Supporting Information

Photoswitchable Rotaxanes Using the Photolysis of Alkoxy acridanes

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Full synthetic details pertaining to the preparations of new compounds**.**
UV-vis and NMR spectra of selected compounds and transients; Table 1: absorptions maxima of rotaxanes and molecular axles observed in different solvents,
Assignment of protons of rotaxanes **31**, **34** – **36**, **39**, **40** and **43**,
Transient decay curve of compound **4**,
Fluorescence spectrum of rotaxane **29**,

9-Methoxy-9-(4-N,N-dimethylaminophenyl)-10-methyl-9,10-dihydroacridine (**4**): MeOH (1 ml) and K_2CO_3 (0.1 g) were added to a solution of **5**[1] (0.1 g, 0.22 mmol as hexafluorophosphate) in MeCN (10 ml). The blue suspension was stirred for 15 min at room temperature. The yellowish suspension was filtrated and the solvents were removed. The residue was treated with chloroform in order to remove the residual K_2CO_3 by filtration. After removing of the solvent compound **4** results as colorless crystals (0.05 g, 66 %), m.p.162 ^oC Lit[2] 170 ^oC.

^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 2.80 (s, 6 H; NCH_3), 2.92 (s, 3 H; OCH_3), 3.47 (s, 3 H; NCH_3), 6.57 (d, *J*(H,H)=9.0 Hz, 2 H; Ar), 6.90 (m, 2 H; acridane, H-2,7), 7.02 (d, *J*(H,H)=9.0 Hz, 2 H; Ar), 7,11 (dd, *J*(H,H)=1,8.8 Hz, 2 H; acridane, H-4,5), 7.3 (m, 4 H; acridane, H-1,3,6,8).

2-(2-(2-(4-bromophenoxy)ethoxy)ethoxy)ethanol (**6**)

4-Bromo-phenol (4.0 g, 23.12 mmol) and NaOEt (3.14 g, 46.24 mmol) in MeCN solution (200 mL) were stirred for 30 min at room temperature. The solution was heated under reflux and triethylene glycol tosylate (7.04 g, 23.12 mmol) in MeCN (50 ml) was dropped in. Reflux boiling was continued for 5 h. After filtration the solvent was removed under reduced pressure and the remaining mixture was worked up by column chromatography (silica gel, cyclohexane/acetone 4:1). yellowish oil, 1.82 g (26 %).

^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ= 3.58 (m, 2 H; ethyleneoxy), 3.69 (m, 6 H; ethyleneoxy), 3.82 (m, 2 H; ethyleneoxy), 4.06, (m, 2 H; ethyleneoxy), 6.77 (d, *J*(H,H)=9.0 Hz, Ar), 7.34 (d, *J*(H,H)=9.0 Hz, 2 H; Ar). $C_{12}H_{17}BrO_4$ (305.16): calcd. (%): C 47.23, H 5.61, Br 26.18; found (%): C 47.14, H 5.75, Br 25.98.

9-(4-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)phenyl)-10-methylacridinium hexafluorophosphate (**7**)

2-(2-(2-(4-bromophenoxy)ethoxy)ethoxy)ethanol (1.16 g, 3.8 mmol) was dissolved in dry THF (50 mL) under an argon atmosphere. The solution was cooled to -78^{o}C and BuLi (1.6 M in n-hexane, 4.8 mL, 7.6 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 (5 mL) was added to the yellow 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 (150 mL) and

purified by column chromatography (MeCN/NH_4PF_6 in MeCN solution (5 %), 40:1), yellow solid, m.p.185 ^oC, 0.7 g (33 %).^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 2.6 (br, 1 H; OH), 3.5 (m, 2 H; ethyleneoxy), 3.6 (m, 2 H; ethyleneoxy), 3.64 (m, 2 H; ethyleneoxy), 3.7 (m, 2 H; ethyleneoxy), 3.9 (m, 2 H; ethyleneoxy), 4.3 (m, 2 H; ethyleneoxy), 4.80 (s, 3 H; NMe), 7.28 (d, *J*(H,H)=8.9 Hz, 2 H; Ar), 7.46 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7,84 (m, 2 H; acridinium, H-2,7), 8.12 (d, *J*(H,H)=8.8 Hz, 2 H; acridinium, H-1,8), 8.36 (m, 2 H; acridinium, H-3,6), 8.57 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5). $C_{26}H_{28}F_6NO_4P$ (563.23): calcd. (%): C 55.40, H 5.01, N 2.49; found (%): C 55.70, H 5.20, N 2.66.

1-bromo-4-(2-(2-(2-(3-(4-((2-methoxyethoxy)methoxy)phenyl)propoxy)
ethoxy)ethoxy)ethoxy)benzene (**8**)

a) 2-(2-(2-(4-bromophenoxy)ethoxy)ethoxy)ethyl tosylate

Triethyleneglykol bistosylate (45.1 g, 89.45 mmol) and 4-bromophenol (4.25 g, 24.61 mmol) dissolved in MeCN (300 mL) were treated with NaOEt (3.35 g, 49.23 mmol). The mixture was boiled under reflux for 5 h. The precipitate was filtered off and the solvent was evaporated. The residue was dissolved in acetone (25 mL). Diethylether (600 mL) was added in order to precipitate the excess of the triethylene glykol bistosylate. After evaporation of the solvent the residue was purified by column chromatography (cyclohexane/acetone (8:1), oil (8.9 g, 76 %). $C_{19}H_{23}BrO_6$ (459.04) calcd. (%): C 49.68, H 5.04, Br 17.39; found (%) C 49.81, H 5.20, Br 17.04. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H; Me), 3.6-3.8 (m, 6 H; ethyleneoxy), 3.8 (m, 2 H; ethyleneoxy), 4.1 (m, 2 H; ethyleneoxy), 4.2 (m, 2 H; ethyleneoxy), 6.80 (d, *J*(H,H)=9.1 Hz, 2 H; Ar), 7.5 (m, 4 H; Ar), 8.80 (d, *J*(H,H)=8.4 Hz, 2 H; Ar).

b) 3-(4-((2-methoxyethoxy)methoxy)phenyl)propan-1-ol

A dichloromethane solution (25 mL) of 4-(3-hydroxypropyl)phenol (3 g, 19.71 mmol) and di-*i*-propylethylamine (5.1 g, 39.42 mmol) was cooled down to -5 ^oC. A dichloromethane solution (25 mL) of 1-chloro-2-(2-methoxyethoxy)ethane (2.45 g, 19.71 mmol) was given to this solution within 2 h. The solution was warmed up to room temperature. The dichloromethane solution was extracted with water (2x50 mL) and 2n NaCl (50 mL). The organic phase was dried (Na_2SO_4). The solvent was removed and the remaining mixture was separated by column chromatography (cyclohexane/acetone 4:1). The first fractions contained the doubly protected product, the desired product was present in the second fraction; oil (1.16 g, 25 %). ^{1}H-NMR (400 MHz, CD_3CN): δ = 1.7 (s, br, 1 H; OH), 1.84 (m, 2 H; CH_2), 2.62 (m, 2 H; CH_2), 3.38 (s, 3 H; OMe), 3.54 (m, 2 H; ethyleneoxy), 3.62 (t, br, 2 H; CH_2OH),

3.90 (m, 2 H; ethyleneoxy), 5.22 (s, 2 H; OCH_2O), 6.95 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.08 (d, *J*(H,H)=8.8 Hz, 2 H; Ar). $C_{13}H_{20}O_4$ (240.29) calcd. (%): C 64.98, H 8.39; found (%): C 65.02, H 8.41.

c) 2-(2-(2-(4-bromophenoxy)ethoxy)ethoxy)ethyl tosylate (3.05 g, 6.67 mmol) dissolved in DMSO (20 mL) was given to a hot DMSO-solution of 3-(4-((2-methoxyethoxy)methoxy)phenyl)propan-1-ol (1.39 g, 5.79 mmol) and NaOEt (0.98 g, 14.98 mmol). The solution was stirred for 1 h at 90 ^oC. DMSO was removed in vacuo. The residue was treated with water and extracted with dichloromethane. The dichloromethane phase was dried and evaporated. The crude product was purified by column chromatography (cyclohexane/acetone 8:1 and 4:1) to give **8** as an oil (1.67 g, 55 %). ^1H-NMR (400 MHz, $CDCl_3$): δ = 1.84 (m, 2 H; CH_2), 2.60 (t, *J*(H,H)=7.7 Hz , 2 H; CH_2), 3.35 (s, 3 H; OMe), 3.43 (t, *J*(H,H)=6.5 Hz , 2 H; OCH_2), 3.5 (m, 4 H; ethyleneoxy), 3.6 - 3.7 (m, 4 H; ethyleneoxy), 3.8 (m, 6 H; ethyleneoxy), 4.1 (m, 2 H; ethyleneoxy), 5.22 (s, 2 H; OCH_2O), 6.77 (d, *J*(H,H)=9.1 Hz, 2 H; Ar), 6.94 (d, *J*(H,H)=9.4 Hz, 2 H; Ar), 7.07 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.33 (d, *J*(H,H)=9.0 Hz, 2 H; Ar). $C_{24}H_{33}BrO_7$ (513.42) calcd. (%): C 56.93, H 6.69; found (%): C 56.62, H 6.69.

9-(4-(2-(2-(2-(3-(4-hydroxyphenyl)propoxy)ethoxy)ethoxy)ethoxy)phenyl)-10-methylacridinium hexafluorophosphate (**9**)

N-methylacridinone (0.79 g, 3.76 mmol) dissolved in THF (30 mL) was given within 0.5 h to a cold (-78 ^oC) solution of **8** (1.98 g, 3.76 mmol) and BuLi 2.4 mL, 1.6 n in n-hexane). After warming up to room temperature the solution was stirred for 12 h. Water (4 mL) was added. The filtered solution was evaporated. The remaining oil was purified by column chromatography (1. butanol/acetic acid/water, 5:1:2; 2. MeCN/5% NH_4PF_6 5%, 40:1) to give the de-protected product **9** as yellow solid, m.p. 204-208 ^oC. ^1H-NMR (400 MHz, CD_3CN): δ = 1.7 (m, 2 H; CH_2), 2.52 (m, 2 H; CH_2), 3.43 (m, 2 H; OCH_2), 3.7 (m, 4 H; ethyleneoxy), 3.8 (m, 2 H; ethyleneoxy), 3.9 (m, 2 H; ethyleneoxy), 4.1 (m, 2 H; ethyleneoxy), 4.3 (m, 2 H; ethyleneoxy), 4.79 (s, 3 H; NMe), 6.82 (d, *J*(H,H)=8.7 Hz, 2 H; Ph), 7.05 (d, *J*(H,H)=8.5 Hz, 2 H; Ph), 7.27 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.42 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.85 (m, 2 H; acridinium, H-2,7), 8.10 (dd, *J*(H,H)=1.0, 8.8 Hz, 2 H; acridinium, H-1,8), 8.35 (m, 2 H; acridinium, H-3,6), 8.56 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5), $C_{35}H_{38}F_6NO_5P$ (697.65) calcd. (%): C 60.26, H 5.49, N 2.01; found (%): C 59.99, H 5.87, N 1.86.

2-(2-(2-(phenylamino)ethoxy)ethoxy)ethanol (**11**)

Na_2CO_3 (1.43 g) was added to a mixture of aniline (3.30 g, 35 mmol) and triethylene glykol monotosylate (3.69 g, 12 mmol). The mixture was stirred at 150°C for 3 h. After cooling down water (30 mL) was added. The mixture was extracted with diethylether (3x30 mL). The organic phases were combined, dried ($MgSO_4$); and the solvent was removed in vacuum. The remaining oil was purified by column chromatography (cyclohexane/ethylacetate 1:4) to give **11** as oil (1.66 g, 61%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 3.29 (m, 2 H; ethyleneoxy), 3.59 (m, 2 H; ethyleneoxy), 3.63 – 3.67 (m, 4 H; ethyleneoxy), 3.69 (m, 2 H; ethyleneoxy), 3.73 (m, 2 H; CH_2OH), 6.64 (m, 2 H; Ar), 6.71 (m, 1 H; Ar), 7.18 (m, 2 H; Ar). $C_{13}H_{21}NO_3$ (239.31) calcd. (%): C 63.98, H 8.50, N 6.22; found (%) C 63.79, H 8.32, N 5.99. HRMS (ESI): calcd for $C_{12}H_{20}NO_3$: 226.1438; found: 226.1438 $[M+H^+]^+$.

3-(4-(2-(2-(2-(phenylamino)ethoxy)ethoxy)ethoxy)phenyl)propan-1-ol (**13**)

a) 2-(2-(2-(4-(3-hydroxypropyl)phenoxy)ethoxy)ethoxy)ethyl tosylate

3-(4-Hydroxyphenyl)propanol (2 g, 13.14 mmol) and NaH (in hexane, 60%) (0.58 g, 14.5 mmol) in acetonitrile solution (150 mL) were boiled under reflux for 45 min. Triethylene glykol bistosylate (12 g, 26.2 mmol) was added and the mixture was refluxed for 26 h. The solvent was removed in vacuo. The residue was distributed between water (200 mL) and dichloromethane (200 mL). The aqueous phase was extracted with dichloromethane (2x100 mL). The combined organic phases were dried ($MgSO_4$). The solvent was evaporated. The remaining oil was dissolved in acetone (10 mL) and diethylether (200 mL) was added. Triethylene glycol bistosylate was separated by filtering. The solution was evaporated. The residue was purified by column chromatography (cyclohexane/ethylacetate 2:3); oil (2.6 g (49%). ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 7.78 (d, *J*=8.3, 2 H, Ar); 7.31 (d, *J*=8.0, 2 H; Ar), 7.08 (d, *J*=8.7, 2 H; Ar), 6.81 (d, *J*=8.7, 2 H; Ar), 4.14 (m, 2 H, ethyleneoxy), 4.07 (m, 2 H; ethyleneoxy), 3.79 (m, 2 H; ethyleneoxy); 3.56-3.69 (m, 8 H; ethyleneoxy), 2.62 (m, 2 H; CH_2), 2.41 (s, 3 H), 1.76-.189 (m, 2 H; CH_2). $C_{22}H_{30}O_7S$ (438.53) calcd. (%): C 60.25, H 6.90; found (%): C 60.18, H 7.01.

b) 2-(2-(2-(4-(3-hydroxypropyl)phenoxy)ethoxy)ethoxy)ethyl tosylate (1.71 g, 3.90 mmol) was dissolved together with aniline (2 mL, 22 mmol) and triethylamine (4 mL, 29 mmol) in toluene. The solution was refluxed under argon for 13 d. The solvents were evaporated in vacuo. The residue was distributed between water (40 mL) and dichloromethane (40 mL). The aqueous phase was extracted with dichloromethane (2x 40 mL). The combined organic phases

were dried ($MgSO_4$). After evaporating of the solution the residue was purified by column chromatography (1. dichloromethane/acetone 500:3, 2. dichloromethane/acetone 5:1) to give **13** as oil (0.692 g, 49 %).

