Supporting Information

Dynamic covalent synthesis of [2]- and [3]rotaxanes both in solution and on solid supports.

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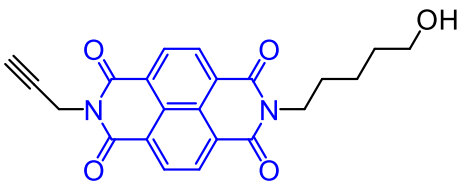
1. Experimental details and HPLC and LC MS methods

General considerations

Unless otherwise stated, reagents were purchased from commercial sources (*e.g.* Sigma Aldrich, Alfa Aesar, CTI) and used without further purification. The following solvents (AR grade) were distilled and dried prior to use according to standard procedures: acetonitrile, tetrahydrofuran and *N,N*-dimethylformamide were purified by a solvent purification system - Innovative Technologies PureSolv Micro; ethyl acetate, methanol and hexane were distilled under reduced pressure. Triethylamine was dried over KOH. All silica gel column chromatography was performed using Merck silica gel 60 (grade 9835, 230-400 mesh). Analytical TLC was carried out on Merck silica gel F_{254} precoated aluminium sheets. The TentaGel™ S-SH, resins were purchased from AnaSpec with a quoted loading of 0.2 mmol/g and a particle size of approximately 130 mm. Solution NMR spectra were recorded on a Bruker Avance 400 MHz or a Bruker advance 600 MHz spectrometer and referenced to the relevant solvent peak. High resolution magic angle spinning NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 298 K using a Bruker HR MAS probe. Rotors containing a suspension of the beads in $CDCl_3$, Acetone-d_6 or CD_3CN were spun at 4 or 5 kHz. One-dimensional HR MAS spectra were obtained with 64 scans. Unless otherwise stated, the CPMG pulse sequences used contained either 0, 8, 32 or 128 π-pulses with a repetition time of 30 ms. A Dionex Ultimate 3000 RSLC was used for HPLC separations. ESI high-resolution mass spectra were obtained using a Thermo Fisher Scientific Orbitrap Elite™ mass spectrometer. UV-visible spectra were recorded on a Shimadzu UV-1800 UV-vis spectrophotometer. IR spectra were obtained using a Thermo Nicolet Nexus 870 esp spectrometer equipped with a 45 ° Ge ATR accessory at 4 cm^{-1} resolution using 64 scan averaging. Melting points were measured by the capillary method on a Gallen Kamp variable-temperature melting point apparatus and are uncorrected.

Synthetic procedures

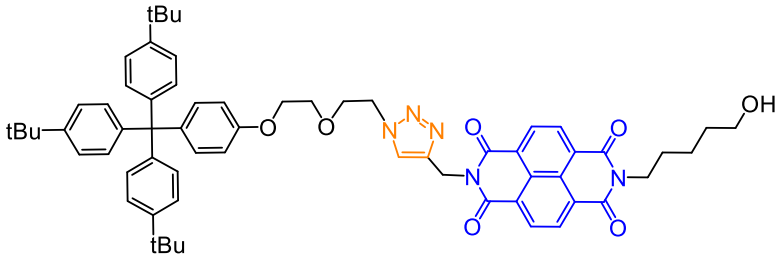
Synthesis of N-(5-Hydroxypentyl)-N'-(3-butynyl) naphthalene diimide 6



A solution of 5-amino-1-pentanol (200 mg, 1.9 mmol) and propargyl amine (0.2 mL, 1.9 mmol) dissolved in dry, degassed DMF (3 mL) was added dropwise to a solution of 1,4,5,8-napthalenetetracarboxylic dianhydride (495 mg, 1.83 mmol) in dry, degassed DMF (2 mL).

The reaction mixture was then stirred under argon at 120 °C for 2 hours. After this time the solvent was evaporated to yield a crude pink solid which was purified by column chromatography using DCM:EtOAc (80:20) as the eluent to give the pure product as a cream solid (233 mg, 32 %). ESI-MS found *m/z* 391.1291 $[C_{22}H_{18}N_2O_5 + H]^+$ (calc. *m/z* 391.1288, Δ = 0.5 ppm). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (dd, J_{HH} = 20.8, 7.6 Hz, 4H, NDI-H), 4.98 (d, J_{HH} = 2.4 Hz, 2H, CH_2), 4.28 – 4.18 (m, 2H, CH_2), 3.68 (t, J_{HH} = 6.4 Hz, 2H, CH_2), 2.24 (t, J_{HH} = 2.4 Hz, 1H, CH), 1.80 (t, J_{HH} = 7.7 Hz, 2H, CH_2), 1.72 – 1.62 (m, 2H, CH_2), 1.56 – 1.46 (m, 2H, CH_2). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.9, 162.2, 131.5, 131.2, 127.1, 126.9, 126.4, 71.4, 62.8, 41.0, 32.4, 30.0, 28.0, 23.4. The physical data collected was consistent with that previously reported.[1]

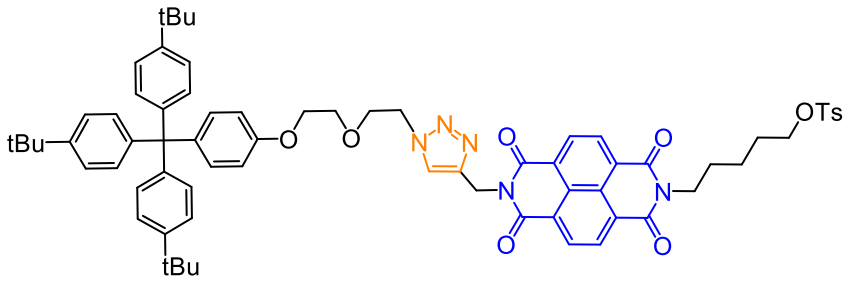
Synthesis of N-(5-Hydroxypentyl)-N'-((1-(2-(2-(4-(tris(4-(tert-butyl)phenyl)methyl) phenoxy)ethoxy)ethyl)-1,2,3-triazol-4-yl)methyl) naphthalene diimide 8



Unsymmetrical NDI **6** (400 mg, 1.0 mmol) and stopper azide **7**[2] (670 mg, 1.0 mmol) were dissolved in dry degassed DCM (60 mL) to which $Cu(MeCN)_4PF_6$ (38 mg, 0.12 mmol), *N,N*-diisopropylethylamine (DIPEA, 0.2 mL, 1.1 mmol) and a catalytic amount of tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) were added. The reaction was stirred for 3 days before being washed with HCl (40 mL, 1M) and water (2 x 50 mL). The organic phase was dried over Na_2SO_4 then evaporated under reduced pressure. The product was purified by column chromatography using DCM:EtOAc (60:40) as the eluent to afford the product as a pale yellow solid (635 mg, 62 % yield). ESI-MS found *m/z* 1030.5105 $[C_{63}H_{69}N_5O_7 + Na]^+$ (calc. *m/z* 1030.5089, Δ = 1.5 ppm). m.p. 225 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79–8.66 (m, 4H), 7.86 (s, 1H), 7.23 (d, J_{HH} = 8.6 Hz, 6H), 7.12 (d, J_{HH} = 8.9 Hz, 2H), 7.08 (d, J_{HH} = 8.6 Hz, 6H), 6.79 (d, J_{HH} = 8.9 Hz, 2H), 5.47 (s, 3H), 4.52 (t, J_{HH} = 5.0 Hz, 2H), 4.21 (t, J_{HH} = 7.2 Hz, 3H), 4.06 (t, J_{HH} = 4.2 Hz, 3H), 3.90 (t, J_{HH} = 5.0 Hz, 2H), 3.77 (t, J_{HH} = 4.8 Hz, 3H), 3.67 (t, J_{HH} = 6.4 Hz, 2H), 1.79 (p, J_{HH} = 7.6 Hz, 3H), 1.66 (dt, J_{HH} = 14.0, 6.7 Hz, 2H), 1.52 (q, J_{HH} = 8.5, 7.6 Hz, 2H), 1.28 (s, 27H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.9, 162.6, 156.4, 148.5, 144.2, 140.2, 132.5, 131.3, 131.1, 130.8, 126.9, 126.8, 126.8, 126.6, 124.8, 124.2, 113.2,

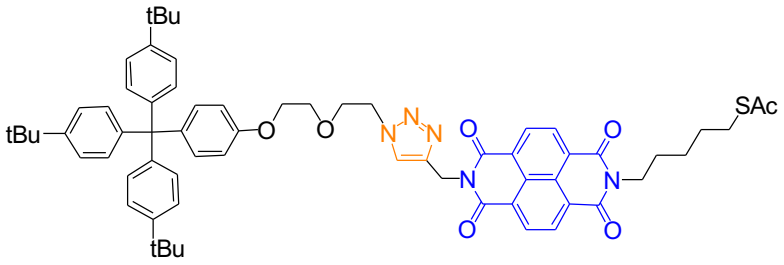
70.0, 69.7, 67.2, 63.2, 62.8, 50.6, 40.9, 35.6, 34.4, 32.4, 31.5, 27.9, 23.4. Purity determined by HPLC: >95 %.

Synthesis of *N*-(5-Hydroxypentyl)-*N′*-((1-(2-(2-(4-(tris(4-(tert-butyl)phenyl)methyl) phenoxy)ethoxy)ethyl)-1,2,3-triazol-4-yl)methyl) naphthalene diimide *p*-toluylsulfonate 9



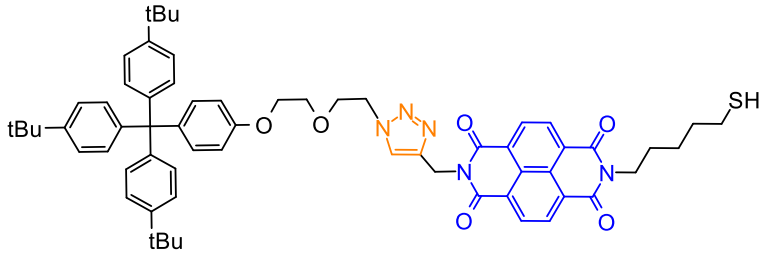
The half-dumbbell NDI **8** (1.6 g, 1.6 mmol) was dissolved in dry, degassed DCM (100 mL) with triethylamine (TEA, 0.45 mL) and 4-dimethylaminopyridine (DMAP, cat.), to which a solution of tosyl chloride (1.2 g, 6.3 mmol) in DCM (60mL) was added dropwise at 0 °C. The reaction was stirred for 3 days under argon. After this time, the reaction was quenched over an ice/water mixture, before being extracted with DCM (3 x 30 mL). The organic extracts were combined and washed with water (2 x 50 mL) and brine (30 mL) then dried over Na_2SO_4 and evaporated. The crude material was purified by column chromatography over silica using DCM:MeOH (99:1) as the eluent to give the product as an off white solid (1.8 g, 95 %). m.p. 218 °C. ESI-MS found *m/z* 1162.5388 [$C_{70}H_{75}N_5O_9S$ + H]$^+$ (calc. *m/z* 1162.5358, Δ = 2.5 ppm). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (q, J_{HH} = 20.0, 7.6 Hz, 4H), 7.86 (s, 1H), 7.78 (d, J_{HH} = 8.3 Hz, 2H), 7.34 (d, J_{HH} = 8.0 Hz, 2H), 7.26 (s, 1H), 7.23 (d, J_{HH} = 8.6 Hz, 6H), 7.12 (d, J_{HH} = 9.0 Hz, 2H), 7.09 (d, J_{HH} = 8.7 Hz, 6H), 6.79 (d, J_{HH} = 9.0 Hz, 2H), 4.52 (t, J_{HH} = 5.0 Hz, 3H), 4.17 – 4.13 (m, 2H), 4.08 – 4.01 (m, 4H), 3.90 (t, J_{HH} = 5.0 Hz, 3H), 3.79 – 3.75 (m, 3H), 2.43 (s, 4H), 2.04 (s, 1H), 1.77 – 1.67 (m, 4H), 1.46 (p, J_{HH} = 7.7 Hz, 2H), 1.28 (s, 27H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.8, 162.7, 156.4, 148.5, 144.8, 144.2, 142.4, 140.3, 133.2, 132.5, 131.3, 131.1, 130.8, 130.0, 128.5, 128.0, 126.9, 126.8, 126.6, 125.8, 125.0, 124.2, 113.2, 70.4, 70.0, 69.5, 67.2, 63.2, 50.8, 40.6, 35.4, 34.4, 31.5, 28.6, 27.5, 23.07, 21.8, 21.4.

