Supporting information for:

Exploiting Donor–Acceptor Interactions in Aqueous Dynamic Combinatorial Libraries: exploratory studies of simple systems

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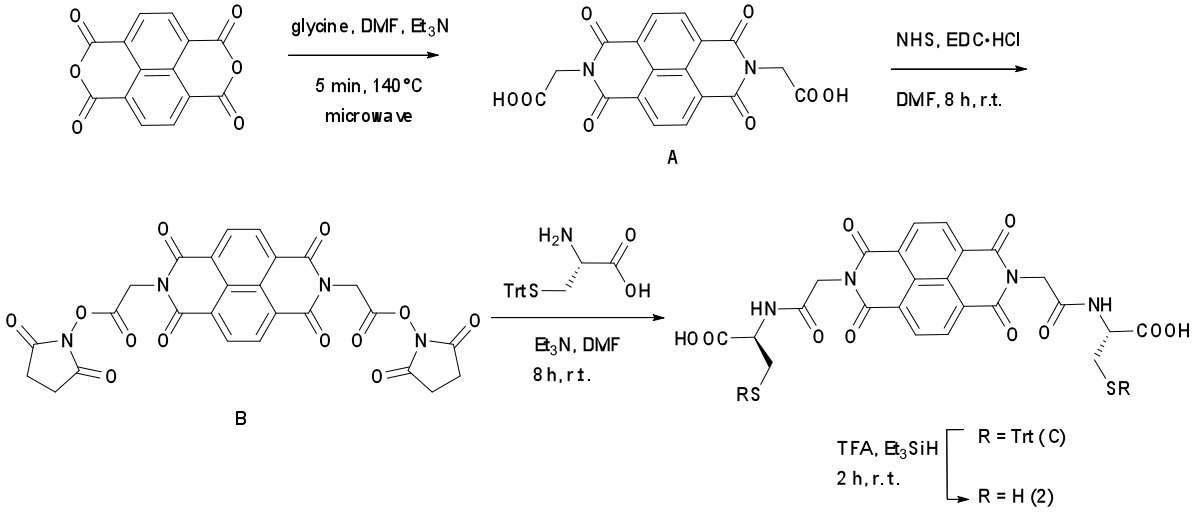
Synthesis

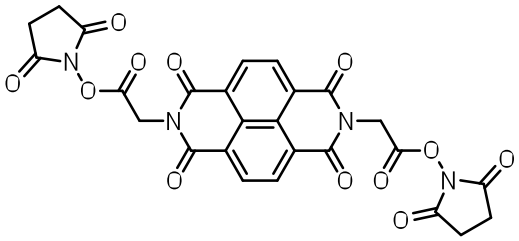
General. All solvents were of reagent grade. Acetone was distilled and dimethylformamide (DMF) was dried over 4 Å molecular sieve. All commercially purchased chemicals (1,5-dihydroxynaphthalene, methyl bromoacetate, *N*-hydroxysuccinimide, *S*-trityl-L-cysteine, glutathione, triethylamine, trifluoroacetic acid (TFA), triethylsilane *N*-(3-(dimethylaminopropyl))-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl), **G3**–**G8** and **G10**) were used as received. Building blocks **1**[1,2] and **4**,[3] and guests **G1** and **G2**[2,4,5] and **G9**[2] were synthesised according to published procedures. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-400 or Avance 500 TCI Cryo Spectrometers. All signals were internally referenced to the solvent residue. All high-resolution (HR) electrospray ionisation (ESI) mass spectra were recorded on Waters LCT Premier XE instrument. Melting points were measured by a Gallenkamp instrument in an open capillary.

- **Synthesis of NDI building block 2**

NDI dithiol building block **2** was synthesised according to the following scheme:

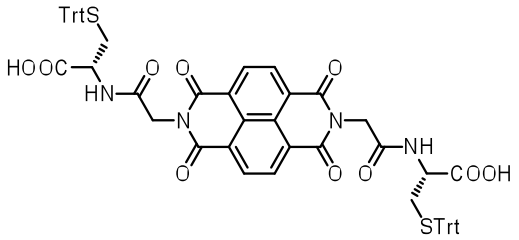


*Synthesis of **B**:*



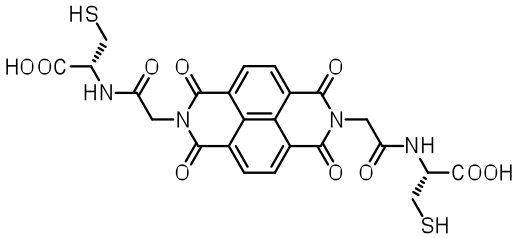
To a mixture of **A**[1] (0.57 g, 1.5 mmol) and *N*-hydroxylsuccinimide (0.70 g, 6.0 mmol) was dissolved in DMF (50 ml) and cooled with an ice bath. EDC·HCl (1.15 g, 6.0 mmol) was added to the solution, and the mixture was stirred in the melting ice bath for 15 minutes. Stirring was continued at room temperature for 8 hours. The precipitate formed was collected by filtration and dried *in vacuo*. Yield: 0.76 g, 88%. ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 8.80 (s, 4 H, NDI), 5.28 (s, 4 H, Gly), 2.82 (s, 8 H, NC(O)CH_2). ^{13}C{^{1}H} NMR (125.75 MHz, DMSO-d_6, 300 K) δ (ppm): 169.9, 164.6, 162.2, 131.4, 126.6, 126.1, 25.6.

*Synthesis of **C**:*



To a mixture of **B** (0.63 g, 1.09 mmol) and *S*-trityl-L-cysteine (0.87 g, 2.4 mmol) in DMF (50 ml) was added Et_3N (0.4 ml, 2.9 mmol). The solution was stirred under N_2 for 8 hours at room temperature. Solvent was removed and acetone (15 ml) was added to the residue. The acetone mixture was added dropwise to a vigorously stirred solution of 1 M HCl (200 ml). The precipitate was collected by filtration and dried. The product was purified by silica flash column chromatography ($CHCl_3$/MeOH = 8:1 with 0.1% formic acid). Yield: 0.28 g, 24%. M.p.: >300 °C (decomposed). ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 8.72 (s, 4 H, NDI), 8.58 (br, 2 H, NH), 7.36–7.22 (m, 30 H, Trt), 4.80 (d, J = 16 Hz, 2 H, Gly), 4.73 (d, J = 16 Hz, 2 H, Gly), 4.17 (dd, J = 7.6 Hz, 13 Hz, 2 H, α–Cys), 2.46–2.37 (m, 4 H, β–Cys). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6, 300 K) δ (ppm): 171.4, 166.1, 162.4, 144.4, 130.8, 129.2, 128.2, 126.8, 126.4, 65.9, 51.8, 42.6, 33.8. HRMS (ESI+) calcd. for $C_{62}H_{48}N_4O_{10}S_2Na$ $[M+Na]^+$ (*m/z*): 1095.2704, found: 1095.2732.

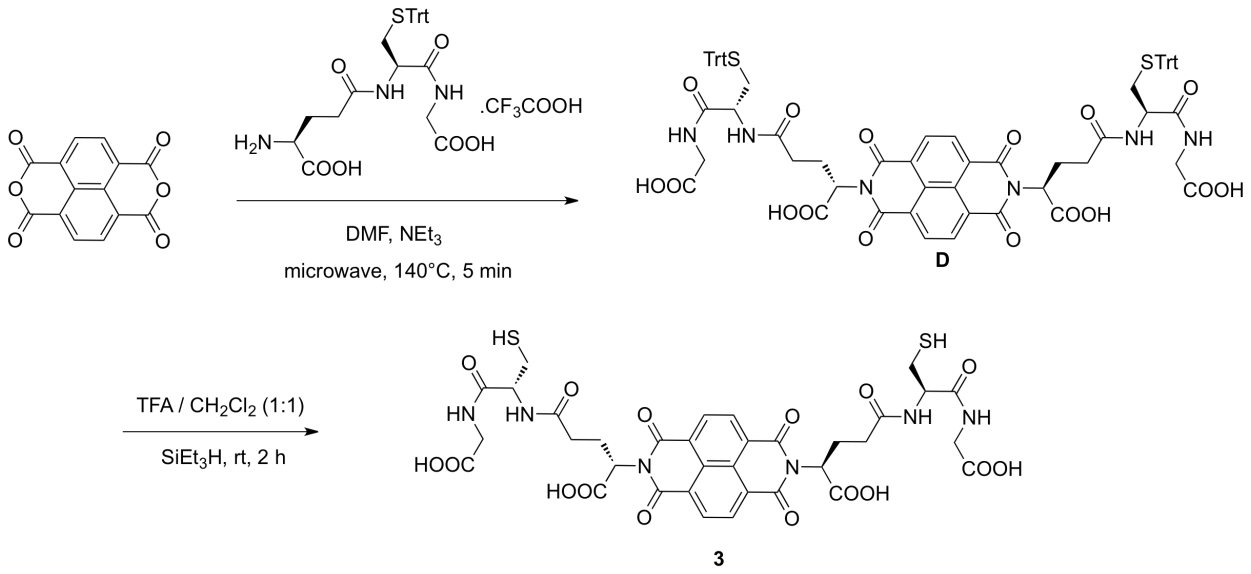
*Synthesis of **2**:*



To a Schlenk flask charged with **C** (0.28 g, 0.26 mmol) was added degassed TFA (3 ml, 40 mmol). The solution was stirred under N_2 at room temperature for 1.5 hour and added $SiEt_3H$ (0.2 ml, 1.3 mmol). Stirring was continued for 30 minutes. Volatiles were removed *in vacuo*. The solid left was washed with Et_2O (20 ml) and collected by filtration. Yield: 0.13 g, 87%. M.p.: > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 12.93 (br, 2 H, COOH), 8.73 (s, 4 H, NDI), 8.68 (d, J = 7.9 Hz, 2 H, NH), 4.82 (d, J = 16 Hz, 2 H, Gly), 4.77 (d, J = 16 Hz, 2 H, Gly), 4.48–4.43 (m, 2 H, α–Cys), 2.91–2.84 (m, 2 H, β–Cys), 2.81–2.73 (m, 2 H, β–Cys), 2.40 (t, J = 8.4 Hz, 2 H, SH). ^{13}C{^{1}H} NMR (100.60 MHz, DMSO-d_6, 300 K) δ (ppm): 171.7, 162.8, 152.4, 131.2, 129.4, 126.6, 54.9, 42.9, 26.0. HRMS (ESI+) calcd. for $C_{24}H_{21}N_4O_{10}S_2$ $[M+H]^+$ (*m/z*): 589.0699, found: 589.0718.

