Supplementary Information

Naphthalimide-containing conjugated polyelectrolytes with different chain configurations

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Catalogue

Experimental

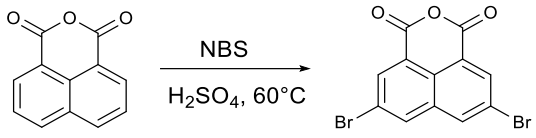
1. Materials

1,8-Naphthalenedicarboxylic anhydride, 3,5-dibromophenol, taurine, triethylene glycol monomethyl ether, ethynyltrimethylsilane, cuprous iodide (CuI), tetrakis-(triphenylphosphine) palladium ($Pd(PPh_3)_4$), 1,3-propanesultone were purchased from Energy Chemical Co. (Shanghai, China). Methylene blue were purchased from Aladdin Chemical Co. (Shanghai, China). Ruthenium(III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$), 2-(pyridin-2-yl)pyridine and 1,10-phenanthroline-5,6-dione, (S)-propane-1,2-diol, 2-(2-methoxyethoxy)ethanol were purchased from Innochem Co. (Shanghai, China). 2,5-Diethynylhydroquinone was purchased from Shanghai Dibo Biotechnology Co., Ltd (Shanghai, China). The solvents used in all experiments were purchased from General Reagent Co. and used without further purification. The water used in all experiments was prepared by a Milli-Q water purification system and displayed a resistivity of $\geq$18.2 MΩ cm^{-1}.

2. Instrumentation

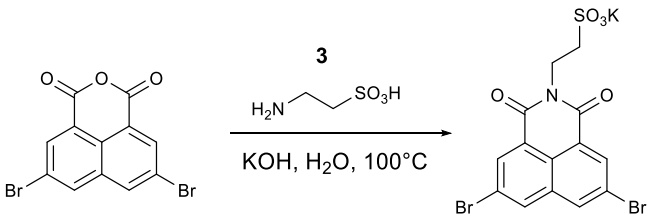
^1H NMR and ^{13}C NMR spectra were acquired on a Bruker Advance III 400 MHz spectrometer system. Mass spectra of monomers were acquired on a Waters Q-TOF Premier system. Fluorescence spectra were acquired on a HORIBA Fluorolog-3 system with 1 cm path length cuvette. Absorption spectra were acquired on an Agilent Cary 100 UV-Vis spectrophotometer with 1 cm path length cuvette. Circular dichroism spectra were acquired on an Applied Photophysics Chirascan system with 1 cm path length cuvette. Fluorescence quantum yields of polymers in solution were measured using relative method, using coumarin 6 as a standard, which had a reported quantum yield of 0.78 in ethanol upon excitation at 400 nm.

3. Synthesis and characterization



1 **2**

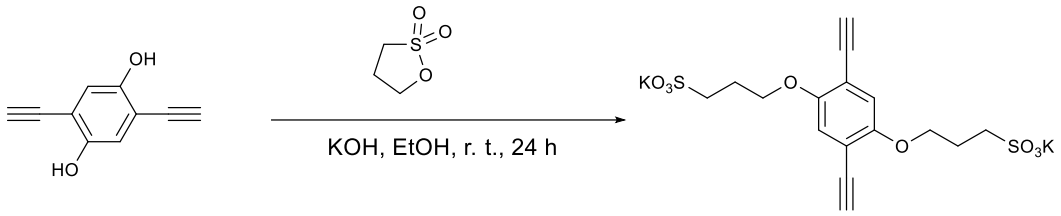
Synthesis of compound 2. Compound 2 was synthesized by improved literature methods.[1] N-Bromosuccinimide (7.83 g, 44.0 mmol, commercially available) was added to a solution of **1** (4.00 g, 20.0 mmol) in concentrated sulfuric acid (20.0 mL) and the mixture was stirred at 60 ℃ for 10 h. After cooling to room temperature, poured the mixture into ice water and filtered. The precipitate was washed with water and acetonitrile for several times and then recrystallization was carried out with boiled DMF to get pure a pale pink solid **2** (1.50 g, yield 20.0%). The product can only be dissolved in DMSO-d6 when heated to 150 ℃ for more than 5 min and should be tested within several minutes, which will precipitate quickly after cooling. Due to the extremely poor solubility of this compound, only the ^{1}H NMR spectrum was obtained. ^{1}H NMR (400 MHz, DMSO) δ 8.79 (d, J = 1.8 Hz, 2H; 2Ar-*H*), 8.54 (d, J = 1.8 Hz, 2H; 2Ar-*H*).



2 **N**

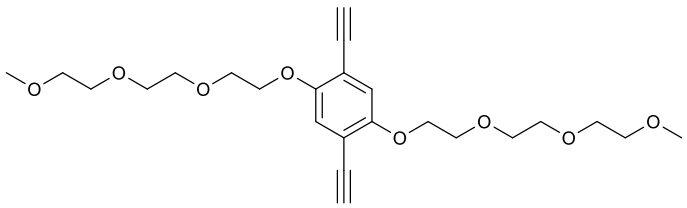
Synthesis of compound N. A solution of taurine (384 mg, 3.07 mmol, commercially available) and KOH (172 mg, 3.07 mmol) in H_2O (2.0 mL) was added to the suspension of compound **2** (1.10 g, 3.07 mmol) in H_2O (30.0 mL), then the reaction was refluxed for 20 h before cooling to room temperature. Yellow precipitation was formed. After filtration and washing with ice water, the pure amidated product **N** was obtained (791 mg, yield 47.0%). ^{1}H NMR (400 MHz, DMSO) δ 8.67 (d, *J* = 1.8 Hz, 2H; 2Ar-*H*), 8.43 (d, *J* = 1.8 Hz, 2H; 2Ar-*H*),

4.40 - 4.17 (m, 2H; CH_2), 2.84 - 2.64 (m, 2H; CH_2). ^{13}C NMR (101 MHz, DMSO) δ 161.72 (2*C*=O), 134.44 (2*C*), 133.78 (2*C*-Br), 132.57 (*C*), 124.64 (2*C*H), 124.40 (2*C*H), 121.10 (*C*), 48.42 (*C*H_2), 37.13 (*C*H_2). HRMS (ESI) *m/z*: [M] calcd for $C_{14}H_8Br_2NO_5S^-$, 459.8495; found: 459.8493.



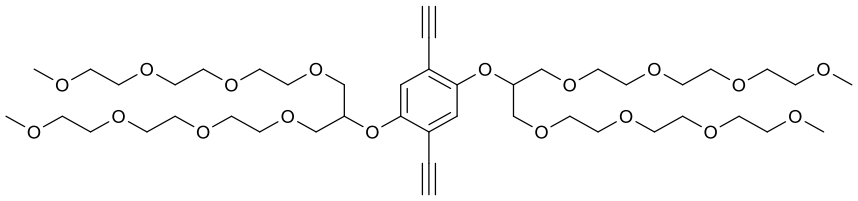
4 **pPE-1**

Synthesis of compound pPE-1. 1,3-propanesultone (289 mg, 2.36 mmol, commercially available) was added to a mixture of compound **4** (166 mg, 1.05 mmol, commercially available) and KOH (137 mg, 2.44 mmol) in ethanol (30.0 mL) in a round-bottomed flask. The reaction was stirred at room temperature for 24 h. A brown precipitate was formed. Filtration and recrystallization from ethanol gave the product as brown solid **pPE-1** (393 mg, yield 78.3%). ^{1}H NMR (400 MHz, DMSO) δ 7.02 (s, 2H, 2Ar-*H*), 4.39 (s, 2H, 2C*H*), 4.05 (t, J = 6.4 Hz, 4H, 2OCH_2), 2.58 - 2.53 (t, 4H, 2CH_2), 2.07 - 1.89 (m, 4H. 2CH_2). ^{13}C NMR (101 MHz, DMSO) δ 153.12 (2O*C*), 117.16 (2*C*H), 112.58 (2*C*), 85.90 (2*C*H), 79.63 (2*C*H), 67.97 (2*C*H_2), 47.82 (2*C*H_2), 25.18 (2*C*H_2). HRMS (ESI) *m/z*: [M] calcd for $C_{16}H_{16}O_8S_2^{2-}$, 200.0149; found: 200.0150.



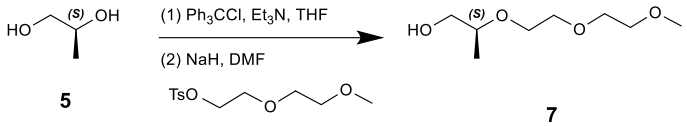
pPE-2

Synthesis of compound pPE-2. Compound **pPE-2** was synthesized according to a literature method.[2]

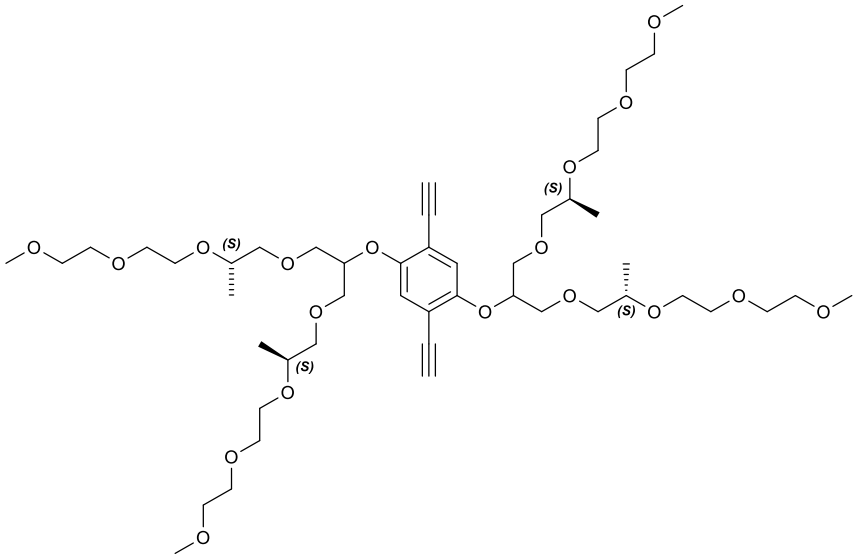


pPE-3

Synthesis of compound pPE-3. Compound **pPE-3** was synthesised according to a literature method.[3]



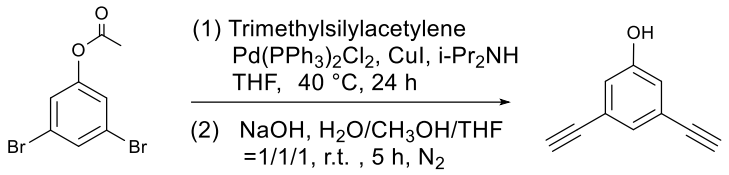
Synthesis of compound 7. Compound **5** is a commercially available compound. Compound **6** and **7** was synthesised according to a literature method.[4]



pPE-4

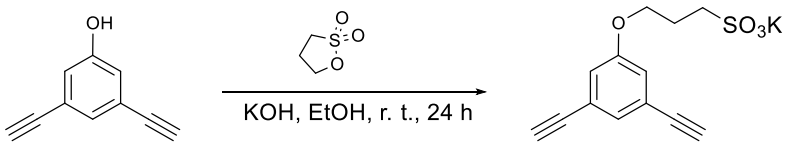
Synthesis of compound pPE-4. Compound **pPE-4** was synthesized according to the similar procedure used for **pPE-3**, except replacing triethylene glycol monomethyl ether with compound **7** (yield 30.0, total yield of all steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H, Ar-*H*), 4.47 – 4.35 (m, 2H, 2OC*H*), 3.73 – 3.60 (m, 40H, 20CH_2), 3.54 (m, 12H, 4CH, 4OCH_2), 3.37 (s, 12H, 4OCH_3), 3.32 (s, 2H, 2C*H*), 1.13 (d, *J* = 6.2 Hz, 12H, 4CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.15 (2O*C*), 121.37 (2*C*H), 114.94 (2*C*), 82.69 (2*C*H), 79.90 (2*C*H), 79.74 (2O*C*H),

75.70 (4O*C*H_2), 75.57 (4O*C*H_2), 75.01 (4O*C*H_2), 71.96 (4O*C*H_2), 70.88 (4O*C*H_2), 70.51 (4O*C*H_2), 68.66 (4*C*H), 59.02 (4O*C*H_3), 17.23 (4*C*H_3). HRMS (ESI) m/z: [M+Na^+] calcd for $C_{48}H_{82}O_{18}S$, 969.5393; found: 969.5393. $[\alpha]^{20}_D$ = -13.6° (c = 0.3, $CHCl_3$).



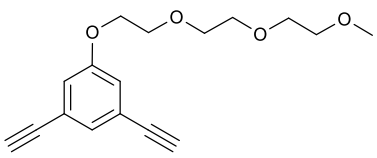
7 **8**

Synthesis of compound 8. Compound **8** was synthesised from compound **7**[5] according to a literature method.[6]



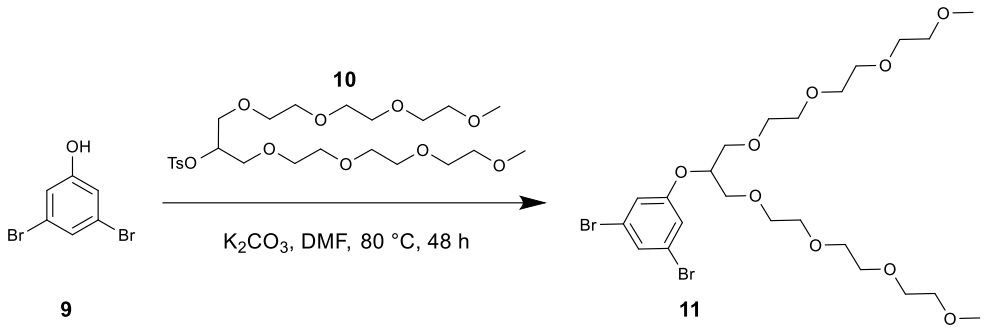
8 **mPE-1**

Synthesis of compound mPE-1. Compound **mPE-1** was synthesized according to the same procedure used for **pPE-1** except that 1,3-Propanesultone (289 mg, 2.36 mmol, commercially available), compound **8** (298 mg, 2.09 mmol), KOH (137 mg, 2.44 mmol) and ethanol (30.0 mL) were used. The product was brown solid (546 mg, yield 86.0%).^{1}H NMR (400 MHz, DMSO) δ 7.09 (s, 1H, Ar-*H*), 7.03 (d, J = 1.1 Hz, 2H, 2Ar-*H*), 4.25 (s, 2H. 2C*H*), 4.08 (t, J = 6.5 Hz, 2H, CH_2), 2.55 – 2.51 (t, 2H, CH_2), 2.01 – 1.93 (m, 2H, CH_2). ^{13}C NMR (101 MHz, DMSO) δ 158.46 (O*C*), 126.76 (2*C*H), 123.24 (*C*H), 118.31 (2*C*), 82.23 (2*C*H), 81.40 (2*C*), 67.09 (*C*H_2), 47.62 (*C*H_2), 25.00 (*C*H_2). HRMS (ESI) m/z: [M] calcd for $C_{13}H_{11}O_4S^-$, 263.0384; found: 263.0384.

