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Electronic Supplementary Information

Supramolecular polymerization and cyclization of dioxynaphthalene motif bridged bifunctional UPys: minor variations in molecular skeleton and drastic differences in self-assembly

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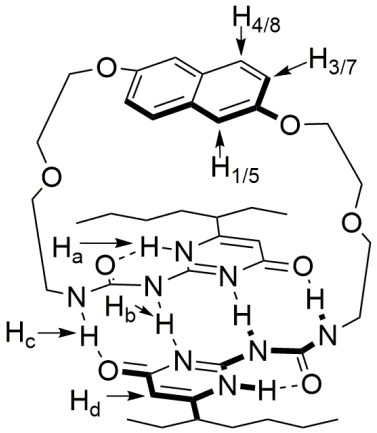
1. Materials and methods

All reactions were carried out under normal pressure unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. All yields were given as isolated yields. **DNP2**[S1] and **L1**[S2] and blue-box[S3] were prepared according to literature procedure. NMR spectra were recorded on a Bruker AVANCE III 300 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, where $CDCl_3$, CD_3CN and DMSO-d_6 were dried using neutral aluminum oxide. NOESY experiments were performed on a Bruker AVANCE III 400 MHz spectrometer. DOSY experiments were performed on a Bruker AVANCE III 600 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on LCMS2020. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass. Scanning electron microscopy (SEM) images were recorded on a JSM-6360LA. For theory calculation, the Minnesota density functional M06-2X[S4] provides a computational approach suitable for the study of the systems including both H-bonding and stacking.[S5] In order to have a reliable description of both H-bonding and stacking interactions the M06-2X functional and the valence triple zeta basis set, augmented with both polarization and diffuse functions (6-311+G(d.p))[S6] were used in the calculations. The GAUSSIAN 09 system of DFT programs[S7] was used for all computations.

2. NOESY of DNP1 and DNP2



Scheme S1 Chemical structure of **DNP1** in its cyclic monomer form

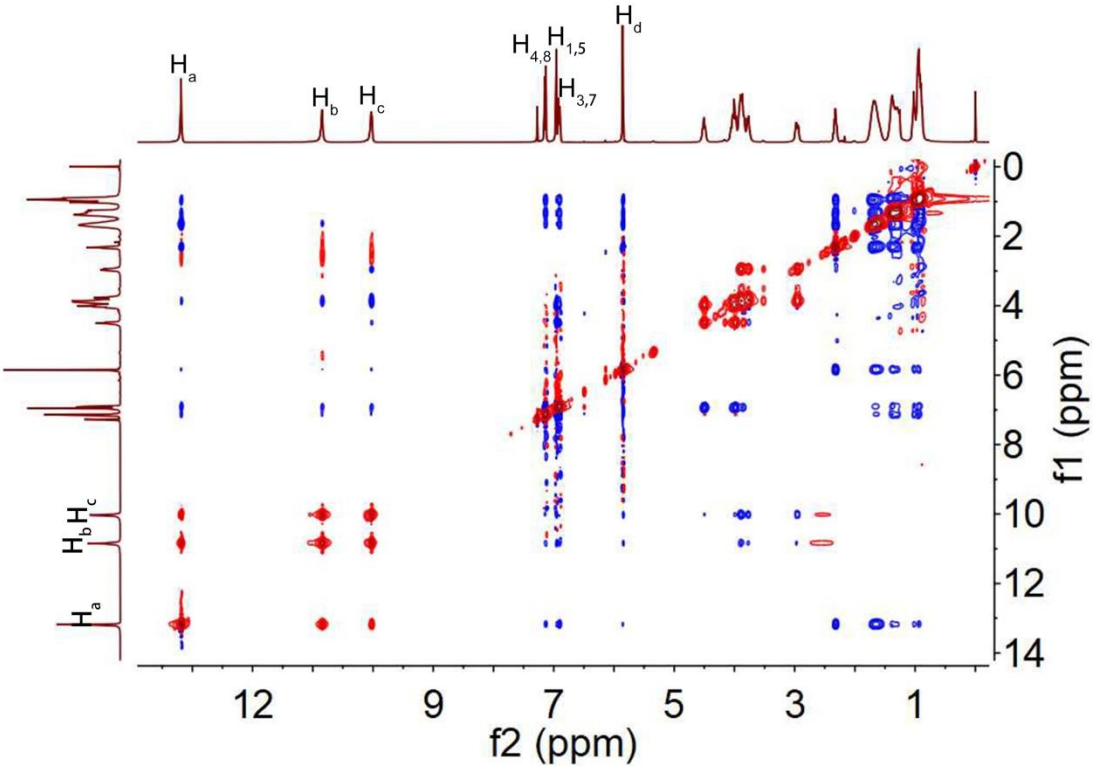
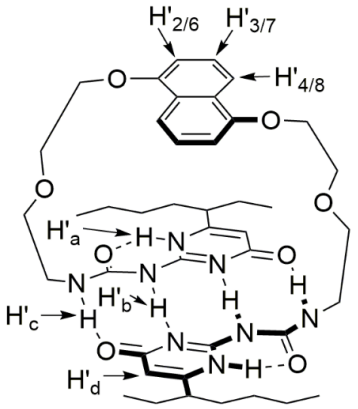


Figure. S1 NOESY NMR spectrum (400 MHz, $CDCl_3$, 298 K, 128 mM) of **DNP1**.



Scheme S2 Chemical structure of **DNP2** in its cyclic monomer form

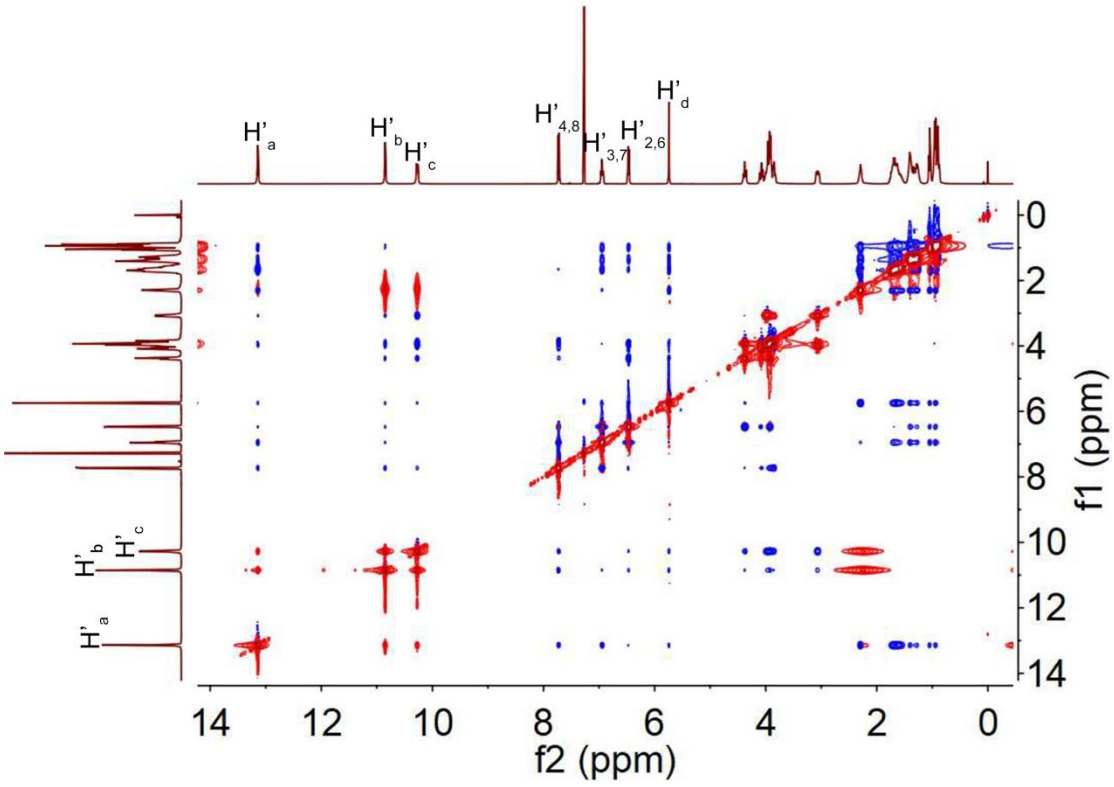


Figure. S2 NOESY NMR spectrum (400 MHz, $CDCl_3$, 298 K, 128 mM) of **DNP2**.

