ChemComm
RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 3404

Received 4th December 2012,
Accepted 6th March 2013

DOI: 10.1039/c3cc38699f

www.rsc.org/chemcomm

Studies of hybrid organic–inorganic [2] and [3]rotaxanes bound to Au surfaces†

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Hybrid organic–inorganic [2]- and [3]rotaxanes have been synthesised, and their ability to bind to Au surfaces studied; the length of the tethering group is found to control how the supramolecular assembly binds to the surface and we find that [2]rotaxanes show improved stability over previous studies of simple inorganic rings.

Many proposed applications of molecular nanomagnets involve supporting these species on surfaces. There have been beautiful results reported using XMCD studies of $\{Fe_4\}$ on Au surfaces showing retention of single molecule magnetism,[1] and a report of a terbium phthalocyanine molecules forming part of molecular spin valves and transistors,[2] and where the blocking temperature for relaxation of the magnetisation can be raised above 100 K by binding to a Ni ferromagnet.[3] Recently we have shown we can form an organised monolayer of $\{Cr_7Ni\}$ anti-ferromagnetic rings on an Au surface by sublimation.[4] For applications it would be advantageous if more complex molecules could be attached to surfaces. Here we attach hybrid organic–inorganic rotaxanes[5,6] to surfaces, inspired by some of the beautiful surface chemistry shown previously for catenanes bound to surfaces.[7]

We have designed and synthesized interlocked hybrid organic–inorganic systems with functionalized axles where the organic axles are stoppered by 4-methylthio phenyl and/or 4-pyridyl groups contain templating ammonium group(s) around which the inorganic heterometallic ring(s) are grown. The rings contain one Ni^{2+} and seven Cr^{3+} centres arranged in an octagon, held together by fluoride and carboxylates.[8]

We have made five [2]rotaxanes ($Ar{=}C_6H_4$):
$[(MeSArCH_2)NH_2C_2H_4Ph][Cr_7NiF_8(O_2C^tBu)_{16}]$ **1**
$[(MeSArCH_2)_2NH_2][Cr_7NiF_8(O_2C^tBu)_{16}]$ **2**
$[(MeSArCH_2)NH_2C_2H_4Py][Cr_7NiF_8(O_2C^tBu)_{16}]$ **3**
$[(MeSArC_2H_4)NH_2CH_2Ph][Cr_7NiF_8(O_2C^tBu)_{16}]$ **4**
$[MeC(O)S(CH_2)_6NH_2CH_2Ph][Cr_7NiF_8(O_2C^tBu)_{16}]$ **5**
and three related [3]rotaxanes: $[(MeSArCH_2)NH_2(CH_2)_6]_2$-$[Cr_7NiF_8(O_2C^tBu)_{16}]_2$ **6**
$[(MeSArCH_2)NH_2(CH_2)_{12}NH_2(CH_2Py)][Cr_7NiF_8(O_2C^tBu)_{16}]_2$ **7**
$\{[(MeSArCH_2)NH_2C_2H_4Py][Cr_7NiF_8(O_2C^tBu)_{16}]\}_2[Cu(O_2C^tBu)_2]_2$ **8**

The crystal structures of compounds **1–4**, **6** and **8** have been determined; **2**, **3**, **6** and **8** are shown in Fig. 1. The secondary amine threads were designed with a methylene spacer between the ammonium site and the bulky aromatic stoppers such as 4-methylthiophenyl at each end of the axle. This creates sufficient space to accommodate the heterometallic $\{Cr_7Ni\}$ rings. Both NMR and electrospray mass spectrometry confirm these are rotaxanes, not *pseudo*-rotaxanes (see ESI†). To construct the [3]rotaxane **6** we used a C_{12} chain between the two ammonium sites as this allows two rings to be bound. The threads were made *via* a Schiff base condensation followed by reduction (see ESI†).[9] The [2]rotaxane **3** was designed with a pyridyl-head group so that it could be used to bind to a further metal site. Reaction of **3** with $[Cu(O_2C^tBu)_2]_2$ then leads to a [3]rotaxane **8**, where the dimetallic copper complex forms part of the organic thread (Fig. 1d).

