Metallacycle-cored fluorescent supramolecular polymer networks for the detection of acidic environment

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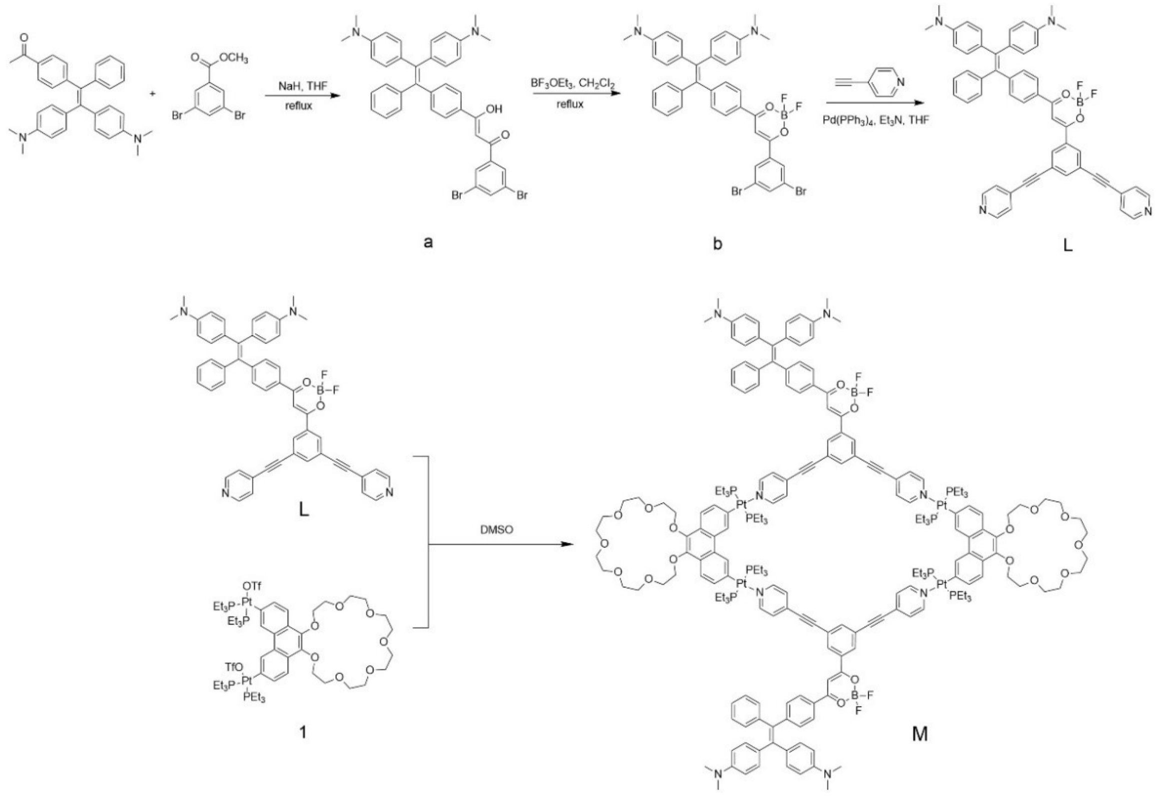
Supporting Information

1. *Materials and methods*

All reagents were commercially available from Energy Chemical Company and used as supplied without further purification. 1-(4-(2,2-Bis(4-(dimethyl amino)phenyl)-1-phenylvinyl)phenyl) ethan-1-one was prepared according to the related literature.[1] ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were collected on a Bruker Advance 500 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as deuterated solvent. Mass spectra were recorded on an Agilent Technologies 6530 Accurat-Mass Q-TOF LC/MS instrument. UV-Vis absorption spectra were performed on a Hitachi U-5300 absorption spectrophotometer. The fluorescent emission spectra were conducted on an Edinburgh FLS 980 or Hitachi F-7000 fluorescence spectrophotometer. Scanning electron microscopy (SEM) was performed on a Carl Zeiss Jena supra 55 sapphire instrument. Waters 2414 refractive index detector was used to perform gel permeation chromatography measurements at 25 °C using THF as eluent. The system was calibrated with polystyrene standards. THF and sample solutions were filtered over a filter with a pore size of 0.22 μm (PTFE, Millex-HN 13 mm Syringes Filters, Millipore, US). Rheological data were obtained by using an ARES-G2 rheometer.

2. *Synthetic procedures and characterization data*



Scheme S1 Synthetic route to **L** and **M**.

*2.1 Synthesis of **a***

The THF solution (20 mL) of 1-(4-(2,2-bis(4-(dimethylamino) phenyl)-1-phenylvinyl)phenyl)ethan-1-one (400 mg, 0.869 mmol) and methyl 3,5-dibromobenzoate (1.02 g, 3.476 mmol) was added to solution of sodium hydride (83 mg, 3.476 mmol, 60% in mineral oil) in THF (10 mL) at 0°C. The mixture was stirred at room temperature for 20 min and then refluxed for 24 h. After cooling down, diluted HCl was slowly added to quench the reaction. The solvent was removed under vacuum and the residue was partitioned between brine and dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was purified by chromatography (silica gel, PE/EA, 100:1, *v*/*v*) to afford compound **a** as a dark red solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ (ppm): 7.99 (d, J = 1.8 Hz, 2H), 7.80 (t, J = 1.8 Hz, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.04–7.17 (m, 7H), 6.91 (d, J = 2.4 Hz, 2H), 6.89 (d, J = 2.4 Hz, 2H), 6.67 (s, 1H), 6.46 (dd, J = 6.3 Hz, 4H), 2.91 (s, 6H), 2.89 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ (ppm): 186.1, 181.9, 151.3, 149.2, 149.1, 144.7, 143.6, 139.2, 137.2, 135.6, 132.8, 132.7, 132.1, 131.7, 131.4, 128.8, 127.9, 126.8, 126.0, 123.4, 111.4, 111.3, 93.3, 40.4. ESI-HRMS [**a** + H]$^+$: calcd for $[C_{39}H_{35}Br_2N_2O_2]^+$: 721.1060, found 721.1047.

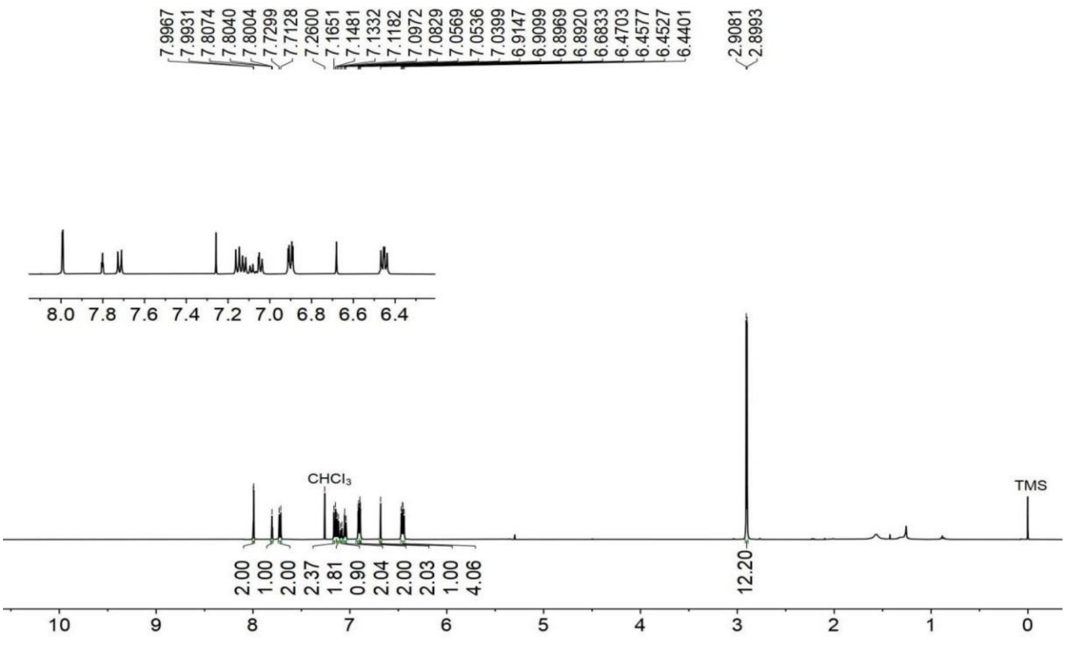


Figure S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **a**.

