Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplementary Information

From simple Katritzky salts to AIEgens: mechanochromic luminescence and heparin detection

Faxu Lin,[ab] Yang Feng,[a] Xiaoqing Liu,[c] Lei Wang,[a] Zhen-Qiang Yu,[bd] Yi Liu[*ad]

[a] *Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China. E-mail: liuyiacee@szu.edu.cn.*

[b] *School of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China.*

[c] *Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen 518005, China*

[d] *Centre for AIE Research, Shenzhen University, Shenzhen 518060, China.*

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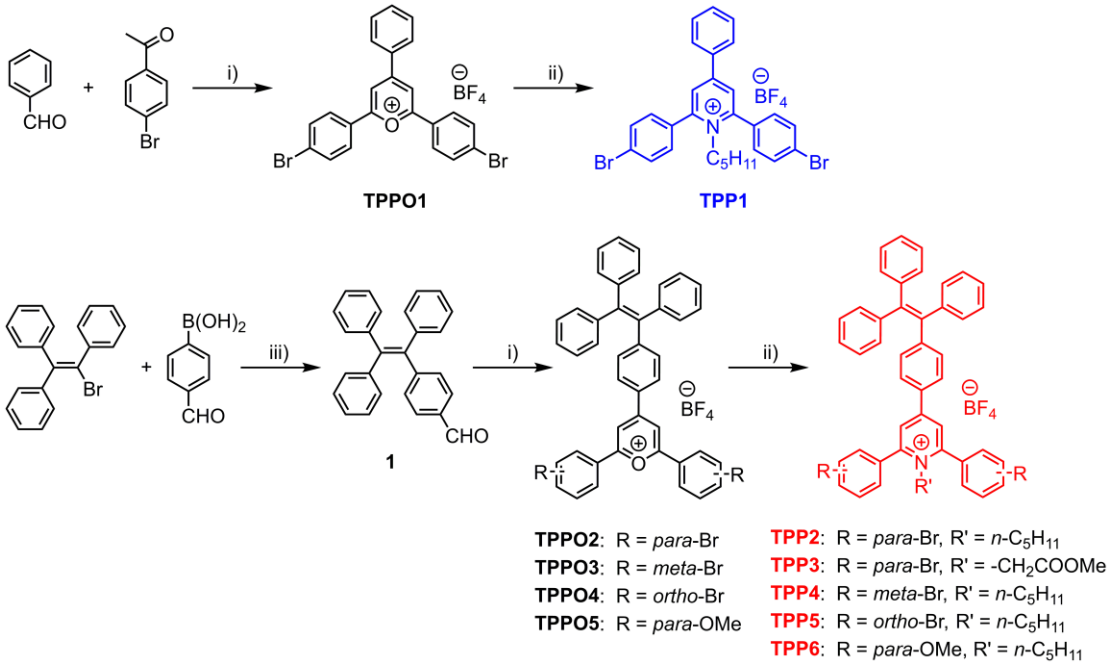
1. General materials

Materials: 1-(4-Bromophenyl)ethan-1-one, boron trifluoride diethyl etherate, benzaldehyde, (2-bromoethene-1,1,2-triyl)tribenzene, K_2CO_3, tetrahydrofuran, ethanol, (4-formylphenyl)boronic acid, tetrakis(triphenylphosphine)palladium, toluene, diethyl ether, 1-pentylamine, glycine methyl ester hydrochloride, triethylamine, 1-(3-bromophenyl)ethan-1-one, 1-(2-bromophenyl)ethan-1-one, 1-(4-methoxyphenyl)ethan-1-one, ferrocene, tetrabutylammonium hexafluorophosphate, heparin (Hep), chondroitin 4-sulfate (Chs), and hyaluronic acid (HA) were all purchased from Energy Chemical (Shanghai, China). All these materials are analytical grade and used as received.

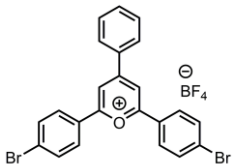
Characterizations and instruments: ^{1}H,^{13}C NMR spectra, 2D ^{1}H-^{1}H correlation spectroscopy (COSY) and nuclear overhauser effect spectroscopy (NOESY) were measured on a Bruker AVANCE Ⅲ 500MHZ or 600MHZ spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal standard. Electrospray ionization (ESI) mass spectra (ESI-MS) were recorded on a TRIPLETOF 6600+ mass spectrometer. Absorption spectra were taken on a Thermo-fisher Evolution 220 spectrometer. Emission spectra were taken on a Thermo Lumina Fluorescent spectrometer. The fluorescence quantum yield (QY) data have been measured by Hamamatsu Absolute PL quantum yield spectrometer C11347. The sizes of the nanoaggregates were measured with dynamic light scattering (ZetasizerNano ZSP, Malvern Instruments, Malvern, UK). Powder XRD patterns were recorded on a RigakuSmartLab X-ray Diffractometer. Electrochemical properties was measured on a CHI 660E electrochemical workstation.

2. Synthetic procedures



Scheme S1. Synthetic routes toward cationic AIEgens. Condition: i) BF_3-Et_2O, toluene, acetonphenone, 80 ℃; ii) 1-Aminopentane, EtOH, or glycine methyl ester hydrochloride, triethylamine, EtOH, 80 ℃; iii) $Pd(PPh_3)_4$, K_2CO_3, THF/EtOH/H_2O, 80 ℃.

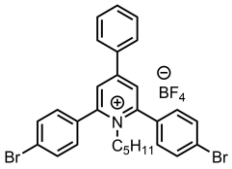
2,6-bis(4-bromophenyl)-4-phenylpyrylium tetrafluoroborate (TPPO1)



TPPO1

To a flask containing 1-(4-bromophenyl)ethan-1-one (2.1 eq, 1.97 g, 9.9 mmol) was added benzaldehyde (1.0 eq, 500 mg, 4.71 mmol) and BF_3-Et_2O (10 ml) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask with vigorous stirring to precipitate the desired pyrylium salt. After filtration and thoroughly washing with Et_2O, 1.20 g of the title compound was obtained as a red solid (46.0% yield). This compound was used directly in the next step without further characterization and purification.

2,6-bis(4-bromophenyl)-1-pentyl-4-phenylpyridin-1-ium tetrafluoroborate (TPP1)



TPP1

To a flask containing TPPO1 (1.0 eq, 50 mg, 0.09 mmol) was added 1-pentylamine (1.3 eq, 10.3 mg, 0.12 mmol) and EtOH (15 ml) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask to precipitate the desired pyridinum salt. After filtration and thoroughly washing with Et_2O, 39 mg of the title compound was obtained as a white solid (69% yield). ESI-MS m/z: $[TPP1\text{-}BF_4]^+$ calcd. for $C_{28}H_{26}Br_2N$: 536.0427. Found: 536.0410. ^1H NMR (500 MHz, DMSO-d_6) δ8.50 (s, 2H), 8.24 (d,J = 7.1 Hz, 2H), 7.95 (d,J = 8.4 Hz, 4H), 7.80 (d,J = 8.4 Hz, 4H), 7.69 – 7.60 (m, 3H),4.27 (t,J = 7.9 Hz, 2H), 1.36 (m, 2H), 0.84 – 0.77 (m, 2H), 0.75 – 0.68 (m, 2H), 0.56 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 132.57 , 132.52 , 131.84 , 130.08 , 129.12 , 126.79 , 125.25 , 54.87, 28.68 , 27.81 , 21.13 , 13.65.

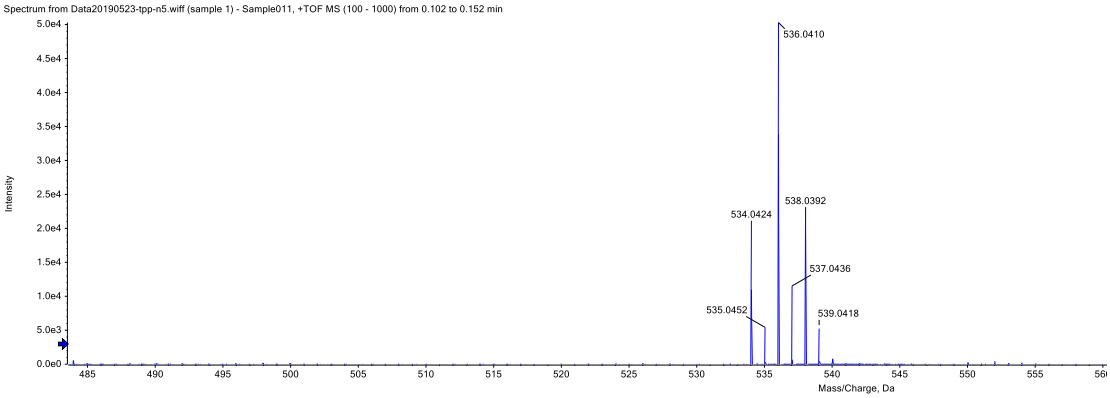
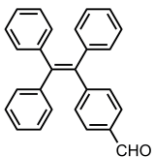


Figure S1 ESI mass spectrum of cationic AIEgen TPP1.

4-(1,2,2-triphenylvinyl)benzaldehyde(1)

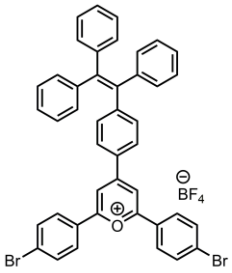


1

Into a two-necked 250 mL round-bottom flask, was added K_2CO_3 (3.0 eq, 2.47 g, 17.9 mmol), (2-bromoethene-1,1,2-triyl)tribenzene (1.0 eq, 2.00 g, 5.97 mmol), (4-formylphenyl)boronic acid (1.1 eq, 0.98 g, 6.56 mmol), and $Pd(PPh_3)_4$ (0.03 eq, 344 mg, 0.29 mmol). The flask was evacuated and refilled with Argon gas for three times, followed by the addition of degassed

THF/EtOH/H_2O mixture (80mL / 10mL / 10 mL). The mixture was then heated to 80 ℃ and kept refluxing with stirring overnight. After cooling to room temperature, the reaction mixture was extracted with dichloromethane (3 × 100 mL), and the combined organic layers were dried in vacuum. After evaporating the solvent, the crude product was purified via silica gel column chromatography with DCM/petroleum ether = 1/5 as eluent to obtain 2.0 g of the title compound as a yellow solid (93% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.90 (s, 1H), 7.62 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 7.13 (q, J = 3.6 Hz, 9H), 7.02 (dd, J = 7.5, 4.2 Hz, 6H).

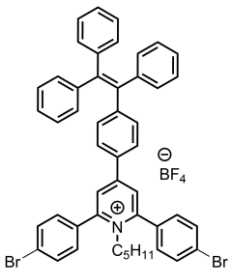
2,6-bis(4-bromophenyl)-4-(4-(1,2,2-triphenylvinyl)phenyl)pyrylium tetrafluoroborate (TPPO2)



TPPO2

To a flask containing 1-(4-bromophenyl)ethan-1-one (2.5 eq, 1.10 g, 5.55 mmol) was added 4-(1,2,2-triphenylvinyl)benzaldehyde (**1**, 1.0 eq, 800 mg, 2.22 mmol), anhydrous toluene (5 ml), and BF_3-Et_2O (1.5 eq, 0.47 ml, 3.33 mmol) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask with vigorous stirring to precipitate the desired pyrylium salt. After filtration and thoroughly washing with Et_2O, 800 mg of the title compound was obtained as a red solid (45% yield). This compound was used directly in the next step without further characterization and purification.

2,6-bis(4-bromophenyl)-1-pentyl-4-(4-(1,2,2-triphenylvinyl)phenyl)pyridin-1-ium tetrafluoroborate (TPP2)



TPP2

To a flask containing TPPO2 (1.0 eq, 50 mg, 0.06 mmol) was added 1-pentylamine (1.2 eq, 6.6 mg, 0.12 mmol) and EtOH (15 ml) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask to precipitate the desired pyridinum salt. After filtration and thoroughly washing with Et_2O, 50 mg of the title compound was obtained as a yellow solid (92% yield). ESI-MS m/z: $[TPP2\text{-}BF_4]^+$ calcd. for $C_{48}H_{40}Br_2N$: 790.1502. Found: 790.1523. ^1H NMR (500 MHz, DMSO-d_6) δ 8.42 (s, 2H), 8.07 (d,J = 6.7 Hz, 2H), 7.93 (d,J = 8.5 Hz ,4H), 7.78 (d,J = 8.5 Hz 4H), 7.19 – 7.13 (m, 11H), 7.02 (m, 6H), 4.25 (t,J = 7.8 Hz, 2H), 1.33 (dq, J = 12.7, 7.4 Hz, 2H), 0.85 – 0.70 (m, 4H), 0.56 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ155.22 , 153.56 , 148.28 , 143.19 , 143.13 , 142.92 , 142.83 , 139.86 , 132.53 , 132.26 , 131.83 , 131.15 , 131.12 , 131.04 , 131.03 , 128.58 , 128.52 , 128.47 , 128.34 , 127.51 , 127.39 , 126.23 , 125.21 , 54.76 , 28.68 , 27.77 , 21.13 , 13.64.

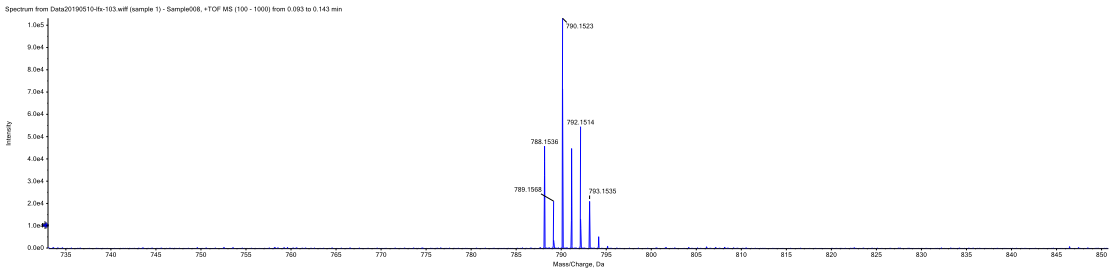
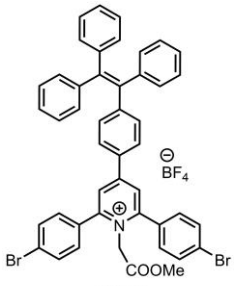


Figure S2 ESI mass spectrum of cationic AIEgen TPP2.

2,6-bis(4-bromophenyl)-1-(2-methoxy-2-oxoethyl)-4-(4-(1,2,2-triphenylvinyl)phenyl)pyridin-1-ium tetrafluoroborate (TPP3)



TPP3

To a flask containing glycine methyl ester hydrochloride (1.1 eq, 8.7 mg, 0.07 mmol) was added triethylamine (1.1 eq, 7.0 mg, 0.07 mmol) and EtOH (5 ml). After keeping stirring the mixture for 30minutes, the mixture was added into a flask containing TPPO2 (1.0 eq, 50 mg, 0.06 mmol)

under Argon atmosphere following with the addition of EtOH (10 ml). The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask to precipitate the desired pyridinum salt. After filtration and thoroughly washing with Et_2O, 47 mg of the title compound was obtained as a yellow solid (86% yield). ESI-MS m/z: $[TPP3\text{-}BF_4]^+$ calcd. for $C_{48}H_{40}Br_2N$: 792.0930. Found: 792.0936. ^1H NMR (500 MHz, DMSO-d_6) δ 8.53 (s, 2H), 8.07 (d,J = 8.6 Hz, 2H), 7.91 (d,J = 7.4 Hz, 4H), 7.63 (d, J = 8.2 Hz, 4H), 7.21 – 7.13 (m, 11H), 7.07 – 6.98 (m, 6H), 5.18 (d, J = 5.0 Hz, 2H), 3.47 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.49 , 160.67 ,153.50 ,147.89 , 144.57 , 137.50 , 137.39 , 136.63 , 135.88 , 133.71 , 133.27 , 132.15 , 130.48 , 61.53, 58.48.

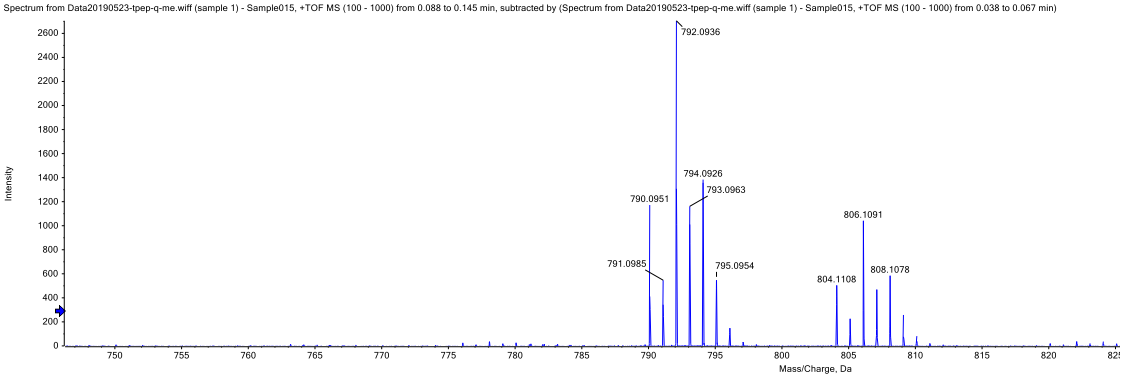
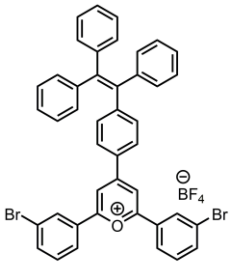


Figure S3 ESI mass spectrum of cationic AIEgen TPP3.

2,6-bis(3-bromophenyl)-4-(4-(1,2,2-triphenylvinyl)phenyl)pyrylium tetrafluoroborate (TPPO3)

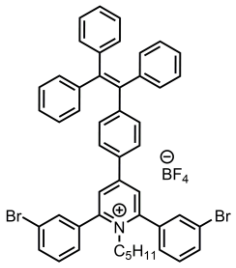


TPPO3

To a flask containing 1-(3-bromophenyl)ethan-1-one (2.2 eq, 607 mg, 3.05 mmol) was added 4-(1,2,2-triphenylvinyl)benzaldehyde (**1**, 1.0 eq, 500 mg, 1.39 mmol), anhydrous toluene (5 ml), and BF_3-Et_2O (1.5 eq, 0.26 ml, 2.08 mmol) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask with vigorous stirring to precipitate the desired pyrylium salt. After filtration and thoroughly washing with Et_2O, 430 mg of the title compound was

obtained as a red solid (38% yield). This compound was used directly in the next step without further characterization and purification.

