Electronic Supplementary Information (ESI) for:

Squaraine [2]Catenanes: Synthesis, Structure and Molecular Dynamics

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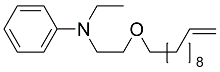
Content :

1. Synthesis

General Information

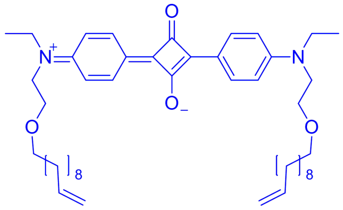
Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C-NMR spectra were recorded by using Varian Unity Plus spectrometers. Electrospray ionization time-of-flight (ESI-TOF) mass spectra were obtained using a Bruker micrOTOF II. Mass spectra data was analyzed using Bruker Compass DataAnalysis 4.0.

Methods



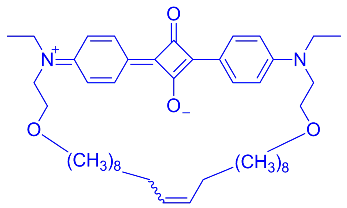
S1

S1. A solution of 2-(*N*-Ethyl-anilino)ethanol (3.1 g, 19 mmol) and 11-bromo-1-undecene (5.3 g, 23 mmol) in benzene (100 mL) was added to tetrabutylammonium bisulfate (0.62 g) and 50% NaOH solution (100 mL).The resulting biphasic solution was stirred for 24 hours. The reaction mixture was extracted with ethyl ether and the organic layer was dried over Na_2SO_4. After filtration the solvent was removed and then the crude product was purified by column chromatography (hexane:dichloromethane 4:6) to give compound **S1** (4.7 g, 15 mmol, 79%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.24 (m, 2H), 6.73 (m, 3H), 5.88 (m, 1H), 5.00 (m, 2H), 3.53 (m, 8H), 2.08 (m, 2H), 1.62 (m, 2H), 1.41 (m, 12H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.1, 139.5, 129.6, 115.9, 114.5, 111.9, 71.8, 68.7, 50.4, 45.7, 34.2, 30.1, 29.9, 29.8, 29.8, 29.5, 29.3, 26.5, 12.5; MS(ESI): calcd. for $C_{21}H_{36}NO$ $(M + H)^+$ 318.2791, found 318.2816.



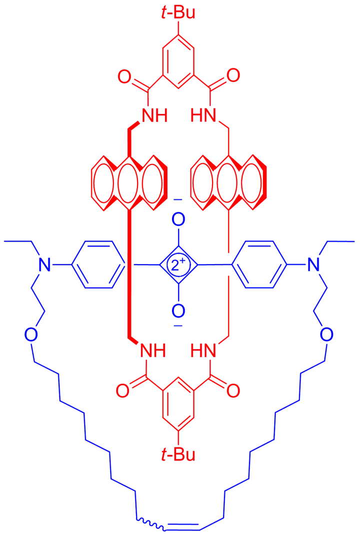
4

Squaraine Dye 4. S1 (2.3 g, 7.2 mmol), squaric acid (0.38 g, 3.3 mmol), benzene (100 mL) and n-butanol (50 mL) were added to a 250 mL round bottom flask fitted with Dean-Stark apparatus. The mixture was heated to 100 °C for 24 hours. Evaporation of solvent and column chromatography (methanol:chloroform 1:49) to give compound **4** (1.2 g, 1.7 mmol, 52%) as a blue solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 9.0 Hz, 4H), 6.80 (d, *J* = 9.5 Hz, 4H), 5.84 (m, 2H), 5.00 (m, 4H), 3.65 (m, 12H), 3.45 (t, *J* = 6.5 Hz, 4H), 2.06 (m, 4H), 1.57 (m, 4H), 1.37 (m, 4H), 1.29 (m, 26H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 188.5, 183.7, 153.7, 139.5, 133.6, 120.1, 114.4, 112.6, 72.7, 68.5, 50.8, 46.7, 34.1, 29.9, 29.8, 29.7, 29.7, 29.4, 29.2, 26.3, 12.6; MS(ESI): calcd. for $C_{46}H_{69}N_2O_4$ $(M + H)^+$ 713.5252, found 713.5272.