^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 1.8 (m, 2 H; CH_2), 2.64 (m, 2 H; benzyl-H), 3.30 (m, 2 H; NCH_2), 3.64 (t, *J*(H,H)=6.5 Hz, 2 H; ethyleneoxy), 3.68 (m, 2 H; ethyleneoxy), 3.70 – 3.76 (m, 4 H; ethyleneoxy), 3.86 (t, *J*(H,H)=5.0 Hz, 2 H; ethyleneoxy), 4.12 (t, *J*(H,H)=5.0 Hz, 2 H; ethyleneoxy), 6.64 (m, 2 H; Ar), 6.72 (d, *J*(H,H)= 7.3 Hz, 2 H, Ar), 6.86 (d, *J*(H,H)= 8.7 Hz, 2 H, Ar), 7.10 (d, *J*(H,H)= 8.6 Hz, 2 H, Ar), 7.17 (m, 2 H, Ar). $C_{21}H_{29}NO_4$ (359.21) calcd. (%): C 70.17, H 8.13, N 3.90; found (%) C 69.89, H 7.77, N 3.62. HRMS (ESI): calcd for $C_{21}H_{30}NO_4$: 360.2169; found: 360.2164 $[M+H^+]^+$.

3-(4-(2-(2-(2-(methyl(phenyl)amino)ethoxy)ethoxy)ethoxy)phenyl)propan-1-ol (**14**)

To 2-(2-(2-(4-(3-hydroxypropyl)phenoxy)ethoxy)ethoxy)ethyl tosylate (1.47 g, 3.36 mmol) and N-methylaniline (1.47 g, 13.72 mmol) dissolved in acetonitrile (30 mL) K_2CO_3 (1.57 g, 3.38 equ.) was added. The reaction mixture was refluxed under an argon atmosphere for 2 d. After stirring for 17 d at room temperature the solvent was removed. The residue was treated with water (30 mL) and diethylether 30 mL). The aqueous phase was extracted with diethylether (4x30 mL). The combined organic phases were dried ($MgSO_4$). The solvent was removed. The residue was purified by column chromatography (dichloromethane/acetone 20:1). Oil (0.81 g, 64%, ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 1.8 (m, 2 H; CH_2), 2.65 (m, 2 H; benzyl-H), 2.98 (s, 3 H; NMe), 3.55 (m, 2 H; ethyleneoxy), 3.61 – 3.73 (m, 8 H; ethyleneoxy), 3.84 (m, 2 H; ethyleneoxy), 4.09 (t, *J*(H,H)=4.9 Hz, 2 H; ethyleneoxy), 6.66 – 6.74 (m, 3 H; Ar), 6.68 (t, *J*(H,H)= 7.2 Hz, 2 H; Ar), 6.72 (d, *J*(H,H)= 8.8 Hz, 2 H; Ar), 6.85 (d, *J*(H,H)= 8.7 Hz, 2 H; Ar), 7.11 (d, *J*(H,H)= 8.7 Hz; 2 H, Ar), 7.23 (m, 2 H; Ar). $C_{22}H_{31}NO_4$ (373.49) calcd. (%): C 70.75, H 8.37, N 3.75; found (%) C 70.57, H 8.47, N 3.53. HRMS (ESI): calcd for $C_{22}H_{32}NO_4$: 374.2253; found: 374.2322 $[M+H^+]^+$.

9-(4-(2-(2-(2-hydroxyethoxy)ethoxy)ethylamino)phenyl)-10-methylacridinium hexafluorophosphate (**15**)

15 was prepared according to the procedure given in the literature[2]. **11** (1.57 g, 6.97 mmol) and N-methylacridinium iodide (2.20 g, 6.85 mmol) were suspended in n-butanol (40 mL). The suspension was heated to 120 ^{o}C for 3 h while air was bubbled through the mixture. The solvent was evaporated in vacuo. The crude product was purified by column chromatography (i-PrOH/acetic acid/water 5:1:2). The violet fractions were evaporated. The remaining oil was

treated with water and NH_4PF_6 in order to exchange the anion. The aqueous solution was extracted with dichloromethane (3x20 mL). The combined organic phases were dried ($MgSO_4$) and evaporated to give **13** (0.9 g, 23%), viscous oil.

^{1}H-NMR (400 MHz, CD_3CN): δ = 2.9 (t, br, 1 H; OH), 3.40 (t, *J*(H,H)=5.5 Hz, 2 H; NCH_2), 3.5 (m, 2 H; CH_2OH), 3.6 (m, 6 H; ethyleneoxy), 3.7 (t, *J*(H,H)=5.5 Hz, 2 H; ethyleneoxy), 4.73 (s, 3 H; NMe), 5.3 (s, br, 1 H; NH), 6.94 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.33 (d, *J*(H,H)=8.6 Hz, 2 H; Ar), 7.81 (m, 2 H; acridinium, H-2,7), 8.24 (dd, *J*(H,H)=1.0, 8.8 Hz, 2 H; acridinium, H-1,8), 8.30 (m, 2 H, acridinium, H-3,6), 8.51 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5).

HRMS (ESI): calcd for $C_{26}H_{29}N_2O_3$: 417.2173; found: 417.2172 $[M- PF_6^-]^+$,

UV-Vis (MeCN), λ/nm (ε/cmM^{-1}): 257 (73000), 358 (15100), 409 (6700), 537.5 (8140).

9-(4-((2-(2-(2-hydroxyethoxy)ethoxy)ethyl)(methyl)amino)phenyl)-10-methylacridinium hexafluorophosphate (**16**)

2-(2-(2-(methyl(phenyl)amino)ethoxy)ethoxy)ethanol (**12**)[3] (0.861 g, 3.60 mmol) and N-methylacridinium iodide (1.10 g, 3.42 mmol) were suspended in n-butanol (20 mL). The suspension was heated to 120 ^{o}C for 6 h while air was bubbled through the mixture. The solvent was evaporated in vacuo. The crude product was purified by column chromatography (i-propanol/acetic acid/water 8:1:2). The violet fractions were evaporated and treated with water and NH_4PF_6 and extracted with dichloromethane. The organic phase was dried ($MgSO_4$) and evaporated to give **16** (1.402 g, 71%), viscous oil. ^{1}H-NMR (400 MHz, CD_3CN): δ = 3.10 (s, 3 H; NCH_3), 3.48 (t, *J*(H,H)=5.1 Hz, 2 H; ethyleneoxy), 3.6 (m, 6 H; ethyleneoxy), 3.66 (t, *J*(H,H)=5.6 Hz, 2 H; NCH_2), 3.72 (t, *J*(H,H)=5.6 Hz, 2 H; ethyleneoxy), 4.71 (s, 3 H; NMe), 7.00 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.33 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.76 (m, 2 H; acridinium, H-2,7), 8.20 (d, *J*(H,H)=8.7 Hz, 2 H; acridinium, H-1,8), 8.30 (m, 2 H; acridinium, H-3,6), 8.49 (d, *J*(H,H)=9.2 Hz, 2 H; acridinium, H-4,5).

HRMS (ESI): calcd for $C_{27}H_{31}N_2O_3$: 431.2329; found: 431.2329 $[M- PF_6^-]^+$,

9-(4-(2-(2-(2-(4-(3-hydroxypropyl)phenoxy)ethoxy)ethoxy)ethylamino)phenyl)-10-methylacridinium hexafluorophosphate (**17**)

13 (0.669 g, 1.86 mmol) and N-methylacridinium iodide (0.613 g, 1.91 mmol) were suspended in n-butanol (15 mL). The suspension was heated to 120 ^{o}C for 3 h while air was bubbled through the mixture. After cooling down to room temperature, diethylether (60 mL) was added. The insoluble residue was purified by column chromatography (*i*-

PrOH/water/acetic acid). In order to exchange the anion the resulting acetate was treated with NH_4PF_6 (saturated solution in MeCN, blue viscous oil (0.890 g, 48 %).

^{1}H-NMR (400 MHz, CD_3CN): δ = 1.62 (m, 2 H; CH_2), 2.44 (m, 2 H; CH_2), 3.39 (m, 2 H; NCH_2), 3.43 (m, 2 H; CH_2OH), 3.69 (m, 4 H; ethyleneoxy), 3.74 (m, 2 H; ethyleneoxy), 3.78 (m, 2 H; ethyleneoxy), 4.01 (m, 2 H; ethyleneoxy), 4.70 (s, 3 H; NMe), 6.72 (d, *J*(H,H)=8.5 Hz, 2 H; Ph), 6.88 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 6.97 (d, *J*(H,H)=8.5 Hz, 2 H; Ph), 7.23 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.73 (m, 2 H; acridinium, H-2,7), 8.17 (d, *J*(H,H)=8.6 Hz, 2 H; acridinium, H-1,8), 8.27 (m, 2 H; acridinium, H-3,6), 8.48 (d, *J*(H,H)=9.2 Hz, 2 H; acridinium, H-4,5). HRMS (ESI): calcd for $C_{35}H_{39}N_2O_4$: 551.2904; found: 551.2901 $[M]^+$.

9-(4-((2-(2-(2-(4-(3-hydroxypropyl)phenoxy)ethoxy)ethoxy)ethyl)(methyl)amino)phenyl)-10-methylacridinium hexafluorophosphate (**18**)

14 (0.662 g, 1.77 mmol) and N-methylacridinium iodide (0.57 g, 1.77 mmol) were suspended in n-butanol (20 mL). The suspension was heated to 120 ^{o}C for 3.5 h while air was bubbled through the mixture. The solvent was removed in vacuo. The residue was purified by column chromatography (1. 800 ml MeCN, 20 ml H_2O, 1 g NH_4PF_6, 2. *i*-PrOH/water/acetic acid 5:2:1). The resulting acetate was treated with NH_4PF_6, water and dichloromethane in order to exchange the anion. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried ($MgSO_4$). After removing of the solvent, **18** resulted as blue viscous oil (0.13 g, 25 %).

^{1}H-NMR (400 MHz, CD_3CN): δ = 1.63 (m, 2 H; CH_2), 2.45 (t, *J*(H,H)=7.6 Hz , 2 H; CH_2), 3.11 (s, 3 H; NCH_3), 3.45 (t, , *J*(H,H)=6.5 Hz 2 H; CH_2OH), 3.5-3.7 (m, 6 H; ethyleneoxy), 3.71-3.77 (m, 4 H; ethyleneoxy), 3.97 (m, 2 H; ethyleneoxy), 4.71 (s, 3 H; NMe), 6.69 (d, *J*(H,H)=8.6 Hz, 2 H; Ar), 6.95 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.07 (d, *J*(H,H)=8.9 Hz, 2 H; Ar), 7.34 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 7.76 (m, 2 H; acridinium, H-2,7), 8.21 (d, *J*(H,H)=8.7 Hz, 2 H; acridinium, H-1,8), 8.29 (m, 2 H; acridinium, H-3,6), 8.49 (d, *J*(H,H)=9.2 Hz, 2 H; acridinium, H-4,5).

HRMS (ESI): calcd for $C_{36}H_{41}N_2O_4$: 565.30608; found: 565.3061 $[M]^+$.

Compound **19**

7 (0.2 g) dissolved in MeCN (5 mL) and EtOH (1 mL) was treated with K_2CO_3 (0.1 g) under stirring for 5 h. The decolorized reaction mixture was filtrated; the solution was evaporated under reduced pressure. The remaining residue was dissolved in chloroform. The resulting suspension was filtered. The solvent was removed. The resulting acridane **19** was used

without further purification (oil, 0.15 g, 94%). ^{1}H-NMR (400 MHz, CD_3CN): δ = 1.13 (t, *J*(H,H)=7.0 Hz, 2 H; CH_3), 3.05 (q, *J*(H,H)=7.0 Hz, 2 H; OCH_2), 3.5 (m, 5 H; NMe, ethyleneoxy), 3.6 (m, 6 H; ethyleneoxy), 3.7 (m, 2 H; ethyleneoxy), 4.00 (m, 2 H; ethyleneoxy), 6.75 (d, *J*(H,H)=9.0 Hz, 2 H; Ar), 6.90 (m, 2 H; acridane, H-2,6), 7.12 (d, *J*(H,H)=8.0 Hz, 2H; acridane, H-4,5), 7.16 (d, *J*(H,H)=9.0 Hz, 2 H; Ar), 7.3 (m, 4H; acridane, H-3,5,1,8), 7.57 (s, 1 H; OH).

4-(3-(2-(2-(2-(4-(9-ethoxy-10-methyl-9,10-dihydroacridin-9-yl)phenoxy)ethoxy)ethoxy)ethoxy)propyl)phenol (**20**)

10 (0.37 g, 0.53 mmol) dissolved in MeCN (6 mL) and ethanol (0.5 mL) were treated with K_2CO_3 (0.10 g) for 4 h under stirring. The suspension was filtered, and the solvent was removed in vacuo. The product was separated from K_2CO_3 by dissolution in chloroform. **20** was obtained as an oil (0.36 g, 96 %) after evaporation of the solvent which was used without further purification. ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 1.14 (t, *J*(H,H)=7.0 Hz, 3 H; CH_3), 1.8 (m, 2 H; CH_2), 2.52 (m, 2 H; benzyl-H), 3.05 (q, *J*(H,H)=7.0 Hz, 2 H; OCH_2), 3.35 (t, *J*(H,H)=6.5 Hz, 2 H; OCH_2), 3.46 (m, 5 H; ethyleneoxy, NCH_3), 3.53 (m, 6 H; ethyleneoxy), 3.7 (m, 2 H; ethyleneoxy), 4.0 (m, 2 H; ethyleneoxy), 6.68 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 6.73 (d, *J*(H,H)= 9.0 Hz, 2 H; Ar), 7.1 (d, *J*(H,H)= 8.5 Hz, 2 H; Ar), 7.0-7.2 (m, 6 H; acridane, Ar), 7.3 (m, 4 H; acridane), HRMS (ESI): calcd. for $C_{35}H_{38}NO_5$: 552,2750; found 552.2746 $[M\text{-}EtO^-]^+$.

2-(2-(2-(4-(9-methoxy-10-methyl-9,10-dihydroacridin-9-yl)phenylamino)ethoxy)ethoxy)ethanol (**21**)

15 (0.21 g) dissolved in MeCN (5 mL) and MeOH (1 mL) was treated with K_2CO_3 (0.1 g) under stirring for 1 h. The reaction mixture was filtered and the solution was evaporated under reduced pressure. The remaining residue was dissolved in chloroform. The resulting suspension was filtered. The solvent was removed. The resulting acridane **21** was used without further purification (oil, 0.16 g, 94%).

