Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Supporting Information for

Studies of Hybrid Organic-Inorganic [2] and [3] Rotaxanes Bound to Au Surfaces

Harapriya Rath,[a] Grigore A. Timco,[a] Valdis Corradini,[b] Alberto Ghirri,[b,c] Antonio Fernandez Lisardo,[a] Robin G. Pritchard,[a] Christopher A. Muryn,[a] Marco Affronte[b] and Richard E. P. Winpenny[a]**

a. School of Chemistry and Photon Science Institute, The University of Manchester Oxford Road. M13 9PL, Manchester (UK), Fax: (+44)161-275-4616
E-mail: richard.winpenny@manchester.ac.uk

b. CNR, Institute Nanoscience, S3 Centre and Dipartimento di Fisica, Universita di Modena e Reggio Emilia, Via Campi 213/A, 41125 Modena, Italy

c. CNR, Institute Nanoscience, S3 Centre and Dipartimento di Fisica, Universita di Milano, Via Celoria 16, 20133 Milano, Italy

Contents:

1. SYNTHESIS

1.1. Experimental Details

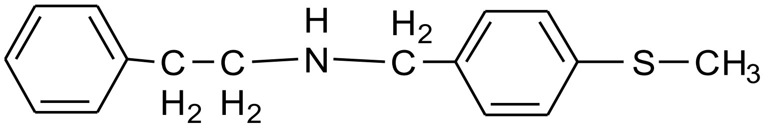
Unless stated otherwise, all commercially available reagents and solvents were used without further purification.

[$Ni_2(H_2O)(O_2CCMe_2)_4(HO_2CCMe_2)_4$] was prepared according to a procedure reported in G. Chaboussant, R. Basler, H.-U. Güdel, S. Ochsenbein, A.Parkin, S. Parsons, G. Rajaraman, A. Sieber, A. A. Smith, G. A. Timco, R. E. P.Winpenny, *Dalton Trans.*, 2004, 2758-2766. The 4-(Methylmercapto)phenylethylamine was prepared according to a procedure reported H. C. Englert, U. Gerlach, H. Goegelein, J. Hartung, H. Heitsch, D. Mania, S. Scheidler, *J. Med. Chem.* **2001,** *44,* 1085-1098. The $Me(O)CS(CH_2)_6Br$ was prepared according to a procedure reported in L. Tauk , A. P. Schröder, G. Decher, N. Giuseppone, Nature Chemistry, 1(8), 649-656; 2009.

The syntheses of the hybrid organic-inorganic rotaxanes were carried out in Erlenmeyer Teflon® FEP flasks supplied by Fisher. Column chromatography was carried out using Silica 60A (particle size 35-70 µm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light. NMR spectra were recorded on Bruker AV 400, and Bruker DMX 500 instruments. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. ESI mass spectrometry was carried out by the services at the University of Manchester.

1.2 Synthesis of $[(MeSArCH_2)NH_2C_2H_4Ph][Cr_7NiF_8(O_2C^tBu)_{16}]$ 1 (Ar = C_6H_4):

Thread $MeSArCH_2NHC_2H_4Ph$.

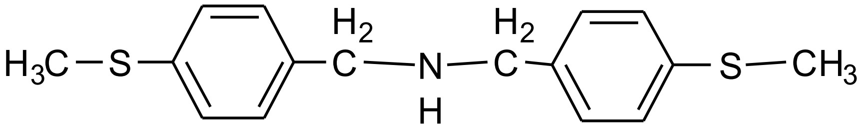


To a solution of phenylethylamine (1mL, 10mmol) in 30mL methanol, 4-methylthiobenzaldehyde (1.33mL, 10mmol) in 5mL methanol was added and the reaction mixture was refluxed for 3 hr under nitrogen atmosphere, then stirred at room temperature overnight. Then an excess of $NaBH_4$ was added and the reaction mixture was stirred during 24h under nitrogen atmosphere. Afterward the reaction was quenched with water and the solvents evaporated under reduced pressure evaporated. The residue s was extracted with chloroform, organic extract dried over anhydrous magnesium sulphate and evaporated under reduced pressure. Product $MeSArCH_2NHC_2H_4Ph$ was obtained as a light yellow liquid in 84% yield (2.1g). ES-MS (sample dissolved in MeOH, run in MeOH): m/z = 258 $[M+H]^+$. ^1H NMR (400 MHz, 293K, $CDCl_3$):$\delta = 2.4$(s, 3H), 2.70 (t, 2H), 2.8 (t, 2H), 3.60 (s, 2H), 7.00-7.2(m Ph, 9H).

Rotaxane 1. Me_3CCO_2H (20.0 g, 195 mmol), $MeSArCH_2NHC_2H_4Ph$ (0.616 g, 2.4 mmol), and $CrF_3\cdot4H_2O$ (3.0 g, 16 mmol) were heated at 140°C with stirring in a Teflon flask for 0.5 h, then $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$ (0.35 g, 0.6 mmol) was added. After 1 h the temperature of the reaction was increased to 160°C for 20 h. The flask was cooled to room temperature, and then acetone (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetone, dried in air. Flash chromatography (toluene, followed by gradient elution up to 8:1 toluene: EtOAc) afforded desired [2] rotaxane as a green crystalline solid. Yield: 1.9 g (32%, calculated from $CrF_3\cdot4H_2O$ used). Elemental analysis (%) calcd for $C_{96}H_{164}Cr_7F_8NNiO_{32}S$: Cr 14.85, Ni 2.39, C 47.06, H 6.70, N 0.57, S 1.30; found: Cr 14.04, Ni 2.30, C 46.77, H 7.08, N 0.61, S 1.20. ES-MS (sample dissolved in THF, run in MeOH): m/z = 2474 $[M+Na]^+$; 2451$[M]^+$. X-ray quality crystals were obtained by recrystallization from a mixture of Et_2O/acetone.

1.3 Synthesis of $[(MeSArCH_2)_2NH_2][Cr_7NiF_8(O_2C^tBu)_{16}]$ 2

Thread $(MeSArCH_2)_2NH$.

