Electronic Supplementary Material (ESI) for ChemComm.

Potential-controlled rotaxane molecular shuttles based on electron-deficient macrocyclic complexes

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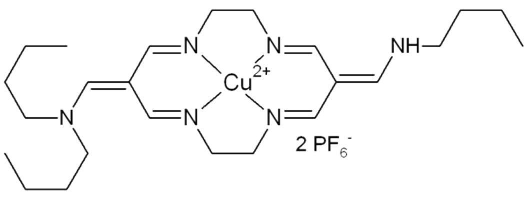
SUPPORTING INFORMATION

Synthesis

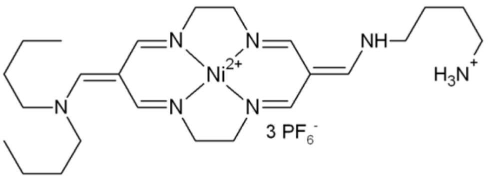
Acetonitrile (HPLC grade, purchased from POCh) was dried over P_2O_5 and distilled. Dibenzo-24-crown-8 (TCI Chemicals, >98%) was dried and kept over P_2O_5 *in vacuo*. All other solvents and reagents were reagent grade or better and used without purification: 1,4-diaminobutane (TCI Chemicals, >98.0%); ammonium hexafluorophosphate (Apollo Scientific, 99.8%); hexafluorophosphoric acid ca. 60% aqueosu solution (ABCR); *n*-butylamine (Aldrich, >99%); *N*,*N*-dimethylformamide puriss, absolute, over molecular sieve (Aldrich); phosphorous(V) oxide (ABCR, 98%); *p*-xylylenediamine (TCI Chemicals, >99.0%); silica gel 60 silanized for column chromatography (0.063-0.200 mm, Merck); triethylamine (ABCR, 99%); trifluoromethanesulfonic acid (TCI Chemicals, >98.0%).

Equipment: elemental analyzer PERKIN-ELMER type 240; mass spectrometer MALDI Synapt G2-S (*m*/*z* peaks listed according to decreasing peak intensity); nuclear magnetic resonance spectrometers Varian VNMRS 500 and Varian Mercury 400 (chemical shifts reported in reference to solvent residual peak (1.94 ppm (^{1}H) and 118.26 ppm (^{13}C) for acetonitrile)); potentiostat Autolab (ECO Chemie, Netherlands).

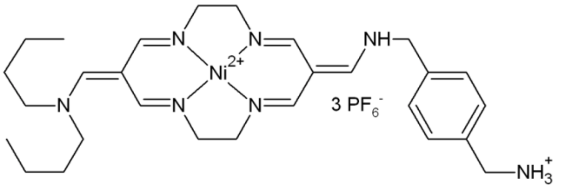
Compounds **1Ni**, **1Cu** (a mixed salts of dicationic TAM complex and PF_6^- and $CF_3SO_3^-$ counterions in 1:1 ratio), and complex **2Ni** were synthesized according to known procedures (see M. Woźny et al., *Chem. Sci.*, **2014**, 5, 2836.). The remaining compounds were synthesized as follows:



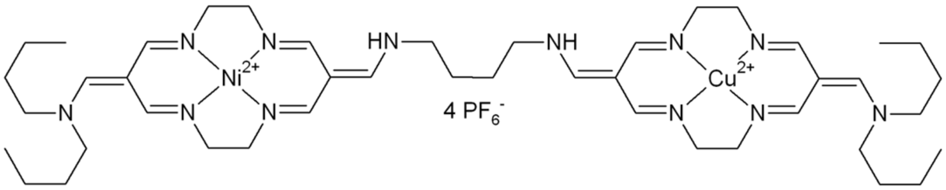
2Cu: 80.2 mg of complex **1Cu** (0.110 mmol) was dissolved in 3 mL of anhydrous CH_3CN and 1.1 eq. of *n*-butylamine (11.9 μL) was added. The mixture was left for 15 minutes. Then 1 g of silanized silica gel was added and the suspension was evaporated to dryness. The solid was transferred to the top of silanized silica gel column and eluted with a mixture containing 10 g NH_4PF_6, 550 mL H_2O and 450 mL CH_3CN. The main, orange-red fraction was collected and concentrated. The precipitate formed during evaporation of CH_3CN was filtered, washed with 5 × 3 mL H_2O and dried *in vacuo* over P_2O_5. Yield 41.3 mg (49%). *Anal.* Calc. for $C_{24}H_{42}CuN_6{\cdot}2PF_6$ (768.1): C 37.53, H 5.51, N 10.94%; found C 37.50, H 5.31, N 10.75%. TOF MS ES+ (CH_3CN, *m/z*): 238.6 $[C_{24}H_{42}CuN_6]^{2+}$, 476.3 $[C_{24}H_{41}CuN_6]^{+}$. ^{1}H NMR (400 MHz, CD_3CN) δ 0.87, 1.07, 1.22, 1.52 and 1.65 (5 × br, $CH_2CH_2CH_3$).