3. Analysis of CPC value of DNP1 from ^{1}H NMR

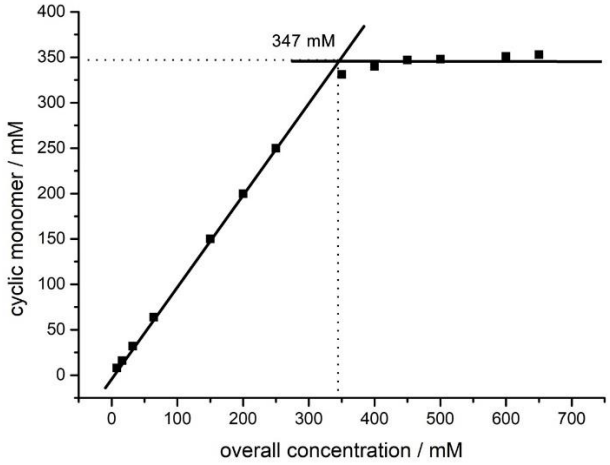


Figure. S3 Concentration of cyclic oligomers versus total concentration of **DNP1** upon concentration increasing. H_b in ^{1}H NMR (300 MHz, $CDCl_3$) was used for calculation.

4. Variable-temperature ^{1}H NMR spectra of DNP1 and DNP2

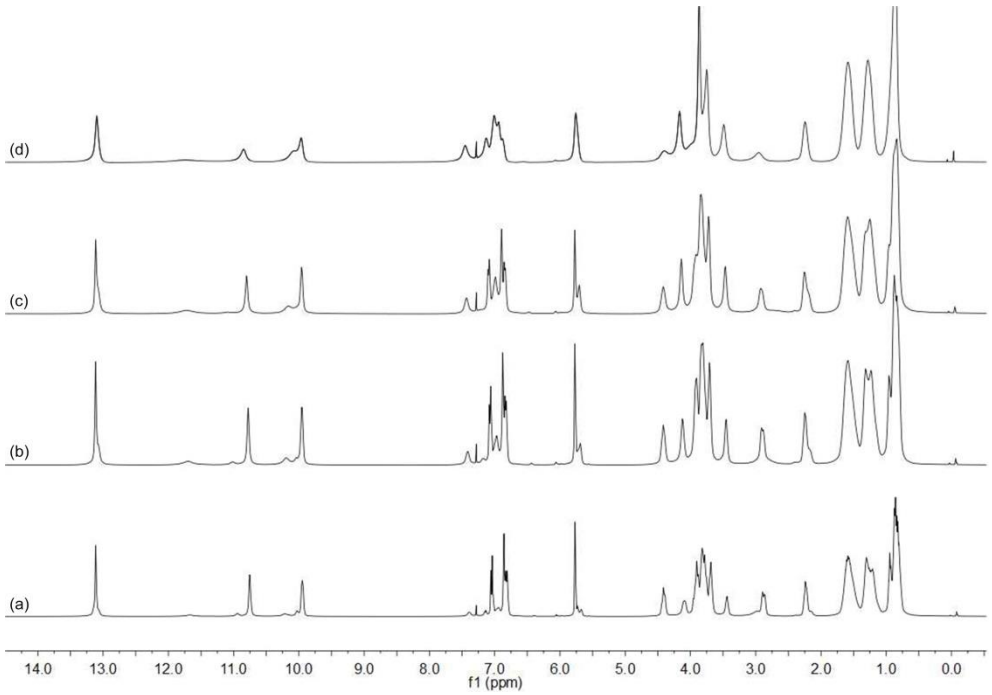


Figure. S4 Partial ^{1}H NMR spectrum(400 MHz, $CDCl_3$, 350 mM) of **DNP1** at different temperature: (a) 298, (b) 308, (c) 318, (d) 333 K.

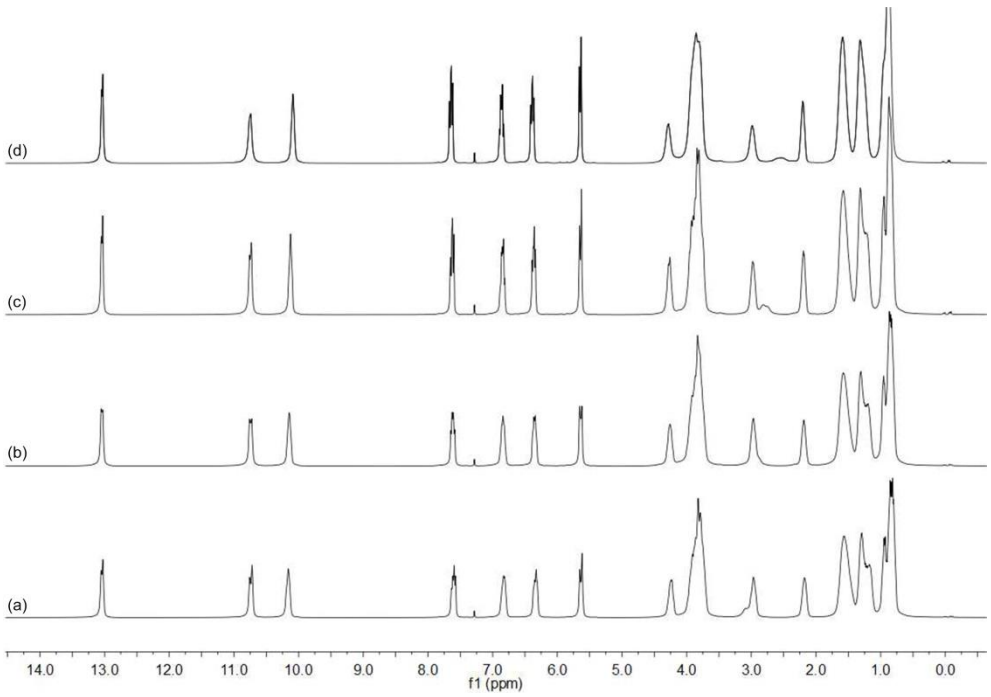


Figure. S5 Partial ^{1}H NMR spectrum(400 MHz, $CDCl_3$, 350 mM) of **DNP2** at different temperature: (a) 298, (b) 308, (c) 318, (d) 333 K.

