Supplementary Materials

Nitrogen atom modulation enables high-sensitive mechanofluorochromism of tetraphenylethylene-based luminescent materials

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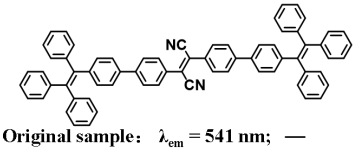
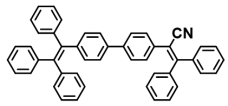
1. Materials and methods

General procedure. All raw materials and reagents were commercially available from Bidepharm, Aladdin and used without further purification. Column chromatography was conducted using SiO_2 (Qingdao ocean column chromatography silica gel, 200-300 mesh) and the separated products were visualized by UV light. NMR spectra data were recorded on Qone AS 400-MHz NMR spectrometer in $CDCl_3$. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyl]prop-2 -enenitrile (DCTB) as the matrix and data were collected in linear mode on a Bruker Autoflex III mass spectrometer. The UV-Vis spectra of solution samples were recorded with a Shimadzu UV2550 spectrophotometer. The emission spectra of solution samples were measured on a Shimadzu RF-5301 PC spectrometer (CCD) and Maya2000Pro optical fiber spectrophotometer. The emission spectra of solid samples and solid-state quantum yields were determined by Edinburgh FLS920 Steady State and Transient State Fluorescence Spectrometer. Single-crystal X-ray diffraction analysis was measured by a Bruker D8 Venture X-ray single crystal diffractometer using a Mo·Kα radiation at 100 K. Powder X-ray diffraction (PXRD) measurements were collected on a PANalytical B.V. Empyrean powder diffractometer operating at 40 kV/30 mA using the Cu·Kα line. Thermogravimetric Analysis (TGA) was conducted using a TA Instruments TGA550 instrument within a temperature range from room temperature to 800°C, with a heating rate of 10°C/min, under a nitrogen gas atmosphere. Differential Scanning Calorimetry (DSC) measurements were performed using a METTLER TOLEDO DSC3 instrument under a nitrogen gas atmosphere, with a heating rate of 10°C/min. The TEM images were taken with JEM-2100 transmission electron microscope. The mixed clear solution was drop cast on an ultra-thin carbon-coated Cu grid (200 mesh) for TEM measurements.

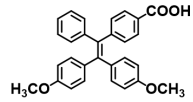
2. A partial summary of TPE-based MFC compounds



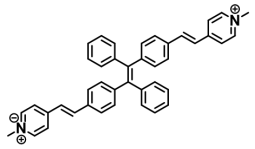
Original sample: λ_{em} = 541 nm; —
Groud sample: λ_{em} = 563 nm; —
J. Phys. Chem. C 2013, 117, 7334−7347



Original sample: λ_{em} = 443 nm; Φ_F= 52%
Groud sample: λ_{em} = 515 nm; Φ_F= 42%
Adv. Mater. 2013, 25, 2837–2843



Original sample: λ_{em} = 451 nm; —
Groud sample: λ_{em} = 496 nm; Φ_F= 10%
Adv. Funct. Mater. 2019, 29, 1900516



Original sample: λ_{em} = 560 nm; Φ_F= 43%
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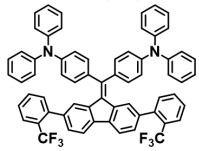
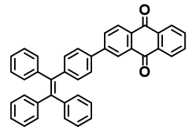
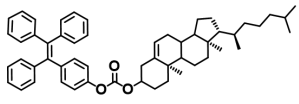
Chem. Commun.,2015, 51, 8849



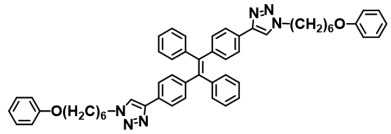
Original sample: λ_{em} = 583 nm; Φ_F= 64%
Groud sample: λ_{em} = 461 nm; Φ_F= 58%
Sci. Adv. 2024, 10, eadk5444



Original sample: λ_{em} = 520 nm; Φ_F= 4%
Groud sample: λ_{em} = 572 nm; Φ_F= 24%
Chem. Eur. J. 2023, 29, e202301070



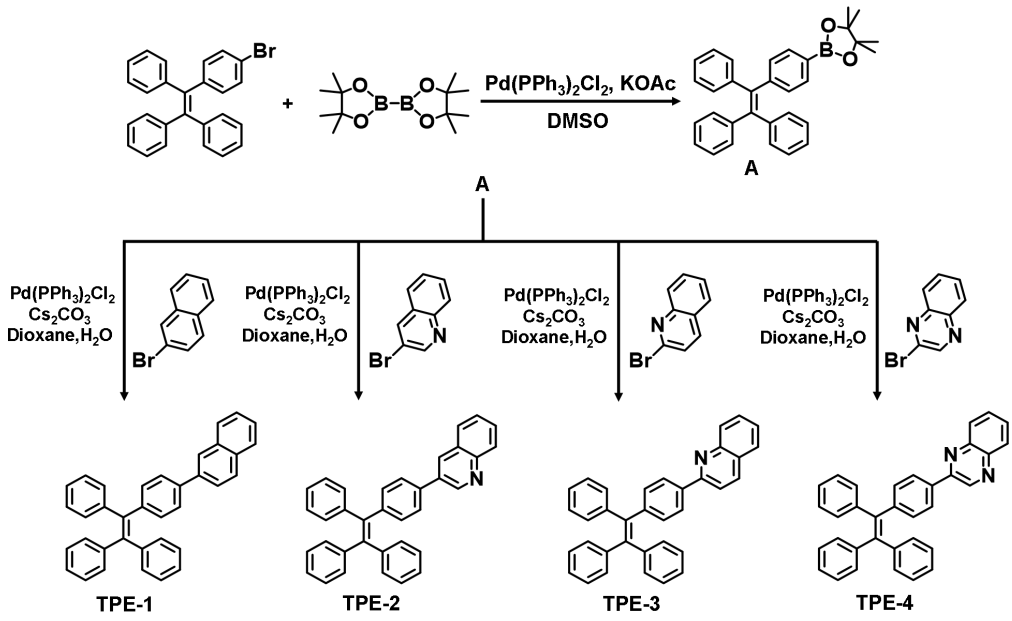
Original sample: λ_{em} = 450 nm; Φ_F=24.8%
Groud sample: λ_{em} = 465 nm; Φ_F=22.0%
Angew. Chem. Int. Ed. 2019, 58, 17814 – 17819



Original sample: λ_{em} = 447 nm; Φ_F= 100%
Groud sample: λ_{em} = 477 nm; —
J. Am. Chem. Soc. 2012, 134, 9956−9966

Supplementary Figure 1. A partial summary of TPE-based MFC compounds (λ_{em} represents the maximum fluorescence emission peak of the compounds).

3. Synthetic routes of TPE-1, TPE-2, TPE-3 and TPE-4



Supplementary Scheme 1. Synthetic routes of **TPE-1**, **TPE-2**, **TPE-3** and **TPE-4**.

3.1 Compound **A**: Accurately weigh (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (2.0 g, 4.88 mmol), bis(pinacolyl)diborane (1.36 g, 5.34 mmol), $Pd(PPh_3)_2Cl_2$ (0.172 g, 0.245 mmol) and KOAc (2.93 g, 29.855 mmol) were placed in a 200 mL Schlenk flask, which was evacuated and filled with nitrogen three times. The flask was then injected with 120 mL of dry DMSO, and the reaction was carried out at 80 °C overnight. After cooling to room temperature, the mixture was extracted with dichloromethane and water, the organic phase was retained, and the operation was repeated three times. The solvent in the organic phase was evaporated under vacuum, and the crude product was purified by silica gel column chromatography using dichloromethane as the eluent to obtain compound **A** (2.06 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H), 7.07−7.13 (m, 9H), 7.00−7.07 (m, 8H), 1.33 (s, 12H).

3.2 **TPE-1**: Accurately weigh compound **A** (0.61 g, 1.33 mmol), 2-bromonaphthalene (0.274 g, 1.33 mmol), $Pd(PPh_3)_2Cl_2$ (0.077 g, 0.110 mmol), and Cs_2CO_3 (0.873 g, 2.679 mmol) and place them in a 200 mL Schlenk flask. Repeat the process of evacuating and filling with nitrogen three times in the reaction flask, and under a nitrogen atmosphere,

add 40 mL of dioxane and 10 mL of ultrapure water. Maintain a temperature of 88 °C in an oil bath and stir the reaction overnight. After cooling to room temperature, the mixture was extracted with dichloromethane and water, retain the organic phase, and repeat the operation three times. Evaporate the solvent in the organic phase under vacuum, and purify the crude product by column chromatography using silica gel with dichloromethane as the eluent to obtain **TPE-1** (0.537 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.92 – 7.82 (m, 3H), 7.73 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.0 Hz, 4H), 7.22 – 7.01 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.87, 143.01, 141.31, 140.64, 138.87, 138.12, 133.78, 132.69, 132.02, 131.58, 131.50, 128.44, 128.29, 127.93, 127.85, 127.78, 127.74, 126.66, 126.61, 126.36, 125.97, 125.61, 125.47. MALDI-TOF: calcd. for $[C_{36}H_{26}+H]^+$ 459.20 (found 459.15). Appearance: white powder. Melting point: 217 °C.