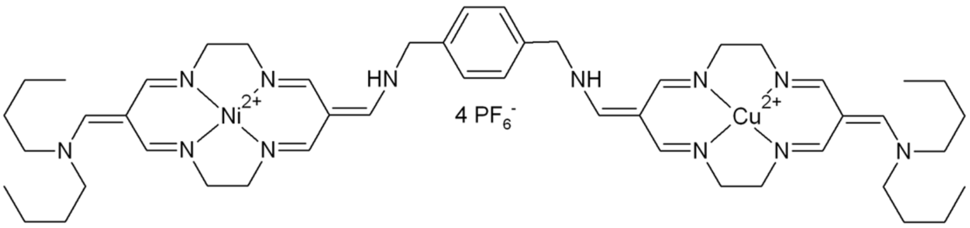
3Ni: To 581.0 mg of complex **1Ni** (0.801 mmol) dissolved in 5 mL of anhydrous CH_3CN, a solution of 1 eq. of trifluoromethanesulfonic acid (70.9 μL) and 1 eq. of putrescine (80.5 mg) in 3 mL of CH_3CN was added. Each of the mixtures was stirred for 5 minutes, followed by the addition of 2 g of silanized silica gel. The suspension was evaporated to dryness and solids transferred to the top of the silanized silica gel column. A solution of 2 g NH_4PF_6 and 15 μL of 60% HPF_{6aq} in 100 mL of H_2O was passed through, followed by 300 mL of distilled water. The title compound was eluted with 10% CH_3CN in H_2O, and collected as the first yellow-colored, broad band. The eluate was evaporated to dryness and resulting solid was further dried *in vacuo*, over P_2O_5. Yield: 324.6 mg (43%). *Anal.* Calc. for $C_{24}H_{44}N_7Ni{\cdot}3PF_6{\cdot}H_2O$ (**3Ni**$\cdot H_2O$) (942.3): C 30.59, H 4.92, N 10.41%; found C 30.43, H 4.84, N 10.28%. TOF MS ES$^+$ (CH_3CN, *m/z*): 486.2 $[C_{24}H_{42}N_7Ni]^{+}$. ^{1}H NMR (500 MHz, CD_3CN) δ 0.97 (comp, 2 × 3 H, CH_3); 1.34, 1.42 (2 × m, 2 × 2 H, $C\underline{H_2}CH_3$); 1.69 (comp, 8 H, CH_2 β to N); 2.98 (t, *J* = 7.3 Hz, 2 H, $C\underline{H_2}NH_3^+$); 3.47-3.62 (comp, 14 H, NCH_2); 5.60-7.20 (br, 4 H, NH_3^+, NH); 7.53 (s, 2 H), 7.66 (br, 3 H), 8.11 (br, 1 H) (CH=N, =CHN). ^{13}C NMR (125 MHz, CD_3CN) δ 13.8, 13.8 (CH_3); 20.1, 20.4 ($\underline{C}H_2CH_3$); 24.3, 27.0, 29.2, 31.3 (CH_2 β to N); 40.6 ($CH_2NH_3^+$); 50.7, 52.6, 59.3, 60.1, 61.3 (NCH_2); 103.9, 104.4 ($\underline{C}$=CHN); 155.3, 160.7 (CH=N); 162.4, 164.1 (=CHN).



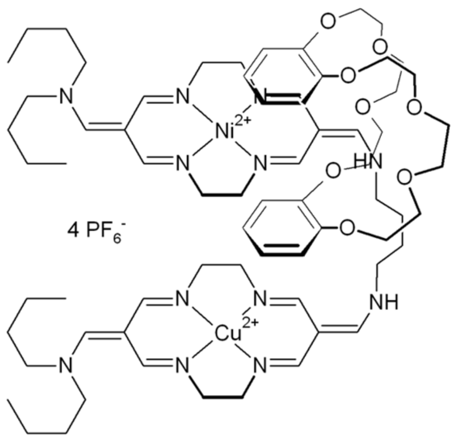
3’Ni: To 460.7 mg of complex **1Ni** (0.635 mmol) dissolved in 4 mL of anhydrous CH_3CN, a solution of 1 eq. of trifluoromethanesulfonic acid (56.2 μL) and 1 eq. of *p*-xylylenediamine (86.5 mg) in 3 mL of degassed and warm DMF was added. The mixture was stirred for 5 min, and then treated analogously to the procedure described for complex **3Ni**. Yield: 213.8 mg (34%). *Anal.* Calc. for $C_{28}H_{44}N_7Ni{\cdot}3PF_6{\cdot}H_2O$ (990.3): C 33.96, H 4.68, N 9.90%; found C 33.87, H 4.50, N 9.83%. TOF MS ES^+ (CH_3CN, *m/z*): 536.3 $[C_{28}H_{44}N_7Ni]^+$, 268.7 $[C_{28}H_{45}N_7Ni]^{2+}$. ^1H NMR (400 MHz, CD_3CN) δ 0.97 (comp, 2 × 3 H, CH_3); 1.34, 1.42 (2 × m, 2 × 2 H, $C\underline{H}_2CH_3$); 1.65-1.78 (comp, 2 × 2 H, CH_2 β to N); 3.50-3.63 (comp, 12 H, NCH_2CH_2N and $NC\underline{H}_2(CH_2)_2CH_3$); 4.15 (q, J = 6.0 Hz, 2 H, $ArC\underline{H}_2NH_3^+$); 4.69 (d, J = 6.0 Hz, 2 H, $ArC\underline{H}_2NH$); 6.66 (br, 3 H, NH_3^+); 7.45 (comp, 4 H, H_{Ar}); 7.49, 7.53, 7.56, 7.67 br, 7.78, 7.81, 8.07 (6 H, =CHN and CH=N); 8.54 (br, 1 H, NH). ^{13}C NMR (100 MHz, CD_3CN) δ 13.8 (CH_3); 20.1, 20.5 ($\underline{C}H_2CH_3$); 29.2, 31.3 (CH_2 β to N); 44.3 ($CH_2NH_3^+$); 52.6, 54.4, 59.4, 60.3, 61.4 (NCH_2); 103.9, 104.8 ($\underline{C}$=CHN); 129.6, 130.8 ($C_{sp2}H$ in benzene ring); 133.2, 138.1 ($\underline{C}_{sp2}C$ in benzene ring); 155.4, 161.0 (CH=N); 162.5, 164.1 (=CHN).



