Supporting information

Full-color tunable mechanofluorochromism and excitation-dependent emissions of single-arm extended tetraphenylethylenes

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Experimental details

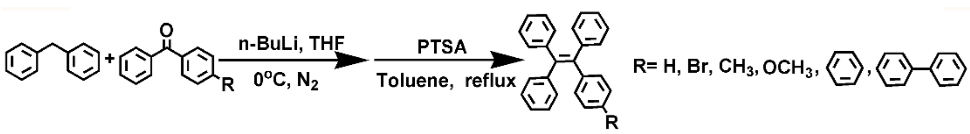
Materials

All raw materials (such as diphenylmethane,4-methylbenzophenone, triethyl phosphite and various aromatic aldehydes) were purchased from commercial sources and used without further purification.

Characterization

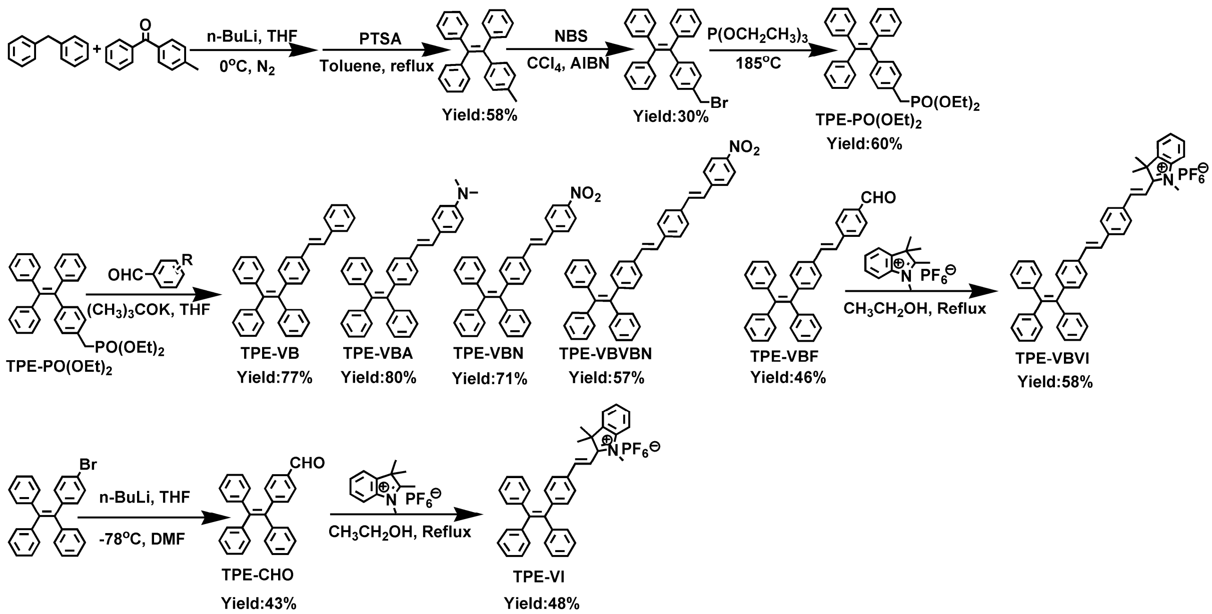
^{1}H NMR (300 MHz) spectra were recorded on a Varian Mercury using TMS as a standard at room temperature.^{13}C NMR (125 MHz) spectra were recorded on a Bruker AVANCE500 using TMS as a standard at room temperature.The time of flight mass spectra was recorded using a Kratos MALDI-TOF mass system. UV-Vis absorption spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer. The fluorescence quantum yields (Φ_f) and lifetime were measured on FLS 920 lifetime and steady state spectrometer. Steady State fluorescence spectra were measured using a Shimadzu RF-5301 PC spectrophotometer. Reflection spectroscopy was performed on a Maya 2000PRO fiber optical spectrometer with Ocean DH-2000-BAL UV-Vis-NIR light source using $BaSO_4$ as background. True-color optical images were obtained by using a Canon camera. DSC experiments were recorded on a NETZSCH DSC 204 instrument at a scanning rate of 10 K·min^{-1}. Powder XRD patterns were obtained from a PANalytical B.V.Empyrean X-ray diffractomer with Cu-Kα radiation (λ = 1.5418 Å).

Synthetic scheme for monosubstituted tetraphenylethylene derivatives (group I)



Take **TPE-CH$_3$** as an example, the general synthetic procedure is shown as follow: To a solution of diphenylmethane (3.8 g, 22.6 mmol, 1.0 eq) in dry THF (20 mL) was added 10 mL of n-butyllithium hexane solution (2.5 mol/L) (equivalently 25.0 mmol n-butyllithium, 1.1 eq) at 0 °C under nitrogen atmosphere. The resulting orange-red solution was stirred for one hour at that temperature. To this solution was added 4-methylbenzone (4.0 g, 20.4 mmol, 0.9 eq) and the reaction mixture was allowed to warm to room temperature with stirring for 12 hours. Then the reaction was quenched with the addition of an aqueous solution of ammonium chloride, the organic layer was extracted with dichloromethane, and the combined organic layers were washed with a saturated brine solution and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the resulting crude alcohol was dissolved in about 50 mL of toluene in a 100 mL Schlenk flask fitted with a Dean-Stark trap. A catalytic amount of p-toluenesulphonic acid (PTSA) (0.42 g, 2.4 mmol, 0.1 eq) was added, and the mixture was refluxed for 6 hours and cooled to room temperature. The toluene layer was washed with 10 % aqueous $NaHCO_3$ solution, dried over anhydrous $MgSO_4$ and evaporated to afford the crude **TPE-CH$_3$**. The crude product was recrystallized in alcohol to afford a white powder with the yield of 60%.

Synthetic scheme for single-arm extended tetraphenylethylene derivatives (group II)

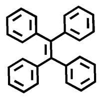


TPE-PO(OEt)$_2$ and **TPE-CHO** were synthesized according to reported literatures.[1]

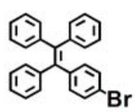
The single-arm extended tetraphenylethylene derivatives were synthesized according to typical Witting-Horner reaction. Taking **TPE-VB** as an example, the general synthetic procedure is shown as follow: To a solution of **TPE-PO(OEt)$_2$** (240 mg, 0.5 mmol, 1eq) and benzaldehyde (53 mg, 0.5 mmol, 1eq) in dry THF (10 mL) cooled to 0 ^{o}C, was stepwise added 2 mL dry THF solution of potassium tert-butoxide (70 mg, 0.6 mmol, 1.2 eq). After 10 hours, the reaction mixture was poured into a large amount of water (around 100 mL). Then the crude was filtered out and recrystallized with hot ethanol to afford white powders (yield: 77%).

TPE-VI and **TPE-VBVI** were synthesized as following synthetic procedure: A mixture of 1,2,3,3-tetramethyl-3H-indolium hexafluorophosphate (1 mmol) and the corresponding aldehydes (1 mmol) in ethanol (10 mL) were refluxed for 24 hours under nitrogen. When the reaction mixture was cool to room temperature, the crude was filtered out and purified with column chromatography (CH_2Cl_2/petroleum ether) to afford the target products.

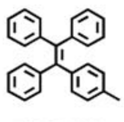
Detailed characterization of tetraphenylethylene and its derivatives


TPE

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.10-7.08 (12H, m), 7.04-7.02 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.76, 140.98, 131.38, 127.69, 126.45. MS (MALDI-TOF): m/z calcd. $[M]^+$ 332.16 found 331.95.

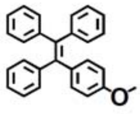

TPE-Br

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.23-7.19 (2H, m), 7.13-7.07 (9H, m), 7.03-6.98 (6H, m), 6.90-6.87 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.75, 143.45, 143.36, 143.26, 142.73, 141.62, 139.68, 133.03, 131.37, 131.34, 131.29, 131.27, 130.89, 127.92, 127.82, 127.73, 127.68, 126.74, 126.69, 126.64, 126.44, 120.49. MS (MALDI-TOF): m/z calcd. $[M]^+$ 410.07 found 410.34.



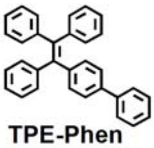
TPE-CH_3

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.10-7.02 (15H, m), 6.90 (4H, s), 2.25 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.98, 143.96, 140.93, 140.77, 140.48, 136.09, 131.39, 131.36, 131.26, 128.42, 127.70, 127.64, 126.37, 126.32, 21.24. MS (MALDI-TOF): m/z calcd. $[M]^+$ 346.17 found 346.00.



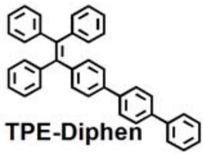
TPE-OCH_3

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.10-7.01 (15H, m), 6.93 (2H, d, J=8.9 Hz), 6.63 (2H, d, J=8.9 Hz), 3.73 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 158.10, 144.07, 144.02, 144.01, 140.55, 140.11, 136.14, 132.57, 131.42, 131.40, 131.37, 127.75, 127.64, 126.39, 126.28, 113.07, 55.12. MS (MALDI-TOF): m/z calcd. $[M]^+$ 362.17 found 362.06.



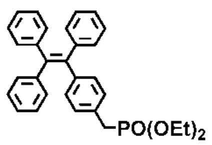
TPE-Phen

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.56-7.54 (2H, m), 7.41-7.29 (5H, m), 7.14-7.02 (17H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.83, 143.78, 142.81, 141.17, 141.15, 140.68, 140.58, 138.90, 131.84, 131.49, 131.41, 128.75, 127.82, 127.76, 127.70, 127.21, 126.91, 126.54, 126.48, 126.26. MS (MALDI-TOF): m/z calcd. $[M]^+$ 408.19 found 407.93.



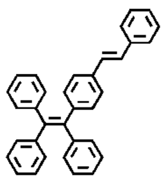
TPE-Diphen

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.64-7.61 (6H, m), 7.47-7.34 (5H, m), 7.14-7.02 (17H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.79, 143.75, 143.74, 142.89, 141.18, 140.70, 140.53, 139.96, 139.55, 138.31, 131.86, 131.46, 131.38, 128.83, 127.80, 127.73, 127.67, 127.43, 127.34, 127.21, 127.02, 126.53, 126.52, 126.46, 126.10. MS (MALDI-TOF): m/z calcd. $[M]^+$ 484.22 found 484.11.



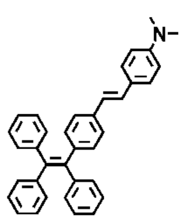
TPE-PO(OEt)$_2$

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.10-6.96 (19H, m), 3.98-3.89 (4H, m), 3.10 (1H, s), 3.02 (1H, s), 1.21(6H, t); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.77, 143.64, 143.59, 142.49, 142.46, 141.05, 140.55, 140.54, 131.53, 131.51, 131.32, 131.31, 129.60, 129.53, 129.27, 129.22, 127.67, 126.49, 126.47, 126.41, 62.25, 62.20, 34.13, 33.03, 16.47, 16.42. MS (MALDI-TOF): m/z calcd. $[M]^+$ 482.20 found 482.00.



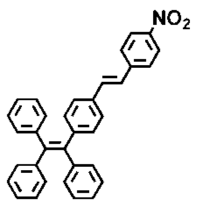
TPE-VB

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.47 (2H, d, J=7.4 Hz), 7.34 (2H, t), 7.27-7.21 (4H, m), 7.13-7.00 (18H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.76, 143.68, 143.24, 141.12, 140.60, 137.41, 135.32, 131.74, 131.44, 131.37, 128.68, 128.44, 128.40, 127.79, 127.71, 127.65, 127.54, 126.54, 126.51, 126.45, 125.84. MS (MALDI-TOF): m/z calcd. $[M]^+$ 434.20 found 434.58.



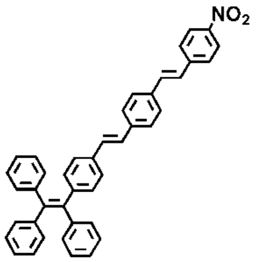
TPE-VBA

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 7.36 (2H, d, J=8.8 Hz), 7.20 (2H, d, J=8.4 Hz), 7.13-6.94 (18H, m), 6.81 (1H, d, J=16.2 Hz), 6.70 (2H, d, J=8.3 Hz), 2.97 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 143.90, 143.87, 143.81, 143.72, 140.80, 131.66, 131.46, 131.39, 131.37, 128.55, 127.76, 127.64, 127.61, 127.54, 126.44, 126.43, 126.34, 125.30, 124.14, 120.00, 112.46, 40.49. MS (MALDI-TOF): m/z calcd. $[M]^+$ 477.25 found 477.70.



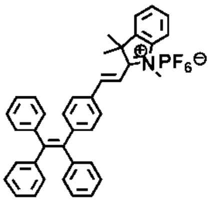
TPE-VBN

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 8.20 (2H, d, J=8.9 Hz), 7.58 (2H, d, J=8.9 Hz), 7.29 (1H, d, J=8.3 Hz), 7.20-7.01 (20H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 146.68, 144.64, 143.97, 143.60, 143.53, 143.46, 141.66, 140.31, 134.16, 133.07, 131.92, 131.38, 131.35, 131.32, 127.82, 127.77, 127.68, 126.74, 126.66, 126.62, 126.40, 125.92, 124.17. MS (MALDI-TOF): m/z calcd. $[M]^+$ 479.19 found 479.66.



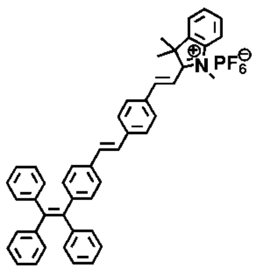
TPE-VBVBN

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 8.23 (2H, d, J=8.9 Hz), 7.63 (2H, d, J=8.9 Hz), 7.53 (2H, d, J=8.7 Hz), 7.49 (2H, d, J=8.8 Hz), 7.29-7.24 (3H, m), 7.17-7.01 (20H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 146.70, 143.91, 143.74, 143.70, 143.63, 143.59, 141.27, 140.53, 138.07, 135.35, 135.09, 132.90, 131.82, 131.44, 131.39, 131.38, 129.18, 127.81, 127.74, 127.68, 127.63, 127.44, 126.93, 126.84, 126.58, 126.56, 126.51, 125.99, 125.96, 124.21. MS (MALDI-TOF): m/z calcd. $[M]^+$ 581.24 found 581.03.



TPE-VI

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 8.01 (1H, d, J=16.3 Hz), 7.61-7.53 (6H, m), 7.33 (1H, d, J=15.7 Hz), 7.20-7.11 (11H, m), 7.08-7.00 (6H, m), 4.11 (3H, s), 1.76 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 182.14, 152.78, 149.05, 144.08, 143.31, 143.19, 142.96, 142.93, 142.28, 140.22, 133.13, 132.04, 131.24, 131.23, 131.10, 130.43, 129.89, 129.44, 128.53, 128.52, 128.37, 127.60, 127.43, 127.42, 123.33, 115.66, 113.40, 52.60, 34.88, 25.70. HRMS (ESI, positive): m/z calcd. $[M-PF_6^-]^+$ 516.2686 found 516.2685.

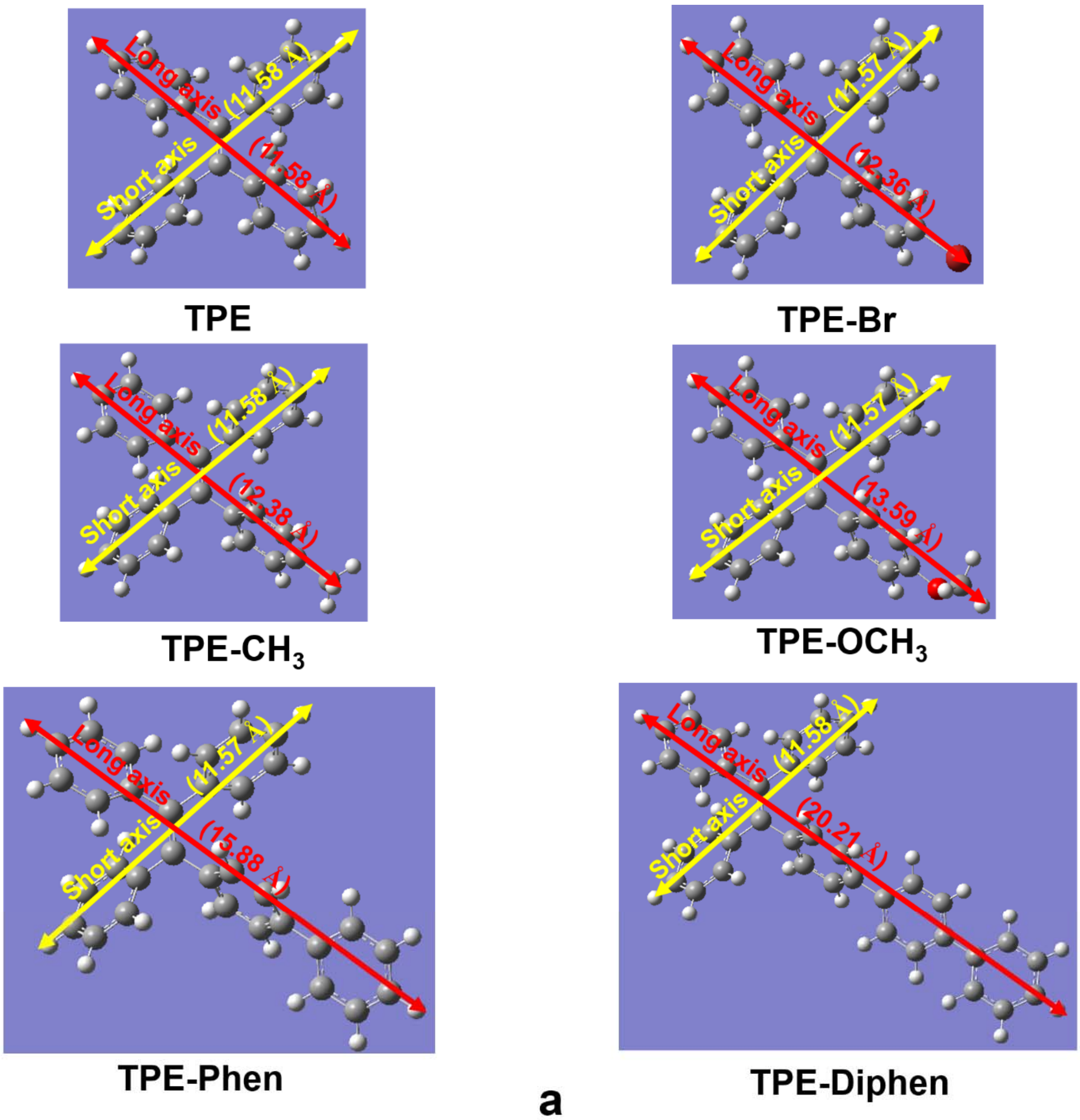


TPE-VBVI

^{1}H NMR (300 MHz, $CDCl_3$): δ(TMS, ppm): 8.41 (1H, d, J=16.3 Hz), 8.22 (2H, d, J=8.3 Hz), 7.91-7.86 (2H, m), 7.78 (2H, d, J=8.2 Hz), 7.72-7.62 (3H, m), 7.48-7.42 (3H, m), 7.30 (1H, d, J=16.6 Hz), 7.18-7.13 (9H, m), 7.03-6.93 (8H, m), 4.16 (3H, s), 1.80 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ(TMS, ppm): 182.05, 152.88, 144.06, 143.89, 143.66, 143.58, 143.46, 142.65, 142.33, 141.48, 140.67, 135.30, 134.11, 131.91, 131.68, 131.53, 131.22, 131.17, 131.13, 129.82, 129.45, 128.40, 128.37, 128.29, 127.96, 127.61, 127.19, 127.15, 127.09, 126.92, 123.32, 115.60, 112.99, 52.59, 34.88, 25.82. HRMS (ESI, positive): m/z calcd. $[M-PF_6^-]^+$ 618.3155 found 618.3154.

Figure S1. (a) Optimized structures of **TPE** and its group I derivatives using B3LYP/6-31G (d,p) by Gaussian 09[2]. (b) Long-to-short axis ratio (LSAR) of **TPE** and its group I derivatives.

Long-to-short axis ratio (LSAR) is obtained through molecular long axis divided by molecular short axis.

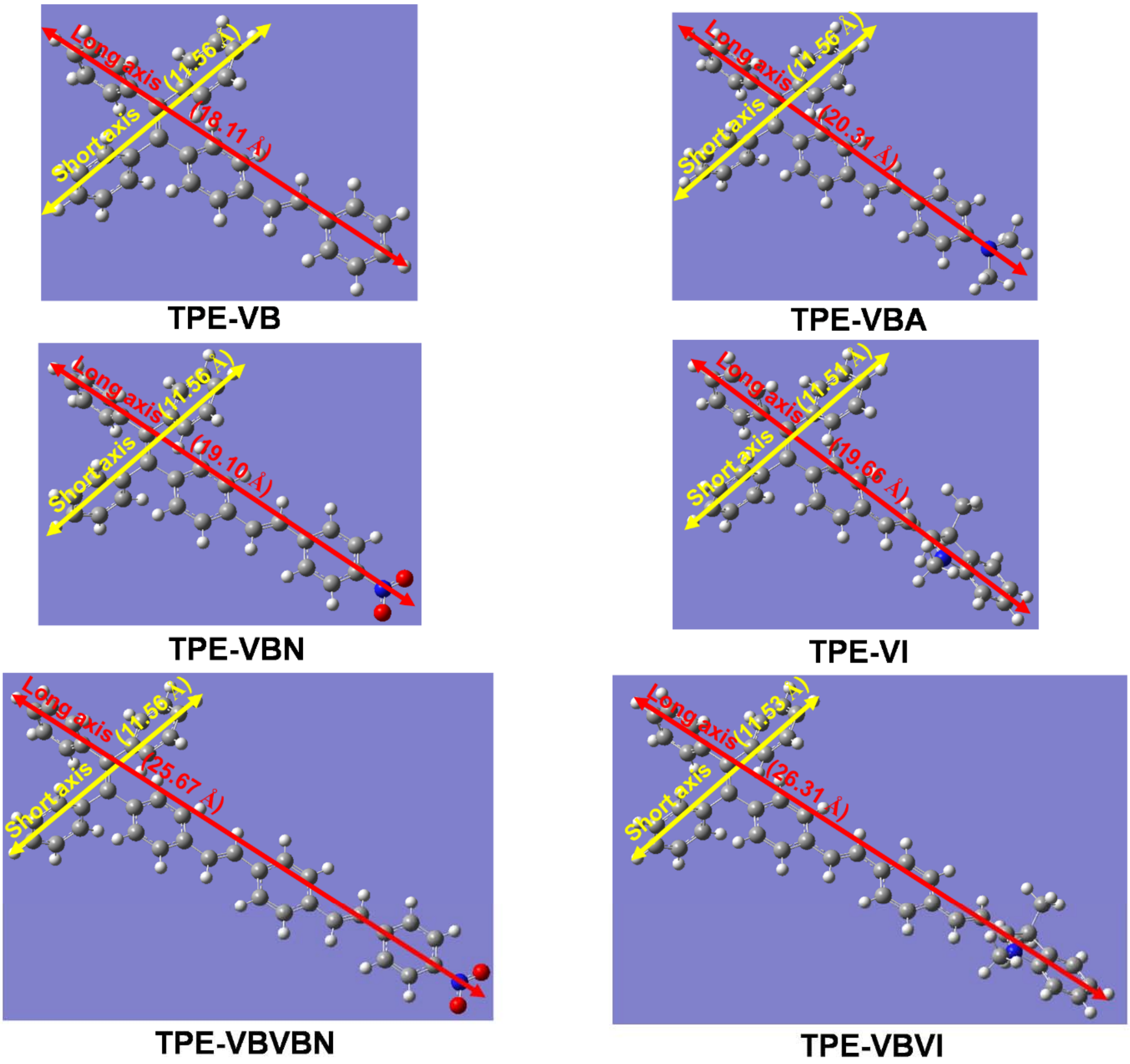


a

Compound	TPE	TPE-Br	TPE-CH_3	TPE-OCH_3	TPE-Phen	TPE-Diphen
Long-to-short axis ratio	1.00	1.07	1.07	1.17	1.37	1.75

b

Figure S2. (a) Optimized structures of single-arm extended **TPE** derivatives (group II) using B3LYP/6-31G (d,p) by Gaussian 09[2]. (b) Long-to-short axis ratio (LSAR) and dipole moments of these six single-arm extended **TPE** derivatives (group II).



a

Compound	TPE-VB	TPE-VBA	TPE-VBN	TPE-VI	TPE-VBVBN	TPE-VBVI
Long-to-short axis ratio	1.57	1.76	1.65	1.71	2.22	2.28
Dipole moment (Debye)	0.13	3.63	7.11	12.73	7.71	24.02

b

Figure S3. Molecular orbital amplitude plots of HOMO and LUMO energy levels of the six single-arm extended tetraphenylethylene derivatives (group II) calculated using B3LYP/6-31G(d,p) by Gaussian 09[2].