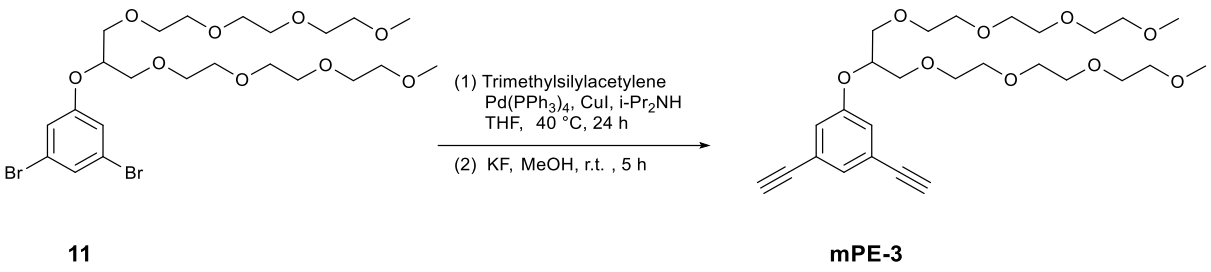


mPE-2

Synthesis of compound mPE-2. Compound **mPE-2** was synthesized according to a literature method.[7]



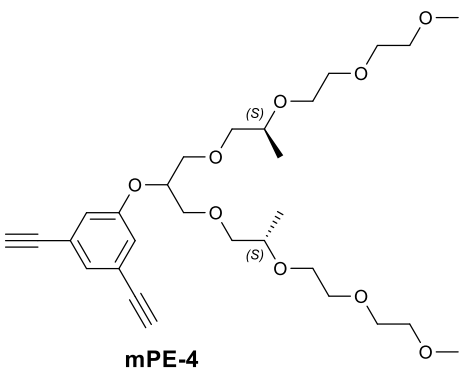
Synthesis of compound 11. In a round-bottomed flask, compound **9** (2.69 g, 5.00 mmol, commercially available) was added to a mixture of compound **10**[8] (1.26 g, 5.00 mmol) and K_2CO_3 (1.04 g, 7.50 mmol) in DMF (8.0 mL), then the reaction was stirred at 80℃ for 48 h. After that, 30.0 mL H_2O was added to the mixture and extracted with dichloromethane (50.0 mL×3). The organic solution was dried by Na_2SO_4 and then the solvent was removed in vacuo to get yellow oil **11**. This compound was used for the next step reaction without further purification and characterization.



11 **mPE-3**

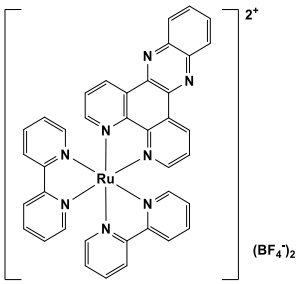
Synthesis of compound mPE-3. (1) Compound **11** (3.25 g, 5 mmol), CuI (50 mg, 0.26 mmol) and $Pd(PPh_3)_4$ (303 mg, 0.26 mmol) were added to a Schlenk flask. Then added trimethylsilylacetylene (3.0 mL, 20.0 mmol), THF (45.0 mL) and triethylamine (15.0 mL) to the mixture under nitrogen atmosphere, the solution was stirred at 50 ℃ under nitrogen atmosphere for 24 h. (2) The mixture was filtrated with siliceousearth and removed the liquid under vacuo. After that, CH_3OH (30.0 mL) and KF (2.03 g, 35.0 mmol) were added to the mixture, and the solution was stirred at room temperature overnight. After that, 50.0 mL

dichloromethane was added to the mixture and washed with H_2O, following by a column chromatography (eluting by EtOAc) to get yellow oil **mPE-3** (806 mg, yield 40.0%, total yield of three steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H, Ar-*H*), 7.11 (d, *J* = 1.1 Hz, 2H, 2Ar-*H*), 4.58 - 4.46 (m, 1H, OC*H*), 3.72 - 3.60 (m, 24H, 12OCH_2), 3.54 (dd, *J* = 5.7, 3.5 Hz, 4H, 2OCH_2), 3.38 (s, 6H, 2OCH_3), 3.06 (s, 2H, 2C*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.45 (O*C*), 128.18 (2*C*H), 122.82 (*C*H), 120.15 (2*C*), 81.95 (2*C*H), 77.13 (2*C*), 76.97 (*C*H), 76.65 (2*C*H_2), 71.37 (2*C*H_2), 70.57 (2*C*H_2), 70.09 (2*C*H_2), 70.06 (2*C*H_2), 70.00 (2*C*H_2), 69.95 (2*C*H_2), 58.45 (2*C*H_3). HRMS (ESI) *m/z*: [M+H^+], [M+NH_4^+], [M+Na^+], [M+K^+] calcd for $C_{27}H_{40}O_9$, 509.2745, 526.3011, 531.2565, 547.2304; found: 526.3027, 531.2564, 547.2301.

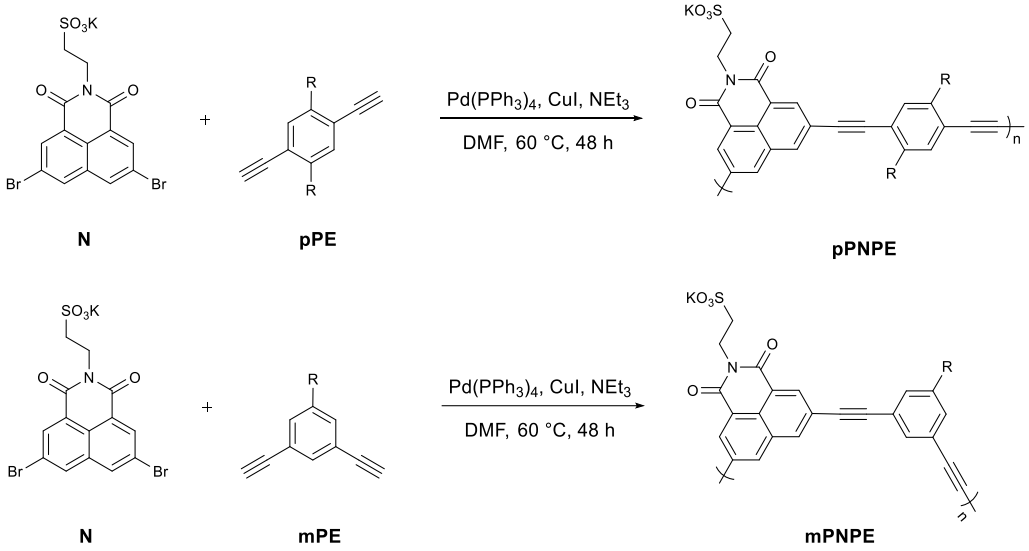


mPE-4

Synthesis of compound mPE-4. Compound **mPE-4** was synthesized according to the same procedure used for **pPE-4** (yield 42.3%, total yield of all steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H, Ar-*H*), 7.12 (d, J = 1.1 Hz, 2H, 2Ar-*H*), 4.62 - 4.43 (m, 1H, OC*H*), 3.77 - 3.58 (m, 20H, 10CH_2), 3.52 (m, J = 13.0, 7.7, 4.5 Hz, 6H, 2C*H*, 2OCH_2), 3.38 (s, 6H, 2OCH_3), 3.07 (s, 2H, 2C*H*), 1.14 (d, J = 6.3 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.53 (O*C*), 128.12 (2*C*H), 122.80 (*C*H), 120.10 (2*C*), 81.93 (2*C*H), 77.17 (2*C*), 76.91 (O*C*H), 75.06 (2O*C*H_2), 74.44 (2O*C*H), 71.36 (2O*C*H_2), 70.28 (2O*C*H_2), 70.17 (2O*C*H_2), 69.91 (2O*C*H_2), 68.02 (2O*C*H_3), 58.44 (2O*C*H_3), 16.54 (2*C*H_3). HRMS (ESI) m/z: [M+NH_4^+], [M+Na^+], [M+K^+] calcd for $C_{29}H_{44}O_9$, 554.3324, 559.2878, 575.2617; found: 554.3320, 559.2867, 575.2599. $[\alpha]^{20}_D$ = -9.2° (c = 0.3, $CHCl_3$).



Synthesis of $[Ru(bpy)_2(dppz)]^{2+}(BF_4^-)_2$. $[Ru(bpy)_2(dppz)]^{2+}(BF_4^-)_2$ was synthesised according to a literature method.[9]



Synthesis of polymers: the bisalkyne monomers **pPE** or **mPE** (0.1 mmol), the dibromo-substituted naphthalimide monomers **N** (0.1 mmol), CuI (1.4 mg, 0.0075 mmol) and $Pd(PPh_3)_4$ (8.7 mg, 0.0075 mmol) were added to a Schlenk flask under nitrogen atmosphere. Then injected degassed DMF (3.0 mL) and triethylamine (1.0 mL) into the mixture. The mixture was stirred at 60 ℃ under nitrogen atmosphere for 24 h. The obtained reaction solution was diluted with water (15.0 mL) and filter, then the filtrate was purified by dialysis against deionized water with a regenerated cellulose membrane (3.5 kDa cutoff) ([polymer] is the polymer repeat unit concentration). Finally, polymers solution was obtained and stored.

Molecular weights of these polymers were analyzed by pulsed-gradient spin-echo (PGSE) NMR technique (*PULPROG = stebpgp1s*, PEO with known molecular weight as standards,

solvent is DMSO-d6, 1 mg/mL,) instead of commonly used gel permeation chromatography (GPC) as reporetd before[10-12] due to strong adsorption of the polymers on GPC columns.

pPNPE-1. ^{1}H NMR (400 MHz, DMSO) δ 8.87 (m, 2H, 2Ar-*H*), 8.48 (m, 2H, 2Ar-*H*), 7.38 (m, 2H, 2Ar-*H*), 4.25 (br, 6H, 3CH_2), 2.83 (br, *J* = 6H, 3CH_2), 2.16 - 2.08 (br, 4H, 2CH_2). $\overline{M_n}$ = 10.1 kDa.

pPNPE-2. ^{1}H NMR (400 MHz, DMSO) δ 9.15 - 6.58 (br, 6H, 6Ar-*H*), 4.53 - 3.48 (br, 24H, 10OCH_2,2CH_2), 3.14 (m, 10H, 2OCH$_2$, 2OCH_3). $\overline{M_n}$ = 11.7 kDa.

pPNPE-3. ^{1}H NMR (400 MHz, D$_2$O) δ 8.95 - 6.71 (br, 6H, 6Ar-*H*), 3.63 (br, 62H, 2OC*H*, 28OCH_2, 2CH_2), 3.33 (br, 12H, 4OCH_3). $\overline{M_n}$ = 18.5 kDa.

pPNPE-4. ^{1}H NMR (400 MHz, D$_2$O) δ 8.86 – 6.64 (br, 6H, 6Ar-*H*), 4.19 - 2.46 (br, 70H, 2OC*H*, 24OCH_2, 4CH$_3$C*H*, 2CH_2, 4OCH_3), 0.95 (br, 12H, 4OCH_3). $\overline{M_n}$ = 14.3 kDa.

mPNPE-1. ^{1}H NMR (400 MHz, DMSO) δ 8.60 (m, 4H, 4Ar-*H*), 7.66 - 7.12 (m, 2H, 2Ar-*H*), 4.14 (m, 4H, 2CH_2), 2.79 (br, 2H, CH_2), 2.69 – 2.56 (br, 2H, CH_2), 2.07 (br, 2H, CH_2). $\overline{M_n}$ = 6.5 kDa.

mPNPE-2. ^{1}H NMR (400 MHz, DMSO) δ 9.48 – 6.71(br, 7H, 7Ar-*H*), 4.52 – 3.28 (m, 19H, 6OCH_2, 2CH_2, OCH_3,). $\overline{M_n}$ = 9.3 kDa.

mPNPE-3. ^{1}H NMR (400 MHz, D$_2$O) δ 7.24 (br, 7H, 7Ar-*H*), 4.17 - 2.47 (br, 39H, OC*H*, 14OCH_2, 2CH_2, 2OCH_3). $\overline{M_n}$ = 11.4 kDa.

mPNPE-4. ^{1}H NMR (400 MHz, D$_2$O) δ 7.34 (br, 7H, 7Ar-*H*), 3.45 (br, 37H, OC*H*, 12OCH_2, 2CH$_3$C*H*, 2CH_2, 2OCH_3), 1.15 (br, 6H, 2CH_3). $\overline{M_n}$ = 10.3 kDa.

4. Molecular modeling

The molecular models were obtained using a modified method as literature.[13, 14] The *pcff* force field in Materials Studio program and the simplified protonated 10-mer model of polymers were used for simulating. The water environment was built by the Amorphous Cell

module (a = 80 Å, b = 80 Å, c = 80 Å; α = 90º, β = 90º, γ = 90º), and single polymer chains were placed in the center of the solvent cell (density 1.0 g/mL).

Results

1. Molecular weight and solubility

Table S1. Self-diffusion coefficient (D) of the PEO references in DMSO-d6

	PEO 100,000	PEO 20,000	PEO 8,000	PEO 6,000	PEO 4,000
D * 10^{12} (m^2/s)	13.94	28.441	53.41	66.56	73.86

The relationship between polymer self-diffusion coefficient (D) and its molecular weight (M) is given by

$$D = kM^{-\nu} \quad \text{(eq. 1)}$$

A least square optimization of eq. 1 for the six standards afforded k =7.17×10^{-9} and ν = 0.55, which yielded the molecular weigut for the polymers.