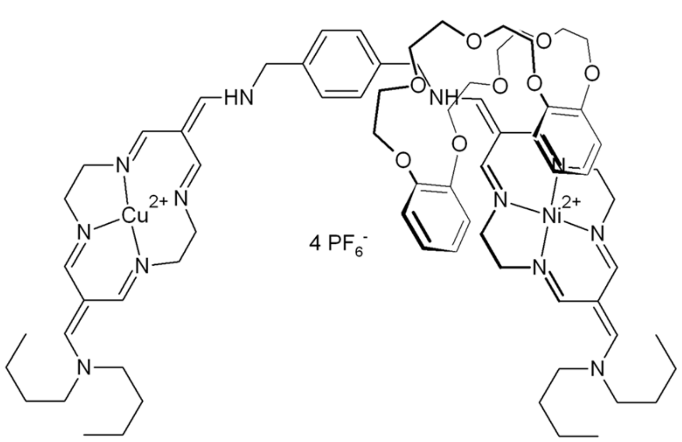
4CuNi: 32.0 mg of monohydrate $\mathbf{3Ni}{\cdot}H_2O$ (0.034 mmol) was dehydrated by triple dissolution/evaporation (3 × 5 mL of anhydrous CH_3CN). The remaining solid, **3Ni**, was then dissolved in 0.7 mL of CH_3CN and poured into the solution of 1 eq. of **1Cu** (24.9 mg) in 0.3 mL of CH_3CN, followed by the addition of a solution of 2 eq. of triethylamine (9.5 μL) in 0.5 mL of CH_3CN. The mixture was stirred for 30 minutes and a solution of 100 mg NH_4PF_6 in 20 mL H_2O was added. CH_3CN was evaporated, precipitate filtered and dissolved again in 5 mL of CH_3CN. Then, 0.5 g of silanized silica gel 60 (Merck) was added, the suspension was evaporated to dryness, solids transferred to the top of the silanized silica gel column, and eluted with a mixture of 1 g NH_4PF_6 : 100 mL H_2O : 150 mL CH_3CN. The first and main, orange-colored fraction was collected. The precipitate formed during evaporation of CH_3CN was filtered, washed with 2 × 5 mL of H_2O, 3 mL of CH_3OH, 3 mL Et_2O, and dried *in vacuo* over P_2O_5. Yield 32.1 mg (64%). *Anal.* Calc. for $C_{44}H_{74}CuN_{12}Ni{\cdot}4PF_6$ (1473.2): C 35.87, H 5.06, N 11.41%; found C 36.07, H 4.88, N 11.17%. TOF MS ES+ (CH_3CN, *m/z*): 222.9 $[C_{44}H_{74}CuN_{12}Ni]^{4+}$, 296.8 $[C_{44}H_{73}CuN_{12}Ni]^{3+}$, 444.7 $[C_{44}H_{72}CuN_{12}Ni]^{2+}$, 517.7 $[C_{44}H_{73}CuN_{12}Ni{\cdot}PF_6]^{2+}$, 590.6 $[C_{44}H_{74}CuN_{12}Ni{\cdot}2PF_6]^{2+}$. ^1H NMR (500 MHz, CD_3CN) δ 0.88, 1.08 (2 × br, CH_3 in Cu unit); 0.97 (comp, 2 × 3 H, CH_3 in Ni unit); 1.19, 1.27 (2 × br, 2 × 2 H, $C\underline{H}_2CH_3$ in Cu); 1.34, 1.42 (2 × m, 2 × 2 H, $C\underline{H}_2CH_3$ in Ni); 1.58 br, 1.65 br, 1.71 m (CH_2 β to N); 3.43, 3.57 (2 × br, 14 H, NCH_2); 7.53 s, 7.63 br, 7.67 br, 7.99 br, 9.00-10.00 br (CH=N, =CHN, NH) (for ^1H NMR, see below). ^{13}C NMR (125 MHz, CD_3CN) δ 13.5, 15.0 (CH_3 in Cu unit); 13.81, 13.84 (CH_3 in Ni unit); 20.1, 20.4 ($\underline{C}H_2CH_3$ in Ni unit); 20.3 ($\underline{C}H_2CH_3$ in Cu unit); 27.0 (CH_2 β to N in the linker, on the side of Ni unit); 29.2, 31.3 (CH_2 β to N in NBu_2, in Ni unit); 50.7, 52.5 (NCH_2CH_2N in Ni); 59.3 br, 60.2 br, 61.3 (NCH_2 in the linker and NBu_2, in Ni unit); 103.9, 104.3 ($\underline{C}$=CHN in Ni unit); 155.1 br, 160.7 br (CH=N in Ni unit); 162.4, 163.9 (=CHN in Ni unit).