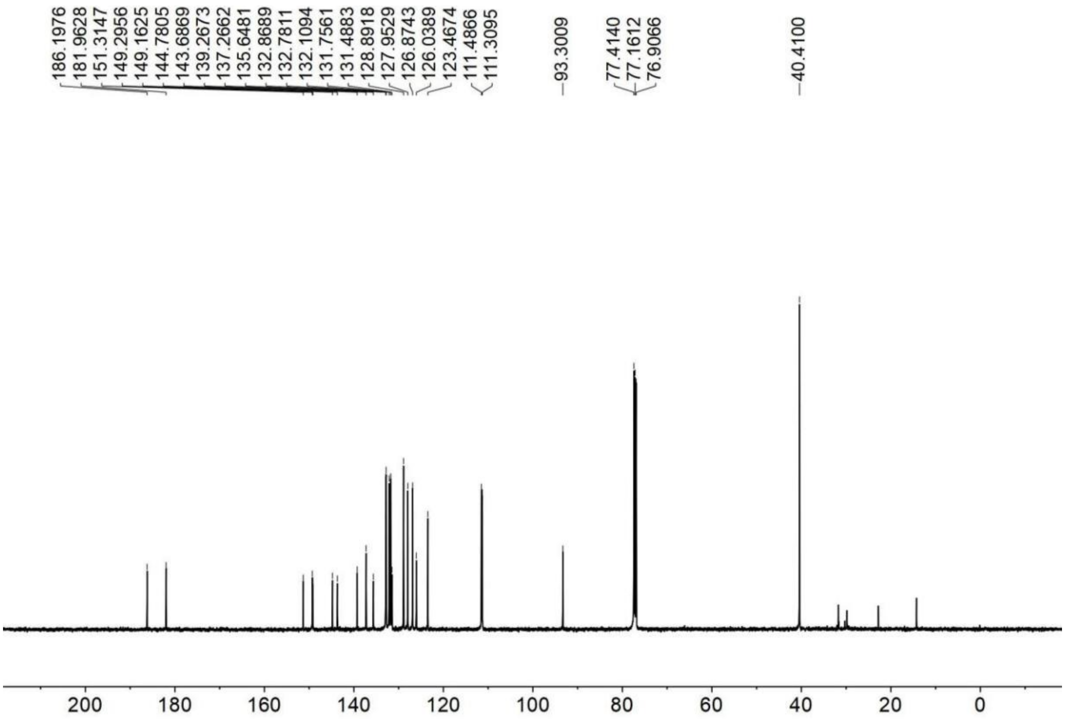


Figure S2 ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **a**.

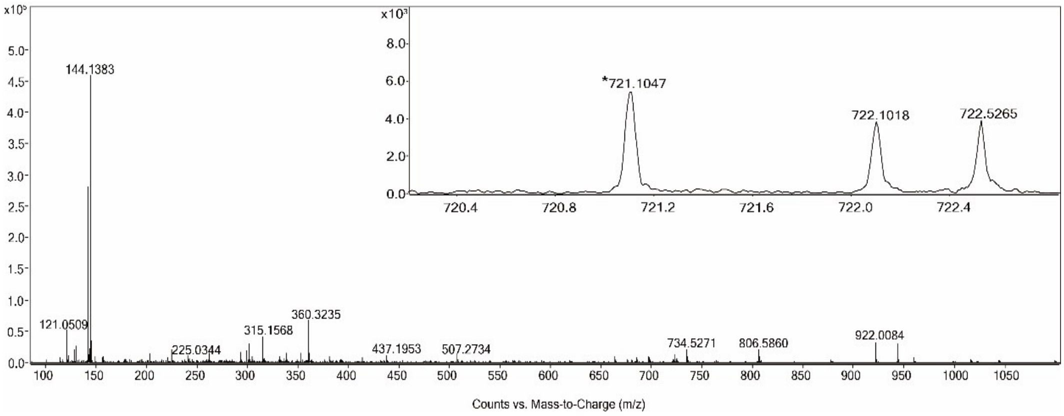


Figure S3 ESI-HRMS spectrum of **a**.

2.2 Synthesis of ***b***

A solution of $BF_3{\cdot}Et_2O$ (73.670 mg, 0.519 mmol) in CH_2Cl_2 (10 mL) was added to **a** (250 mg, 0.346 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred for 12 h at room temperature, then partitioned between brine and dichloromethane. The organic layer was dried over $MgSO_4$ and evaporated. The residue was purified by chromatography using CH_2Cl_2 as eluent to get compound **b** as a blue-black solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ (ppm): 8.11 (d, J = 1.7 Hz, 2H), 7.90 (t, J = 1.7 Hz, 1H), 7.88 (d, J = 8.7 Hz, 2H), 7.04–7.20 (m, 7H), 6.99 (s, 1H), 6.90 (dd, J = 2.7 Hz, 4H), 6.47 (dd, J = 8.8 Hz, 4H), 2.94 (s, 6H), 2.92 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ (ppm): 184.0, 177.8, 155.6, 149.7, 149.4, 145.9, 144.4, 139.4, 135.8, 133.1, 132.9, 132.6, 131.8, 131.1, 130.0, 129.0, 128.1, 127.7, 126.3, 123.8, 111.4, 111.2, 93.8, 40.3. ESI-HRMS [**b** + H]$^+$: calcd for: $[C_{39}H_{34}BBr_2F_2N_2O_2]^+$ 768.1079, found 768.1018.

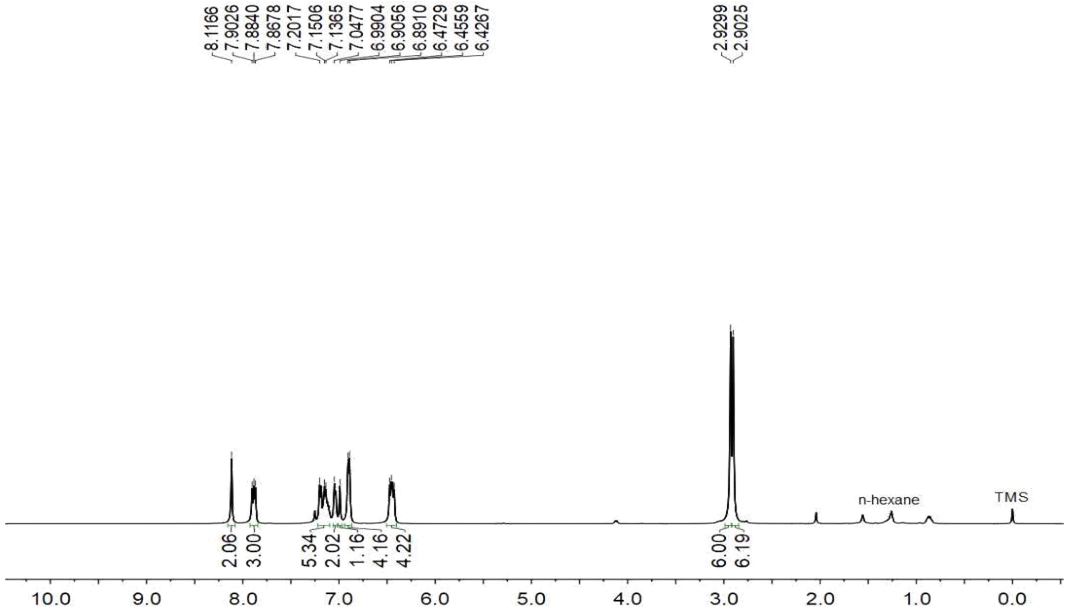


Figure S4 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **b**.

