Supporting Information

pH and light-controlled self-assembly of [c2]

daisy chain rotaxanes

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1. Synthesis

General Methods

All reactions were performed under an atmosphere of argon unless otherwise indicated. All reagents and solvents were purchased at the highest commercial quality and used without further purification unless otherwise noted. Dry solvents were obtained using a double column SolvTech purification system. Yields refer to purified spectroscopically (¹H NMR) homogeneous materials. Thin Layer Chromatographies were performed with TLC silica on aluminium foils (Silica Gel/UV254, Aldrich). In most cases, irradiation using a Bioblock VL-4C UV-Lamp (6 W, 254 nm and/or 365 nm) as well as p-anisaldehyde, phosphomolybdic acid and Cerium ammonium molybdate stainings were used for visualization. Ultra Performance Liquid Chromatographies coupled to Mass Spectroscopy (UPLC-MS) were carried out on a Waters Acquity UPLC-SQD apparatus equipped with a PDA detector (190-500 nm, 80Hz), using a reverse phase column (Waters, BEH C18 1.7 µm, 2.1mm x 50 mm), and the MassLynx 4.1 – XP software. Preparative Adsorption Flash Column Chromatographies were performed using silica gel (60 Å, 230–400 mesh, 40–63 µm, Sigma-Aldrich). ¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz and ¹³C spectra at 100 MHz in CDCl₃ or CD₃CN at 25°C. The spectra were internally referenced to the residual proton solvent signal (CDCl₃: 7.26 ppm, CD₃CN: 1.94 pm for ¹H spectrum, and CDCl₃: 77.16 ppm and CD₃CN: 118.26 and 1.32 ppm for ¹³C spectrum). For ¹H NMR assignments, the chemical shifts are given in ppm. Coupling constants J are listed in Hz. The following notation is used for the ¹H NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m), large (l).

Synthetic Procedures



То of 4-(benzyloxy)-N-(4-(benzyloxy)phenyl)-N-(4stirred. sticky suspension а nitrophenyl)aniline¹ (188 mg, 398 µmol, 1.00 eq) in MeOH (5 mL) a 1 M HCl solution (6 mL) was added slowly, followed by two drops of conc. HCl. The mixture was then cooled down to 0°C. After 15 min at this temperature, NaNO₂ (129 mg, 1.87 mmol, 4.70 eq) in water (0.8 mL) was added dropwise within about 2 min. The yellow-orange suspension immediately turned brown after the first drop. The mixture was further stirred for 35 min. NaN₃ (259 mg, 3.98 mmol, 10.0 eq) was added in two equal portions dissolved in water (1.3 mL each). The brown suspension was further stirred for 40 min, while allowing the mixture to heat up to room temperature. Dichloromethane (90 mL) was added and the mixture was washed with water (90 mL). The organic phase was washed with sat. NaHCO₃ (25 mL) followed by brine (25 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The oily brown crude product was purified by flash column chromatography (SiO₂, dichloro-methane/cyclohexane: 1/1; R_f (dichloromethane/cyclohexane: 1/1) = 0.27) to afford compound 1 (131 mg, 263 μ mol, 66 % over two steps) as a brown waxy solid. ¹H NMR (CDCl₃, 400 MHz, 25°C): $\delta = 7.50$ -7.33 (m, 10H, H_C), 7.04 (d, ${}^{3}J = 9.2$ Hz, 4H, H_B), 6.98 (d, ${}^{3}J = 8.8$ Hz, 2H, H_A), 6.92 (d, ${}^{3}J =$ 8.8 Hz, 4H, H_B), 6.86 (d, ${}^{3}J$ = 8.8 Hz, 2H, H_A), 5.06 (s, 4H, $H\delta$); ${}^{13}C$ NMR (CDCl₃, 100 MHz, 25° C): $\delta = 155.1, 146.1, 141.3, 137.2, 132.3, 128.7, 128.1, 127.6, 126.1, 122.9, 119.8, 115.8,$ 70.5; ESI-MS: m/z calcd for C₃₂H₂₆N₄O₂: 470.19 [M-N₂]⁺, 498.21 [M]⁺, found 470.34, 498.35.