4’CuNi: 21.4 mg of **3’Ni**$\cdot H_2O$ (0.022 mmol) was dehydrated as above, dissolved in 0.5 mL of CH_3CN and poured into the solution of 1 eq. of **1Cu** (16.1 mg) in 0.3 mL of CH_3CN, followed by the addition of a solution of 2 eq. of triethylamine (6.1 µL) in 0.3 mL of CH_3CN. The mixture was stirred for 30 minutes and then treated analogously to the procedure described for complex **4CuNi**. Yield 20.4 mg (61%). *Anal.* Calc. for $C_{48}H_{74}CuN_{12}Ni{\cdot}4PF_6$ (1521.3): C 37.90, H 4.90, N 11.05%; found C 37.73, H 4.82, N 10.91%. TOF MS ES+ (CH_3CN, *m/z*): 234.9 $[C_{48}H_{74}CuN_{12}Ni]^{4+}$, 312.8 $[C_{48}H_{73}CuN_{12}Ni]^{3+}$, 614.7 $[C_{48}H_{74}CuN_{12}Ni{\cdot}2PF_6]^{2+}$, 468.7 $[C_{48}H_{72}CuN_{12}Ni]^{2+}$. ^1H NMR (500 MHz, CD_3CN) δ 0.88, 1.08 (2 × br, CH_3 in Cu unit); 0.97 (comp, CH_3 in Ni unit); 1.18 (br, $C\underline{H}_2CH_3$ in Cu unit); 1.34 and 1.42 (2 × m, $C\underline{H}_2CH_3$ in Ni); 1.56-1.77 (comp, CH_2 β to N); 3.45-3.68 (comp, NCH_2); 4.64 (s, 4 H, CH_2Ar); 7.15-7.39 (comp, br with 7.28 and 7.34 ppm, H_{Ar} of *p*-xylyl linker); 7.53 s, 7.67 br, 7.78 s (CH=N, =CHN, NH) (for ^1H NMR spectra, see below). ^{13}C NMR (125 MHz, CD_3CN) δ 13.5, 15.0 (CH_3 in Cu unit); 13.83, 13.85 (CH_3 in Ni unit); 20.1, 20.4 ($\underline{C}H_2CH_3$ in Ni unit); 20.3 ($\underline{C}H_2CH_3$ in Cu unit); 29.2, 31.3 (CH_2 β to N in NBu_2, in Ni unit); 52.6, 54.5, 60.4 br, 61.3 (NCH_2); 103.9, 104.7 ($\underline{C}$=CHN in Ni unit); 129.3, 129.4 ($C_{sp2}H$ in benzene ring); 136.7 ($\underline{C}_{sp2}C$ in benzene ring); CH=N in Ni unit unobserved; 162.5, 164.0 (=CHN in Ni unit).



