Supporting Information

Controlling Ring Translation of Rotaxanes

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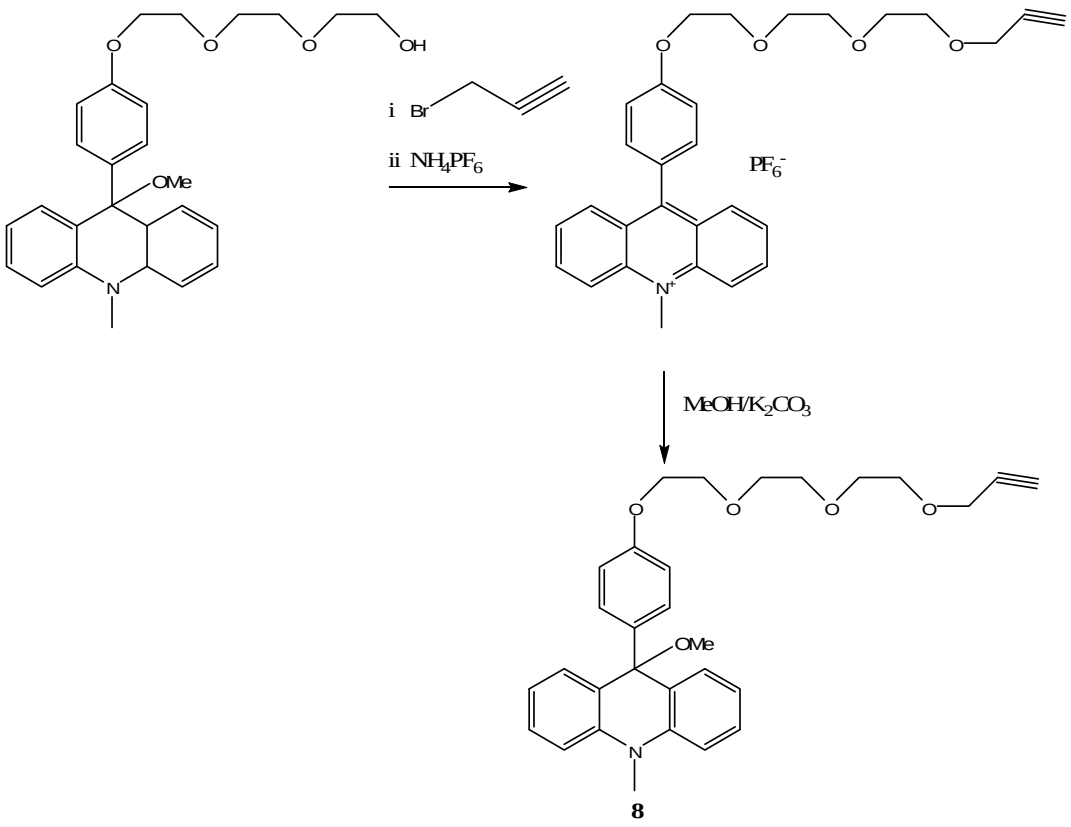
Full synthetic details pertaining to the preparations of new compounds**.**
UV-vis and NMR spectra of selected compounds and transients; Assignment of protons of rotaxanes **3**, **4**, **6**, **10**, **12**, **14**, **16**, **19** and **21** and the molecular axles **22 - 24**
Transient decay curves of compound **12**, **25**, **21**,**22** and **26;** absorption spectrum and decay curve of the transient observed upon irradiation of **CBQT**$^{4+}$ in MeOH.

9-(4-(2-(2-(2-(4-(2-carboxyethyl)phenoxy)ethoxy)ethoxy)ethoxy)phenyl)-10-methylacridinium hexafluorophosphate (**2**)

A solution of **1**[1] (0.404 g, 0.57 mmol) in acetone (30 mL) were cooled to 0 ^{o}C.CrO_3 (0.315 g, 3.15 mmol) dissolved in H_2SO_4 (3 $moll^{-1}$) were slowly dropped into the acetone solution whereby the temperature was hold below 5 ^{o}C. The suspension was stirred for 3 h at 0 ^{o}C. Water (30 mL) and dichloromethane (DCM) (40 mL) were added. The organic phase was seoarated and the aqueous phase was extracted with DCM (2 x 40 mL). The combined organic phases were were dried ($MgSO_4$), the solvent was removed in vacuo. The residue was chromatographed (silica gel, acetonitrile (200 mL)/0.5% NH_4PF_6 aqueous solution (5 mL)). The solvent was evaporated and the residue was dissolved in water (30 mL) and DCM (30 mL). The organic layer was separated. The aqueous solution was extracted with DCM (3 x 30 mL). The combined organic solutions were dried ($MgSO_4$). The solvent was evaporated to give pure **2** as orange resin, 0.320 g, (79 %).

^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 2.50 (t, *J*=8 Hz, 2 H; CH_2), 2.77 (t, *J*=8 Hz, 2 H; CH_2), 3.67-3.69 (m, 4 H; ethyleneoxy), 3.79 (t, *J*=5 Hz, 2 H; ethyleneoxy), 3.89 (t, *J*=5 Hz, 2 H; ethyleneoxy), 3.89 (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.07 (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.28 (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.79 (s, 3 H; $N^{+}Me$), 6.83 (d, *J*=9 Hz, 2 H; aryl), 7.09 (d, *J*=9 Hz, 2 H; aryl), 7.27 (d, *J*=9 Hz, 2 H; aryl), 7.44 (d, *J*=9 Hz, 2 H; aryl), 7.85 (m, 2 H; acridinium); 8.11 (d. *J*=9 Hz, 2 H; acridinium), 8.35 (m, 2 H; acridinium), 8.58 (d, *J*=9 Hz, 2 H; acridinium); HRMS (ESI) found 566,2531, calcd for $(M\text{-}PF_6^{-})[C_{35}H_{36}O_6N]^{+}$) 566.2537.



Scheme S1 Synthesis of the western part of the molecular axle **8**

10-Methyl-9-(4-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethoxy)phenyl)acridinium hexafluorophosphate: **2-(2-(2-(4-(9-methoxy-10-methyl-4a,9,9a,10-tetrahydroacridin-9-yl)phenoxy)ethoxy)ethoxy)ethanol**[1] (0.80 g, 1.73 mmol) dissolved in THF (50 mL) were treated with NaH (0.117 g, 0.29 mmol, 60% in hexane). The mixture was stirred for 30 min. Propargyl bromide (0.28 g, 1.90 mmol) was added and the solution was heated under reflux for 5 hours and stirred at room temperature for 12 hours. NH_4PF_6 (15 mL, 5% in water) was added. The solvent was removed in vacuo. The residue was treated with water (15 mL) and dichloromethane (DCM) (30 mL). The organic phase was separated. The aqueous phase was extracted with DCM (3x 30 mL). The combined organic phases were dried ($MgSO_4$); the solvent was removed in vacuo. The remaining residue was purified by column chromatography (CC) (SiO_2/acetone (400 mL)/cyclohexane (40 mL)/NH_4PF_6 (0.5 g). The obtained product was isolated; the solvents were evaporated. Water (30 mL) was added to the remaining solid. The aqueous phase was extracted with DCM (3x 30 mL). The combined organic phases were dried ($MgSO_4$). The solvent was removed in vacuo to give the substituted acridinium salt (0.43 g, 41%) as orange-red resin.

^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 2.68 (t, *J*=2 Hz, 1 H; propargyl), 3.63-3.61 (m, 6 H; ethyleneoxy), 3.69-3.67 (m, 2 H; ethyleneoxy), 3.89 (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.14 (d, *J*=2 Hz, 2 H; CH_2), 4.29 (t, J = 5 Hz, 2H; ethyleneoxy), 4.81 (s, 3 H; N^+Me), 7.27 (d, *J*=9 Hz, 2 H; aryl), 7.46 (d, *J*=9 Hz, 2 H; aryl), 7.84 (t, *J*=8 Hz, 2 H; acridinium); 8.11 (d. *J*=9 Hz, 2 H; acridinium), 8.37 (t, *J*=8 Hz, 2 H; acridinium), 8.60 (d, *J*=9 Hz, 2 H; acridinium); HRMS (ESI) found 456.2167, calcd for (M-PF_6^-)[$C_{29}H_{30}O_4N]^+$) 456.2169.

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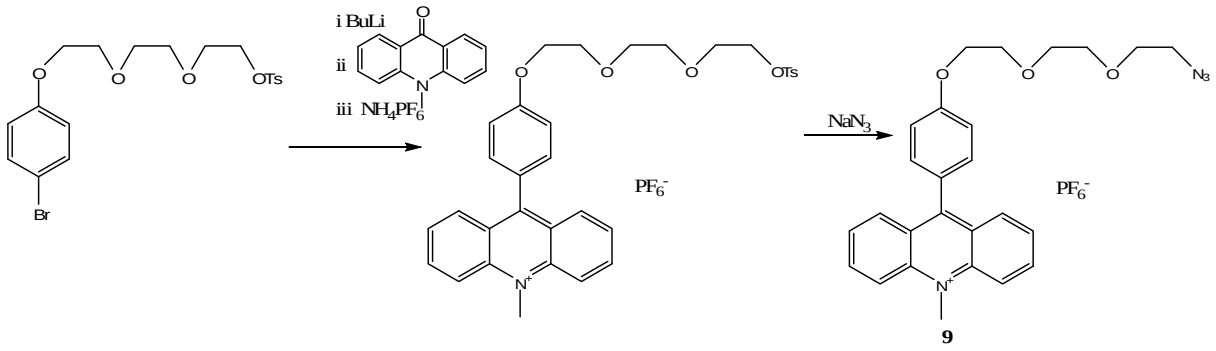
9-Methoxy-10-methyl-9-(4-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethoxy)phenyl)-9,10-dihydroacridine (**8**)

The suspension of **10-Methyl-9-(4-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethoxy)phenyl)acridinium hexafluorophosphate** (0.18 g, 0.30 mmol) dissolved in MeCN (5 mL) and MeOH (0.5 mL) and K_2CO_3 (0.1 g) was stirred for 12 h. After filtration the solvent was removed in vacuo. The residue was extracted with chloroform (5 mL). The solid was filtered and the solvent was removed in vacuo to give **8** (0.145 g, 99%), brown oil.

^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ= 2.39 (t, *J*=2 Hz, 1 H; propargyl), 2.95 (s, 3 H; OMe), 3.50 (s, 3 H; NMe), 3.71-3.63 (m, 8 H; ethyleneoxy), 3.79 (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.05 (t, *J*=5 Hz; 2H; ethyleneoxy), 4.16 (d, *J* = 2 Hz, 2 H; OCH_2), 6.76 (d, *J*=9 Hz, 2 H; aryl); 6.92 (t, *J*=8 Hz, 2 H; acridane H-5,7), 7.02 (d, *J*=8 Hz, 2 H; acridane H-4,5), 7.21 (d, *J*=9 Hz, 2 H; aryl), 7.28 (t, *J*=8 Hz, 4 H; acridane H-3,6); HRMS (ESI) found 456.2167 calcd for (M-MeO^-), $[C_{29}H_{30}O_4N]^+$ 456.2169.



Scheme S2 Synthesis of the eastern part of the molecular axle **9**

10-Methyl-9-(4-(2-(2-(2-(tosyloxy)ethoxy)ethoxy)ethoxy)phenyl)acridinium hexafluorophosphate

2-(2-(2-(4-bromophenoxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate[1] (3.1 g, 6.8 mmol) was dissolved in dry THF (30 mL) under an argon atmosphere. The solution was cooled to -78°C and BuLi (1.6 M in n-hexane, 4.2 mL, 6.8 mmol) was dropped into the solution within 30 min. A solution of N-methylacridinone (0.80 g, 3.8 mmol) in THF solution (50 mL) was dropped in this

solution at -78^{O}C. The reaction mixture was stirred for 30 min. at -78^{o}C and then for 20 h at room temperature. Water (2 mL) was added to the violet solution. After filtration and removing of the solvent in vacuum the remaining oil was purified by column chromatography (n-butanol/acetic acid/water 5:1:2) to separate the product from N-methylacridinone. The product (as acetate) was treated with an aqueous saturated solution of NH_4PF_6 (50 mL), dissolved in dichloromethane and purified by column chromatography (MeCN/NH_4PF_6 in MeCN solution (5 %), 40:1), yellow solid, m.p.140 ^{o}C, 1.6 g (33 %). ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 2.40 (s, 3 H; CH_3), 3.5 (m, 2 H; ethyleneoxy), 3.6 (m, 4 H; ethyleneoxy), 3.8 (m, 2 H; ethyleneoxy), 4.1 (m, 2 H; ethyleneoxy), 4.3 (m, 2 H; ethyleneoxy), 7.27 (d, *J*(H,H)=8.7 Hz, 2 H; Ar), 7.41 (d, *J*(H,H)=8.1 Hz, 2 H; Ar), 7.45 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.76 (d, *J*(H,H)=8.2 Hz, 2 H; Ar), 7,83 (m, 2 H; acridinium, H-2,7), 8.16 (d, *J*(H,H)=7.5 Hz, 2 H; acridinium, H-1,8), 8.35 (m, 2 H; acridinium, H-3,6), 8.57 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5). $C_{33}H_{34}F_6NO_6PS$ (717.66): calcd. (%): C 55.23, H 4.77, N 1.45, S 4.47; found (%): C 55.17, H 5.08, N 1.60, S 4.37.

9-(4-(2-(2-(2-azidoethoxy)ethoxy)ethoxy)phenyl)-10-methylacridinium hexafluorophosphate (9)

10-Methyl-9-(4-(2-(2-(2-(tosyloxy)ethoxy)ethoxy)ethoxy)phenyl)acridinium hexafluorophosphate (0.8 g, 1.11 mmol) dissolved in dry DMF (20 mL) and NaN_3 (0.8 g (12.3 mmol) were stirred for 14 hours at 60 ^{o}C. After cooling water (40 mL) and ethyl acetate (40 mL) were added. The organic phase was separated. The water phase was extracted with ethyl acetate (4x 50 mL). The combined organic phases were dried ($MgSO_4$). The solvent was removed in vacuo. The residue was purified by CC (SiO_2/ acetone (400 mL)/cyclohexane (40 mL)/NH_4PF_6 (0.5 g)). The yellow product fraction was evaporated. The residue was treated with water (30 mL) and DCM (30 mL). The aqueous phase was extracted with DCM (2x 30 mL). The combined organic phases were dried ($MgSO_4$) and evaporated to give **9** as orange resin (0.43 g, 65%).

^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 3.39 (t, *J*=5 Hz, 2 H; CH_2N_3), 3.64 (m, 4 H; ethyleneoxy), 3.71 (t, *J*=5 Hz, 2 H; CH_2O), 3.90 (t, *J*=5 Hz, 2 H; CH_2O), 4.30 (t, *J*=5 Hz, 2 H; OCH_2), 4.80 (s, 3 H; $N^{+}Me$), 7.29 (d, *J*=9 Hz, 2 H; aryl), 7.47 (d, *J*=9 Hz, 2 H; aryl), 7.86 (m, 2 H; acridinium, H-2,7), 8.13 (d, *J*=9 Hz, 2 H; acridinium, H-1,8), 8.37 (m, 2 H; acridinium, H-3,6), 8.59 (d, *J*=9 Hz, 2 H; acridane, H-4,5); HRMS: found 443.2075, calcd for (M-PF_6^{-}), $[C_{26}H_{27}O_3N_4)]^{+}$ 443.2078; IR: 2160 cm^{-1}.