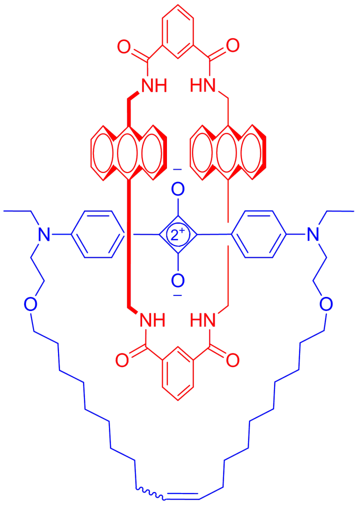
5

Squaraine Macrocycle 5. First generation Grubbs' catalyst (10% mol) was added to a solution of **1** (1.4 g, 2.0 mmol) in anhydrous dichloromethane (700 mL). The solution was stirred at room temperature for 24 hours, concentrated *in vacuo* and the crude residue was purified by column chromatography (methanol:chloroform 1:49) to give compound **5** (0.38 g, 0.557 mmol, 28%) as a blue solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.39 (d, J = 9.3 Hz, 4H), 6.83 (m, 4H), 5.33 (m, 75% *trans*), 4.95 (m, 25%, *cis*), 3.58 (m, 12H), 3.41 (t, J = 6.6 Hz, 4H), 1.90 (m, 4H), 1.49 (m, 4H), 1.26 (m, 30H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 187.8, 184.6, 154.0, 133.4, 130.5, 120.1, 112.9, 71.8, 68.3, 50.8, 46.3, 37.3, 32.9, 30.2, 30.0, 29.7, 29.5, 29.4, 26.1, 12.6; MS(ESI): calcd. for $C_{44}H_{65}N_2O_4$ $(M + H)^+$ 685.4939, found 685.4948.



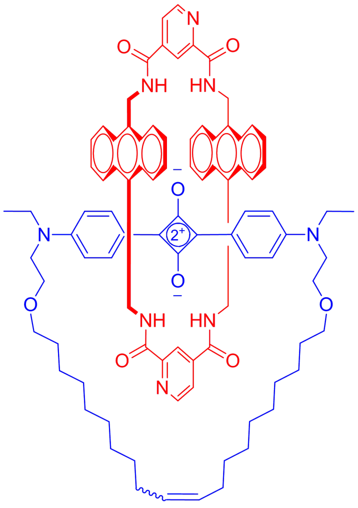
1

Squaraine Catenane 1. Solutions of 9,10-bis(aminomethyl)anthracene (0.17 g, 0.72 mmol) and 5-*tert*-butylisophthaloyl dichloride (0.19 g, 0.72 mmol) in dry chloroform (50 mL) were simultaneously added over a period of 5 h to a solution of the squaraine macrocycle **5** (0.10 g, 0.15 mmol) and triethylamine (0.14 g, 1.4 mmol) in dry chloroform (100 mL) under a nitrogen atmosphere. The mixture was stirred for a further 20 h and then filtered through filter paper. The filter paper was washed with chloroform (100 mL) and the filtrate was concentrated. Purification of the crude material by column chromatography (methanol:chloroform 1:49) to give squaraine catenane **1** (0.049 g, 0.032 mmol, 22%) as a green solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.44 (s, 2H), 8.56 (s, 4H), 8.33 (bs, 4H), 7.76 (bs, 8H), 7.00 (d, J = 9.4 Hz, 4H), 6.71 (dd, J = 6.8, 2.8 Hz, 8H), 6.17 (d, J = 8.8 Hz, 4H), 5.25 (d, J = 2.9 Hz, 8H), 4.39 (t, J = 4.6 Hz, 25% *cis*), 4.15 (t, J = 3.5 Hz, 75%, *trans*), 3.74 (bs, 4H), 3.69 (bs, 4H), 3.62 (t, J = 7.2 Hz, 4H), 3.55 (t, J = 6.6 Hz, 4H), 1.57 (s, 18H), 1.66 – 0.40 (m, 38H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 184.3, 179.2, 167.4, 153.4, 133.6, 133.2, 130.7, 129.4, 129.2, 129.0, 128.7, 126.1, 124.1, 123.0, 117.2, 111.9, 72.1, 68.6, 51.1, 47.0, 38.9, 35.7, 32.6, 31.7, 30.0, 29.6, 29.6, 29.5, 29.4, 29.3, 25.9, 12.8; MS(ESI): calcd. for $C_{100}H_{117}N_6O_8$ $(M + H)^+$ 1530.8960, found 1530.8911.