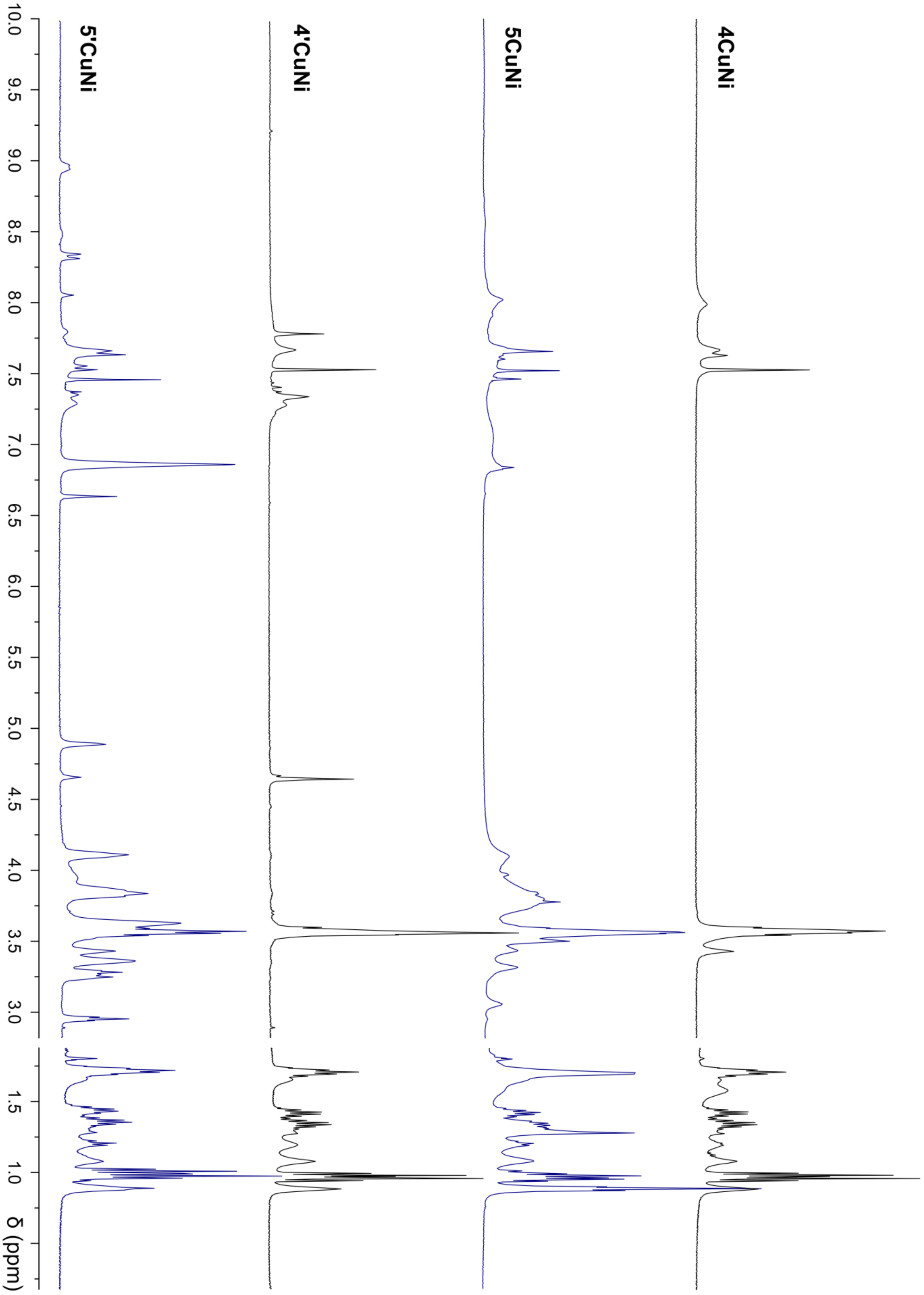
5CuNi: 34.3 mL of anhydrous CH_3CN was added to the mixture of 195.9 mg of **1Cu** (0.268 mmol), 1 eq. of **3Ni** (252.8 mg before dehydration) and 20 eq. of dibenzo-24-crown-8 (2.404 g). The suspension was degassed and filled with argon, then heated gently until all crown ether dissolved. After cooling to room temperature, a solution of 1 eq. of triethylamine (37.4 μL) in 1 mL of CH_3CN was added dropwise over the period of 3 h. From time to time the flask was gently heated in order to dissolve DB24C8, which crystallizes from the supersaturated solution. The solution was stirred overnight, followed by filtering off the DB24C8 precipitate. The filtrate was evaporated to dryness and solids were washed by shaking with 5 × 15 mL of anhydrous benzene to extract remnants of DB24C8. Then, the orange-colored oil remaining in the flask was dried *in vacuo*, dissolved in 5 mL CH_3CN and poured to the solution of 1 g of NH_4PF_6 in 50 mL of H_2O. The immediately formed precipitate was filtered, washed with 15 mL of H_2O, dissolved in 8 mL CH_3CN, and adsorbed on 1 g of silanized silica gel. The solid was transferred to the top of silanized silica gel column. Distilled water (A) and a solution of 15 gL^{-1} of NH_4PF_6 in CH_3CN (B) were prepared. The product was isolated by means of gradient elution with 20, 30, 40 and 50% of B in A+B mixture. The main and last orange-colored fraction was collected. The precipitate formed during evaporation of CH_3CN was filtered, washed with 5 × 10 mL H_2O, 3 mL CH_3OH and 3 mL Et_2O, and dried *in vacuo* over P_2O_5. Yield 139.1 mg (27%). *Anal.* Calc. for $C_{68}H_{106}CuN_{12}NiO_8\cdot 4PF_6$ (1921.7): C 42.50, H 5.56, N 8.75%; found C 42.53, H 5.62, N 8.64%. TOF MS ES+ (CH_3CN, *m/z*): 335.0 $[C_{68}H_{106}CuN_{12}NiO_8]^{4+}$, 446.3 $[C_{68}H_{105}CuN_{12}NiO_8]^{3+}$, 741.9 $[C_{68}H_{105}CuN_{12}NiO_8\cdot PF_6]^{2+}$. ^1H NMR (500 MHz, CD_3CN) δ 0.89 br t, 0.97 comp, 1.08 br (CH_3); 1.15-1.50 a set of signals with visible maxima at 1.21, 1.28, 1.42 ($C\underline{H}_2CH_3$); 1.50-1.85 with maxima at 1.70 and 1.71 (CH_2 β to N); 2.85-3.65 with maxima at 2.95, 3.06, 3.32, 3.43, 3.50 and 3.56 (NCH_2); 3.65-4.30 with maxima at 3.78 and 4.10 (OCH_2); 6.60-7.35 with maxima at 6.84 and 7.06 (H_{Ar}); 7.35-8.90 with maxima at 7.46, 7.52, 7.60, 7.66, 8.02, 8.58, 8.72, and 8.90-10.50 br (CH=N, =CHN, NH) (for ^{1}H NMR spectra, see below). ^{13}C NMR (125 MHz, CD_3CN) δ 13.5, 13.8, 13.9 and 15.0 (CH_3); 20.10, 20.12, 20.3, 20.4 ($\underline{C}H_2CH_3$); 27.1, 27.5 (CH_2 β to N in the linker); 29.2, 31.3, 31.4 (CH_2 β to N in NBu_2); 49.0, 50.4, 51.1, 52.5, 52.6, 58.7 br, 59.7 br, 60.1 br, 61.3, 68.5 br, 69.3, 70.3 br, 71.2 br, 71.5 br (NCH_2 and OCH_2); 103.8, 104.3 ($\underline{C}$=CHN); 112.9 (C *ortho* to O); 121.5, 122.4 (C *meta* to O); 149.1 br (C_{sp2}–O); 154.4 br, 159.3 br (CH=N); 162.1, 162.4, 163.9, 166.2 (=CHN).