5. Study of DNP1 in mixed $CDCl_3$/DMSO-d_6 solvent

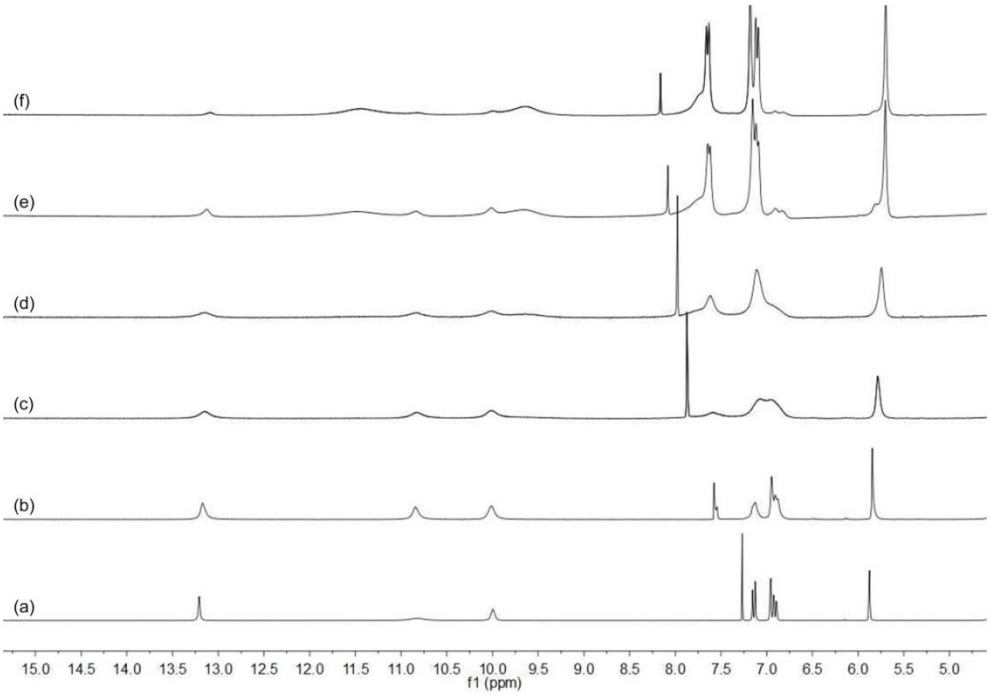


Figure. S6 ^{1}H NMR spectra (300 MHz, 298 K) of **DNP1** in mixtures of $CDCl_3$/DMSO-d_6 (v/v). From bottom to top: χ_{DMSO} = (a) 0, (b) 0.15, (c) 0.30, (d) 0.40, (e) 0.50, (f) 0.60.

6. Host-guest behavior of DNP1 and blue-box in mixed solvents

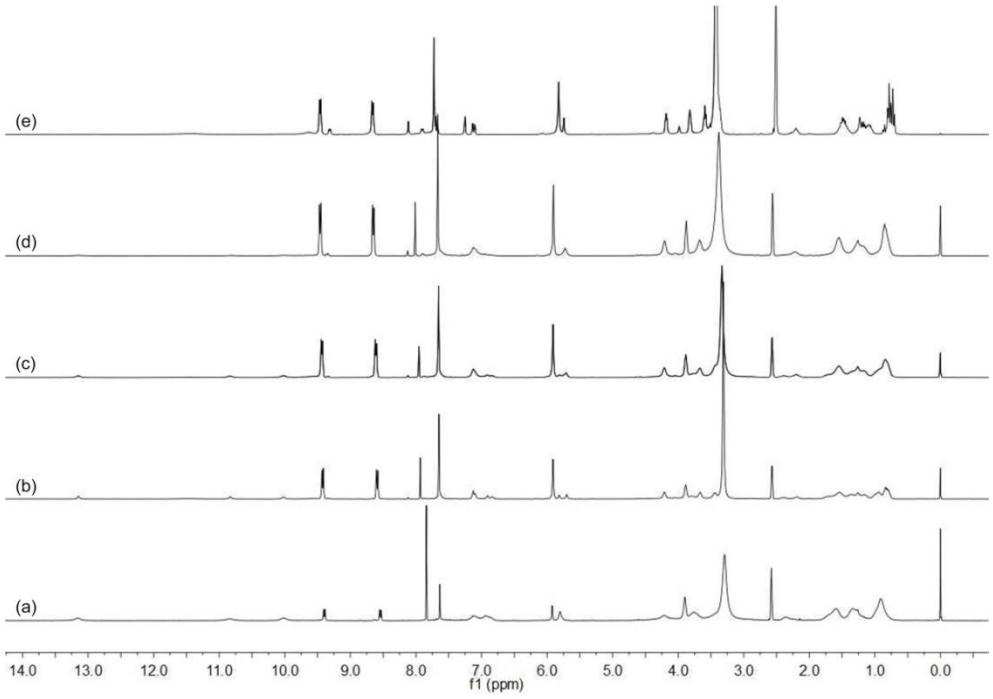


Figure. S7 ^{1}H NMR spectra (300 MHz, 298 K) of **DNP1** and blue-box in mixtures of $CDCl_3$/DMSO-d_6 (v/v). From bottom to top: χ_{DMSO} = (a) 0.30, (b) 0.37, (c) 0.40, (d) 0.45, (e) 1.00.

7. Host-guest behavior of DNP2 and blue-box in mixed solvents

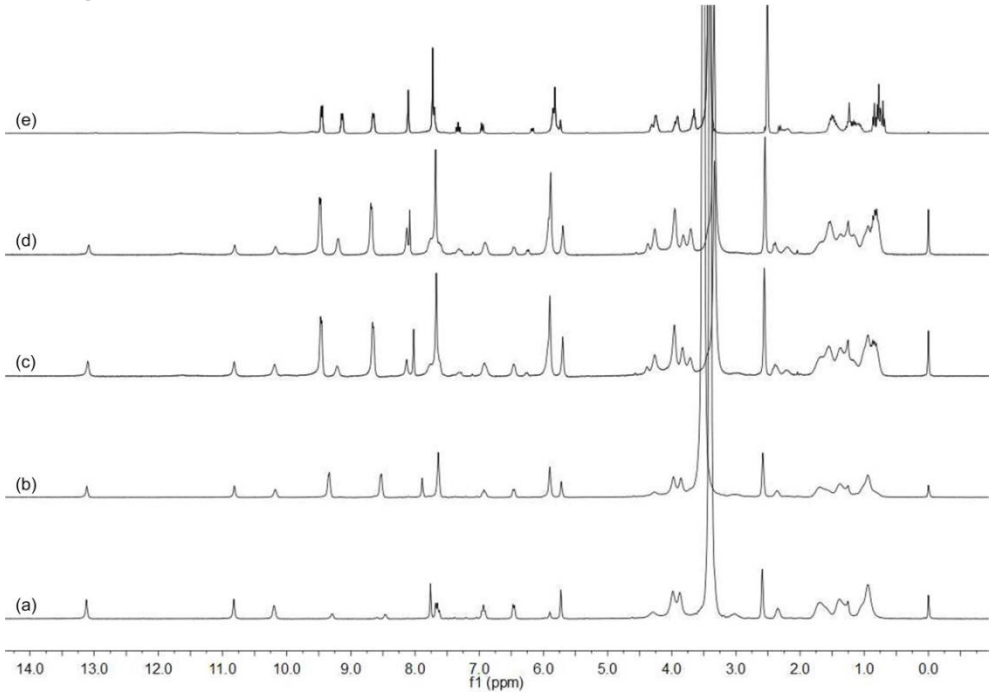
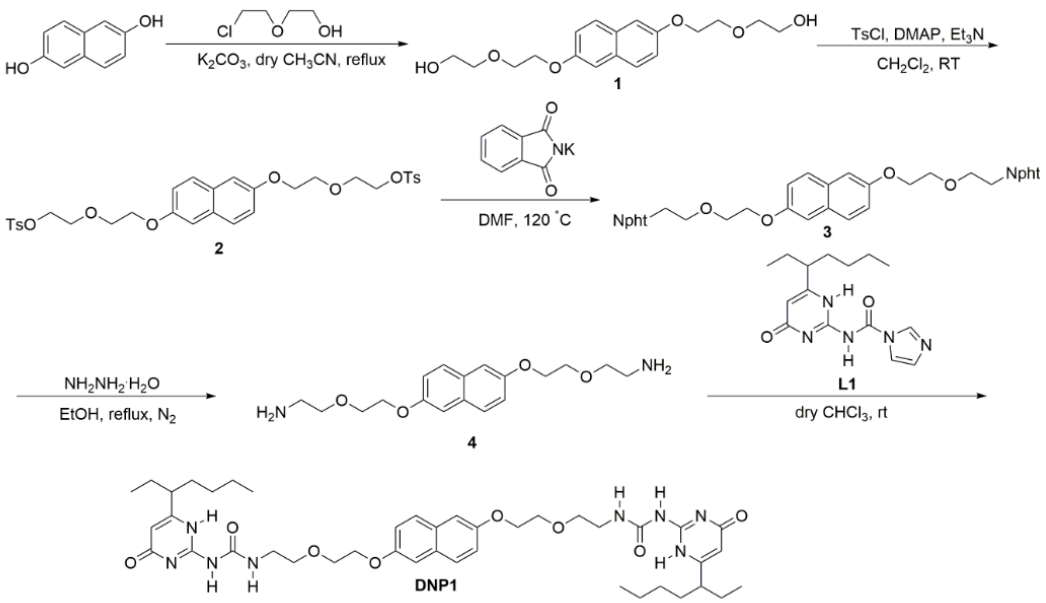