^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 2.5 (s, br, 1 H; OH), 2.9 (s, 3 H ; OCH_3), 3.2 (t, *J*(H,H)=5.3 Hz, 2 H; NCH_2), 3.41 (s, 3 H; NCH_3), 3.5 (m, 4 H; ethyleneoxy), 3.6 (m, 4 H; ethyleneoxy), 3.7 (m, 2 H; ethyleneoxy), 6.37 (d, *J*(H,H)=9 Hz, 2 H; Ar), 6.84 (m, 2 H; acridane, H-2,7), 6.94 (d, *J*(H,H)=7.5 Hz, 2 H; acridane, H-4,5), 7.03 (d, *J*(H,H)=8.9 Hz, 2 H; Ar), 7.2 (m, 2 H; acridane, H-3,6), 7.26 (dd, *J*(H,H)=1.4, 7.8 Hz, 2 H; acridane, H-1,4).

HRMS (ESI): calcd for $C_{26}H_{29}N_2O_3$: 417.2173; found: 417.2171 $[M\text{-}OCH_3^-]^+$, UV-Vis (MeCN), λ/nm (ε/cmM^{-1}): 282 (15800), 313 (sh) (4100).

2-(2-(2-((4-(9-methoxy-10-methyl-9,10-dihydroacridin-9-yl)phenyl)(methyl)amino)ethoxy)ethoxy)ethanol (**22**)

16 (1.14 g, 1.93 mmol) dissolved in MeCN (6 mL) and MeOH (1 mL) was treated with K_2CO_3 (0.4 g) under stirring for 2 h. The reaction mixture was filtered and the solution was evaporated under reduced pressure. The remaining residue was dissolved in chloroform. The resulting suspension was filtered. The solvent was removed. The resulting acridane **22** (dark oil, 0.8 g, 88%) was used without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 2.90 (s, 3 H ; OCH_3), 3.42-3.49 (m, 2 H; ethyleneoxy), 3.48 (s, 3 H; NCH_3), 3.53-3.61 (m, 8 H; ethyleneoxy), 3.64-3.68 (m, 2 H; ethyleneoxy), 6.48 (d, *J*(H,H)=9.0 Hz, 2 H; Ar), 6.84 (m, 2 H; acridane, H-2,7), 6.93 (d, *J*(H,H)=8.2 Hz, 2 H; acridane, H-4,5), 7.05 (d, *J*(H,H)=8.9 Hz, 2 H; Ar), 7.2 (m, 2 H; acridane, H-3,6), 7.28 (dd, *J*(H,H)=1.5, 7.6 Hz, 2 H; acridane, H-1,4), HRMS (ESI): calcd for $C_{28}H_{35}N_2O_4$: 463.2591; found: 463.2598 $[M+H^+]^+$; calcd for $C_{27}H_{31}N_2O_3$: 431.2329; found: 431.2330 $[M\text{-}OCH_3^-]^+$.

3-(4-(2-(2-(2-(4-(9-methoxy-10-methyl-9,10-dihydroacridin-9-yl)phenylamino)ethoxy)ethoxy)ethoxy)phenyl)propan-1-ol (**23**)

17 (0.084 g, 0.16 mmol) dissolved in MeCN (5 mL) and methanol (1 mL) was treated with K_2CO_3 (0.10 g) for 1 h under stirring. The suspension was filtered, and the solvent was removed in vacuo. The product was separated from K_2CO_3 by dissolution in chloroform. **23** was obtained as an dark oil (0.068 g, 97 %) after evaporation of the solvent which was used without further purification. ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 1.8 (m, 2 H; CH_2), 2.61 (m, 2 H; benzyl-H), 2.95 (s, 3 H; OCH_3), 3.5 (s, 3 H; NCH_3), 3.6 (m, 6 H; ethyleneoxy), 3.8 (m, 2 H; ethyleneoxy), 4.1 (m, 2 H; ethyleneoxy), 6.46 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 6.81 (d, *J*(H,H)=8.8 Hz, 2 H; Ar), 6.9 (m, 2 H; acridane, H-2,7), 7.0 (d, *J*(H,H)=7.5 Hz, 2 H; acridane, H-4,5), 7.1 (m, 4 H; Ar), 7.2 (m, 2 H; acridane, H-3,6), 7.32 (dd, *J*(H,H)=1.5, 7.5 Hz, 2 H; acridane, H-1,8); HRMS (ESI): calcd for $C_{35}H_{39}N_2O_4$: 551.2904; found: 551.2896 $[M\text{-}CH_3O^-]^+$.

3-(4-(2-(2-(2-((4-(9-methoxy-10-methyl-9,10-dihydroacridin-9-yl)phenyl)(methyl)amino) ethoxy)ethoxy)ethoxy)phenyl)propan-1-ol (**24**)

18 (0.28 g, 0.40 mmol) dissolved in MeCN (4 mL) and methanol (1 mL) were treated with K_2CO_3 (0.50 g) for 40 min under stirring. The suspension was filtered, and the solvent was removed in vacuum. The product was separated from K_2CO_3 by dissolution in chloroform. **24** was obtained as an oil (0.21 g, 89 %) after evaporation of the solvent which was used without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 1.9 (m, br, 2 H; CH_2), 2.72 (m, br, 2 H; CH_2), 2.99 (s, 3 H; NCH_3), 3.1 (s, 3 H; OCH_3), 3.6 (m, 5 H; NCH_3, ethylenoxy), 3.7 (m, 4 H; ethyleneoxy), 3.7 (m, 2 H; ethyleneoxy), 3.9 (m, 2 H; ethyleneoxy), 4.1 (m, 2 H; ethyleneoxy), 6.7 (m, 2 H; Ar), 6.9 (m, 2 H; Ar), 7.0 (m, 2 H; acridane, Ar), 7.1-7.2 (m, 4 H; Ar, acridane), 7.2-7.4 (m, 4 H; Ar, acridane), 7.5 (m, 2 H; acridane); HRMS (ESI): calcd for $C_{36}H_{42}N_2O_4$: 566.3145; found: 551.2896 $[M\text{-}CH_3O^-]^+$.

Rotaxane 27

A solution of **19** (0.30 g, 0.65 mmol) dissolved in MeCN (3.5 mL), **26**[4] (0.86 g, 0.78 mmol) and 2,6-di-*t*-butyl-4-methylpyridine (0.15 g, 0.71 mmol) was stirred for 30 min under an argon atmosphere. A solution of adamantane-1-carbonyl chloride (0.13 g, 0.65 mmol) was added. The resulting suspension was stirred at room temperature for 7 days. A white precipitate was removed and the filtrate was evaporated. The resulting oil was extracted with dichloromethane in order to dissolve compound **28**. The residue was treated with 5 mL of a solution of NH_4PF_6 in MeCN (400 mL), ethyl acetate (200 mL) and cyclohexane (100 mL). Free **26** was filtered off. The solution was chromatographed (NH_4PF_6 in MeCN/ethylacetate/cyclohexane 2:1:0.5). The yellow fractions were collected and the solvents were removed. The resulting yellow solid was washed with water and dried in vacuum to give **27** (0.12 g, 10%), m.p. 255-260 ^{o}C. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.3 (m, br, 2 H; ethyleneoxy), 1.7 (m, 9 H; adamantane), 2.0 (s, br, 6 H; adamantane), 3.05 (m, br, 2 H; ethyleneoxy), 3.34 (t, *J*(H,H)=5.0 Hz, 2 H; ethyleneoxy), 3.4 (m, 4 H; ethyleneoxy), 3.84 (t, *J*(H,H)=5.2 Hz, 2 H; OCH_2), 4.22 (d, *J*(H,H)=8.6 Hz, 2 H; Ar), 4.90 (s, 3 H; NMe), 5.75, 5.78, 5,82, 5.85 (m, 8 H; ring **26**, benzyl-H), 6.95 (d, *J*(H,H)=8.6 Hz, 2 H; Ar), 7.70 (s, 8 H; ring **26**), 7.76 (dd, *J*(H,H)=1, 7.8 Hz, 2 H; acridinium, H-1,8), 8.11 (d, *J*(H,H)=7.0 Hz, 8 H; ring **26**), 8.17 (m, 2 H; acridinium, H-2,7), 8.30 (m, 2 H; acridinium, H-3,6), 8.70 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5), 9.01 (d, *J*(H,H)=7.0 Hz, 8 H; ring **26**).

MS (ESI): calcd for $C_{73}H_{74}F_{18}N_5O_5P_3$: 767.7302; found: 767.7289 $[M\text{-}2\ PF_6^-]^{2+}$calcd for

$C_{73}H_{74}F_{12}N_5O_5P_2$: 463.4986; found: 463.4981 [M-3 PF_6^-]$^{3+}$); calcd for $C_{73}H_{74}F_6N_5O_5P$: 311.3827; found: 311.3824 [M-4 PF_6^-]$^{4+}$; elemental analysis calcd (%) for $C_{73}H_{74}F_{30}N_5O_5P_5$: C 48.01, H 4.08, N 3.83; found: C 48.28, H 4.01, N 3.68.

The dichloromethane solution containing the acylated axle was evaporated. The remaining residue was purified by column chromatography (NH_4PF_6 (7 g) in MeCN/ethylacetate/cyclohexane 2:1:0.5) to give pure **28** (0.17 g, 73%) as an oily compound. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.7 (s, br, 9 H; adamantane), 1.9 (s, br, 6 H; adamantane), 3.6 (m, 6 H; ethyleneoxy), 3.9 (m, 2 H; ethyleneoxy), 4.15 (m, 2 H; ethyleneoxy), 4.26 (m, 2 H; ethylenoxy), 4.80 (s, 3 H; NMe), 7.27 (d, *J*(H,H)=8.8 Hz, 2 H, Ar), 7.46 (d, *J*(H,H)=8.6 Hz, 2 H; Ar), 7.84 (m, 2H; acridinium, H-2,7, 8.11 (dd, *J*(H,H)=1, 8.8 Hz, 2 H, acridinium, H-1,8), 8.35 (m, 2 H; acridinium, H-3,6), 8.70 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5); elemental analysis calcd (%) for $C_{36}H_{39}F_6NO_5P$: C 60.84, H 5.53, N 1.97; found: C 60.69, H 5.74, N 1.80.

Rotaxane 31

26 (0.44 g, 0.40 mmol) dissolved in MeCN (4 mL) and 2,6-di-*t*-butyl-4-methylpyridine (0.16 g, 0.75 mmol) were added to 1 mL of the dichloromethane solution of **22** (0.174 g, 0.38 mmol). The solution was stirred for 30 min under an argon atmosphere. An acetonitrile solution (2 mL) of adamantane-1-carbonyl chloride (0.17 g, 0.85 mmol) was added. The resulting suspension was stirred at room temperature for 5 days. A white precipitate was removed and the filtrate was evaporated. The resulting oil was extracted with dichloromethane in order to dissolve compound **32**. The remaining red solid was treated with 3 mL of a solution of NH_4PF_6 (7 g) in MeCN (400 mL), ethyl acetate (200 mL) and cyclohexane (100 mL). Free **26** (0.14 g) was filtered off. The solution was chromatographed (NH_4PF_6 in MeCN/ethylacetate/cyclohexane 2:1:0.5). The red fraction was collected and the solvents were removed. The resulting red solid was washed with water and dried in vacuum to give **31** (0,081 g, 12%). M.p. 198-205^{o}C (dec.);

^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.1 (s, br, 3 H, N-CH_3), 1.13 (s, br, 2 H; NCH_2), 1.76 (m, 6 H; adamantane), 1.80 (s, br, 6 H; adamantane), 1.9 (s, br, 3 H; adamantane), 3.2 (s, br, 2 H; ethyleneoxy), 3.3 (s, br, 2 H; ethyleneoxy), 3.5 (s, br, 2 H; ethyleneoxy), 3.6 (s, br, 2 H; ethyleneoxy), 3.8 (s, br, 2 H; ethyleneoxy), 3.67 (d, br, 2 H, Ar), 4.87 (s, 3 H; NMe), 5.74, 5.78, 5,81, 5.84 (m, 8 H; ring **26**, benzyl-H), 6.65 (d, *J*(H,H)=8.2 Hz, 2 H; Ar), 7.75 (s, 8 H; ring **26**), 7.80 (d, *J*(H,H)=8.8 Hz, 2 H; acridinium, H-1,8), 8.04 (s, br, 8 H; ring **26**), 8.20 (m, 2 H; acridinium, H-2,7), 8.50 (m, 2 H; acridinium, H-3,6), 8.69 (d,

J(H,H)=9.3 Hz, 2 H; acridinium, H-4,5), 9.04 (d, *J*(H,H)=6.2 Hz, 8 H; ring **26**);
MS (ESI): calcd for $C_{74}H_{77}F_{18}N_6O_4P_3$: 774.2460; found: 774.2457 $[M\text{-}2\ PF_6^-]^{2+}$, calcd for $C_{74}H_{77}F_{12}N_6O_4P_2$: 467.8425; found: 467.8423 $[M\text{-}3\ PF_6^-]^{3+}$, $C_{74}H_{77}F_6N_6O_4P$: 314.6407; found: 314.6405 $[M\text{-}4\ PF_6^-]^{4+}$.

The dichloromethane solution was evaporated to give **32**. The separation and purification was performed with the help of column chromatography [MeOH/H_2O/NH_4Cl (saturated aqueous solution) 300:50:1]. The blue fractions were collected, the solvents were evaporated, and the remaining blue solid was dissolved with a mixture of H_2O (30 mL)/dichloromethane (30 mL)/NH_4PF_6 (0.2 g). The organic phase was dried. The solvent was evaporated to give compound **32** (0.17 g, 33%) as oily compound. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.69 (m, 6 H; adamantane), 1.80 (s, br, 6 H; adamantane), 1.9 (s, br, 3 H; adamantane), 3.15 (s, 3 H; N-CH_3), 3.6 (m, br, 6 H; ethyleneoxy), 3.71 (m, br, 2 H; ethyleneoxy), 3.77 (m, 2 H; ethyleneoxy), 4.13 (t, *J*(H,H)=5.5 Hz, 2 H; NCH_2), 4.76 (s, 3 H; N^+Me), 7.07 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.41 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.82 (m, 2 H; acridinium, H-2,7), 8.27 (d, *J*(H,H)=8.8 Hz, 2 H; acridinium, H-1,8), 8.33 (m, 2 H; acridinium, H-3,6), 8.55 (d, *J*(H,H)=9.1 Hz, 2 H; acridinium, H-4,5); MS (ESI): calcd for $C_{38}H_{45}N_2O_5$: 593.3374; found: 593.3365 $[M\text{-}2\ PF_6^-]^{2+}$.

