.20 g, 0.47 mmol), 2-nitrobenzyl bromide (**3**, 0.12 g, 0.57 mmol) and cesium carbonate (0.18 g, 0.57 mmol) were dissolved in 7 mL acetonitrile under nitrogen atmosphere. The mixture was heated at 70 °C overnight. After being cooled to room temperature, the mixture was extracted with dichloromethane for three times. The organic phase was combined and washed with water and dried over anhydrous sodium sulfate Na₂SO₄. After the evaporation of solvents, the crude product was purified by silica gel column chromatography using DCM/hexane in the volume ratio of 1:4 as eluent. The pale yellow solid was obtained in the yield of 70%. ¹H NMR (400 MHz, CD₂Cl₂): 8.14 (dd, 1H, *J* = 8.0 Hz), 7.88 (dd, 1H, *J* = 7.6 Hz), 7.69 (t, 1H, *J* = 7.6 Hz), 7.15 -7.48 (m, 3H), 7.32 (dd, 2H, *J* = 8.0 Hz), 7.13 -7.01 (m, 19H), 5.49 (s, 2H). ¹³C NMR (100 MHz, CD₂Cl₂): 157.1, 146.5, 143.2, 141.7, 140.4, 137.6, 133.3, 133.1, 131.0, 130.6, 130.5, 128.0, 127.8, 127.3, 127.09, 127.0, 125.8, 125.7, 125.0, 124.3, 114.5. HRMS (MALDI-TOF) *m/z* 559.2153 (M⁺, calcd. 559.6925).

Photo-irradiation experiments

Stock THF solution of TPE-C with a concentration of 1mM was prepared. An aliquot (0.1 mL) of this stock solution was transferred to a 10 mL volumetric flask. Adding an appropriate amount of THF, water was added dropwise under vigorous stirring to furnish 10 μM THF/water mixtures with water fraction (*f_w*) of 85 and 95 vol%. The solution (3mL) in a quartz cuvette was irradiated by a hand-held UV lamp at 365 nm. PL measurements were carried out in a specific time.

Photo-patterning and pattern erasing experiments

Stock THF solution of TPE-C with a concentration of 1mM was prepared. A filter paper was soaked in the stock solution and then taken out and dried by compressed air. A projector transparent film with pattern was covered on the filter paper. The filter paper was irradiated for 5 min by using hand-held UV lamp with 365 nm to generate the pattern on the filter paper. To erase the pattern, the filter paper was irradiated for another 15 min without the film.

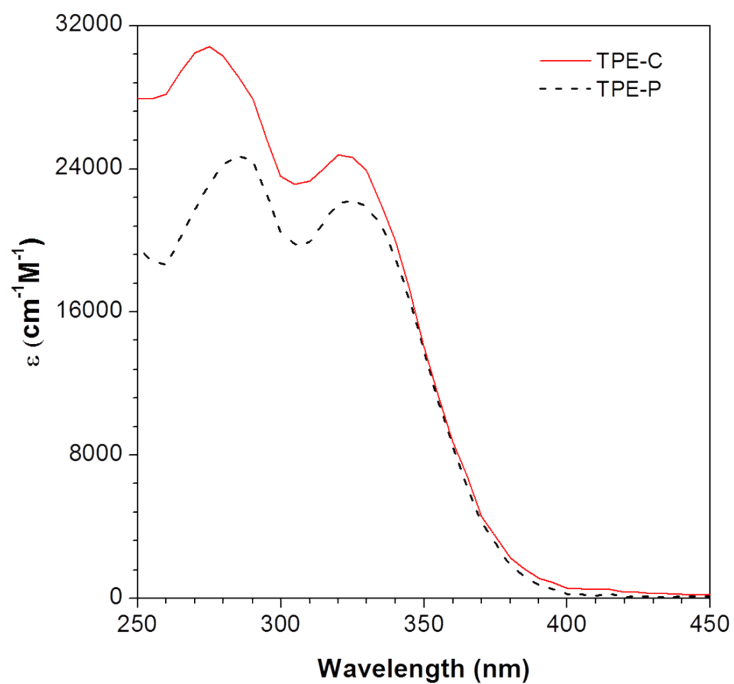


Fig. S1 Absorption spectra of TPE-P and TPE-C in THF solution. Concentration: 10 μM .