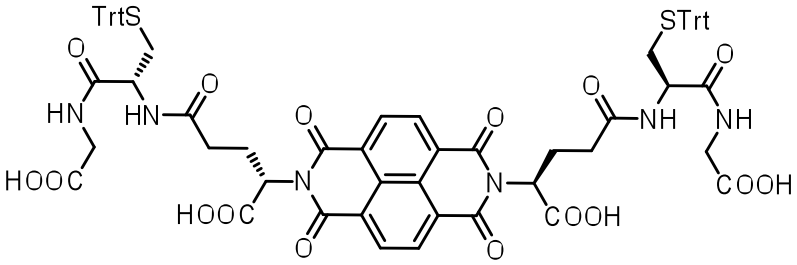
- **Synthesis of NDI building block 3**

NDI dithiol building block **3** was synthesised according to the following scheme:



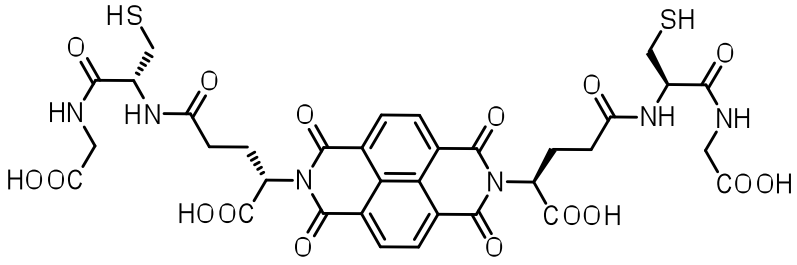
Trityl protected glutathione was synthesised according to the literature.[6]

*Synthesis of **D***:



1,4,5,8-Naphthalenetetracarboxylic dianhydride (80 mg, 0.300 mmol) and the trityl protected glutathione[6] (396 mg, 0.600 mmol) were suspended in 3 mL of DMF in a pressure-tight 20-mL microwave vial. To this suspension was added 0.1 mL of dry Et_3N. The suspension was sonicated until the mixture became homogeneous. The reaction mixture was heated for 5 min at 140 ± 5 °C (direct flask temperature measurement) under microwave irradiation using a dedicated microwave system. The solvent was removed under reduced pressure. The residue was taken up into a minimum volume of acetone. This solution was added under stirring to 100 mL of 1 M HCl. The resulting suspension was filtered using a Büchner funnel. The solid was then washed with 100 mL deionized water and dried *in vacuo*. The product was obtained in the form of a brown solid. Yield: 306 mg, 77%. M.p.: > 250 °C (decomposed). ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 13.1–12.3 (br, 4 H, COOH), 8.69 (s, 4 H, NDI), 8.06 (t, J = 6 Hz, 2 H, NH–Gly), 7.99 (d, J = 8 Hz, 2 H, NH–Cys), 7.33–7.11 (m, 30 H, Trt), 5.57 (dd, J = 16 Hz, 11 Hz, 2 H, α–Glu), 4.29 (dd, J = 14 Hz, 8 Hz, 2 H, α–Cys), 3.64 (d, J = 5.6 Hz, 4 H, Gly), 2.42–2.21 (m, 12 H). ^{13}C{^{1}H} NMR (100.60 MHz, DMSO-d_6, 300 K) δ (ppm): 171.6, 171.1, 170.8, 170.4, 162.7, 144.7, 131.4, 129.4, 128.7, 128.4, 127.0, 126.7, 126.4, 66.1, 53.5, 51.5, 34.2, 32.2, 31.0, 24.6. HRMS (ESI+) calcd. for $C_{72}H_{63}N_6O_{16}S_2$ $[M+H]^+$ (*m/z*): 1331.3736, found: 1331.3654.

*Synthesis of **3***:

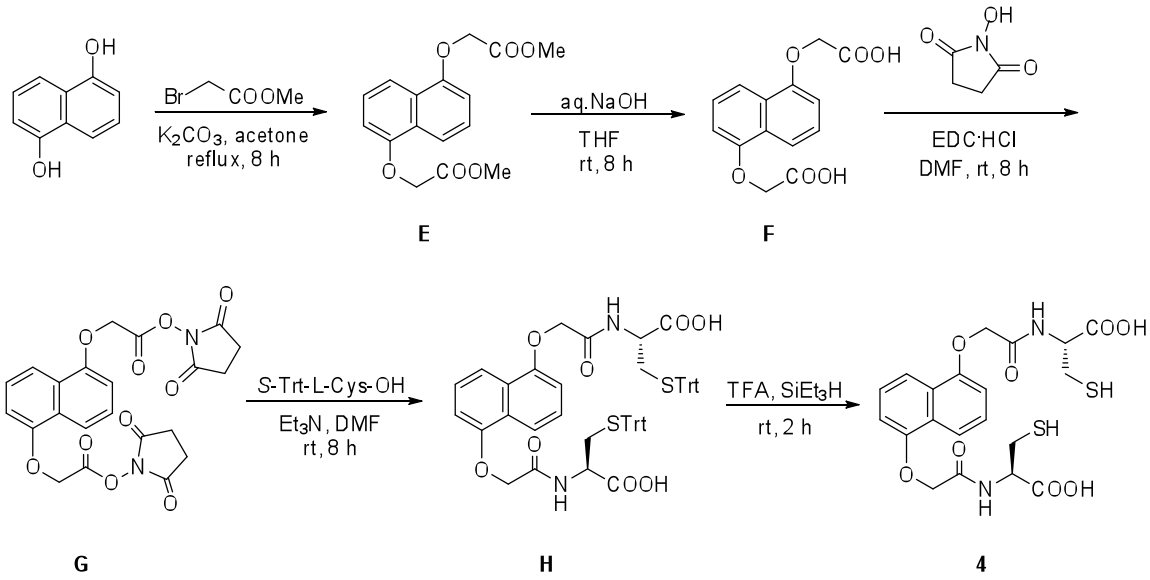


To a Schlenk flask charged with **D** (306 mg, 0.230 mmol) was added degassed trifluoroacetic acid (3 ml, 40 mmol), dichloromethane (3 ml), and triethylsilane (110 µl, 0.690 mmol). The solution was stirred under N_2 at room temperature. After 2 hours, all the volatiles were removed in vacuo. The residue was washed with Et_2O (20 ml) and dried *in vacuo*. Yield: 154 mg, 79 %. M.p.: > 250 °C (decomposed). ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 12.85 (br, 4 H,

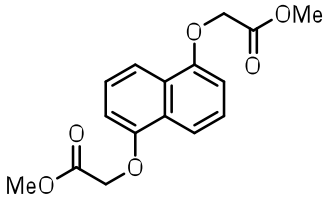
COOH), 8.75 (s, 4 H, NDI), 8.23 (t, *J* = 6 Hz, 2 H, NH–Gly), 7.90 (d, *J* = 8 Hz, 2 H, NH–Cys), 5.58 (dd, *J* = 9 Hz, 5 Hz, 2 H, α–Glu), 4.35 (dd, *J* = 13 Hz, 7 Hz, 2 H, α–Cys), 3.73 (dd, *J* = 11 Hz, 6 Hz, 4 H, Gly), 2.80–2.63 (m, 4 H), 2.42–2.24 (m, 10 H). $^{13}C\{^{1}H\}$ NMR (100.62 MHz, DMSO-d_6, 300 K): 173.4, 171.8, 171.3, 170.8, 170.4, 162.8, 131.6, 65.3, 56.7, 54.8, 32.0, 26.7, 24.4, 15.5. HRMS (ESI+) calcd. for $C_{34}H_{35}N_6O_{16}S_2$ $[M+H]^+$ (*m/z*): 847.1545, found: 847.1571.

- **Synthesis of DN building block 4**

DN dithiol building block **4** was synthesised according to the following scheme:

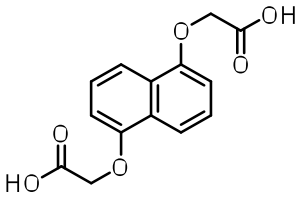


*Synthesis of DN ester **E***:



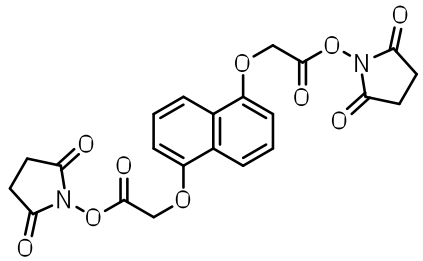
To a solution of 1,5-dihydroxynaphthalene (1.61 g, 10 mmol) in acetone (200 ml) was added finely ground K_2CO_3 (7 g, 50 mmol) and methyl bromoacetate (2.2 ml, 22 mmol). The mixture was heated to reflux for 8 hours. The resulting solution was filtered, Et_2O (100 ml) was added, and washed successively with 1 M HCl (50 ml), water (50 ml) and brine (50 ml). Evaporation of solvents from the organic layer gave the product as a yellow crystalline solid which was used in the next step without further purification. Yield: 3.06 g, quant. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ (ppm): 7.98 (d, *J* = 8.4 Hz, 2 H, DN), 7.36 (t, *J* = 7.6 Hz, 2 H, DN), 6.76 (d, *J* = 7.2 Hz, 2 H, DN), 4.81 (s, 4 H, CH_2), 3.82 (s, 6 H, CH_3).