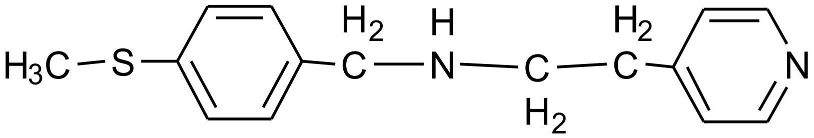


To a solution of 4-methylthiobenzylamine (0.64mL, 4.5mmol) in 30mL methanol, 4-methylthiobenzaldehyde (0.61mL, 4.5mmol) in 5mL methanol was added dropwise and the reaction mixture was refluxed for 3 hr under nitrogen atmosphere, then stirred at room temperature overnight. Then an excess of $NaBH_4$ was added and the reaction mixture stirred over night under nitrogen atmosphere. Afterward the reaction was quenched with water and the solvents evaporated under reduced pressure. The residue was extracted with chloroform. The organic extract was dried over anhydrous magnesium sulphate and then solvent removed under reduced pressure. The product $(MeSArCH_2)_2NH$ was obtained as light yellow liquid in 81% yield (1.1g). ES-MS (sample dissolved in MeOH, run in MeOH): m/z = 290 $[M+H]^+$. ^1H NMR (400 MHz, 293K, $CDCl_3$):δ = 2.4(s, 6H), 3.70 (s, 4H), 7.16(d, 4H), 7.23(d, 4H).

Rotaxane 2. Me_3CCO_2H (20.0 g, 195 mmol), $(MeSArCH_2)_2NH$ (0.7 g, 2.4 mmol), and $CrF_3{\cdot}4H_2O$ (3.0 g, 16 mmol) were heated at 140°C with stirring in a Teflon flask for 0.5 h, then $2NiCO_3{\cdot}3Ni(OH)_2{\cdot}4H_2O$ (0.35 g, 0.6 mmol) was added. After 1 h the temperature of the reaction was increased to 160°C for 20 h. The flask was cooled to room temperature, and then acetone (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetone and dried. Flash chromatography (toluene, then gradient elution up to 8:1 toluene: EtOAc) afforded desired [2] rotaxane as green crystalline solid. Yield: 1.6 g (26%, calculated from $CrF_3{\cdot}4H_2O$ used). Elemental analysis (%) calcd for $C_{96}H_{164}Cr_7F_8NNiO_{32}S_2$: Cr 14.66, Ni 2.36, C 46.45, H 6.62, N 0.56, S 2.58; found: Cr 14.62, Ni 2.31, C 45.48, H 6.46, N 0.58, S 2.44 . ES-MS (sample dissolved in THF, run in MeOH): m/z = 2506 $[M+Na]^+$; 2483$[M]^+$. X-ray quality crystals were obtained by recrystallization from acetone.

1.4 Synthesis of $[(MeSArCH_2)NH_2C_2H_4Py][Cr_7NiF_8(O_2C^tBu)_{16}]$ 3

Thread $(MeSArCH_2)NHC_2H_4Py$.

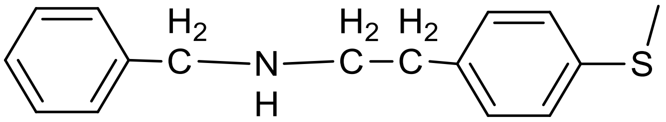


To a solution of 4-(2-aminoethyl)pyridine (0.5mL, 4.5mmol) in 30mL methanol, 4-methylthiobenzaldehyde (0.61mL, 4.5mmol) in 5mL methanol was added dropwise and the reaction mixture was refluxed for 3 h under nitrogen atmosphere, then allowed to stir at room temperature overnight. Then an excess of $NaBH_4$ was added and reaction mixture stirred over night under nitrogen atmosphere. The reaction was quenched with water and the solvents evaporated under reduced pressure. The residue was extracted with chloroform. The organic extract was dried over anhydrous magnesium sulphate and evaporated under reduced pressure. $(MeSArCH_2)NHC_2H_4Py$ was obtained as a light yellow liquid in 90% yield (1g). ES-MS (sample dissolved in MeOH, run in MeOH): m/z = 259 $[M+H]^+$. NMR (400 MHz, 293K, $CDCl_3$):δ = 2.4(s, 3H), 2.70 (t, 2H), 2.85 (t, 2H), 3.70 (s, 2H), 7.17(d, 2H), 7.23(d, 4H), 8.4 (d, 2H).

Rotaxane 3. Me_3CCO_2H (20.0 g, 195 mmol), $(MeSArCH_2)NHC_2H_4Py$ (0.619 g, 2.4 mmol), and $CrF_3\cdot4H_2O$ (3.0 g, 16 mmol) were heated at 140°C with stirring in a Teflon flask for 0.5 h, then $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$ (0.35 g, 0.6 mmol) was added. After 1 h the temperature of the reaction was increased to 160°C for 20 h. The flask was cooled to room temperature, and then acetone (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetone, dried in air. Flash chromatography (toluene, then gradient elution up to 5:1 toluene: EtOAc) afforded desired [2] rotaxane as green crystalline solid. Yield: 2.4 g (40%, calculated from $CrF_3\cdot4H_2O$ used). Elemental analysis (%) calcd for $C_{95}H_{163}Cr_7F_8N_2NiO_{32}S$: Cr 14.84, Ni 2.39, C 46.53, H 6.70, N 1.14, S 1.30; found: Cr 14.13, Ni 2.32, C 47.65, H 6.81, N 1.11, S 1.09. ES-MS (sample dissolved in THF, run in MeOH): m/z = 2475 $[M+Na]^+$; 2452$[M]^+$. X-ray quality crystals were obtained by recrystallization from ethylacetate.