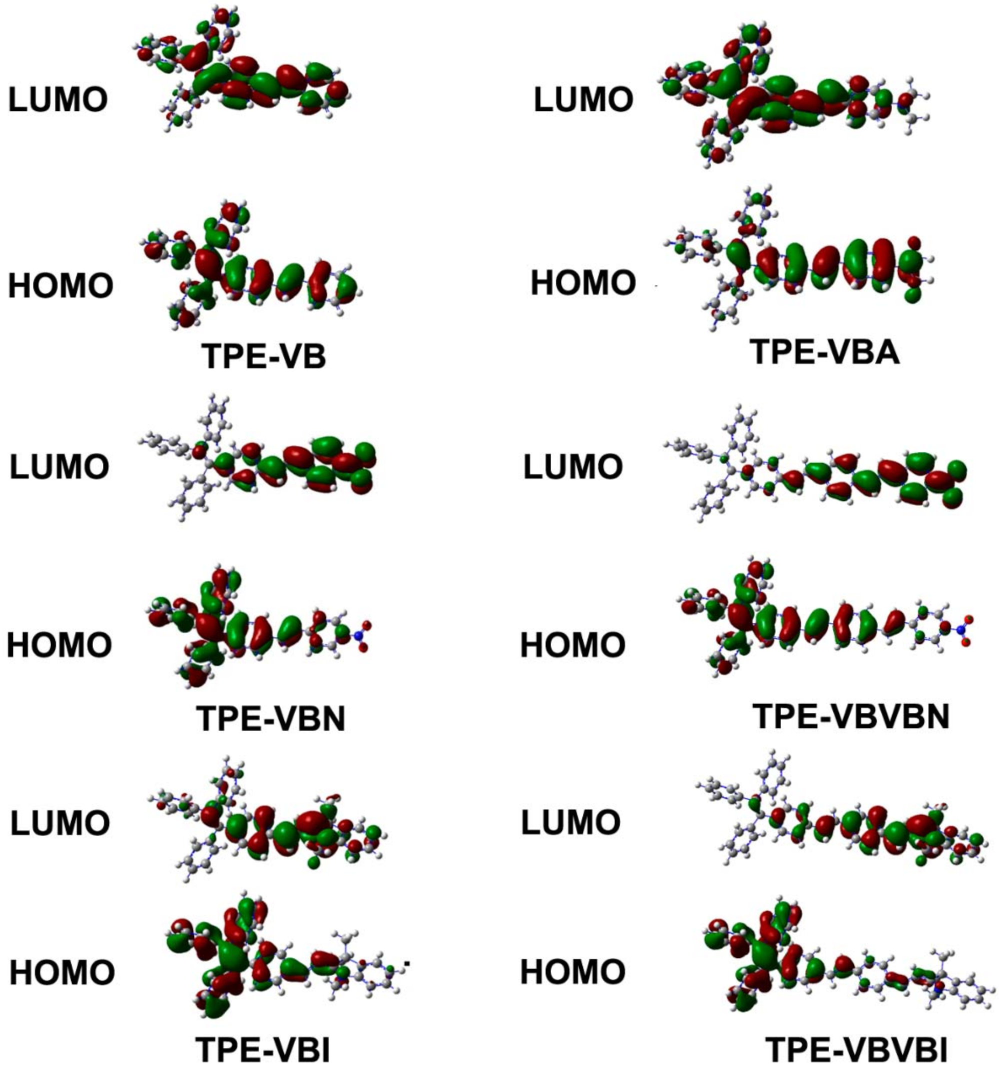
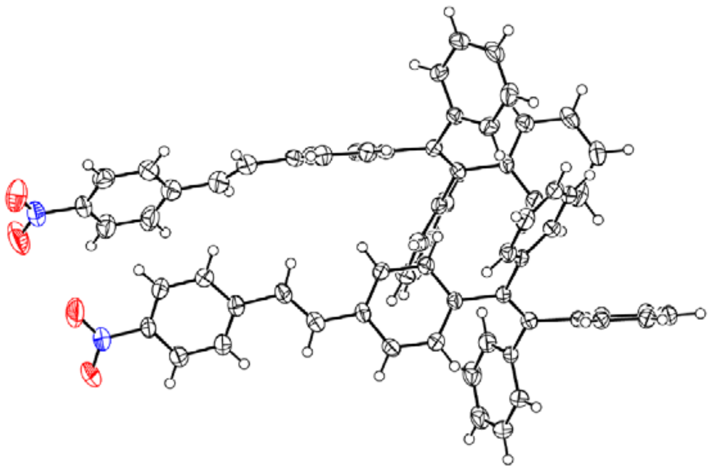


Table S1. Summary of crystal data and intensity collection parameters for **TPE-VBN** and **TPE-VBVBN**.

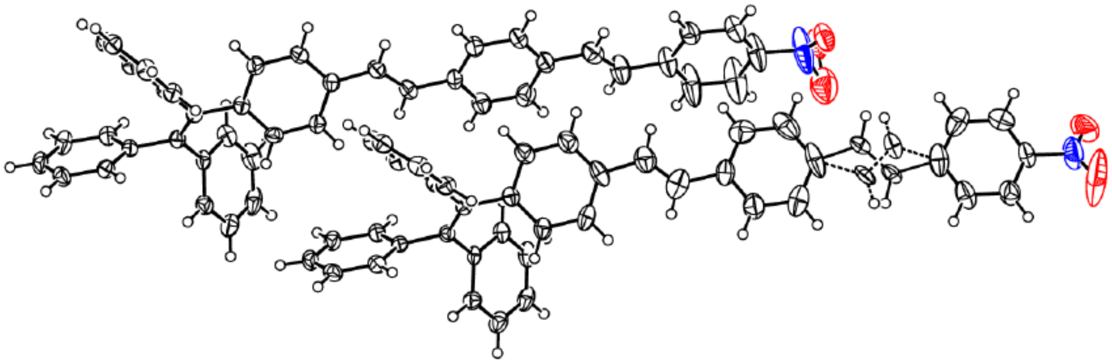
Compound	**TPE-VBN**	**TPE-VBVBN**
Formula	$C_{34}H_{25}NO_2$	$C_{42}H_{31}NO_2$
Formula mass	479.55	581.68
Space group	P 21	P -1
a/ Å	10.202(5)	9.396(5)
b/ Å	18.970(7)	17.959(6)
c/ Å	13.263(5)	18.690(7)
α/°	90	79.896(14)
β/°	98.310(15)	83.610(15)
γ/°	90	86.117(15)
V/Å^3	2539.9(18)	3082(2)
Z	4	4
ρ/g.cm^{-3}	1.254	1.254
F_{000}	1008	1224
Temp, (K)	153(2)	153(2)
Absorption coefficient, μ/mm^{-1}	0.077	0.076
No. of reflections measured	23987	23103
No. of independent reflections	9887	10341
R_{int}	0.0554	0.0575
Final R_1 values ($I > 2\sigma(I)$)	0.0539	0.0674
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1241	0.1864
Final $R1$ values (all data)	0.0840	0.1355
Final $wR(F^2)$ values (all data)	0.1391	0.2445
Goodness-of-fit on F^2	1.018	0.987
CCDC numbers	1053198	1053197

The crystal data for **TPE-VBN** and **TPE-VBVBN** were deposited into Cambridge Crystallographic Data Centre with CCDC numbers of 1053198 and 1053197, respectively.

Figure S4. Single-crystal X-ray structure of **TPE-VBN** and **TPE-VBVBN** (50% probability ellipsoids).



TPE-VBN



TPE-VBVBN

Figure S5. (a) Absorption spectra and (b) fluorescent spectra of **TPE-VB** (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of **TPE-VB** with different water fractions). (c) Absorption spectra and (d) fluorescent spectra of **TPE-VBA** (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of **TPE-VBA** with different water fractions).

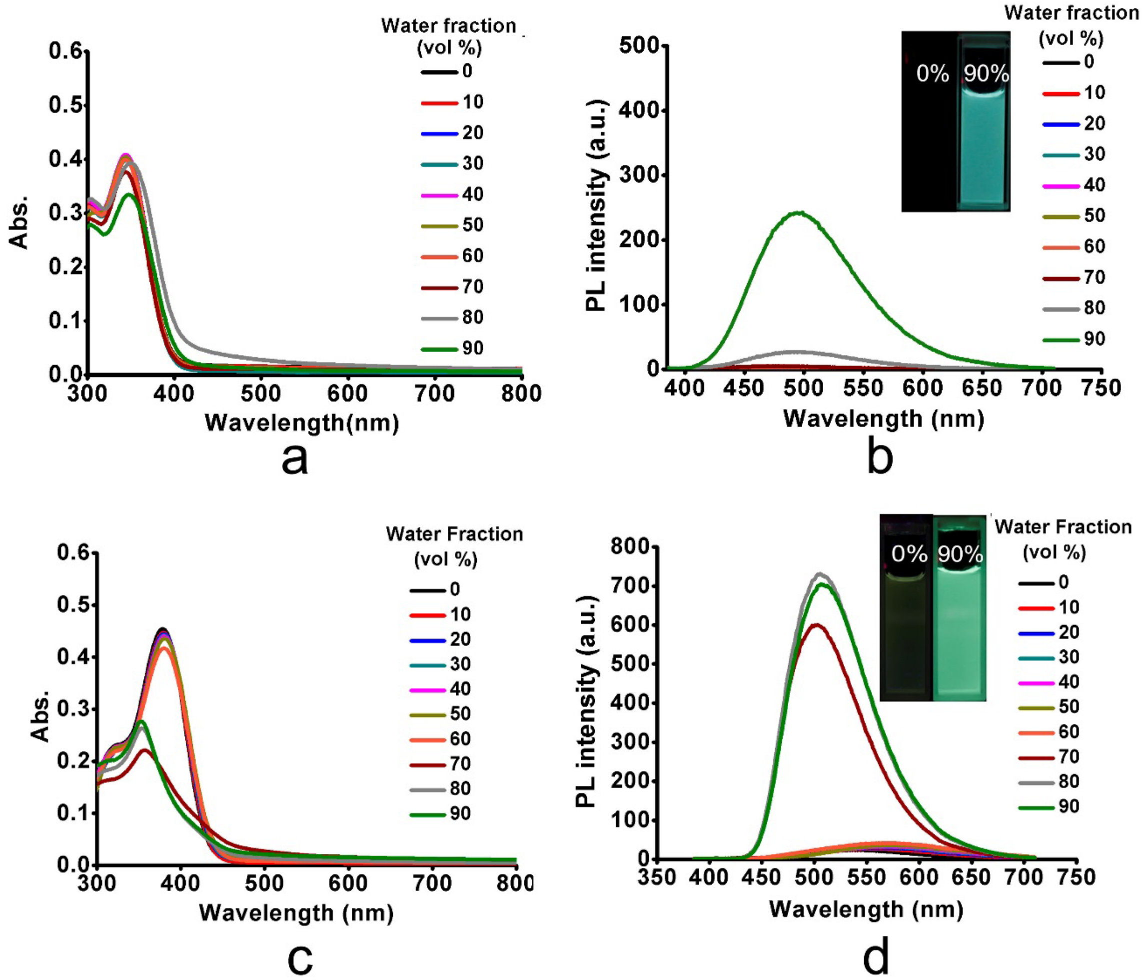


Figure S6. (a) Absorption spectra and (b) fluorescent spectra of **TPE-VI** (1×10^{-5} M) in THF and hexane mixtures with different hexane fractions (inset: real fluorescent images of **TPE-VI** with different hexane fractions). (c) Absorption spectra and (d) fluorescent spectra of **TPE-VBVI** (1×10^{-5} M) in THF and hexane mixtures with different hexane fractions (inset: real fluorescent images of **TPE-VBVI** with different hexane fractions).

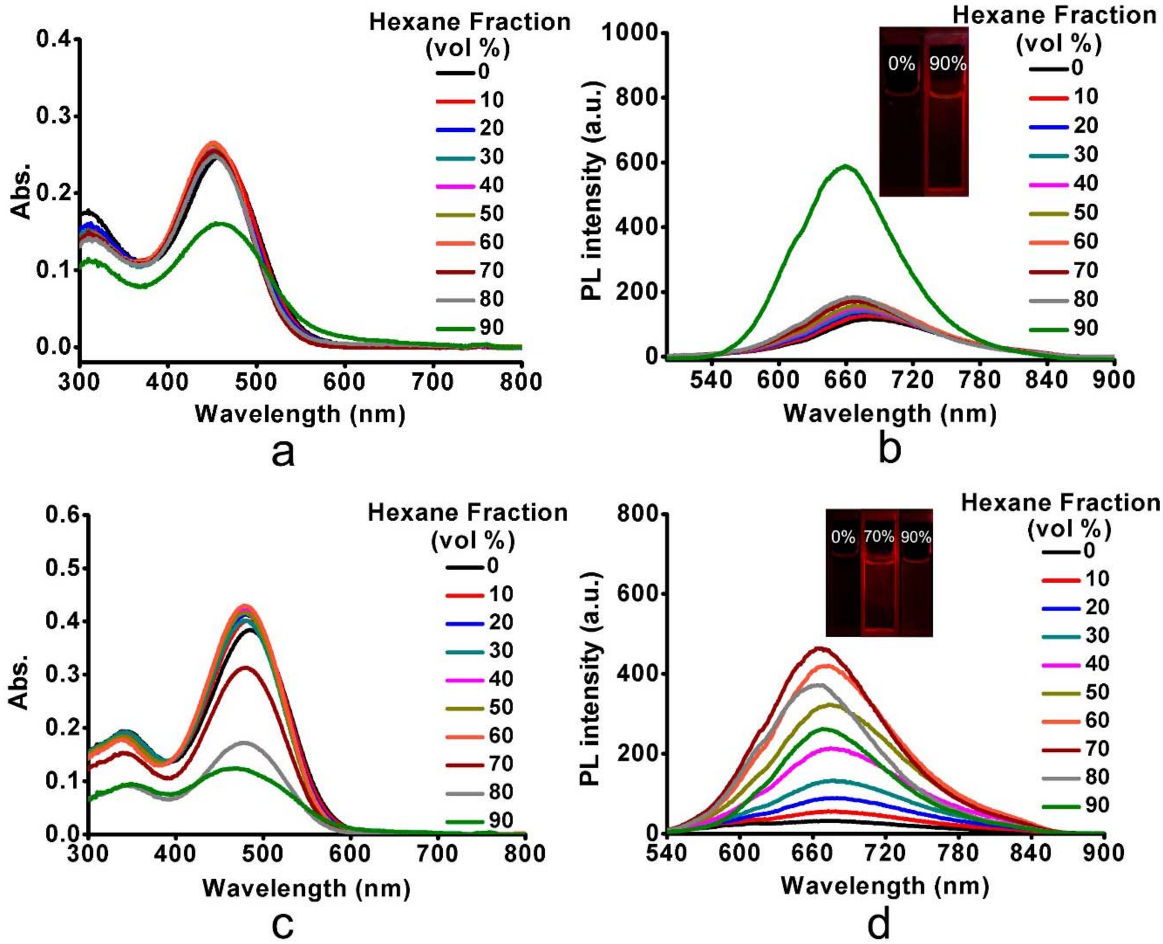


Figure S7. (a) Absorption spectra and (b) fluorescent spectra of **TPE-VBN** (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of **TPE-VBN** with different water fractions). (c) Absorption spectra and (d) fluorescent spectra of **TPE-VBVBN** (1×10^{-5} M) in THF and water mixtures with different water fractions (inset: real fluorescent images of **TPE-VBVBN** with different water fractions).

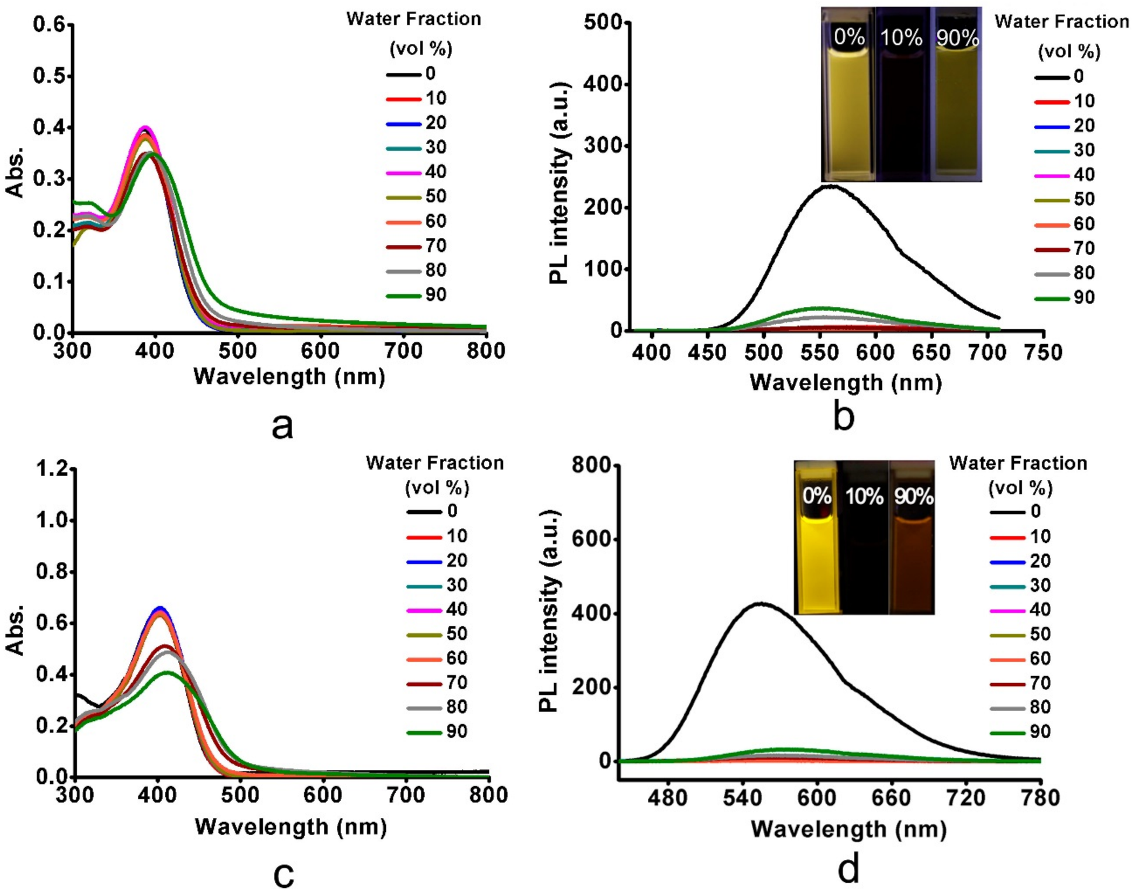


Figure S8. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra (λ_{Ex}=365 nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of **TPE-VBA** in different states.

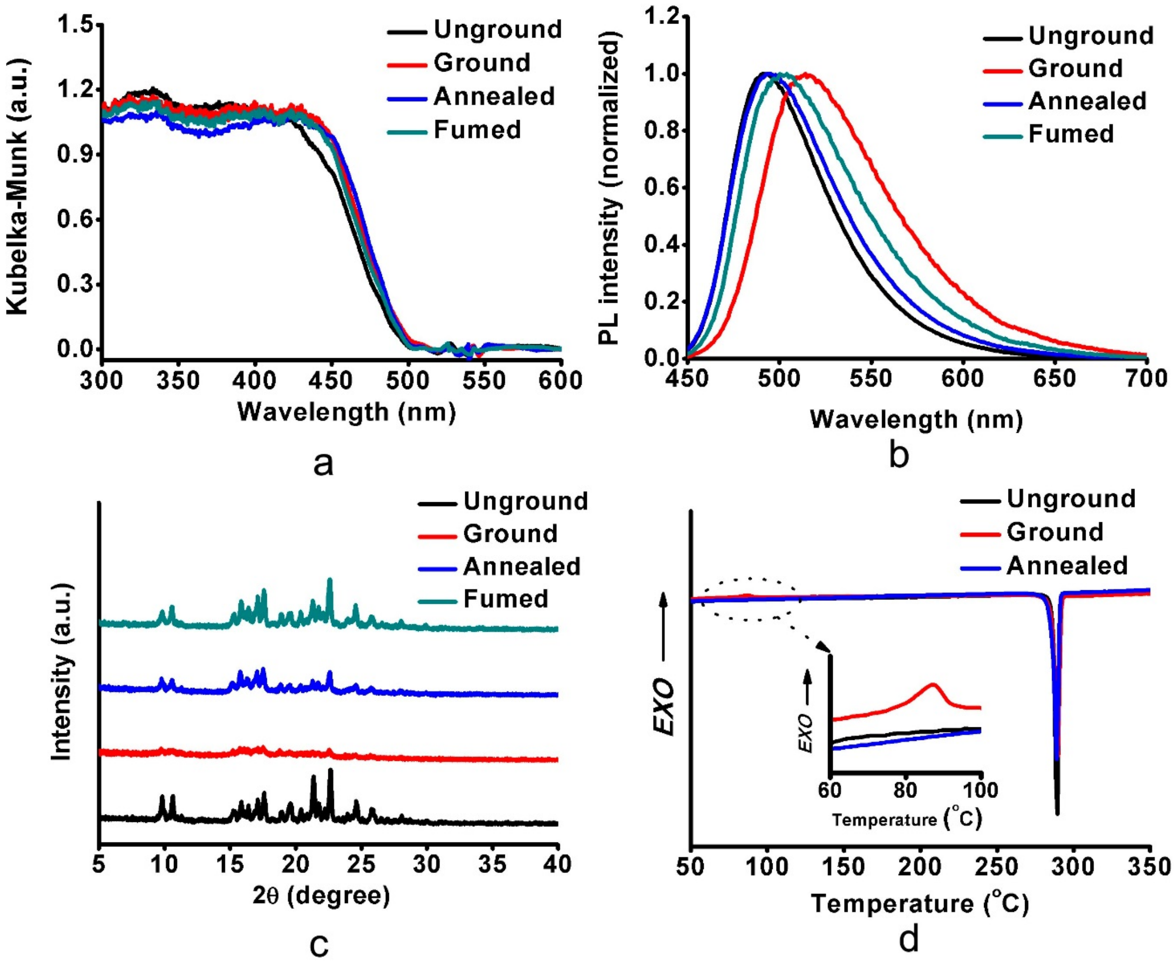


Figure S9. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra (λ_{Ex}=365 nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of **TPE-VBN** in different states.

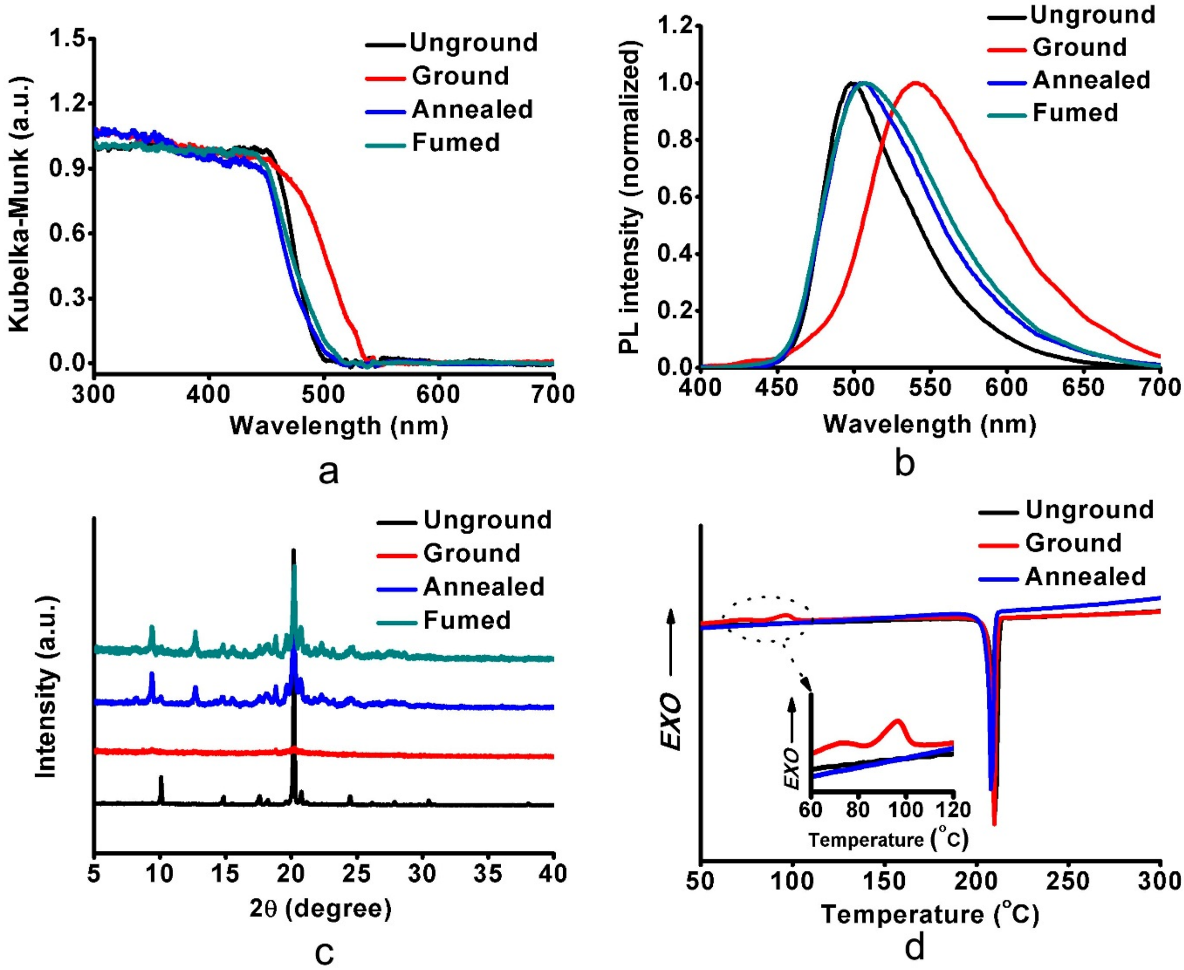


Figure S10. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra (λ_{Ex}=365 nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of **TPE-VBVBN** in different states.