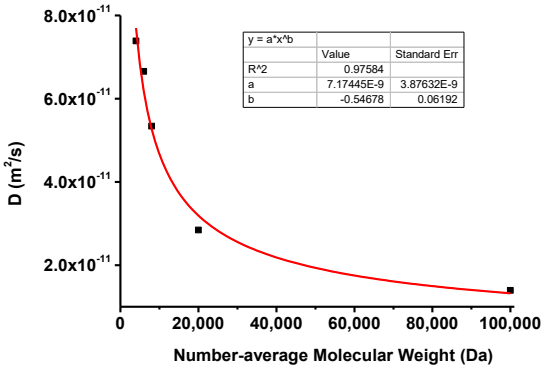


Fig. S1 Fit curve of D and $\overline{M_n}$ of PEO

Table S2. Molecular weight of the polymers

	pPNPE-1	pPNPE-2	pPNPE-3	pPNPE-4	mPNPE-1	mPNPE-2	mPNPE-3	mPNPE-4
D * 10^{12} (m^2/s)	44.9	41.4	32.3	38.4	57.2	47.2	42.0	44.6
$\overline{M_n}$ [a] (Da)	10138	11749	18451	14264	6528	9258	11446	10262
$\overline{DP}$ [b]	12.4	14.8	15.0	11.1	10.1	14.7	13.5	11.7
$\overline{X_n}$ [c]	24.8	29.6	30.0	22.2	20.2	29.4	27.0	23.4

[a] Number average molecular weight; [b] number of repeating unit; [c] number of structural unit.

Table S3. Water solubility of the polymers

	pPNPE-1	pPNPE-2	pPNPE-3	pPNPE-4	mPNPE-1	mPNPE-2	mPNPE-3	mPNPE-4
Water solubility (mg/mL)	5.5	2.1	15.7	10.5	5.2	4.0	14.5	11.8

2. UV-Vis absorption and fluorescence emission characterizaion

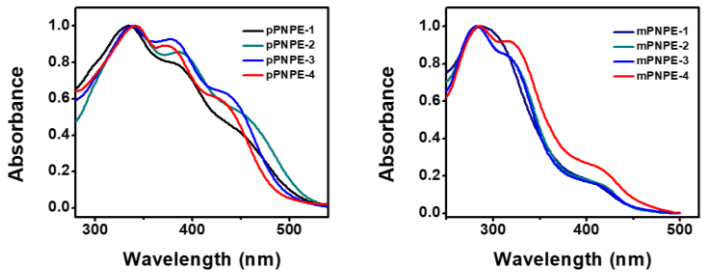


Fig. S2 UV-Vis absorption spectra of pPNPEs (left) and mPNPEs (right) in THF. [polymer] is the polymer repeat unit concentration, which is 10.0 μM in these measurements.

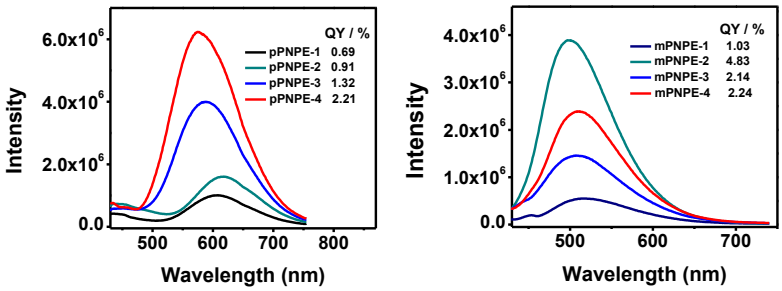


Fig. S3 Fluorescence emission spectra of pPNPEs (left) and mPNPEs (right) in THF. [polymer] is the polymer repeat unit concentration, which is 10.0 μM in these measurements. Excitation wavelength is 400 nm.

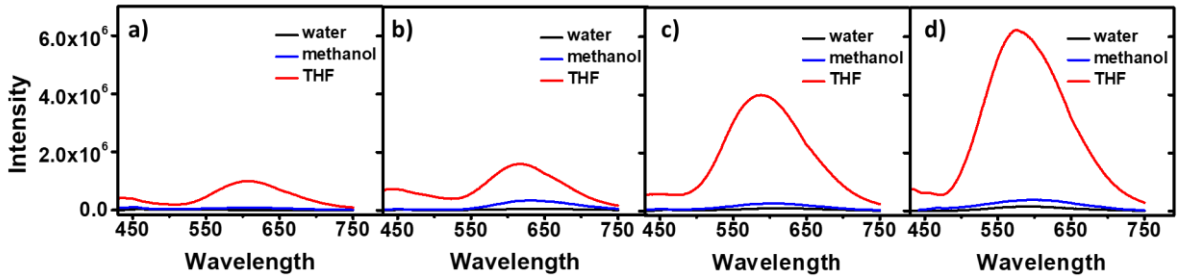


Fig. S4 Fluorescence emission spectra of pPNPE-1 (a), pPNPE-2 (b), pPNPE-3 (c) and pPNPE-4 (d) in differet solvents. ([polymer] is the polymer repeat unit concentration, which is 10.0 μM in these measurements. Excitation wavelength is 400 nm.

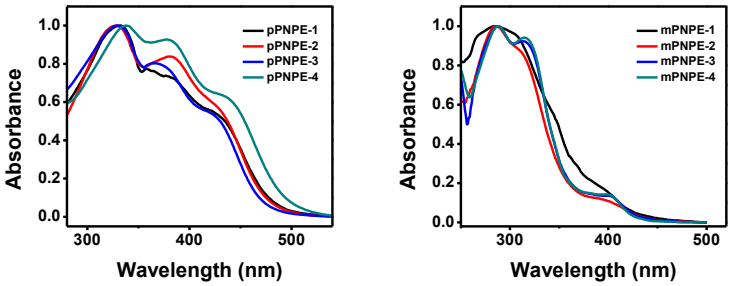


Fig. S5 UV-Vis absorption spectra of pPNPEs (left) and mPNPEs (right) in THF. [polymer] is the polymer repeat unit concentration, which is 10.0 μM in these measurements.

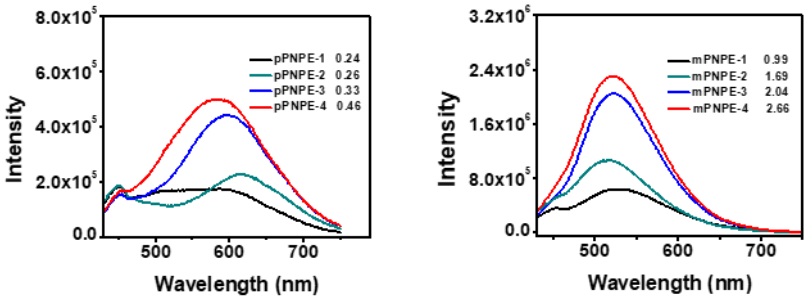


Fig. S6 Fluorescence emission spectra of pPNPEs (left) and mPNPEs (right) in DMSO. [polymer] is the polymer repeat unit concentration, which is 10.0 μM in these measurements. Excitation wavelength is 400 nm.

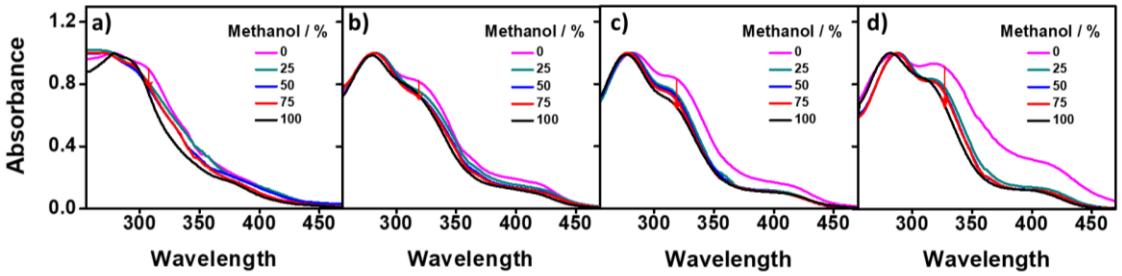


Fig. S7 Normalized UV-Vis absorption spectra of mPNPE-1 (a), mPNPE-2 (b), mPNPE-3 (c) and mPNPE-4 (d) in methanol/THF mixture with different methanol volume fraction from 0 to 100%.

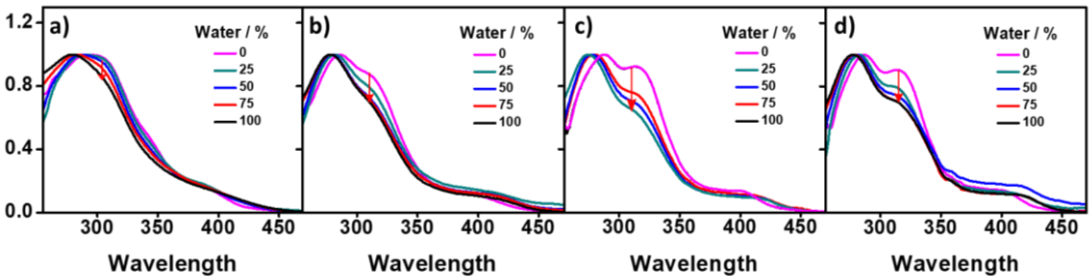


Fig. S8 Normalized UV-Vis absorption spectra of mPNPE-1 (a), mPNPE-2 (b), mPNPE-3 (c) and mPNPE-4 (d) in water/DMSO mixture with different water volume fraction from 0 to 100%.

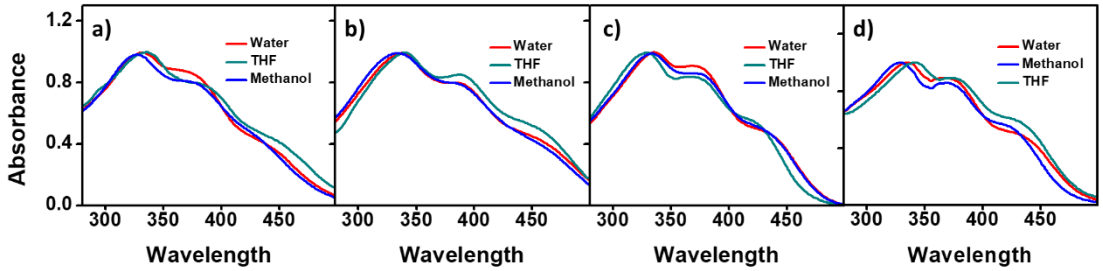


Fig. S9 Normalized UV-Vis absorption spectra of mPNPE-1 (a), mPNPE-2 (b), mPNPE-3 (c) and mPNPE-4 (d) in different solutions.

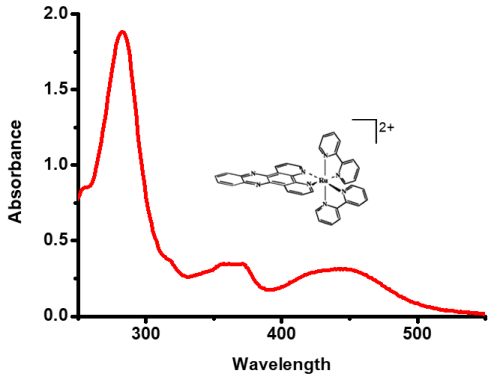


Fig. S10 UV-Vis absorption spectrum of $[Ru(bpy)_2(dppz)]^{2+}(BF_4^-)_2$ in aqueous solution.

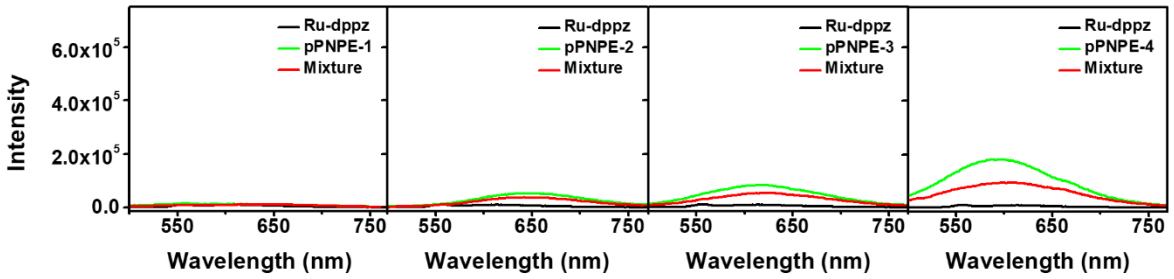


Fig. S11 Fluorescence emission spectra of pPNPE (150 μM), Ru-dppz (20 μM) and their mixture. ([polymer] is the polymer repeat unit concentration). Exciation wavelength is 470 nm.

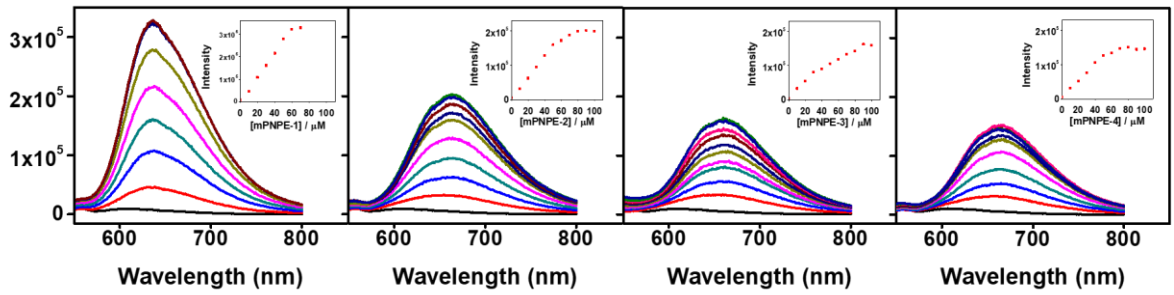


Fig. S12 Fluorescence spectra of Ru-dppz (20 μM) in aqueous solution containing different amounts of mPNPEs. Insets are plots of the maxima fluorescence intensity against mPNPEs concentrations. Exciation wavelength is 470 nm.

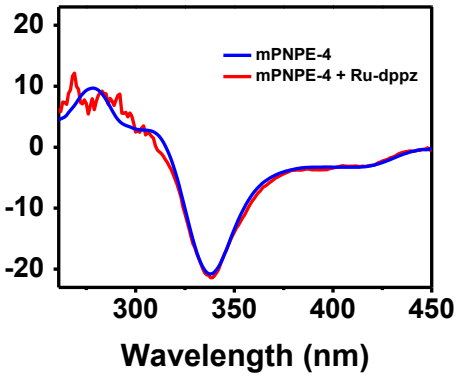


Fig. S13 CD spectra of mPNPE-4 and mPNPE-4 / Ru-dppz mixture in water ([mPNPE-4] is 55.7 μM, [Ru-dppz] is 11 μM).