Synthesis of *N*-(5-(*S*-acetyl)sulfoxypentyl)-*N'*-((1-(2-(2-(4-(tris(4-(*tert*butyl)phenyl) methyl) phenoxy)ethoxy)ethyl)-1,2,3-triazol-4-yl)methyl) naphthalene diimide 10



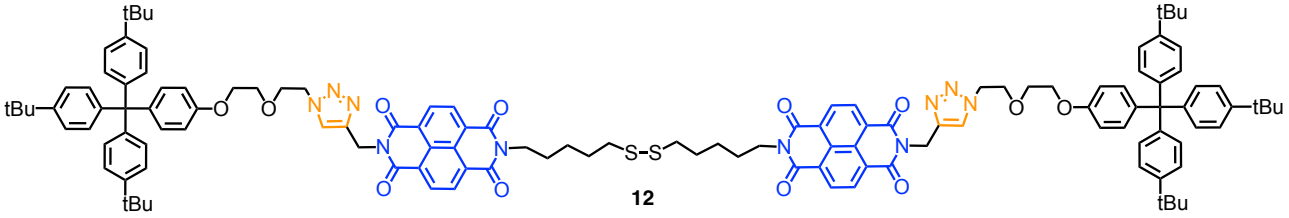
The tosylate **9** (1.35 g, 1.16 mmol) was dissolved in dry degassed DMF (100 mL) to which potassium thioacetate (590 mg, 5.16 mmol) was added. The reaction was stirred for 3 days and the reaction mixture was passed through a silica plug. The product was then purified by column chromatography over silica using DCM:EtOAc (30%) to afford the product as a yellow brown solid (900 mg, 72 %). ESI-MS found *m/z* 1088.4967 $[C_{65}H_{71}N_5O_7S + Na]^+$ (calc. *m/z* 1088.4966, Δ = 0.1 ppm). m.p.: 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (q, J_{HH} = 7.6 Hz, 4H), 7.87 (s, 1H), 7.24 (s, 2H), 7.12 (d, J_{HH} = 8.9 Hz, 2H), 7.08 (d, J_{HH} = 8.6 Hz, 5H), 6.79 (d, J_{HH} = 9.0 Hz, 2H), 5.30 (s, 2H), 4.52 (t, J_{HH} = 5.0 Hz, 2H), 4.22 – 4.16 (m, 2H), 4.08 – 4.04 (m, 2H), 3.91 (t, J_{HH} = 5.0 Hz, 2H), 3.80 – 3.75 (m, 2H), 2.88 (t, J_{HH} = 7.3 Hz, 2H), 1.77 – 1.73 (m, 2H), 1.66 (p, J_{HH} = 7.5 Hz, 2H), 1.50 (p, J_{HH} = 7.6 Hz, 2H), 1.29 (s, 27H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.8, 162.6, 156.4, 148.5, 144.2, 140.3, 132.48, 131.3, 131.0, 130.9, 130.8, 126.8, 126.6, 124.2, 113.1, 70.0, 69.6, 67.2, 63.2, 50.7, 40.8, 38.8, 35.5, 34.4, 31.5, 29.0, 27.7, 26.0.

Synthesis of *N*-(5-Sulfoxypentyl)-*N'*-((1-(2-(2-(4-(tris(4-(tert-butyl)phenyl)methyl)phenoxy) ethoxy)ethyl) -1,2,3-triazol-4-yl)methyl) naphthalene diimide 2



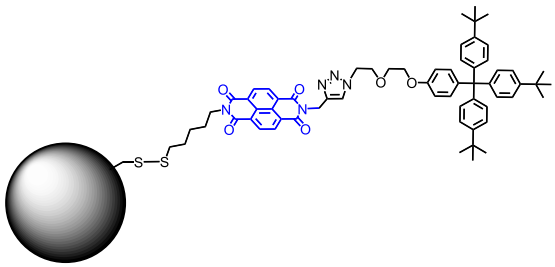
The thioacetate protected NDI thread **10**, (50 mg, 0.05 mmol) was dissolved in dry, degassed DCM (2 mL). Sodium methoxide (25 m, 0.5 mmol) dissolved in dry degassed MeOH (1 mL) was then added, and the mixture stirred under argon for 15 minutes. After this time the reaction was quenched with HCl (5 mL, 1M). The solution was diluted with additional DCM (10 mL) and the organic phase

washed with HCl (5 mL, 1M), and water (2 x 5 mL) to afford the product which rapidly oxidised to the disulfide homo dimer **12** (44 mg, quantitative yield); ESI-MS found *m/z* 2045.9885 $[C_{126}H_{137}N_{10}O_{12}S_2 + H]^+$ (calc. *m/z* 2045.9853, Δ = 1.6 ppm). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 – 8.62 (dd, J_{HH} = 11.5, 7.7 Hz, 4H), 7.85 (s, 1H), 7.23 (d, J_{HH} = 8.5 Hz, 6H), 7.12 (d, J_{HH} = 8.9 Hz, 2H), 7.08 (d, J_{HH} = 8.4 Hz, 6H), 6.79 (d, J_{HH} = 8.8 Hz, 2H), 5.46 (s, 2H), 4.51 (t, J_{HH} = 5.0 Hz, 2H), 4.18 (t, J_{HH} = 7.6 Hz, 2H), 4.06 (t, J_{HH} = 4.5 Hz, 2H), 3.90 (t, J_{HH} = 5.1 Hz, 2H), 3.82 – 3.75 (m, 2H), 2.71 (t, J_{HH} = 7.3 Hz, 2H), 1.78 (p, J_{HH} = 7.5 Hz, 4H), 1.60 – 1.48 (m, 2H), 1.29 (s, 27H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.8, 162.8, 162.6, 162.5, 156.4, 148.4, 144.2, 140.2, 132.4, 131.3, 131.0, 131.0, 130.8, 126.8, 126.8, 126.7, 126.7, 126.7, 126.5, 126.5, 124.2, 113.2, 69.9, 69.6, 67.2, 63.2, 50.6, 40.8, 35.5, 34.4, 31.6, 31.5, 31.4, 28.9, 28.8, 28.5, 28.5, 27.7, 27.7, 26.0, 25.98, 26.0, 25.9.



12

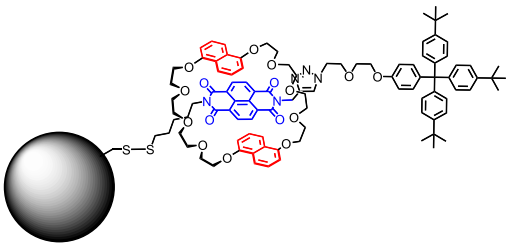
Synthesis of the NDI half-dumbbell functionalised TentaGel beads 17



The half-dumbbell disulfide **12** (20.5 mg, 10 x 10^{-3} mmol) was added as the disulfide to a suspension of the TentaGel™ S–SH resins 0.2 mmol/g (20.3 mg, 4 x 10^{-3} mmol) in $CHCl_3$ (4 mL) in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 40 equiv) and dithioerythritol (DTE, 10 equiv). The suspension was stirred gently and alternatively for 15 min every hour for 2 weeks. The reaction was then quenched with iodine (10 mg) in $CHCl_3$ (2 mL) and stirred for 30 min. The beads were then filtered through a fritted funnel and washed alternatively with DCM (2 x 1mL) followed by hexane (2 x 1 mL) 5 iterations terminating on a wash with DCM. This cycle of washing was designed to shrink and swell the beads to ensure complete removal of any residual material from the reaction solution. The beads were finally washed with acetone (2 x 1 mL) and water (2 x 1 mL) for five

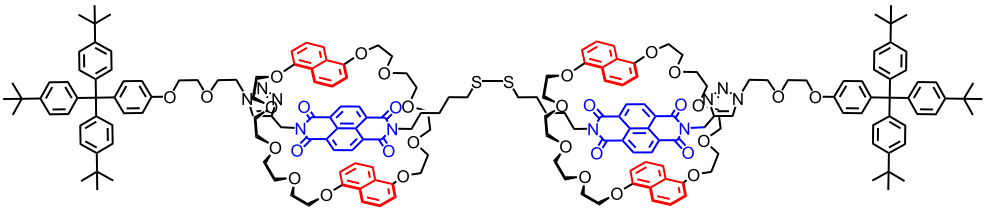
additional cycles, finishing with acetone (2 x 1 mL) and DCM (5 x 1 mL) washes before being air dried. ^{1}H HR MAS NMR (400 MHz, $CDCl_3$) δ 8.75 (2d, J_{HH} = 6.9 Hz, 4H), 7.89 (d, J_{HH} = 6.9 Hz, 1H), 7.26 (d, J_{HH} = 8.4 Hz, 6H), 7.12 (d, J_{HH} = 8.2 Hz, 8H), 6.82 (d, J_{HH} = 8.8 Hz, 2H), 5.47 (d, J_{HH} = 14.4 Hz, 2H), 4.58 – 4.49 (m, 2H), 4.05 (t, J_{HH} = 4.8 Hz,2H), 3.15 (m, 2H), 3.00 (t, J_{HH} = 7.1 Hz, 2H), 2.69 – 2.58 (t, J_{HH} = 7.1 Hz, 2H), 1.35 – 1.28 (s, 27H).

Synthesis of the rotaxane functionalised TentaGel beads 4



The half-dumbbell disulfide **12** (20.5 mg, 10 x 10^{-3} mmol) and DNQ[38]crown-10 **3** (127.4 mg, 200 x 10^{-3} mmol) were added to a suspension of the TentaGel^{TM} S–SH resins 0.2 mmol/g (20.3 mg, 4 x 10^{-3} mmol) in $CHCl_3$ (4 mL) in the presence of DBU (40 equiv) and DTE (10 equiv). The suspension was stirred gently and alternatively for 15 min every hour for 2 weeks. The reaction was then quenched with iodine (10 mg) in $CHCl_3$ (2 mL) and stirred for 30 min. The beads were then filtered through a fritted funnel and washed alternatively with DCM (2 x 1mL) followed by hexane (2 x 1 mL) for 5 iterations. The beads were then washed with acetone (2 x 1 mL) and water (2 x 1 mL) for five additional cycles, before final washes with acetone (2 x 1 mL) and DCM (5 x 1 mL). The resins were then left to air dry. ^{1}H HR MAS NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 4H), 8.36 – 8.24 (m, 4H), 8.12 (s, 1H), 7.89 (s, 1H), 7.27 – 7.21 (m, 6H), 7.09 (d, J_{HH} = 8.1 Hz, 8H), 6.82 (d, J_{HH} = 8.2 Hz, 2H), 6.75 (d, J_{HH} = 8.6 Hz, 2H), 6.48 – 6.40 (m, 2H), 6.00 (d, J_{HH} = 7.6 Hz, 2H), 5.48 (s, 2H), 5.41 (s, 2H), 4.66 (s, 2H), 4.54 (s, 2H), 3.15 (s, 2H), 3.01 (t, J_{HH} = 6.8 Hz, 2H), 2.64 (t, J_{HH} = 6.8 Hz, 2H), 2.19 (t, J_{HH} = 3.0 Hz, 2H), 1.32 (s, 27H).