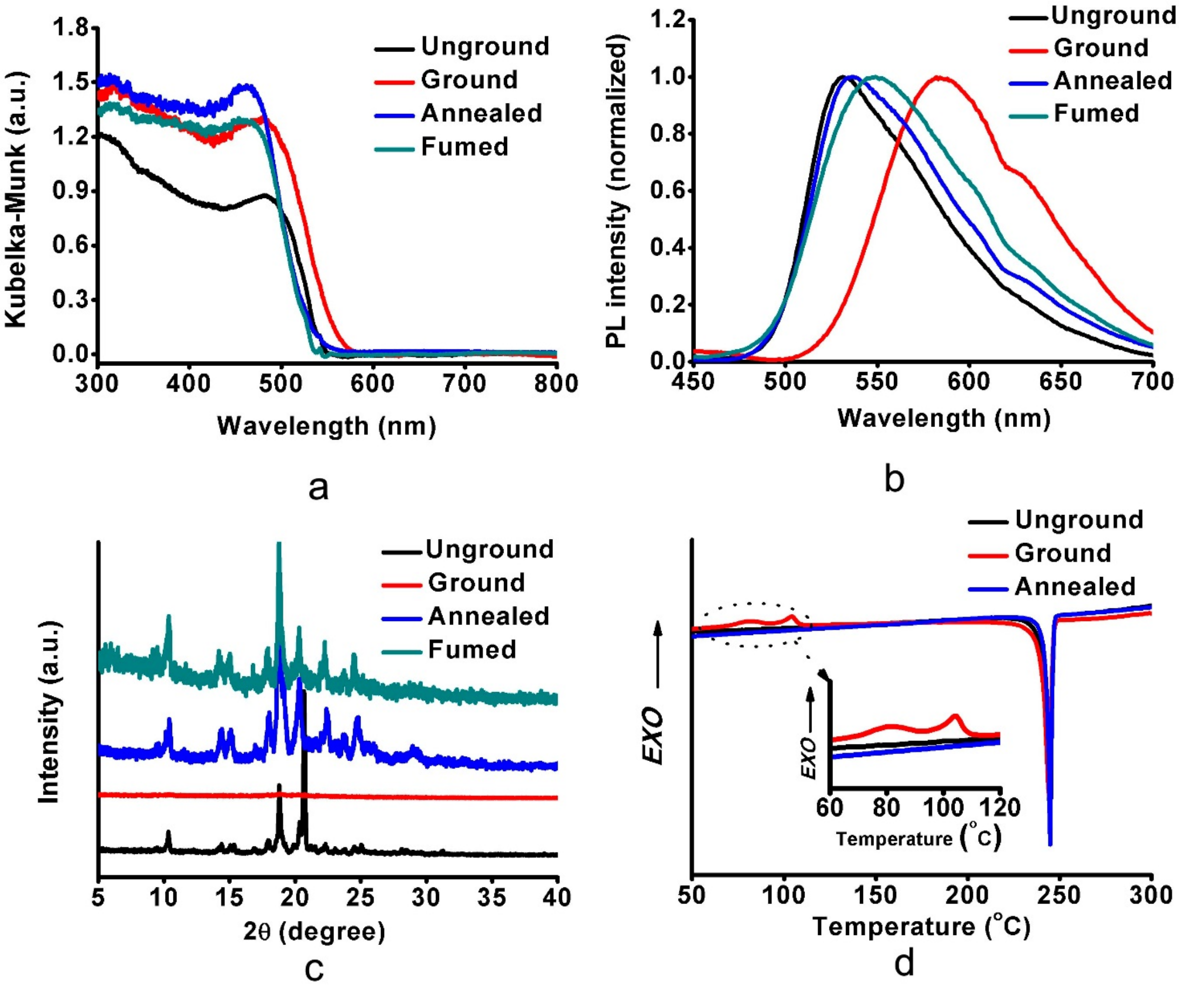


Figure S11. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra (λ_{Ex}=500 nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of **TPE-VI** in different states.

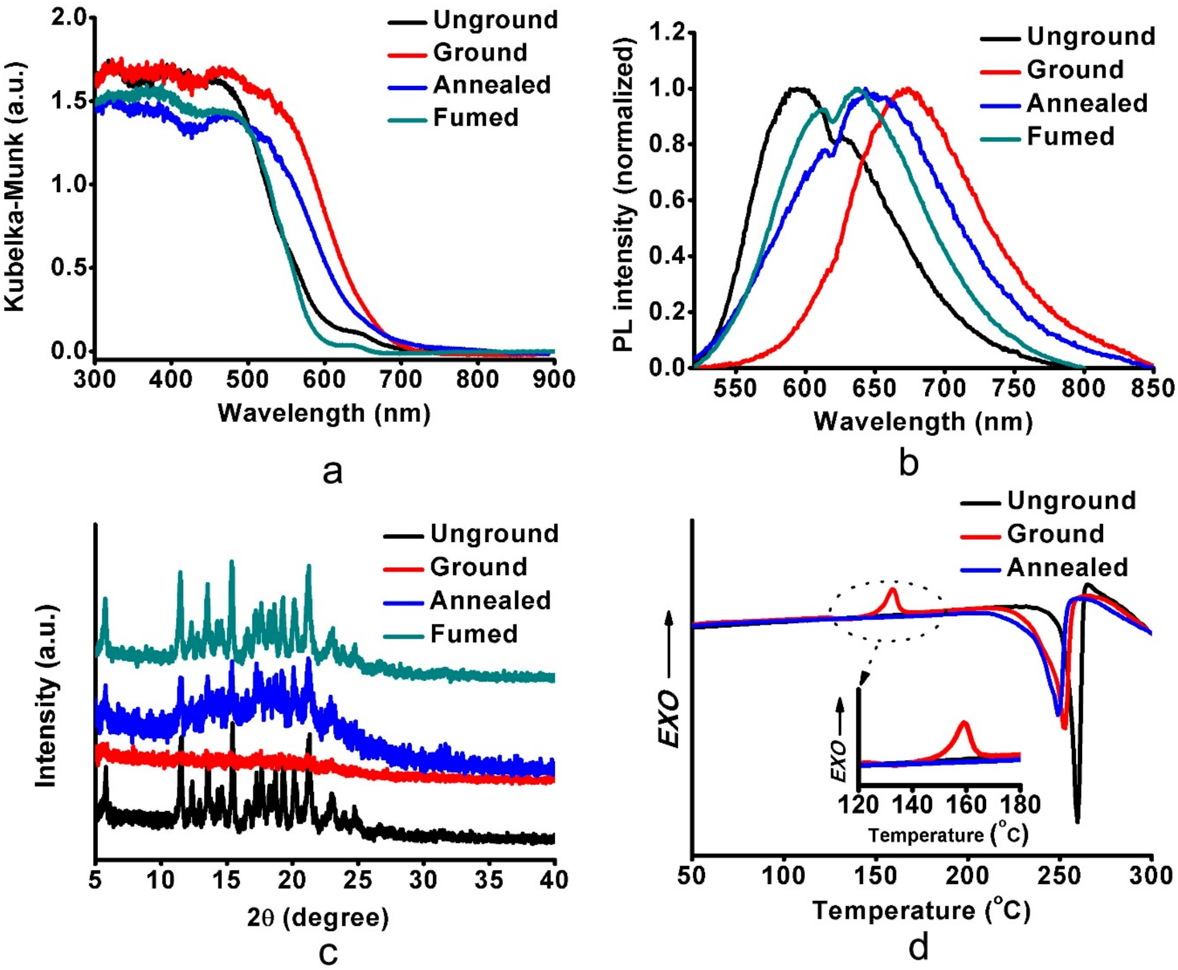


Figure S12. (a) Kubelka–Munk diffuse reflectance absorption spectra, (b) fluorescent spectra (λ_{Ex}=500 nm), (c) powder X-ray diffraction (PXRD) patterns and (d) DSC curves of **TPE-VBVI** in different states.

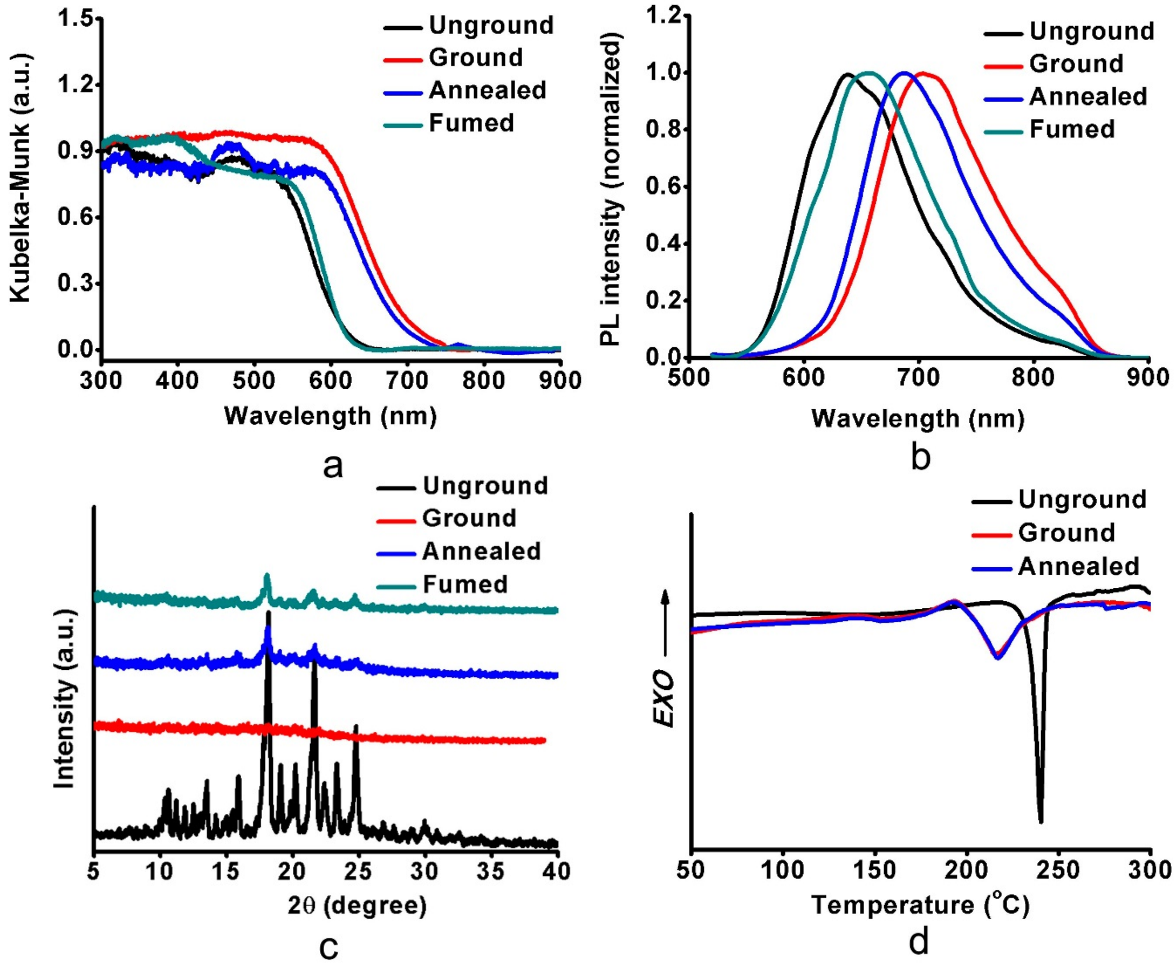


Figure S13. (a) Emission spectra of unground **TPE** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

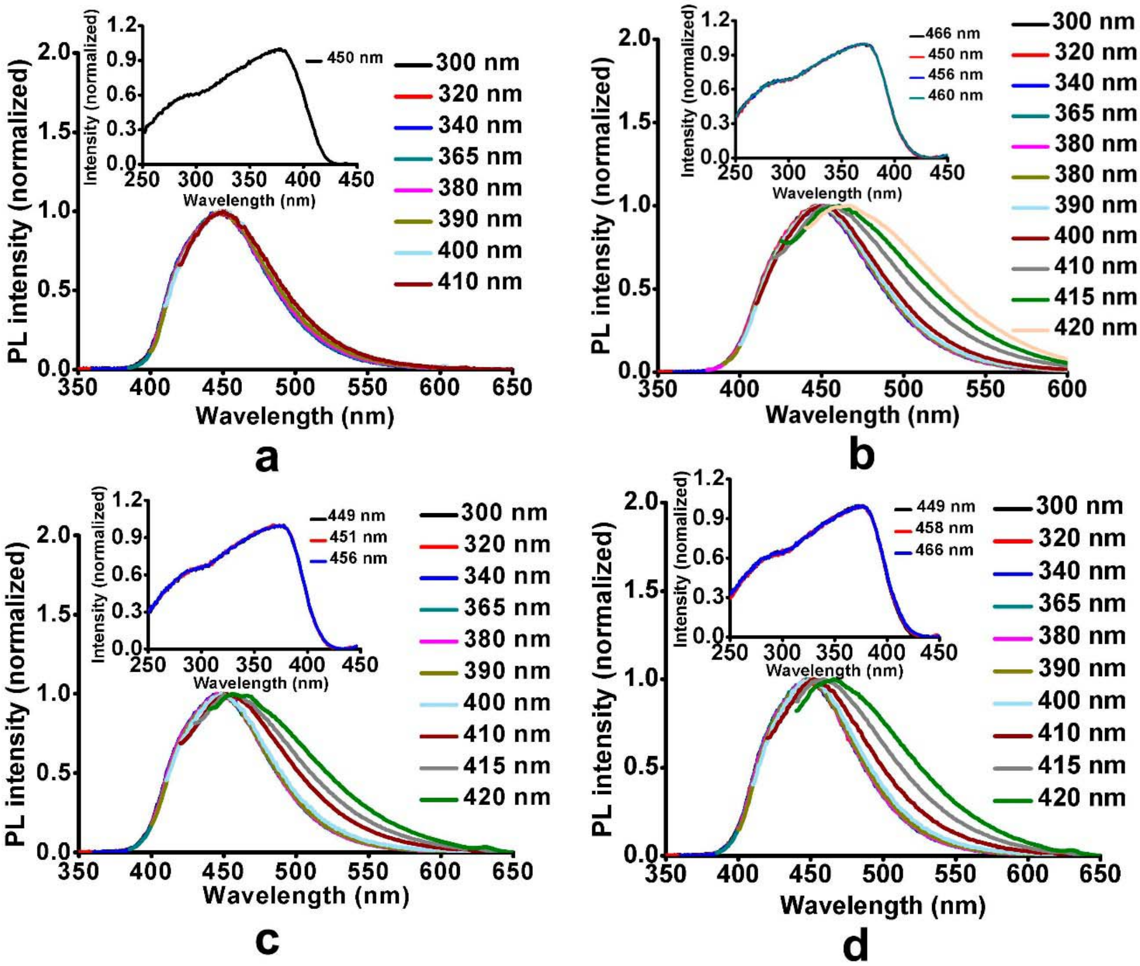


Figure S14. (a) Emission spectra of unground **TPE-Br** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-Br** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-Br** with different excitation lights (inset: the corresponding excitation spectrum). (d) Emission spectra of fumed **TPE-Br** with different excitation lights (inset: the corresponding excitation spectrum).

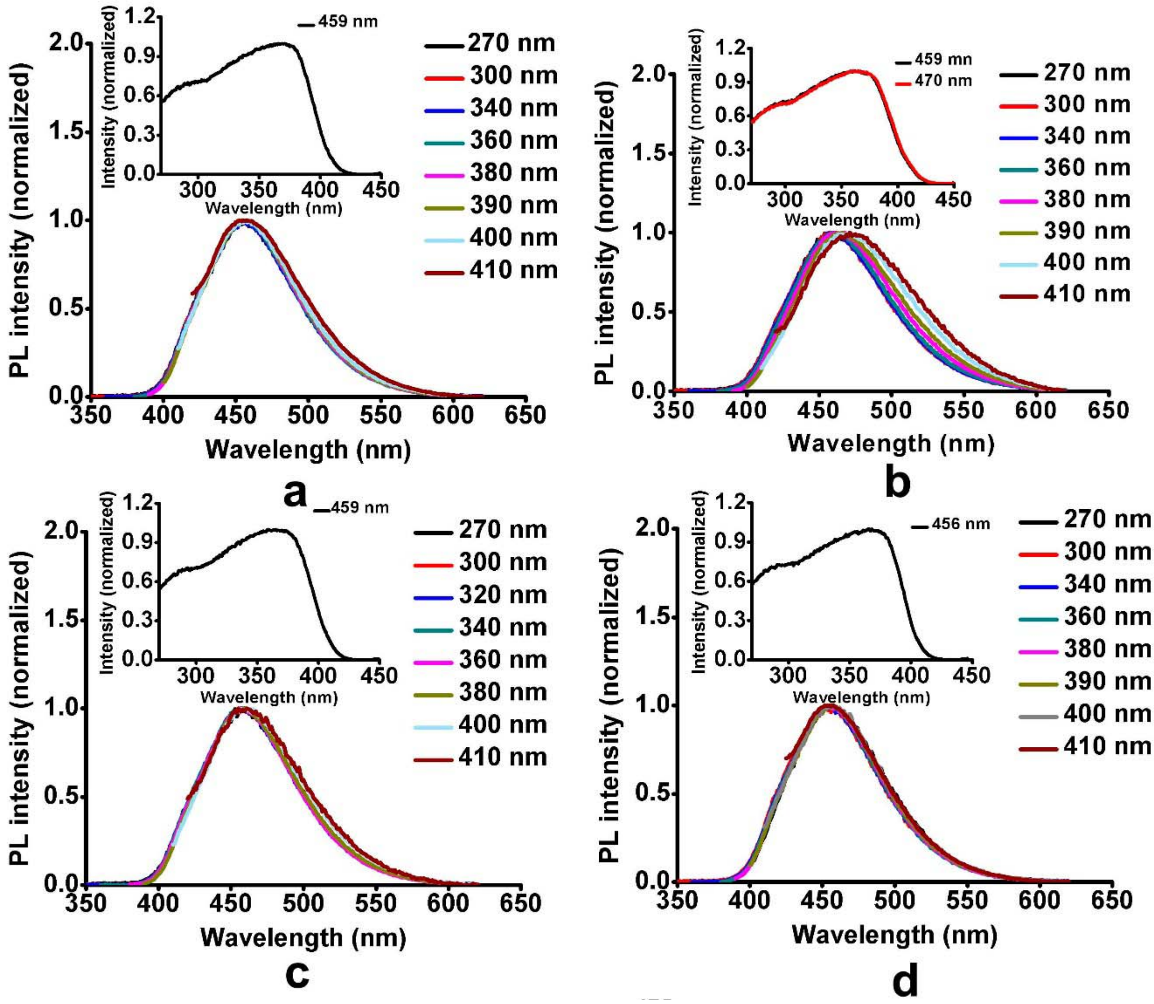


Figure S15. (a) Emission spectra of unground **TPE-CH$_3$** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (b) Emission spectra of ground **TPE-CH$_3$** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-CH$_3$** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-CH$_3$** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

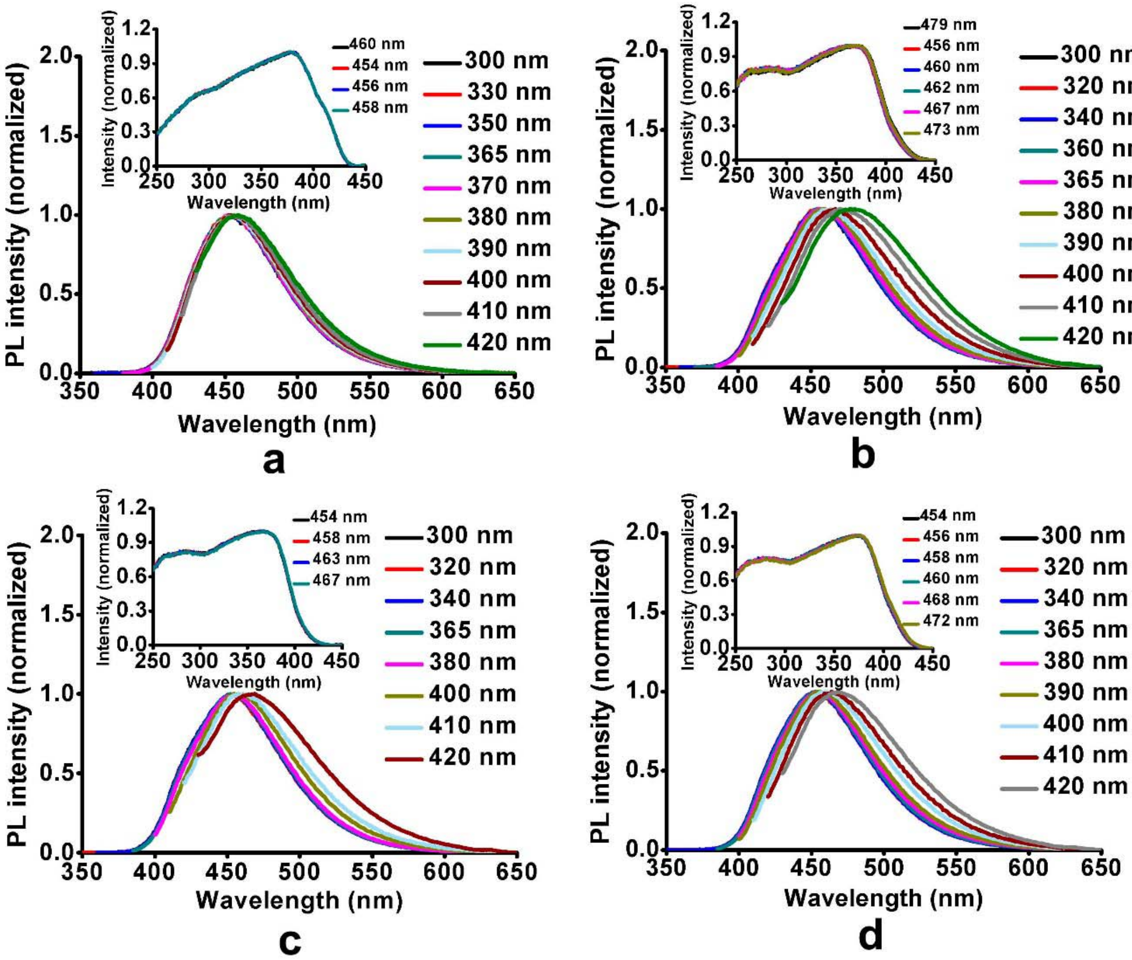


Figure S16. (a) Emission spectra of unground **TPE-OCH$_3$** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-OCH$_3$** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-OCH$_3$** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-OCH$_3$** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

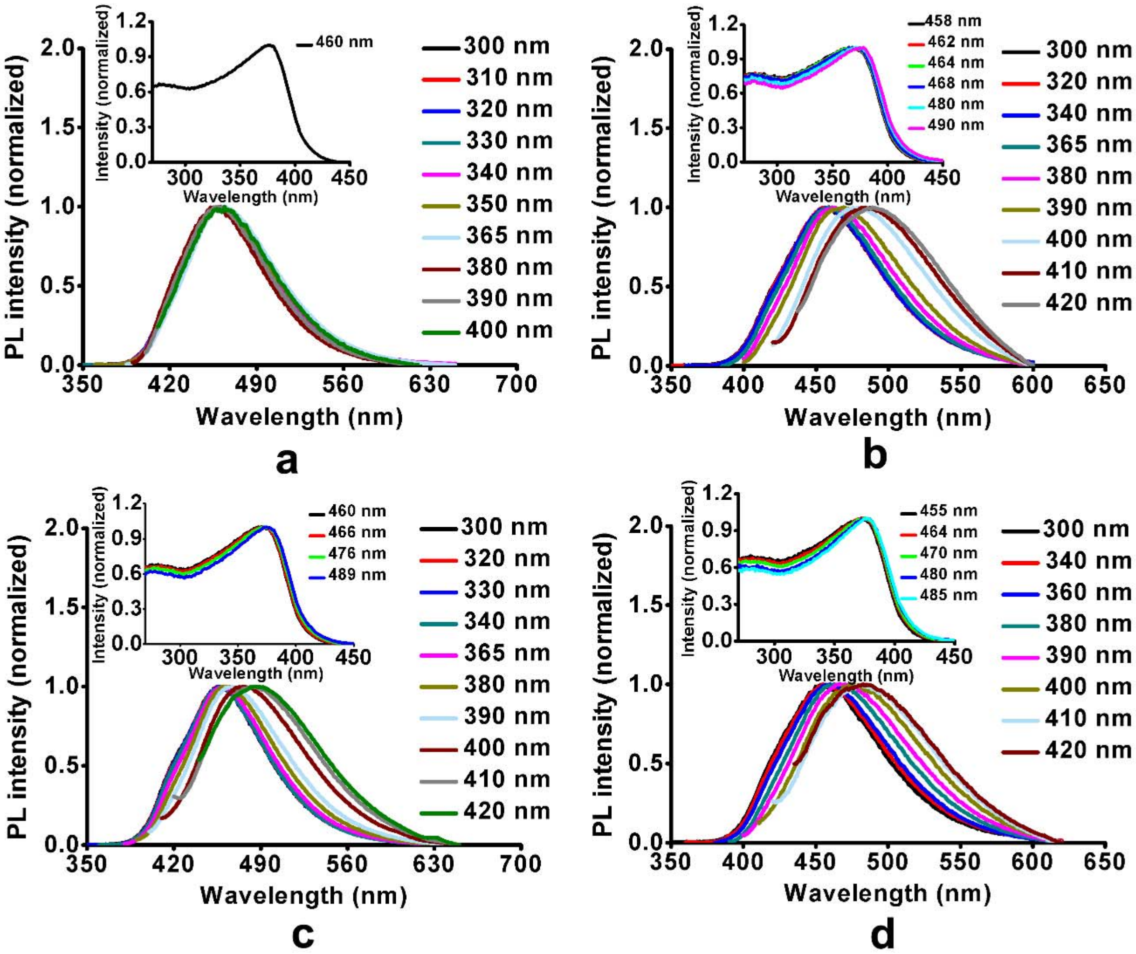


Figure S17. (a) Emission spectra of unground **TPE-Phen** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-Phen** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-Phen** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-Phen** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

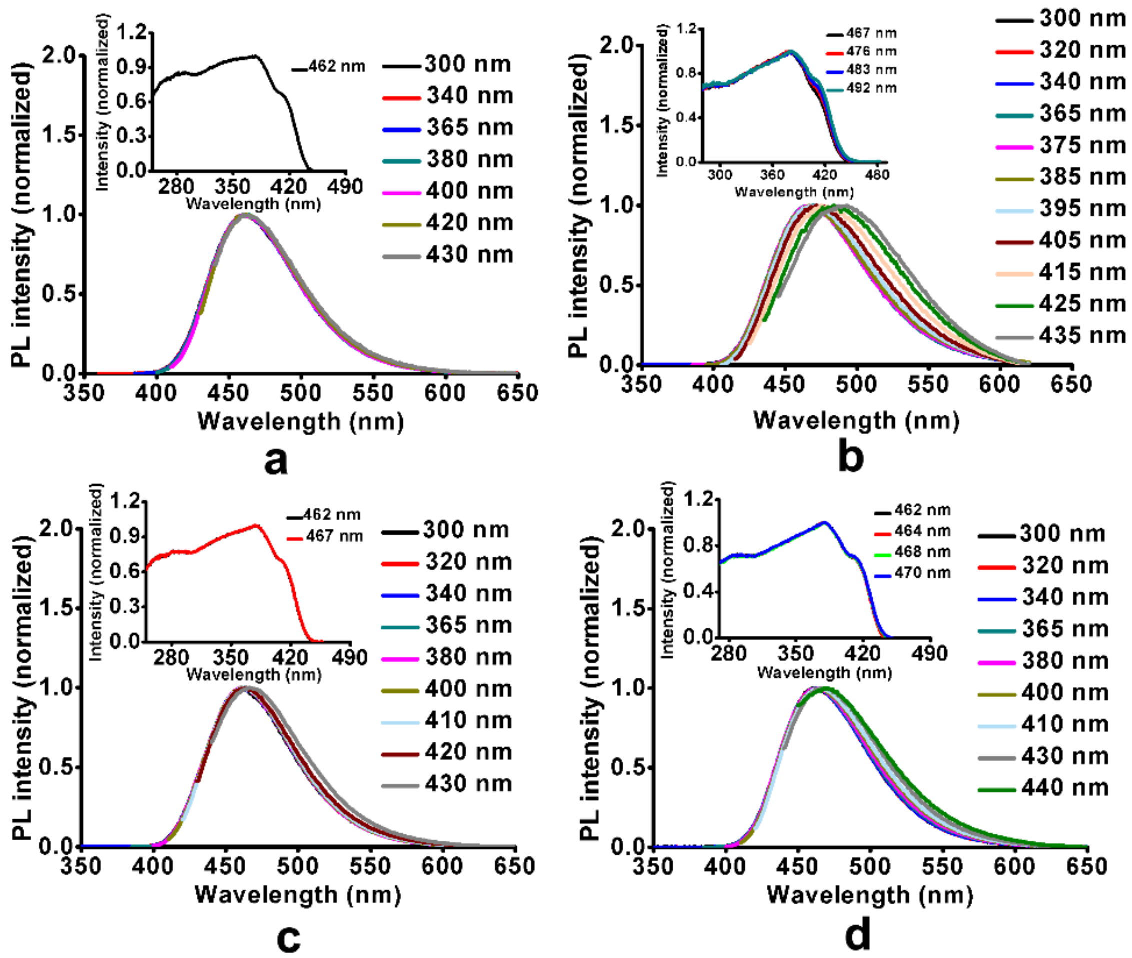


Figure S18. (a) Emission spectra of unground **TPE-Diphen** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-Diphen** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-Diphen** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-Diphen** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