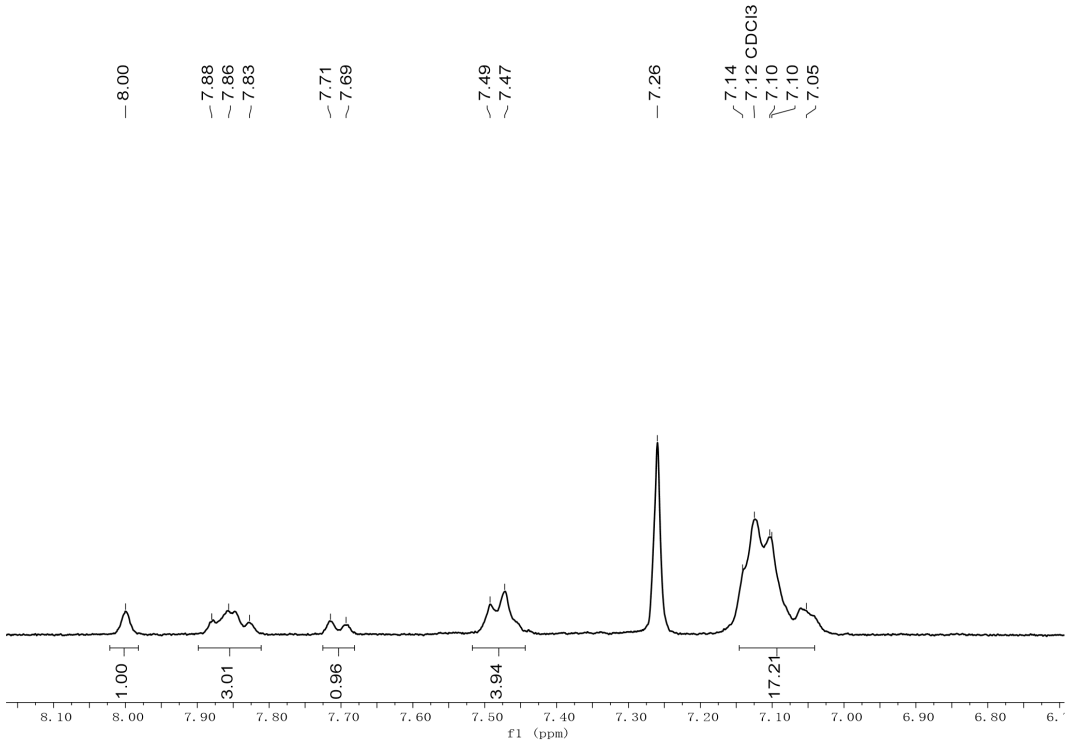
3.3 **TPE-2**: Accurately weigh compound **A** (0.82 g, 1.788 mmol), 3-bromoquinoline (0.37 g, 1.788 mmol), $Pd(PPh_3)_2Cl_2$ (0.103 g, 0.148 mmol), and Cs_2CO_3 (1.174 g, 3.601 mmol) were placed in a 200 mL Schlenk flask, which was evacuated and filled with nitrogen three times. The flask was then injected with 40 mL of dioxane and 10 mL of ultrapure water, and the reaction was carried out at 88°C overnight. After cooling to room temperature, the mixture was extractedwith dichloromethane and water, retain the organic phase, and repeat the operation three times. Evaporate the solvent in the organic phase under vacuum, and purify the crude product by column chromatography using silica gel with a mixture of dichloromethane and ethanol (100:1) as the eluent to obtain compound **TPE-2** (0.625 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, J = 2.3 Hz, 1H), 8.29 (d, J = 2.1 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.23 – 7.03 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.65, 143.98, 143.70, 141.75, 140.29, 135.52, 133.53, 133.33, 132.35, 131.53, 131.48, 131.45, 129.61, 129.08, 128.18, 128.11, 128.00, 127.92, 127.81, 127.23, 126.81, 126.74, 126.69, 126.64. MALDI-TOF: calcd. for $[C_{35}H_{25}N+H]^+$ 460.20 (found 460.18). Appearance: light green powder. Melting point: 200 °C.

3.4 **TPE-3**: Accurately weigh compound **A** (0.75 g, 1.635 mmol), 2-bromoquinoline (0.338 g, 1.635 mmol), $Pd(PPh_3)_2Cl_2$ (0.095 g, 0.135 mmol), and Cs_2CO_3 (1.073 g, 3.294 mmol) and place them in a 200 mL Schlenk flask. Repeat the process of evacuating and filling with nitrogen three times in the reaction flask, and under a nitrogen atmosphere, add 40 mL of dioxane and 10 mL of ultrapure water. Maintain a temperature of 88°C in an oil bath and stir the reaction overnight. After cooling to room temperature, the mixture was extracted with dichloromethane and water, retain the organic phase, and repeat the operation three times. Evaporate the solvent in the organic phase under vacuum, and purify the crude product by column chromatography using silica gel with a mixture of dichloromethane and ethanol (100:1) as the eluent to obtain compound **TPE-3** (0.676 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 7.9 Hz, 2H), 7.83 (t, J = 7.9 Hz, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.9 Hz, 2H), 7.18 – 7.04 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.10, 143.82, 143.71, 141.64, 140.55, 140.55, 137.53, 136.81, 132.08, 131.58, 131.52, 131.49, 129.78, 127.97, 127.84, 127.80, 127.57, 127.25, 127.02, 126.76, 126.67, 126.36, 119.08. MALDI-TOF: calcd. for $[C_{35}H_{25}N + H]^+$ 460.20 (found 460.22). Appearance: white powder. Melting point: 235 °C.

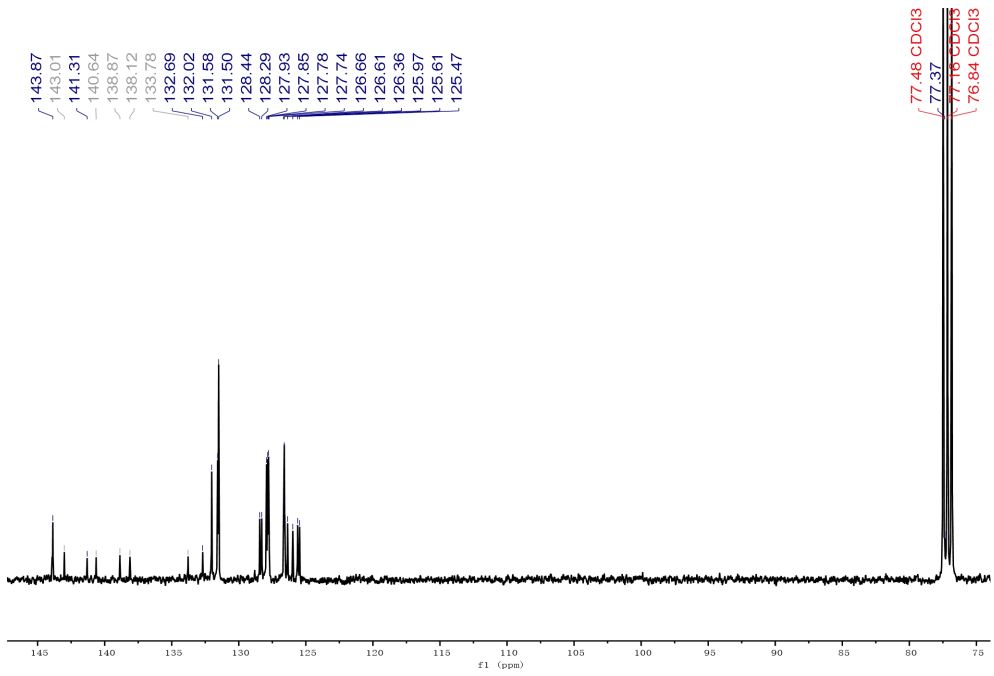
3.5 **TPE-4**: Accurately weigh compound **A** (0.88 g, 1.443 mmol), 2-bromoquinoxaline (0.4 g, 1.443 mmol), $Pd(PPh_3)_2Cl_2$ (0.111 g, 0.159 mmol), and Cs_2CO_3 (1.259 g, 3.865 mmol) were placed in a 200 mL Schlenk flask, which was evacuated and filled with nitrogen three times. The flask was then injected with 40 mL of dioxane and 10 mL of ultrapure water, and the reaction was carried out at 88°C overnight. After cooling to room temperature, the mixture was extracted with dichloromethane and water, retain the organic phase, and repeat the operation three times. Evaporate the solvent in the organic phase under vacuum, and purify the crude product by column chromatography using silica gel with a mixture of dichloromethane and ethanol (100:1) as the eluent to obtain compound **TPE-4** (0.751 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.13 (ddd, J = 8.3, 6.7, 1.6 Hz, 2H), 8.01 – 7.96 (m, 2H), 7.77 (dddd, J = 19.8, 8.3, 6.9,

1.7 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.05 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.66, 146.24, 143.62, 143.55, 143.48, 142.40, 142.12, 141.56, 140.25, 134.67, 132.37, 131.54, 131.50, 131.46, 130.42, 129.64, 129.58, 129.22, 128.03, 127.93, 127.83, 126.99, 126.91, 126.79. MALDI-TOF: calcd. for $[C_{34}H_{24}N_2+H]^+$ 461.19 (found 461.19). Appearance: light yellow powder. Melting point: 199 °C.

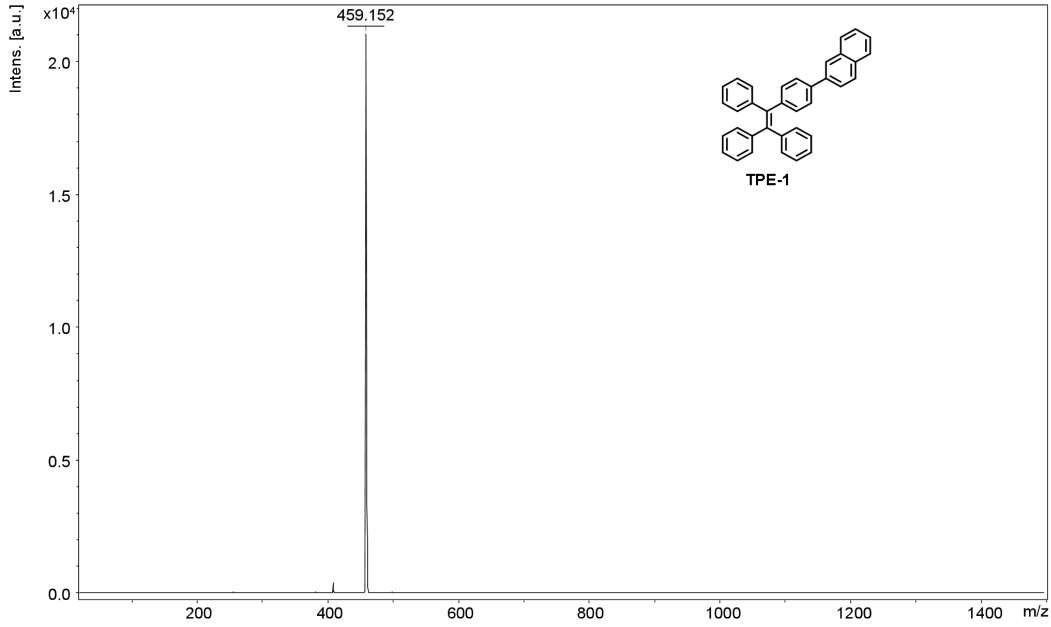
4. ^{1}H NMR, ^{13}C NMR and MALDI-TOF-MS