2,6-bis(3-bromophenyl)-1-pentyl-4-(4-(1,2,2-triphenylvinyl)phenyl)pyridin-1-ium tetrafluoroborate (TPP4)



TPP4

To a flask containing TPPO3 (1.0 eq, 50 mg, 0.06 mmol) was added 1-pentylamine (1.2 eq, 6.6 mg, 0.12 mmol) and EtOH (15 ml) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask to precipitate the desired pyridinum salt. After filtration and thoroughly washing with Et_2O, 45 mg of the title compound was obtained as a yellow solid (83% yield). ESI-MS m/z: $[TPP4\text{-}BF_4]^+$ calcd. for $C_{48}H_{40}Br_2N$: 790.1502. Found: 790.1490. ^1H NMR (500 MHz, DMSO-d_6) δ 8.46 (s, 2H), 8.11 – 8.06 (m, 4H), 7.92 (d, J = 8.1 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.66 (t, J = 7.9 Hz, 2H), 7.20 – 7.12 (m, 10H), 7.06 – 6.98 (m, 6H) , 4.24 (s, 2H), 1.36 (t, J = 7.7 Hz, 2H), , 0.83 – 0.72 (m, 4H), 0.58 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 154.46 , 142.84 , 135.26 , 134.25 , 132.26 , 131.62 , 131.15 , 131.12 , 131.03 , 128.80 , 128.66 , 128.52 , 128.48 , 128.34 , 127.40 , 126.44 , 122.54 , 54.88, 28.79 , 27.76 , 21.12 , 13.65.

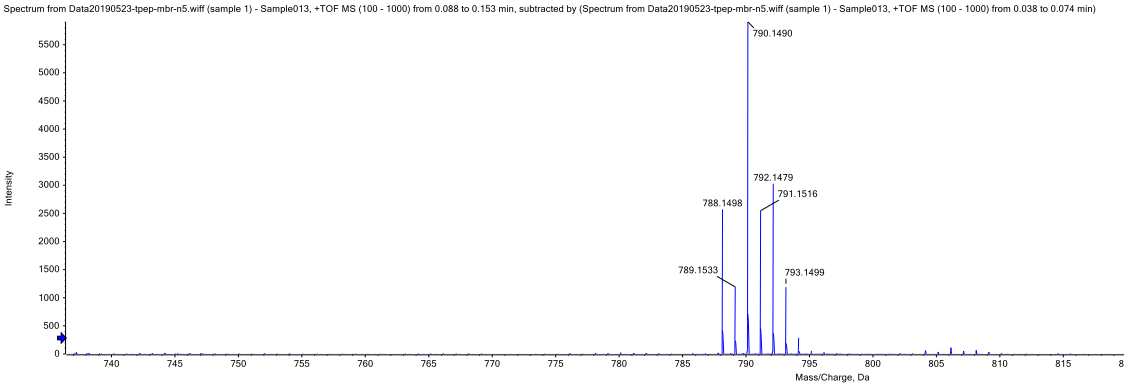
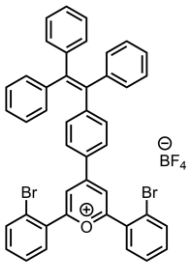


Figure S4 ESI mass spectrum of cationic AIEgen TPP4.

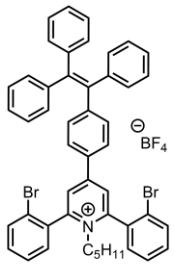
2,6-bis(2-bromophenyl)-4-(4-(1,2,2-triphenylvinyl)phenyl)pyrylium tetrafluoroborate (TPPO4)



TPPO4

To a flask containing 1-(2-bromophenyl)ethan-1-one (2.2 eq, 607 mg, 3.05 mmol) was added 4-(1,2,2-triphenylvinyl)benzaldehyde (**1**, 1.0 eq, 500 mg, 1.39 mmol), anhydrous toluene (5 ml), and BF_3-Et_2O (1.0 eq, 0.18 ml, 1.39 mmol) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask with vigorous stirring to precipitate the desired pyrylium salt. After filtration and thoroughly washing with Et_2O, 213 mg of the title compound was obtained as a red solid (19% yield). This compound was used directly in the next step without further characterization and purification.

2,6-bis(2-bromophenyl)-1-pentyl-4-(4-(1,2,2-triphenylvinyl)phenyl)pyridin-1-ium tetrafluoroborate (TPP5)



TPP5

To a flask containing TPPO4 (1.0 eq, 50 mg, 0.06 mmol) was added 1-pentylamine (1.1 eq, 6.0 mg, 0.069 mmol) and EtOH (15 ml) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask to precipitate the desired pyridinum salt. After filtration and thoroughly washing with Et_2O, 36 mg of the title compound was obtained as a yellow solid (66% yield). ESI-MS m/z: $[TPP5\text{-}BF_4]^+$ calcd. for $C_{48}H_{40}Br_2N$: 790.1502. Found: 790.1503. ^1H NMR (500 MHz, DMSO-d_6) δ8.65 (s, 2H), 8.12 (d, J = 8.6, 3H), 7.98 (dd, J = 8.1, 1.1 Hz, 2H), 7.83 (dd,

J = 7.6, 1.7 Hz, 2H), 7.74 (td, J = 7.6, 1.2 Hz, 2H), 7.67 (td, J = 7.8, 1.7 Hz, 2H), 7.20 – 7.13 (m, 12H), 7.05 – 6.99 (m, 7H), 3.97 – 3.93 (m, 2H), 1.50 – 1.46 (m, 2H), 0.89 – 0.82 (m, 2H), 0.77 – 0.69 (m, 5H), 0.56 – 0.52 (m, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ154.89 , 154.57 , 143.16 , 143.10 , 142.95 , 139.79 , 133.62 , 133.52 , 132.41 , 132.17 , 131.17 , 131.15 , 131.04 , 128.92 , 128.66 , 128.51 , 128.49 , 128.35 , 127.57 , 127.42 , 126.79 , 122.48 , 54.55 , 29.46 , 28.77 , 27.95 , 20.94 , 13.67.

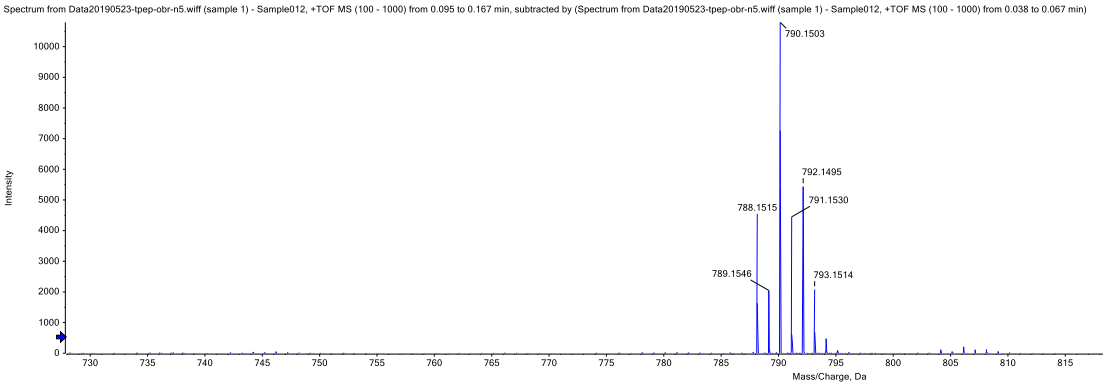
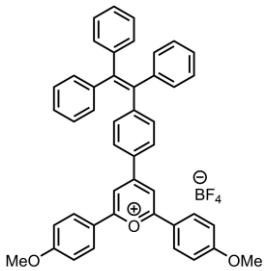


Figure S5 ESI mass spectrum of cationic AIEgen TPP5.

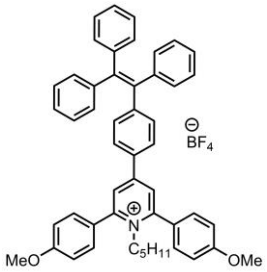
2,6-bis(4-methoxyphenyl)-4-(4-(1,2,2-triphenylvinyl)phenyl)pyrylium tetrafluoroborate (TPPO5)



TPPO5

To a flask containing 1-(4-methoxyphenyl)ethan-1-one (2.2 eq, 458 mg, 3.05 mmol) was added 4-(1,2,2-triphenylvinyl)benzaldehyde (**1**, 1.0 eq, 500 mg, 1.39 mmol), anhydrous toluene (5 ml), and BF_3-Et_2O (1.5 eq, 0.26 ml, 2.08 mmol) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask with vigorous stirring to precipitate the desired pyrylium salt. After filtration and thoroughly washing with Et_2O, 490 mg of the title compound was obtained as a red solid (50% yield). This compound was used directly in the next step without further characterization and purification.

2,6-bis(4-methoxyphenyl)-1-pentyl-4-(4-(1,2,2-triphenylvinyl)phenyl)pyridin-1-ium tetrafluoroborate (TPP6)



TPP6

To a flask containing TPPO5 (1.0 eq, 93 mg, 0.13 mmol) was added 1-pentylamine (1.1 eq, 13.0 mg, 0.15 mmol) and EtOH (15 ml) under Argon atmosphere. The reaction mixture was heated to 80 ℃ with vigorous stirring overnight. After cooling the mixture to room temperature, 50 mL of Et_2O was added into the flask to precipitate the desired pyridinum salt. After filtration and thoroughly washing with Et_2O, 100 mg of the title compound was obtained as a yellow solid (98% yield). ESI-MS m/z: $[TPP6\text{-}BF_4]^+$ calcd. for $C_{48}H_{40}Br_2N$: 692.3523. Found: 692.3535. ^1H NMR (500 MHz, DMSO-d_6) δ8.27 (s, 2H), 8.05 (d, J = 8.6 Hz, 2H), 7.78 (d,J = 8.7 Hz 4H),7.22 (d,J = 8.6 Hz, 4H), 7.18 – 7.12 (m, 10H), 7.01 (m, 6H), 4.37 (t, J = 7.8 Hz, 2H), 3.88 (s, 6H), 1.33 – 1.24 (m, 2H), 0.84 – 0.76 (m, 2H), 0.73 – 0.66 (m, 2H), 0.55 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 166.25, 161.20, 157.92, 135.87 , 133.25 ,132.11, 119.59, 60.81 , 33.23, 32.53, 25.95, 19.40.

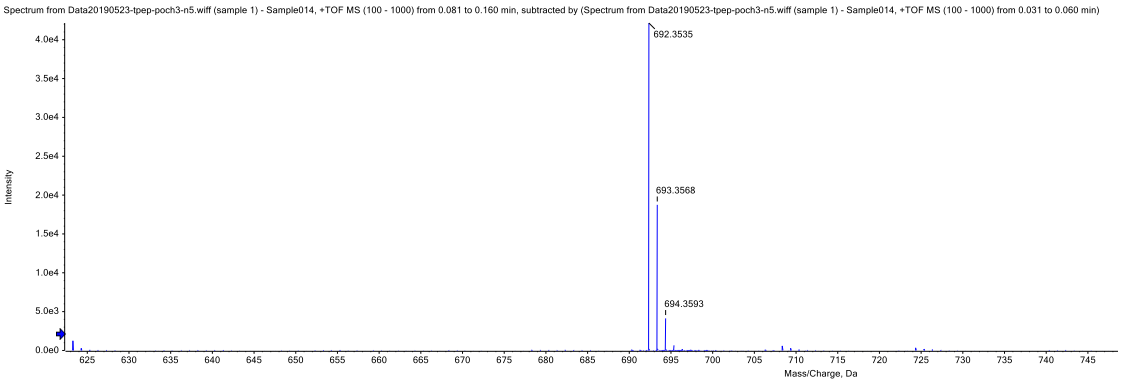


Figure S6 ESI mass spectrum of cationic AIEgen TPP6.

3. Figures and charts

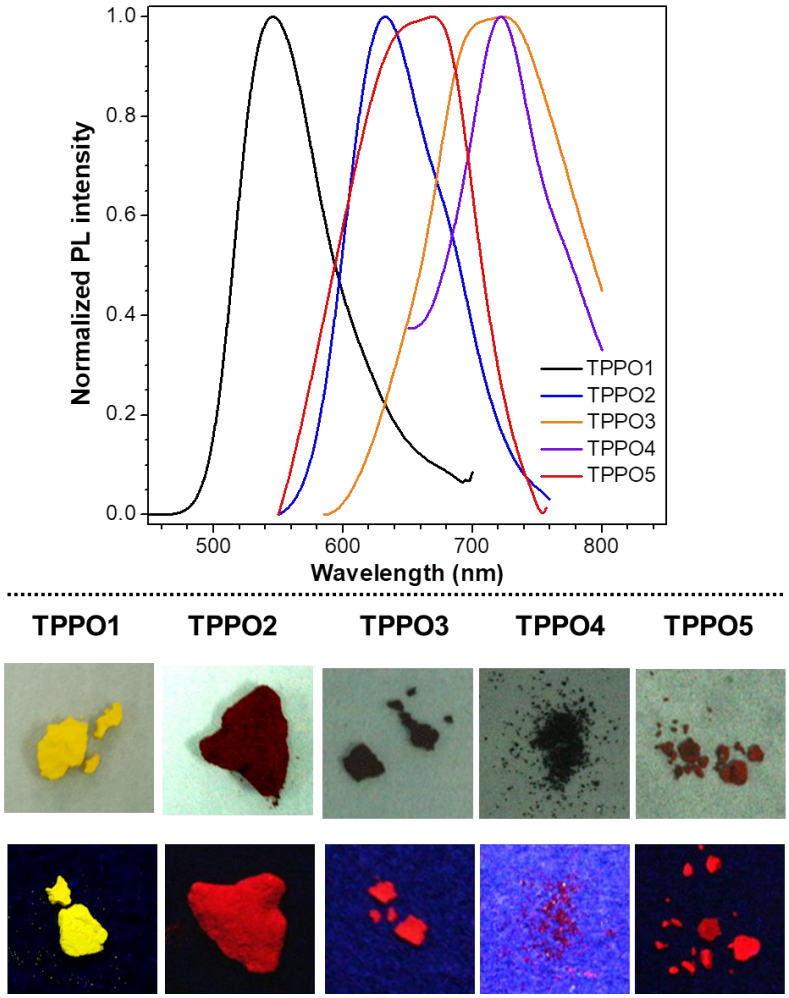


Figure S7. (Up) Photoluminescence spectra of as-prepared TPPOs samples in the solid state. (Bottom) Fluorescent images of as-prepared TPPOs samples under sun light and UV irradiation.

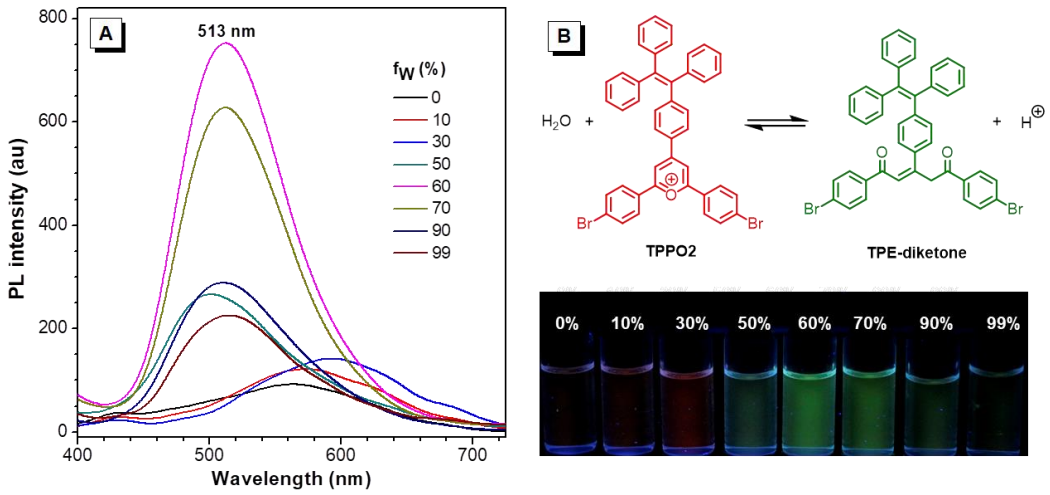


Figure S8. (A) Photoluminescence spectra of TPPO2 in DMSO and DMSO/water mixtures with different water fraction (f_w). Concentration = 10 μM. (B) Hydrolysis and the fluorescent images of of TPPO2 in aqueous media.

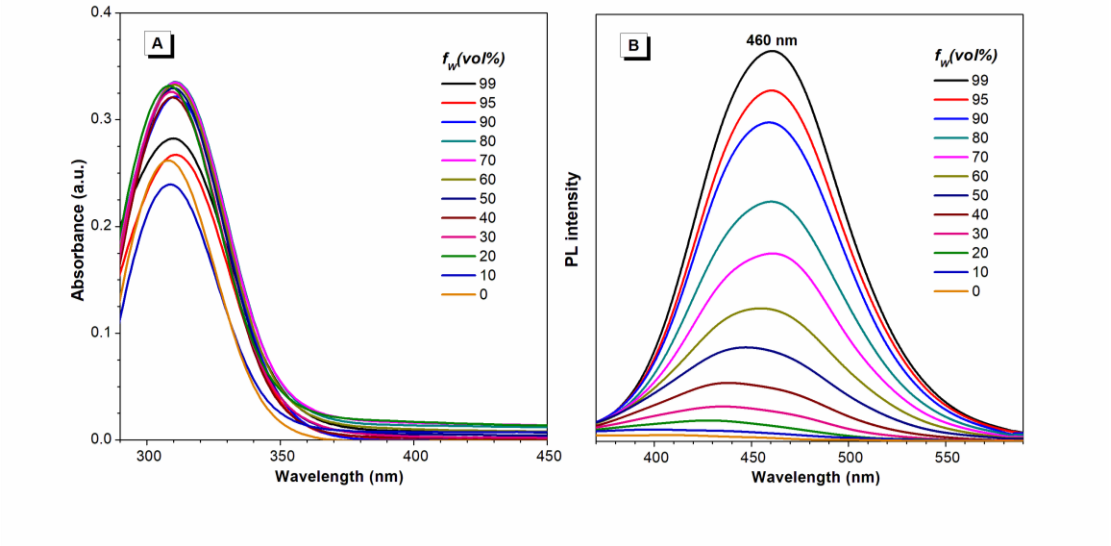


Figure S9. (A) UV-Vis absorption spectra and (B) photoluminescence spectra of TPP1 in DMSO and DMSO/water mixtures with different water fraction (f_w). Concentration = 10 μM.