Isolation of [3]rotaxane 16



The initial $CHCl_3$ and CH_2Cl_2 washings of the functionalised resins **4** were collected and purified by column chromatography over silica using $CHCl_3$:MeOH (99:1) as the eluent. From this, the naphthalene diimide [3]rotaxane **16** was isolated as a pure red solid. ESI-MS found $[M]^+$ *m/z* 3318.5871 $[C_{198}H_{225}N_{10}O_{32}S_2]^+$ (calc. *m/z* 3318.5722, Δ = 4.5 ppm). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (s, 8H), 8.07 (s, 2H), 7.22 (d, *J* = 8.5 Hz, 12H), 7.08 (d, *J* = 8.6 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 12H), 6.79 (d, *J* = 8.3 Hz, 8H), 6.72 (d, *J* = 8.9 Hz, 4H), 6.42 (t, *J* = 7.7 Hz, 8H), 5.95 (d, *J* = 7.3 Hz, 8H), 5.37 (s, 4H), 4.63 (t, *J* = 4.9 Hz, 4H), 4.09 – 4.03 (m, 4H), 4.03 – 3.95 (m, 20H), 3.92 – 3.88 (m, 8H), 3.86 (m, 12H), 3.77 – 3.74 (m, 4H), 2.93 – 2.84 (m, 4H), 1.96 (m, 4H), 1.90 (m, 5H), 1.73 – 1.66 (m, 9H), 1.58 – 1.49 (m, 8H), 1.29 (s, 54H).

HPLC and LC MS methods

HPLC-grade MeCN and isopropanol were filtered with a 0.45 μm Millipore filter, degassed appropriately and used without further purification. HPLC analysis was carried out on a Dionex Ultimate 3000 RSLC system coupled in parallel to a diode array detector and a Thermo Fisher Scientific Orbitrap Elite mass spectrometer, with the flow split ~4:1 by adjusting the dimensions of the connective tubing. The data was processed using Thermo Xcalibur software. ESI mass spectra in positive ion mode were acquired with a resolution 120000 (Δm/m, defined at *m/z* 400).

All quantitative analysis was performed using chromatogram recorded at 420 nm. Despite repeated attempts, it was not possible to isolate each individual component of the equilibrium and calculate molar extinction coefficients. For the purpose of calculating relative proportions of each component is was assumed that the porphyrin absorbance was similar for each unit. The presence of two porphyrin subunits in porphyrin homodimer **11** doubles the expected absorbance and this was taken into account when performing the calculations.

At this wavelength however only the porphyrin species are detected. This simplifies the analysis of the system from five to three species in the thread synthesis and from nine to four species in the

rotaxane synthesis. The chromatograms were also recorded at λ = 380 nm, the wave-length of the NDI centre, which in combination with the MS data gave information about the presence of the NDI species. However, using the data collected at this wavelength for any calculations was not possible due to the large difference in extinction coefficients between the porphyrin and NDI moieties. Given these limitations, for Rxns 1-5 the precise quantity of NDI homo dimer **12** cannot be calculated, however is expected to be similar to that of the porphyrin homo dimer **11**, due to the statistically nature of this equilibrium.

Table S1: ESI-MS Orbitrap source settings for the HPLC-MS studies of the exchange experiments.

ESI-MS parameters	
Heater temperature (°C)	300
Sheath Gas flow rate (arb.)	25
Aux Gas flow (arb.)	5
Sweep Gas flow rate (arb.)	1
Capillary temperature (°C)	350

Table S2: LC-UV-vis detector settings for the HPLC-MS studies of the exchange experiments.

Detection wavelength (nm)	Detection window (nm)	Reference wavelength (nm)	Reference window (nm)
254	8	600	8
292	8	600	8
380	8	600	8
420	8	600	8

2. Supplementary Schemes and Figures

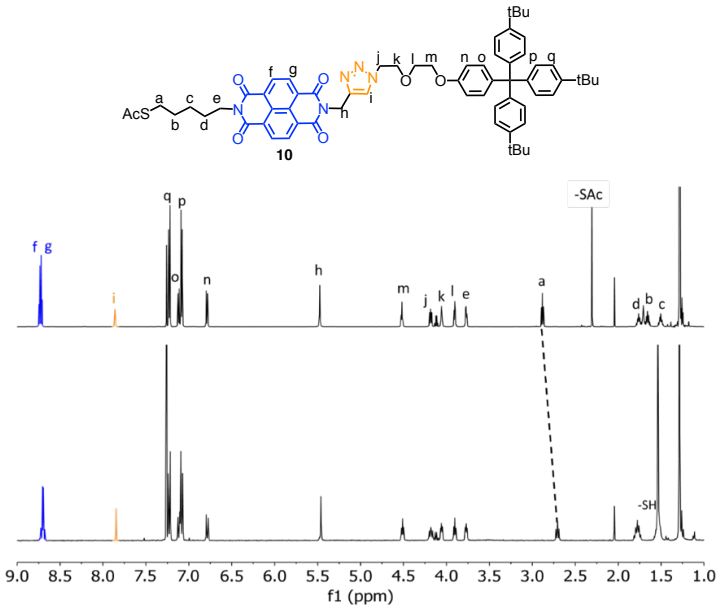
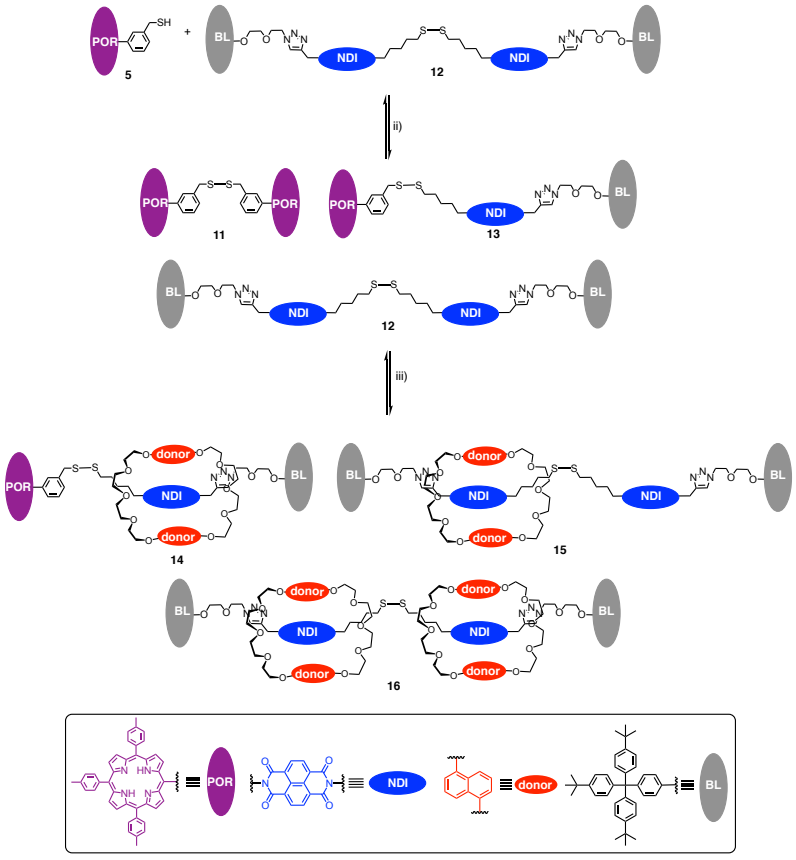
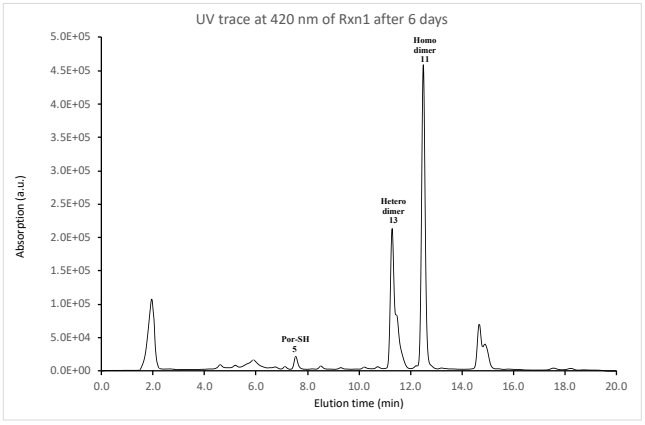
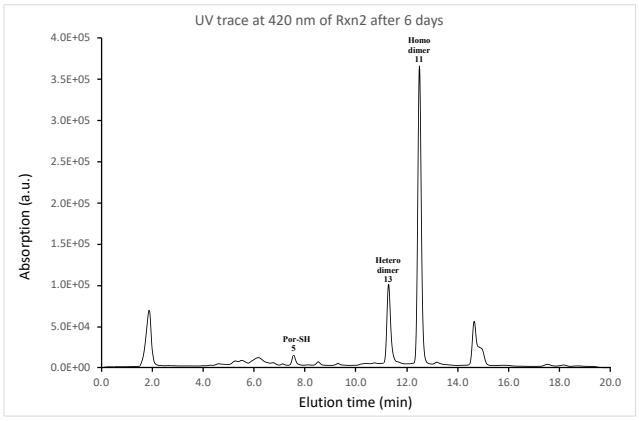


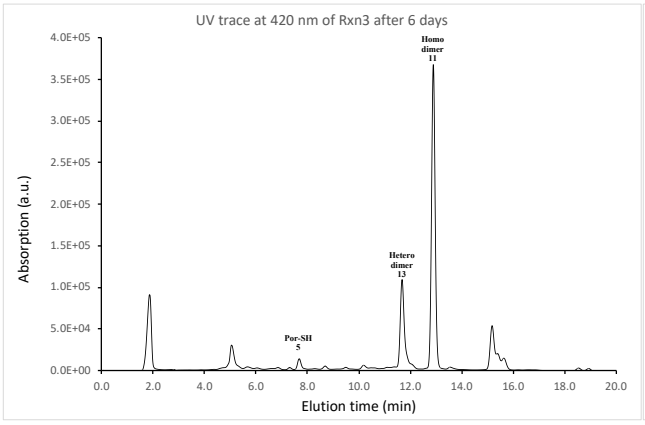
Figure S1: Comparison of the ^{1}H NMR ($CDCl_3$, 400 MHz) of the naphthalene diimide thioacetate **10** (top) and the naphthalene diimide disulfide **12** (bottom).