*Synthesis of the DN acid **F***:



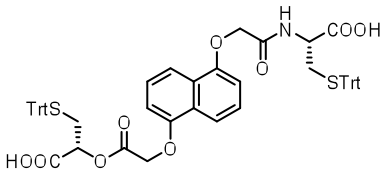
To a solution of **E** (3.04 g, 10 mmol) in THF (150 ml) was added 0.5 M NaOH (200 ml). The mixture was vigorously stirred at room temperature for 8 hours, and poured into 1 M HCl (200 ml). The precipitate formed was collected by filtration, washed with Et_2O and dried. Yield: 2.40 g, 87%. M.p.: >250 °C (decomposed). ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 13.05 (br, 2 H, COOH), 7.80 (d, J = 8.8 Hz, 2 H, DN), 7.40 (t, J = 8.0 Hz, 2 H, DN), 6.91 (d, J = 7.6 Hz, 2 H, DN), 4.87 (s, 4 H, CH_2). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6, 300 K) δ (ppm): 170.0, 153.1, 125.9, 125.3, 114.3, 106.0, 64.9. HRMS (ESI+) calcd. for $C_{14}H_{12}O_6Na$ $[M+Na]^+$ (*m/z*): 299.0532, found: 299.0527.

*Synthesis of active ester **G***:



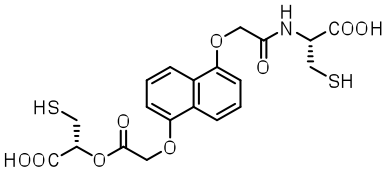
A mixture of **F** (0.41 g, 1.5 mmol) and *N*-hydroxylsuccinimide (0.70 g, 6.0 mmol) was dissolved in DMF (50 ml) and cooled with an ice bath. EDC·HCl (1.15 g, 6.0 mmol) was added to the solution, and the mixture was stirred in the melting ice bath for 15 minutes. Stirring was continued at room temperature for a further 8 hours. The precipitate formed was collected by filtration and dried *in vacuo*. Yield: 0.60 g, 85%. M.p.: 240–243 °C (decomposed). ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 7.84 (d, J = 8.4 Hz, 2 H, DN), 7.46 (t, J = 8.0 Hz, 2 H, DN), 7.08 (d, J = 7.6 Hz, 2 H, DN), 5.53 (s, 4 H, OCH_2), 2.84 (s, 8 H, $NC(O)CH_2$). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6, 300 K) δ (ppm): 169.9, 165.3, 152.4, 125.8, 125.6, 114.8, 106.8, 63.4, 25.5. HRMS (ESI+) calcd. for $C_{22}H_{18}N_2O_{10}Na$ $[M+Na]^+$ (*m/z*): 493.0859, found: 493.0848.

*Synthesis of trityl protected dithiol **H***:



To a mixture of **G** (0.47 g, 1 mmol) and *S*-trityl-L-cysteine (0.80 g, 2.2 mmol) in DMF (50 ml) was added Et_3N (0.3 ml, 2.2 mmol). The solution was stirred under N_2 for 8 hours at room temperature. Solvent was removed and the residue re-dissolved in acetone (10 ml). The acetone solution was added dropwise to a vigorously stirred solution of 1 M HCl (200 ml). The yellowish-brown solid was collected by filtration and dried. Yield: 0.79 g, 82%. M.p.: 207–209 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 12.91 (br, 2 H, COOH), 8.43 (d, J = 8.4 Hz, 2 H, NH), 7.91 (d, J = 8.4 Hz, 2 H, DN), 7.34–7.22 (m, 32 H, Trt, DN), 6.97 (d, J = 7.6 Hz, 2 H, DN), 4.73 (s, 4 H, OCH_2), 4.33 (dt, J = 5.2 Hz, 8.4 Hz, 2 H, α), 2.70 (dd, J = 8.4 Hz, 12.0 Hz, 2 H, β); ^{1}H NMR (400 MHz, acetone-d_6, 300 K) δ (ppm): 7.98 (d, J = 8.0 Hz, 2 H, NH), 7.74 (d, J = 8.0 Hz, 2 H, DN), 7.40–7.21 (m, 32 H, Trt, DN), 7.05 (d, J = 7.6 Hz, 2 H, DN), 4.75 (s, 4 H, OCH_2), 4.63 (ddd, J = 8.0 Hz, 6.8 Hz, 5.2 Hz, 2 H, α), 2.84 (dd, J = 12 Hz, 6.8 Hz, 2 H, β), 2.72 (dd, J = 12 Hz, 5.2 Hz, 2 H, β). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6, 300 K) δ (ppm): 171.3, 167.4, 153.0, 144.2, 129.1, 128.1, 126.8, 125.8, 125.3, 114.8, 106.7, 67.2, 66.2, 50.8, 33.0. HRMS (ESI+) calcd. for $C_{58}H_{50}N_2O_8S_2Na$ $[M+Na]^+$ (*m/z*): 989.2906, found: 989.2911.

*Synthesis of DN dithiol **4***:



To a Schlenk tube charged with **H** (0.48 g, 0.5 mmol) was added degassed TFA (5 ml, 65 mmol) under N_2. The solution was stirred at room temperature for 1.5 hour, and triethylsilane added (0.4 ml, 2.5 mmol). Immediate precipitation was observed, and the mixture was stirred for an additional 30 minutes. Volatiles were removed *in vacuo*. The resulting yellow solid was washed with Et_2O (50 ml). Yield: 0.23 g, 94%. M.p.: 175–179 °C (decomposed). ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) δ (ppm): 13.01 (br, 2 H, COOH), 8.37 (d, J = 7.6 Hz, 2 H, NH), 7.91 (d, J = 8.4 Hz, 2 H, DN), 7.42 (t, J = 8.0 Hz, 2 H, DN), 7.00 (d, J = 8.0 Hz, 2 H, DN), 4.78 (s, 4 H, OCH_2), 4.55 (dt, J = 7.2 Hz, 4.8 Hz, 2 H, α), 3.02–2.95 (m, 2 H, β), 2.93–2.86 (m, 2 H, β), 2.43 (t, J = 8.4 Hz, 2 H, SH). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6, 300 K) δ (ppm): 171.3, 167.6, 153.0, 125.8, 125.4, 114.7, 106.6, 67.2, 53.9, 25.4. HRMS (ESI+) calcd. for $C_{20}H_{23}N_2O_8S_2$ $[M+H]^+$ (*m/z*): 483.0896, found: 483.0907.

DCL setup and HPLC/LCMS methods

A typical analytical DCL was prepared in 1 ml scale by dissolving the building blocks in 10 mM NaOH to give a 5 mM solution, followed by titration with 100 mM NaOH to pH 8. Templates or salt ($NaNO_3$) were added either as a concentrated solution or directly in solid form where appropriate. The library solutions were stirred in close-capped vials for at least 5 days before HPLC or LCMS analysis. Preparative DCLs were prepared using the same method in 10 ml scale.

HPLC grade MeOH (Fisher or Romil) and formic acid (FA) (Fluka or Romil) were used without further purification. MilliQ water was obtained from a Millipore water purification system. HPLC analyses were carried out on Hewlett Packard 1050 or 1100 systems coupled to diode array or multiple wavelength UV/Vis detectors. Data was processed using HP ChemStation software. In general, analytical separations were achieved by injecting 5 μl aliquots of 5 mM library solution onto a reverse phase Symmetry C_8 column (150 x 4.6 cm, 3 μm particle size). Separations were achieved by running the column either with THF/water, acetonitrile/water, or MeOH/water as eluent at a flow rate of 1 ml/min at 32.5 °C. UV/Vis absorbance was monitored at 292 nm (for 1,5-DN containing DCLs) and 383 nm (for NDI containing DCLs).

Preparative separations were performed on a HP 1050 system coupled to a single variable wavelength UV detector. Samples were injected onto a reverse phase SymmetryPrep C_{18} column (300 x 7.8 mm, 7 μm particle size) by using a Gilson 234 auto-injector. Solvent systems used were the same as that for the analytical separation with elution profiles modified from the corresponding analytical methods. Fractions were manually collected and combined. Solvents were removed from the combined fractions by a rotary evaporator and the isolated sample stored in a fridge.

LCMS was carried out on an Agilent 1100 LC/MSD trap XCT system. Data was processed using ChemStation and LC/MSD trap software. Influx of analyte solution was maintained at a flow rate of 50 μl/min and ionised with an electrospray source (ESI). ESI-MS spectra (negative ion) were acquired in ultra scan mode with drying temperature of 350 °C, nebuliser pressure of 18 psi, drying gas flow of 5 l/min. Capillary voltage was set to 4000 V. An ICC target of 20,000 ions or accumulation time of 100 ms, and a target mass of 1000 was set for the trap. Unless otherwise stated, dissociation amplitude of 1 V was used for MS/MS studied.

Analytical HPLC methods for DCLs of NDIs

*Analytical HPLC method for DCL containing only NDI **1** (5 mM total):*

Time/min	Water (0.1% FA)	THF
0	60%	40%
40	60%	40%

Analytical HPLC method of the other NDI DCLs (5 mM total):

Time/min	Water (0.1% FA)	Acetonitrile (0.1% FA)
0	90%	10%
30	30%	70%
40	30%	70%

- **Analytical HPLC methods for DCLs of DNs**

*Analytical HPLC method for DCLs containing either **4** or **5** (5 mM total):*

Time/min	Water (0.1% FA)	MeOH (0.1% FA)
0	40%	60%
9	40%	60%
20	0%	100%
30	0%	100%

*Analytical method for DCL containing both **4** and **5** (1:1, 5 mM total):*

Time/min	Water (0.1% FA)	MeOH (0.1% FA)
0	45%	55%
6	45%	55%
7	40%	60%
14	40%	60%
20	20%	80%
30	20%	80%

- **Preparative HPLC methods**

Preparative HPLC methods:

DCL	*NDI **1***	*DN **4** or **5***
Injection volume	200 µl	300 µl
Flow rate	2.5 ml/min	3 ml/min
Temperature	45 °C	32.5 °C
Elution	45% THF/water (0.1% FA, isocratic elution)	65% MeOH/water (0.1% FA, isocratic elution)
Run time	35 minutes	20 minutes

HPLC analysis of DCLs

- **HPLC analysis of DCLs of NDI building block 2**

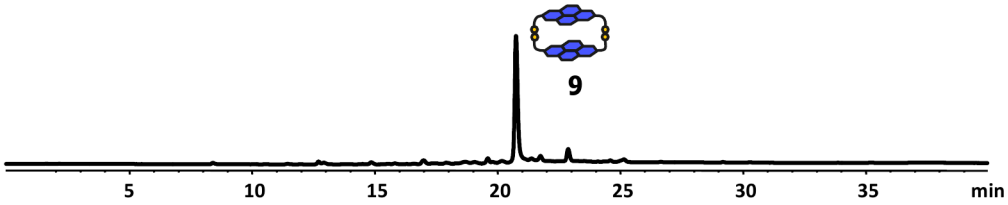


Figure S1. HPLC analysis of 5 mM DCL of **2** (5 mM). No change was observed upon addition of template (2.5 mM) or $NaNO_3$ (1M).