¹ E. Moulin, F. Niess, M. Maaloum, E. Buhler, I. Nyrkova, N. Giuseppone, *Angew. Chem. Int. Ed.*, 2010, **49**, 6974.



N-(4-(bis(4-(benzyloxy)phenyl)amino)phenyl)-2-chloroacetamide¹ (300 mg, 546 µmol, 1.00 eq) and NaN₃ (710 mg, 10.9 mmol, 20.0 eq) were suspended in dry DMF (4.80 mL) under an argon atmosphere. The yellow-brown mixture was vigorously stirred at room temperature overnight. After this time, the resulting creamy-white suspension was poured into brine (20 mL) and extracted with EtOAc (115 mL). The organic phase was washed with brine (2 × 75 mL). The aqueous phases were extracted with EtOAc (75 mL). The combined organic phases were dried over Na₂SO₄ and then evaporated to give a brown oil. The crude product was purified by flash column chromatography (SiO₂, cyclohexane/ethyl acetate: $5/1 \rightarrow 3/1$; R_f (cyclohexane/ethyl acetate: 3/1) = 0.33) to give compound **2** (281 mg, 506 µmol, 93 %) as a creamy-white solid. ¹H NMR (CDCl₃, 400 MHz, 25°C): δ = 7.86 (s, 1H, *H_a*), 7.47–7.29 (m, 12H, *H_AH_C*), 7.01 (d, ³*J* = 9.2 Hz, 4H, *H_B*), 6.93 (d, ³*J* = 9.2 Hz, 2H, *H_A*), 6.89 (d, ³*J* = 8.8 Hz, 4H, *H_B*), 5.03 (s, 4H, *H* δ), 4.13 (s, 2H, *H* α); ¹³C NMR (CDCl₃, 100 MHz, 25°C): δ = 164.3, 155.1, 146.1, 141.4, 137.2, 130.0, 128.7, 128.1, 127.7, 126.2, 122.0, 121.5, 115.8, 70.5, 53.2; ESI-MS: *m/z* calcd for C₃₄H₂₉N₅O₃: 555.23 [M]⁺, found 555.39.



To a stirred solution of pseudorotaxane **3** (99.7 mg, 68.1 μ mol, 1.00 eq), azide **1** (68.0 mg, 136 μ mol, 2.00 eq) and Cu(MeCN)₄PF₆ (50.8 mg, 136 μ mol, 2.00 eq) in dry dichloromethane (2.6 mL), 2,6-lutidine (1.60 μ L, 13.6 μ mol, 0.20 eq) was added under an argon atmosphere.

The brown mixture was stirred at room temperature. After 3 days, Cu(MeCN)₄PF₆ (12.7 mg, 34.1 µmol) was added. The black-brown mixture was stirred for 1 hour, before 2,6-lutidine (0.80 µL, 6.83 µL) was added. The mixture was stirred for another day. The crude mixture was then directly loaded onto a chromatography column (SiO₂, dichloromethane/methanol: $100/0 \rightarrow 100/5$; R_f (dichloromethane/methanol: 100/6) = 0.24) to give compound 4 (54.7 mg, 22.2 μ mol, 33 %) as a greyish-brown solid. ¹H NMR (CDCl₃, 400 MHz, 25°C): δ = 7.64 (s, 2H, H_{T1}), 7.52–7.28 (m, 24H, $H_{A1 \text{ or } A2} H_C$), 7.08 (d, ${}^{3}J = 8.8 \text{ Hz}$, 8H, $H_{B1 \text{ or } B2}$), 6.99 (d, ${}^{3}J =$ 8.8 Hz, 4H, $H_{A1 \text{ or } A2}$), 6.93 (d, ${}^{3}J$ = 8.8 Hz, 8H, $H_{B1 \text{ or } B2}$), 6.90 (d, ${}^{3}J$ = 9.2 Hz, 2H, $H_{ar, DB24C8}$), 6.86–6.73 (m, 8H, $H_{ar, DB24C8}$), 6.68 (d, ${}^{3}J$ = 8.4 Hz, 2H, $H_{ar, DB24C8}$), 6.62 (s, 2H, $H_{ar, DB24C8}$), 5.04 (s, 8H, Hd), 4.54-4.32 (m, 4H, Hg), 4.32-3.52 (m, 48H, H_{CH2O, DB24C8}), 3.52-3.30 (m, 4H, H_8), 2.70 (t, ${}^{3}J = 7.4$ Hz, 4H, H_3), 1.78–1.58 (m, 8H, $H_4 H_7$), 1.46–1.16 (m, 8H, $H_5 H_6$); ¹³C NMR (CDCl₃, 100 MHz, 25°C): δ = 155.7, 149.2, 148.4, 147.9, 147.7, 146.9 (2C), 146.4, 146.2, 140.5, 137.0, 129.8, 128.7, 128.1, 127.6, 127.0, 124.8, 123.8, 123.1, 121.4, 121.2, 121.1, 120.4, 119.0, 116.0, 113.1, 112.8, 112.0, 111.9, 72.4, 71.9, 71.0, 70.9, 70.8, 70.4, 67.7, 67.6, 67.1 (2C), 66.8, 52.2, 48.9, 32.0, 29.8, 29.3, 28.7, 26.7, 26.6, 25.5; ESI-MS: m/z calcd for C₁₃₀H₁₄₈F₁₂N₁₀O₂₀P₂: 1085.05 [M-2PF₆]²⁺, found 1085.23.



