Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Solvatochromic Rotaxane Molecular Shuttles

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1. General Experimental Section

Unless stated otherwise, all reagents and anhydrous solvents were purchased and used without further purification. The following compounds were prepared according to literature procedures: *N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide **3**,[1] 1,6,9-Tribromo-*N*-(2,5-di-*tert*-butyl-phenyl) perylene-3,4-dicarboximide **4**,[2] 2-(acetic acid)-5-8-di-*tert*-butyl-benzo[de]isoquinoline-1,3-dione **10**[3] and *tert*-butyl (10-aminononyl)carbamate.[4]

^{1}H and ^{13}C spectra were recorded on a Bruker Avance 400 spectrometer, with working frequencies of 400 and 100 MHz for ^{1}H and ^{13}C nuclei, respectively. Chemical shifts are quoted in parts per million (ppm) relative to tetramethylsilane (TMS) using the residual solvent peak as a reference. The coupling constants (*J*) are reported in hertz (Hz). Multiplicities are given as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet) and b (broad). The full assignment of the ^{1}H NMR signals was performed using COSY (Correlation Spectroscopy) and ROESY (Rotating-Frame Overhauser Effect spectroscopy) experiments at 298 K. Acquisition parameters for ROESY experiments: data points= 2048, relaxation delay = 2 s, mixing time = 200 ms; Processing parameters: size = 2048 × 2048, window function = sine. Fast atom bombardment (FAB) mass spectra were obtained using a JEOL JMS SX/SX 102A four-sector mass spectrometer, equipped with Xenon primary atom beam, utilizing a 3-nitrobenzoyl alcohol matrix. Other abbreviations used: DMF = dimethylformamide, Et_2O = diethylether, MeOH = methanol, *t*BuOH = *tert*-butanol, TFA = trifluoroacetic acid, $Pd_2(dba)_3$ = Tris (dibenzylideneacetone)dipalladium(0), BINAP = (±)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene, NaO*t*Bu = Sodium *tert*-butoxide, Et_3N = triethylamine, BOP = Benzotriazole-1-yl-oxy-tris-(dimethylamino)-phosphonium hexafluorophosphate, DIPEA = diisopropylethylamine.

1.1 UV-Vis Absorption Spectroscopy

Electronic absorption spectra of solutions were recorded in quartz cuvettes (1 cm, Hellma) on a Hewlett-Packard 8543 diode array (range 190-1000 nm) or a Varian Cary 3E (range 190-900 nm) spectrophotometer. Concentrations were typically 10^{-6} to 10^{-5} M.

1.2 Steady-State Fluorescence Spectroscopy

Emission spectra were measured on a Spex Fluorolog 3 spectrometer, equipped with a Xe arc light source, a Hamamatsu R928 photomultiplier tube detector and double excitation and emission monochromators. The fluorescence spectra were corrected for the wavelength response of the detection system. The fluorescence of compounds in solution was detected in right angle geometry. Fluorescence quantum yields[5] were estimated by comparison of a standard solution of *N,N'*-(2,6-diisopropylphenyl)-1,6,7,12- tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide (Φ_{Fl} = 0.96 in $CHCl_3$)[6] and calculated according to the following:

$$\Phi_{Fl} = \Phi_r \frac{A_r I_s n_s^2}{A_s I_r n_r^2} \qquad \text{(S1)}$$

where Φ_{Fl} is the quantum yield, A is the absorption factor (absorbance ~ 0.1) at the excitation wavelength, I is the integrated emission intensity and n is the refractive index of the solvents. Subscripts s and r refer to the sample and the reference solutions, respectively.

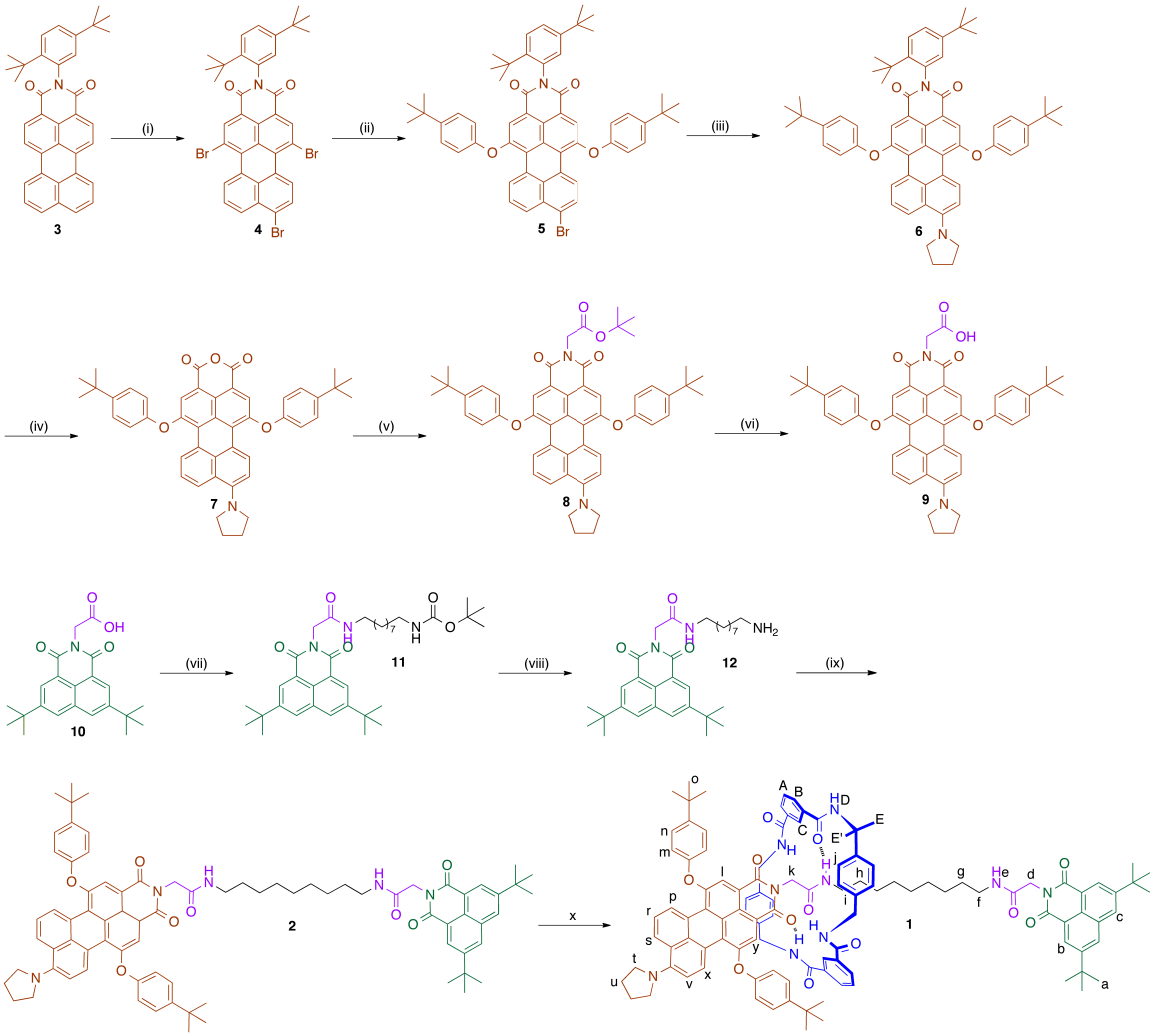
1.3 Time-Resolved Fluorescence Spectroscopy

Time-resolved emission measurements were performed using a picosecond time-correlated single photon counting (TCSPC) set-up.[7] A mode-locked Ar^+ laser (Coherent 486 AS Mode Locker and Coherent Innova 200 laser) was operated at λ = 514.5 nm (laser pulses of ca. 60 ps with a repetition rate of 76 MHz) and used to pump a DCM dye laser (Coherent model 700) coupled with a cavity dumper (Coherent 7200). The output at 3.8 MHz was doubled with a BBO crystal resulting in an excitation wavelength of 323 nm. Fluorescence was detected at a right angle to the incident beam direction after passing though a polarizer set to the magic angle (54.7°), and a monochromator (Carl Zeiss M20 67583) before reaching the microchannel plate photomultiplier tube (Hamamatsu R3809). The instrument response (~18 ps) was recorded using the Raman scattering of a doubly ionized water sample. Time windows (4000 channels) of 5 ns (1.25 ps/channel) – 50 ns (12.5 ps/channel) could be used facilitating a window for measurements going from 5 ns to 50 ns. The recorded traces were fitted to model decay functions convoluted with the system response using the computer program Fluofit (PicoQuant) or using similar procedures implemented in Igor Pro (Wavemetrics).

For fluorescence decay measurements at λ_{exc}= 405 nm a continuously tunable (690-1040 nm) Coherent Chameleon laser was used as the excitation source (fwhm=140 fs with a pulse repetition rate of 80 MHz). A pulse picker (Angewandte Physics and Electronics (APE)) was employed to decrease the repetition rate to 4 MHz. The laser beam was passed through a BBO crystal to double the frequency yielding an excitation wavelength of 405 nm. A dichroic mirror separated the excitation beam from the fundamental beam. The rest of the set-up is the same as described above.