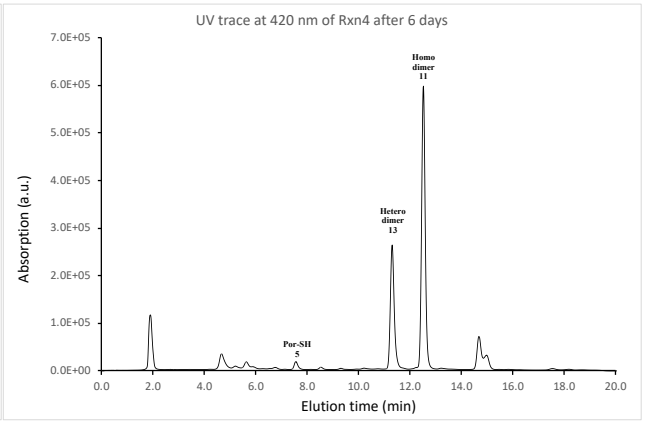


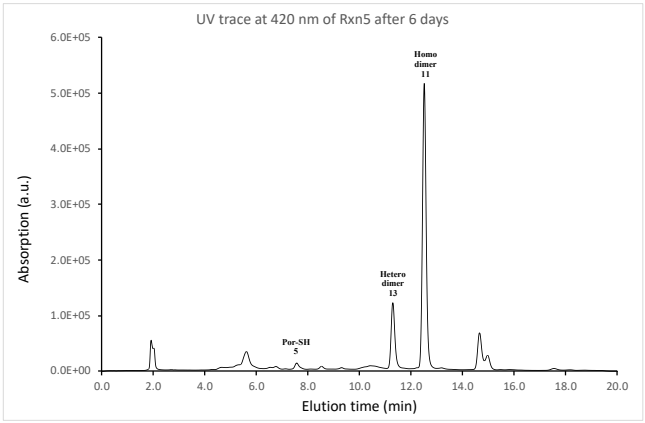
Scheme S1: Scope of initial HPLC investigations to optimise disulfide exchange; i) the formation of a porphyrin homodimer **11**, diimide homodimer **12** and heterodimer **13** via disulfide exchange. When under thermodynamic exchange, a statistical distribution of the three dimers would be expected. ii) addition of 1 equiv. of macrocycle allows for the possible formation of rotaxanes (**14**-**16**).







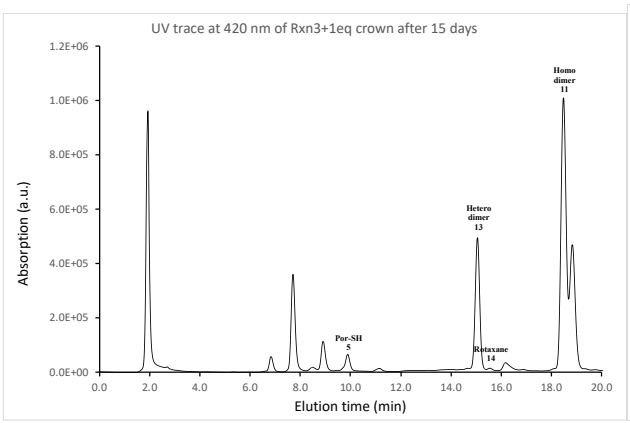


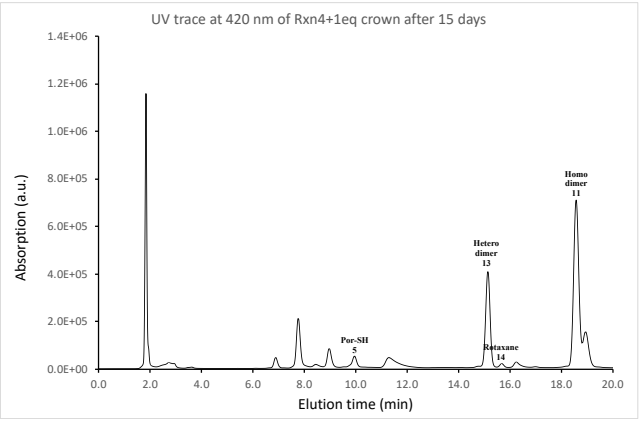


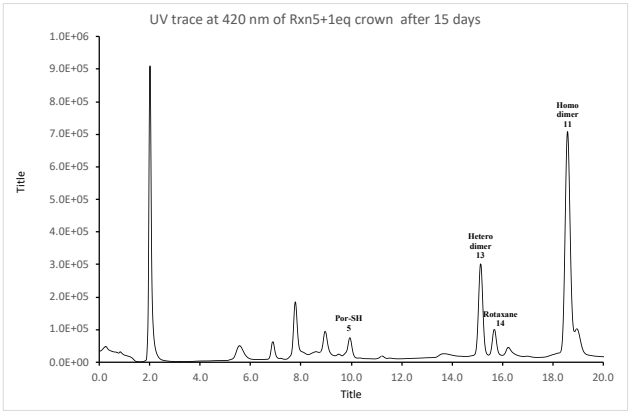
HPLC Solvent Gradient

Time (min)	%MeCN	%^{i}Prop
0.0	80	20
2.0	80	20
15.0	60	40
17.0	60	40
19.0	0	100
19.5	0	100
21.0	80	20

Figure S2: HPLC traces of Rxn 1-5 after 6 days.







HPLC Solvent Gradient

Time (min)	%MeCN	%^{i}Prop
0.0	80	20
2.0	80	20
15.0	50	50
17.0	50	50
19.0	0	100
19.5	0	100
21.0	80	20

Figure S3: HPLC trace of Rxn 3-5, 15 days after addition of one equivalent of macrocycle **3**.

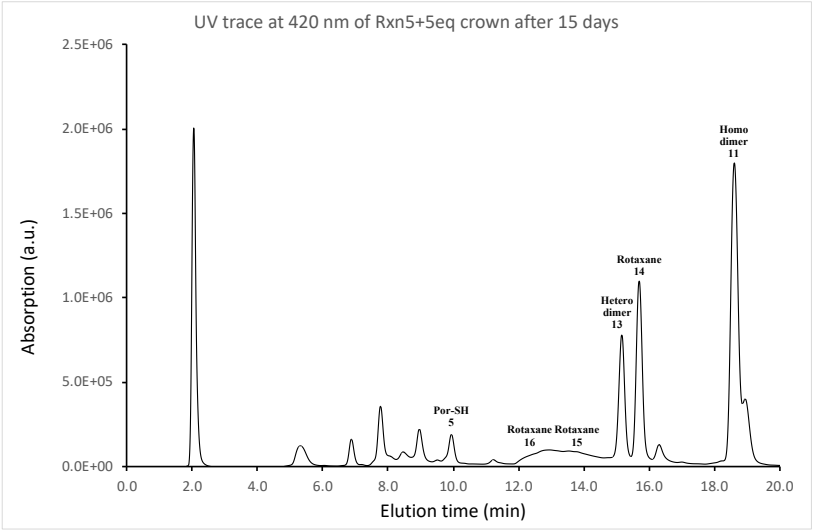


Figure S4: HPLC trace of Rxn 3, 15 days after addition of one equivalent of macrocycle **3**.

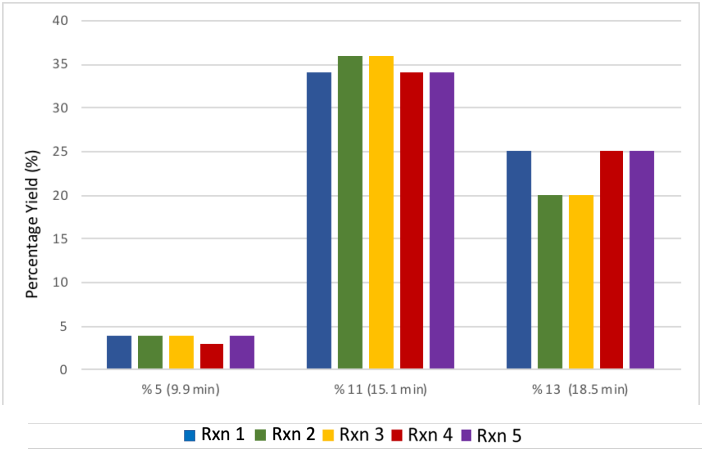


Figure S5: Evaluation of the efficacy of disulfide exchange between **12** and **5**. Chart shows relative proportions of homo porphyrin dimer **11** and heterodimer **13** present in solution after 6 days equilibration time at room temperature.

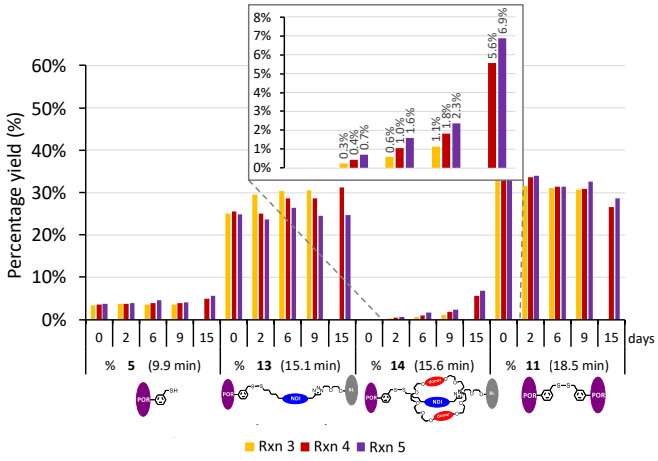


Figure S6: Relative product distribution observed following addition of crown macrocycle **3** to equilibrated solution of NDI disulfide **12** and porphyrin thiol **5**. The insert focusses on the evolution of the [2]rotaxane **14**.

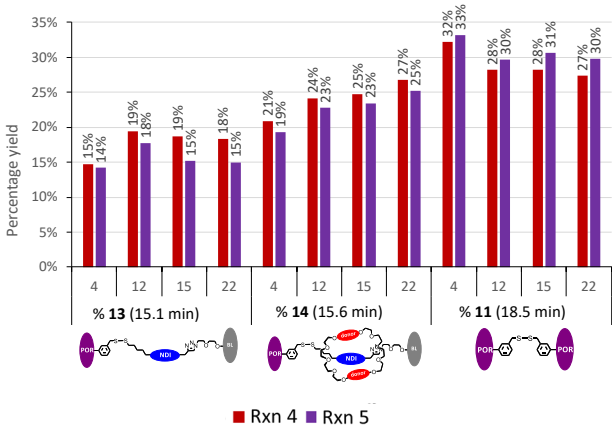


Figure S7: Relative proportions of the major components from the equilibration of **12** and **5** in the presence of 5 equivalents of macrocycle **3**. The percentage yield of the porphyrin homodimer **11**, porphyrin heterodimer **13** and heterorotaxane **14** in $CHCl_3$ over time is shown.

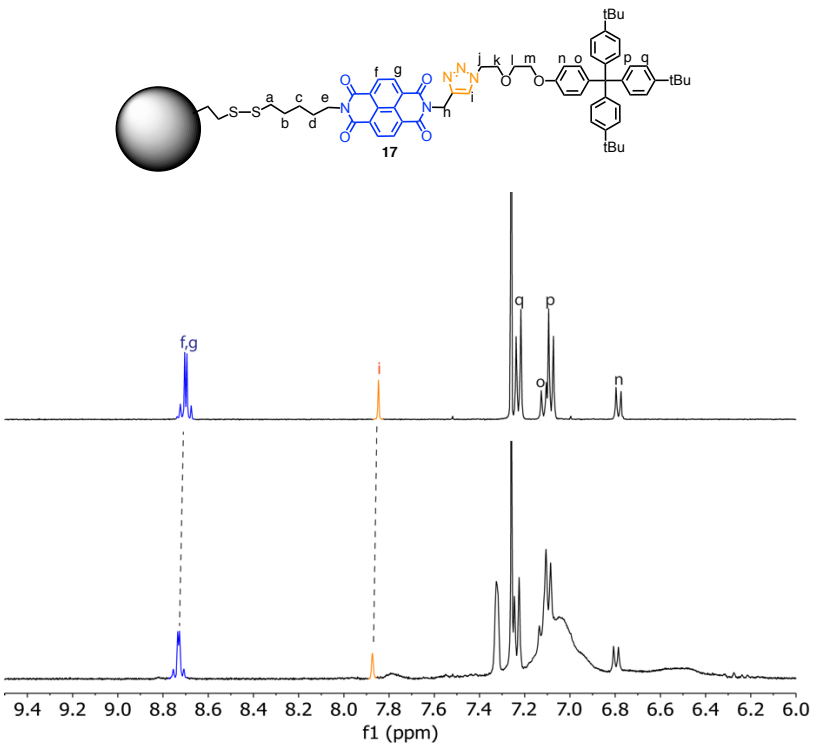


Figure S8: Comparison of the partial ^{1}H NMR spectrum ($CDCl_3$, 600MHz) of naphthalene disulfide **12** (top) with the HR-MAS ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 128 CPMG loops) of the naphthalene functionalised resins **17**.