Previous studies[10–12] have shown that S-functionalised $\{Cr_7Ni\}$ derivatives can be deposited from liquid phase. The S-terminated amine assures strong grafting of the ring to surface, but also leads to the formation of an S-containing self-assembled monolayer (SAM). At best we achieved around 30% $\{Cr_7Ni\}$ and about 30% S-containing SAM coverage.[10] The $\{Cr_7Ni\}$ rings deposited retain their chemical composition and show magnetic behaviour similar to bulk materials. Here we study rotaxanes as they present severe challenges for liquid deposition onto Au(111); we wish to establish the limits of this approach.

The rotaxanes were attached to the Au(111) surface from a 10^{-3} M CH_2Cl_2 solution. X-ray photoelectron spectroscopy (XPS) was performed to demonstrate that the rotaxanes were intact, and to study the binding mode of the ligands. The results show that the

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† Electronic supplementary information (ESI) available: Experimental details and crystallographic data for **1–4**, **6** and **8**. CCDC 907149–907152, 912256 and 923150. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc38699f

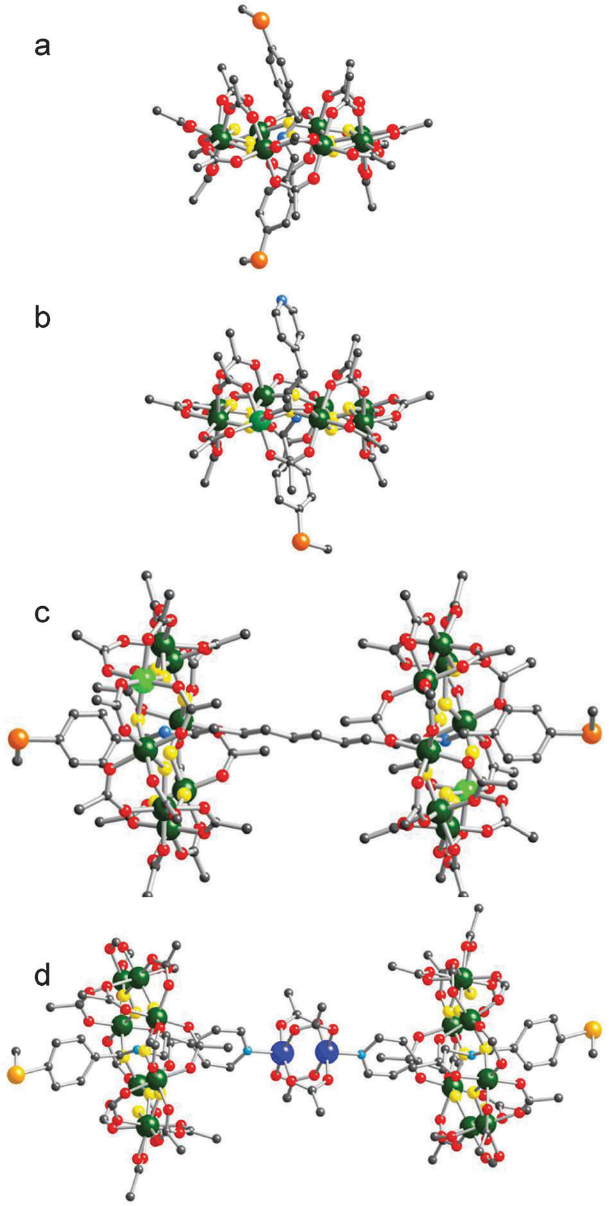

Fig. 1 The structures of compounds (a) **2**, (b) **3**, (c) **6** and (d) **8** in the crystal. Me-groups of pivalates and H-atoms removed for clarity. Colours: Cr, Ni, green; F, yellow; O, red; N, light blue; S, orange; C, grey; Cu, blue.

Table 1 XPS data for compounds **1–8**

	Ratios of XPS peaks				Surface coverage/%	
	F-1s/Cr-2p [1.14]	Cr-2p/ Ni-2p[7]	S-2p/ Cr-2p	S1/S2	MeS-SAM	Cr$_7$Ni rotax
1	1.17 ± 0.05	6.5 ± 2	5 ± 5 [1]	4 : 1	15 ± 5	35 ± 5
2	1.15 ± 0.05	5 ± 2	70 ± 5 [2]	9 : 1	95 ± 5	15 ± 5
3	1.15 ± 0.05	5.5 ± 2	10 ± 5 [1]	4 : 1	10 ± 5	12 ± 5
4	1.17 ± 0.05	6 ± 2	6 ± 5 [1]	7 : 3	20 ± 5	50 ± 5
5	1.18 ± 0.05	6.5 ± 2	10 ± 5 [1]	4 : 1	50 ± 5	60 ± 5
6	1.12 ± 0.05	5 ± 2	6 ± 5 [2]	1 : 9	10 ± 5	38 ± 5
7	1.16 ± 0.05	7 ± 2	5 ± 5 [1]	4 : 1	20 ± 5	50 ± 5
8	1.10 ± 0.05	6 ± 2	20 ± 5 [2]	4 : 1	20 ± 5	10 ± 5