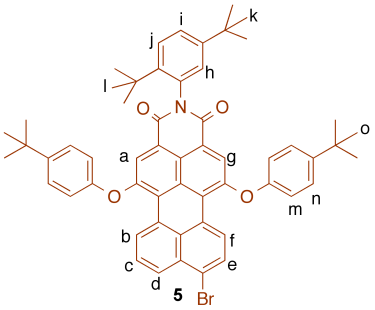
2. Synthesis and Characterization

Scheme 1. Synthesis of molecular shuttle **1**[a]



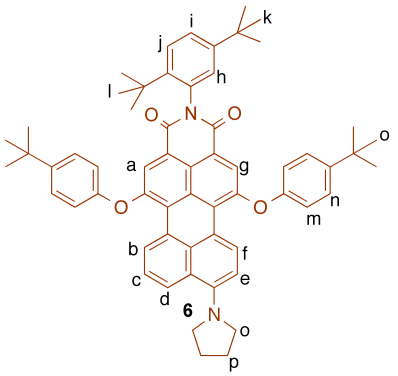
[a] (i) Br_2, $CHCl_3$, reflux, 19 h, 40%; (ii) 4-*tert*-butylphenol, K_2CO_3, DMF, 100 °C, 16 h, 50%; (iii) Pyrrolidine,$Pd_2(dba)_3$, BINAP, NaO*t*Bu, toluene, 100 °C, overnight, 80%; (iv) a) KOH, *t*BuOH, reflux, 3 h; b) AcOH, overnight, 60%; (v) Glycine *tert*-butyl ester hydrochloride, K_2CO_3, DMF, 100 °C, overnight, 70%; (vi) TFA, CH_2Cl_2, 0 °C to RT, 99%; (vii) *tert*-butyl (10-aminononyl)carbamate, BOP, DIPEA, DMF, RT, overnight, 75%; (viii) TFA, CH_2Cl_2, 0°C to RT, 98%; (ix) Compound **9**, BOP, DIPEA, DMF, RT, overnight, 80%; (x) Isophthaloyl dichloride, *p*-xylylene diamine, Et_3N, $CHCl_3$, RT, 20 h, 16%.

1-Bromo-6,9-di(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (5)[2]



Compound **5** was prepared using a modification of the literature procedure.[2] A solution of 1,6,9-Tribromo-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide 4 (1.50 g, 2.00 mmol) in DMF (50 mL) was treated with 4-*tert*-butylphenol (0.634 g, 4.22 mmol) and anhydrous potassium carbonate (1.99 g, 14.4 mmol) and stirred at 100 °C for 16 h. the reaction mixture was cooled to room temperature and water (100 mL) was added. The resulting solid was collected by vacuum filtration over a glass filter, washed with H_2O/MeOH (1:1) and dried in an oven at 130 °C. The solid obtained was dissolved in CH_2Cl_2 and subjected to column chromatography (SiO_2, eluent: 1:1 CH_2Cl_2/*n*-pentane) to afford compound **5** as a red solid (0.778 g, 44%); mp = 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (d, J = 7.8, 1H, H_b), 9.20 (d, J = 8.5, 1H, H_f), 8.38 (d, J = 8.3, 1H, H_d), 8.32 (s, 1H, H_a), 8.31 (s, 1H, H_g), 7.91 (d, J = 8.5, 1H, H_i), 7.72 (t, J = 8.1, 1H, H_c), 7.56 (d, J = 8.7, 1H, H_j), 7.43 (d, J = 7.5, 4H, H_n), 7.16-7.06 (m, 5H, H_m+ H_e, 6.94 (d, J = 2.1, 1H, H_h), 1.33 (s, 18H, H_o), 1.31 and 1.25 (s, 2 × 9H, H_k and H_l). HRMS calc. for ^{79}Br and ^{81}Br isotopomers: 883.3236/885.3231, found 883.3270/885.3235.

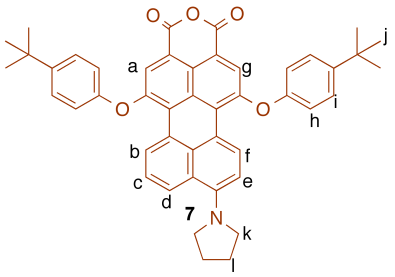
1-(*N*-pyrrolidino)-6,9-di(*tert*-butoxyphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide. (6)[2]



An oven dried Schlenk flask equipped with a magnetic stirring bar was charged with dry toluene (10 mL), $Pd_2(dba)_3$ (5 mol%), BINAP (10 mol%), NaO*t*Bu (0.042 g, 0.441 mmol), compound **5** (0.600 g, 0.339 mmol) and pyrrolidine (226 μL, 2.70 mmol). The reaction mixture was heated at 100 °C overnight. After cooling to room temperature, water (100 mL) and Et_2O (100 mL) were added and the phases were separated. The aqueous phase was extracted with Et_2O and the combined organic phases

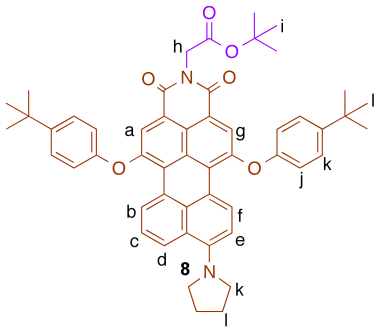
were dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel (solvent gradient elution: 60/40 *n*-pentane/CH_2Cl_2, to 10/90) to give compound **6** as a blue solid (0.474 g, 80%); mp = 284-285 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.34 (d, *J* = 8.1, 4H, H_b), 9.26 (d, *J* = 8.9, 4H, H_f), 8.36 (d, *J* = 8.3, 1H, H_d), 8.27 (s, 1H, H_a), 8.26 (s, 1H, H_g), 7.53 (d, *J* = 8.5, 1H, H_i), 7.49 (t, *J* = 8.1, 1H, H_c), 7.44-7.35 (m, 5H, H_n+ H_j), 7.07-7.04 (m, 4H, H_m), 6.95 (d, *J* = 7.9, 1H, H_e), 6.94 (d, *J* = 2.0, 1H, H_h), 3.64 (bs, 4H, H_p), 2.07 (bs, 4H, H_r), 1.32 (s, 18H, H_o), 1.28 and 1.25 (2 × s, 18H, H_k and H_l). HRMS calc. 875.4788, found 875.4790.

1-(*N*-pyrrolidino)-6,9-di(*tert*-butoxyphenoxy)perylene-3,4-dicarboxylic anhydride (7)[2]



Following a standard procedure,[1, 2] a mixture of **6** (0.300 g, 0.342 mmol), and KOH (1.34 g, 23.8 mmol) in *t*BuOH (60 mL) was refluxed for 3 h, affording quantitative hydrolysis of the imide. The hot reaction mixture was poured into acetic acid (70 mL) and the reaction mixture was vigorously stirred overnight at room temperature. To this mixture was added CH_2Cl_2 (100 mL). The organic layer was washed with water (3x50 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was subjected to column chromatography on silica gel with a solvent gradient of CH_2Cl_2/*n*-Hexane (80:20) to CH_2Cl_2/ *n*-hexane (95:5) to obtain **7** as a blue solid (141 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.35 (d, *J* = 8.1, 4H, H_b), 9.24 (d, *J* = 9.0, 4H, H_f), 8.40 (*J* = 8.3, 1H, H_d), 8.16 (s, 1H, H_a), 8.13 (s, 1H, H_g), 7.53 (t, *J* = 8.3, 1H, H_c), 7.44-7.41 (m, 4H, H_n), 7.07-6.98 (m, 5H, H_m+ H_e), 3.73 (bs, 4H, H_k), 2.12 (bs, 4H, H_l), 1.37 and 1.36 (2 × s, 18H, H_j).

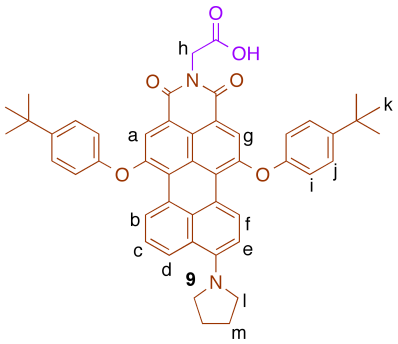
***N*-(*tert*-butoxycarbonylmethylene)-1-(*N*-pyrrolidino)-6,9-di(*tert*-butoxyphenoxy)perylene-3,4-dicarboximide (8)**



Anhydride **7** (0.138 g, 0.198 mmol) and glycine *tert*-butyl ester hydrochloride (0.066 g, 2.4 mmol) were dissolved in DMF (15 mL). Then, K_2CO_3 (0.138 g, 0.990 mmol) was added and the reaction mixture was stirred at 100 °C overnight. DMF was removed under reduced pressure and the resulting

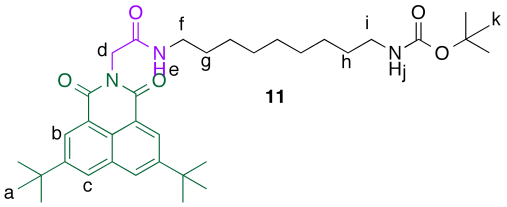
solid was redissolved in CH_2Cl_2 (100 mL). The resulting solution was washed with water (3 × 50 mL) and dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/*n*-pentane (96:4) to give **8** as a blue solid (0.162 g, 80%); mp = 158-160 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.36 (d, *J* = 8.1, 1H, H_b), 9.21 (d, *J* = 8.7, 1H, H_f), 8.28 (d, *J* = 8.3, 1H, H_d), 8.23 (s, 1H, H_a), 8.20 (s, 1H, H_g), 7.46, (t, *J* = 8.3, 1H, H_c), 7.41-7.34 (m, 4H, H_k), 7.05-6.99 (m, 4H, H_j), 6.92 (d, *J* = 8.6, 1H, H_e), 4.79 (s, 4H, H_h), 3.62 (bs, 4H, H_m), 2.04 (bs, 4H, H_n), 1.47 (s, 9H, H_i), 1.34 and 1.33 (s, 18H, H_l); ^{13}C NMR (100 MHz, CD_2Cl_2): 167.1 (CO), 162.7 (ArC), 162.6 (ArC), 162.6 (ArC), 154.1 (ArC), 153.9 (ArC), 151.9 (ArC), 150.4 (ArC), 146.6 (ArC), 146.4 (ArC), 131.0 (ArC), 130.9 (ArC), 130.8 (ArCH), 129.3 (ArC), 129.1 (ArCH), 128.5 (ArC), 128.0 (ArCH), 127.0 (ArC),126.8 (ArCH), 126.7 (ArCH), 125.1 (ArC), 124.8 (ArCH), 124.2 (ArCH), 123.5 (ArC), 123.4 (ArCH), 119.8 (ArC), 117.7 (ArCH), 117.5 (ArCH), 109.9 (ArCH), 81.7 (C_q), 41.7 (CH_2), 34.0 (2xC_q), 31.0 (CH_3), 27.6 (CH_3), 25.6 (CH_2). FAB-MS (3-NOBA matrix): m/z = 801.381 $[M+H]^+$ (Calcd for $C_{52}H_{52}N_2O_6$ + H^+: m/z = 801.383).