Figure. S8 ^{1}H NMR spectra (300 MHz, 298 K) of **DNP2** and blue-box in mixtures of $CDCl_3$/DMSO-d_6 (v/v). From bottom to top: χ_{DMSO} = (a) 0.30, (b) 0.40, (c) 0.45, (d) 0.50, (e) 1.00.

8. Synthetic procedures and characterization of DNP1



Scheme S3 Synthesis of **DNP1**

8.1 Synthesis of compound 1:

To a suspension of 2,6-dihydroxynaphtalene (6.83 g, 42.6 mmol) and dry K_2CO_3 (58.87 g, 426.0 mmol) in anhydrous CH_3CN (300 mL) was added 2-(2-chloroethoxy)ethanol (15.94 g, 127.9 mmol) and the mixture was then refluxed for 4 d under N_2 atmosphere. Then the resulting mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in DCM (200 mL) and the solution was washed with brine (150 mL × 3) and dried over anhydrous $MgSO_4$. After the solvent was evaporated, the residue was purified by recrystallization in ethyl acetate to obtain **1** as a white solid (11.00 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.63 (d, *J* = 8.8 Hz, 2H, naphthalene-*H*), 7.16 (dd, *J* = 8.8 Hz, *J* = 2.5 Hz, 2H, naphthalene-*H*), 7.11 (d, *J* = 2.5 Hz, 2H, naphthalene-*H*), 4.29-4.18 (m, 4H, OCH_2), 3.98-3.88 (m, 4H, OCH_2), 3.83-3.76 (m, 4H, OCH_2), 3.74-3.64 (m, 4H, OCH_2), 1.96 (s, 2H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 155.2, 129.8, 128.3, 119.2, 107.2, 72.6, 69.7, 67.5, 61.8. ESI-MS: *m/z* calcd for $[M + Na]^+$ = 359.15, found = 359.10; HR-ESI-MS ($C_{18}H_{24}O_6$): *m/z* calcd for $[M + Na]^+$ = 359.1465, found = 359.1464.