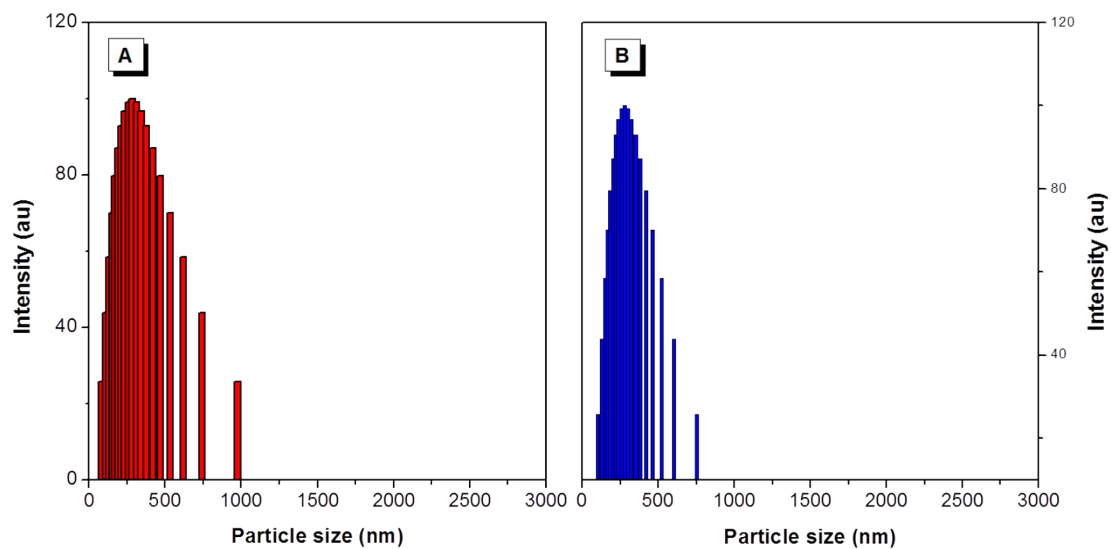
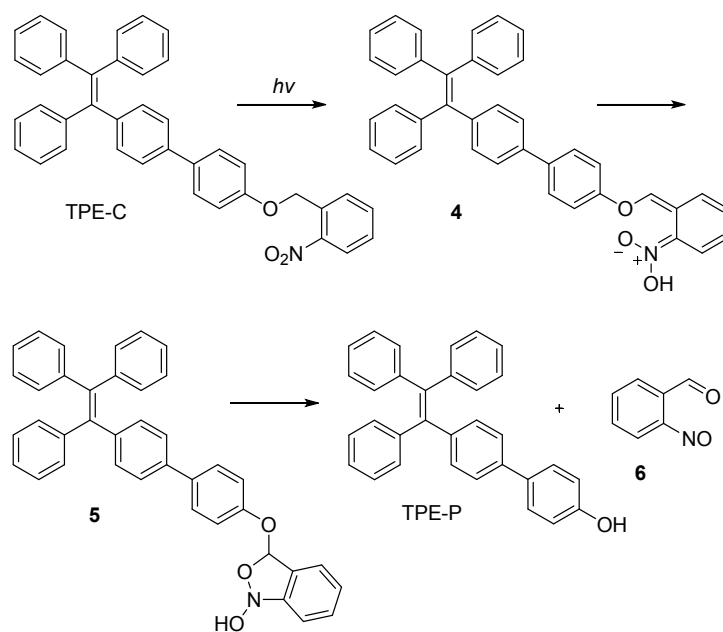


Fig. S2. Particle size analysis of TPE-P (A) and TPE-C (B) in the mixture of THF/water with $f_w = 95 \text{ vol}\%$



Scheme. S1. Proposed uncaging mechanism of TPE-C.²

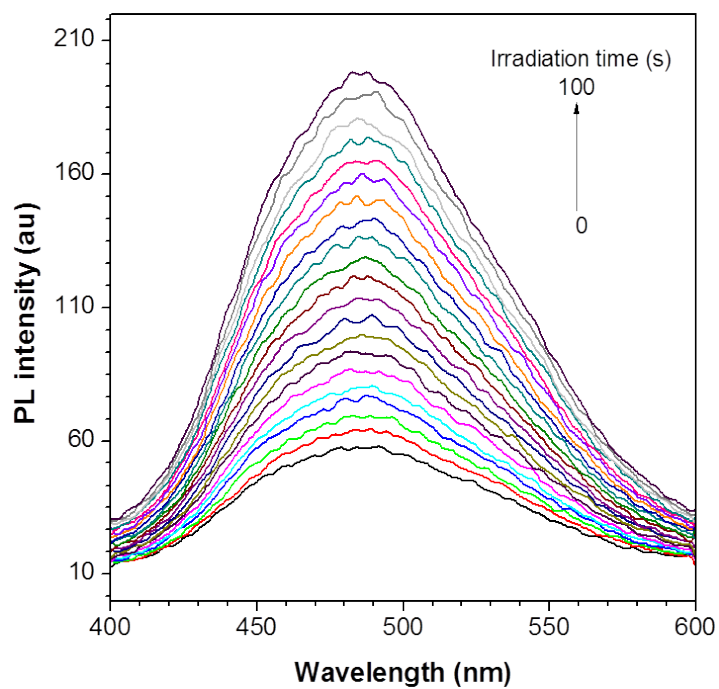


Fig. S3 PL spectra of TPE-C in THF/water mixtures with $f_w = 85$ vol% at different irradiation time. Concentration: $10 \mu\text{M}$; excitation wavelength: 320 nm

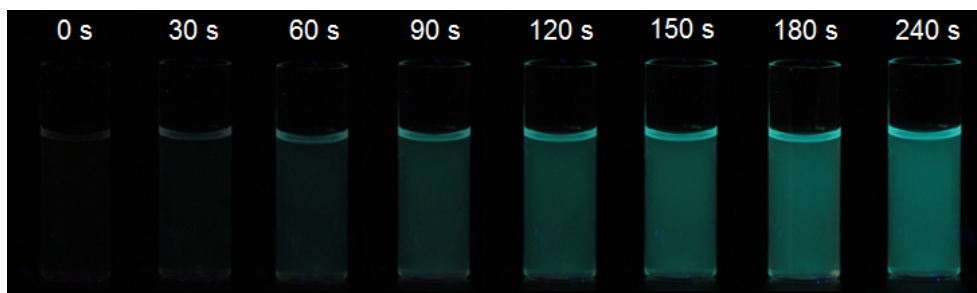


Fig. S4 Fluorescent photographs of TPE-C in the mixture of THF/water with $f_w = 95$ vol% taken at different irradiation time.