5’CuNi: 19.3 mL of anhydrous CH_3CN was added to the mixture of 110.7 mg of **1Cu** (0.151 mmol), 1 eq. of **3’Ni** (149.9 mg before dehydration) and 20 eq. of dibenzo-24-crown-8 (1.354 g). The suspension was degassed and filled with argon, then heated gently until all crown ether dissolved. After cooling to room temperature, a solution of 1 eq. of triethylamine (21.1 μL) in 1 mL of CH_3CN was added dropwise over the period of 3 h. Then the synthesis and isolation was performed analogously to the procedure described for rotaxane **5CuNi**. Yield 74.4 mg (25%). *Anal.* Calc. for $C_{72}H_{106}CuN_{12}NiO_8 \cdot 4PF_6$ (1969.8): C 43.90, H 5.42, N 8.53%; found C 43.67, H 5.38, N 8.46%. TOF MS ES+ (CH_3CN, *m/z*): 346.9 $[C_{72}H_{106}CuN_{12}NiO_8]^{4+}$, 462.2 $[C_{72}H_{105}CuN_{12}NiO_8]^{3+}$, 765.8 $[C_{72}H_{105}CuN_{12}NiO_8 \cdot PF_6]^{2+}$, 692.8 $[C_{72}H_{104}CuN_{12}NiO_8]^{2+}$, 838.8 $[C_{72}H_{106}CuN_{12}NiO_8 \cdot 2PF_6]^{2+}$. ^{1}H NMR (500 MHz, CD_3CN) δ 0.89 br, 0.93-1.03 comp, 1.08 br (CH_3); 1.15-1.50 a set of signals with visible maxima at 1.21, 1.28, 1.36, 1.43 ($C\underline{H_2}CH_3$); 1.60-1.80 with maximum at 1.72 (CH_2 β to N); 2.90-3.60 with maxima at 2.95, 3.25, 3.28, 3.36, 3.43, and 3.57 (NCH_2); 3.60-4.20 with maxima at 3.63, 3.84 and 4.11 (OCH_2); 4.66 and 4.89 (2 × br, CH_2Ar); 6.63 (s, 1 H, one of NCH_2CH_2N protons in Ni unit); 6.86 (br, H_{Ar} of DB24C8 ring); 7.20-7.40 with maxima at 7.29 and 7.35 (H_{Ar} of the p-xylyl linker); 7.40-9.05 with maxima at 7.46, 7.53, 7.55, 7.63, 7.66, 7.80, 8.05, 8.31, 8.34, 8.49 and

8.96 (CH=N, =CHN, NH) (for ^{1}H NMR spectra, see below). ^{13}C NMR (125 MHz, CD_3CN) δ 13.5, 13.8, 13.9 and 15.0 (CH_3); 20.1, 20.3, 20.5 ($\underline{C}H_2CH_3$); 29.2, 31.3, 31.4 (CH_2 β to N); 52.5, 54.2, 58.5, 59.5, 61.3, 68.3, 70.8, 71.0 (NCH_2 and OCH_2); 103.8, 104.5 ($\underline{C}$=CHN); 112.6 (C "*ortho*" to O in benzene ring of DB24C8); 121.8 (C "*meta*" to O in benzene ring of DB24C8); 128.9 and 129.7 ($C_{sp2}H$ in benzene ring of the *p*-xylyl linker); 138.1 ($\underline{C}_{sp2}C$ in benzene ring of the *p*-xylyl linker); 148.9 (C_{sp2}–O); 154.7 and 158.6 (CH=N); 162.0 and 167.1 (=CHN).

^{1}H NMR spectra of 4CuNi, 4'CuNi, 5CuNi and 5'CuNi (500 MHz, CD_3CN, 298.15 K)



Electroanalytical measurements

Square wave voltammetry (SWV) and cyclic voltammetry (CV) experiments were carried out using the Autolab potentiostat (ECO Chemie, Netherlands) in a three electrode arrangement, with a silver/silver chloride (Ag/AgCl) electrode as the reference, platinum foil as the counter and the glassy carbon electrode (GCE, BAS, 3 mm diameter) as the working electrode. The reference electrode were separated from the working solution by an electrolytic bridge filled with 0.1 M tetrabutylammonium hexafluorophosphate/acetonitryl (TBAHFP/AN) solution. The reference potential electrode was calibrated by using the ferrocene oxidation process in the same TBAHFP/AN solution. 0.1 M TBAHFP/AN was used as the supporting electrolyte solution. Argon was used to deaerate the solution and an argon blanket was maintained over the solution during all experiments. All experiments were carried out at 25 °C. The GC electrode was polished mechanically with 1.0, 0.3 and 0.05 μm alumina powder on a Buehler polishing cloth to a mirror-like surface. Finally, it was rinsed with acetonitrile and sonificated in pure acetonitrile.