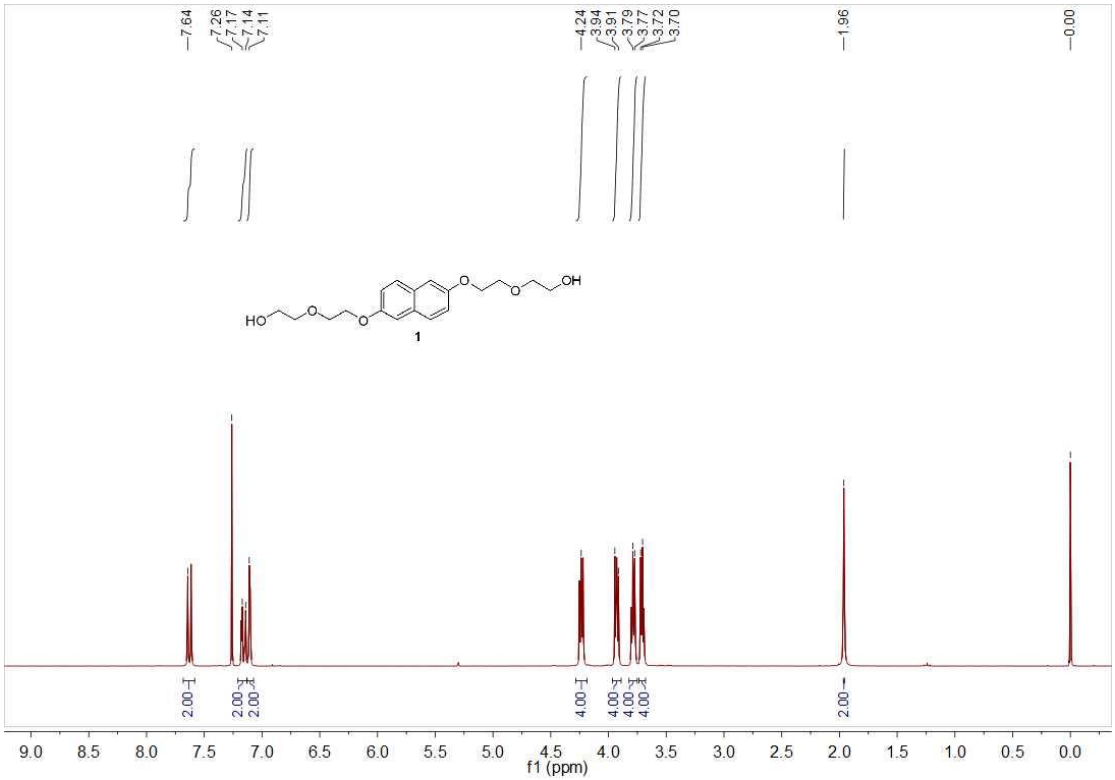


Figure. S9 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **1**

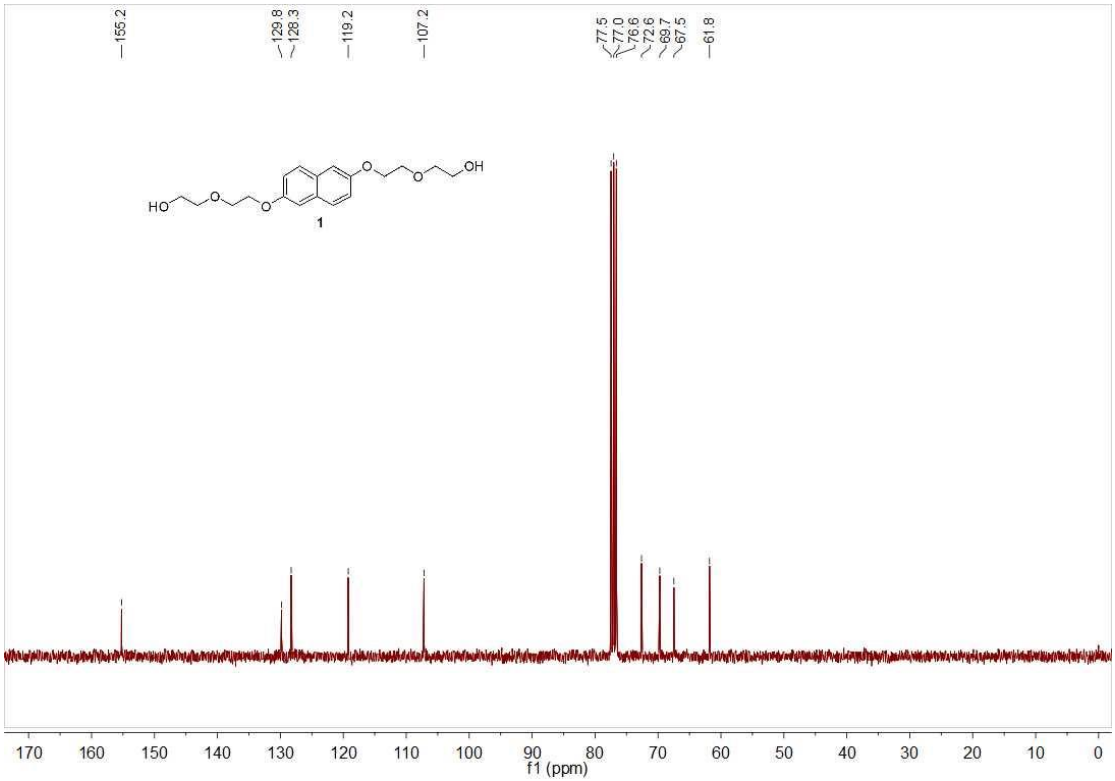


Figure. S10 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **1**

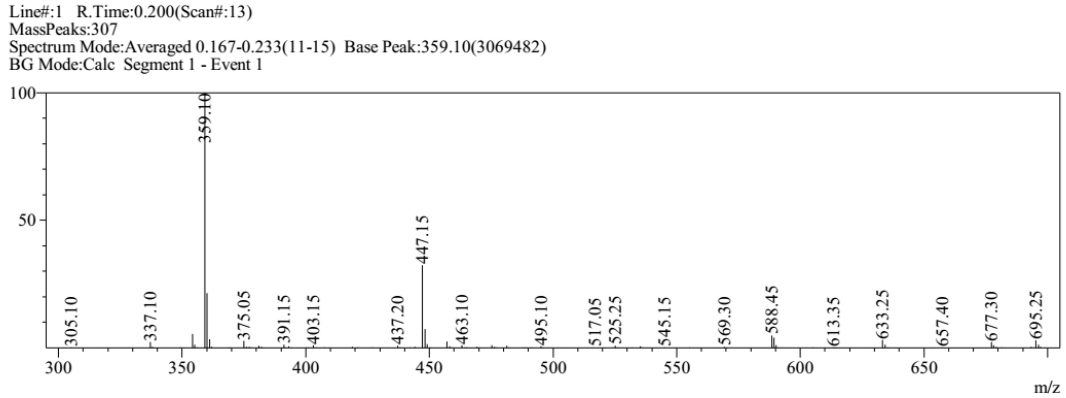


Figure. S11 Electrospray ionization mass spectrum of **1**

8.2 Synthesis of compound 2:

To a solution of compound **1** (4.20 g, 12.5 mmol) and tosyl chloride (5.60 g, 29.3 mmol) in DCM (200 mL) at 0 °C under N_2 atmosphere was added triethylamine (3.79 g, 37.5 mmol) through a dropping funnel over a period of 10 min. The mixture was allowed to warm slowly to room temperature and stirred for 12 h, and then washed with 1N HCl (50 mL × 3), saturated aqueous $NaHCO_3$ (150 mL × 3) and brine (150 mL × 2), dried over anhydrous $MgSO_4$. The resulting mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by precipitation in hexane to obtain **2** as a white solid (7.32 g, 91%). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.78 (d, *J* = 8.3 Hz, 4H, Ts-*H*), 7.72 (d, *J* = 8.9 Hz, 2H, naphthalene-*H*), 7.42 (d, *J* = 8.0 Hz, 4H, Ts-*H*), 7.26 (d, *J* = 2.5 Hz, 2H, naphthalene-*H*), 7.12 (dd, *J* = 8.9 Hz, *J* = 2.5 Hz, 2H, naphthalene-*H*), 4.21-4.04 (m, 8H, OCH_2), 3.78-3.60 (m, 8H, OCH_2), 2.35 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 155.2, 145.3, 132.8, 130.6, 129.9, 128.6, 128.1, 119.4, 107.5, 70.5, 69.3, 68.5, 67.5, 21.5. ESI-MS: *m/z* calcd for $[M + Na]^+$ = 667.16, found = 667.20; HR-ESI-MS ($C_{32}H_{36}O_{10}S_2$): *m/z* calcd for $[M + Na]^+$ = 667.1642, found = 667.1637.