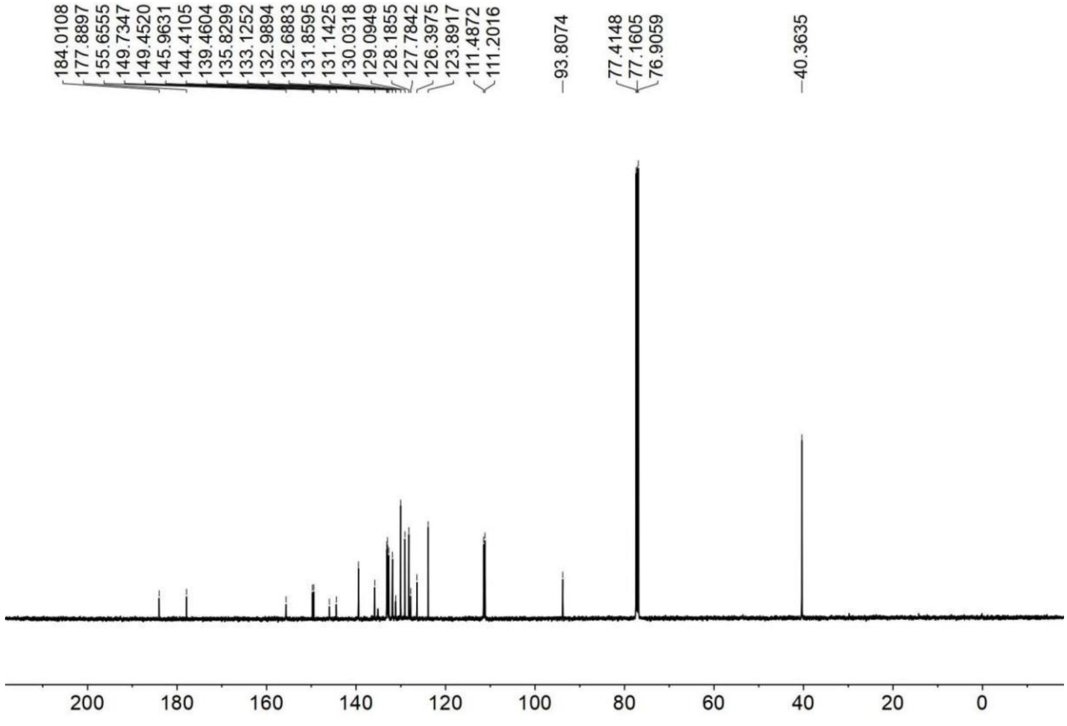


***Figure S*5** ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **b**.

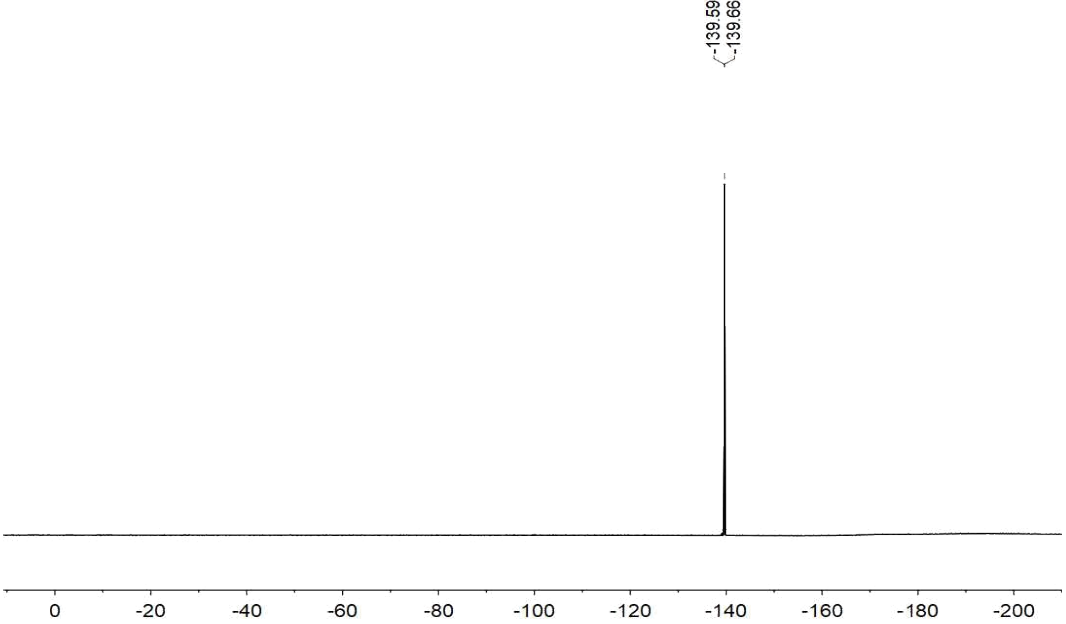


Figure S6 ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of **b**.

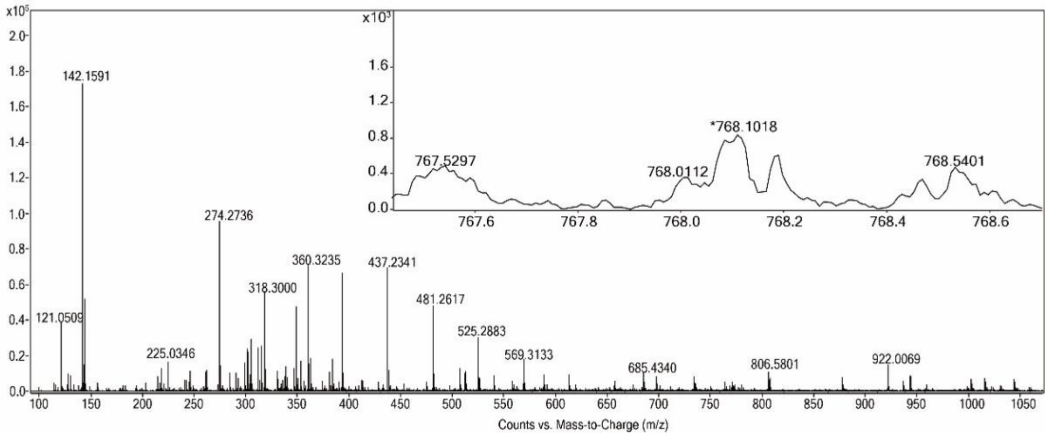


Figure S7 ESI-HRMS spectrum of **b**.

