Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Fast thermal-responsive azatriphenylene ionic discotic liquid crystalline polymers with shape memory properties

Xiao-Ping Xiong,[a] Qian Yang,[a] Ruo-Jun Wang,[a] Ling-Yi Zeng,[a] Wen-Hao Yu,[a,b]*

Hong-Mei Chen,[a] Hai-Liang Ni,[a] Chun Feng,[a] Ke-Qing Zhao[a] and Ping Hu[a]*

[a]College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, Sichuan Province, 610068, People's Republic of China.

[b] College of Polymer Science & Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, People's Republic of China.

Corresponding author:

Wenhao Yu* Email: yuwenhao@sicnu.edu.cn

Ping Hu* Email: hp_x@sicnu.edu.cn

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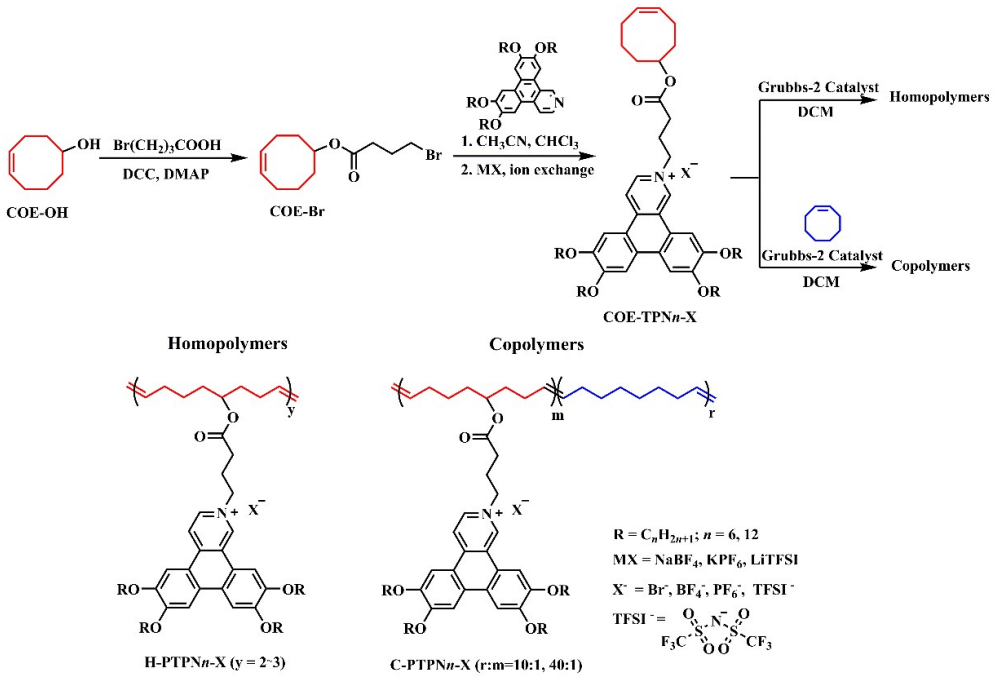
Experimental Section



Scheme 1. Synthetic route of the azatriphenylene IDLC monomers and polymers.

Instruments and Materials

^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a Bruker 600 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in units of parts per million (ppm) by assigning the TMS resonance in the ^{1}H spectrum as 0.00 ppm and the $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet. IR spectra were recorded on a Bruker VERTEX70 spectrometer using KBr discs. High-resolution mass spectra were obtained using a Bruker BioTOF-Q mass spectrometer and/or a Varian 7.0T FTMS mass spectrometer. Mesomorphic textures were observed and recorded using a polarizing optical microscope (POM, Zeiss, AXIO Scope A1), equipped with a hot stage (Mettler, FP80HT) and controller (Linkam Scientific, T95-STD). Phase transition temperatures and enthalpies of compounds were investigated using a differential scanning calorimetry (DSC) TA-discovery calorimeter under a nitrogen atmosphere, with heating and cooling rates of 10 ℃/min.

Temperature-variation X-ray diffraction (XRD) experiments were conducted on a Rigaku Smartlab (3) X-ray diffractometer equipped with a TCU 110 temperature control unit, and the sample temperature was controlled within ±1 K. The X-ray source (Cu Kα, λ = 0.154 nm) was provided by 40 kW ceramic tubes. Ultraviolet-visible (UV-vis) absorption spectra were measured at room temperature on a Perkin Elmer Lambda 950 spectrophotometer. Photoluminescence spectra were recorded on a Horiba

Fluorolog-4 spectrophotometer. Dynamic mechanical analysis (DMA) was performed on a DMA Q850 (TA Instruments) in film tension mode (stress control). Uniaxial tensile tests were conducted at room temperature using an Instron 5567 (Instron Corporation, Norwood, MA, USA). Electrochemical impedance spectroscopy (EIS) experiments were recorded on an Autolab PGSTAT302 voltammetric analyser. The molecular weight and polydispersity were investigated using gel permeation chromatography (GPC) on a Waters Associates GPC system. Degassed THF was used as the eluent at a flow rate of 1.0 mL/min.

All other chemicals were purchased commercially and used as received unless otherwise indicated. Column chromatography was performed on silica gel (200-300 mesh), and all reported yields are isolated yields.

Synthesis of all ionic monomers and polymers

Synthesis of COE-Br

A 50 mL flask equipped with a magnetic stir bar was charged with cyclooct-4-enol (0.5 g, 4.0 mmol), 4-bromobutyric acid (1.0 g, 6.0 mmol), 4-dimethylaminopyridine (DMAP, 96.8 mg, 0.8 mmol), dicyclohexylcarbodiimide (DCC, 3.3 g, 16.0 mmol), and dichloromethane (CH_2Cl_2, 20 mL). The mixture was stirred at room temperature under a nitrogen atmosphere for 18 hours. The resulting precipitate was filtered off, and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel, eluting with petroleum ether/CH_2Cl_2 (2:1, v/v), to afford a colorless oily liquid **COE-Br** (0.98 g, 89%). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 5.63 ~ 5.55 (m, 2H, CH=CH), 4.79 ~ 4.76 (m, 1H, CH), 3.40 ~ 3.38 (m, 2H, CH_2), 2.40 ~ 2.37 (m, 2H, CH_2), 2.28 ~ 2.25 (m, 1H, CH_2), 2.12 ~ 2.08 (m, 4H, CH_2), 2.06 ~ 2.02 (m, 1H, CH_2), 1.83 ~ 1.78 (m, 2H, CH_2), 1.66 ~ 1.62 (m, 1H, CH_2), 1.57 ~ 1.50 (m, 3H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.84, 128.81, 128.55, 74.89, 32.70, 32.64, 31.86, 31.78, 26.82, 24.54, 23.81, 21.26.

Synthesis of COE-TPN6-Br and COE-TPN12-Br

A solution containing a mixture of **COE-Br** (0.4 g, 1.5 mmol), **TPN6** (0.8 g, 1.3 mmol), 2 mL acetonitrile, and 4 mL trichloromethane was stirred at 82 ℃ for 48 hours. After cooling, the solution was concentrated under vacuum. The residue was purified by column chromatography on silica gel, first eluting with CH_2Cl_2/ethyl acetate (5:1, v/v) to remove starting reactants, and then eluting with a mixture of CH_2Cl_2:ethanol (2:1, v/v) to give a light yellow solid (0.92 g, 80%) as the product **COE-TPN6-Br**. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ: 10.98 (s, 1H, ArH), 8.59 (d, J = 6.8 Hz, 1H, ArH), 8.43 (d, J = 6.8 Hz, 1H, ArH), 8.36 (s, 1H, ArH), 7.56 (s, 1H, ArH), 7.52 (s, 1H, ArH), 7.48 (s, 1H, ArH), 5.61 ~ 5.53 (m, 2H, CH=CH), 5.33 (t, J = 7.2 Hz, 2H, NCH_2), 4.71 ~ 4.65 (m, 1H, OCH), 4.55 (t, J = 6.4 Hz, 2H,

OCH_2), 4.27 (t, J = 6.4 Hz, 2H, OCH_2), 4.21 (t, J = 6.4 Hz, 2H, OCH_2), 4.16 (t, J = 6.4 Hz, 2H, OCH_2), 2.55 (t, J = 6.8 Hz, 2H, $COCH_2$), 2.37 ~ 2.30 (m, 2H, CH_2), 2.27 ~ 2.23 (m, 1H, CH_2), 2.11 ~ 2.06 (m, 2H, CH_2), 2.02 ~ 1.91 (m, 9H, CH_2), 1.79 ~ 1.71 (m, 4H, CH_2), 1.67 ~ 1.56 (m, 8H, CH_2), 1.55 ~ 1.49 (m, 2H, CH_2), 1.47 ~ 1.35 (m, 16H, CH_2), 0.97 ~ 0.91(m, 12H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 171.89, 153.87, 151.70, 150.95, 149.50, 142.71, 137.24, 135.41, 129.76, 129.52, 129.08, 125.35, 124.57, 120.20, 119.94, 118.17, 106.95, 106.57, 105.55, 104.98, 70.87, 69.53, 69.43, 69.35, 59.22, 33.67, 33.57, 31.92, 31.74, 31.68, 30.78, 29.37, 29.24, 29.20, 27.45, 26.08, 26.06, 25.97, 25.87, 25.82, 25.53, 24.78, 22.70, 22.67, 22.21, 14.15, 14.07, 14.06. FT-IR (KBr, cm^{-1}): 3431, 2932, 2853, 1724, 1607, 1522, 1468, 1425, 1377, 1288, 1178, 1016, 825, 723. HRMS (ESI): *m/z* 824.5894 (calcd $[M]^+$ = 824.5824).

COE-TPN12-Br was prepared with a yield of 77% (0.48 g) in a similar manner from **COE-Br** (0.16 g, 0.6 mmol) and **TPN12** (0.5 g, 0.5 mmol). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ: 11.00 (s, 1H, ArH), 8.61(d, J = 6.8 Hz, 1H, ArH), 8.41 (d, J = 6.8 Hz, 1H, ArH), 8.37 (s, 1H, ArH), 7.55 (s, 1H, ArH), 7.51 (s, 1H, ArH), 7.46 (s, 1H, ArH), 5.63 ~ 5.51 (m, 2H, CH=CH), 5.34 (t, J = 7.6 Hz, 2H, NCH_2), 4.70 ~ 4.64 (m, 1H, OCH), 4.54 (t, J = 6.0 Hz, 2H, OCH_2), 4.26 (t, J = 6.8 Hz, 2H, OCH_2), 4.20 (t, J = 6.8 Hz, 2H, OCH_2), 4.15 (t, J = 6.8 Hz, 2H, OCH_2), 2.55 (t, J = 6.8 Hz, 2H, $COCH_2$), 2.37 ~ 2.31 (m, 3H, CH_2), 2.29 ~ 2.20 (m, 2H, CH_2), 2.11 ~ 2.06 (m, 2H, CH_2), 2.03 ~ 1.91 (m, 9H, CH_2), 1.80 ~ 1.70 (m, 4H, CH_2), 1.66 ~ 1.51(m, 10H, CH_2), 1.50 ~ 1.24 (m, 62H, CH_2), 0.89 ~ 0.86 (m, 12H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 171.82, 153.82, 151.66, 150.93, 149.48, 142.50, 137.20, 135.42, 129.75, 129.52, 129.01, 125.25, 124.52, 120.12, 119.89, 118.14, 106.85, 106.50, 105.53, 104.97, 70.88, 69.51, 69.37, 69.34, 59.18, 33.66, 33.57, 31.97, 30.76, 29.81, 29.77, 29.74, 29.69, 29.63, 29.43, 29.30, 27.43, 26.44, 26.26, 26.19, 25.53, 24.87, 24.77, 22.72, 22.21, 18.46, 14.13. HRMS (MALDI): *m/z* 1160.9570 (calcd$[M]^+$ = 1160.9580).

Synthesis of COE-TPN6-BF_4

All of the anion-exchange reactions used in this study were similar. **COE-TPN6-BF_4** was used as an example. Firstly, **COE-TPN6-Br** (0.3 g, 0.3 mmol) was dissolved in 3 mL of CH_2Cl_2, and $NaBF_4$ (0.3 g, 3 mmol) was dissolved in 2 mL of deionized water. Then, the two reaction solutions were mixed and stirred at room temperature for 48 hours. After that, the reaction mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was washed with deionized water several times until the eluent remained clear without the formation of yellow precipitate, as confirmed by the addition of $AgNO_3$ solution. The organic phases were combined, dried with anhydrous magnesium sulfate, filtered, concentrated under vacuum, and the yellow solid was obtained with a yield of 83.9% (0.23 g). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ: 9.77 (s, 1H, ArH), 8.43 (d, J = 6.8 Hz, 1H, ArH), 8.30 (d, J = 6.8 Hz, 1H,

ArH), 7.90 (s, 1H, ArH), 7.53 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.49 (s, 1H, ArH), 5.66 ~ 5.54 (m, 2H, CH=CH), 4.77 ~ 4.73 (m, 2H, NCH_2), 4.72 ~ 4.70 (m, 1H, OCH), 4.31 (t, *J* = 6.4 Hz, 2H, OCH_2), 4.28 ~ 4.22 (m, 4H, OCH_2), 4.11 (t, *J* = 6.4 Hz, 2H, OCH_2), 2.48 (t, *J* = 6.8 Hz, 2H, $COCH_2$), 2.33 ~ 2.20 (m, 3H, CH_2), 2.14 ~ 2.09 (m, 2H, CH_2), 2.07 ~ 1.90 (m, 9H, CH_2), 1.84 ~ 1.76 (m, 2H, CH_2), 1.65 ~ 1.54 (m, 10H, CH_2), 1.51 ~ 1.36 (m, 16H, CH_2), 1.29 ~ 1.25 (m, 2H, CH_2), 0.98 ~ 0.86 (m, 12H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 171.78, 154.02, 151.82, 150.83, 149.650, 141.18, 137.40, 134.70, 129.79, 129.53, 129.94, 125.31, 124.74, 120.45, 119.47, 118.08, 106.37, 105.55, 105.11, 104.93, 69.52, 69.46, 69.33, 69.25, 60.09, 33.69, 33.56, 31.83, 31.75, 31.73, 31.69, 30.55, 29.71, 29.36, 29.30, 29.22, 27.22, 27.11, 25.86, 25.79, 25.55, 25.03, 24.80, 24.59, 22.67, 22.21, 14.11, 14.08, 14.05. FT-IR (KBr, cm^{-1}): 3435, 2933, 2856, 1717, 1602, 1525, 1472, 1427, 1379, 1285, 1180, 1057, 837, 721. HRMS (ESI): *m/z* 824.5894 (calcd $[M]^+$ = 824.5824).

Synthesis of COE-TPN6-PF_6

Yellow solid, yield: 86%. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) *δ*: 9.34 (s, 1H, ArH), 8.39 (d, *J* = 6.8 Hz, 1H, ArH), 8.18 (d, *J* = 6.8 Hz, 1H, ArH), 7.63 (s, 1H, ArH), 7.48 ~ 7.46 (m, 3H, ArH), 5.63 ~ 5.59 (m, 2H, CH=CH), 4.74~4.73 (m, 1H, OCH), 4.65 (t, *J* = 8.0 Hz, 2H, NCH_2), 4.27 ~ 4.21 (m, 6H, OCH_2), 4.06 (t, *J* = 6.8 Hz, 2H, OCH_2), 2.44 (t, *J* = 6.8 Hz, 2H, $COCH_2$), 2.29 ~ 2.22 (m, 3H, CH_2), 2.14 ~ 2.09 (m, 2H, CH_2), 2.04 ~ 1.89 (m, 9H, CH_2), 1.83 ~ 1.77(m, 2H, CH_2), 1.67 ~ 1.53 (m, 10H, CH_2), 1.48 ~ 1.35 (m, 16H, CH_2), 1.29 ~ 1.25 (m, 2H, CH_2), 0.98 ~ 0.91 (m, 12H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 171.65, 154.10, 151.93, 150.70, 149.76, 140.09, 137.52, 134.53, 129.79, 129.53, 128.75, 125.01, 124.88, 120.65, 118.97, 118.02, 106.15, 105.44, 104.86, 104.48, 69.43, 69.35, 69.33, 69.20, 60.09, 33.69, 33.54, 31.89, 31.80, 31.76, 31.71, 30.46, 29.79, 29.71, 29.34, 29.25, 29.22, 26.94, 25.87, 25.83, 25.76, 25.55, 24.81, 22.67, 22.20, 14.10, 14.07, 14.06. FT-IR (KBr, cm^{-1}): 3439, 2928, 2862, 1726, 1614, 1527, 1470, 1429, 1382, 1279, 1182, 1022, 840, 723. HRMS(ESI): *m/z* 824.5894 (calcd $[M]^+$ = 824.5824).

Synthesis of COE-TPN6-TFSI

Yellow solid, yield: 87%. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) *δ*: 9.75 (s, 1H, ArH), 8.64 (d, *J* = 6.8 Hz, 1H, ArH), 8.53 (d, *J* = 6.8 Hz, 1H, ArH), 7.93 (s, 1H, ArH), 7.73 (s, 1H, ArH), 7.66 (s, 1H, ArH), 7.64 (s, 1H, ArH), 5.68 ~ 5.56 (m, 2H, CH=CH), 4.83 (t, *J* = 7.2 Hz, 2H, NCH_2), 4.79 ~ 4.75 (m, 1H, OCH), 4.32 ~ 4.24 (m, 6H, OCH_2), 4.14 (t, *J* = 6.4 Hz, 2H, OCH_2), 2.49 (t, *J* = 6.4 Hz, 2H, $COCH_2$), 2.39 ~ 2.20 (m, 3H, CH_2), 2.16 ~ 2.11 (m, 2H, CH_2), 2.09 ~ 2.04 (m, 1H, CH_2), 2.02 ~ 1.90 (m, 6H, CH_2), 1.86 ~ 1.80 (m, 2H, CH_2), 1.68 ~ 1.55 (m, 12H, CH_2), 1.51 ~ 1.40 (m, 14H, CH_2), 1.29 ~ 1.25 (m, 4H, CH_2), 0.98 ~ 0.86 (m, 12H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 171.85, 154.29, 152.15, 150.91, 149.95,

140.85, 138.04, 135.24, 129.83, 129.52, 129.12, 125.46, 125.29, 120.93, 119.39, 118.81, 118.37, 106.57, 105.76, 105.21, 105.06, 69.69, 69.50, 69.43, 60.30, 33.72, 33.55, 31.72, 31.67, 30.51, 29.30, 29.16, 26.99, 25.88, 25.84, 25.73, 25.58, 24.84, 22.66, 22.19, 14.05. FT-IR (KBr, cm^{-1}): 2939, 2860, 1726, 1604, 1525, 1463, 1431, 1384, 1340, 1276, 1182, 1136, 1053, 829, 736, 648. HRMS (ESI): *m/z* 824.5894 (calcd $[M]^+$ = 824.5824).