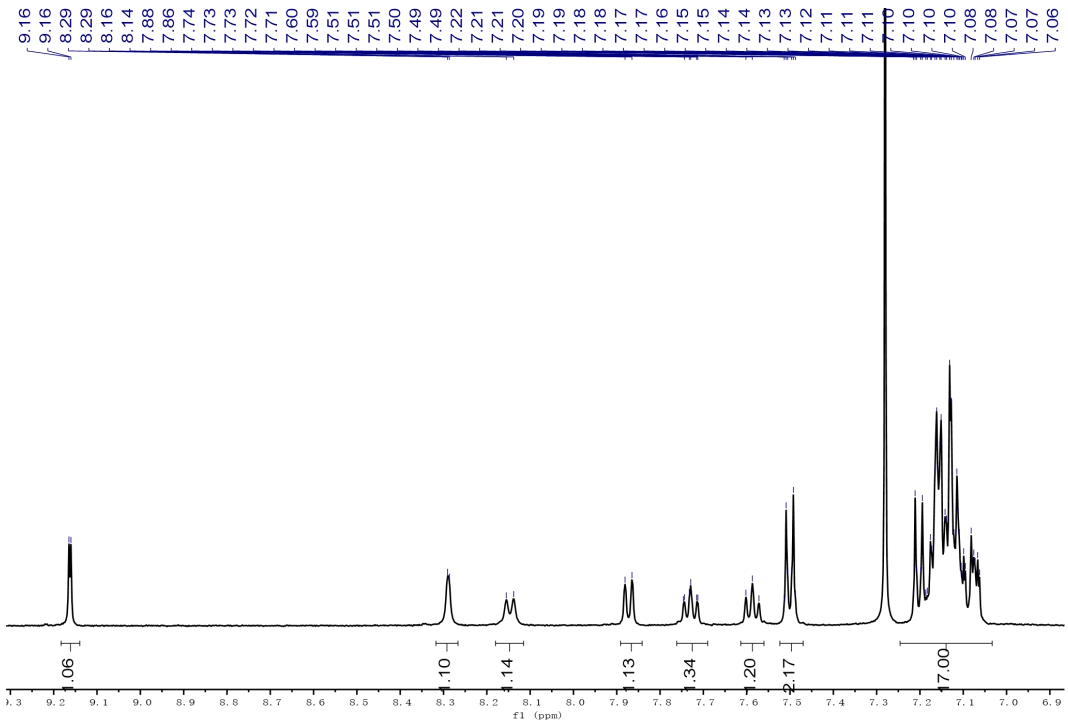
Supplementary Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) spectrum of **TPE-1**.



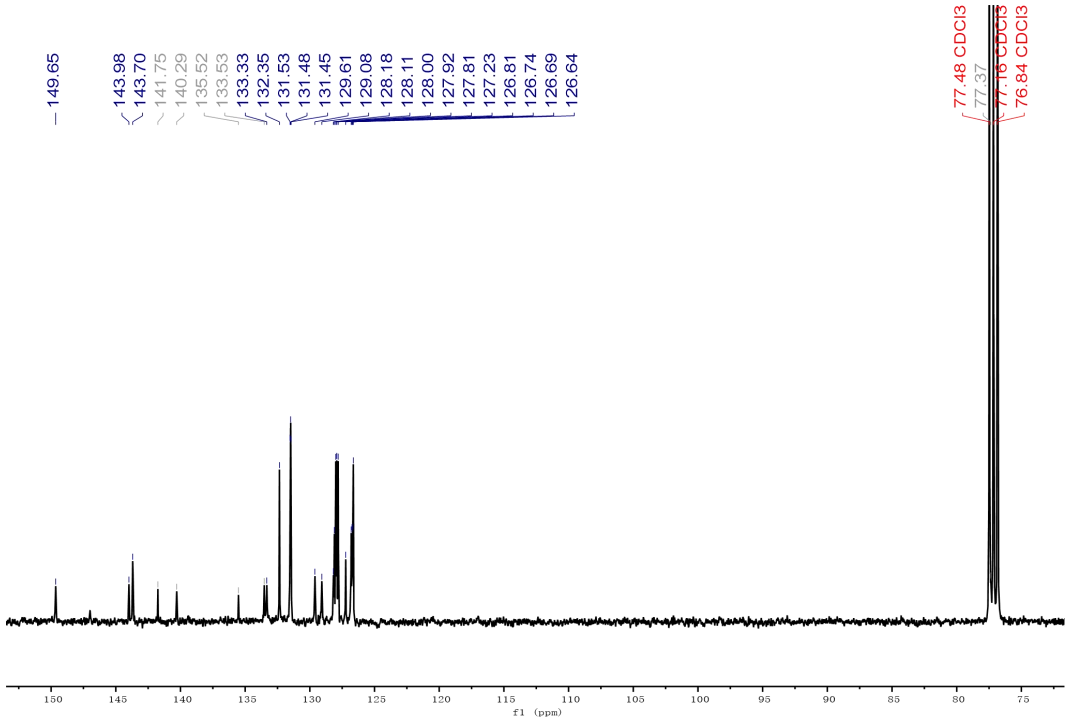
Supplementary Figure 3. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) spectrum of **TPE-1**.



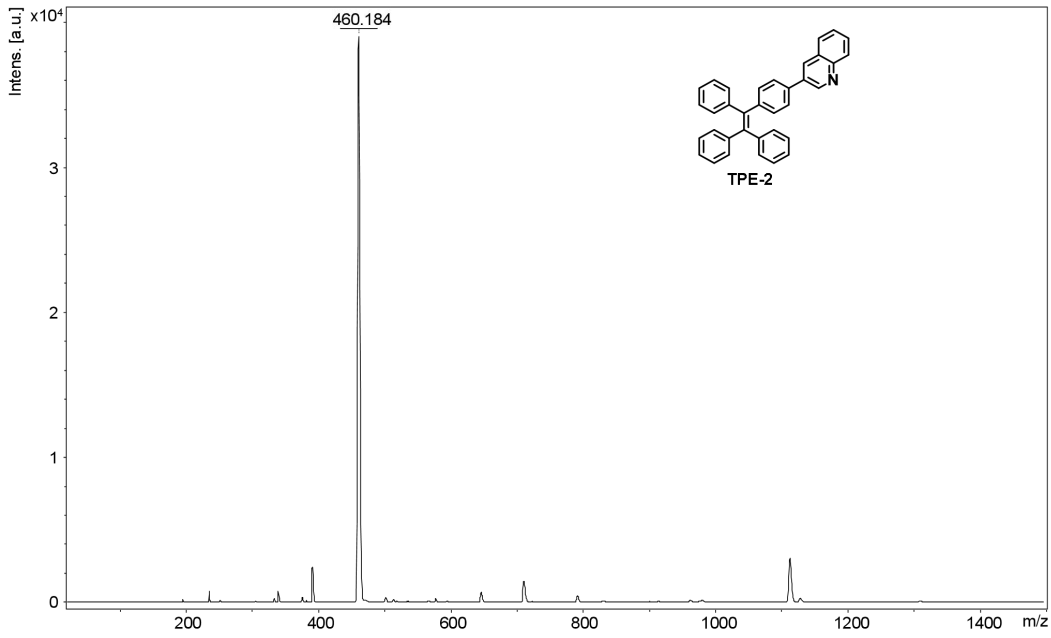
Supplementary Figure 4. MALDI-TOF-MS spectrum of **TPE-1**.



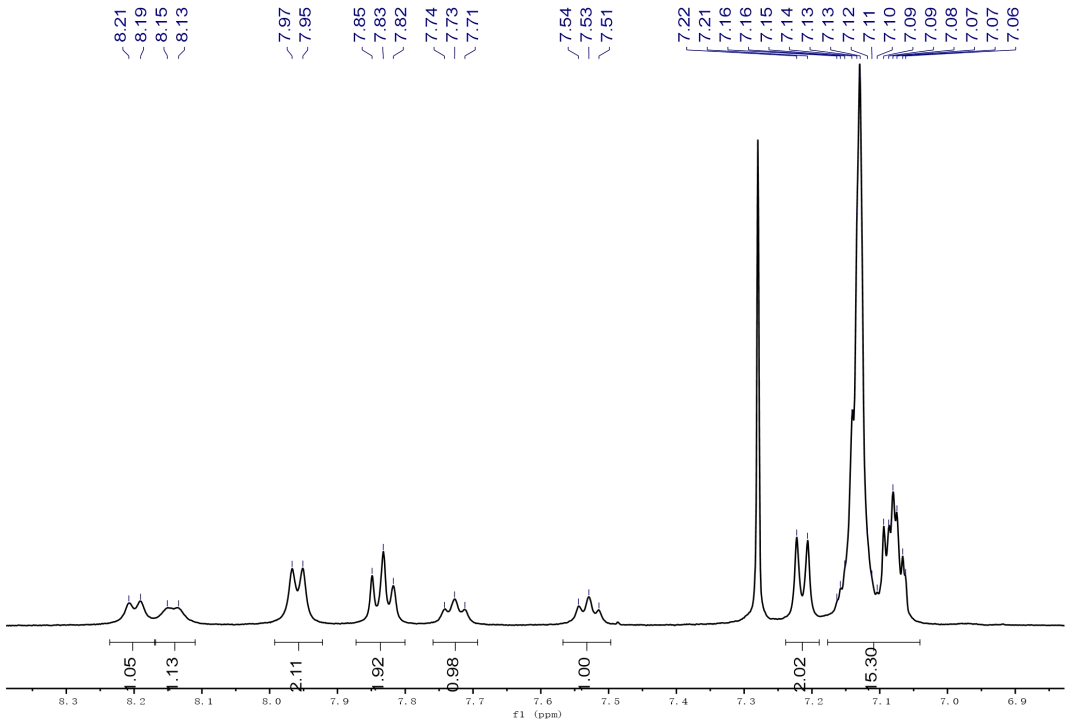
Supplementary Figure 5. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) spectrum of **TPE-2**.