1.5 Synthesis of [(MeSArC$_2$H$_4$)NH$_2$CH$_2$Ph][Cr$_7$NiF$_8$(O$_2$C^{t}Bu)$_{16}$] 4

Thread MeSArC$_2$H$_4$NHCH$_2$Ph :

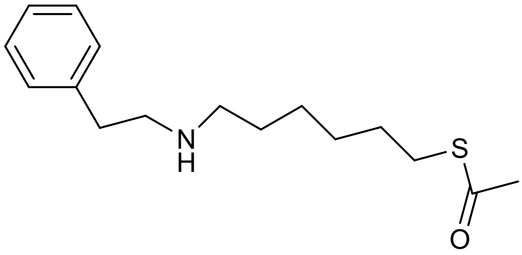


To a solution of 4-(Methylmercapto)phenylethylamine (0.5g, 2mmol) in 30mL methanol, benzaldehyde (0.25mL, 2mmol) in 5mL methanol was added and the reaction mixture was refluxed for 3 hr under nitrogen atmosphere, then allowed to stir at room temperature overnight. Then an excess of NaBH$_4$ was added and the reaction mixture was stirred during 24h under nitrogen atmosphere. Afterward the reaction was quenched with water and the solvents evaporated under reduced pressure. The residue was extracted with chloroform, washed with water and extract dried over anhydrous magnesium sulphate, and evaporated under reduced pressure. MeSArC$_2$H$_4$NHCH$_2$Ph was obtained as a light yellow liquid in 70% yield (0.44g). ES-MS (sample dissolved in MeOH, run in MeOH): m/z = 258 $[M+H]^+$. ^{1}H NMR (400 MHz, 293K, CDCl$_3$):δ = 2.4(s, 3H), 2.70 (t, 2H), 3.2 (t, 2H), 3.60 (s, 2H), 7.00-7.2(Ph 9H).

Rotaxane 4. Me$_3$CCO$_2$H (20.0 g, 195 mmol), MeSArC$_2$H$_4$NHCH$_2$Ph (0.6 g, 2.3 mmol), and CrF$_3$·4H$_2$O (2.8 g, 15 mmol) were heated at 140°C with stirring in a Teflon flask for 0.5 h, then [Ni$_2$(H$_2$O)(O$_2$CCMe$_2$)$_4$(HO$_2$CCMe$_2$)$_4$] (1.55 g) was added. After 1 h the temperature of the reaction was increased to 160°C for 20 h. The flask was cooled to room temperature, and then acetonitrile (35 mL) was added while stirring. The product was collected by filtration, washed with a large quantity of acetonitrile, dried in air, and then extracted with hexane and extract evaporated under reduced pressure. The green residue was purified by flash column chromatography (eluent toluene). An initial faint green band eluted off the column first, followed later by the main second band (intense green) which contained the desired product. The solvents were removed under reduced pressure and the green solid obtained was washed with acetonitrile and then dried under vacuum. Yield: 1.7g (30%, calculated
from CrF$_3$·4H$_2$O used). Elemental analysis (%) calcd for $C_{96}H_{164}Cr_7F_8NNiO_{32}S_1$: Cr 14.85, Ni 2.39, C 47.06, H 6.70, N 0.57, S 1.30; found: Cr 14.67, Ni 2.21, C 46.70, H 7.17, N 0.6, S 1.38. ES-MS (sample dissolved in THF, run in MeOH): m/z = 2451 $[M]^+$; 2474$[M+Na]^+$. X-ray quality crystals were obtained by recrystallization from acetone.

1.6 Synthesis of[(Me(O)CSC$_6$H$_{12}$)NH$_2$C$_2$H$_4$Ph][Cr$_7$NiF$_8$(O$_2$C^{t}Bu)$_{16}$] 5

Thread Me(O)CSC$_6$H$_{12}$NHC$_2$H$_4$Ph:

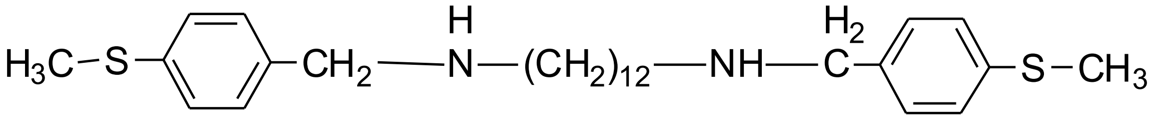


To a mixture of benzylethylamine (0.26mL, 2 mmol) and KF/Celite (1.1g) in acetonitrile (30 ml) was added a solution of Me(O)CS(CH$_2$)$_6$Br (0.5g, 2 mmol) in MeCN (15 ml) within 1 h. The mixture was stirred at r.t. for 2 days and then filtered. The solid was washed with MeCN. The combined organic phase was evaporated and the residue was purified by Flash chromatography (CH$_2$Cl$_2$/MeOH 10:1) to afford **Me(O)CSC$_6$H$_{12}$NHC$_2$H$_4$Ph** (0.28g, 50. ES-MS (sample dissolved in Dichloromethane, run in MeOH): m/z = 280 [M+H]$^+$. ^{1}H NMR (400 MHz, 293K, CDCl$_3$)= 1.3-1.6(m, 8H), 2.2(s, 3H), 2.60 (t, 2H), 2.80 (t, 2H), 3.70 (s, 2H), 7.10-7.3(m, Ph 5H).

Rotaxane 5. Me$_3$CCO$_2$H (20.0 g, 195 mmol), **Me(O)CSC$_6$H$_{12}$NHC$_2$H$_4$Ph** (0.55 g, 1.9 mmol), and CrF$_3$·4H$_2$O (2.37 g, 13 mmol) were heated at 140°C with stirring in a Teflon flask for 0.5 h, then [Ni$_2$(H$_2$O)(O$_2$CCMe$_2$)$_4$(HO$_2$CCMe$_2$)$_4$] (0.35 g) was added. After 1 h the temperature of the reaction was increased to 160°C for 20 h. The flask was cooled to room temperature, and then acetonitrile (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetonitrile, dried in air, and then extracted with hexane. Flash chromatography (hexane/toluene (1/9) and then toluene) afforded the desired [2] rotaxane as a green crystalline solid (0.8g) in 13% yield. Elemental analysis (%) calcd for C$_{96}$H$_{170}$Cr$_7$F$_8$NNiO$_{33}$S$_1$: Cr 14.73, Ni 2.38, C 46.62, H 6.89, N 0.57, S 1.29; found: Cr 14.84, Ni 2.33, C 46.76, H 7.08, N 0.59, S 1.31. ES-MS (sample dissolved in THF, run in MeOH): m/z = 2494 [M+Na]$^+$; 2471[M]$^+$.