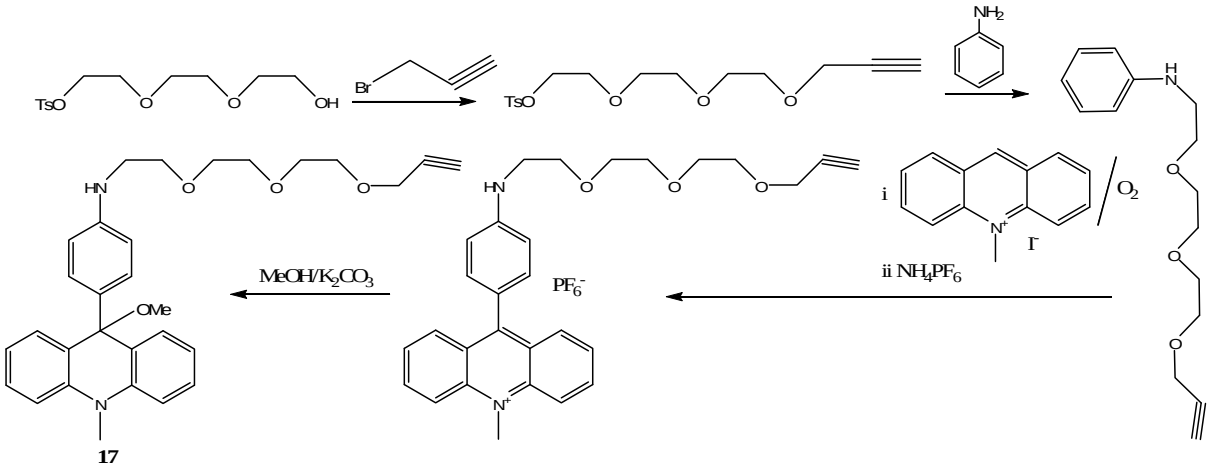
Compound 13

4-(3-(2-(2-(2-(4-(9-ethoxy-10-methyl-9,10-dihydroacridin-9-yl)phenoxy)ethoxy)ethoxy)ethoxy)propyl)phenol[1] (0.400 g, 0.69 mmol) and propargylbromide (0.163 g, 163 mmol) were dissolved in MeCN (30 mL). K_2CO_3 (0.190 g, 1.37 mmol) was added.

The suspension was refluxed for 8 h and stirred for 12 h at room temperature. The solvent was evaporated. The residue was treated 5% aqueous NH_4PF_6 solution and DCM (30 mL). The aqueous solution was extracted with DCM (2 x 30 mL). The combined organic phases were dried ($MgSO_4$) and evaporated. The crude product was purified by CC (silica gel, acetone (400 mL)/cyclohexane (40 mL)/NH_4PF_6 (0.5 g)). The yellow fractions were evaporated and NH_4PF_6 was dissolved with water (30 mL). The aqueous suspension was extracted with DCM (3 x 30 mL). The DCM solutions were dried and evaporated to give the acridinium salt as an orange resin, 0.287 g (57 %). ^{1}H-NMR (400 MHz, CD_3CN, TMS) (^{13}C 100 MHz): δ= 1.81-1.73 (31.0) (m, 2 H; CH_2) , 2.59 (31.4) (t, *J*=7 Hz, 2 H; CH_2), 2.74 (t, *J*=2 Hz, 1 H: propargyl), 3.42 (75.6) (t, *J*=7 Hz, 2 H; CH_2O), 3.51-3.53 (m, 2 H; ethyleneoxy), 3.56-3.58 (m, 2 H; ethyleneoxy), 3.61-3.63 (m, 2 H; ethyleneoxy), 3.67-3.69 (m, 2 H; ethyleneoxy), 3.88 (69.2) (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.28 (68.0) (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.62 (55.5) (d, *J*=2 Hz, 2 H, propargyl,CH_2), 4.79 (38.7) (s, 3 H; N^+Me), 6.82 (114.6) (d, *J*=9 Hz, 2 H; aryl); 7.11 (129.4) (d, *J*=9 Hz, 2 H; aryl), 7.27 (114.9) (d, *J*=9 Hz, 2 H; aryl), 7.44 (130.5) (d, *J*=9 Hz, 2 H; aryl), 7.84 (127.6) (m, 2 H; acridinium, H-3,6), 8.11 (132.0) (m, 2 H; acridinium, H-4,5), 8.37 (138.6) (m, 2 H; acridinium, H-2,7), 8.58 (118.4) (m, 4 H; acridinium, H-1,8), HRMS (ESI) found 590.2900, calcd for (M-PF_6^-)$[C_{38}H_{40}O_5N]^+$ 590.2901

The resin was transformed into the acridane compound **13**. K_2CO_3 (0.1 g) was added to 0.250 g (0.34 mmol) resin dissolved in MeCN (5 mL) and MeOH (0.5 mL). The suspension was stirred for 12 h. After filtration the solvent was removed in vacuo. The residue was extracted with chloroform (5 mL). The solid was filtered and the solvent was removed in vacuo to give **13**, 0.200 g (95 %).

^{1}H-NMR (400 MHz, $CDCl_3$, TMS) (^{13}C 100 MHz): δ= 1.81-1.85 (31.3) (m, 2 H; CH_2) , 2.49 (75.3) (t, *J*=2 Hz, 1 H; propargyl), 2.61 (31.3) (t, *J*=7 Hz, 2 H; CH_2), 2.94 (55.8) (s, 3 H; OCH_3), 3.43 (t, *J*=7 Hz, 2 H; CH_2O), 3.49 (33.4) (s, 3 H; N^+Me), 3.60-3.73 (m, 8 H; ethyleneoxy), 3.79 (69.7) (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.05 (67.2) (t, *J*=5 Hz, 2 H; ethyleneoxy), 4.63 (d, *J*=2 Hz, 2 H; propargyl), 6.75 (113.7) (d, *J*=9 Hz, 2 H; aryl); 6.85-6.89 (114.7, 120.1) (m, 4 H; aryl, acridane-H3,6), 7.02 (112.1) (d, *J*=9 Hz, 2 H; acridane-H1,8), 7.09 (129.3) (d, *J*=9 Hz, 2 H; aryl), 7.21 (127.4) (d, *J*=9 Hz, 2 H; aryl), 7.29 (128.3, 129.3) (m, 4 H; acridane-H-2,4,5,7), HRMS (ESI) found 644.2994, calcd for (M+Na^{23})$[C_{39}H_{43}O_6N^{23}Na]$ 644.2983, found 590.2900, calcd for (M-MeO^-)$[C_{38}H_{40}O_5N]^+$ 590.2901.



Scheme S3 Synthesis of the molecular axle **17**

N-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethyl)aniline

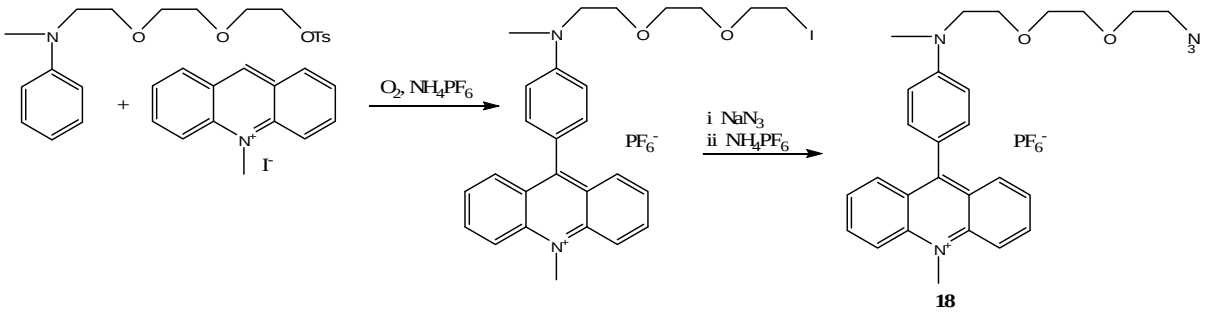
K_2CO_3 (4.7 g, 34.01 mmol) was added to the solution of 2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate[2] (3.63 g , 10.6 mmol) and aniline (3.22 g, 34.58 mmol) in MeCN (40 mL). The suspension was refluxed for 20 h. The solvent was evaporated in vacuo. The remaining residue was treated with water (30 mL) and diethylether (30 mL). The organic layer was separated. The aqueous phase was extracted with diethylether (3 x 30 mL). The combined organic phases were dried ($MgSO_4$). After removing the solvent the residue was purified by CC (silica gel, cyclohexane/ethylacetate 2:1) to give 2.1 g (75 %) oil. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ= 3.29 (t, *J*=5 Hz, 2 H; NCH_2), 3.64-3.67 (m, 10 H; ethyleneoxy), 4.19 (d, *J*=2 Hz, 2 H; propargyl), 4.41 (t, *J*=5 Hz, 1 H; propargyl), 6.63 (d, *J*=8 Hz, 2 H; Ar), 6.71 (t, *J*=8 Hz, 1 H; Ar), 7.17, (t, *J*=8 Hz, 2 H; Ar).

10-methyl-9-(4-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethylamino)phenyl)acridinium hexafluorophosphate

N-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethyl)aniline (1.00 g, 3.8 mmol) and N-methylacridinium iodide (1.22 g, 3.8 mmol) in n-butanol (40 mL) were refluxed for 8 h.while air bubbled through the suspension.. The solvent was evaporated in vacuo. The residue was purified by CC (silica gel, acetone (400 mL)/cyclohexane 40 mL)/0.5 g NH_4PF_6). The violet fractions were collected. The solvents were evaporated in vacuo. The residue was treated with water (30 mL). The suspension was extracted with DCM (3 x 30 mL). The DCM-solution was dried ($MgSO_4$) and evaporated to give a violet resin, 1.09 g (48 %). ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 2.68 (t, *J*=2 Hz, 1 H; propargyl), 3.41 (t, *J*=5 Hz, 2 H; NCH_2), 3.61-3.63 (m, 8 H; ethyleneoxy), 3.73 (t, *J*=5 Hz, 2 H; OCH_2), 4.15 (d, *J*=2 Hz, 2 H; propargyl), 4.72 (s, 3 H; N^+Me), 6.94 (d, *J*=9 Hz, 2 H; aryl), 7.33 (d, *J*=9 Hz, 2 H; aryl), 7.82 (m, 2 H; acridinium, H-2,7); 8.26 (d. *J*=8 Hz, 2 H; acridinium, H-1,8), 8.37 (m, 2 H; acridinium, H-3,6), 8.51 (d, *J*=9 Hz, 2 H; acridinium, H-4,5).

4-(9-methoxy-10-methyl-9,10-dihydroacridin-9-yl)-N-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethyl)aniline (**17**)

The suspension of **10-methyl-9-(4-(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)ethylamino)phenyl)acridinium hexafluorophosphate** (0.50 g, 0.83 mmol) dissolved in MeCN (5 mL) and MeOH (0.5 mL) and K_2CO_3 (0.1 g) was stirred for 12 h. After filtration the solvent was removed in vacuo. The residue was extracted with chloroform (5 mL). The solid was filtered and the solvent was removed in vacuo to give **17** (0.402 g, 100%), red oil. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ= 2.39 (t, *J*=2 Hz, 1 H; propargyl), 2.95 (s, 3 H; OMe), 3.23 (t, *J*=6 Hz, 2 H; NCH2), 3.48 (s, 3 H; NMe), 3.61-3.73 (m, 10 H; ethyleneoxy), 4.17 (d, *J* = 2 Hz, 2 H; propargyl), 6.76 (d, *J*=9 Hz, 2 H; aryl); 6.48 (d, *J*=9 Hz, 2 H; aryl), 6.92 (m, 2 H; acridane H-2,7), 7.01 (d, *J*=9 Hz, 2 H; acridane, H-4,5), 7.09 (d, *J*=9 Hz, 2 H; Ar), 7 .27 (m, 4 H; acridane H-3,6), 7.33 (d, *J*=9 Hz, 2 H; acridane, H-1,8).



Scheme S4 Synthesis of the molecular thread **18**

2-(2-(2-(methyl(phenyl)amino)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate

Toluene sulfochloride (5.83 g, 30.58 mmol) dissolved in DCM (20 mL) were added to 2-(2-(2-(methyl(phenyl)amino)ethoxy)ethoxy)ethanol[4] (1.34 g, 5.58 mmol) in DCM (10 mL). NaOH (5.81 g, 145.26 mmol) and DCM (30 mL) were added. The blue solution was refluxed for 7 h. The formed suspension was given to water (150 mL) and DCM (50 mL). The organic layer was separated. The aqueous phase was extracted with DCM (3 x 50 mL). The combined organic phases were dried ($MgSO_4$) and evaporated. Purification by CC (silica gel, cyclohexane/ethylacetate 2:1) affords a yellowish oil, 2.00 g (91 %). ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 2.42 (s, 3 H; methyl), 2.94 (s, 3 H; NCH_3), 3.48-3.55 (m, 6 H; ethyleneoxy), 3.59 (s br, 2 H; OCH_2), 3.65 (t, *J*=5 Hz, 2 H; NCH_2), 4.12 (t, *J*=5 Hz, 2 H; OCH_2), 6.68 (s br, 3 H; aryl), 7.20 (s br, 2 H; aryl), 7.32 (d, *J*=8 Hz, 2 H; Ar), 7.78 (d, *J*=8 Hz, 2 H; Ar).

9-(4-((2-(2-(2-iodoethoxy)ethoxy)ethyl)(methyl)amino)phenyl)-10-methylacridinium hexafluorophosphate

2-(2-(2-(methyl(phenyl)amino)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (1.06 g, 2.69 mmol) and N-methylacridinium iodide (0.86 g, 2.69 mmol) were heated in boiling n-butanol (40 mL) for 7 h while air bubbled through the suspension. The solvent was evaporated in vacuo. The residue was purified by CC (silica gel, acetone (400 mL)/cyclohexane (40 mL)/NH_4PF_6 (0.5 g). The violet fractions were treated with water (30 mL). The mixture was extracted with DCM (3 x 30 mL). The combined DCM-solutions were dried ($MgSO_4$) and evaporated in vacuo to give a violet resin, 1.38 g (75 %). ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 3.13 (s, 3 H; NMe), 3.26 (t, *J*=6 Hz, 2 H; CH_2I), 3.60 (s, 4 H; ethyleneoxy), 3.70 (t, *J*=6 Hz, 4 H; NCH_2, OCH_2), 3.74 (m, 2 H; OCH_2), 4.71 (s, 3 H; N^+Me), 7.05 (d, *J*=9 Hz, 2 H; aryl), 7.40 (d, *J*=9 Hz, 2 H; aryl), 7.82 (m, 2 H; acridinium, H-2,7); 8.26 (d, *J*=8 Hz, 2 H; acridinium, H-1,8), 8.31 (m, 2 H; acridinium, H-3,6), 8.50 (d, *J*=9 Hz, 2 H; acridinium, H-4,5).

9-(4-((2-(2-(2-azidoethoxy)ethoxy)ethyl)(methyl)amino)phenyl)-10-methylacridinium hexafluorophosphate (**18**)

9-(4-((2-(2-(2-iodoethoxy)ethoxy)ethyl)(methyl)amino)phenyl)-10-methylacridinium hexafluorophosphate (1.24 g, 1.81 mmol) and NaN_3 (1.3 g (19.91 mmol) dissolved in dry DMF (30 mL) were stirred for 16 h at 80 ^{o}C. The suspension was treated with water (40 mL) and DCM (40 mL). The organic layer was separated. The aqueous solution was extracted with DCM (2 x 30 mL). The combined DCM-solutions were dried ($MgSO_4$) and evaporated. The remaining violet resin was dried in vacuo to give 1.08 g (98 %). ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 3.13 (s, 3 H; NMe), 3.39 (t, *J*=5 Hz, 2 H; OCH_2), 3.64 (m, 4 H; OCH_2), 3.71 (t, *J*=5 Hz, 2 H; ethyleneoxy), 3.90 (t, *J*=5 Hz, 2 H; NCH_2), 4.30 (t, *J*=5 Hz, 2 H; CH_2N_3), 4.71 (s, 3 H; N^+Me), 7.05 (d, *J*=9 Hz, 2 H; aryl), 7.40 (d, *J*=9 Hz, 2 H; aryl), 7.82 (m, 2 H; acridinium, H-2,7), 8.26 (d. *J*=9 Hz, 2 H; acridinium, H-1,8), 8.31 (m, 2 H; acridinium, H-3,6), 8.50 (d, *J*=9 Hz, 2 H; acridinium, H-4,5). HRMS: found 456.2395, calcd for (M-PF_6^-), $[C_{27}H_{30}O_2N_5]^+$ 456.2394.

Molecular axle 22

The axle **11** (0.16 g, 0.13 mmol) dissolved in MeCN/MeOH (5mL/0.5 mL) was stirred with K_2CO_3(0.1g) for 12 hours. The precipitate was filtered off. The solvent was removed in vacuo. The residue was extracted with dry chloroform (3x 5mL). The solution was evaporated to afford **21** (0.12 g, 93 %) which was used without further purification.