_N_-(carboxymethyl)-1-(_N_-pyrrolidino)-6,9-di(*tert*-butoxyphenoxy)perylene-3,4-dicarboximide (9)



A solution of compound **8** (0.160 g, 0.198 mmol) in anhydrous CH_2Cl_2 (10 mL) at 0 °C was treated with TFA (2 mL). After stirring at room temperature for 3 h, the solvent was evaporated. The residue was diluted with CH_2Cl_2 and concentrated under reduced pressure to afford **9** as a blue solid (0.146 g, 99%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.23 (d, *J* = 8.0, 1H, H_b), 9.10 (d, *J* = 8.4, 1H, H_f), 8.25 (d, *J* = 8.0, 1H, H_d), 8.04 (s, 1H, H_a), 8.03 (s, 1H, H_g), 7.40-7.34 (m, 5H, H_c+ H_j), 7.05-6.99 (m, 4H, H_i), 6.83 (d, *J* = 8.6, 1H, H_e), 4.81 (s, 2H, H_h), 3.60 (bs, 4H, H_l), 2.03 (bs, 4H, H_m), 1.34 and 1.33 (s, 18H, H_k).

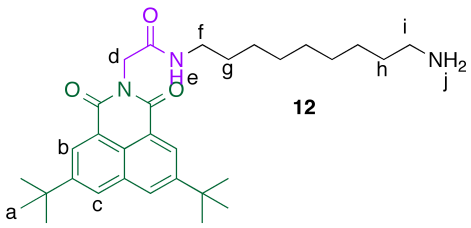
***tert*-Butyl-*N*-(9-aminononyl)-2-(5,8-di-*tert*-butyl-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl) acetamido)nonyl)carbamate (11)**



To a stirred solution of compound **10** (0.200 g, 0.544 mmol) in DMF (15 mL) under nitrogen was added BOP (0.360 g, 0.816 mmol) in one portion. The reaction mixture was stirred for 30 min at room

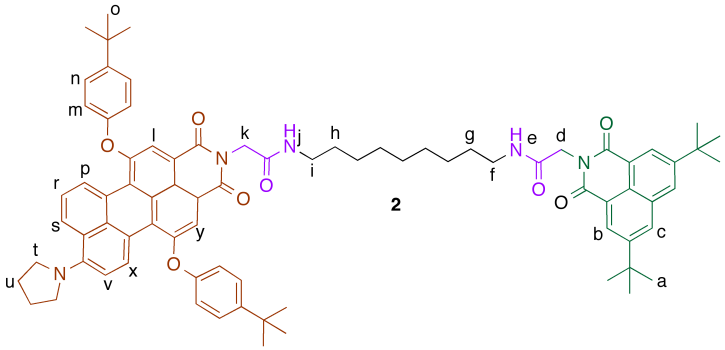
temperature. Then, DIPEA (568 µL, 3.26 mmol) and *tert*-butyl (10-aminononyl)carbamate (0.144 g, 0.598 mmol) were dissolved in anhydrous DMF (10 mL) and added to the reaction mixture. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The oily residue was redissolved in CH_2Cl_2 (100 mL), washed with water (3 × 50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica gel with CH_2Cl_2/Acetone (95:5) yielded **11** as a white solid (0.248 g, 75%); mp = 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 1.8 Hz, 2H, H_b), 8.17 (d, *J* = 1.8 Hz, 2H, H_c), 5.77 (bs, 1H, H_e), 4.87 (s, 2H, H_d), 4.51 (s, 1H, H_j), 3.31 (td, *J* = 6.8, *J* = 6.4, 2H, H_f), 3.11 (td, *J* = 6.8, *J* = 5.2, 2H, H_i), 1.57 (s, 4H, H_g and H_h), 1.49 (s, 18H, H_a), 1.46 (s, 9H, H_k), 1.29 (bs, 10H, CH_2 alkyl chain).

***N*-(9-aminononyl)-2-(5,8-di-*tert*-butyl-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)acetamide (12)**



Procedure as for acid **9**, starting from amide **11** (0.150 g, 0.247 mmol), gave amine **12** as a white solid (0.123 g, 98%); mp = 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 1.8 Hz, 2H, H_b), 8.17 (d, *J* = 1.8 Hz, 2H, H_c), 5.77 (bs, 1H, H_e), 4.87 (s, 2H, H_d), 3.30 (td, *J* = 8.0, *J* = 4.0, 2H, H_f), 3.11 (t, *J* = 8.0, 2H, H_i), 1.51-1.46 (m, 22 H, H_a+ H_g+ H_h), 1.29-1.25 (m, 10H, CH_2 alkyl chain); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (CO), 164.3 (CO), 150.1 (ArC), 131.9 (ArC), 129.5 (ArCH), 129.4 (ArCH), 124.8 (ArC), 121.5 (ArC), 43.0 (CH_2), 39.7 (CH_2), 35.1 (C_q), 31.0 (CH_3), 29.3 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 26.7 (2 × CH_2). HRMS calc. 508.3539, found 508.3539.

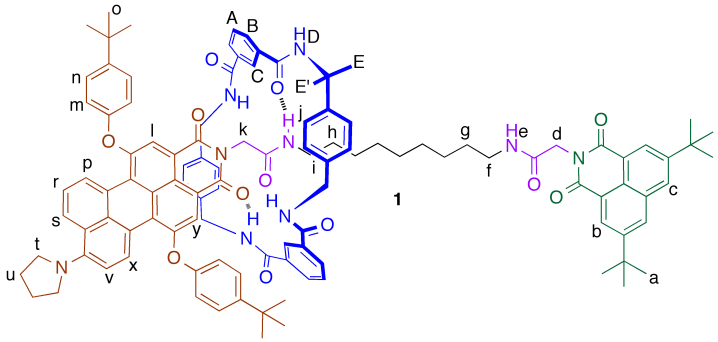
2-(5,12-bis(4-(*tert*-butyl)phenoxy)-1,3-dioxo-9-(pyrrolidin-1-yl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinolin-2(3*H*,3a^1*H*,13a*H*)-yl)-*N*-(9-(2-(5,8-di-*tert*-butyl-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)acetamido)nonyl)acetamide-Thread 2



To a stirred solution of compound **9** (0.128 g, 0.172 mmol) in anhydrous DMF (10 mL) under nitrogen BOP (0.114 g, 0.258 mmol) was added in one portion. The reaction mixture was stirred for 30 min at

room temperature. A solution of compound **12** (0.096 g, 0.19 mmol) in DMF (5mL) was then added, followed by DIPEA (499 µL, 1.20 mmol). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, followed by redissolving of the blue residue in CH_2Cl_2 (100 mL), which was washed with water, and then dried over $MgSO_4$. Removal of the solvent gave a blue solid from which the product was isolated by column chromatography (SiO_2, eluent: 95:5 CH_2Cl_2/Acetone) as a dark blue solid (0.170 g, 80%); mp = 182-184 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.15 (d, *J* = 7.1, 1H, H_p), 9.06 (d, *J* = 7.1, 1H, H_x), 8.53 (d, *J* = 1.8, 2H, H_b), 8.23 (dd, *J* = 8.4, *J* = 0.9, 1H, H_s), 8.14 (s, 1H, H_l), 8.10 (s, 1H, H_y), 8.05 (d, *J* = 1.8, 2H, H_c), 7.45-7.36 (m, 5H, H_n+ H_r), 7.11-7.00 (m, 4H, H_m), 6.81 (d, *J* = 9.1, 1H, H_v), 6.14 (t, *J* = 5.7, 1H, H_j), 6.00 (t, *J* = 5.7, 1H, H_e), 4.69 (s, 2H, H_d), 4.60 (s, 2H, H_k), 3.59 (bs, 4H, H_t), 3.24-3.16 (m, 4H, H_f+ H_i), 2.02 (bs, 4H, H_u), 1.50-1.44 (m, 2H, H_g), 1.40 (bs, 20H, H_a+ H_h) , 1.33 and 1.32 (s, 18H, H_o), 1.26 (bs, 10H, CH_2 alkyl chain); ^{13}C NMR (100 MHz, DMF-*d*$_7$): δ = 166.8 (CO), 164.3 (CO), 162.5 (ArC), 162.4 (ArC), 154.0 (ArC), 153.8 (ArC), 151.9 (ArC), 150.4 (ArC), 149.9 (ArC), 146.8 (ArC), 146.5 (ArC), 132.2 (ArC), 130.9 (ArC), 130.8 (ArCH), 130.7 (ArC), 129.6 (ArCH), 129.0 (ArCH), 128.5 (ArC), 128.2 (ArCH), 128.0 (ArCH), 127.7 (ArC), 127.2 (ArCH), 127.1 (ArCH),126.7 (ArC), 124.9 (ArC), 124.7 (ArCH), 124.6 (ArC), 123.6 (ArCH), 123.5 (ArCH), 123.2 (ArC), 122.8 (ArCH), 121.8 (ArC), 120.2 (ArC), 118.2 (ArCH), 117.8 (ArCH), 117.7 (ArC), 117.0 (ArC), 52.3 (CH_2), 42.5 (CH_2), 42.4 (CH_2), 38.9 (CH_2), 38.8 (CH_2), 30.8 (CH_3), 30.5 (CH_3), 26.3 (CH_2), 25.0 (CH_2), 22.5 (CH_2). FAB-MS (3-NOBA matrix): *m/z* = 1236.670 $[M+H]^+$ (Calcd for $C_{79}H_{89}N_5O_8$ + H^+: m/z = 1236.671).