*2.2 Synthesis of **L***

4-Alkynylpyridine (480 mg, 4.668 mmol), **b** (600 mg, 0.778 mmol), $Pd(PPh_3)_4$ (250 mg, 0.216 mmol) and CuI (80 mg, 0.421 mmol) were dissolved into THF (50 mL) and triethylamine (0.2 mL, 1.440 mmol). After the mixture was deoxygenated with liquid nitrogen three times, the mixture was refluxed at 65 °C for 48 h. After cooling down, the solvent was removed with rotary evaporator, and the residue was extractd with CH_2Cl_2 for three times. The organic layer was dried over $MgSO_4$ and evaporated. The residue was purified by chromatography (silica gel, CH_2Cl_2/CH_3OH, 70:1, *v*/*v*) to get compound **L** as a blue-black solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ (ppm): 8.66 (d, J = 5.1 Hz, 4H), 8.23 (s, 2H), 7.96 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 5.6 Hz, 4H), 7.12–7.21 (m, 5H), 7.10 (s, 1H), 7.05 (d, J = 6.8 Hz, 2H), 6.91 (d, J = 8.2 Hz, 4H), 6.48 (dd, J = 8.7 Hz, 4H), 2.94 (s, 6H), 2.93 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ (ppm): 183.7, 178.7, 155.4, 150.0, 149.6, 149.4, 145.8, 144.4, 139.6, 135.0, 133.5, 133.1, 132.9, 132.6, 131.8, 131.7, 131.1, 130.4, 129.0, 128.1, 127.8, 126.3, 125.6, 124.1, 111.4, 111.1, 93.6, 91.1, 89.0, 77.4, 77.1, 96.9. ESI-HRMS [**L** + H]$^+$: calcd for: $[C_{53}H_{42}BF_2N_4O_2]^+$ 814.3400, found 814.3365.

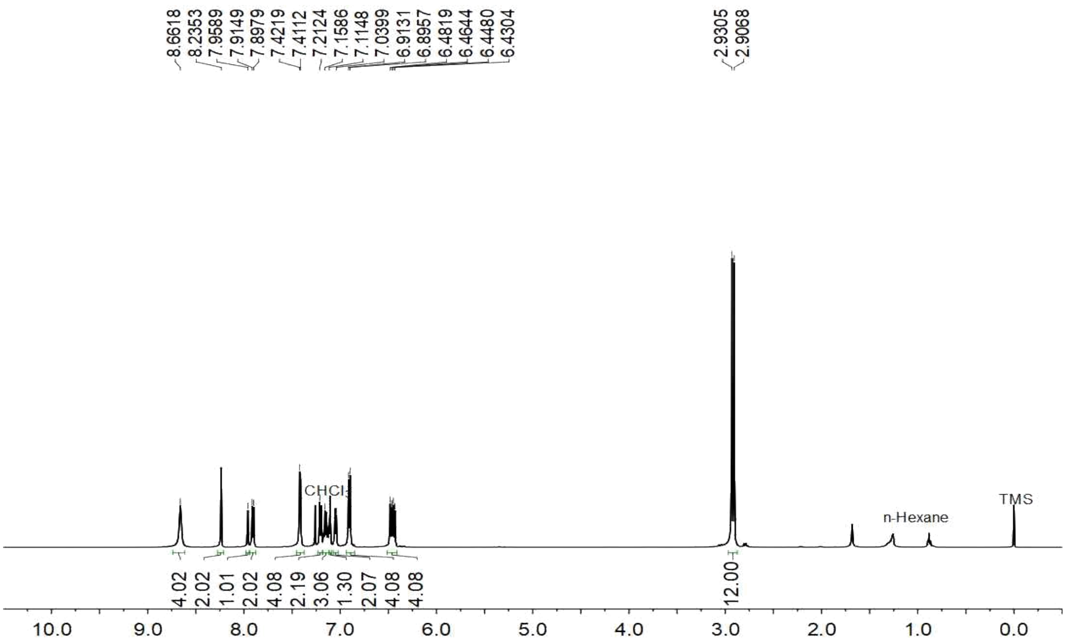


Figure S8 ^1H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **L**.

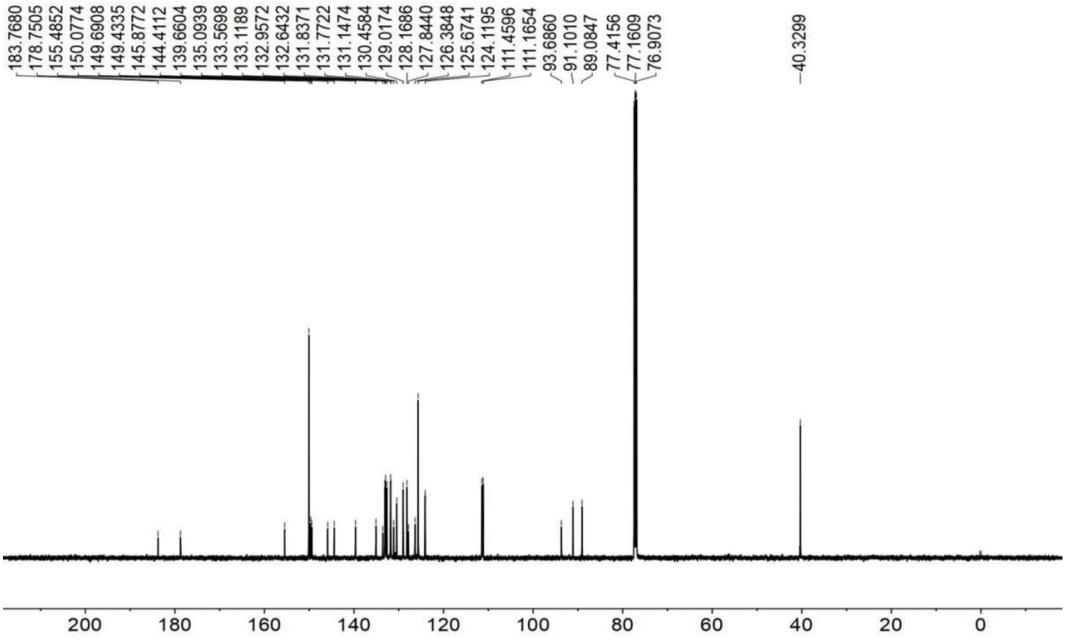


Figure S9 ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **L**.

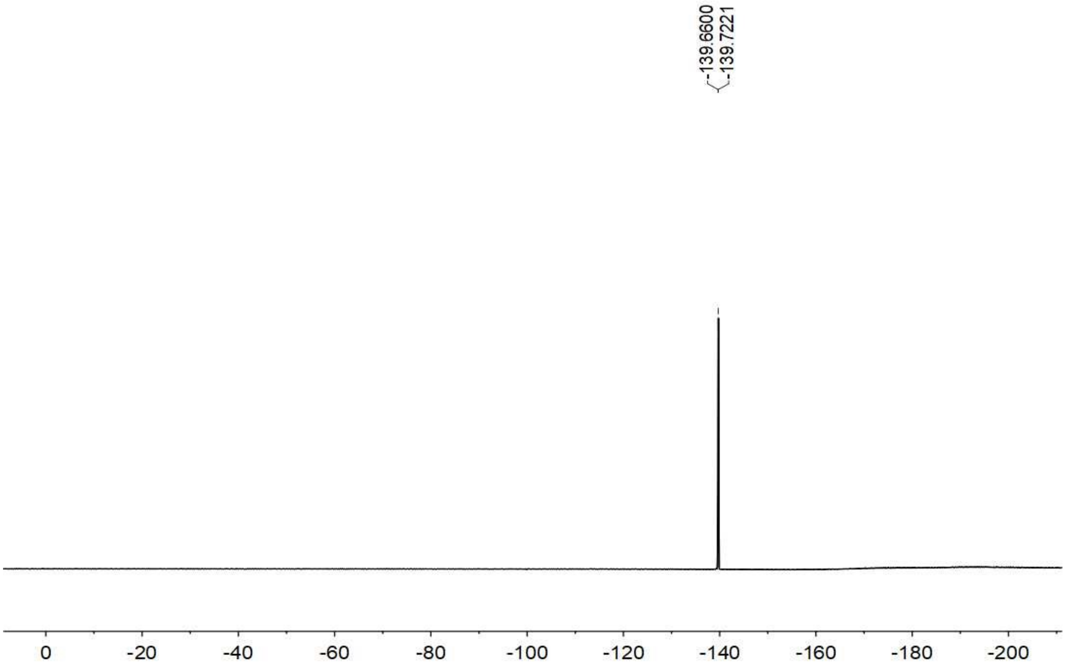


Figure S10 ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of **L**.