^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C 100 MHz): δ = 2.9 (50.6) (s, 6 H; OMe), 3.42 (33.1) (s, 6 H; NMe), 3.5 (70.1, 70.3) (m, 12 H; ethyleneoxy), 3.6 (69.3) (m, 4 H; ethyleneoxy), 3.72 (69.0) (t, *J*(H,H)=5.0 Hz, 2 H; ethyleneoxy), 3.9 (67.3) (m, 4 H; ethyleneoxy), 4.37 (49.6) (t, *J*(H,H)=5.0 Hz, 2 H; NCH_2), 4.43 (63.9) (s, 2 H; OCH_2), 6.70 (112.8) (dd, *J*(H,H)=9.0, 8.8 Hz, 4 H; Ar), 6.88

(120.1) (m, 4 H; acridane, H-2,7), 7.07 (113.6) (d, *J*(H,H)=7.5 Hz, 4 H; acridane, H-4,5), 7.13 (d, *J*(H,H)=8.6 Hz, 4 H; Ar), 7.2 (128.6) (m, 8 H; acridane, H-1,3,6,8), 7.72 (124.0) (s, 1 H; triazole); HRMS (ESI): found 930.4436; calcd for [M-MeO$^-$] $[C_{56}H_{60}O_8N_5]^+$: 930.4425; found 449.7130; calcd for. [M-2 MeO$^-$] $[C_{56}H_{60}O_8N_5]^{2+}$: 449.7124.

Molecular axle 23

The axle **15** (0.158 g, 0.10 mmol) dissolved in MeCN/MeOH (5mL/0.5 mL) was stirred with K_2CO_3(0.1g) for 12 hours. The precipitate was filtered off. The solvent was removed in vacuo. The residue was extracted with dry chloroform (3x 5mL). The solution was evaporated to afford **23** (0.011 g, 87 %) which was used without further purification.

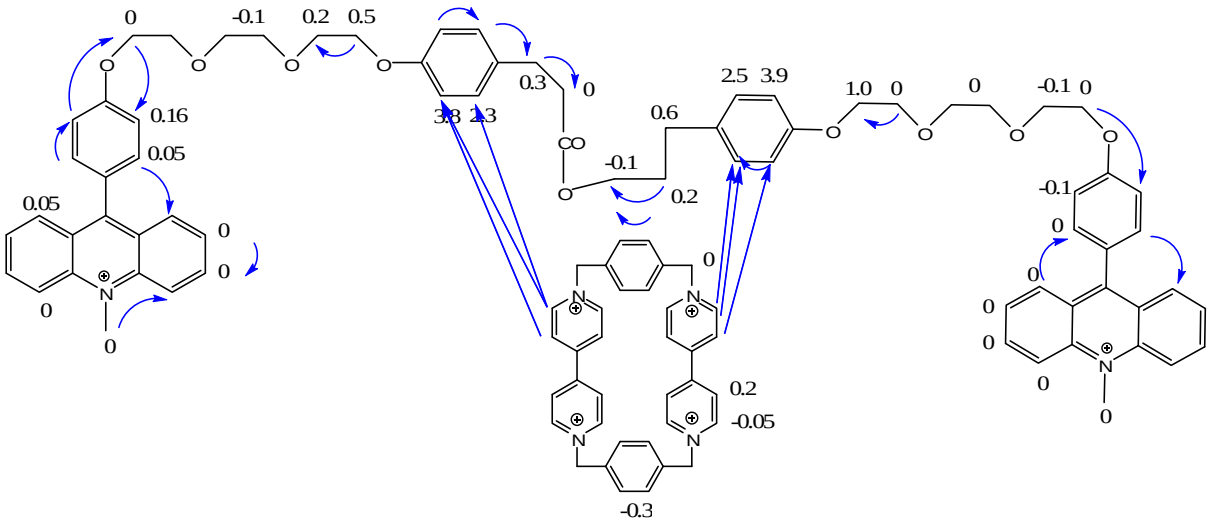
^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C 100 MHz): δ = 1.72 (31.2) (m, 2 H; CH_2), 2.52 (30.8) (t, *J*(H,H)=8 Hz, 2.9 (50.3) (s, 6 H; OMe), 3.34 (70.1) (t, *J*(H,H)=6 Hz, 2 H; OCH_2), 3.42 (32.8) (s, 6 H; NMe), 3.4-3.5 (69.1-70.0) (m, 12 H; ethyleneoxy), 3.6 (69.3) (m, 4 H; ethyleneoxy), 3.72 (69.0) (t, *J*(H,H)=5.0 Hz, 2 H; OCH_2), 3.9 (67.1) (m, 4 H; ethyleneoxy), 4.42 (49.8) (t, *J*(H,H)=5.0 Hz, 2 H; NCH_2), 4.96 (61.1) (s, 2 H; OCH_2), 6.66 (113.3), 6.69 (113.6) (dd, *J*(H,H)=9.0, 8.8 Hz, 4 H; Ar), 6.88 (119.8) (m, 4 H; acridane, H-2,7), 7.07 (126.7) (d, *J*(H,H)=9 Hz, 4 H; Ar), 7.1 (112.5, 126.7) (m, 8 H; Ar, acridane, H-4,5), 7.3 (128.3) (m, 8 H; acridane, H-1,3,6,8), 7.84 (124.0) (s, 1 H; triazole); HRMS (ESI): found 1067.5362; calcd for [M-MeO$^-$] $[C_{65}H_{69}D_2O_9N_5]^+$: 1067.5372; found 516.7495; calcd for. [M-2 MeO$^-$] $[C_{65}H_{69}D_2O_9N_5]^{2+}$: 516.7489.

Molecular axle 24

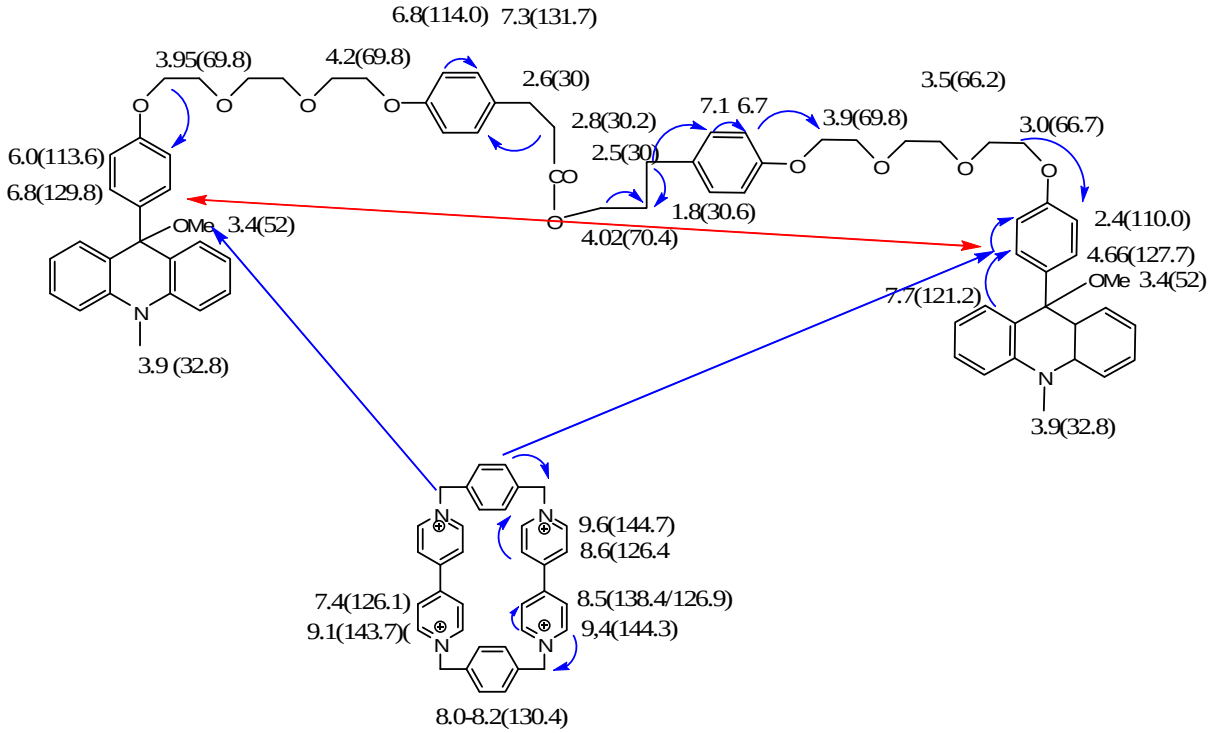
The axle **20** (0.15 g, 0.13 mmol) dissolved in MeCN/MeOH (5 mL/0.5 mL) was stirred with K_2CO_3(0.1 g) for 12 h. The precipitate was filtered off. The solvent was removed in vacuo. The residue was extracted with dry chloroform (3x 5mL). The solution was evaporated to afford **23** (0.04 g, 38 %) as red-brown oil that was used without further purification.

^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C 100 MHz): δ = 2.8 (38.4) (s, 3 H; NMe), 3.89 (50.8) (s, 3 H; OMe), 3.91 (50.7) (s, 3 H; OMe), 3.1 (43.3) (m, 2 H; NHC$\underline{H_2}$), 3.3 (52.0) (m, 2 H; MeN$\underline{CH_2}$), 3.43-3.5 (33.3, 69.2,69.4,69.6,70.2,70.3,70.3) (m, 22 H; ethyleneoxy, NMe), 3.67 (68.4) (t, *J*(H,H)=4.7 Hz, 2 H; OCH_2), 4.29 (50.0) (t, *J*(H,H)=5.0 Hz, 2 H; NCH_2), 4.47 (64.1) (s, 2 H; OCH_2), 6.40 (111.9) (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 6.51 (111.4) (d, *J*(H,H)=9.0 Hz, 2 H; Ar), 6.87 (117.6) (m, 4 H; acridane, H-2,7), 6.94 (126.7) (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 6.99 (126.7) (d, *J*(H,H)=9.0 Hz, 2 H; Ar), 7.07 (112.8) (d, *J*(H,H)=8.3 Hz, 4 H; acridane, H-4,5), 7.3 (128.7, 128.9) (m, 8 H; acridane, H-1,3,6,8), 7.65 (124.1) (s, 1 H; triazole); HRMS (ESI):

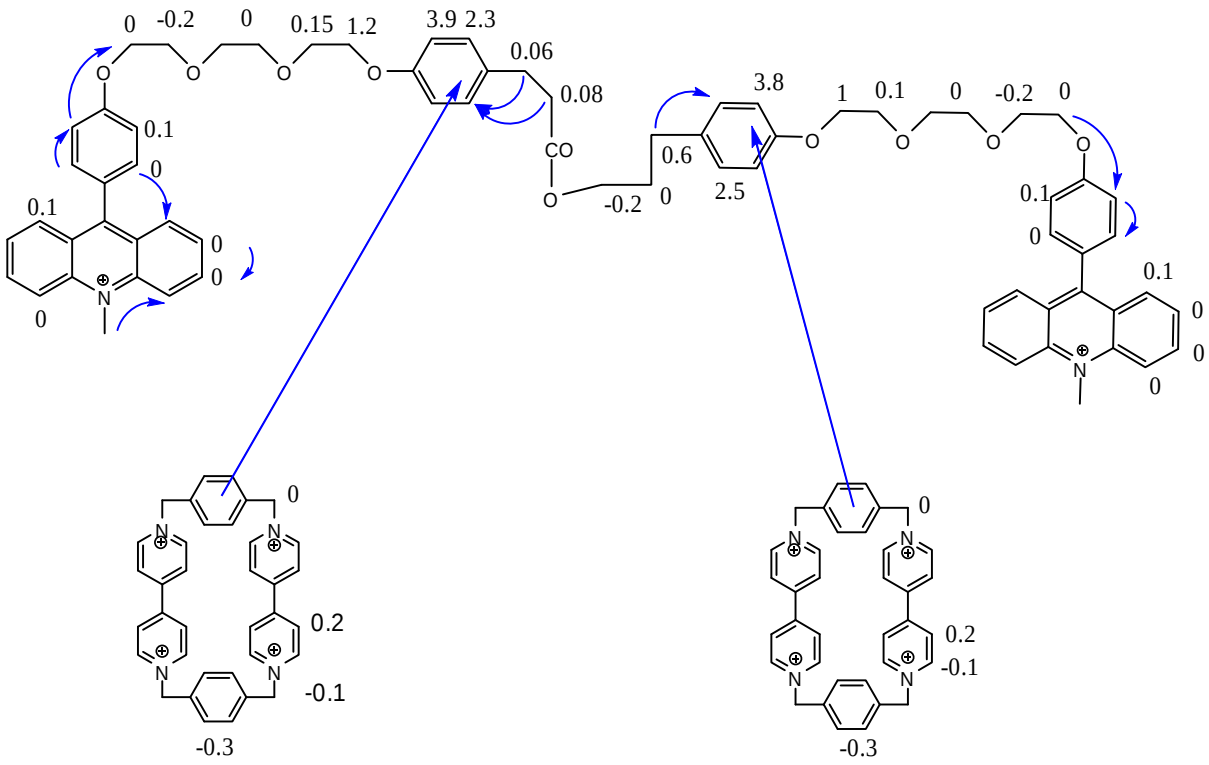
found 942.4910 calcd for [M-MeO$^-$] [$C_{57}H_{64}O_6N_7$]$^+$]: 942.4913; found 455.7365 calcd for [M-2 MeO$^-$] [$C_{56}H_{61}O_5N_7$]$^{2+}$: 455.7362.



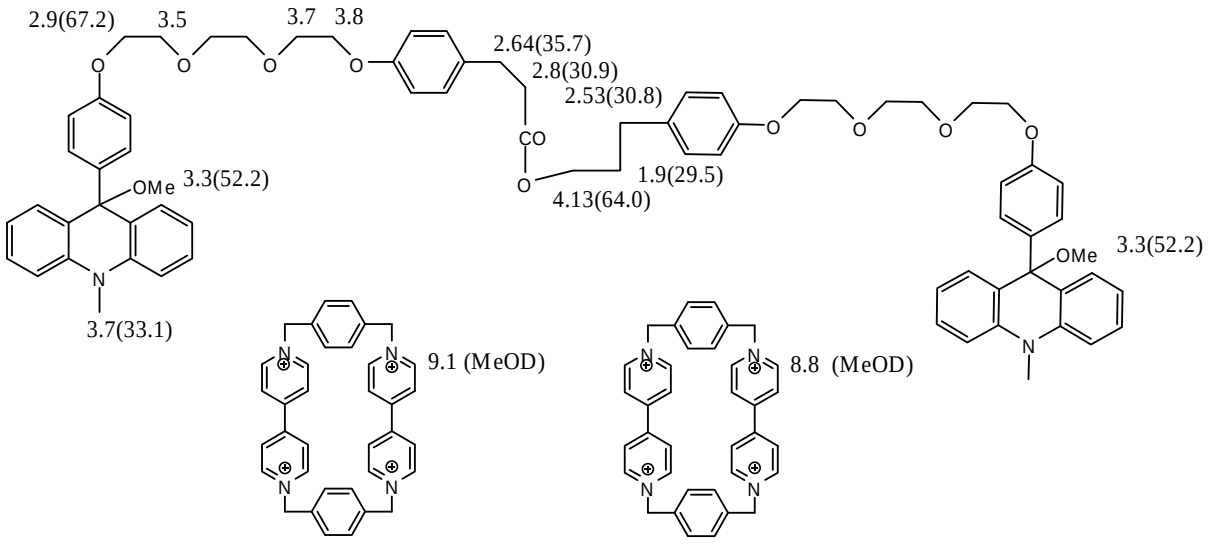
Scheme S5 Chemical shift differences of proton resonances of rotaxane **3** obtained by comparison of the proton resonances of compound **5** with related proton resonances observed in the rotaxane ($\delta_{\mathbf{4}}$ - $\delta_{\text{rotaxane }\mathbf{3}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.



Scheme S6 Assignable proton signals together with ^{13}C signals (in brackets) of rotaxane **6** in acetone-d_6 solution at 233 K. Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra. The red arrow marks the exchange cross peak between protons of two aryl groups of the acridane moieties



Scheme S7 Chemical shift differences of proton resonances of rotaxane **4** obtained by comparison of the proton resonances of compound **4** with related proton resonances observed in the rotaxane ($\delta_{\mathbf{5}}$ - $\delta_{\text{rotaxane }\mathbf{4}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.



Scheme S8 Assignable proton signals together with ^{13}C signals (in brackets) of rotaxane **7** in CD_3CN solution at 298 K.