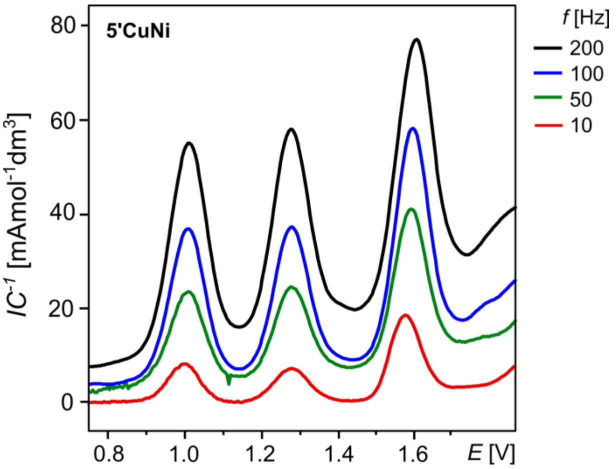


Fig. 1 Square wave voltammograms (SWV) of rotaxane **5'CuNi** (CH_3CN, ΔE = 5 mV, 25 mV amplitude, *E* [V] *vs.* Ag/AgCl).

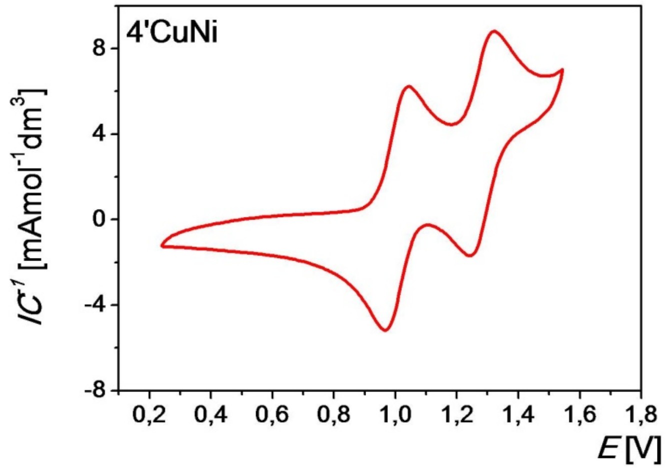


Fig. 2 Cyclic voltammogram (CV) of **4’CuNi** (CH_3CN, v = 50 mVs^{-1}, E [V] *vs.* Ag/AgCl).

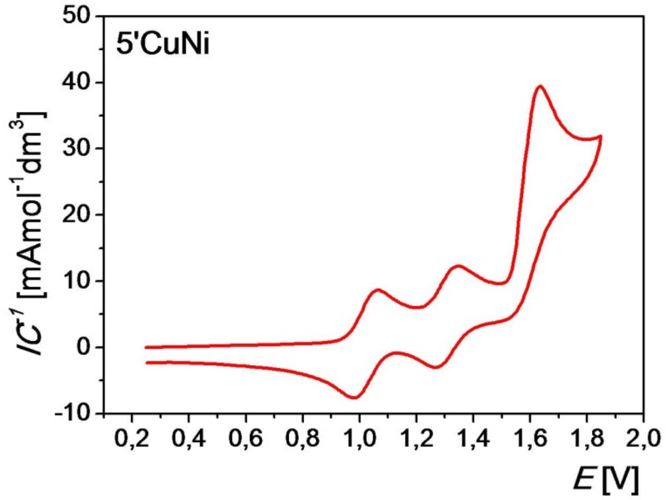


Fig. 3 Cyclic voltammogram (CV) of rotaxane 5’**CuNi** (CH_3CN, v = 50 mVs^{-1}, E [V] *vs.* Ag/AgCl).

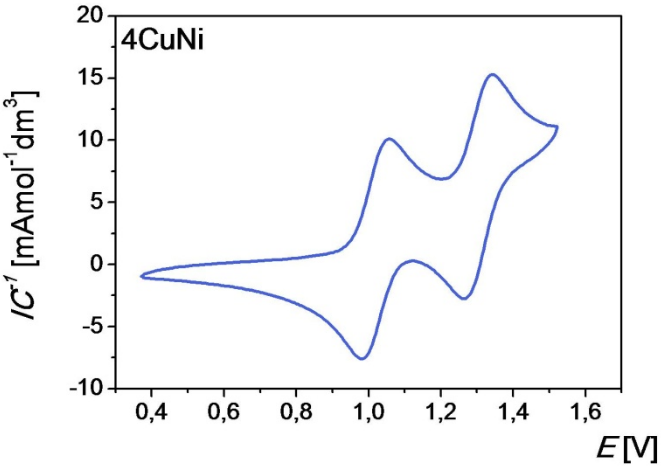


Fig. 4 Cyclic voltammogram (CV) of **4CuNi** (CH_3CN, v = 50 mVs^{-1}, E [V] *vs.* Ag/AgCl).