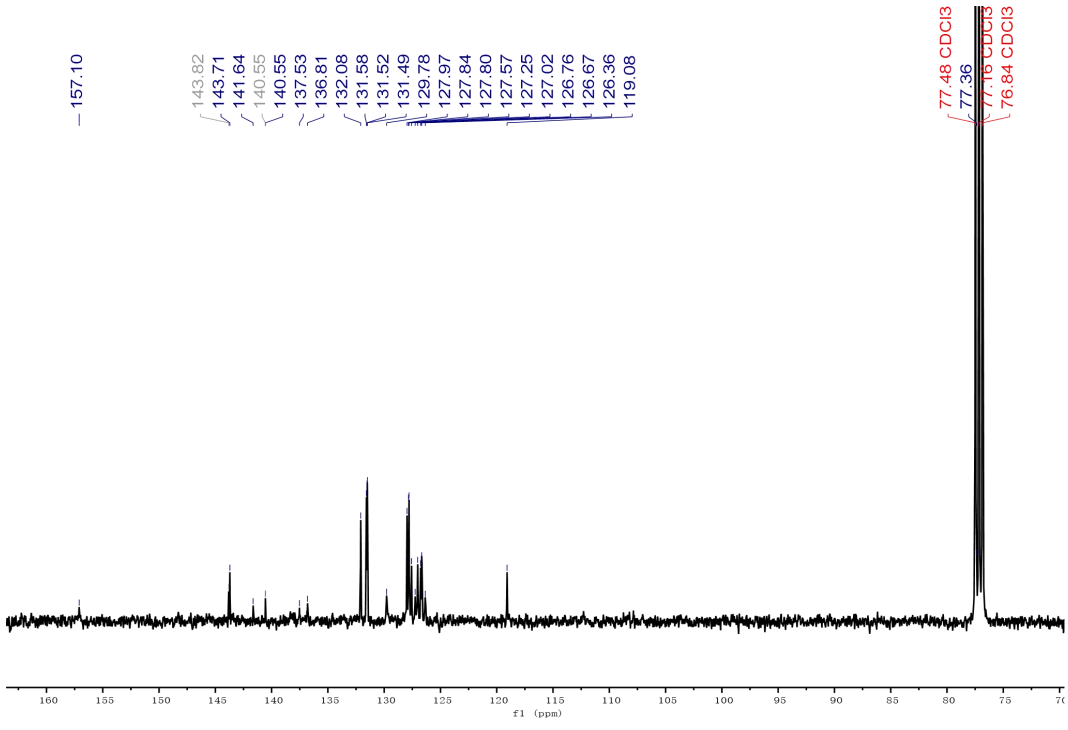
Supplementary Figure 6. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) spectrum of **TPE-2**.



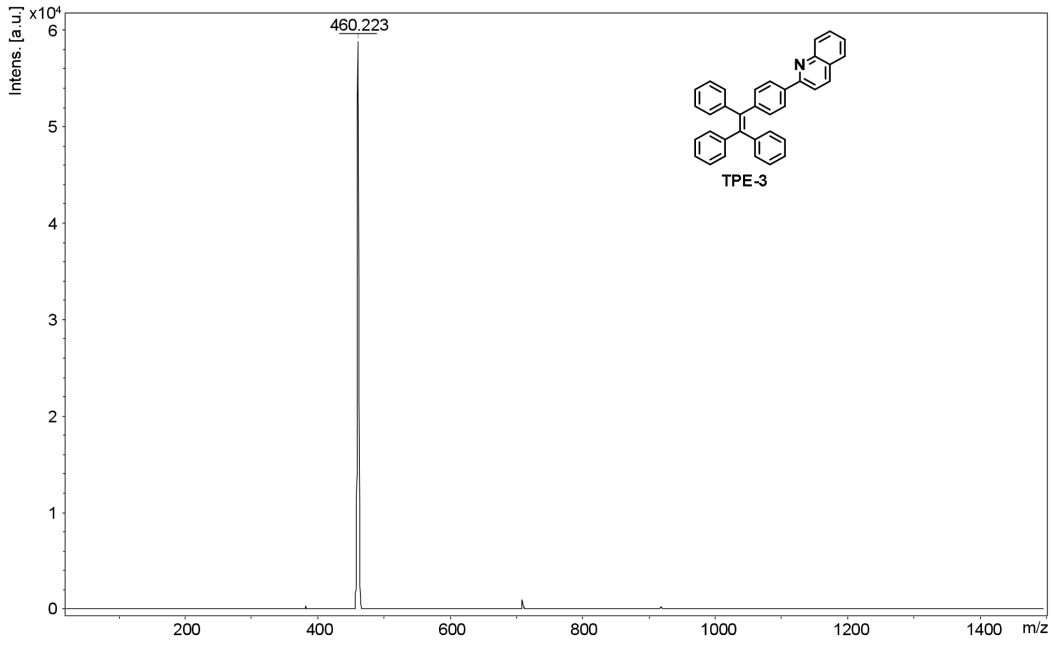
Supplementary Figure 7. MALDI-TOF-MS spectrum of **TPE-2**.



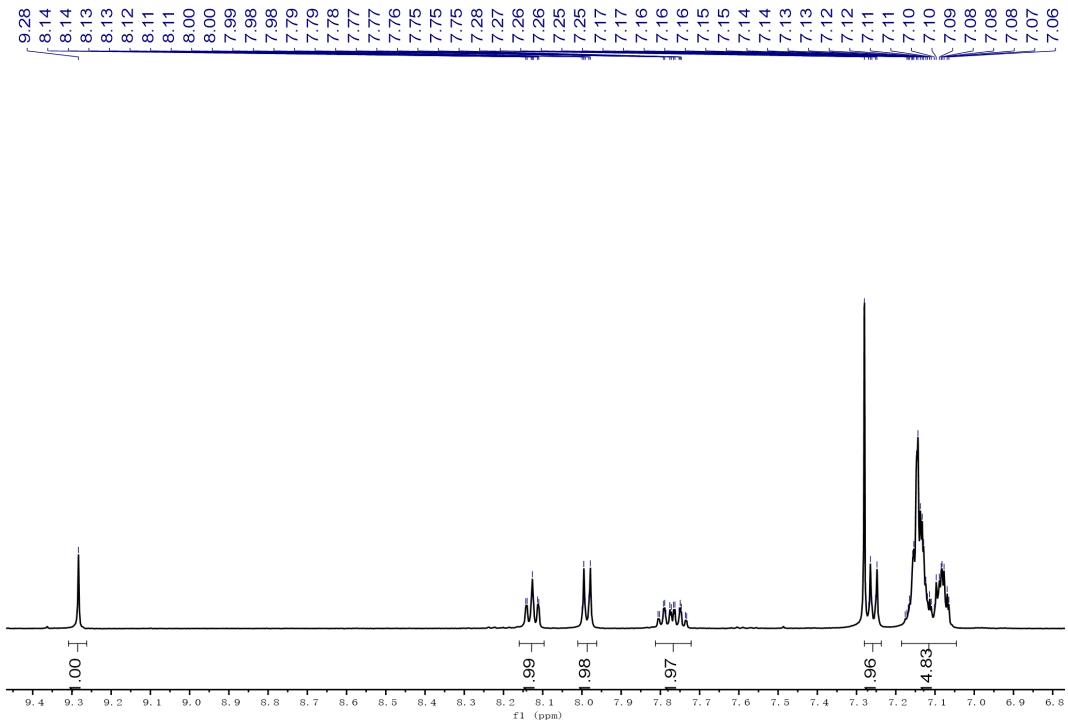
Supplementary Figure 8. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) spectrum of **TPE-3**.



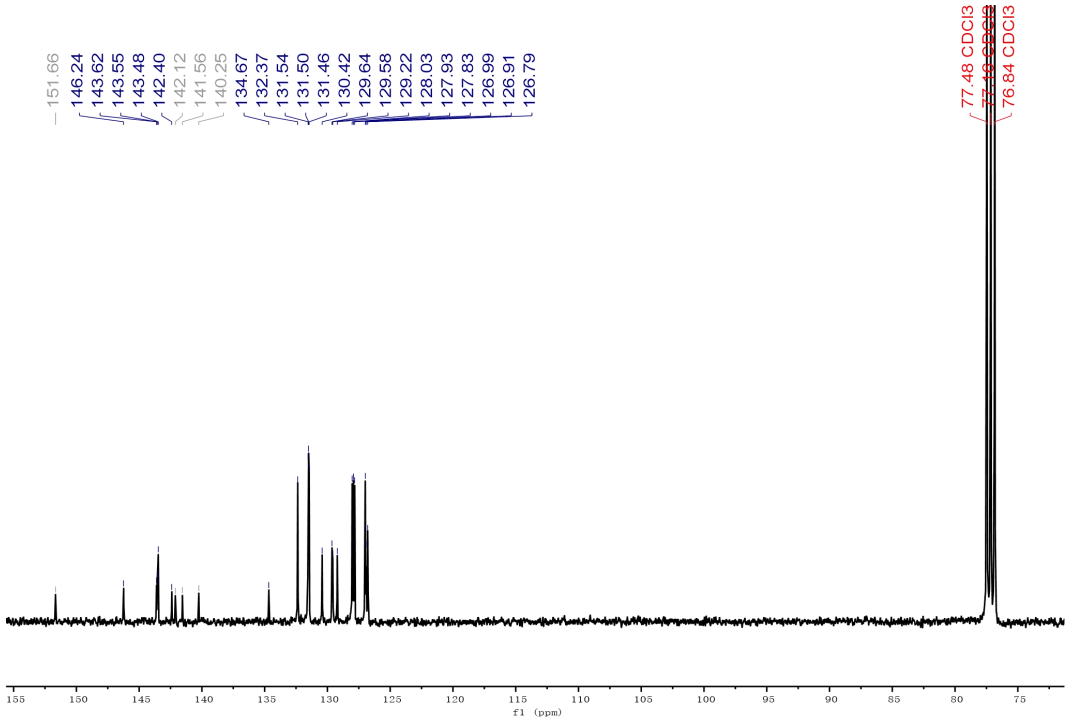
Supplementary Figure 9. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) spectrum of **TPE-3**.