1.7 Synthesis of $[(MeSArCH_2NH_2)_2(CH_2)_{12}][Cr_7NiF_8(O_2C^tBu)_{16}]_2$ 6

Thread $(MeSArCH_2NH)_2(CH_2)_{12}$:

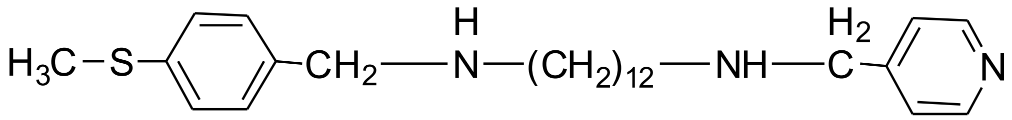


To a solution of 1,12-diamino dodecane (2.2g, 11mmol) in 30mL methanol, 4-methylthio- benzaldehyde (2.9mL, 22mmol) in 5mL methanol was added dropwise and the reaction mixture was refluxed for 3 h under nitrogen atmosphere, the allowed to stir at room temperature overnight. An excess of $NaBH_4$ was added and the reaction mixture stirred over night under nitrogen atmosphere. Then the reaction was quenched with water and the solvents evaporated under reduced pressure. The residue was extracted with chloroform, extract dried over anhydrous magnesium sulphate and then evaporated. The product was obtained as a white solid after recrystallisation from $CHCl_3$/Pentane in 78% yield (4g). ES-MS (sample dissolved in MeOH, run in MeOH): m/z = 473 $[M+H]^+$. NMR (400 MHz, 293K, $CDCl_3$):δ = 1.2 (s, 16H), 1.4 (m, 4H), 2.4(s, 6H), 2.50 (t, 4H), 3.70 (s, 4H), 7.10(d, 4H), 7.13(d, 4H).

Rotaxane 6. Me_3CCO_2H (20.0 g, 195 mmol), $(MeSArCH_2NH)_2(CH_2)_{12}$ (0.566 g, 1.2 mmol), and $CrF_3\cdot4H_2O$ (3.0 g, 16 mmol) were heated at 140°C with stirring in a Teflon flask for 0.5 h, then $2NiCO_3\cdot3Ni(OH)_2\cdot4H_2O$ (0.35 g, 0.6 mmol) was added. After 1 h the temperature of the reaction was increased to 160°C for 20 h. The flask was cooled to room temperature, and then acetone (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetone, dried in air. The solid was filtered and dried. Flash column chromatography (toluene, then gradient elution up to 4:1 toluene: EtOAc) afforded desired [3] rotaxane as a green crystalline solid. Yield: 2.2 g (37%, calculated from $CrF_3\cdot4H_2O$ used). Elemental analysis (%) calcd for $C_{188}H_{334}Cr_{14}F_{16}N_2Ni_2O_{64}S_2$: Cr 14.98, Ni 2.41, C 46.47, H 6.88, N 0.57, S 1.32; found: Cr 14.62, Ni 2.43, C 45.29, H 7.13, N 0.50, S 1.29. X-ray quality crystals were obtained by recrystallization from THF.

1.8. Synthesis of $[(MeSArCH_2)NH_2(CH_2)_{12}NH_2(CH_2Py)][Cr_7NiF_8(O_2C^tBu)_{16}]_2$ 7

Thread $(MeSArCH_2)NH(CH_2)_{12}NH(CH_2Py)$:



To a solution of 1,12 diaminododecane (2g, 10mmol) in 30mL methanol, 4-methylthiobenzaldehyde (1.35mL, 10mmol) in 5mL methanol was added and the reaction mixture was refluxed for 3 h under nitrogen atmosphere and then cooled to room temperature. The formed precipitated was filtered and washed with MeOH. Then it was redisolved under reflux in 30mL Methanol, and to the obtained solution 4-Pyridinecarboxaldehyde (0.95mL, 10mmol) in 5mL methanol was added, and the reaction mixture was refluxed for 3 hr under nitrogen atmosphere, afterward stirred at room temperature overnight. Then an excess of NaBH4 was added and reaction mixture stirred over night under nitrogen atmosphere. The reaction was quenched with water and the solvents evaporated under reduced pressure. The residue was extracted with chloroform, washed with water and dried over anhydrous magnesium sulphate and then evaporated Yield 60%. ES-MS (sample dissolved in dichloromethane, run in MeOH): m/z = 428 $[M+H]^+$. ^1H NMR (400 MHz, 293K, $CDCl_3$):δ = 1.3-1.6(m, 20H), 2.4(s, 3H), 2.70 (t, 2H), 2.80 (t, 2H), 3.60 (s, 2H), 3.70 (s, 2H), 7.09-7.3(Ph+py, 7 Hs), 8.4(d, py, 2H).

Rotaxane 7. Me_3CCO_2H (20.0 g, 195 mmol), $(MeSArCH_2)NH(CH_2)_{12}NH(CH_2Py)$ (0.67 g, 1.5 mmol), and $CrF_3\cdot4H_2O$ (3.9 g, 21 mmol) were heated at 140°C with stirring in a Teflon flask for 0.5 h, then $[Ni_2(H_2O)(O_2CCMe_2)_4(HO_2CCMe_2)_4]$ (2.1 g, 4.47 mmol) was added. After 1 h the temperature of the reaction was increased to 160°C for 24 h. The flask was cooled to room temperature, and then acetonitrile (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetonitrile, dried in air, and extracted with hexane. Flash chromatography (toluene then toluene/ethyl acetate 9/1) afforded the desired [3] rotaxane as a green crystalline solid (1.1 g) in 20% yield (calculated from $CrF_3\cdot4H_2O$ used). Elemental analysis (%) calcd for $C_{186}H_{331}Cr_{14}F_{16}N_3Ni_2O_{64}S_1$: Cr 15.12, Ni 2.44, C 46.42, H 6.89, N 0.87, S 0.67; found: Cr 14.57, Ni 2.23, C 46.97, H 7.43, N 0.84, S 0.63.