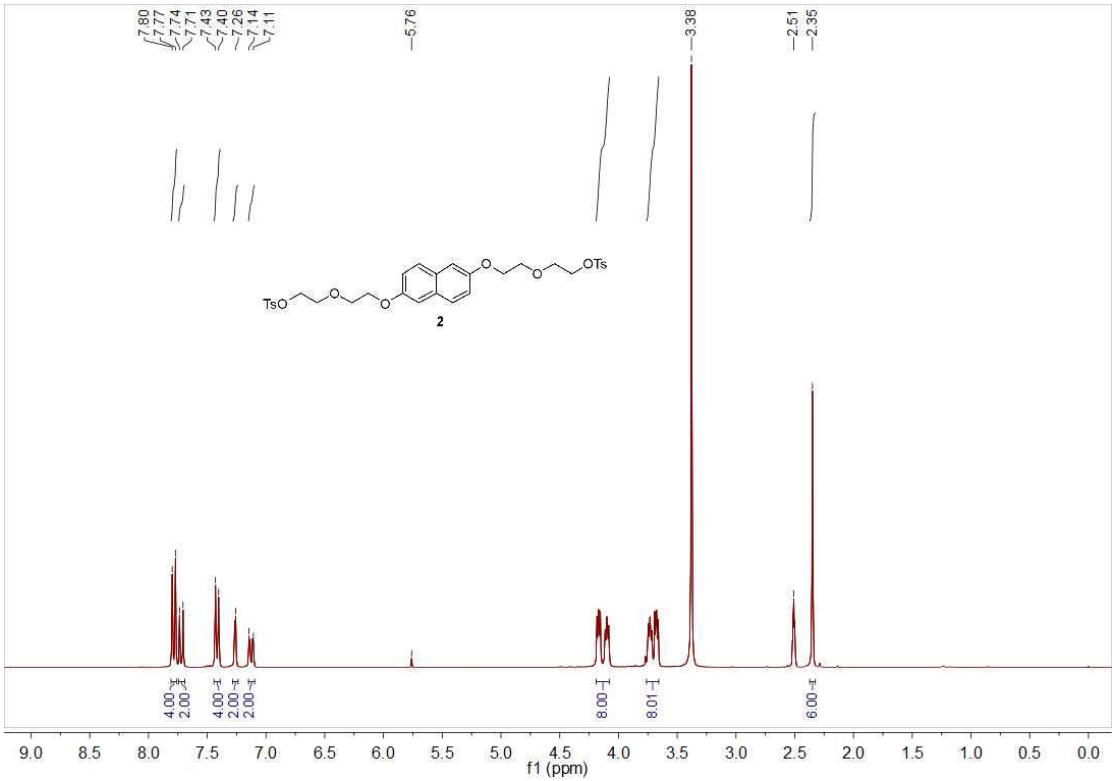


Figure. S12 ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **2**

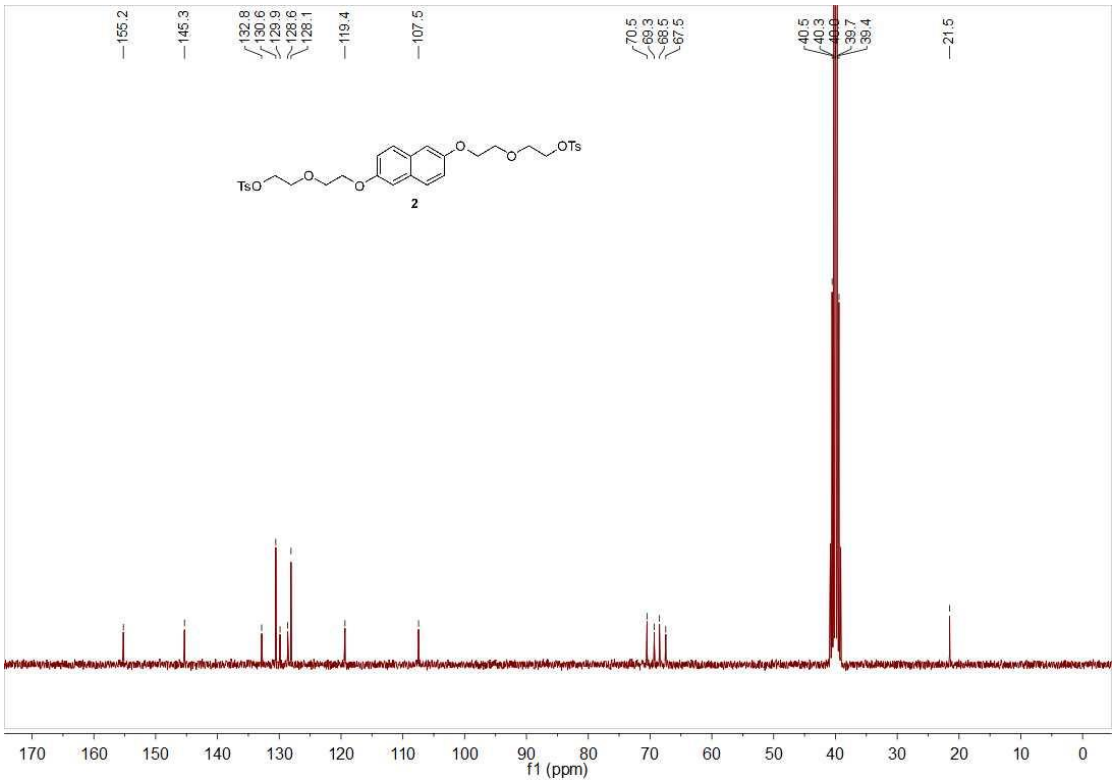


Figure. S13 ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **2**

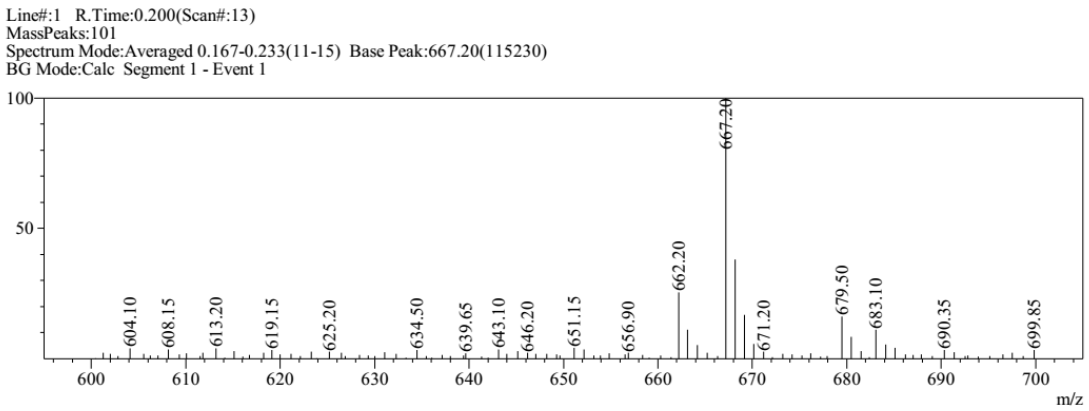


Figure. S14 Electrospray ionization mass spectrum of **2**

8.3 Synthesis of compound 3:

To a solution of compound **2** (3.50 g, 5.4 mmol) in DMF (100 mL) was added potassium phthalimide (3.02 g, 16.3 mmol) at room temperature under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 12 h and then poured into 200 mL of water. The resulting mixture was extracted with DCM (200 mL × 3) and then washed with 1N NaOH aqueous solution(200 mL × 3), the combined extracts was washed with brine (200 mL × 3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The compound **3** was afforded as a white solid (2.18 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.83-7.74 (m, 4H, phthlimide-*H*), 7.69-7.61 (m, 4H, phthlimide-*H*), 7.52 (d, *J* = 8.8 Hz, 2H, naphthalene-*H*), 7.08-6.97 (m, 4H, naphthalene-*H*), 4.18-4.11 (m, 4H, OC*H*$_2$), 3.98-3.82 (m, 12H, OC*H*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 168.3, 155.2, 133.9, 132.1, 129.7, 128.1, 123.2, 119.1, 107.0, 69.1, 68.1, 67.5, 37.3. ESI-MS: *m/z* calcd for $[M + Na]^+$ = 617.19, found = 617.20; HR-ESI-MS ($C_{34}H_{30}N_2O_8$): *m/z* calcd for $[M + Na]^+$ = 617.1894, found = 617.1890.

