Supplementary Material (ESI) for Organic & Biomolecular Chemistry


**Supporting Information**

# Photoswitchable rotaxanes on gold nanoparticles

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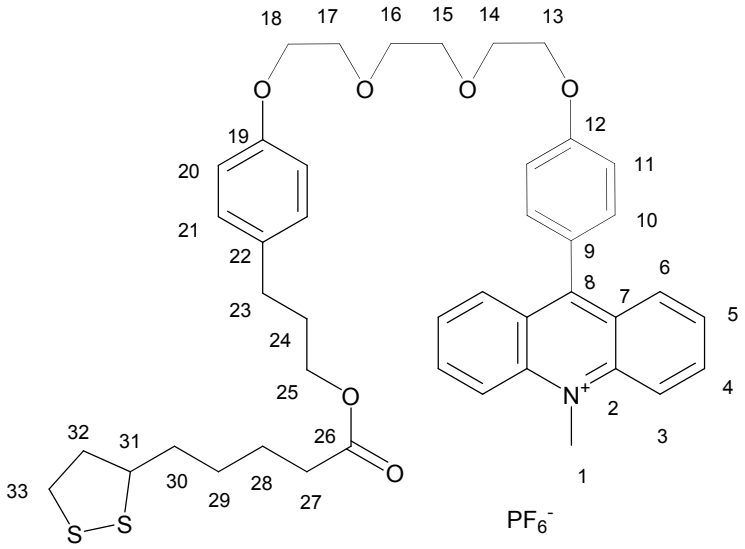
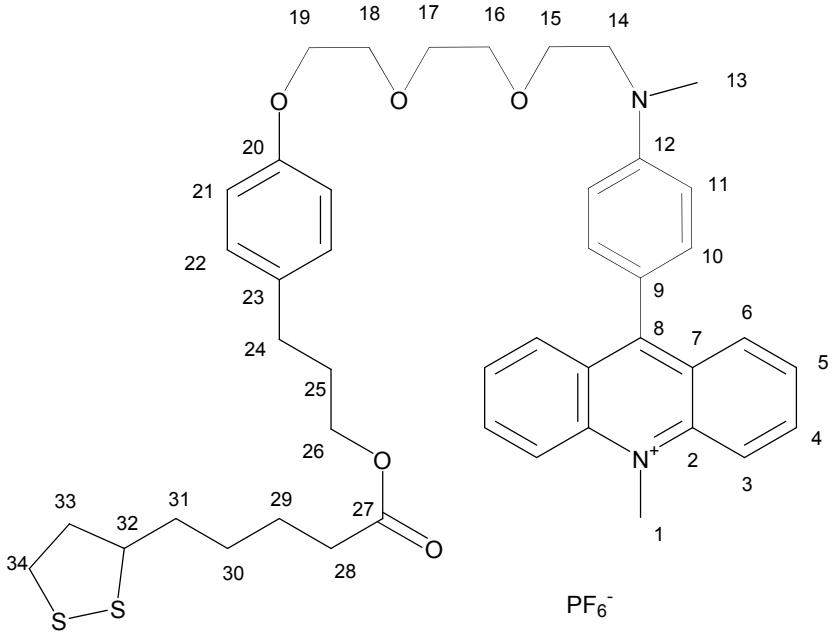
NMR signals of new compounds. Preparation and functionalization of Au-NPs.
UV-vis and NMR spectra of selected compounds and transients; Assignment of protons of rotaxanes **12** and **13;** Assignment of protons of rotaxanes **5**/**CBQT**$^{4+}$**, 6**/**CBQT**$^{4+}$ **13** on Au-NP,
Transient decay curves of rotaxanes **6**/**CBQT**$^{4+}$ and **13**.

**9-(4-(2-(2-(2-(4-(3-(5-(1,2-Dthiolan-3-yl) pentanoyloxyl) propyl) phenoxy) ethoxy)ethoxy)ethoxy)phenyl)-10-methylacridinium hexafluorophosphate** (**2**)



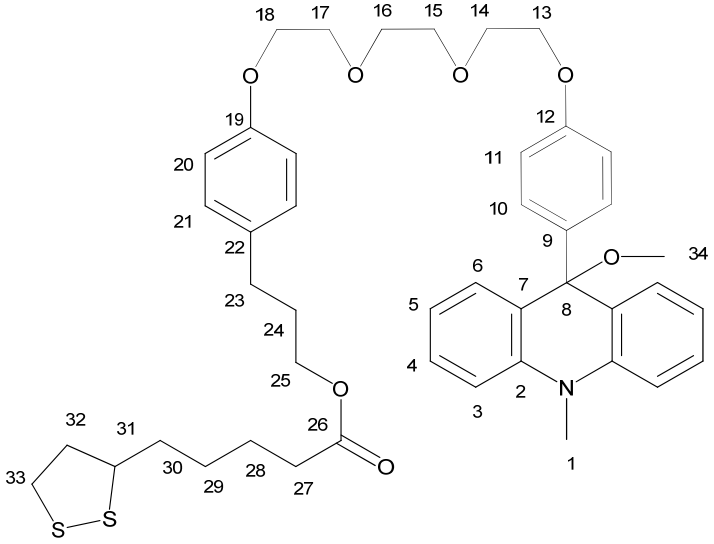

$^{1}$H-NMR (400MHz,$CDCl_3$): δ=8.61(d, *J* = 9 Hz, 2 H;H-3), 8.34 (m, 2 H; H-4), 8.09 (dd, *J* = 1, 9 Hz, 2 H; H-6), 7.78(m, 2 H; H-5), 7.41 (d, *J* = 9.0 Hz, 2 H; H-10), 7.21 (d, *J* = 8.9 Hz, 2 H; H-11), 7.08 (d, J = 8.8 Hz, 2 H; H-21), 6.85 (d, *J* = 8.8 Hz, 2 H; H-20), 4.93 (s, 3 H; H-1), 4.31 (m, 2 H; H-13), 4.13 (m, 2 H; H-18), 4.05 (m, 2 H; ethyleneoxy), 3.98 (m, 2 H; ethyleneoxy), 3.89 (t, J = 6.3 Hz, 2 H; $OCH_2$), 3.81 (m, 4 H; ethyleneoxy), 3.56(m,1H; H-31), 3.11 (m, 2 H; H-33), 2.60 (m, 2 H; H-23), 2.45 (m, 1 H; H-32), 2.31 (t, *J* = 7.2 Hz, 2 H; H-27), 1.89 (m, 3 H; H-24,H-32), 1.57 (m, 4 H; H-28,H-30), 1.4 (m, 2 H; H-29);
$^{13}$C-NMR(100 MHz, $CDCl_3$): δ=178.5, 173.5, 161.8, 160.5, 156.7, 141.4, 138.9, 133.4, 131.6, 130.3, 129.2, 127.6, 126.1, 124.8, 118.3, 115.1, 70.8, 70.7, 69.7, 69.5, 67.7, 63.5, 56.3, 49.2, 40.1, 38.6, 34.0, 33.7, 33.5, 31.1, 30.3, 28.6, 25.4.

**9-(4-(2-(2-(2-(4-(3-(5-(1,2-Dithiolan-3-yl)pentaoyloxy)propyl)phenoxy) ethoxy)ethoxy)ethyl)methylamino)phenyl)-10-methylacridinium hexafluorophosphate (4)**




$^{1}$H-NMR (400MHz, $CDCl_3$): δ=8.55 (d, *J* = 9.2 Hz, 2 H; H-3), 8.32 (m, 2 H; H-4), 8.23 (d, *J* = 8.7 Hz, 2 H; H-6), 7.74 (m, 2 H; H-5), 7.36 (d, *J* = 8.7 Hz, 2 H; H-10), 7.00 (m, 4 H; H-11, H-22), 6.79 (d, *J* = 8.3 Hz, 2 H; H-21), 4.86 (s, 3 H; H-1), 4.08 (m, 2 H; ethyleneoxy), 3.85 (t, *J* = 6.3 Hz, 2 H; H-26), 3.71 (m, 8 H; ethyleneoxy), 3.57 (m, 3H; $NCH_2$, H-32), 3.19 (s, 3 H; H-13), 3.11 (m, 2 H; H-34), 2.59 (t, *J* = 7.4 Hz, 2 H; H-24), 2.46 (m, 1 H; H-33), 2.31 (t, *J* = 7.1 Hz, 2 H; H-28), 1.91 (m, 3 H; H-25, H-33), 1.6 (m, 4 H; H-29, H-31), 1.4 (m, 2 H; H-30); $^{13}$C-NMR (100MHz, $CDCl_3$): δ=173.5, 157.0, 141.5, 138.5, 133.4, 132.8, 131.0, 129.2, 127.2, 125.9, 118.1, 114.5, 70.8, 70.7, 69.8, 67.4, 63.6, 56.3, 40.2, 38.4, 38.3, 34.5, 34.0, 31.1, 30.31, 28.7, 24.6.

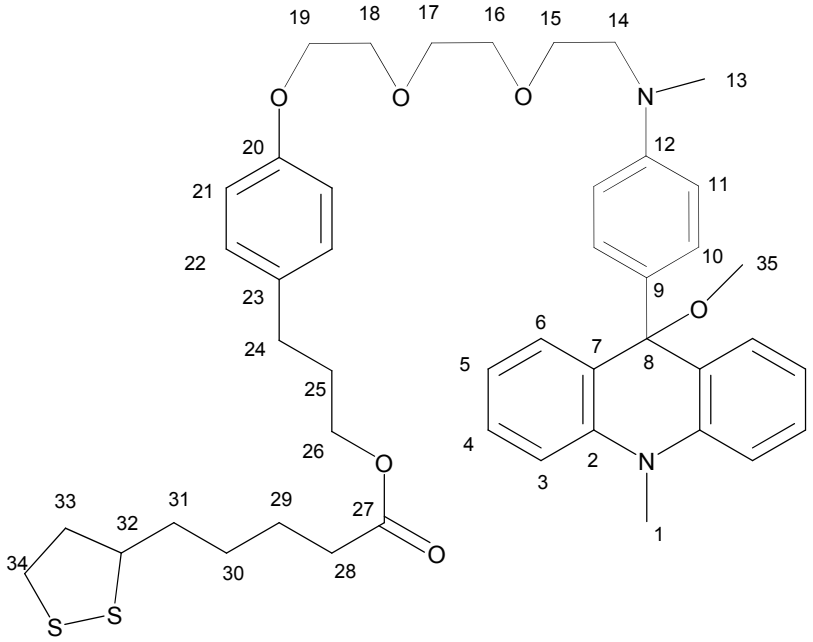
**3-(4-(2-(2-(2-(4-Methoxy-10-methyl-4a,9,9a,10-tetrahydroacdrin-9-yl)phenoxy)ethoxy)ethoxy)ethoxy)phenyl)propyl-5-(1,2-dithiolan-3-yl)pentanoate (5)**




$^{1}$H-NMR (400MHz, $CD_3CN$): δ=7.25 (m, 4 H; H-4, H-6), 7.18 (d, J = 8.6 Hz, 2 H; Ar), 7.13 (d, J = 8.3 Hz, 2 H; H-3), 7.05 (d, *J* = 8.5 Hz, 2 H; Ar), 6.9 (m, 2 H; H-5), 6.79 (d, J = 8.7 Hz, 2 H; Ar), 6.72 (d, J = 9 Hz, 2 H; Ar), 3.98 (m, 4 H; ethyleneoxy), 3.68 (m, 4 H; ethyleneoxy), 3.57 (m, 5 H; ethyleneoxy, H-31), 3.46 (m, 5 H; H-1, H-25), 3.1 (m, 5 H; H-33, H-34), 2.57 (m, 2 H; H-23), 2.45 (m, 1 H; H-32), 2.39 (m, 2 H; H-27), 1.8 (m, 3 H; H-24, H-32), 1.6 (m, 4 H; H-28, H-30), 1.4 (m, 2 H; H-29);

$^{13}$C-NMR (100MHz, $CD_3CN$): δ= 173.2, 157.2, 156.9, 142.9, 141.0, 134.6, 133.7, 129.4, 129.3, 126.8, 124.5, 120.1, 114.4, 113.6, 112.7, 77.9, 71.1, 70.3, 69.4, 69.3, 67.4, 67.2, 63.2, 60.9, 56.4, 51.0, 49.5, 40.08, 38.3, 33.3, 33.1, 30.8, 28.5, 24.5.