- **HPLC analysis of DCLs of NDI building block 3**

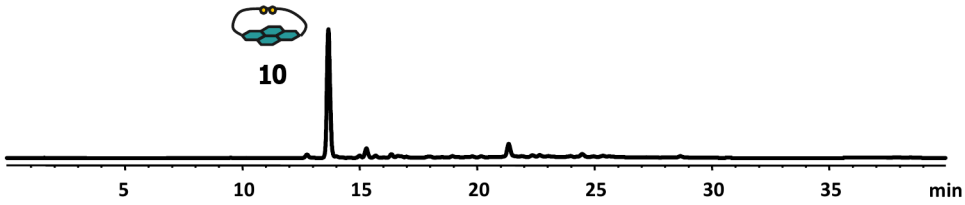


Figure S2. HPLC analysis of 5 mM DCL of **3** (5 mM). No change was observed upon addition of template (2.5 mM) or $NaNO_3$ (1M).

- **HPLC analysis of DCLs of NDI building blocks 1 and 2**

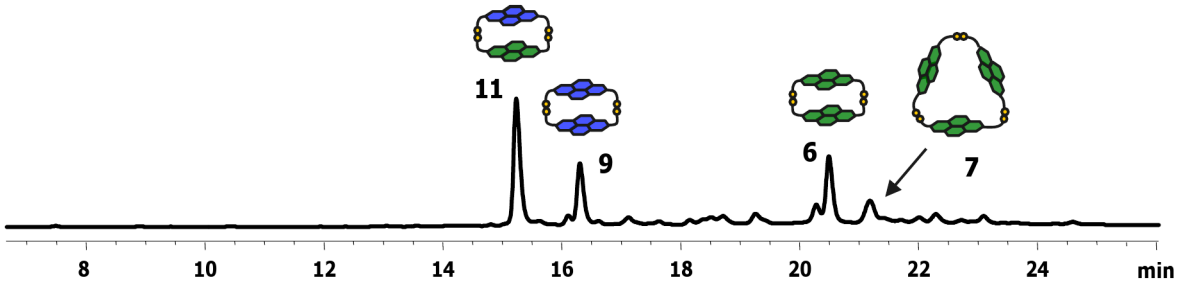


Figure S3. HPLC analysis of 5 mM DCL of **1** and **2** (1:1 molar ratio, 5 mM total).

Table S1. Amplification factors of library members of DCL of **1** and **2** (1:1 molar ratio, 5 mM total, 2.5 mM guest). In the presence of the other templates, no change in the library distribution was observed.

Guest	**6**	**7**	**9**	**11**
G1	0.8	0.8	0.8	1.2
G2	0.1	0.2	0.4	1.9

- **HPLC analysis of DCLs of NDI building blocks 1 and 3**

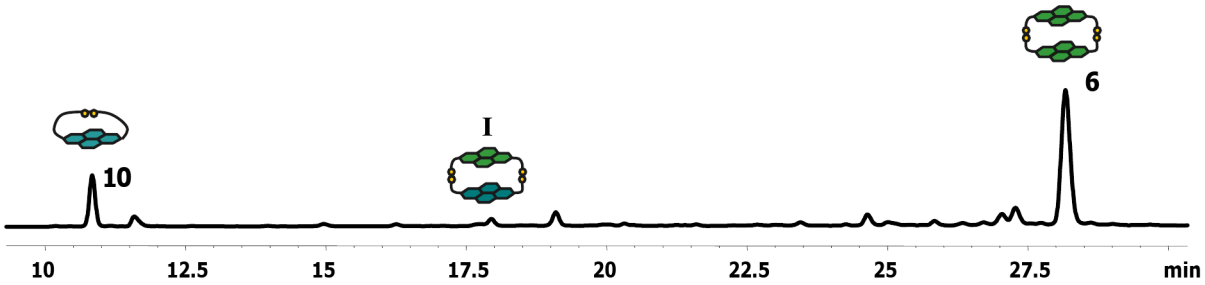


Figure S4. HPLC analysis of 5 mM DCL of **1** and **3** (1:1 molar ratio, 5 mM total).

Table S2 Amplification factors of library members of DCL of **1** and **3** (1:1 molar ratio, 5 mM total, 2.5 mM guest). In the presence of the other templates, no change in the library distribution was observed.

Guest	**6**	**10**	**I**
G1	0.6	0.9	12.5
G2	0.5	0.1	13.0

- **HPLC analysis of DCLs of NDI building blocks 2 and 3**

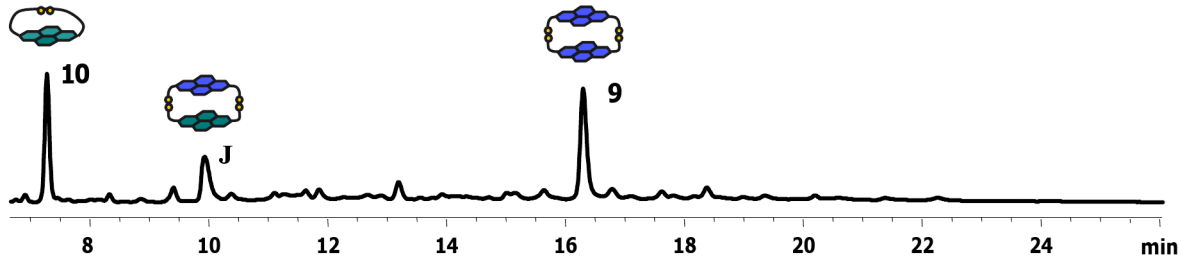


Figure S5. HPLC analysis of 5 mM DCL of **2** and **3** (1:1 molar ratio, 5 mM total).

Table S3 Amplification factors of library members of DCL of **2** and **3** (1:1 molar ratio, 5 mM total, 2.5 mM guest). In the presence of the other templates, no change in the library distribution was observed.

Guest	**9**	**10**	**J**
G2	0.7	0.8	1.6

HPLC analysis of DCLs of NDI building blocks 1, 2 and 3

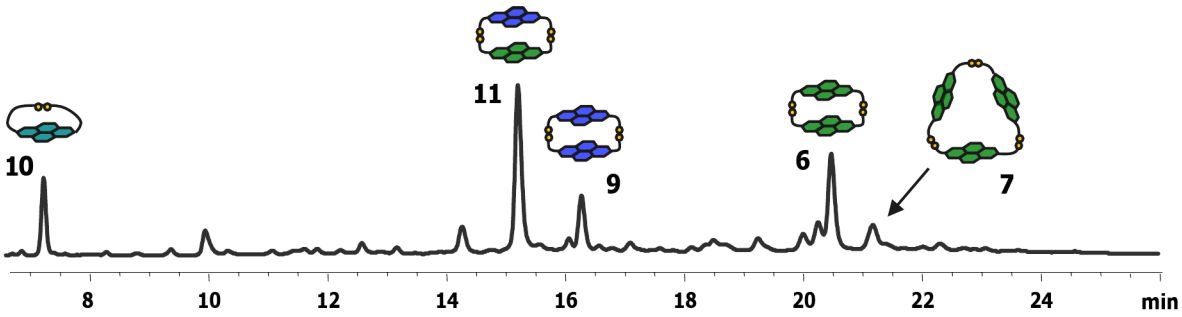


Figure S6. HPLC analysis of 5 mM DCL of **1**, **2** and **3** (1:1:1 molar ratio, 5 mM total).

Table S4. Amplification factors of library members of DCL of **1**, **2** and **3** (1:1:1 molar ratio, 5 mM total, 2.5 mM guest).

Guest	**6**	**7**	**9**	**10**	**11**
G1	0.9	0.7	0.8	1	1.2
G2	0.2	0.2	0.1	1	2.3

- **HPLC analysis of DCLs of DN building blocks**

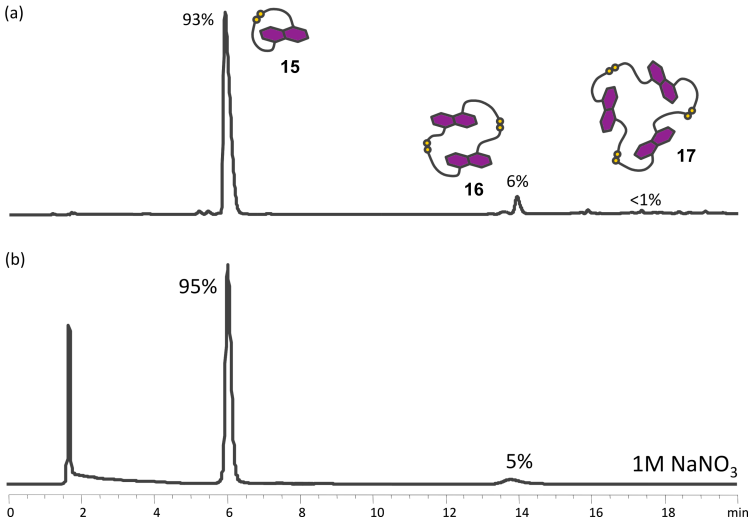


Figure S7. HPLC analysis of 5 mM DCL of **5** in (a) the absence of salt, (b) the presence of 1 M $NaNO_3$.