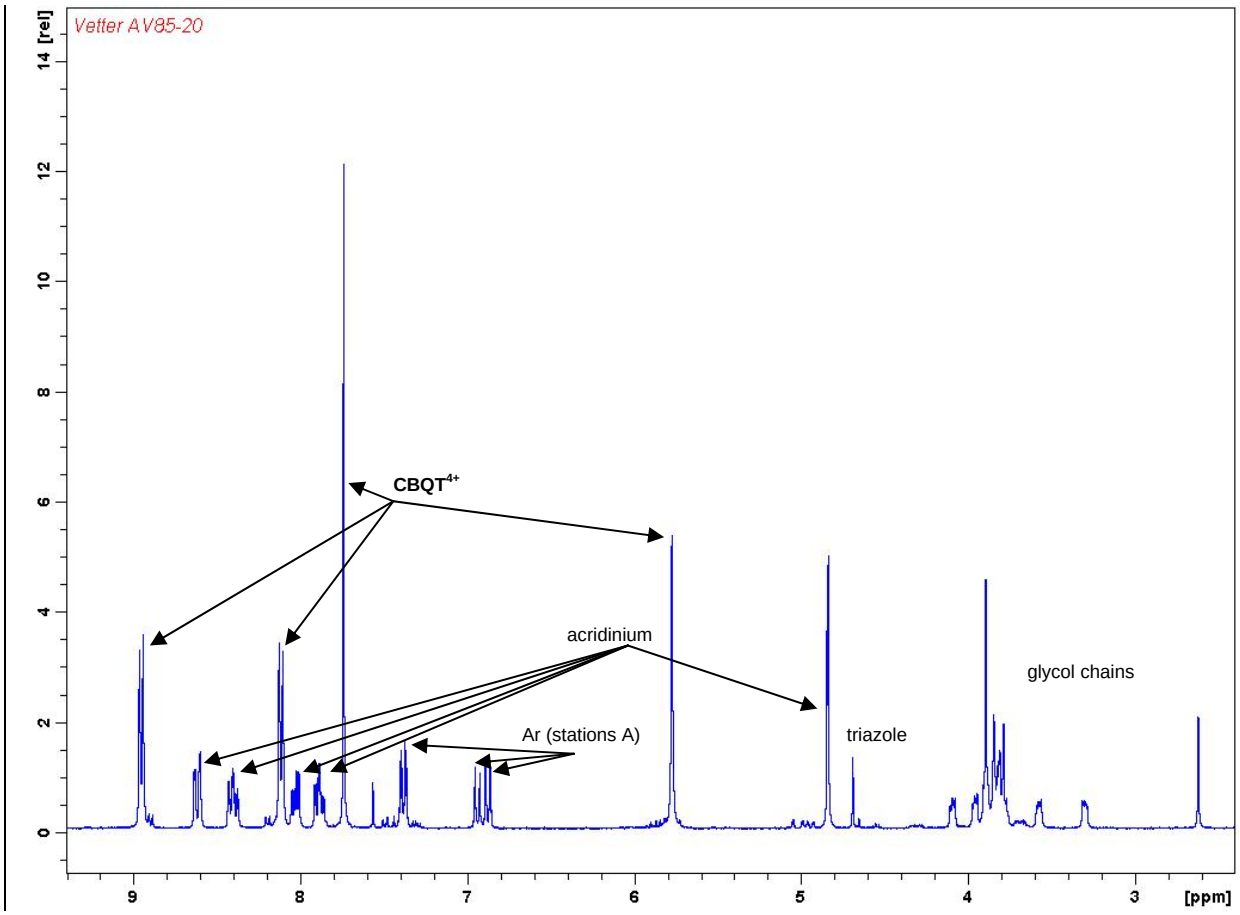
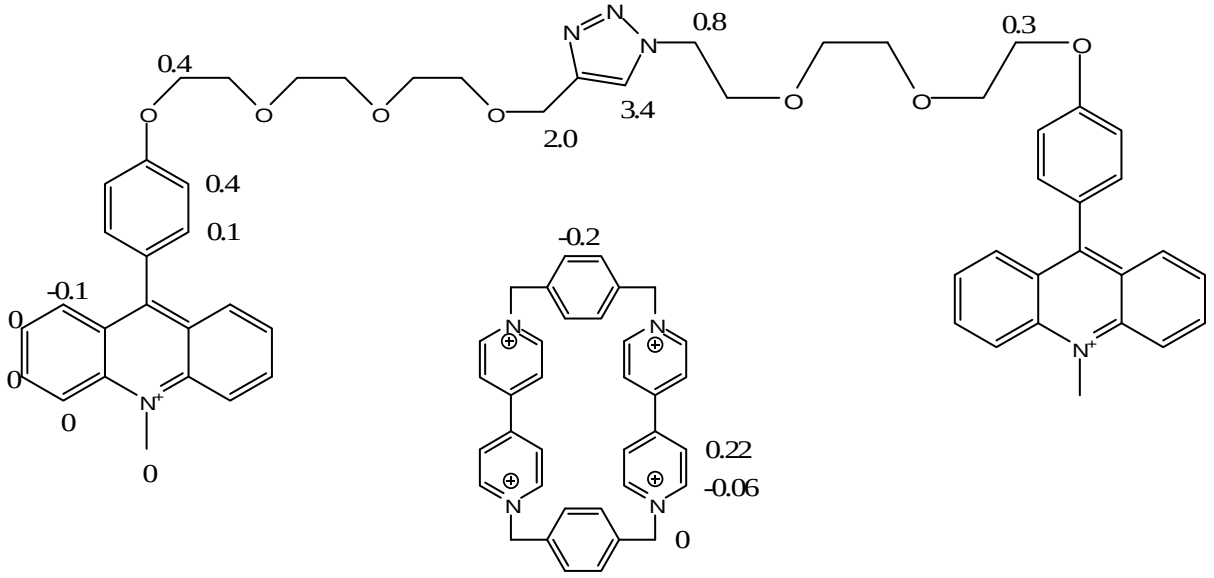


Figure S1 ^{1}H NMR spectrum of rotaxane **10** (CD_3CN) at 298 K



Scheme S9 Chemical shift differences of proton resonances of rotaxane **10** obtained by comparison of the proton resonances of compound **11** with related proton resonances observed in the rotaxane ($\delta_{\mathbf{11}} - \delta_{\text{rotaxane }\mathbf{10}}$).

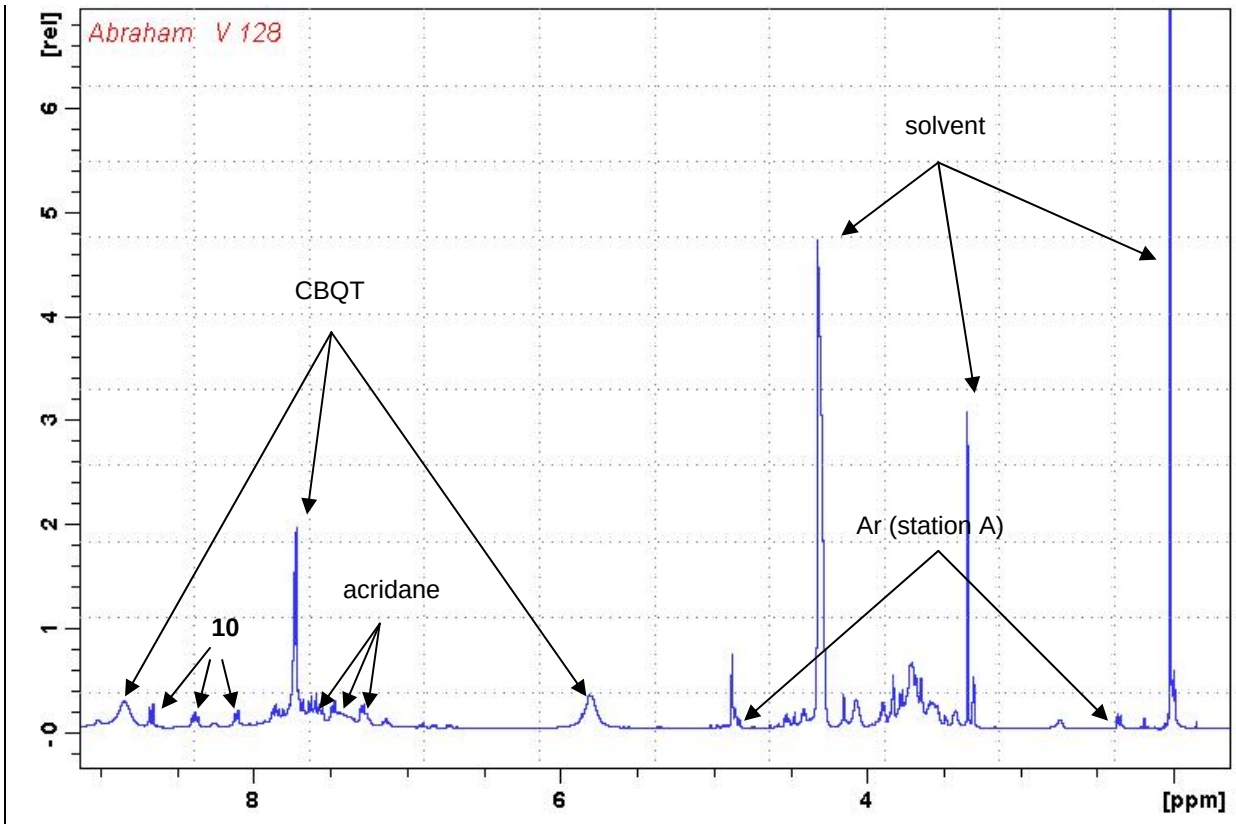


Figure S2 ^{1}H NMR spectrum of rotaxane **12** containing 20 % **10** (CD_3OD/CD_3CN 3:1) at 298 K

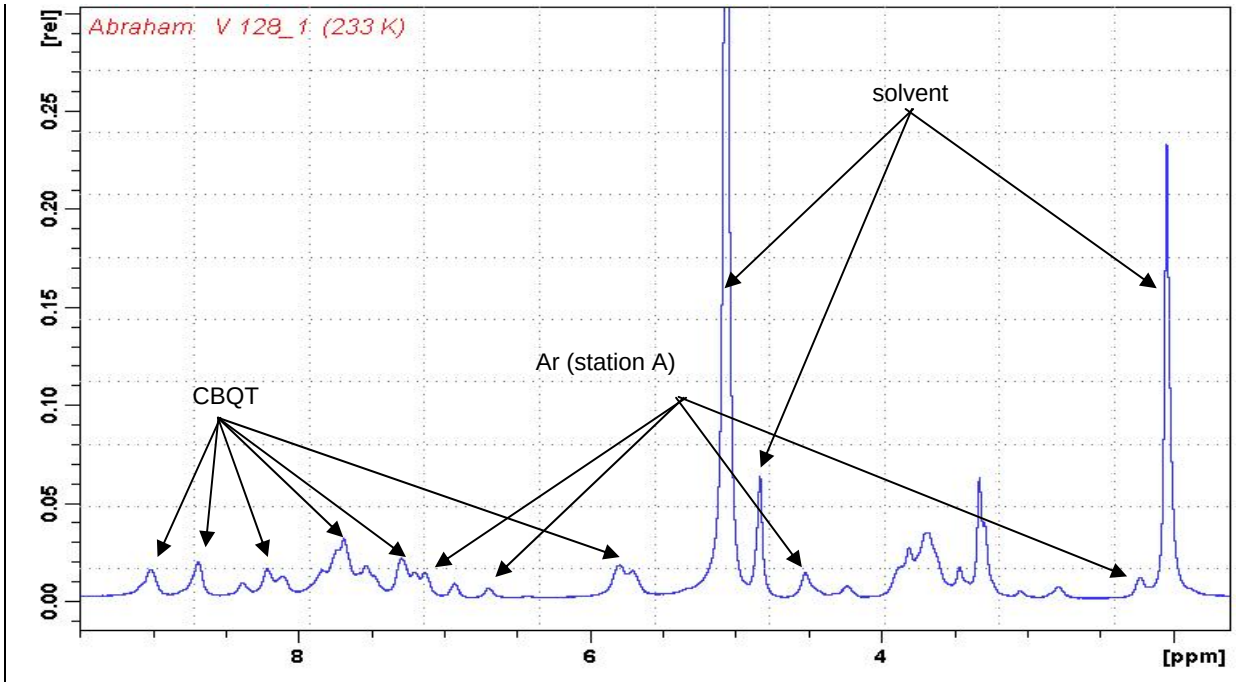
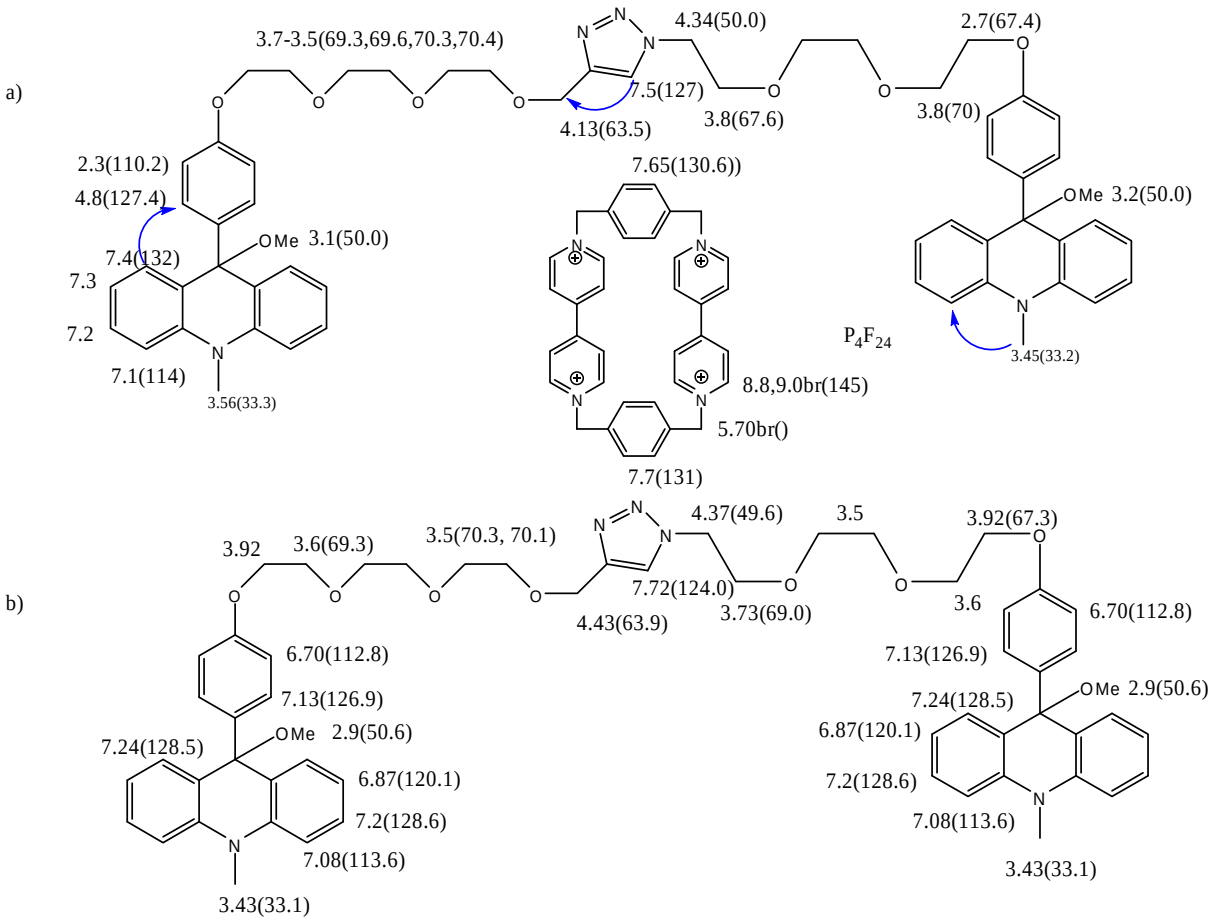


Figure S3 ^{1}H NMR spectrum of rotaxane **12** containing 20 % **10** (CD_3OD/CD_3CN 3:1) at 233 K



Scheme S10 Assignment of proton and (^{13}C) resonances for a) the rotaxane **12** and b) the axle **22** based on two-dimensional NMR-spectroscopy. Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