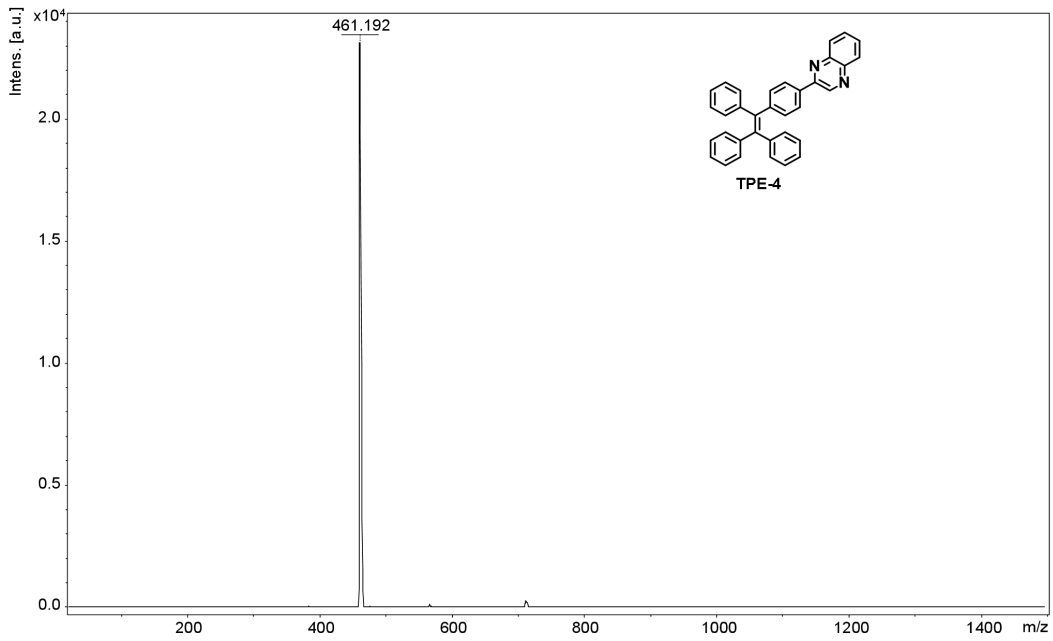
Supplementary Figure 10. MALDI-TOF-MS spectrum of **TPE-3**.



Supplementary Figure 11. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) spectrum of **TPE-4**.

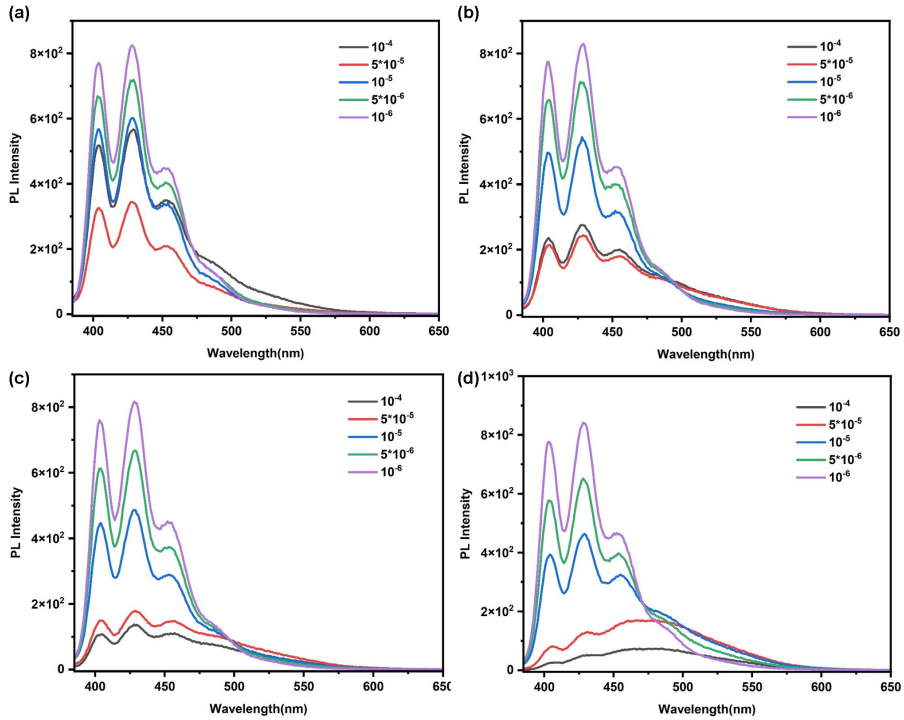


Supplementary Figure 12. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) spectrum of **TPE-4**.

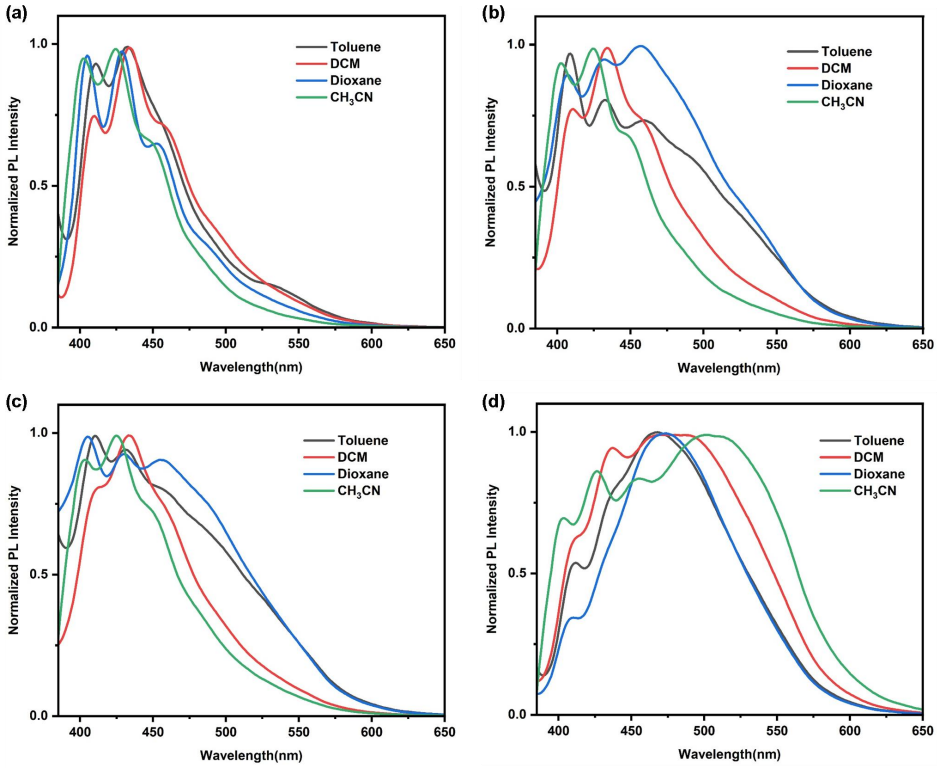


Supplementary Figure 13. MALDI-TOF-MS spectrum of **TPE-4**.

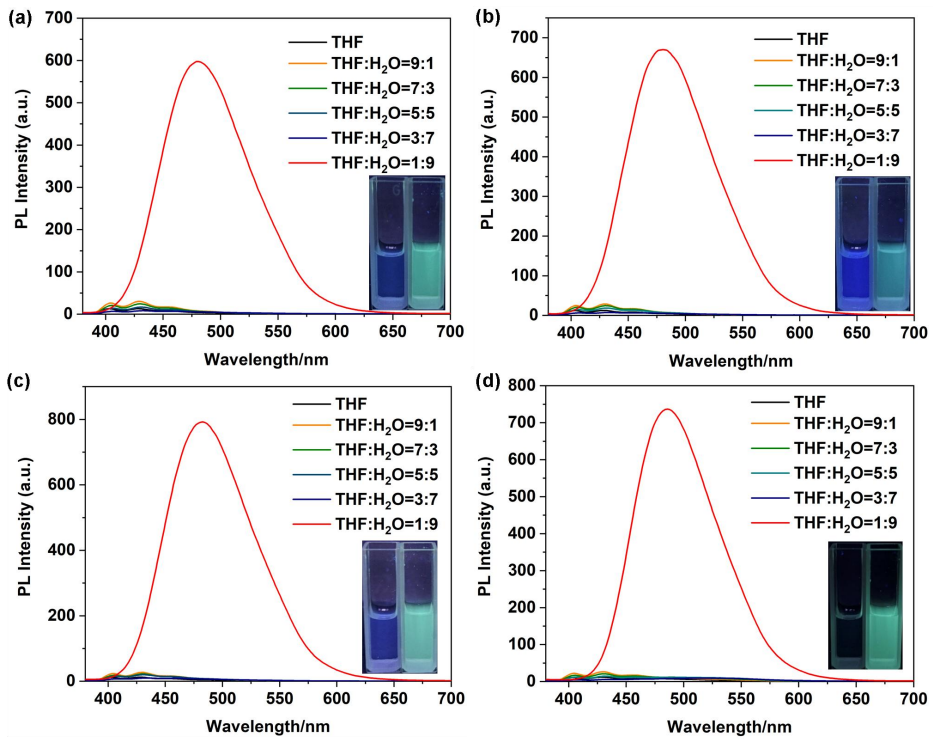
5. The spectra, PXRD, TGA and DSC characterization of TPE-1, TPE-2, TPE-3 and TPE-4



Supplementary Figure 14. The fluorescence spectra of (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3**, and (d) **TPE-4** in THF at different concentrations.