Rotaxane 33

20 (0.24 g, 0.40 mmol), **26** (0.53 g, 0.48 mmol) and 2,6-di-*t*-butyl-4-methylpyridine (0.091 g, 0.44 mmol) were dissolved in MeCN (2.5 mL). The yellow solution was stirred for 1 h under an argon atmosphere. After that time an acetonitrile solution (0.5 mL) of adamantane-1-carbonyl chloride (0.080 g, 0.40 mmol) was added. The resulting suspension was stirred at room temperature for 3 days. A white precipitate was removed and the filtrate was evaporated. The resulting oil was extracted with dichloromethane in order to dissolve **20** and compound **34**. The yellow solid was treated with 5 mL of a solution of NH_4PF_6 in MeCN (400 mL), ethyl acetate (200 mL) and cyclohexane (100 mL). Free **26** (0.12 g) was filtered. The solution was chromatographed (NH_4PF_6 (7 g) in 400 mL MeCN/ethylacetate/cyclohexane 2:1:0.5). The yellow fractions were collected and the solvents were removed. The resulting yellow solid was washed with water and dried in vacuum to give **33** (0,204 g, 26%). M.p. 188-194^{o}C; ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.1 (m, br, 2 H; CH_2), 1.56 (m, 2 H; CH_2), 1.9 (s, br, 6 H; adamantane), 2.1 (m, 6 H; adamantane), 2.2 (s, br, 3 H; adamantane), 3.55 (t, *J*(H,H)=5.7 Hz, 2 H; OCH_2), 3.71 (d, *J*(H,H)=8.4 Hz, 2 H; Ar), 3.76-3.78 (m, 12 H; ethyleneoxy, phenyl), 4.2 (m, 2 H;

ethyleneoxy), 4.83 (s, 3 H; NMe), 5.77 (m, 8 H; ring **26**, benzyl-H), 7.18 (d, *J*(H,H)=8.7 Hz, 2 H; Ar), 7.45 (d, *J*(H,H)=8.7 Hz, 2 H; Ar), 7.83 (s, 8 H; ring **26**), 7.9 (m, 2 H; acridinium, H-2,7), 8.08 (dd, *J*(H,H)=1, 7.7 Hz, 2 H; acridinium, H-1,8), 7.98 (d, *J*(H,H)=7.0 Hz, 8 H; ring **26**), 8.39 (m, 2 H; acridinium, H-3,6), 8.61 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5), 8.95 (d, *J*(H,H)=7 Hz, 8 H; ring **26**); MS (ESI): calcd for $C_{82}H_{84}F_{18}N_5O_6P_3$: 834.7668; found: 834.7676 [M-2 PF_6^-]$^{2+}$, calcd for $C_{82}H_{84}F_{12}N_5O_6P_2$: 508.1896; found: 508.1903 [M-3 PF_6^-]$^{3+}$, calcd for $C_{82}H_{84}F_6N_5O_6P$: 344.9010; found: 344.9015 [M-4 PF_6^-]$^{4+}$.

The dichloromethane solution was evaporated to give the compounds **20** and **34**. The separation and purification was performed with the help of CC (NH_4PF_6 (7 g) in 650 mL MeCN/ethylacetate/cyclohexane 2:1:0.5). The yellow fractions were collected, the solvents were evaporated and the remaining solid was washed with water to give compound **34** (0.20 g, 59%) as yellow solid. M.p. 75^{o}C; ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.7 (m, 6 H; adamantane), 1.8 (m, 2 H; CH_2), 1.9 (s, br, 6 H; adamantane), 2.0 (s, br, 3 H; adamantane), 2.63 (m, 2 H; CH_2), 3.4 (t, *J*(H,H)=6.3 Hz, 2 H; ethyleneoxy), 3.5 (m, 2 H; ethyleneoxy), 3.6 (m, 2 H; ethyleneoxy), 3.7 (m, 2 H; ethyleneoxy), 3.9 (m, 2 H, ethyleneoxy), 4.3 (m, 2 H; ethyleneoxy), 4.80 (s, 3 H, N^+Me), 6.87 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.19 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.25 (d, *J*(H,H)=8.3 Hz, 2 H; Ar), 7.43 (d, *J*(H,H)=8.0 Hz, 2 H; Ar), 7.83 (m, 2 H; acridinium, H-2,7), 8.11 (dd, *J*(H,H)=1.1, 7.8 Hz 2 H; acridinium, H-1,8), 8.34 (m, 2 H; acridinium, H-3,6), 8.57 (d, *J*(H,H)=9.3 Hz, 2 H; acridinium, H-4,5); MS (ESI): calcd for $C_{46}H_{52}NO_6$: 714.3789; found: 714.3788 [M- PF_6^-]$^+$.

Rotaxanes 35, 36

An acetonitrile solution (4 mL) of **23** (0.090 g, 0.16 mmol), **26** (0.195 g, 0.18 mmol) and 2,6-di-*t*-butyl-4-methylpyridine (0.033 g, 0.16 mmol) was stirred for 1 h under an argon atmosphere. After that time an acetonitrile solution (1 mL) of adamantane-1-carbonyl chloride (0.032 g, 0.16 mmol) was added. The solution was stirred at room temperature for 4 days. The solution was evaporated and the residue was extracted with dichloromethane. The red solid was treated with 1 mL of a solution of NH_4PF_6 (7 g) in MeCN (400 mL), ethyl acetate (200 mL) and cyclohexane (100 mL). Free **26** (0.13 g) was filtered. The solution was chromatographed (NH_4PF_6 (7 g) in 400 mL MeCN/ethylacetate/cyclohexane 2:1:0.5). The violet fractions were collected and the solvents were removed. The resulting solid was washed with water and dried in vacuum to

give a mixture of **35** and **36** (1:1) (0,030 g, 9.5%).

Rotaxane **35**: ^{1}H-NMR (400 MHz, CD_3CN, TMS): δ = 1.7 (m, br, 8 H; adamantane, CH_2), 1.9 (m, 6 H; adamantane), 2.1 (s, br, 5 H; adamantane, CH_2), 2.98 (d, *J*(H,H)=8.5 Hz, 2 H; Ph), 3.0 (m, br, 2 H; ethyleneoxy), 3.37 (t, br, 2 H, NCH_2), 3.77 (m, 2 H; ethyleneoxy), 3.9 (m, 6 H; ethyleneoxy), 4.12 (m, 2 H; CH_2), 4.60 (d, *J*(H,H)=8.4 Hz, 2 H; Ar), 4.77 (s, 3 H; N^+Me), 5.77 (m, 8 H; ring **26**, benzyl-H), 7.32 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.9 (m, 18 H; ring **26**, acridinium, H-2,7), 8.15 (dd, *J*(H,H)=1, 7.7 Hz, 2 H; acridinium, H-1,8), 8.3 (m, 2 H; acridinium, H-3,6), 8.57 (d, *J*(H,H)=9.2 Hz, 2 H; acridinium, H-4,5), 8.93 (d, *J*(H,H)=7 Hz, 8 H; ring **26**); MS (ESI): calcd for $C_{82}H_{85}F_{18}N_6O_5P_3$: 834.2748; found: 834.2755 [M-2 PF_6^-]$^{2+}$, calcd for $C_{82}H_{84}F_{12}N_6O_5P_2$: 507.8616; found: 507.8623 [M-3 PF_6^-]$^{3+}$, calcd for $C_{82}H_{84}F_6N_6O_5P$: 344.6550; found: 344.6556 [M-4 PF_6^-]$^{4+}$.

Rotaxane **36**: ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.6 (m, br, 2 H; CH_2), 1.7 (m, br, 12 H; adamantane, CH_2), 1.9 (m, 12 H; adamantane), 2.1 (s, br, 8 H; adamantane, CH_2), 2.85 (d, *J*(H,H)=8.6 Hz, 2 H; Ph), 2.9 (m, br, 2 H; ethyleneoxy), 3.75 (m, 2 H; ethyleneoxy), 3.9 (m, br, 6 H; ethyleneoxy, NCH_2), 4.1 (m, 2 H; CH_2), 4.75 (d, *J*(H,H)=9 Hz, 2 H; Ph), 4.88 (s, 3 H; N^+Me), 5.77 (m, 8 H; ring **26**, benzyl-H), 7.57 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.67 (d, *J*(H,H)=8.5 Hz, 2 H; Ar), 7.9 (m, 18 H; ring **26**, acridinium, H-2,7), 8.18 (dd, *J*(H,H)=1, 7.8 Hz, 2 H; acridinium, H-1,8), 8.4 (m, 2 H; acridinium, H-3,6), 8.66 (d, *J*(H,H)=9.2 Hz, 2 H; acridinium, H-4,5), 8.98 (d, *J*(H,H)=6.8 Hz, 8 H; ring **26**); MS (ESI): calcd for $C_{93}H_{99}F_{18}N_6O_6P_3$: 915.3270; found: 915.3274 [M-2 PF_6^-]$^{2+}$, calcd for $C_{93}H_{99}F_{12}N_6O_6P_2$: 561.8964; found: 561.8971 [M-3 PF_6^-]$^{3+}$, calcd for $C_{93}H_{99}F_6N_6O_6P$: 385.1811; found: 385.1818 [M-4 PF_6^-]$^{4+}$.

Rotaxane 39

Prepared according to the general procedure from rotaxane **27** (0.034 g), yield 0.29 g, (91%), dark green oily solid. ^{1}H NMR (400 MHz, MeOD/CD_3CN 5:1, TMS): δ = 1.7 (m, br, 6 H; adamantane), 1.8 (s, br, 6 H; adamantane), 1.9 (s, br, 3 H; adamantane), 2.38 (d, *J*(H,H)=8.8 Hz, 2 H; phenyl), 2.80 (s, br, 2 H; ethyleneoxy), 3.4 (s, 3 H; NMe), 3.6 (s, br, 2 H; ethyleneoxy), 3.7 (m, br, 2 H; ethyleneoxy), 3.8 (m, 2 H; ethyleneoxy), 4.0 (m, 2 H; ethyleneoxy), 4.26 (t, *J*(H,H)=6.7 Hz, 2 H; $CH_2O(CO)$), 4.85 (d, *J(*H,H)= 8.7 Hz, 2 H; phenyl), 5.8 (s, br, 8 H; ring **26**), 7.5 (d, *J(*H,H)= 6.7 Hz, 2 H; acridane), 7.6 (m, 4 H; acridane), 7.6-7.74 (m br, 18 H; acridane, ring **26**); MS (ESI): calcd for $C_{74}H_{77}F_{12}N_5O_6P_2$: 710.7573; found: 710.7587 [M-2 PF_6^-]$^{2+}$.

Rotaxane 41

Prepared according to the general procedure from rotaxane **31** (0.030 g), yield 0.22 g, 85%), dark solid. M.p. 149-154 ^{o}C; ^{1}H NMR (400 MHz, /CD_3CN, TMS): δ = 1.7 (m, br, 12 H; adamantane), 1.9 (m, br, 3 H; adamantane), 2.2 (d, br, 2 H; phenyl), 2.4 (s, br, 3 H; NCH_3), 3.3 (m, 6 H; NCH_2, ethyleneoxy), 3.4 (s, 3 H; OCH_3), 3.8 (m, 4 H; ethyleneoxy), 4.0 (m, 2 H; $CH_2O(CO)$), 4.5 (d, br, 2 H; phenyl), 5.7 (s, br, 8 H; ring **26**), 7.50-7.7 (m, 24 H; acridane, ring **26**), 8.8 (s, br, 8 H; ring **26**); MS (ESI): calcd for $C_{75}H_{80}F_{12}N_6O_5P_2$: 717.2737; found: 717.2742 $[M\text{-}2\ PF_6^-]^{2+}$, calcd for $C_{75}H_{80}F_6N_6O_5P$: 429.8611; found: 429.8614 $[M\text{-}3\ PF_6^-]^{3+}$, calcd for $C_{75}H_{80}N_6O_5$: 286.1548; found: 286.1553 $[M\text{-}4\ PF_6^-]^{4+}$.

Rotaxane 42

To an acetonitrile solution (6 mL) of the rotaxane **33** (0.047 g, 0.024 mmol) $NaHCO_3$ (0.20 g) and MeOH (0.2 mL) were added. The suspension was stirred for 1 day. After filtration the dark solution was evaporated to give **42** (0.039 g, 87%) as dark oil that was used without further purification.

^{1}H NMR (400 MHz, CD_3OD/CD_3CN 5:1): δ = 1.15 (m, 2 H; CH_2), 1.8 (s, br, 6 H; adamantane), 2.0 (s, br, 6 H; adamantane), 2.1 (s, br, 3 H; adamantane), 2.23 (t, br, 2 H; CH_2), 2.48 (d, br, 2 H; aryl), 2.7 (m, br, 2 H; ethyleneoxy), 3.03 (t, *J*(H,H)=6.5 Hz, 2 H; OCH_2), 3.30 (m 2 H; ethyleneoxy), 3.33 (s, 3 H; OCH_3), 3.5 (m, 2 H; ethyleneoxy), 3.7 (m, 5 H; ethyleneoxy, NCH_3), 3.8 (m, br, 4 H: ethyleneoxy), 4.87 (d, br, 2 H; aryl), 5.7 (s br, 8 H; ring **26**), 6.9 (s br, 4 H; phenyl), 7.47 (d, *J*(H,H)=8.3 Hz, 2 H; acridane, H-4,5), 7.52 (d, *J*(H,H)=6.5 Hz, 2 H; acridane, H-1,8), 7.6-7.7 (m, 20 H; acridane, ring **26**), 8.8 (s, br, 8 H; ring **26**); MS (ESI): calcd for $C_{83}H_{87}F_{12}N_5O_7P_2$: 777.7939; found: 777.7947 $[M\text{-}2\ PF_6^-]^{2+}$, calcd for $C_{83}H_{87}F_6N_5O_7P$: 470.2077; found: 470.2082 $[M\text{-}3\ PF_6^-]^{3+}$.

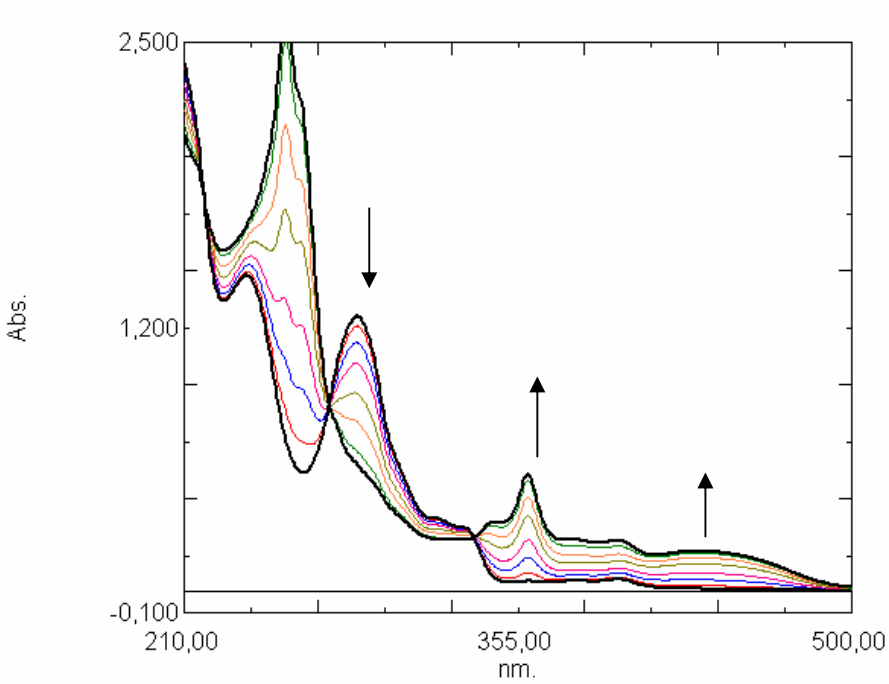


Figure 1a: UV-Vis spectra recorded after consecutive irradiations of compound **2** with light of the wavelength 313 nm in acetonitrile solution, 10s …. 12 min.