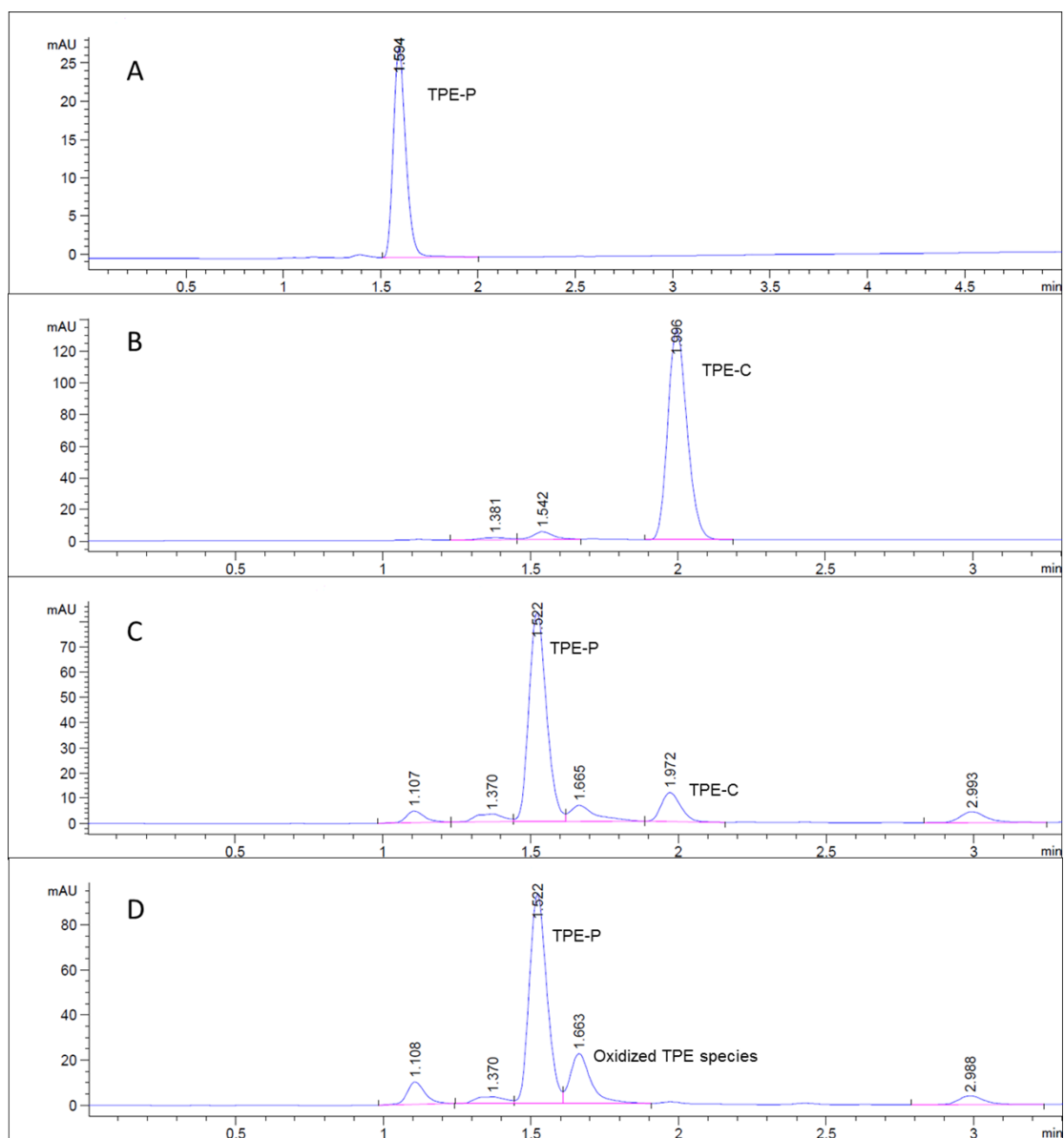


Fig. S5 HPLC spectra of TPE-P (A) and TPE-C before (B), and after being irradiated under UV light for 3 (C) and 8 (D) min respectively. All samples were eluted with acetonitrile at a flow rate of 1 mL/min.