2

Squaraine Catenane 2. Solutions of 9,10-bis(aminomethyl)anthracene (0.17 g, 0.72 mmol) and isophthaloyl dichloride (0.15 g, 0.72 mmol) in dry chloroform (50 mL) were simultaneously added over a period of 5 h to a solution of the squaraine macrocycle **4** (0.10 g, 0.15 mmol) and triethylamine (0.14 g, 1.4 mmol) in dry chloroform (100 mL) under a nitrogen atmosphere. The mixture was stirred for a further 20 h and then filtered through filter paper. The filter paper was washed with chloroform (100 mL) and the filtrate was concentrated. Purification of the crude material by column chromatography (methanol:chloroform 1:49) to give squaraine catenane **2** (0.074 g, 0.052 mmol, 35%) as a green solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.63 (s, 2H), 8.52 (d, *J* = 7.9 Hz, 4H), 8.35 (bs, 4H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.75 (dd, *J* = 6.8, 3.2 Hz, 8H), 7.01 (d, *J* = 8.9 Hz, 4H), 6.71 (dd, *J* = 7.0, 3.0 Hz, 8H), 6.19 (t, *J* = 9.1 Hz, 4H), 5.25 (d, *J* = 3.6 Hz, 8H), 4.42 (t, *J* = 4.4 Hz, 25% *cis*), 4.16 (t, *J* = 2.1 Hz, 75%, *trans*), 3.74 (bs, 4H), 3.69 (bs, 4H), 3.62 (t, *J* = 7.1 Hz, 4H), 3.55 (t, *J* = 6.8 Hz, 4H), 1.66 – 0.45 (m, 38H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 184.4, 178.9, 167.0, 153.5, 133.9, 133.2, 130.7, 129.6, 129.4, 129.0, 128.7, 128.6, 126.1, 124.1, 117.2, 112.0, 72.1, 68.6, 51.1, 47.0, 38.5, 35.7, 32.6, 31.7, 30.0, 29.8, 29.7, 29.5, 29.4, 29.3, 26.0, 12.8; MS(ESI): calcd. for $C_{92}H_{101}N_6O_8$ $(M + H)^+$ 1418.7709, found 1418.7690.



3

Squaraine Catenane 3. Solutions of 9,10-bis(aminomethyl)anthracene (0.057 g, 0.24 mmol) and pyridind-2,4-dicarbonyl dichloride (0.049 g, 0.24 mmol) in dry chloroform (20 mL) were simultaneously added over a period of 5 h to a solution of the squaraine macrocycle **4** (0.033 g, 0.048 mmol) and triethylamine (0.024 g, 0.24 mmol) in dry chloroform (20 mL) under a nitrogen atmosphere. The mixture was stirred for a further 20 h and then filtered through filter paper. The filter paper was washed with chloroform/triethylamine (30 mL of 100:1 v/v) and the filtrate was concentrated. Purification of the crude material by column chromatography (methanol:chloroform 1:99) to give squaraine catenane **3** (0.012 g, 0.0086 mmol, 18%) as a green solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 9.58 (s, 2H), 9.19 (s, 2H), 8.46 (t, *J* = 3.7 Hz, 2H), 8.29 (s, 4H), 7.78 – 7.69 (m, 8H), 6.89 (d, *J* = 8.4 Hz, 4H), 6.73 – 6.70 (m, 8H), 6.19 (d, *J* = 9.0 Hz, 4H), 5.30 (bs, 4H), 5.22 (bs, 4H), 4.35 (t, *J* = 4.7 Hz, 25% *cis*), 4.11 (t, *J* = 3.7 Hz, 75% *trans*), 3.74 (bs, 4H), 3.69 (bs, 4H), 3.63 (t, *J* = 7.2 Hz, 4H), 3.54 (t, *J* = 6.6 Hz, 4H), 1.66 – 0.40 (m, 38H); ^{13}C (150 MHz, $CDCl_3$): δ 184.6, 177.8, 165.5, 165.3, 153.8, 153.6, 151.9, 151.8, 142.2, 133.0, 130.7, 130.6, 129.3, 128.9, 128.5, 128.2, 126.3, 126.2, 124.1, 124.0, 123.9, 123.8, 116.9, 112.1, 72.2, 72.1, 68.5, 51.1, 51.0, 47.0, 46.7, 38.7, 38.5, 32.7, 32.5, 30.5, 30.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.6, 26.1, 25.9, 14.3, 12.7; MS(ESI): calcd. for $C_{90}H_{99}N_8O_8$ $(M + H)^+$ 1419.7580, found 1419.7581.