Synthesis of COE-TPN12-TFSI

Yellow solid, yield: 85%. ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ: 9.67 (s, 1H, ArH), 8.55 (d, J = 6.8 Hz, 1H, ArH), 8.47 (d, J = 6.8 Hz, 1H, ArH), 7.87 (s, 1H, ArH), 7.60 (s, 1H, ArH), 7.56 (s, 1H, ArH), 7.54 (s, 1H, ArH), 5.67 ~ 5.56 (m, 2H, CH=CH), 4.81 ~ 4.74 (m, 3H, CH_2), 4.30 ~ 4.22 (m, 6H, OCH_2), 4.07 (t, J = 6.4 Hz, 2H, OCH_2), 2.47 (t, J = 6.4 Hz, 2H, $COCH_2$), 2.37 ~ 2.31 (m, 2H, CH_2), 2.30 ~ 2.26 (m, 1H, CH_2), 2.15 ~ 2.10 (m, 2H, CH_2), 2.08 ~ 1.88 (m, 9H, CH_2), 1.85 ~ 1.76 (m, 2H, CH_2), 1.69 ~ 1.51 (m, 12H, CH_2), 1.48 ~ 1.05 (m, 64H, CH_2), 0.90 ~ 0.86 (m, 12H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 171.78, 154.20, 152.11, 150.89, 149.91, 140.45, 137.95, 135.09, 129.81, 129.52, 129.00, 125.37, 125.21, 120.94, 120.81, 119.31, 118.80, 106.43, 105.70, 105.03, 104.99, 69.60, 69.45, 69.39, 60.31, 60.20, 33.68, 33.53, 31.97, 30.43, 29.81, 29.76, 29.66, 29.62, 29.59, 29.43, 29.40, 29.26, 29.19, 26.92, 26.27, 26.22, 26.09, 25.56, 24.52, 22.72, 22.19, 14.13. HRMS (MALDI): *m/z* 1160.9570 (calcd $[M]^+$ = 1160.9580).

Synthesis of H-PTPN6-TFSI

H-PTPN6-TFSI was used as an example. **COE-TPN6-TFSI** (0.1 g, 0.1 mmol) was added to a solution of Grubb's second-generation catalyst (0.8 mg, 0.96 μmol) in 2 mL of anhydrous CH_2Cl_2. The reaction solution was then degassed with three freeze–vacuum–thaw cycles. After the reaction mixture was stirred at 45℃ for 18 hours, the solution was precipitated into an excess of methanol. The precipitate was isolated, dried under vacuum for 24 hours, and obtained as a yellow solid in 72% yield.

Synthesis of C-PTPN6-TFSI (10:1)

C-PTPN6-TFSI (10:1) was used as an example. **COE-TPN6-TFSI** (0.1 g, 0.1 mmol) and **COE** (0.1g，1 mmol) were added into a Schlenk flask. The mixture was frozen in an ice water bath, vacuumed and unfrozen, repeating this process three times to remove air from the reaction system. A solution of Grubb's second-generation catalyst (0.2 mg, 0.24 μmol) in 1 mL anhydrous CH_2Cl_2 was added dropwise to the mixture. Under a nitrogen atmosphere, the mixture was heated to 45℃ and stirred at that temperature for 6 hours. After the reaction, the viscous reaction solution was poured onto a Teflon film, and the yellow film was obtained in 96% yield after the organic solvent had evaporated.

Fig. S1. ^{1}H NMR spectrum of **COE-Br**.

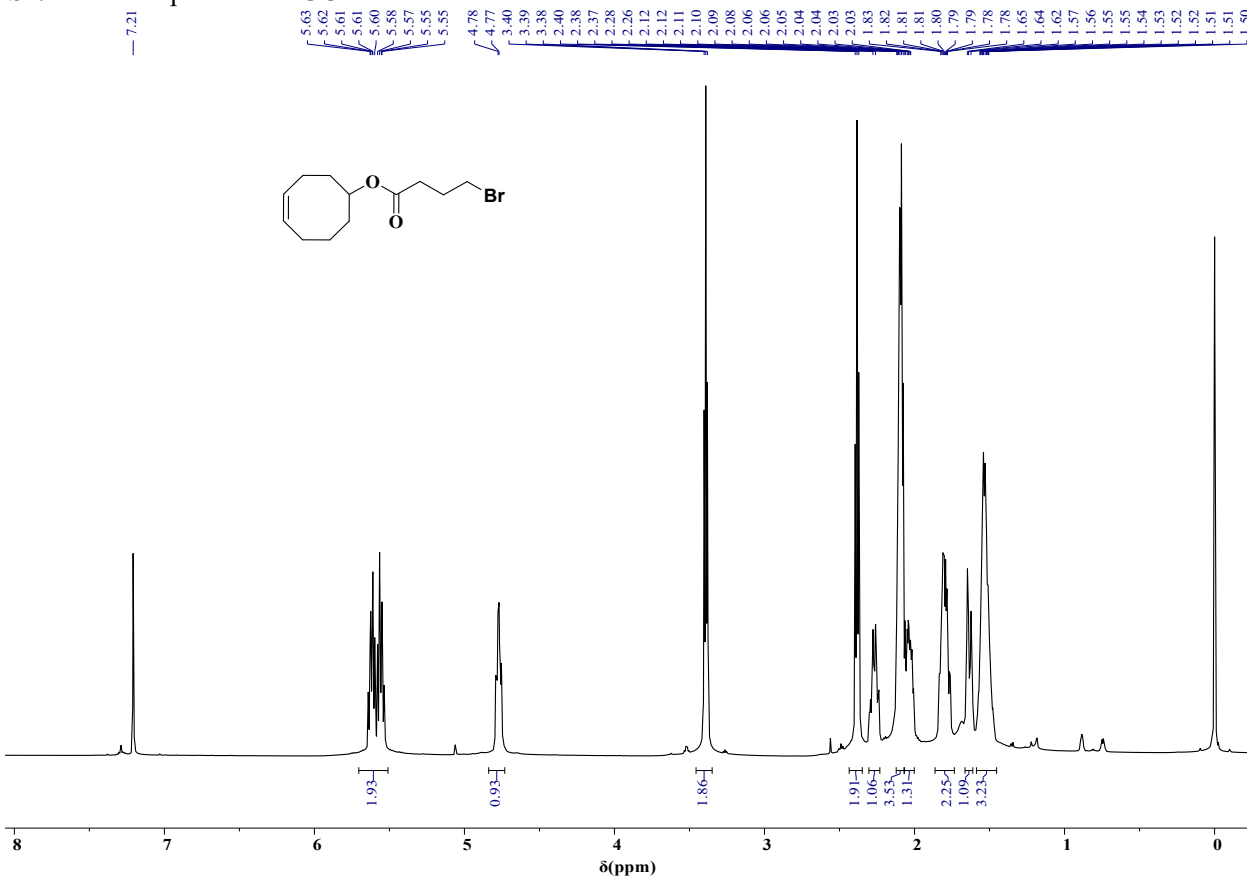


Fig. S2. ^{13}C NMR spectrum of **COE-Br**.

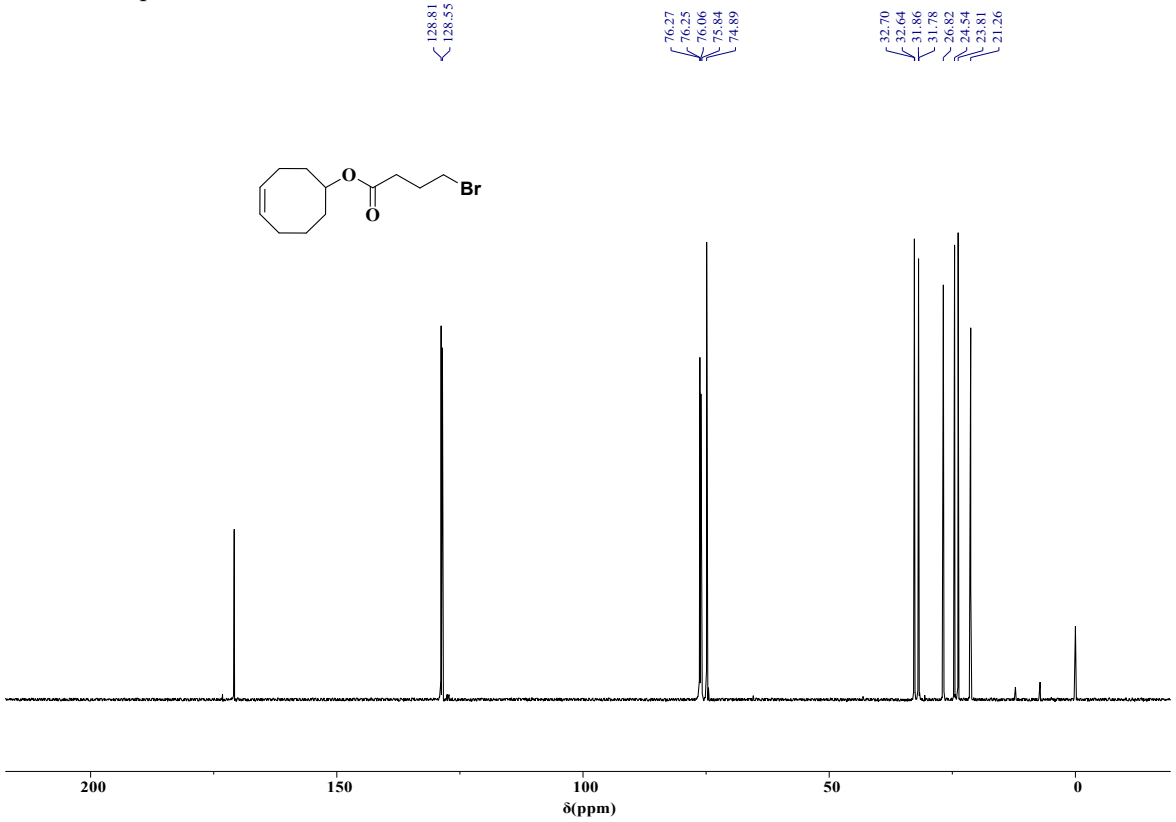


Fig. S3. ^{1}H NMR spectrum of **COE-TPN6-Br**.

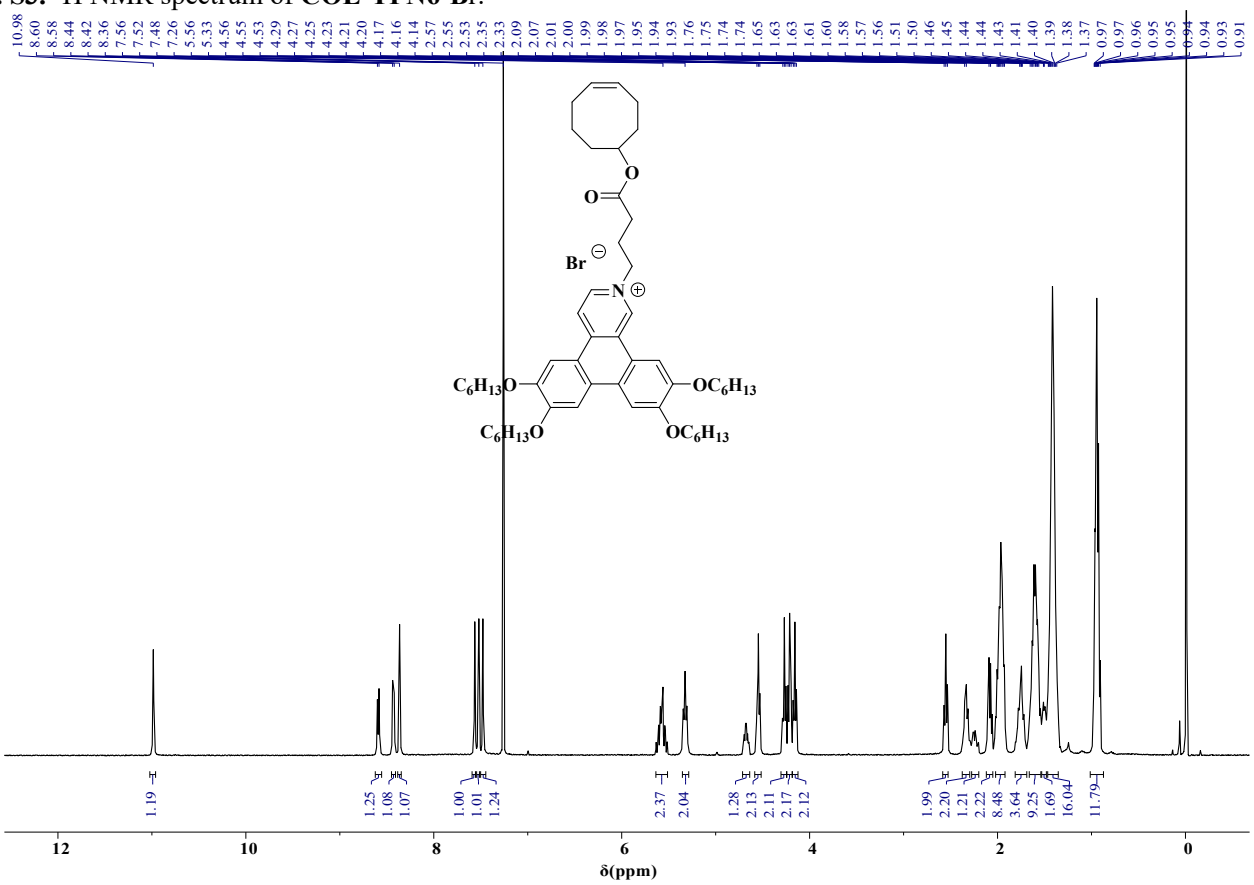


Fig. S4. ^{13}C NMR spectrum of **COE-TPN6-Br**.

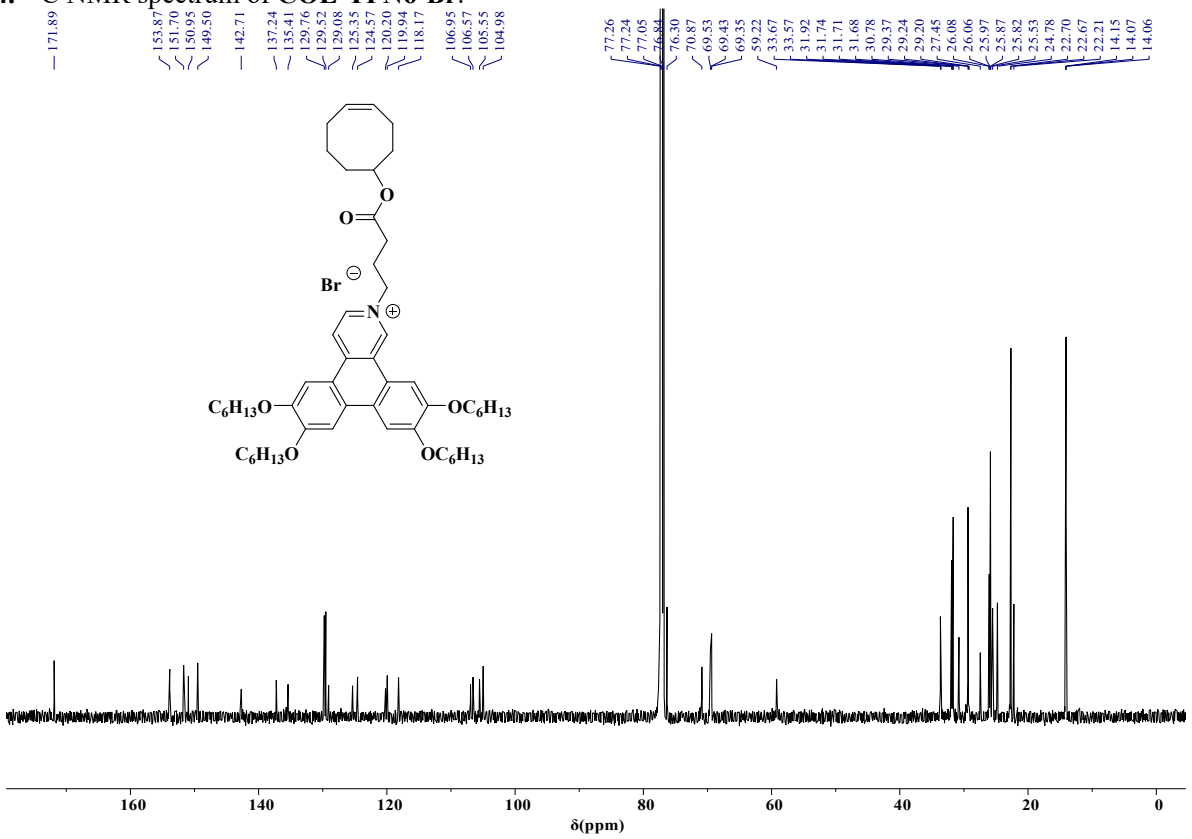


Fig. S5. ^{1}H NMR spectrum of **COE-TPN6-BF$_4$**.