[2]-(1,4,7,14,17,20-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-2-(5,12-bis(4-(*tert*-butyl)phenoxy)-1,3-dioxo-9-(pyrrolidin-1-yl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinolin-2(3*H*,3a^1*H*,13a*H*)-yl)-*N*-(9-(2-(5,8-di-*tert*-butyl-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)acetamido)nonyl)acetamide-Rotaxane 1



Thread **2** (0.170 g, 0.137 mmol) and Et_3N (459 µL, 3.30 mmol) were dissolved in chloroform (75 mL), and stirred vigorously whilst solutions of the *p*-xylylene diamine (0.223 g, 1.64 mmol) and isophthaloyl dichloride (0.332 g, 1.64 mmol) in $CHCl_3$ (20 mL) were simultaneously added over a period of 4 hours using a motor-driven syringe pump. The resulting suspension was stirred overnight and filtered through a pad of Celite to afford the crude product. The solvent was removed and the residue was subjected to column chromatography (silica gel, CH_2Cl_2: Acetone (9:1) to yield unreacted thread **2** (0.135 g, 80%) and rotaxane **1** (0.038 g, 16%) as blue solids; mp = 203-206 °C; ^{1}H NMR (400

MHz, CD_2Cl_2): δ = 9.37 (d, *J* = 8.1, 1H, H_p), 9.26 (d, *J* = 8.9, 1H, H_x), 8.55 (d, (d, *J* = 0.9, 2H, H_b), 8.36 (d, *J* = 8.6, 1H, H_s), 8.18 (d, *J* = 0.9, 2H, H_c), 8.09-8.05 (m, 8H, H_C+ H_l+ H_y+ H_B), 7.91 (t, *J* = 4.9, 1H, H_D), 7.57-7.50 (m, 3H, H_A+ H_r), 7.39-7.36 (m, 4H, H_n), 7.06 (s, 8H, H_F), 7.02-6.99 (m, 4H, H_m), 6.94 (d, *J* = 9.2, 1H, H_v), 6.90 (t, *J* = 6.1, 1H, H_j), 6.74 (t, *J* = 5.4, 1H, H_e), 4.50 (s, 2H, H_d), 4.46 (dd, *J* = 14.0, *J* = 5.4, A-part of ABX system, 4H, H_E), 4.25 (dd, *J* = 14.0, *J* = 4.7, B-part of ABX system, 4H, $H_{E'}$), 4.12 (s, 2H, H_k), 3.68 (bs, 4H, H_t), 2.81-2.76 (m, 2H, H_f), 2.71-2.67 (m, 4H, H_i), 2.06 (bs, 4H, H_u), 1.42 (s, 18H, H_a), 1.32 (bs, 18H, H_o), 1.15-1.06 (m, 4H, H_g+ H_h), 0.970-0.901 (m, 10H, CH_2 alkyl chain); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 168.9 (CO), 168.0 (CO), 166.6 (CO), 166.2 (CO), 164.4 (CO), 161.5 (ArC), 159.8 (ArC), 155.7 (ArC), 155.5 (ArC), 153.7 (ArC), 151.0 (ArC), 149.9 (ArC), 146.9 (ArC), 146.7 (ArC), 146.5 (ArC), 132.3 (ArC), 132.0 (ArC), 131.8 (ArC), 131.1 (ArCH), 130.6 (ArCH), 129.5 (ArCH), 129.4 (ArCH), 129.1 (ArCH), 128.9 (ArCH), 128.8 (ArCH), 128.6 (ArCH), 128.5 (ArC), 128.4 (ArCH), 128.2 (ArCH), 126.7 (ArCH), 126.5 (ArC), 126.4 (ArCH), 124.9 (ArCH), 124.8 (ArC), 124.6 (ArC), 124.5 (ArC), 123.9 (ArC), 123.8 (ArC), 123.4 (ArCH), 122.9 (ArC), 121.6 (ArC), 119.3 (ArCH), 117.4 (ArC), 117.3 (ArCH), 117.1 (ArCH), 117.0(ArC), 50.2 (CH_2), 44.3 (CH_2), 42.4 (CH_2), 40.6 (CH_2), 39.4 (CH_2), 39.3 (CH_2), 35.2 (C_q), 34.9 (CH_2), 33.1 (CH_2), 30.9 (CH_3), 30.6 (CH_3), 29.5 (CH_2), 28.6 (CH_2), 28.1 (CH_2), 28.0 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 25.7 (CH_2). FAB-MS (3-NOBA matrix): *m/z* = 1768.881 $[M+H]^+$ (Calc. for $C_{111}H_{117}N_9O_{12}+H^+$: m/z = 1768.882).

3. NMR Spectra

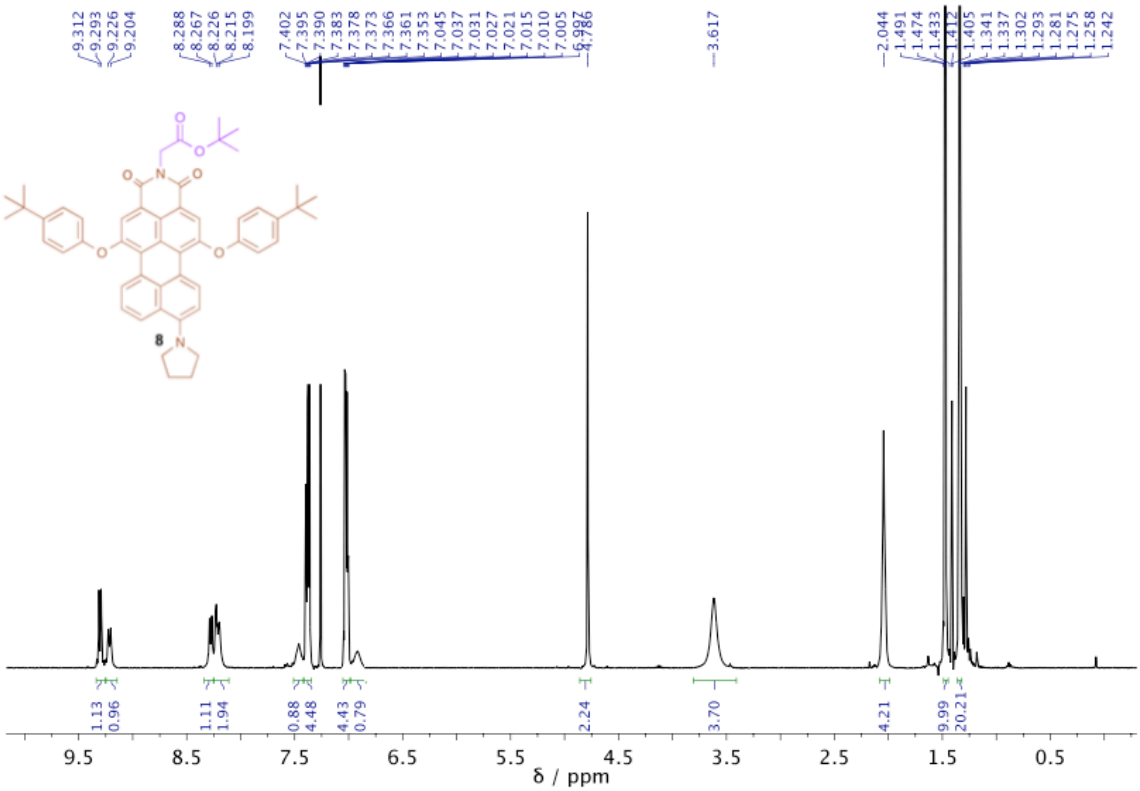


Figure S1. ^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$, 298 K).