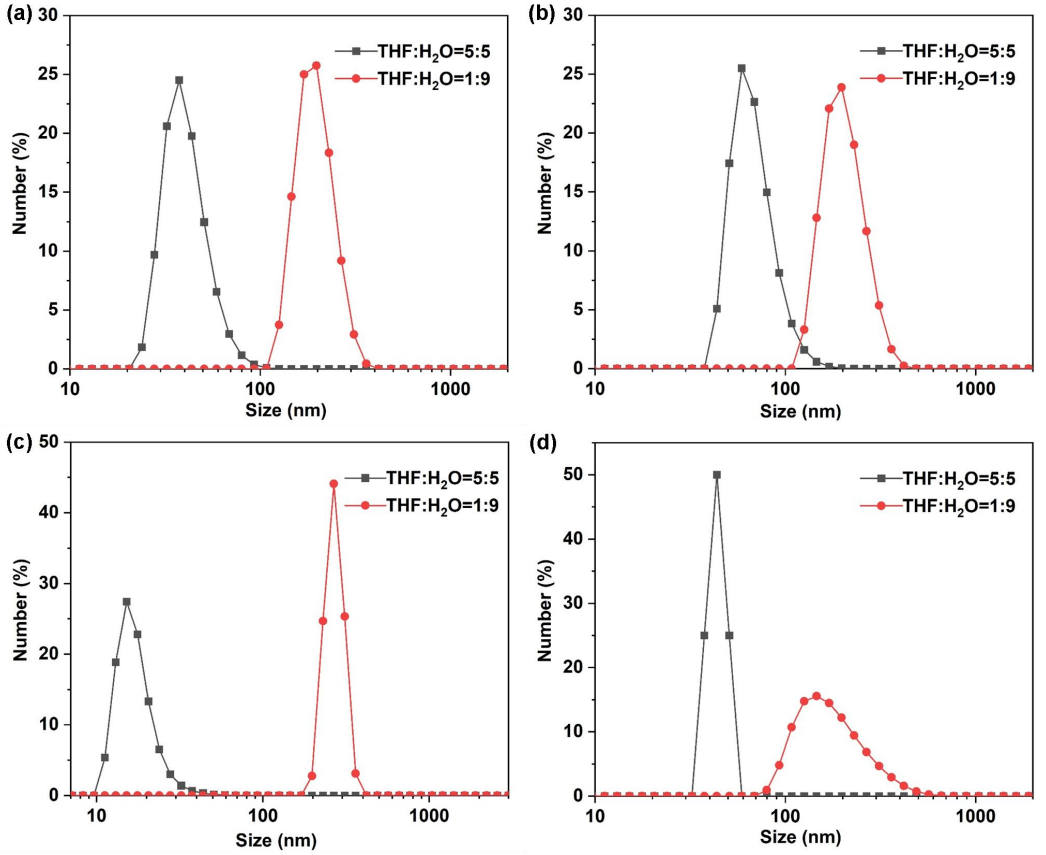


Supplementary Figure 15. The fluorescence spectra of (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3**, and (d) **TPE-4** in different solvents.

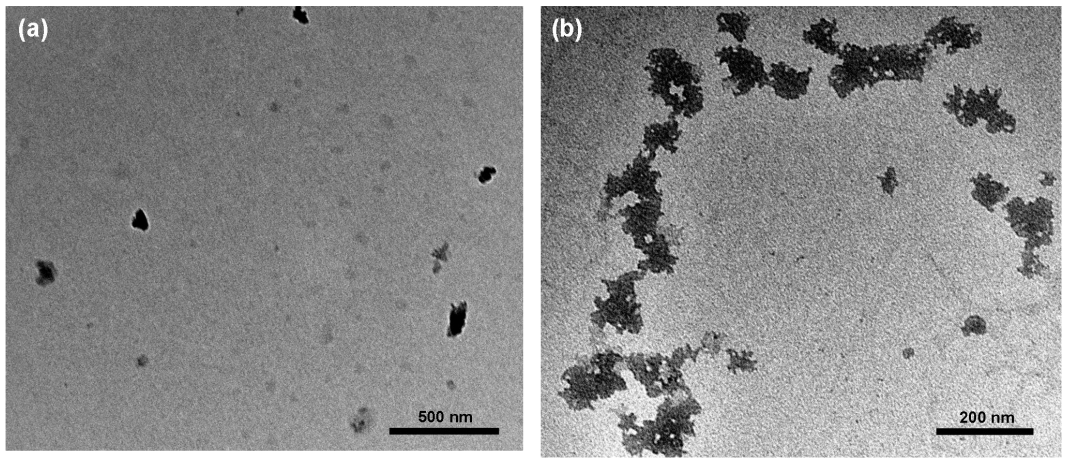


Supplementary Figure 16. The fluorescence emission spectra of (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3** and (d) **TPE-4** in solutions containing poor solvents are shown

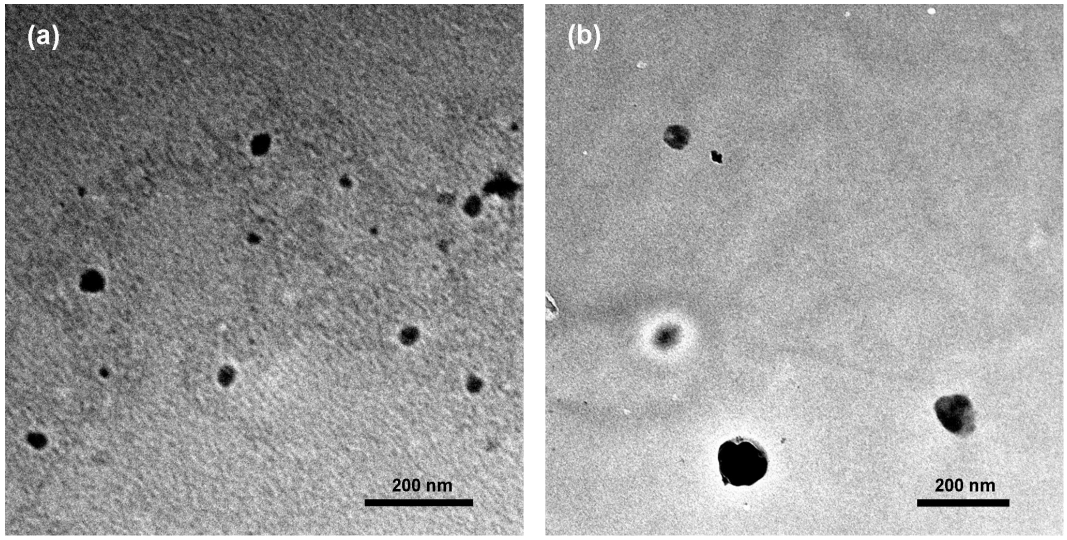
(c=10^{-5} M). The illustrations are the fluorescence images of four compounds in THF (left) and THF:H_2O=1:9 (right).



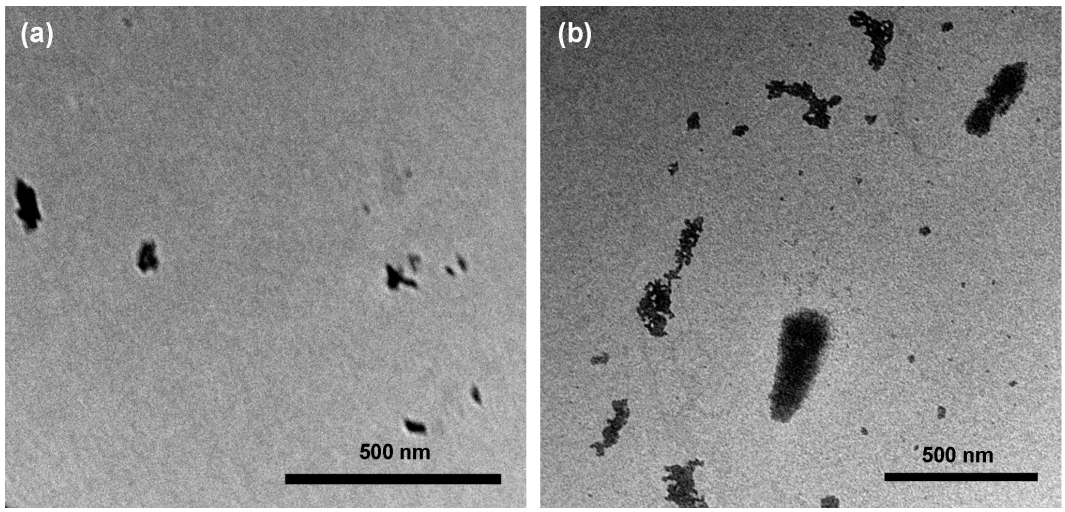
Supplementary Figure 17. Size distributions of (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3** and (d) **TPE-4** in mixed solvent of THF:H_2O =5:5 and THF:H_2O=1:9 (c = 10^{-5} M).



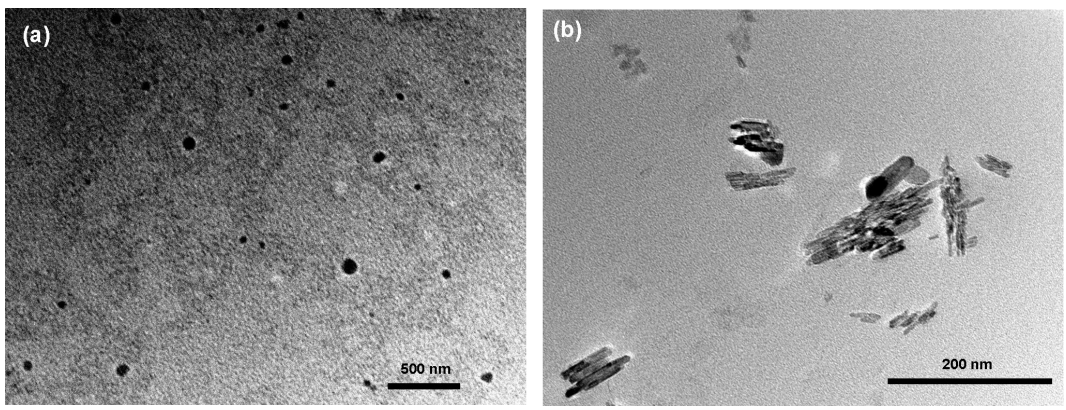
Supplementary Figure 18. TEM images of **TPE-1** in (a) THF:H_2O =5:5 and (b) THF:H_2O=1:9 (c = 10^{-5} M).



