Electronic Supplementary Information (ESI)

Förster Resonance Energy Transfer by Formation of Mechanically Interlocked [2]Rotaxane

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Table of Contents

Experimental section

Materials. All solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. Fluorescence spectra were measured on argon saturated solutions of the compounds in HPLC-grade chloroform using Spex Fluorolog 3 and Hitachi F-2500 fluorescence spectrometers. Absorbances at the excitation wavelengths were $A < 0.2$. For quantum yield measurements, absorbances of ~ 0.1 were used. As standards,[S1] argon saturated solutions of anthracene in ethanol[S2] ($\Phi_f = 0.28$) and perylene in cyclohexane[S3] ($\Phi_f = 0.94$) were used. Because the absorption bands of the systems investigated as well as the reference substances show relatively sharp features, care was taken to minimize errors due to slightly different wavelength calibrations and band widths of the absorption and emission spectrometers by exciting at wavelengths that correspond to a minimum or maximum in the spectra of sample and reference. For excitation of the pyrene absorption band a wavelength of 329 nm was favorable, for the pyrene absorption bands 394 nm was optimal. Since the fluorescence excitation spectra of the standards are identical to their absorption spectra it is safe to use the reported quantum yields irrespective of the excitation wavelengths. Fluorescence decay times were measured with a Time-Correlated Single Photon Counting set-up recently described.[S4] Excitation wavelengths were 349 and 430 nm. UV-Vis absorption spectra were recorded with a JASCO V-630 or a Cary 3.

[2]Rotaxane 3. To a solution of axle **1**[S5] (38.0 mg, 0.0500 mmol), **H1**[S6] (180 mg, 0.125 mmol) and perylene stopper **2**[S7] (18.0 mg, 0.0600 mmol) in chloroform (1 mL), tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA, 26.0 mg, 0.0500 mmol) was added. The reaction mixture was stirred at 25 °C for 1h. To the mixture, $Cu(CH_3CN)_4PF_6$ (18.0 mg, 0.0500 mmol) was added, and the mixture was stirred at 25 °C for 24h. The resulting solution was concentrated under *vacuo*. Column chromatography (silica gel; ethyl acetate : dichloromethane = 1 : 1) afforded a brown solid ([2]rotaxane **3**, 92.0 mg, 0.0370 mmol, Yield: 74%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.21 (d, 1H, pyrene), 7.62−8.15 (m, 26H, pyrene and perylene), 7.45−7.49 (m, 2H, perylene), 7.34 (s, 1H, triazole), 7.28 (s, 2H, triazole), 7.12−7.20 (m, 15H, phenyl), 7.06 (m, 2H, pyridinium), 7.05 (m, 2H, phenyl), 6.83, 6.81, 6.78, 6.74 (s, 4H, phenyl protons of pillar[5]arene moiety), 6.66 (d, 2H, phenyl), 6.63, 6.60, 6.58, 6.55, 6.46, 6.44

(s, 6H, phenyl protons of pillar[5]arene moiety), 6.16 (dd, 2H, methylene), 5.85 (s, 2H, methylene), 5.84 (m, 2H, pyridinium), 5.73 (dd, 2H, methylene), 4.66, 4.46 (dd, 4H, methylene protons of pillar[5]arene moiety), 4.41 (t, 2H, methylene), 3.96 (m, 2H, methylene), 3.26−3.92 (m, 26H, methylene protons of pillar[5]arene moiety), 2.63 (t, 2H, methylene), 2.23 (q, 2H, methylene), 1.56 (q, 2H, methylene), 1.08−1.40 (m, 28H, methyl protons of pillar[5]arene moiety and methylene), 1.03 (m, 2H, methylene), 0.59 (m, 2H, methylene), 0.44 (m, 2H, methylene), -0.18 (m, 2H, methylene), -1.31 (m, 2H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.0, 156.5, 151.6, 150.2, 150.1, 150.0, 149.6, 149.3, 149.2, 149.0, 148.9, 148.8, 148.8, 147.0, 143.9, 143.8, 143.2, 139.3, 134.2, 132.5, 132.2, 131.9, 131.8, 131.7, 131.0, 130.5, 130.3, 130.2, 130.1, 130.0, 129.7,129.5, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.9, 127.4, 127.2, 127.1, 126.7, 126.4, 126.3, 126.2, 125.8, 125.7, 125.6, 125.0, 124.9, 124.9, 127.4,127.2, 127.1, 126.7, 126.4, 126.3, 126.2, 125.8, 125.7, 125.6, 125.0, 124.9, 124.8, 124.4, 124.2, 123.9, 122.5, 122.1, 120.7, 120.4, 120.3, 119.3, 116.6, 116.0, 115.6, 115.3, 115.1, 114.9, 114.8, 114.6, 113.1, 112.5, 68.0, 65.6, 65.2, 64.8, 64.3, 64.0, 63.9, 63.8, 63.3, 62.3, 62.4, 62.4, 62.2, 57.3, 52.2, 52.1, 52.0, 30.6, 29.7, 29.5, 29.4, 29.3, 28.9, 28.8, 28.5, 28.3, 27.7, 26.5, 25.8, 15.4, 15.3, 15.2, 15.1, 15.0. HRESIMS: *m*/*z* Calcd for $C_{156}H_{149}N_{10}O_{12}$ $[M]^+$: 2354.1351, found 2354.1352.