To a stirred solution of pseudorotaxane **3** (132 mg, 90.0 µmol, 1.00 eq), azide **2** (100 mg, 180 µmol, 2.00 eq) and Cu(MeCN)₄PF₆ (67.1 mg, 180 µmol, 2.00 eq) in dry dichloromethane (5.0 mL), 2,6-lutidine (2.08 µL, 18.0 µmol, 0.20 eq) was added under an argon atmosphere. The resulting yellow solution, which turned greenish-yellow after 1–2 hours, was stirred at room temperature. After 2 days, additional Cu(MeCN)₄PF₆ (33.5 mg, 45.0 µmol) and 2,6-lutidine (1.04 µL) were added. The mixture was stirred for another day. The crude mixture was then directly loaded onto a chromatography column (SiO₂, dichloromethane/methanol: 100/0 \rightarrow 100/5; R_f (dichloromethane/methanol: 100/8) = 0.52) to give compound **5** (135 mg, 52.4 µmol, 58 %) as a greyish-brown solid. ¹H NMR (CDCl₃, 400 MHz, 25°C): δ = 8.17 (s, 2H,

H_{am}), 7.49 (s, 2H, *H_{T1}*), 7.45–7.28 (m, 24H, *H_C H_{A1 or A2}*), 6.96 (d, ³*J* = 8.4 Hz, 8H, *H_{B1 or B2}*), 6.92–6.68 (m, 22H, *H_{A1 or A2} H_{B1 or B2} H_{ar, DB24C8}*), 6.66–6.56 (m, 4H, *H_{ar, DB24C8}*), 5.19 (s, 4H, *Hα*), 4.99 (s, 8H, *Hδ*), 4.50–4.30 (m, 4H, *H₉*), 4.28–3.52 (m, 48H, *H_{CH20, DB24C8}*), 3.50–3.28 (m, 4H, *H₈*), 2.65 (t, ³*J* = 7.2 Hz, 4H, *H₃*), 1.80–1.46 (m, 12H, *H₄ H₆ H₇*), 1.40–1.22 (m, 4H, *H₃*); ¹H NMR (CD₃CN, 400 MHz, 25°C): δ = 8.55 (s, 2H, *H_{am}*), 7.57 (s, 2H, *H_{T1}*), 7.47–7.29 (m, 24H, *H_C H_{A1 or A2}*), 6.95 (d, ³*J* = 9.2 Hz, 8H, *H_{B1 or B2}*), 6.90 (d, ³*J* = 9.2 Hz, 8H, *H_{B1 or B2}*), 6.85–6.68 (m, 16H, *H_{A1 or A2} H_{ar, DB24C8}*), 6.39 (d, ³*J* = 8.4 Hz, 2H, *H_{ar, DB24C8}*), 5.13 (s, 4H, *Hα*), 5.03 (s, 8H, *Hδ*), 4.60–4.36 (m, 4H, *H₉*), 4.32–3.52 (m, 48H, *H_{CH20, DB24C8}*), 3.51–3.31 (m, 4H, *H₈*), 2.64 (t, ³*J* = 7.4 Hz, 4H, *H₃*), 1.80–1.69 (m, 4H, *H₇*), 1.69–1.58 (m, 4H, *H₄*), 1.43–1.23 (m, 8H, *H₅ H₆*); ¹³C NMR (CD₃CN, 100 MHz, 25°C): δ = 165.0, 156.0, 148.8 (2C), 148.7, 147.3, 147.1, 146.4, 142.3, 138.5, 132.5, 129.6, 128.9, 128.7, 127.1, 126.4, 124.0, 123.6, 122.6, 122.1, 121.8, 116.8, 114.3, 113.0, 112.9, 73.1, 73.0, 71.6, 71.5 (2C), 71.3, 71.1, 71.0, 68.6, 68.3, 68.1 (2C), 53.4, 52.9, 49.8, 29.8, 29.0, 27.2, 26.9, 26.0; ESI-MS: *m/z* calcd for C₁₃₄H₁₅₄F₁₂N₁₂O₂₂P₂: 1141.57 [M–2PF₆]²⁺, found 1141.80.