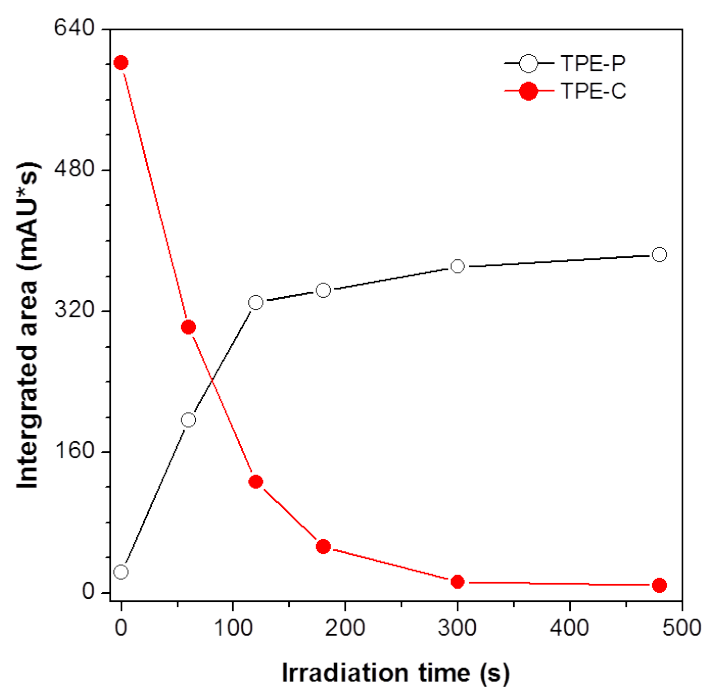


Fig. S6 Change in the integrated area of the specific peaks in HPLC spectra *versus* irradiation time.

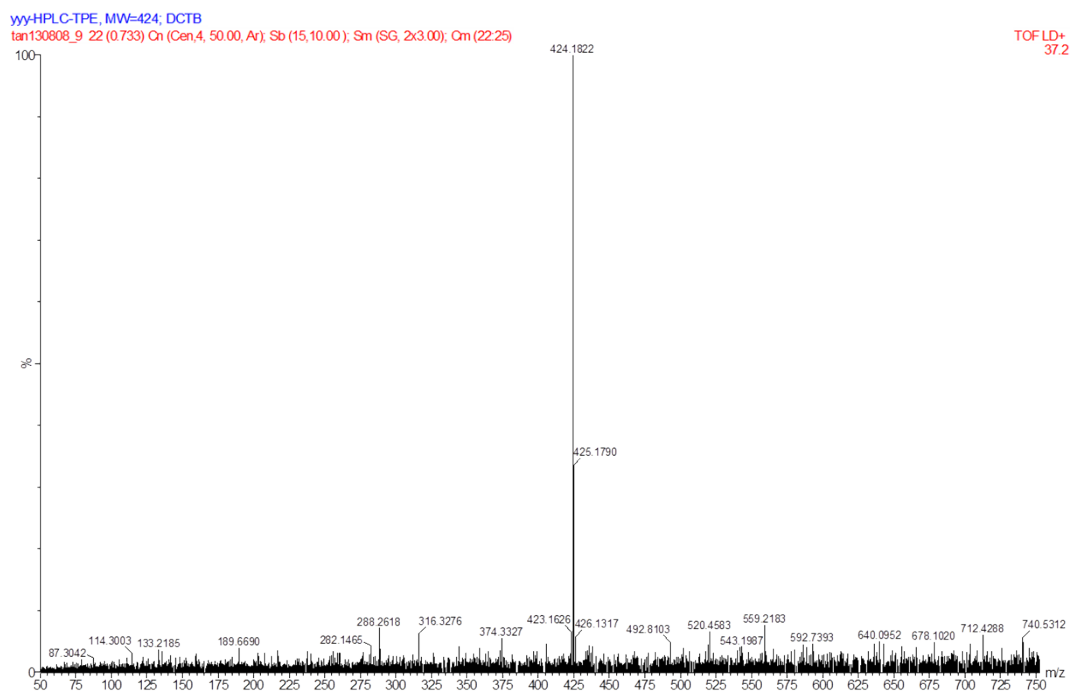


Fig. S7 High resolution mass spectrum (MALDI-TOF) of the peak at 1.5 min in HPLC spectrum.



Fig. S8 Photographs of filter paper at ambient conditions taken under UV irradiation at 365 nm with different irradiation time. Letters “A” and “E” were written by TPE-P and letter “T” was written by TPE-C using capillary tubes.

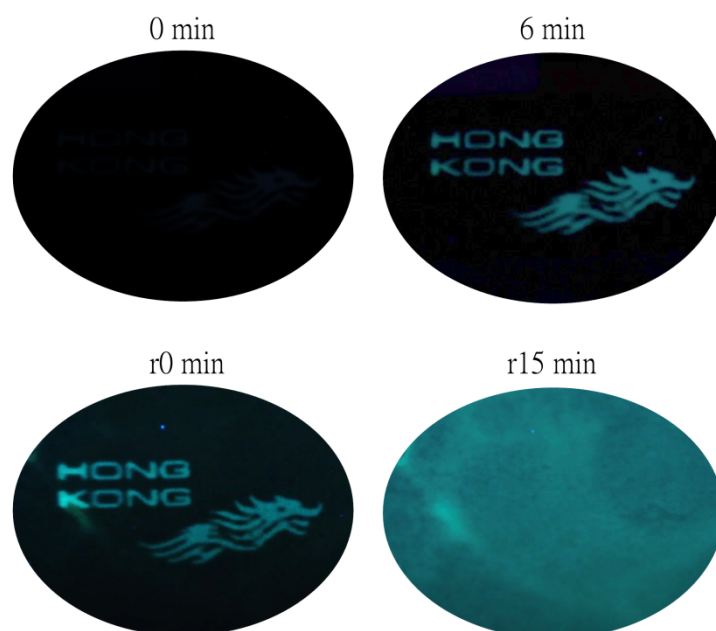


Fig. S9 Photographs of the process of photo-pattern by a mask with HKSAR logo under UV irradiation and pattern erasing process after removing the mask under further UV irradiation.