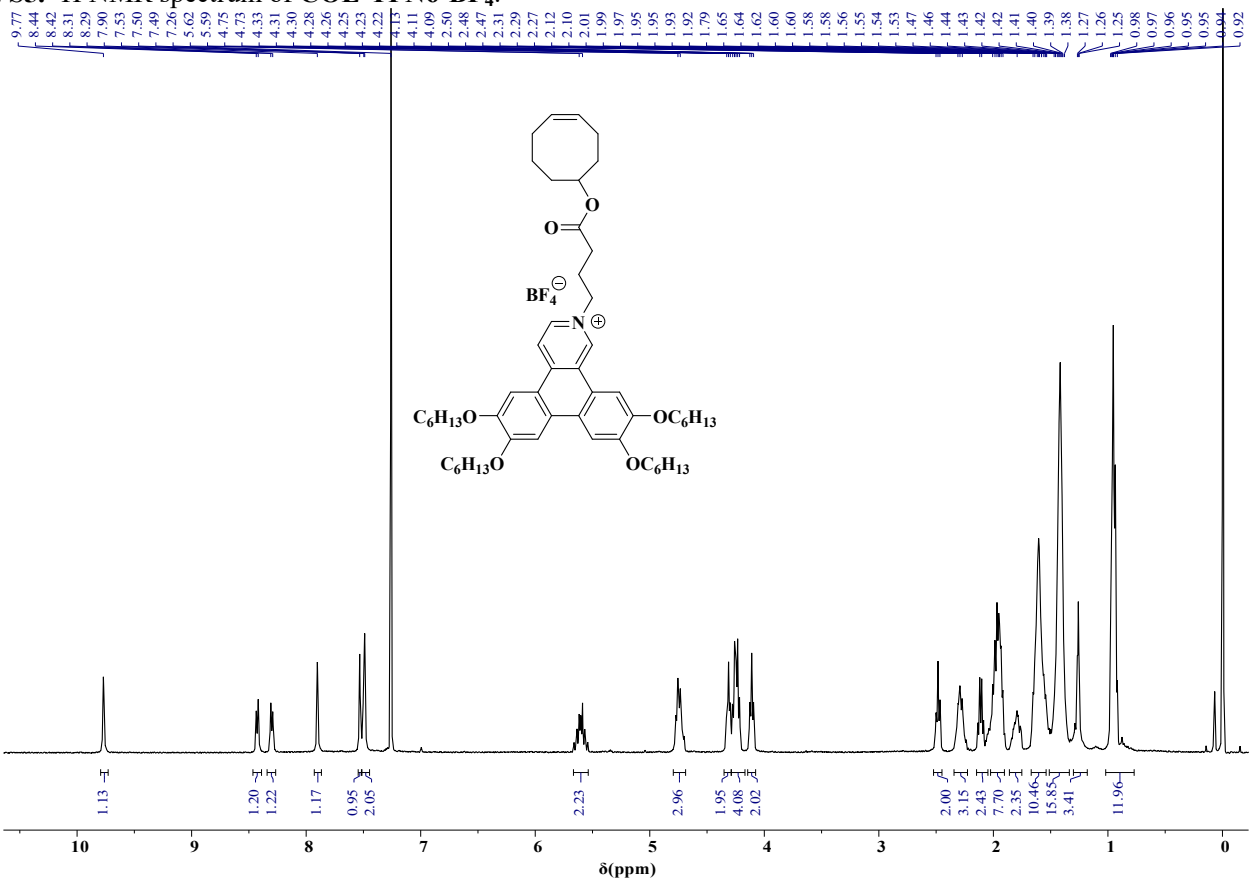


Fig. S6. ^{13}C NMR spectrum of **COE-TPN6-BF$_4$**.

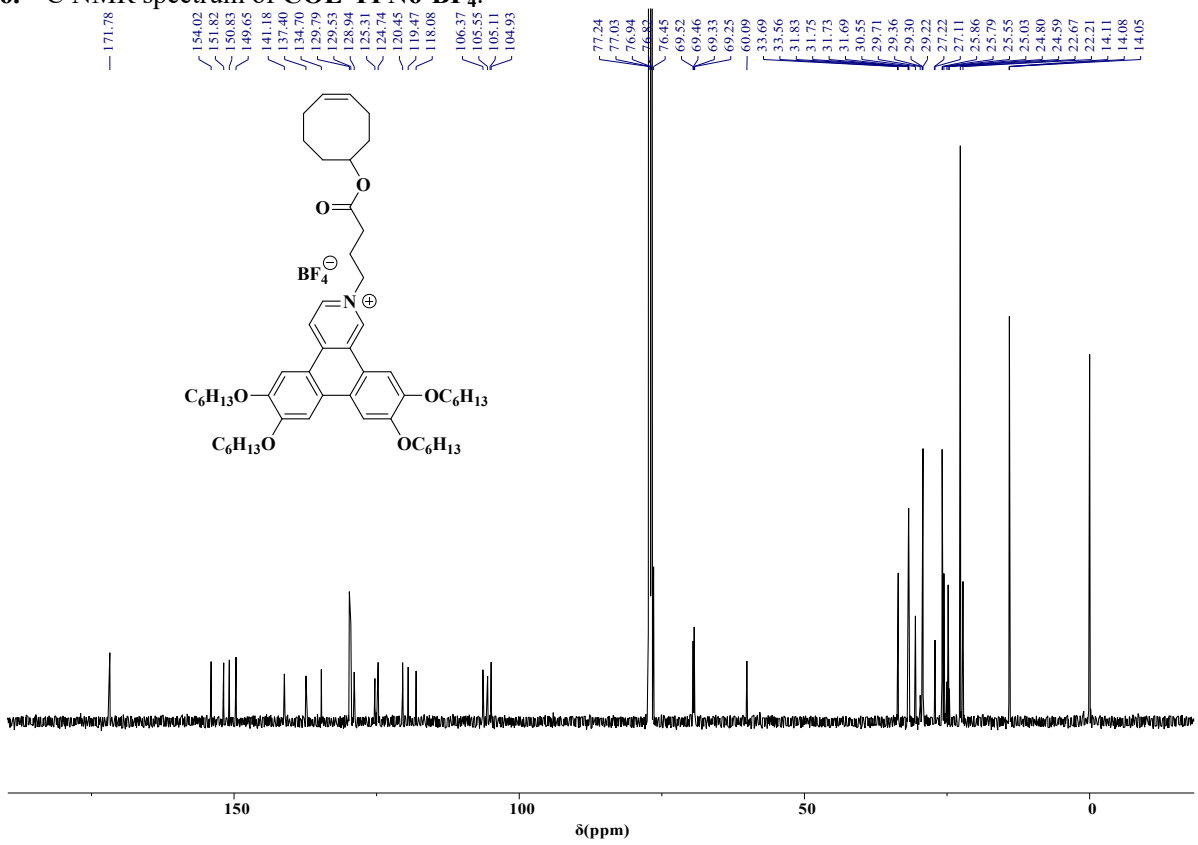


Fig. S7. ^{1}H NMR spectrum of **COE-TPN6-PF$_6$**.

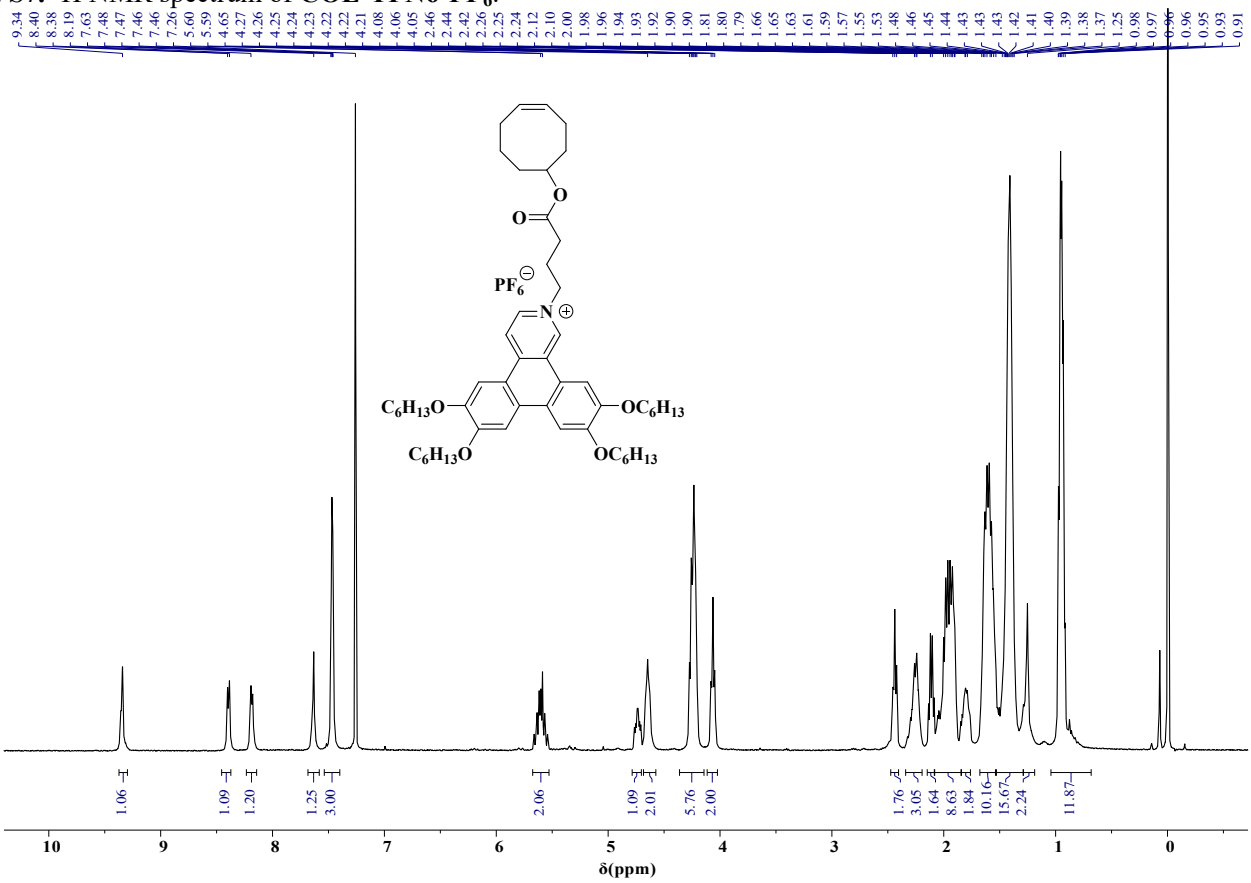


Fig. S8. ^{13}C NMR spectrum of **COE-TPN6-PF$_6$**.

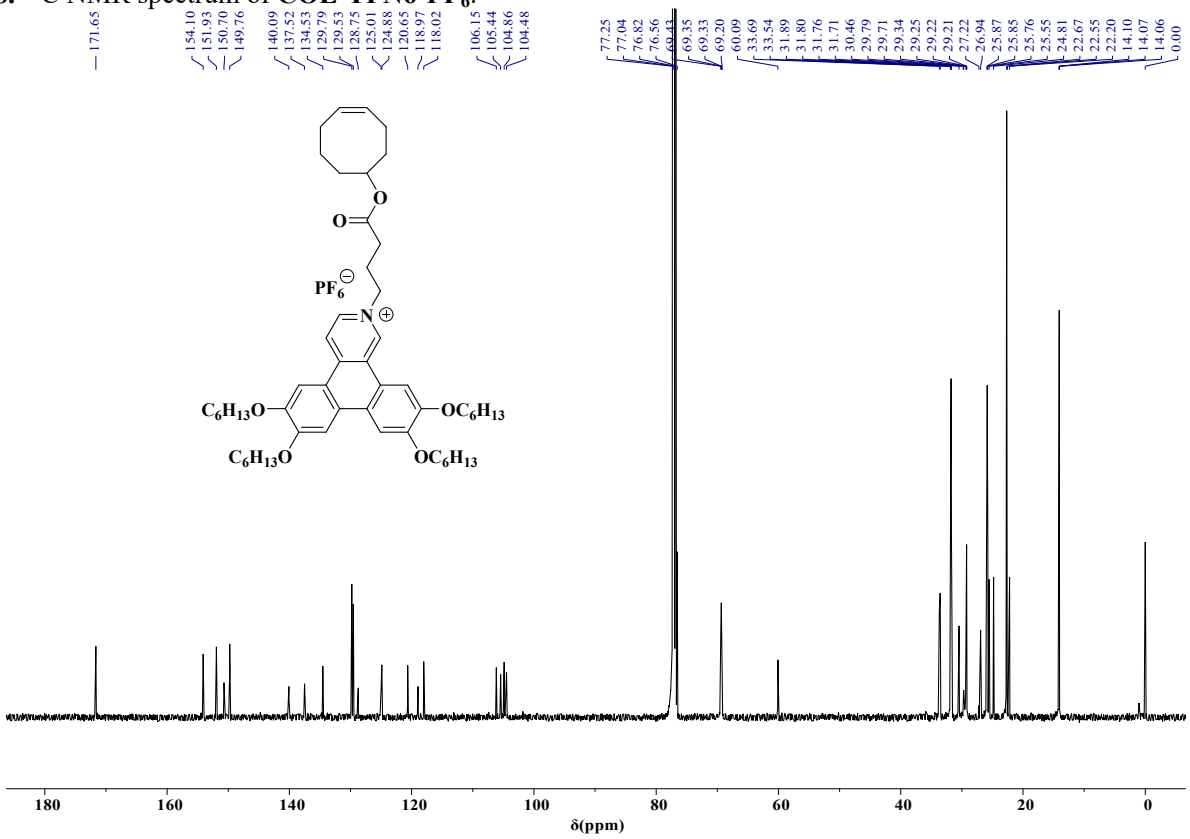


Fig. S9. ^{1}H NMR spectrum of **COE-TPN6-TFSI**.

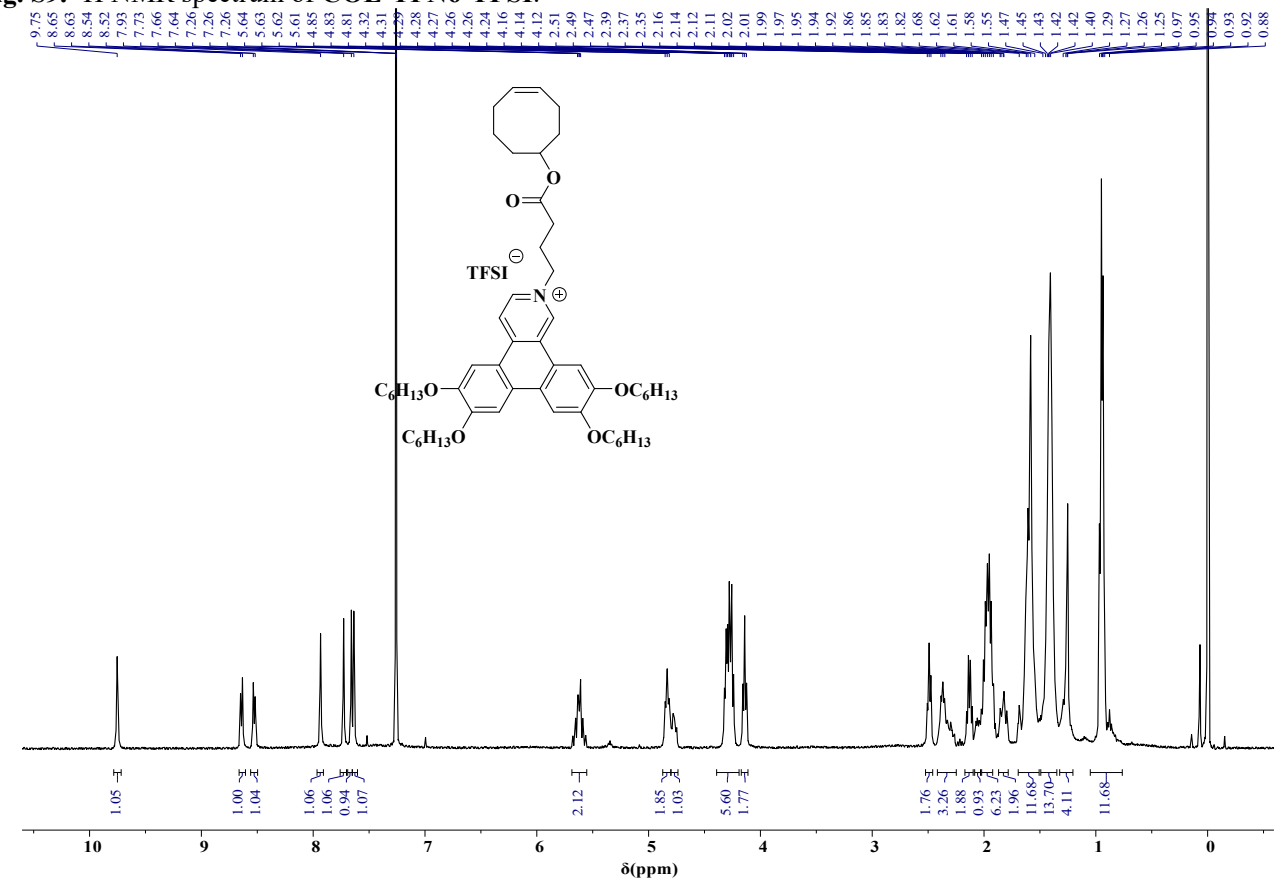


Fig. S10. ^{13}C NMR spectrum of **COE-TPN6-TFSI**.

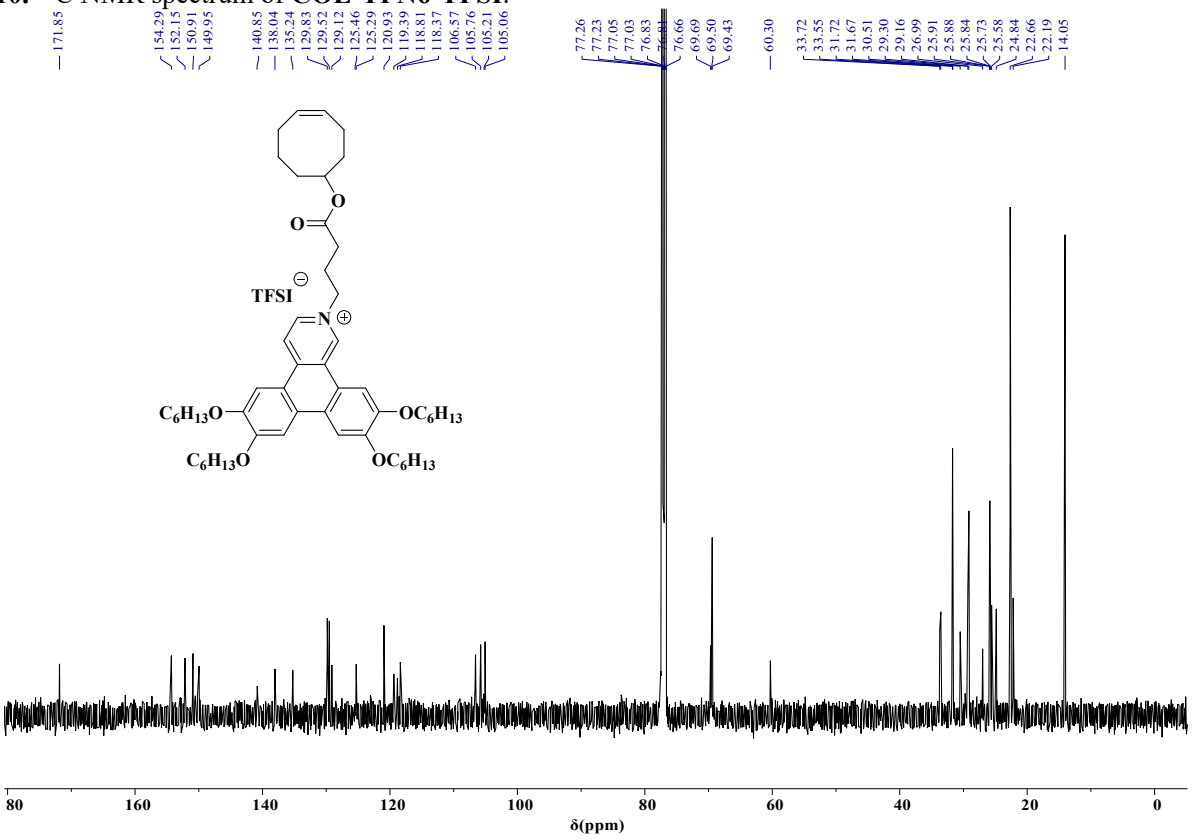


Fig. S11. ^{1}H NMR spectrum of **COE-TPN12-Br**.