First step

To a solution of rotaxane dimer **4** (49.3 mg, 20.0 µmol, 1.00 eq) in dry dichloromethane (2.5 mL), methyl iodide (1.00 mL) was added at once under an argon atmosphere. The solution was stirred at room temperature for 4 days and the solvent was then evaporated to give the intermediate diiodide of **6** (X = I) (50.0 mg). ¹H NMR (CD₃CN, 400 MHz, 25°C): δ = 8.66 (s, 2H, *H*_{*TI*}), 7.63 (d, ³*J* = 9.2 Hz, 4H, *H*_{*A1 or A2*}), 7.50–7.30 (m, 20H, *H*_{*C*}), 7.17 (d, ³*J* = 9.2 Hz, 8H, *H*_{*B1 or B2*}), 7.03 (d, ³*J* = 9.2 Hz, 8H, *H*_{*B1 or B2*}), 6.89 (d, ³*J* = 9.2 Hz, 4H, *H*_{*A1 or A2*}), 6.85–6.68 (m, 12H, *H*_{*ar, DB24C8*), 6.47 (d, ³*J* = 8.4 Hz, 2H, *H*_{*ar, DB24C8*}), 5.09 (s, 8H, *H* δ), 4.60–4.40 (m,}}

4H, H_9), 4.34–4.58 (m, 48H, $H_{CH2O, DB24C8}$), 4.19 (s, 6H, H_{Me}), 3.56–3.38 (m, 4H, H_8), 2.77 (t, ³J = 7.8 Hz, 4H, H_3), 1.82–1.73 (m, 4H, H_8), 1.73–1.62 (m, 4H, H_4), 1.50–1.36 (m, 8H, H_5 H_6); ¹³C NMR (CD₃CN, 100 MHz, 25°C): δ = 157.6, 152.7, 148.8, 147.2, 147.0, 146.1, 140.1, 138.2, 129.5, 129.2, 129.0, 128.7, 126.9, 126.5, 126.3, 123.6, 123.2, 121.7, 118.4, 117.2, 114.2, 113.2, 112.9, 73.1, 71.6 (2C), 71.5, 71.4, 71.2, 71.0, 68.6, 68.4, 68.3, 68.1, 53.0, 49.7, 38.6, 30.2, 27.5, 27.3, 27.0, 23.9; ESI-MS: m/z calcd for C₁₃₂H₁₅₄F₁₂I₂N₁₀O₂₀P₂: 550.04 [M– 2I–2PF₆]⁴⁺, found 550.25.