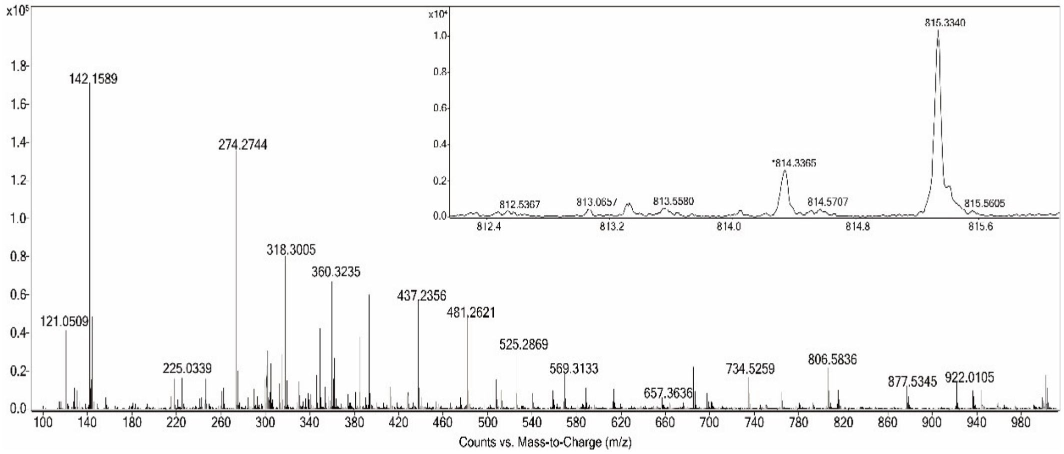


Figure S11 ESI-HRMS spectrum of **L**.

*2.4 Synthesis of **1***

1 was synthesized according to literature procedure.[2] ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ (ppm): 8.33 (s, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 4.50–4.48 (m, 4H), 4.12–4.11 (m, 4H), 3.95–3.93 (m, 4H), 3.81–3.79 (m, 8H), 3.76–3.75 (m, 4H), 1.63–1.62 (m, 24H), 1.15–1.11 (m, 36H). ^{31}P NMR (202 MHz, $CDCl_3$, 298 K) δ (ppm): 19.34 (s, ^{195}Pt satellites, $^1J_{Pt–P}$ = 2793.39 Hz).

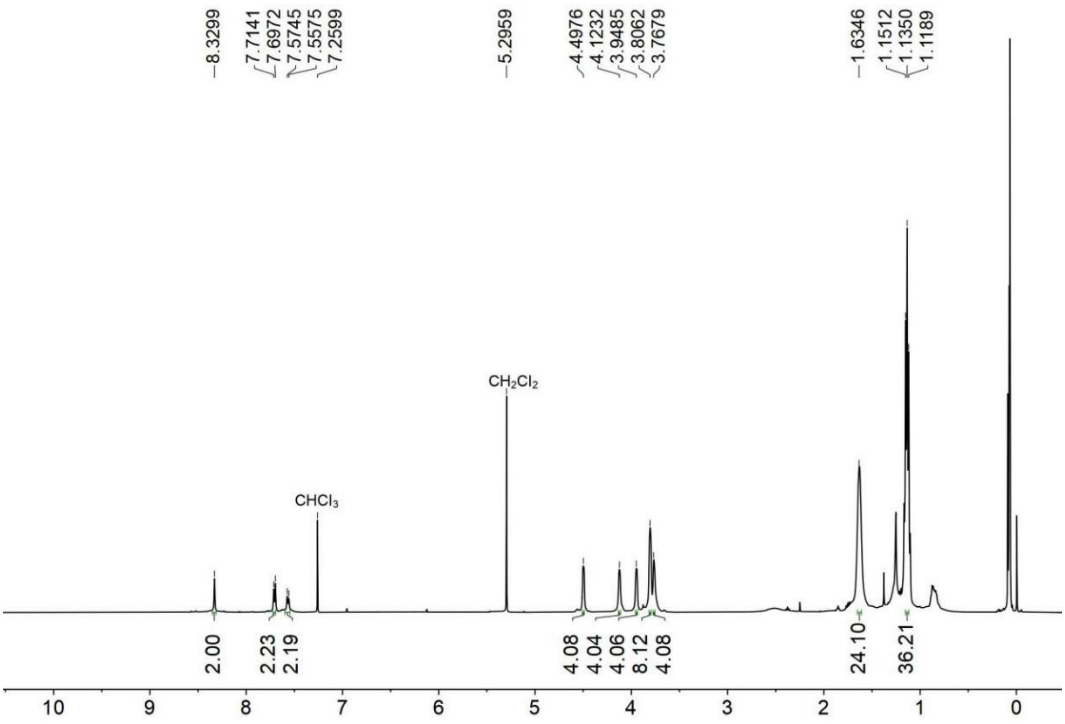


Figure S12 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1**.

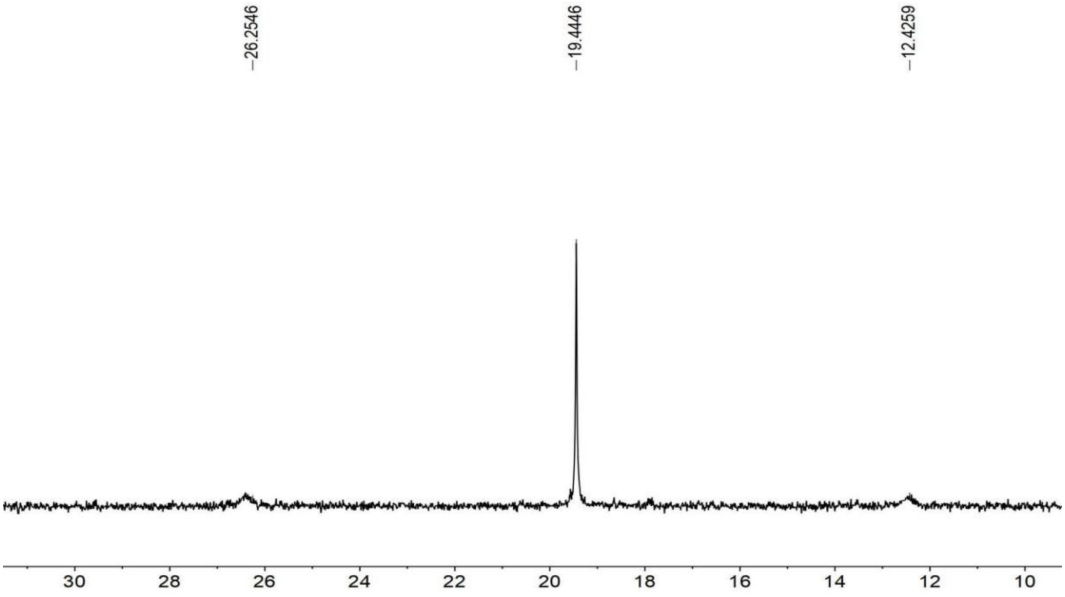


Figure S13 ^{31}P NMR spectrum (202 MHz, $CDCl_3$, 298 K) of **1**.