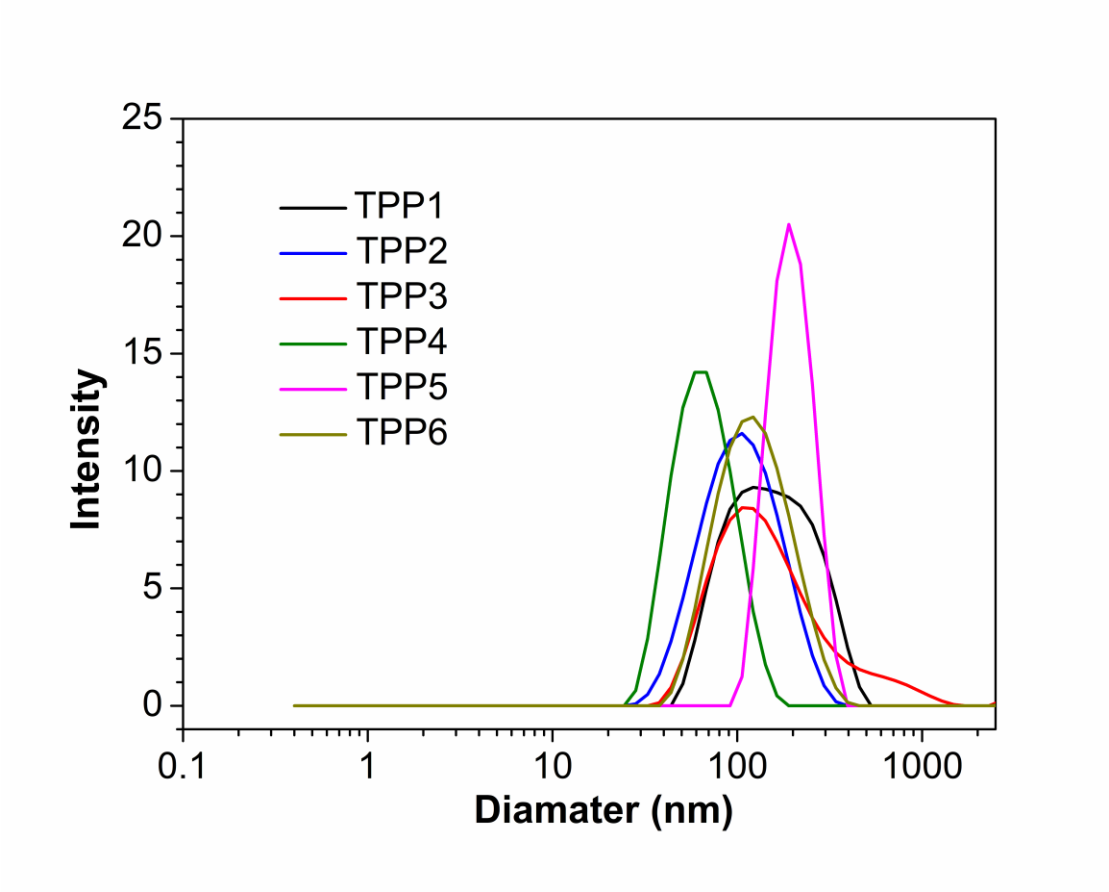


Figure S10. Dynamic light scattering of TPPs in DMSO/Water mixture with water fraction f_w = 95%.

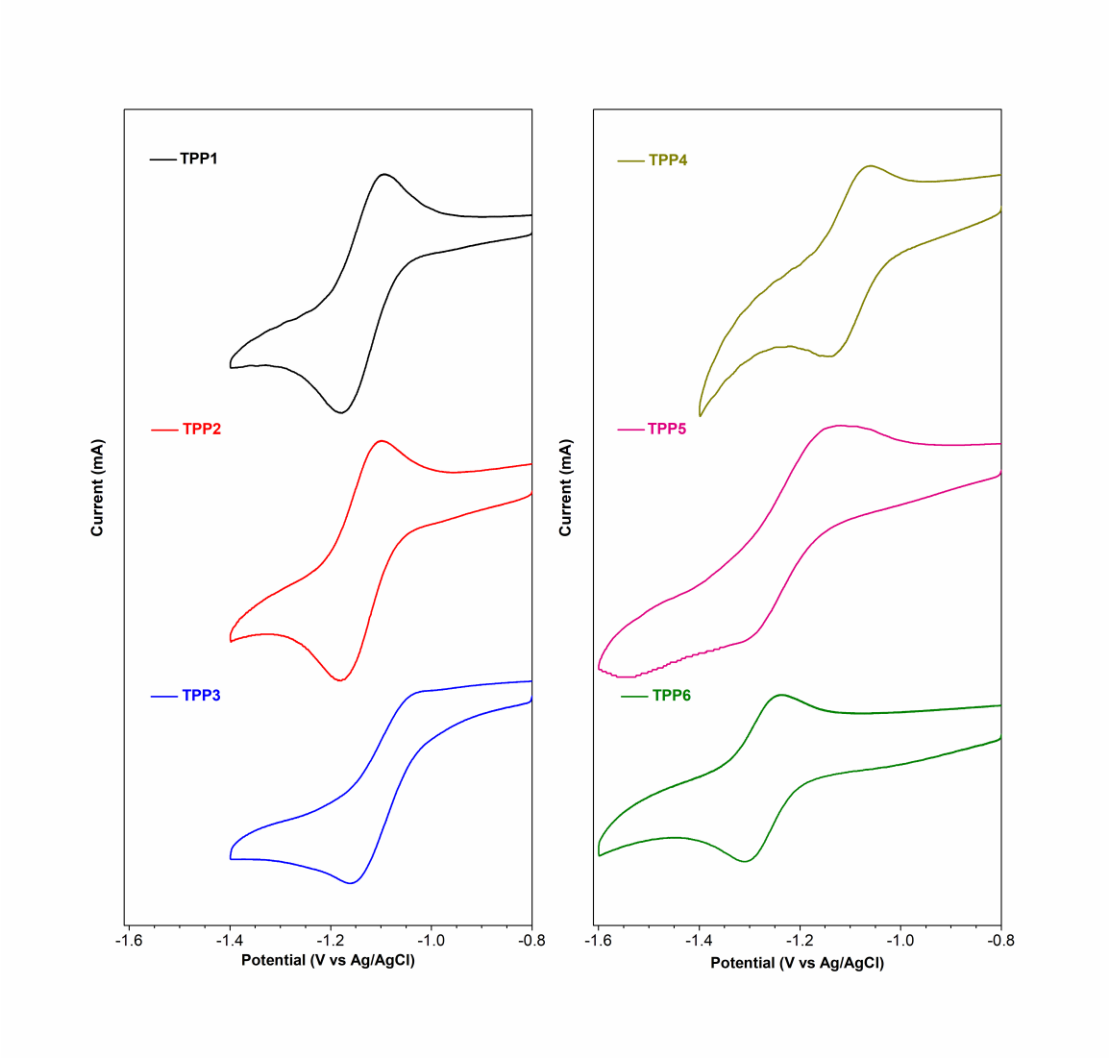


Figure S11. Cyclic voltametry spectra of TPPs in DCM (1 mM) measured with [n-Bu_4N][PF_6] (0.1 M) as a supporting electrolyte with ferrocene as reference.

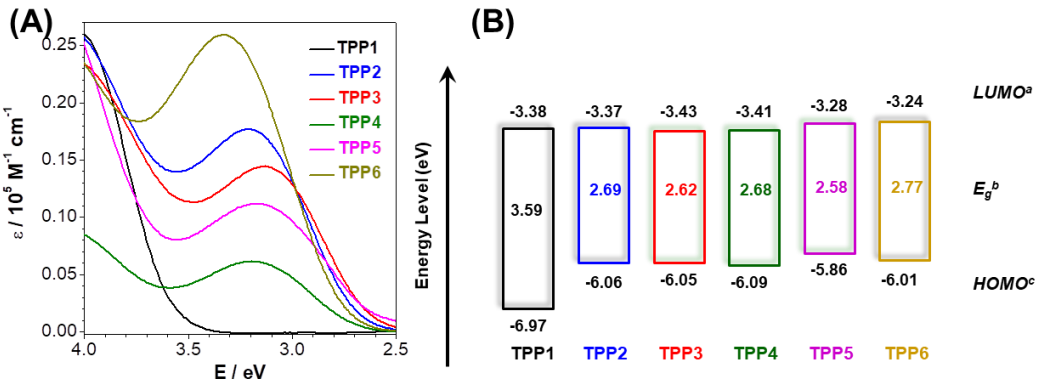


Figure S12. (A) UV-Vis absorption spectra of TPPs in DMSO (10 μM). (B) Energy levels of molecular orbitals of TPPs. [a] LUMO levels were calculated by the first reduction peaks in the electrochemical measurement with respect to ferrocene. [b] Optical Band gap (E_g) was estimated from the absorption edge wavelength, which was obtained from the offset wavelength derived from the low energy absorption band. [c] HOMO = LUMO - E_g.

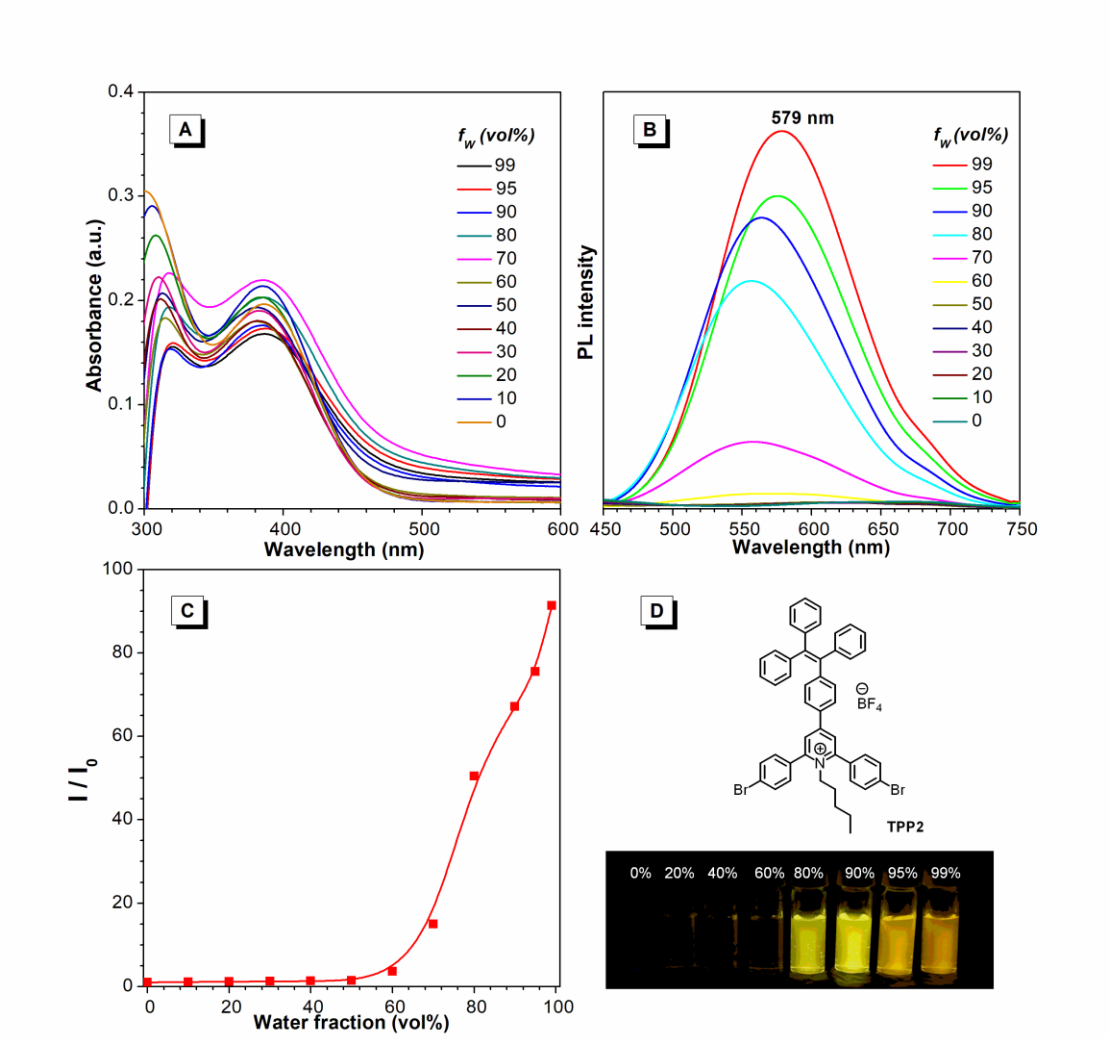


Figure S13. (A) UV-Vis absorption spectra and (B) photoluminescence spectra of TPP2 in DMSO and DMSO/water mixtures with different water fraction (f_w). (C) Plots of the maximum emission intensities of TPP2 in DMSO and DMSO/water mixtures versus f_w. (D) Chemical structure and images of TPP2 under UV lamp in DMSO and DMSO/water mixtures with different f_w. Concentration = 10 μM.

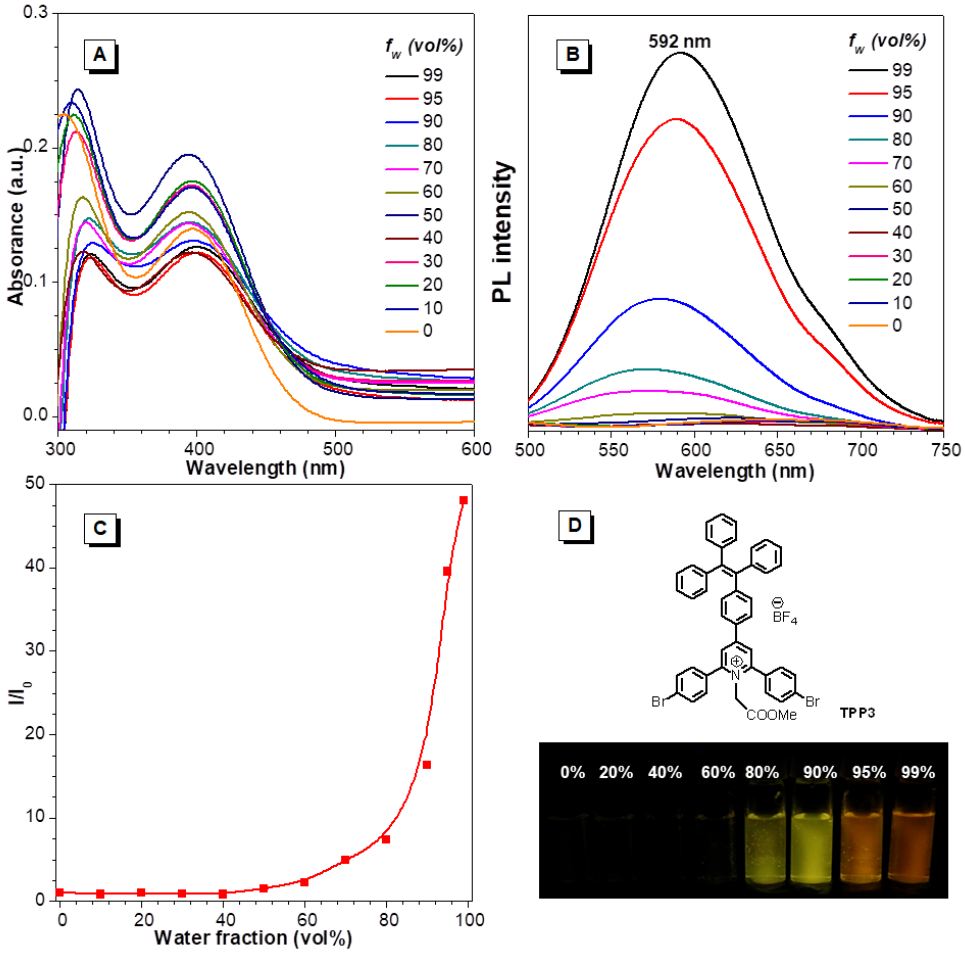


Figure S14. (A) UV-Vis absorption spectra and (B) photoluminescence spectra of TPP3 in DMSO and DMSO/water mixtures with different water fraction (f_w). (C) Plots of the maximum emission intensities of TPP3 in DMSO and DMSO/water mixtures versus f_w. (D) Chemical structure and images of TPP3 under UV lamp in DMSO and DMSO/water mixtures with different f_w. Concentration = 10 μM.

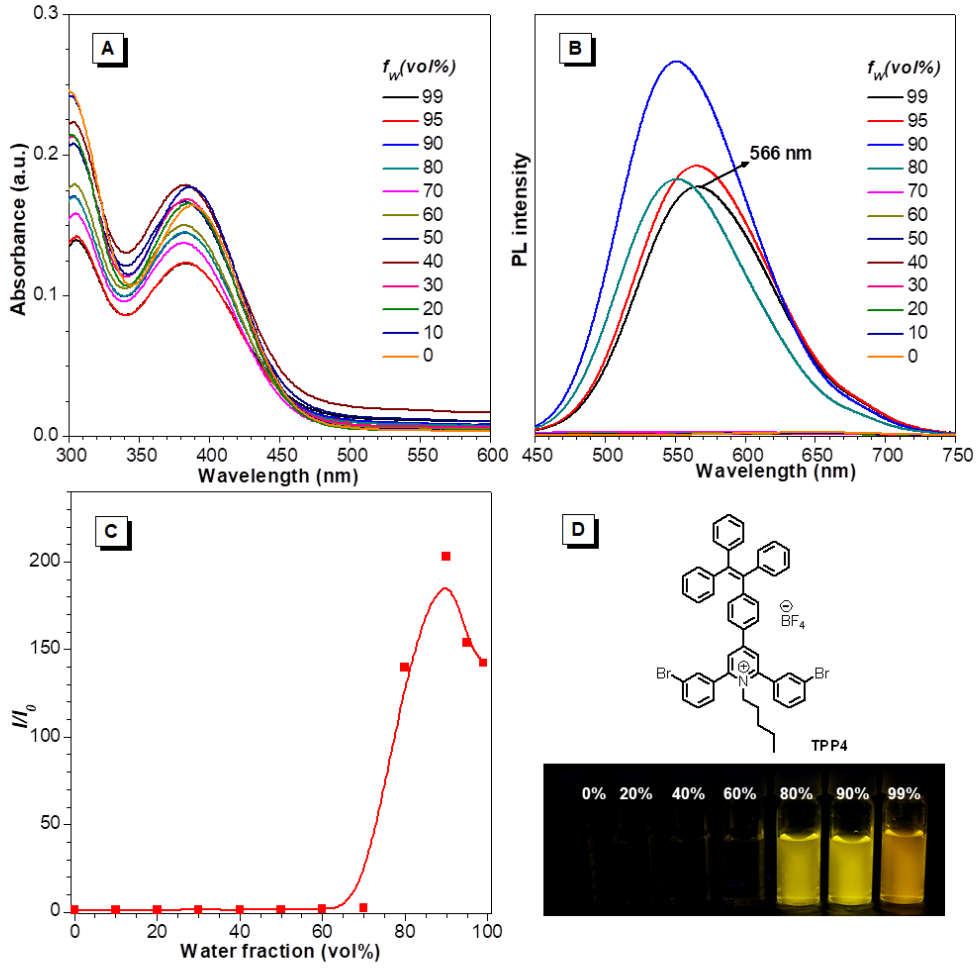


Figure S15. (A) UV-Vis absorption spectra and (B) photoluminescence spectra of TPP4 in DMSO and DMSO/water mixtures with different water fraction (f_w). (C) Plots of the maximum emission intensities of TPP4 in DMSO and DMSO/water mixtures versus f_w. (D) Chemical structure and images of TPP4 under UV lamp in DMSO and DMSO/water mixtures with different f_w. Concentration = 10 μM.