Second step

To a suspension of the diiodide precursor of **6** (X = I) in water (2.7 mL) were added NH₄PF₆ (26.1 mg, 160 µmol, 8.00 eq) and dry dichloromethane (2.7 mL). The resulting biphasic solution was vigorously stirred for 1 hour. The aqueous phase was extracted with DCM (3 × 3.1 mL). The combined organic phases were dried over Na₂SO₄ and evaporated under reduced pressure to give compound **6** (49.5 mg, 17.8 µmol, 89 %) as a yellow solid. ¹H NMR (CD₃CN, 400 MHz, 25°C): δ = 8.41 (s, 2H, *H_{TI}*), 7.56 (d, ³*J* = 9.2 Hz, 4H, *H_{A1 or A2}*), 7.50–7.30 (m, 20H, *H_C*), 7.18 (d, ³*J* = 8.8 Hz, 8H, *H_{B1 or B2}*), 7.03 (d, ³*J* = 9.2 Hz, 4H, *H_{A1 or A2}*), 6.90 (d, ³*J* = 9.2 Hz, 4H, *H_{A1 or A2}*), 6.85–6.68 (m, 12H, *H_{ar, DB24C8}*), 6.45 (d, ³*J* = 8.4 Hz, 2H, *H_{ar, DB24C8}*), 5.10 (s, 8H, *H* δ), 4.60–4.40 (m, 4H, *H₉*), 4.34–4.58 (m, 48H, *H_{CH20, DB24C8}*), 4.17 (s, 6H, *H_{Me}*), 3.56–3.38 (m, 4H, *H₈*), 2.74 (t, ³*J* = 7.8 Hz, 4H, *H₃*), 1.85–1.72 (m, 4H, *H₇*), 1.72–1.60 (m, 4H, *H₄*), 1.52–1.37 (m, 8H, *H₅ H₆*); ¹³C NMR (CD₃CN, 100 MHz, 25°C): δ = 157.7, 152.8, 148.8, 147.2, 147.1, 146.1, 140.2, 138.3, 129.6, 129.2, 129.0, 128.7, 126.9, 126.3, 126.2, 123.7, 123.2, 121.7, 118.5, 117.2, 114.3, 113.1, 112.9, 73.1, 71.6, 71.5 (2C), 71.3, 71.1, 71.0, 68.6, 68.3, 68.2, 68.1, 52.9, 49.7, 38.4, 30.4, 28.9, 27.5, 27.3, 27.0, 23.8; ESI-MS: *m/z* calcd for C₁₃₂H₁₅₄F₂₄N₁₀O₂₀P₄: 550.04 [M–4PF₆]⁴⁺, found 550.25.



To a solution of rotaxane dimer 5 (50 mg, 19.4 µmol, 1.00 eq) in dry dichloromethane (2.4 mL), methyl iodide (0.97 mL) was added at once under an argon atmosphere. The solution was stirred at room temperature for 3 days and the solvent was then evaporated to give a solid. To a suspension of the previous solid in water (2.6 mL) were added NH₄PF₆ (25.3 mg, 155 µmol, 8.00 eq) and dry dichloromethane (2.6 mL). The resulting biphasic solution was vigorously stirred for 1 hour. The aqueous phase was extracted with dichloromethane (3×3) mL). The combined organic phases were dried over Na₂SO₄ and evaporated under reduced pressure to give 7 (54.0 mg, 18.7 µmol, 96 %) as a yellow solid. ¹H NMR (CD₃CN, 400 MHz, 25°C): δ = 8.72 (s, 2H, H_{am}), 8.20 (s, 2H, H_{T1}), 7.50–7.30 (m, 24H, $H_C H_{A1 \text{ or } A2}$), 6.97 (d, 3J = 8.8 Hz, 8H, $H_{B1 \text{ or } B2}$), 6.92 (d, ${}^{3}J = 8.8$ Hz, 8H, $H_{B1 \text{ or } B2}$), 6.84 (d, ${}^{3}J = 9.2$ Hz, 4H, $H_{A1 \text{ or } A2}$), 6.83–6.71 (m, 12H, $H_{ar, DB24C8}$), 6.43 (d, ${}^{3}J$ = 8.4 Hz, 2H, $H_{ar, DB24C8}$), 5.39 (s, 4H, $H\alpha$), 5.05 (s, 8H, $H\delta$), 4.60–4.38 (m, 4H, H_9), 4.34–3.60 (m, 48H, $H_{CH2O, DB24C8}$), 4.15 (s, 6H, H_{Me}), 3.52-3.38 (m, 4H, H_8), 2.72 (t, ${}^{3}J = 7.8$ Hz, 4H, H_3), 1.80-1.68 (m, 4H, H_7), 1.67-1.55 (m, 4H, H_4), 1.48–1.32 (m, 8H, $H_5 H_6$); ¹³C NMR (CD₃CN, 100 MHz, 25°C): δ = 162.0, 156.1, 148.8, 147.2, 147.1, 145.7, 141.1, 138.5, 130.3, 129.5, 128.9, 128.7, 127.3, 126.3, 123.7, 122.2, 122.1, 121.7, 116.8, 114.3, 113.1, 112.9, 73.1, 71.6, 71.5, 71.3, 71.1, 71.0, 68.6, 68.3, 68.2, 68.0, 56.1, 52.9, 49.7, 38.6, 28.9, 27.4, 27.2, 26.9, 23.7; ESI-MS: m/z calcd for $C_{136}H_{160}F_{24}N_{12}O_{22}P_4$: 578.55 [M-4PF₆]⁴⁺, found 578.81.



