Electronic Supplementary Information for

Anion directed synthesis of a hydrogensulfate selective luminescent rotaxane

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Experimental:

Chemicals were commercially available and used as received. All reactions were carried out using pre-dried solvents and nitrogen atmosphere unless otherwise stated. ^{1}H and ^{13}C-NMR spectra were recorded on Varian 500 MHz Unity plus spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer.

3: A solution of **1** (0.44 g, 1.83 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a solution containing **2** (1.1 g, 4.02 mmol) and Et_3N (1.7 ml) in CH_2Cl_2 (25 ml) too, at room temperature. The mixture was stirred overnight. A precipitate was formed which was then filtered and washed with CH_2Cl_2 and Et_2O (98 %). NMR analysis confirmed both the structure and analytical purity of the product.

^{1}H-NMR (DMSO-d_6, δ, ppm): 3.66 (b, 8H), 3.99-4.08 (m, 12H, -NHCH$_2$*CH$_2$*OAr- & -ArO*CH$_2$*CH$_2$- & -CH$_2$O*CH$_2$*CH=CH$_2$), 5.11-5.27 (m, 4H, -CH=*CH$_2$*), 5.85 (b, 2H, -*CH*=CH$_2$), 6.86 (bs, 8H, *CH $_{Ar}$*), 7.84 (bs, 2H, *CH$_{(5,5')\ bipy}$*), 8.78 (bs, 2H, *CH$_{(3,3')\ bipy}$*), 8.84 (m, 2H, *CH$_{(6,6')\ bipy}$*), 9.16 (b, 2H, *NH*).
^{13}C-NMR (DMSO-d_6, δ, ppm): 39.25, 66.26, 67.44, 68.18, 71.07, 115.23, 115.35, 116.40, 118.14, 121.87, 134.99, 142.49, 149.93, 152.28, 152.46, 155.32, 164.71.
MS (+FAB): 683 (M^++1)

4: Compound **3** (0.44 g, 0.64 mmol) and $Re(CO)_5Cl$ (0.25 g, 0.69 mmol) were refluxed together in THF (80 ml) overnight to obtain an orange solution of the corresponding complex. Solvent was evaporated under reduced pressure and the crude was purified by liquid chromatography (Silica gel; CH_2Cl_2/MeOH, 9/1). The Re(I) complex was isolated as a bright yellow solid (90%).

^{1}H-NMR ($CDCl_3$, δ, ppm): 3.74 (t, *J*= 4.5 Hz, 4H, -NH*CH$_2$*-), 4.00-4.07 (m, 12H, -NHCH$_2$*CH$_2$*OAr- & -ArO*CH$_2$*CH$_2$- & -CH$_2$*CH$_2$*Oallyl), 4.18-4.31 (m, 4H, -CH$_2$O*CH$_2$*CH=CH$_2$), 5.18 (dd, J_{cis}= 10.2 Hz, J_{gem}= 1.5 Hz, 2H, -CH=*CH$_2$*), 5.28 (dd, J_{trans}= 17.4 Hz, J_{gem}= 1.5 Hz, 2H, -CH=*CH$_2$*), 5.93 (ddd, J_{trans}= 17.4 Hz, J_{cis}= 10.2 Hz, J_{vic}= 5.4 Hz, 2H, -*CH*=CH$_2$), 6.84 (d, J_{ortho}= 9 Hz, 4H, *CH $_{Ar}$*), 6.91 (d, J_{ortho}= 9 Hz, 4H, *CH $_{Ar}$*), 7.63 (bs, 2H, *NH*), 7.83 (d, J_{ortho}= 5.4 Hz, 2H, *CH$_{(5,5')\ bipy}$*), 8.43 (s, 2H, *CH$_{(3,3')\ bipy}$*), 8.91 (d, J_{ortho}= 5.4 Hz, 2H, *CH$_{(6,6')\ bipy}$*).
^{13}C-NMR ($CDCl_3$, δ, ppm): 40.53, 66.82, 68.03, 68.60, 72.40, 115.67, 115.86, 117.40, 120.26, 126.47, 134.46, 143.20, 152.51, 153.35, 153.70, 155.04, 161.75, 187.21, 195.89.

MS (Electrospray): 1027 (M^++K^+), 1011 (M^++Na^+), 953 (M^+-Cl^-).

5: Grubbs' catalyst (0.03 g) was added to a solution of **4** (0.3 g, 0.3 mmol) in dichloromethane (20 ml). After six hours a second aliquot of catalyst (0.03 g) was added and the mixture was stirred overnight. The solvent was evaporated under reduced pressure and the crude was purified by column chromatography (Silica gel; Acetone/CH_2Cl_2, 1/1). The product was isolated as a bright yellow solid (40%).