[2]Rotaxane 4. To a solution of axle **1** (38.0 mg, 0.0500 mmol), **H2**[S8] (111 mg, 0.125 mmol) and perylene stopper **2** (18.0 mg, 0.0600 mmol) in chloroform (1 mL), TBTA (26.0 mg, 0.0500 mmol) was added. The reaction mixture was stirred at 25 °C for 1h. To the mixture, $Cu(CH_3CN)_4PF_6$ (18.0 mg, 0.0500 mmol) was added, and the mixture was stirred at 25 °C for 24h. The resulting solution was concentrated under *vacuo*. Column chromatography (silica gel; ethyl acetate : dichloromethane = 1 : 1) afforded a brown solid ([2]rotaxane **4**, 78.0 mg, 0.0400 mmol, Yield: 80%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.21 (m, 4H, perylene), 7.85 (d, 1H, perylene), 7.71 (m, 3H, perylene), 7.46-7.56 (m, 3H, perylene), 7.23 (s, 1H, triazole), 7.15−7.20 (m, 15H, phenyl), 7.12 (d, 2H, phenyl), 6.98 (d, 2H, pyridinium), 6.86 (s, 5H, phenyl protons of pillar[5]arene moiety), 6.81 (d, 2H, phenyl), 6.65 (s, 5H, phenyl protons of pillar[5]arene moiety), 6.04 (d, 2H, pyridinium), 5.91 (s, 2H ,methylene), 4.47 (m, 2H, methylene), 4.20 (m, 2H, methylene), 3.61-3.92 (m, 30H, methylene and methylene bridge of pillar[5]arene moiety), 2.69 (t, 2H, methylene), 2.41 (m, 2H, methylene), 1.65 (m, 2H, methylene), 1.38 (t, 15H, methyl of pillar[5]arene moiety), 1.33 (t, 15H, methyl of pillar[5]arene moiety), 1.05 (m, 2H, methylene), 0.63 (m, 2H, methylene), 0.54 (m, 2H, methylene), -0.21 (m, 2H, methylene), -1.30 (m, 2H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.3, 156.7, 150.3, 149.4, 148.5, 147.1, 144.0, 139.3, 134.6, 133.2, 132.8, 132.3, 129.9, 129.4, 129.2, 128.9, 128.8, 127.8, 127.5, 126.8, 126.7, 125.9, 122.7, 120.9, 120.8, 120.3, 119.6, 116.2, 115.0, 113.3, 112.4, 68.4, 65.5, 64.4, 64.0, 63.7, 57.3, 52.5, 31.7, 30.9, 29.7, 29.4, 27.6, 26.6, 23.8, 23.3, 22.7, 15.5, 15.4. HRESIMS: *m*/*z* Calcd for $C_{120}H_{131}N_4O_{12}$ $[M]^+$: 1819.9758, found 1819.9752.

Dumbbell 5. To a solution of axle **1** (38.0 mg, 0.0500 mmol) and perylene stopper **2** (18.0 mg, 0.0600 mmol) in chloroform (1 mL), TBTA (26.0 mg, 0.0500 mmol) was added. To the mixture, $Cu(CH_3CN)_4PF_6$ (18.0 mg, 0.0500 mmol) was added, and the mixture was stirred at 25 °C for 24h. The resulting solution was concentrated under *vacuo*. Column chromatography (silica gel; ethyl acetate : dichloromethane = 1 : 1) afforded a brown solid (dumbbell **5**, 52.0 mg, 0.0485 mmol, Yield: 97%). ^{1}H NMR (500 MHz, ppm): δ 8.20 (d, 2H, pyridinium), 8.06 (m, 3H, perylene), 8.01 (d, 1H, perylene), 7.72 (d, 1H, perylene), 7.61 (m, 2H, perylene), 7.39 (m, 3H, perylene), 7.26 (s, 1H, triazole), 7.13−7.22 (m, 16H, perylene and phenyl), 7.09 (m, 4H, phenyl and pyridinium), 6.70 (d, 2H, phenyl), 5.76 (s, 2H, methylene), 4.25 (t, 2H, methylene), 4.13 (t, 2H, methylene), 3.98 (t, 2H, methylene), 2.57 (m, 2H, methylene), 2.17 (m, 2H, methylene), 1.71 (m, 2H, methylene), 1.52 (m, 2H, methylene), 1.07−1.25 (m, 10H, methylene). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 170.1, 156.3, 147.0. 145.1, 139.5, 134.4, 132.4, 132.3, 132.2, 131.7, 131.0, 130.6, 130.4, 129.8, 128.9, 128.4, 128.3, 128.2, 128.1, 127.5, 127.4, 126.8, 126.7, 125.9, 122.7, 120.8, 120.6, 119.7, 113.8, 113.2, 67.8, 64.3, 63.0, 60.3, 52.1, 30.8, 28.9, 28.6, 28.5, 28.3, 25.6, 25.4. HRESIMS: *m*/*z* Calcd for $C_{65}H_{61}N_4O_2$ $[M]^+$: 929.4789, found 929.4798.