1.9. Synthesis of $\{[(MeSArCH_2)NH_2C_2H_4Py][Cr_7NiF_8(O_2C^tBu)_{16}]\}_2[Cu(O_2C^tBu)_2]_2$ 8

Rotaxane8: $[Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_2]$ (0.015 g, 0.02mmol) was added to a solution of **3** (0.1 g,0.04mmol) in toluene (3 mL), and the mixture was stirred until the copper complex dissolved. The reaction mixture was heated for 0.5h and then slowly brought to room temperature during which time nice crystals started forming. The crystalline product was filtered, washed with toluene and acetone and dried in air. Yield: 0.09g (50%; yields based on Cu). Elemental analysis (%) calcd for $C_{210}H_{362}Cr_{14}F_{16}N_4Ni_2O_{72}S_2Cu_2$: Cr 13.39, Ni 2.16,Cu 2.34, C 46.40, H 6.71, N 1.03, S 1.18; found: Cr 13.13, Ni 2.22, Cu 2.19, C 47.65, H 6.81, N 1.01, S 1.09.

2. **PROOF OF ROTAXANE FORMATION**

2.1 Calculation based on X-ray structure

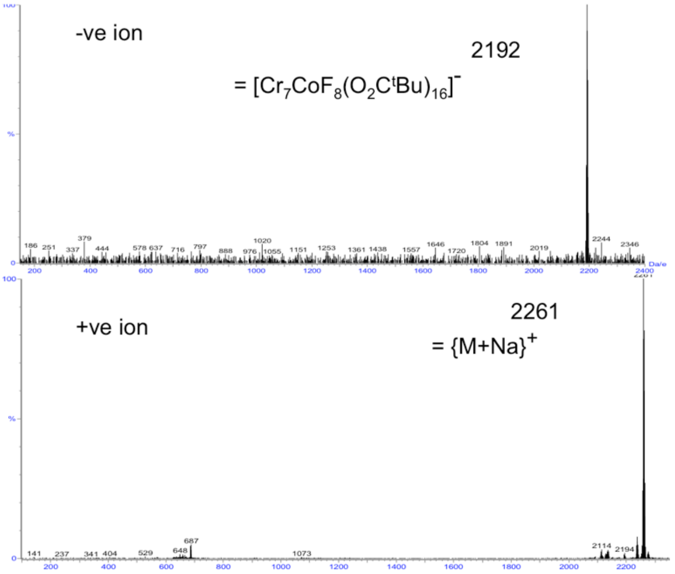
To check that phenyl-groups are large enough to prevent the rings slipping off the threads we did the following calculation. The size of the cavity of the rings is controlled by the distances between opposite fluorine atoms and the van der Waals radius for fluorine. The smallest distance between two opposite F atoms in compound **1** is 6.342 Å and the van der Waals radius 1.47 Å. So the size of the cavity is 6.34 – (2 x 1.47) = 3.40 Å. The average F….F distance is 6.57 Å, giving a cavity of 3.63 Å.

In the phenyl stoppers the average distance between opposite H-atoms is 4.00 Å. If we add in the van der Waals radius for hydrogen (1.2 Å) the space needed by stopper to move out of the ring is 5.4 Å. This is around 1.8 Å bigger than the cavity.

The calculation shows that the phenyl stoppers are big enough to keep the ring on the thread.

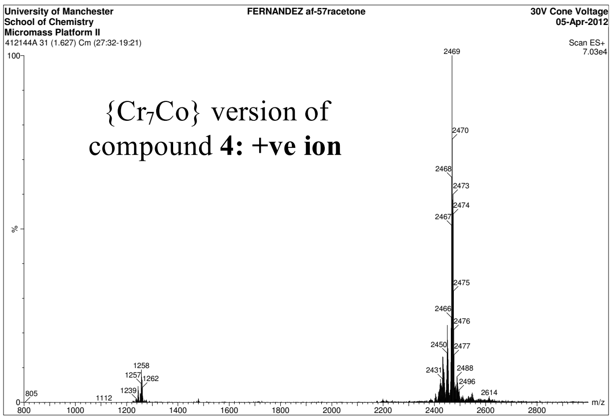
2.2 Electrospray Mass Spectrometry (ES-MS)

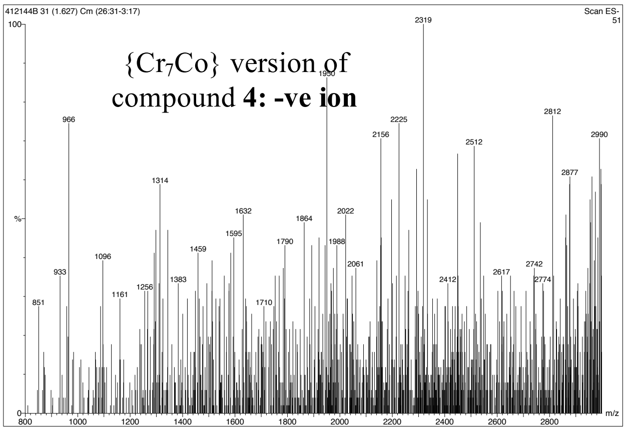
When heterometallic rings are templated about simple ammonium cations with small side-chains peaks are seen in both the positive ion and negative ion channels of an ES-MS experiment. In the positive ion we typically see the molecular ion plus one sodium ion. In the negative ion we see the heterometallic ring, without the organic template, i.e. the ammonium ion is sufficiently label we see the negative ring alone.



For example, for $[Me_2NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$, see right above.