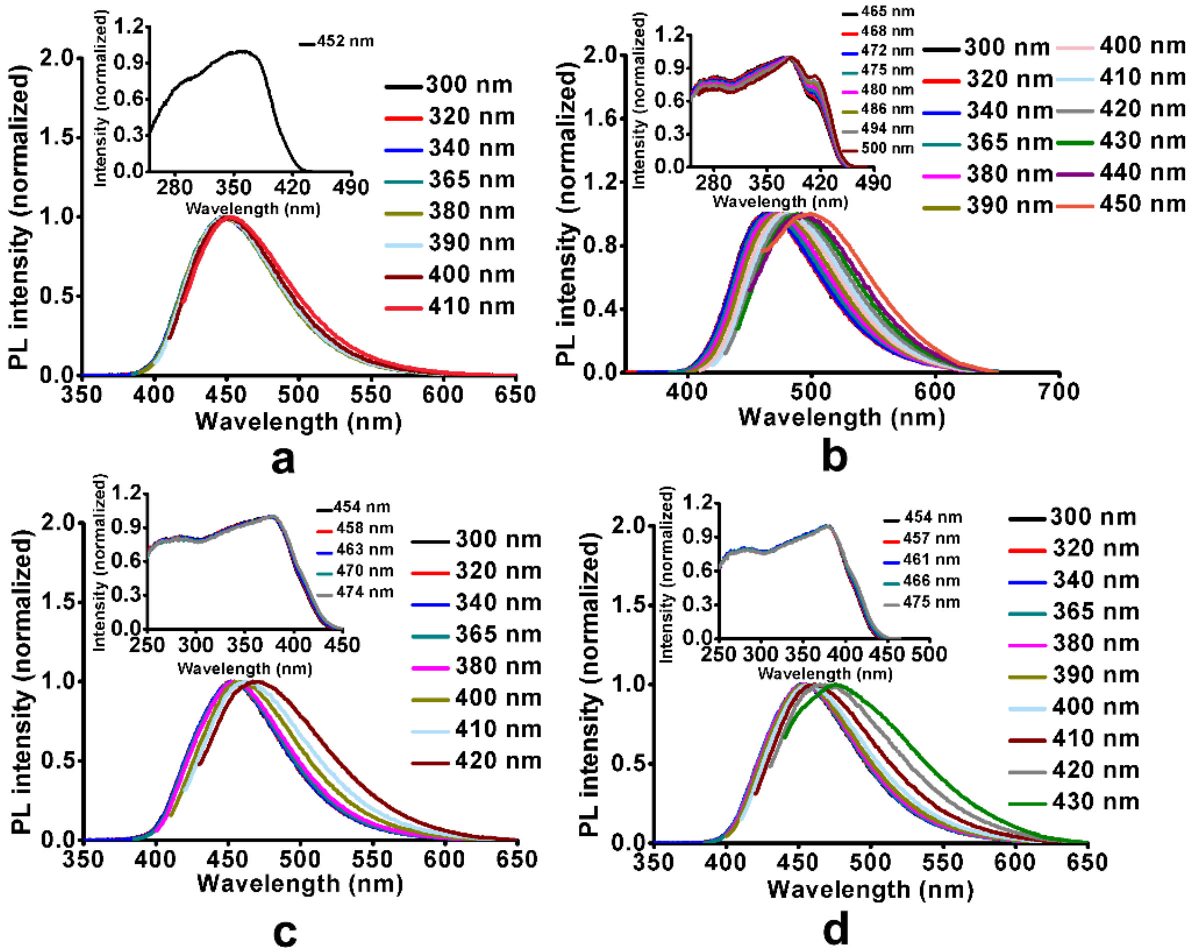


Figure S19. (a) Emission spectra of unground **TPE-VB** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-VB** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-VB** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-VB** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

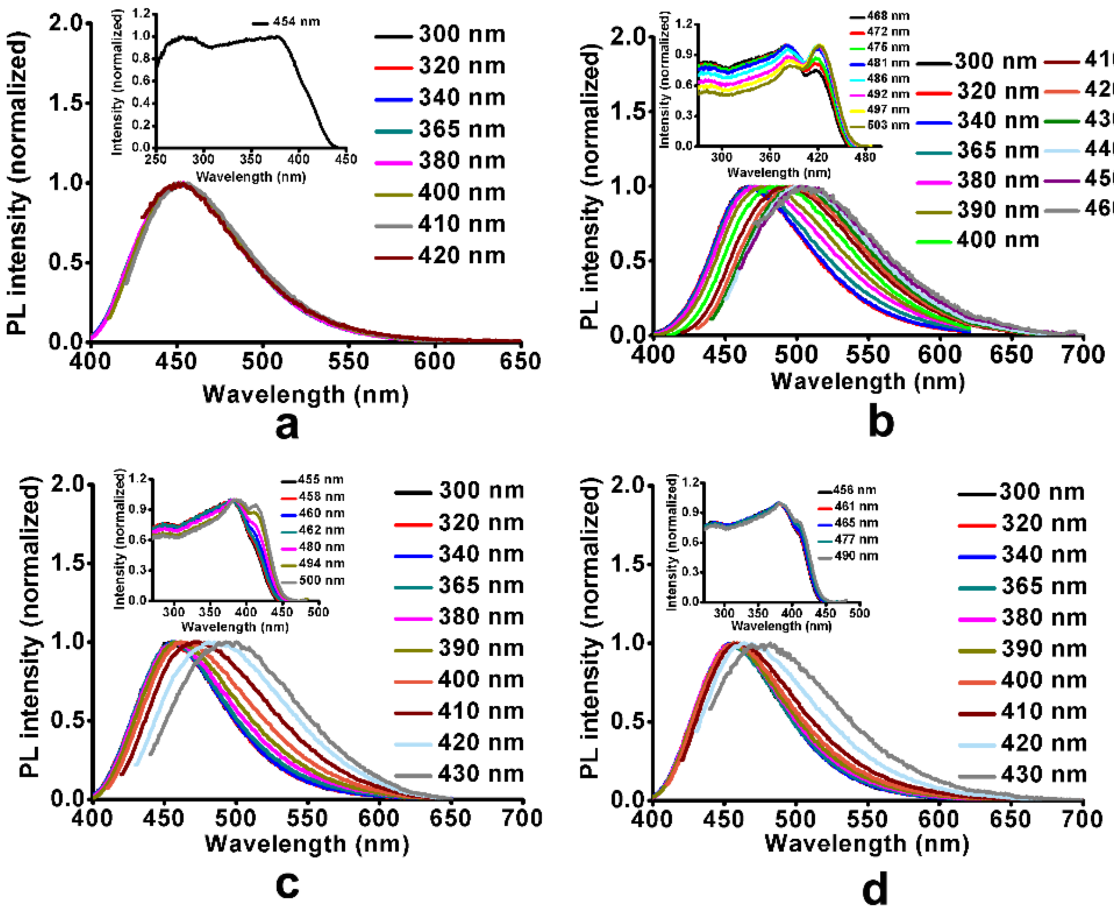


Figure S20. (a) Emission spectra of unground **TPE-VBA** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-VBA** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-VBA** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-VBA** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

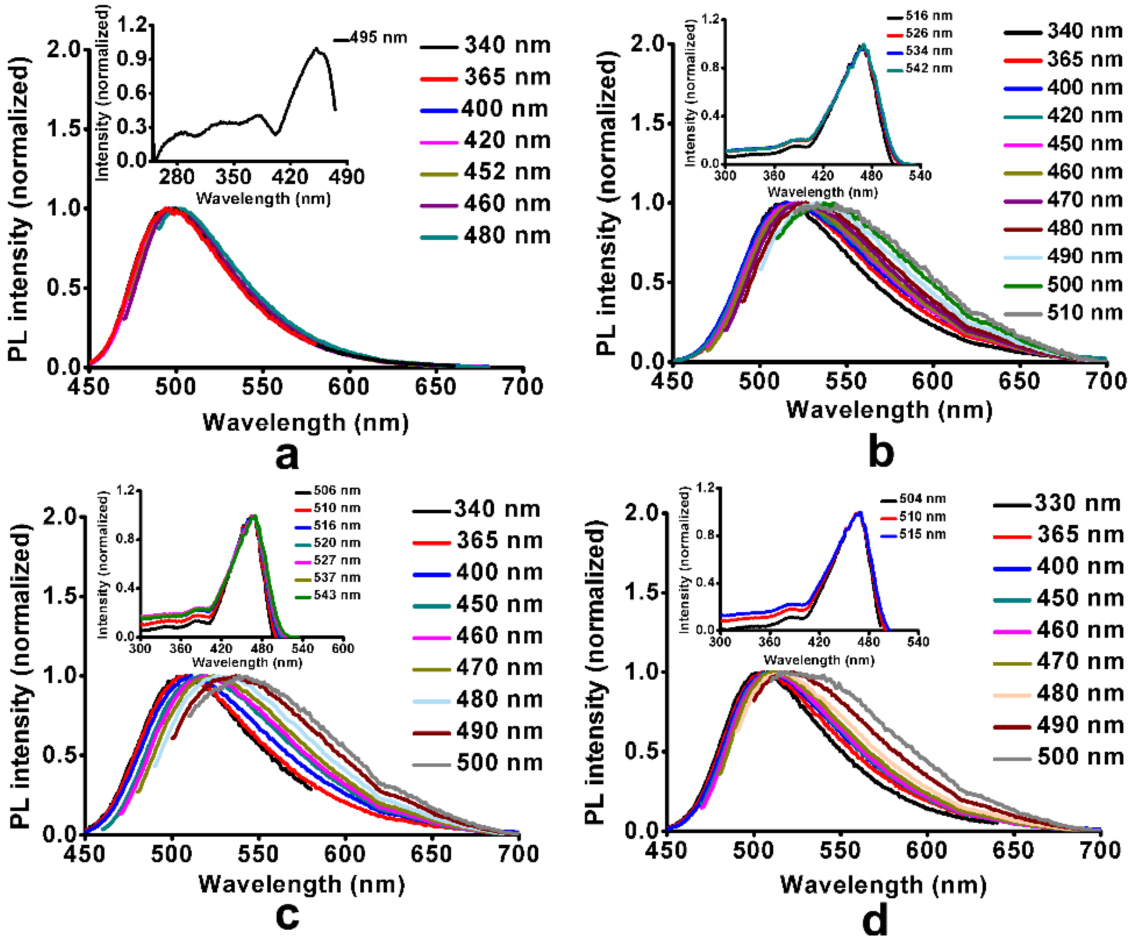


Figure S21. (a) Emission spectra of unground **TPE-VBN** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (b) Emission spectra of ground **TPE-VBN** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-VBN** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-VBN** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

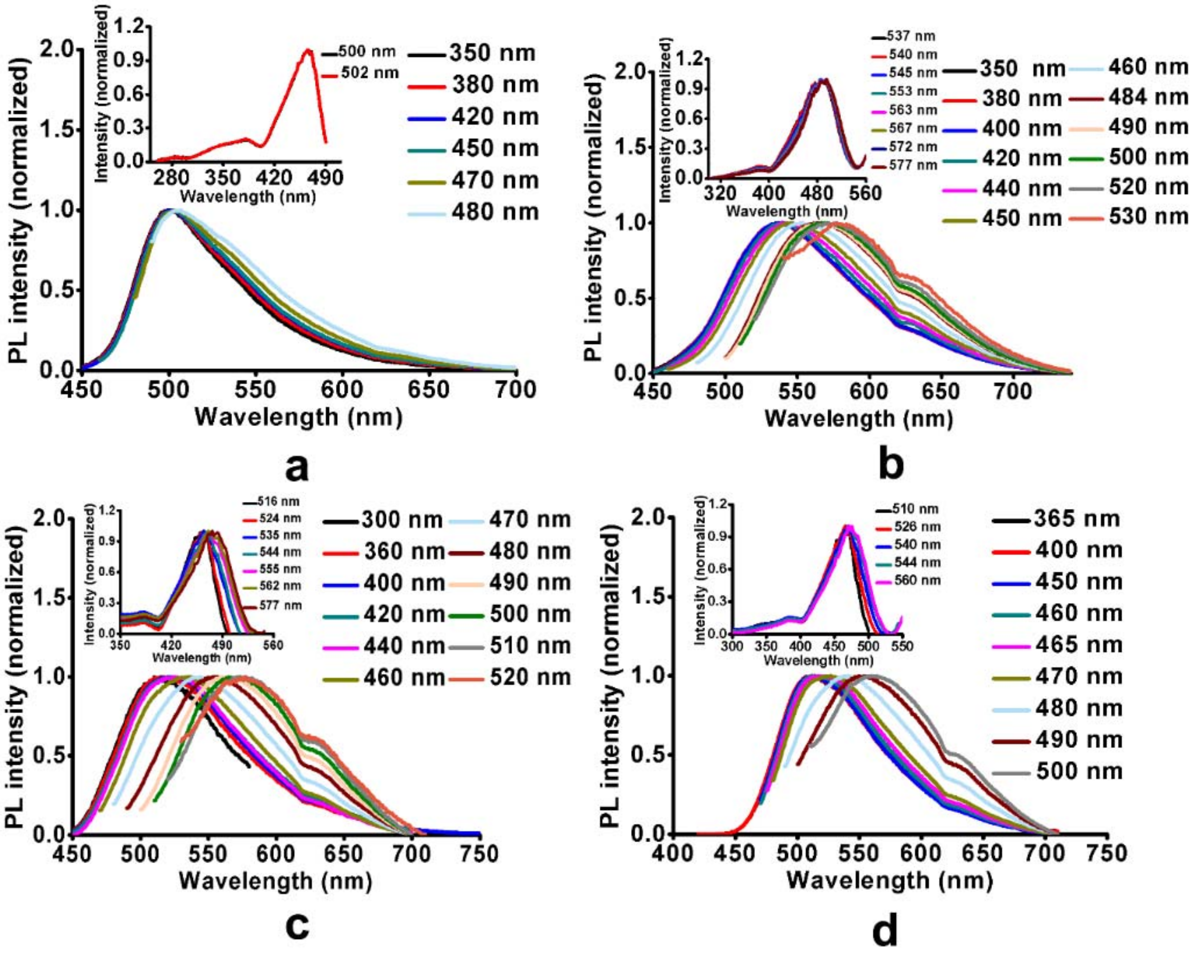


Figure S22. (a) Emission spectra of unground **TPE-VBVBN** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-VBVBN** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-VBVBN** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-VBVBN** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

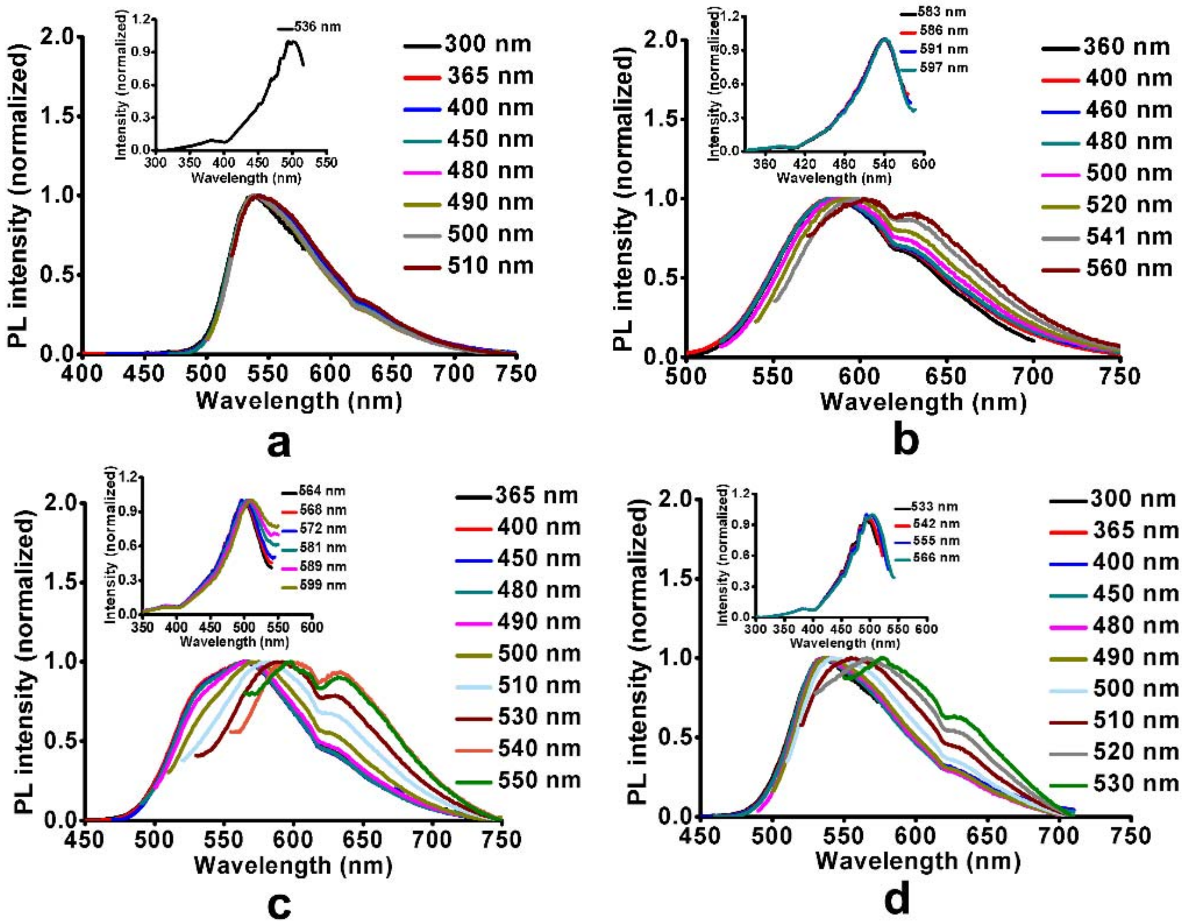


Figure S23. (a) Emission spectra of unground **TPE-VI** with different excitation lights (inset: the corresponding excitation spectrum). (b) Emission spectra of ground **TPE-VI** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-VI** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-VI** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

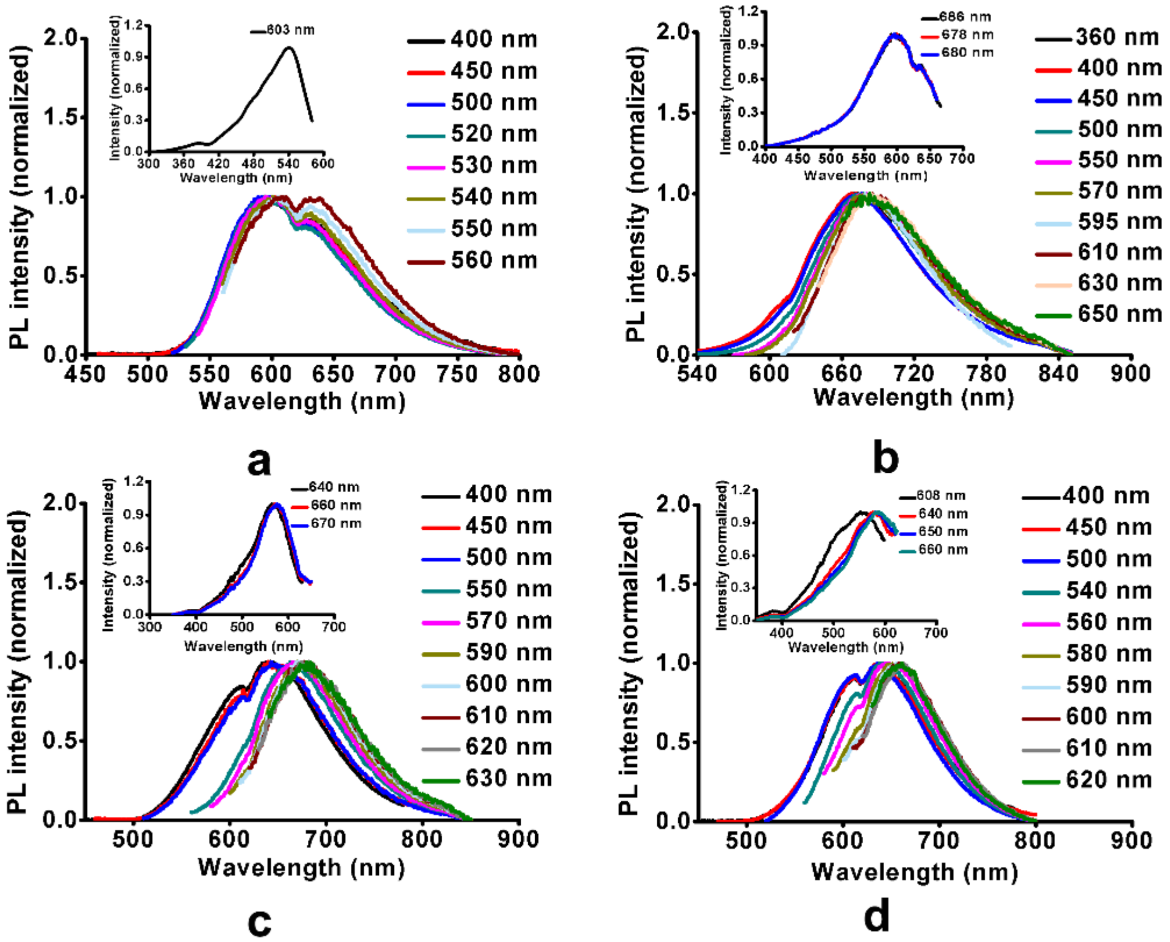


Figure S24. (a) Emission spectra of unground **TPE-VBVI** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (b) Emission spectra of ground **TPE-VBVI** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (c) Emission spectra of annealed **TPE-VBVI** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths). (d) Emission spectra of fumed **TPE-VBVI** with different excitation lights (inset: the corresponding excitation spectra with different emission wavelengths).

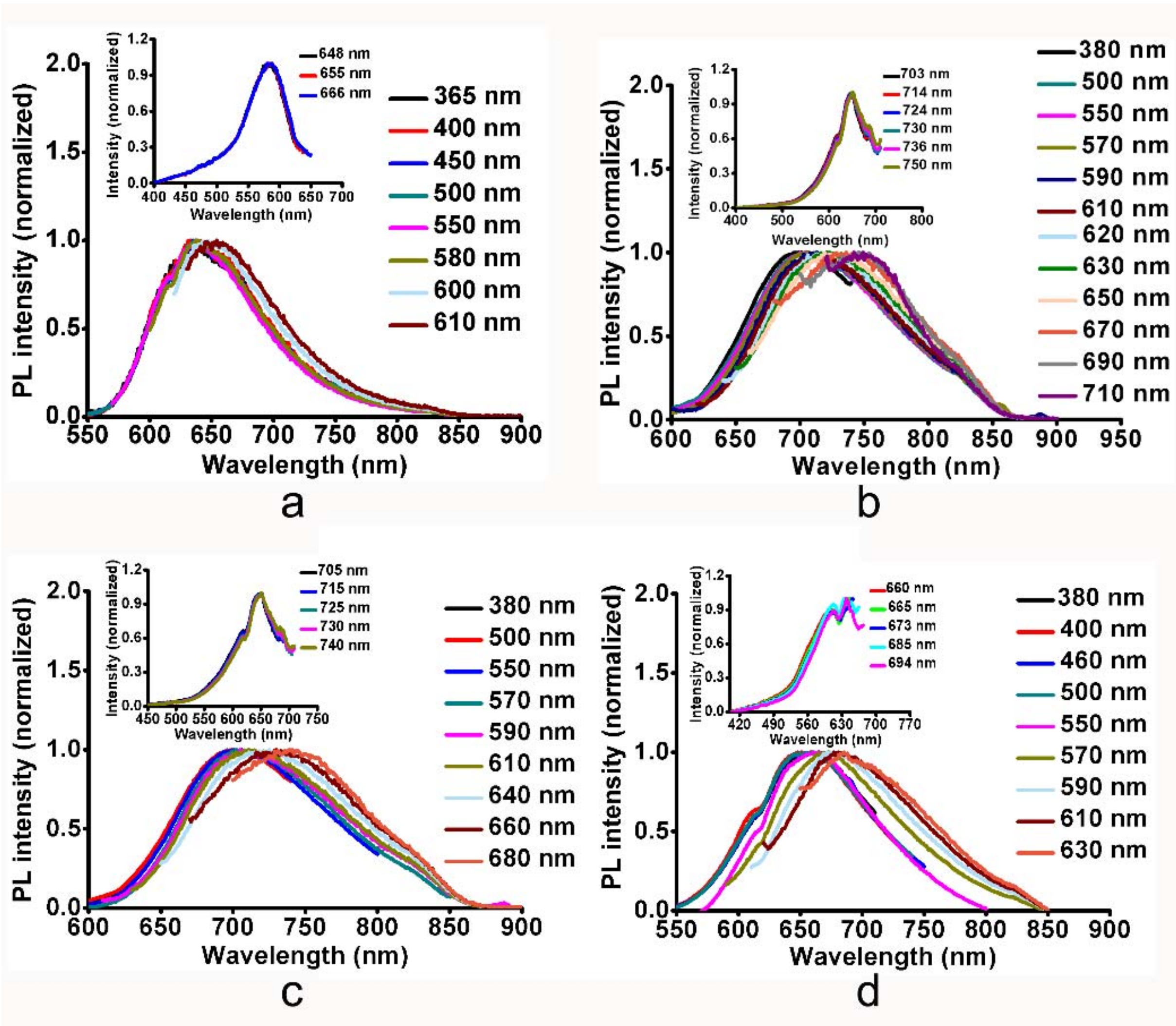


Figure S25. (a) Normalized emission spectra of **TPE-VB** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of **TPE-VB** in THF solution (1×10^{-5} M).