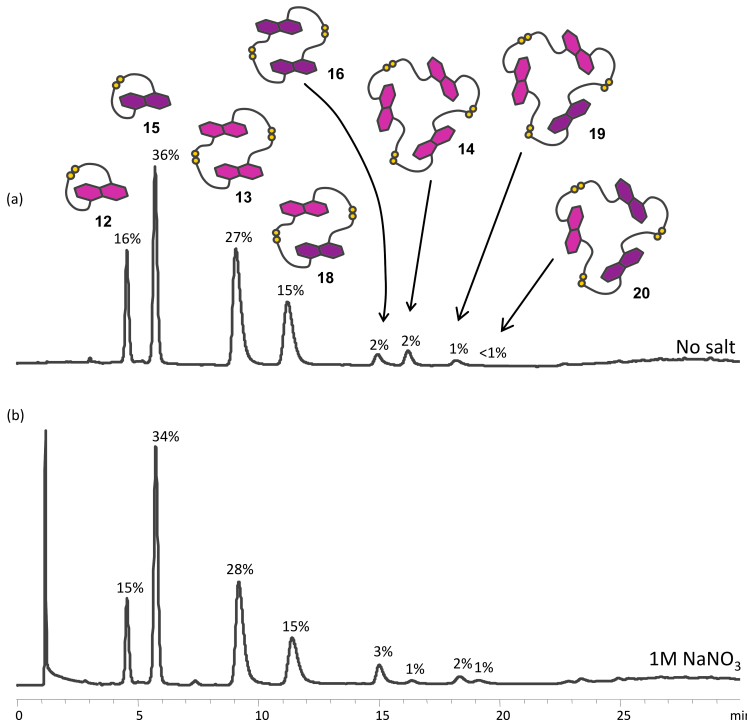


Figure S8. HPLC analysis of 5 mM DCL of **4** and **5** (1:1 molar ratio, 5 mM total) in (a) the absence of salt, (b) the presence of 1 M $NaNO_3$.

Table S5. Amplification factors of library members of DCL of **4** (5 mM, 2.5 mM guest).

Guest	Monomer **12**	Dimer **13**	Trimer **14**
G5	0.9	1.3	1.1
G6	1.0	1.1	1.0
G7	1.0	0.9	1.0

Table S6. Amplification factors of library members of DCL of **4** and **5** (1:1 molar ratio, 5 mM, 2.5 mM guest).

Guest	Monomer		Dimer			Trimer		
	12	**15**	**13**	**16**	**18**	**14**	**19**	**20**
G6	0.8	0.9	0.9	1.1	1.4	1.2	1.0	1.1
G8	0.9	0.6	0.8	1.4	1.5	2.0	2.0	1.5

MS spectra

- **MS spectra of NDI macrocycles**

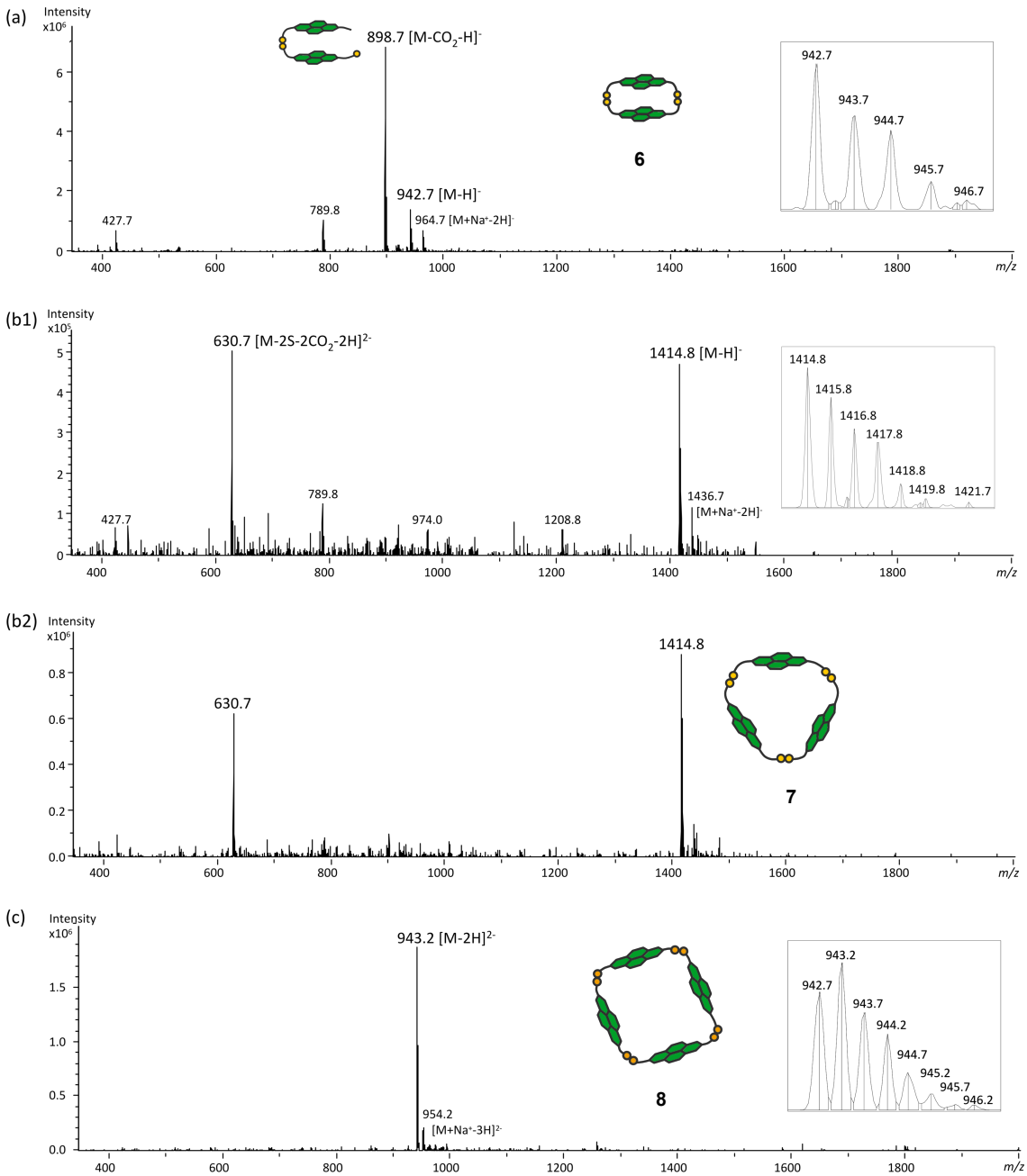


Figure S9. ESI-MS spectra of NDI macrocycles (a) **6**, (b1) minor isomer of **7** at 19 min, (b2) major isomer of **7** at 23 min, and (c) **8** (as dianion). Expansions of the molecular ion are shown as insets.

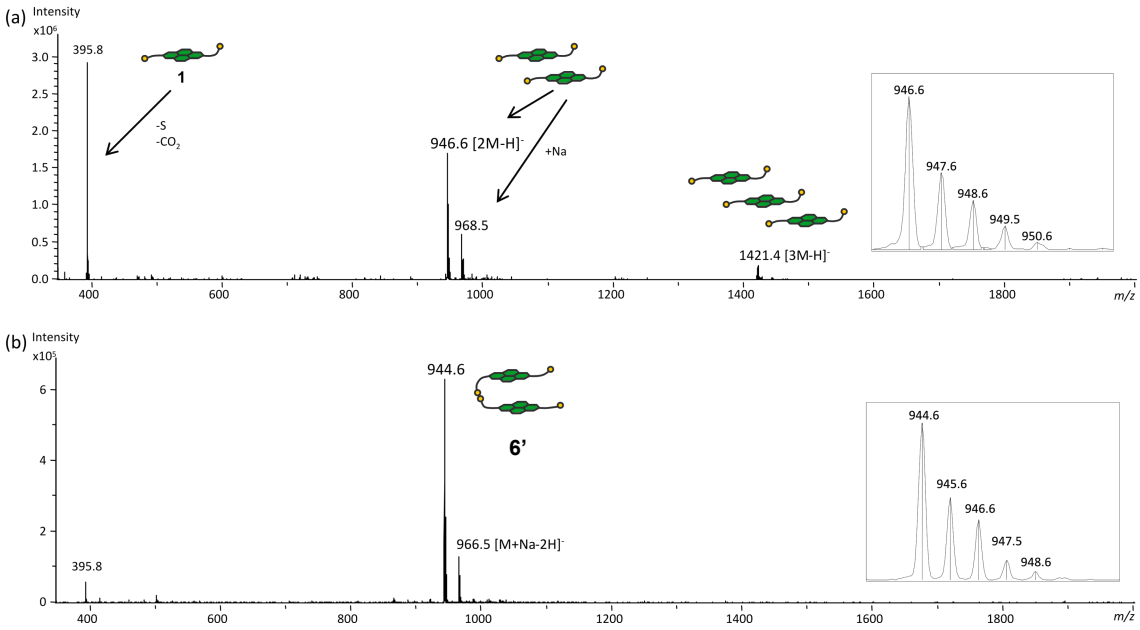


Figure S10. ESI-MS spectra of the NDI intermediates observed during equilibration (a) the dithiol building block **1**, and (b) the linear dimer **6'**. Expansions of the molecular ions are shown as insets.