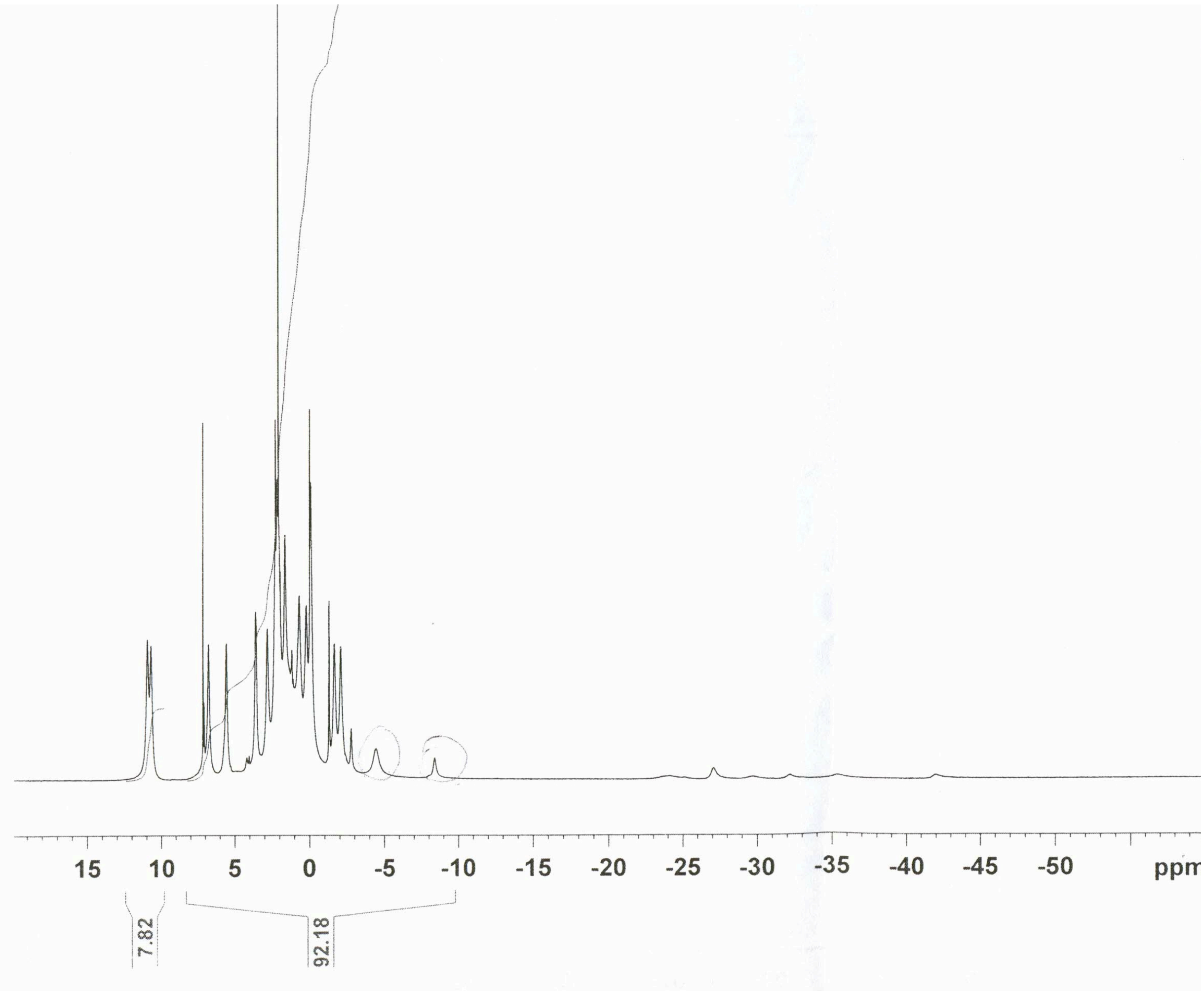
For the [2]rotaxanes reported here we only see significant peaks in the positive channel; no peaks are seen in the negative channel for the ring alone, as the thread cannot fall out of the ring. This is shown over, with the positive ion spectra for the $\{Cr_7Co\}$ version of **4** shown left and the negative ion shown right. No peaks above background are seen in the negative ion channel. This is direct evidence that **4** is a [2]rotaxane, not a *pseudo*-rotaxane.





2.3 NMR spectroscopy

The NMR spectra of the {Cr_7Co} ring complexes give interpretable paramagnetically shifted spectra. For the [2]rotaxanes discussed here the resonances for the organic thread are found shifted to negative chemical shifts; no resonances are seen for free thread (see below for the {Cr_7Co} version of **4**).



3. Experimental details on STM and XPS

The gold surface was prepared by sputtering and annealing of a Au(111) single-crystal (STM experiments) or flame annealing of Au/mica substrates (XPS experiments). We prepared mM solutions of derivatives **1-8** by dissolving microcrystalline powders in CH_2Cl_2. Monolayer depositions were obtained by dipping the gold surface for 10 minutes in a 1 mM solution of the specific derivative, followed by rinse with clean CH_2Cl_2 for 20 seconds and nitrogen blow-drying. Thick films were obtained by drop casting the saturated solution on HOPG substrates.

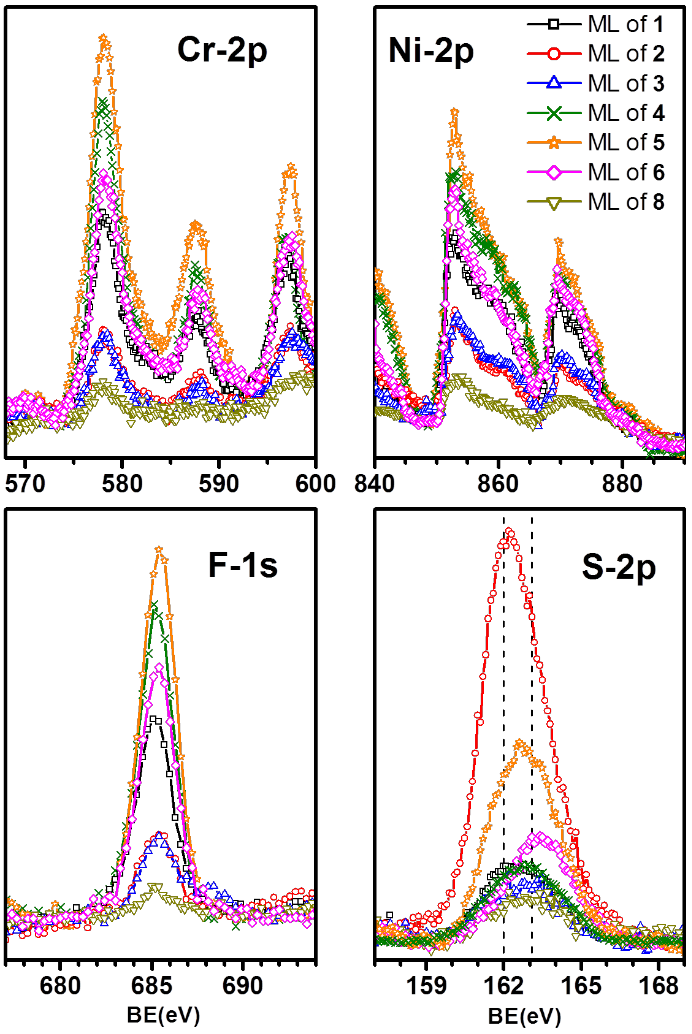


Fig. 3.1. Comparison among the core level spectra measured for monolayers of **1**, **2**, **3**, **4**, **5**, **6** and **8**.