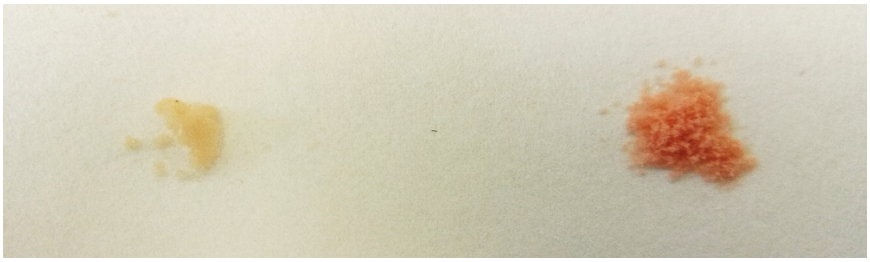


Figure S9: Photograph of the dumbbell functionalised resins **17** (left) and the rotaxanes functionalised resins **4** (right).

3. ^{1}H, ^{13}C NMR, HPLC and Mass Spectra of Select Molecules

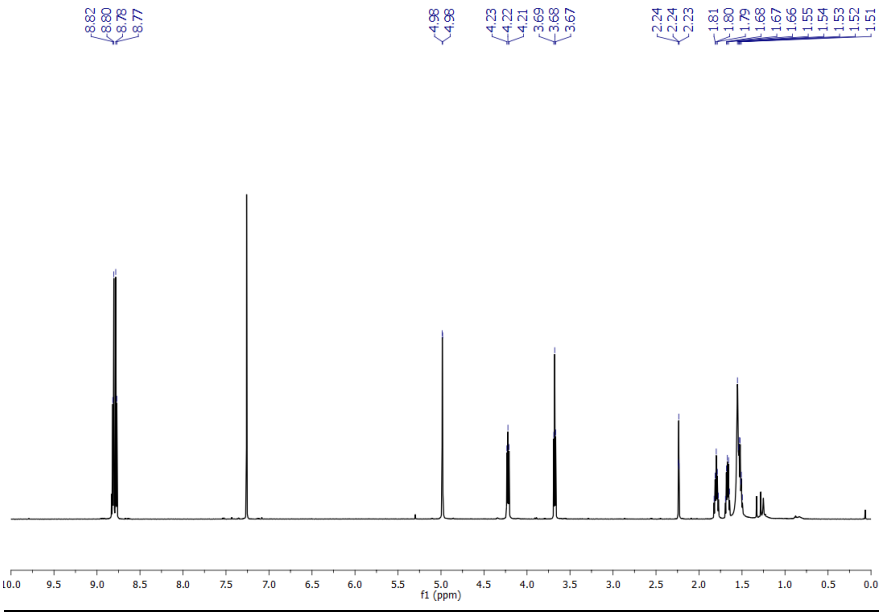


Figure S10: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**.

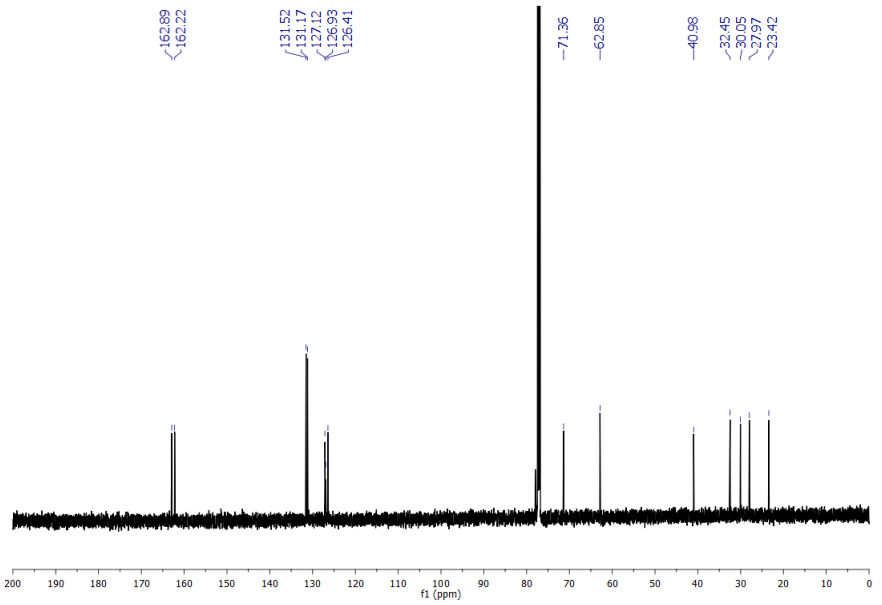


Figure S11: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6**.

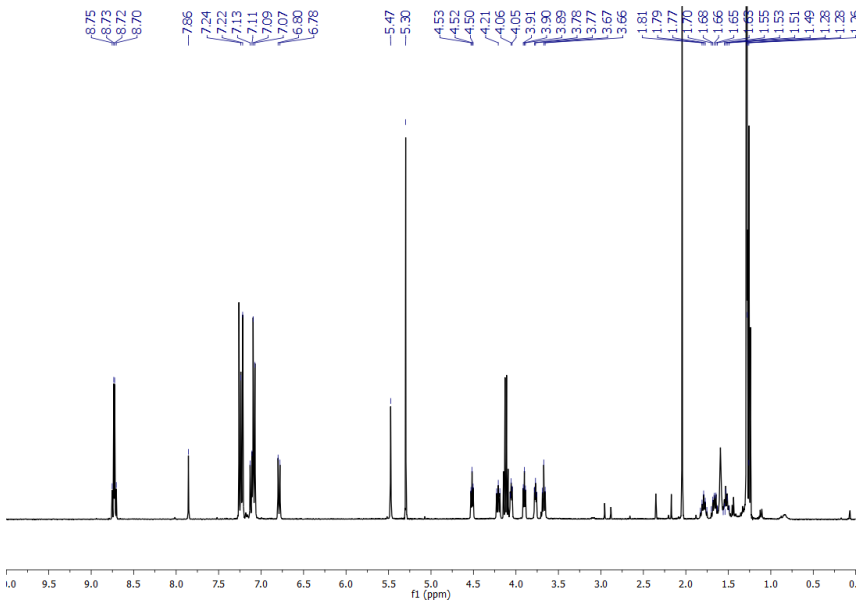


Figure S12: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**.

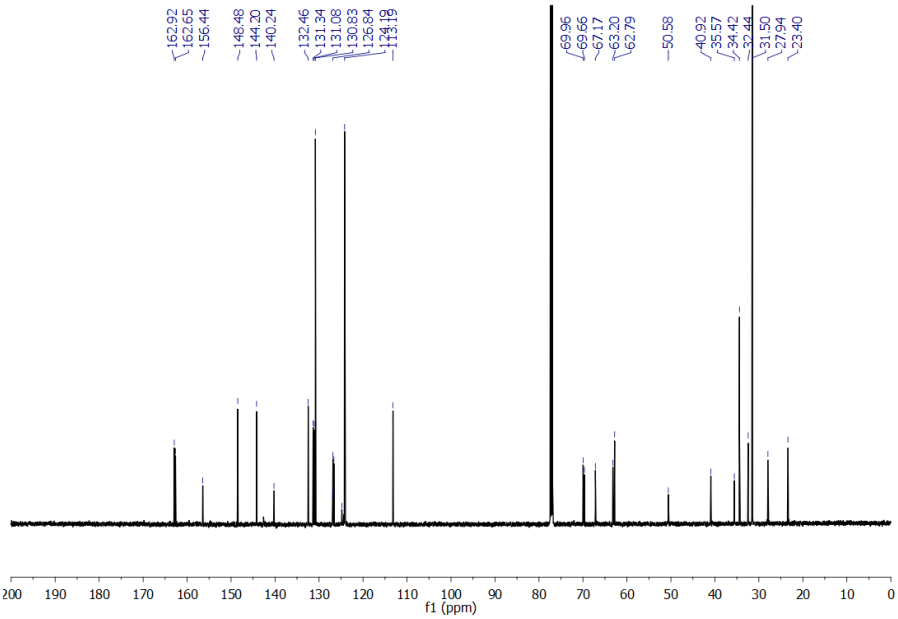


Figure S13: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8**.

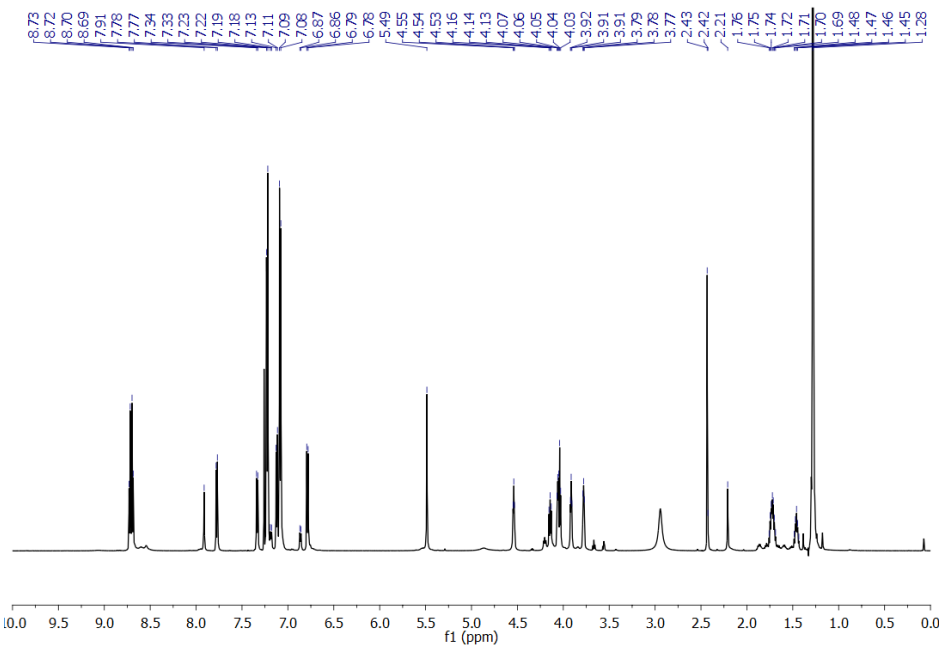


Figure S14: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**.