^{1}H-NMR (DMSO-d_6, δ, ppm): 3.60-3.69 (m, 8H, -NH*CH*$_2$- & -CH_2*CH*$_2$OCH_2-), 3.94 (bs, 8H, -NHCH_2*CH*$_2$OAr- & -ArO*CH*$_2$$CH_2$-), 4.08 (bs, 4H, -$CH_2$O*CH*$_2$CH=CH-), 5.73 (bs, 2H, -*CH*=*CH*-), 6.78-6.86 (m, 8H, *CH* $_{Ar}$), 8.05 (d, J_{ortho}= 5.1 Hz, 2H, *CH*$_{(5,5')\ bipy}$), 9.07 (s, 2H, *CH*$_{(3,3')\ bipy}$), 9.12 (d, J_{ortho}= 5.1 Hz, 2H, *CH*$_{(6,6')\ bipy}$), 9.41 (b, 2H, *NH*).
^{13}C-NMR (DMSO-d_6, δ, ppm): 38.62, 66.36, 67.70, 68.15, 69.97, 115.38, 115.55, 122.20, 125.76, 128.79, 144.37, 152.36, 152.82, 153.79, 155.69, 163.38, 189.38, 197.46.
MS (Electrospray): 999 (M^++K^+), 983 (M^++Na^+), 925 (M^+-Cl^-).

8: Hydrazine monohydrate (5 ml) was added to a mixture of compound **7** (0.36 g, 0.56 mmol) and Ni-Raney (0.2 g) in 1,4-dioxane (25 ml). The mixture was refluxed for 12 h. After cooling down the reaction was filtered through celite, washed with CH_2Cl_2 (30 ml) and evaporated under reduced pressure. The crude amine, without further purification, was dissolved in dichloromethane (20 ml) with Et_3N (0.25 ml) and a solution of 3,5-dichlorocarbonylpyridine in CH_2Cl_2 (20 ml), prepared from the corresponding dicarboxylic acid (0.51 mmol), was added dropwise, at room temperature and under N_2 atmosphere. The mixture was stirred overnight and the solvent was then evaporated under reduced pressure. The product precipitates in MeOH as a pure white solid (58%).

^{1}H-NMR ($CDCl_3$, δ, ppm): 0.94-1.04 (m, 24H, 8 x -OCH_2CH_2*CH*$_3$), 1.84-1.97 (m, 16H, 8 x -OCH_2*CH*$_2$$CH_3$), 3.09-3.16 (m, 8H, Ar-*CH*$_2$-Ar $_{calix}$), 3.78-3.87 (m, 16H, 8 x -O*CH*$_2$$CH_2CH_3$), 4.41-4.46 (m, 8H, Ar-*CH*$_2$-Ar $_{calix}$), 6.48-6.75 (m, 22H, *CH* $_{calix}$), 7.99 (bs, 2H, *NH*), 8.49 (s, 1H, *CH*$_{(4)\ py}$), 9.08 (s, 2H, *CH*$_{(2,6)\ py}$).
^{13}C-NMR ($CDCl_3$, δ, ppm): 10.50, 10.64, 10.69, 23.43, 23.52, 31.23, 76.74, 76.76, 76.85, 38.62, 120.78, 121.45, 122.13, 128.07, 128.29, 128.44, 130.62, 131.06, 133.57, 135.02, 135.05, 135.49, 135.75, 150.56, 154.11, 156.61, 156.80, 162.8.
MS (Electrospray): 1347 (M^++2), 1346 (M^++1), 1345 (M^+).

9-I, **9-Cl**: Methylation and subsequent anion exchange were carried out according to a previously described procedure.[1] **9-I** (90%) and **9-Cl** (96%).