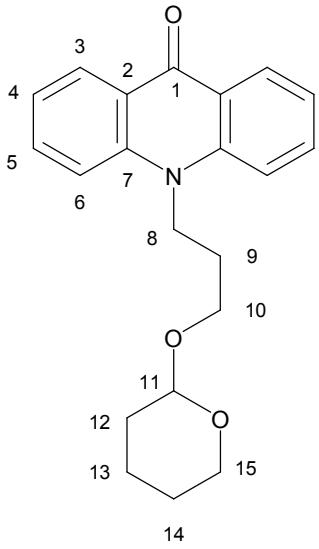
**3-(4-(2-(2-(2-(4-Methoxy-10-methyl-9,10-dihydroacdrin-9-yl)phenyl) methylamino)ethoxy)ethoxy)ethoxy)phenyl)propyl-5-(1,2-dithiolan-3-yl)pentanoate (6)**




$^{1}$H-NMR (400 MHz, $CD_3CN$): δ=7.42 (m, 4 H; H-4,H-6), 7.12 (d, *J* = 7.5 Hz, 2 H; H-3), 6.96 (m, 2 H; Ar), 6.84 (m, 2 H; H-5), 6.75 (d, *J* = 8.5 Hz, 2 H; Ar), 6.55 (d, *J* = 8.3 Hz, 2 H; Ar), 4.1 (m, 2 H; ethyleneoxy), 3.8 (m, 4 H; ethyleneoxy), 3.5 (m, 11 H; ethyleneoxy, H-14, H-26, H-32), 3.31 (s, 3 H, H-1), 3.23 (s, 3 H; H-35), 3.1 (m, 2 H; H-34), 3.13 (s, 3 H; H-13), 2.5 (m, 2 H; H-24), 2.44 (m, 1 H; H-33), 2.3 (m, 2 H; H-28), 1.8 (m, 3 H; H-25, H-33), 1.6 (m, 4 H; H-29, H-31), 1.4 (m, 2H; H-30);

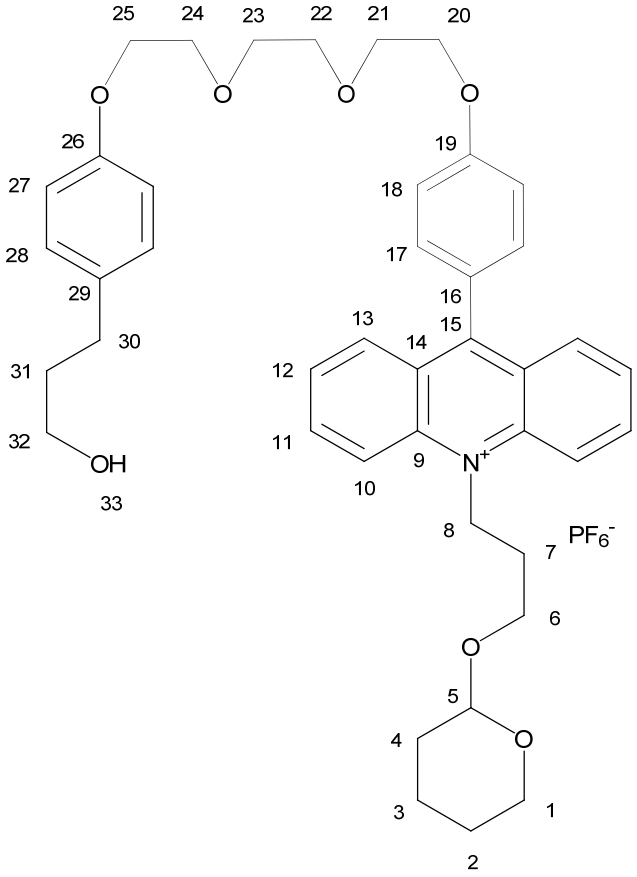
$^{13}$C-NMR (100MHz, $CDCl_3$): δ=157.1, 147.8, 141.0, 138.1, 134.6, 133.2, 129.4, 129.3, 128.5, 128.22, 126.4, 125.0, 120.0, 114.4, 112.1, 111.2, 78.0, 70.3, 69.4, 68.1, 67.4, 63.2, 60.9, 56.4, 51.82, 50.5, 43.3, 40.1, 38.3, 34.6, 33.3, 32.8, 30.8, 30.3, 28.4, 24.4.

**10-(3-(tetrahydro-2H-pyran-2yloxy)propyl)acridin-9(10H)-one** (**7**)




$^{1}$H-NMR (400MHz,$CDCl_3$): δ=8.58 (dd, J = 1.6; 7.92 Hz, 2 H; H-3), 7.71 (m, 2H; H-5), 7.64 (m, 2 H; H-6), 7.29 (m, 2 H; H-4), 4.65 (m, 1 H; H-11), 4.56 (m, 2 H; H-8), 4.0 (m, 1 H; H-15), 3.9 (m, 1 H, H-15), 3.56 (m, 2 H; H-10), 2.22 (m, 2 H; H-9), 1.9 (m, 1 H; H-14), 1.7 (m, 3 H; H-14, H-12), 1.6 (m, 2 H; H-13), $^{13}$C-NMR (100 MHz, $CD_3CN$): δ=177.5, 142.3, 134.2, 127.2, 122.5, 121.4, 115.8, 99.2, 64.5, 62.2, 43.5, 30.9, 27.7, 25.6, 19.7.

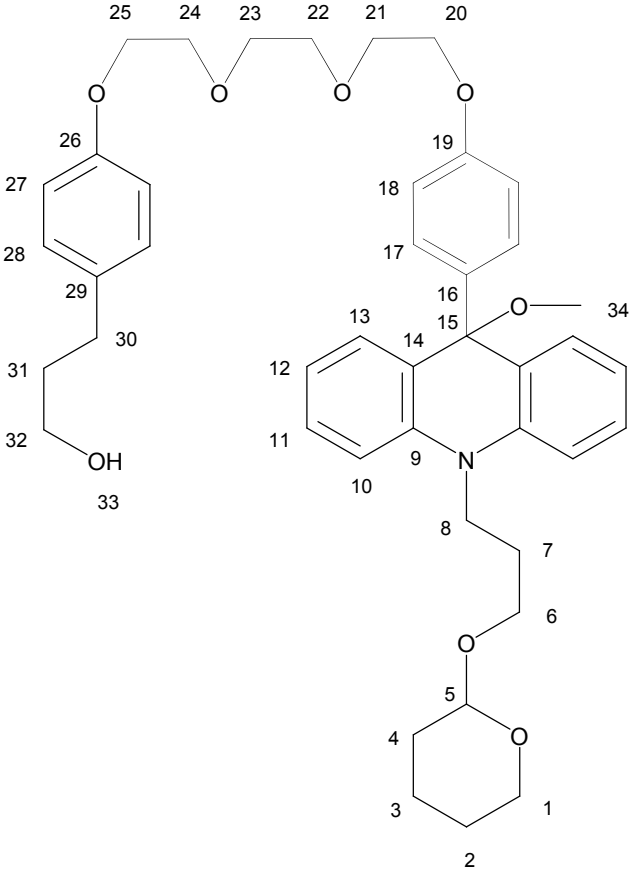
**9-(4-(2-(2-(2-(4-(3-Hydroxypropyl))phenoxy)ethoxy)ethoxy)ethoxy)phenl)-10-(3-(tetrahydro-2H-pyran-2-yloxy)propyl)acridinium hexafluorophosphate (9)**




$^{1}$H-NMR (400 MHz, $CD_3CN$): δ=8.64 (d, *J* = 9.5 Hz, 2 H; H-10), 8.35 (m, 2 H; H-11), 8.09 (d, *J* = 11.8 Hz, 2 H; H-13), 7.82 (m, 2 H; H-12), 7.41 (d, *J* = 9.4 Hz, 2 H; H-17), 7.27 (d, *J* = 9.4 Hz, 2 H; H-18), 7.06 (d, *J* = 9.4 Hz, 2 H; H-28), 6.82 (d, *J* = 9.4 Hz, 2 H; H-27), 5.45 (m, 2 H; H-8), 4.62 (m, 2 H; H-5), 4.2 (m, 2 H; ethyleneoxy), 4.1 (m, 2 H; ethyleneoxy), 3.9 (m, 2 H; ethyleneoxy), 3.8 (m, 2 H; ethyleneoxy), 3.7 (m, 6 H; ethyleneoxy, H-6), 3.4 (m, 4 H; H-1, H-32), 2.4-2.6 (m, 4 H; H-7, H-30), 1.7 (m, 4 H; H-4,H-31), 1.6 (m, 4 H; H-2, H-3),

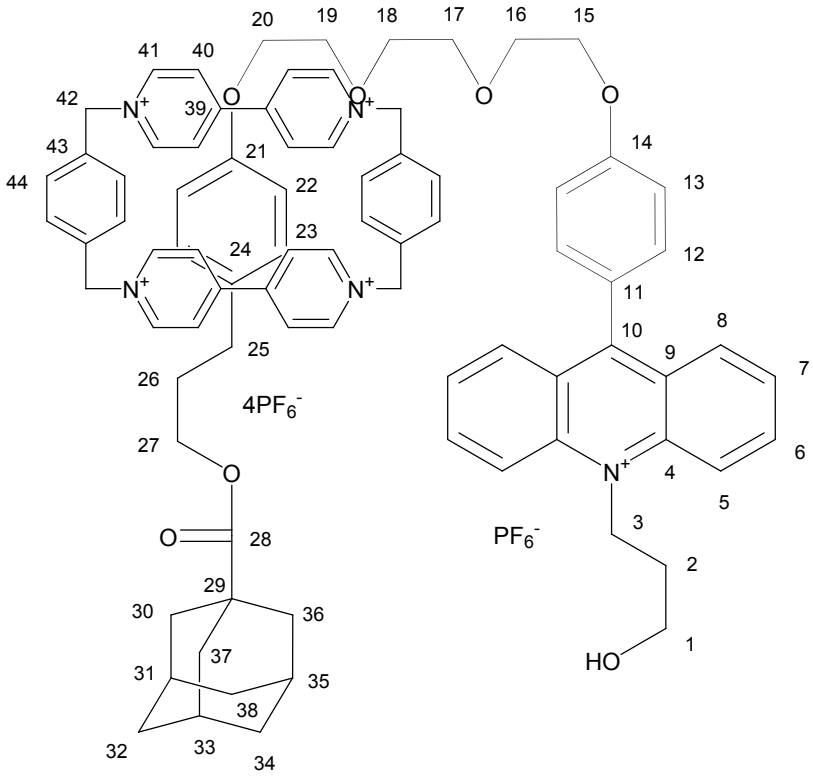
$^{13}$C-NMR (100 MHz, $CD_3CN$): δ=160.6, 159.5, 156.8, 140.0, 136.0, 133.7, 129.8, 129.3, 125.3, 125.1, 124.8, 124.3, 118.6, 115.0, 114.5, 99.5, 71.5, 70.0, 69.3, 64.8, 63.3, 62.5, 59.8, 33.5, 31.8, 30.6, 26.4, 25.5, 20.9.

**3-(4-(2-(2-(2-(4-(9-Methoxy-10-(3-(tetrahydro-2H-pyran-2yloxy)propyl)-9,10-dihydroacridin-9-yl)phenoxy)ethoxy)ethoxy)ethoxy)phenyl)propan-1-ol** (**10**)




$^{1}$H-NMR (400MHz, $CD_3CN$): δ=7.24-7.18 (m, 6 H; acridane), 7.12 (d, *J* = 9.0 Hz, 2 H; H-28), 7.07 (d, *J* = 9.0 Hz, 2 H; H-28), 6.9 (m, 2 H; acridane), 6.78 (d, *J* = 9.0 Hz, 2 H; H-18), 6.73 (d, *J* = 9.0 Hz, 2 H; H-27), 4.61 (m, 1 H; H-5), 4.1 (m, 2 H; ,H-8), 4.0 (m, 4 H; ethyleneoxy), 3.8 (m, 2 H; H-1), 3.7 (m, 4 H; ethyleneoxy), 3.6 (m, 2 H; H-6), 3.57 (m, 2 H; H-32), 2.86 (s, 3 H; H-34), 2.6 (m, 2 H; H-30), 2.1 (m, 2 H; H-7), 1.7 (m, 2 H; H-4), 1.5-1.6 (m, 4 H; H-3, H-4), $^{13}$C-NMR (100 MHz, $CD_3CN$): δ=159.5, 156.8, 140.0, 136.0, 133.7, 129.8, 129.3, 125.3, 125.1, 124.8, 124.3, 118.6, 115.0, 114.5, 98.8, 87.6, 71.5, 70.0, 69.3, 64.8, 63.3, 62.5, 50.5, 42.8, 33.5, 31.8, 30.6, 26.5, 25.5, 20.9.