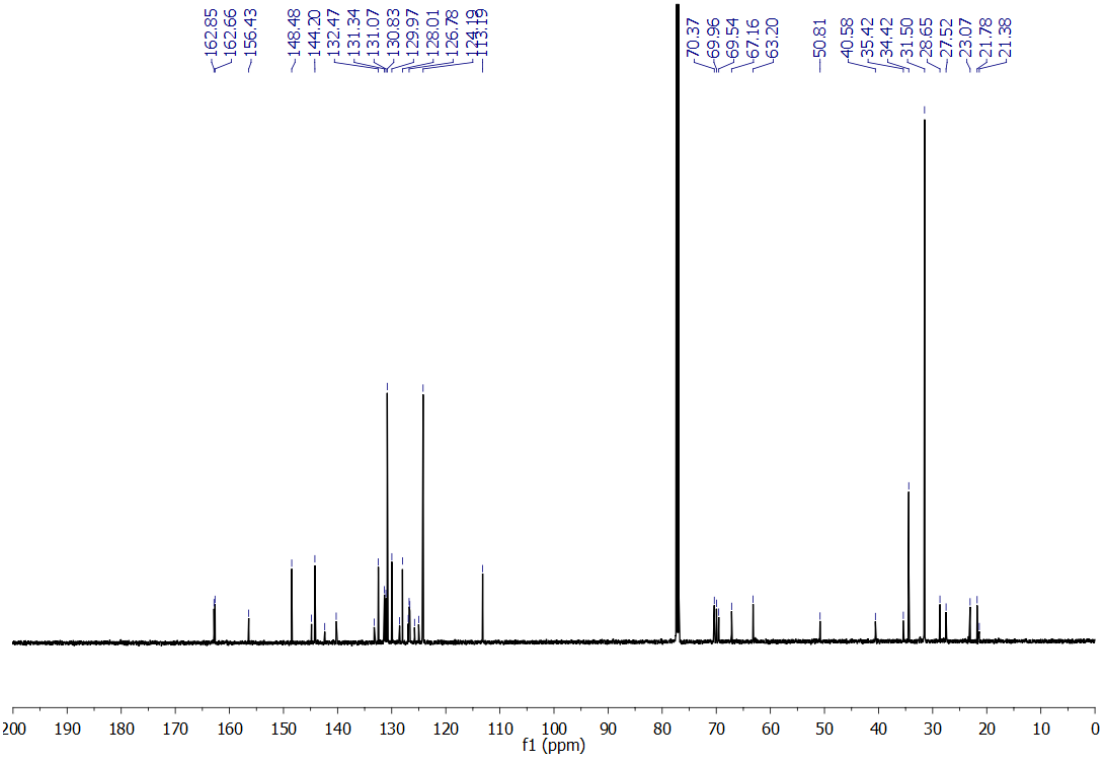


Figure S15: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9**.

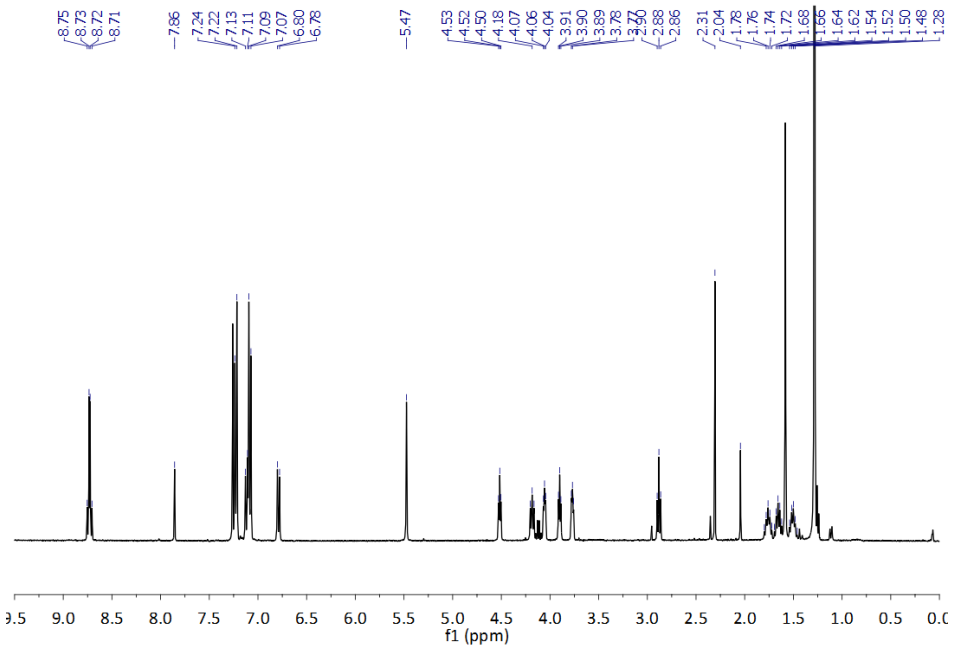


Figure S16: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**.

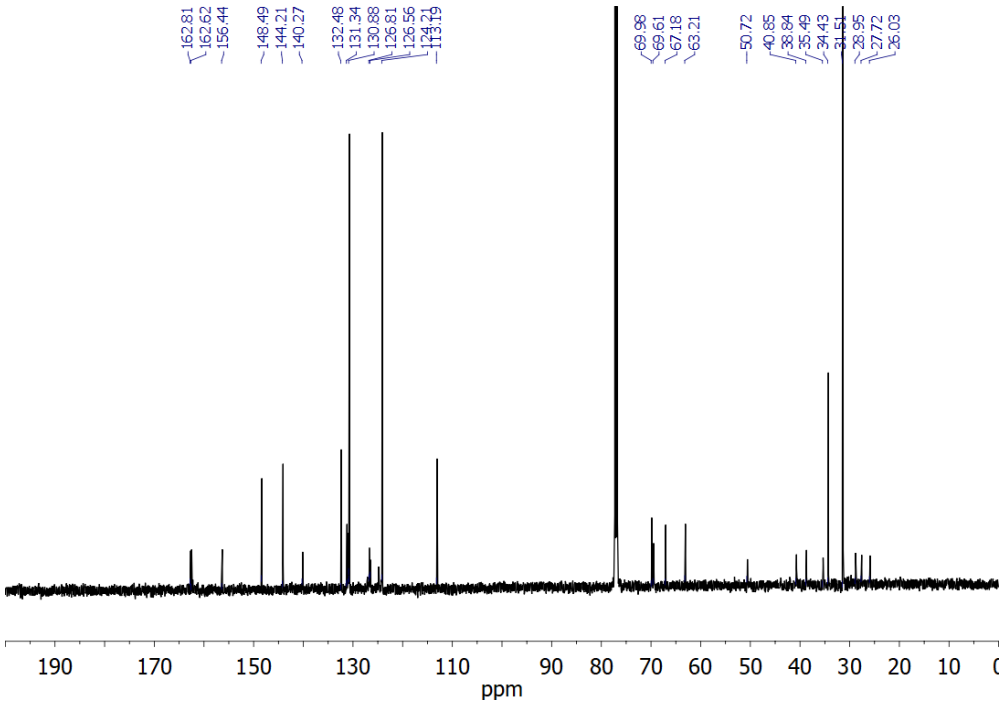


Figure S17: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**.

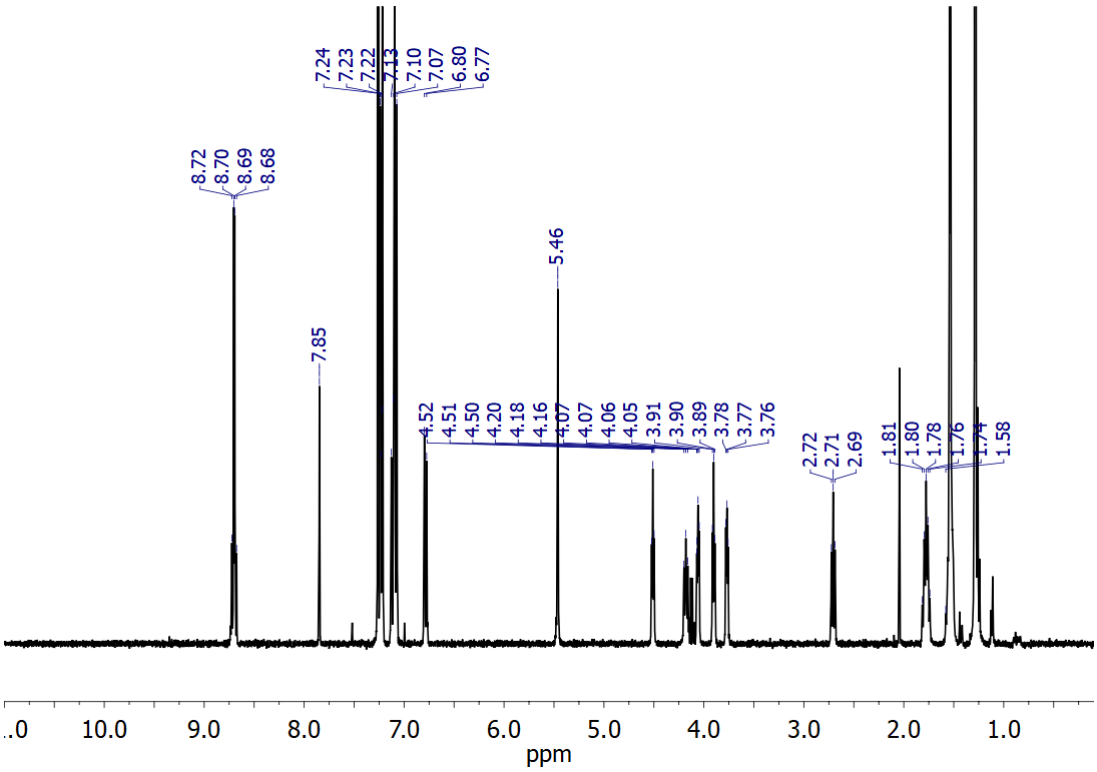


Figure S18: ^{1}H NMR (400 MHz, $CDCl_3$) of naphthalene diimide disulfide **12**.

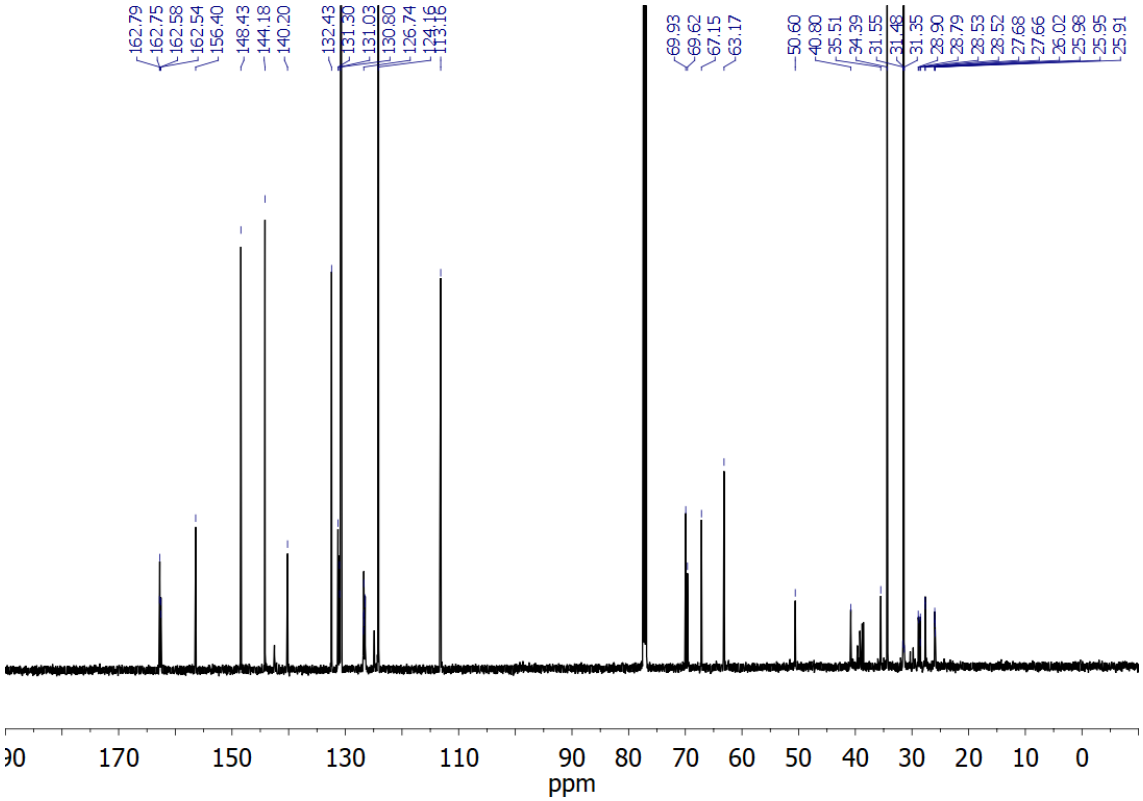


Figure S19: ^{13}C NMR (100 MHz, $CDCl_3$) of naphthalene diimide disulfide **12**.