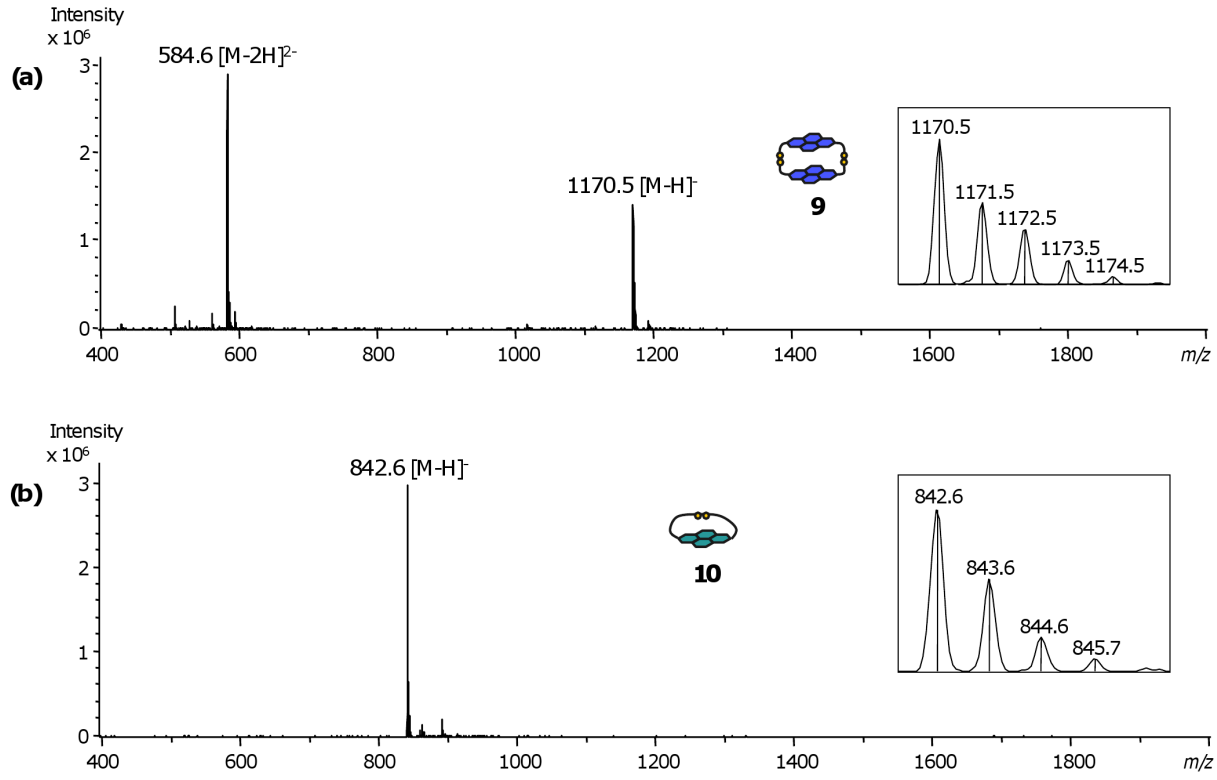


Figure S11. ESI-MS spectra of NDI macrocycles (a) **9**, and (b) **10**. Expansions of the molecular ion are shown as insets.

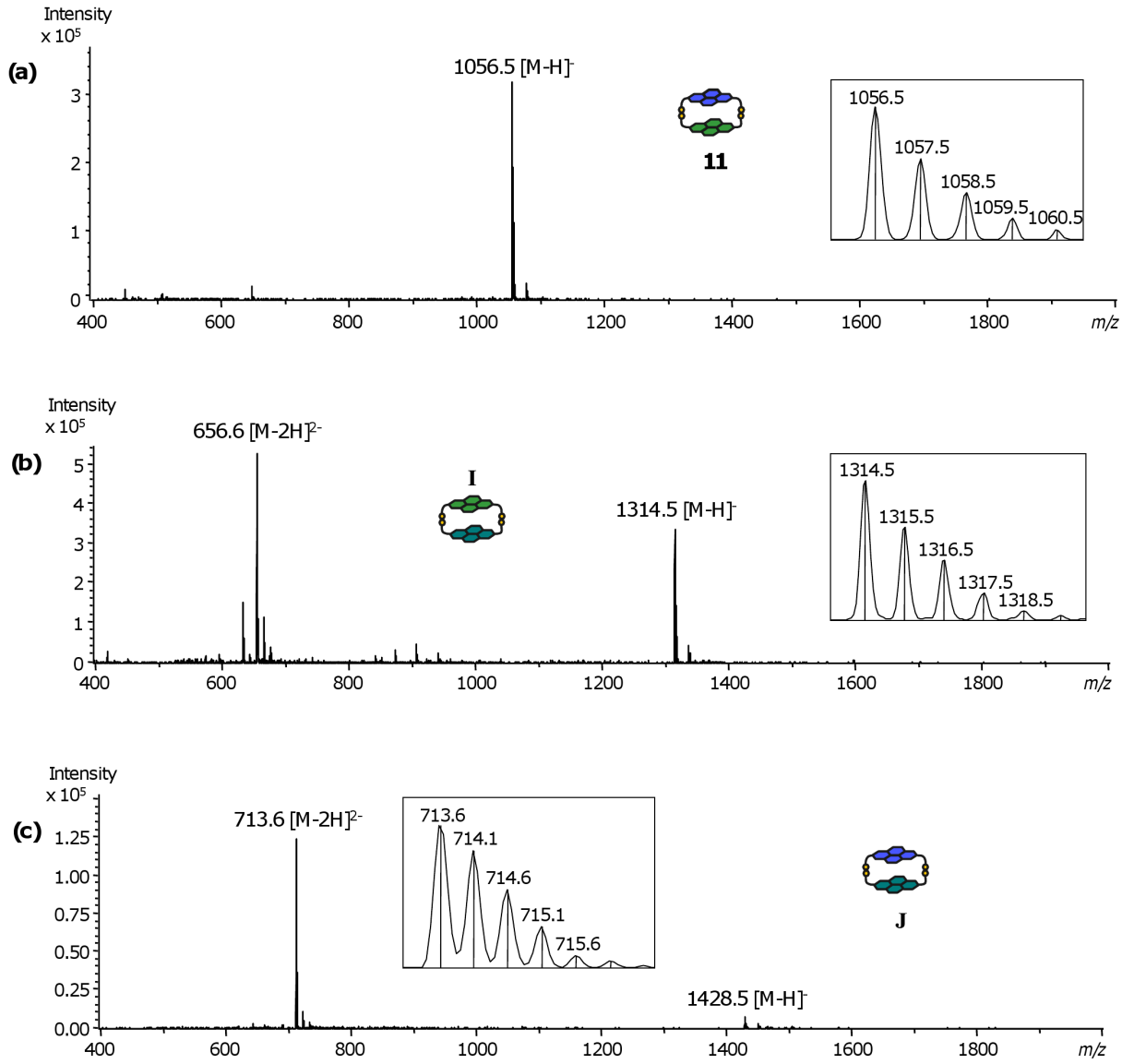


Figure S12. ESI-MS spectra of NDI macrocycles (a) **11**, (b) **I**, and (c) **J**. Expansions of the molecular ion are shown as insets.

- **MS spectra of DN macrocycles**

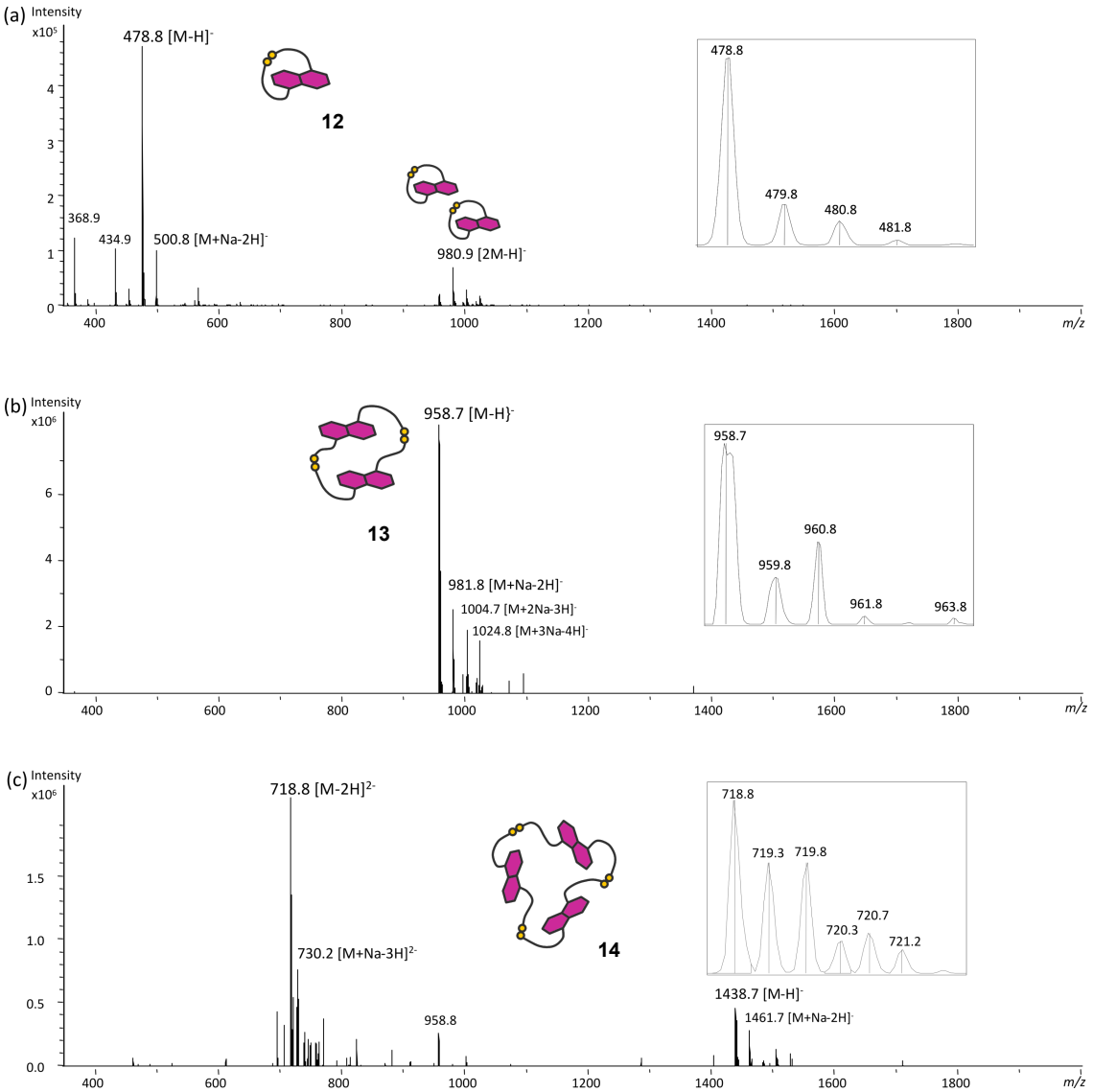


Figure S13. ESI-MS spectra of the DN macrocycles (a) **12**, (b) **13**, and (c) **14**. Expansions of the molecular ions are shown as insets.