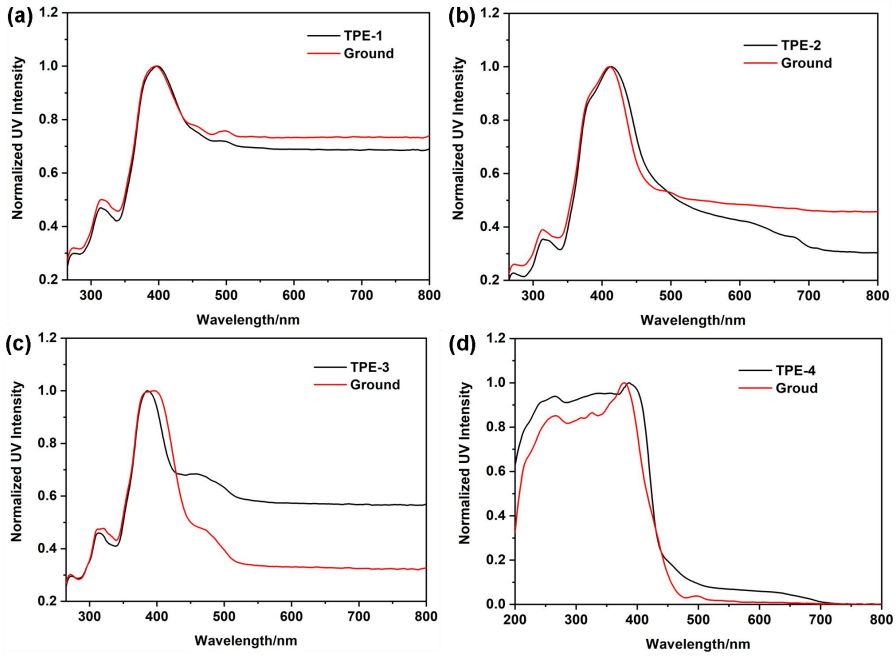
Supplementary Figure 19. TEM images of **TPE-2** in (a) THF:H_2O =5:5 and (b) THF:H_2O=1:9 (c = 10^{-5} M).



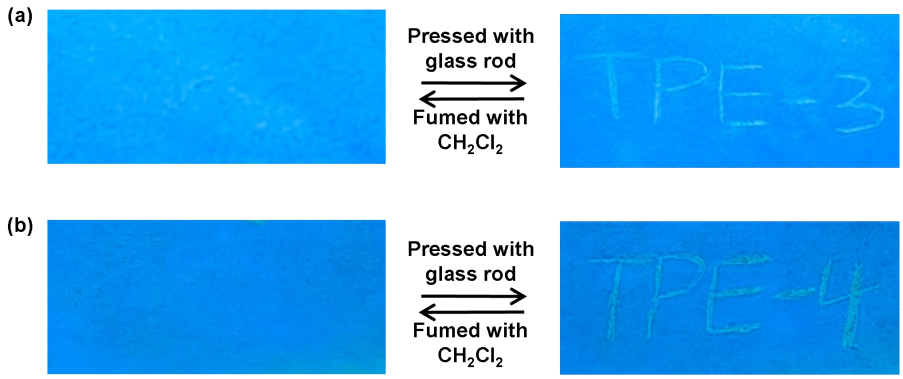
Supplementary Figure 20. TEM images of **TPE-3** in (a) THF:H_2O =5:5 and (b) THF:H_2O=1:9 (c = 10^{-5} M).



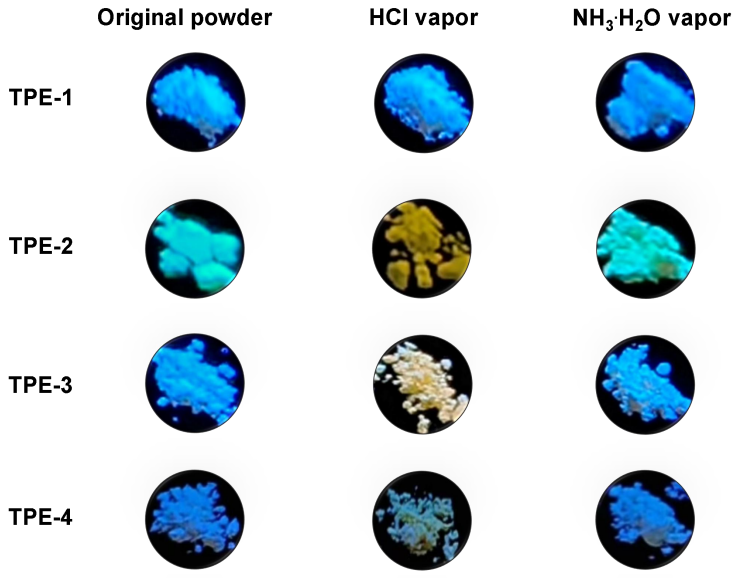
Supplementary Figure 21. TEM images of **TPE-4** in (a) THF:H_2O =5:5 and (b) THF:H_2O=1:9 (c = 10^{-5} M).



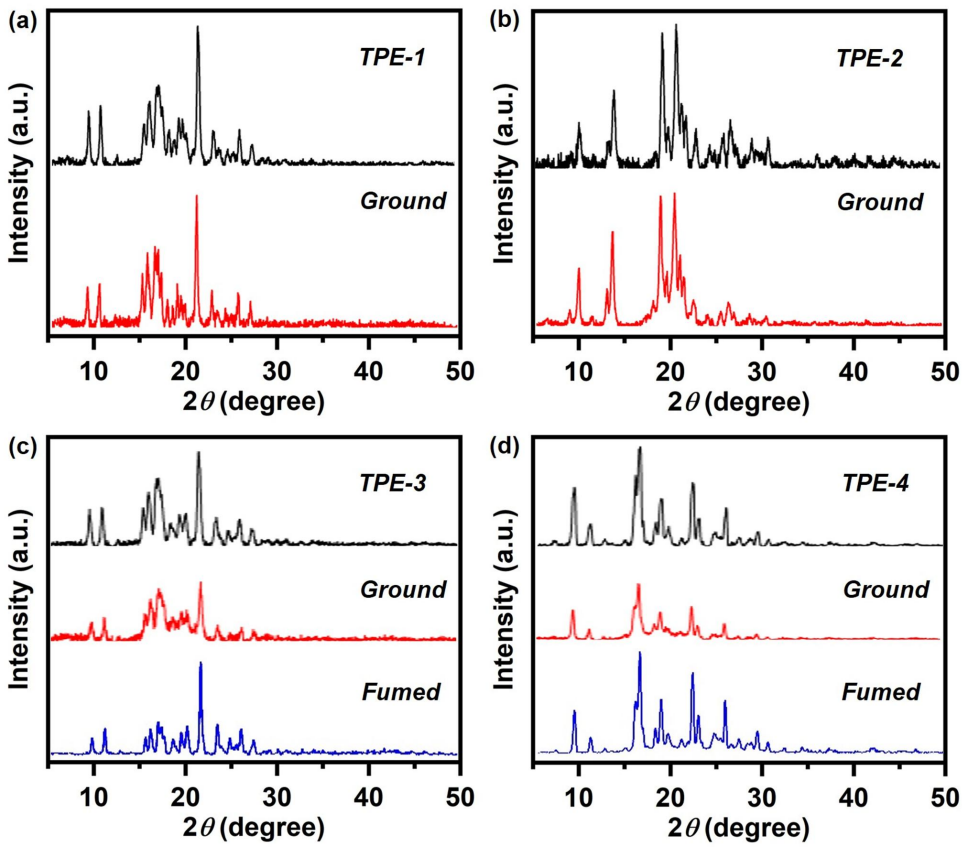
Supplementary Figure 22. Solid-state UV-vis spectra of (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3** and (d) **TPE-4** before and after grinding.



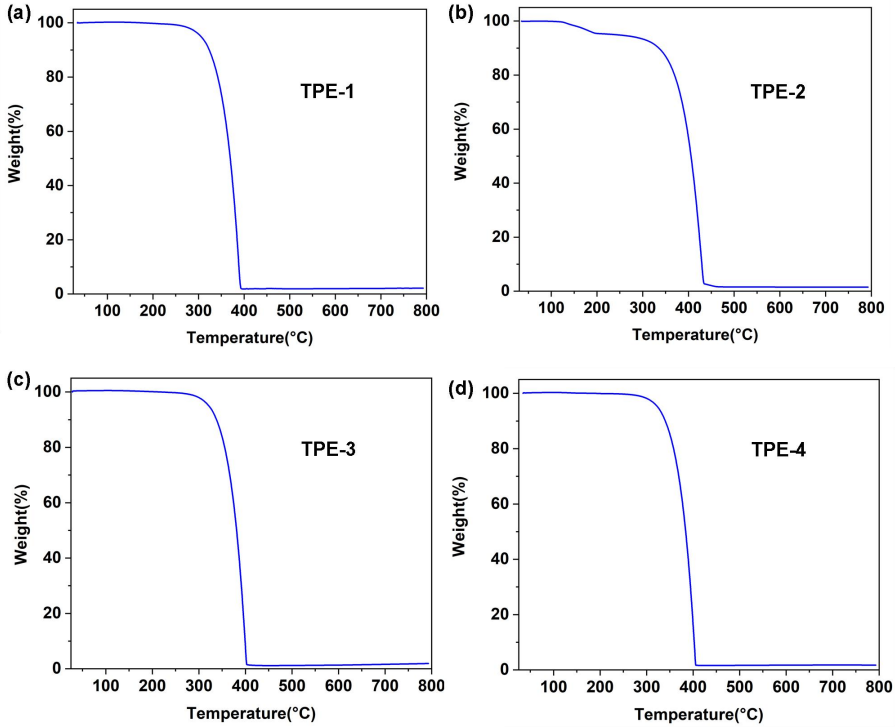
Supplementary Figure 23. The writable MFC material based on (a) **TPE-3** and (b) **TPE-4** (The images are taken under irradiation with a 365 nm UV lamp).



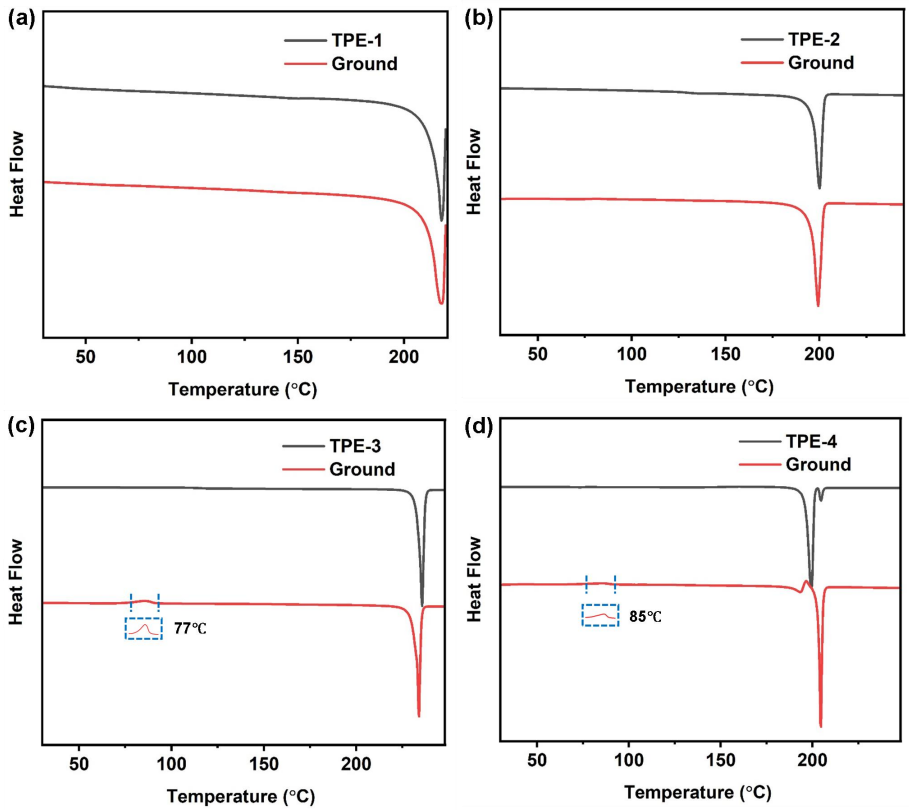
Supplementary Figure 24. Acid-induced fluorescence color change phenomenon of four compounds.