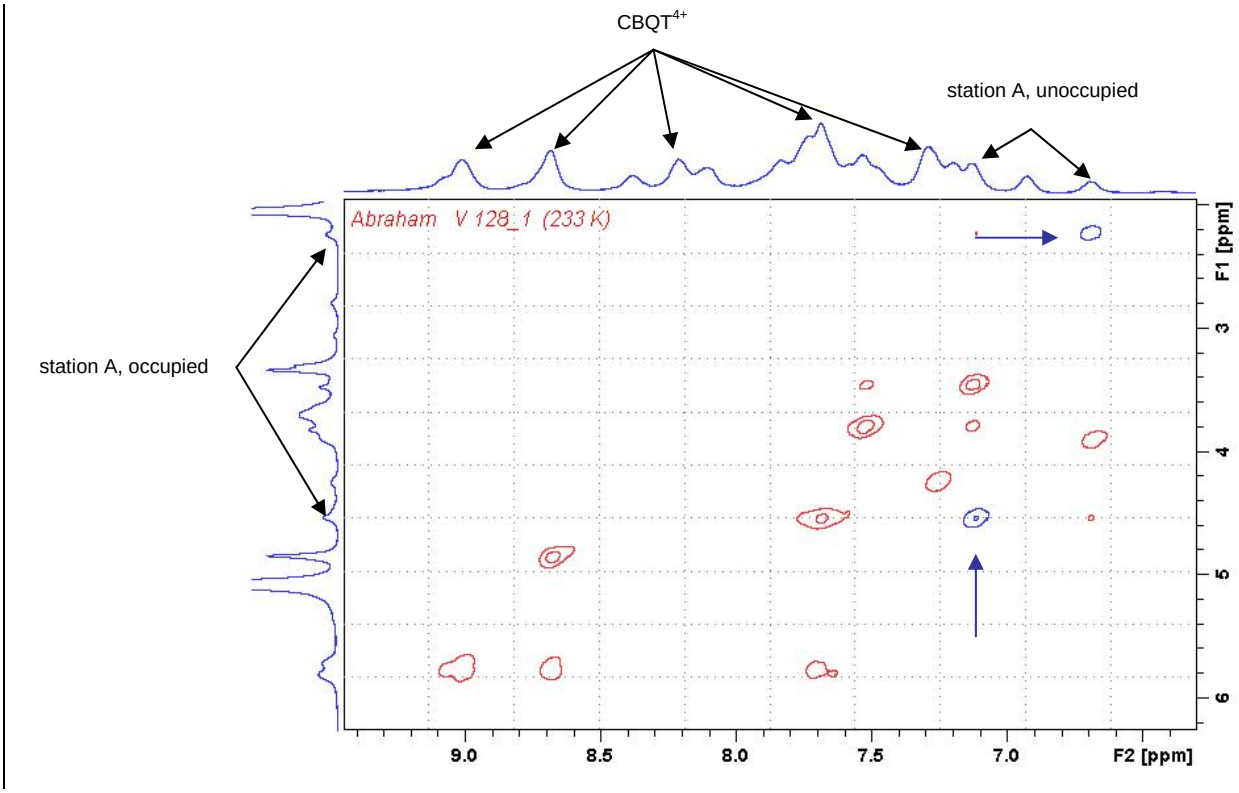
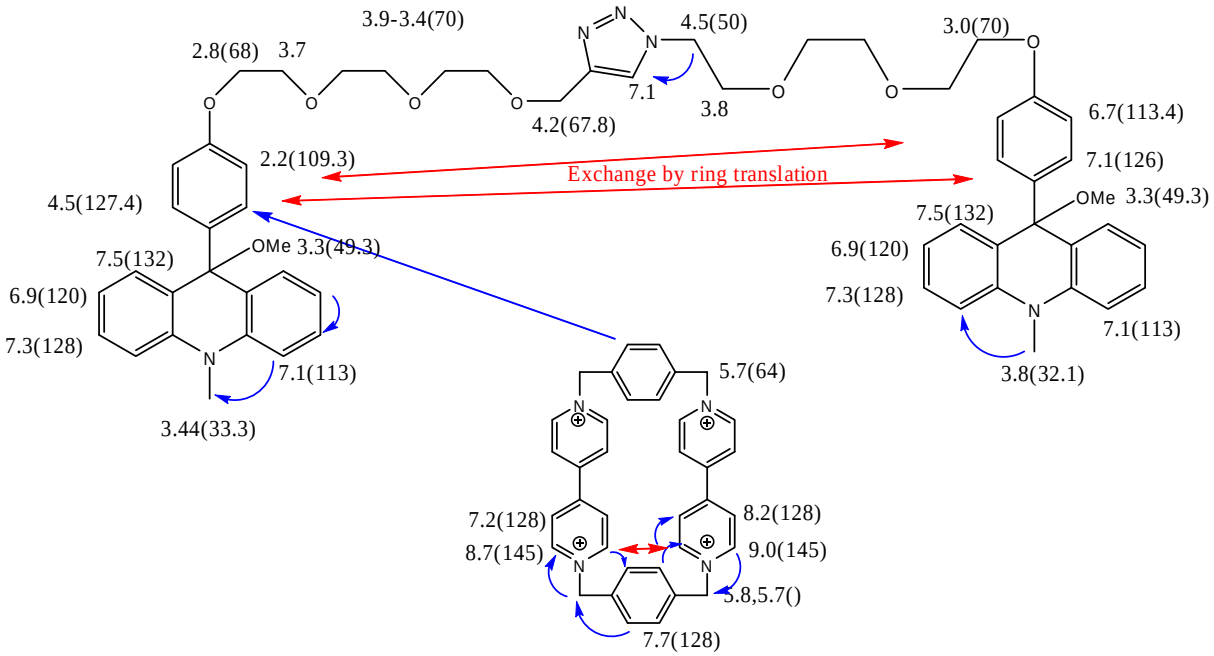
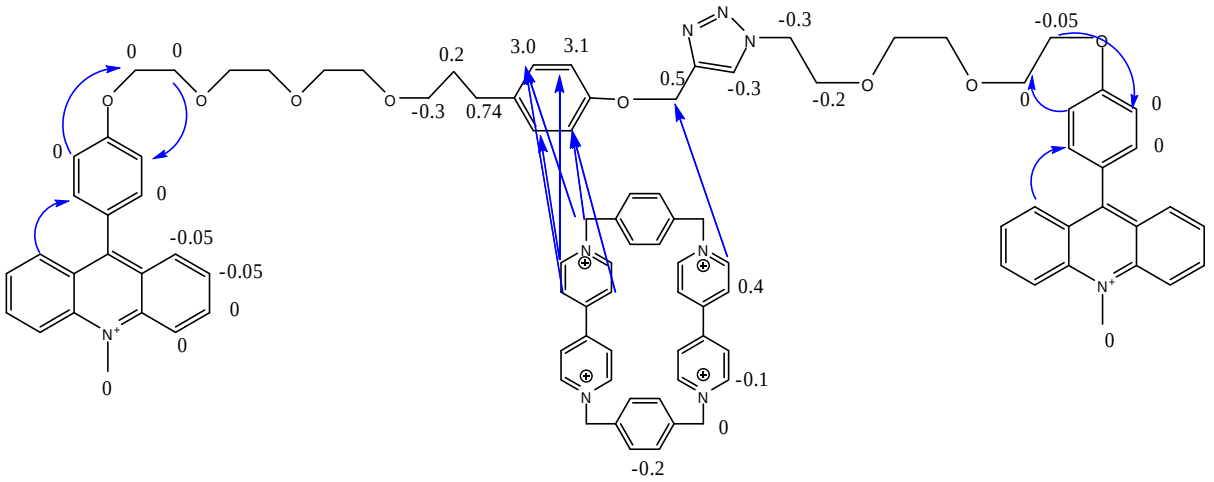


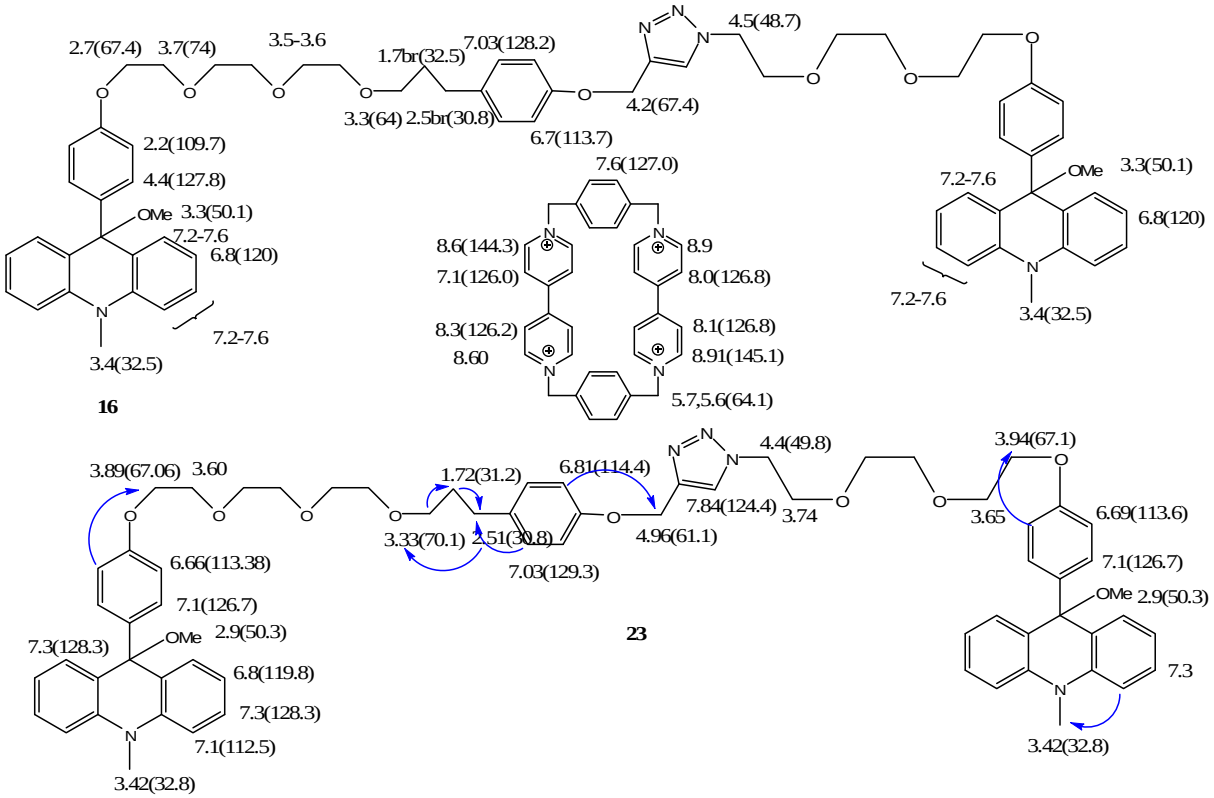
Figure S4 Partial ROESY spectrum of rotaxane **12** at 233 K: red – NOE; blue - exchange cross peaks.



Scheme S11 Assignment of proton and (^{13}C) resonances for the rotaxane **12** in MeOD/CD_3CN (2:1) solution at 233 K. Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra. Red arrows mark exchange peaks observed in the ROESY spectrum at 233 K.



Scheme S12 Chemical shift differences of proton resonances of rotaxane **14** obtained by comparison of the proton resonances of compound **13** with related proton resonances observed in the rotaxane ($\delta_{\mathbf{13}} - \delta_{\text{rotaxane }\mathbf{14}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.



Scheme S13 Assignment of proton and (^{13}C) resonances for rotaxane **16** at 233 K MeOD/CD_3CN 1:1) and the axle **23** (298 K in CD_3CN) based on two-dimensional NMR-spectroscopy. Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

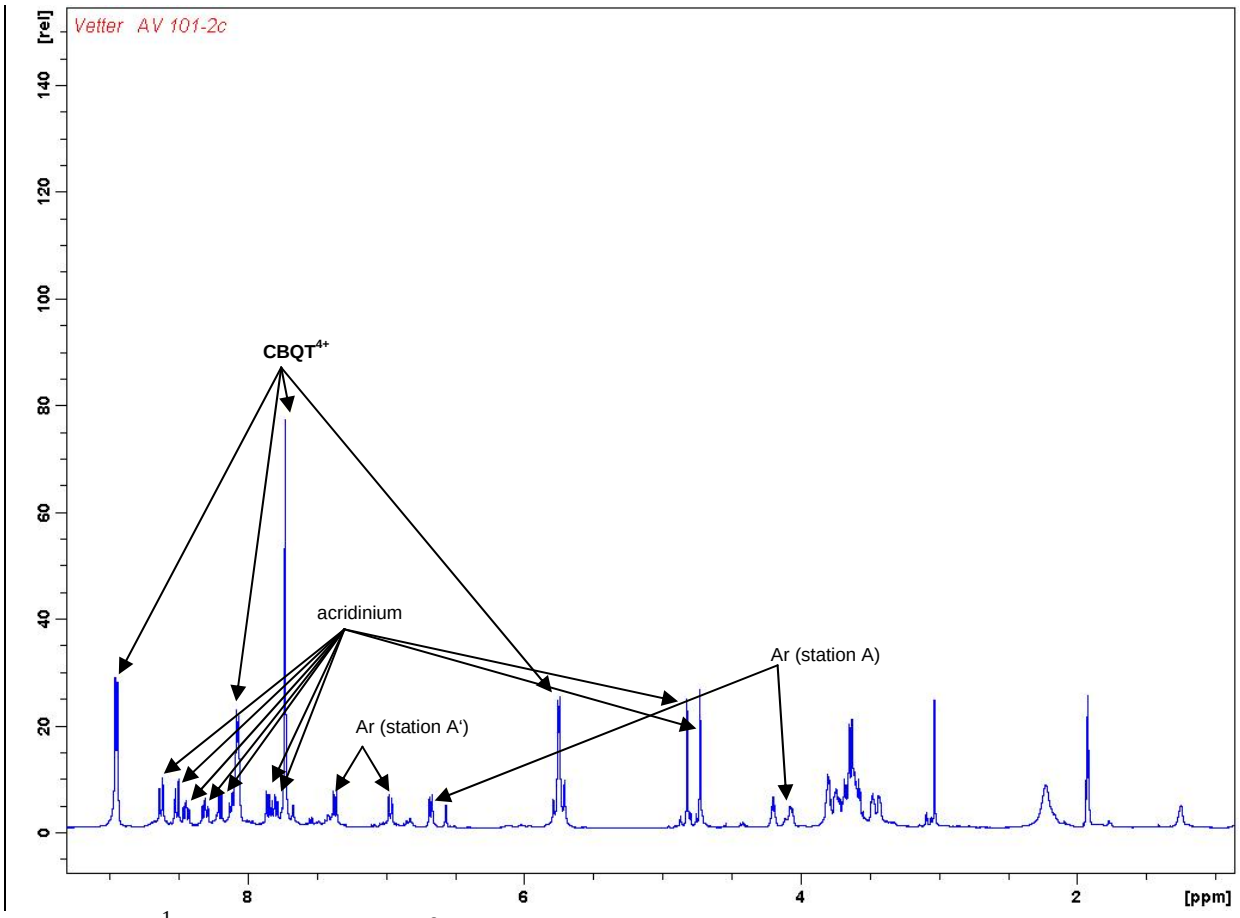
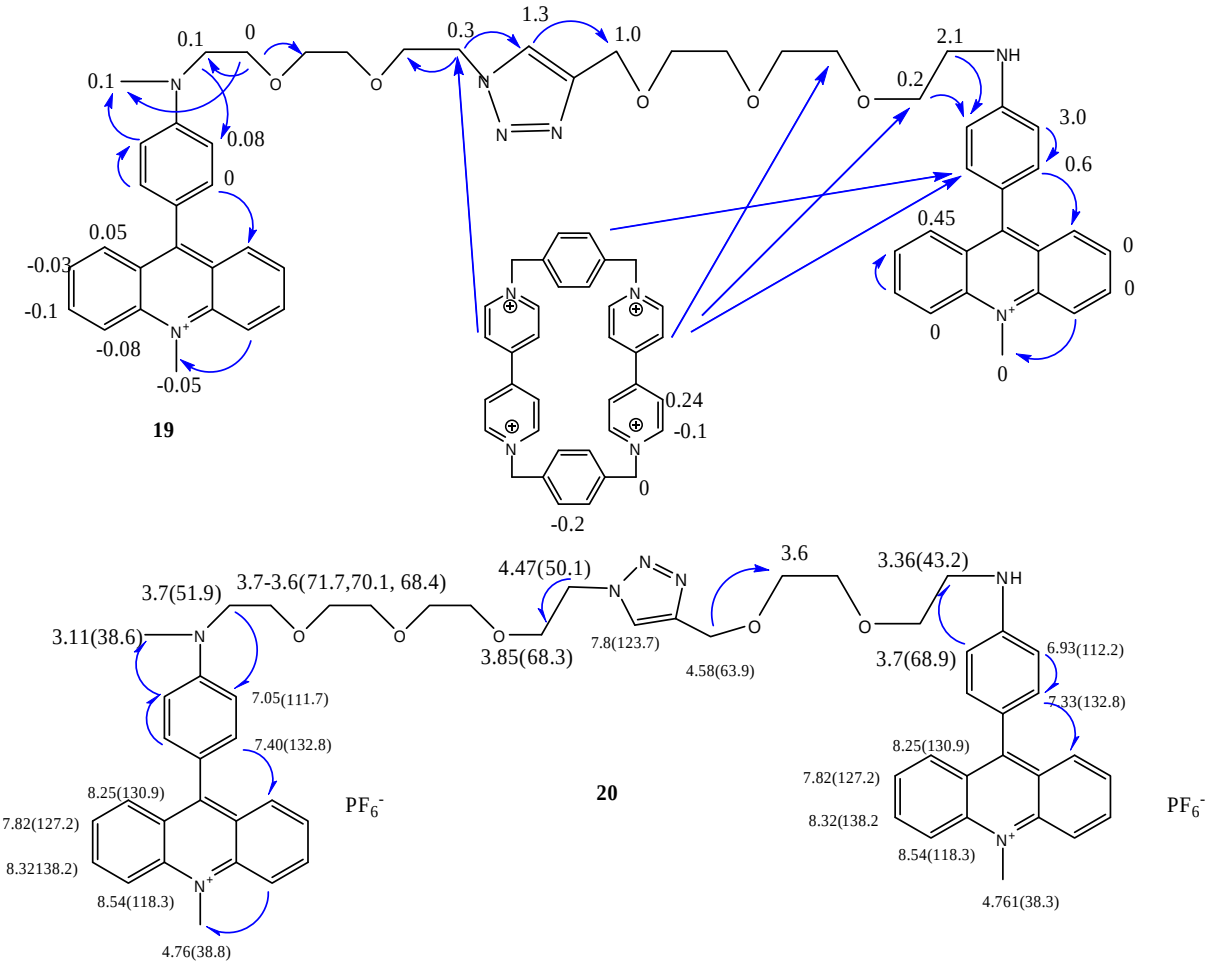