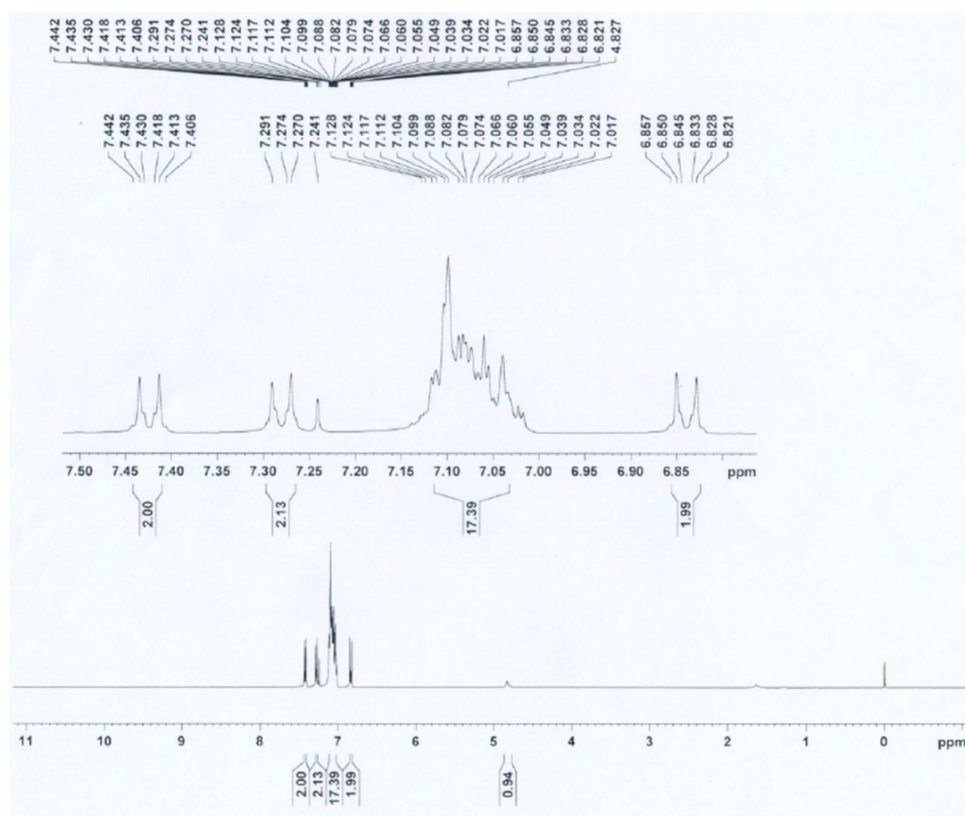


Fig. S10 ^1H NMR spectrum of TPE-P in CDCl_3 .

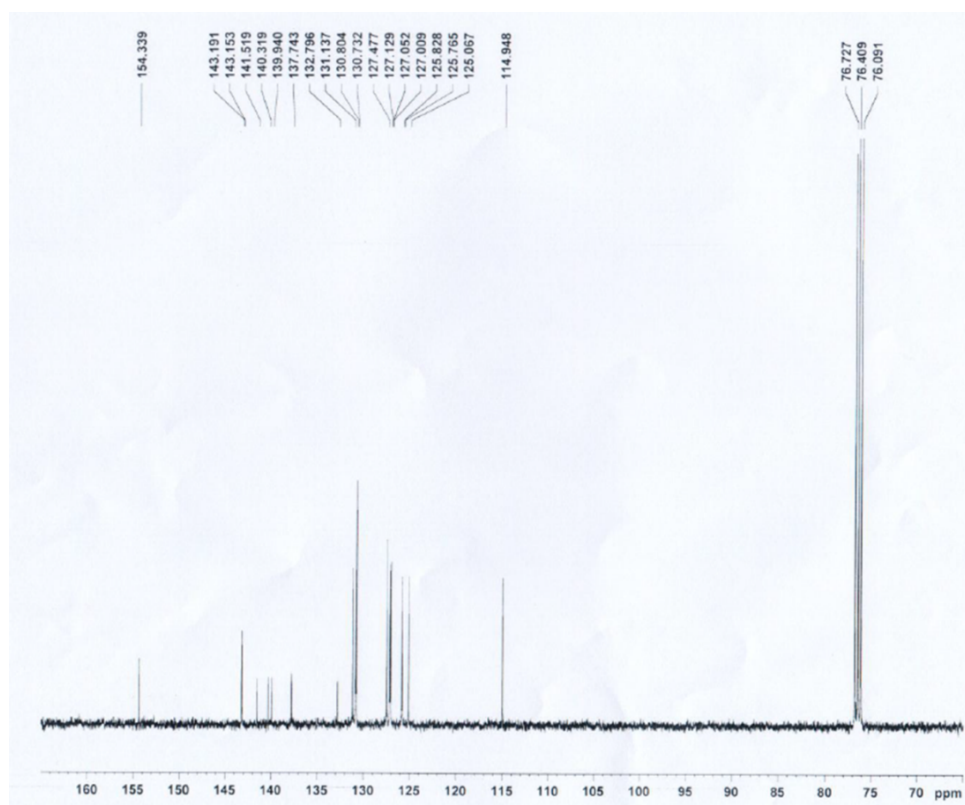


Fig. S11 ^{13}C NMR spectrum of TPE-P in CDCl_3 .