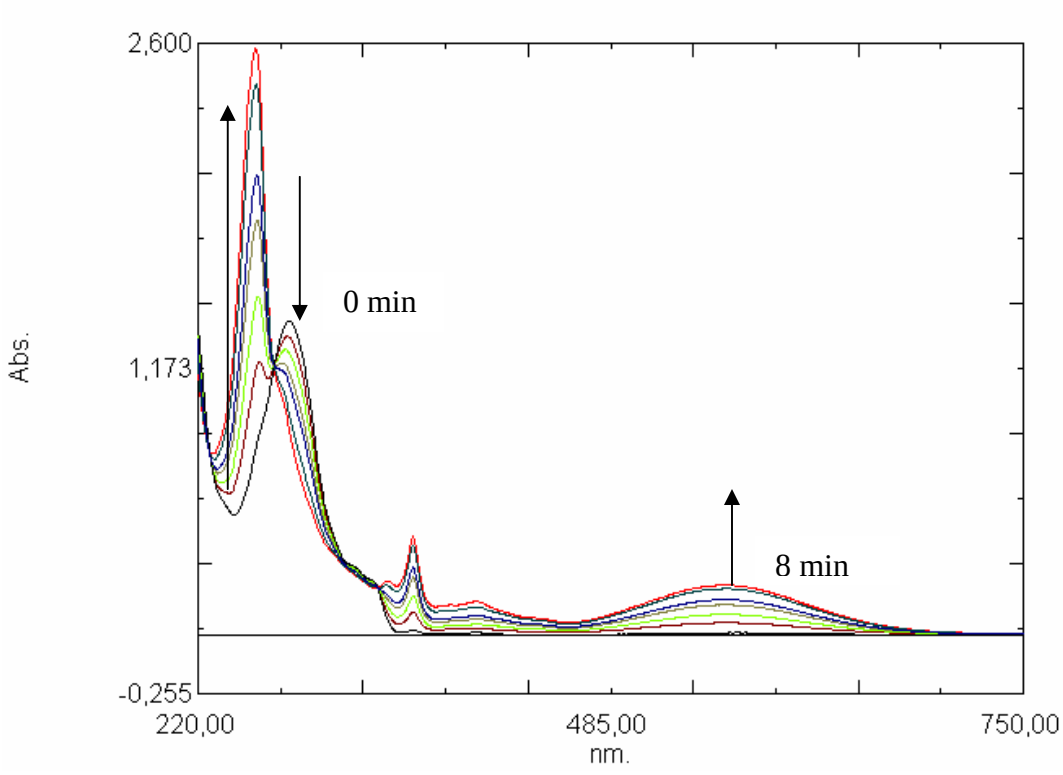


Figure 1b: UV-Vis spectra recorded after consecutive irradiation (20 s …. 8 min) of compound **4** in acetonitrile solution with light of the wavelength 313 nm.

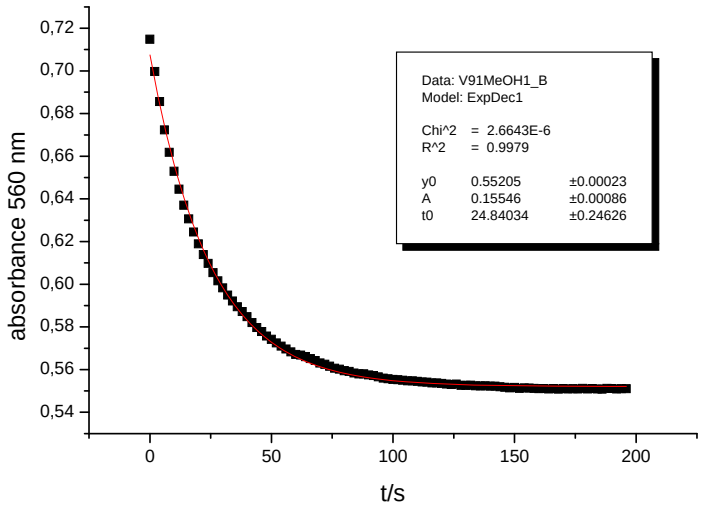


Figure 2a Decay curve of the transient absorption at 360 nm recorded after irradiation of compound **4** for 5 s (HBO 500) in methanol solution

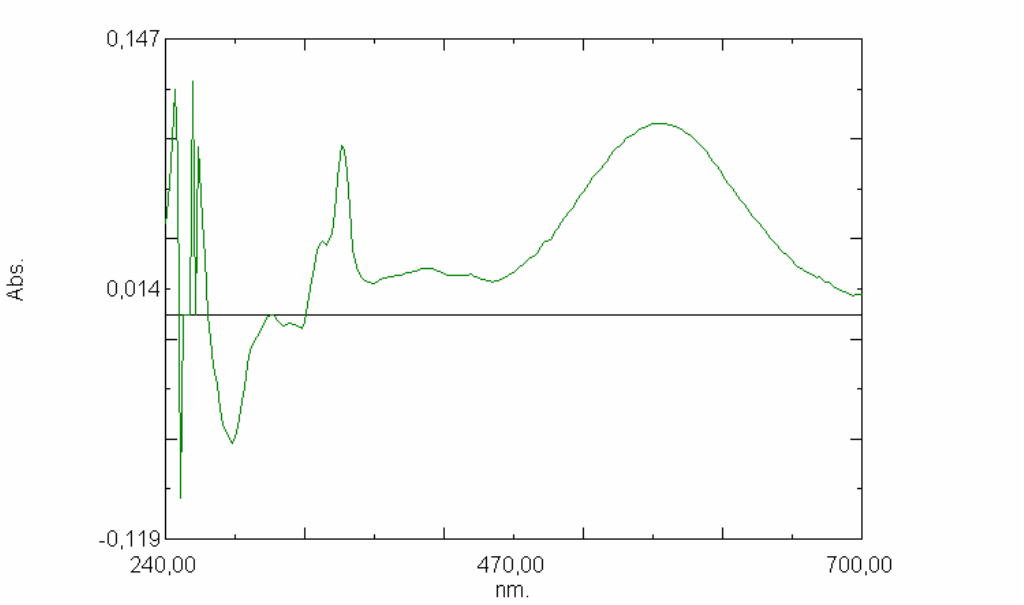


Figure 2b Transient absorption spectrum recorded after irradiation of compound **4** in methanol solution

Table 1 UV-Vis absorption maxima of rotaxanes **27** and **29** and the related molecular axles in different solvents

solvent	**29**	**15**	**27**	**9**
dichloromethane	-	562/415	-	450
THF	496/397	558/413	437	439
acetone	542/410	548/408	430	436
MeCN	507/404	539/423	430	435
Hexafluoro-*i*-propanol	456	525/451	429	431

Table 2 Lifetimes (s) of the intermediate acridinium methoxide rotaxanes in different solvents monitored after excitation (5 s) using a high pressure mercury lamp (500 W)

Rotaxan	MeOH	MeOH/MeCN	EtOH/MeCN
39	150		
40	220	5/1: 460	5/1; 590
41	70	1/1; 400	

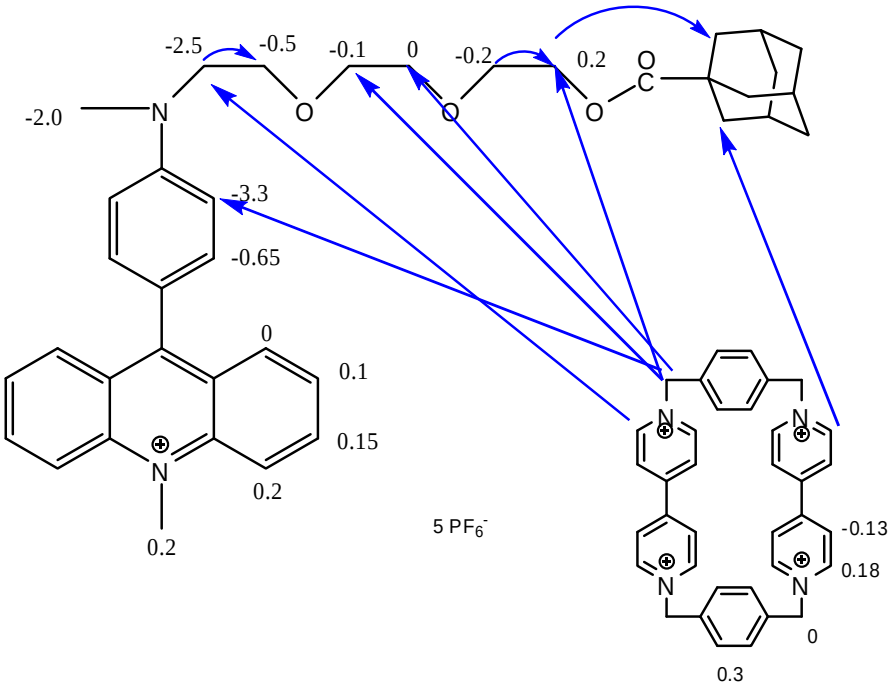


Figure 3 Chemical shift differences of proton resonances of rotaxane **31** obtained by comparison of the proton resonances of compounds **22** and **26** with related proton resonances observed in the rotaxane ($\delta_{\text{rotaxane }\mathbf{31}} - \delta_{\text{free component}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

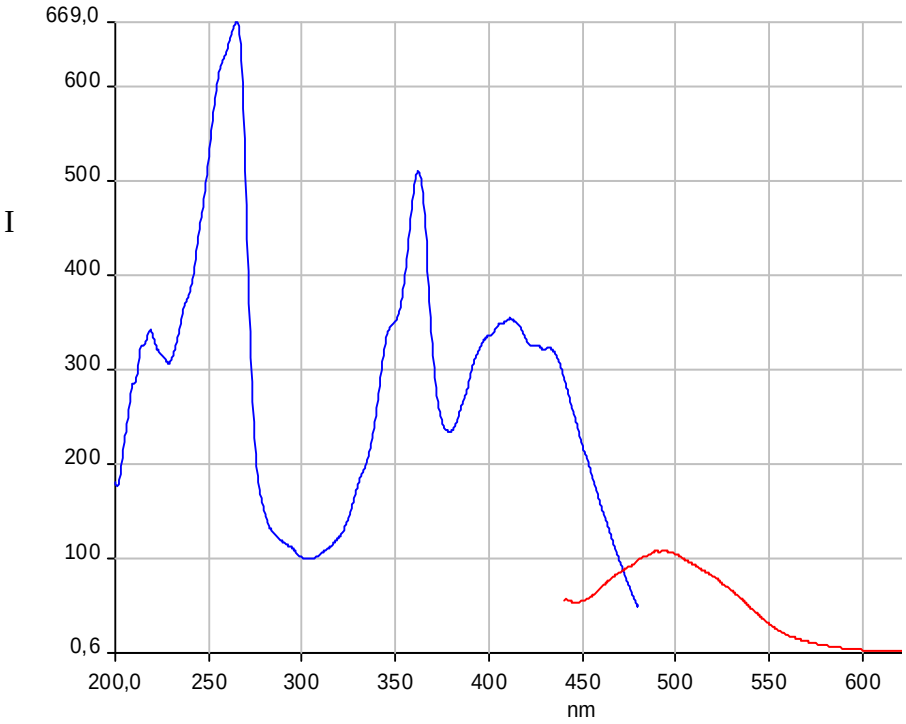


Figure 4 Fluorescence (—) and fluorescence excitation spectrum (—) (based on fluorescence at 500 nm) of rotaxane **29** in acetonitrile solution

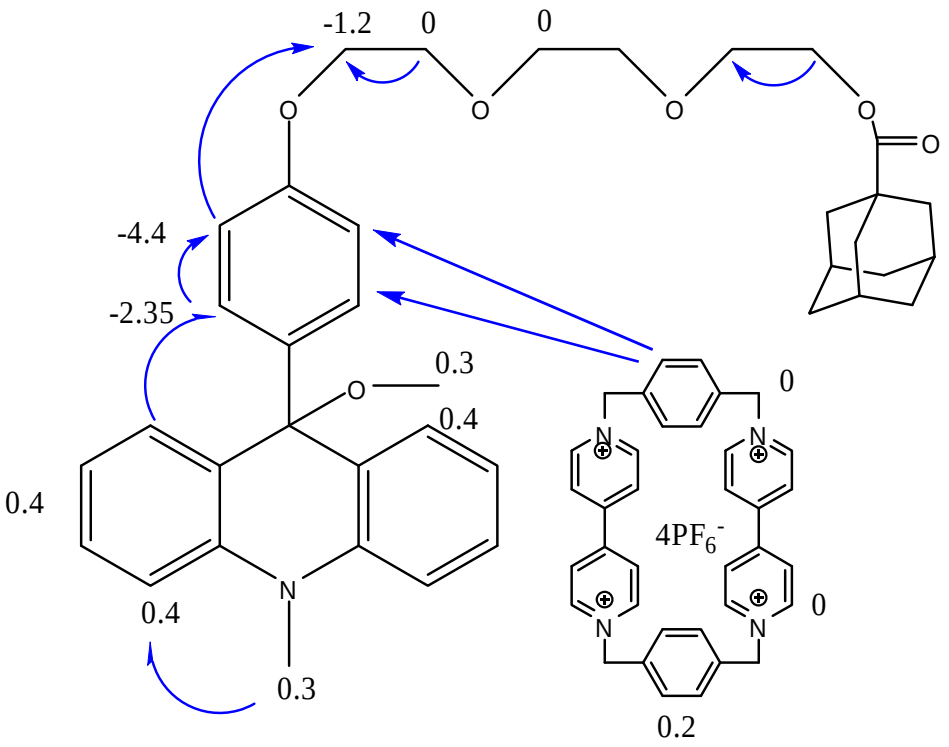


Figure 5a Chemical shift differences of proton resonances of rotaxane **39** obtained by comparison of the proton resonances of compounds **19** and **26** with related proton resonances observed in the rotaxane ($\delta_{\text{rotaxane }\mathbf{39}} - \delta_{\text{free component}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