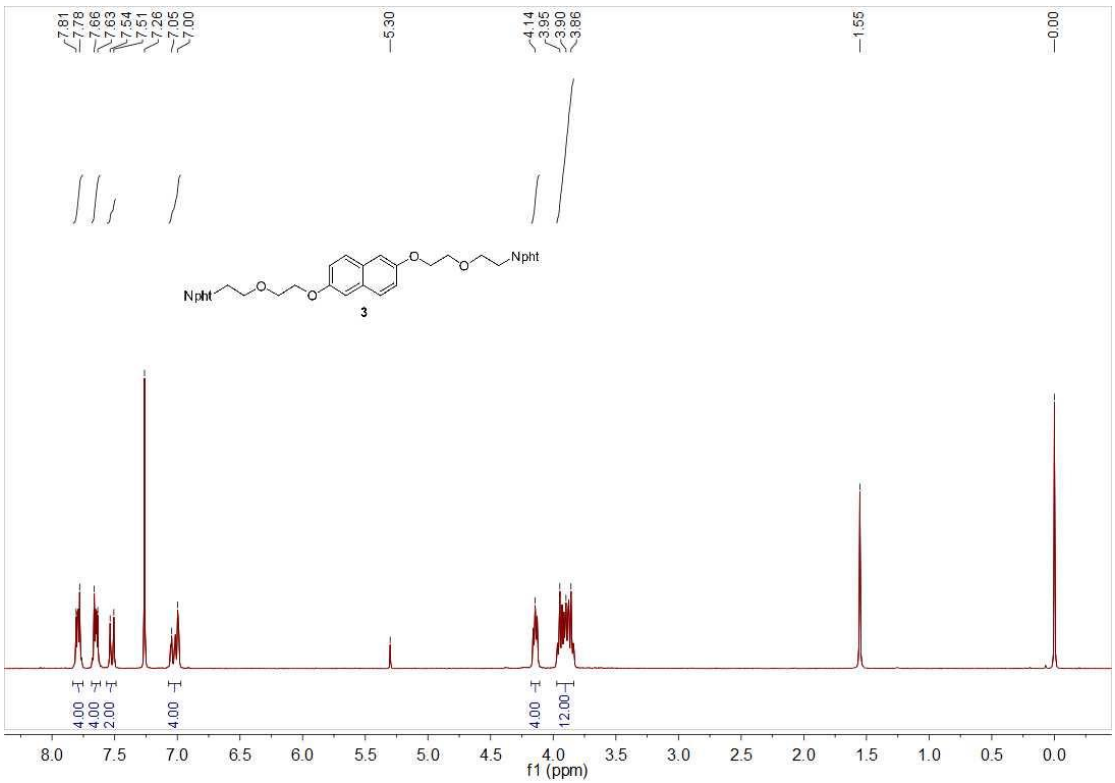


Figure. S15 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3**

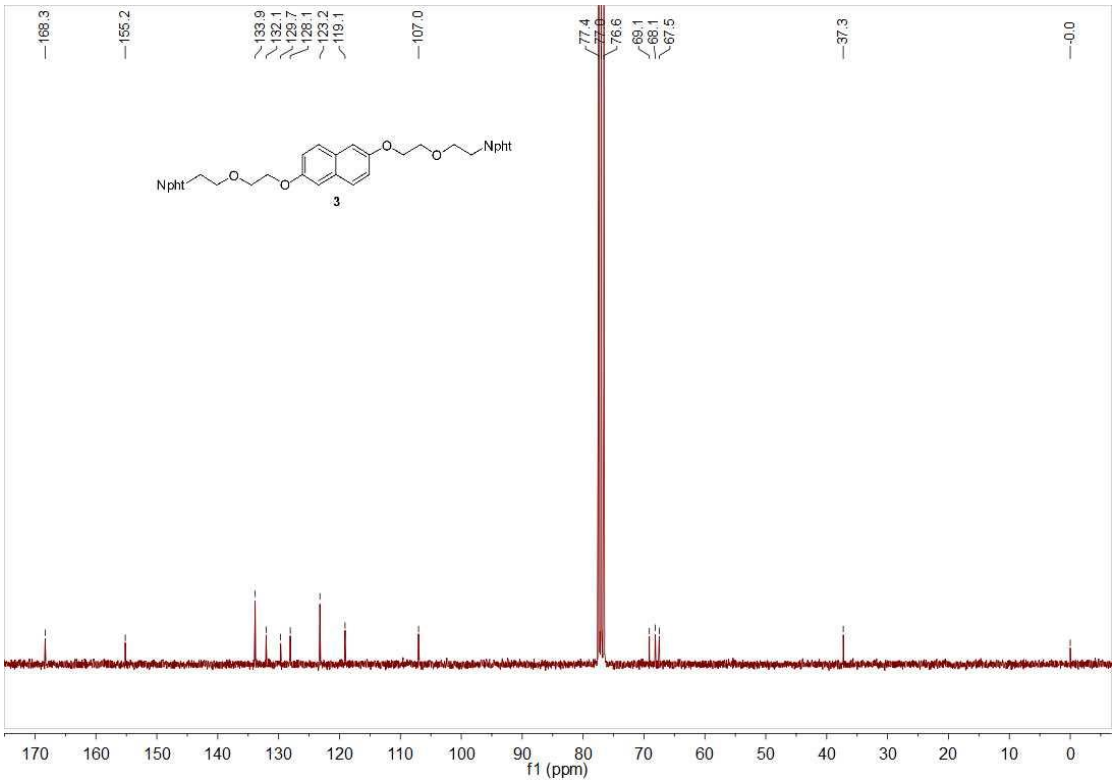


Figure. S16 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **3**

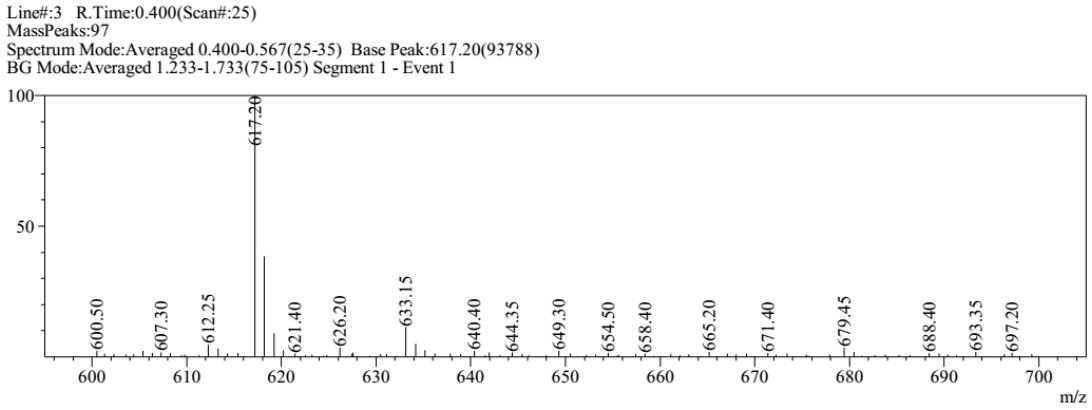


Figure. S17 Electrospray ionization mass spectrum of **3**

8.4 Synthesis of DNP1:

To a solution of **3** (0.70 g, 1.1 mmol) in EtOH (30 mL) was added dropwise hydrazine monohydrate (0.62 g, 12.3 mmol) and the mixture was then refluxed for 24 hours under N_2 atmosphere. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (100 mL × 3), brine (100 mL × 3), and dried over anhydrous $MgSO_4$. After the solvent was removed with an evaporator under reduced pressure, and the resulting yellow solid compound **4** was used in next step without further purification (0.32 g, 85%). Imidazolide **L1** (0.85 g, 2.8 mmol) and **4** (0.32 g, 1.0 mmol) were dissolved in 20 mL of dry $CHCl_3$ and this solution was stirred for 12 h under nitrogen at room temperature. To the reaction mixture was washed with 1 M HCl (20 mL × 2), saturated $NaHCO_3$ (30 mL × 2), brine (30 mL × 2), and dried over anhydrous $MgSO_4$. After the solvent was removed, the resulting residue was subjected to column chromatography over silica gel (eluent: $CHCl_3$) to afford compound **DNP1** as a white solid (0.55 g, 72%). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 11.38 (s, 2H, N*H*), 9.62 (br s, 2H, N*H*), 7.78 (s, 2H, N*H*), 7.69 (d, *J* = 8.9 Hz, 2H, naphthalene-*H*), 7.26 (d, *J* = 2.3 Hz, 2H, naphthalene-*H*), 7.12 (dd, *J* = 8.9 Hz, *J* = 2.4 Hz, 2H, naphthalene-*H*), 5.74 (s, 2H, alkylidene-*H*), 4.48-3.96 (m, 4H, OCH_2), 3.95-3.70 (m, 4H, OCH_2), 3.68-3.48 (m, 4H, OCH_2), 3.42-3.34 (m, 4H, OCH_2), 2.29-2.10 (m, 2H, C*H*(CH_2)$_2$), 1.58-1.35 (m, 8H, CH_2), 1.26-1.02 (m, 8H, CH_2), 0.86-0.62 (m, 12H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 155.3, 154.9, 152.2, 152.1, 129.9, 128.5, 119.3, 107.4, 105.6, 69.7, 69.3, 67.6, 48.4, 33.4, 29.6, 27.0, 22.6, 14.3, 12.2. ESI-MS: *m/z* calcd

for $[M + H]^+$ = 805.46, found = 805.45; HR-ESI-MS ($C_{42}H_{60}N_8O_8$): *m/z* calcd for $[M + H]^+$ = 805.4607, found = 805.4596.