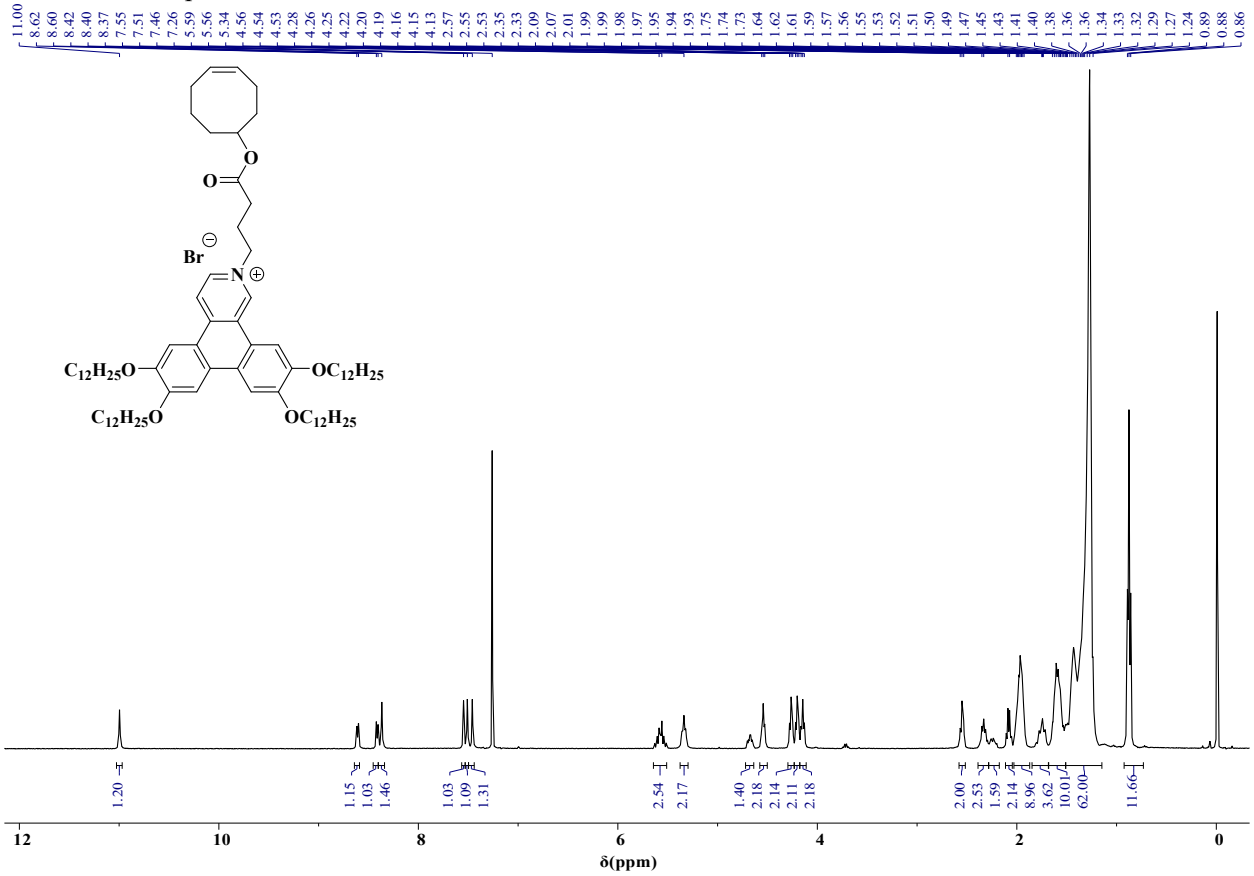


Fig. S12. ^{13}C NMR spectrum of **COE-TPN12-Br**.

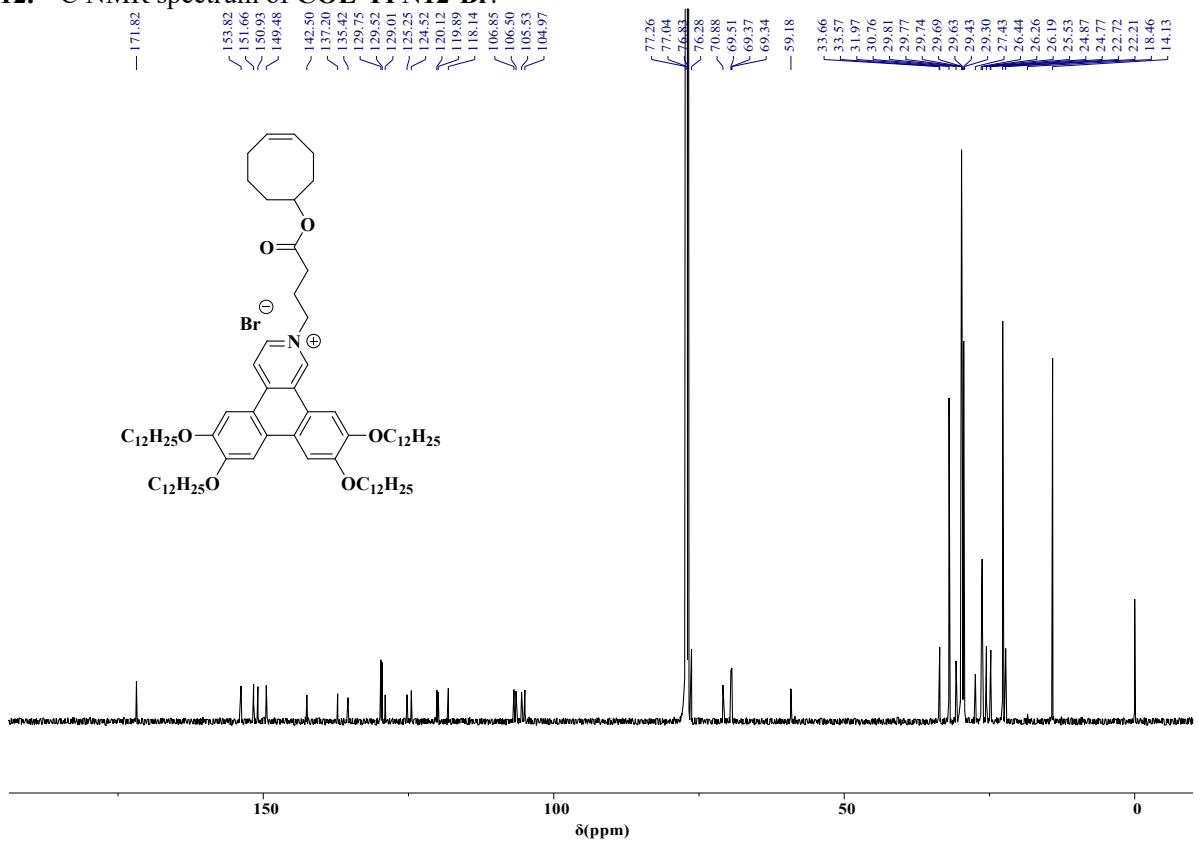


Fig. S13. ^{1}H NMR spectrum of **COE-TPN12-TFSI**.

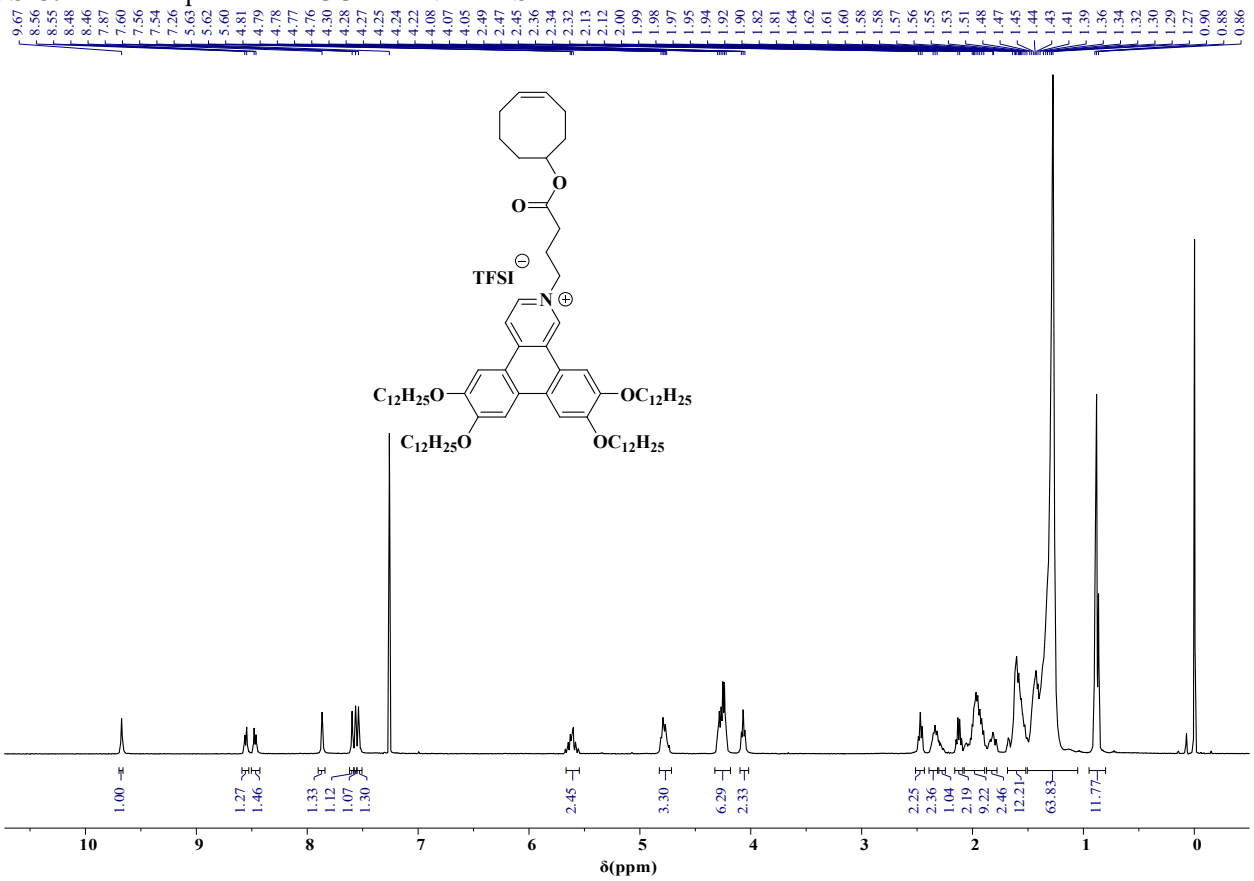


Fig. S14. ^{13}C NMR spectrum of **COE-TPN12-TFSI**.

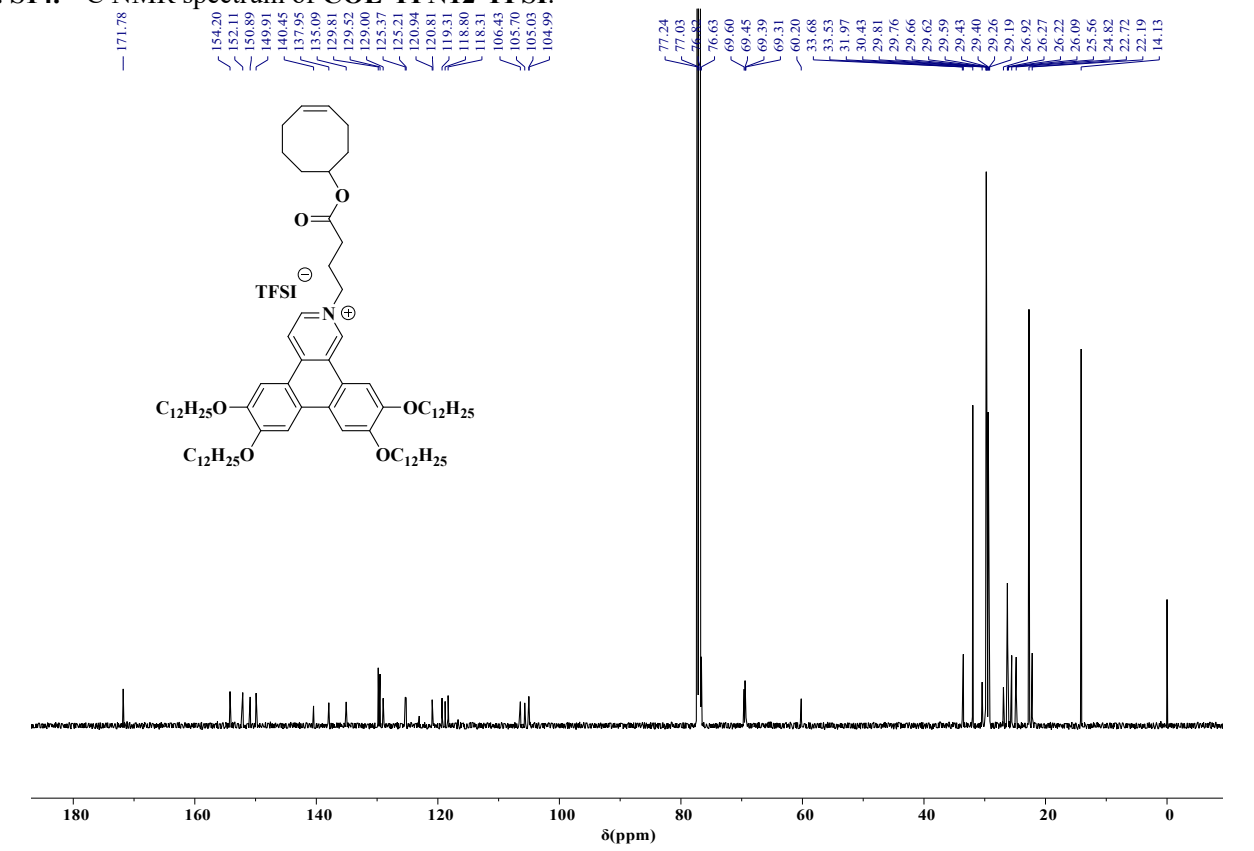


Fig. S15. ^{1}H NMR spectrum of **H-PTPN6-Br**.

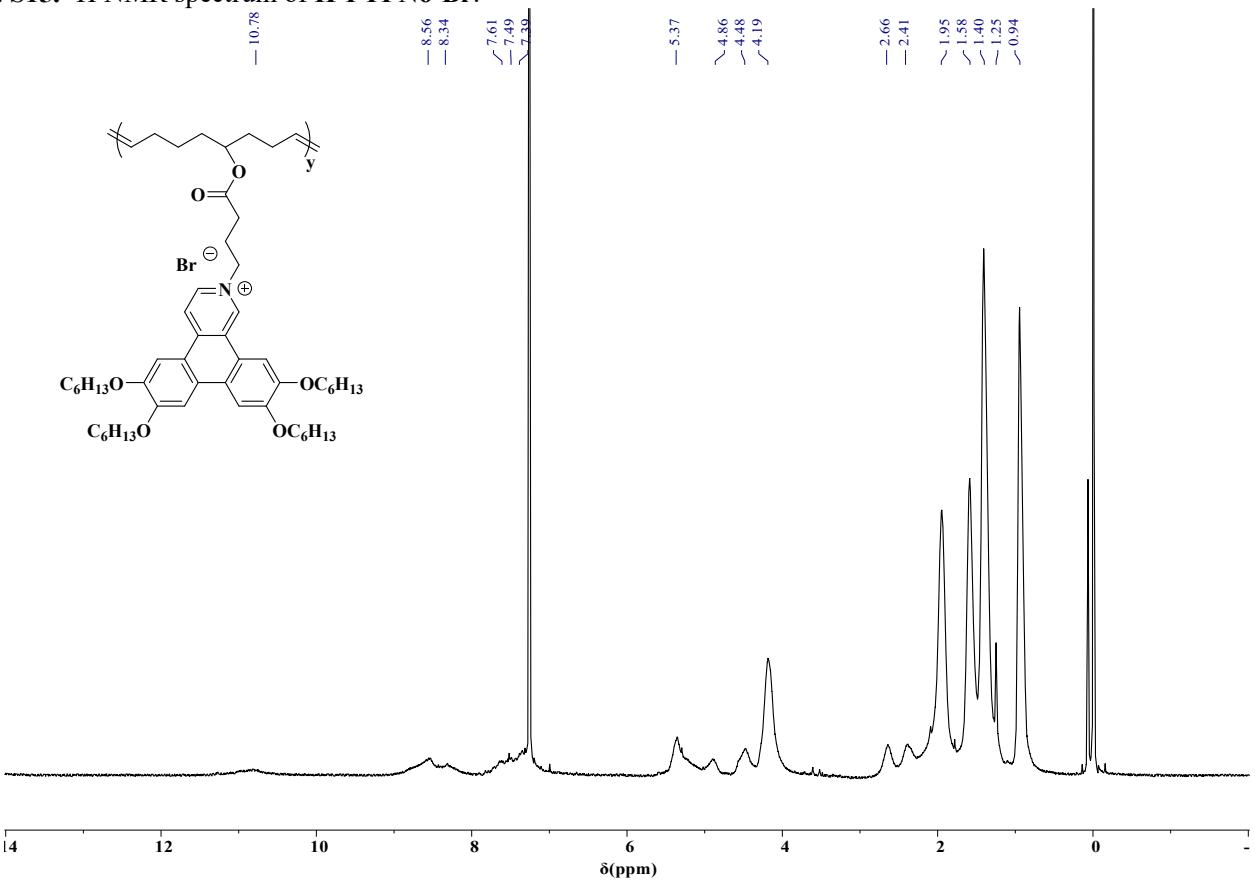


Fig. S16. ^{1}H NMR spectrum of **H-PTPN6-BF$_4$**.