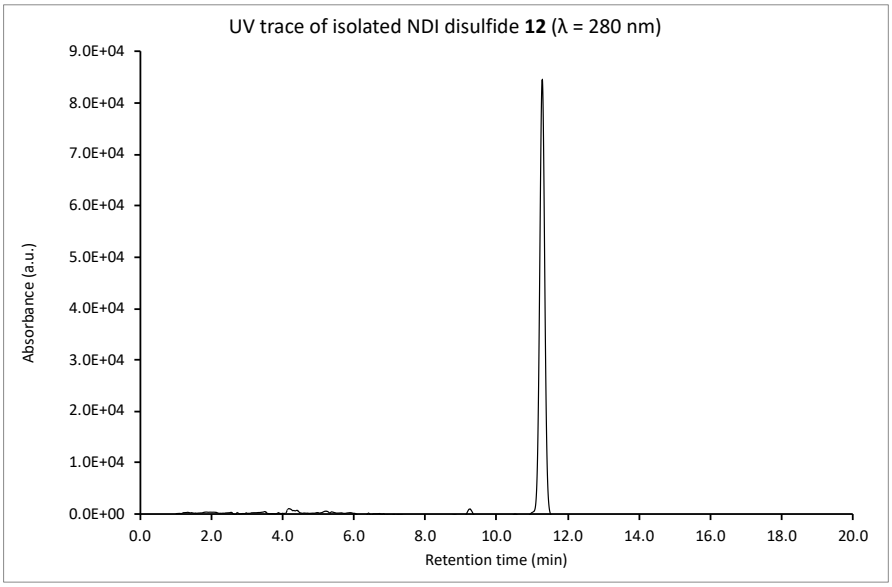


Figure S20: HPLC trace of naphthalene diimide disulfide **12**.

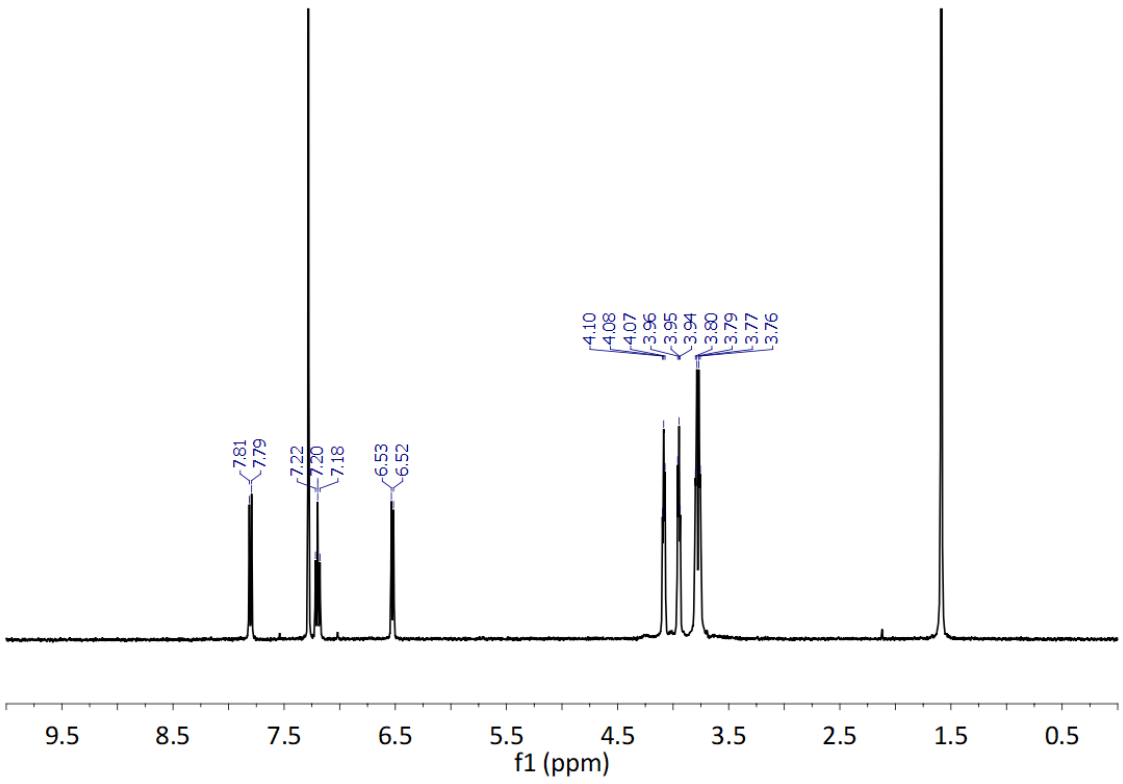


Figure S21: ^{1}H NMR (400 MHz, $CDCl_3$) of 1,5-dinaphtho[38]crown-10 macrocycle **3**.

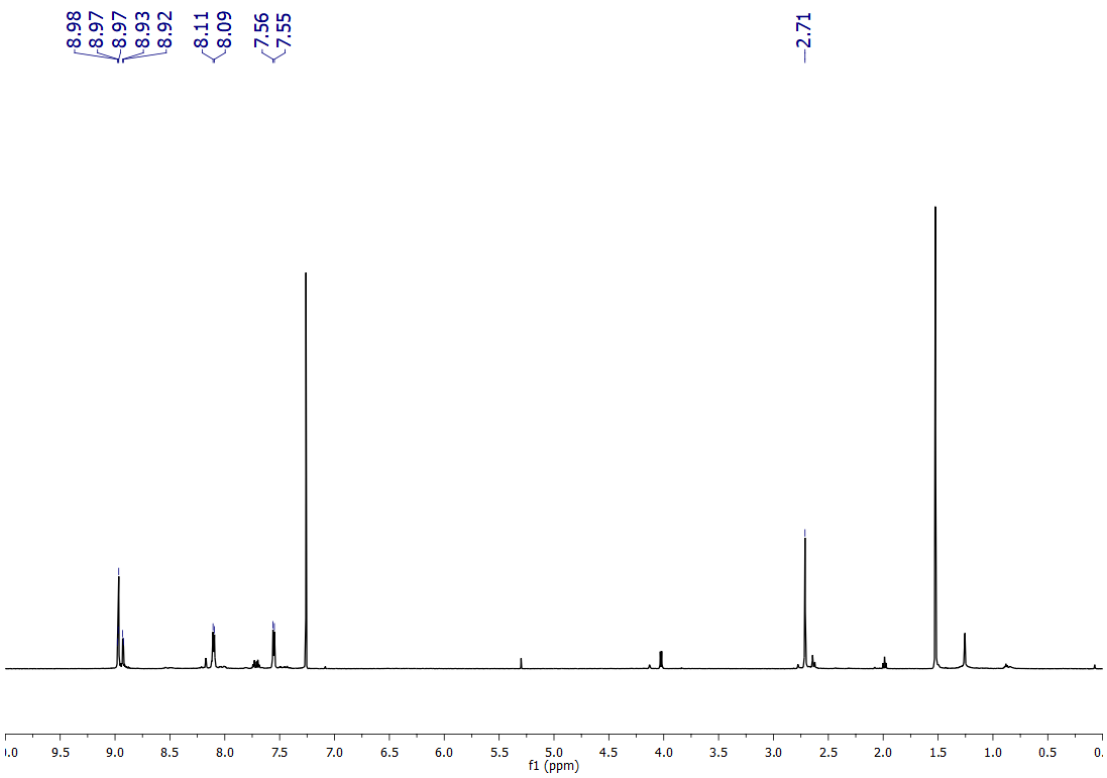


Figure S22: ^{1}H NMR (400 MHz, $CDCl_3$) of porphyrin thiol **5**.

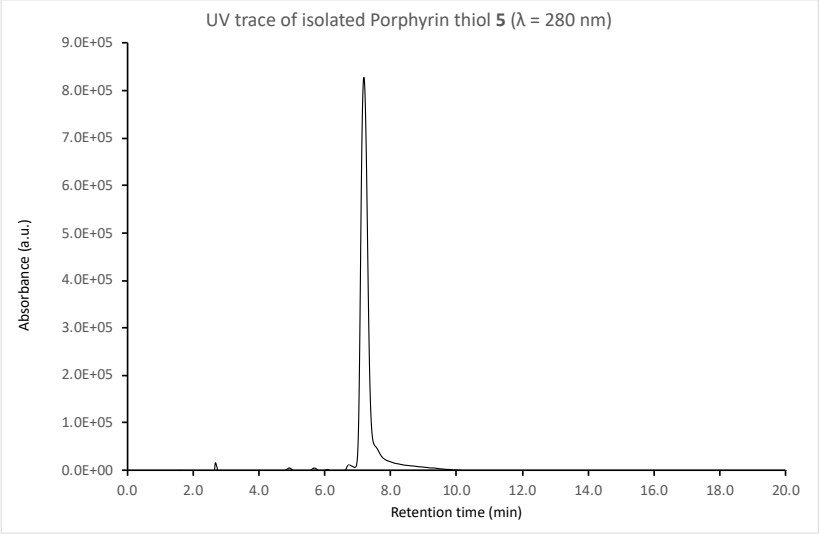


Figure S23: HPLC trace of porphyrin thiol **5**.

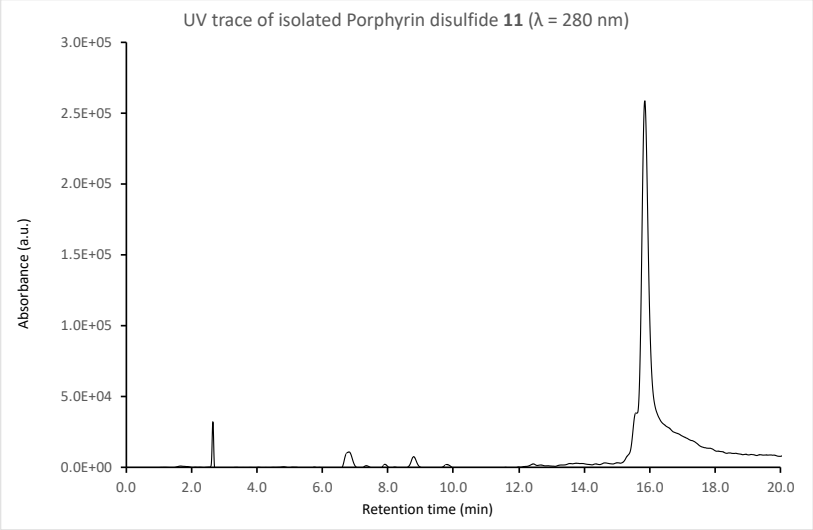


Figure S24: HPLC trace of porphyrin disulfide **11**.