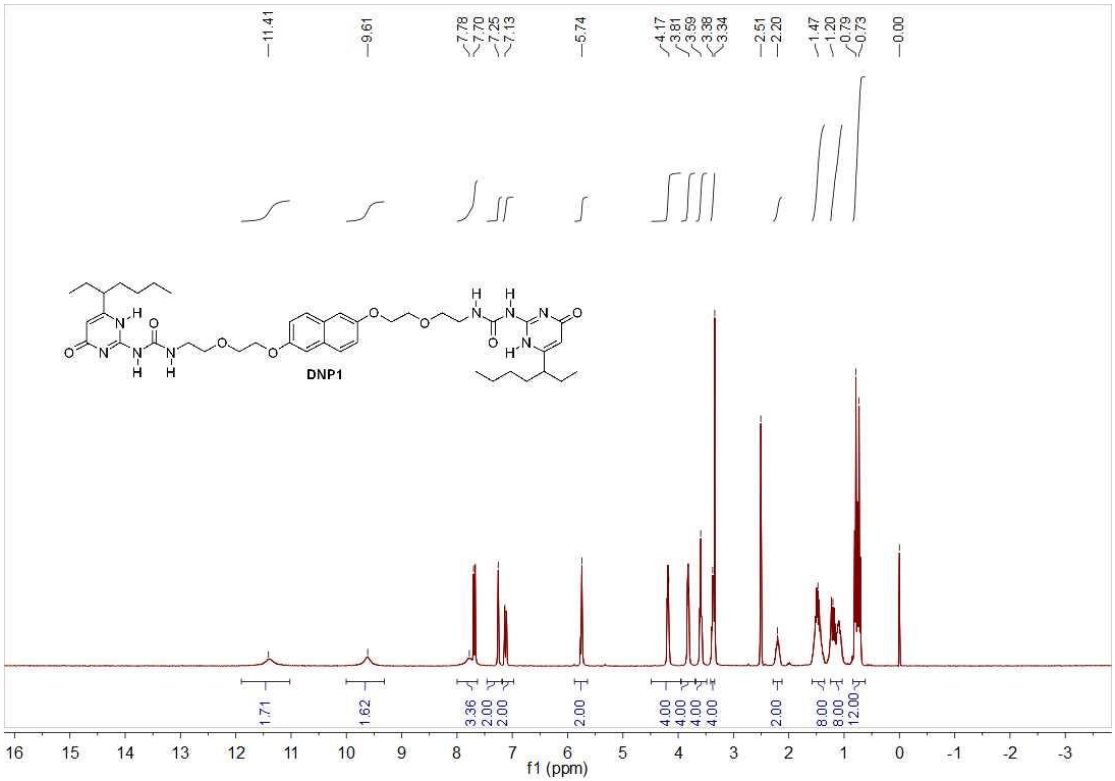


Figure. S18 ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **DNP1**

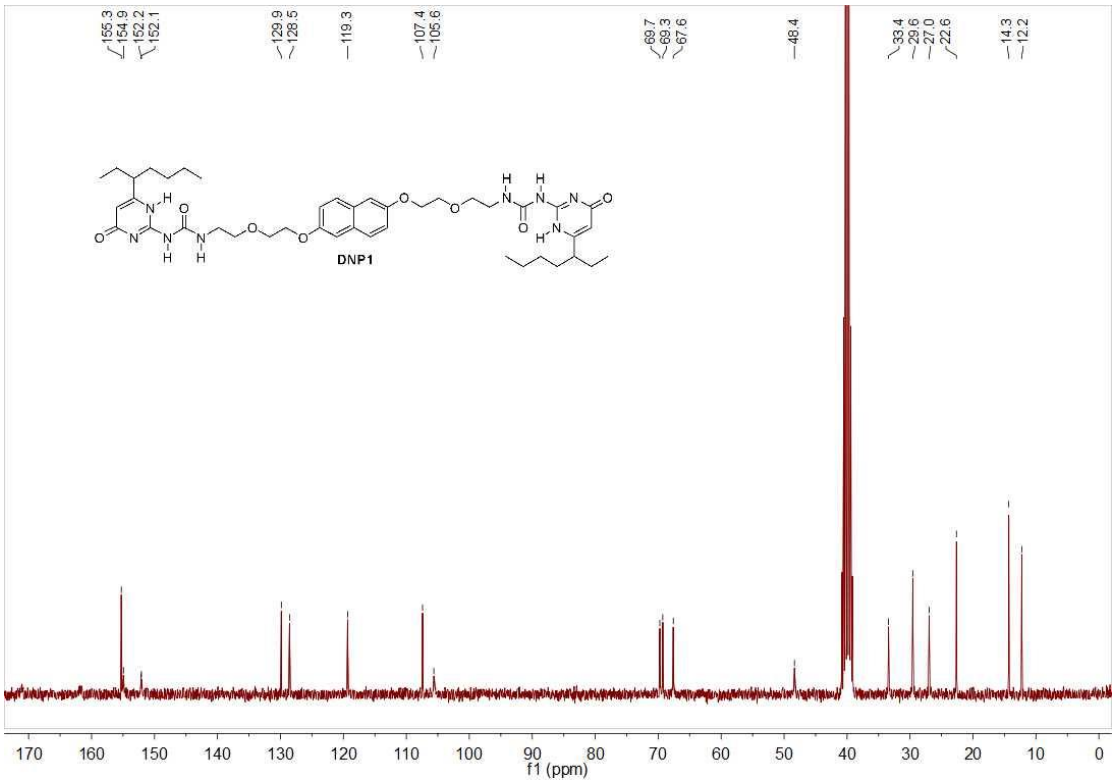


Figure. S19 ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **DNP1**

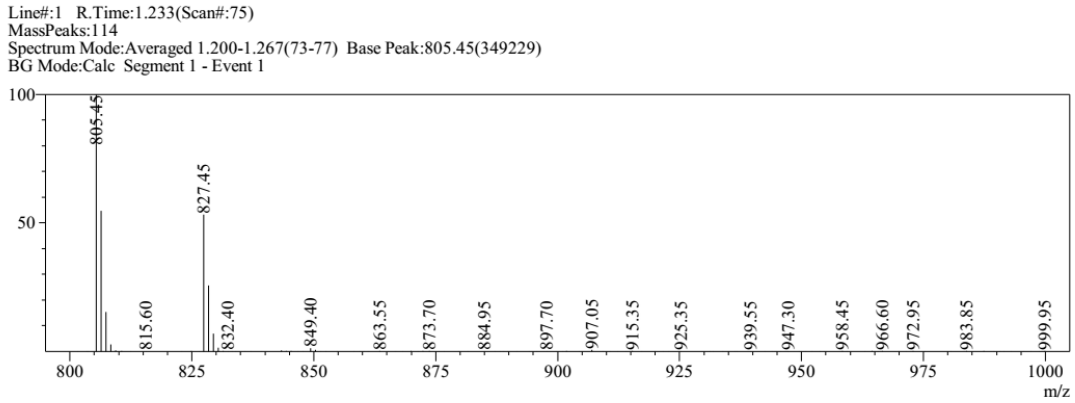


Figure. S20 Electrospray ionization mass spectrum of **DNP1**

9. Reference

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