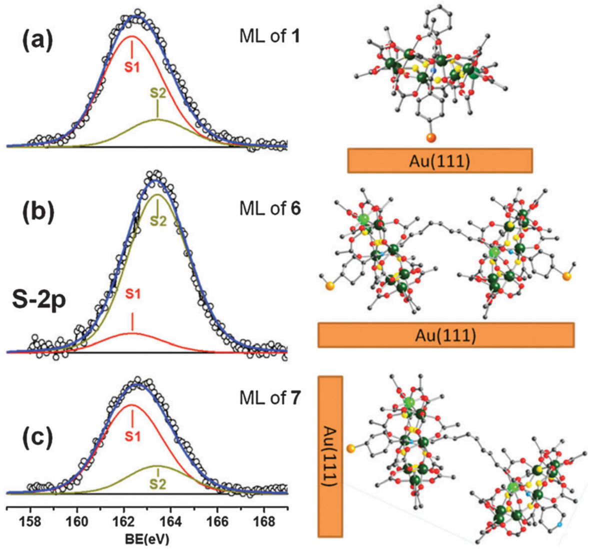

Fig. 2 XPS measurements: S-2p core level best fits for MLs of **1** (a), **6** (b) and **7** (c). In the right panel, a sketch of the surface-binding.

Cr-2p, F-1s and Ni-2p core level line-shapes measured on sub-monolayers (MLs) (see ESI†) are very similar to corresponding data measured on multilayers that were drop cast from saturated solutions onto HOPG. The ratios of the peaks match the stoichiometric values (reported in brackets) calculated for the chemical formulae for these elements, indicating that the molecular core for compounds **1–8** is largely maintained (Table 1). Conversely, the S-2p/Cr-2p ratio indicates in many cases an excess of sulfur in the MLs. This is probably due to formation of an S-containing ML, possibly formed by loss of –SMe from the organic thread.

The nature of the S-bonding has been investigated by evaluating the different contributions to the S-2p core level (Fig. 2 and Table 1). The S-2p fitting procedure has been performed using spin–orbit split doublets (Voigt functions), with the following parameters: spin–orbit splitting equal to 1.2 eV, branching ratio equal to 0.5, Lorentzian width equal to 574 meV and Gaussian width equal to 2400 meV for all components. For all rotaxanes, two components are observed at 162.0 eV (S1 peak) and 163.1 eV (S2). S1 can be assigned to sulfur species after C–S bond cleavage bound to Au, while S2 is due to intact MeSPh groups containing S atoms that are not bound to Au.

The number of S–Me endgroups within the organic thread of the rotaxanes strongly influence their interaction with the surface. In [2]rotaxanes with a single S–Me such as **1**, **3** and **4**, there will be rotaxanes where the S to methyl bound has broken, leading to a strong Au–S bond tethering the rotaxanes to the surface, in addition to some surface bound –SMe groups (see Fig. 2a). In **2**, a [2]rotaxane with two S–Me groups, the S1 peak is very intense, which shows that S–C cleavage is important for **2**.

For **6**, a [3]rotaxane with two S–Me, the S2 peak is dominant (Table 1), suggesting that in this topology the sulfur of the organic thread prefer not to bind to the surface (see Fig. 2b). On the contrary for **7** where only one S–Me is present, the S1 peak is dominant, suggesting that the [3]rotaxane preferably grafts to the surface through an Au–S bond (see Fig. 2c).