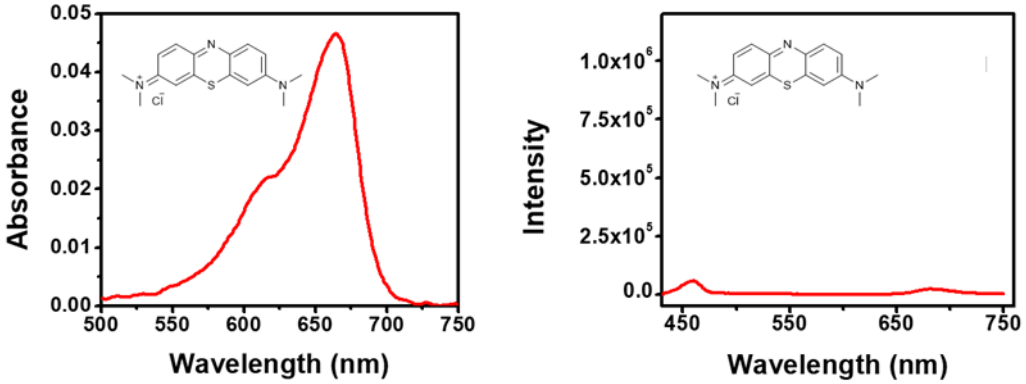
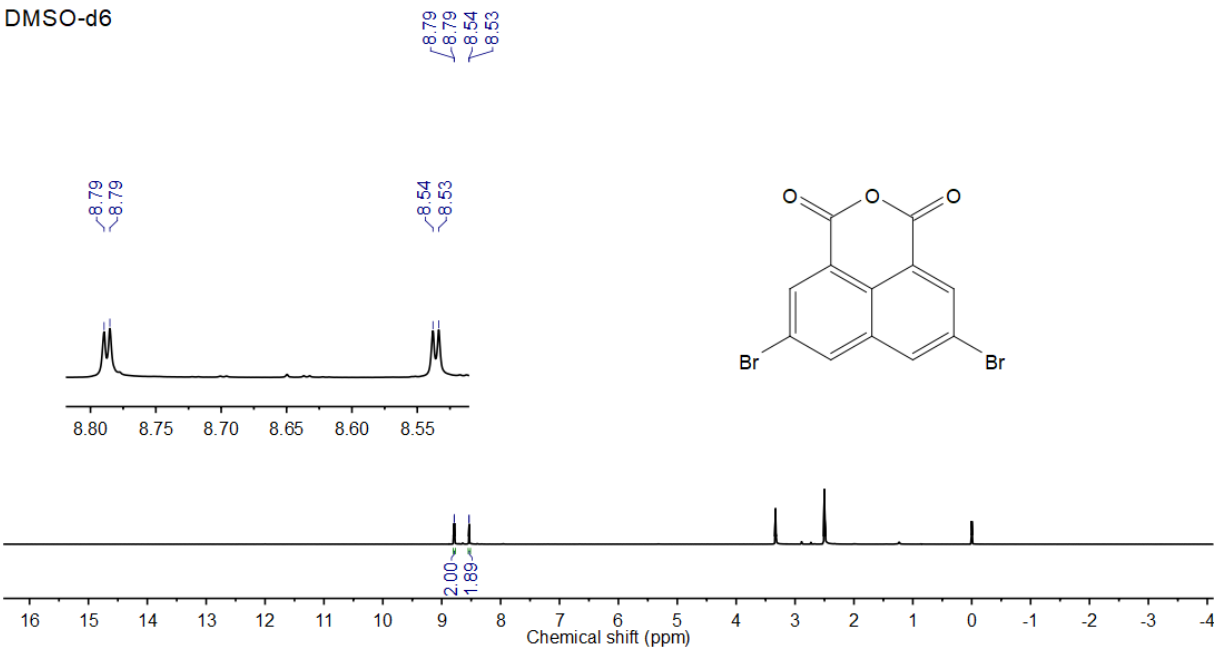
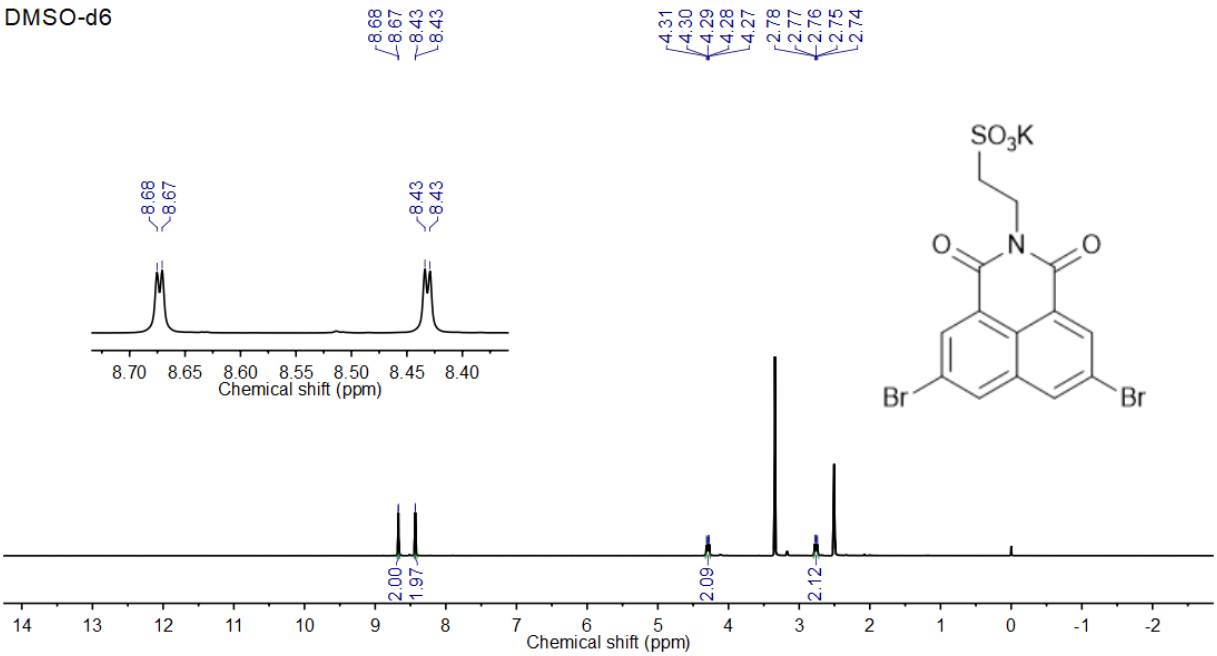
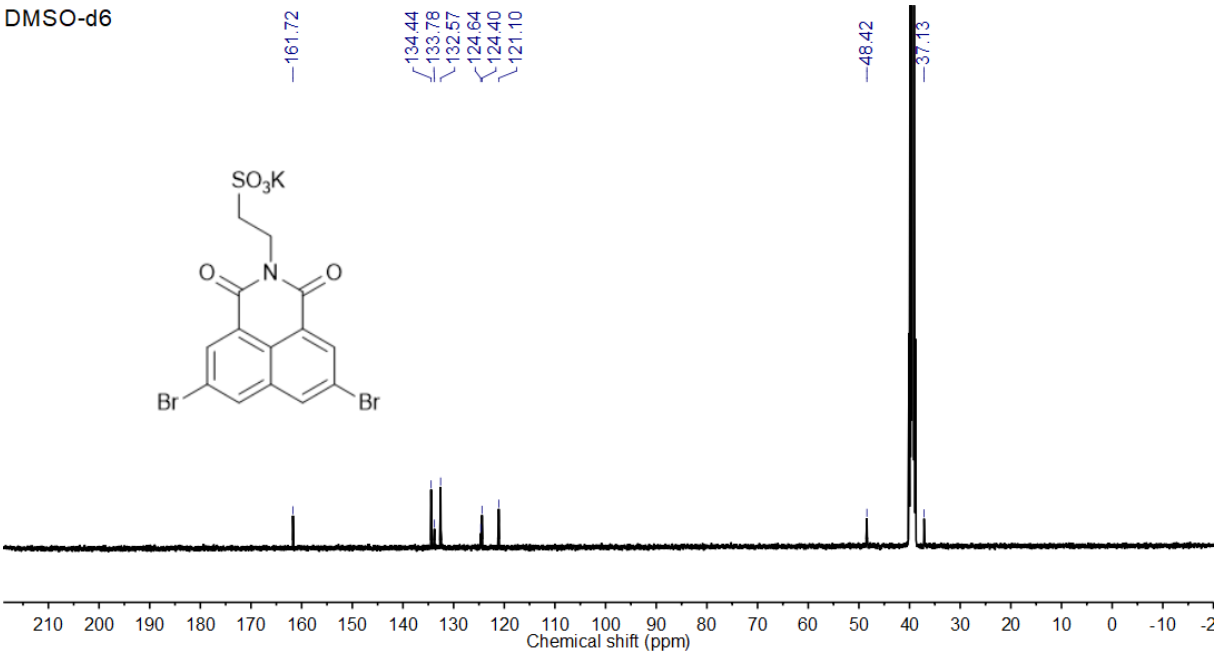


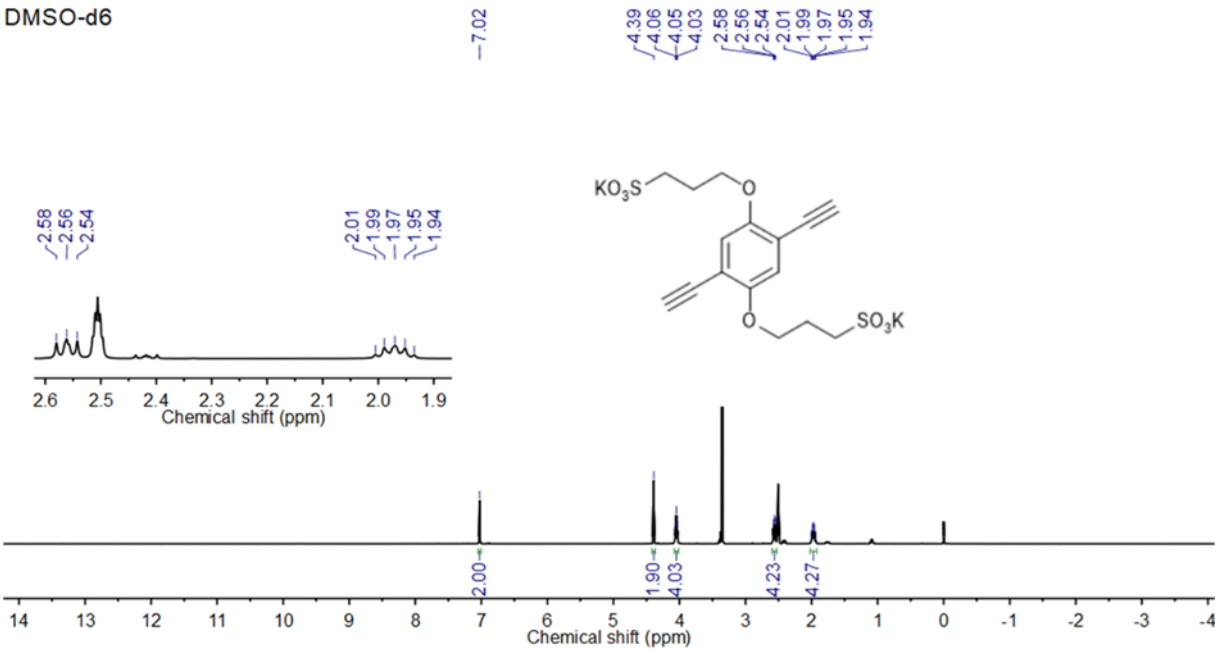
Fig. S14 UV-Vis absorption (left) and fluorescence emission spectra (right) of methylene blue in aqueous solution (0.3 μM). Exciation wavelength is 400 nm.