^{1}H-NMR ($CDCl_3$, δ, ppm): 0.87-0.93 (m, 12H, 4 x -OCH_2CH_2*CH*$_3$), 0.97 (t, *J*= 7.5 Hz, 12H, 4 x -OCH_2CH_2*CH*$_3$), 1.83-1.96 (m, 16H, 8 x -OCH_2*CH*$_2$$CH_3$), 3.12-3.24 (m, 8H, Ar-*CH*$_2$-Ar calix), 3.74 (t, *J*= 7.5 Hz, 8H, 4 x -O*CH*$_2$$CH_2CH_3$), 3.74 (t, *J*= 7.8 Hz, 8H, 4 x -O*CH*$_2$$CH_2CH_3$), 4.40-4.45 (m, 8H, Ar-*CH*$_2$-Ar $_{calix}$), 6.44 (t, *J*= 7.5 Hz, 4H, *CH* $_{calix}$), 6.54 (d, *J*= 7.5 Hz, 4H, *CH* $_{calix}$), 6.62 (t, *J*= 7.5 Hz, 2H, *CH* $_{calix}$), 6.72 (t, *J*= 7.5 Hz, 4H, *CH* $_{calix}$), 6.90 (d, *J*= 7.5 Hz, 4H, *CH* $_{calix}$), (bs, 2H, *NH*), 7.50 (s, 4H, *CH* $_{calix}$), 7.68 (s, 2H, *CH*$_{(2,6)\ py}$), 9.38 (s, 1H, *CH*$_{(4)\ py}$), 10.13 (s, 2H, *NH*).

^{13}C-NMR ($CDCl_3$, δ, ppm): 10.09, 10.16, 10.45, 23.05, 23.12, 23.29, 30.81, 45.60, 76.81, 76.96, 77.05, 121.69, 122.38, 122.88, 128.09, 128.52, 128.62, 131.64, 134.26, 134.29, 134.21, 135.97, 136.35, 140.67, 146.00, 154.62, 155.86, 156.91, 158.99.
MS (Electrospray): 1362 (M^++2), 1361 (M^++1), 1360 (M^+).

^{1}H-NMR ($CDCl_3$, δ, ppm): 0.93-0.97 (m, 12H, 4 x -$OCH_2CH_2CH_3$), 1.04 (t, *J*= 7.5 Hz, 12H, 4 x -$OCH_2CH_2CH_3$), 1.89-2.03 (m, 16H, 8 x -$OCH_2CH_2CH_3$), 3.20-3.29 (m, 8H, Ar-CH_2-Ar *calix*), 3.76 (t, *J*= 7.5 Hz, 8H, 4 x -$OCH_2CH_2CH_3$), 3.94-3.98 (m, 8H, 4 x -$OCH_2CH_2CH_3$), 4.47-4.52 (m, 8H, Ar-CH_2-Ar *calix*), 6.44 (t, *J*= 7.5 Hz, 4H, *CH calix*), 6.56 (d, *J*= 7.5 Hz, 4H, *CH calix*), 6.70 (t, *J*= 7.5 Hz, 2H, *CH calix*), 6.76 (t, *J*= 7.5 Hz, 4H, *CH calix*), 7.05 (d, *J*= 7.5 Hz, 4H, *CH calix*), 7.66 (s, 4H, *CH calix*), 7.94 (s, 2H, *CH(2,6) py*), 10.11 (s, 1H, *CH(4) py*), 11.17 (s, 2H, *NH*).
^{13}C-NMR ($CDCl_3$, δ, ppm): 10.10, 10.20, 10.60, 23.11, 23.16, 23.40, 30.87, 30.93, 45.60, 76.81, 77.02, 77.13, 121.87, 122.54, 122.75, 128.03, 128.39, 128.83, 132.20, 134.22, 134.28, 134.40, 136.33, 136.62, 141.32, 145.93, 154.79, 155.84, 157.16, 159.12.
MS (Electrospray): 1362 (M^++2), 1361 (M^++1), 1360 (M^+).

10: A solution of **4** (0.36 g, 0.26 mmol) and **9-Cl** (0.30 g, 0.31 mmol) in dichloromethane (20 ml) was stirred for 15 minutes. A ring closing metathesis was then carried out as described for compound **5**. The solvent was evaporated under reduced pressure and the crude was purified by preparative TLC (Silica gel; Dichloromethane/Acetone, 3/1). After washing the corresponding fraction of silica gel with acetone (2 x 25 ml) and methanol (2 x 25 ml) the solvent was evaporated under reduced pressure and the product was isolated as a bright yellow solid (21%).