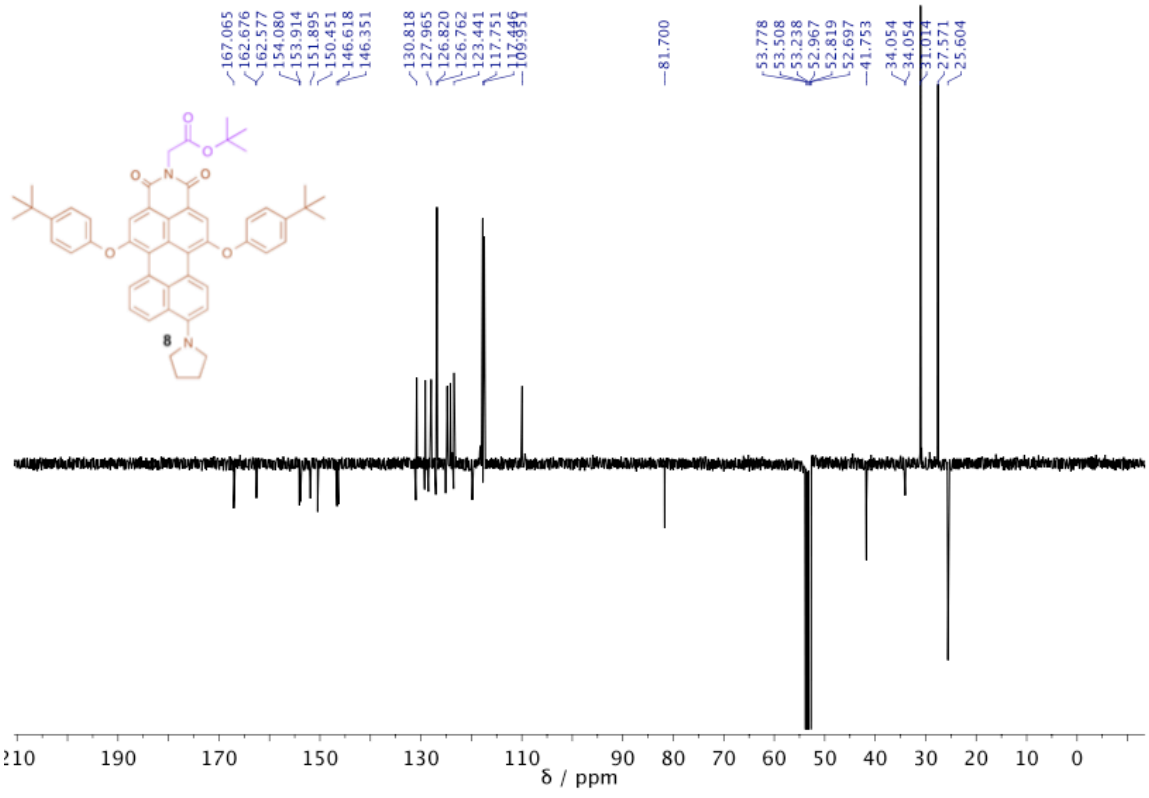


Figure S2. APT spectrum of compound **8** (400 MHz, CD_2Cl_2, 298 K).

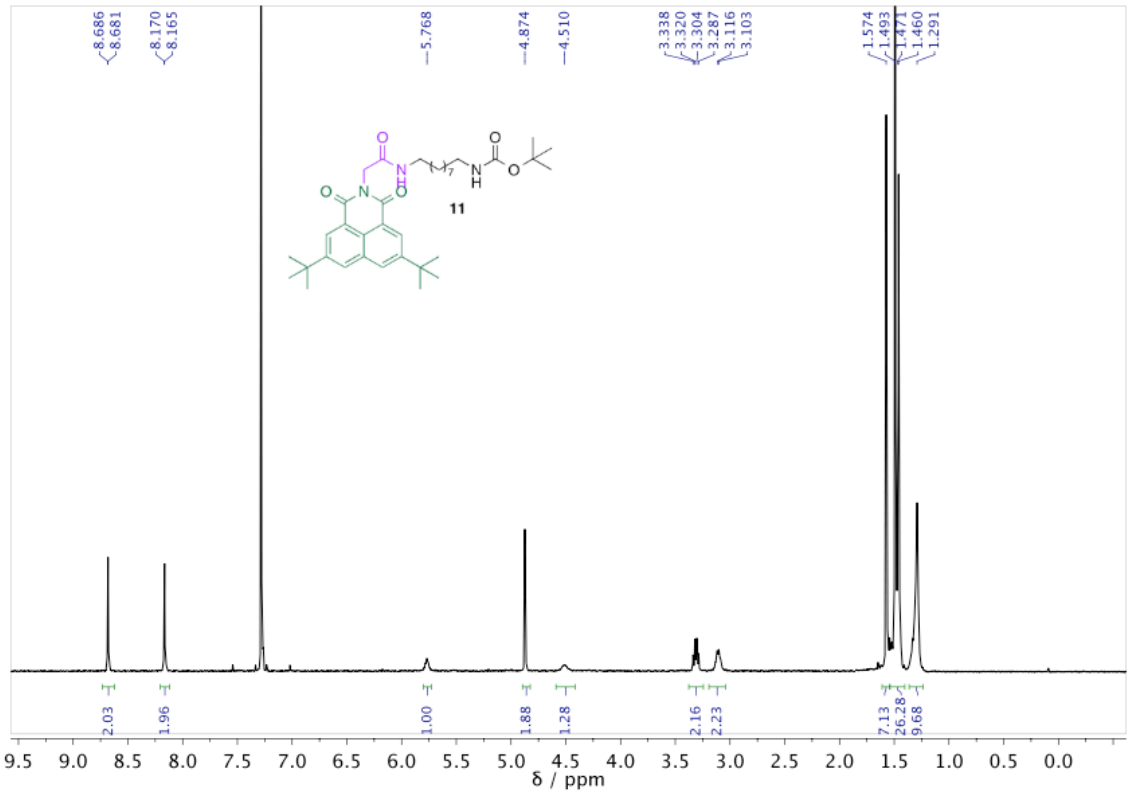


Figure S3. ^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$, 298 K).

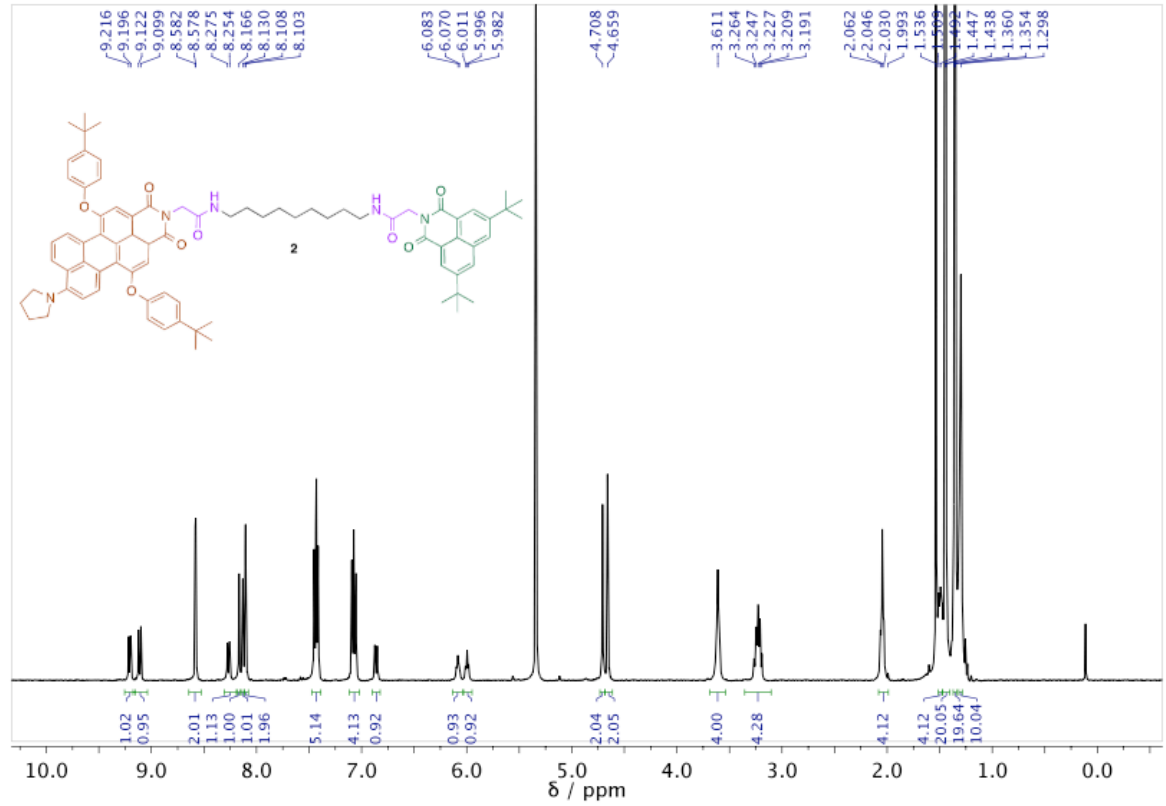


Figure S4. ^{1}H NMR spectrum of thread **2** (400 MHz, CD_2Cl_2, 298 K).

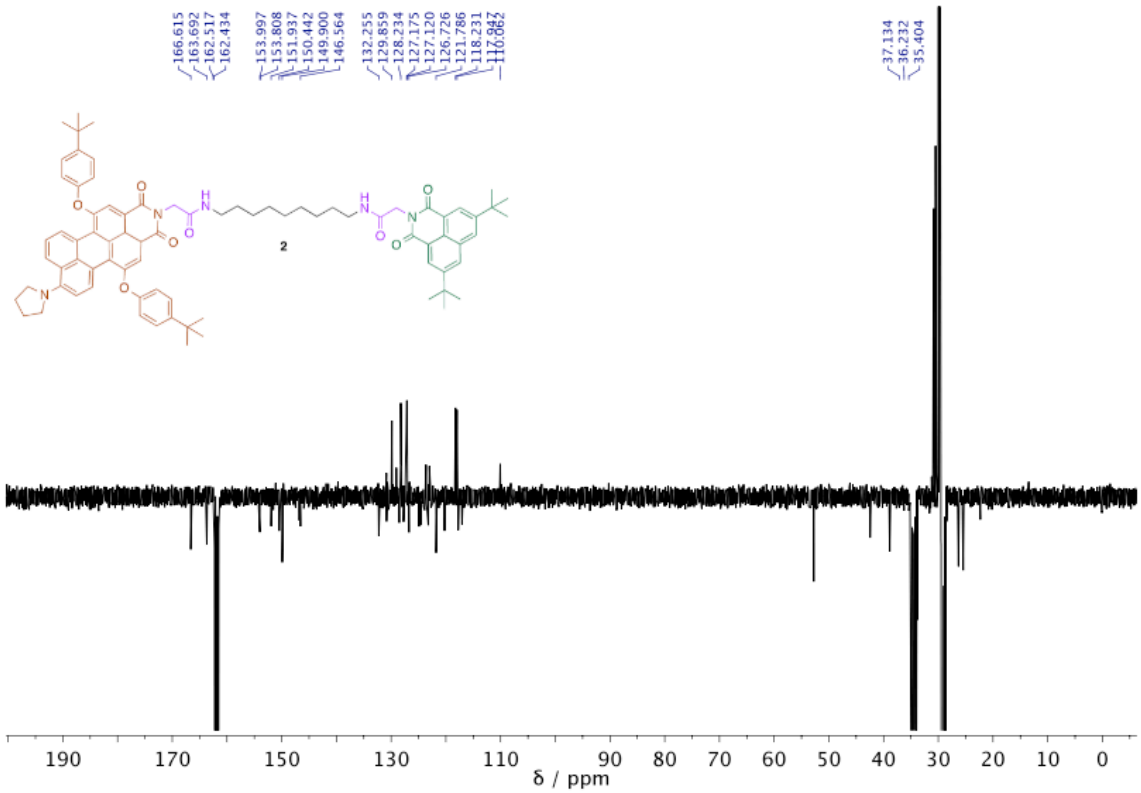


Figure S5. APT spectrum of thread **2** (400 MHz, DMF-d_7, 298 K).