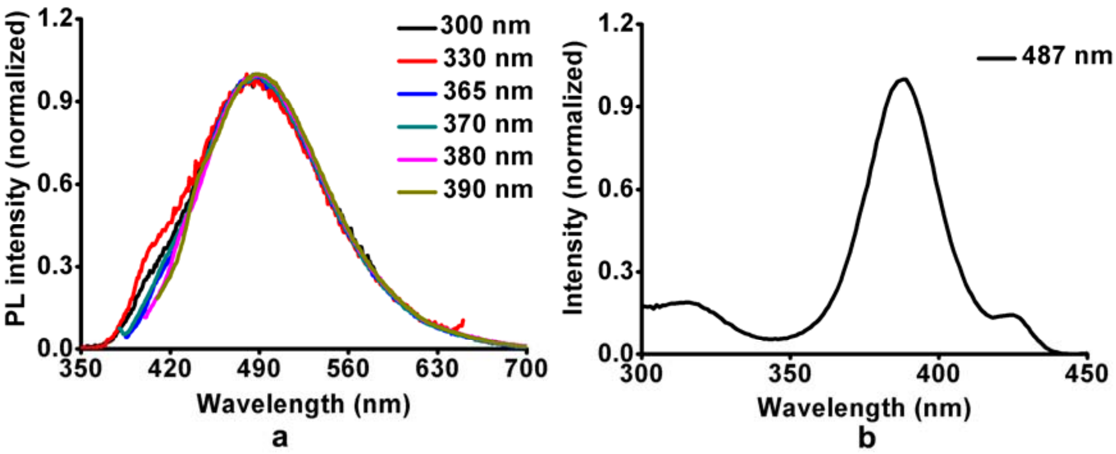


Figure S26. (a) Normalized emission spectra of **TPE-VBA** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of **TPE-VBA** in THF solution (1×10^{-5} M).

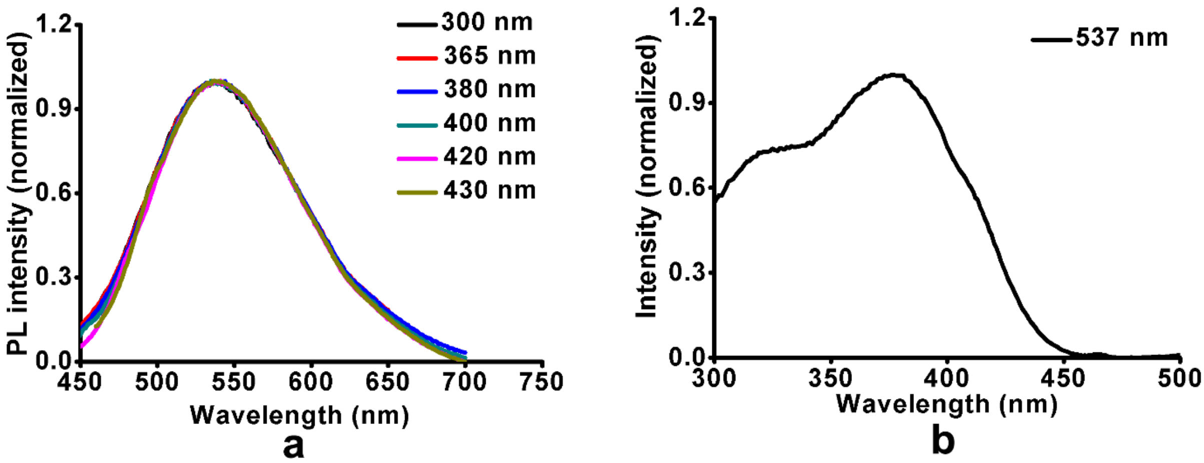


Figure S27. (a) Normalized emission spectra of **TPE-VBN** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of **TPE-VBN** in THF solution (1×10^{-5} M).

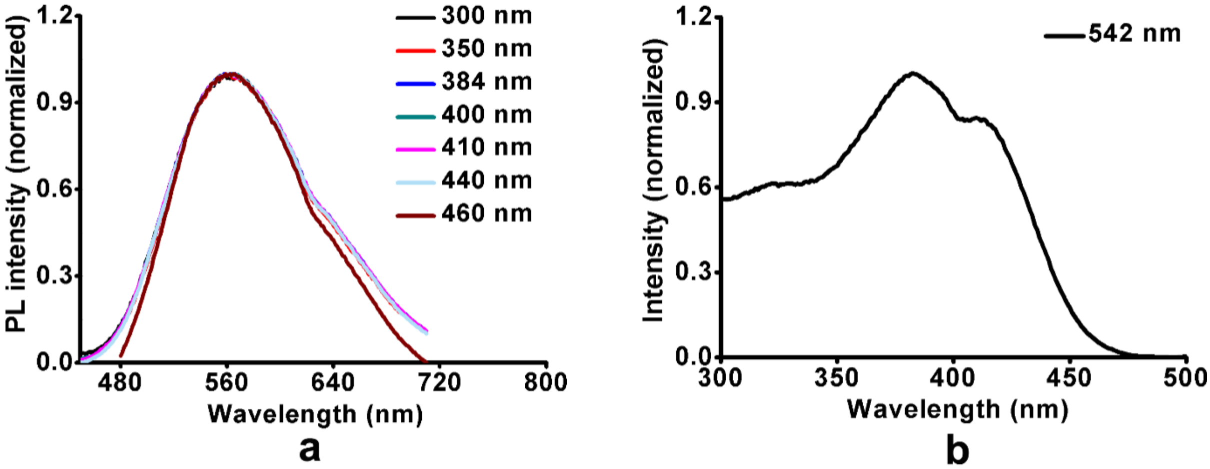


Figure S28. (a) Normalized emission spectra of **TPE-VBVBN** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of **TPE-VBVBN** in THF solution (1×10^{-5} M).

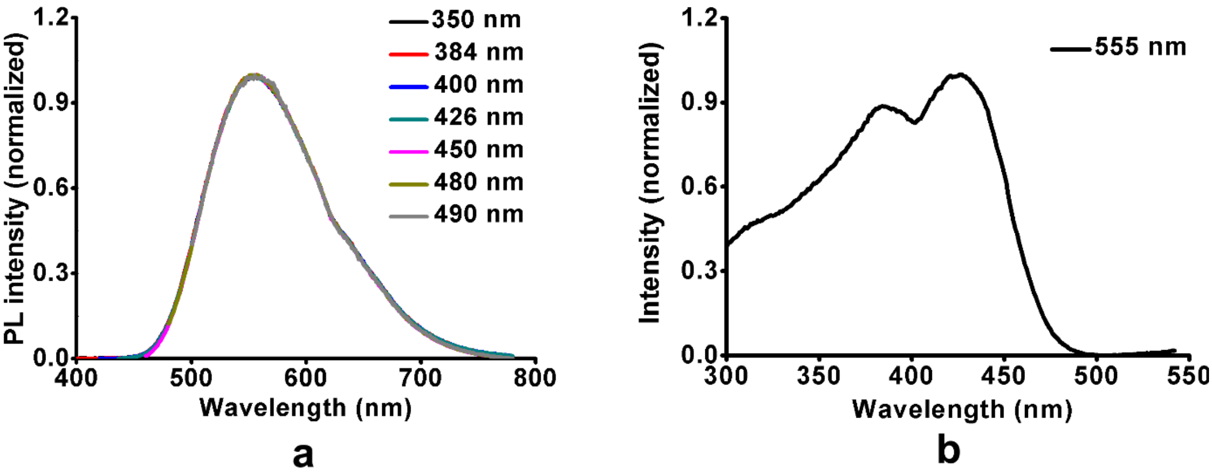


Figure S29. (a) Normalized emission spectra of **TPE-VI** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of **TPE-VI** in THF solution (1×10^{-5} M).

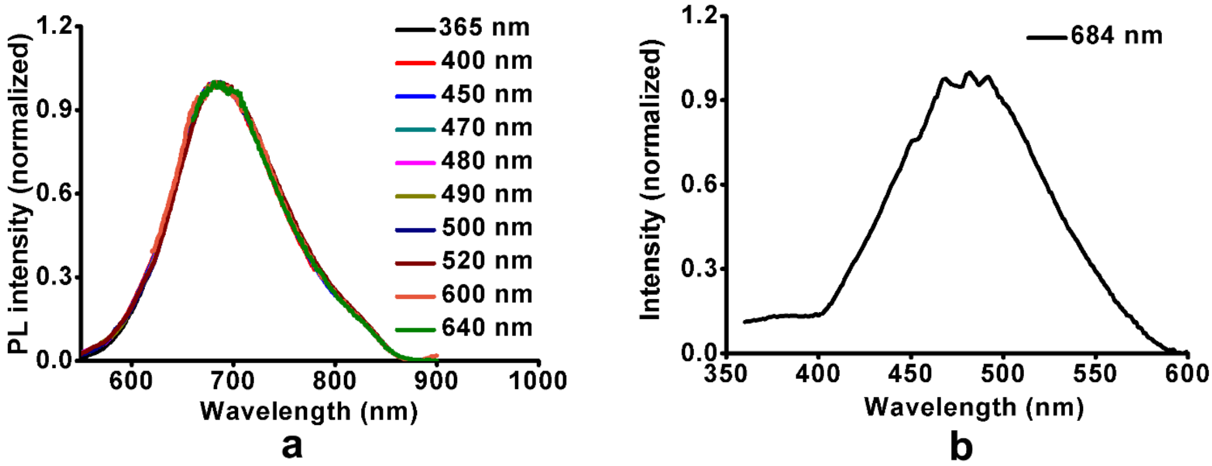


Figure S30. (a) Normalized emission spectra of **TPE-VBVI** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of **TPE-VBVI** in THF solution (1×10^{-5} M).

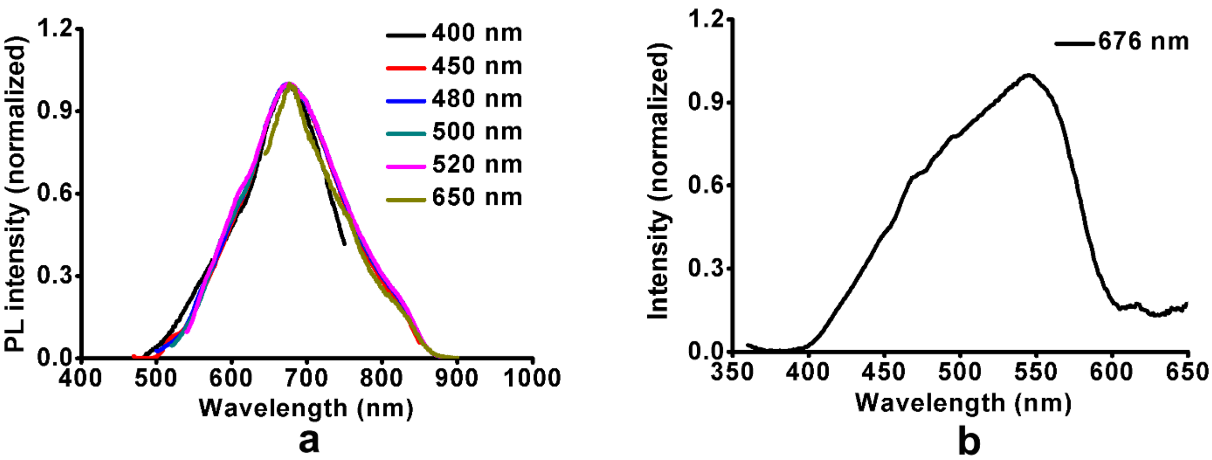


Figure S31. (a) Normalized emission spectra of **Rhodamine 6G** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectrum of **Rhodamine 6G** in THF solution (1×10^{-5} M).

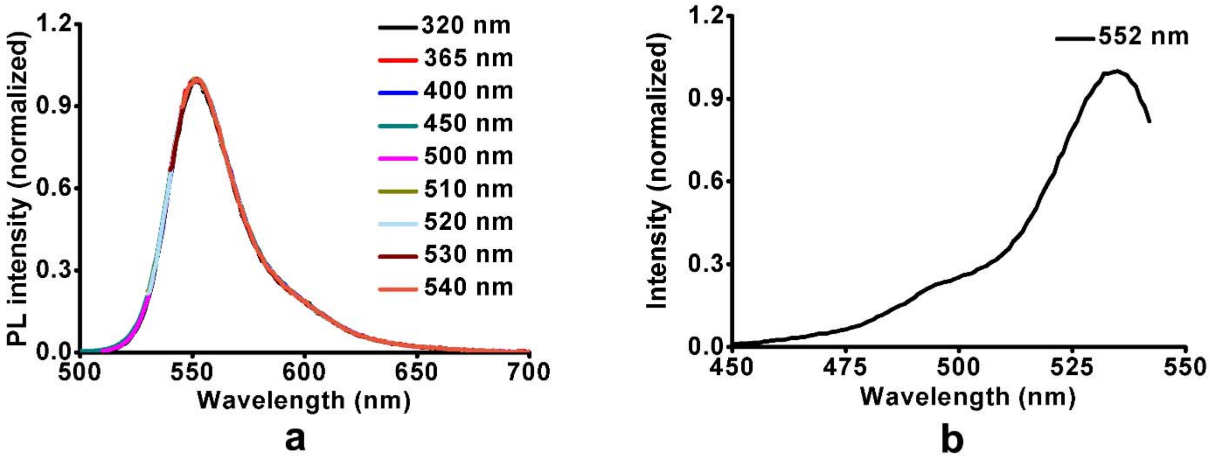


Figure S32. (a) Normalized emission spectra of **Anthracene** in THF solution (1×10^{-5} M) with different excitation lights. (b) Normalized excitation spectra of **Anthracene** in THF solution (1×10^{-5} M) with different emission wavelengths.

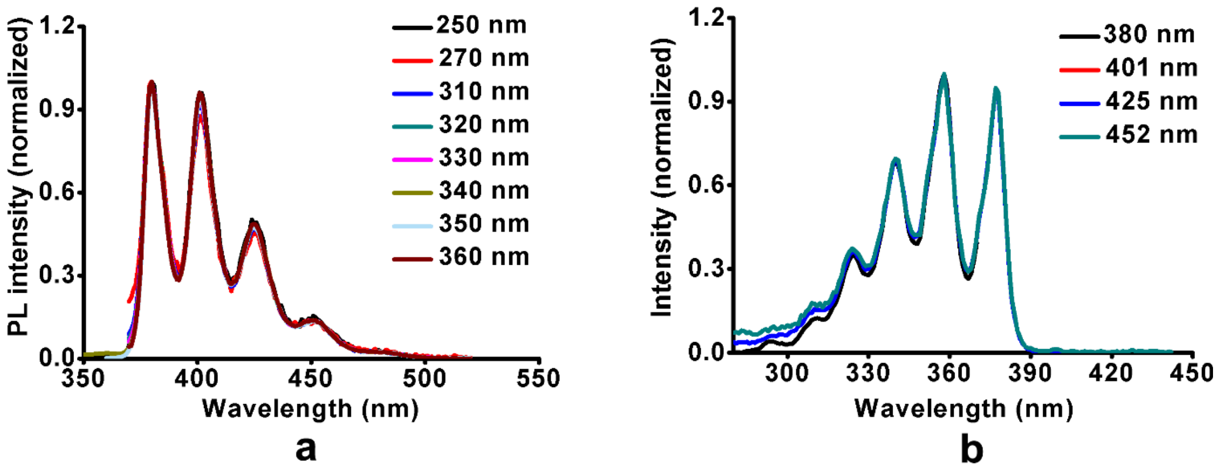


Figure S33. (a) Normalized emission spectra of **Rhodamine 6G** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **Rhodamine 6G** in PMMA film (ω%=1%) with different emission wavelengths.

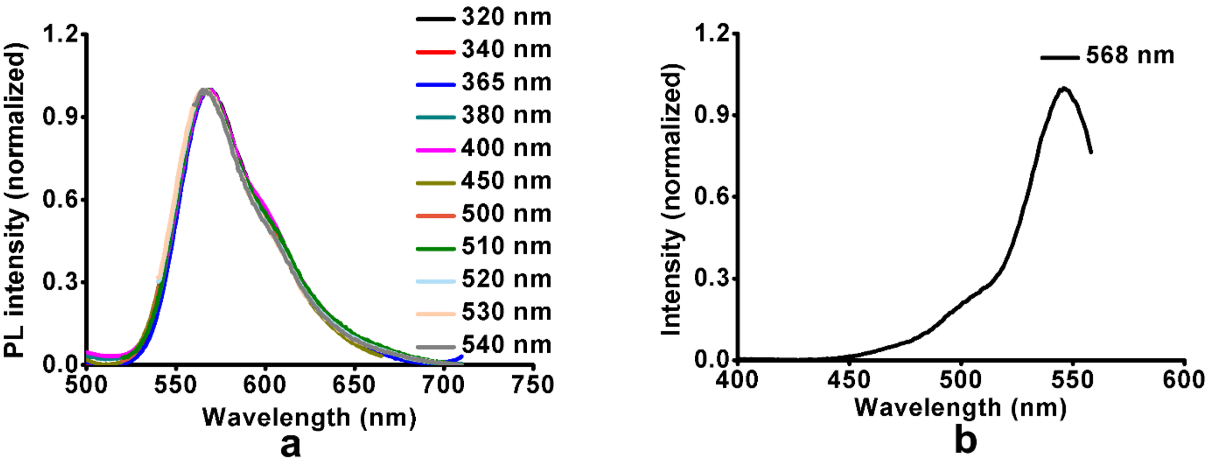


Figure S34. (a) Normalized emission spectra of **Anthracene** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **Anthracene** in PMMA film (ω%=1%) with different emission wavelengths.

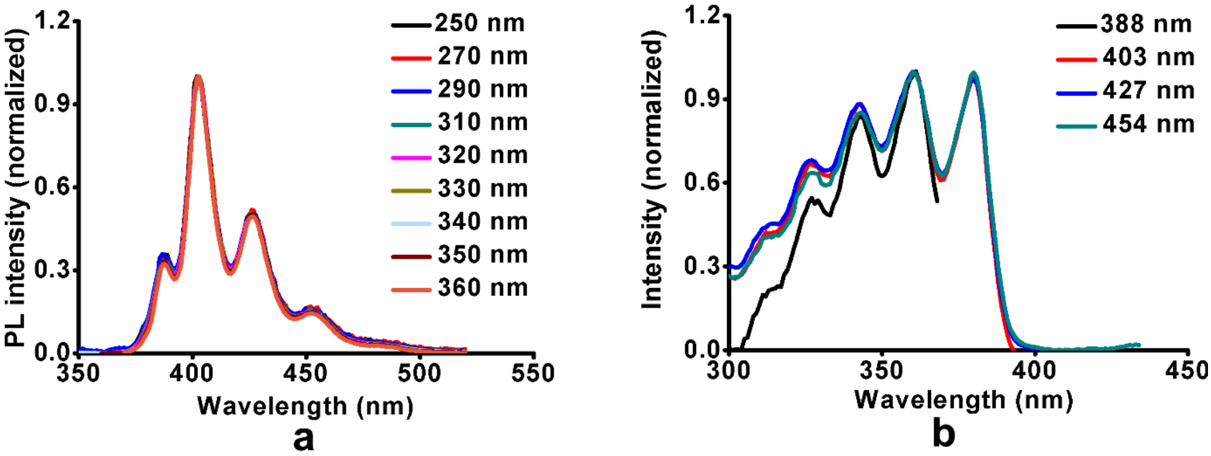


Figure S35. (a) Normalized emission spectra of **TPE** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE** in PMMA film (ω%=1%) with different emission wavelengths.

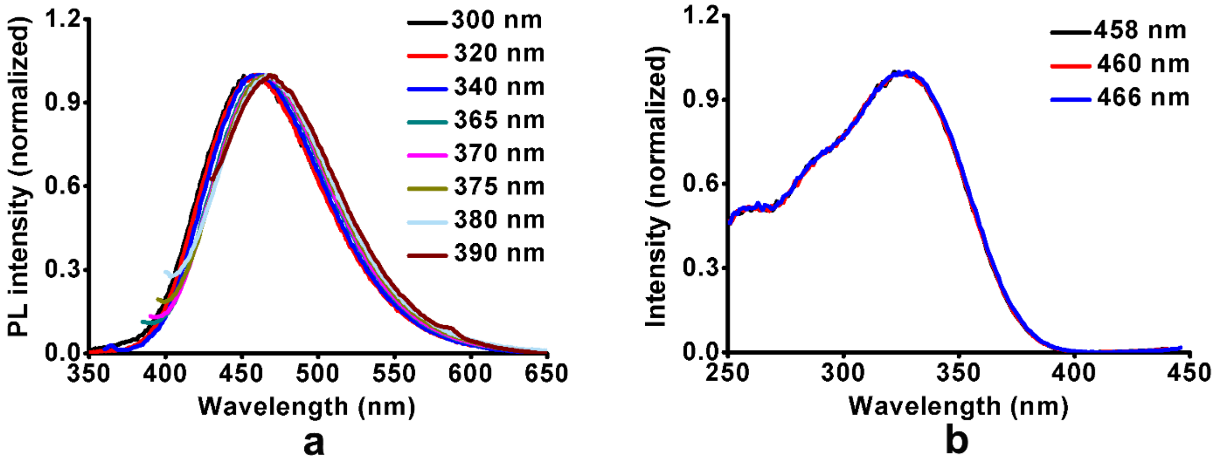


Figure S36. (a) Normalized emission spectra of **TPE-Br** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-Br** in PMMA film (ω%=1%) with different emission wavelengths.

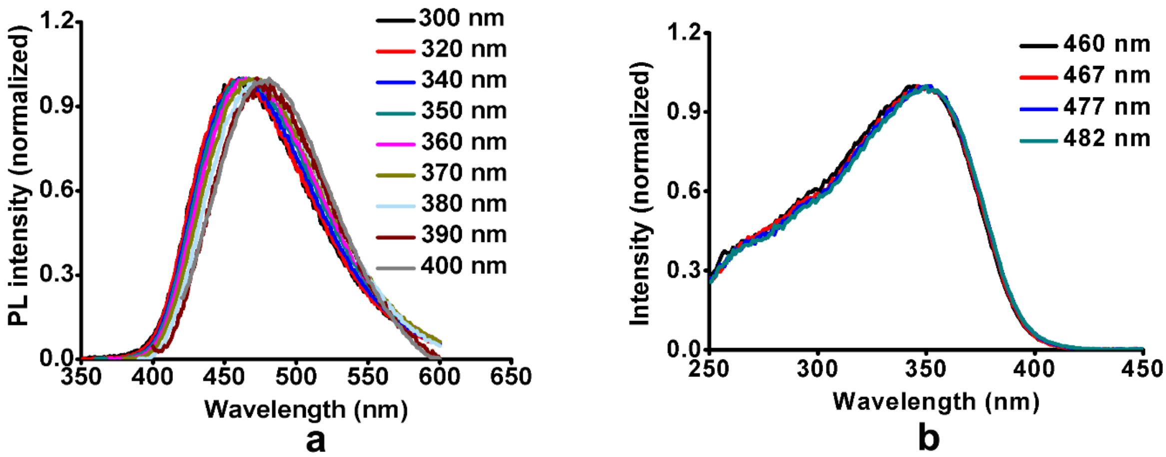
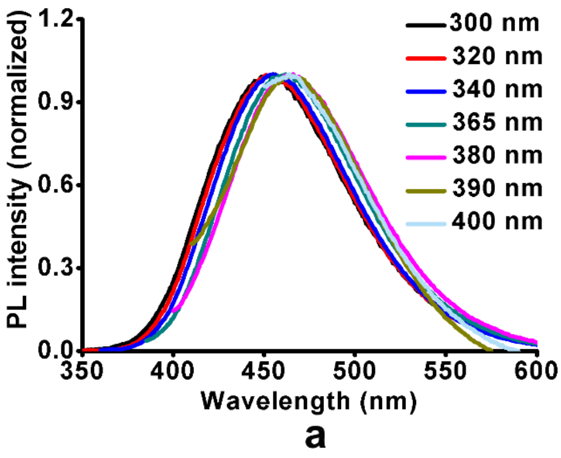


Figure S37. (a) Normalized emission spectra of **TPE-CH$_3$** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-CH$_3$** in PMMA film (ω%=1%) with different emission wavelengths.



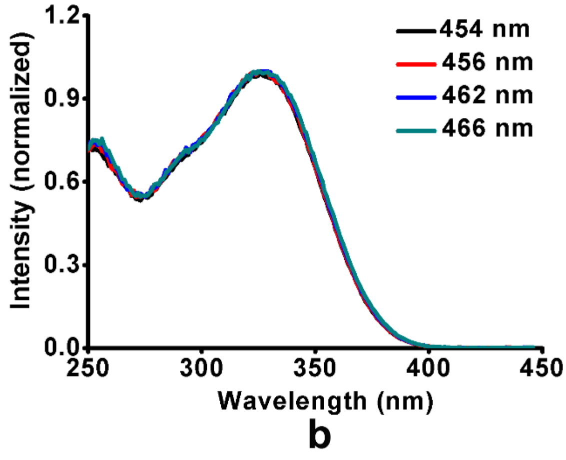
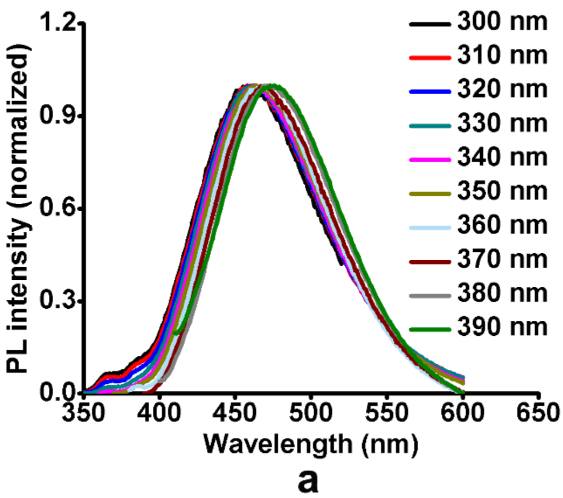


Figure S38. (a) Normalized emission spectra of **TPE-OCH$_3$** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-OCH$_3$** in PMMA film (ω%=1%) with different emission wavelengths.