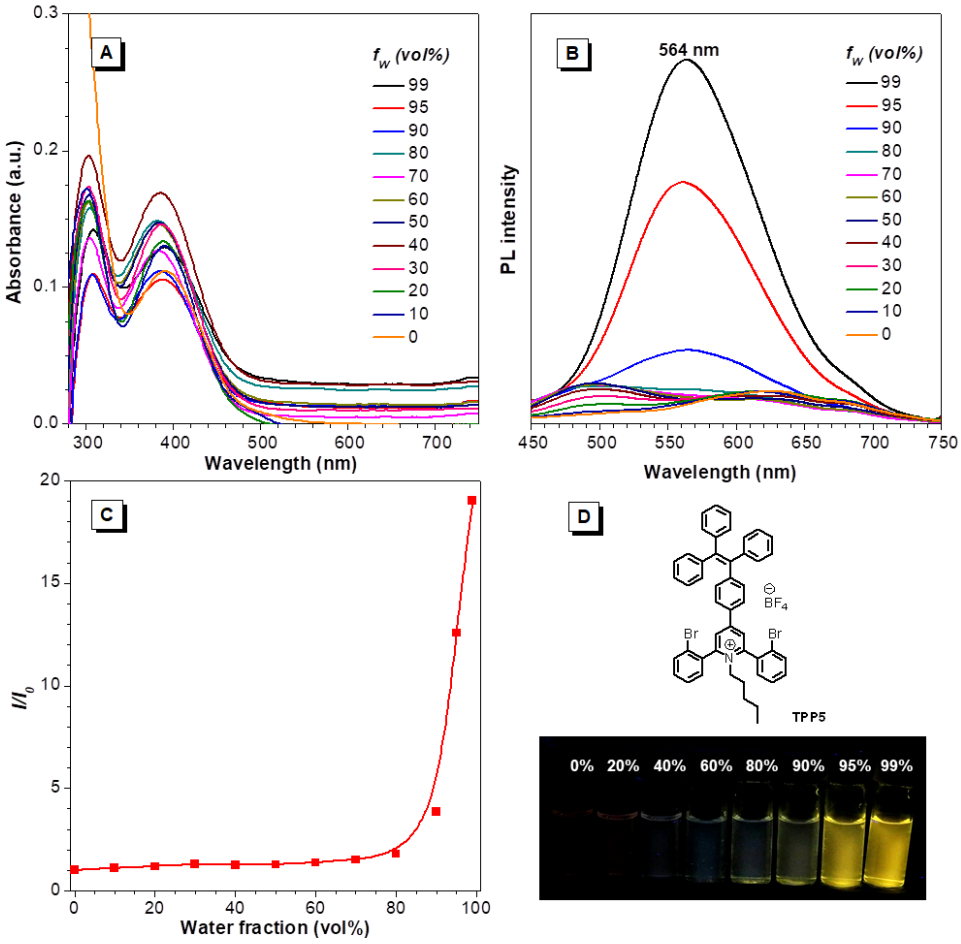


Figure S16. (A) UV-Vis absorption spectra and (B) photoluminescence spectra of TPP5 in DMSO and DMSO/water mixtures with different water fraction (f_w). (C) Plots of the maximum emission intensities of TPP5 in DMSO and DMSO/water mixtures versus f_w. (D) Chemical structure and images of TPP5 under UV lamp in DMSO and DMSO/water mixtures with different f_w. Concentration = 10 μM.

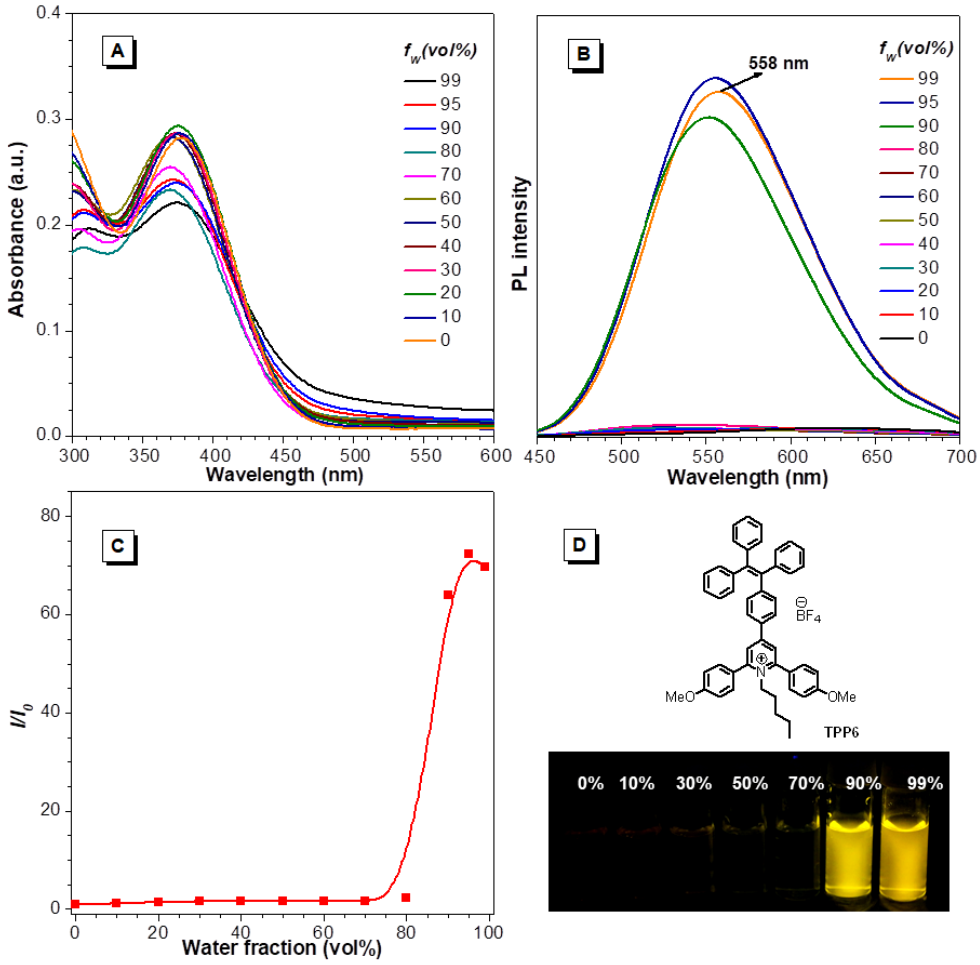


Figure S17. (A) UV-Vis absorption spectra and (B) photoluminescence spectra of TPP6 in DMSO and DMSO/water mixtures with different water fraction (f_w). (C) Plots of the maximum emission intensities of TPP6 in DMSO and DMSO/water mixtures versus f_w. (D) Chemical structure and images of TPP6 under UV lamp in DMSO and DMSO/water mixtures with different f_w. Concentration = 10 μM.

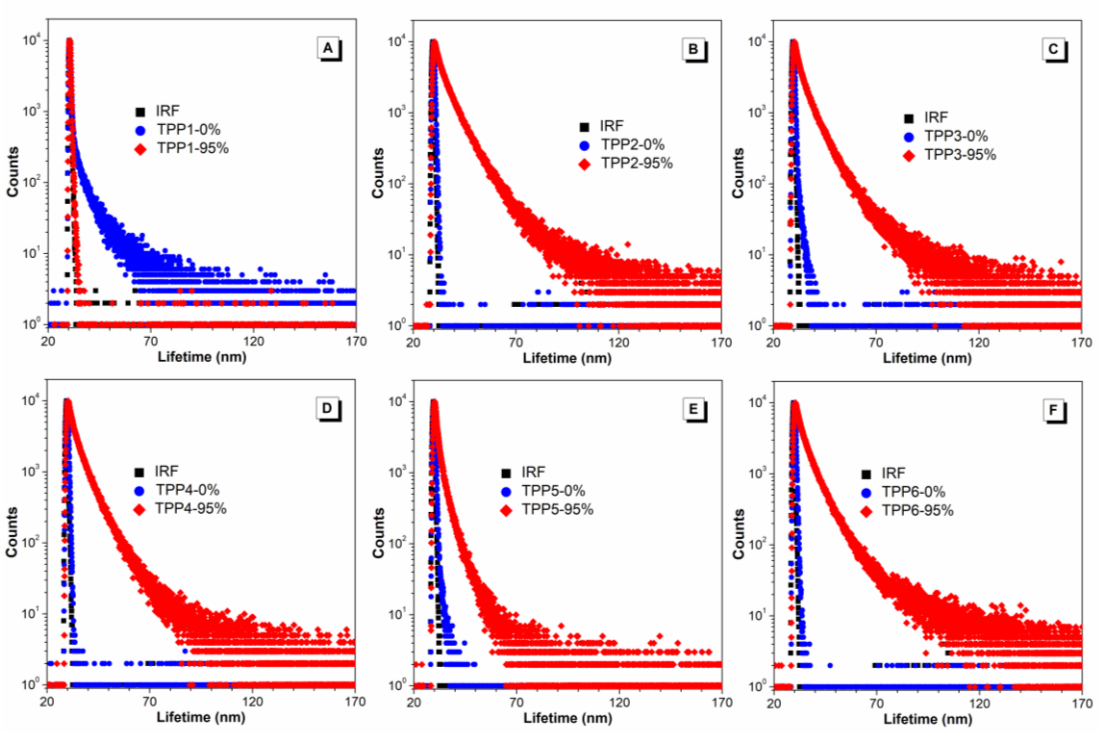


Figure S18. Fluorescence decay curves of TPPs in the pure DMSO solution and DMSO-H_2O mixture (f_W = 95 vol%).

Table S1. Photophysical properties of TPPs fluorophores

AIEgens	Pure DMSO solution						Nano-aggregates (DMSO/H_2O, 5/95 by volume)				Electronic properties		
	λ_{abs} (nm)	ε_{abs} (10^5 M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F (%)	$\triangle\lambda$ (nm)	τ (ns)	λ_{em} (nm)	Φ_F (%)	$\triangle\lambda$ (nm)	τ (ns)	E_g (ev)[c]	LUMO (ev)[d]	HOMO (ev)[e]
TPP1	308	0.26	-	0.17[a]	-	0.70	460	24.9[a]	152	0.62	3.59	-3.38	-6.97
TPP2	300, 386	0.27, 0.18	667	3.4[b]	281	0.66	579	50.3[b]	193	5.02	2.69	-3.37	-6.06
TPP3	304, 397	0.24, 0.14	645	3.4[b]	248	0.70	592	30.8[b]	195	4.15	2.62	-3.43	-6.05
TPP4	299, 388	0.09, 0.06	639	3.0[b]	251	0.67	566	36.8[b]	178	3.97	2.68	-3.41	-6.09
TPP5	283, 391	0.40, 0.11	626	3.6[b]	235	0.65	564	13.6[b]	173	1.63	2.58	-3.28	-5.86
TPP6	270, 373	0.34, 0.26	634	4.4[b]	261	0.71	558	44.9[b]	185	4.38	2.77	-3.24	-6.01

[a] Relative fluorescence quantum yield was measured with Anthracene (Φ_F = 0.27) as reference. [b] Absolute fluorescence quantum yield was measured by Hamamatsu Absolute PL quantum yield spectrometer C11347. [c] Optical Band gap (E_g) was estimated from the absorption edge wavelength, which was obtained from the offset wavelength derived from the low energy absorption band. [d] LUMO levels were calculated by the first reduction peaks in the electrochemical measurement with respect to ferrocene. [e] HOMO = LUMO - E_g.

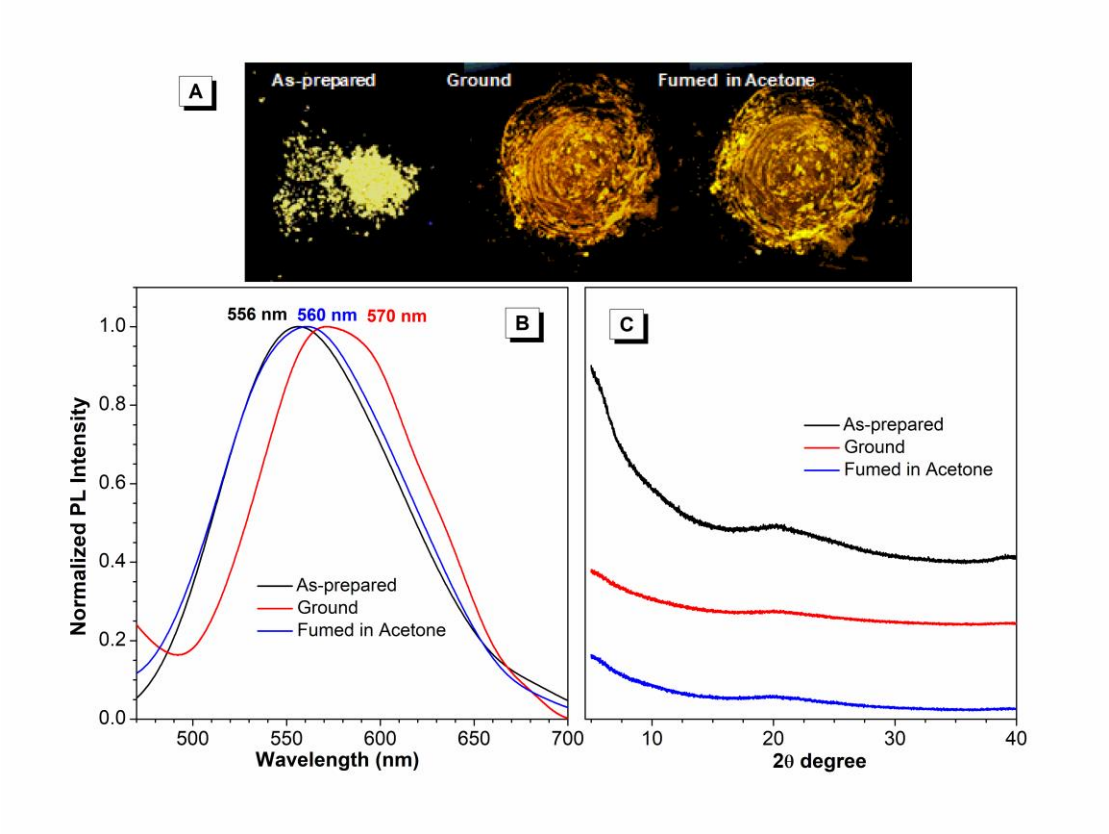


Figure S19. Fluorescent images (A), PL spectra (B), and powder XRD results (C) of as-prepared samples of cationic luminogen TPP4 after grinding and subsequent solvent fuming with acetone for 5 minutes.

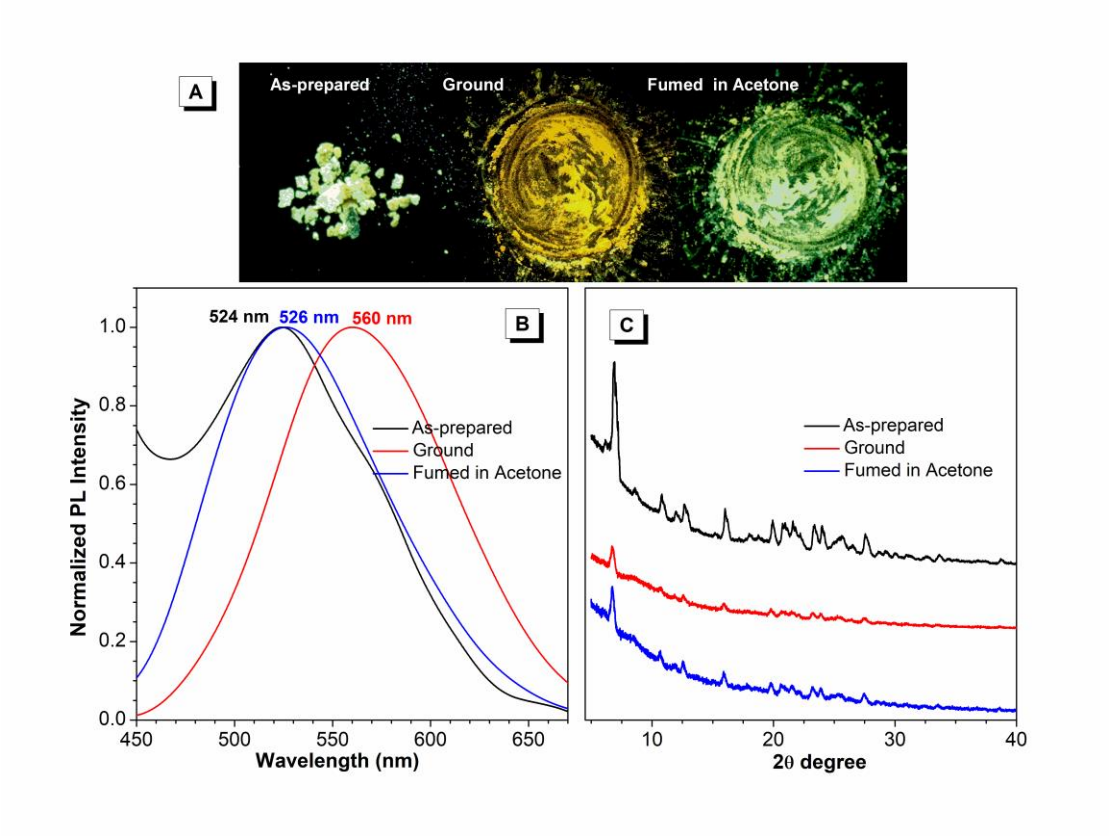


Figure S20. Fluorescent images (A), PL spectra (B), and powder XRD results (C) of as-prepared samples of cationic luminogen TPP5 after grinding and subsequent solvent fuming with acetone for 5 minutes.

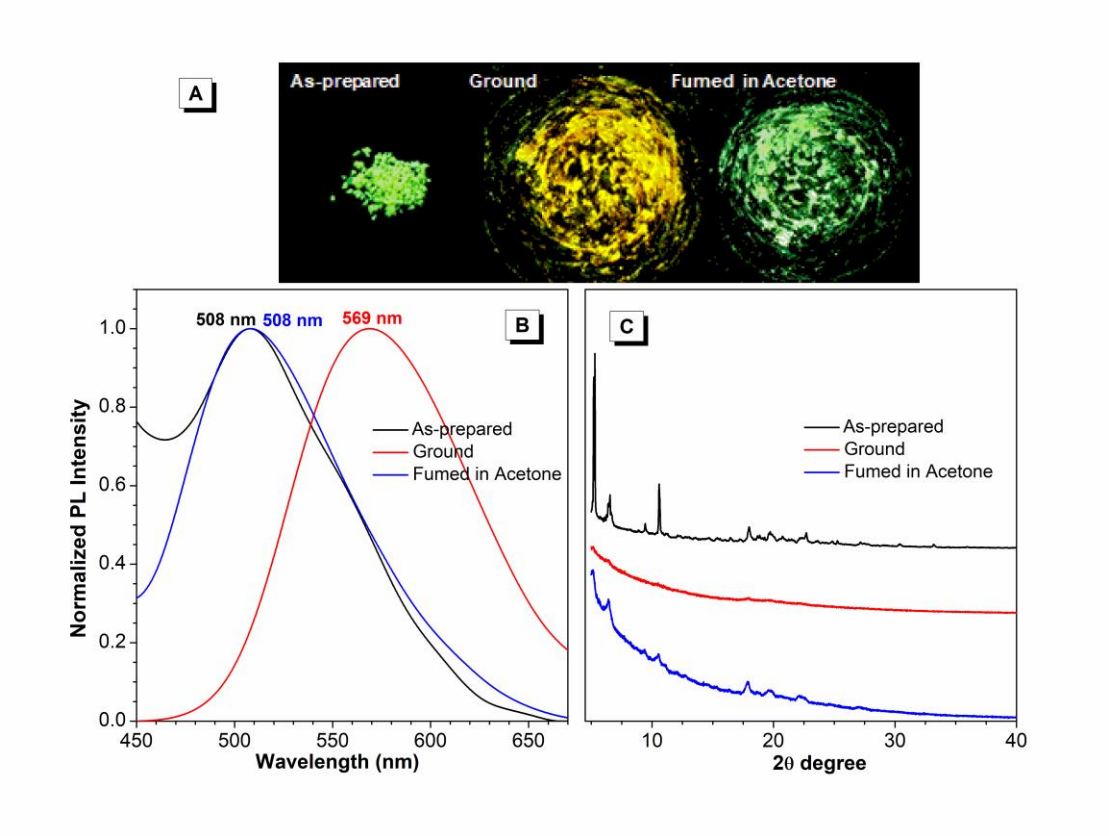


Figure S21. Fluorescent images (A), PL spectra (B), and powder XRD results (C) of as-prepared samples of cationic luminogen TPP6 after grinding and subsequent solvent fuming with acetone for 5 minute.