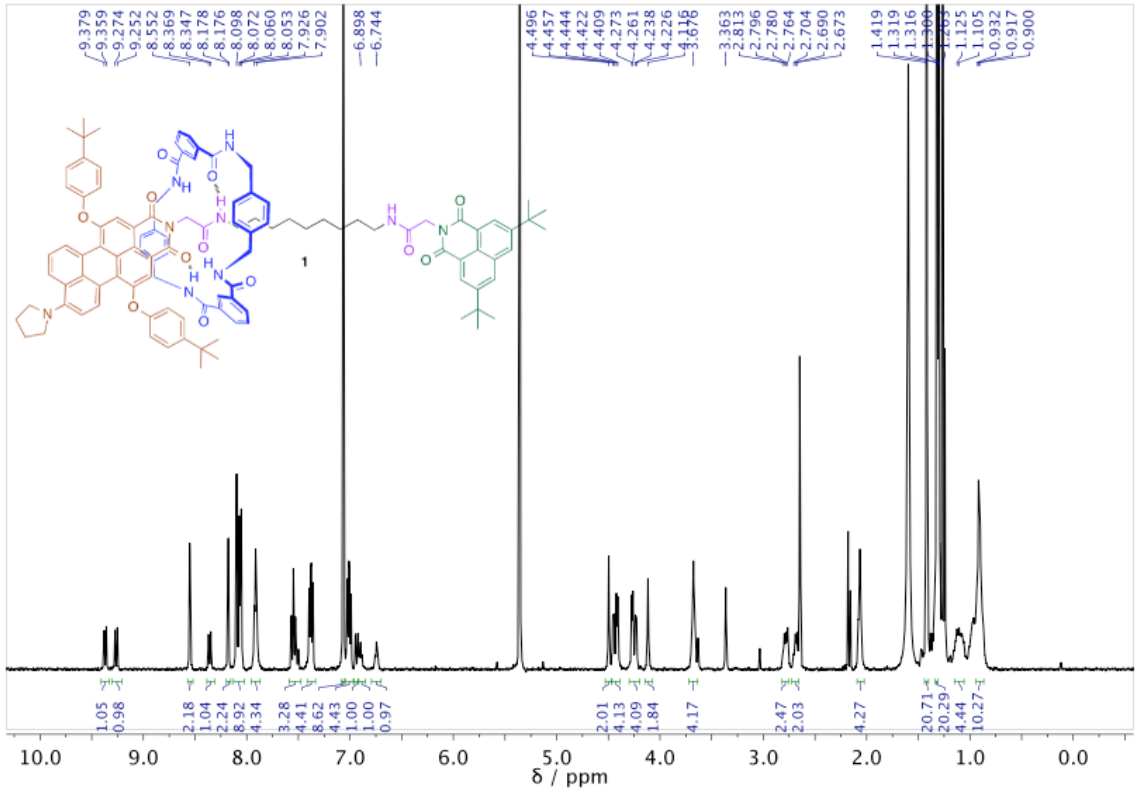
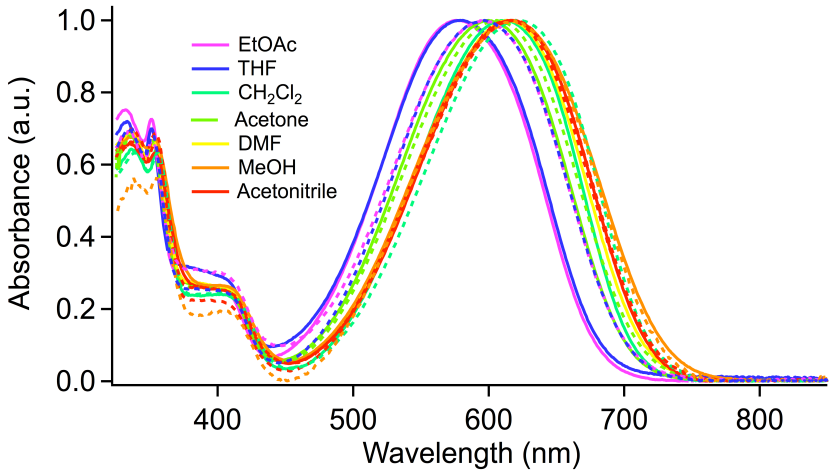


Figure S6. ^{1}H NMR spectrum of rotaxane **1** (400 MHz, CD_2Cl_2, 298 K).

4. Optical Spectroscopic Properties

4.1 Absorption and Emission Spectra

A)



B)

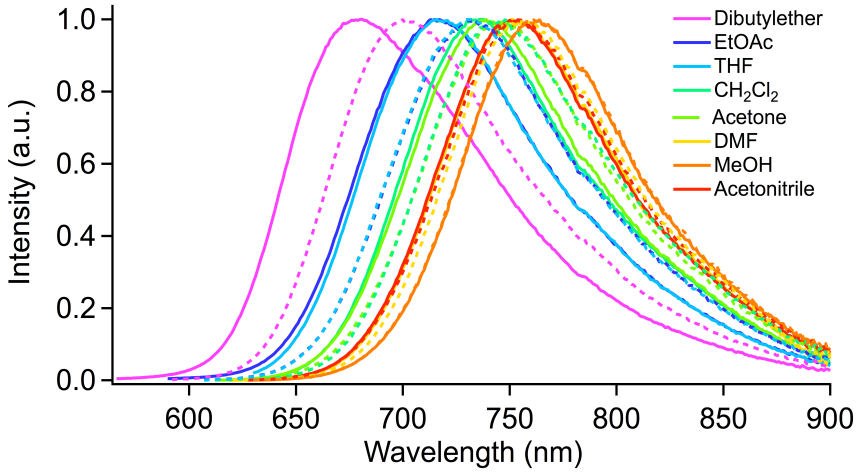


Figure S7. A) Absorption spectra of rotaxane **1** (dotted) and thread **2** (line) in different solvents; B) Emission spectra of rotaxane **1** (dotted) and thread **2** (line) in different solvents. All spectra are scaled to the same maxima. The spectra in toluene and DMSO are shown in the main text (Fig. 2).

4.2 Fluorescence Quantum Yields and Fluorescence Lifetimes

Fluorescence lifetimes of **1** and **2** were determined in various solvents using a single photon counting apparatus with excitation at 405 nm. The obtained values are compiled in Table 4. Detection at different wavelengths ranging from 680 to 720 nm gave identical traces.

Table S1. Fluorescence quantum yields (Φ_{Fl})[a] and fluorescence decay times (τ)[b] with respective amplitudes in brackets of rotaxane **1** and thread **2** in several solvents.

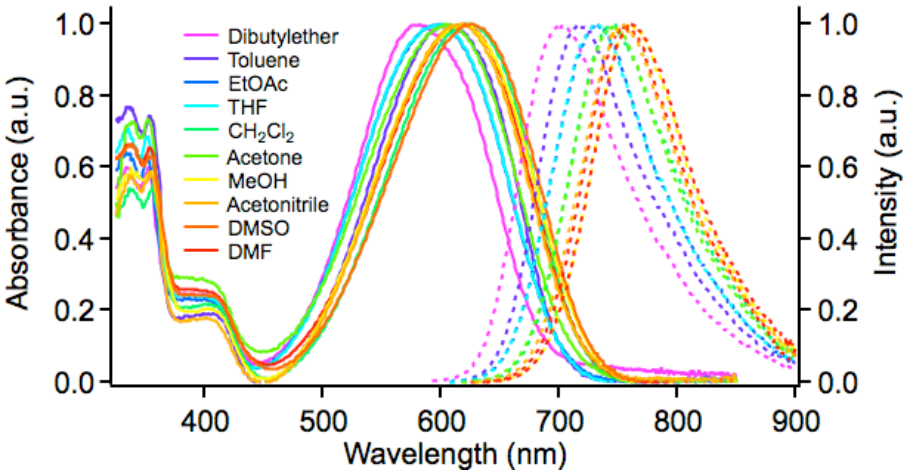
	1		**2**	
Solvent	Φ_{Fl}[c,d]	τ (ns)[e,f]	Φ_{Fl}[c,d]	τ (ns)[f, g]
Toluene	0.45	2.9	0.47	3.4
Dibutyether		3.2		3.8
EtOAc		2.9		3.5
THF		2.9		3.3
CH_2Cl_2	0.36	2.9	0.36	3.1
Acetone	0.32	3.0	0.33	3.3
DMF		2.8		2.9
MeOH		1.8		1.9
Acetonitrile	0.30	2.9	0.27	3.1
DMSO		2.7 (0.80)		2.8 (0.74)
		0.2 (0.20)		0.2 (0.26)

[a] The standard used is perylene red in $CHCl_3$ with a quantum yield of 0.96.[6] [b] Excitation wavelength for lifetimes is 405 nm. [c] λ_{exc} = 560 nm. [d] Φ_{Fl} ± 0.02. Absorbance of the solution ~ 0.1. [e] Detection at 720 nm. [f] Error estimate < 5 %. [g] Detection at 700 nm.