Scanning tunneling microscopy and X-ray photoemission spectroscopy experiments were used to check that the desired two-dimensional distribution of nanometric entities was actually obtained. STM measurements were carried out by an Omicron UHV VT-STM system. The tips used were electrochemically etched tungsten wires. Room temperature STM images were obtained in constant current mode with typical imaging conditions of 2.0 V and the lowest achievable current (20 pA) in order to minimize dragging and damaging of the soft organic materials with the scanning tip. XPS measurements were performed by using an Omicron hemispherical analyzer (EA125) and a non-monochromatized Mg-Kα X-ray source ($h\nu = 1253.6$ eV).

3.1 XPS investigation

Fig. 3.1 shows the systematic comparison among the core levels of the Au(111) surface immersed in a 1 mM solution of all the derivatives from **1** to **8**. The Cr-2p, F-1s and Ni-2p core level line-shapes measured for the ML's fit well with the data obtained for the corresponding thick film. The F-1s/Cr-2p and Cr-2p/Ni-2p ratios are well reproducible and close to the expected ones (see Tab. I of the regular article), thus evidencing the stability of the core for all the Cr_7Ni rotaxanes reported. For the ML of **8**, we observed a strong excess of copper, which indicates that the Cu^{2+} dimer pivalate can undergo fragmentation, probably due to the high reactivity of copper with gold.

In summary, XPS data suggest that the core of these Cr_7Ni rotaxanes is chemically stable and unaffected by the deposition on gold, while the outermost parts (S-Me end groups and Cu dimer) are more susceptible to the presence of the metal surface and their behavior has to be evaluated case by case.

3.2 Further STM images

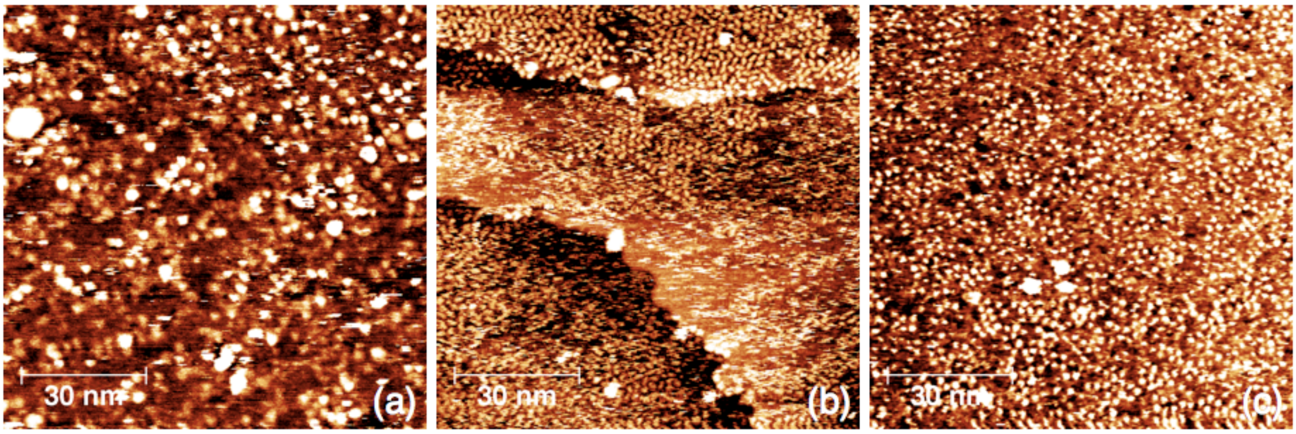


Fig. 3.2. STM images of [2]rotaxanes on Au(111): (a) **1**, (b) **4** and (c) **5**. Scan area is 100 x 100 nm^2.

The STM images in Fig. 3.2 (scan area of 100 x 100 nm^2) give a representative picture of the outcome of the deposition of **1**, **4** and **5** on gold. In detail, while panels (a) and (c) display a homogeneous distribution of isolated molecules respectively for **1** and **5**, panel (b) shows that **4** self –assemble in dense domains that alternates to free regions with a low density of molecules. The surface coverage can be estimated as (30 ± 20)% for **1**, (50 ± 20)% for **4** and (50 ± 20)% for **5**, in reasonable agreement with the values derived from the quantitative XPS analysis (Tab. I).

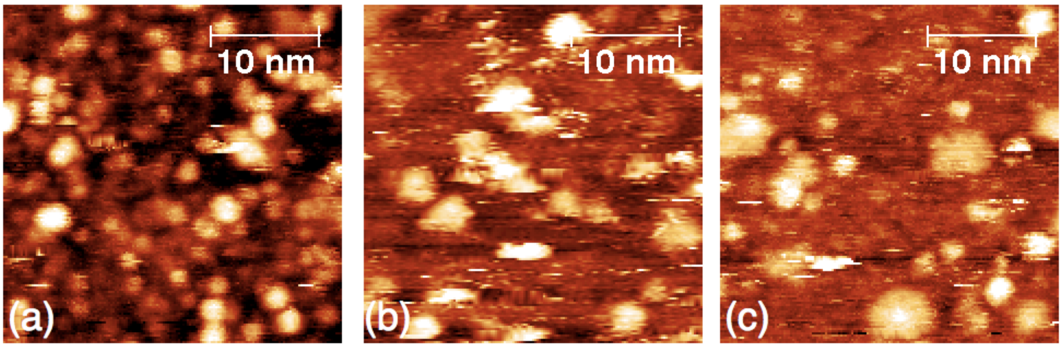


Fig 3.3. STM images showing the gold surface after the deposition of (a) **2**, (b) **3** and (c) **8**.