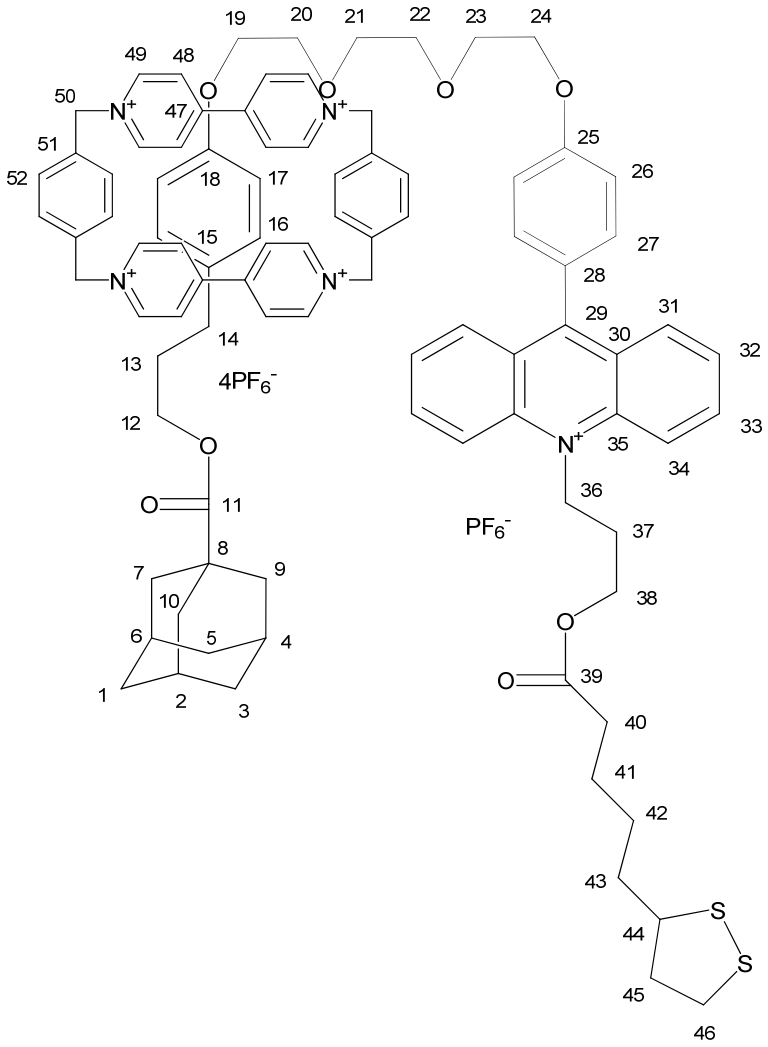
**Rotaxane 11**




$^{1}$H-NMR (400MHz, $CD_3CN$): δ=8.91 (d, *J* = 8.0 Hz, 8 H; H-41), 8.65 (d, *J* = 9.7 Hz, 2 H; H-5), 8.38 (m, 2 H; H-6), 7.91 (d, *J* = 8.0 Hz, 2 H; H-8), 7.9 (s, br, 8 H; H-40), 7.87 (m, 10 H; H-7, H-44), 7.33 (d, *J* = 9.5 Hz, 2 H; H-12), 6.96 (d, *J* = 9.6 Hz, 2 H; H-13), 5.79, 5.76, 5.72, 5.69 (m, 8 H; H-42), 5.42 (m, 2 H; H-3), 4.55(d, *J* = 9.4 Hz, 2 H; 23), 4.28 (m, 2 H; ethyleneoxy), 4.08 (t, J = 7.1 Hz, 2 H; H-27), 4.1 (m, 4 H; ethyleneoxy), 3.96 (m, 2 H; ethyleneoxy), 3.84 (m, 2 H; H-1), 3.76 (m, 2 H; ethyleneoxy), 2.98 (m, br, 2 H; ethyleneoxy), 2.92 (d, J = 9.3 Hz, 2 H; H-22), 2.33 (m, 2 H; H-2), 2.1 (m, 5 H; H-25, adamantane), 2.0 (m, 6 H; adamantane), 1.8 (m, 6 H; adamantane), 1.66 (m, 2 H; H-26),

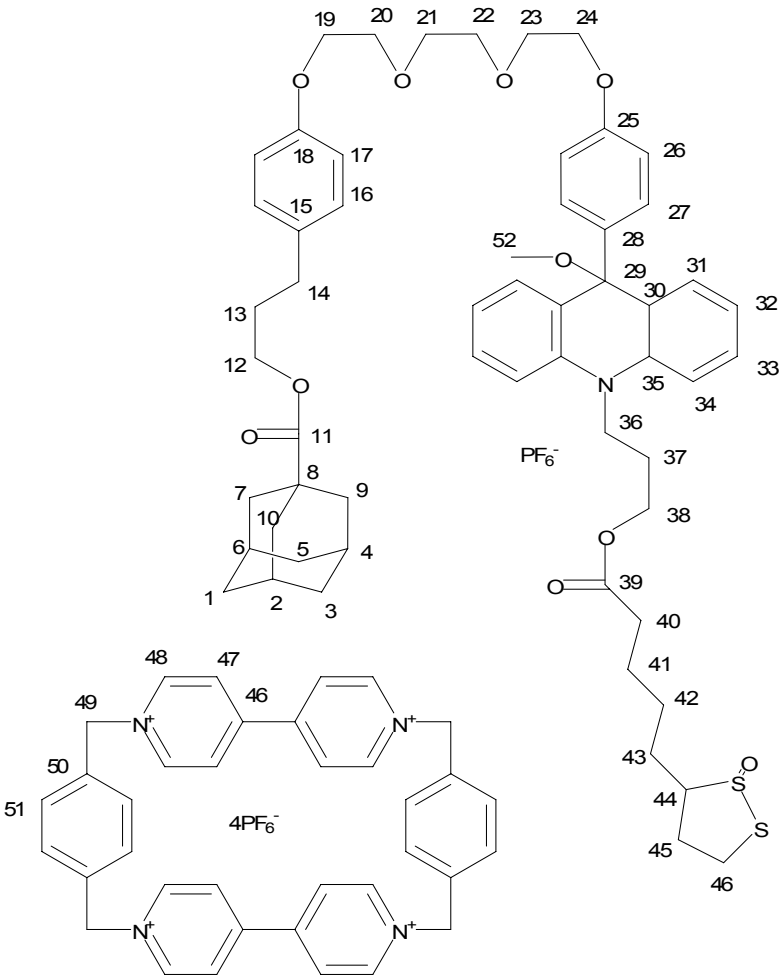
$^{13}$C-NMR(400MHz,$CD_3CN$): δ=177.2(C-28), 160.8(C-10), 159.4(C-14), 157.7(C-21), 150.7(C-39), 144.6(C-41), 139.9(C-4), 138.4(C-6), 133.8(C-24), 131.4(C-43), 130.5(C-12), 130.4(C-13), 128.9(C-44), 128.7(C-7), 128.1(C-8), 128.1(C-23), 126.5(C-40), 125.1(C-11), 124.7(C-9), 117.9(C-5), 111.5(C-22), 70.5(C-17,C-18), 70.4(C-16), 69.2(C-19), 67.3(C-15), 66.7(C-20), 63.2(C-27), 59.6(C-42), 57.8(C-1), 47.9(C-3), 38.5(C-32,C-34,C-38), 35.8(C-30,C-36,C-37), 30.8(C-25), 29.6(C-26), 27.6(C-31,C-33,C-35).

**Acridinium Rotaxane 12**




$^{1}$H-NMR (400MHz, $CD_3CN$): δ=8.91(d, *J* = 6.8 Hz, 8 H; H-49), 8.56 (d, *J* = 9.0 Hz, 2 H; H-34), 8.37 (m, 2 H; H-33), 7.98 (d, *J* = 8.3 Hz, 2 H; H-31), 7.89 (s br, 8H; H-48), 7.83 (m, 10 H, H-32, H-52), 7.33 (d, *J* = 8.8 Hz, 2 H; H-27), 6.97 (d, *J* = 8.8 Hz; H-26), 5.75 (m, 8 H; H-50), 5.41 (t br, 2 H; H-36), 4.53 (d, J = 8.7 Hz, 2 H; H-16), 4.3 (t br, 2 H; H-38), 4.3 (m br, 2 H; H-24), 4.08 (t, *J* = 7.9 Hz, 2 H; H-12), 4.0 (m br, 4 H; ethyleneoxy), 3.96 (m br, 2 H; ethyleneoxy), 3.75 (m br, 2 H; ethyleneoxy), 3.5 (m, 1 H; H-44), 3.1 (m, 2 H; H-46), 3.0 (m br, 2 H; ethyleneoxy), 2.92 (d, *J* = 8.6 Hz, 2 H; H-17), 2.49 (m, 3 H; H-37, H-45), 2.35 (m, 2 H; H-40), 2.0 (m, 5 H; H-14, adamantane), 1.9 (s br, 7 H; H-45, adamantane), 1.8 (m, 7 H; H-13, adamantane), 1.6 (m, 4 H; H-41, H-43), 1.4 (m, 2 H; H-42), $^{13}$C-NMR (100 MHz, $CD_3CN$): δ=177.2, 173.1, 160.8, 159.4, 139.9, 139.7, 133.6, 132.9, 131.6, 128.7, 126.5, 125.1, 124.7, 119.1, 115.7, 112.8, 71.8, 71.7, 70.6, 68.8, 68.1, 64.5, 62.1, 48.9, 39.7, 38.5, 37.2, 37.1, 36.9, 35.5, 30.9, 30.7, 29.9, 28.2, 27.7.

**Acridane Rotaxane 13**




$^{1}$H-NMR (400MHz, $CD_3CN$/MeOD 3:1, 233 K) ($^{13}$C, 100 MHz): δ=8.94 (143.5) (s br, 4 H; H-48), 8.54 (142.6) (s br, 4 H; H-48), 8.13 (126.2) (s br, 4 H; H-47), 7.9 – 7.4 (129.5, 129.0, 126.0, 120, 111.8) (m br, 16 H; H-31-H-34, H-51), 6.86 (125.0) (s br, 4 H; H-47), 6.74 (125.9) (d br, 2 H; H-16), 5.9 (112.2) (d br, 2 H; H-17), 5.7 (64.6) (m, 8 H; H-49), 4.38 (125.8) (d br, 2 H; H-27), 4.3 (40.7, 60.8) ( s br, 4 H; H-36, H-38), 3.95 (61.7) (s br, 2 H; H-12), 3.8 (68.6) ( m, 4 H; ethyleneoxy), 3.7 (68.2) (m, 2 H; ethyleneoxy), 3.6 (68.2) (m, 3 H; H-44, ethyleneoxy), 3.4 (65.1) ( s br, 2 H; ethyleneoxy), 3.2 (46.9) ( s, 3 H; H-52), 3.1 (s br, 2 H; H-46), 2.7 (65.8) (s br, 2 H; ethyleneoxy), 2.6 (29.2) (s br, 3 H; H-14), 2.4 (32.5) (s br, 3 H; H-40, H-45), 2.0 (26.3) (s, 3 H; adamantane), 1.9 (39.2, 26.8) (s br, 7 H; H-45, adamantane), 1.8 (34, 30) (m, 8 H; H-13, adamantane), 1.6 (34, 23) (m, 6 H; H-41-H-43.