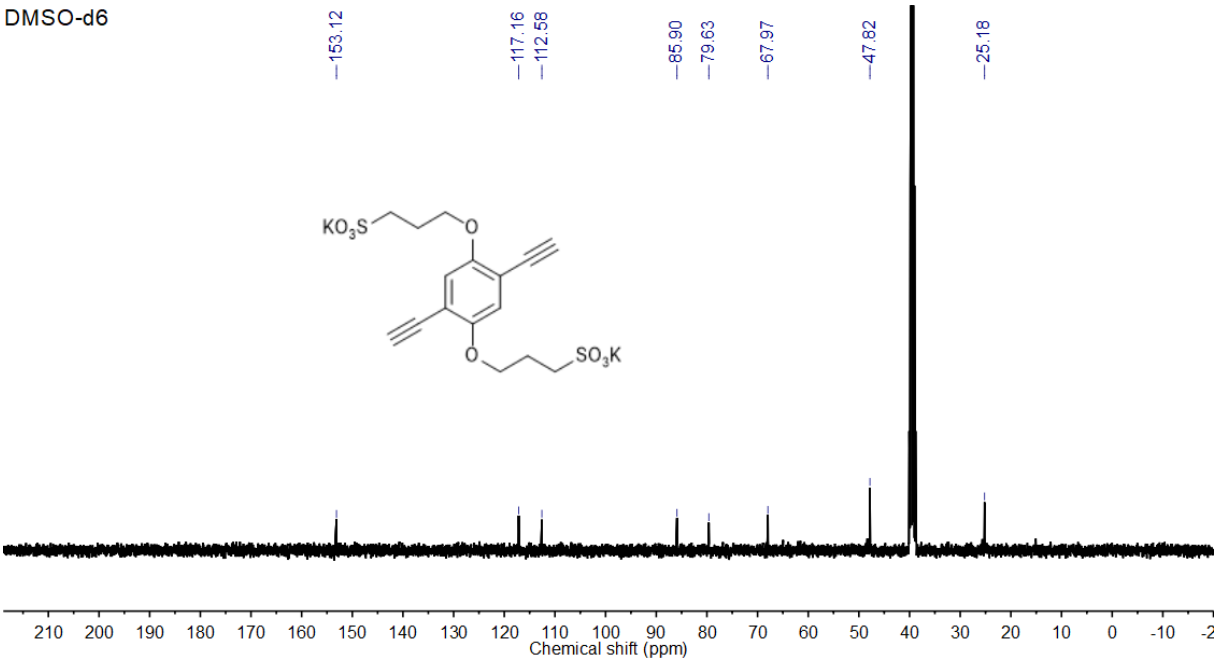
3. NMR spectra

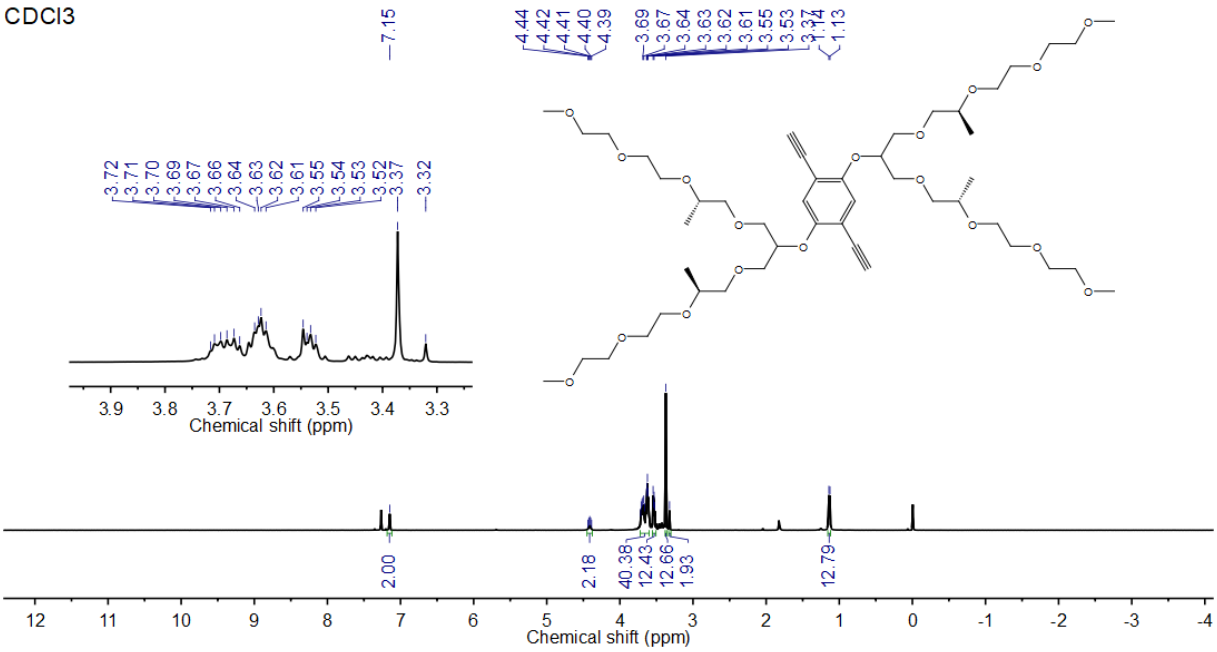


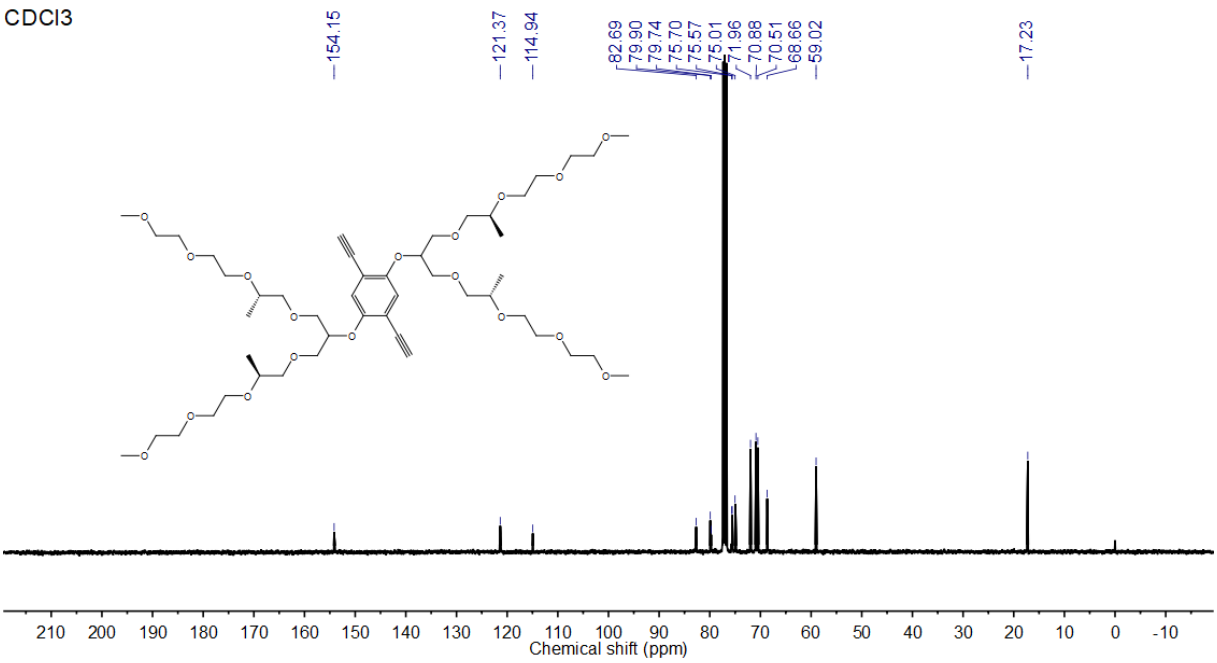


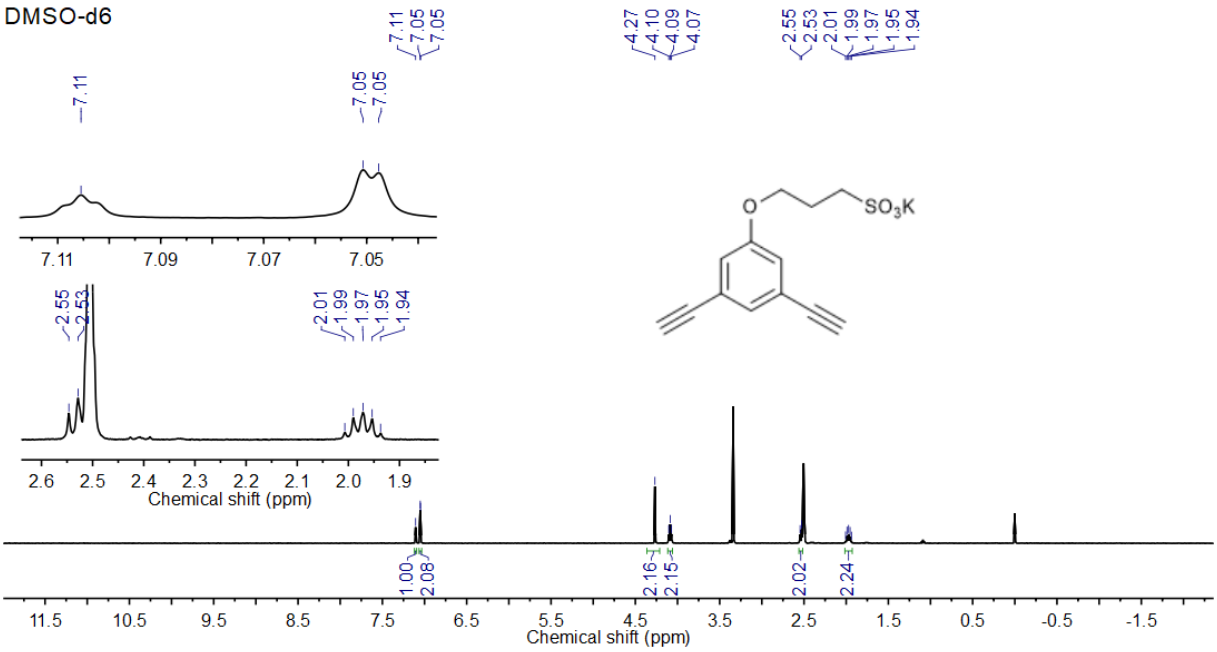

DMSO-d6
161.72
134.44
133.78
132.57
124.64
124.40
121.10
48.42
37.13
SO3K
O
N
O
Br
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
Chemical shift (ppm)

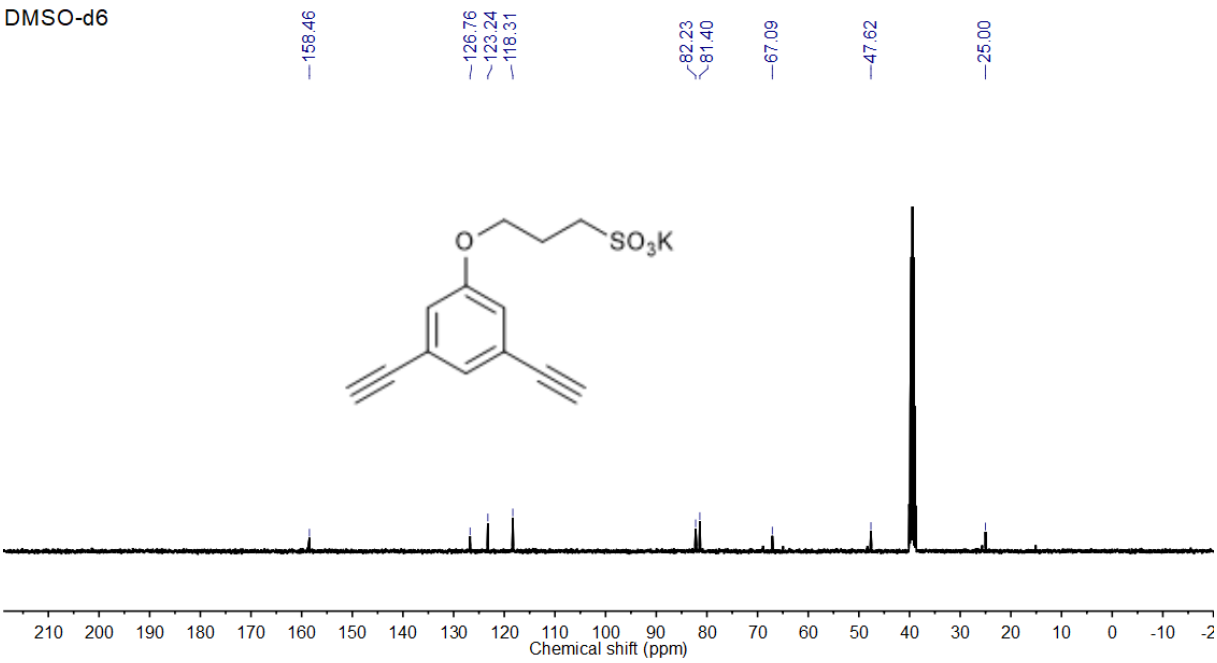

DMSO-d6
7.02
4.39
4.06
4.05
4.03
2.58
2.56
2.54
2.01
1.99
1.97
1.95
1.94
KO3S
O
O
O
SO3K
2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
Chemical shift (ppm)
2.00
1.90
4.03
4.23
4.27
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
Chemical shift (ppm)

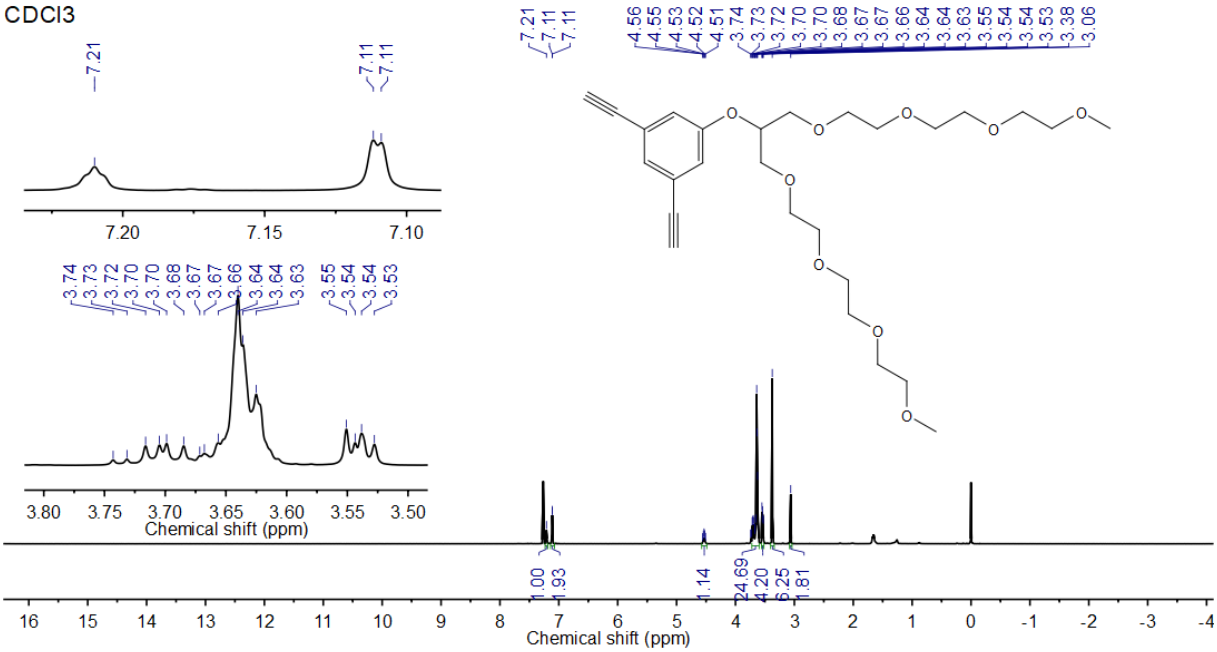

DMSO-d6
153.12
117.16
112.58
85.90
79.63
67.97
47.82
25.18
KO3S
O
O
SO3K
Chemical shift (ppm)