Figure S5 ^{1}H NMR spectrum of rotaxane **19** (CD_3CN) at 298 K



Scheme S14 Chemical shift differences of proton resonances of rotaxane **19** obtained by comparison of the proton resonances of compound **20** with related proton resonances observed in the rotaxane ($\delta_{\mathbf{20}} - \delta_{\text{rotaxane }\mathbf{19}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

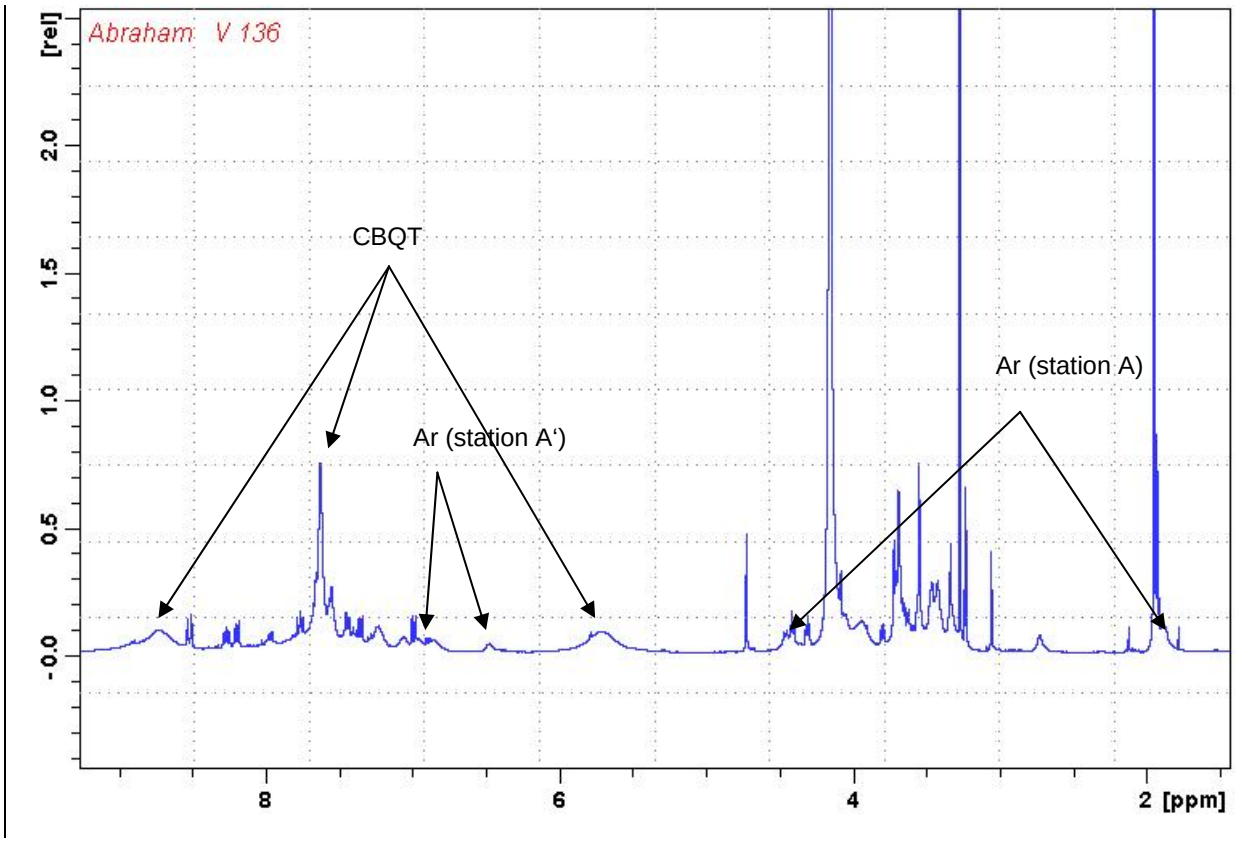
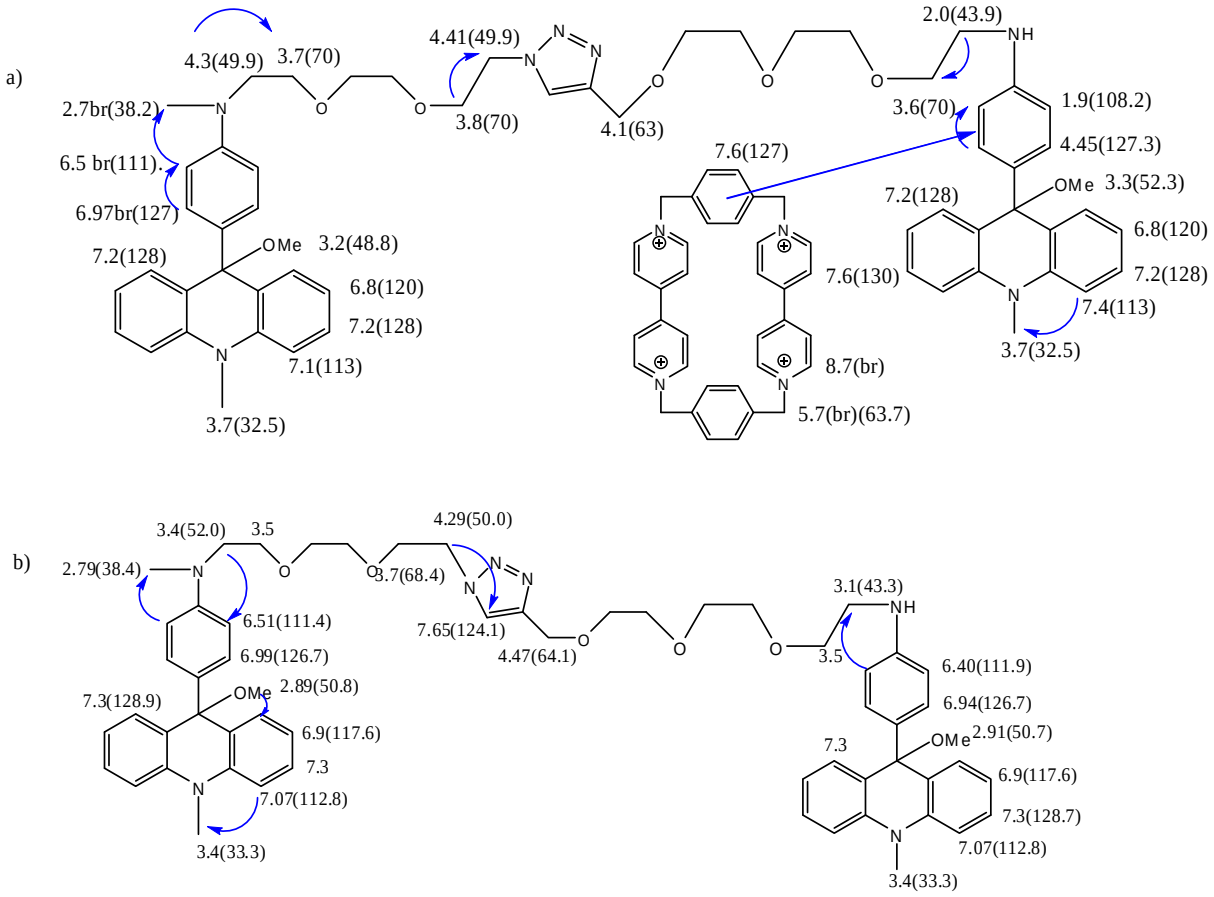
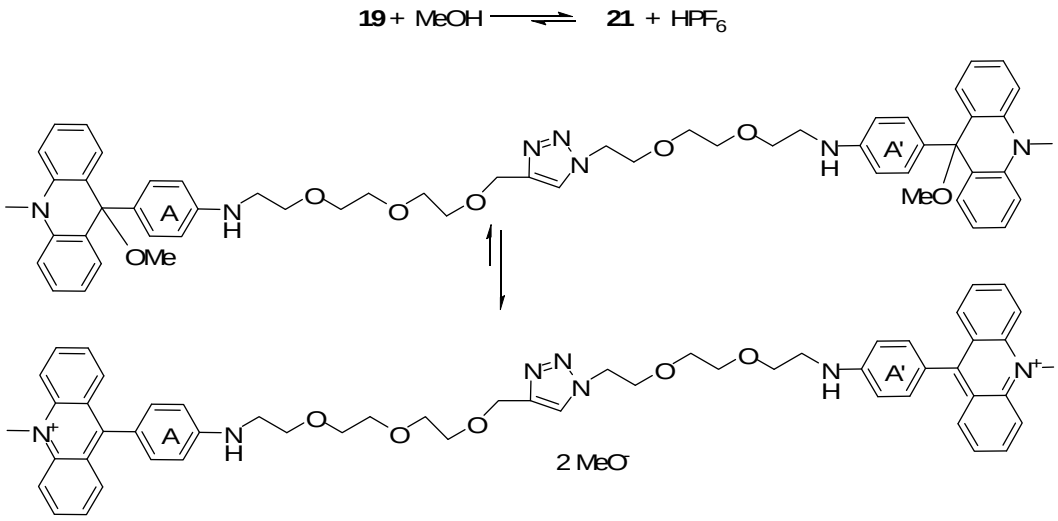


Figure S6 ^{1}H NMR spectrum of rotaxane **21** containing 20 % **19** (CD_3OD/CD_3CN 3:1) at 298 K



Scheme S15 Assignment of proton and (^{13}C) resonances for a) the rotaxane **21** and b) the axle **24** based on two-dimensional NMR-spectroscopy. Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.



Scheme S16 Equilibrium between acridinium and acridane moieties of rotaxane **19** and the axle **24**

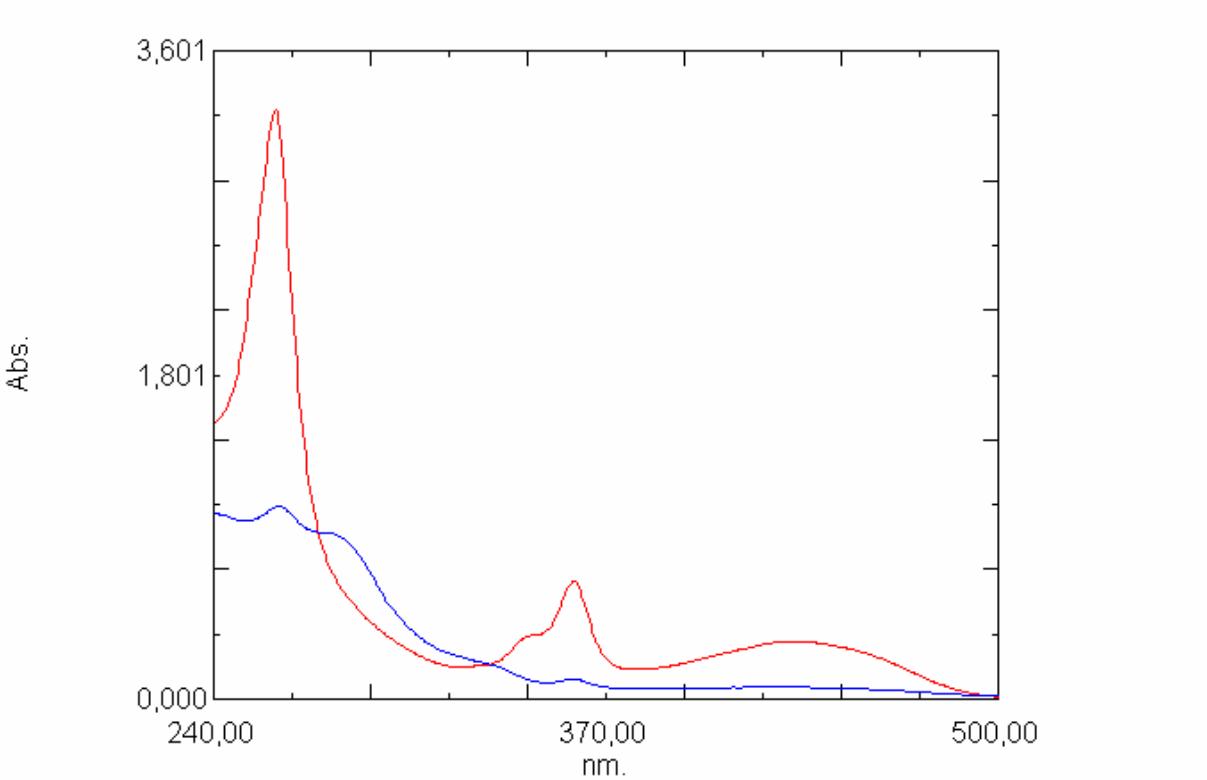


Figure S7 UV-Vis-spectra of rotaxanes **10** (red) and **12** (blue) (2.38×10^{-5} M in acetonitrile solution)

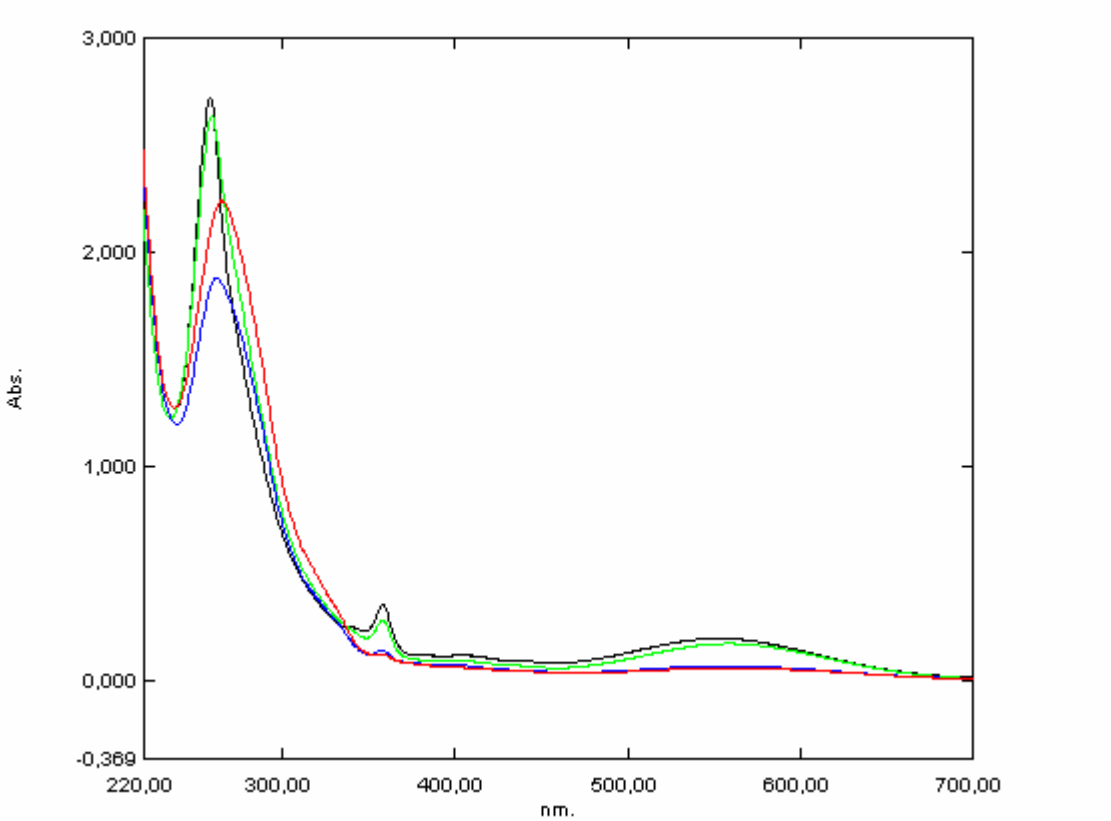


Figure S8 UV/Vis spectra (MeOH, 3.2×10^{-5} M) of **21**: red; after addition of 1 equiv of $HClO_4$: black; after addition of 5 x 5 equiv of ethyl-di-*i*-propylamine: blue; after addition of 5 x 1 equiv of $HClO_4$: green.