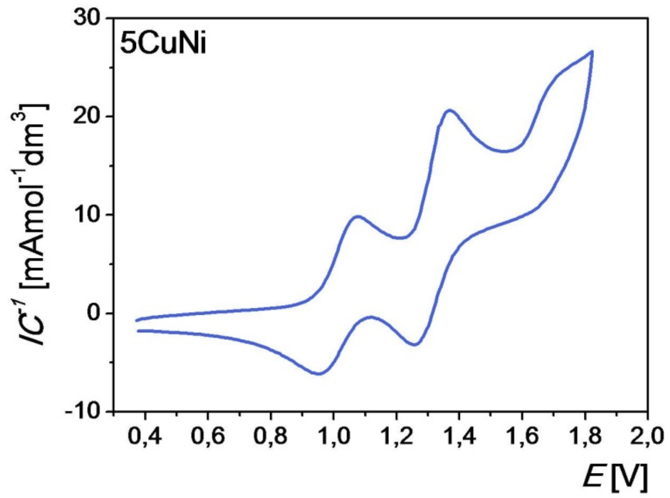


Fig. 5 Cyclic voltammogram (CV) of **5CuNi** (CH_3CN, $v = 50$ mVs^{-1}, E [V] *vs.* Ag/AgCl).

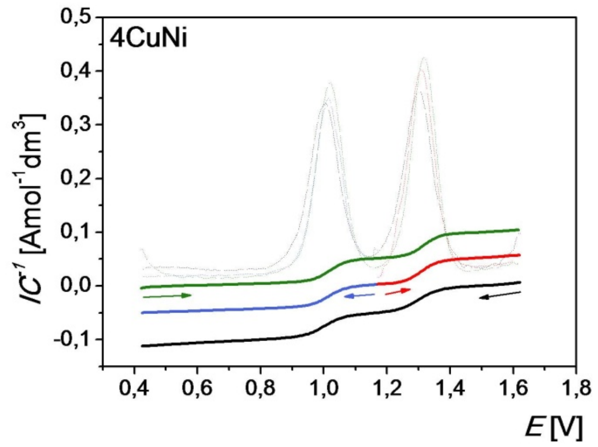


Fig. 6 Normal/reversed pulse voltammograms and their derivatives (NPV/RPV) of **4CuNi** (CH_3CN, $t_p = 70$ms, $t_w = 2$s, E [V] *vs.* Ag/AgCl).

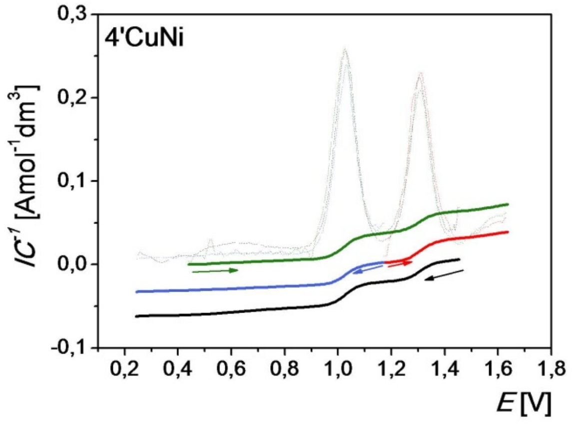


Fig. 7 Normal/reversed pulse voltammograms and their derivatives (NPV/RPV) of **4'CuNi** (CH_3CN, $t_p = 70$ms, $t_w = 2$s, E [V] *vs.* Ag/AgCl).

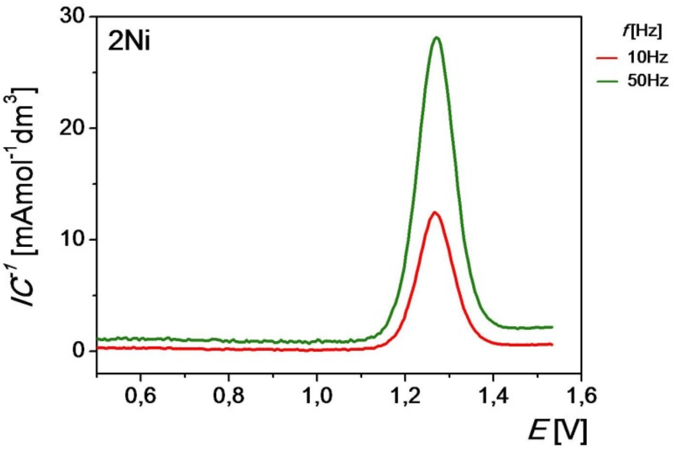


Fig. 8 Square wave voltammograms (SWV) of compound **2Ni** (CH_3CN, ΔE = 5 mV, 25 mV amplitude, E [V] *vs.* Ag/AgCl).

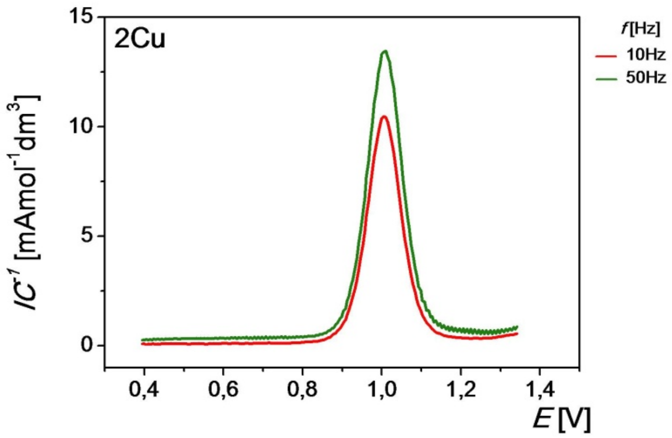


Fig. 9 Square wave voltammograms (SWV) of compound **2Cu** (CH_3CN, ΔE = 5 mV, 25 mV amplitude, E [V] *vs.* Ag/AgCl).