2. Energy barriers from dynamic NMR

Table S1. Data used to calculate free energy of activation (average of 3 trials).

catenane	T_c (K)	$\Delta\nu$ (Hz)	k (s^{-1})	$\Delta G^\ddagger$ (Kcal/mol)
1	240	74	164	11.6 ± 0.3
2	236	76	169	11.4 ± 0.2

The rate of two-site exchange (*k*) at the coalescence temperature was determined using:

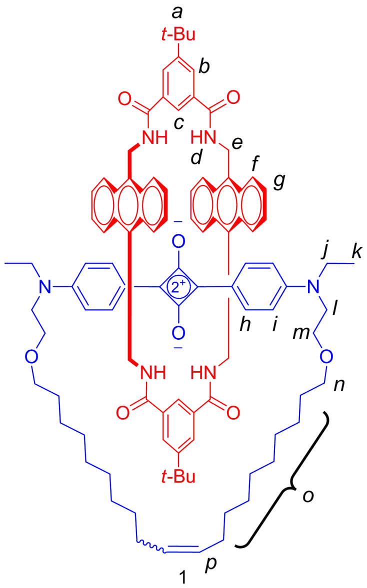
$$k = \frac{\pi}{\sqrt{2}}\ \Delta\nu_0$$

Where $\Delta\nu_0$ is the chemical shift difference of the two protons (in Hz). To determine the activation energy (in kcal·mol^{-1}), the Eyring equation was simplified into the following form:

$$\Delta G^\ddagger = 4.57\ T_C\left[9.97 + \log_{10}\left(\frac{T_C}{\Delta\nu_0}\right)\right]$$

Where T_C is the coalescence temperature (in K).