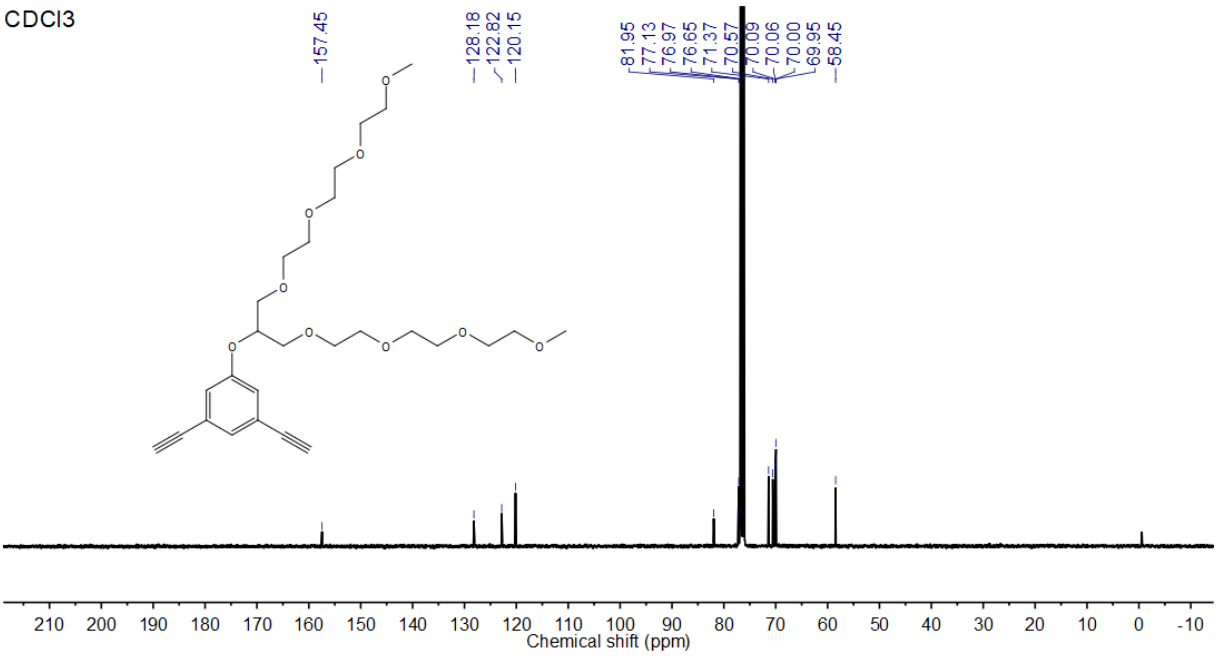

CDCl3
7.15
4.44
4.42
4.41
4.40
4.39
3.69
3.67
3.64
3.63
3.62
3.61
3.55
3.53
3.37
3.14
1.13
3.72
3.71
3.70
3.69
3.67
3.66
3.64
3.63
3.62
3.61
3.55
3.54
3.53
3.52
3.37
3.32
Chemical shift (ppm)
2.00
2.18
40.38
12.43
12.66
1.93
12.79
Chemical shift (ppm)

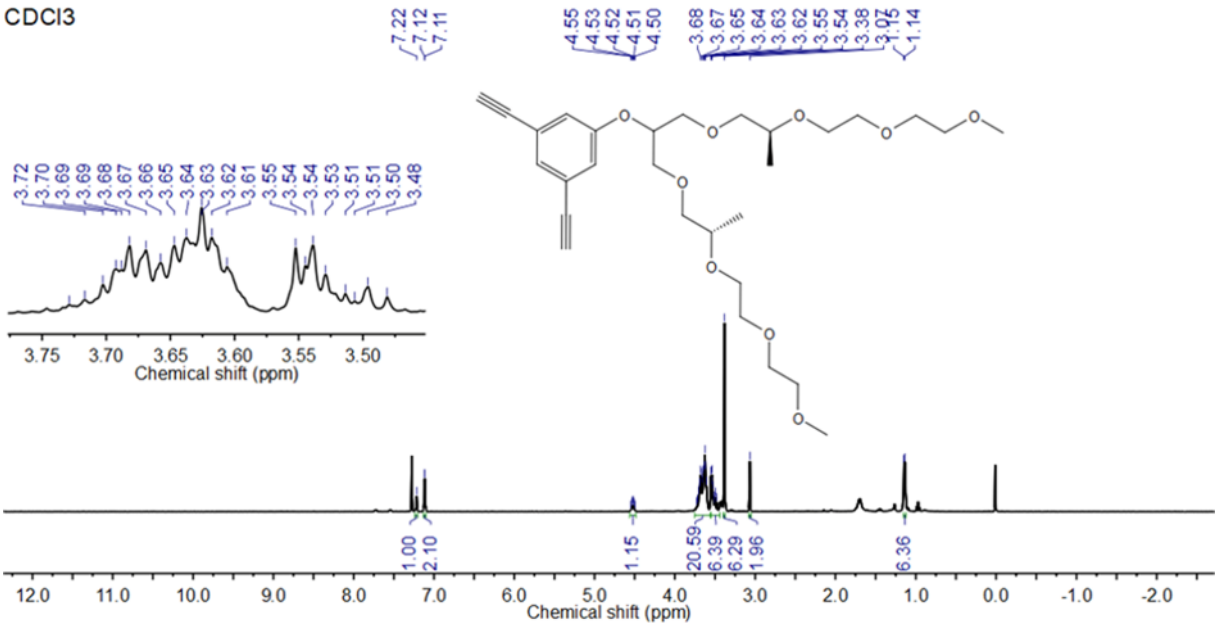

CDCl3
154.15
121.37
114.94
82.69
79.90
79.74
75.70
75.57
75.01
71.96
70.88
70.51
68.66
59.02
17.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift (ppm)

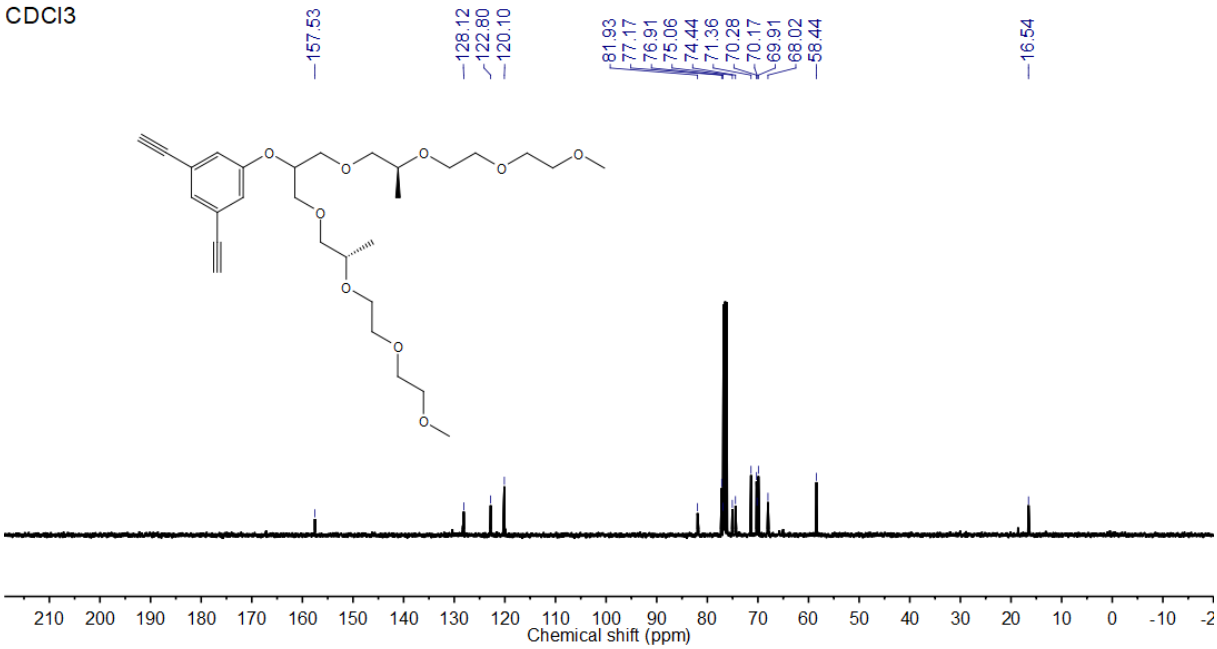

DMSO-d6
7.11
7.05
7.05
4.27
4.10
4.09
4.07
2.55
2.53
2.01
1.99
1.97
1.95
1.94
SO3K
7.11 7.09 7.07 7.05
2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
Chemical shift (ppm)
1.00
2.08
2.16
2.15
2.02
2.24
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
Chemical shift (ppm)

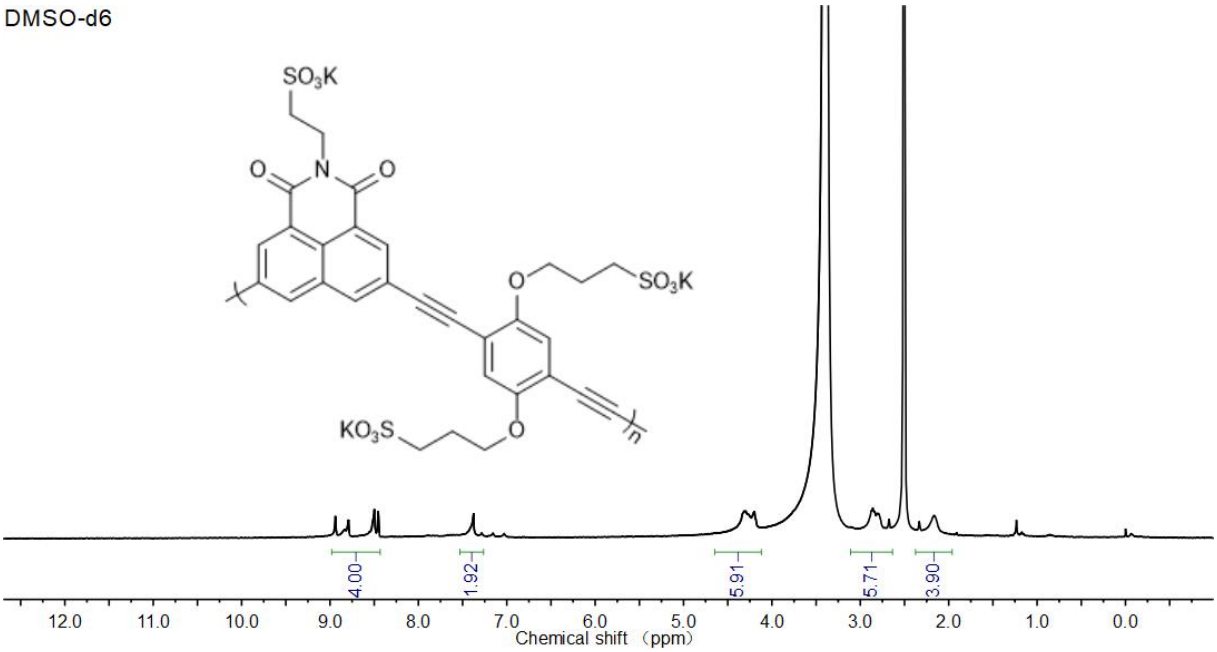

DMSO-d6
158.46
126.76
123.24
118.31
82.23
81.40
67.09
47.62
25.00
O
SO3K
Chemical shift (ppm)


CDCl3
7.21
7.11
7.11
7.20
7.15
7.10
3.74
3.73
3.72
3.70
3.68
3.67
3.67
3.66
3.64
3.64
3.63
3.55
3.54
3.54
3.53
3.80
3.75
3.70
3.65
3.60
3.55
3.50
Chemical shift (ppm)
7.21
7.11
7.11
4.56
4.55
4.53
4.52
4.51
3.74
3.73
3.72
3.70
3.70
3.68
3.67
3.67
3.66
3.64
3.64
3.63
3.55
3.54
3.54
3.53
3.38
3.06
O
1.00
1.93
1.14
24.69
4.20
6.25
1.81
Chemical shift (ppm)

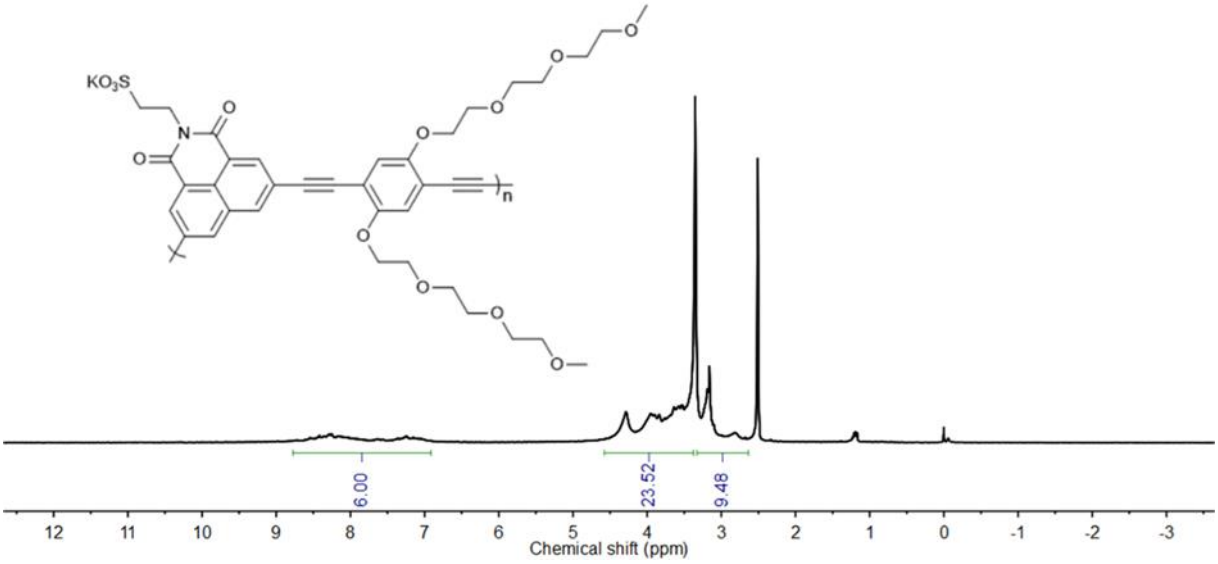

CDCl3
157.45
128.18
122.82
120.15
81.95
77.13
76.97
76.65
71.37
70.57
70.09
70.06
70.00
69.95
58.45
Chemical shift (ppm)


CDCl3
7.22
7.12
7.11
4.55
4.53
4.52
4.51
4.50
3.68
3.67
3.65
3.64
3.63
3.62
3.55
3.54
3.38
1.15
1.14
3.72
3.70
3.69
3.69
3.68
3.67
3.66
3.65
3.64
3.63
3.62
3.61
3.55
3.54
3.54
3.53
3.51
3.51
3.50
3.48
Chemical shift (ppm)
1.00
2.10
1.15
20.59
6.39
6.29
1.96
6.36
Chemical shift (ppm)