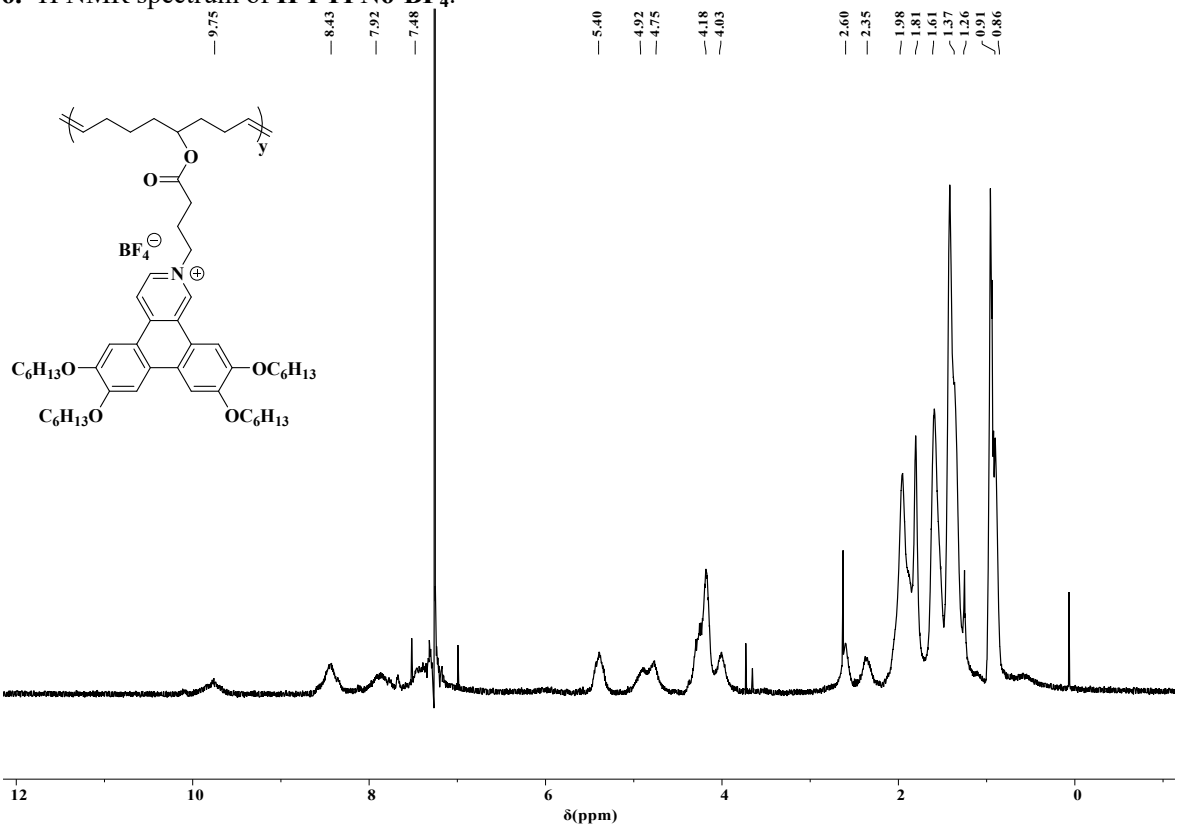


Fig. S17. ^{1}H NMR spectrum of **H-PTPN6-PF$_6$**.

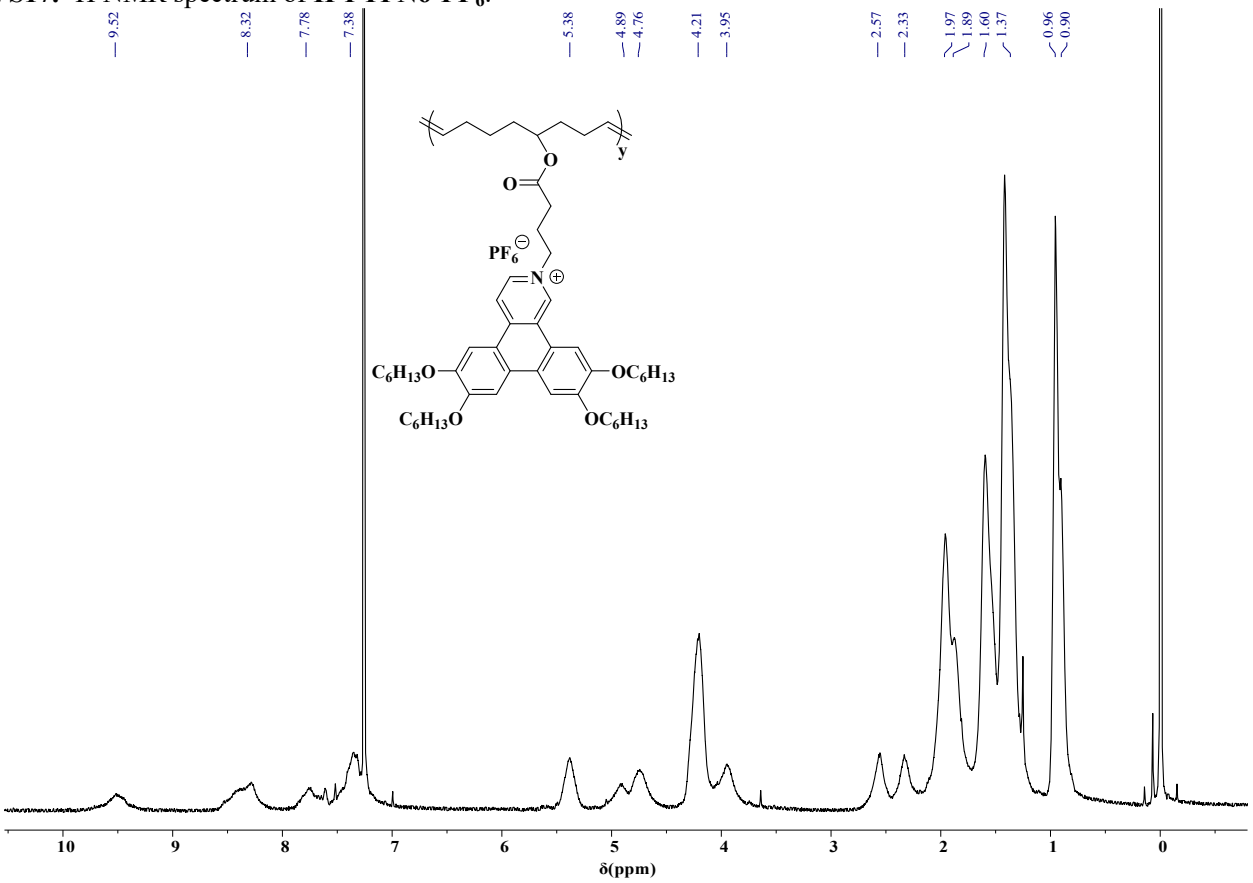


Fig. S18. ^{1}H NMR spectrum of **H-PTPN6-TFSI**.

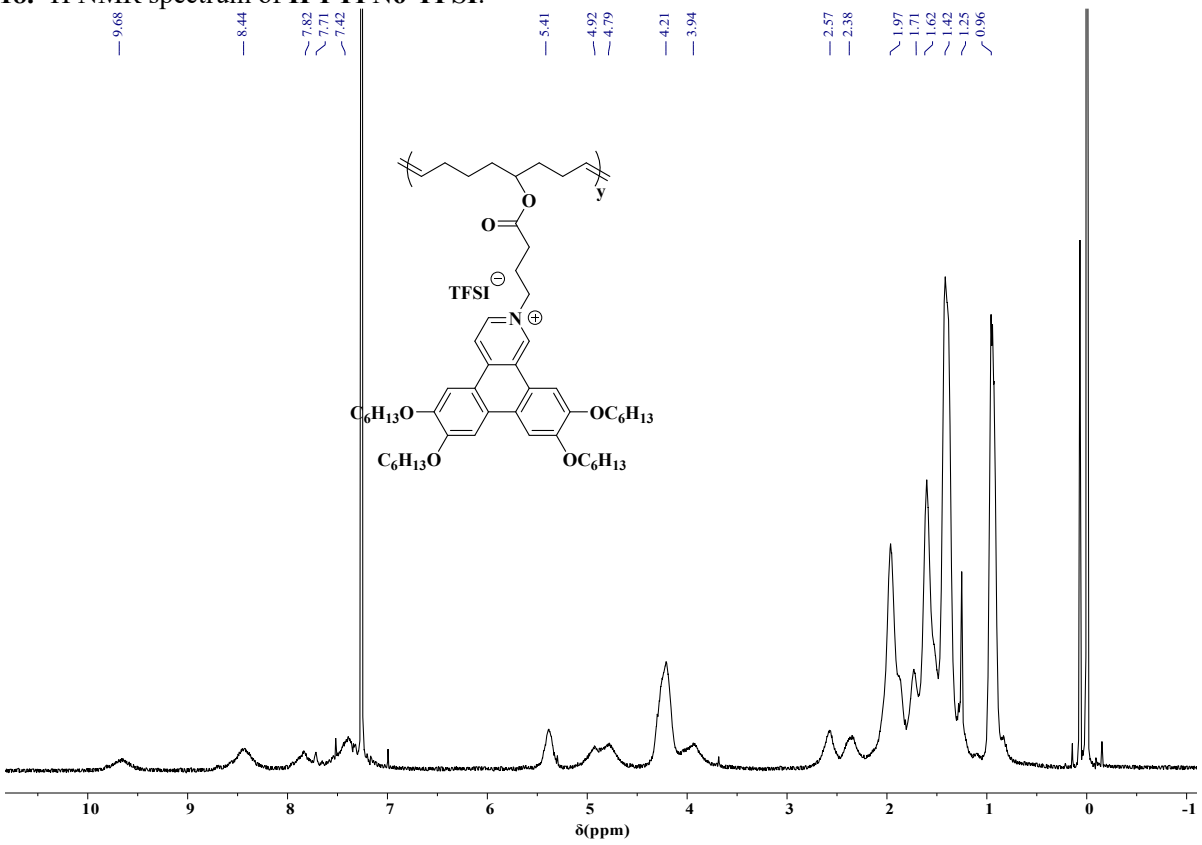


Fig. S19. ^{1}H NMR spectrum of **H-PTPN12-Br**.

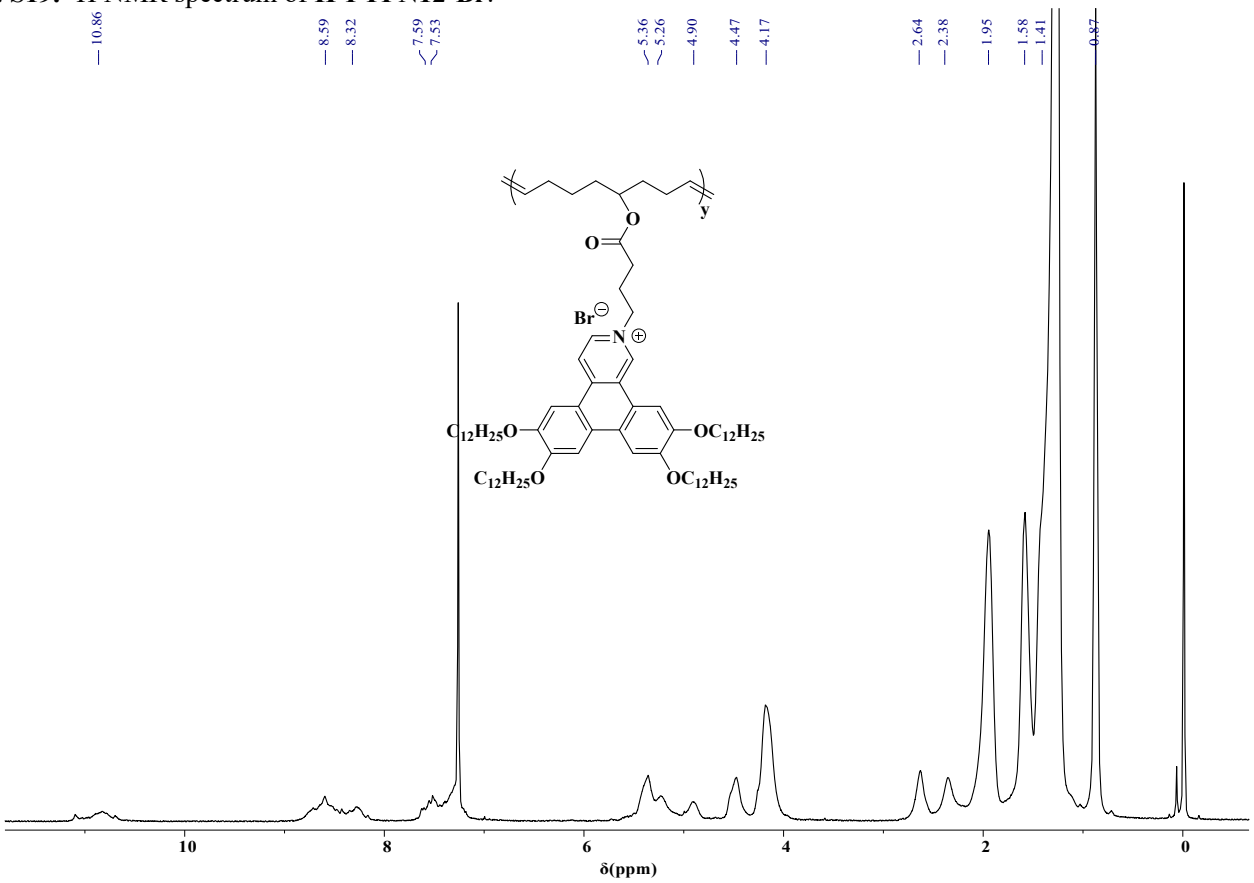


Fig. S20. ^{1}H NMR spectrum of **H-PTPN12-TFSI**.

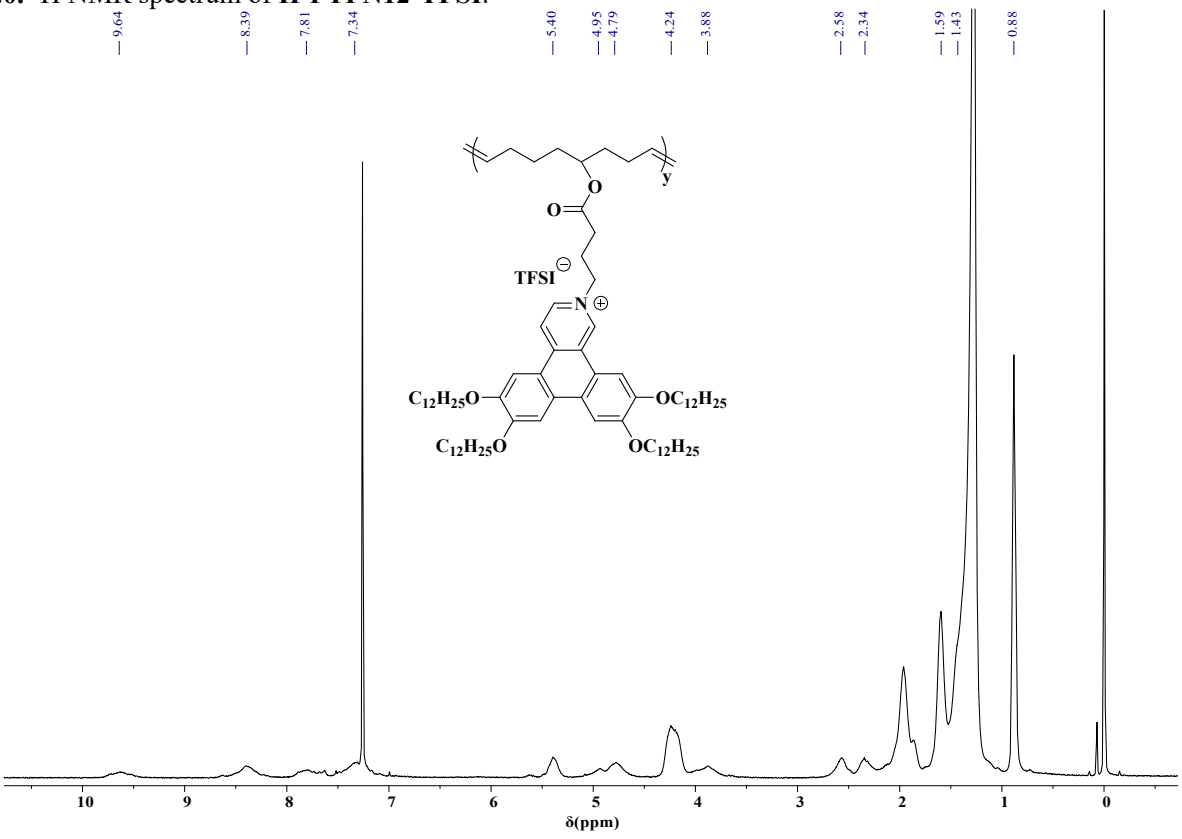


Fig. S21. HRMS m/z (ESI) spectrum of **COE-TPN6-Br**.

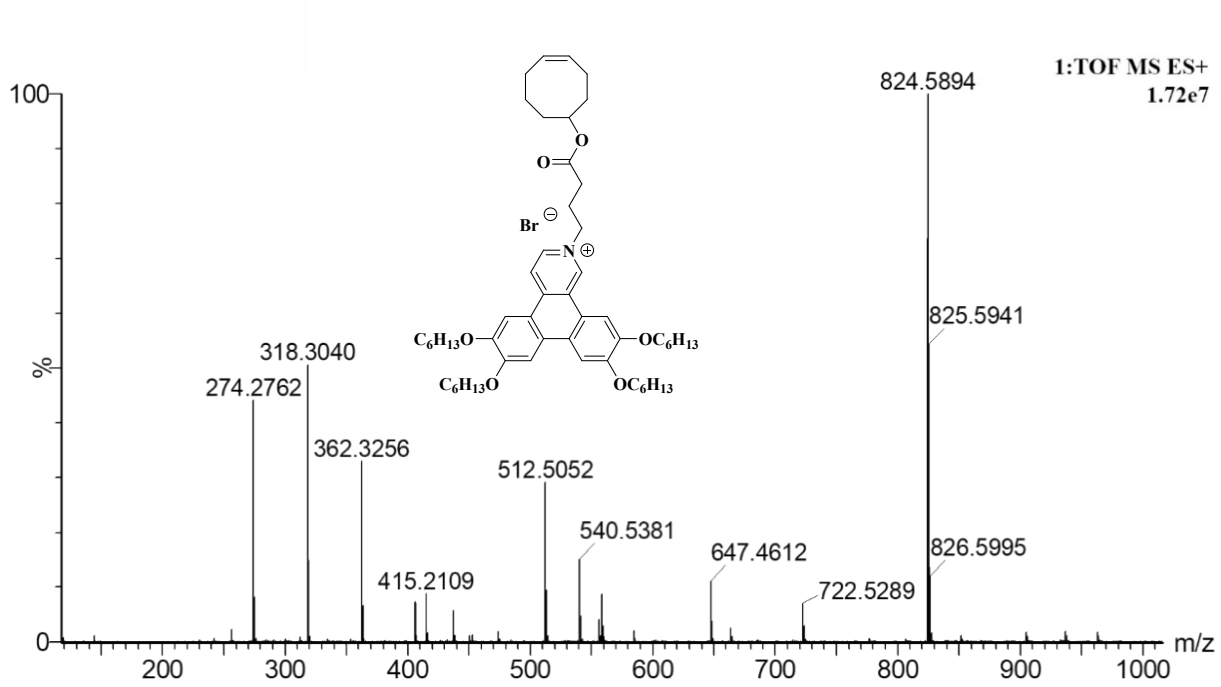


Fig. S22. HRMS m/z (ESI) spectrum of **COE-TPN6-BF_4**.