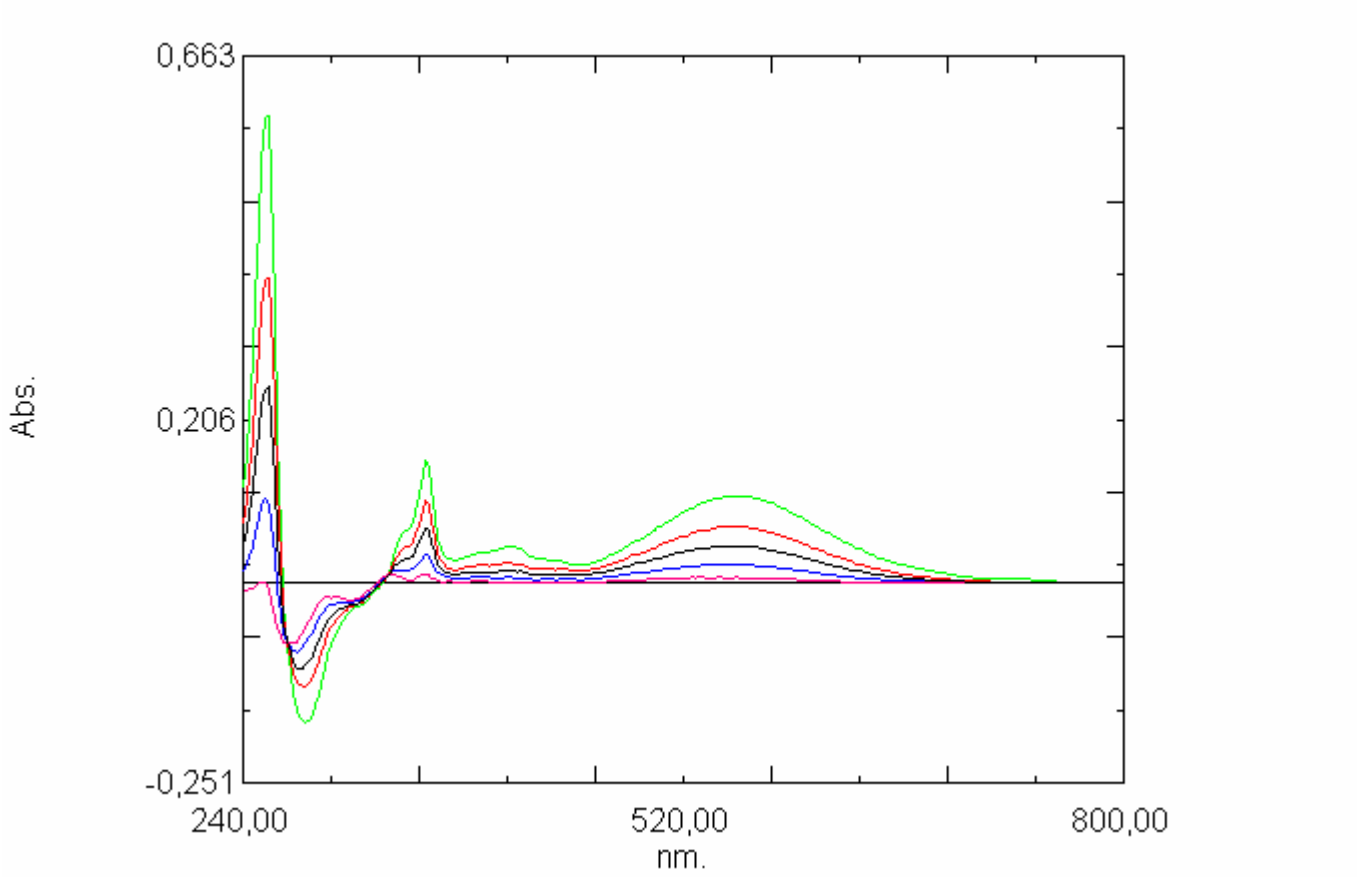


Figure S9 Transient UV-Vis-spectra recorded after excitation of the rotaxane **21** (2.60×10^{-5}M in acetonitrile/MeOH 4:1) obtained in situ from the rotaxane **19** by addition of diisopropylethylamine): green – immediately measured; red – 2 min. delay; black – 4 min. delay; blue – 8 min. delay; pink – 15 min. delay.

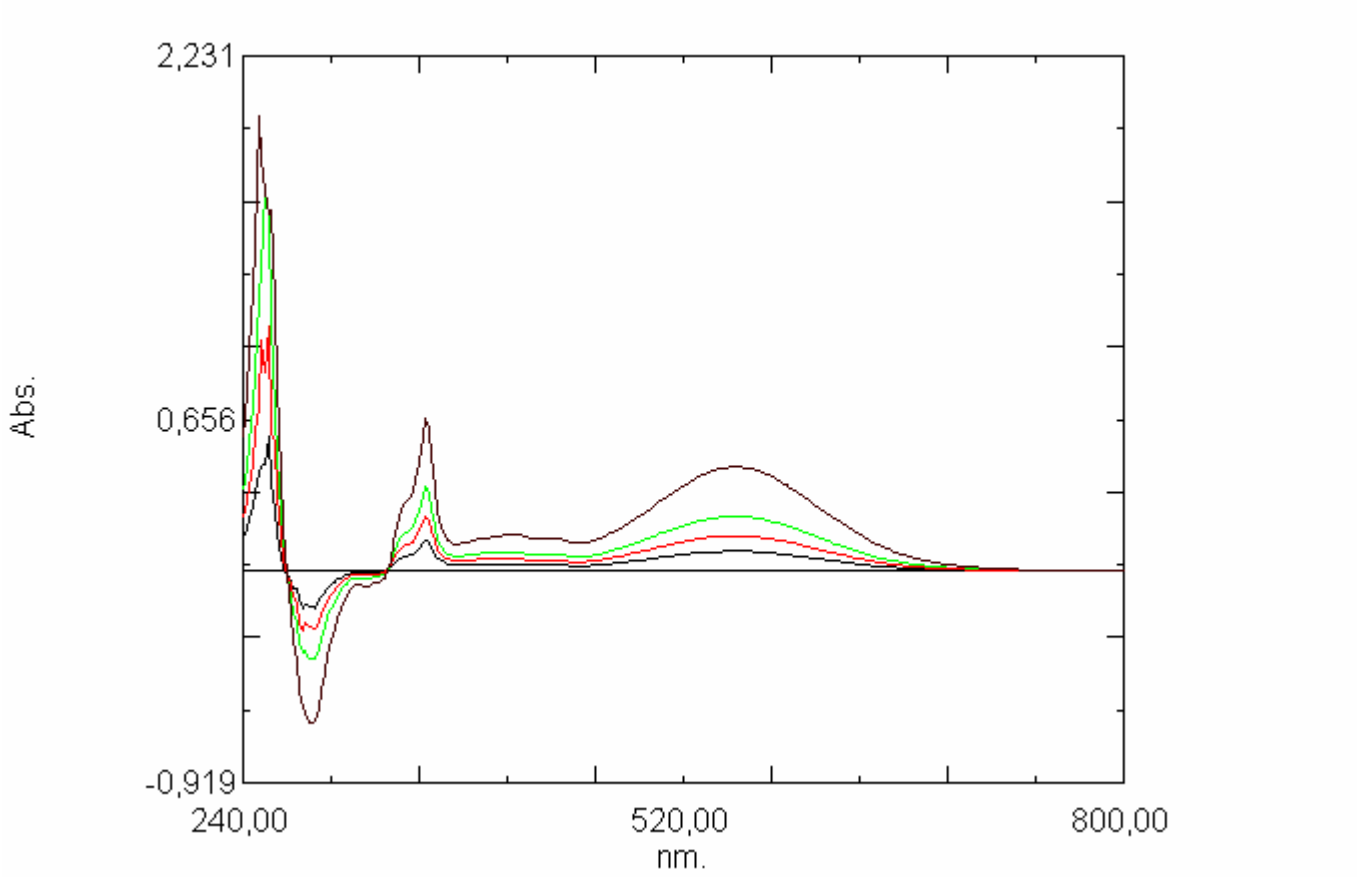


Figure S10 Transient UV-Vis-spectra recorded after excitation of the molecular axle **24** (2.1×10^{-5}M in acetonitrile/MeOH 4:1: black – immediately measured; green – 3 min. delay; red – 6 min. delay; black – 12 min delay.

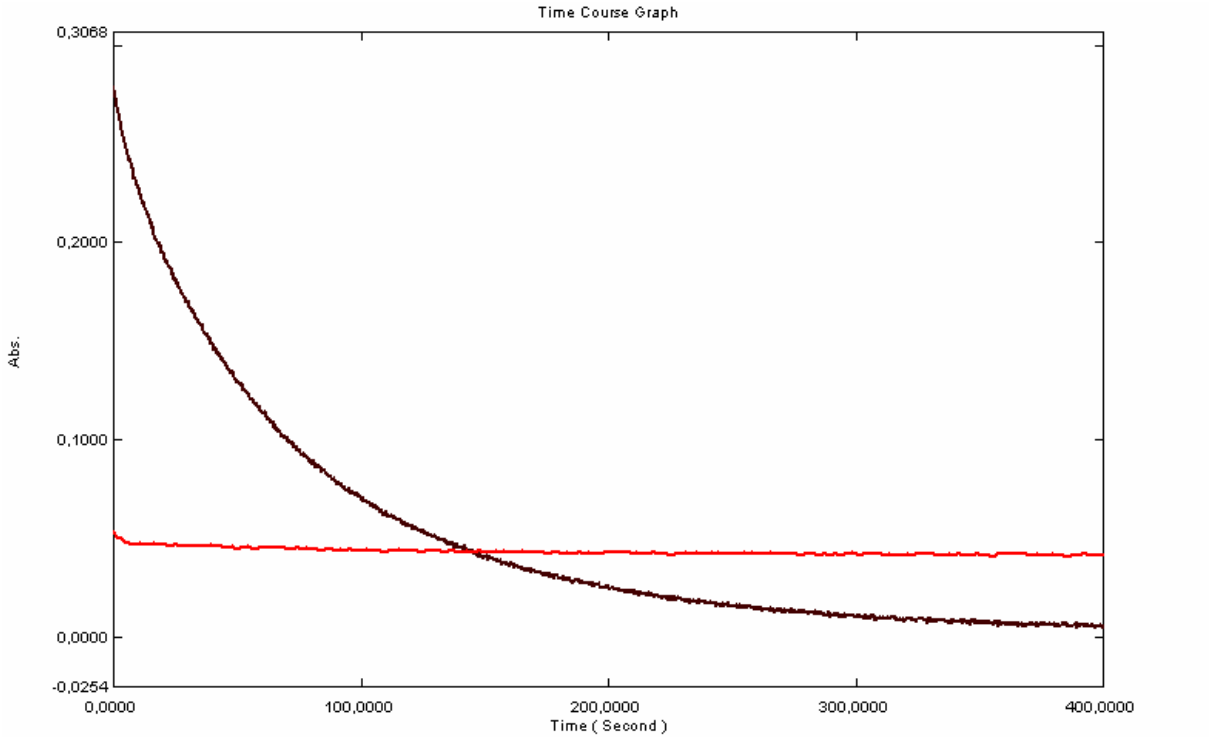
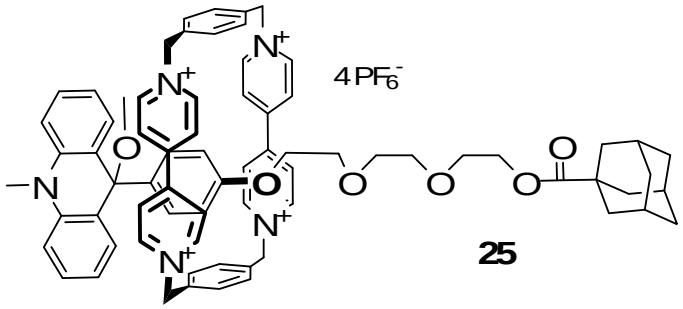


Figure S11 Transient absorbance at 360 nm recorded after photoexcitation of rotaxane **12** ($5x10^{-5}$ M, MeOH solution) (black) and the one-station rotaxane **25**[1] ($6x10^{-5}$M, MeOH solution) (red).



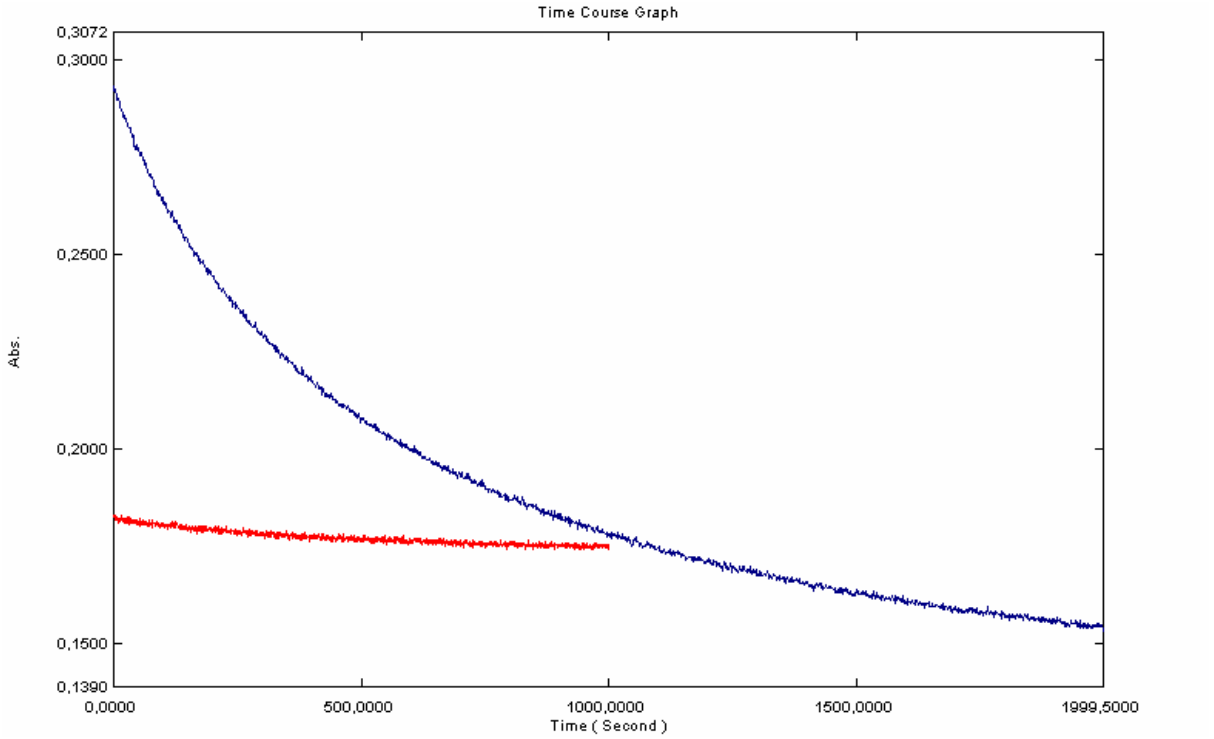
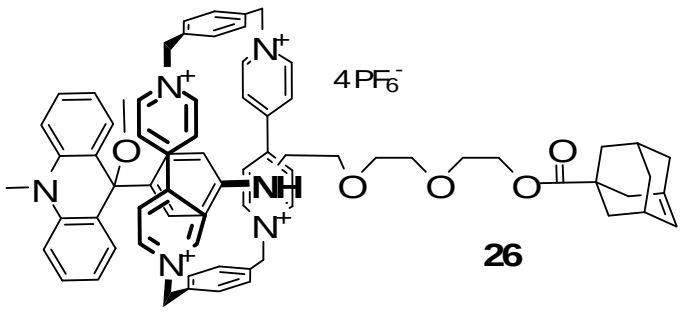


Figure S12 Transient absorbance at 360 nm recorded after photoexcitation of rotaxane **21** ($3x10^{-5}$ M, MeOH solution) (blue) and the one-station rotaxane **26**[1] ($5x10^{-5}$M, MeOH solution) (red).