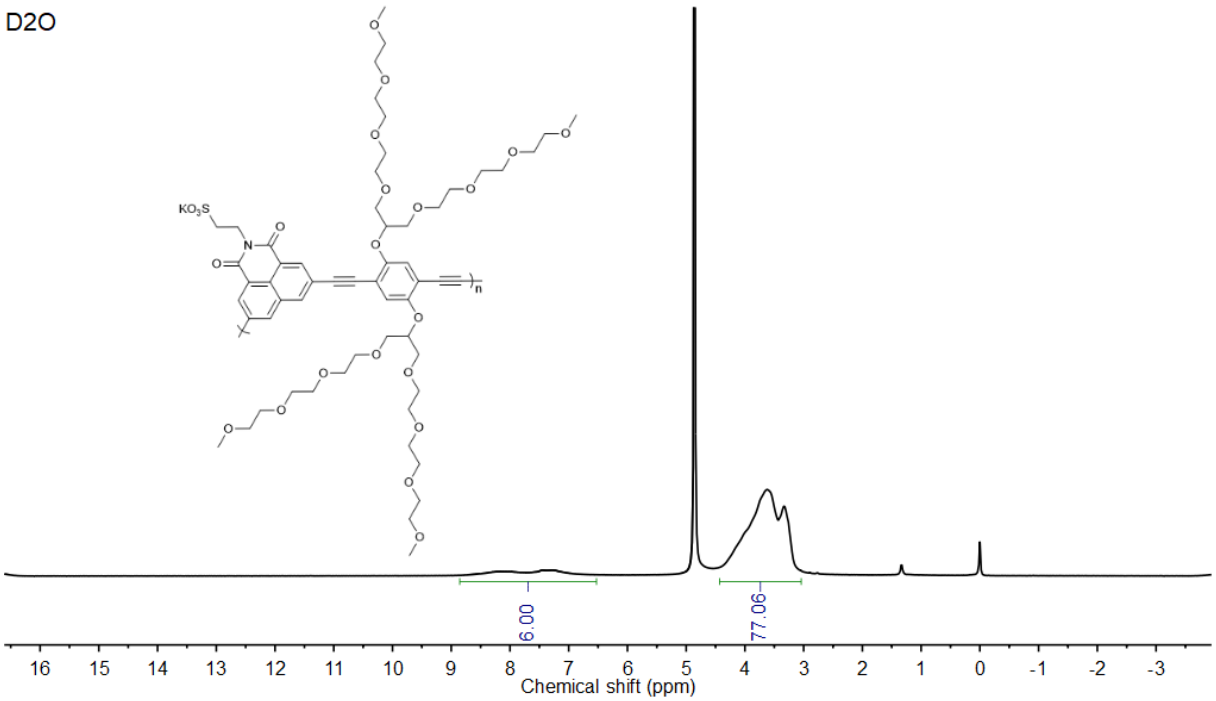

CDCl3
157.53
128.12
122.80
120.10
81.93
77.17
76.91
75.06
74.44
71.36
70.28
70.17
69.91
68.02
58.44
16.54
Chemical shift (ppm)


DMSO-d6
SO3K
KO3S
4.00
1.92
5.91
5.71
3.90
Chemical shift (ppm)

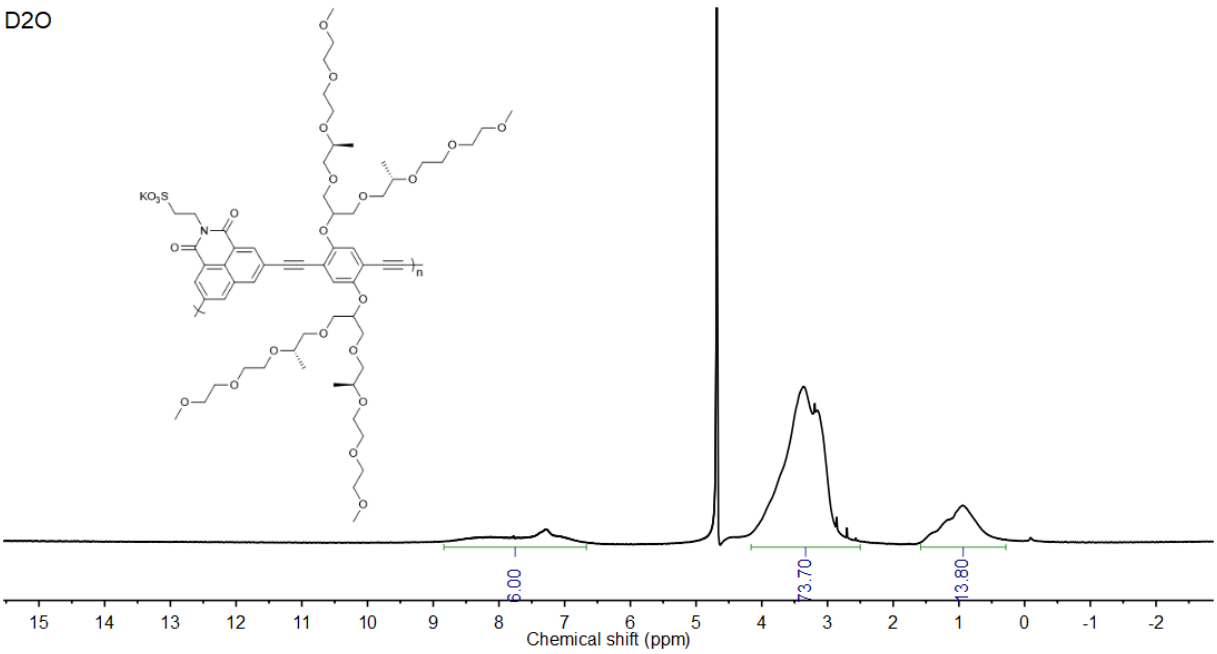
DMSO-d6


KO3S
6.00
23.52
9.48
Chemical shift (ppm)

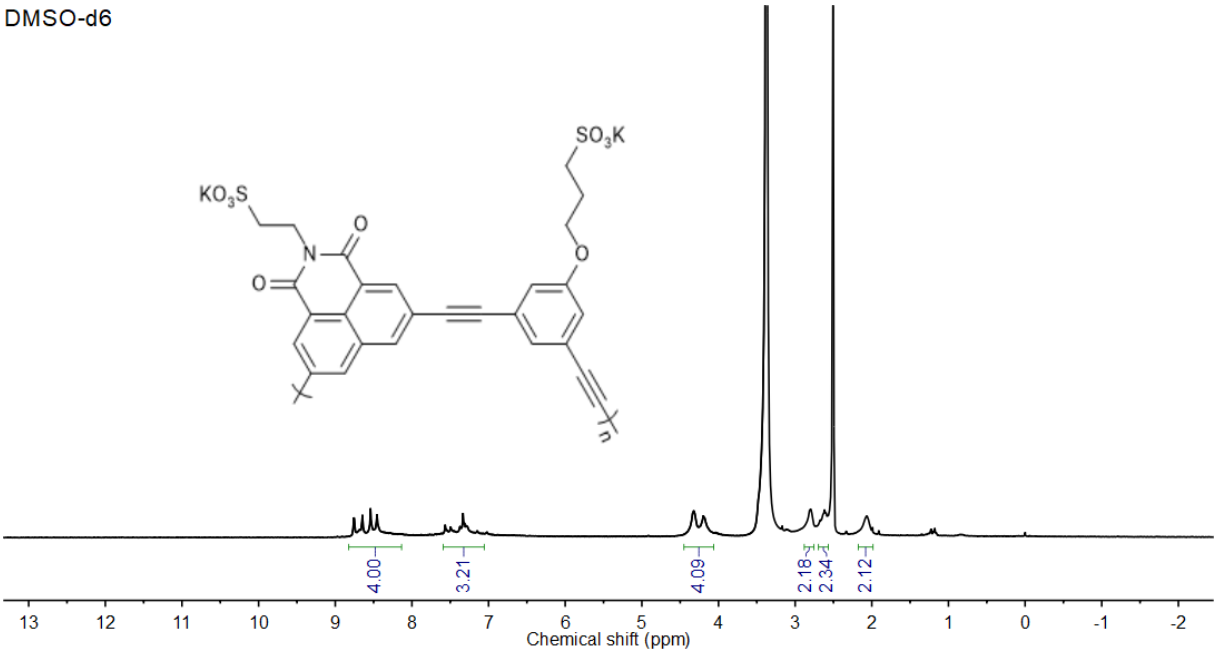
D2O

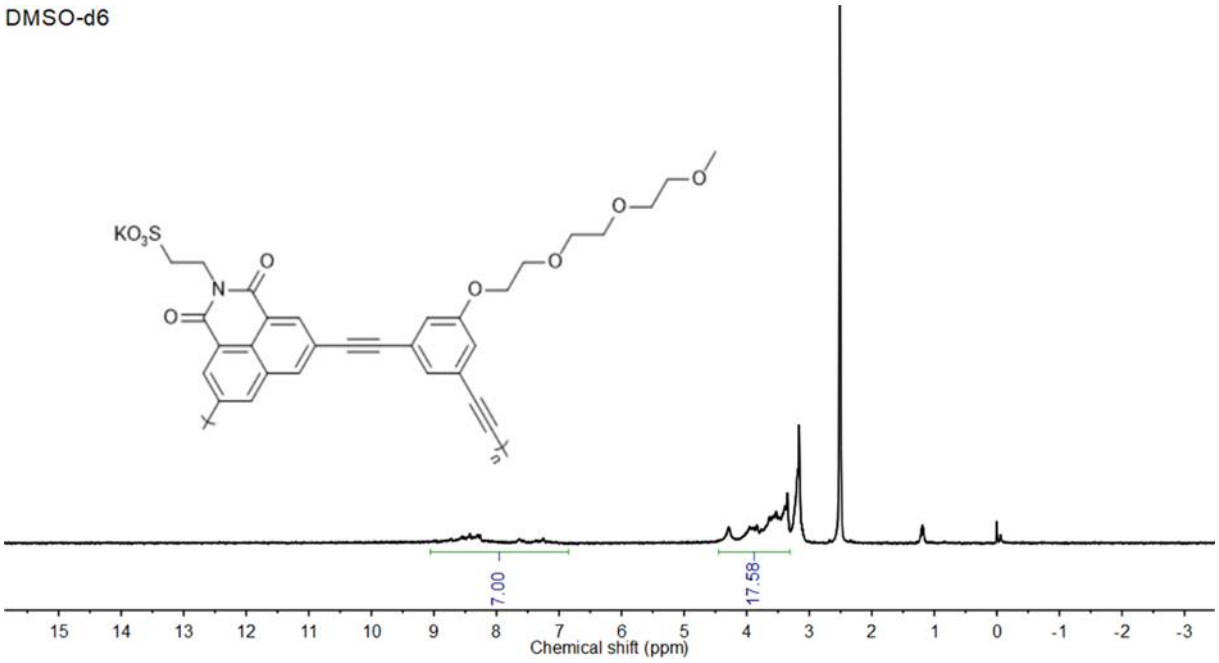

KO3S
6.00
77.06
Chemical shift (ppm)

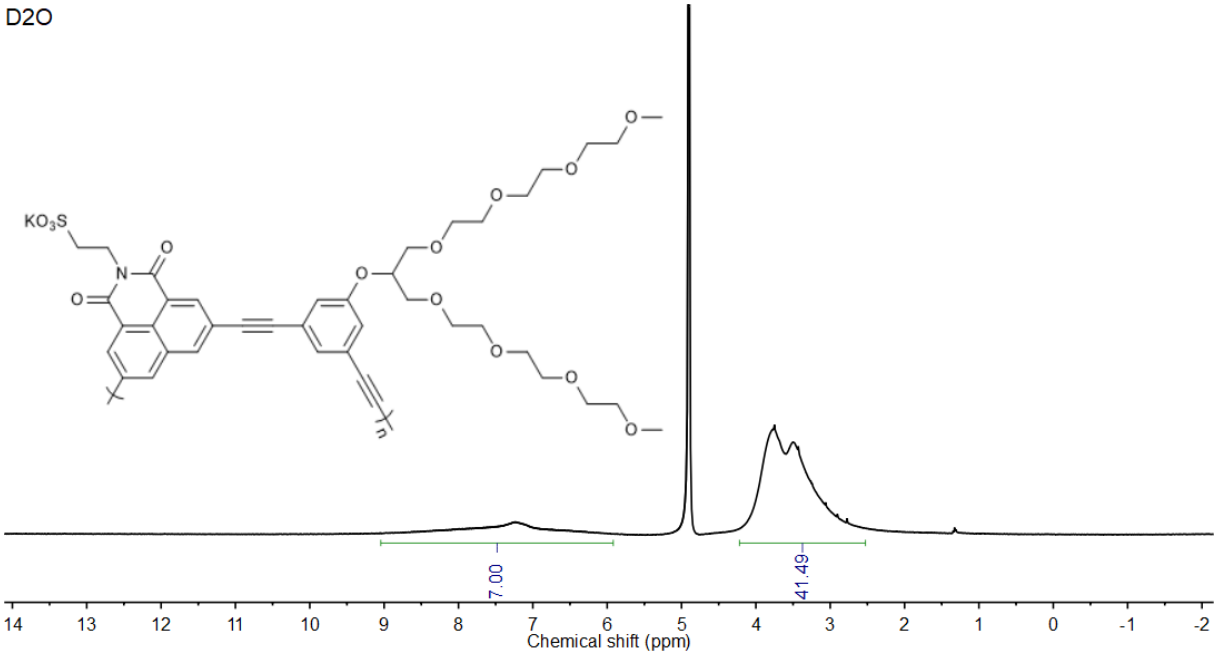
D2O

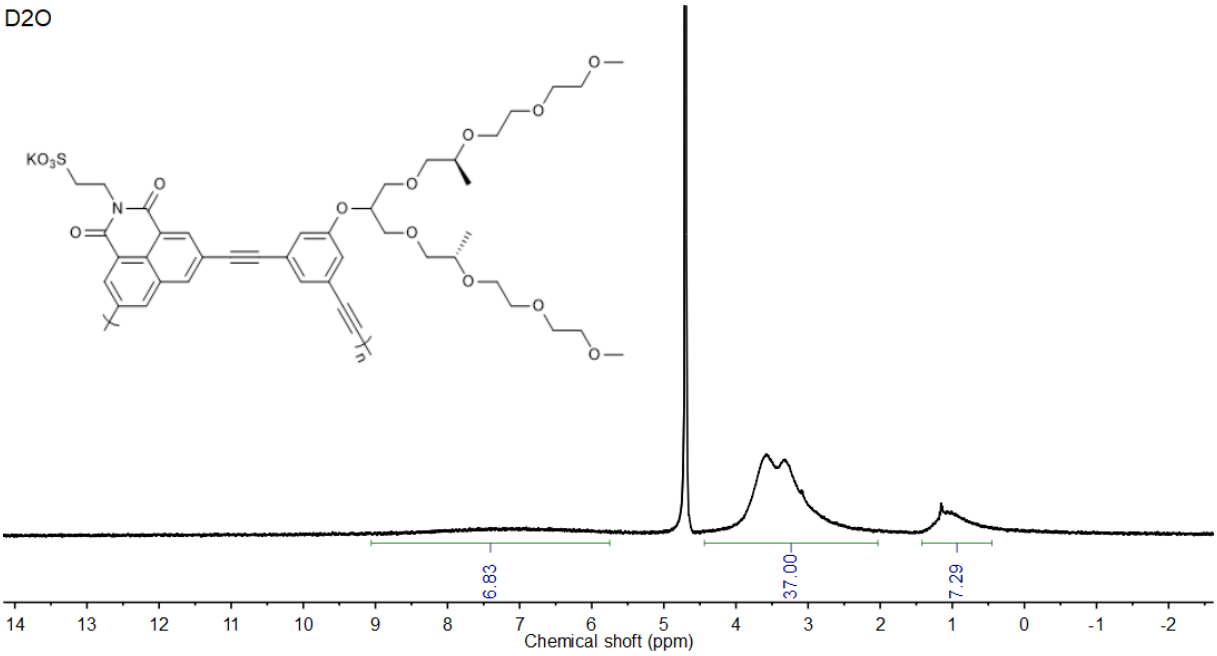

6.00
73.70
13.80
Chemical shift (ppm)