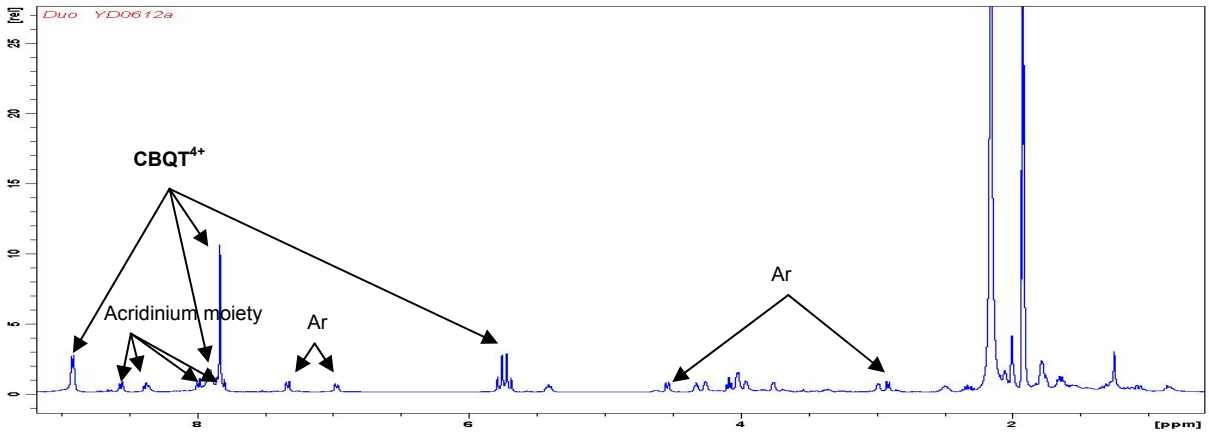



Figure S1. $^{1}$H NMR spectrum ($CD_3CN$) of rotaxane **12**

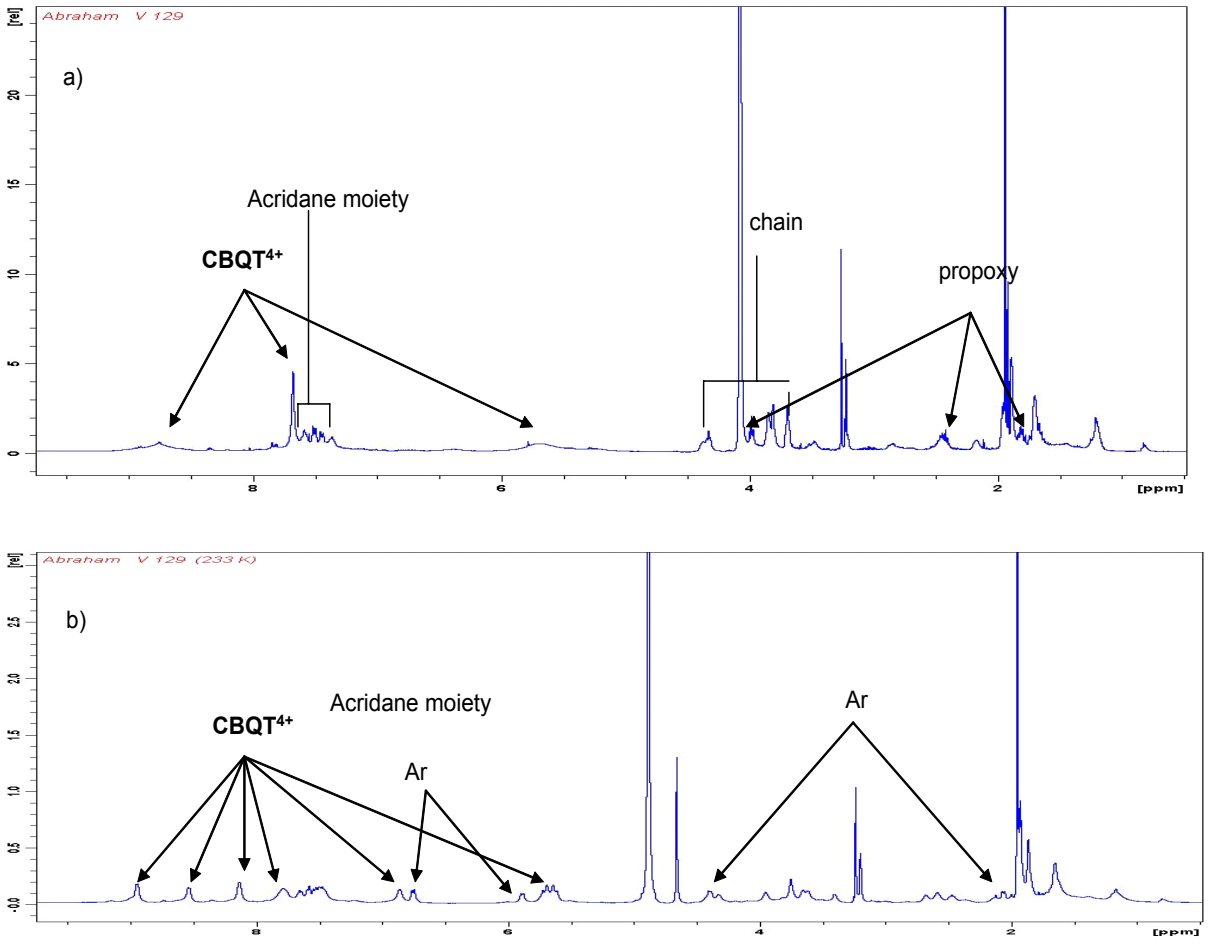
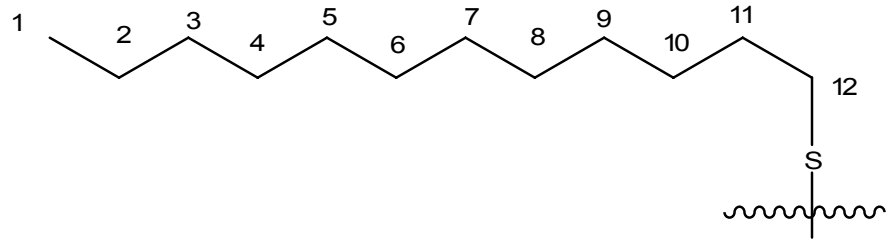



Figure S2. $^{1}$H NMR spectrum ($CD_3CN$) of rotaxane **13** at room temperature and at 233K ($MeOD/CD_3CN$ 3:1).

Colloidal Synthesis

Gold NPs: An aqueous solution of $HAuCl_4$ (0.31g, 0.91 mmol, 30 mL water) was mixed with solution of tetra-n-octylammonium bromide (2.18 g, 4 mmol) in toluene (80ml). The two-phase mixture was vigorously stirred until the aqueous layer was colorless. Dodecanthiol

(0.170 g, 0.84 mmol) was added to the organic layer. An aqueous solution of sodium borohydride (3.8 g, 100 mmol, 25 ml water) was added dropwise with vigorous stirring. After stirring for 4 h the organic phase was separated and the solvents were removed *in vacuo*. The residue was dissolved in toluene (10mL) and mixed with ethanol (400mL) to remove the excess of dodecanethiol. The mixture was kept at -18° overnight and a dark brown precipitate was collected by the centrifugation and washed with toluene and ethanol. The residue was dried *in vacuo* to give the thiol capped gold NPs as dark brown waxy solid (0.214 g). Gold NPs were redissolved in dichloromethane to give the gold NPs that have an averaged diameter, d = 2.8 nm (Figure S3).




$^1$H-NMR (400MHz, $CDCl_3$): δ= 1.56 (s, 18 H,), 1.28(s, 4 H; H-11,12), 0.88 (m, 3 H; H-1); $C_{12}H_{25}SAu_3$ (792.07), calcd (%): C 18.19, H 3.18, S 4.05; found (%) C 18.34, H 3.43; S 3.85.

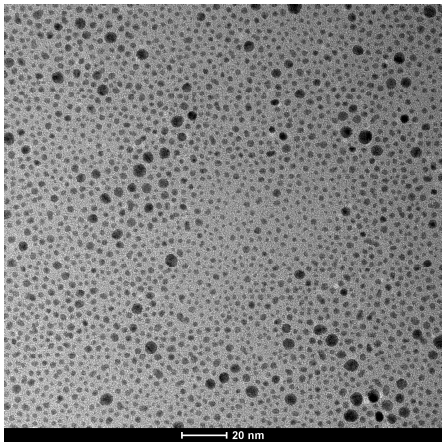


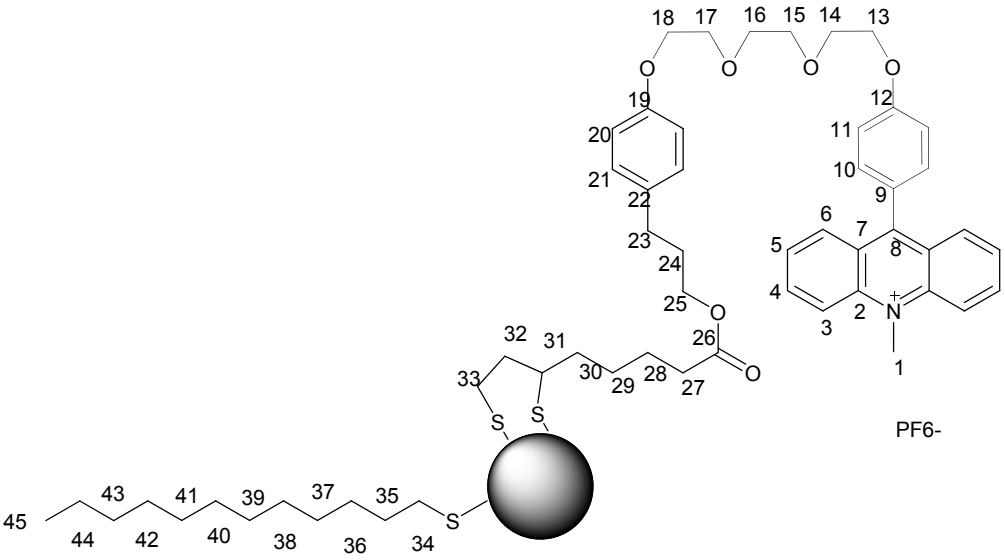

Figure S3. TEM image of the gold NPs. The scale bar corresponds to 20 nm.

Functionalization of gold NPs:

1. Dodacanethiol-capped gold nanoparticles (0.15 g) were redissolved in dichloromethane (1 mL). **2**, **4**, **5** or **6** (0.20 mmol) in MeCN (10 mL) were added. The mixture was stirred under argon for 3 days. After removal of solvents *in vacuo* the residue was washed with acetonitrile to remove free **2**, **4**, **5** or **6** and dodecanethiol until no absorption of

acridinium and acridane compounds, respectively, could be detected in washing solution by the help of UV-Vis-spectroscopy. The precipitate collected by the centrifugation was washed with dichloromethane to remove non-functionalized NPs, and dried *in vacuo* to give the functionalized gold NPs as dark yellow brown powders.

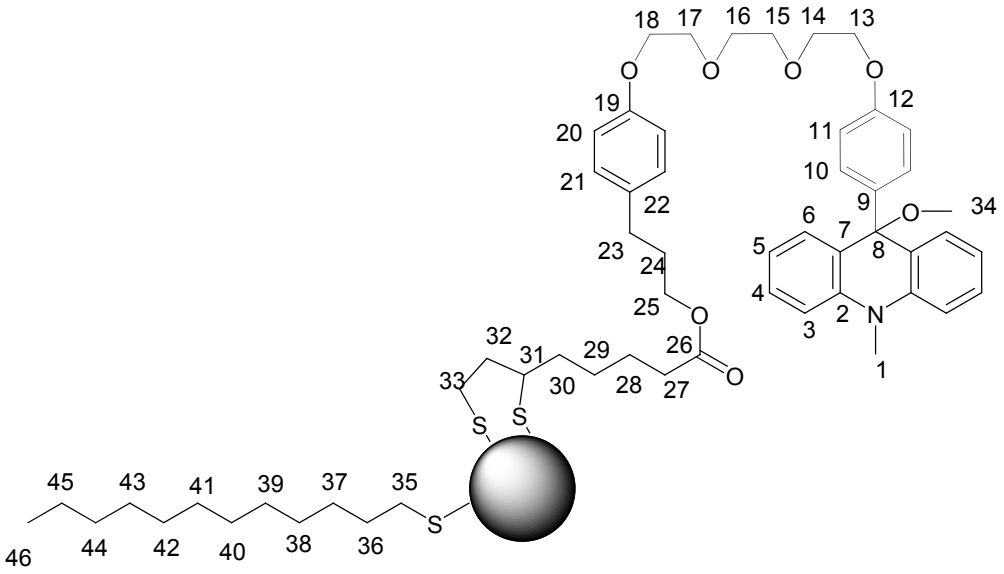
**Gold NPs capped with 2**




**2** (0.155 g, 0.2 mmol) and dodecanethiol-capped gold nanoparticles (0.160 g, 0.2 mmol) were treated according to the procedure described above to give the product as dark-yellow powder (0.110 g).

$^1$H-NMR (400MHz,$CDCl_3$): δ=8.61(d, *J* = 9 Hz, 2 H;H-3), 8.34 (m, 2 H; H-4), 8.09 (dd, *J* = 1, 9 Hz, 2 H; H-6), 7.78(m, 2 H; H-5), 7.41 (d, *J* = 9.0 Hz, 2 H; H-10), 7.21 (d, *J* = 8.9 Hz, 2 H; H-11), 7.08 (d, J = 8.8 Hz, 2 H; H-21), 6.85 (d, *J* = 8.8 Hz, 2 H; H-20), 4.93 (s, 3 H; H-1), 4.31 (m, 2 H; H-13), 4.13 (m, 2 H; H-18), 4.05 (m, 2 H; ethyleneoxy), 3.98 (m, 2 H; ethyleneoxy), 3.89 (t, J = 6.3 Hz, 2 H; $OCH_2$), 3.81 (m, 4 H; ethyleneoxy), 3.56(m,1H; H-31), 3.11 (m, 2 H; H-33), 2.60 (m, 2 H; H-23), 2.45 (m, 1 H; H-32), 2.31 (t, *J* = 7.2 Hz, 2 H; H-27), 1.89 (m, 3 H; H-24, H-32), 1.6 (m, 22 H; H-28, H-30, H-36 – H-44), 1.4 (m, 2 H; H-29), 1.28 (s, 4 H; H-34,35), 0.9 (m, 3 H; H-45); found (%): C 35.34, H 4.15, N 0.81, S 5.24.

**Gold NPs capped with 5**




**5** (0.155 g, 0.2 mmol) and dodecanethiol-capped gold nanoparticles (0.160 g, 0.2 mmol) afforded the product as dark brown solid (0.207 g).