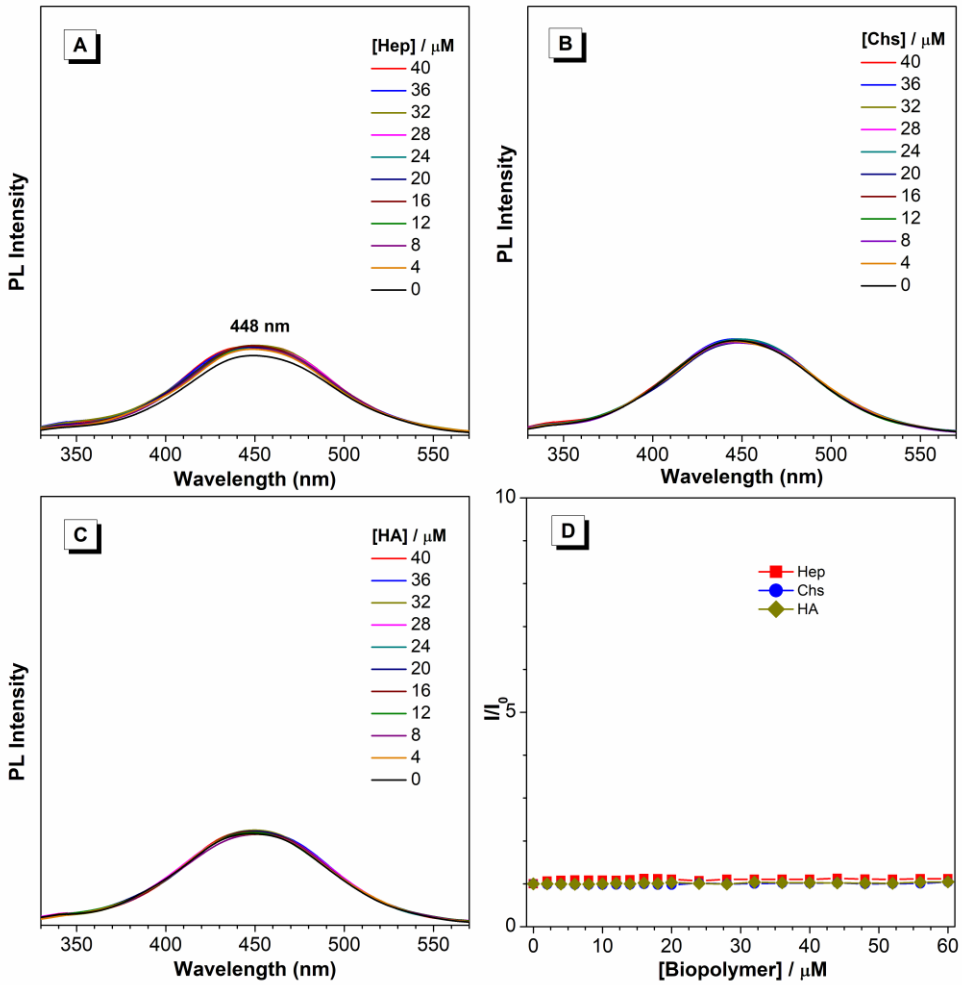


Figure S22. PL spectra of TPP1 with different concentration of (A) heparin (Hep), (B) chondroitin 4-sulfate (Chs), and (C) hyaluronic acid (HA) . (D) Curve of relative fluorescence intensity of TPP1 with biopolymer concentration. Solvent: DMSO/H_2O = 50/50 by volume; concentration of cationic AIEgens: 10 μM.

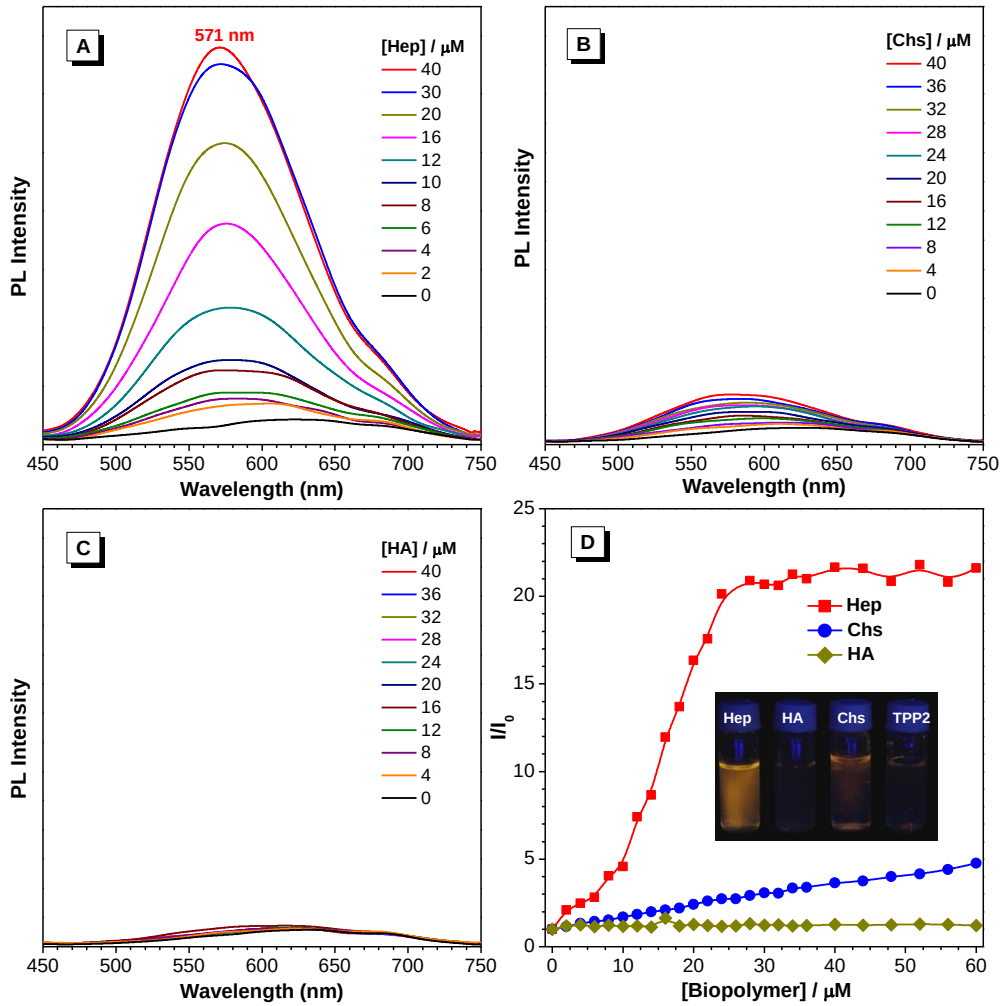


Figure S23. PL spectra of TPP2 with different concentration of (A) heparin (Hep), (B) chondroitin 4-sulfate (Chs), and (C) hyaluronic acid (HA). (D) Curve of relative fluorescence intensity of TPP2 with biopolymer concentration. Solvent: DMSO/H_2O = 50/50 by volume; concentration of cationic AIEgens: 10 μM. Inset: fluorescent images for the mixture of TPP2 in absence or presence of biopolymer (40 μM) under UV lamp.

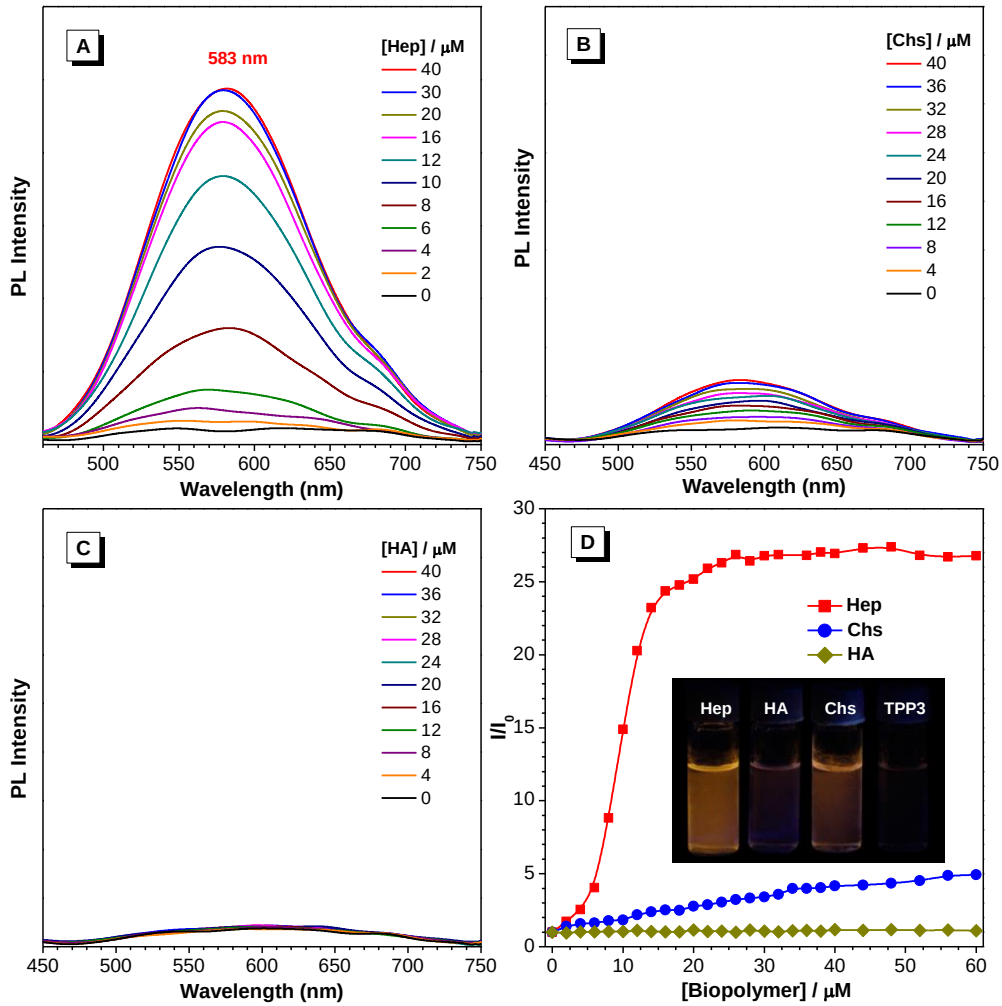


Figure S24. PL spectra of TPP3 with different concentration of (A) heparin (Hep), (B) chondroitin 4-sulfate (Chs), and (C) hyaluronic acid (HA) . (D) Curve of relative fluorescence intensity of TPP3 with biopolymer concentration. Solvent: DMSO/H_2O = 50/50 by volume; concentration of cationic AIEgens: 10 μM. Inset: fluorescent images for the mixture of TPP3 in absence or presence of biopolymer (40 μM) under UV lamp.

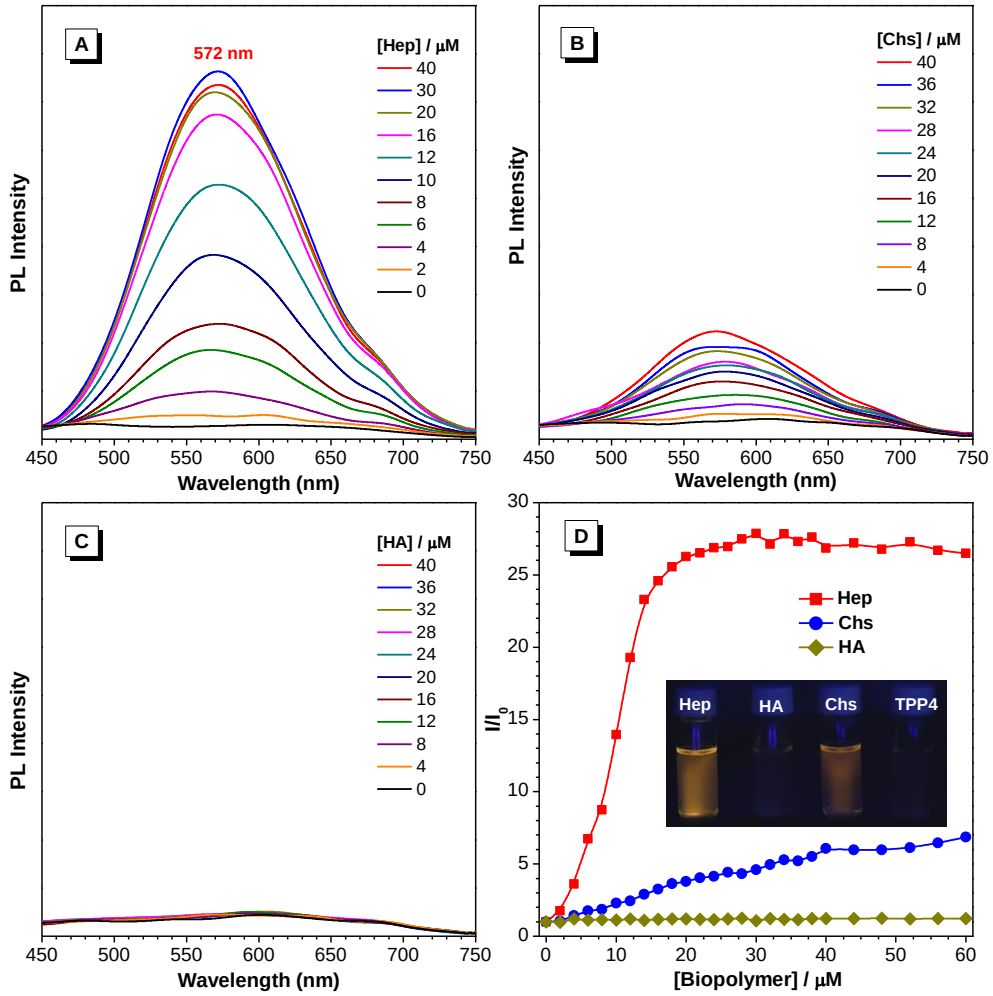


Figure S25. PL spectra of TPP4 with different concentration of (A) heparin (Hep), (B) chondroitin 4-sulfate (Chs), and (C) hyaluronic acid (HA) . (D) Curve of relative fluorescence intensity of TPP4 with biopolymer concentration. Solvent: DMSO/H_2O = 50/50 by volume; concentration of cationic AIEgens: 10 μM. Inset: fluorescent images for the mixture of TPP4 in absence or presence of biopolymer (40 μM) under UV lamp.

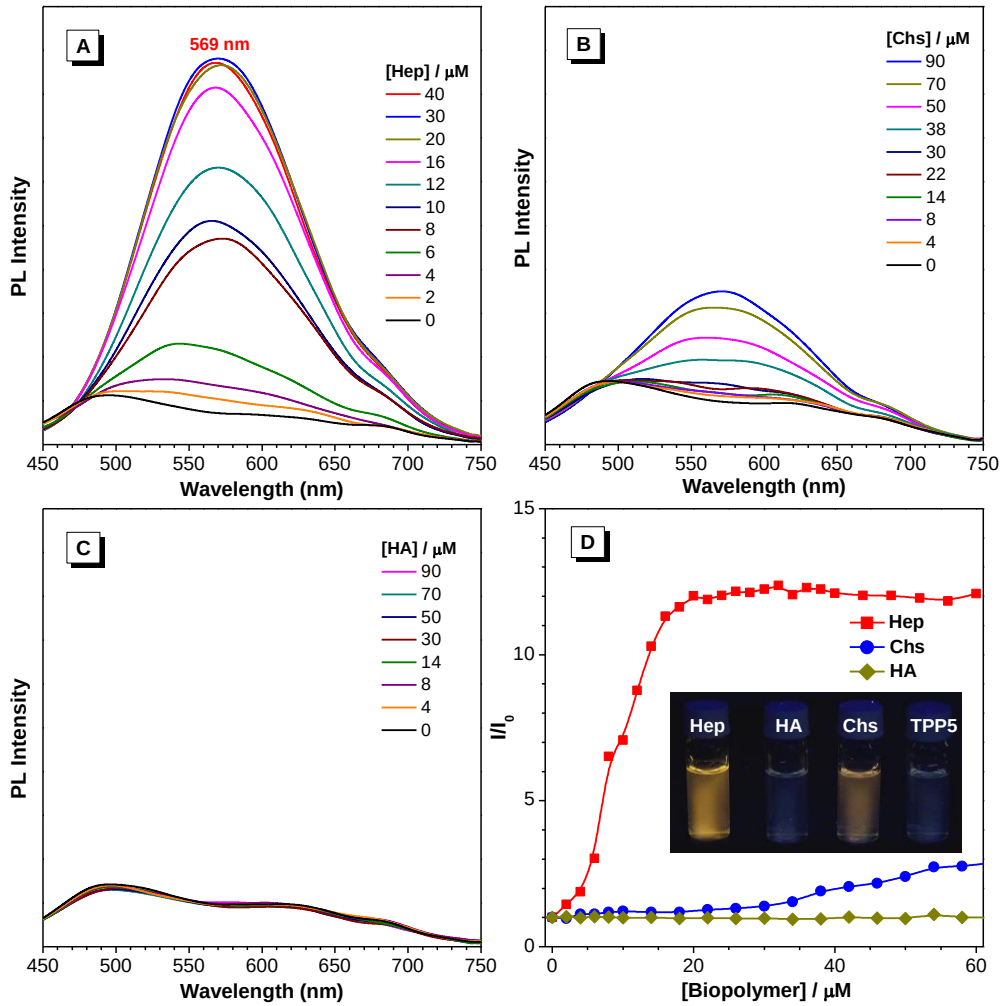


Figure S26. PL spectra of TPP5 with different concentration of (A) heparin (Hep), (B) chondroitin 4-sulfate (Chs), and (C) hyaluronic acid (HA) . (D) Curve of relative fluorescence intensity of TPP5 with biopolymer concentration. Solvent: DMSO/H_2O = 50/50 by volume; concentration of cationic AIEgens: 10 μM. Inset: fluorescent images for the mixture of TPP5 in absence or presence of biopolymer (40 μM) under UV lamp.