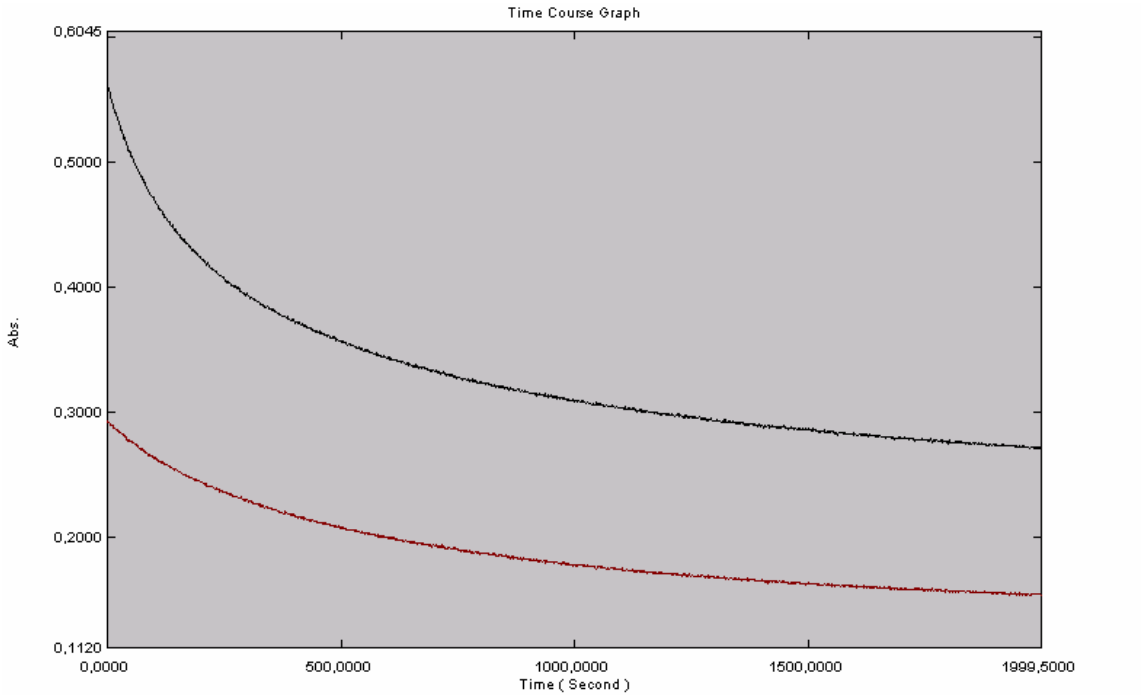


Figure S13 Transient absorbance observed after photoexcitation 313 nm) of the rotaxane **12** ($3.0x10^{-5}$M) (red) and the molecular axle **22** ($2.92x10^{-5}$M) (black) in acetonitrile/MeOH 4:1 with identic absorbance at 324 nm.

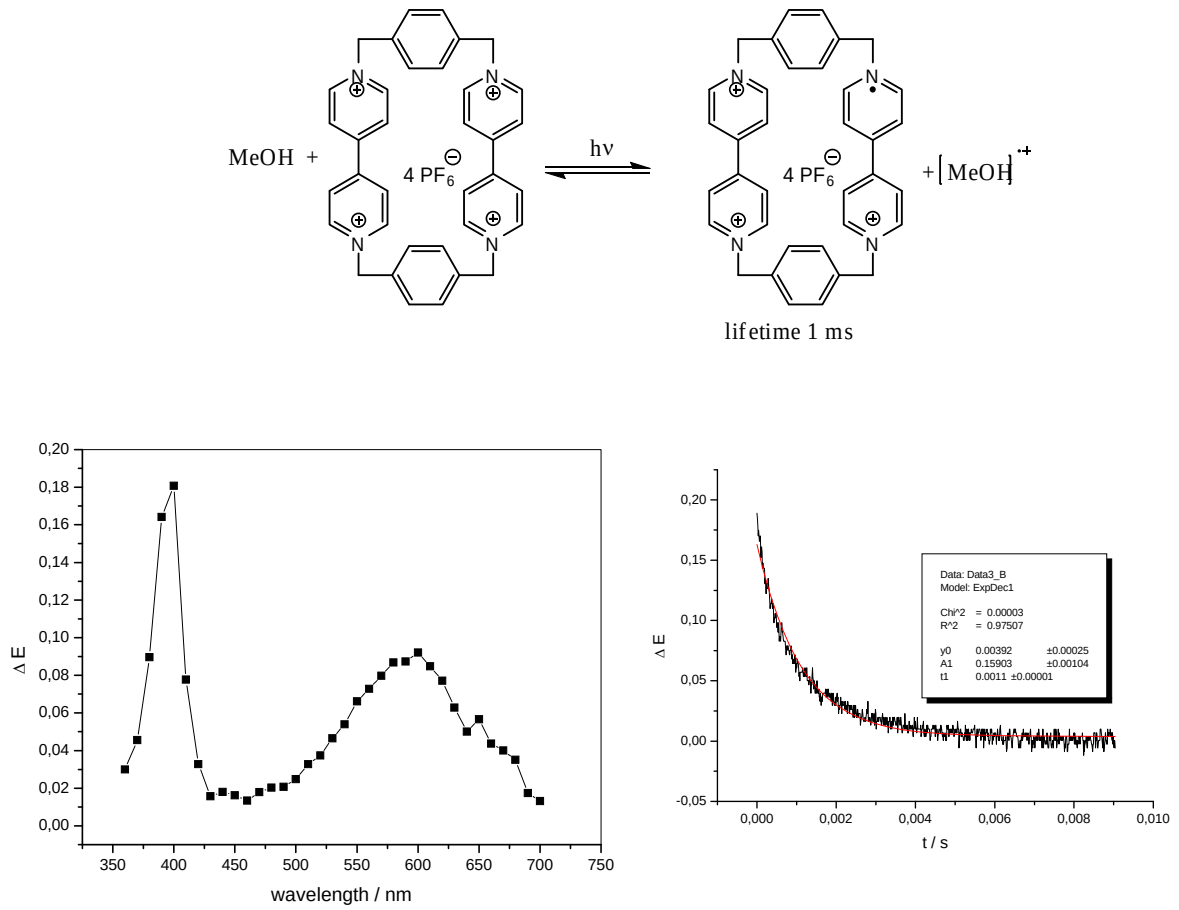


Figure S14 Transient UV-Vis-spectrum recorded after photoexcitation of **CBQT^{4+}** in methanol solution.

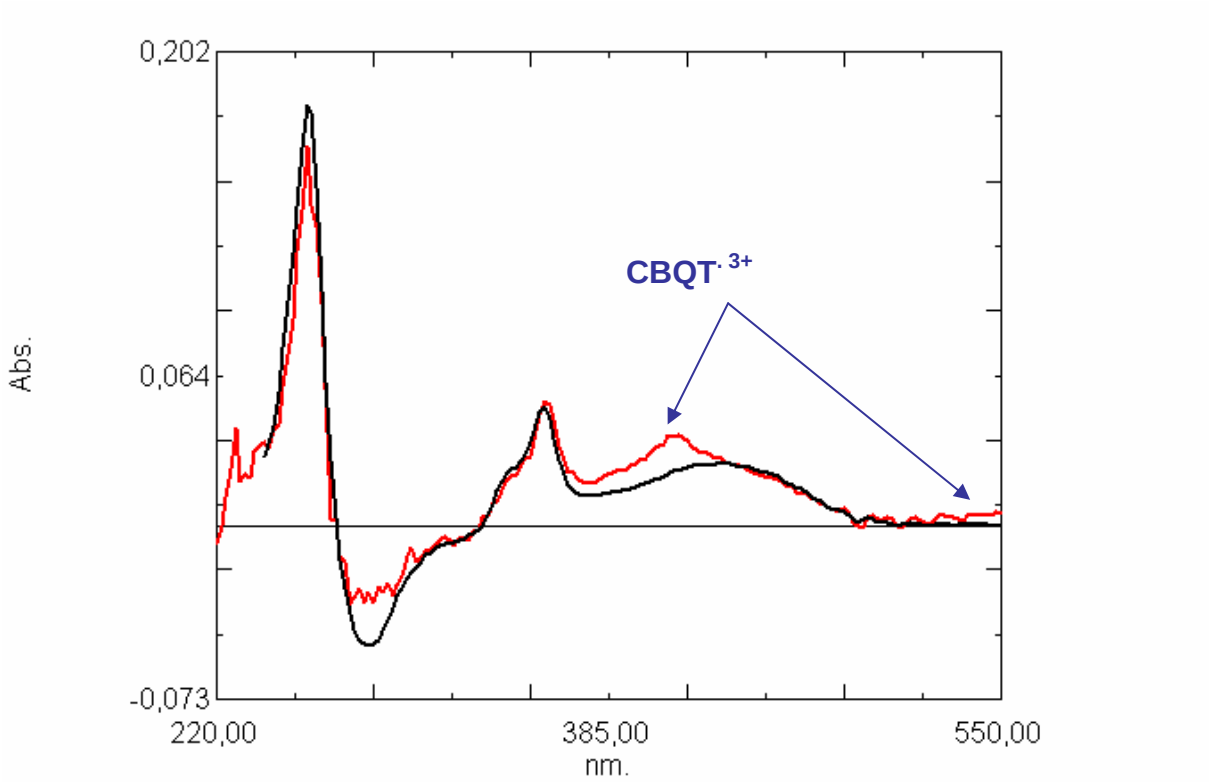
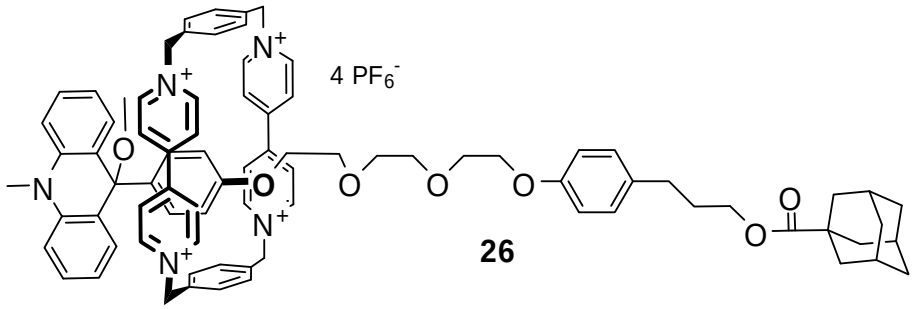


Figure S15 Transient UV-Vis spectra of rotaxane **12** (black) and the rotaxane **26**[3] (red, x 3) recorded after photoexcitation in acetonitrile/methanol 4:1.



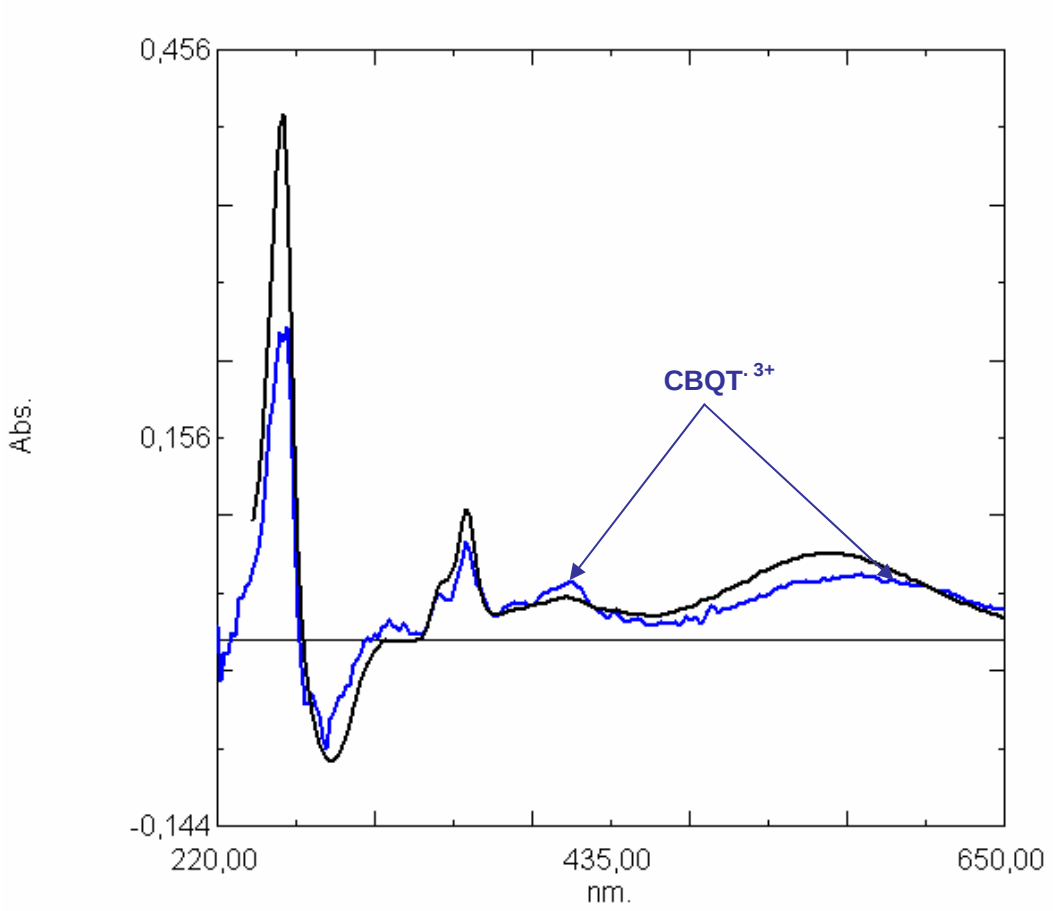
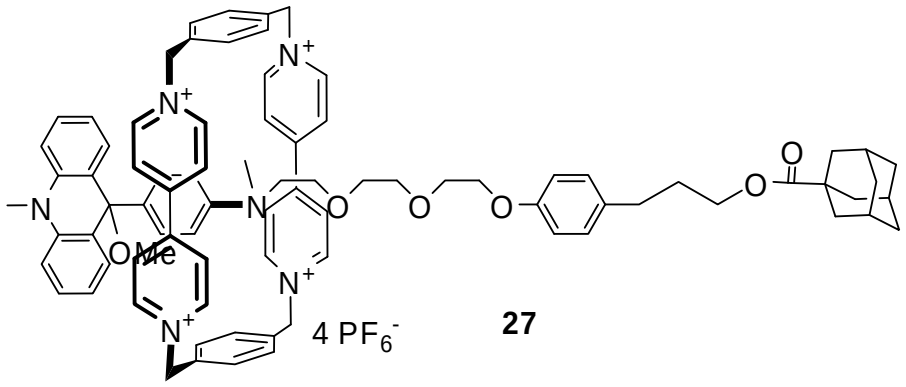


Figure S16 Transient UV-Vis spectra of rotaxane **21** (black) and the rotaxane **27**[1] (blue, x 5) recorded after photoexcitation in acetonitrile/methanol 4:1.



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[2] G. Lu, S. Lam, K. Burgess, *Chem Commun.*, **2006**, 1652.

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[4] R. Janik, S. Kucharski, A. Kubaiska, B. Lyko, *Pol. J. Chem.*, **2001**, 75, 241.