3. Variable temperature ^{1}H NMR spectra of 1 and 2



1

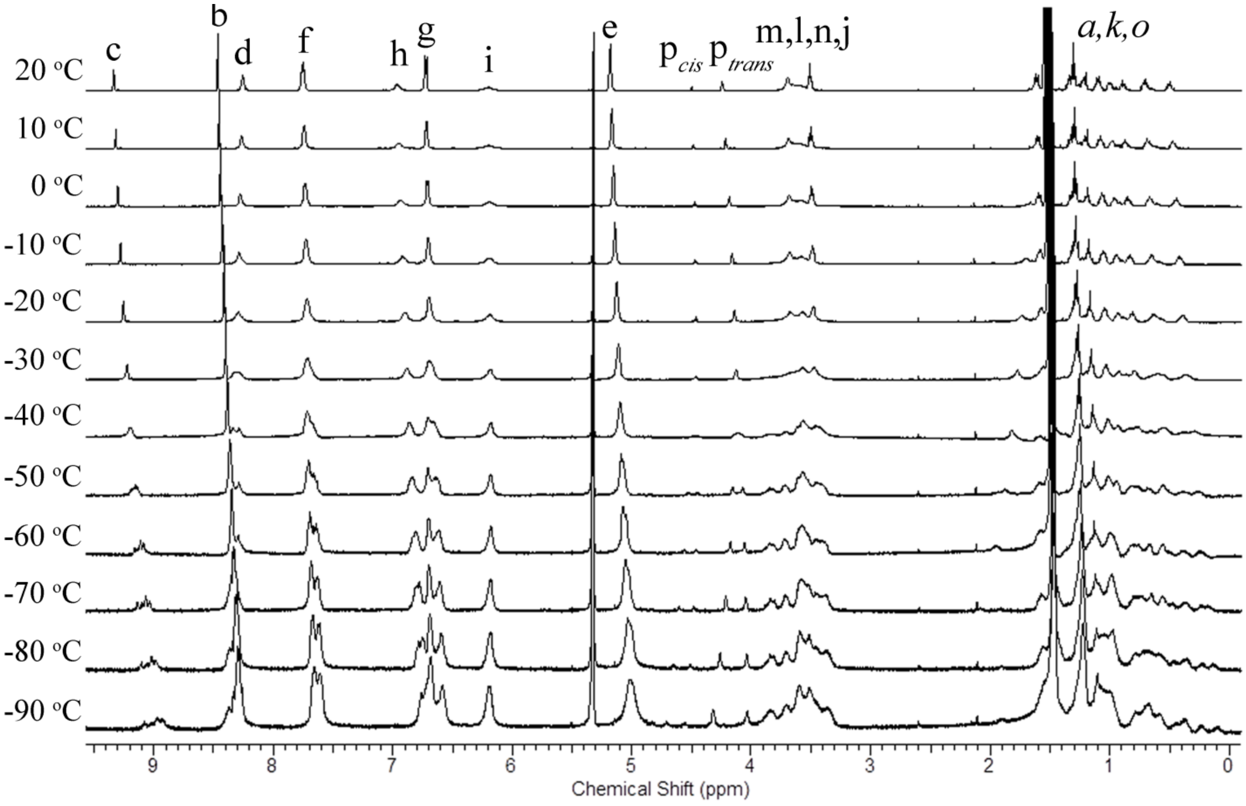


Figure S2. Variable temperature ^{1}H NMR spectra of **1** in CD_2Cl_2

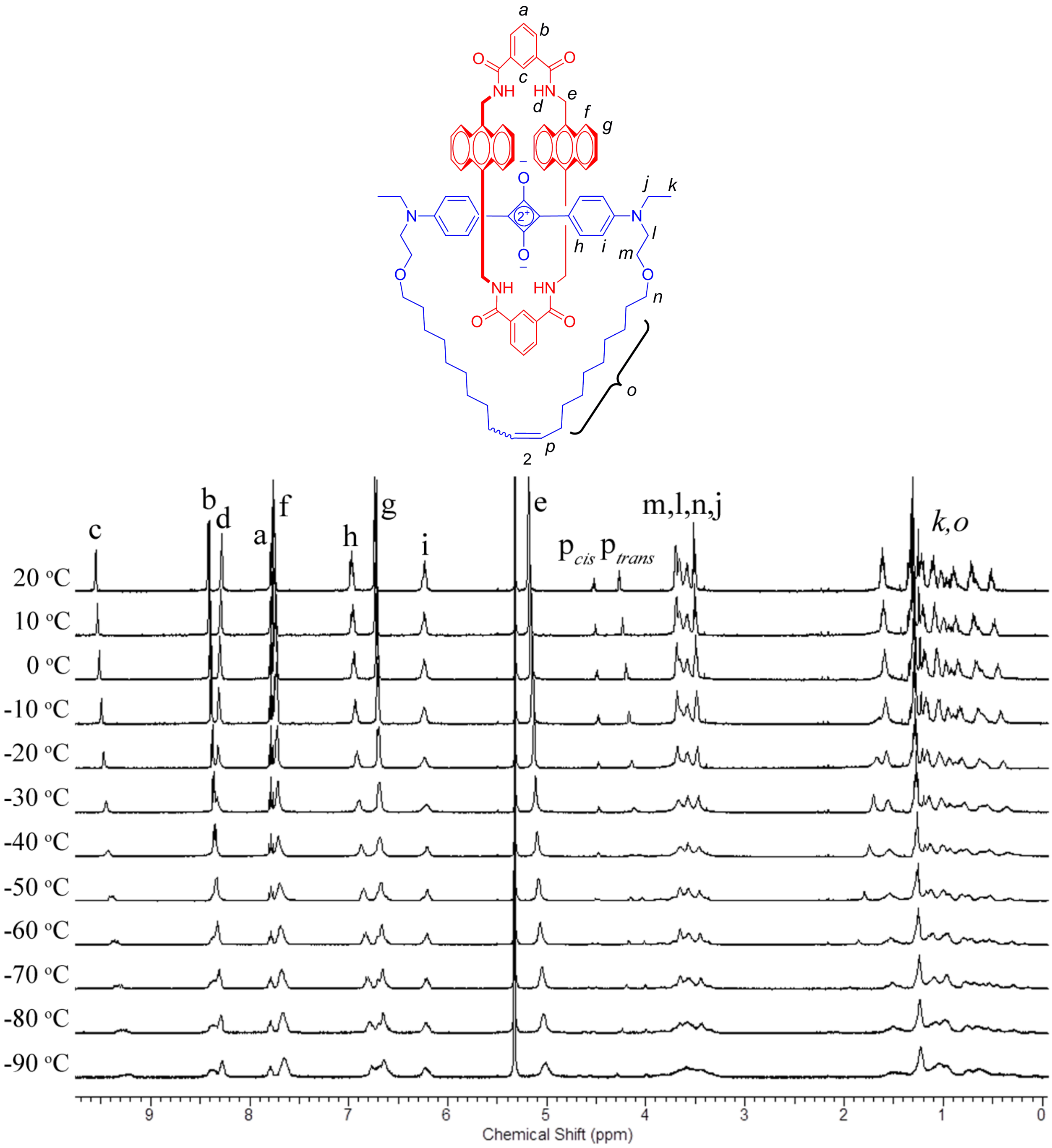


Figure S3. Variable temperature ^{1}H NMR of **2** in CD_2Cl_2

4. X-ray crystallographic data for 3

The catenane **3** crystallizes as pale brown block-like crystals from an acetonitrile solution. There are four molecules of the catenane and eight molecules of acetonitrile in the unit cell of the C-centered monoclinic space group C2/c.