$^1$H-NMR (400MHz, $CD_3CN$): δ=7.25 (m, 4 H; H-4, H-6), 7.18 (m, 4 H; Ar), 7.13 (m, 2 H; H-3), 7.05 (d, *J* = 8.5 Hz, 2 H; Ar), 6.9 (m, 2 H; H-5), 6.79 (d, J = 8.7 Hz, 2 H; Ar), 6.72 (d, J = 9 Hz, 2 H; Ar), 3.98 (m, 4 H; ethyleneoxy), 3.68 (m, 4 H; ethyleneoxy), 3.57 (m, 5 H; ethyleneoxy, H-31), 3.46 (m, 5 H; H-1, H-25), 3.1 (m, 5 H; H-33, H-34), 2.57 (m, 2 H; H-23), 2.45 (m, 1 H; H-32), 2.39 (m, 2 H; H-27), 1.8 (m, 3 H; H-24, H-32), 1.6 (m, 4 H; H-28, H-30), 1.55 (s br, 20 H, H-36 – H-45), 1.4 (m, 2 H; H-29); 1.3 (m, 2 H, H-35), 0.9 (m, 3 H, H-46); found (%): C 32.29, H 4.36, N 0.70, S 3.09.

NPs were redissolved in dichloromethane in order to record TEM images (Figure S4)

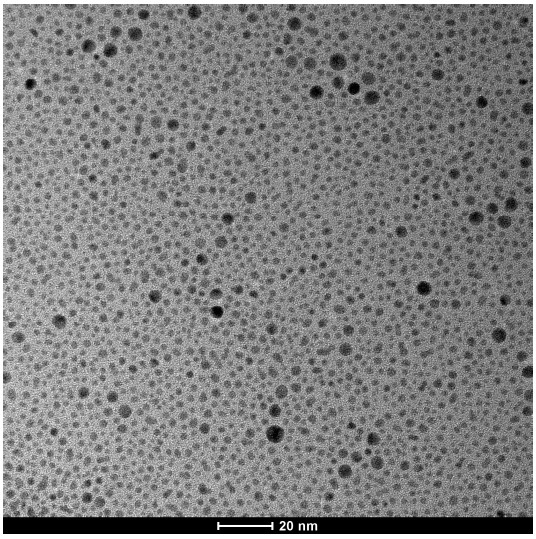
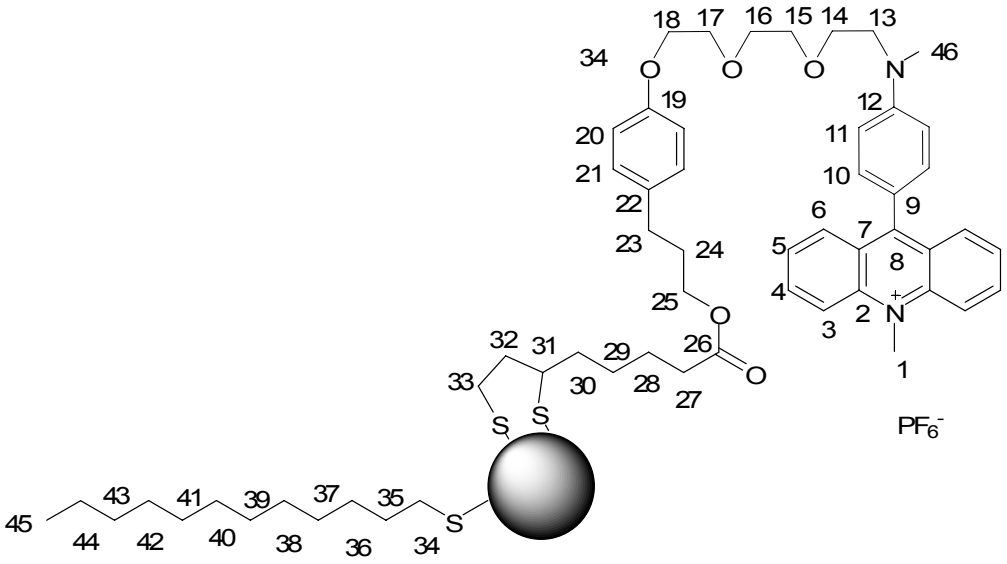



Figure S4. TEM image of gold NPs functionalized with **5**. The scale bar corresponds to 20 nm.

**Gold NPs modified with 4**

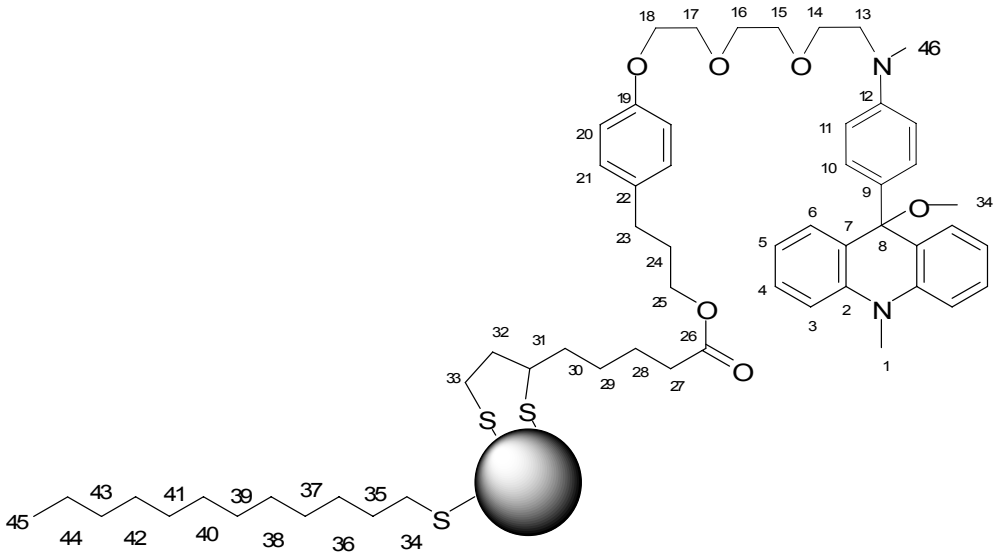


**3** (0.140 g, 0.186 mmol) and dodacanethiol-capped gold nanoparticles (0.150 g, 0.189 mmol) afforded the product as dark yellow brown powders (0.090 g).

$^1$H-NMR (400MHz, $CDCl_3$): δ=8.56 (d, *J* = 9.1 Hz, 2 H; H-3), 8.32 (m, 2 H; H-4), 8.23 (d, *J* = 8.7 Hz, 2 H; H-6), 7.78 (m, 2 H; H-5), 7.36 (d, *J* = 8.7 Hz, 2 H; H-10), 7.00 (m, 4 H; H-11, H-21), 6.79 (d, *J* = 8.3 Hz, 2 H; H-20), 4.85 (s, 3 H; H-1), 4.1 (m, 2 H; ethyleneoxy), 3.85 (t, *J* = 6.3 Hz, 2 H; H-25), 3.7 (m, 8 H; ethyleneoxy), 3.6 (m, 3 H; $NCH_2$, H-31), 3.19 (s, 3 H; H-46), 3.11 (m, 2 H; H-33), 2.56 (t, *J* = 7.4 Hz, 2 H; H-23), 2.47 (m, 1 H; H-32), 2.31 (t, *J* = 7.1

Hz, 2 H; H-27), 1.91 (m, 3 H; H-24, H-32), 1.6 (m, 22 H; H-28, H-30, H-36 – H-44), 1.4 (m, 2H; H-29), 1.28 (s br, 4 H; H-34,35), 0.9 (m, 3 H; H-45); found (%): C 35.82, H 4.22, N 1.55, S 5.11.

**Gold NPs capped with 6**



**39** (0.150 g, 0.196 mmol) and dodecanethiol-capped gold nanoparticles (0.156 g, 0.196 mmol) give the product as dark yellow brown powders (0.110 g).

$^1$H-NMR (400 MHz, $CD_3CN$): δ=7.42 (m, 4 H; H-4,H-6), 7.10 (d, *J* = 7.6 Hz, 2 H; H-3), 6.96 (m, 2 H; Ar), 6.84 (m, 2 H; H-5), 6.75 (d, *J* = 8.5 Hz, 2 H; Ar), 6.55 (d, *J* = 8.4 Hz, 2 H; Ar), 4.1 (m, 2 H; ethyleneoxy), 3.8 (m, 4 H; ethyleneoxy), 3.55 (m, 11 H; ethyleneoxy, H-13, H-25, H-31), 3.30 (s, 3 H, H-1), 3.25 (s, 3 H; H-34), 3.1 (m, 2 H; H-33), 3.13 (s, 3 H; H-13), 2.5 (m, 2 H; H-23), 2.44 (m, 1 H; H-32), 2.3 (m, 2 H; H-27), 1.8 (m, 3 H; H-24, H-32), 1.6 (m, 22 H; H-28, H-30, H-36 – H-44), 1.4 (m, 2H; H-29), 1.3 (s br, 4 H; H-34,35), 0.9 (m, 3 H; H-45); found (%): C 35.32, H 4.55, N 1.17, S 4.90.

2. The procedure described above was also used in order to prepare gold NPs functionalized with rotaxanes. The exchange reaction was performed with thiol capped NPs (0.15 g) in dichloromethane (1 mL) and **5** or **6** (0.20 mmol) in the presence of **CBQT(PF$_6$)$_4$** (0. 20 mmol) in MeCN (10 mL). The mixture was stirred under argon for 3 days. Solvents were removed *in vacuo* and the residue was washed with acetonitrile to remove free **5** or **6, CBQT(PF$_6$)$_4$** and dodecanethiol until no absorption of acridane compounds and

**CBQT(PF$_6$)$_4$**, respectively, could be detected in washing solution by the help of UV-Vis-spectroscopy. The precipitate was dried *in vacuo* to give the functionalized gold NPs as dark yellow brown powders.

NPs functionalized with rotaxanes were redissolved in solvents such as dichloromethane or mixtures from dichloromethane and MeCN to study the NPs by TEM (Figure S5) NMR and UV-Vis spectroscopy, respectively.