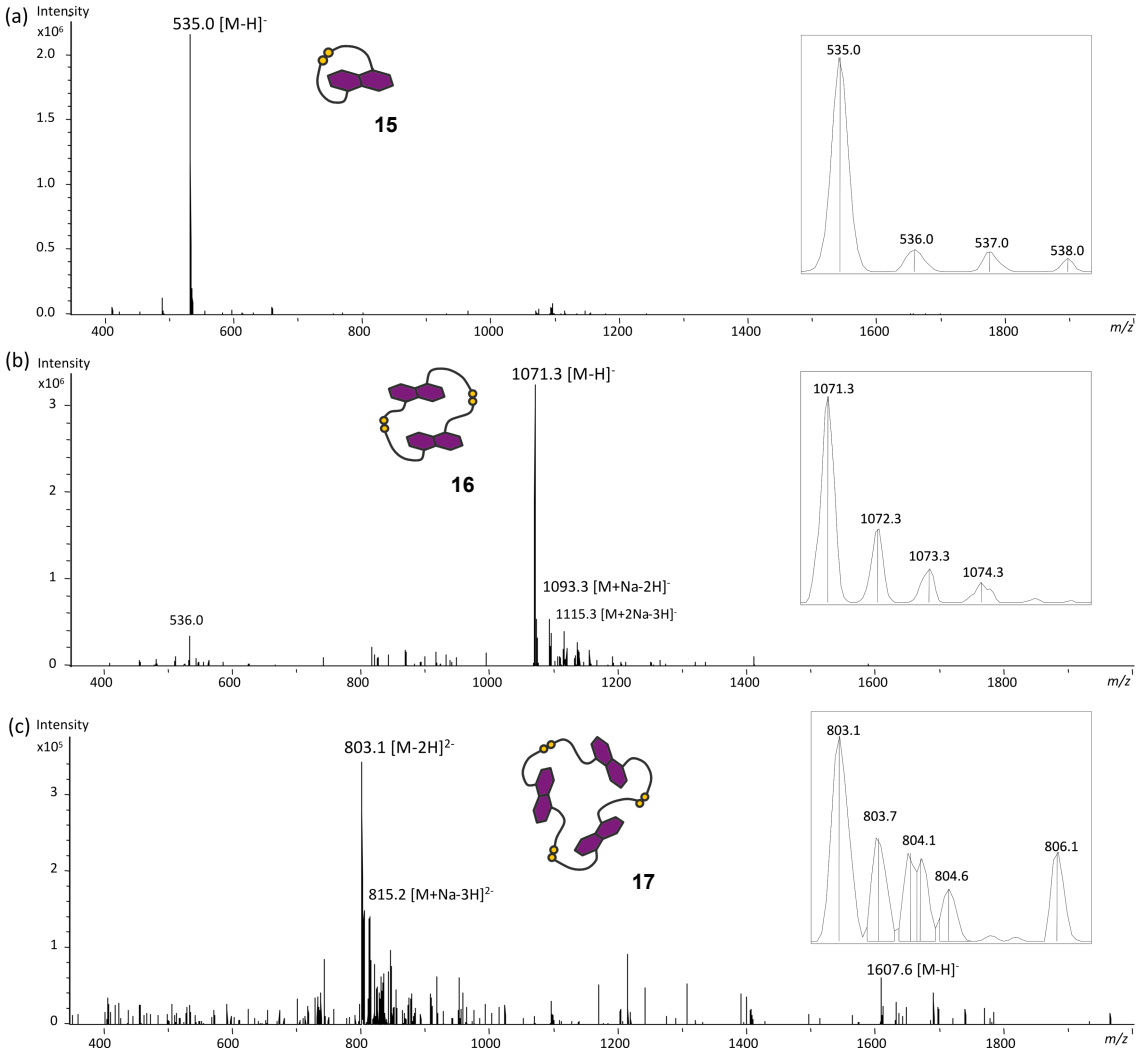


Figure S14. ESI-MS spectra of the DN macrocycles (a) **15**, (b) **16**, and (c) **17**. Expansions of the molecular ions are shown as insets.

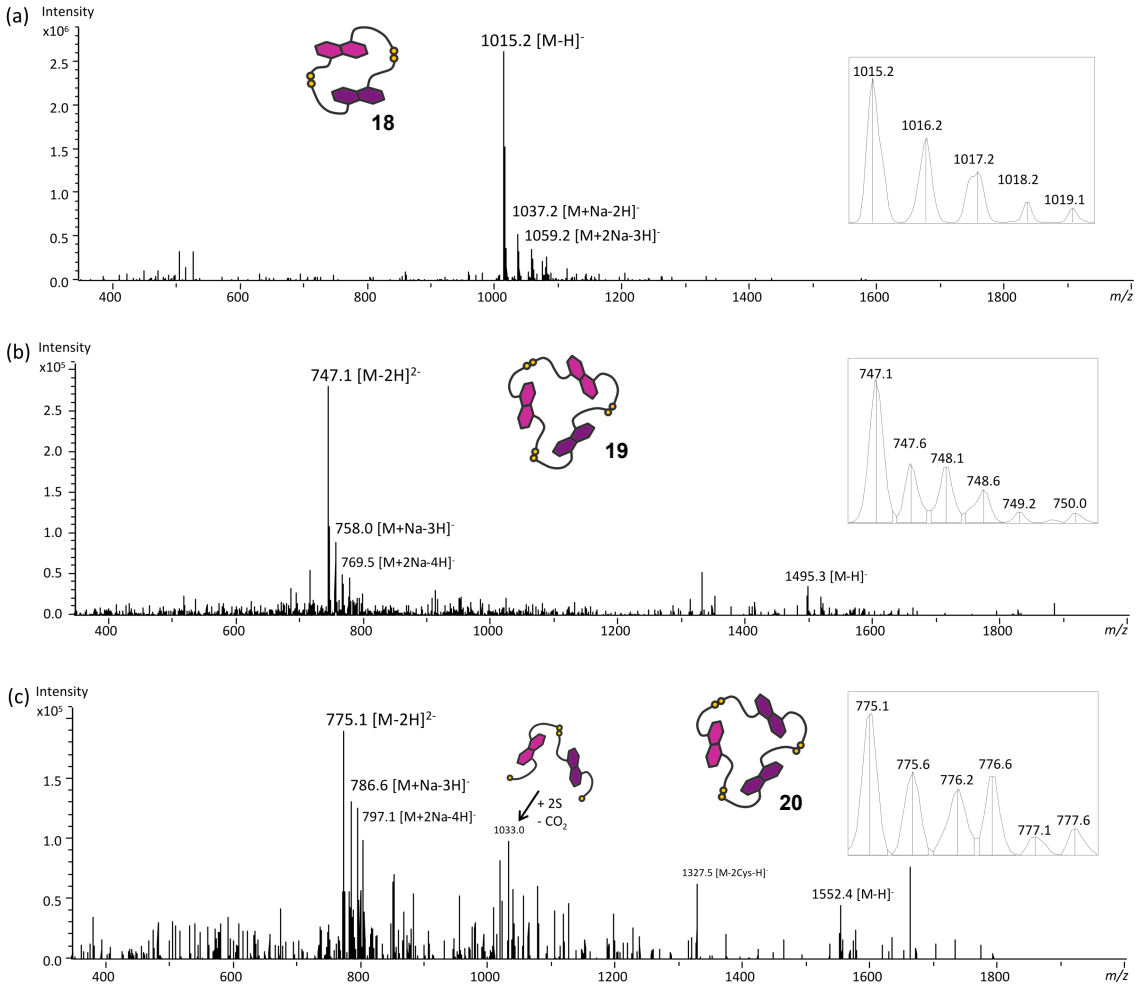


Figure S15. ESI-MS spectra of the mixed DN macrocycles (a) **18**, (b) **19**, and (c) **20**. Expansions of the molecular ions are shown as insets.

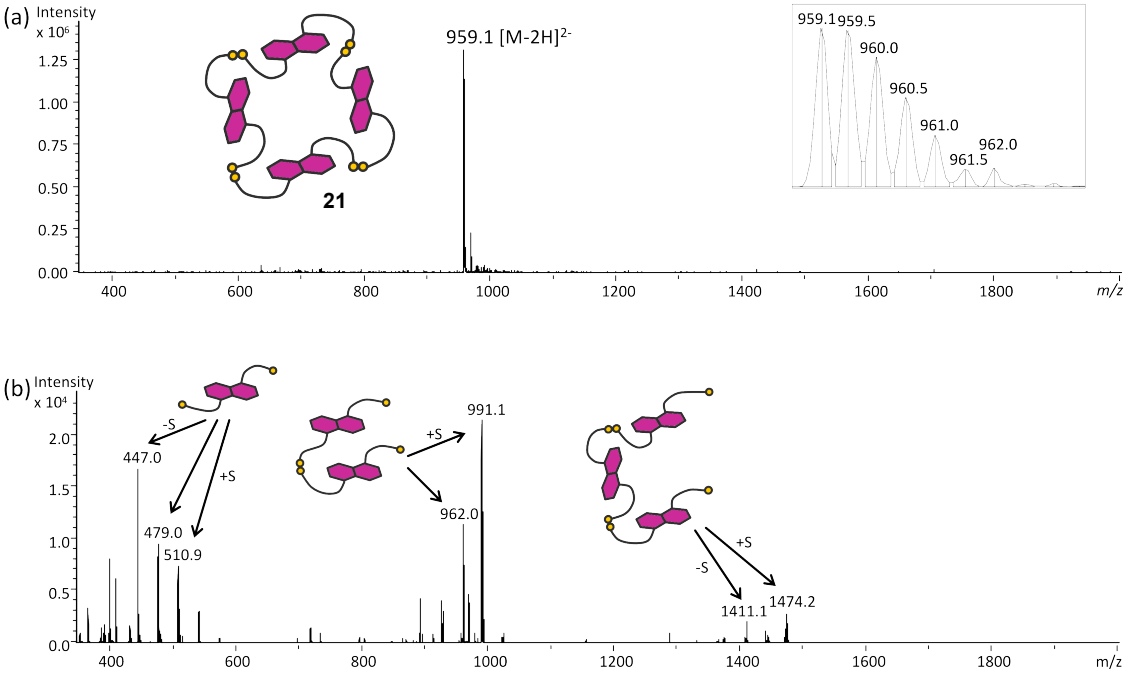


Figure S16. (a) ESI-MS and (b) MS/MS spectra of the DN tetramer **21**. Expansion of the molecular ion is shown as inset.