Fig. 3.3 shows the STM images taken on the Au(111) surface after the deposition respectively of **2**, **3** and **8**. For the derivative **2**, panel (a) shows the Au(111) surface decorated with either a distribution of clusters, with diameter comparable to those in Fig. 3a of the regular paper, and flatter structures that, following XPS, might be assigned to solphur groups detatched from the organic threads and bound to gold. The image (b), obtained after the deposition of **3**, shows flat aggregates and rather unstable STM imaging. The STM image in panel (c), obtained after the deposition of **8,** shows the alternation of uncovered regions toghether with a distribution of clusters, having diameter comparable to a single Cr_7Ni ring, and flat aggregates with size of 3-5 nm. This suggests that **8** undergoes to a fragmentation in smaller components on the Au(111) surface. As pointed out by XPS, this effect most likely produces integer Cr_7Ni rings and moieties containing S or Cu.

4. X-ray Studies

4.1 Experimental Details

Data for compounds **1**, **2**, **3** and **6** were collected on an Oxford Xcaliber-2 diffractometer using Mo Kα radiation and the data reduced using Agilent Technologies CrysAlisPro; data for compounds **4** and **8** were collected at 150 K on a Bruker X8 Prospector diffractometer using CuKα radiation and the data reduced using Bruker APEX2 software. All data were collected at 100 K. Structures were solved using direct methods and refined using least squares minimisation with the SHELX structure solution program.

The large structures show considerable disorder. Details are given in the cif files which have been deposited at the Cambridge Structural Database.

SHELX G. M. Sheldrick , *Acta Cryst.*, 2008, **A64**, 112-122.

3.2 Crystallographic Data

	1	**2**	**3**
empirical formula	$C_{100.5}H_{173}Cr_7F_8NNiO_{33.5}S$	$C_{96}H_{164}Cr_7F_8NNiO_{32}S_2$	$C_{95}H_{163}Cr_7F_8N_2NiO_{34}S$
formula weight	2538.17	2483.13	2484.05
temperature / K	100(2)	100(2)	100(2)
crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	*Pbca*	*Pnn*2	*Pbca*
a / Å	27.3418(6)	14.5209(3)	32.4921(4)
b / Å	32.3342(7)	17.2203(3)	30.3746(3)
c / Å	30.4098(6)	27.2140(5)	27.3877(3)
α / °	90.0	90.0	90.0
β / °	90.0	90.0	90.0
γ / °	90.0	90.0	90.0
volume / Å^3	26884.5(10)	6805.0(2)	27029.9(5)
Z	8	2	8
ρ_{calc} / mg.mm^{-3}	1.254	1.212	1.22
μ / mm^{-1}	0.772	0.775	0.767
F(000)	10680	2606	10423
crystal size / mm^3	0.2 × 0.2 × 0.1	0.27 × 0.2 × 0.12	0.3 × 0.19 × 0.12
reflections collected	32977	52611	35608
independent reflections	18353	12574	18536
data / restraints / parameters	18353 / 2221 / 1385	12574 / 732 / 659	18536/ 1680/ 1333
goodness-of-fit on F^2	1.157	1.147	1.217
final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0707$, $wR_2 = 0.172$	$R_1 = 0.0854$, $wR_2 = 0.2196$	$R_1 = 0.0857$, $wR_2 = 0.2313$
final R indexes [all data]	$R_1 = 0.1143$, $wR_2 = 0.199$	$R_1 = 0.1145$, $wR_2 = 0.2389$	$R_1 = 0.1292$, $wR_2 = 0.257$
largest diff. peak / hole /e.A^{-3}	0.75 / -0.62	0.58 / -0.57	1.61 / -0.79

	4	**6**	**8**
empirical formula	$C_{102}H_{176}Cr_7F_8N_2NiO_{34}S$	$C_{188}H_{334}Cr_{14}F_{16}N_3Ni_2O_{64}S_2$	$C_{238}H_{394}Cr_{14}Cu_2F_{16}N_4Ni_2O_{72}S_2$
formula weight	2567.21	4874.12	5804.20
temperature / K	100(2)	100(2)	100(2)
crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	*Pbca*	$P\,2_1/n$	$C\,2/c$
a / Å	30.2347(12)	30.8780(14)	64.167(6)
b / Å	27.4920(10)	17.2478(8)	17.1756(9)
c / Å	32.1970(12)	54.046(3)	31.0638(19)
α / °	90	90.0	90.0
β / °	90	106.154(2)	113.078(70
γ / °	90	90.0	90.0
volume / Å^3	26762.5(18)	27647(2)	31496(4)
Z	8	4	4
ρ_{calc} / mg.mm^{-3}	1.274	1.171	1.224
μ / mm^{-1}	5.459	0.747	4.836
F(000)	10808	10252	12208
crystal size / mm^3	0.2 x 0.2 x 0.1	0.3 × 0.25 × 0.15	0.2 × 0.1 × 0.1
reflections collected	471822	31648	53274
independent reflections	23309	19385	16265
data / restraints / parameters	23309/62/1387	19385 / 6803 / 2602	16265/ 1631 / 1536
goodness-of-fit on F^2	1.011	1.277	1.388
final R indexes [I≥2σ(I)]	$R_1 = 0.0972$, $wR_2 = 0.2150$	$R_1 = 0.1187$, $wR_2 = 0.2645$	$R_1 = 0.1467$, $wR_2 = 0.4026$
final R indexes [all data]	$R_1 = 0.1562$, $wR_2 = 0.22489$	$R_1 = 0.2211$, $wR_2 = 0.295$	$R_1 = 0.2084$, $wR_2 = 0.4390$
largest diff. peak / hole / e.A^{-3}	1.758/-1.265	0.88/ -0.49	1.127 / -0.64