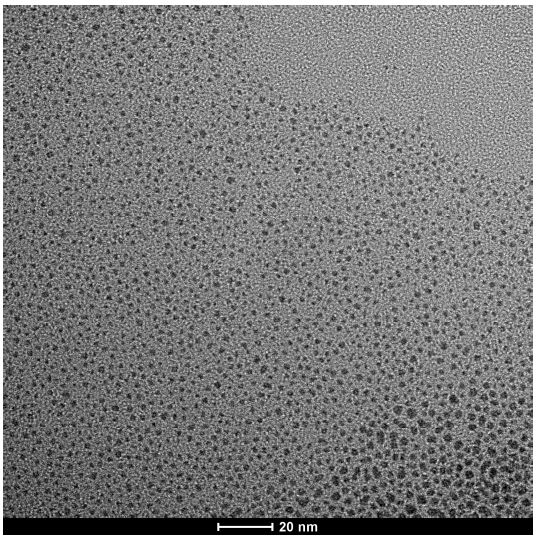
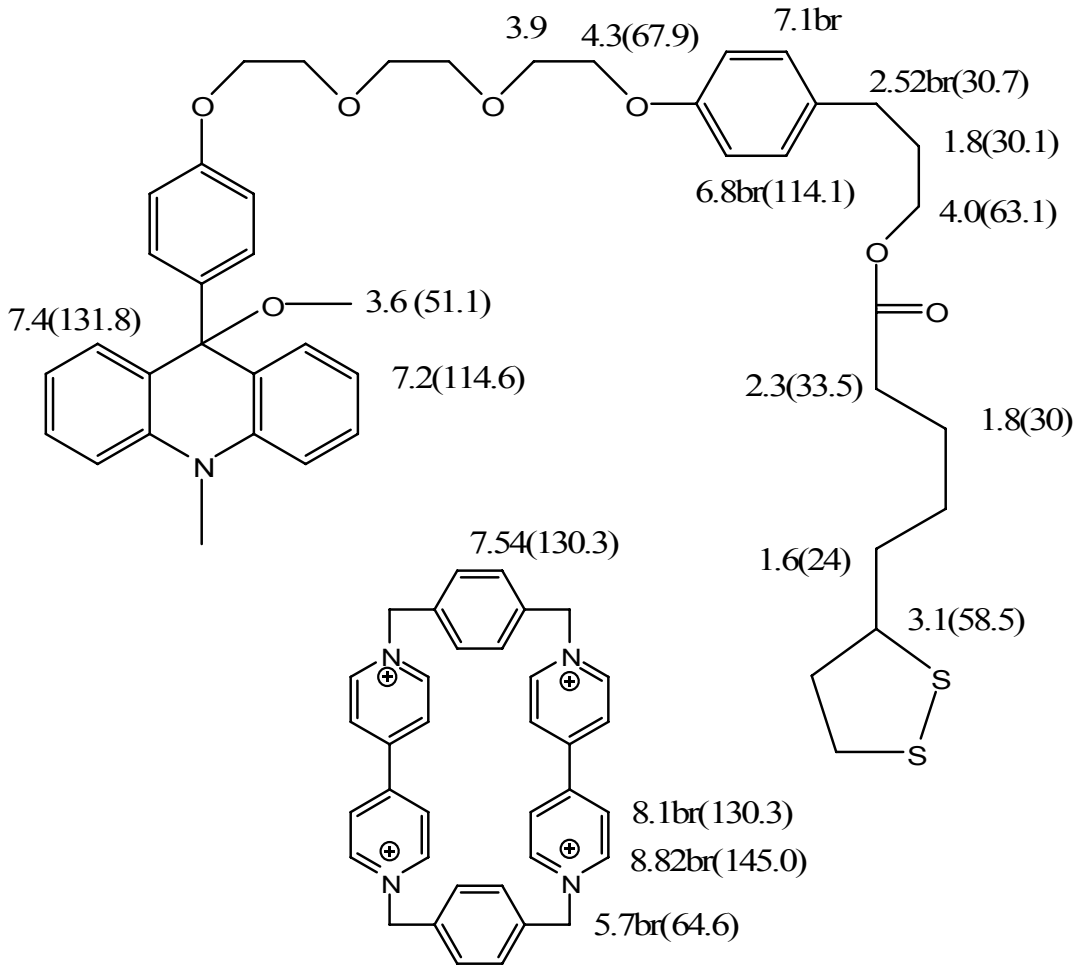
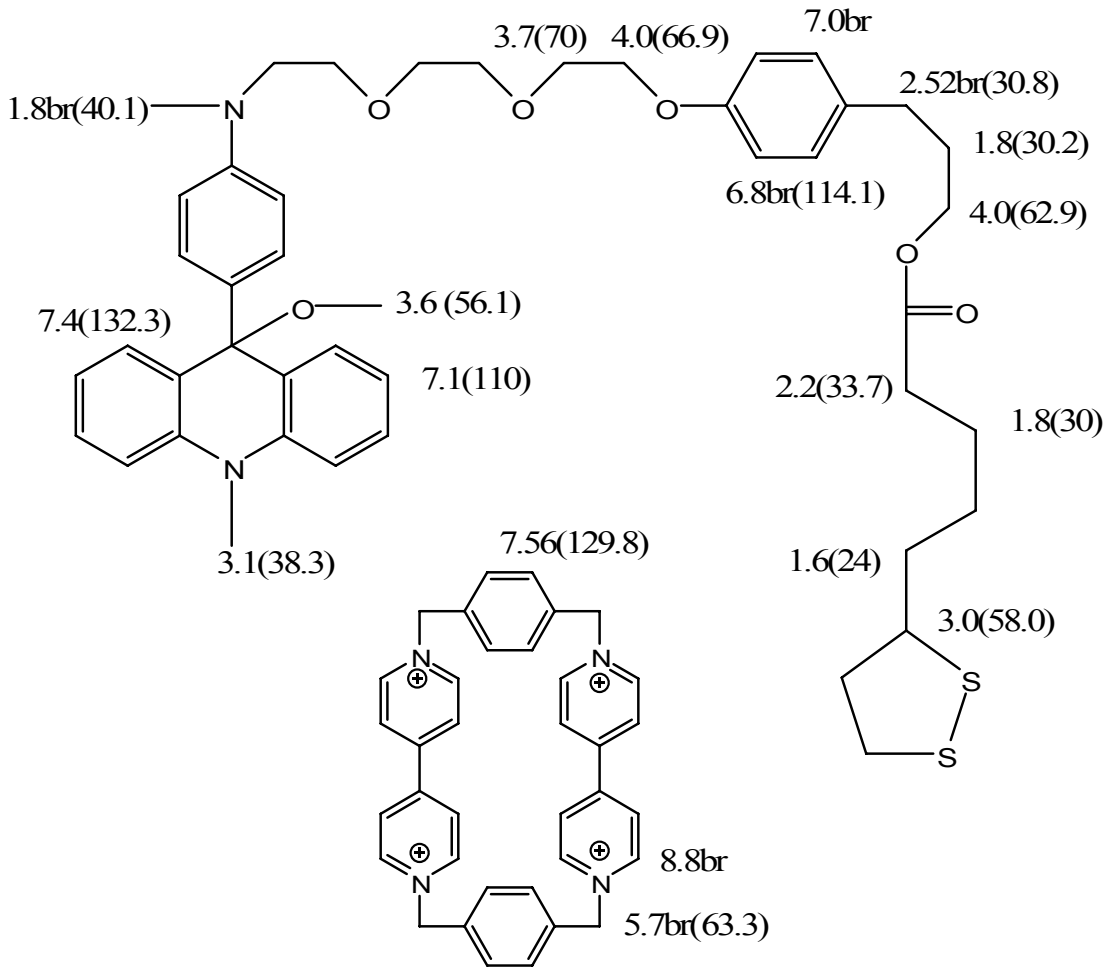



Figure S5. TEM image of gold NPs functionalized with **6**/**CBQT**$^{4+}$. The scale bar corresponds to 20 nm. The average diameter was 3.1 nm.




Scheme S1. Assignable proton signals together with $^{13}C$ signals (in brackets) of rotaxane **5**/**CBQT**$^{4+}$ formed on NPs in $CDCL_3/CD_3CN$ (1:4) solution.




Scheme S2. Assignable proton signals together with $^{13}C$ signals (in brackets) of rotaxane **6**/**CBQT(PF$_6$)$_4$** formed on NPs in $CDCl_3/CD_3CN$ (1:4) solution.

3. Rotaxanes **12** and **13** were deposited on Au NPs by using the procedure described above.

Acridinium rotaxane **12** (0.153 g, 0.070 mmol) in MeCN (10 mL) and dodacanethiol-capped gold nanoparticles (0.06 g, 0.076 mmol) in dichloromethane (1 mL) were mixed and stirred under argon for 3 days. After removal of solvents *in vacuo* the residue was washed with acetonitrile to remove free rotaxane **12** and dodecanethiol until no signal of **12** was detected in the UV-Vis spectrum. The precipitate was washed with dichloromethane and dried *in vacuo* to give the product as dark yellow brown powder (0.115 g).

Acridane rotaxane **13** (150mg, 0.072mmol) in MeCN (16 mL) and dodacanethiol-capped gold nanoparticles (0.060 g, 0.076mmol) in dichloromethane (2 mL) were mixed and stirred under argon for 3 days. After removal of solvents *in vacuo* the residue was washed with acetonitrile to remove free acridane rotaxane **13** and dodecanethiol until no signal of **13** was detected in

the UV-Vis spectrum. The precipitate was washed with dichloromethane to remove non-functionalized AuNPs and dried *in vacuo* to give the product as dark yellow brown powder (0.095 g); found (%) C 45.55, H 2.77, N 2.18, S 3.63.

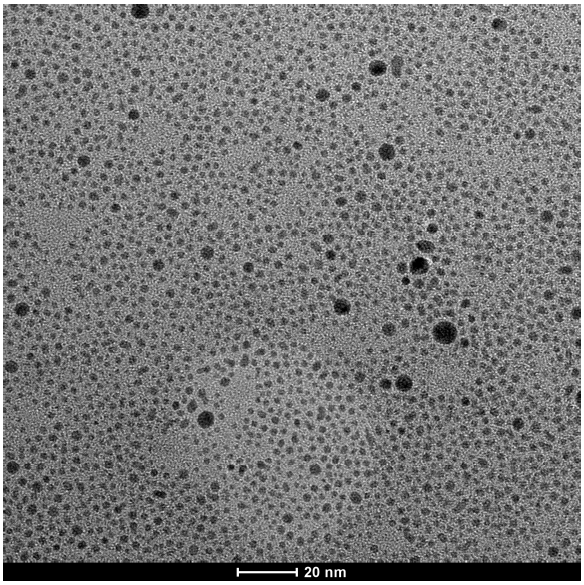



Figure S6. TEM image of gold NPs functionalized with **13**. The scale bar corresponds to 20 nm. The average diameter was 3.4 nm.

Estimation of the average number of thiol and rotaxane units, respectively, around one AuNP: By assuming the core shape of NP to be spherical the average number N of units can be estimated by using the elemental analysis of modified NPs. The sulphur and nitrogen content, respectively, corresponds to the presence of thiol and rotaxane, respectively:
$W_{Au} = 4/3\pi r^3 D_{Au}$, where r is the radius of NP and D is the gold density.
By assuming the bulk gold weight corresponds to the gold content of one NP, the content of thiol units is given by: $N_S = N_{thiol} = \%\ S\ W_{Au}/M_S N_A$ where $M_S$ is the molar number of sulphur and $N_A$ is the Avogadro constant ($6.2 \times 10^{23}$). Accordingly the number of rotaxane units is given by the nitrogen content (elemental analysis) $N_{rotaxane\ \mathbf{13}} = N_N = \%\ N\ W_{Au}/M_N N_A$.