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Compound **6** (10 mg, 3.60 μ M) is dissolved in CH₂Cl₂/CH₃CN (3/1, 3 mL) and shaken with a 1M NaOH solution (3 mL). The organic phase is separated and the aqueous phase extracted 2 times with CH₂Cl₂/CH₃CN (3 x 5 mL). The combined organic are dried over Na₂SO₄, and the solvents are evaporated to yield compound **8** as a greenish solid (8.9 mg, quantitative). ¹H NMR (CD₃CN with CDCl₃ (2.5%), 400 MHz, 25°C) : δ = 9.62 (brs, 2H), 7.71 (brm, 4H), 7.45-7.31 (m, 20H), 7.14 (d, *J* = 8.8 Hz, 8H), 7.01 (d, *J* = 8.8 Hz, 8H), 6.83-6.75 (m, 18H), 5.08 (s, 8H), 4.23-3.97 (m, 23H), 3.79-3.77 (m, 3H), 3.67-3.44 (m, 30H), 3.23-3.01 (m, 10H), 1.65 (brm, 4H), 1.25 (brm, 4H), 0.87-0.83 (brm, 8H).



To a solution of rotaxane 7 (8.2 mg, 2.8 μ mol) in chloroform (2 mL), an aqueous solution of 0.1 M NaOH (2 mL) was added dropwise and the mixture was vigorously stirred at room temperature for 1 hour. The aqueous phase was then extracted three times with chloroform (3

x 5 mL), the organic phase was separated, dried over Na₂SO₄ and concentrated under reduced pressure to give compound **9** (7.0 mg, 2.7 µmol, 95 %) as a dark-green solid. ¹H NMR (CD₃CN, 400 MHz, 25°C): δ = 8.97 (brs, 2H), 8.45 (brs, 2H), 7.44–7.33 (m, 24H), 6.97–6.78 (m, 34H), 6.07 (brs, 4H), 5.04 (s, 8H), 4.18–4.01 (m, 12H), 4.00–3.53 (m, 50H), 3.45–3.29 (m, 4H), 1.56–1.48 (m, 4H), 1.48–1.00 (m, 4H), 0.93–0.69 (m, 8H); ¹³C NMR (CD₃CN, 100 MHz, 25°C): δ = 156.0, 142.3, 138.5, 129.5, 128.9, 128.7, 127.0, 122.5, 122.3, 122.2, 116.8, 115.1, 113.0, 112.9, 71.7 (2C), 71.6, 71.2, 71.0, 70.6, 70.4, 70.1, 69.9, 69.3, 68.5, 30.5, 30.4, 30.4, 30.0, 27.8, 23.5, 23.4.