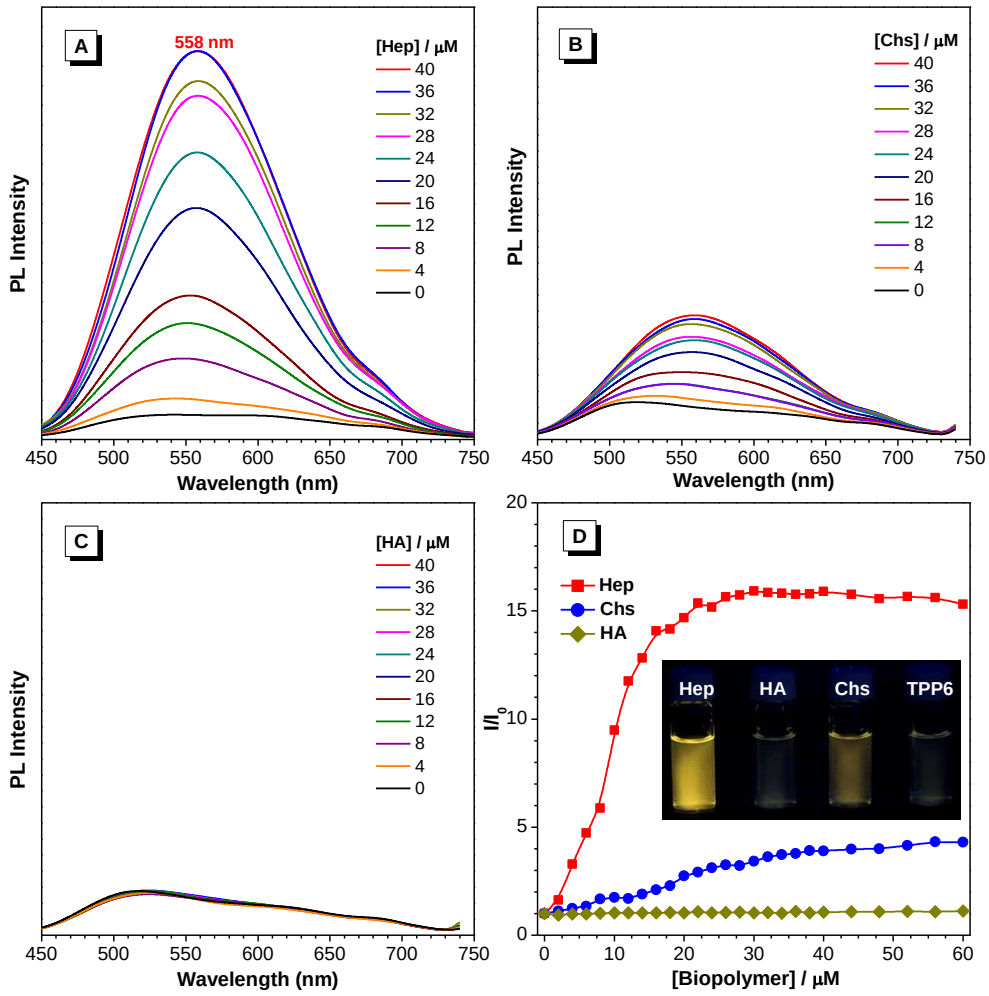


Figure S27. PL spectra of TPP6 with different concentration of (A) heparin (Hep), (B) chondroitin 4-sulfate (Chs), and (C) hyaluronic acid (HA) . (D) Curve of relative fluorescence intensity of TPP6 with biopolymer concentration. Solvent: DMSO/H_2O = 50/50 by volume; concentration of cationic AIEgens: 10 μM. Inset: fluorescent images for the mixture of TPP6 in absence or presence of biopolymer (40 μM) under UV lamp.

4. NMR spectra

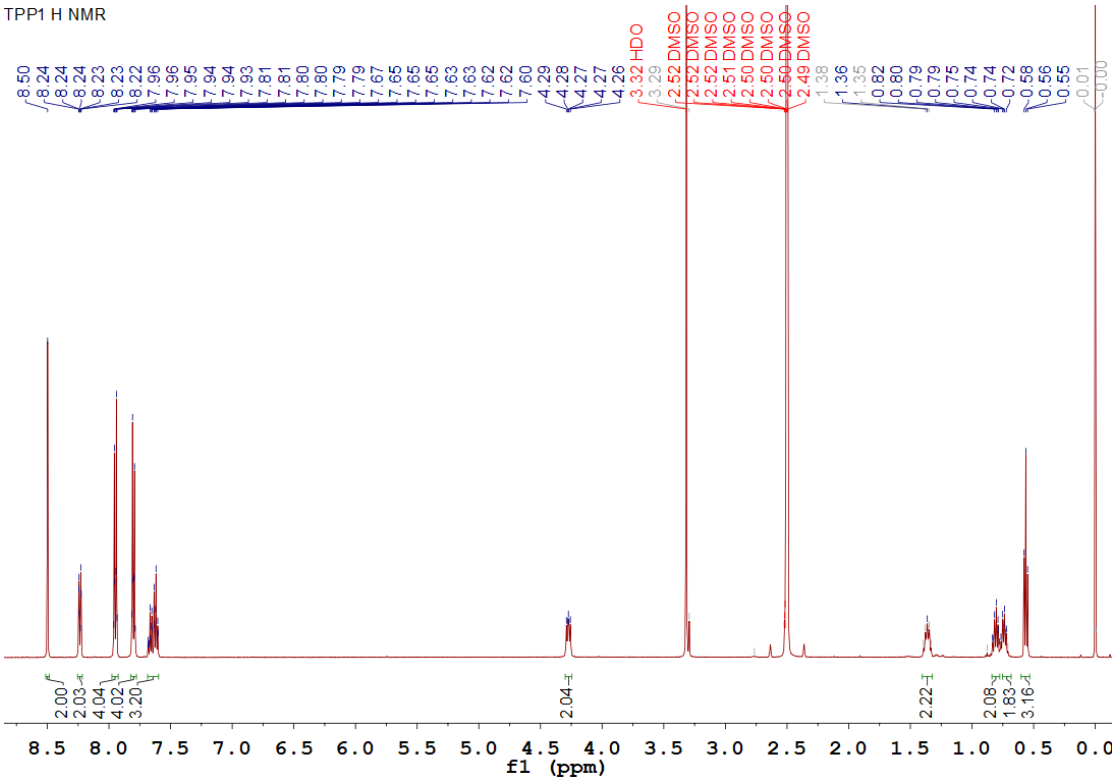


Figure S28. ^{1}H NMR spectrum of TPP1 in DMSO-d_6 at 298K.

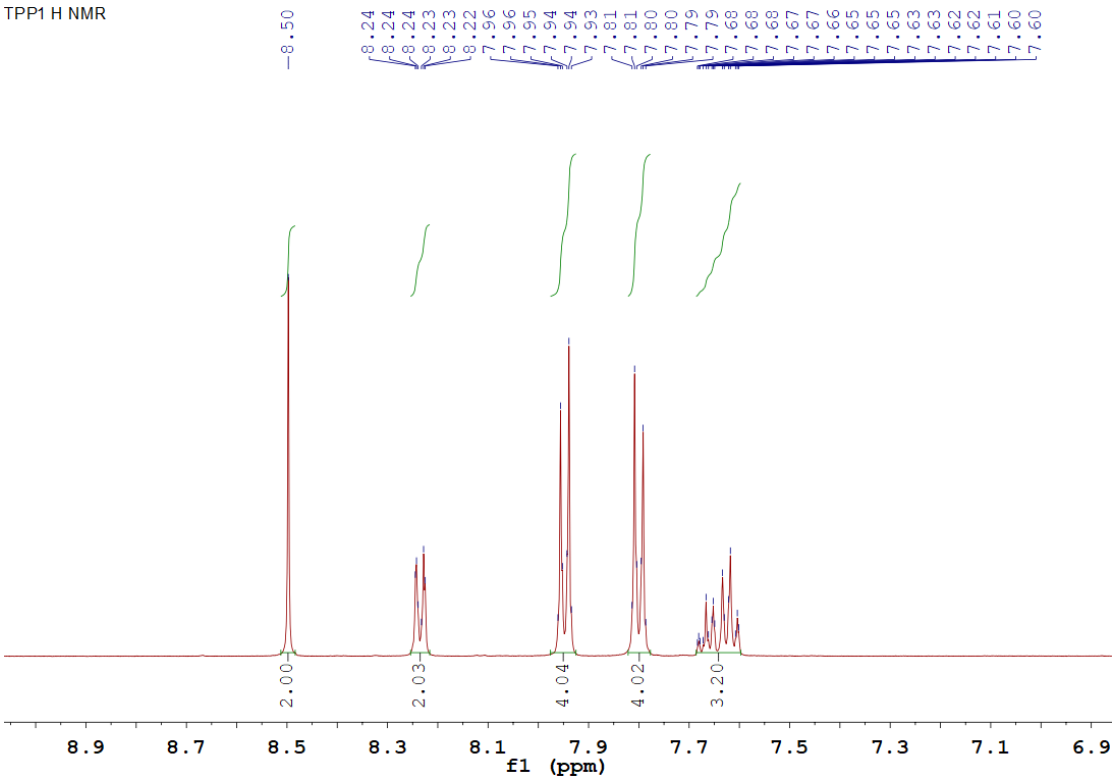


Figure S29. Enlarged aromatic region in the ^{1}H NMR spectrum of TPP1 in DMSO-d_6 at 298K.

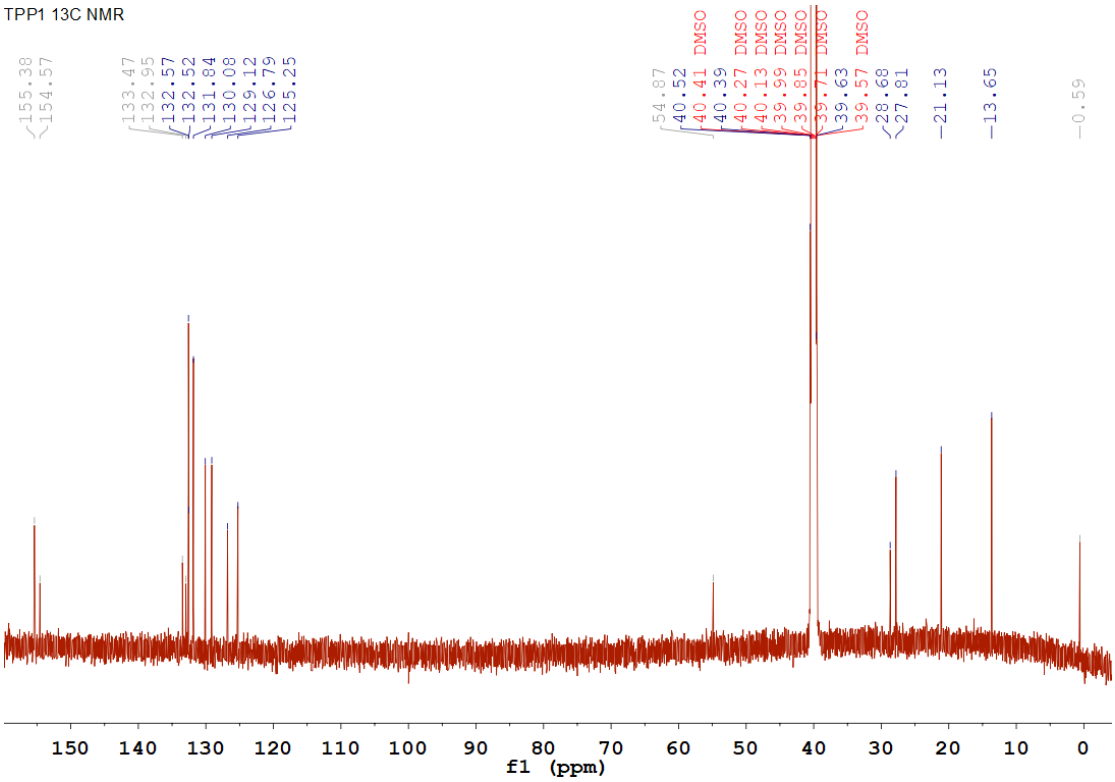


Figure S30. ^{13}C NMR spectrum of TPP1 in DMSO-d_6 at 298K.

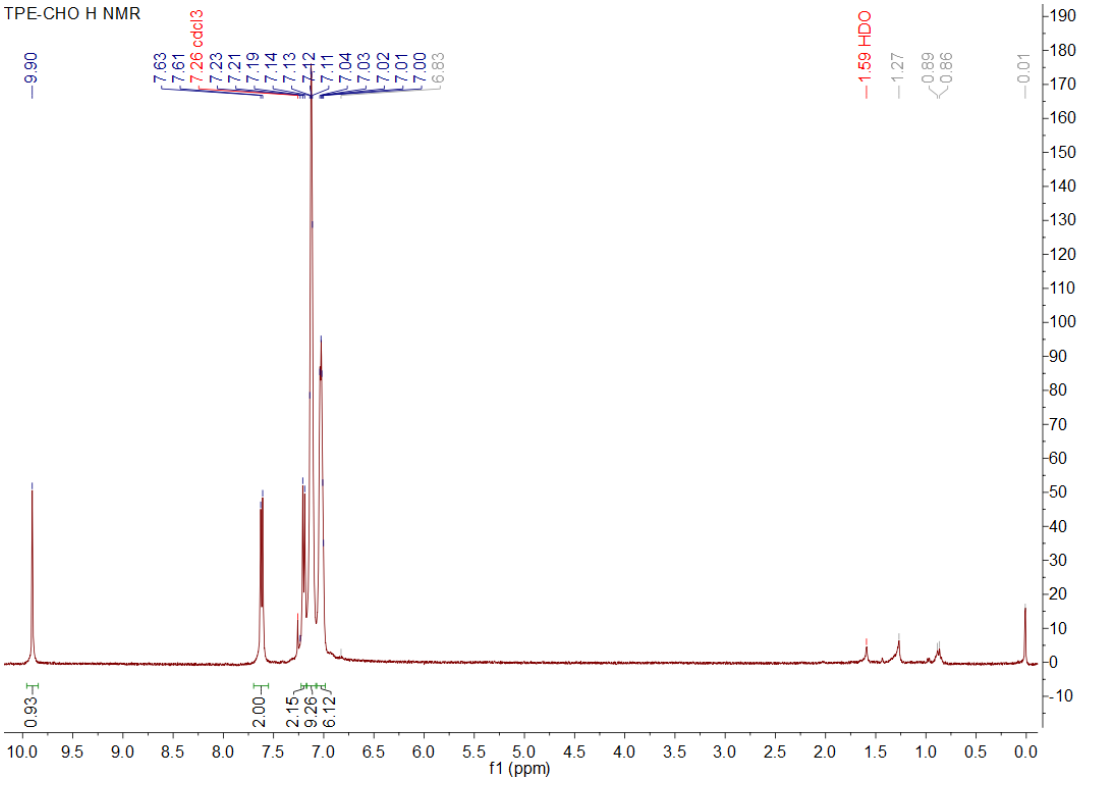


Figure S31. ^{13}C NMR spectrum of compound **1** in $CDCl_3$ at 298K.

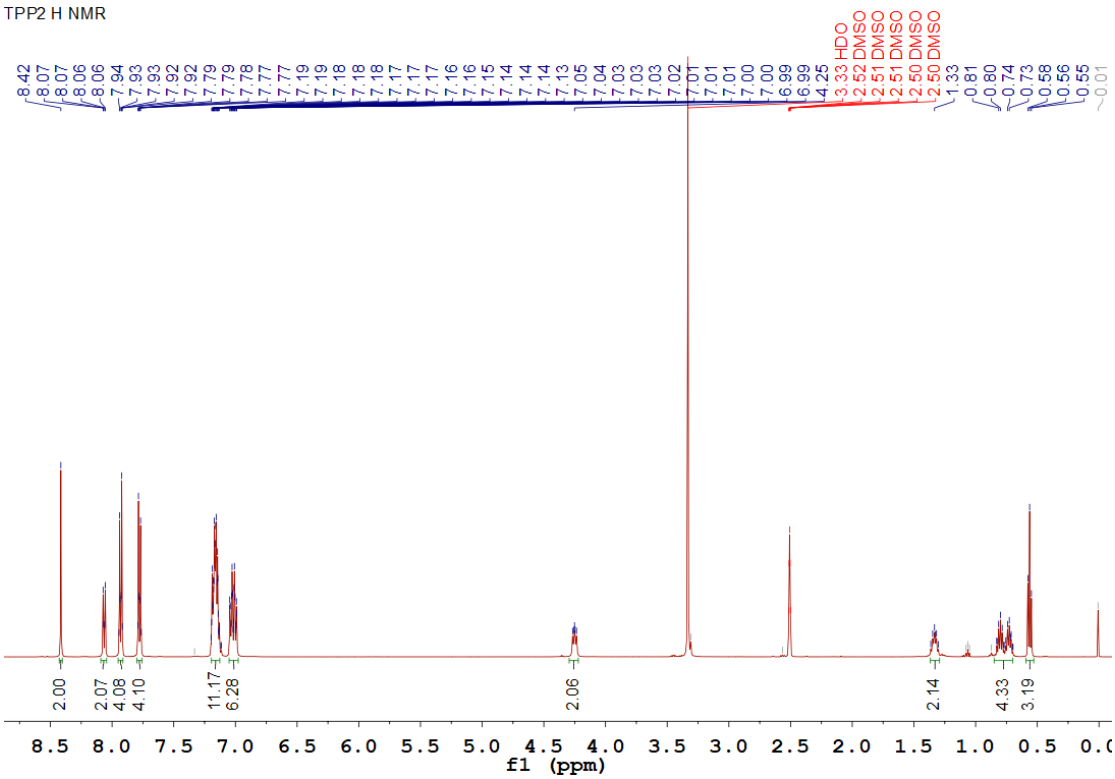


Figure S32. ^{1}H NMR spectrum of TPP2 in DMSO-d_6 at 298K.

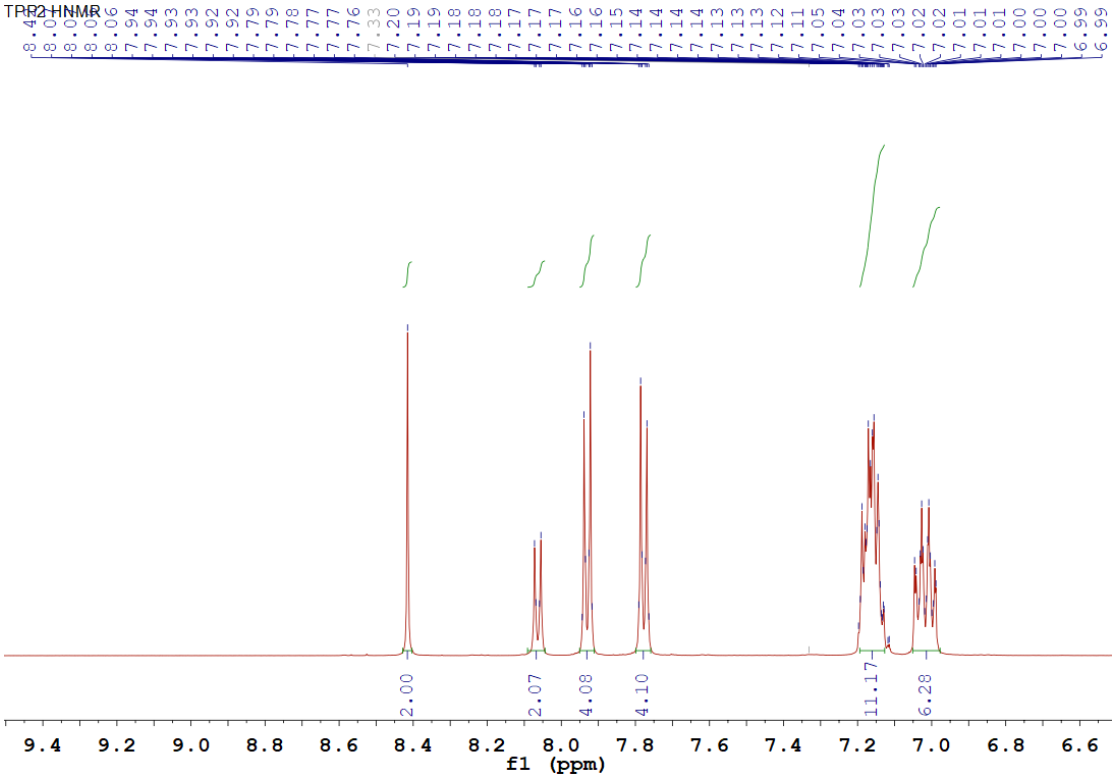


Figure S33. Enlarged aromatic region in the ^{1}H NMR spectrum of TPP2 in DMSO-d_6 at 298K.