^{1}H-NMR ($CDCl_3$, δ, ppm): 0.93-1.06 (m, 24H, 8 x -$OCH_2CH_2CH_3$), 1.88-1.97 (m, 16H, 8 x -$OCH_2CH_2CH_3$), 2.94-3.17 (m, 8H, Ar-CH_2-Ar *calix*), 3.75-4.05 (m, 16H, 8 x -$OCH_2CH_2CH_3$), 4.17 (s, 3H, Py-CH_3), 4.39-4.48 (m, 8H, Ar-CH_2-Ar *calix*), 5.84 (b, 2H, *CH oleph*), 6.34-6.68 (m, 18H, *CH calix*), 6.75 (d, *J*= 7 Hz, 4H, *CH Ar*), 6.85 (d, *J*= 7 Hz, 4H, *CH Ar*), 7.41 (s, 2H, *CH calix*), 7.53 (s, 2H, *CH calix*), 8.11 (d, 2H, *J*= 5.5 Hz, *CH(5, 5') bipy*), 8.72 (s, 1H, *CH(2/6) py*), 8.86 (s, 1H, *CH(6/2) py*), 9.05 (b, 2H, *NH bipy*), 9.10 (d, *J*= 5.5 Hz, 2H, *CH(6, 6') bipy*), 9.84 (s, 2H, *CH(3) bipy*), 9.94 (b, 2H, *NH*), 10.07 (s, 1H, *CH(4) py*).
^{13}C-NMR ($CDCl_3$, δ, ppm): 10.11 (-$OCH_2CH_2CH_3$), 10.17 (-$OCH_2CH_2CH_3$), 10.20 (-$OCH_2CH_2CH_3$), 10.29 (-$OCH_2CH_2CH_3$), 10.46 (2 x -$OCH_2CH_2CH_3$), 10.54 (2 x -$OCH_2CH_2CH_3$), 23.10 (-$OCH_2CH_2CH_3$), 23.16 (-$OCH_2CH_2CH_3$), 23.19 (-$OCH_2CH_2CH_3$), 23.24 (-$OCH_2CH_2CH_3$), 23.29 (2 x -$OCH_2CH_2CH_3$), 23.34 (2 x -$OCH_2CH_2CH_3$), 30.93 (2 x -$OCH_2CH_2CH_3$), 30.99 (2 x -$OCH_2CH_2CH_3$), 31.01 (2 x -$OCH_2CH_2CH_3$), 31.22 (2 x -$OCH_2CH_2CH_3$), 40.32 (-CH_2-), 50.10 (-CH_3), 66.44 (-CH_2-), 68.40 (-CH_2-), 69.46 (-CH_2-), 71.01 (-CH_2-), 76.65 (Ar-CH_2-Ar *calix*), 76.71 (Ar-CH_2-Ar *calix*), 76.80 (2 x Ar-CH_2-Ar *calix*), 76.88 (2 x Ar-CH_2-Ar *calix*), 76.92 (Ar-CH_2-Ar *calix*), 77.02 (Ar-CH_2-Ar *calix*), 115.02 (*CH Ar*), 115.31 (*CH Ar*), 121.08 (*CH calix*), 121.17 (*CH calix*), 121.39 (*CH bipy*), 121.82 (*CH calix*), 121.91 (*CH calix*), 121.99 (*CH calix*), 126.47 (*CH bipy*), 127.43 (*CH calix*), 127.65 (*CH calix*), 128.21 (2 x *CH calix*), 128.23 (*CH calix*), 128.40 (*CH calix*), 128.48 (*Cq*), 129.10 (*Cq*), 129.84 (*CH oleph*),, 130.89 (*Cq*), 131.06 (*Cq*), 133.60 (*Cq*), 134.13 (*Cq*), 134.19 (*Cq*), 134.33 (*Cq*), 134.68 (*Cq*), 134.93 (*Cq*), 135.68 (*Cq*), 135.88 (*Cq*), 136.41 (*Cq*), 136.52 (*Cq*), 137.82 (*CH 4 Py*), 143.34 (*Cq bipy (4,4')*), 145.00 (*CH 2/6 Py*), 145.17 (*CH 6/2 Py*), 152.61 (*Cq Ar*), 152.90 (*Cq Ar*),153.35 (*CH*

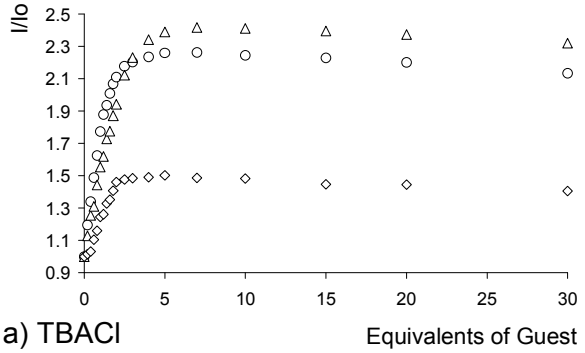
bipy),154.96 (*Cq*), 154.99 (*Cq*), 155.94(*Cq* *bipy(2,2')*), 156.25 (*Cq*), 156.92 (*Cq*), 157.06 (*Cq*), 162.77 (*Cq* *C=O*), 188.66 (*Cq*), 197.24 (*Cq*).
MS (Electrospray): 2323 (M^++3), 2321 (M^++1).