DMSO-d6

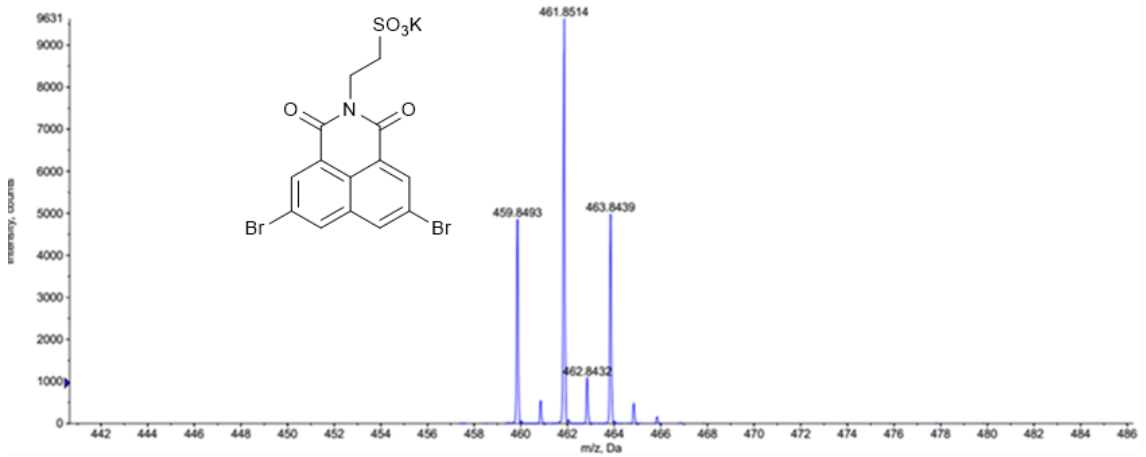

4.00
3.21
4.09
2.18
2.34
2.12
Chemical shift (ppm)

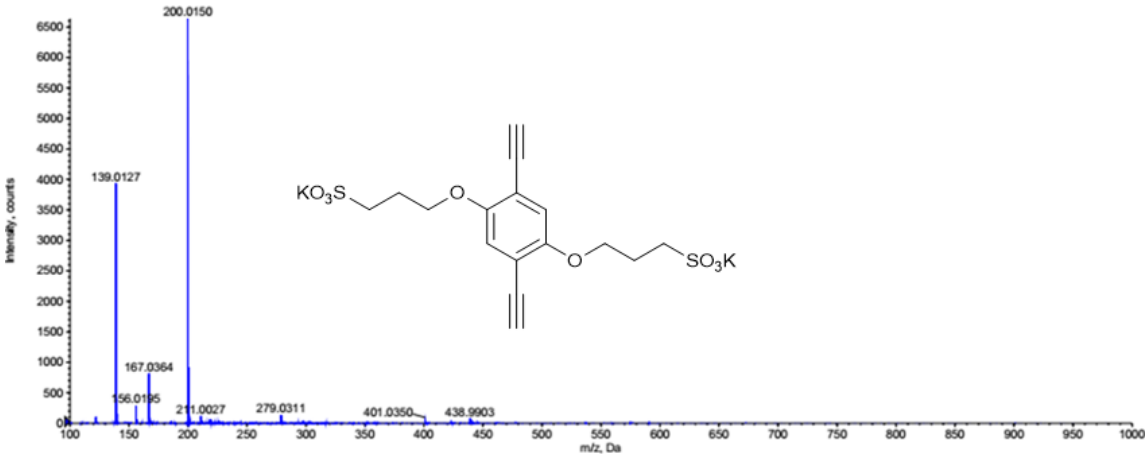

DMSO-d6
KO3S
N
O
7.00
17.58
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
Chemical shift (ppm)

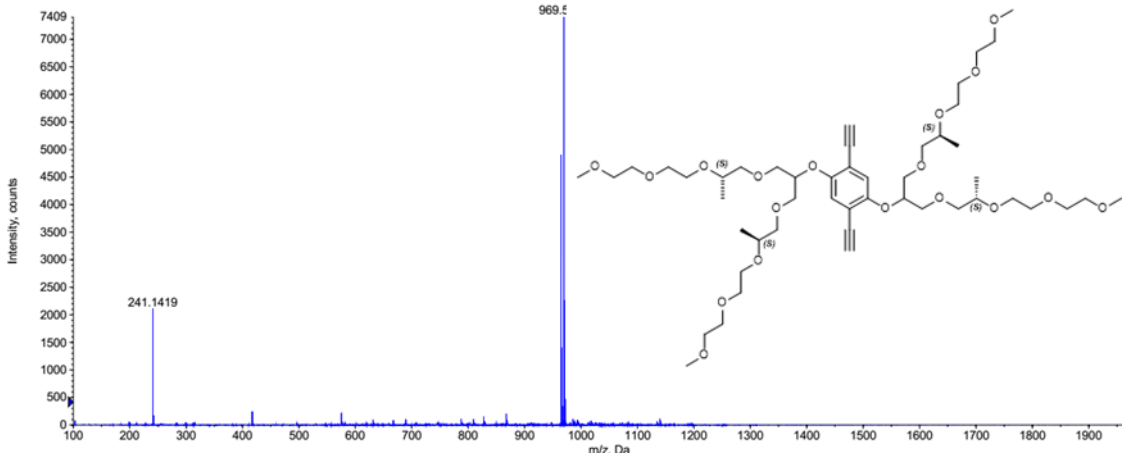

D2O
KO3S
N
O
7.00
41.49
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
Chemical shift (ppm)

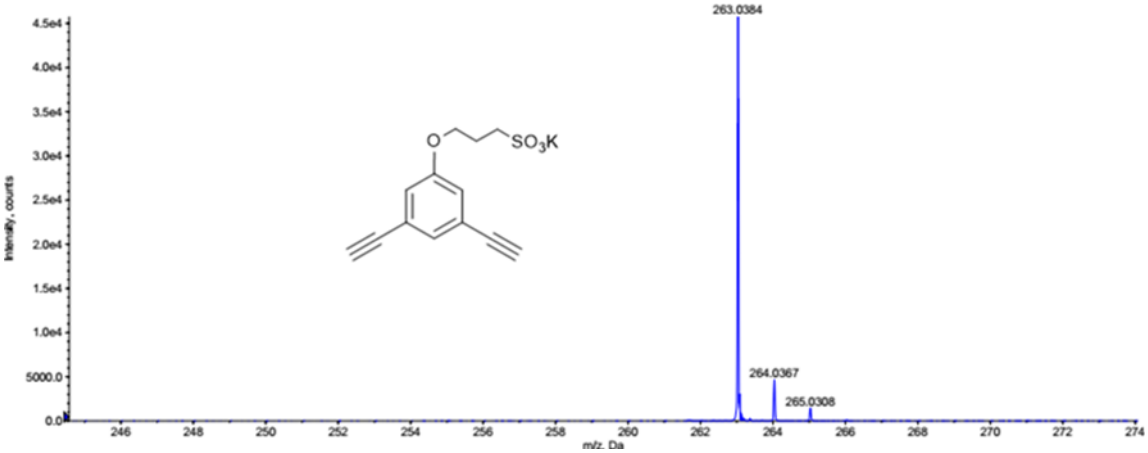


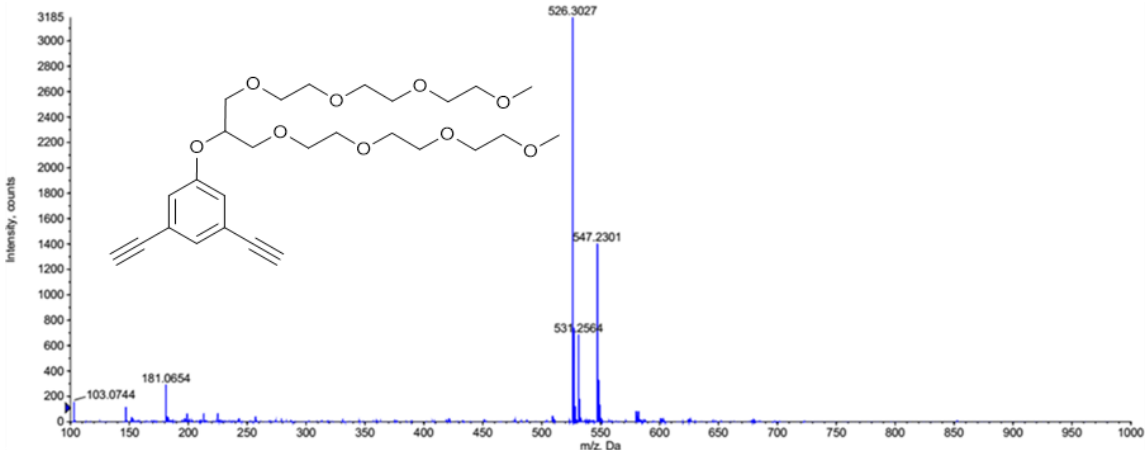
4. Mass spectra

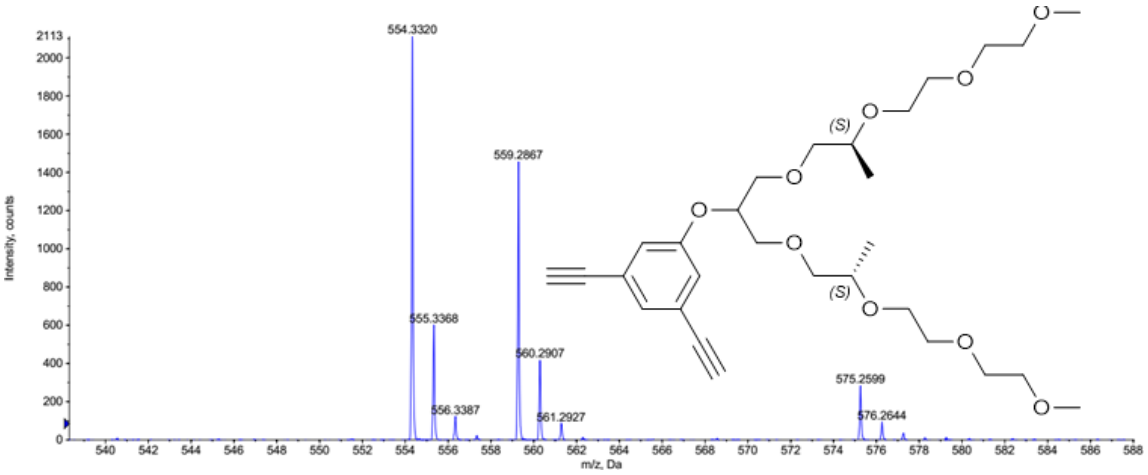



200.0150
139.0127
167.0364
156.0195
211.0027
279.0311
401.0350
438.9903
Intensity, counts
m/z, Da
KO3S
O
O
SO3K


969.5
241.1419
Intensity, counts
m/z, Da
(S)


263.0384
264.0367
265.0308
Intensity, counts
m/z, Da
O
SO3K





References

1 J. Y. Xue, W. Nakanishi, D. Tanimoto, D. Hara, Y. Nakamura and H. Isobe, *Tetrahedron Lett.*, 2013, **54**, 4963-4965.

2 C.-H. Chiang, D. Pangeni and E. E. Nesterov, *Macromolecules*, 2017, **50**, 6961-6966.

3 B. Koo and T. M. Swager, *Macromol. Rapid Commun.*, 2017, 1521-3927.

4 M. Peterca, V. Percec, M. R. Imam, P. Leowanawat, K. Morimitsu and P. A. Heiney, *J. Am. Chem. Soc.*, 2008, **130**, 14840-14852.

5 F. Zhou, S. Li, T. R. Cook, Z. He and P. J. Stang, *Organometallics*, 2014, **33**, 7019-7022.

6 K. Ghosh, H.-B. Yang, B. H. Northrop, M. M. Lyndon, Y.-R. Zheng, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc.*, 2008, **130**, 5320-5334.

7 S. Chen, S. Zhang, C. Bao, C. Wang, Q. Lin and L. Zhu, *Chem. Commun.*, 2016, **52**, 13132-13135.

8 I.-B. Kim, R. Phillips and U. H. F. Bunz, *Macromolecules*, 2007, **40**, 5290-5293.

9 E. Amouyal, A. Homsi, J.-C. Chambron and J.-P. Sauvage, *J. Chem. Soc. Dalton Trans.*, 1990, 1841-1845.

10 E. Ji, D. G. Whitten and K. S. Schanze, *Langmuir*, 2011, **27**, 1565-1568.

11 C. Tan, M. R. Pinto, M. E. Kose, I. Ghiviriga and K. S. Schanze, *Adv. Mater.*, 2004, **16**, 1208-1212.

12 T. Cosgrove and P. C. Griffiths, *Polymer*, 1995, **36**, 3335-3342.

13 T. Ikai, S. Awata, T. Kudo, R. Ishidate, K. Maeda and S. Kanoh, *Polym. Chem.*, 2017, **8**, 4190-4198.

14 T. Ikai, S. Awata and K.-i. Shinohara, *Polym. Chem.*, 2018, **9**, 1541-1546.