NMR spectra

For NMR characterisation of NDI **1** and DN **5**, please refer to our previous communications.[2, 3]

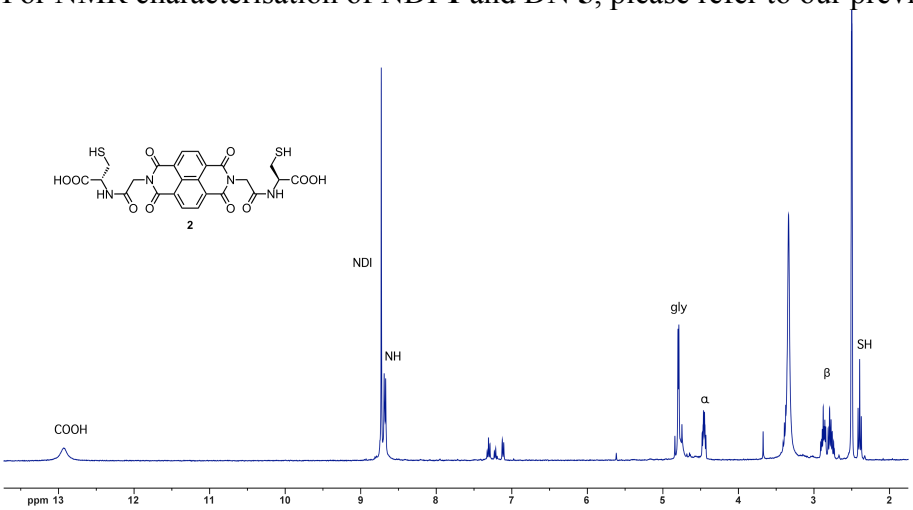


Figure S17. ^{1}H NMR spectra of **2** (400 MHz, 300 K, DMSO-d_6).

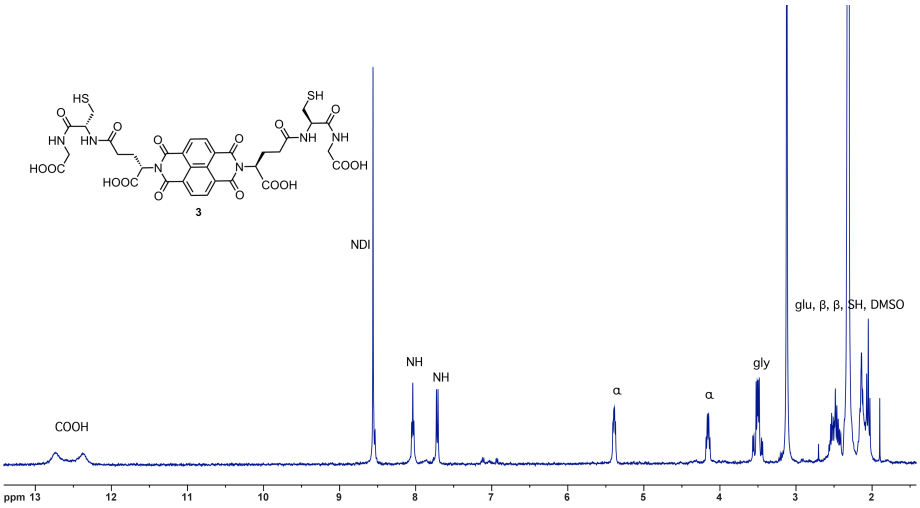


Figure S18. ^{1}H NMR spectra of **3** (400 MHz, 300 K, DMSO-d_6).

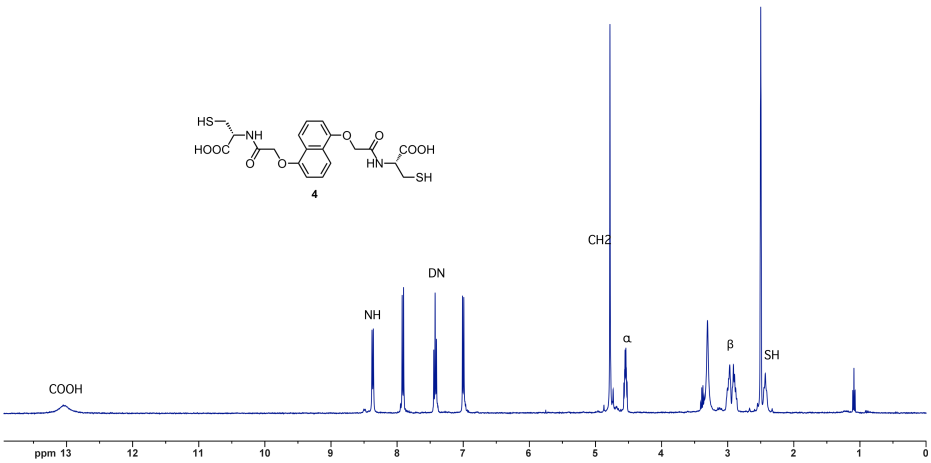


Figure S19. ^{1}H NMR spectra of **4** (400 MHz, 300 K, DMSO-d_6).

For NMR characterisation of NDI macrocycles **6**–**8**, please refer to our previous communication.[2]

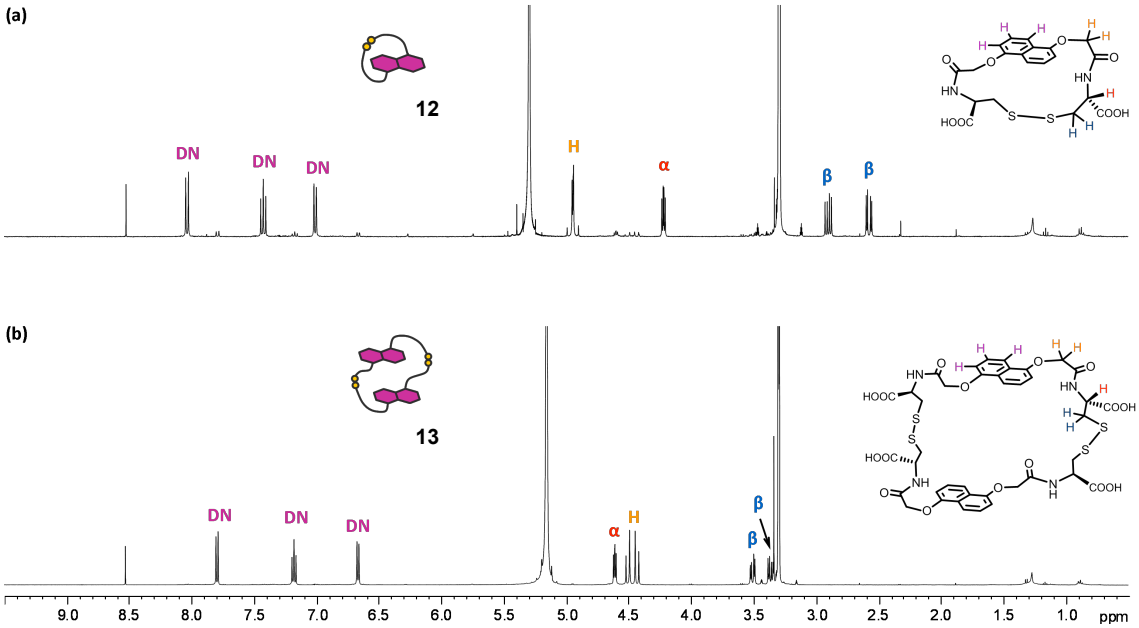


Figure S20. ^{1}H NMR spectra of (a) **12** (400 MHz, 300 K, CD_3OD/NaOD), and (b) **13** (500 MHz, 300 K, CD_3OD/NaOD).

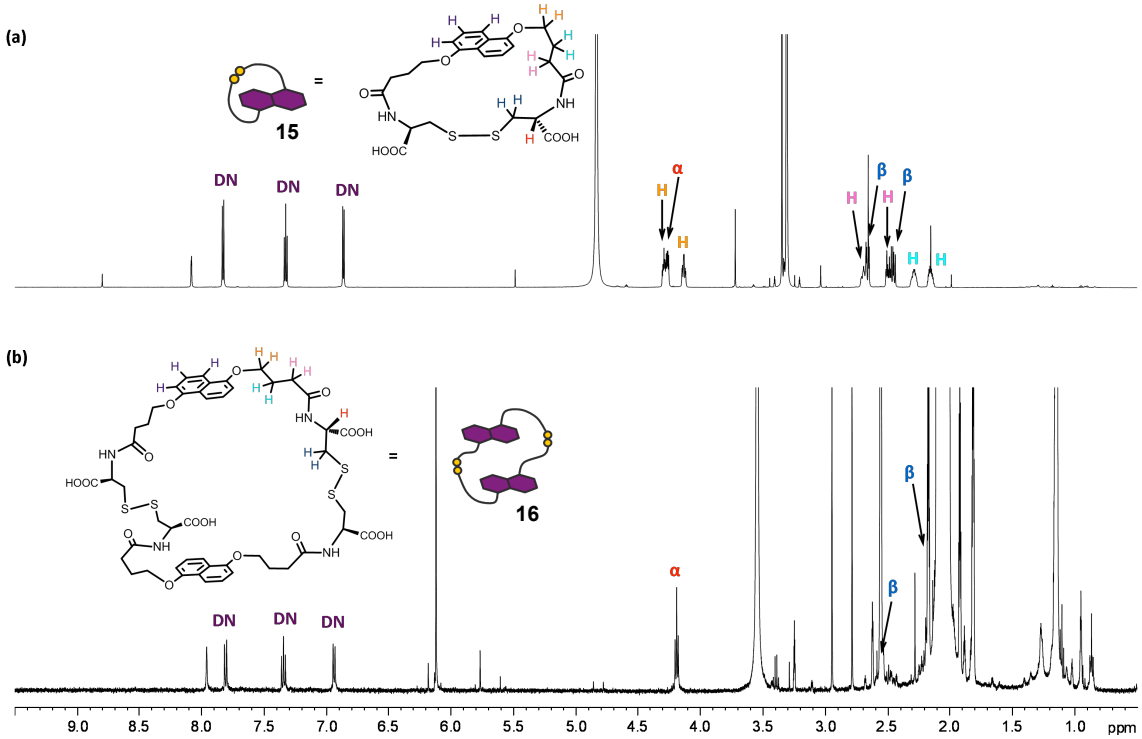


Figure S21. ^{1}H NMR spectra of (a) **15** (500 MHz, 300 K, CD_3OD), and (b) **16** (500 MHz, 300 K, acetone-d_6).

References

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