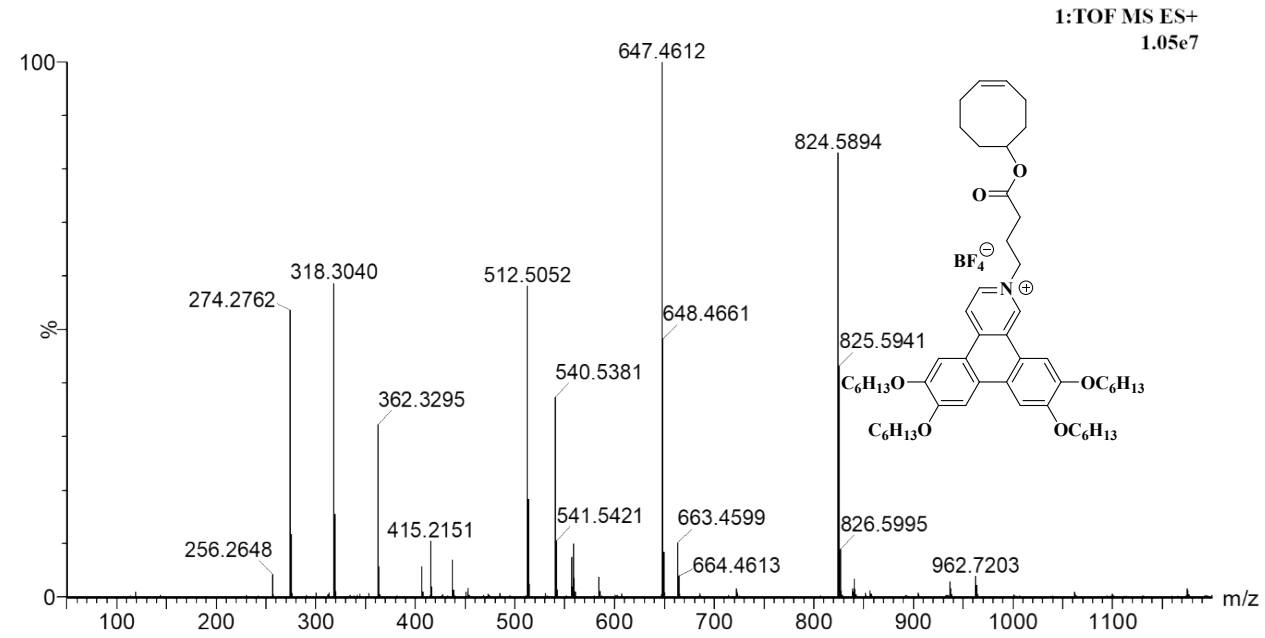


Fig. S23. HRMS m/z (ESI) spectrum of **COE-TPN6-PF$_6$**.

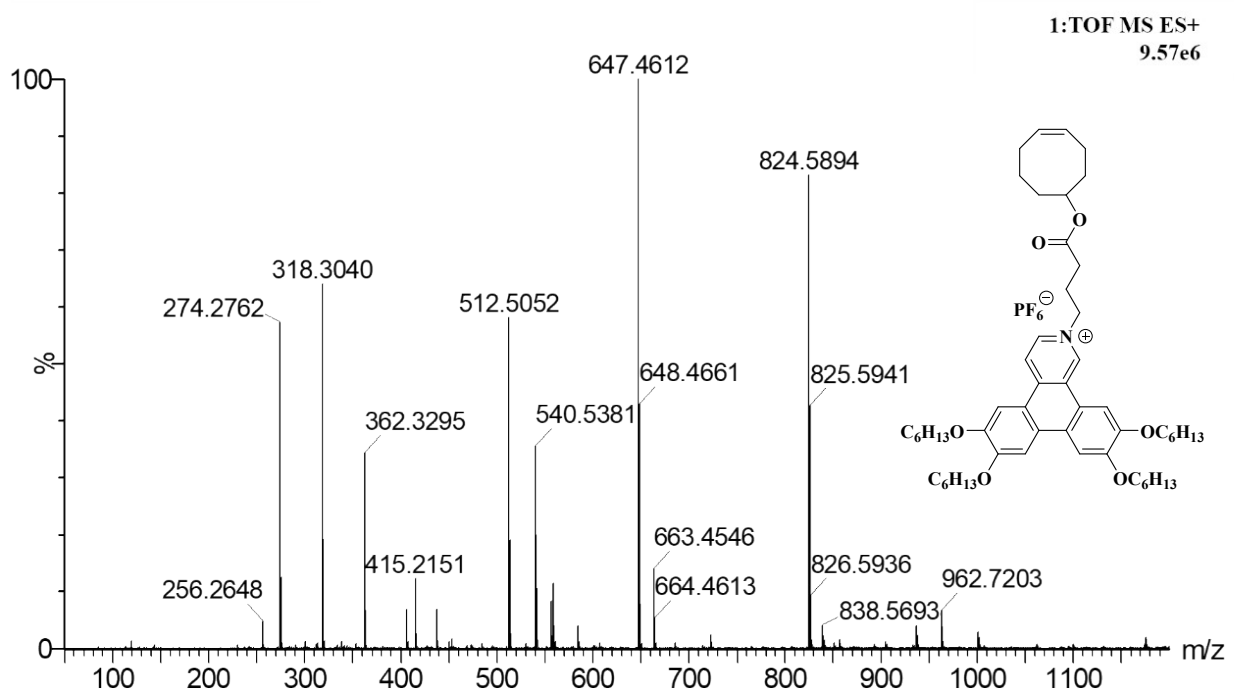


Fig. S24. HRMS m/z (ESI) spectrum of **COE-TPN6-TFSI**.

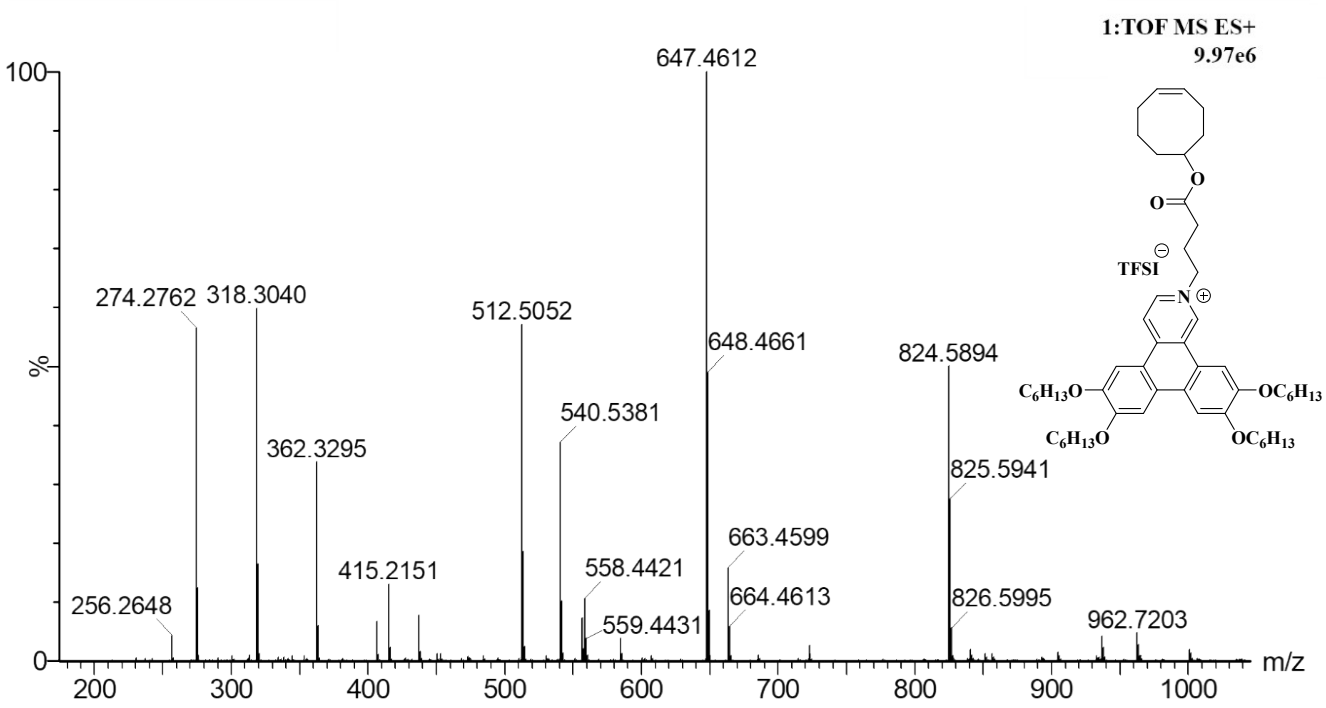


Fig. S25. HRMS m/z (MALDI) spectrum of **COE-TPN12-Br**.

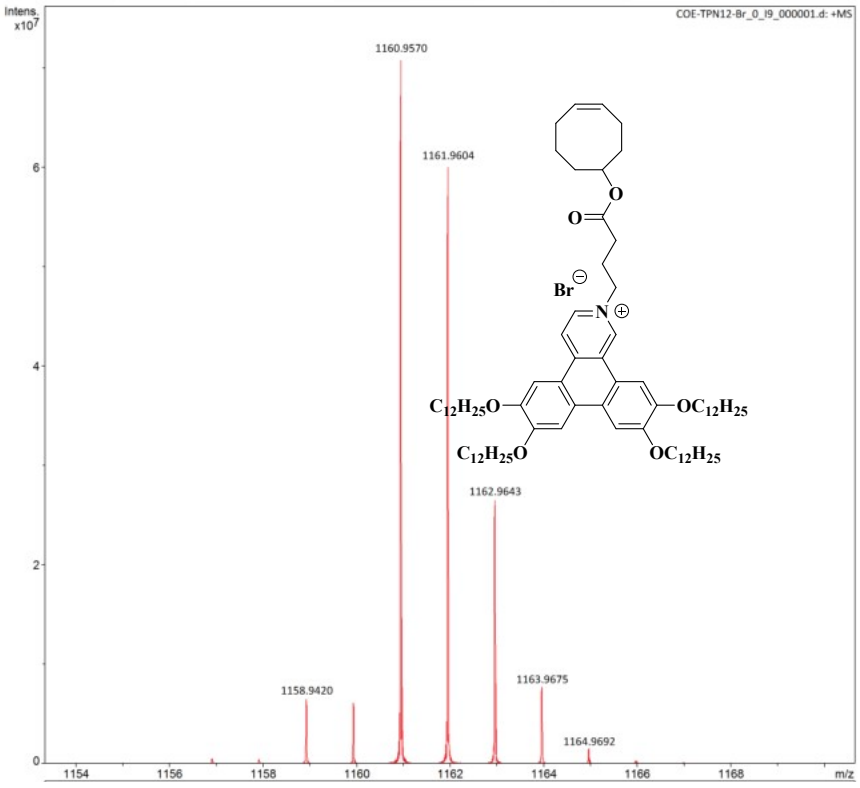


Fig. S26. HRMS m/z (MALDI) spectrum of **COE-TPN12-TFSI**.

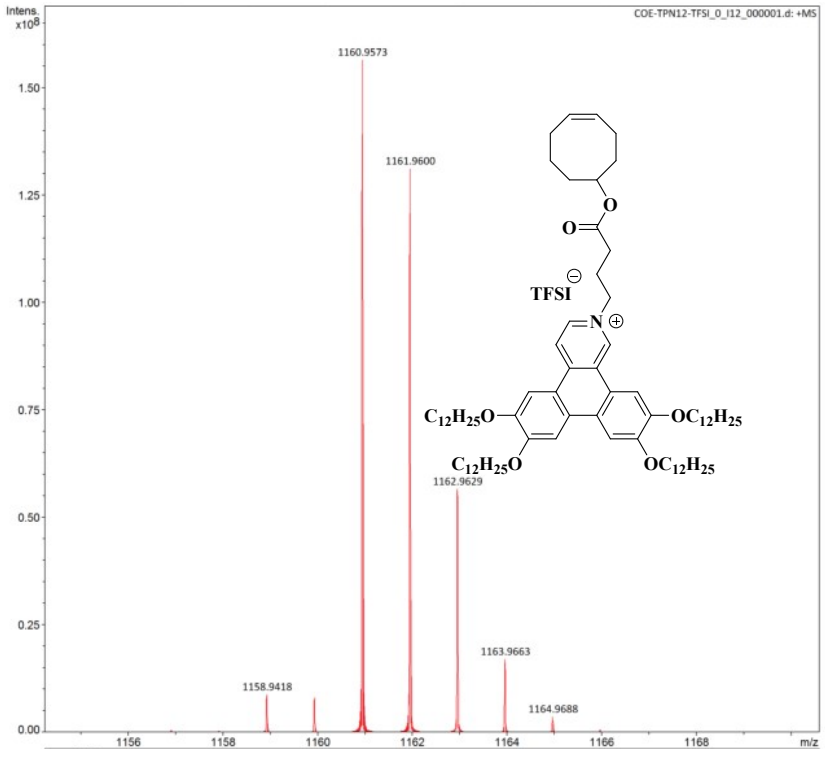


Fig. S27. GPC spectrum of **H-PTPN6-Br**.

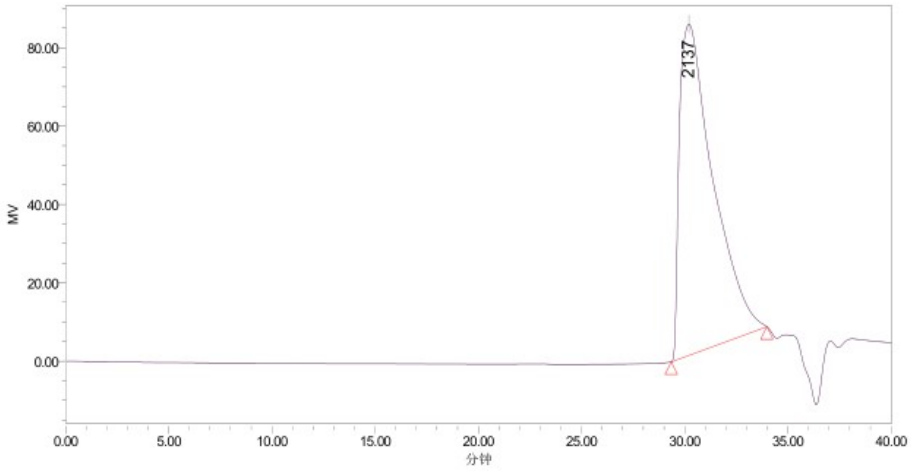


Fig. S28. GPC spectrum of **H-PTPN6-BF_4**.

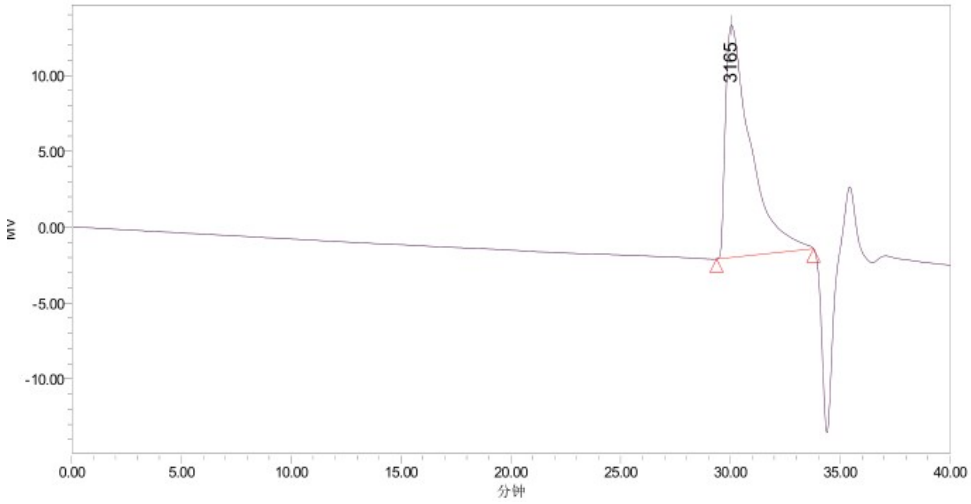


Fig. S29. GPC spectrum of **H-PTPN6-PF_6**.

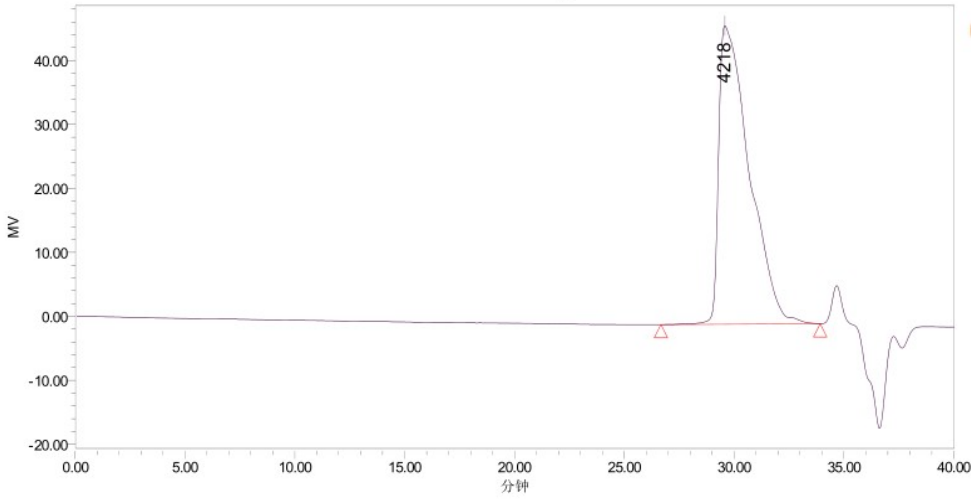


Fig. S30. GPC spectrum of **H-PTPN6-TFSI**.