Due to disorder within the molecule the diffraction resolution was lower than is normally desired. However, the connectivity is correct and the interlinked molecules are present in the structure. The acetonitrile also exhibits large thermal motion; the methyl carbon has an extreme thermal ellipse. However, given the data quality separating this carbon into two components did not seem warranted. It is simply occupying a void within the lattice.

The compound crystallizes on the two-fold axis at [0, y, 0.25]. This leads to disorder in the hydrocarbon chain. The orientation and identity of the squaraine macrocycle alkene is not certain, however, the most reliable model indicates that it is the *trans* isomer, with the double-bond located on the two-fold axis. The location of the atoms within the chain were determined by examination of the electron density map and best fitting the “ribbon” of electron density observed.

The carbon atoms were modeled with refined occupancies. This led to a ratio of approximately 0.66:0.34 on either side of the alkene. These carbon atoms were modeled with isotropic thermal motion parameters. All others were modeled with anisotropic parameters. Mild bond distance restraints were applied to the sp^3 carbons along the chain (SADI) and the model refined as a part, not interacting with the opposite direction disorder (PART -1). The alkene bond was not fixed to any particular value.

The tetralactam pyridyl nitrogen could not be located reliably. As such it was considered to be disordered with the carbon atom that is *meta* to it. Both atoms were modeled at 50 % occupancy with thermal parameters and positions tied to the observed site. Despite the disorder within the molecule and the poor data quality, the bond lengths and angles are expected values.

CRYSTAL SUMMARY

An arbitrary sphere of data were collected on a pale brown block-like crystal, having approximate dimensions of 0.18 × 0.12 × 0.08 mm, on a Bruker Kappa X8-APEX-II diffractometer using a combination of ω- and φ-scans of 0.3°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

Crystal data for $C_{94}H_{104}N_{10}O_8$; M_r = 1501.87; Monoclinic; space group C2/c; a = 21.4062(18) Å; b = 15.2138(13) Å; c = 26.813(4) Å; α = 90°; β = 112.016(5)°; γ = 90°; V = 8095.5(15) $Å^3$; Z = 4; T = 100(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 0.079 mm^{-1}; d_{calc} = 1.232g.cm^{-3}; 20247 reflections collected; 4932 unique (R_{int} = 0.0739); giving R_1 = 0.0758, wR_2 = 0.1827 for 2560 data with [I>2σ(I)] and R_1 = 0.1565, wR_2 = 0.2262 for all 4932 data. Residual electron density (e^-.$Å^{-3}$) max/min: 0.538/-0.391.

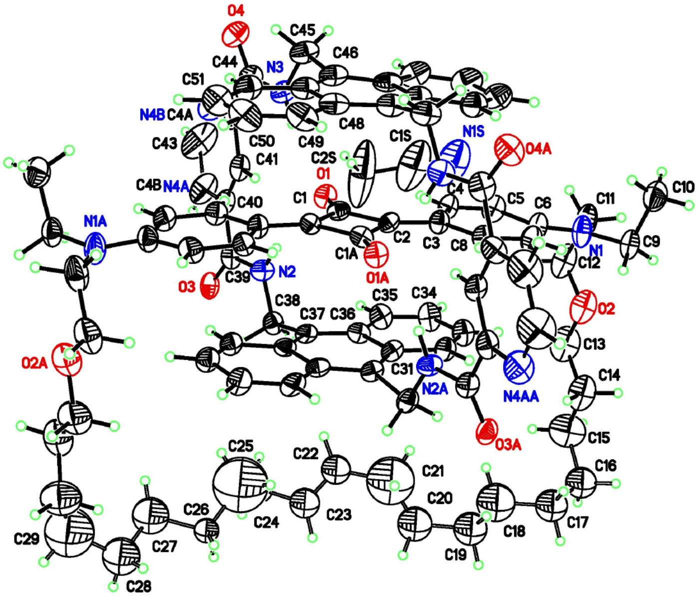


Figure S4: ORTEP diagram of catenane **3**.