^{1}H NMR spectrum of [2]rotaxane 3

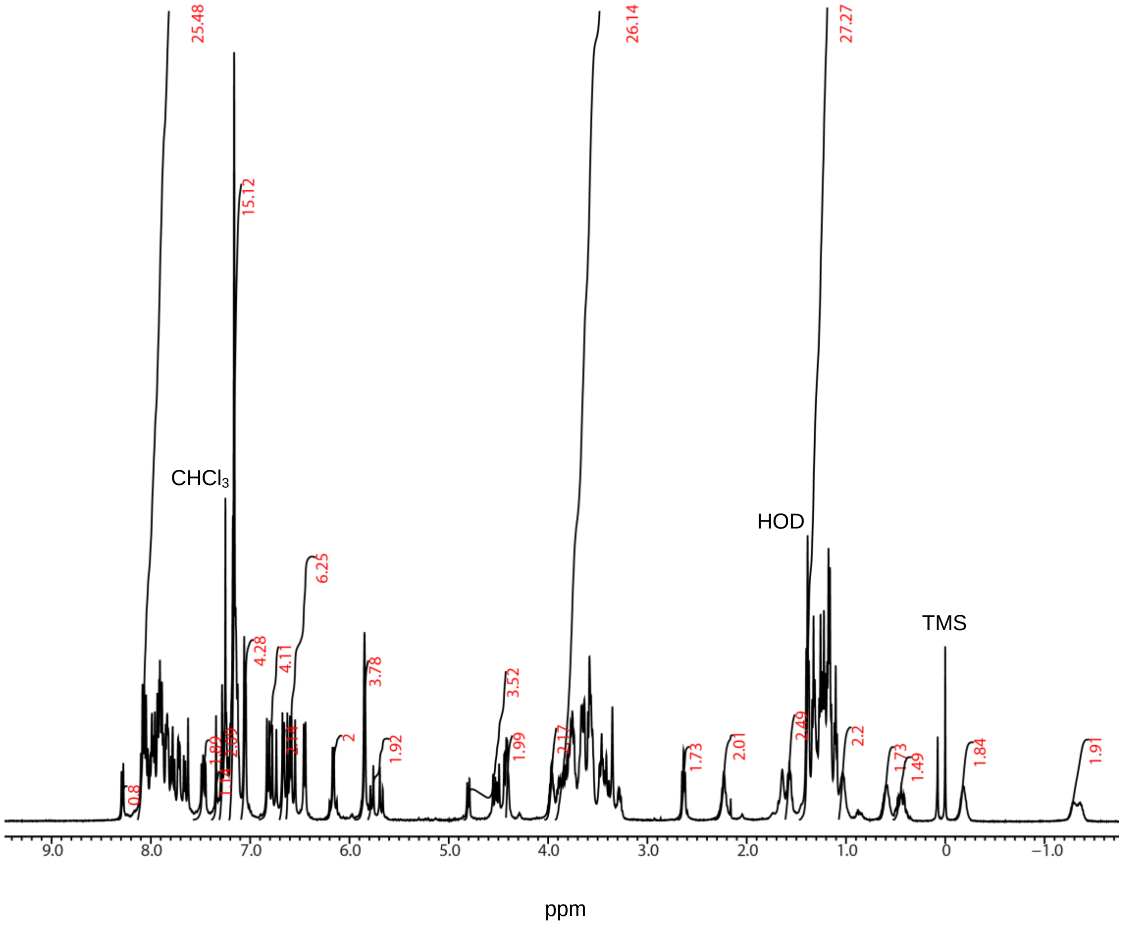


Fig. S1 ^{1}H NMR spectrum of [2]rotaxane **3** in $CDCl_3$ at 25 ^{o}C.

^{13}C NMR spectrum of [2]rotaxane 3

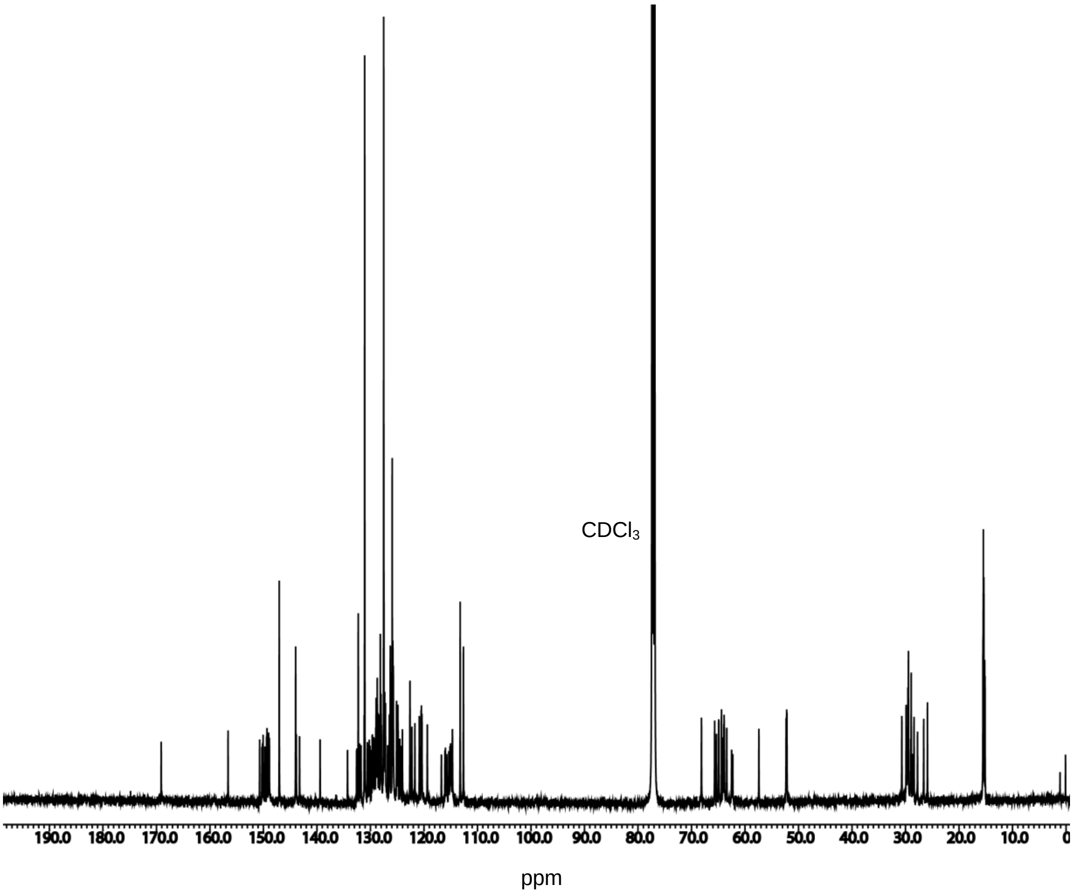


Fig. S2 ^{13}C NMR spectrum of [2]rotaxane **3** in $CDCl_3$ at 25 °C.