*2.5 Synthesis of **M***

L (10.085 mg, 0.012 mmol) and **1** (20.012 mg, 0.012 mmol) were dissolved anhydrous DMSO (1 mL) and the mixture was stirred at 65 ^{0}C for 12 h. After cooling down, diethyl ether (7 mL) were added to obtain a brown solid. ^{1}H NMR (500 MHz, DMSO-d_6, 298K) δ (ppm): 8.99 (m, 4H), 8.91(m, 4H), 8.76 (m, 2H), 8.71 (m, 2H), 8.59 (m, 2H), 8.49 (m, 2H), 8.44 (s, 2H), 8.31 (s, 2H), 8.21–8.19 (m, 2H), 7.99–7.93 (m, 12H), 7.65–7.63 (m, 4H), 7.18–7.14 (m, 12H), 7.01–6.99 (m, 4H), 6.84–6.78 (m, 8H), 6.53–6.47 (m, 8H), 4.31–4.30 (m, 8H), 3.93–3.92 (m, 8H), 3.71–3.51 (m, 32H), 2.86–2.84 (m, 24H), 1.35–1.33 (m, 48H), 1.12–1.09 (m, 72H). ^{31}P NMR (202 MHz, DMSO-*d₆*, 298 K) δ (ppm): 13.61 (s, ^{195}Pt satellites, ${}^{1}J_{\text{Pt–P}}$ = 2654.70 Hz). ESI-TOF-MS: *m/z* 1470.20 [M – 3OTf]$^{3+}$.

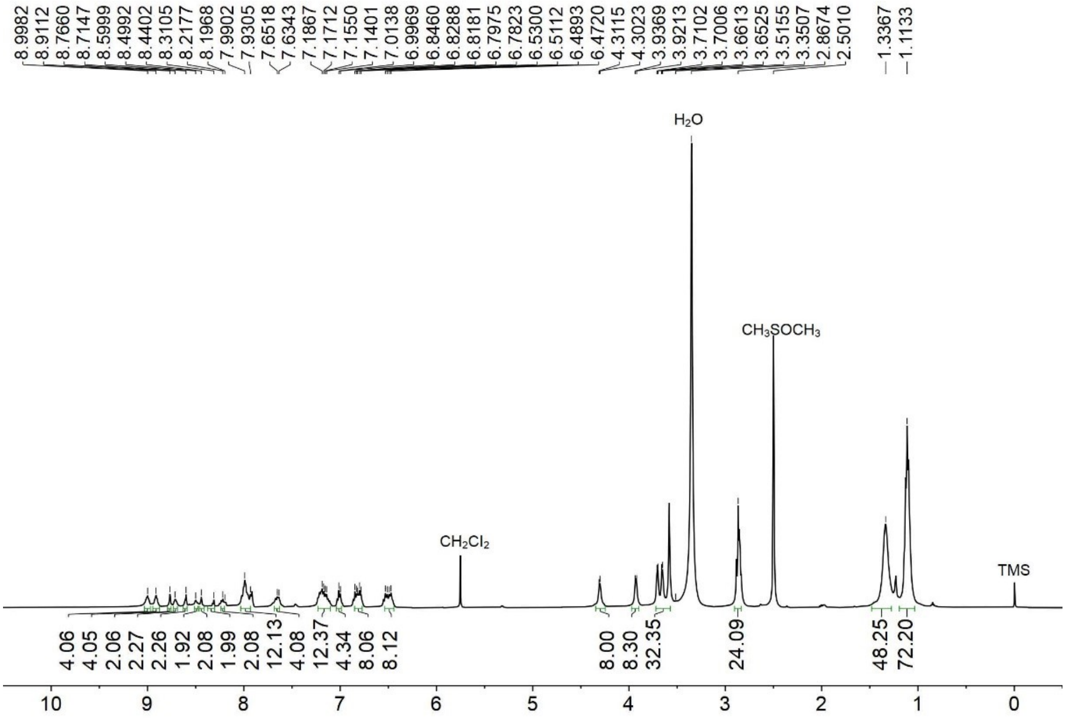


Figure S14 ^{1}H NMR spectrum (500 MHz, DMSO-*d₆*, 298 K) of **M**.

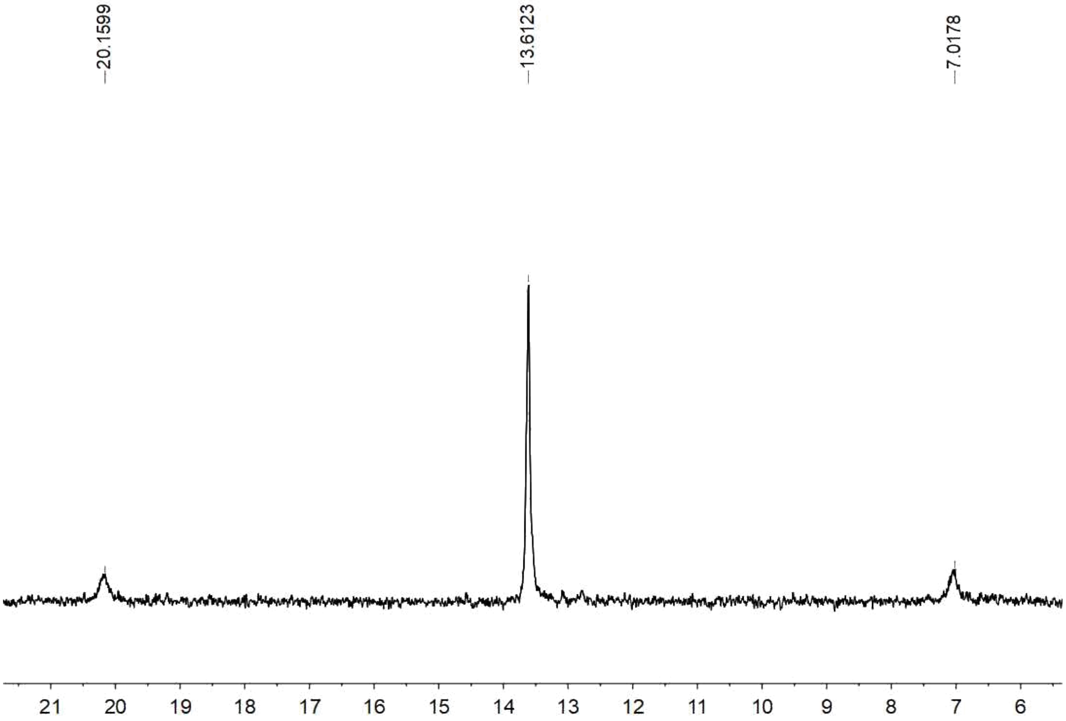


Figure S15 ^{31}P NMR spectrum (202 MHz, DMSO-*d₆*, 298 K) of **M**.