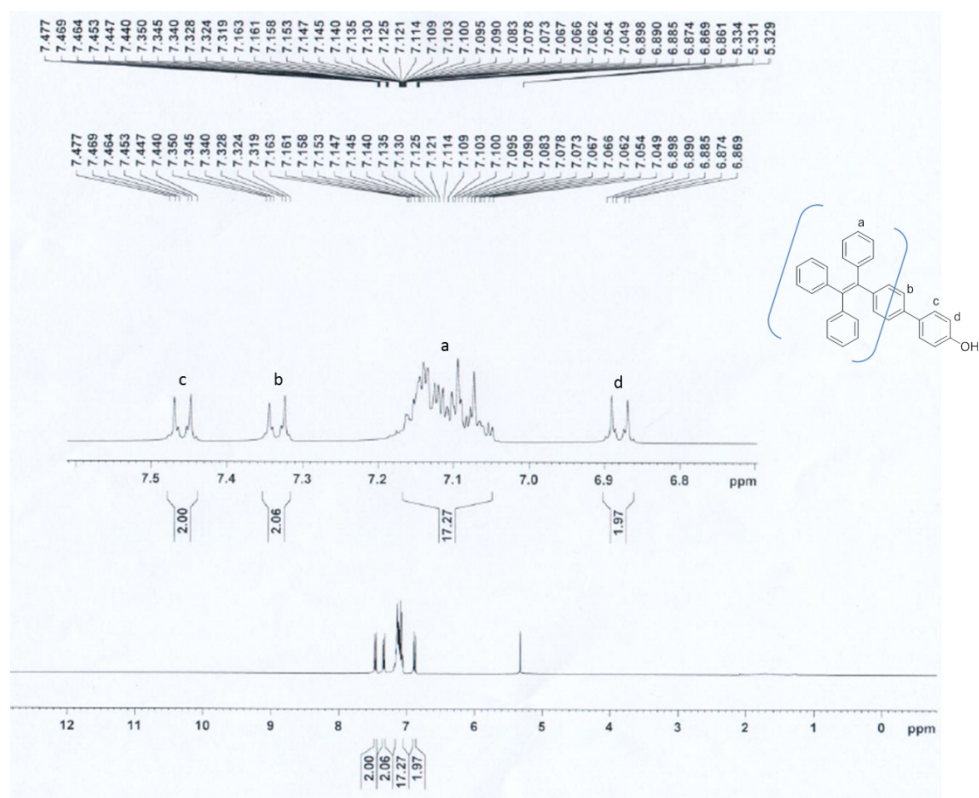


Fig. S12 ^1H NMR spectrum of TPE-P in CD_2Cl_2 .

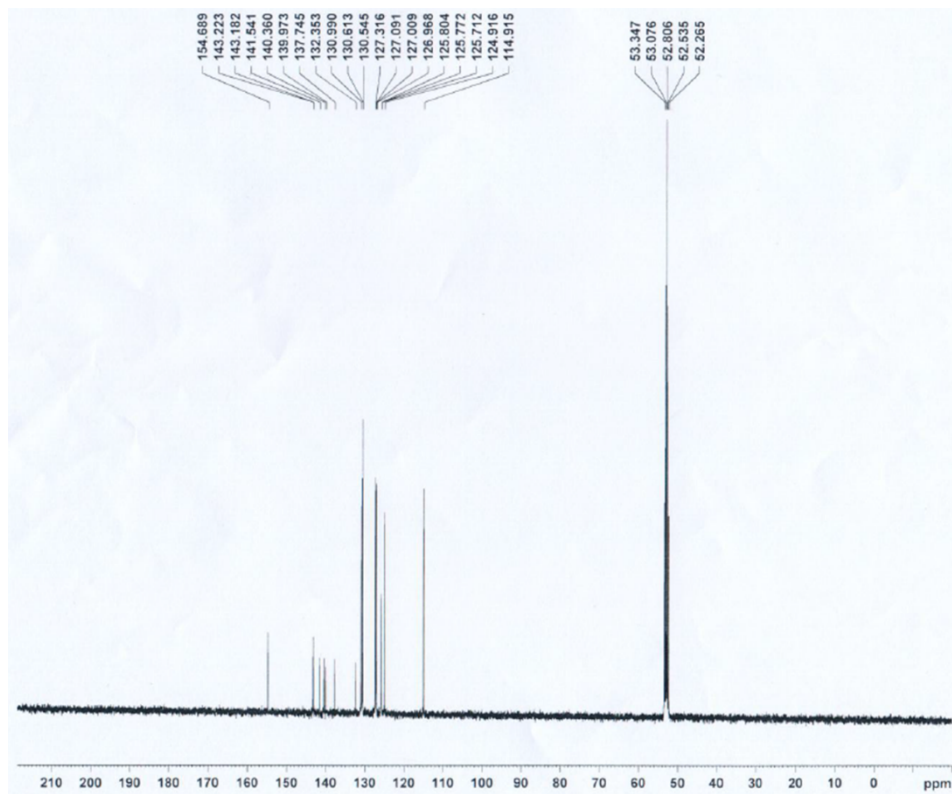


Fig. S13 ^{13}C NMR spectrum of TPE-P in CD_2Cl_2 .