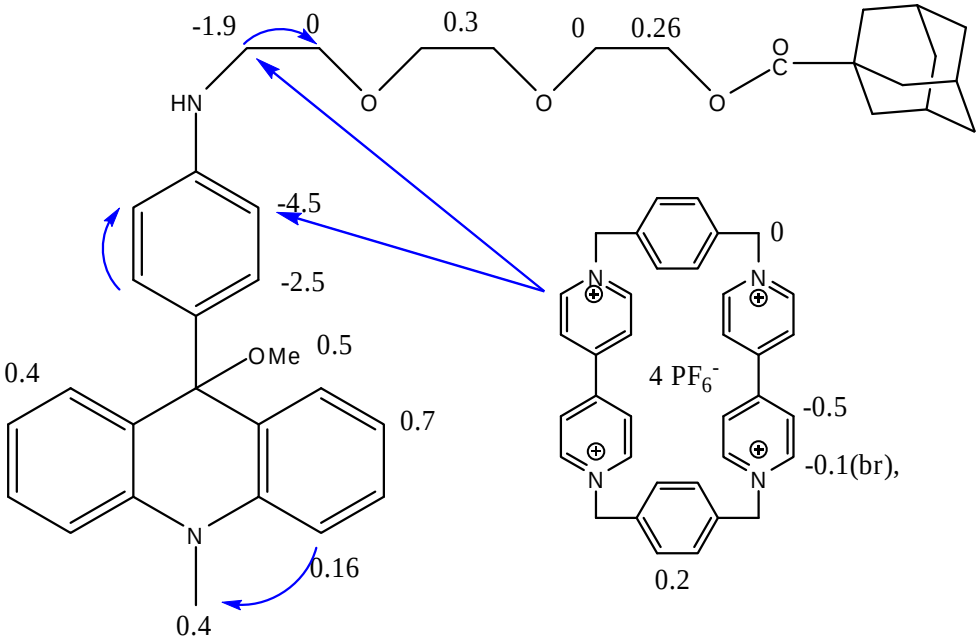


Figure 5b Chemical shift differences of proton resonances of rotaxane **40** obtained by comparison of the proton resonances of compounds **21** and **26** with related proton resonances observed in the rotaxane ($\delta_{\text{rotaxane }\mathbf{40}} - \delta_{\text{free component}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

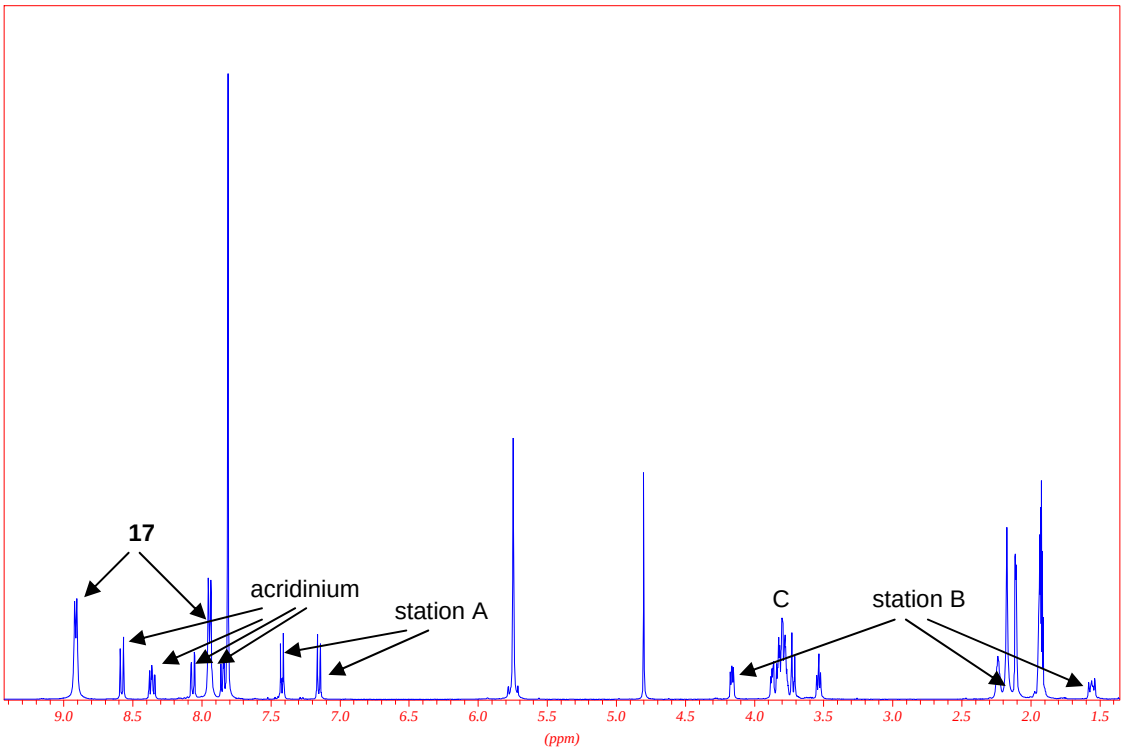


Figure 6 ^{1}H NMR spectrum (CD_3CN) of rotaxane **33**

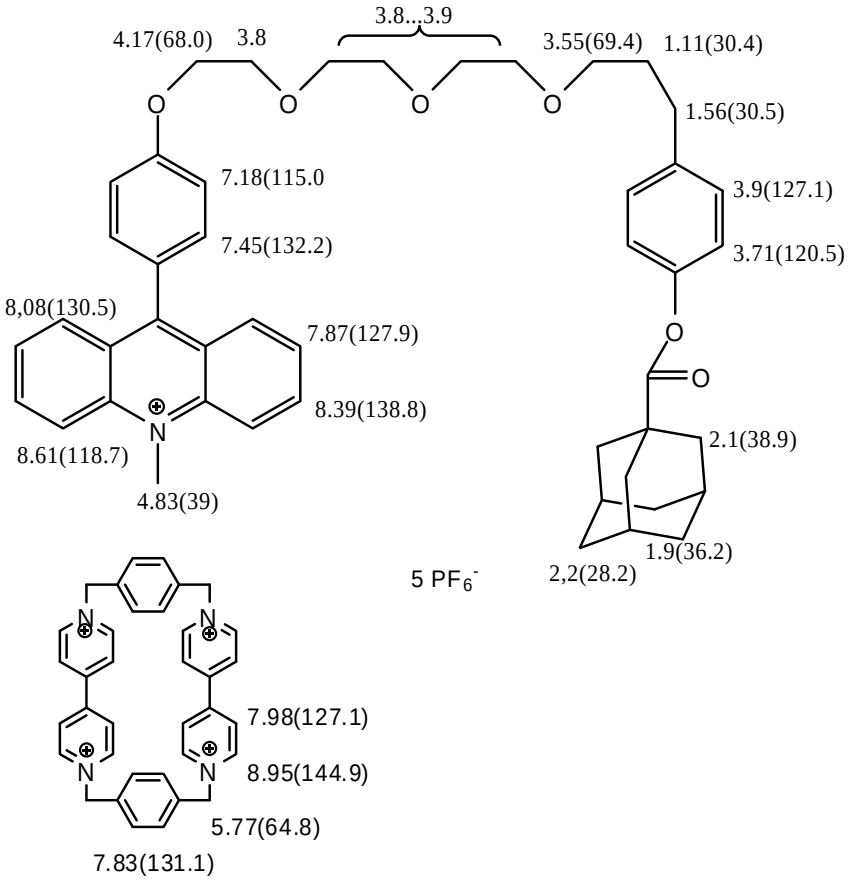


Figure 7 Assignment of proton and (^{13}C) resonances for the rotaxane **33** based on two-dimensional NMR-spectroscopy

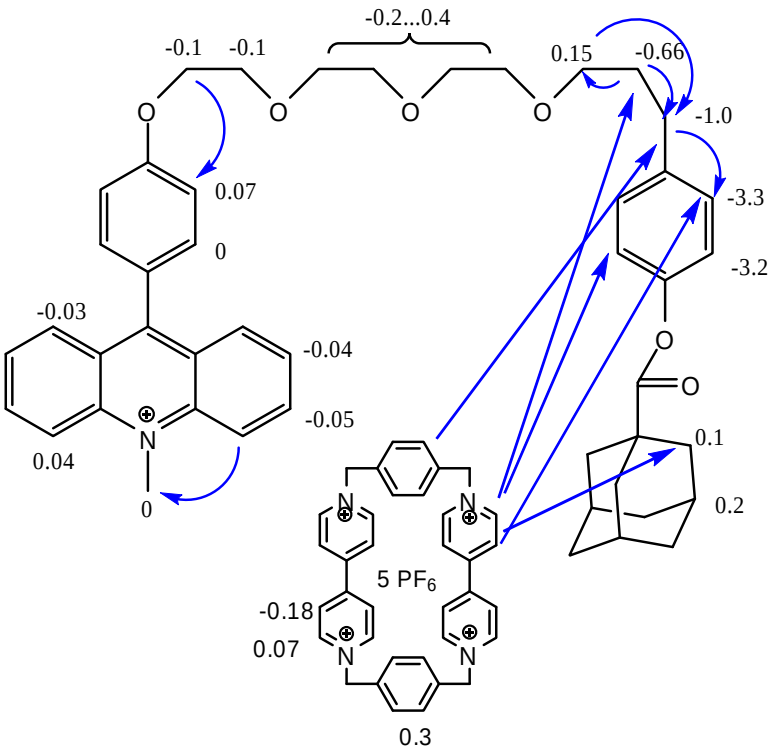


Figure 8 Chemical shift differences of proton resonances of rotaxane **33** obtained by comparison of the proton resonances of compounds **34** and **26** with related proton resonances observed in the rotaxane $\delta_{\text{rotaxane 33}} - \delta_{\text{free component}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

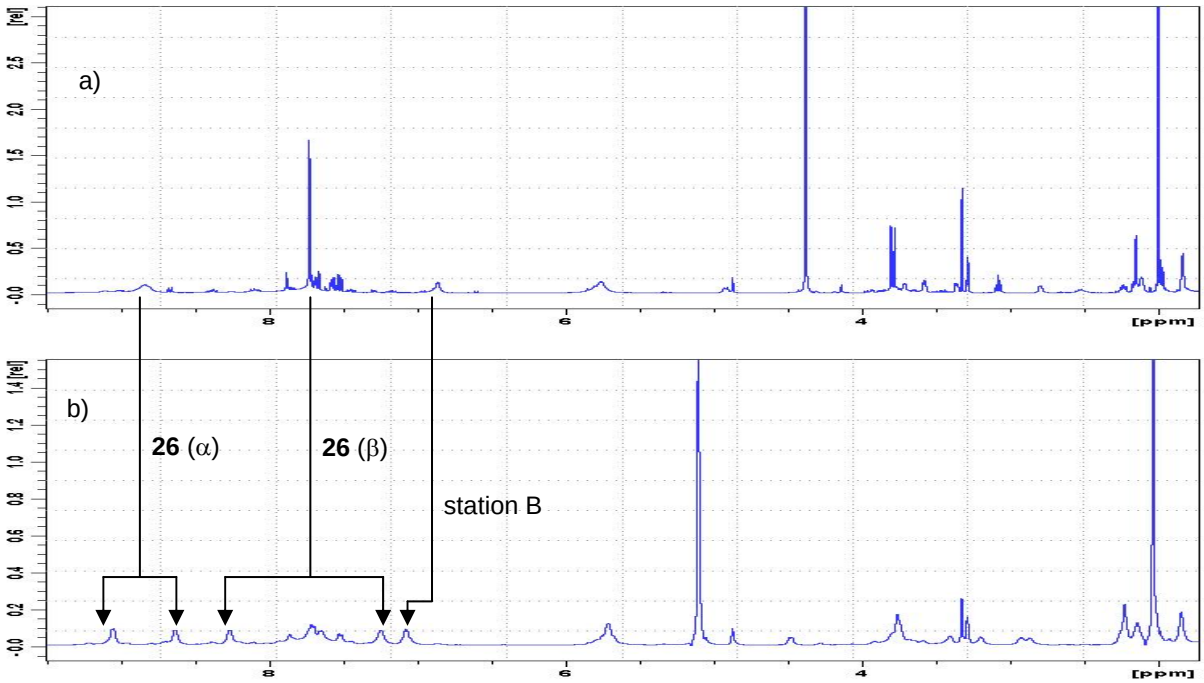
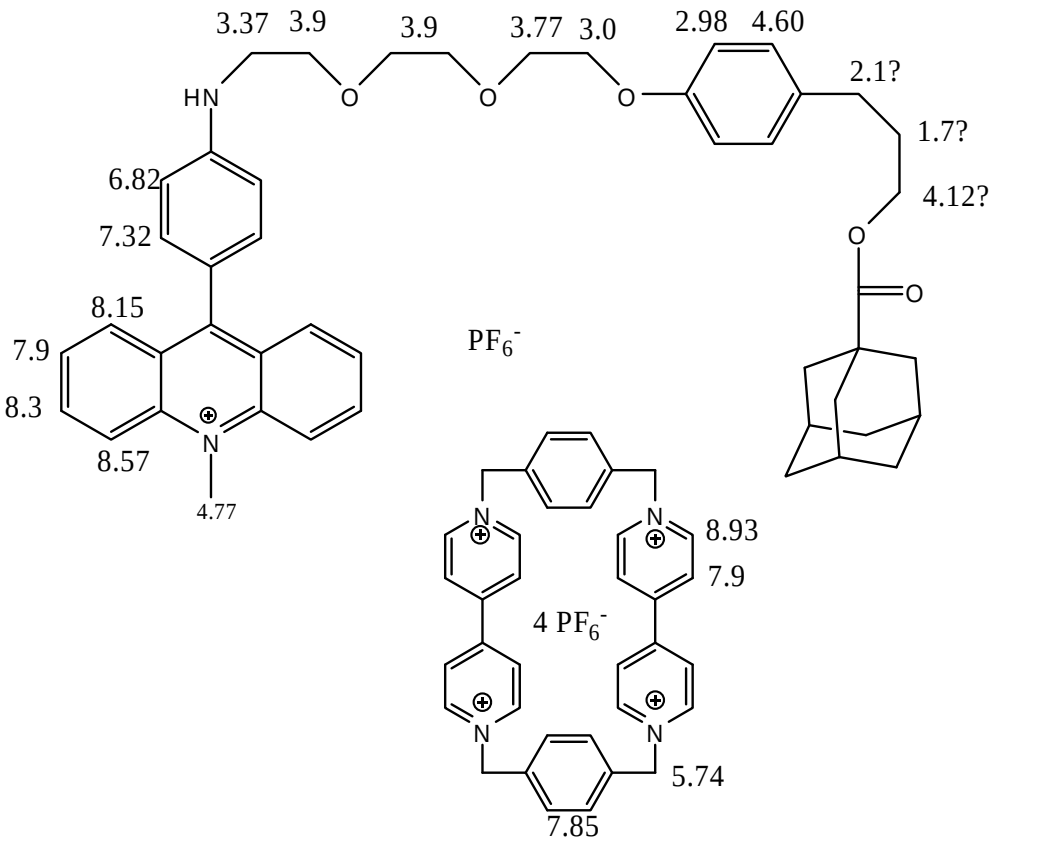


Figure 9 ^{1}H NMR spectra of rotaxane **42** (CD_3OD/CD_3CN 5:1) at 298 (a) and 233 K (b).