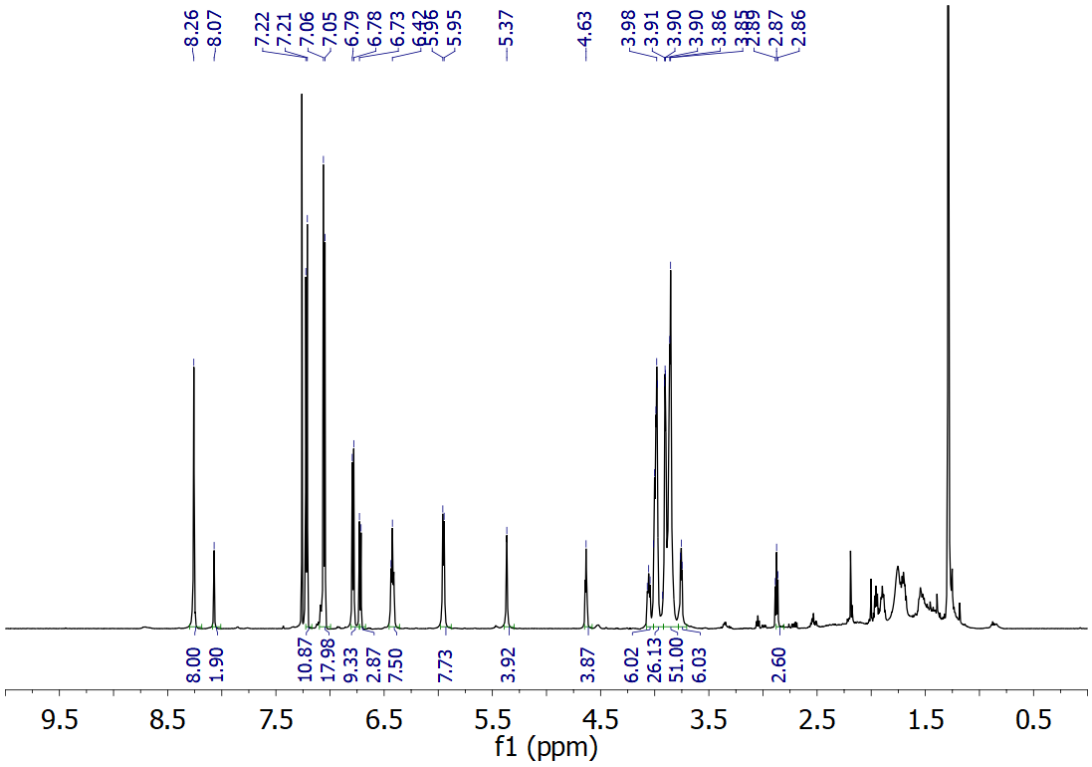


Figure S25: ^{1}H NMR (400 MHz, $CDCl_3$) of naphthalene diimide [3]rotaxane **16**.

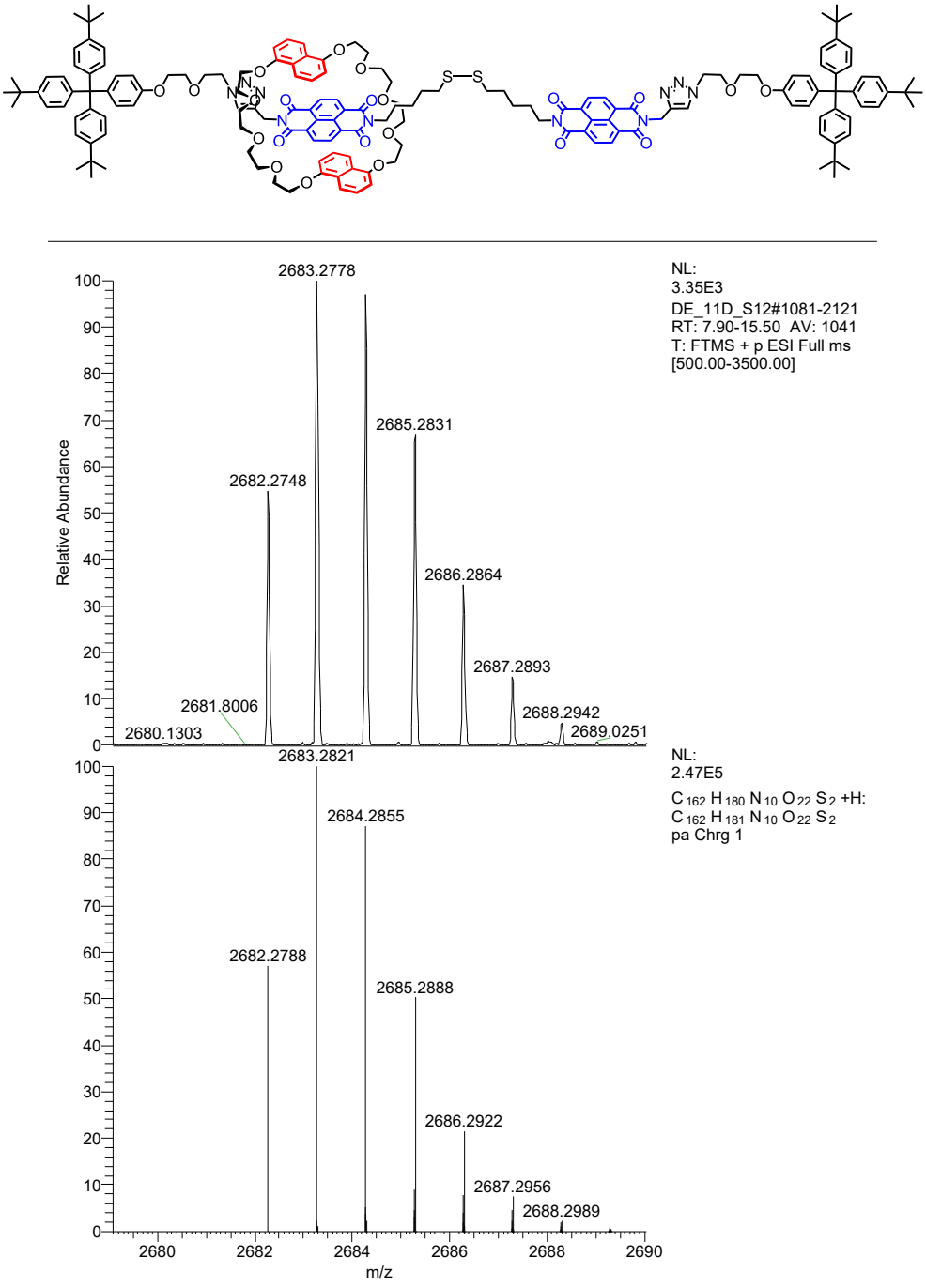
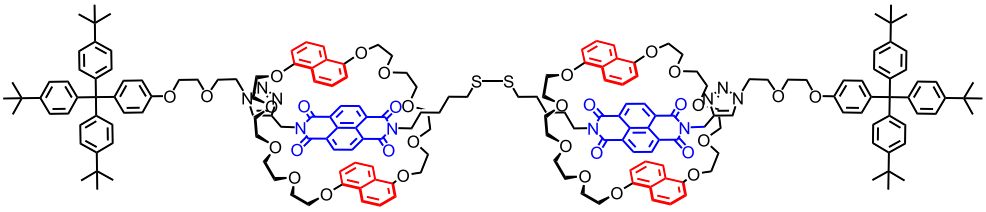


Figure S26: Mass spectrum of naphthalene diimide [2]rotaxane **15** (top) compared to expected isotopic distribution for the M+H species (bottom).



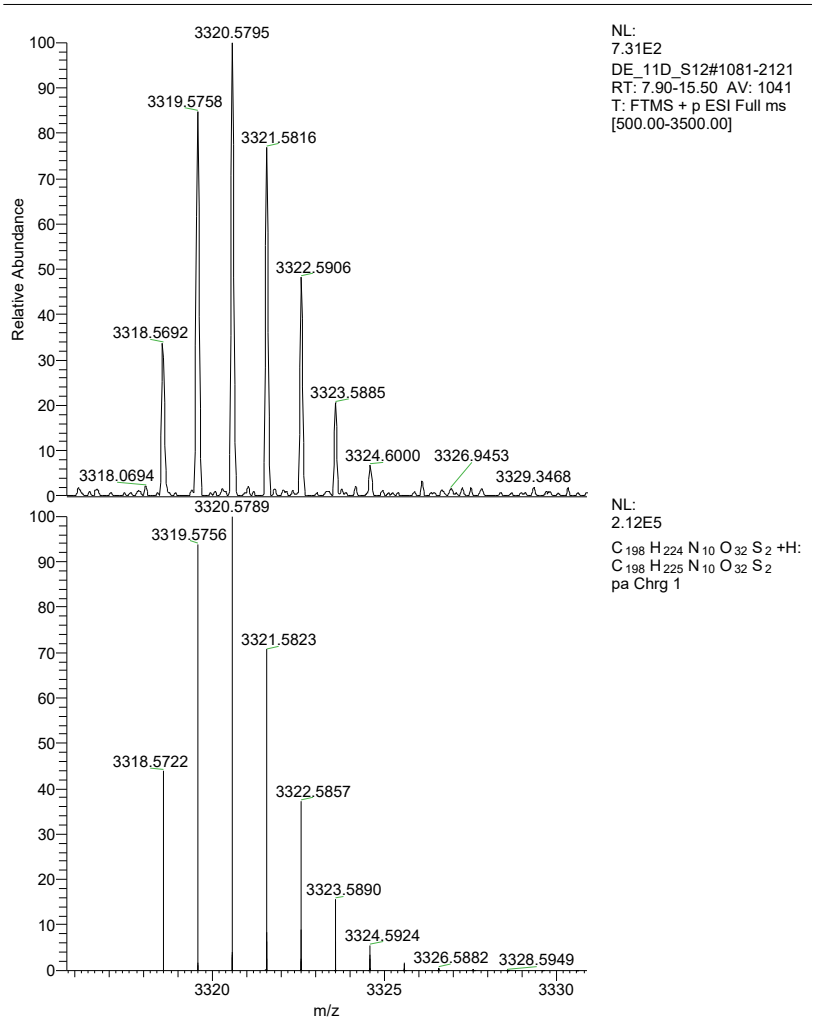


Figure S27: Mass spectrum of naphthalene diimide [3] rotaxane **16** (top) compared to expected isotopic distribution for the M+H species (bottom).

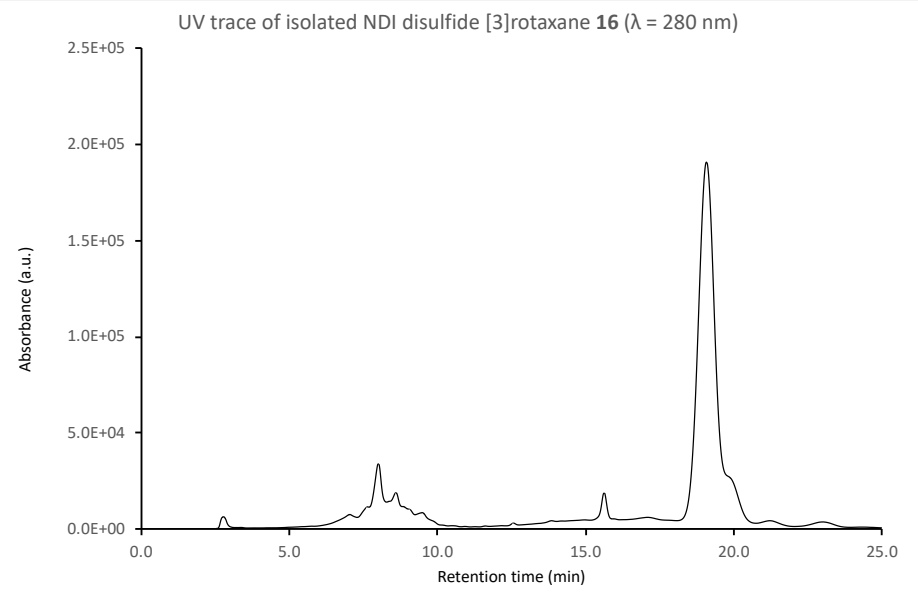


Figure S28: HPLC trace of naphthalene diimide [3] rotaxane **16**

References

[1] H. Wilson, S. Byrne, N. Bampos, K. M. Mullen, *Org. Biomol. Chem.* **2013**, *11*, 2105-2115.
[2] K. M. Mullen, M. J. Gunter, *J.Org. Chem.,* **2008**, *73*, 3336-3350.