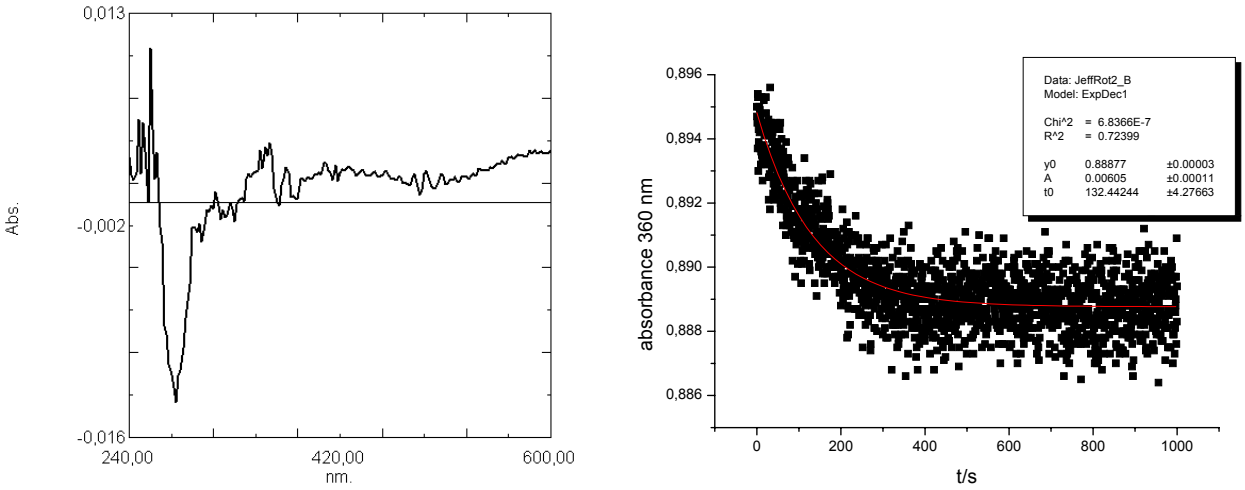
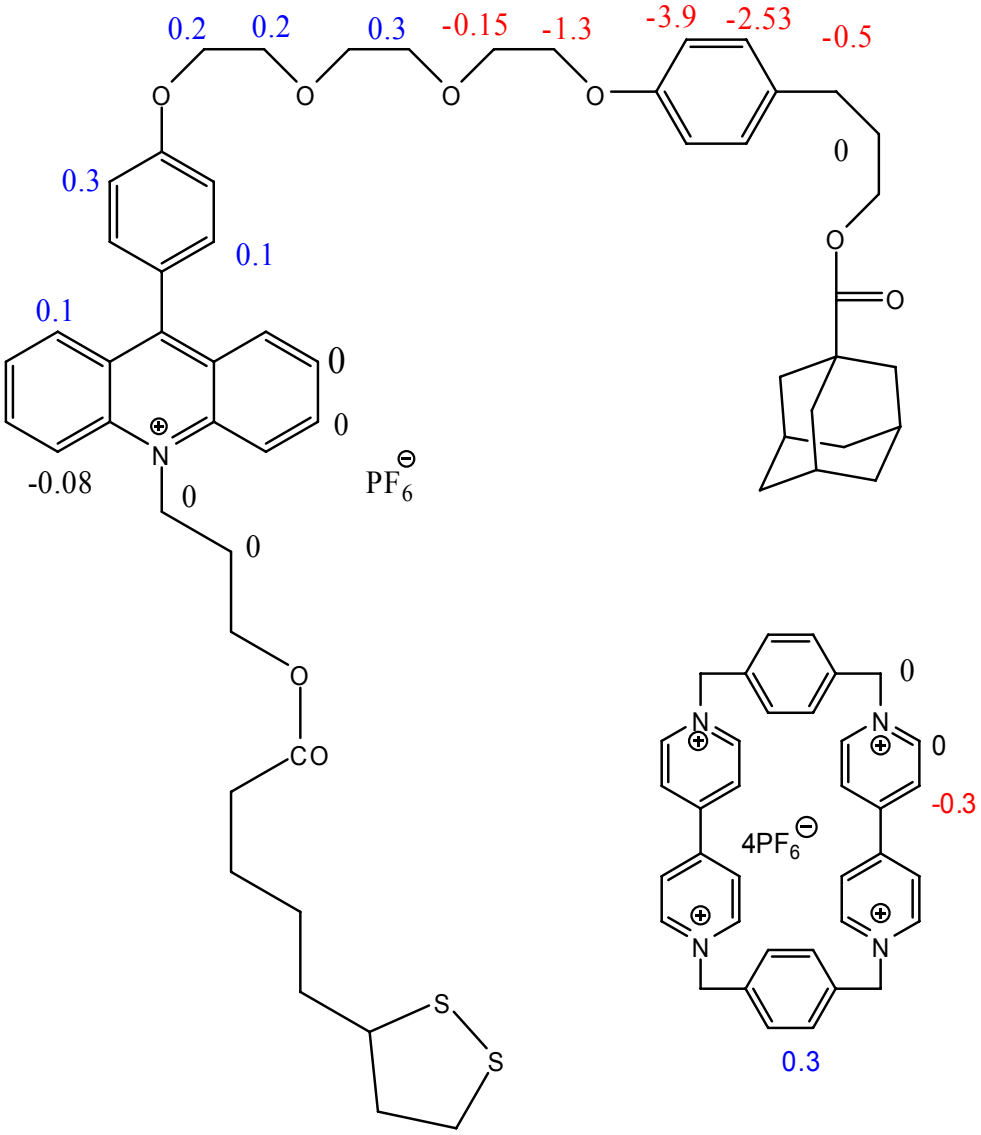
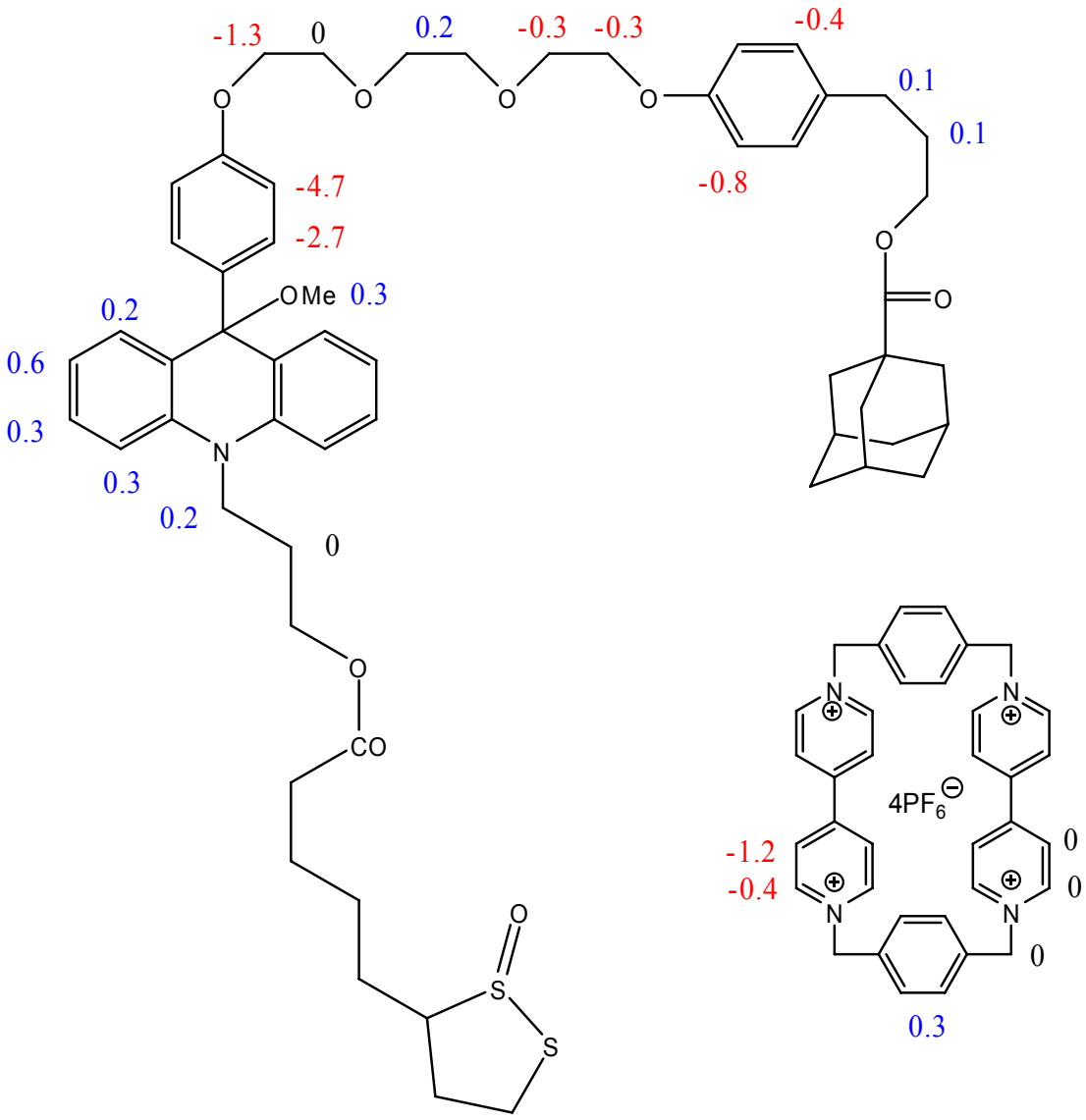



Figure S7. Transient absorption spectrum recorded after irradiation (<300 nm) of pseudorotaxane **6**/**CBQT**$^{4+}$ immobilised on AuNP in DCM/MeOH/MeCN (1:10:10 solution); b) decay curve of the transient absorbance at 360 nm




Scheme S3. Chemical shift differences (ppm) of proton resonances of rotaxane **12** obtained by comparison of the proton resonances of compound **9** with related proton resonances observed in the rotaxane ($\delta_{\text{rotaxane } \mathbf{12}} - \delta_{\mathbf{9}}$ ). Upfield shift: red; downfield shift: blue.




Scheme S4. Chemical shift differences (ppm) of proton resonances of rotaxane **13** (233 K) obtained by comparison of the proton resonances of compound **10** with related proton resonances observed in the rotaxane ($\delta_{\text{rotaxane }\mathbf{13}} - \delta_{\mathbf{10}}$ ). Upfield shift: red; downfield shift: blue.

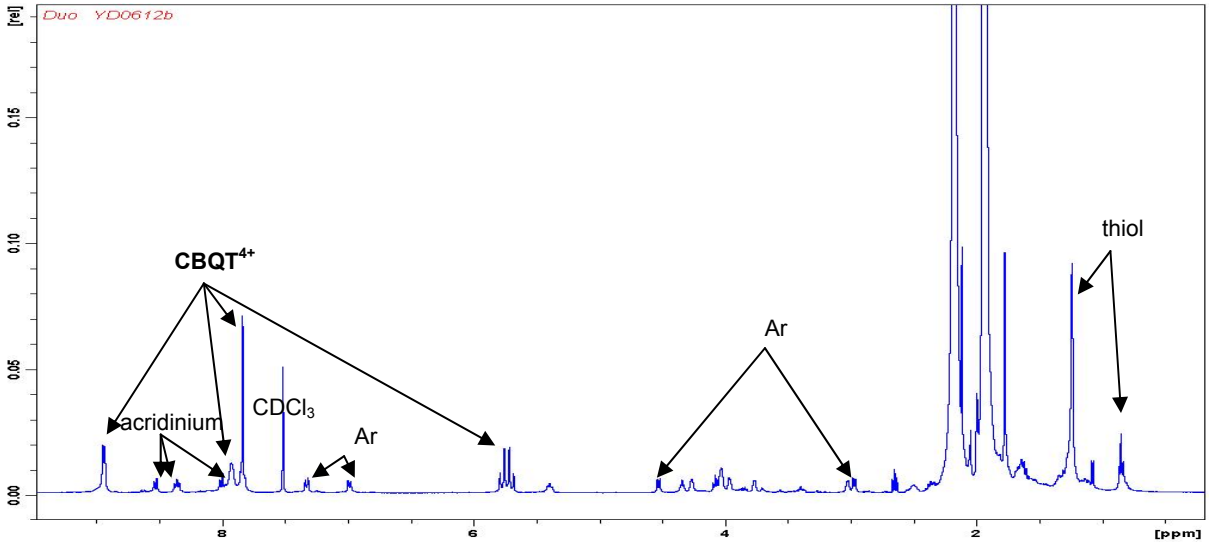
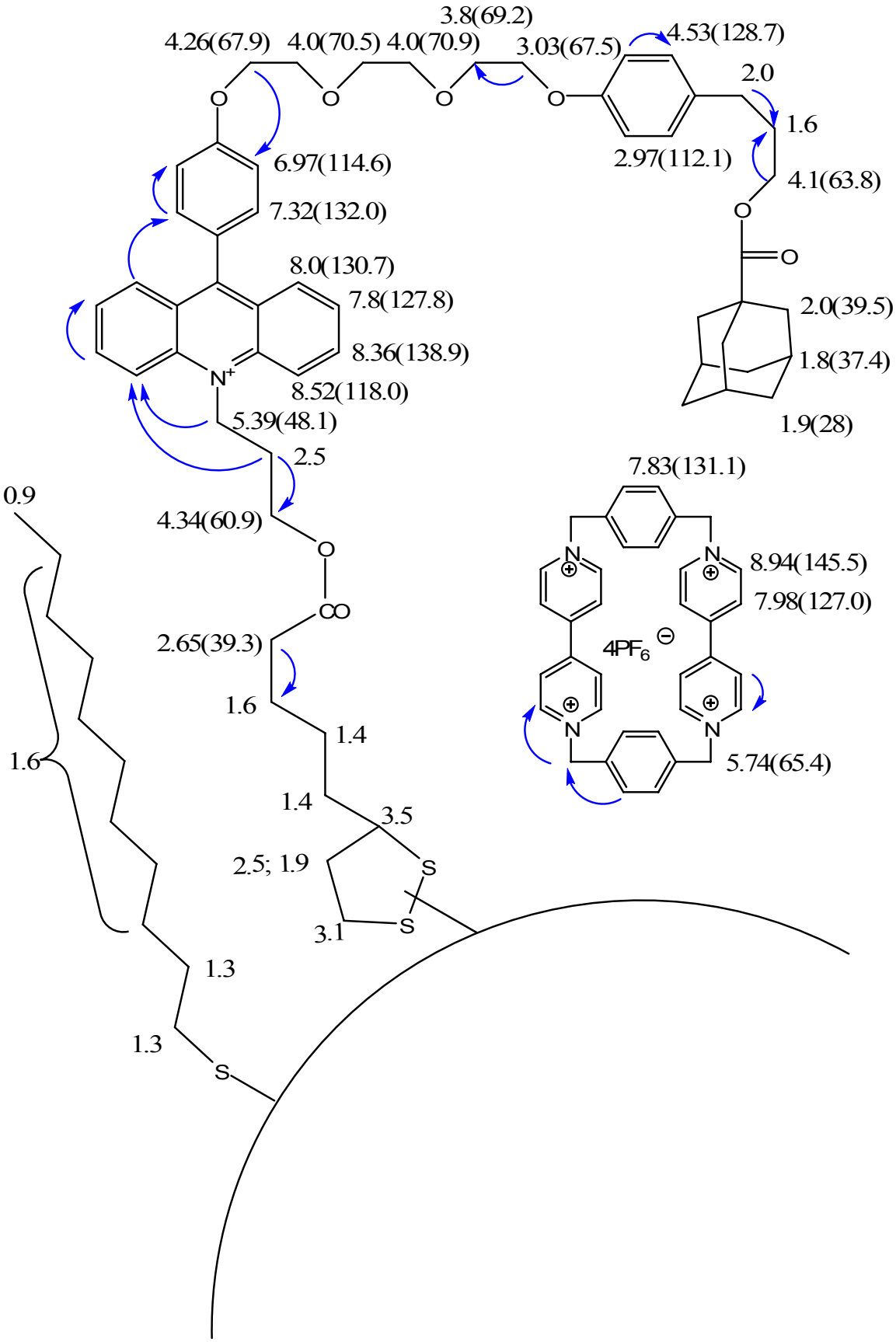



Figure S8. $^{1}$H NMR spectrum of AuNPs capped with rotaxane **12** ($CDCl_3/CD_3CN$).