^{1}H NMR spectrum of [2]rotaxane 4

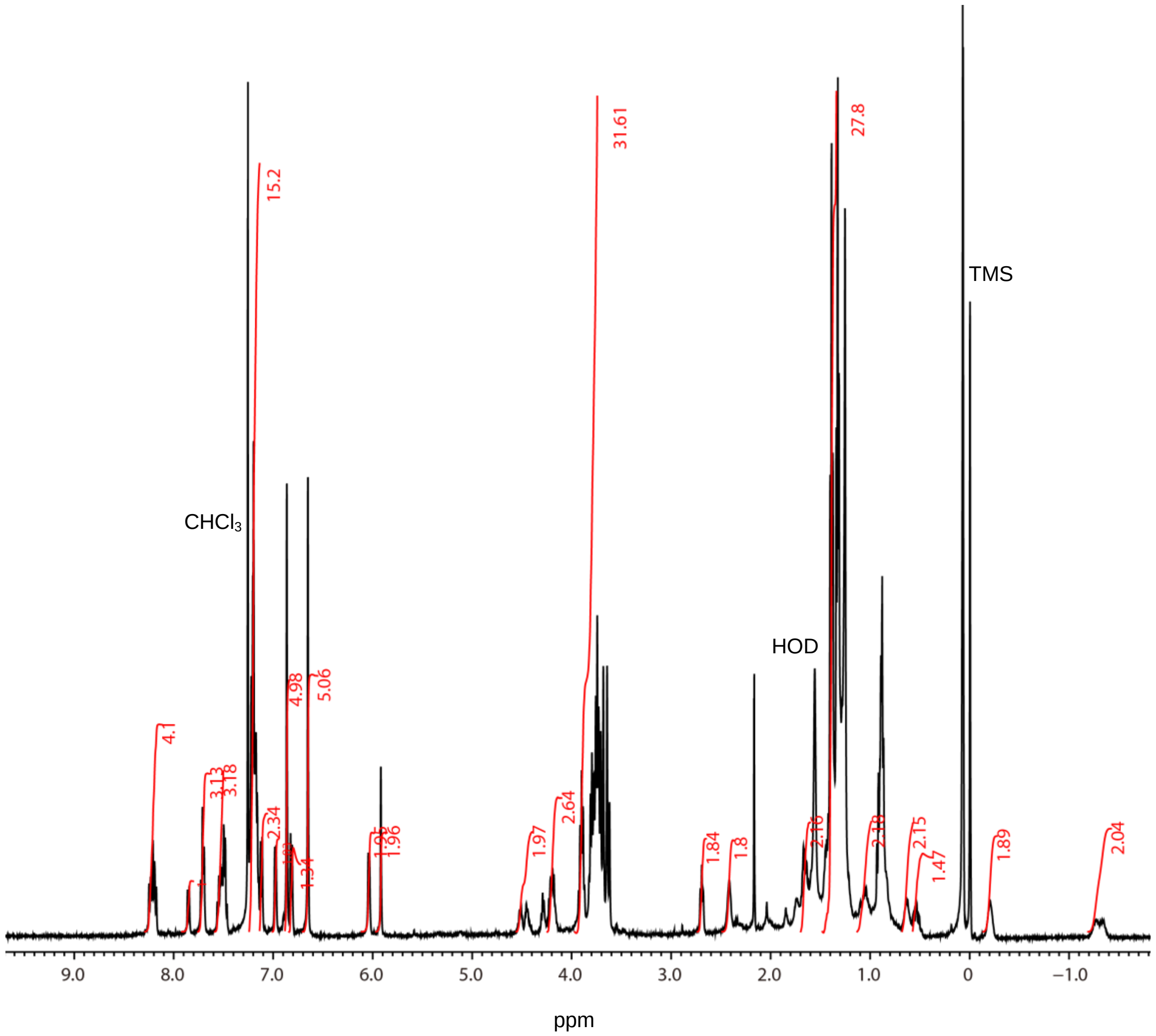


Fig. S3 ^{1}H NMR spectrum of [2]rotaxane **4** in $CDCl_3$ at 25 ^{o}C.

^{13}C NMR spectrum of [2]rotaxane 4

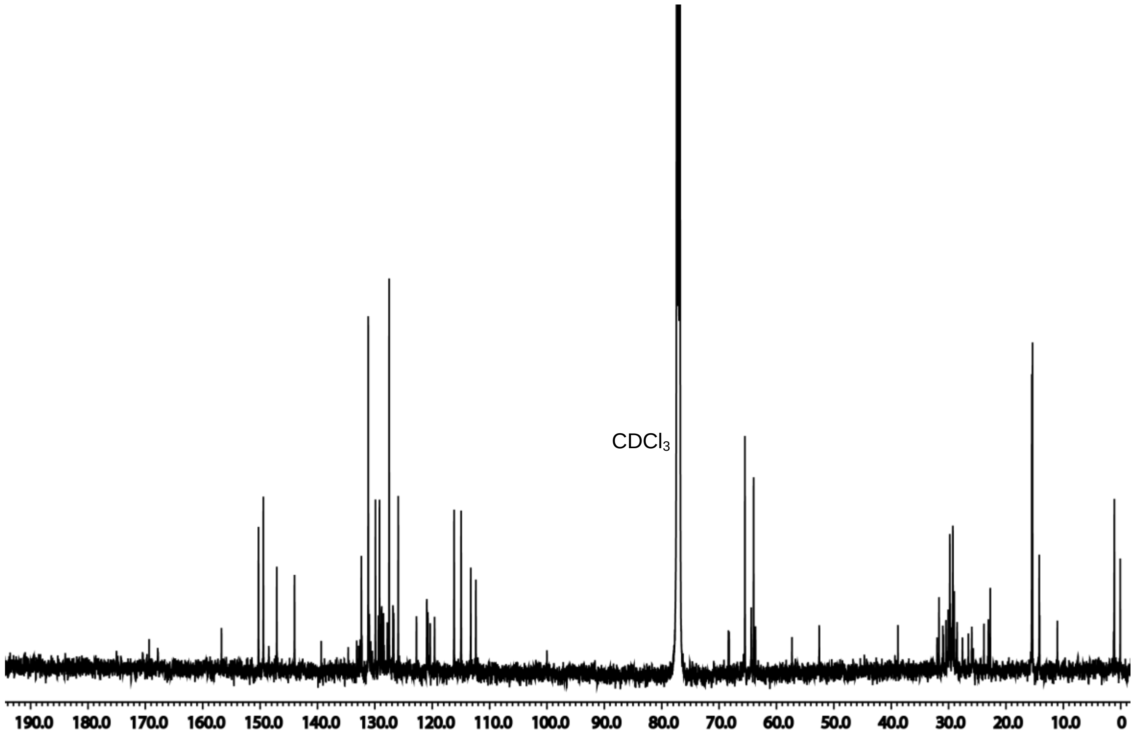


Fig. S4 ^{13}C NMR spectrum of [2]rotaxane **4** in $CDCl_3$ at 25 °C.