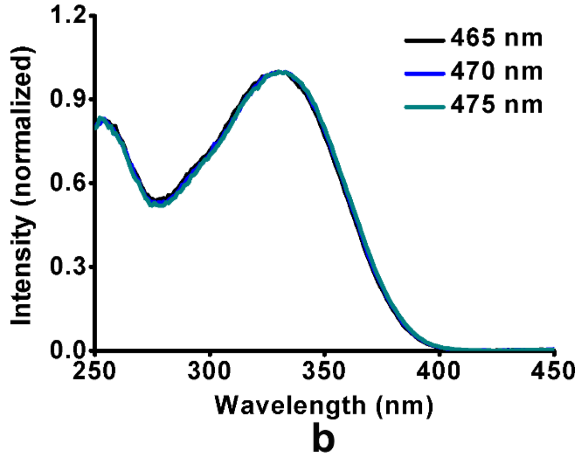


Figure S39. (a) Normalized emission spectra of **TPE-Phen** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-Phen** in PMMA film (ω%=1%) with different emission wavelengths.

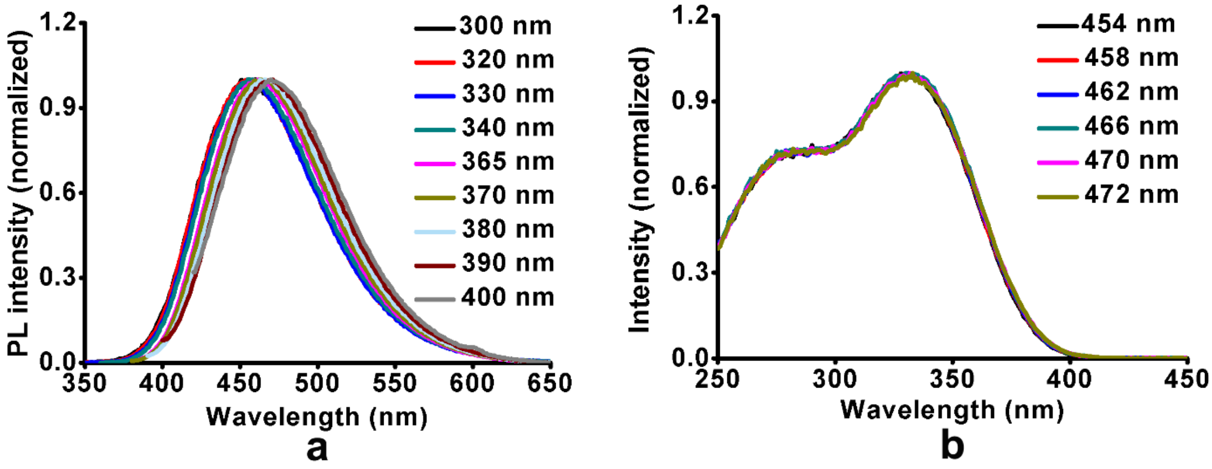


Figure S40. (a) Normalized emission spectra of **TPE-Diphen** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-Diphen** in PMMA film (ω%=1%) with different emission wavelengths.

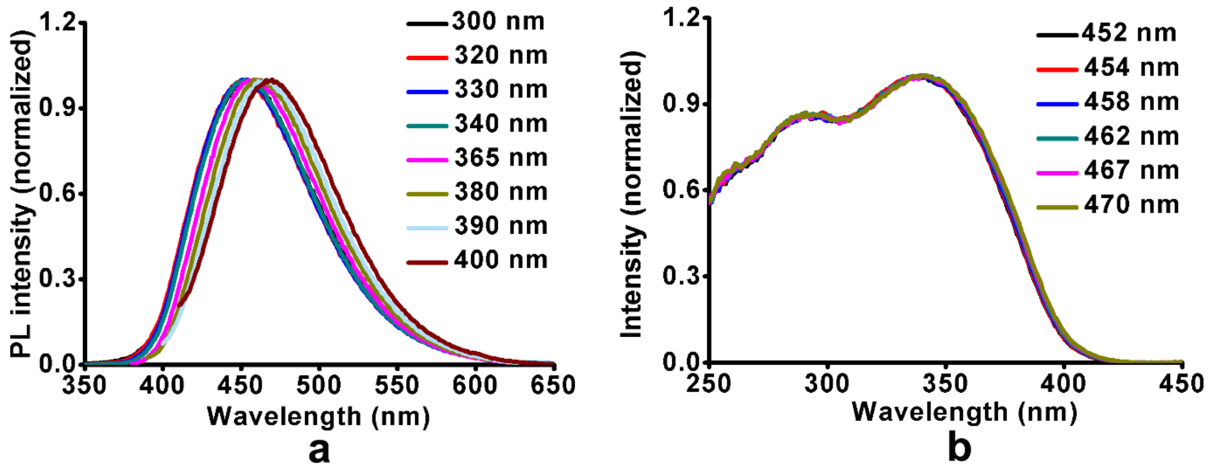


Figure S41. (a) Normalized emission spectra of **TPE-VB** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-VB** in PMMA film (ω%=1%) with different emission wavelengths.

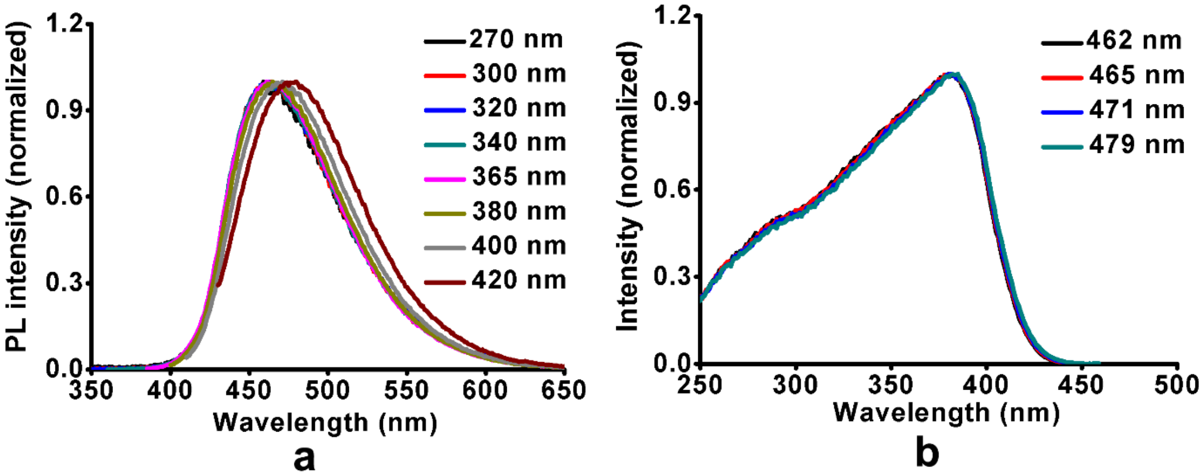


Figure S42. (a) Normalized emission spectra of **TPE-VBA** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-VBA** in PMMA film (ω%=1%) with different emission wavelengths.

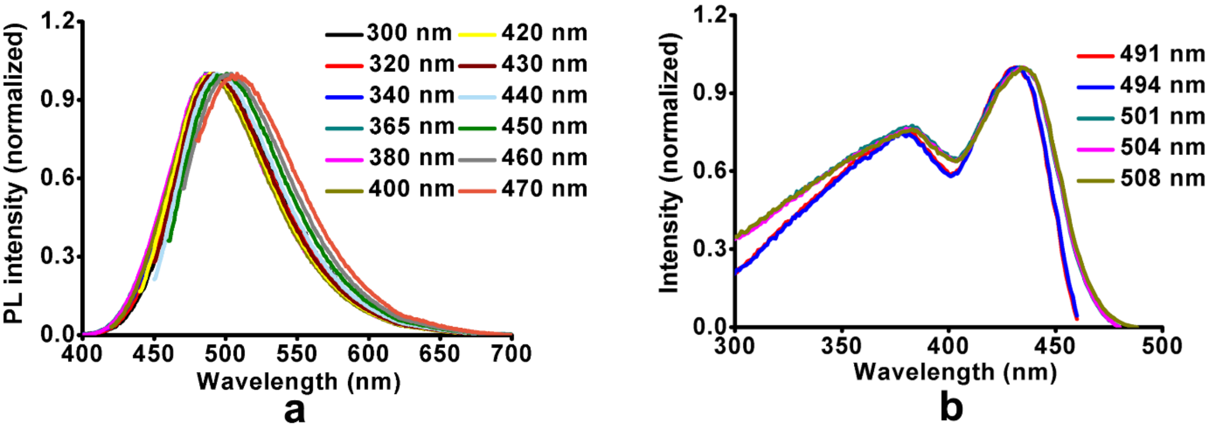


Figure S43. (a) Normalized emission spectra of **TPE-VBN** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-VBN** in PMMA film (ω%=1%) with different emission wavelengths.

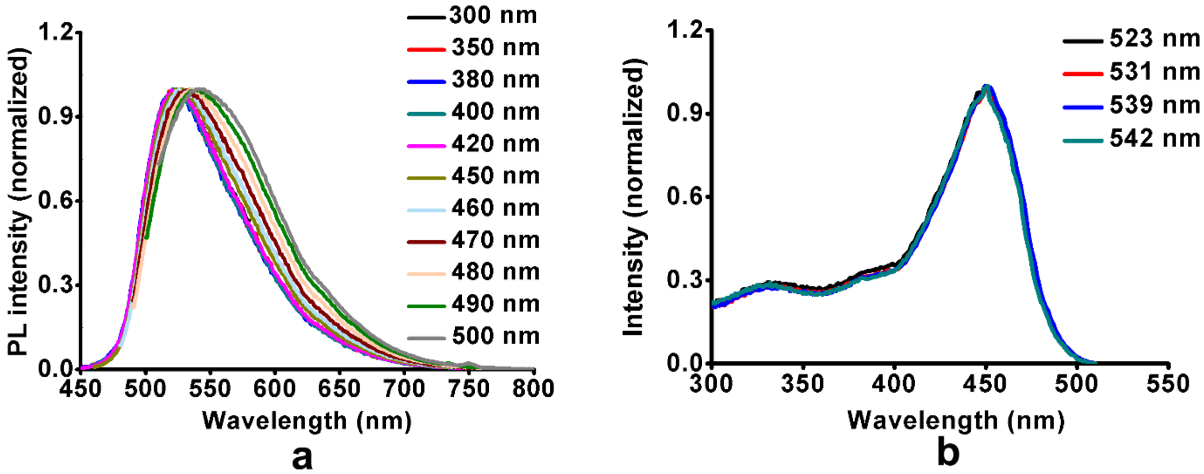


Figure S44. (a) Normalized emission spectra of **TPE-VBVBN** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-VBVBN** in PMMA film (ω%=1%) with different emission wavelengths.

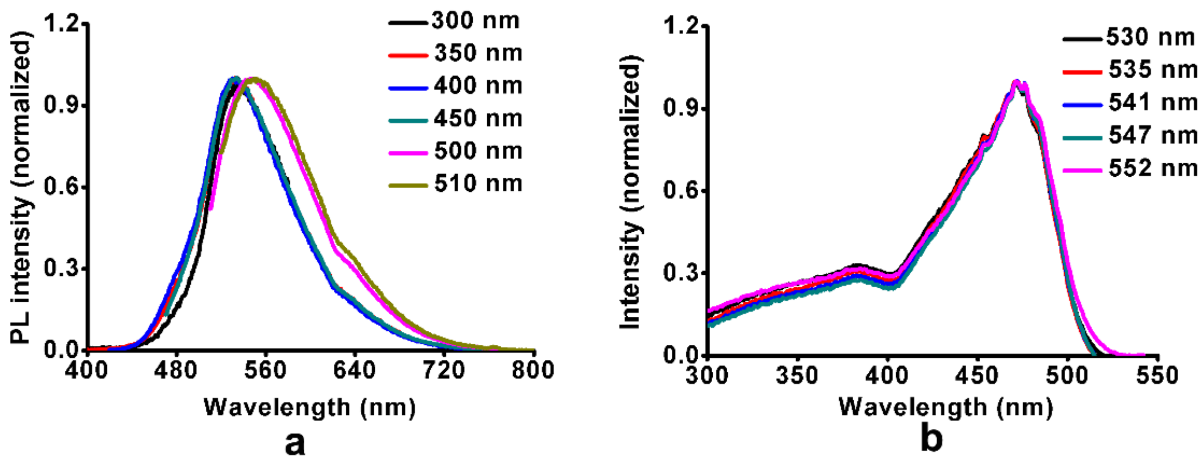


Figure S45. (a) Normalized emission spectra of **TPE-VI** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-VI** in PMMA film (ω%=1%) with different emission wavelengths.

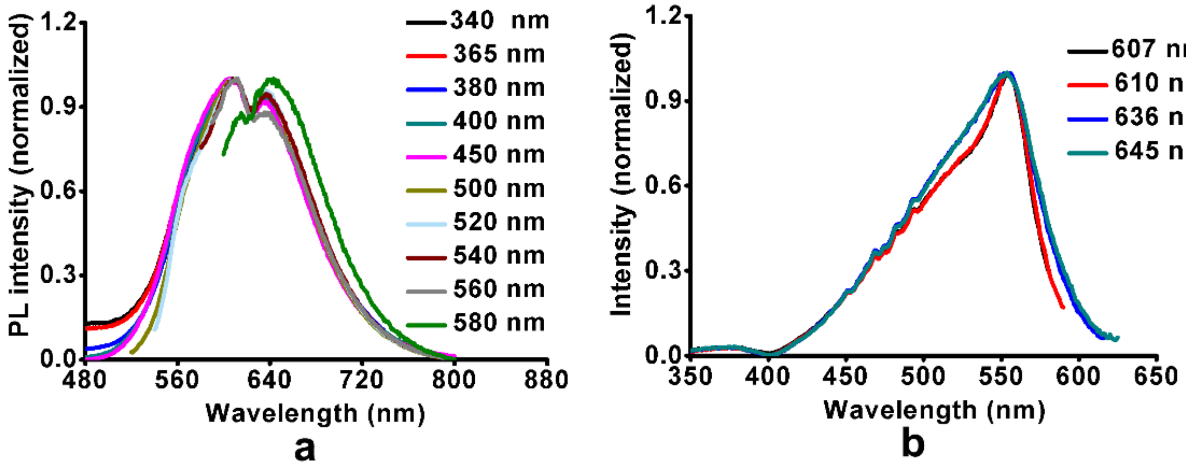


Figure S46. (a) Normalized emission spectra of **TPE-VBVI** in PMMA film (ω%=1%) with different excitation lights. (b) Normalized excitation spectra of **TPE-VBVI** in PMMA film (ω%=1%) with different emission wavelengths.

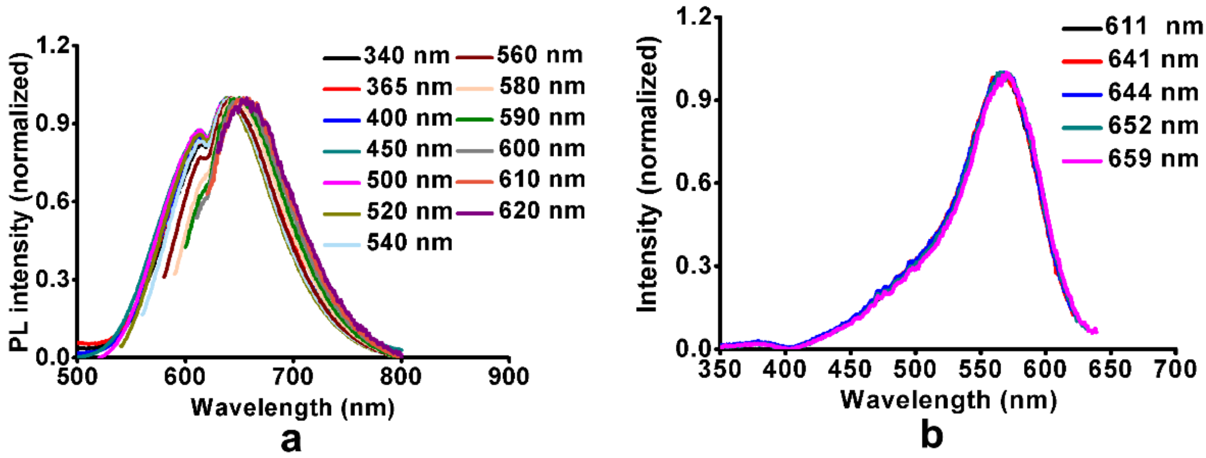
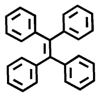


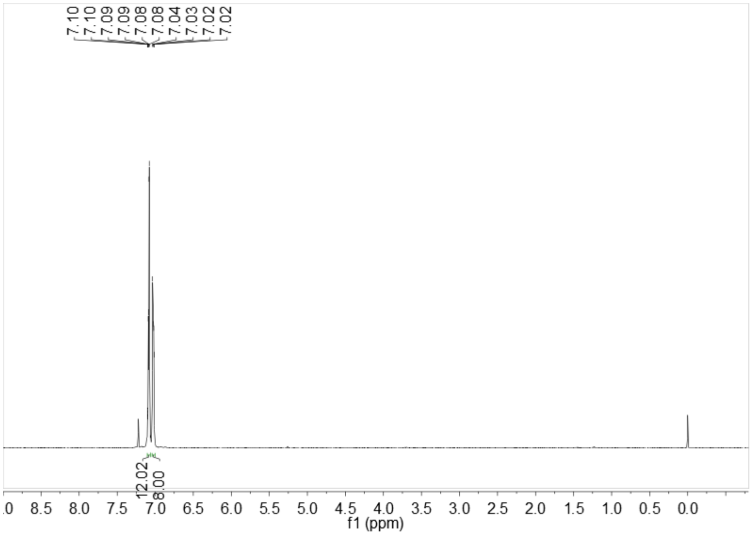
Figure S47. Summary on the maximum emission wavelengths of the studied fluorescent compounds in different states.

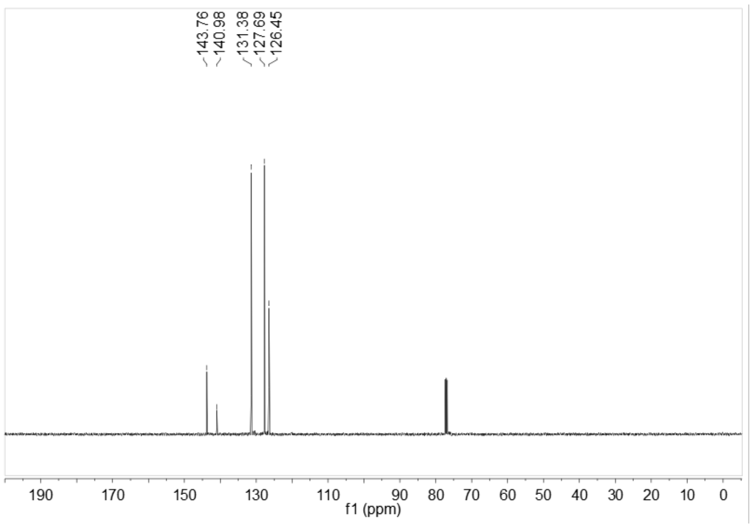
For **TPE-VI** and **TPE-VBVI**, their as-prepared (unground) samples exhibit relatively large maximum wavelength differences, which might be ascribed to the diversified molecular configurations in the non-ignorable surfaces, interfaces and defects of poorly-crystallized powders (broad and weak X-ray diffraction peaks in **Figure S11c** and **S12c**).

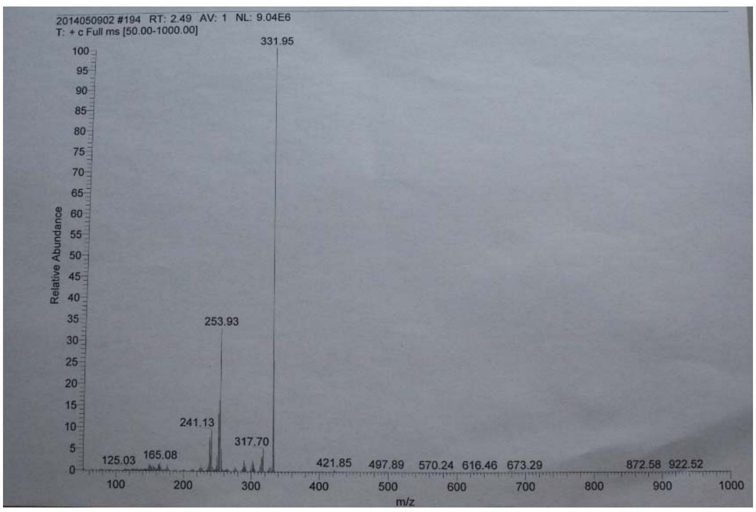
Powders	Unground	Ground	Annealed	Fumed	1% PMMA film	THF solution
TPE	449 nm	446-466 nm 20 nm	445-457 nm 12 nm	447-466 nm 19 nm	458-468 nm 10 nm	
TPE-Br	457 nm	458-471 nm 12 nm	455-461 nm 6 nm	452-458 nm 6 nm	460-481 nm 21 nm	
$TPE-CH_3$	455 nm	456-478 nm 21 nm	453-469 nm 16 nm	454-468 nm 14 nm	455-464 nm 9 nm	
$TPE-OCH_3$	459 nm	456-486 nm 30 nm	456-489nm 33 nm	455-485 nm 30 nm	458-476 nm 18 nm	
TPE-Phen	461 nm	467-493 nm 26 nm	460-464 nm 4 nm	460-470 nm 10 nm	455-471 nm 16 nm	
TPE-Diphen	450 nm	462-499 nm 37 nm	452-479 nm 27 nm	453-476 nm 23 nm	452-470 nm 18 nm	
TPE-VB	453 nm	468-509 nm 41 nm	457-500 nm 43 nm	453-482 nm 29 nm	459-480 nm 21 nm	487 nm
TPE-VBA	494 nm	514-540 nm 26 nm	508-539 nm 31 nm	508-519 nm 11 nm	486-508 nm 22 nm	538 nm
TPE-VBN	498 nm	539-577 nm 38 nm	516-577 nm 61 nm	511-564 nm 53 nm	521-543 nm 22 nm	562 nm
TPE-VBVBN	539 nm	582-602 nm 20 nm	564-598 nm 28 nm	535-576 nm 41 nm	530-550 nm 20 nm	555 nm
TPE-VI	594-608 nm 14 nm	668-685 nm 17 nm	640-682 nm 42 nm	636-662 nm 26 nm	605-643 nm 38 nm	683 nm
TPE-VBVI	635-654 nm 19 nm	697-742 nm 45 nm	699-741 nm 42 nm	660-685 nm 25 nm	638-657 nm 19 nm	675 nm
Rhodamine 6G					568 nm	552 nm
Anthracene					388 nm, 403 nm 426 nm, 451 nm	380 nm, 401 nm 425 nm, 450 nm

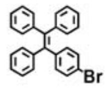
^{1}H NMR, ^{13}C NMR and mass spectra of TPE and its derivatives


TPE

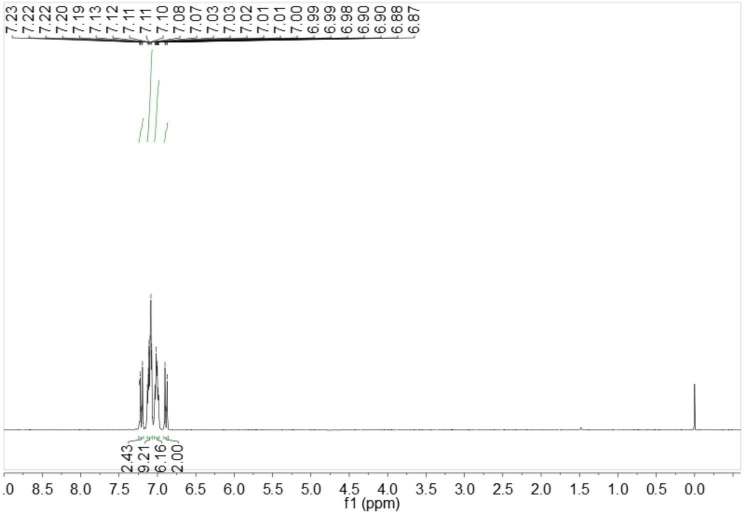


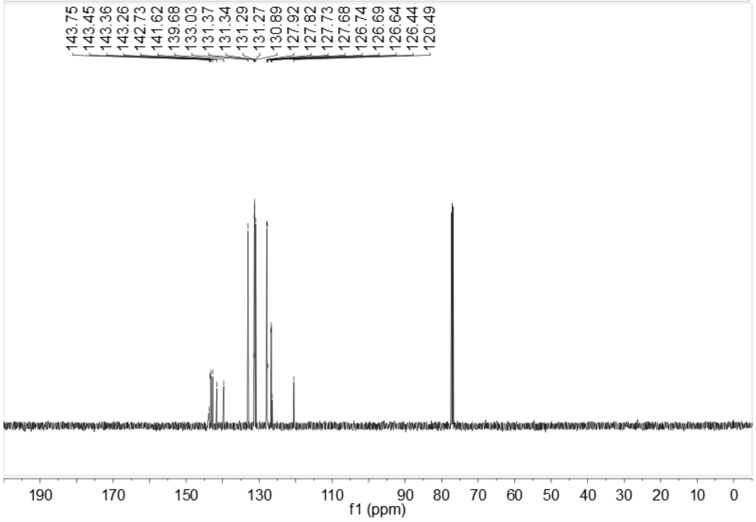


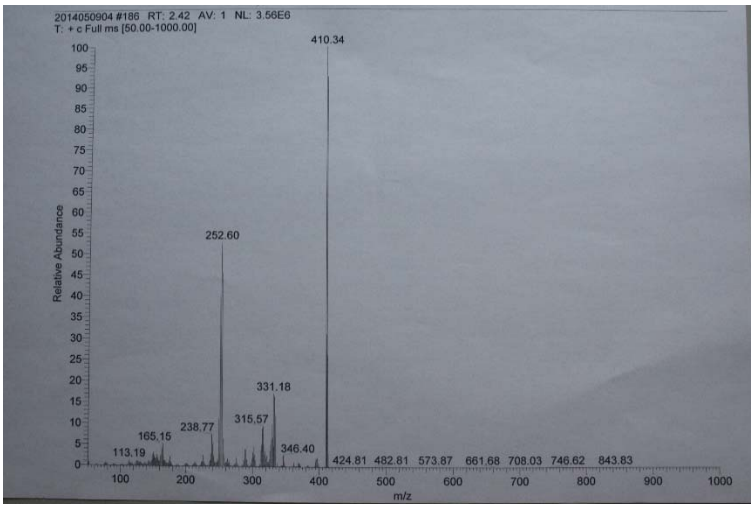


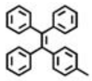


TPE-Br

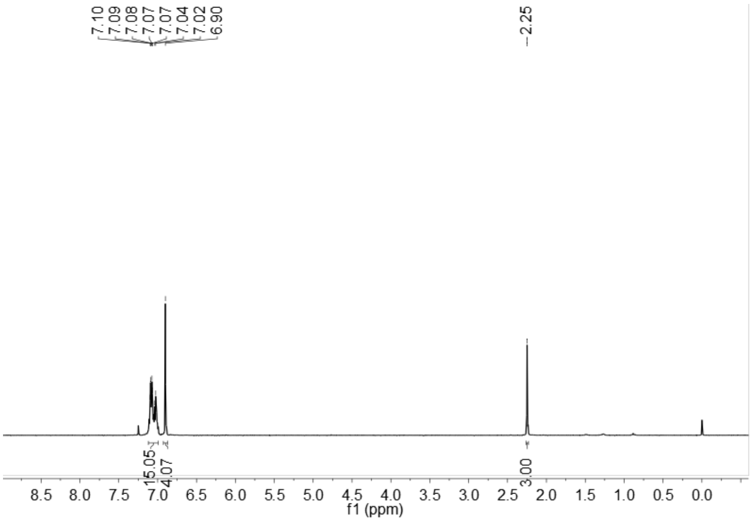

7.23
7.22
7.22
7.20
7.19
7.13
7.12
7.11
7.11
7.10
7.08
7.07
7.03
7.03
7.02
7.01
7.01
7.00
6.99
6.99
6.98
6.90
6.90
6.88
6.87
2.43
9.21
6.16
2.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.75
143.45
143.36
143.26
142.73
141.62
139.68
133.03
131.37
131.34
131.29
131.27
130.89
127.92
127.82
127.73
127.68
126.74
126.69
126.64
126.44
120.49
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