Scheme S5. Assignable proton signals together with $^{13}C$ signals (in brackets) of rotaxane **12** on NPs in $CDCl_3/CD_3CN$ (1:4) solution. Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

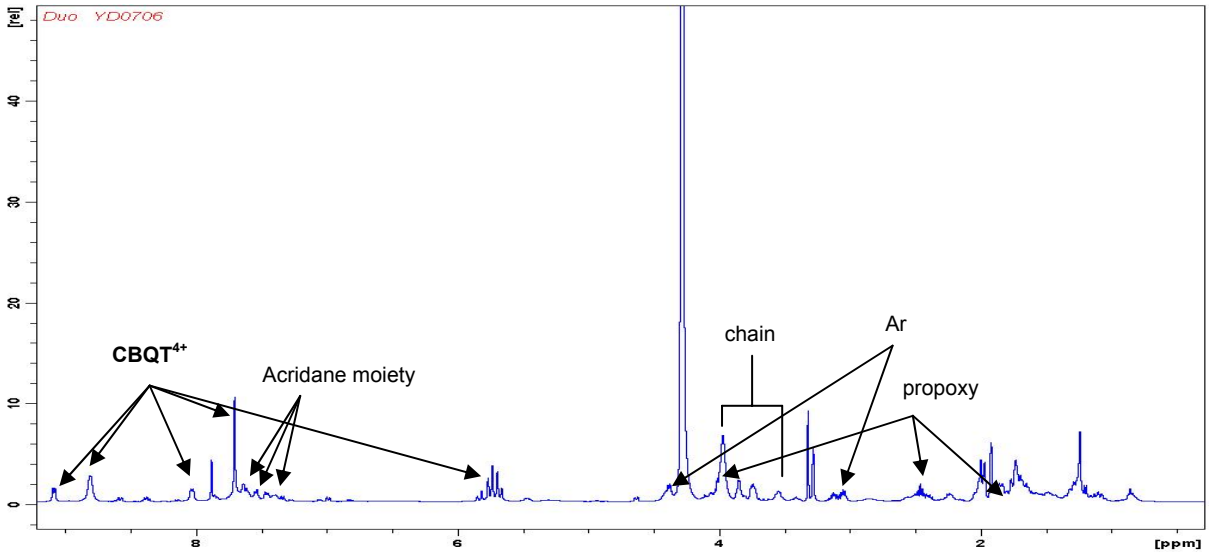
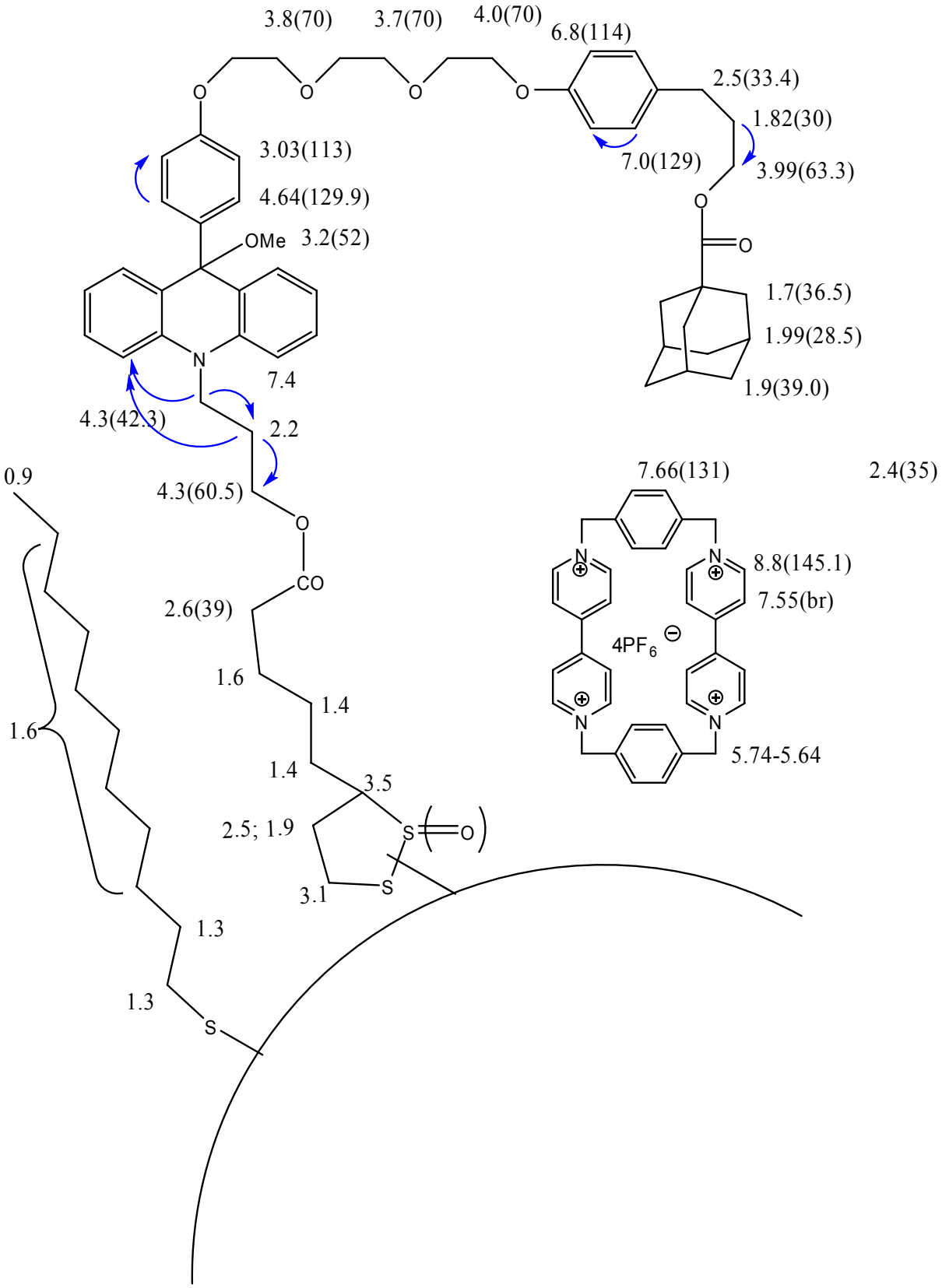



Figure S9. $^{1}$H NMR spectrum of AuNPs capped with rotaxane **13** ($CDCl_3/CD_3CN$).




Scheme S6. Assignable proton signals together with $^{13}C$ signals (in brackets) of rotaxane **13** on NPs in $CDCl_3/CD_3CN$ (1:4) solution. Blue arrows mark NOE's between protons observed as correlation peaks of ROESY spectra.

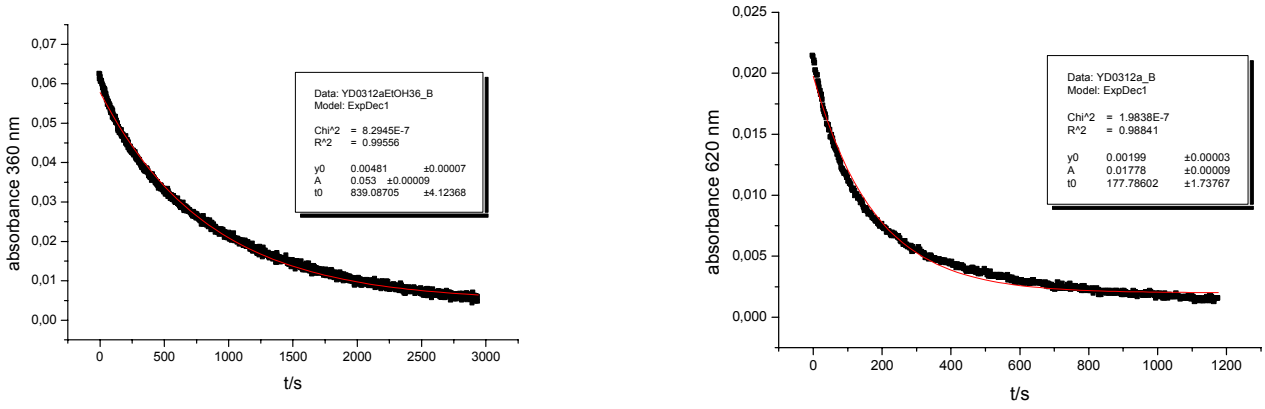



Figure S10. Decay curves of the transient absorption of rotaxane **13** in EtOH solution monitored at 360 and 620 nm, respectively (5s HBO 500; >300 nm).

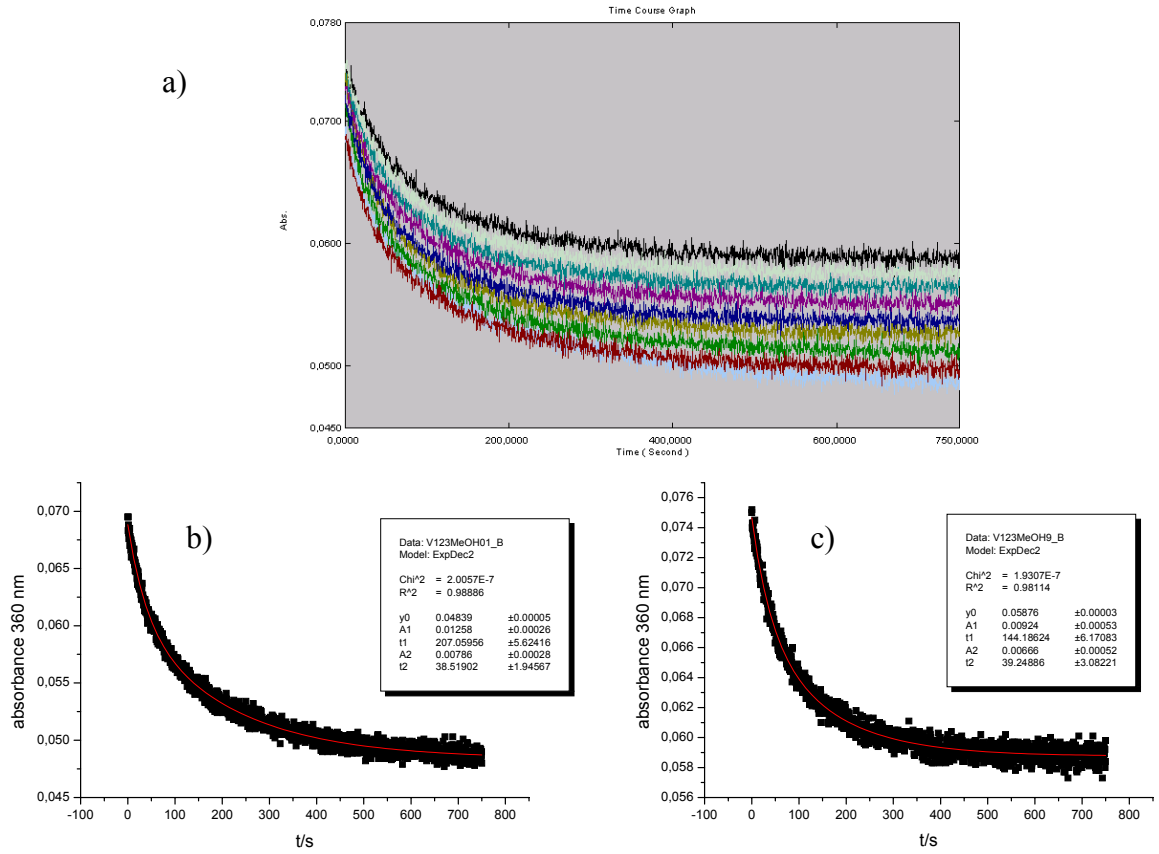



Figure S11. a) Decay curves of the transient absorption recorded after repeated irradiation of rotaxane **13** in methanol solution (5s HBO 500; >300 nm); b) decay after 1x 5s irradiation; c) decay after 10x 5s.

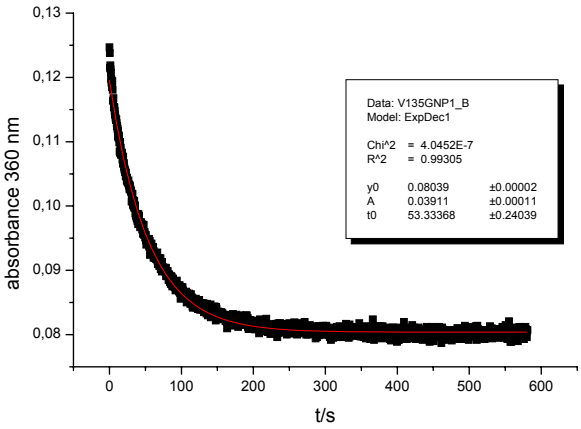



Figure S12. Decay curve of the transient absorption recorded after irradiation of rotaxane **13** deposited on Au NPs in DCM/MeOH/MeCN (1:10:10) solution (5s HBO 500; >300 nm) monitored at 360 nm.