Supplementary Figure 25. The PXRD patterns of (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3** and (d) **TPE-4**.

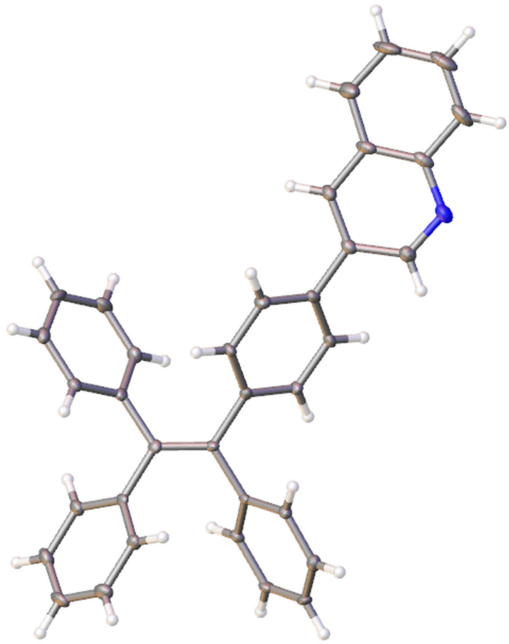


Supplementary Figure 26. TGA curves for (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3** and (d) **TPE-4**.

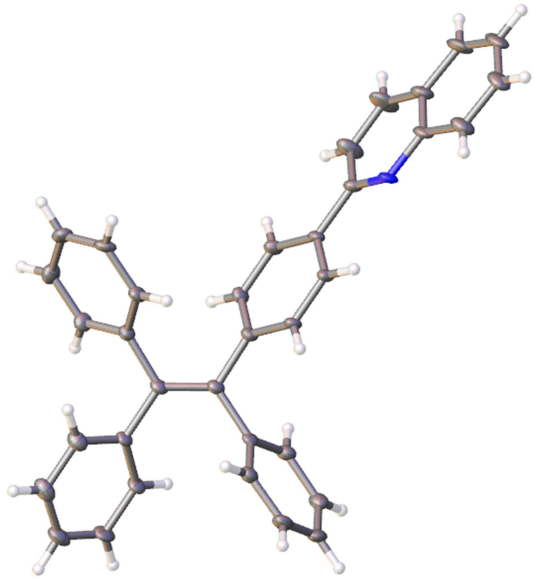


Supplementary Figure 27. DSC curves for (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3**, and (d) **TPE-4**.

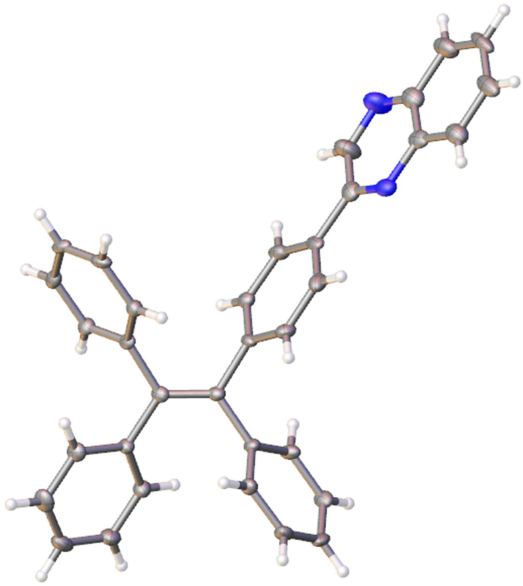
6. X-ray crystallographic data and structures



Supplementary Figure 28. The ORTEP drawing of compound **TPE-2.**



Supplementary Figure 29. The ORTEP drawing of compound **TPE-3.**



Supplementary Figure 30. The ORTEP drawing of compound **TPE-4.**

Supplementary Table 1. Crystal data and structure refinement for TPE-2.

Identification code	**TPE-2**
CCDC number	2349736
Empirical formula	$C_{35}H_{25}N$
Formula weight	459.56
Temperature/K	273.15
Crystal system	Monoclinic
Space group	*P2₁*
a/Å	9.8618(9)
b/Å	9.2134(7)
c/Å	27.026(2)
α/°	90
β/°	98.017(3)
γ/°	90
Volume/Å^3	2431.6(4)
Z	4
ρ_{cal}cg/cm^3	1.255
μ/mm^{-1}	0.072
F(000)	968.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.522 to 54.238
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -34 ≤ l ≤ 34
Reflections collected	28120
Independent reflections	10202 [Rint = 0.0687, Rsigma = 0.0764]
Data/restraints/parameters	10202/1/649
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R1 = 0.0737, wR2 = 0.1865
Final R indexes [all data]	R1 = 0.0788, wR2 = 0.1957
Largest diff. peak/hole / e Å^{-3}	0.51/-0.49
Flack parameter	-0.1(10)

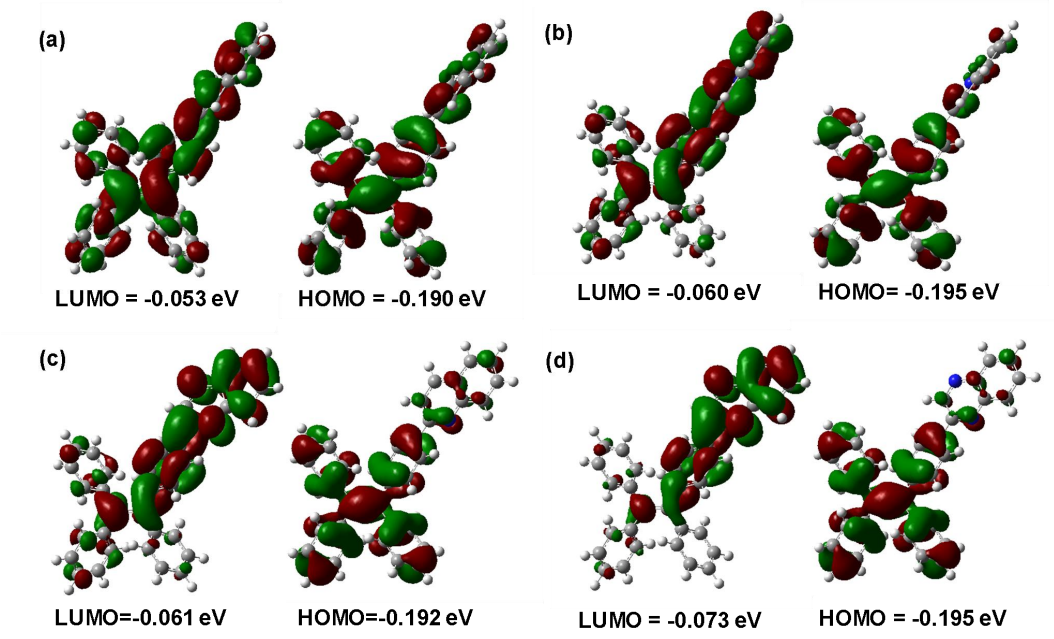
Supplementary Table 2. Crystal data and structure refinement for TPE-3.

Identification code	**TPE-3**
CCDC number	2349738
Empirical formula	$C_{35}H_{25}N$
Formula weight	459.56
Temperature/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.4600(7)
b/Å	11.6938(9)
c/Å	23.7139(18)
α/°	86.877(2)
β/°	81.440(2)
γ/°	71.899(3)
Volume/Å^3	2465.6(3)
Z	4
ρ_{cal}cg/cm^3	1.238
μ/mm^{-1}	0.071
F(000)	968.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.474 to 54.214
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -29 ≤ l ≤ 29
Reflections collected	33934
Independent reflections	9389 [Rint = 0.0618, Rsigma = 0.0598]
Data/restraints/parameters	9389/0/649
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R1 = 0.0907, wR2 = 0.2461
Final R indexes [all data]	R1 = 0.0961, wR2 = 0.2568
Largest diff. peak/hole / e Å^{-3}	0.63/-0.65

Supplementary Table 3. Crystal data and structure refinement for TPE-4.

Identification code	**TPE-4**
CCDC number	2349739
Empirical formula	$C_{34}H_{24}N_2$
Formula weight	460.55
Temperature/K	273.15
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.4072(7)
b/Å	11.6109(9)
c/Å	23.5484(18)
α/°	88.735(3)
β/°	81.569(3)
γ/°	72.635(2)
Volume/Å^3	2427.7(3)
Z	4
ρ_{cal}cg/cm^3	1.260
μ/mm^{-1}	0.073
F(000)	968.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.498 to 54.244
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -30 ≤ l ≤ 30
Reflections collected	34215
Independent reflections	9360 [Rint = 0.0336, Rsigma = 0.0309]
Data/restraints/parameters	9360/0/649
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R1 = 0.0654, wR2 = 0.1877
Final R indexes [all data]	R1 = 0.0784, wR2 = 0.2043
Largest diff. peak/hole / e Å^{-3}	1.17/-0.45

7. Frontier molecular orbitals for TPE-1, TPE-2, TPE-3 and TPE-4



Supplementary Figure 31. Calculated frontier molecular orbitals of (a) **TPE-1**, (b) **TPE-2**, (c) **TPE-3** and (d) **TPE-4**.