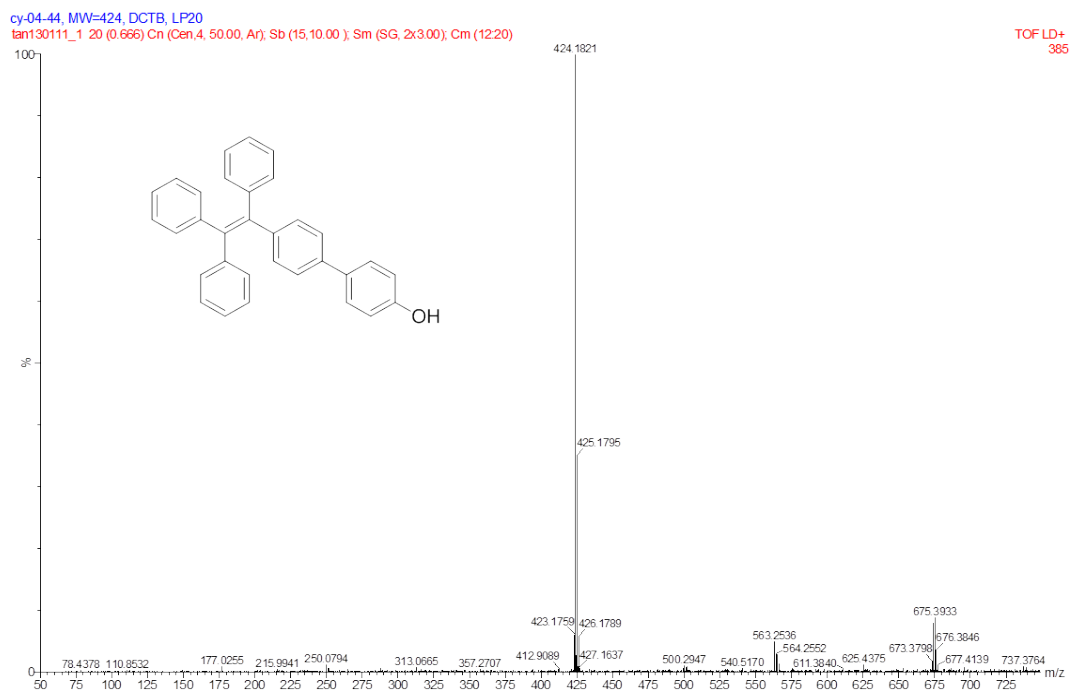


Fig. S14 High resolution mass spectrum (MALDI-TOF) of TPE-P.

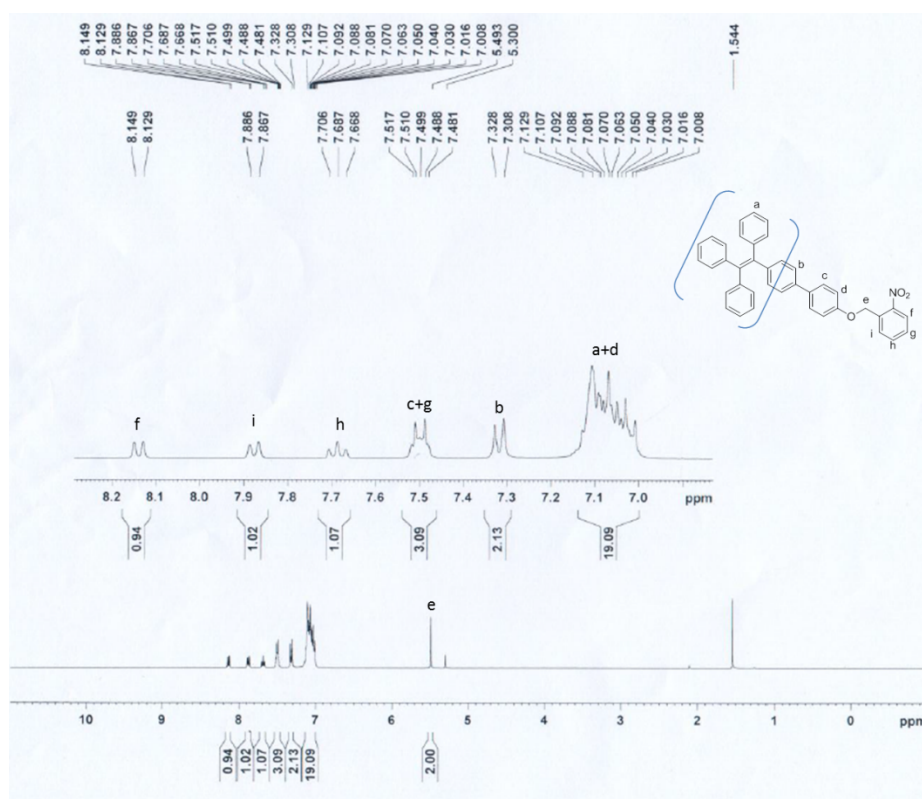


Fig. S15 ^1H NMR spectrum of TPE-C in CD_2Cl_2 .