^{1}H NMR spectrum of dumbbell 5

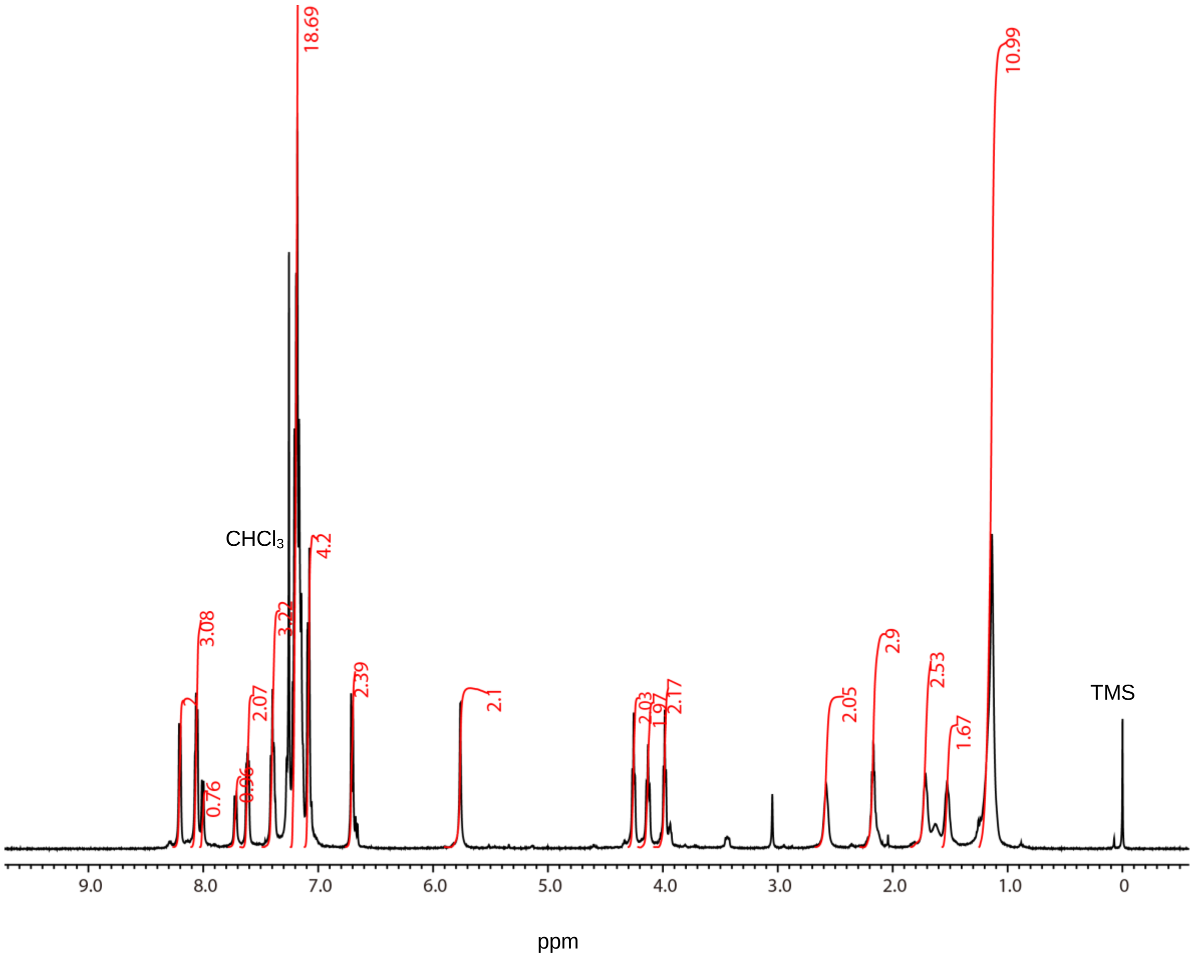


Fig. S5 ^{1}H NMR spectrum of dumbbell **5** in CDCl$_3$ at 25 ^{o}C.

^{13}C NMR spectrum of dumbbell 5

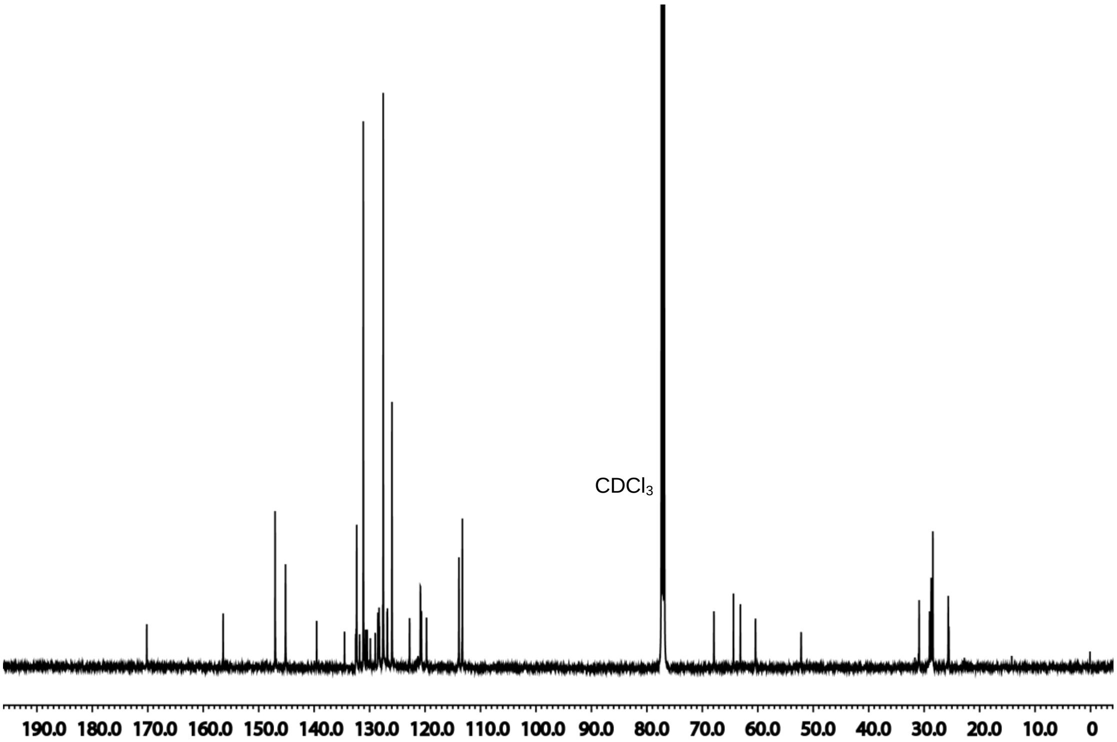


Fig. S6 ^{13}C NMR spectrum of dumbbell **5** in $CDCl_3$ at 25 °C.