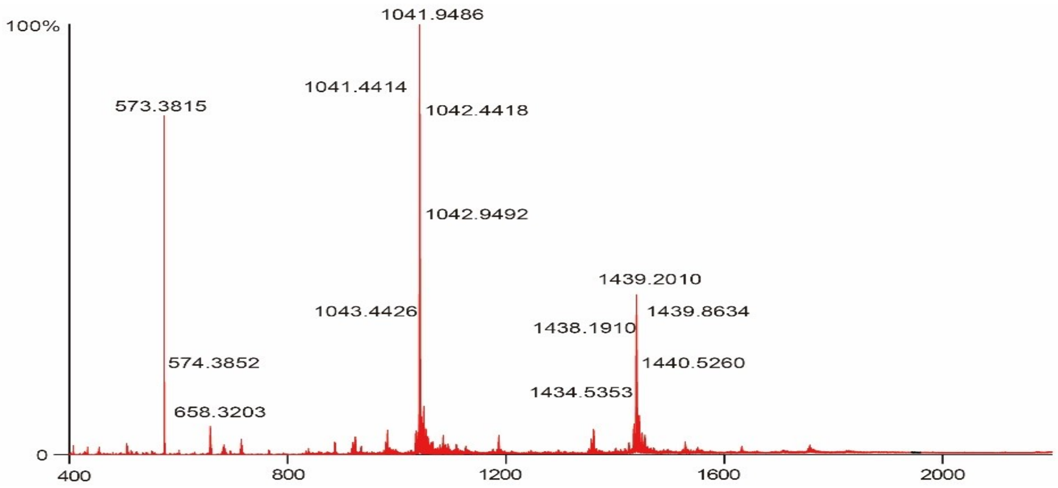
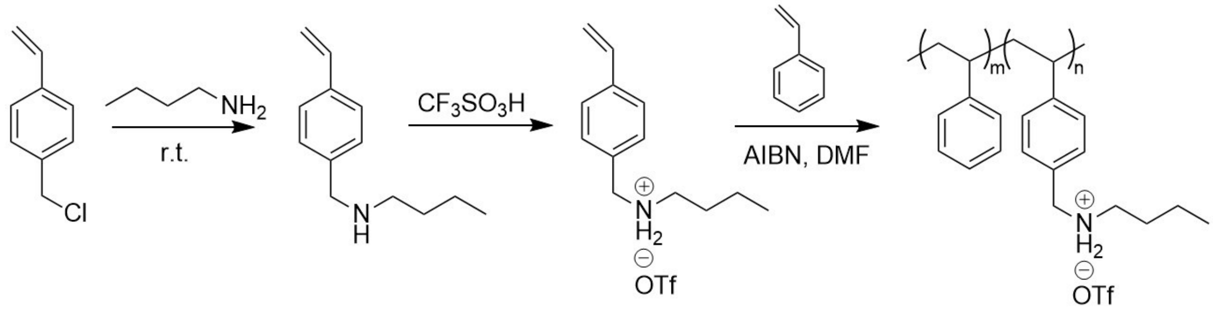


Figure S16 ESI-TOF-MS spectrum of **M**.



Scheme S2 Synthetic route to **2**.

*2.6 Synthesis of **2***

2 was synthesized according to literature procedure.[2] ^{1}H NMR (500 MHz, CDCl$_3$, 298K) δ (ppm): 7.07–7.01 (m, H$_{Ar}$), 6.57–6.43 (m, H$_{Ar}$), 4.10–3.99 (m, H$_a$), 2.76–2.64 (m, H$_b$).

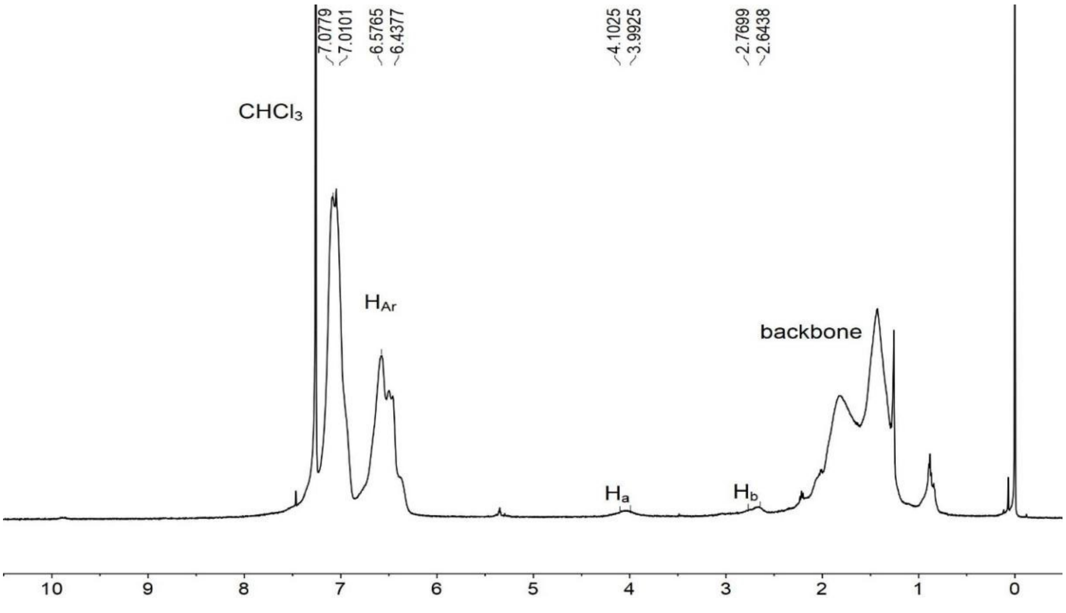
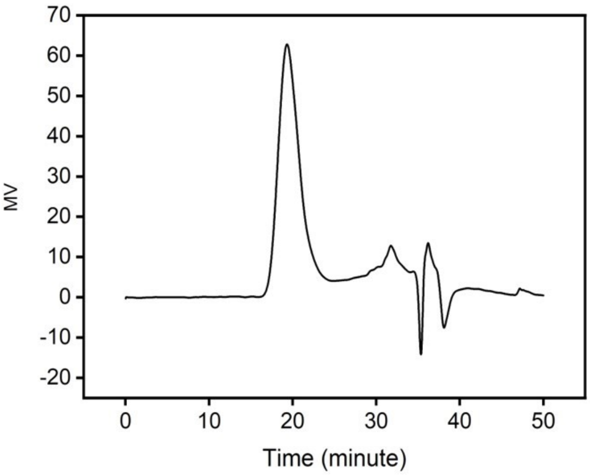


Figure S17 ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of **2**.



RT (min)	Mn(Da)	PDI
19.33	6.5×10^4	1.51

Figure S18 GPC spectrum of **2-Boc**.