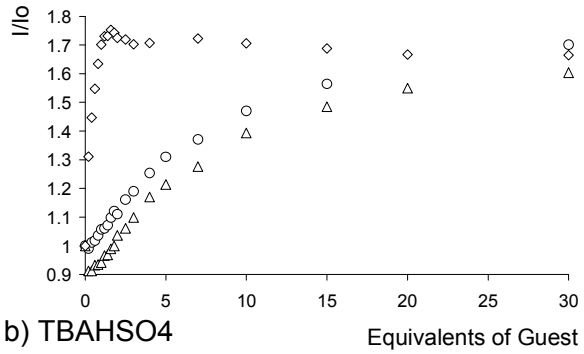
11: Anion exchange was carried out as described elsewhere (91%).[1]

^{1}H-NMR ($CDCl_3$, δ, ppm): 0.88-1.10 (m, 24H, 8 x -OCH_2CH_2*CH_3*), 1.89-1.93 (m, 16H, 8 x -OCH_2*CH_2*CH_3), 3.20-3.24 (m, 8H, Ar-*CH_2*-Ar *calix*), 3.69-4.10 (m, 16H, 8 x -OCH_2*CH_2*CH_3), 4.22 (s, 3H, Py-*CH_3*), 4.41-4.49 (m, 8H, Ar-*CH_2*-Ar *calix*), 6.04 (b, 2H, *CH oleph*), 6.55-6.73 (m, 18H, *CH calix*), 6.99 (b, 4H, *CH Ar*), 7.06-7.12 (m, 4H, *CH Ar*), 7.49 (s, 2H, *CH calix*), 7.54 (s, 2H, *CH calix*), 8.18 (b, *CH(5, 5') bipy*), 9.08-9.58 (m, 6H, *CH(2&6) py*, *NH bipy*, *CH(6, 6') bipy*), 9.58 (s, 2H, *CH(3, 3') bipy*), 10.79 (b, 2H, *NH py*), 10.95 (s, 1H, *CH(4) py*).

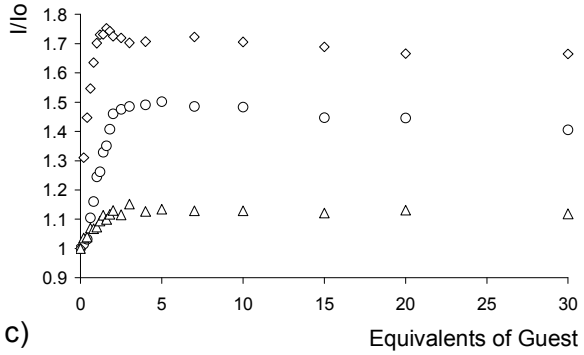
^{13}C-NMR ($CDCl_3$, δ, ppm): 9.83, 9.88, 9.91, 9.96, 10.60, 10.66, 22.85, 23.18, 23.42 , 30.97, 31.00, 31.11, 40.33, 49.28, 66.80, 68.25, 69.34, 70.95, 76.77, 76.87, 76.80, 76.88, 76.92, 77.02, 115.20, 115.87, 122.65, 122.82, 122.92, 123.27, 126.28, 127.62, 128.02, 128.98, 129.15, 129.47, 132.36, 134.08, 134.26, 136.53, 136.81, 137.23, 137.47, 138.51, 142.09, 145.28, 145.81, 152.68, 152.90, 153.41, 156.53, 156.55, 156.66, 157.35, 157.50, 159.02, 159.26, 162.77, 187.41, 196.62.
MS (Electrospray): 2285 (M^+-Cl)

Figure 1 Fluorescence titration curves in acetone at room temperature (λ_{exc}= 400 nm); [Host]= 10^{-5} M; a) ○ = **4**, △ = **5**, ◇ = **11** with TBACl; b) ○ = **4**, △ = **5**, ◇ = **11** with $TBAHSO_4$; c) titration curves of **11** with ◇ = $TBAHSO_4$, ○ = TBACl and △ = $TBANO_3$.





b) TBAHSO4



c)

Refereces:

1 J. A. Wisner, P. D. Beer, M. G. D. Beer, M. R. Sambrook, *J. Am. Chem. Soc.* **2002**, *124*, 12469-12476.