Comparison between the excitation and absorption spectra of [2]rotaxane 3

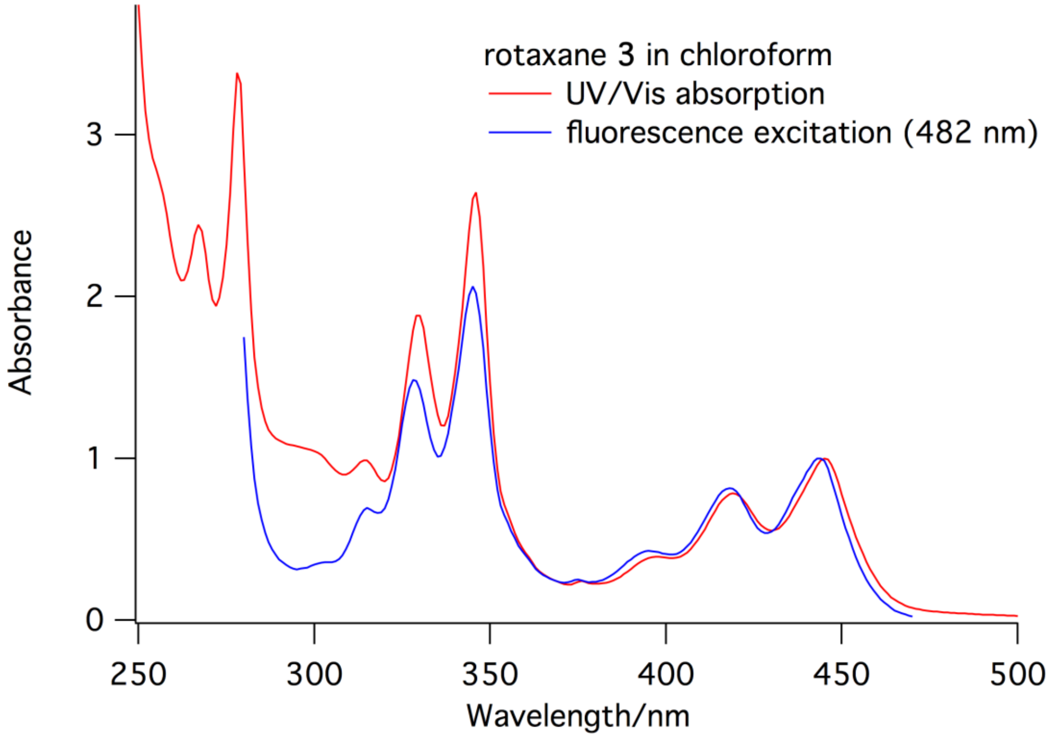
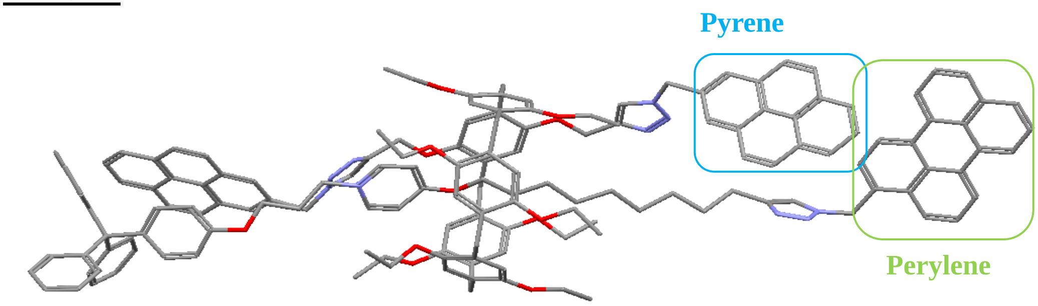


Fig. S7 Excitation spectrum (chloroform, 4.0 × 10^{-6} M) of [2]rotaxane **3** detected at 482 nm compared with the UV/Vis absorption spectrum, scaled to equal intensity at the perylene absorption maximum (445 nm). The relative intensity of the excitation spectrum at the pyrene absorption maximum (346 nm) is 0.78.

Molecular modeling of [2]rotaxane 3

Side View



Top View

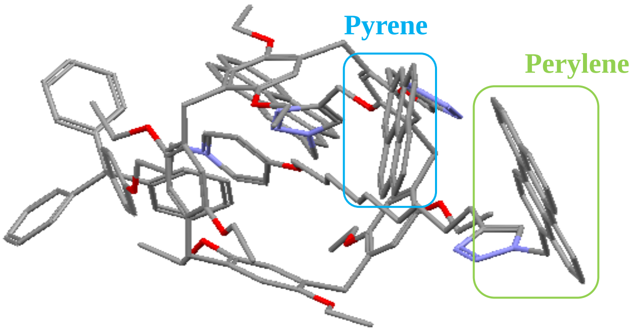


Fig. S8 Molecular structure of [2]rotaxane **3**.