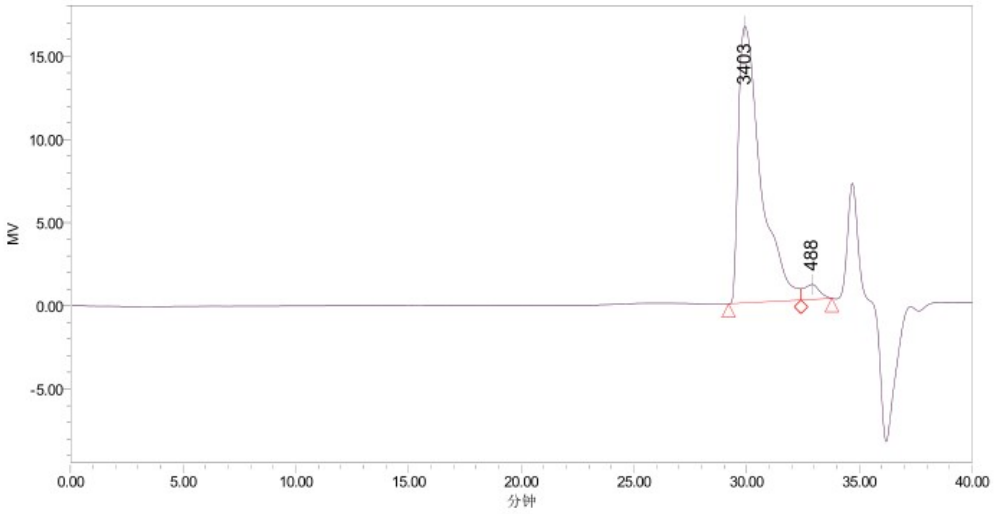


Fig. S31. GPC spectrum of **H-PTPN12-Br**.

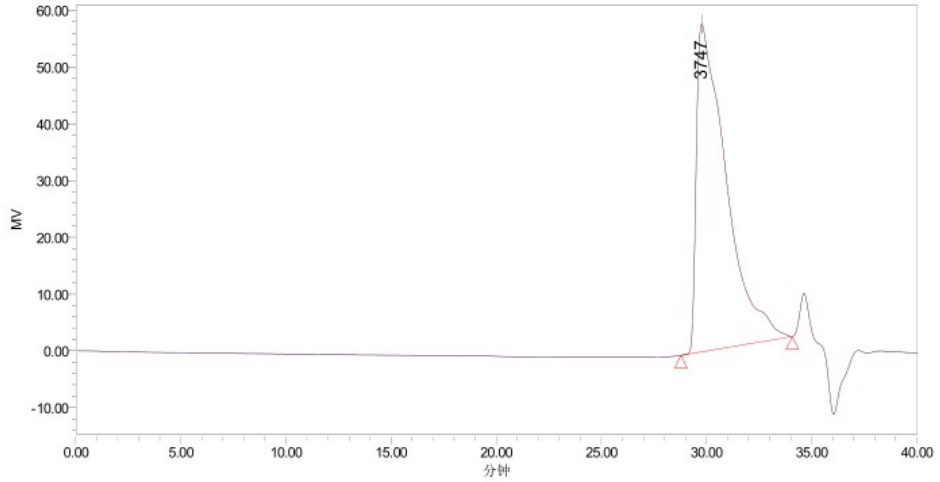


Fig. S32. GPC spectrum of **H-PTPN12-TFSI**.

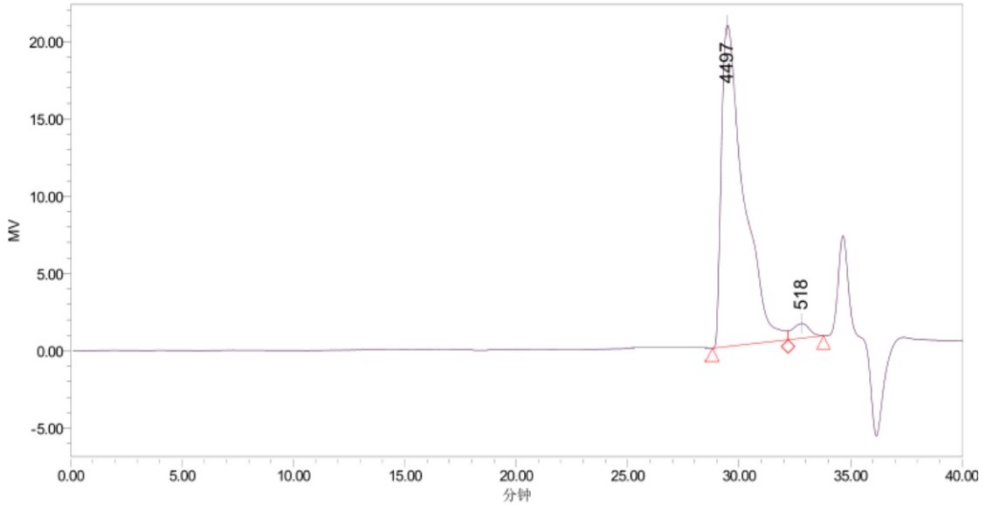


Fig. S33. GPC spectrum of **C-PTPN6-TFSI(10:1)** .

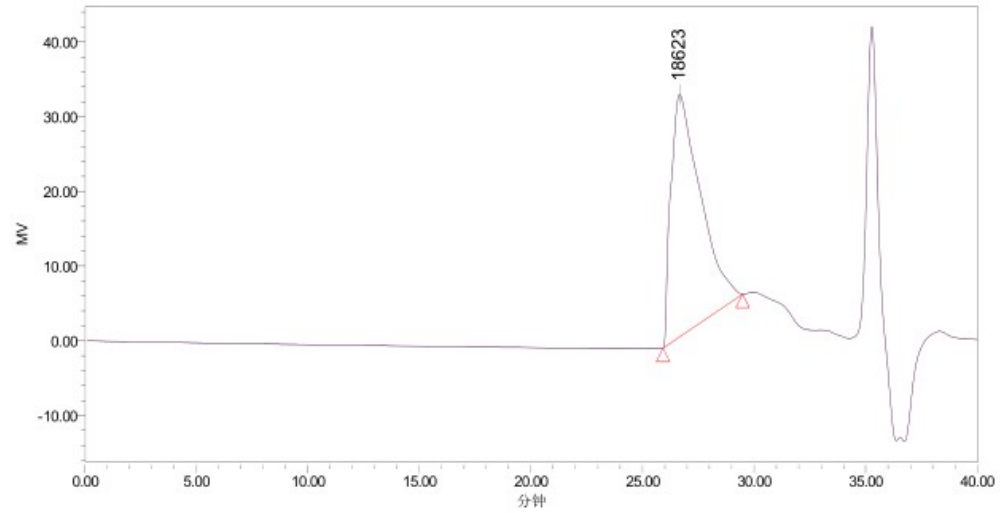


Fig. S34. GPC spectrum of **C-PTPN12-TFSI(10:1)** .

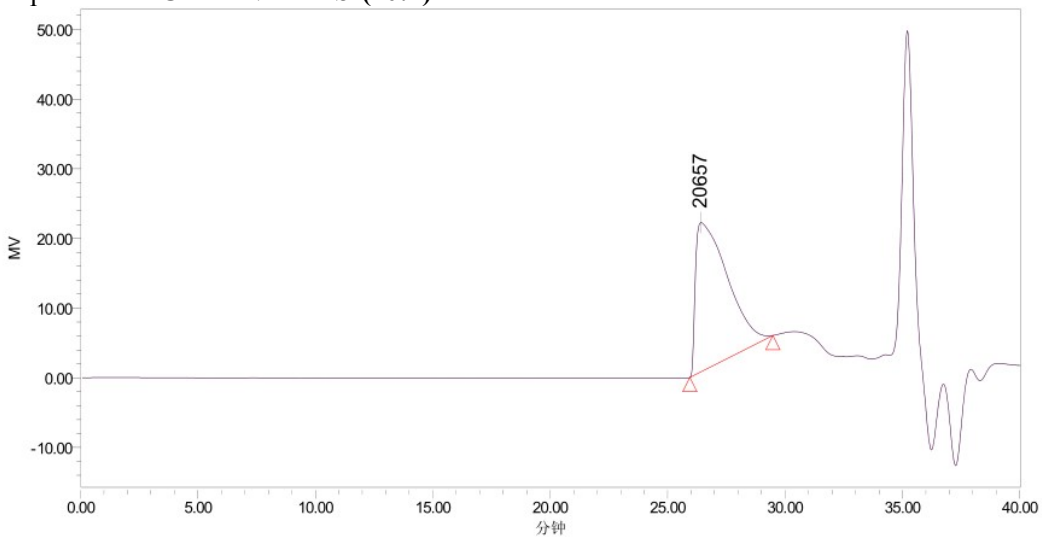
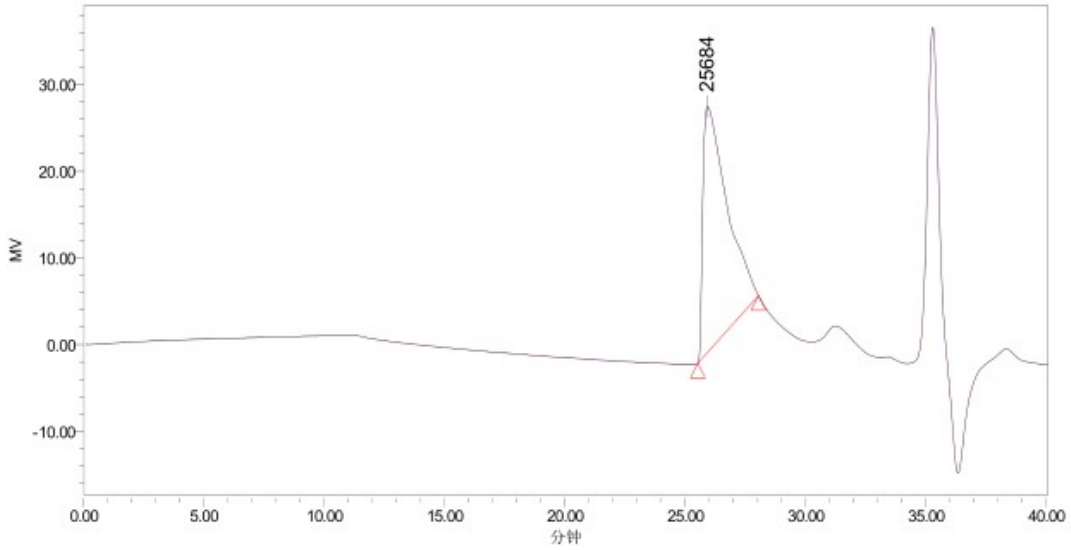


Fig. S35. GPC spectrum of **C-PTPN6-TFSI(40:1)** .



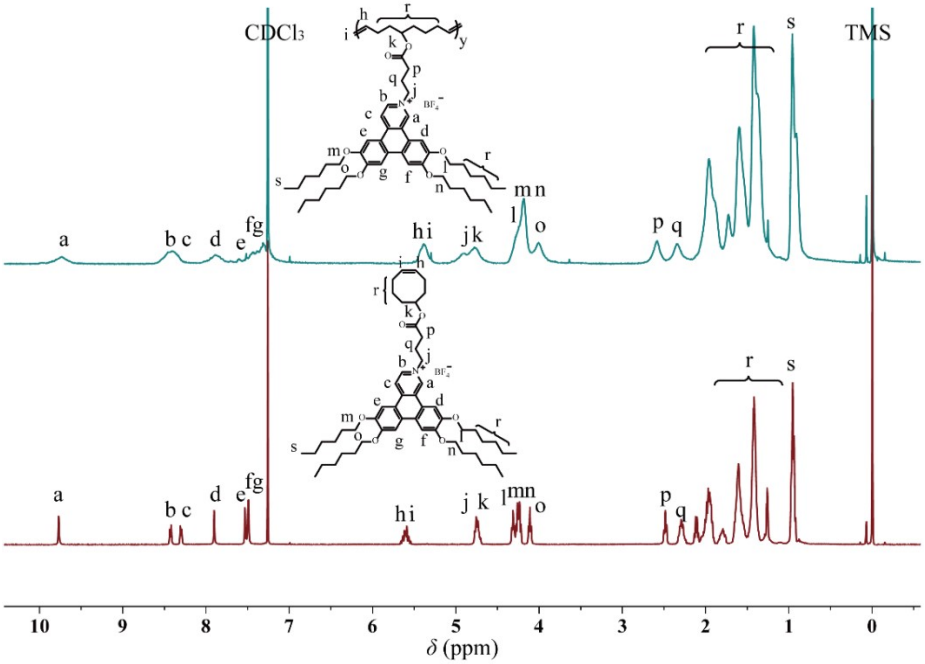


Fig. S36. ^{1}H NMR spectra of **COE-TPN6-BF$_4$** and **H-PTPN6-BF$_4$**.

Table S1. Molecular characteristics of the ionic monomers and polymers.

Samples	T_d (℃)	Samples	T_d[a] (℃)	*Mn*[b] (kDa)	PDI[b]
COE-TPN6-Br	230	**H-PTPN6-Br**	239	1.262	1.25
COE-TPN6-BF$_4$	279	**H-PTPN6-BF$_4$**	288	1.840	1.30
COE-TPN6-PF$_6$	285	**H-PTPN6-PF$_6$**	290	2.504	1.24
COE-TPN6-TFSI	289	**H-PTPN6-TFSI**	309	2.424	1.56
COE-TPN12-Br	236	**H-PTPN12-Br**	253	1.927	1.35
COE-TPN12-TFSI	309	**H-PTPN12-TFSI**	312	3.153	1.16
		C-PTPN6-Br (10:1) [c]	231	-	-
		C-PTPN6-TFSI (10:1)	308	14.421	1.10
		C-PTPN12-TFSI (10:1)	306	14.764	1.09
		C-PTPN6-TFSI (40:1)	309	20.131	1.06

[a]Temperature of 5% weight loss evaluated by TGA under nitrogen atmosphere at a heating rate of 10℃/min;
[b]Determined by GPC in THF using polystyrene (PS) standards.
[c]This polymer is poorly soluble in THF.

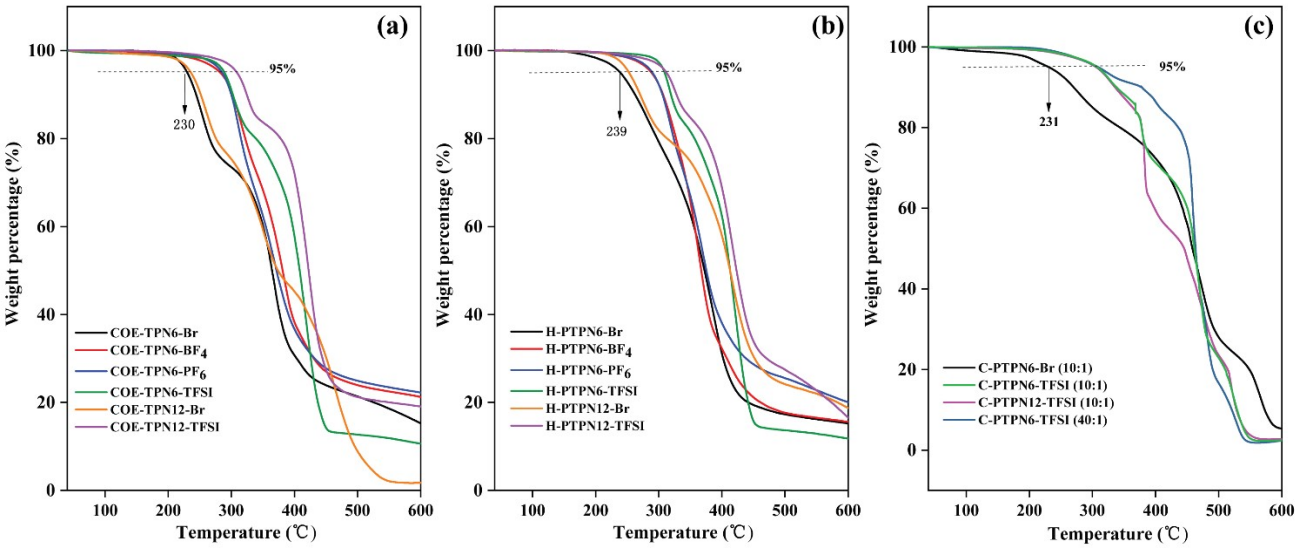


Fig. S37. TGA thermograms of (a) **COE-TPN*n*-X** (X = Br^-, BF_4^-, PF_6^-, $TFSI^-$), (b) **H-PTPN*n*-X** and (c) **C-PTPN*n*-X** measured under nitrogen at a rate of 10 °C/min.