For thread **2**, fluorescence decay times between 3.4 and 2.1 ns were determined and they are similar to the values reported by Zoon *et al.* for a closely related pyrrolidine-substituted perylene imide compound.[8] The obtained fluorescence decay in each solvent was well described by a mono-exponential curve except in the case of DMSO. In DMSO, a small contribution (26%) from an additional fast decay time component (0.2 ns) has been detected, which might be ascribed to some conformational relaxation in the excited state. For rotaxane **1**, fluorescence lifetimes are between 3.2 and 2.1 ns and show no clear dependence on solvent polarity. Notably, the decay times are shorter than those of thread **2**. These trends are rationalized - in line with previous work - on the basis of hydrogen-bond induced non-radiative decay pathways.[9] The decay curves for **1** exhibit a bi-exponential nature for each detection wavelength in DMSO but a mono-exponential behavior in all the other solvents studied. Furthermore, as the data in Table 4 reveal, quantum yields of **1** and **2** show a slight decrease with increasing solvent polarity and they are in accordance with the values described for structurally related perylene derivatives.[8]

4.3 Solvatochromism

A)



B)

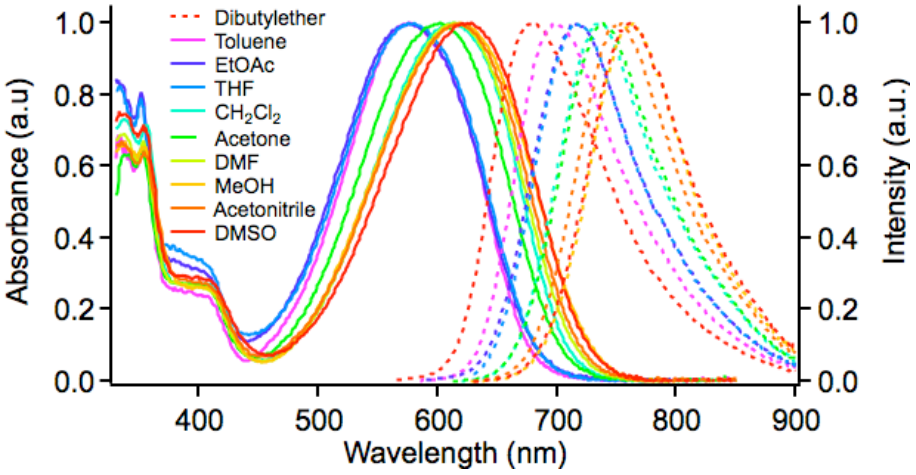


Figure S8. Absorption and emission spectra of A) Rotaxane **1** B) Thread **2** in various solvents. All spectra are scaled to the same maxima.

Table S2. Observed absorption and fluorescence maxima in wavenumbers (cm^{-1}) of rotaxane **1** and thread **2** in different solvents and the relevant solvent parameters[10] for Kamlet-Taft expression.

	1		**2**		Parameters		
Solvent	$\nu_{abs}(\times10^{-4})^a$	$\nu_{em}(\times10^{-4})^a$	$\nu_{abs}(\times10^{-4})^a$	$\nu_{em}(\times10^{-4})^a$	α^b	β^c	π^{*d}
Toluene	1.66	1.38	1.74	1.41	0.00	0.11	0.54
Dibutylether	1.73	1.41	1.80	1.46	0.00	0.49	0.27
EtOAc	1.67	1.36	1.73	1.39	0.00	0.45	0.55
THF	1.67	1.35	1.73	1.38	0.00	0.55	0.58
CH_2Cl_2	1.60	1.34	1.72	1.35	0.30	0.00	0.82
Acetone	1.65	1.33	1.64	1.35	0.08	0.48	0.71
DMF	1.62	1.31	1.66	1.32	0.00	0.69	0.88
MeOH	1.61	1.30	1.63	1.31	0.93	0.62	0.54
Acetonitrile	1.61	1.32	1.61	1.33	0.75	0.31	0.75
DMSO	1.59	1.31	1.62	1.31	0.00	0.76	1.00

[a] Value ± 0.01. [b] Hydrogen-bond donating ability. [c] Hydrogen-bond accepting ability. [d] Dipolarity-polarizability values.

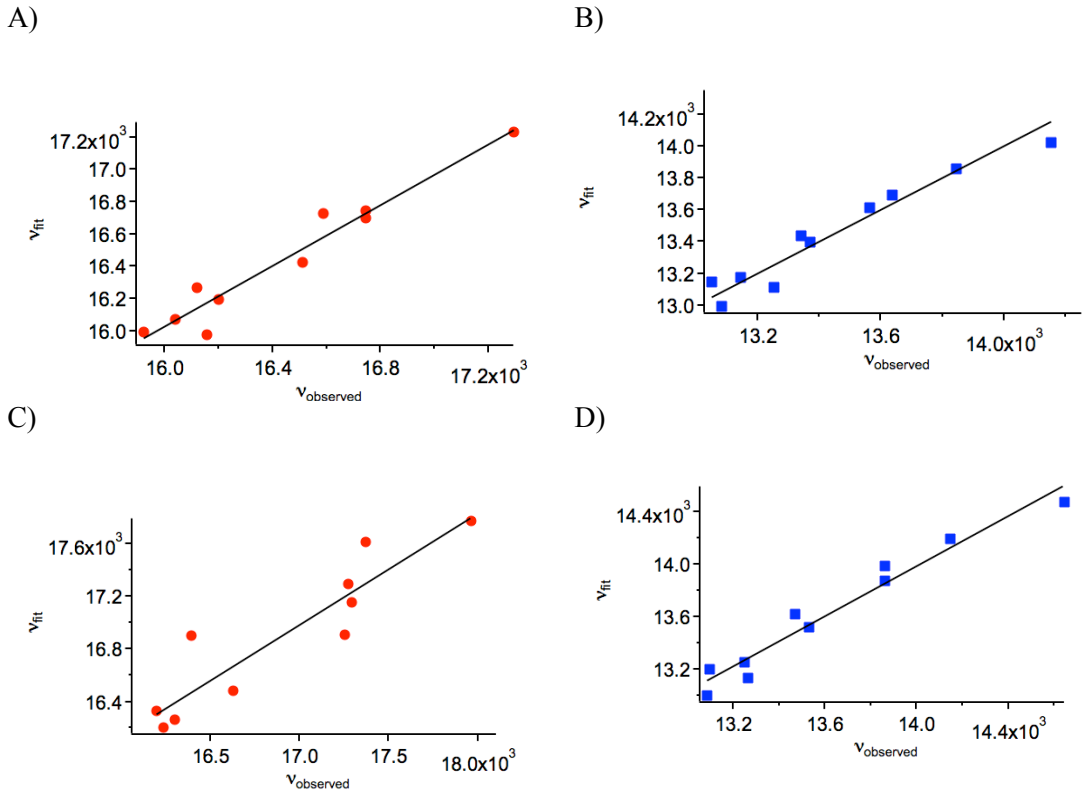
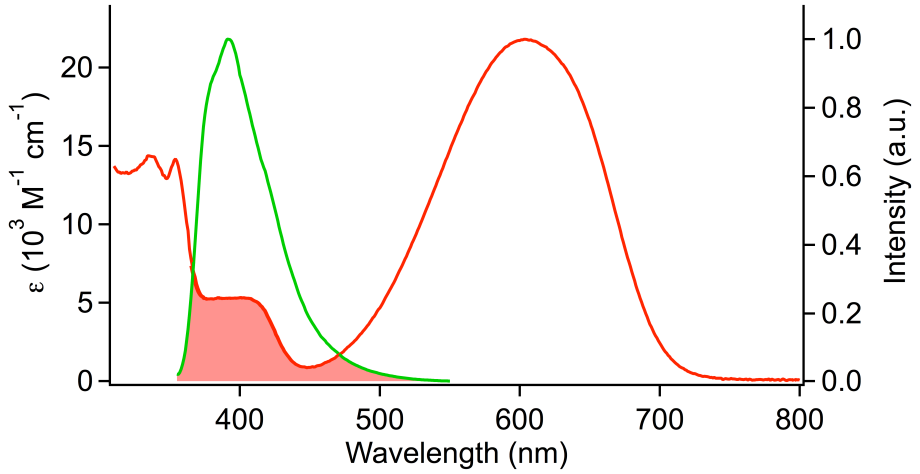


Figure S9. Plots of the maxima obtained from fitting the absorption and fluorescence maxima of rotaxane **1** (A and B, respectively) and thread **2** (C and D, respectively) to the Kamlet-Taft Equation versus observed maxima.

4.4 Fluorescence Resonance Energy Transfer (FRET)

On the basis of the efficient overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor chromophoric units in rotaxane **1** and thread **2** we can expect the possibility of an efficient FRET process (Figure S10). Indeed, upon excitation of **1** and **2** at 345 nm, fluorescence emission of the perylene unit at about 700-800 nm was observed in all the solvents studied indicating an energy transfer from the naphthalimide to the perylene imide chromophore (Figure S11). The emission arising from naphthalimide unit at ~ 380 nm, however, is still detectable. FRET occurs mainly via a higher excited state of the perylene unit absorbing at 400 nm, which is not solvatochromic.