Emission spectrum of [2]rotaxane 3 with the different components from the decay time measurements

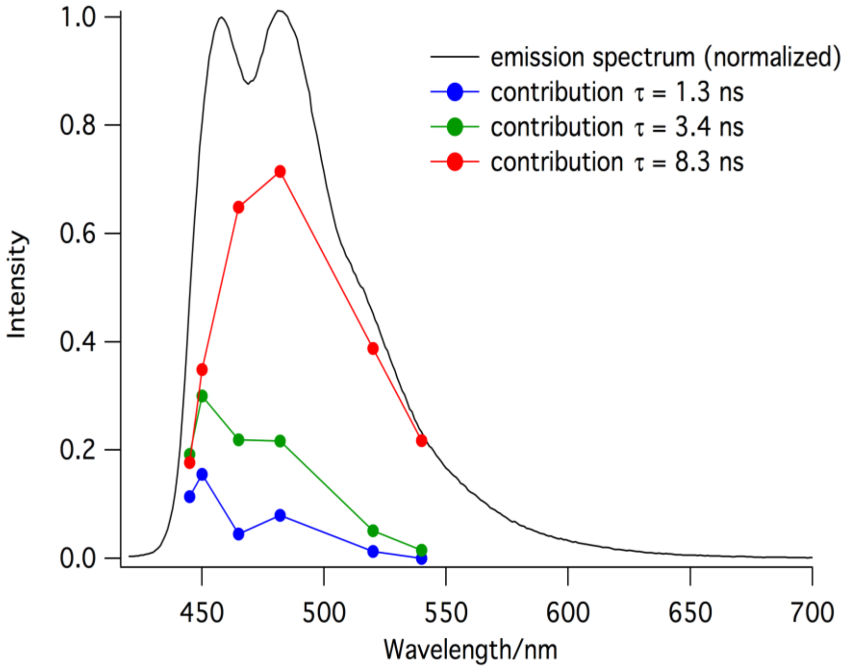


Fig. S9 Emission spectrum (excited at 350 nm, chloroform, 4.0×10^{-6} M) of rotaxane **3** with the relative contributions of the different components from the decay time measurements.

Time profiles of the fluorescence decay

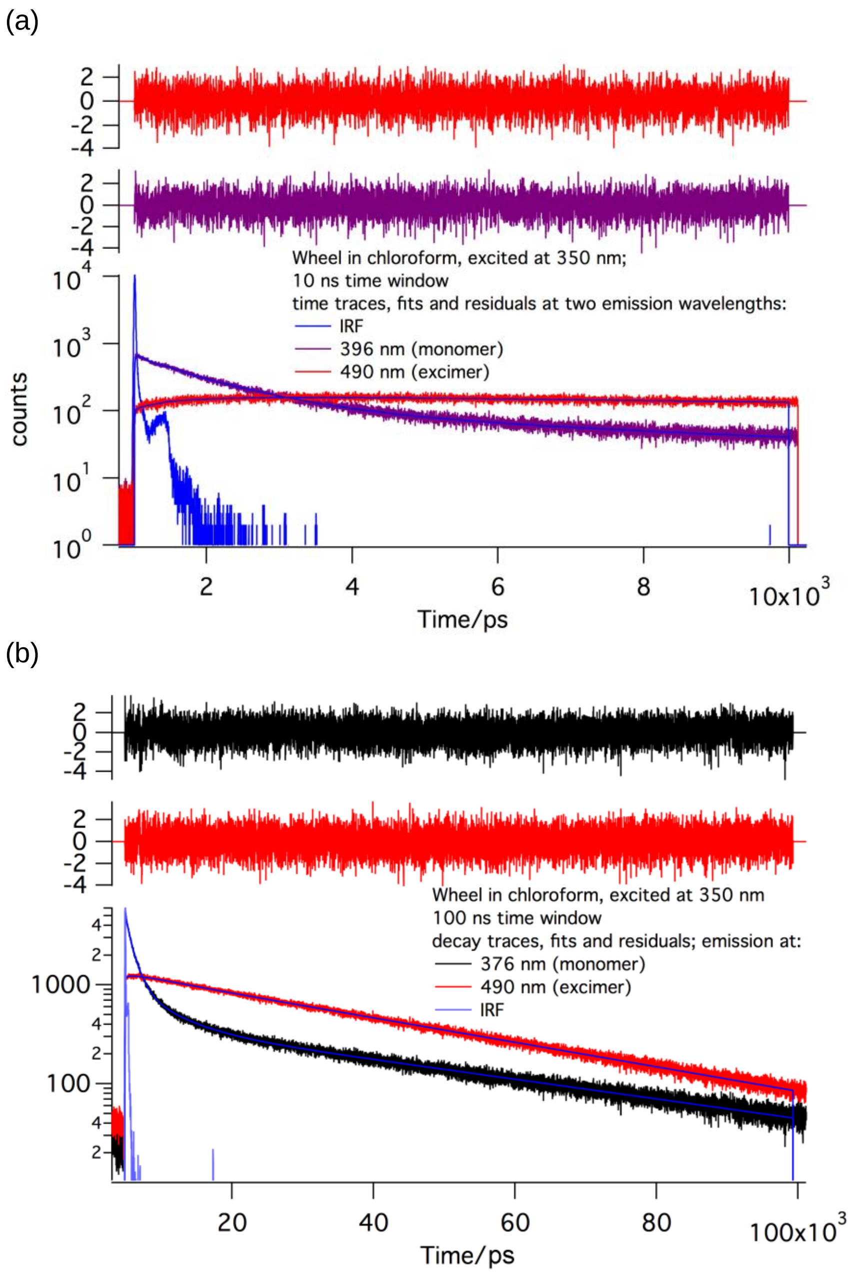


Fig. S10 Fluorescence decay profiles (excited at 350 nm, chloroform, 4.0 × 10^{-6} M) of wheel **H1** in (a) 10 ns and (b) 100 ns.

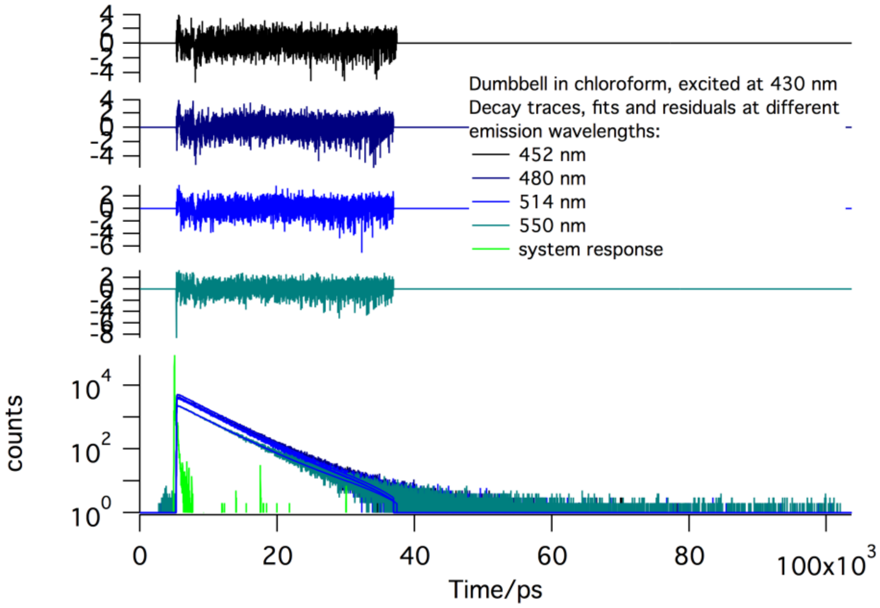


Fig. S11 Fluorescence decay profiles (excited at 430 nm, chloroform, 4.0 × 10^{-6} M) of dumbbell **5**.