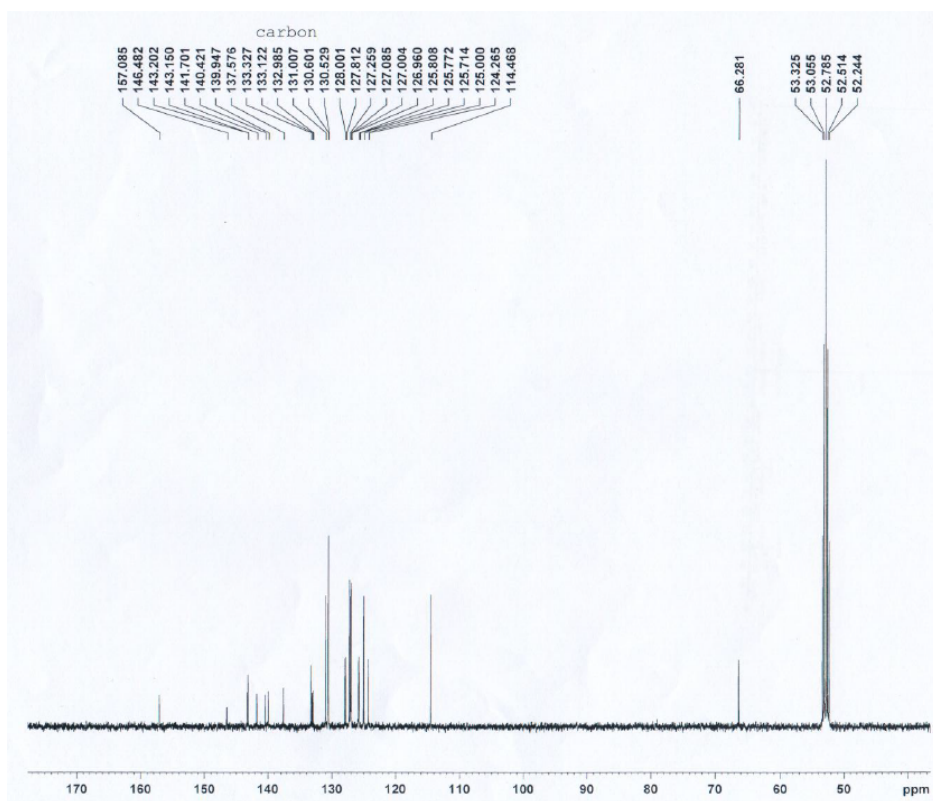


Fig. S16 ^{13}C NMR spectrum of TPE-C in CD_2Cl_2 .

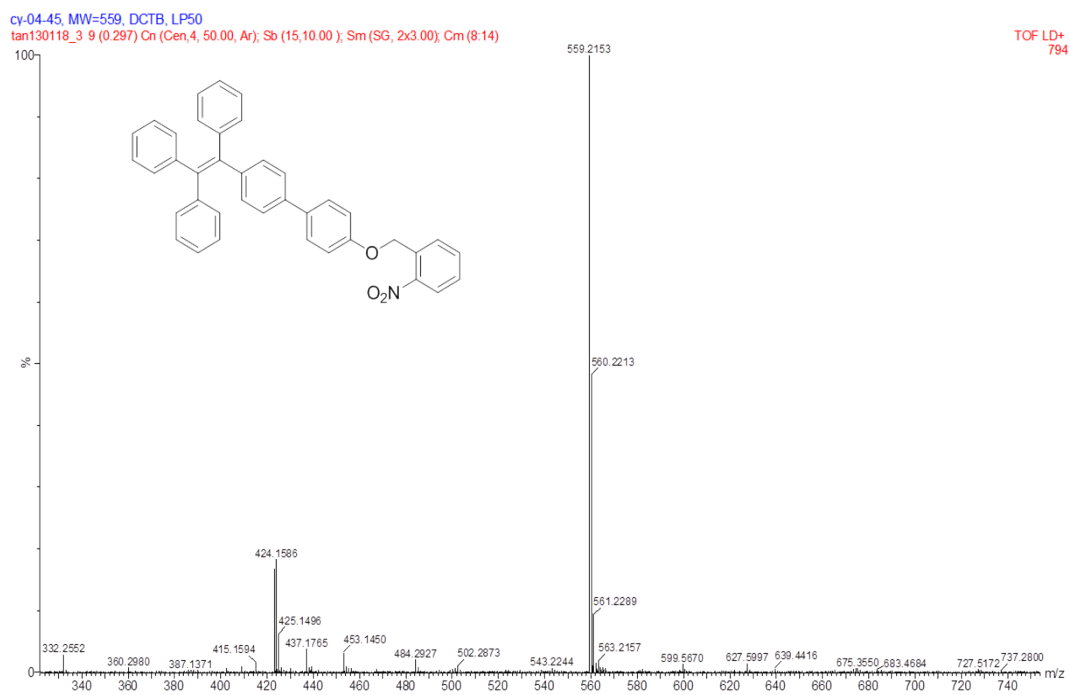


Fig. S17 High resolution mass spectrum (MALDI-TOF) of TPE-C.

Reference

- 1 Y. Hong, S. Chen, C. W. T. L., J. W. Y. Lam, J. Liu, N.-W. Tseng, R. T. K. Kwok, Y. Yu, Z. Wang and B. Z. Tang, *ACS Appl. Mater. Interfaces*, 2011, **3**, 3411.
- 2 Y. V. Il'ichev, M. A. Schworer and J. Wirz, *J. Am. Chem. Soc.*, 2004, **126**, 4581.