Compound **5** (40.0 mg, 15.5 µmol, 1.00 eq) was dissolved in dry dichloromethane (7 mL) and an aqueous solution of NaOH (1 M, 7 mL) was added. The resulting biphasic solution was vigorously stirred for 1 hour. The organic phase was dried over Na₂SO₄ and evaporated under reduced pressure to give **5^{deprot}** (32.8 mg, 14.4 µmol, 93 %) as a beige solid. ¹H NMR (CDCl₃, 400 MHz, 25°C): $\delta = 7.92$ (s, 2H, H_{Tl}), 7.66 (d, ³*J* = 8.8 Hz, 4H, $H_{A1 \text{ or } A2}$), 7.48–7.29 (m, 20H, H_C), 6.95 (d, ³*J* = 9.2 Hz, 8H, $H_{B1 \text{ or } B2}$), 6.90–6.66 (m, 26H, $H_{A1 \text{ or } A2}$ $H_{B1 \text{ or } B2}$ $H_{ar, DB24C8}$), 5.58 (s, 4H, $H\alpha$), 5.01 (s, 8H $H\delta$), 4.23–3.32 (m, 52H, H_9 $H_{CH20, DB24C8}$), 2.54 (t, ³*J* = 7.0 Hz, 4H, H_3), 2.19 (t, ³*J* = 7.0 Hz, 4H, H_8), 1.52–1.34 (m, 8H, H_4 H_7), 1.34–1.12 (m, 8H, H_5 H_6); ¹³C NMR (CDCl₃, 100 MHz, 25°C): δ = 165.2, 154.6, 148.2, 148.1, 148.0, 147.6, 147.1, 146.9, 144.0, 141.8, 137.3, 133.4, 133.0, 128.7, 128.1, 127.6, 125.7, 125.6, 124.0, 122.7, 122.3, 121.3, 120.9, 120.8, 115.6, 112.4, 112.1, 70.5, 70.4, 70.3, 69.9, 69.8, 68.3, 68.1, 53.8, 49.6, 30.2, 29.8, 29.5, 29.4, 29.3, 27.3, 25.5.

2. NMR Spectra



Figure S1. ¹H NMR (400 MHz, CDCl₃, 25°C) spectra of **4** (**A**) and **5** (**B**) and ¹H NMR (400 MHz, CD₃CN, 25°C) spectrum of **5** (**C**) from 10 to 0 ppm.



Figure S2. JMOD ¹³C NMR (100 MHz, CDCl₃, 25°C) spectrum of **4** (**A**) and JMOD ¹³C NMR (100 MHz, CD₃CN, 25°C) spectrum of **5** (**B**) from 200 to 0 ppm.



Figure S3. (A) ¹H NMR (400 MHz, CD₃CN, 25°C) spectrum of **6** and (B) JMOD ¹³C NMR (100 MHz, CD₃CN, 25°C) spectra of **6**.



Figure S4. ¹H NMR (400 MHz, CD₃CN, 25°C) (**A**) and JMOD ¹³C NMR (100 MHz, CD₃CN, 25°C) (**B**) spectra of **7**.



Figure S6. ¹H NMR (400 MHz, CD₃CN, 25°C) spectra of (A) compound 7 irradiated for 1h (20W power lamp) and further treated with NaOD and (B) compound 7 irradiated for 1h (20W power lamp). Red dots (●) indicate NMR peaks corresponding to the triarylamine core.



Figure S7. ¹H NMR (400 MHz, CD₃CN, 25°C) (A) and JMOD ¹³C NMR (100 MHz, CD₃CN, 25°C) (B) spectra of 9.



Figure S8. ¹H NMR (400 MHz, CDCl₃, 25°C) (**A**) and JMOD ¹³C NMR (100 MHz, CDCl₃, 25°C) (**B**) spectra of **5**^{deprot.}



Figure S9. Direct comparison of the ¹H NMR spectra (CDCl₃, 400 MHz, 25°C) of a solution (c = 6.9 mM) of non-irradiated compound **5** in chloroform before (**A**) and after (**B**) light irradiation (20 W power lamp) for 20 min.



Figure S10. Direct comparison of the ¹H NMR spectra (CDCl₃, 400 MHz, 25°C) of a solution of compound $5^{deprot.}$ (A) and compound 5 (B). Upon deprotonation, protons T1, α , am and A1 are downfield shifted, thus indicating that the amide might act as a station for the macrocycle.

3. Optical Spectroscopies

UV-Vis spectra were recorded using a Varian Cary 5000 apparatus with quartz glass cuvettes of 1 cm optical path under ambient conditions, unless otherwise stated.



Figure S11. UV-Vis-NIR spectra obtained as a function of time of irradiation for an initial 0.1 mM solution of compounds 4-9 in chloroform.