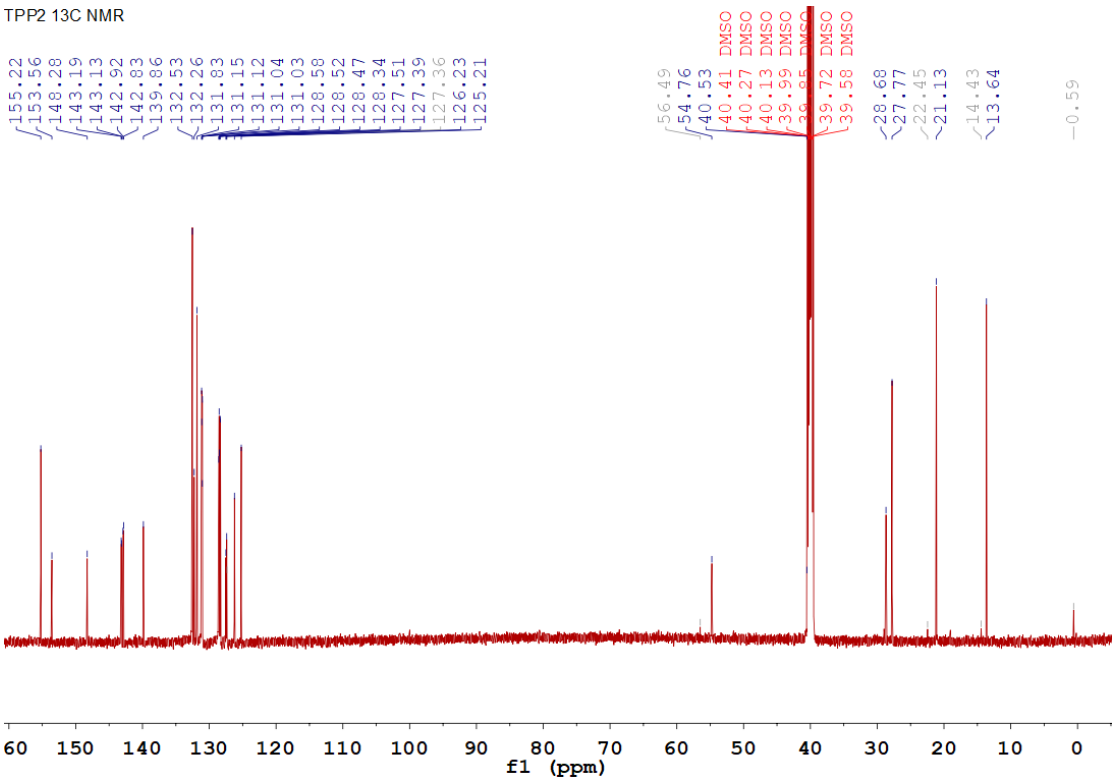


Figure S34. ^{13}C NMR spectrum of TPP2 in DMSO-d_6 at 298K.

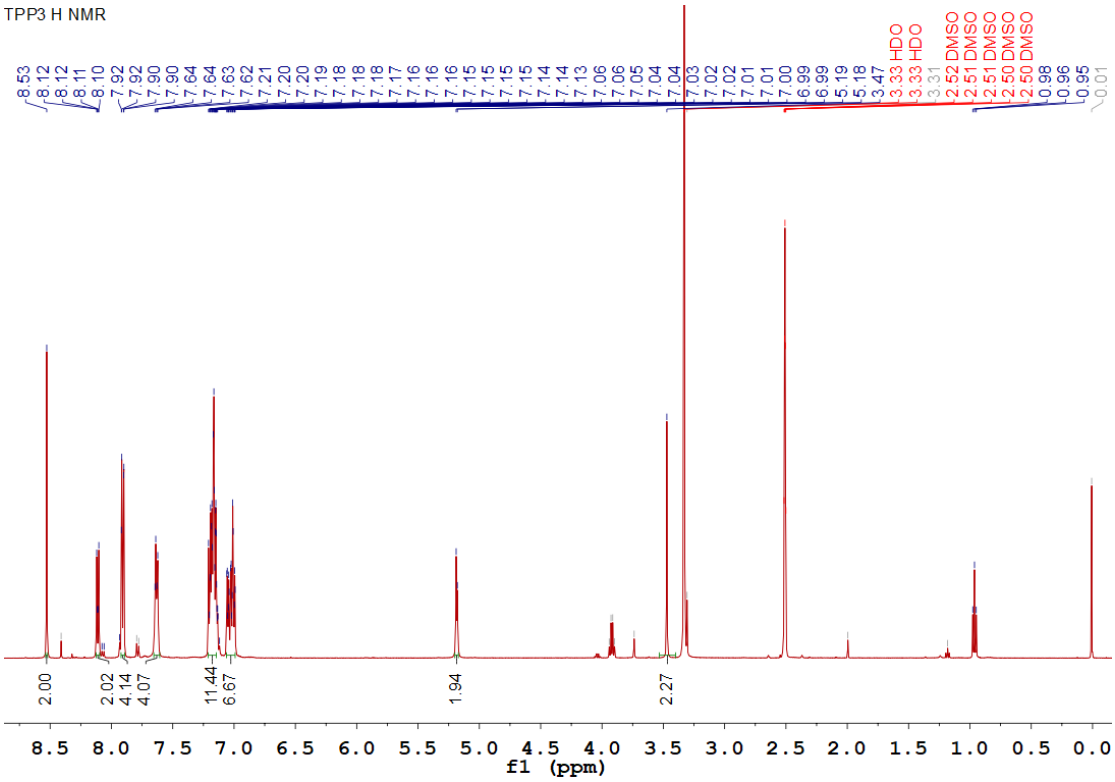


Figure S35. ^{1}H NMR spectrum of TPP3 in DMSO-d_6 at 298K.

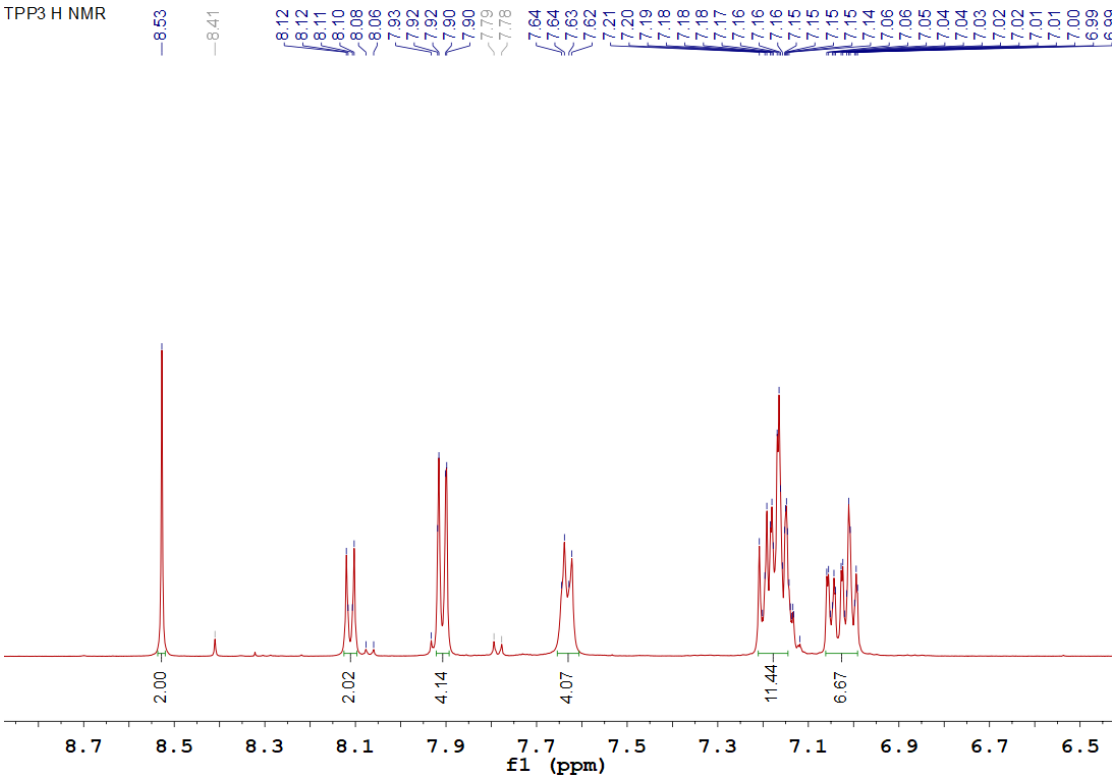


Figure S36. Enlarged aromatic region in the ^{1}H NMR spectrum of TPP3 in DMSO-d_6 at 298K.

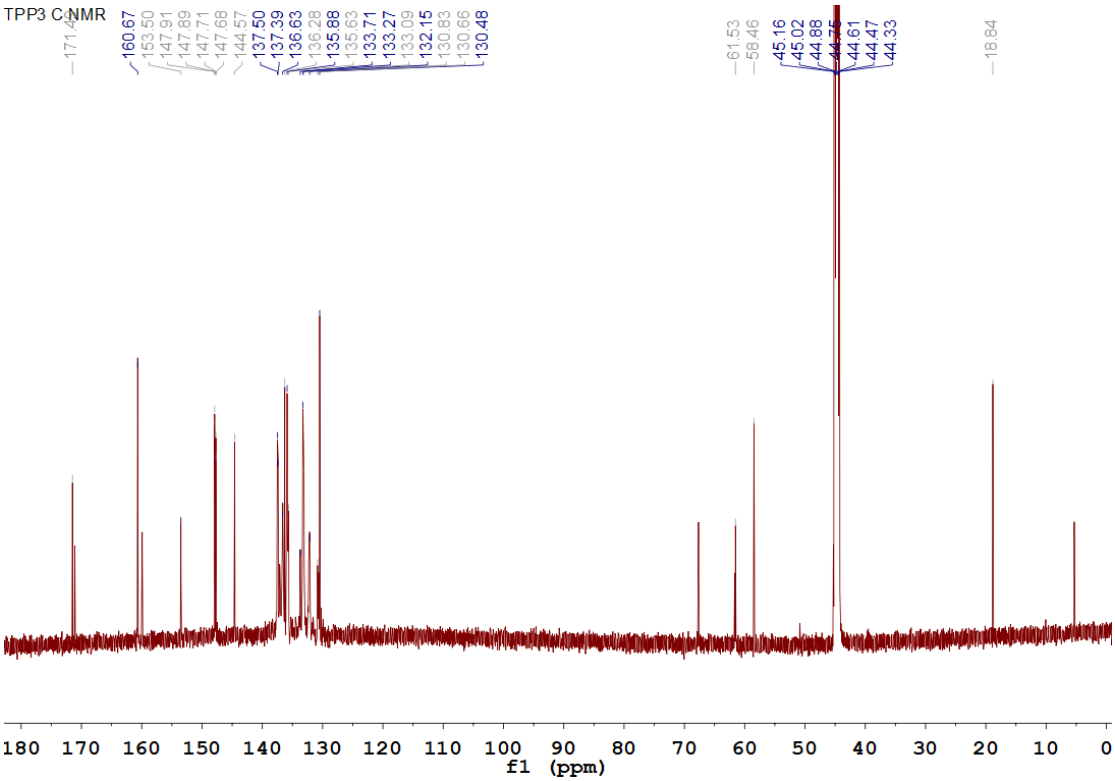


Figure S37. ^{13}C NMR spectrum of TPP3 in DMSO-d_6 at 298K.

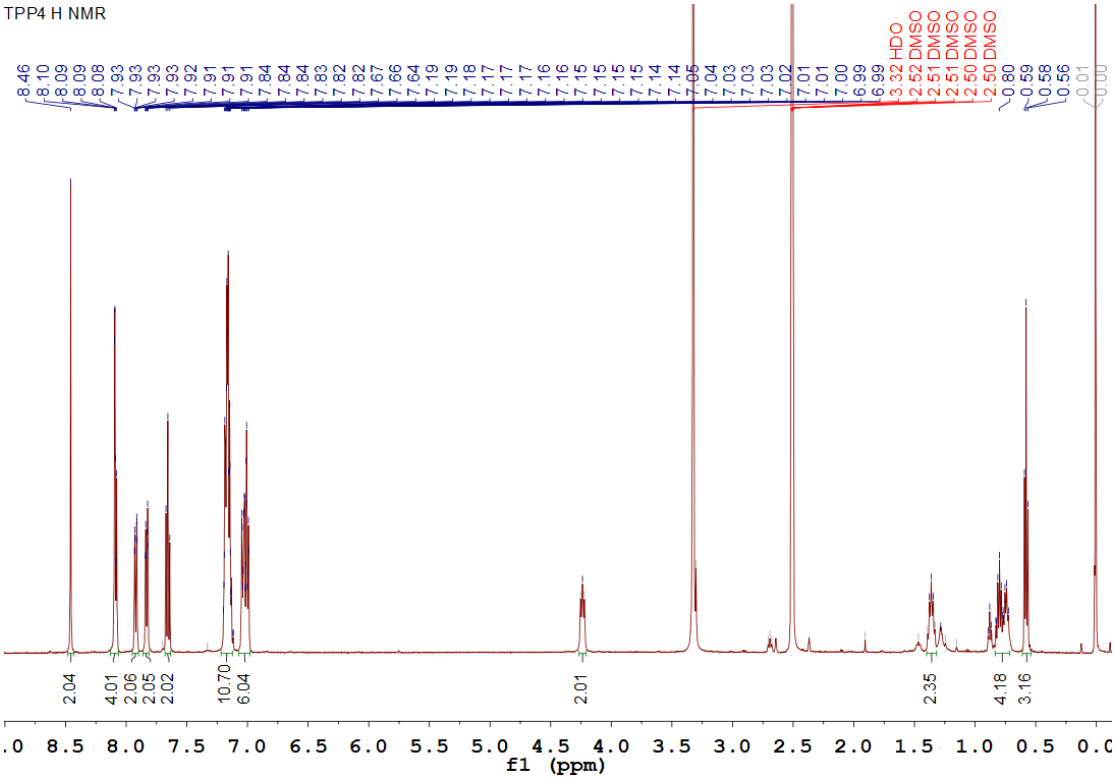


Figure S38. ^{1}H NMR spectrum of TPP4 in DMSO-d_6 at 298K.

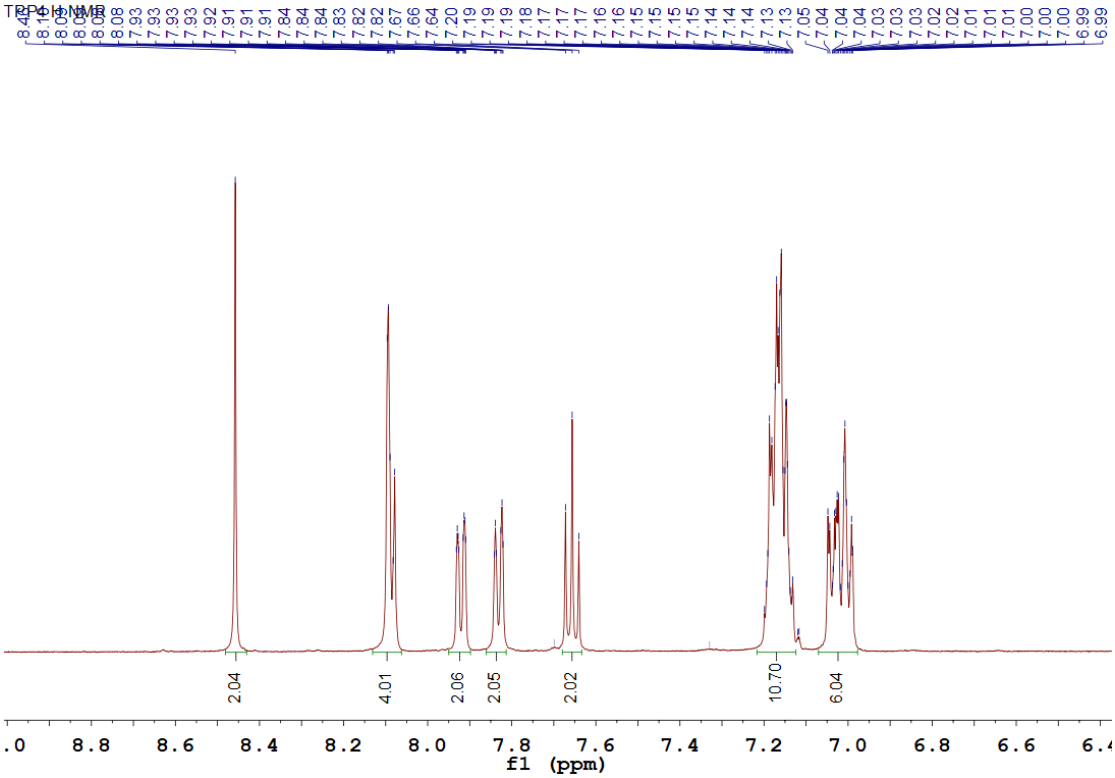


Figure S39. Enlarged aromatic region in the ^{1}H NMR spectrum of TPP4 in DMSO-d_6 at 298K.