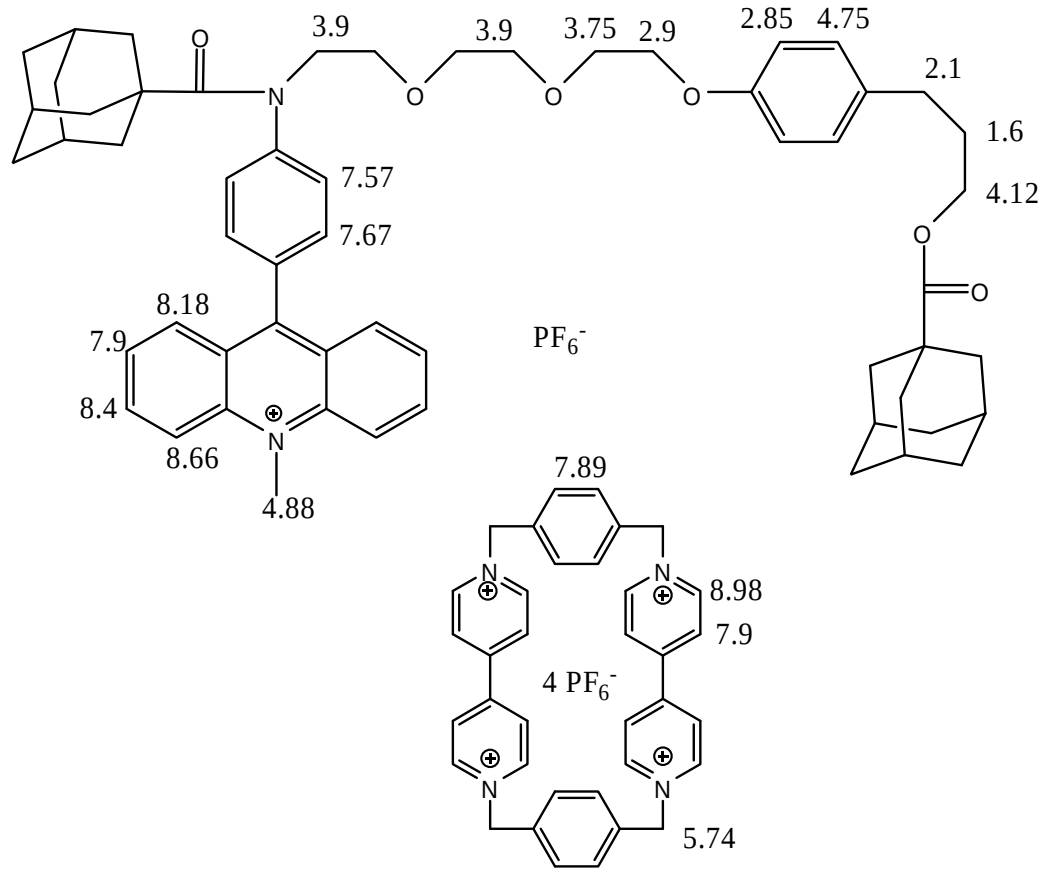


Figure 10 Assignment of proton resonances of rotaxanes **35** and **36**

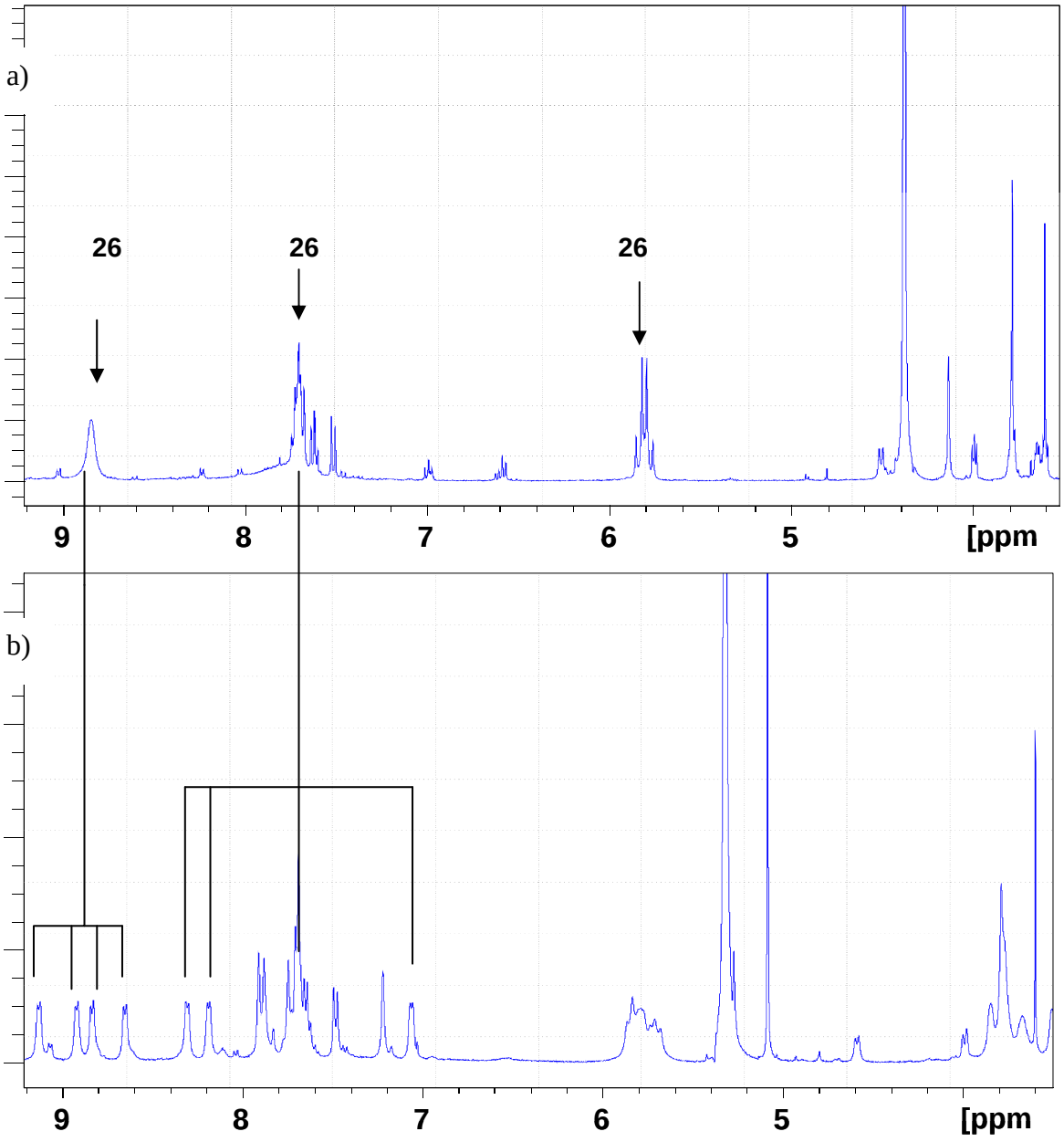


Figure 11 ^{1}H NMR spectra of **40** at 273 K (a) and 213 K (b)

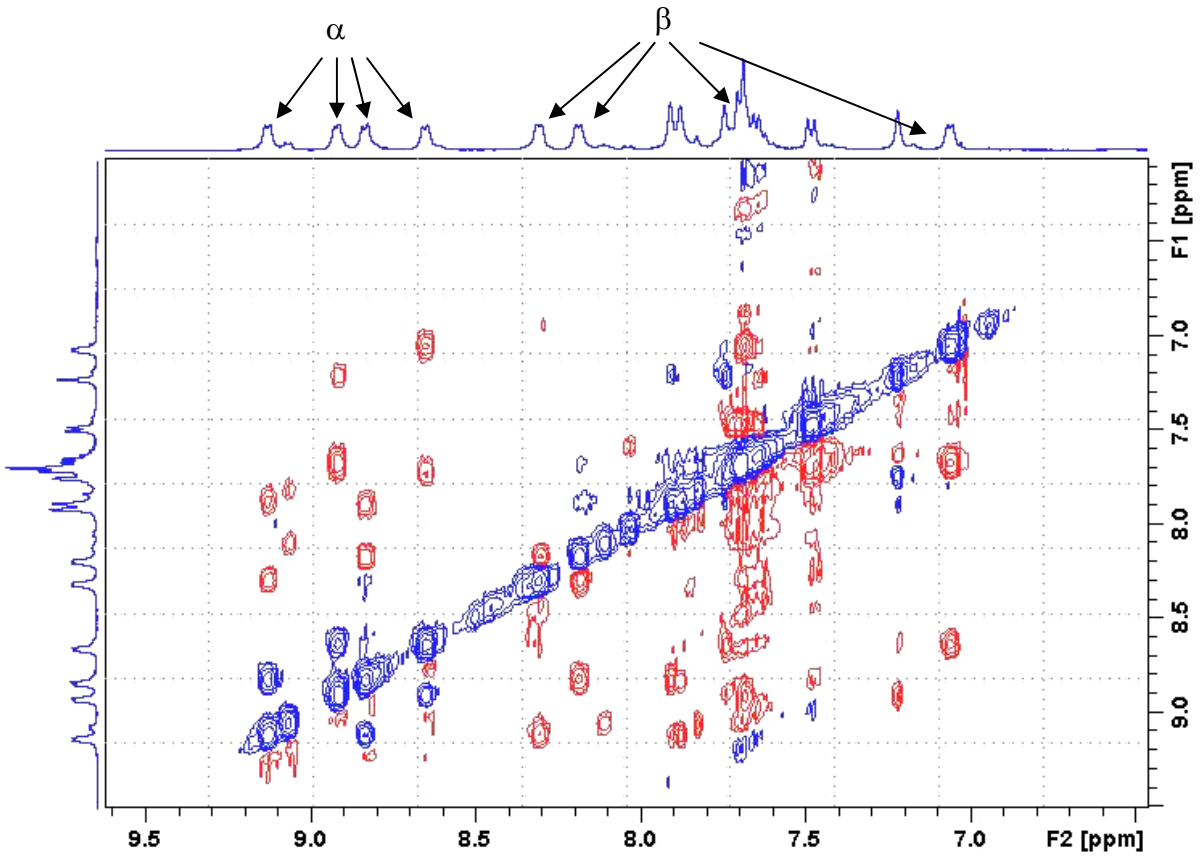


Figure 12 Partial ROESY-spectrum of **40** in CD_3OD/CD_3CN (5:1) at 233 K (blue: exchange peak; red: NOE; α and β denote the protons of the cyclophane **26** with respect to N^+).

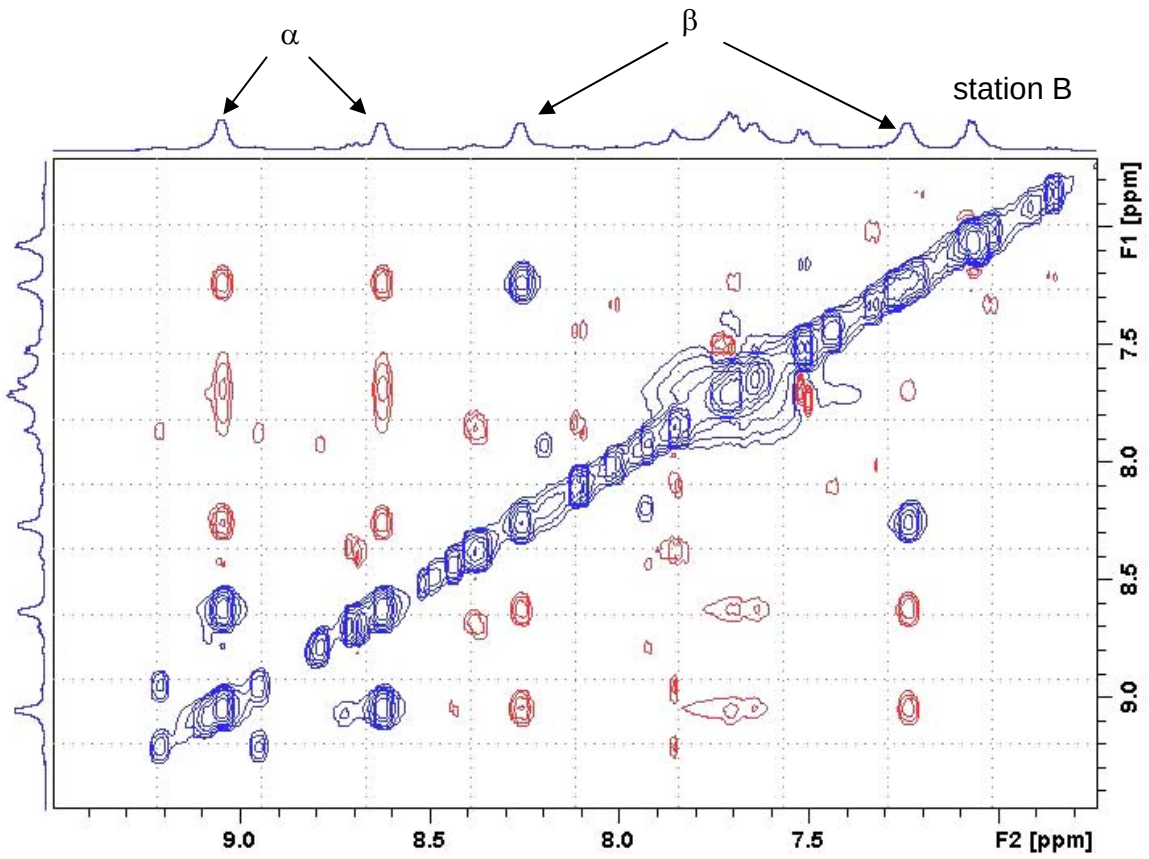


Figure 13 Partial ROESY-spectrum of **42** in CD_3OD/CD_3CN (5:1) at 233 K (blue: exchange peak; red: NOE; α and β denote the protons of the cyclophane **26** with respect to N^+).