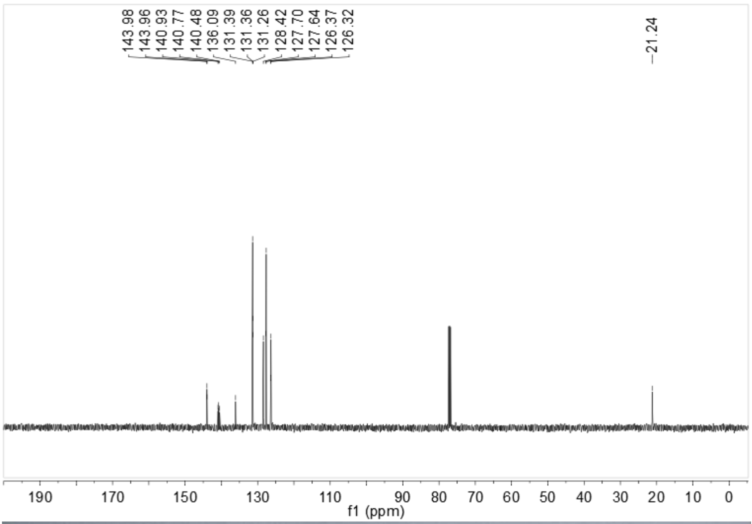

2014050904 #186 RT: 2.42 AV: 1 NL: 3.56E6
T: + c Full ms [50.00-1000.00]
Relative Abundance
410.34
252.60
331.18
315.57
238.77
165.15
113.19
346.40
424.81 482.81 573.87 661.68 708.03 746.62 843.83
m/z



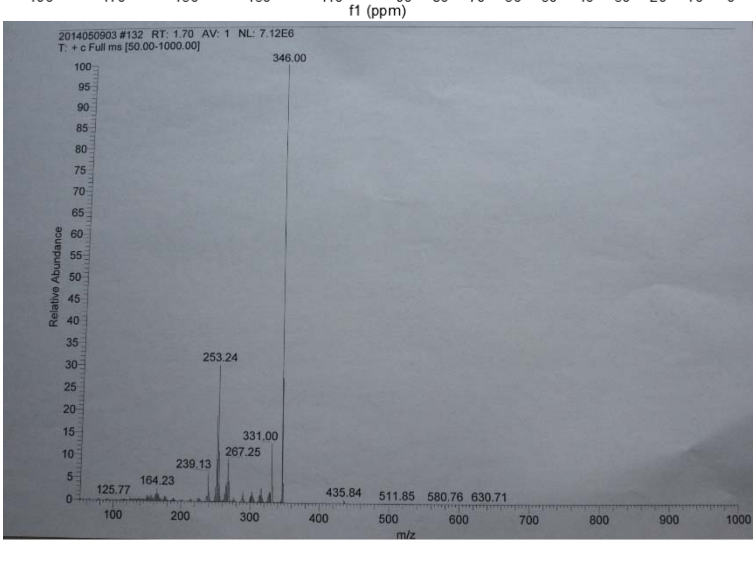
TPE-CH$_3$



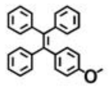
7.10
7.09
7.08
7.07
7.07
7.04
7.02
6.90
2.25
15.05
4.07
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



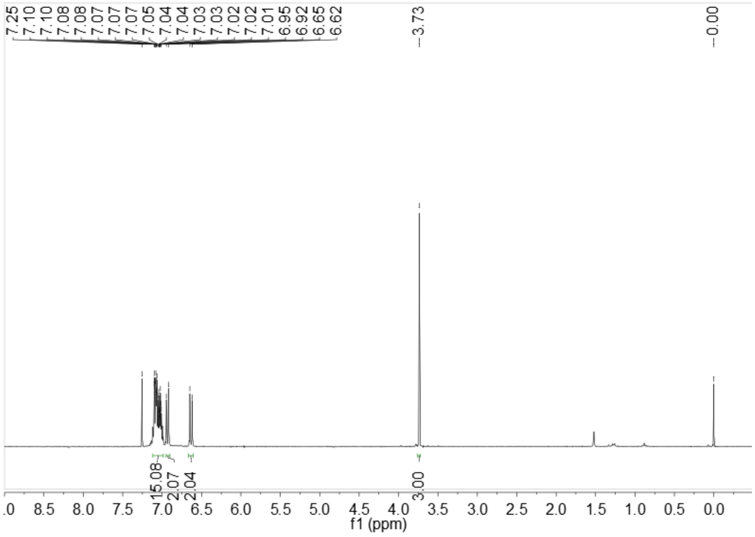
143.98
143.96
140.93
140.77
140.48
136.09
131.39
131.36
131.26
128.42
127.70
127.64
126.37
126.32
21.24
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



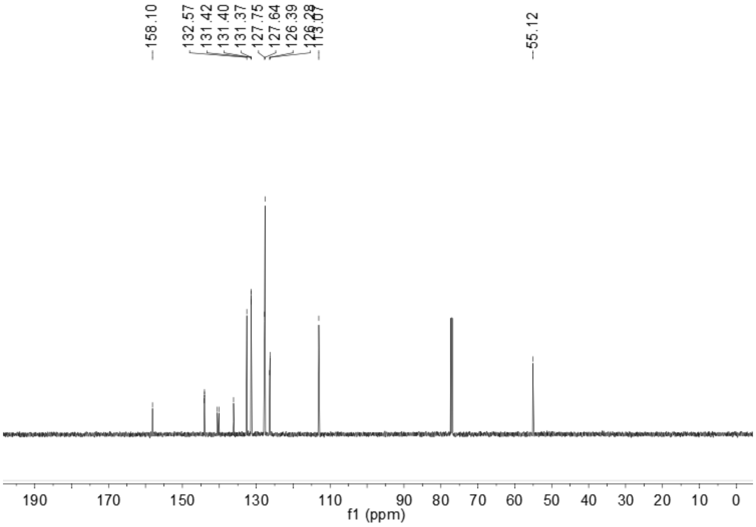
2014050903 #132 RT: 1.70 AV: 1 NL: 7.12E6
T: + c Full ms [50.00-1000.00]
Relative Abundance
346.00
253.24
331.00
267.25
239.13
164.23
125.77
435.84
511.85
580.76
630.71
m/z



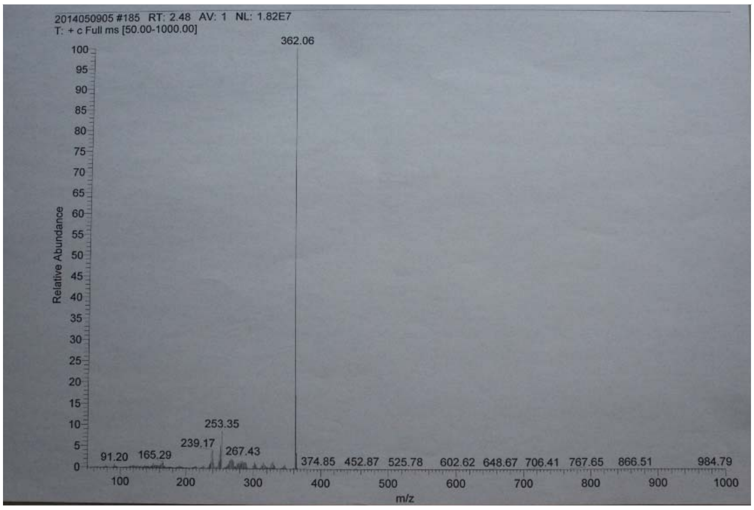
TPE-OCH$_3$



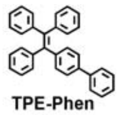
7.25 7.10 7.08 7.08 7.07 7.07 7.05 7.04 7.03 7.03 7.02 7.02 7.01 6.95 6.92 6.65 6.62
3.73
0.00
15.08 2.07 2.04
3.00
f1 (ppm)



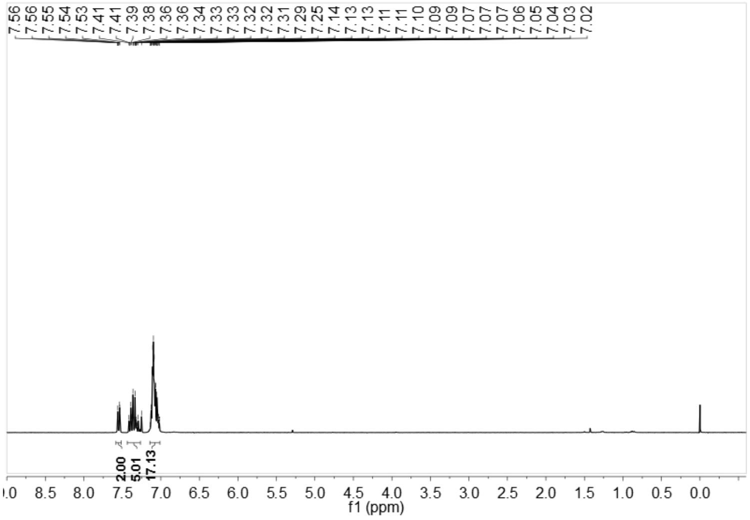
158.10
132.57 131.42 131.40 131.37 127.75 127.64 126.39 126.28 113.07
55.12
f1 (ppm)

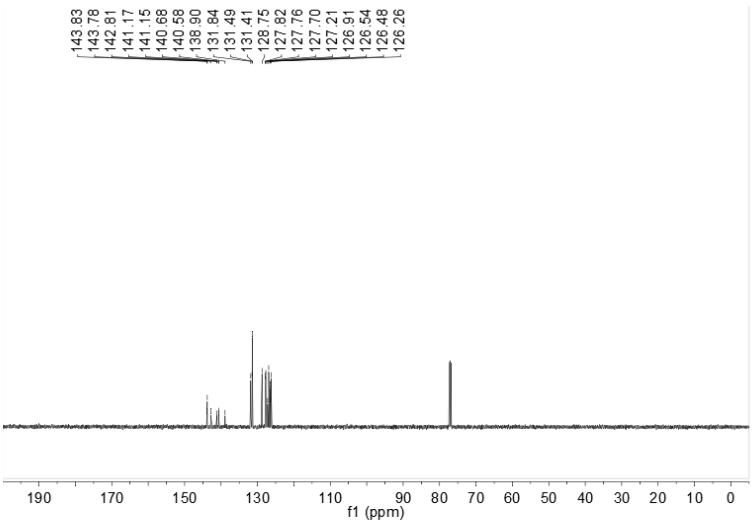


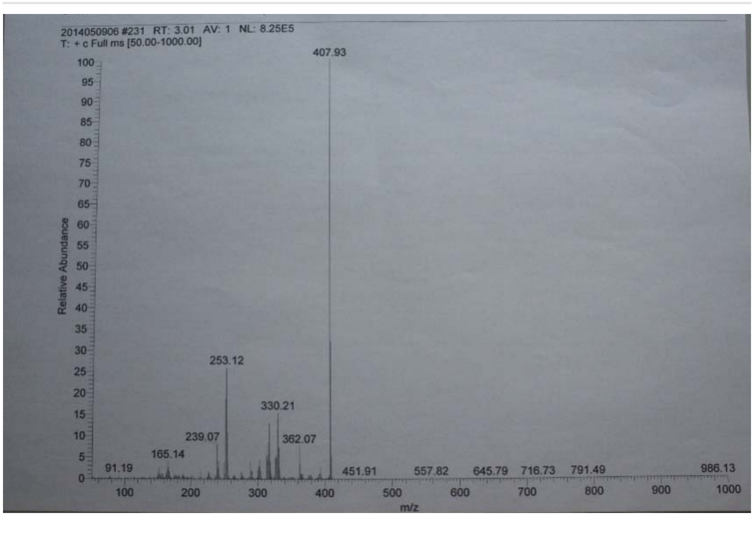
2014050905 #185 RT: 2.48 AV: 1 NL: 1.82E7
T: + c Full ms [50.00-1000.00]
362.06
253.35
239.17
267.43
91.20
165.29
374.85 452.87 525.78 602.62 648.67 706.41 767.65 866.51 984.79
Relative Abundance
m/z

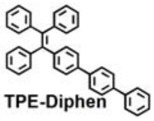


TPE-Phen

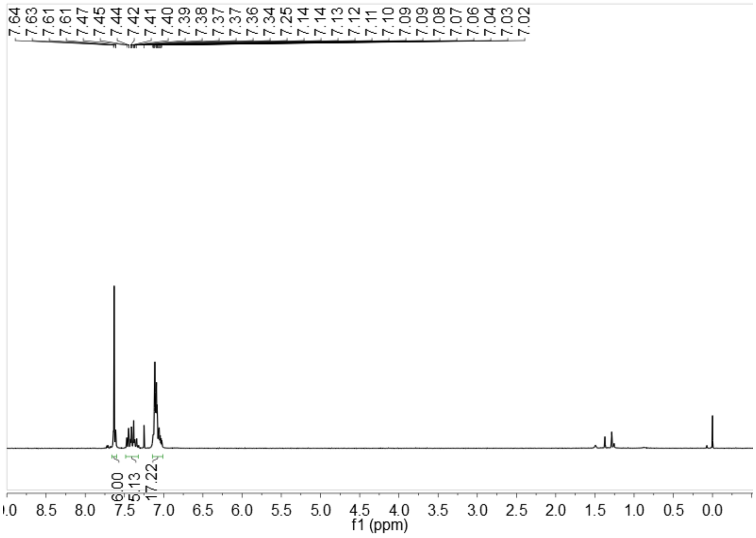

7.56 7.56 7.55 7.54 7.53 7.41 7.41 7.39 7.38 7.36 7.36 7.34 7.33 7.33 7.32 7.31 7.29 7.25 7.14 7.13 7.13 7.11 7.11 7.10 7.09 7.09 7.07 7.07 7.07 7.06 7.05 7.04 7.03 7.02
2.00
5.01
17.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

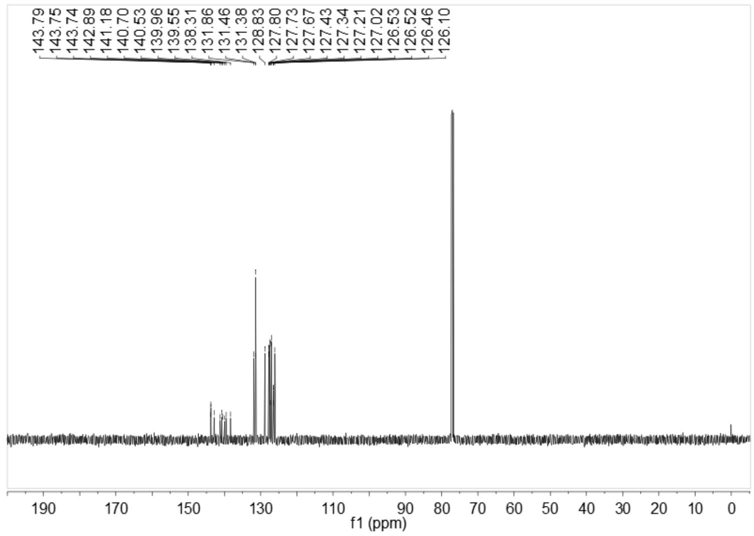

143.83 143.78 142.81 141.17 141.15 140.68 140.58 138.90 131.84 131.49 131.41 128.75 127.82 127.76 127.70 127.21 126.91 126.54 126.48 126.26
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

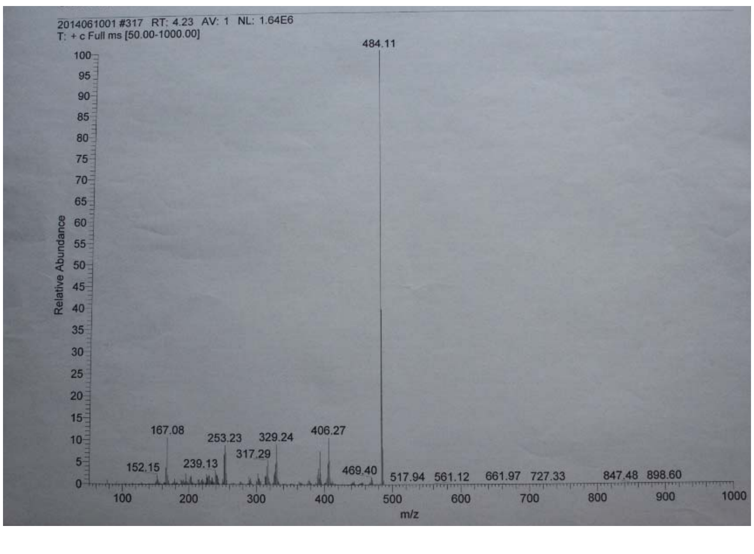

2014050906 #231 RT: 3.01 AV: 1 NL: 8.25E5
T: + c Full ms [50.00-1000.00]
Relative Abundance
407.93
253.12
330.21
239.07
362.07
165.14
91.19
451.91
557.82
645.79
716.73
791.49
986.13
m/z

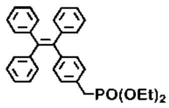


TPE-Diphen

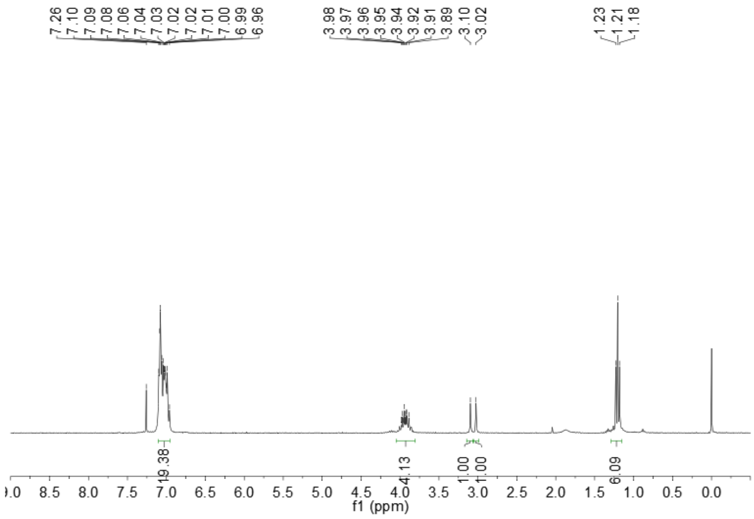

7.64
7.63
7.61
7.61
7.47
7.45
7.44
7.42
7.41
7.40
7.39
7.38
7.37
7.37
7.36
7.34
7.25
7.14
7.14
7.13
7.12
7.11
7.10
7.09
7.09
7.08
7.07
7.06
7.04
7.03
7.02
6.00
5.13
17.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

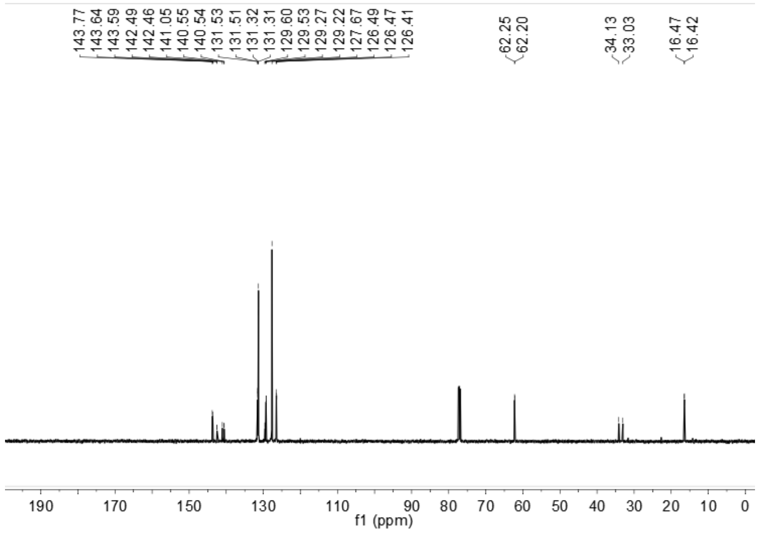

143.79
143.75
143.74
142.89
141.18
140.70
140.53
139.96
139.55
138.31
131.86
131.46
131.38
128.83
127.80
127.73
127.67
127.43
127.34
127.21
127.02
126.53
126.52
126.46
126.10
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

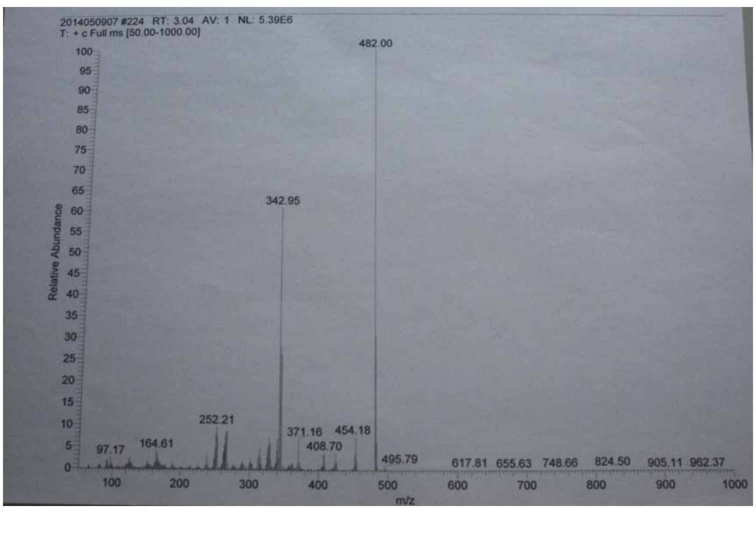

2014061001 #317 RT: 4.23 AV: 1 NL: 1.64E6
T: + c Full ms [50.00-1000.00]
484.11
167.08
253.23
329.24
406.27
317.29
239.13
152.15
469.40
517.94
561.12
661.97
727.33
847.48
898.60
Relative Abundance
m/z

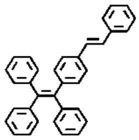

PO(OEt)2

TPE-PO(OEt)$_2$

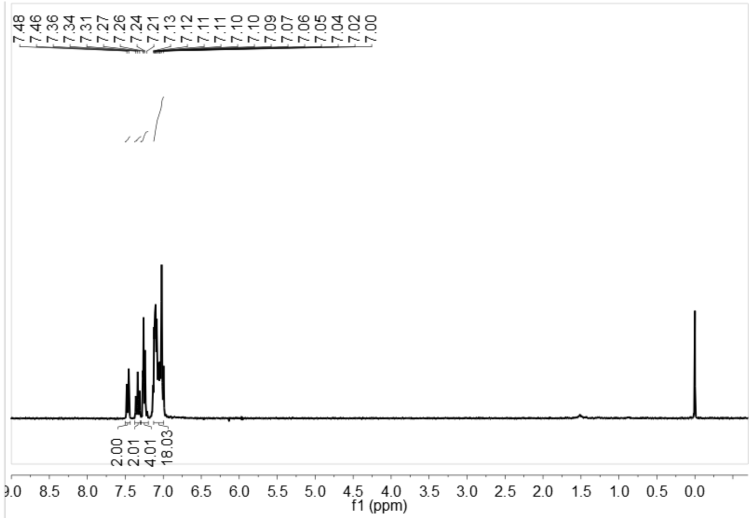

7.26 7.10 7.09 7.08 7.06 7.04 7.03 7.02 7.01 7.00 6.99 6.96
3.98 3.97 3.96 3.95 3.94 3.92 3.91 3.89 3.10 3.02
1.23 1.21 1.18
19.38
4.13
1.00 1.00
6.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.77 143.64 143.59 142.49 142.46 141.05 140.55 140.54 131.53 131.51 131.32 131.31 129.60 129.53 129.27 129.22 127.67 126.49 126.47 126.41
62.25 62.20
34.13 33.03
16.47 16.42
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