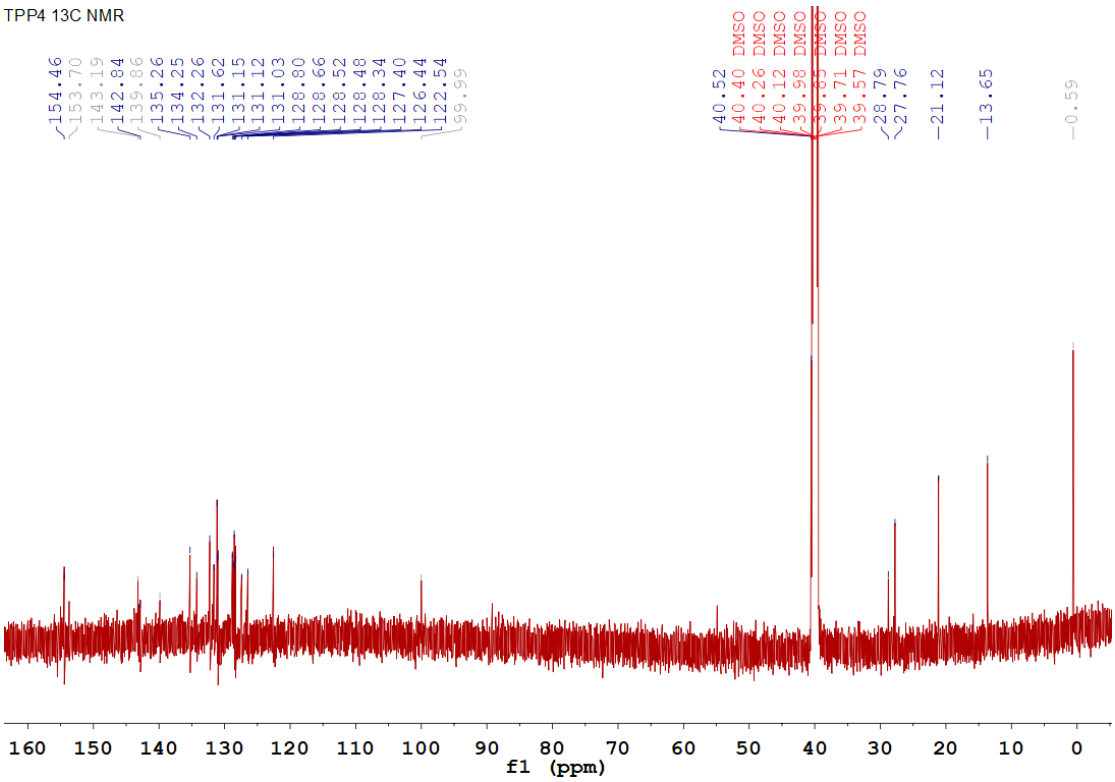


Figure S40. ^{13}C NMR spectrum of TPP4 in DMSO-d_6 at 298K.

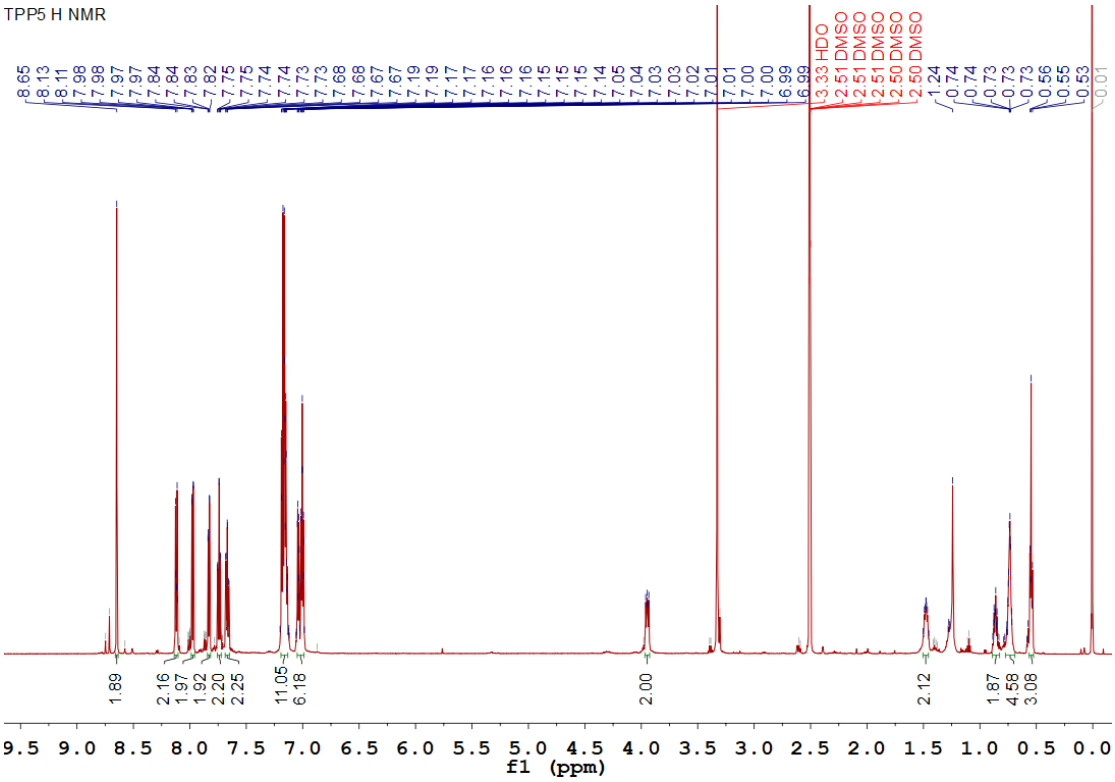


Figure S41. ^{1}H NMR spectrum of TPP5 in DMSO-d_6 at 298K.

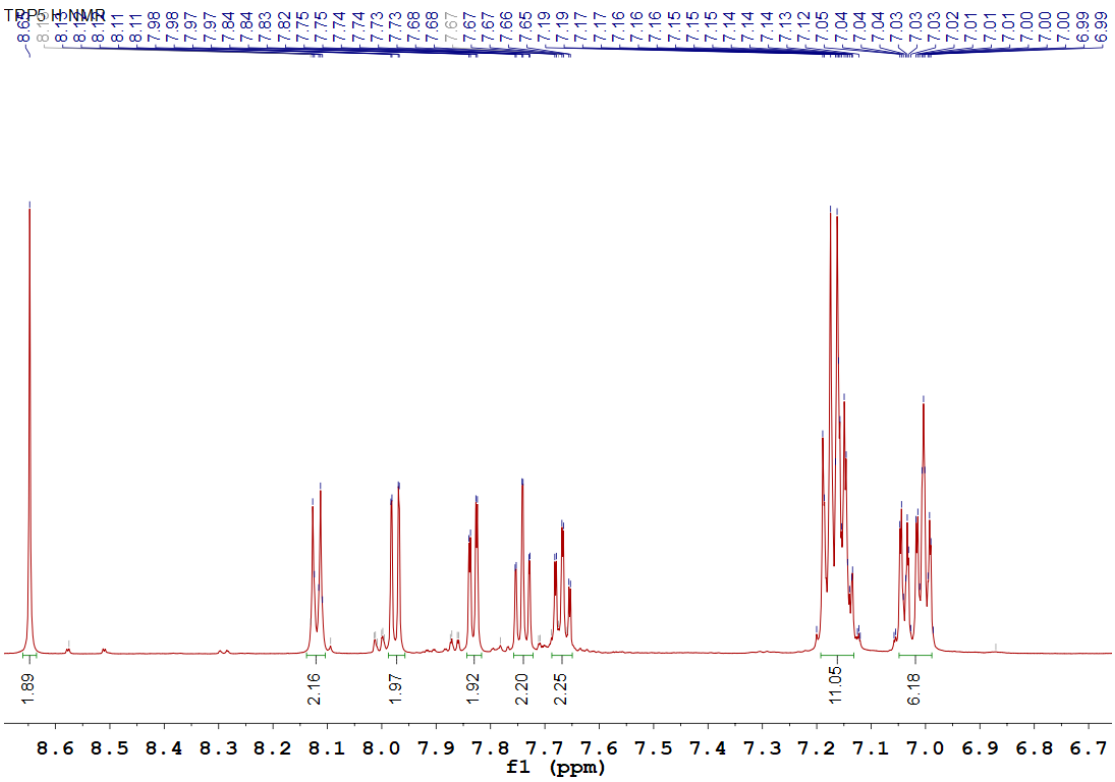


Figure S42. Enlarged aromatic region in the ^{1}H NMR spectrum of TPP5 in DMSO-d_6 at 298K.

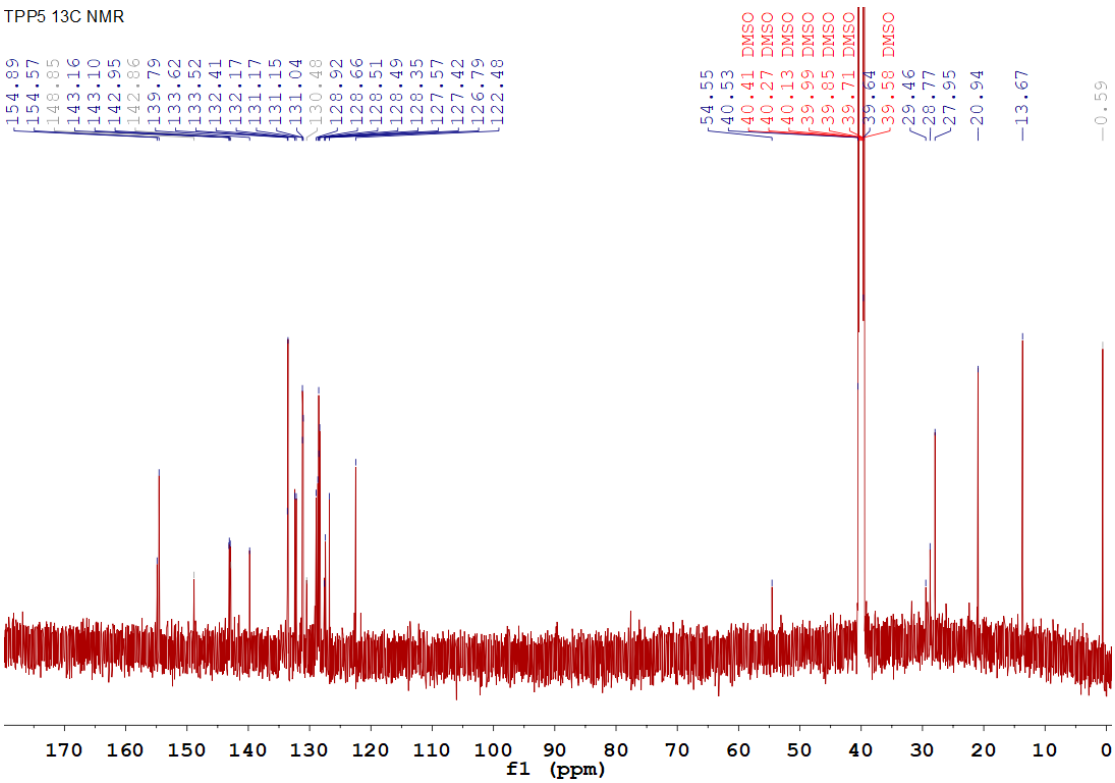


Figure S43. ^{13}C NMR spectrum of TPP5 in DMSO-d_6 at 298K.

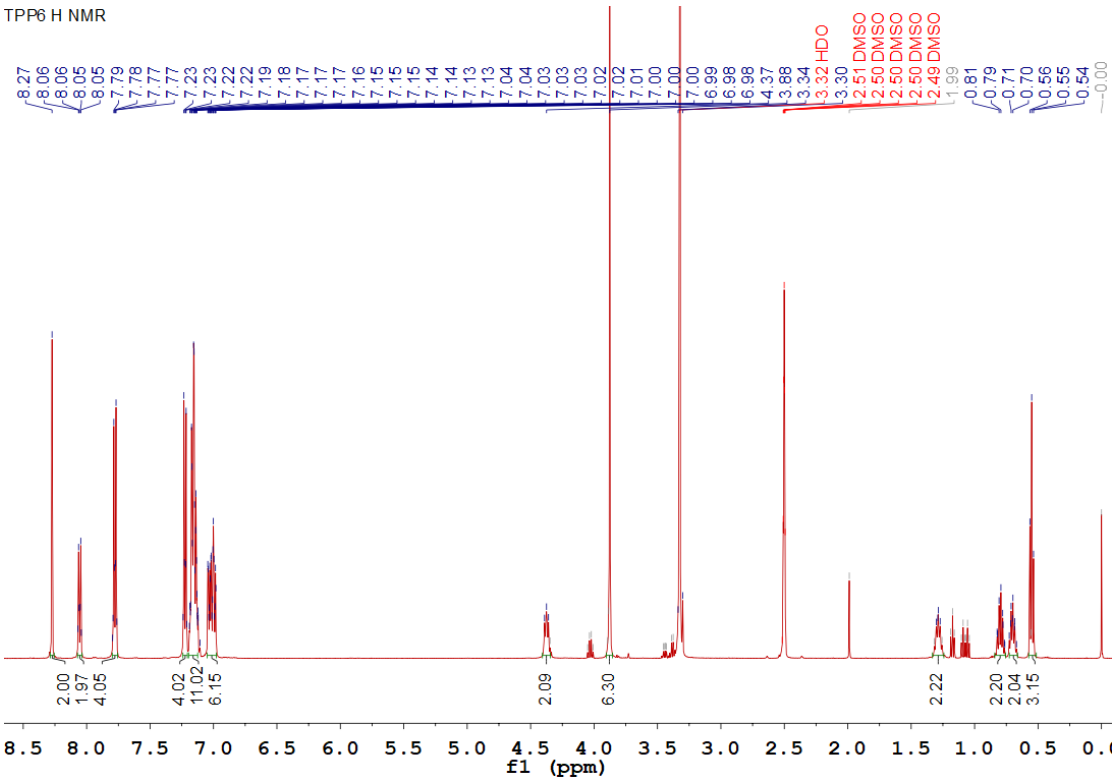


Figure S44. ^{1}H NMR spectrum of TPP6 in DMSO-d_6 at 298K.

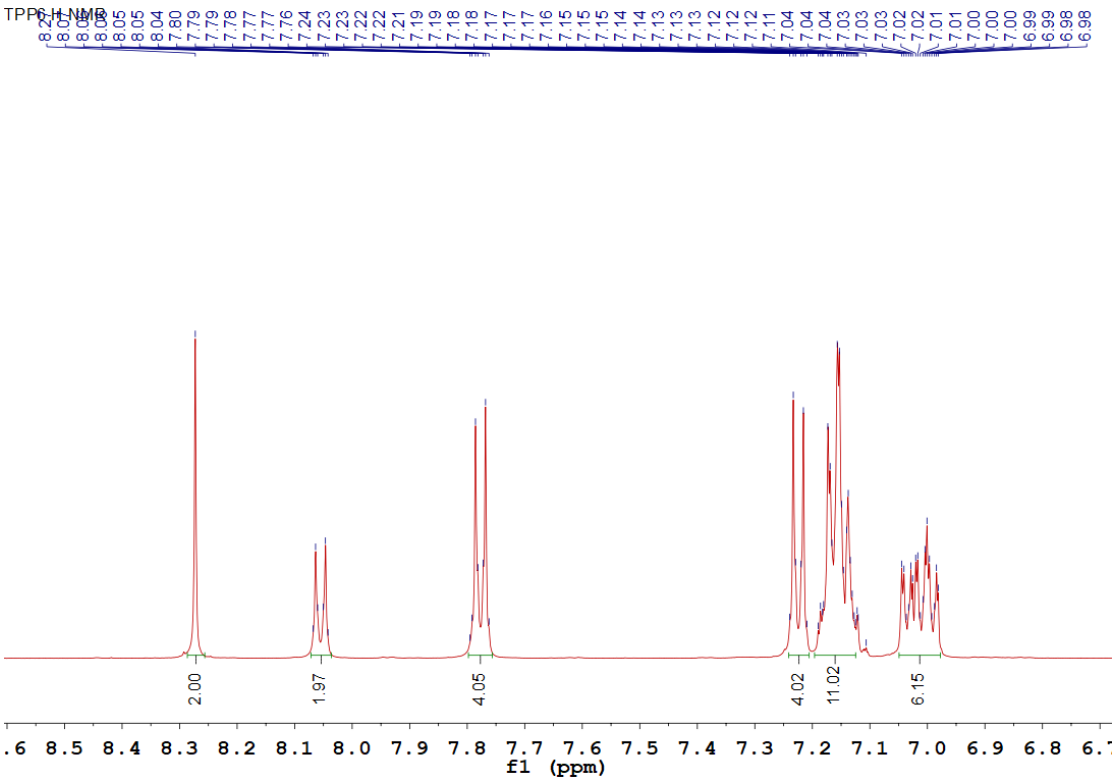


Figure S45. Enlarged aromatic region in the ^{1}H NMR spectrum of TPP6 in DMSO-d_6 at 298K.

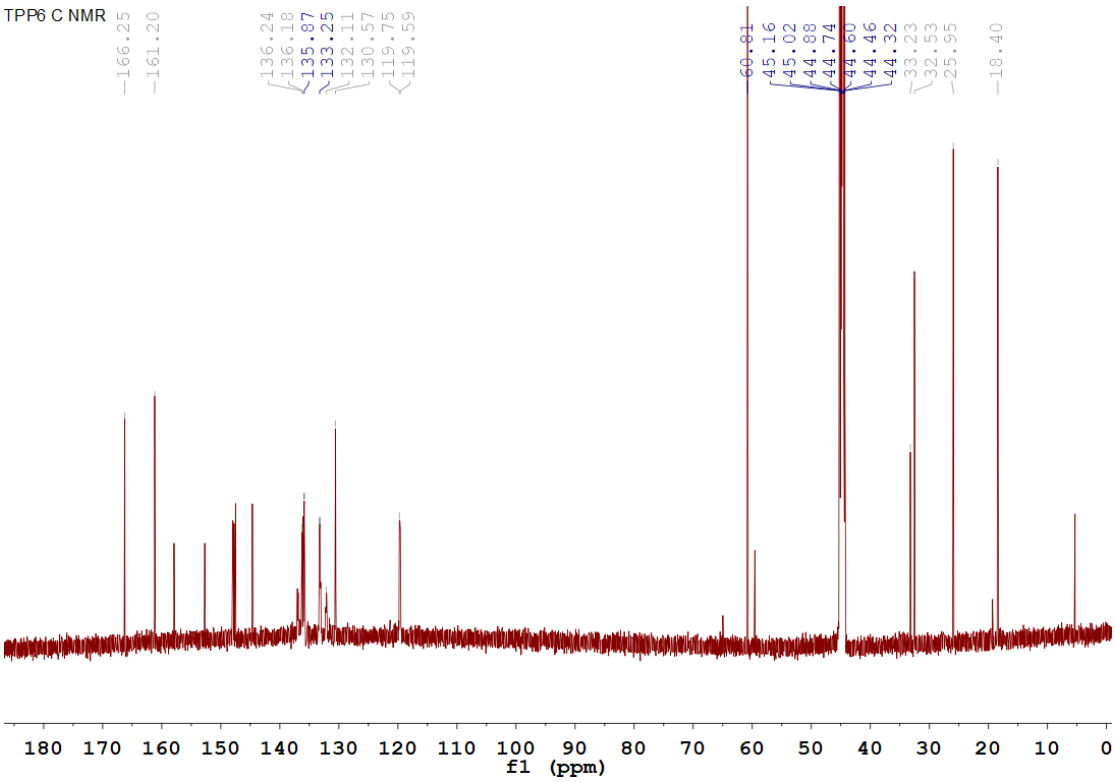


Figure S46. ^{13}C NMR spectrum of TPP6 in DMSO-d_6 at 298K.