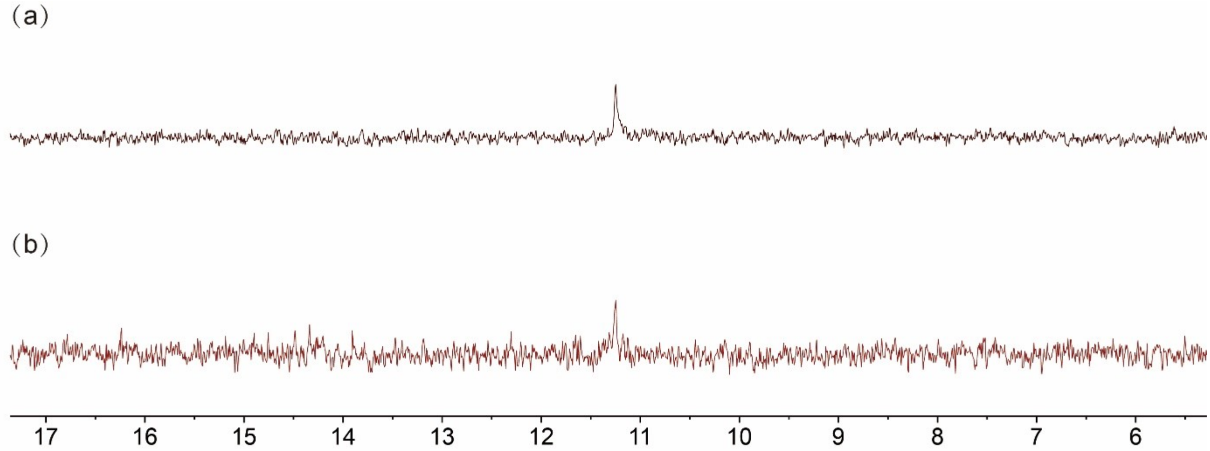


Figure S19 (a) ^{31}P NMR of SP. (b) ^{31}P NMR of SP after acid-base cycle.

3. *Optical characterization*

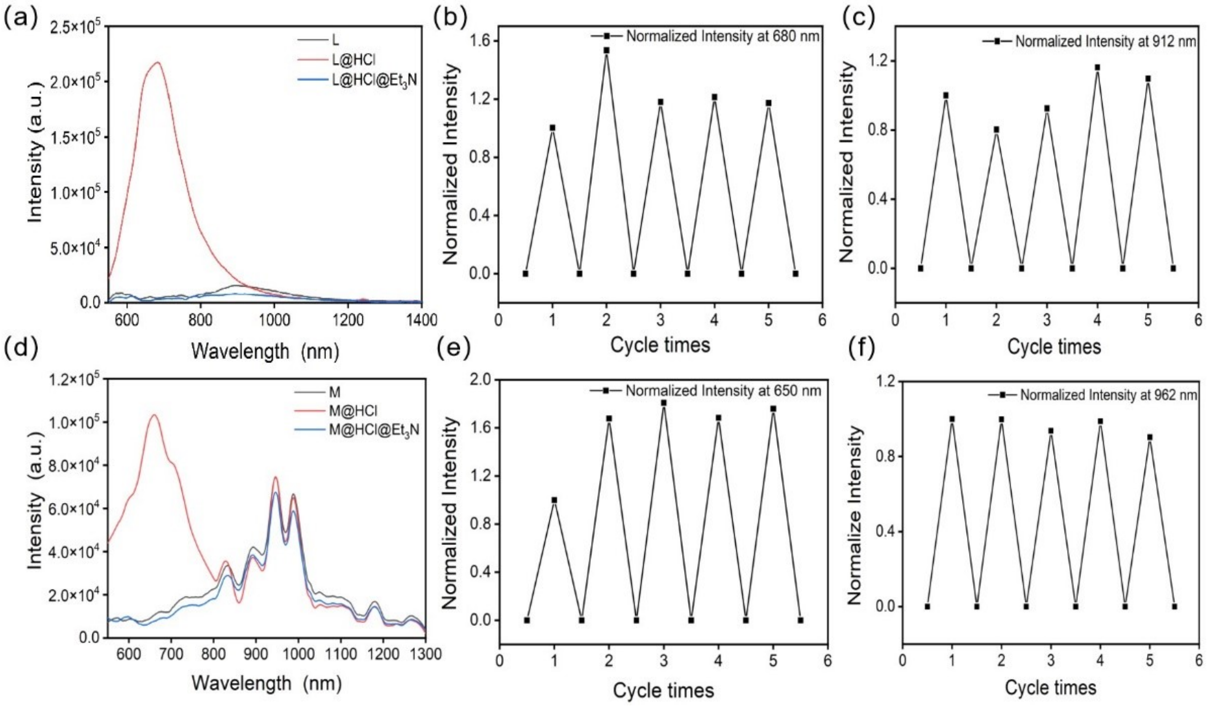


Figure S20 (a) Emission spectra of **L** in HCl steam and Et_3N steam. (b) & (c) Circulation of **L** in HCl and Et_3N; (d) Emission spectra of **M** in HCl steam and Et_3N steam. (e) & (f) Circulation of **M** in HCl and Et_3N.

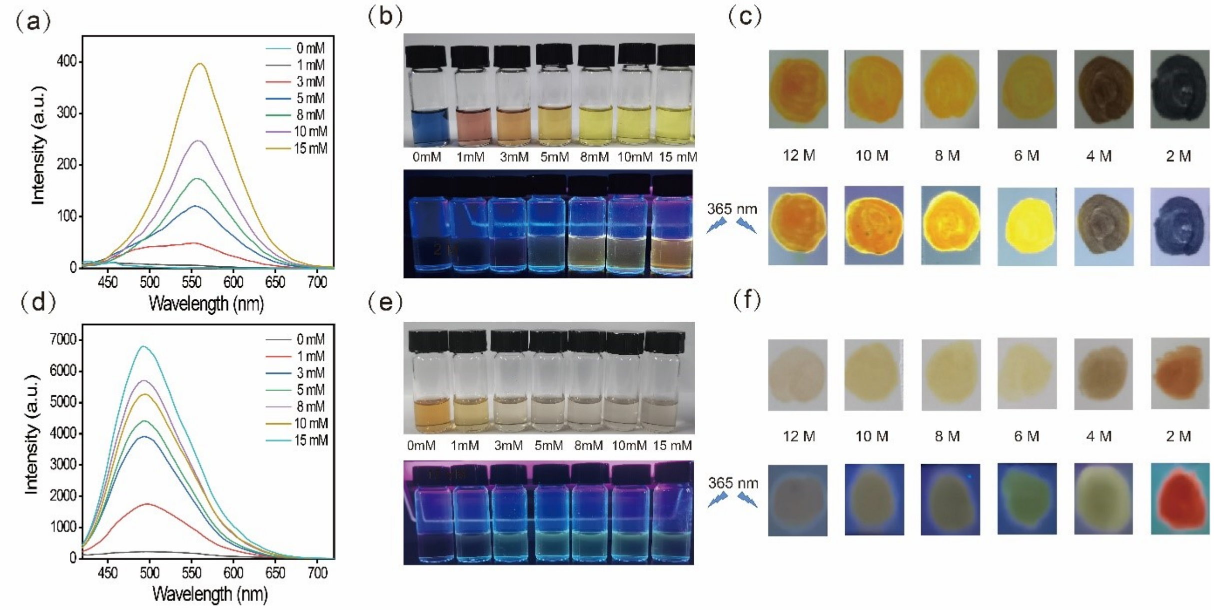


Figure S21 (a) & (b) Emission spectra and image of **L** (50 μ M) in different CF_3COOH concentrations (0–20 mM). (c) Image of **L** in HCl steam of different concentrations for 12 h under 365 nm. (d) & (e) Emission spectra and image of **M** (50 μ M) in different CF_3COOH concentrations for 12 h under 365 nm. (f) Image of **M** in HCl steam of different concentrations for 12 h under 365 nm.

4. Reference

(1) J. D. Zheng, Q. Zeng, R. J. Zhang, D. Xing and T. Zhang, *J. Am. Chem. Soc.,* **2019**, *141*, 19226-19230.

(2) Y. Y. Zhang, F. Chen, Y. Li, H. Y. Qiu, J. J. Zhang and S. C. Yin, *Chin. J. Chem.,* **2021**, *39*, 2731-2737.