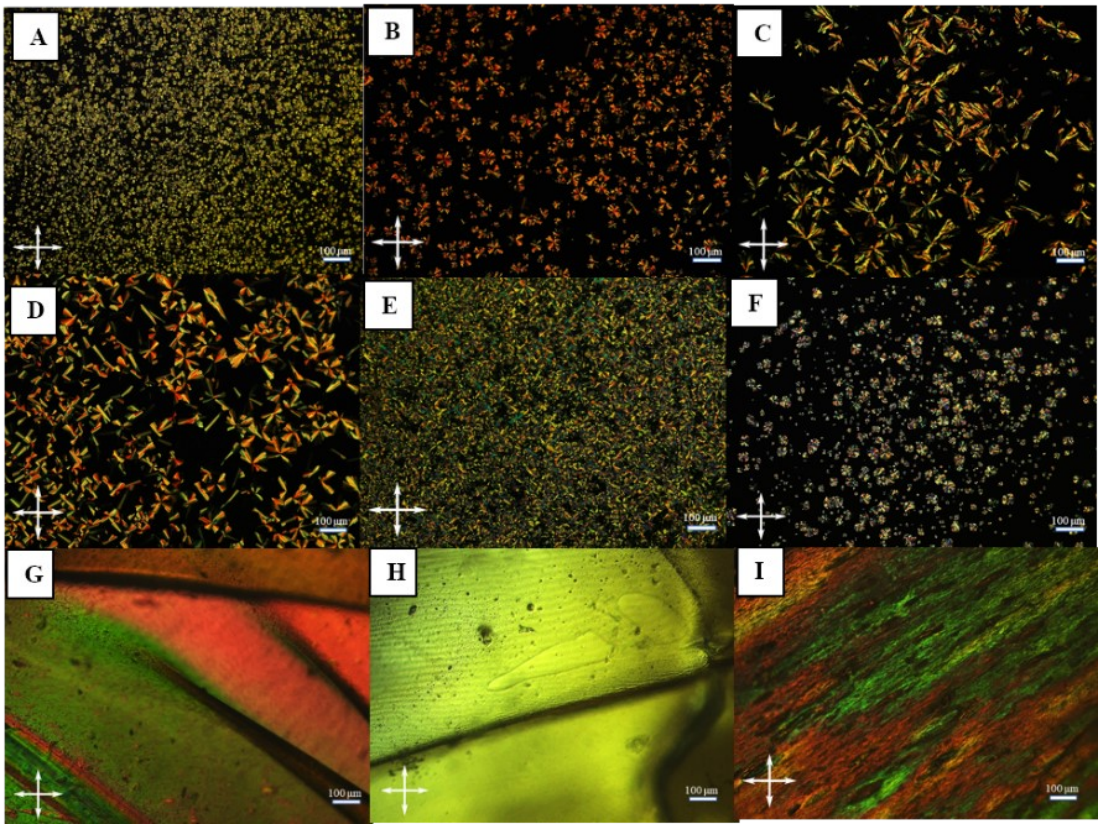


Fig. S38. Textures of **COE-TPN6-BF_4** at 60 °C (A), **COE-TPN6-PF_6** at 88 °C (B), **COE-TPN6-TFSI** at 145 °C (C), **COE-TPN12-TFSI** at 140 °C (D), **H-PTPN6-TFSI** at 150 °C (E), **H-PTPN12-TFSI** at 145 °C (F), **C-PTPN6-TFSI**(10:1) at 60 °C (G), **C-PTPN12-TFSI** (10:1) at 60 °C (H), **C-PTPN6-TFSI** (40:1) at 22 °C (I). Typical optical textures are obtained after slow cooling from the isotropic liquid into the mesophases.

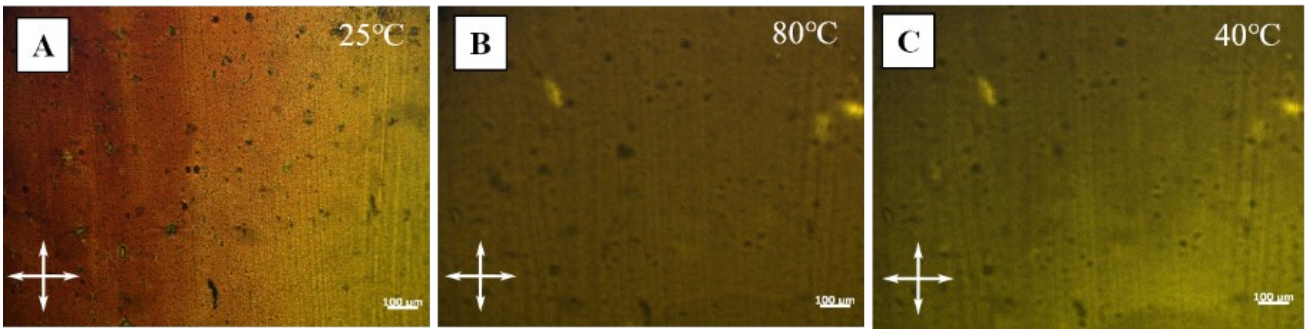


Fig. S39. Textures of **C-PTPN12-TFSI** (10:1) was heated from 25 °C (A) to 80 °C (B), then cooled to 40 °C(C).

Table S2. Mesophases, transition temperatures and enthalpy changes of monomers and polymers.

Compounds	2nd heating /°C (*Δ*H, kJ/mol)	1st cooling /°C (*Δ*H, kJ/mol)
COE-TPN6-Br	g 46 I	I 45 g
COE-TPN12-Br	g 38 I	I 37 g
COE-TPN6-BF_4	g 16 Col_h 98 (3.1) I	I 81 (-1.8) Col_h 15 g
COE-TPN6-PF_6	g 20 Col_h 115 (4.5) I	I 108 (-4.0) Col_h 16 g
COE-TPN6-TFSI	Col_h 157 (15.6) I	I 151 (-15.6) Col_h
COE-TPN12-TFSI	Cr 22 (8.5) Col_h 156 (13.6) I	I 151 (-15.4) Col_h 8 (-14.0) Cr
H-PTPN6-Br	g 97 I	I 94 g
H-PTPN12-Br	g 81 I	I 80 g
H-PTPN6-BF_4	g 88 I	I 88 g
H-PTPN6-PF_6	g 98 I	I 95 g
H-PTPN6-TFSI	Col_h 165 I	I 157 Col_h
H-PTPN12-TFSI	Cr -14 Col_h 163 I	I 154 Col_h -17 Cr
C-PTPN6-Br (10:1)	g 31 I	I -24 g
C-PTPN6-TFSI (10:1)	Cr 18 Col_h 82 I	I 67 Col_h -20 Cr
C-PTPN12-TFSI (10:1)	Cr -15 Col_h 94 I	I 67 Col_h -33 Cr
C-PTPN6-TFSI (40:1)	Cr 11 Col_h 91 I	I 68 Col_h -11 Cr

Cr, crystalline phase; Col_h, hexagonal columnar mesophase; I, isotropic phase; g, glass state.

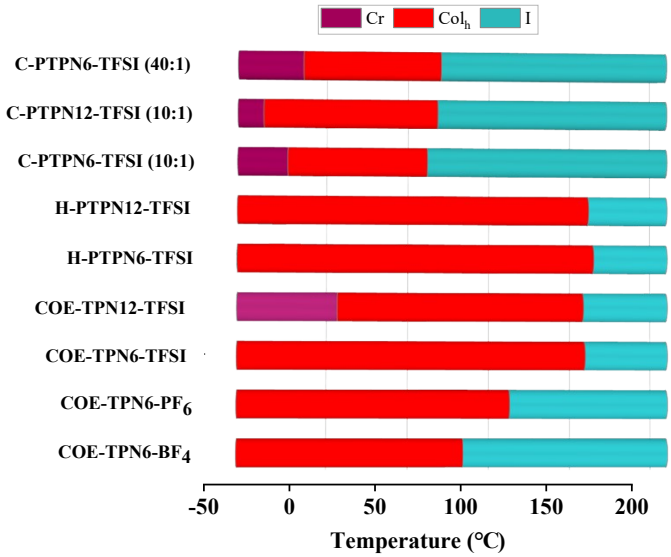


Fig. S40. Thermal and thermotropic mesophase diagram of all ionic monomers and polymers. (1st cooling cycle).

Table S3. X-Ray data for the mesophases of monomers and polymers

Samples	2θ (º)	d (Å)	hkl	Mesophase parameters
COE-TPN6-BF_4 60℃ Col_h	4.74	18.61	100	a = 21.49 Å
	8.17	10.81	110	A = 399.91 Å^2
	20.18	4.40	h_{ch}	Z = 0.93
	25.34	3.51	h_π	V = 1403.68 Å^3
COE-TPN6 -PF_6 80℃ Col_h	4.85	18.20	100	a = 21.02 Å A = 382.48 Å^2 Z = 0.84 V = 1353.99 Å^3
	8.62	10.25	110	
	9.51	9.29	200	
	20.74	4.28	h_{ch}	
	25.11	3.54	h_π	
COE-TPN6-TFSI 80℃ Col_h	4.79	18.43	100	a = 21.28 Å A = 392.21 Å^2 Z = 0.77 V = 1408.04 Å^3
	8.11	10.89	110	
	9.35	9.45	200	
	13.95	6.34	300	
	19.98	4.44	h_{ch}	
	24.76	3.59	h_π	
COE-TPN12-TFSI 30℃ Col_h	4.14	21.31	100	a = 24.61 Å
	7.08	12.47	110	A = 524.37 Å^2
	20.87	4.25	h_{ch}	Z = 0.76
	25.63	3.47	h_π	V = 1819.56 Å^3
H-PTPN6-TFSI 80℃ Col_h	4.80	18.39	100	a = 21.23 Å
	8.17	10.82	110	A = 390.51 Å^2
	21.37	4.15	h_{ch}	
	24.60	3.61	h_π	
H-PTPN12-TFSI 80℃ Col_h	4.03	21.92	100	a = 25.31 Å
	6.81	12.98	110	A = 554.82 Å^2
	20.82	4.26	h_{ch}	
C-PTPN6-TFSI (10:1) 40℃ Col_h	3.48	25.35	100	a = 29.27 Å
	20.57	4.32	h_{ch}	A = 742.04 Å^2
	25.30	3.52	h_π	
C-PTPN12-TFSI (10:1) 60℃ Col_h	3.38	26.11	100	a = 30.15 Å
	20.72	4.28	h_{ch}	A = 787.20 Å^2

Col_h: hexagonal columnar phase; 2θ and d are the experimentally measured diffraction angles [º] and distances [Å]; $d = \lambda/(2\sin\theta)$; hkl are the Miller indices of the reflections, h_{ch}: liquid-like lateral distances between molten chains; h_π: average distances between stacked triphenylene units. a = lattice parameter = $\sqrt{(4/3)} \times$ d100; lattice area $A = a^2 \sin 60^o$; lattice volume $V = a^2 \sin 60^o \times h_\pi$; number of molecules per slice of column (Z) = $(\sqrt{3}\times N_a \times \rho \times a^2 \times h_\pi)/2M$; N_a = Avogadro number; $\rho = 10^3$ kg·m^{-3}, density; a = lattice parameter; h_π = core-core peak; M = molecular weight in kg·m^{-3}.

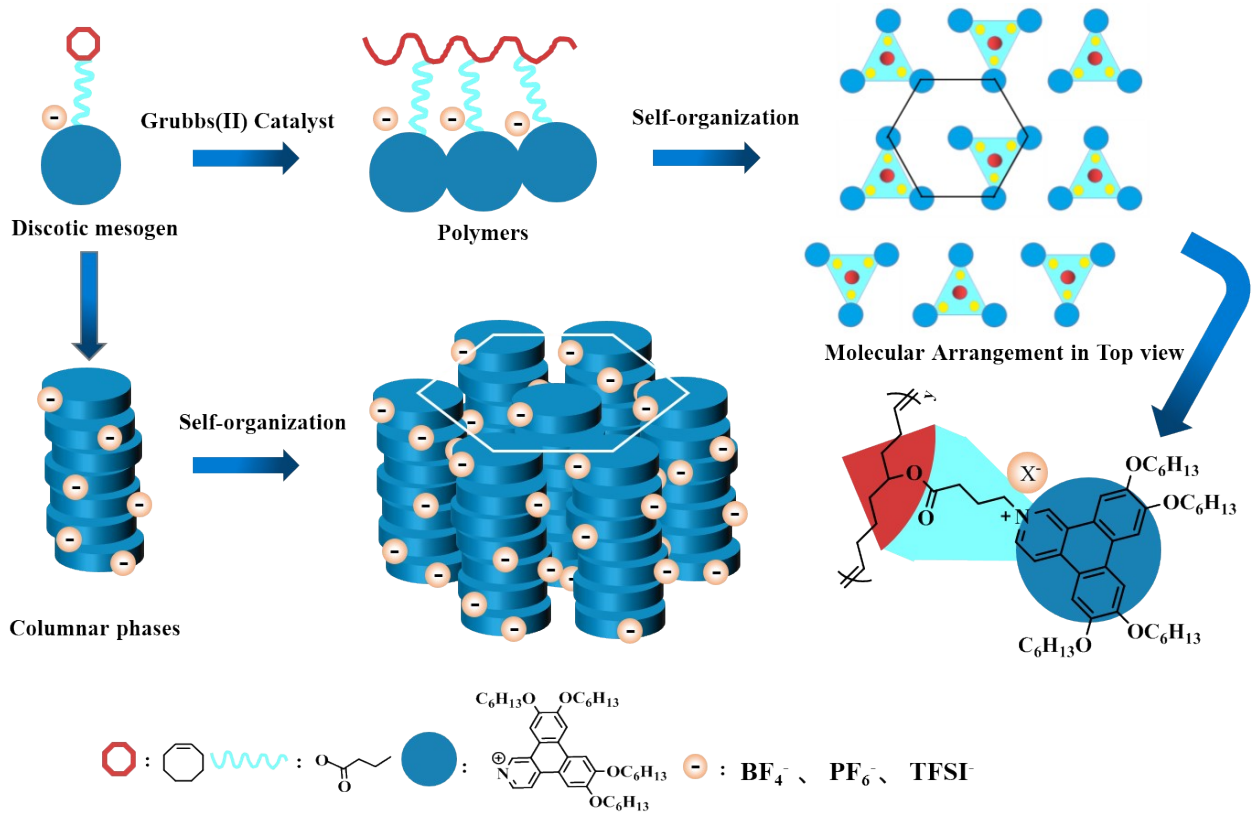


Fig. S41. Schematic drawing of the supramolecular structure for **COE-TPN6-X** (X = BF_4^-, PF_6^-, $TFSI^-$) and **H-PTPN6-TFSI**.

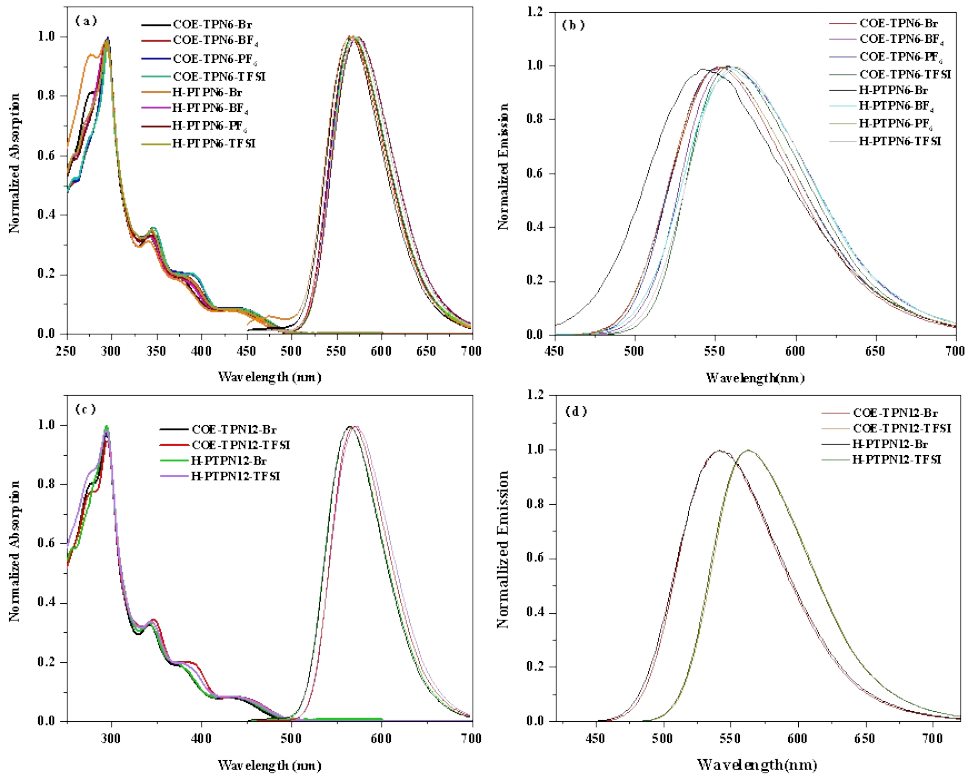


Fig. S42. (a) (c) UV/Vis absorption spectra and photoluminescence in dilute solution; (b) (d) photoluminescence in thin-films.

Table S4. Photo-physical properties of all ionic monomers and polymers[a]

Compounds	λ_{abs} (nm) solution	λ_{em}(nm) solution	λ_{em}(nm) film	Quantum yield (%)[a]
COE-TPN6-Br	294	537	555	15.9
COE-TPN6-BF_4	294	541	557	33.6
COE-TPN6-PF_6	295	542	553	29.5
COE-TPN6-TFSI	295	545	560	33.8
COE-TPN12-Br	294	538	541	20.4
COE-TPN12-TFSI	295	544	564	32.1
H-PTPN6-Br	294	536	542	14.6
H-PTPN6-BF_4	293	550	561	28.6
H-PTPN6-PF_6	294	546	554	15.2
H-PTPN6-TFSI	294	544	562	31.4
H-PTPN12-Br	294	538	542	11.1
H-PTPN12-TFSI	294	545	562	21.3
C-PTPN6-Br (10:1)	296	538	530	---
C-PTPN6-TFSI (10:1)	296	542	561	17.0
C-PTPN12-TFSI (10:1)	296	542	549	19.0
C-PTPN6-TFSI (40:1)	296	542	554	---

[a] Fluorescence spectra of monomers and homopolymers were measured at λ_{exc} = 380 nm and copolymers at λ_{exc} = 365 nm. The absolute quantum yield of fluorescence was measured at a solution concentration of 1 × 10^{-5} mol/L for the monomer and 0.1 mg/mL for the polymer.

Table S5. Mechanical properties of copolymers.

Samples	Fracture stress (Mpa)	Fracture strain (%)	Young's modulus (Mpa)
C-PTPN6-Br (10:1)	9.60	120	0.95
C-PTPN6-TFSI (10:1)	8.94	937	0.65
C-PTPN12-TFSI (10:1)	9.65	806	1.00
C-PTPN6-TFSI (40:1)	15.22	232	2.17

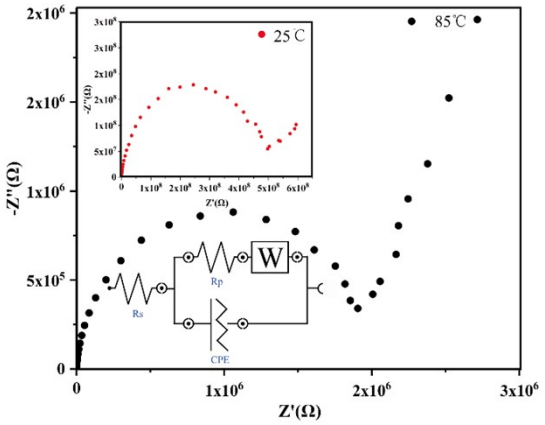


Fig. S43. Typical impedance spectrum presented in the form of the Nyquist plots for captured **C-TPN6-TFSI (10:1)** at different temperatures. The inserted figure is a fitting procedure for the impedance spectrum of the equivalent circuit at 85℃.