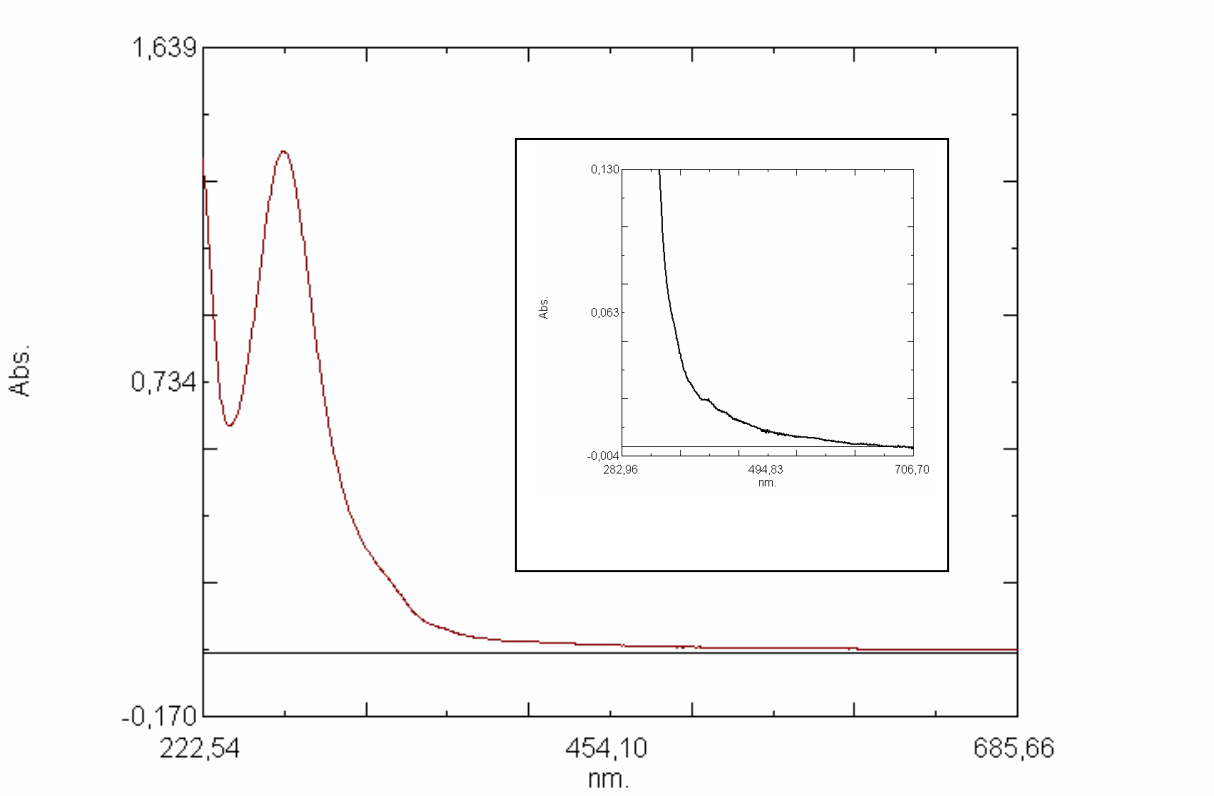


Figure 14 UV-Vis spectrum of the rotaxane **43** ($2x10^{-5}$ M) in methanol solution (inset: increased long wavelength region).

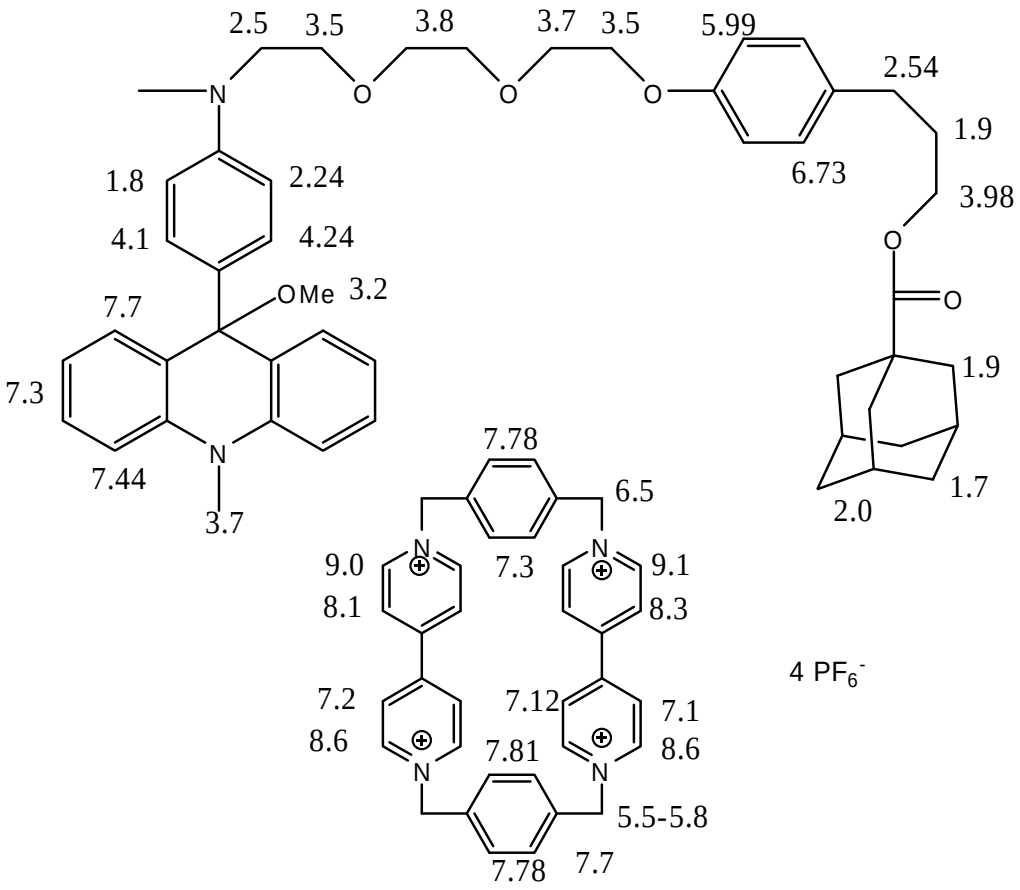


Figure 15 Assignment of proton resonances of the rotaxane **43** based on two-dimensional ^{1}H-NMR spectroscopy (COSY and ROESY) at 233 K

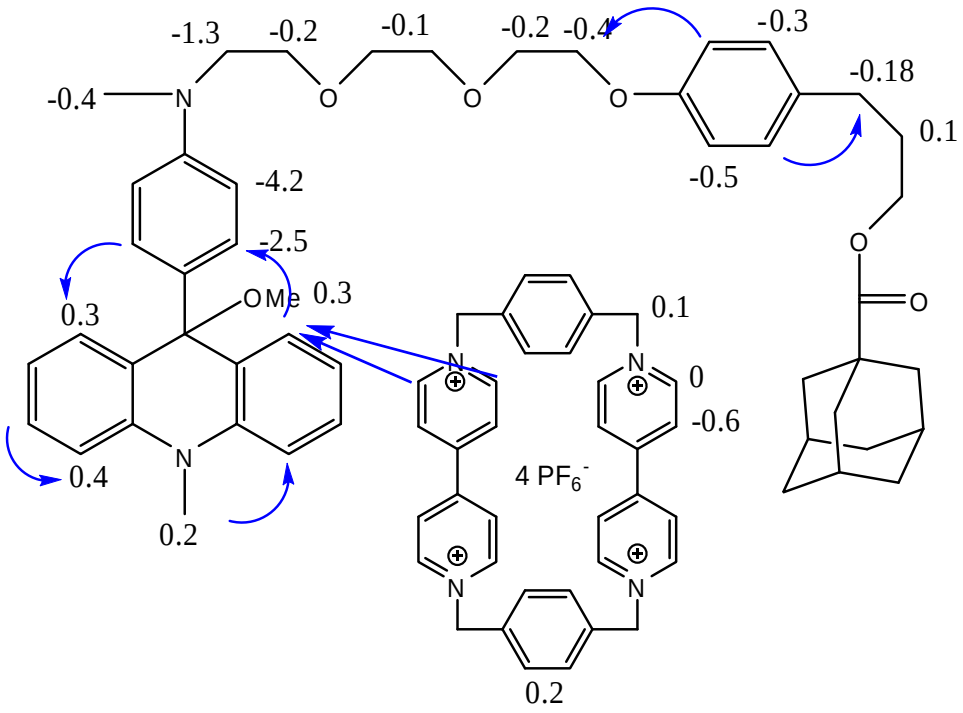


Figure 16 Chemical shift differences of proton resonances of rotaxane **43** obtained by comparison of the proton resonances of compounds **24** and **26** with related proton resonances observed in the rotaxane ($\delta_{\text{rotaxane }\mathbf{43}} - \delta_{\text{free component}}$). Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra at 233 K.

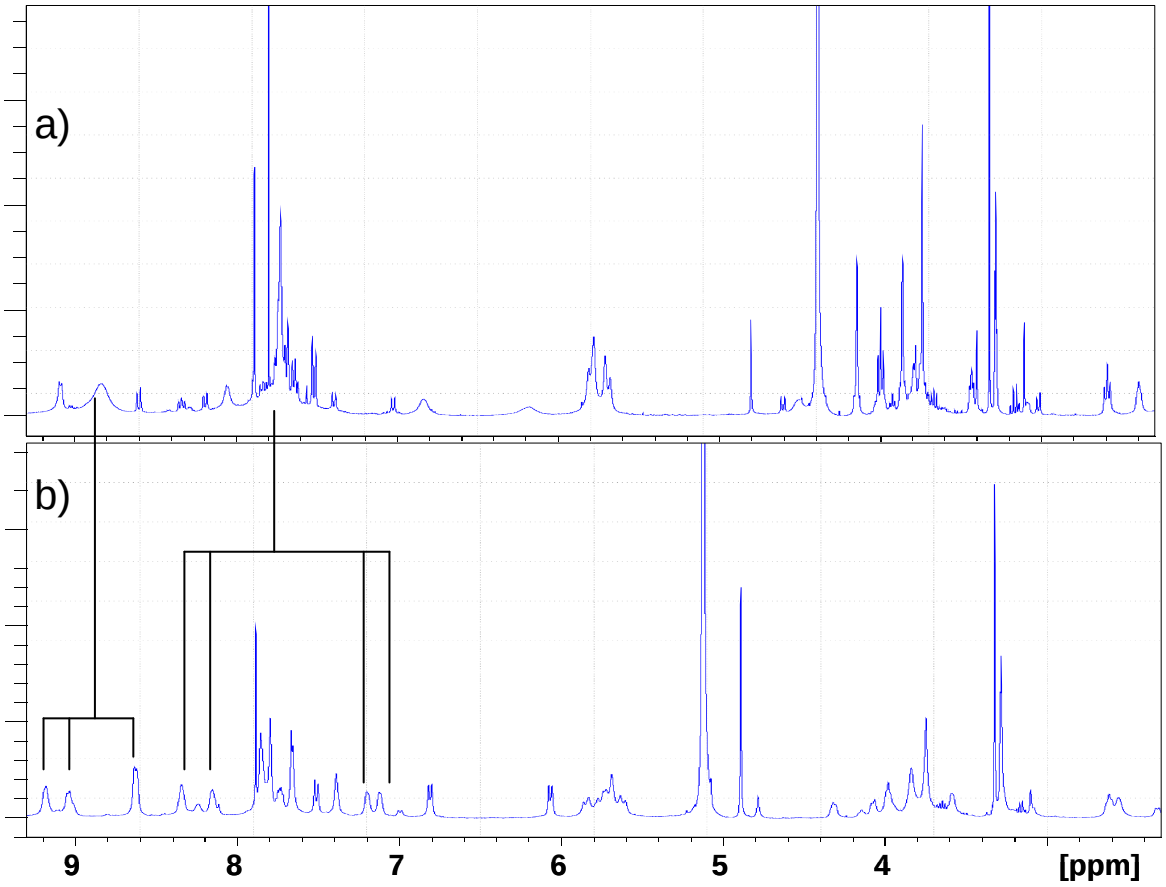


Figure 17 1H NMR spectra of **43** containing 30 % **37** in CD_3OD/CD_3CN (5:1) solution at 298 K (a) and 233 K (b)

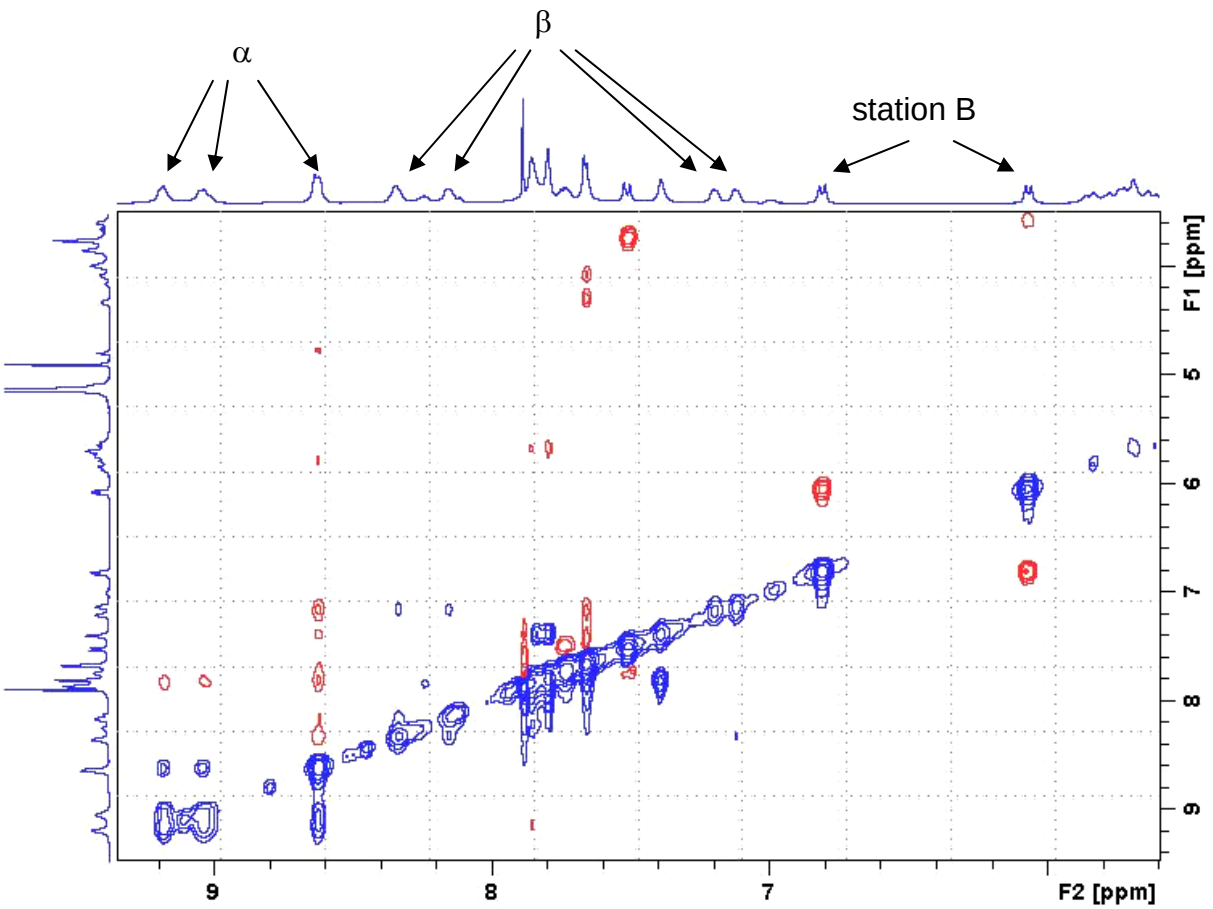


Figure 18 Partial ROESY-spectrum of **43** in CD_3OD/CD_3CN (5:1) at 233 K (blue: exchange peak; red: NOE; α and β denote the protons of the cyclophane **26** with respect to N^+).

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