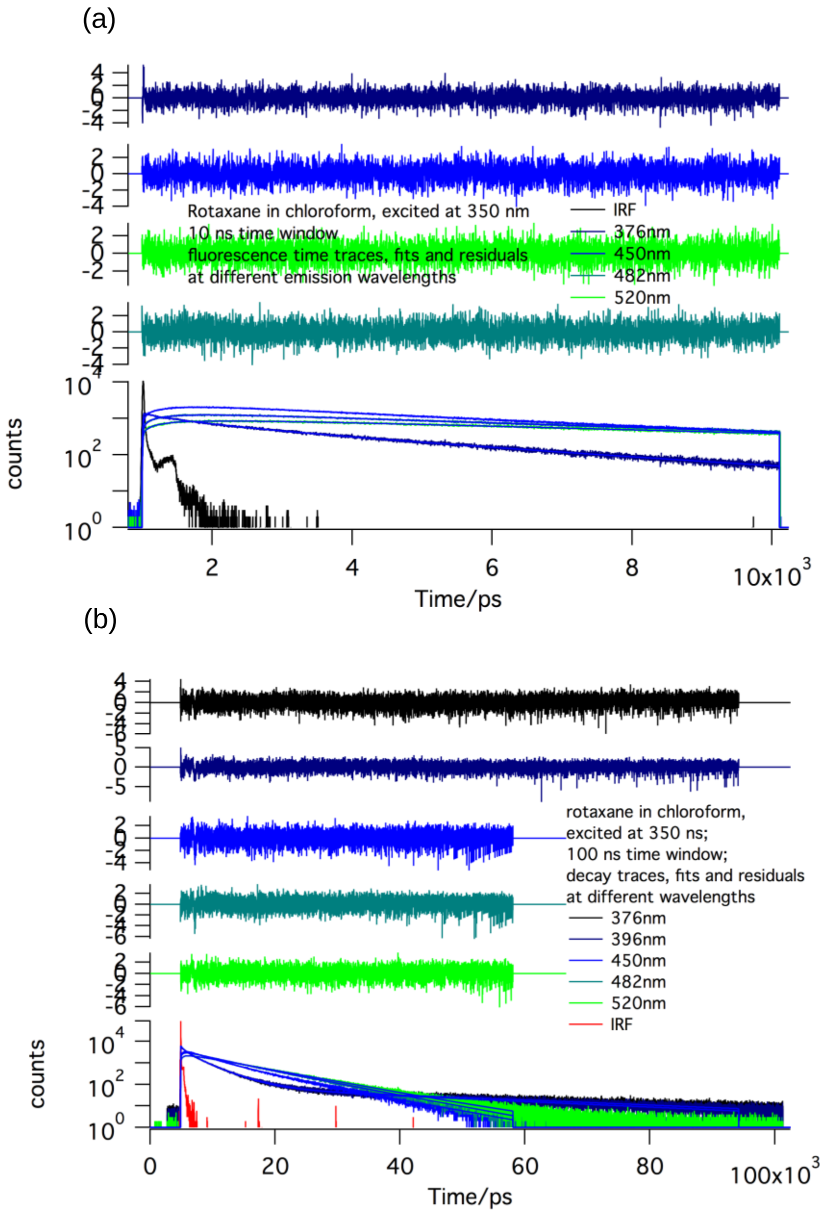


Fig. S12 Fluorescence decay profiles (excited at 350 nm, chloroform, 4.0 × 10^{-6} M) of rotaxane **3** in (a) 10 ns and (b) 100 ns.

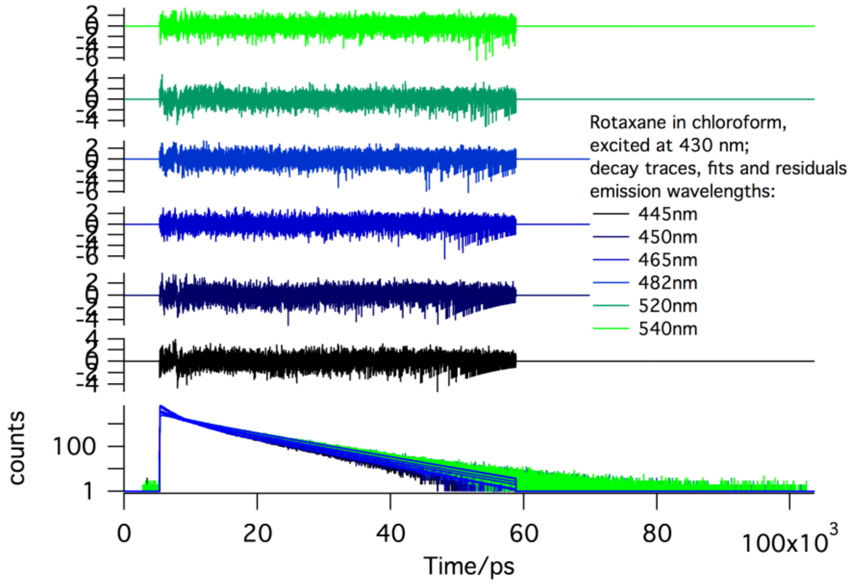


Fig. S13 Fluorescence decay profiles (excited at 430 nm, chloroform, 4.0 × 10^{-6} M) of [2]rotaxane **3**.

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