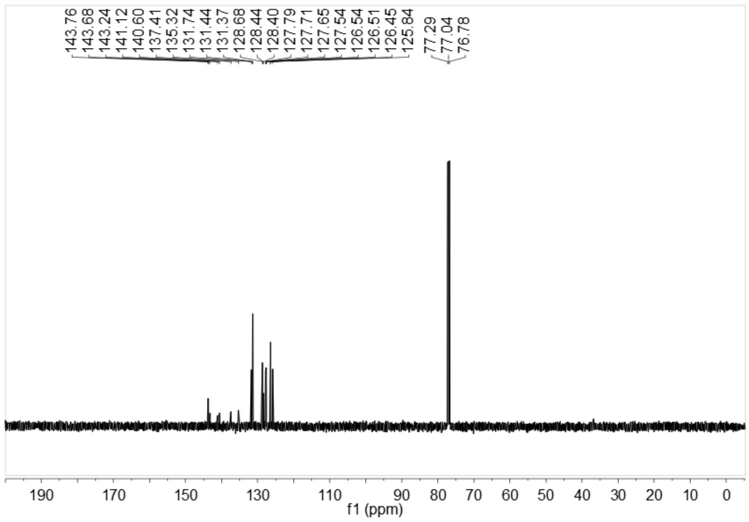

2014050907 #224 RT: 3.04 AV: 1 NL: 5.39E6
T: + c Full ms [50.00-1000.00]
Relative Abundance
482.00
342.95
252.21
371.16
454.18
408.70
97.17
164.61
495.79
617.81 655.63 748.66 824.50 905.11 962.37
100 200 300 400 500 600 700 800 900 1000
m/z



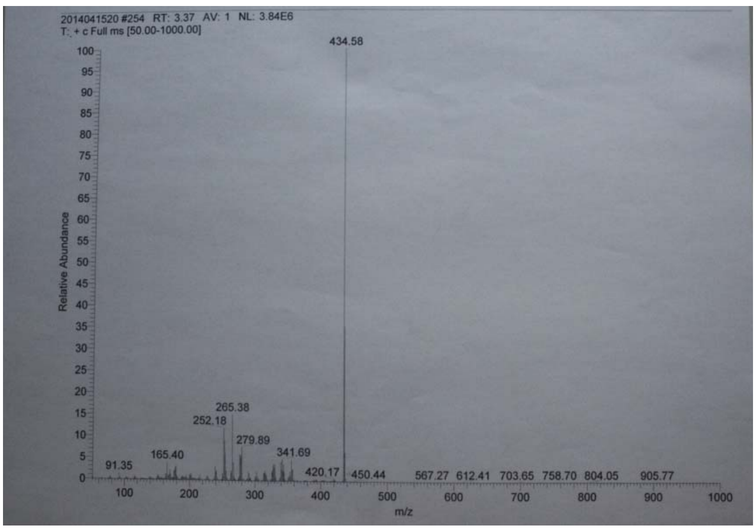
TPE-VB



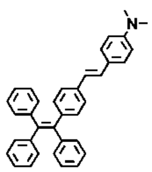
7.48
7.46
7.36
7.34
7.31
7.27
7.26
7.24
7.21
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.07
7.06
7.05
7.04
7.02
7.00
2.00
2.01
4.01
18.03
f1 (ppm)



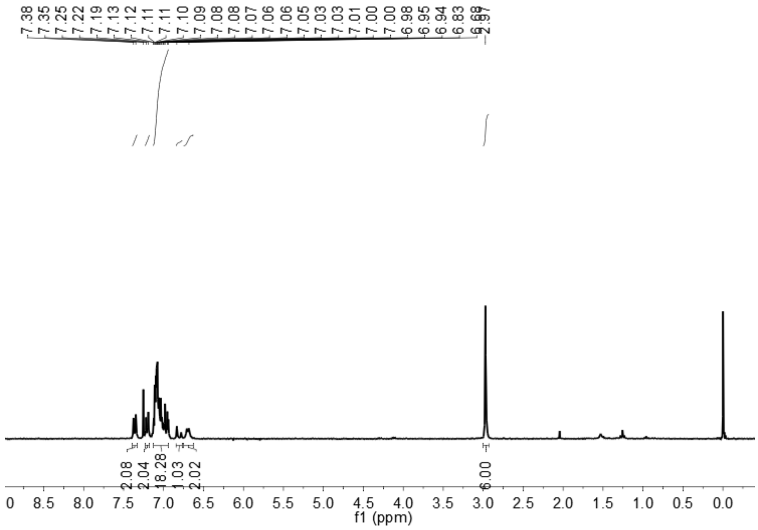
143.76
143.68
143.24
141.12
140.60
137.41
135.32
131.74
131.44
131.37
128.68
128.44
128.40
127.79
127.71
127.65
127.54
126.54
126.51
126.45
125.84
77.29
77.04
76.78
f1 (ppm)

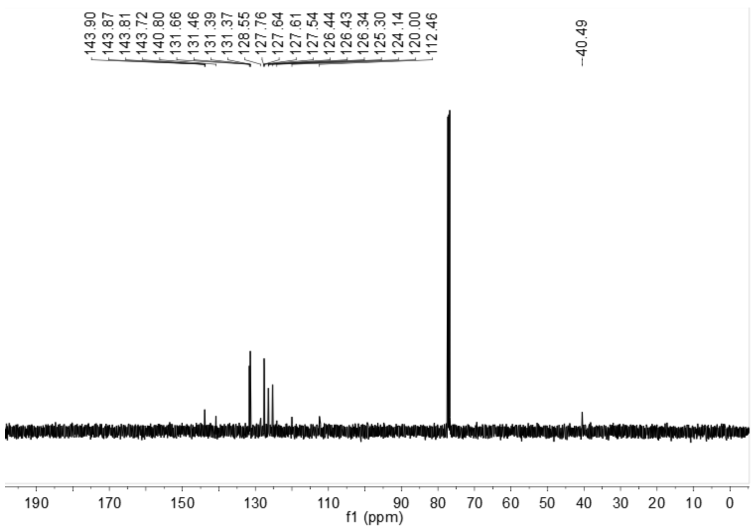


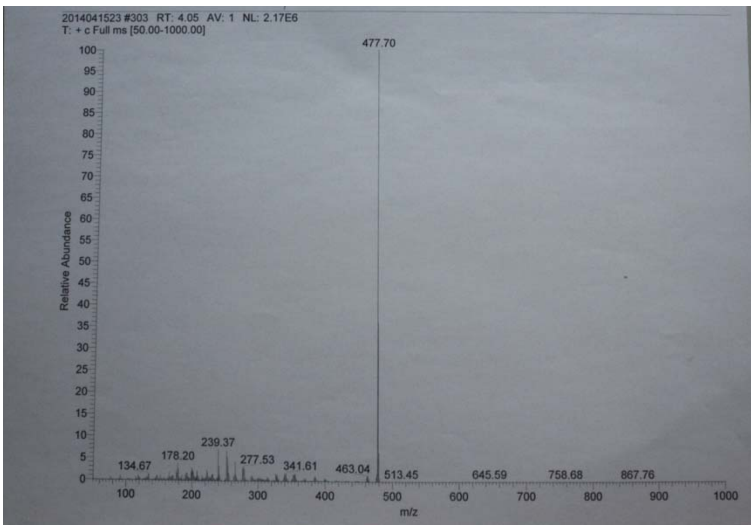
2014041520 #254 RT: 3.37 AV: 1 NL: 3.84E6
T: + c Full ms [50.00-1000.00]
434.58
Relative Abundance
265.38
252.18
279.89
165.40
341.69
91.35
420.17
450.44
567.27
612.41
703.65
758.70
804.05
905.77
m/z

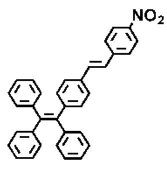

N

TPE-VBA

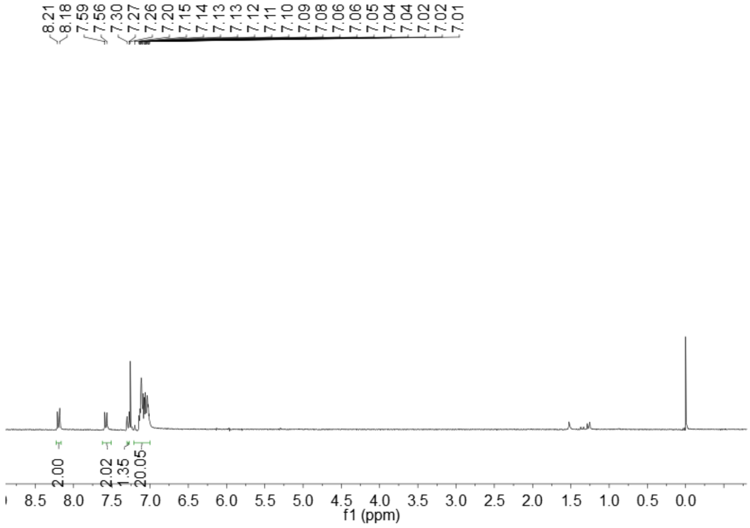

7.38 7.35 7.25 7.22 7.19 7.13 7.12 7.11 7.11 7.10 7.09 7.08 7.08 7.07 7.06 7.06 7.05 7.03 7.03 7.01 7.00 7.00 6.98 6.95 6.94 6.83 6.69 2.97
2.08 2.04 18.28 1.03 2.02 6.00
f1 (ppm)

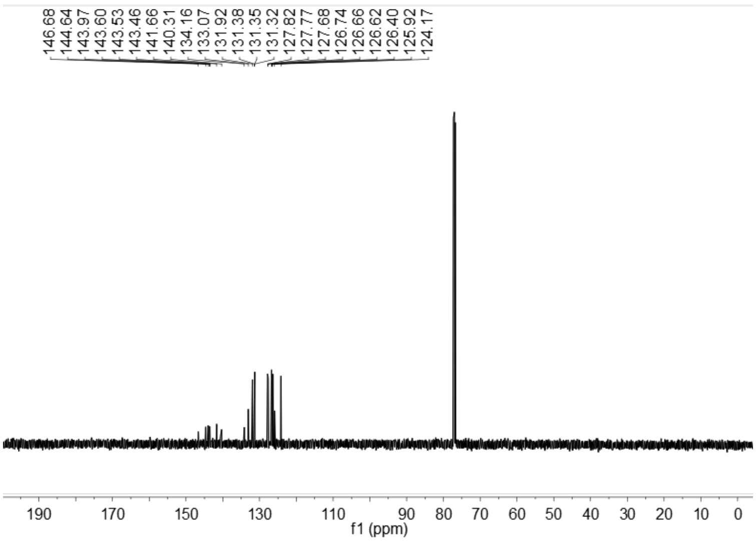

143.90 143.87 143.81 143.72 140.80 131.66 131.46 131.39 131.37 128.55 127.76 127.64 127.61 127.54 126.44 126.43 126.34 125.30 124.14 120.00 112.46
40.49
f1 (ppm)

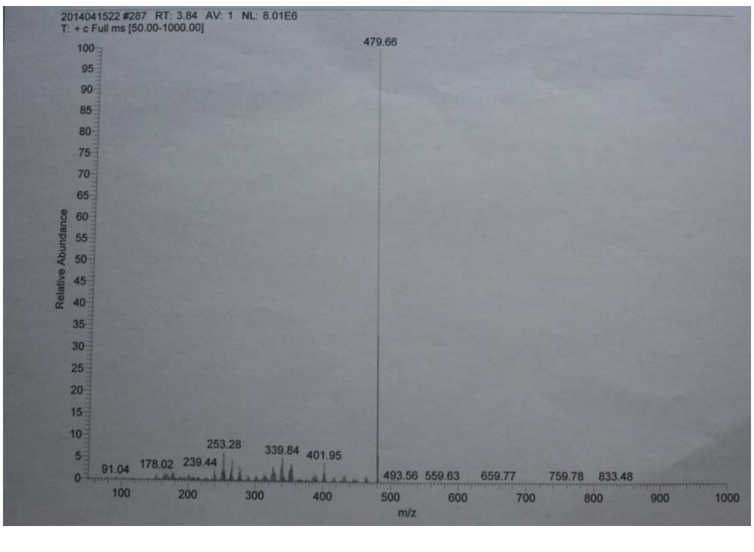

2014041523 #303 RT: 4.05 AV: 1 NL: 2.17E6
T: + c Full ms [50.00-1000.00]
477.70
239.37
178.20
134.67
277.53
341.61
463.04
513.45
645.59
758.68
867.76
Relative Abundance
m/z

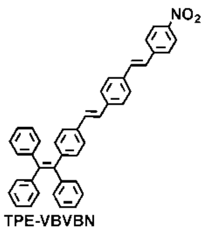

NO2

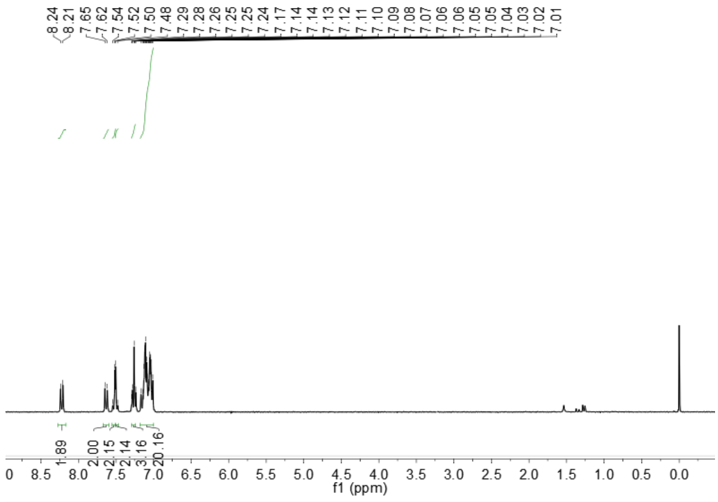
TPE-VBN

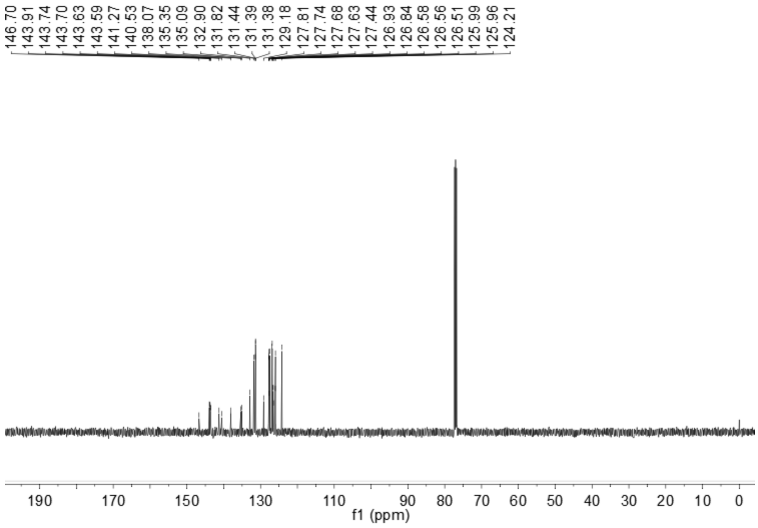

8.21
8.18
7.59
7.56
7.30
7.27
7.26
7.20
7.15
7.14
7.13
7.13
7.12
7.11
7.10
7.09
7.08
7.06
7.06
7.05
7.04
7.04
7.02
7.02
7.01
2.00
2.02
1.35
20.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

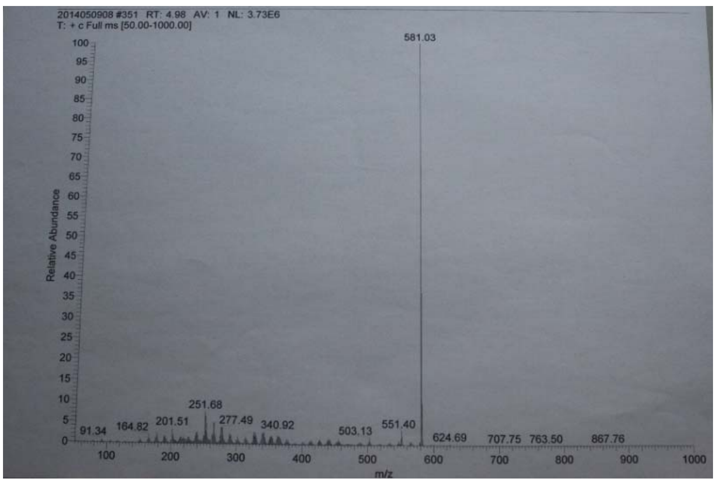

146.68
144.64
143.97
143.60
143.53
143.46
141.66
140.31
134.16
133.07
131.92
131.38
131.35
131.32
127.82
127.77
127.68
126.74
126.66
126.62
126.40
125.92
124.17
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

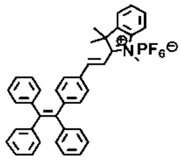

2014041522 #287 RT: 3.84 AV: 1 NL: 8.01E6
T: + c Full ms [50.00-1000.00]
479.66
Relative Abundance
91.04
178.02
239.44
253.28
339.84
401.95
493.56
559.63
659.77
759.78
833.48
m/z


NO2
TPE-VBVBN



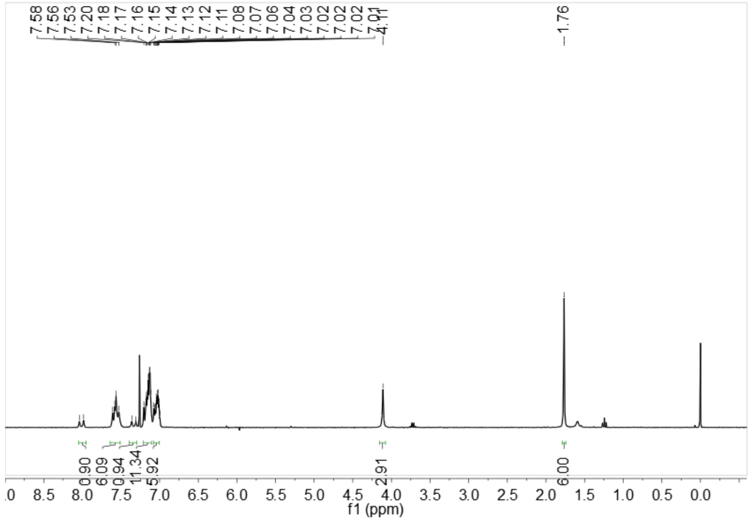




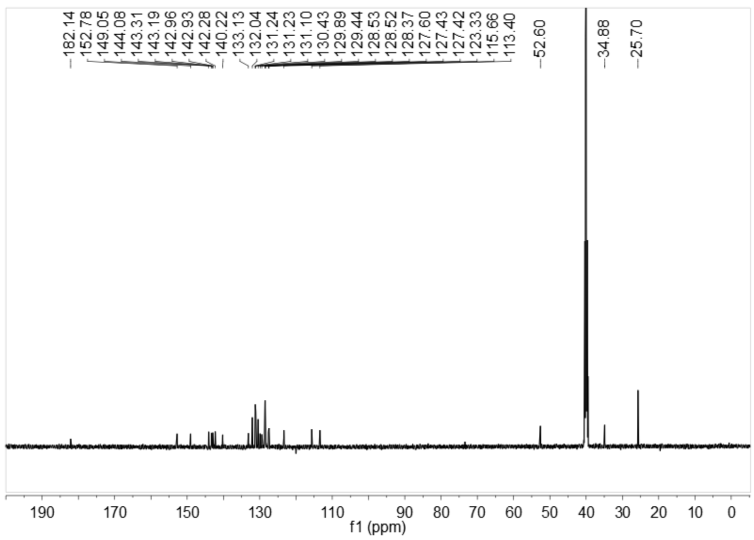


PF6

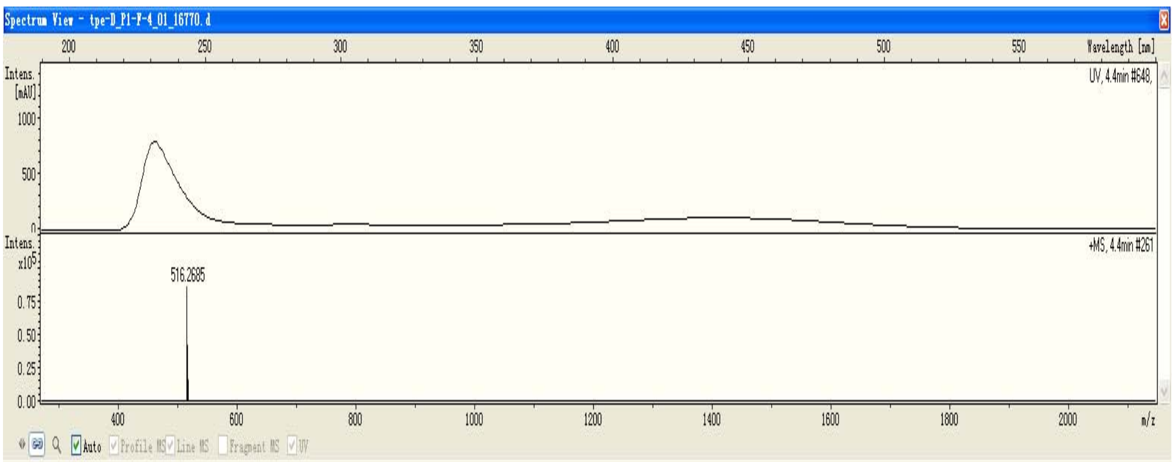
TPE-VI



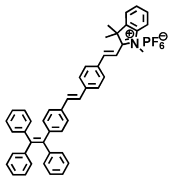
7.58
7.56
7.53
7.20
7.18
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.08
7.07
7.06
7.04
7.03
7.02
7.02
7.01
4.11
1.76
0.90
6.09
0.94
11.34
5.92
2.91
6.00
f1 (ppm)



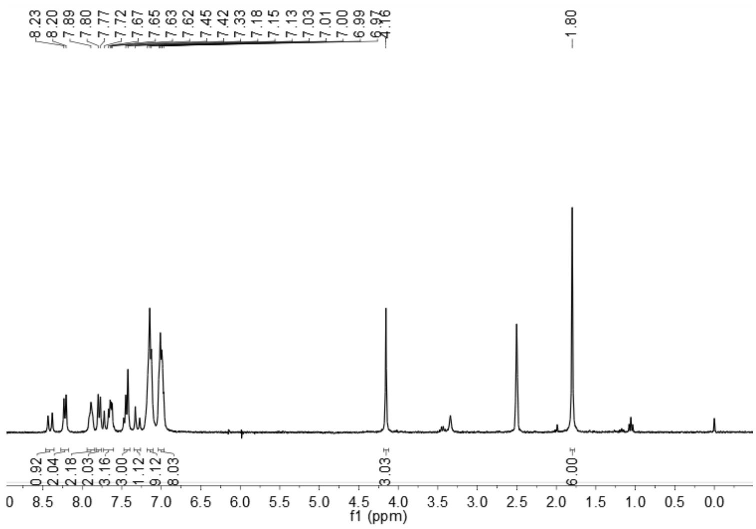
182.14
152.78
149.05
144.08
143.31
143.19
142.96
142.93
142.28
140.22
133.13
132.04
131.24
131.23
131.10
130.43
129.89
129.44
128.53
128.52
128.37
127.60
127.43
127.42
123.33
115.66
113.40
52.60
34.88
25.70
f1 (ppm)

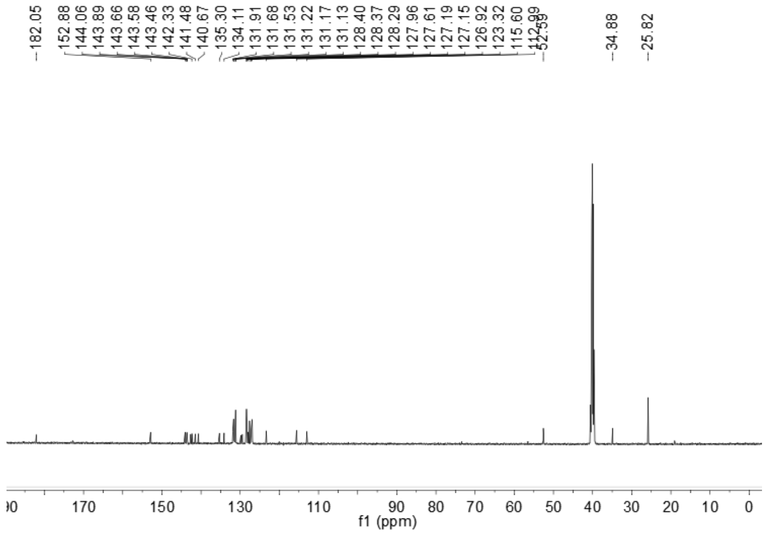


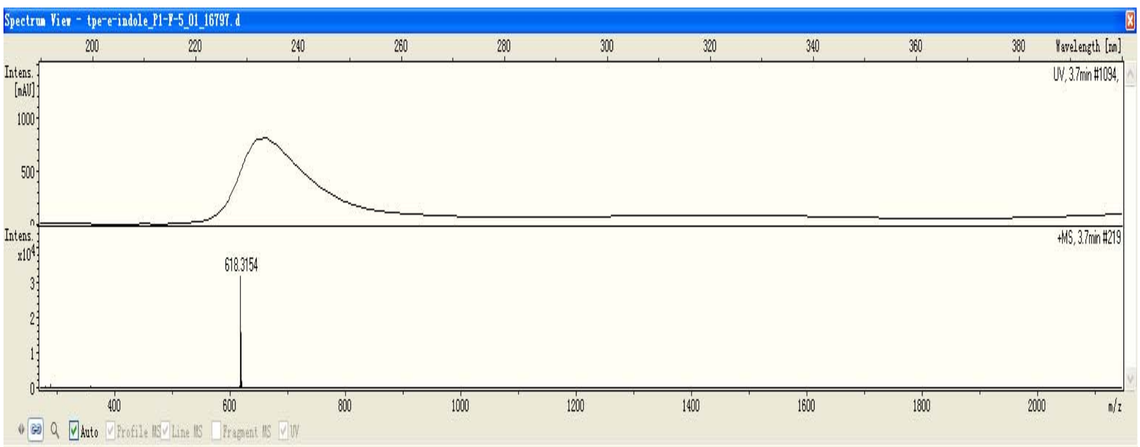
Spectrum View - tpe-D_P1-F-4_01_16770.d
Wavelength [nm]
Intens. [mAU]
UV, 4.4min #648,
Intens. x10^5
+MS, 4.4min #261
516.2685
m/z
Auto
Profile MS
Line MS
Fragment MS
UV



TPE-VBVI







Reference

(1) (a) Q. Lu, X. Li, J. Li, Z. Yang, B. Xu, Z. Chi, J. Xu and Y. Zhang, *J. Mater. Chem. C,* 2015, **3**, 1225. (b) Q. Qi, X. Fang, Y. Liu, P. Zhou, Y. Zhang, B. Yang, W. Tian and S. X. –A. Zhang, *RSC Adv.* 2013, **3**, 16986.

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