A)



B)

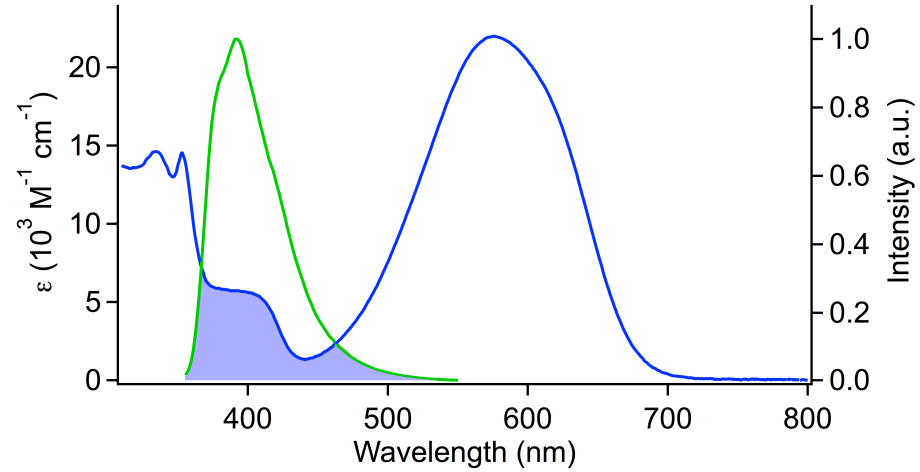
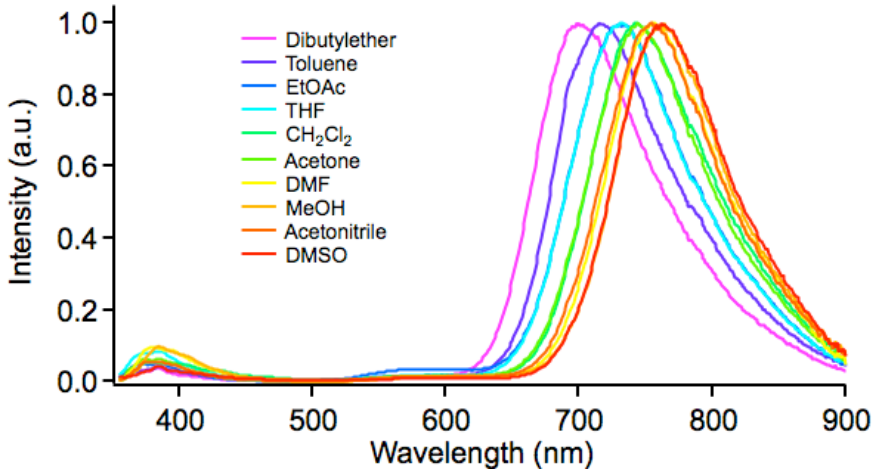


Figure S10. A) Fluorescence emission spectra of compound **11** (donor, green line) and absorption spectrum of rotaxane **1** (red line, left axis) in toluene with shaded area representing the spectral overlap. B) Fluorescence emission spectra of compound **11** (donor, green line) and absorption spectrum of thread **2** (blue line, left axis) in toluene with shaded area representing the spectral overlap.

A)



B)

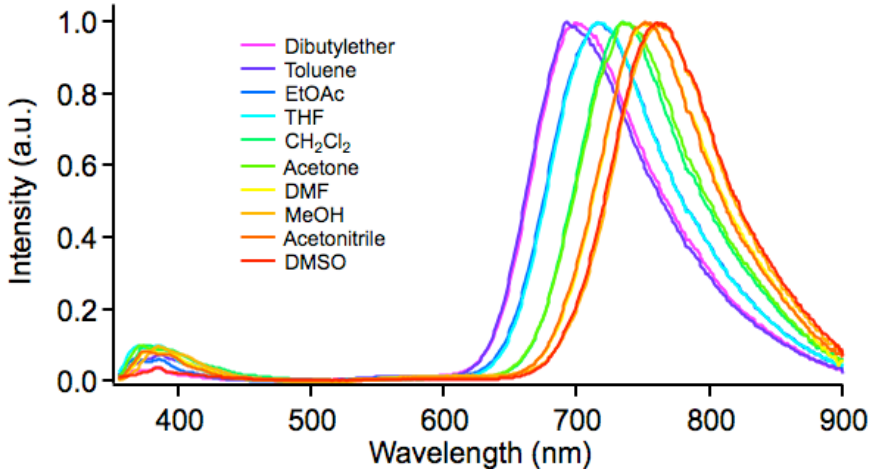


Figure S11. Fluorescence emission spectra (λ_{exc} = 345 nm, 298 K) of A) Rotaxane **1**, B) Thread **2** in various solvents.

For a better quantification of the FRET, time-resolved fluorescence spectroscopy was employed. The observed fluorescence lifetimes are collected in Table S2. For comparison, model compound **11** was used to obtain the donor-only decay times. On excitation of the naphthalimide unit in **2** at 324 nm in toluene, strong quenching of its fluorescence was observed as the fluorescence lifetime was drastically reduced to 0.2 and 0.09 ns for non polar toluene and highly polar acetonitrile, respectively, compared to the reference compound **11** (τ = 2.6 and τ = 2.2 ns for toluene and acetonitrile, respectively). Likewise, for rotaxane **1**, significantly shortened fluorescence lifetimes were found for the naphthalimide unit upon detection at 390 nm compared with those of reference compound **11**. The observed lifetimes are reduced to values of 0.1 ns (in toluene) and 0.08 ns (in acetonitrile). Fluorescence quenching of the naphthalimide unit in **1** is more pronounced than in thread **2**. In both **1** and **2**, the acceptor is always excited to some extent because the acceptor absorbs (ε_{324} = 6130

$M^{-1}cm^{-1}$) at the excitation wavelength used to excite the donor. Since the acceptor is fluorescent, the light absorbed by the donor and transferred to the acceptor appears as enhanced acceptor emission. In the time domain, the characteristics of an excited state reaction are a rise time in the time dependent intensities and a negative pre-exponential factor in the multi-exponential analysis. In the present case, however, a sensitization of the emission of the perylene imide unit with a rise time could not be detected because most of the perylene emission is due to the intrinsic decay of the directly excited perylene imide chromophore rather than by FRET. The decays at 720 nm were fitted mono-exponentially for both rotaxane **1** and thread **2** in all solvents. Fluorescence lifetimes range from 3.1 (in Toluene) to 1.9 ns (in MeOH) for rotaxane **1** and they are similar to those found for thread **2**. As expected, the decay times at 720 nm are very similar to those obtained with direct excitation at 405 nm (Table 4).

Table S3. Fluorescence lifetimes (τ)[a, b] with respective amplitudes in brackets of rotaxane **1**, thread **2** and the reference compound **11** in various solvents.[b]

	1		**2**		**11**
Solvent	τ (ns)[d]	τ (ns)[e]	τ (ns)[d]	τ (ns)[e]	τ (ns)[d]
Toluene	0.10 (0.97)	3.0	0.2 (0.95)	3.4	2.6
THF	1.3 (0.03) 0.09 (0.98)	3.0	1.4 (0.05) 0.10 (0.97)	3.3	1.2
CH_2Cl_2	0.60 (0.02) 0.10	2.9	0.70 (0.03) 0.10 (0.98)	3.2	1.5
Acetone	0.09 (0.85)	3.1	1.3 (0.20) 0.10 (0.80)	3.3	1.7
DMF	1.8 (0.15) 0.11 (0.96)	2.8	1.8 (0.20) 0.11 (0.98)	2.9	1.0
MeOH	0.30 (0.04) 0.08	1.9	0.50 (0.02) 0.09 (0.93)	1.8	2.8
Acetonitrile	0.08	2.9	2.7 (0.07) 0.09 (0.95)	3.0	2.2
DMSO	nd[e]	2.7 (0.80) 0.2 (0.20)	2.1 (0.05) nd[e]	2.8 (0.80) 0.2 (0.20)	nd[e]

[a] λ_{exc} = 324 nm. [b] Error estimate < 5 %. [c] All spectra were recorded at room temperature. [d] λ_{det} = 390 nm. [e] λ_{det} = 720 nm.

[f] Values could not be determined as the signal falls within the time response of the instrument (~ 20 ps).

Based on the above-mentioned photophysical data, the influence of the solvent polarity on the energy transfer rates and efficiencies was studied. The rate of energy transfer was calculated using the following equation:

$$k_T = \frac{1}{\tau_{DA}} - \frac{1}{\tau_D} \qquad \text{(S2)}$$

where τ_{DA} and τ_D represent the decay of the donor in the presence and in the absence of acceptor, respectively. Furthermore, the efficiency of the energy transfer can be calculated according to Equation S3.

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \qquad \text{(S3)}$$

The results for both rotaxane **1** and thread **2** are summarized in Table S3. The respective rate constants for **1** are $k_T = 1.0 \times 10^{10}$ s^{-1} for all solvents, whereas they range from $k_T = 4.6 \times 10^9$ s^{-1} (in toluene) to $k_T = 1.1 \times 10^{10}$ s^{-1} (in acetonitrile) for the corresponding thread **2**. The efficiency of the transfer process from naphthalimide to perylene imide chromophore is close to 1.0 for both compounds in all solvents. No general trend for the effect of solvent polarity on the transfer rates was observed which is in good agreement with the solvent independency usually observed for Förster-type resonance energy transfer.

Table S4. Efficiencies and rate constants of energy transfer in rotaxane **1** and thread **2**.

	1		**2**	
Solvent	k_T (10^{10} s^{-1})	E^a	k_T (10^{10} s^{-1})	E^a
Toluene	0.96 ± 0.02	0.96	0.46 ± 0.01	0.92
THF	1.0 ± 0.1	0.92	0.92 ± 0.01	0.92
CH_2Cl_2	1.0 ± 0.1	0.94	0.93 ± 0.01	0.93
Acetone	1.0 ± 0.2	0.95	0.94 ± 0.01	0.94
DMF	1.1 ± 0.1	0.92	0.81 ± 0.01	0.90
MeOH	1.2 ± 0.1	0.97	1.1 ± 0.1	0.96
Acetonitrile	1.2 ± 0.1	0.96	1.1± 0.1	0.96

[a] Value ± 0.02

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