We calculated the surface coverage of the sulfur-bound species by taking the ratio of the S-2p with the Au-4f peak; this

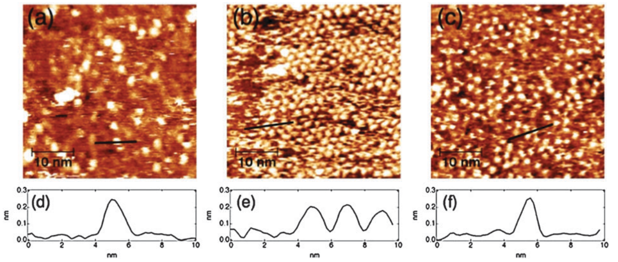

Fig. 3 STM images on Au(111) of: (a) **1**, (b) **4** and (c) **5**. Scan area is 40 × 40 nm^2. (d–f) Height profiles along lines shown in panels (a–c).

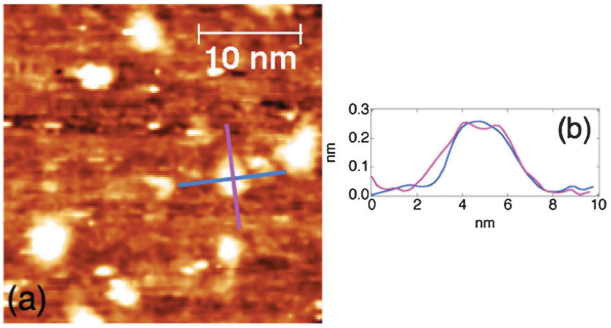

Fig. 4 (a) STM image of [3]rotaxane **6** on Au(111). (b) Line profiles taken along the two orthogonal directions shown in panel (a). Scan area is 30 × 30 nm^2.

suggests that for **2** we have a complete sulfur-ML, while for the other compounds the coverage is below 50% (Table 1). By comparing the Au-4f peak with the Cr-2p, and taking into account the gold signal attenuation due to the overlayer, we have also derived the coverage of the $\{Cr_7Ni\}$ rotaxanes on the surface (Table 1). This varies substantially, with the highest coverage for **4**, **5** and **7**, which approaches 50–60%.

Sub-monolayers of rotaxanes **1–8** on Au(111) have been investigated by means of scanning tunnelling microscopy (STM). For [2]rotaxanes **1**, **4** and **5** stable imaging conditions were obtained at low tunnelling current (20 pA) and high bias voltage (2 V) (Fig. 3). Line profiles show structures in close agreement to those expected.[4] The three [2]rotaxanes give different coverage: for **1** and **5**, (Fig. 3a and c respectively) there are homogeneous distributions of clusters separated by a few nm. The coverage is much higher for the latter, suggesting that the long thread containing a C_6 chain in **5** is more effective for the grafting of the cluster on the surface.

The STM images for **4** (Fig. 3b) differ significantly from those of **1** and **5**. Here molecules pack together in dense 2D-domains that alternate with regions of low coverage (see ESI†). Rotaxanes **1** and **4** differ only in the length of the thread, *i.e.* in **1** the S···N distance is 0.69 nm in **1** and 0.82 nm in **4** in the crystal structures. Such small structural modifications have significant influence on the deposition process.

We also investigated the deposition of [3]rotaxanes such as **6** on Au(111) (see ESI†) by STM (Fig. 4). Here we observe the presence of slightly elongated clusters with fairly reproducible shapes. In most cases the line profiles have FWHM of 3.1 nm as the shortest side, and 3.8 nm as the longest one (Fig. 3d) which is close to the size of **6** determined by crystallography (1.7 nm and 2.8 nm, respectively). The presence of a double peak in the height profile along the longest side might suggest that the structure of **6**, with two $\{Cr_7Ni\}$ rings, is retained after the deposition on Au(111) (Fig. 1c). In agreement with XPS analysis, the grafting of the [3]rotaxane thus preferentially occurs with the longest side of the complex lying flat on the surface.

These results show that [2]- and [3]rotaxanes deposit from solution while preserving the core of the structure. The S-containing ligands can detach themselves and form SAMs, but also assure strong attachment of the rotaxanes. For [2]rotaxanes the best results for **1** and **4**, show that the use of [2]rotaxanes increases the coverage of $\{Cr_7Ni\}$ molecules and decreases the coverage of S-containing SAMS compared with previous studies.[10]

For the [3]rotaxanes the configuration of the molecule on the surface is determined by the interplay of the Van der Waals interaction between the $\{Cr_7Ni\}$ rings and the surface. In **6** the bulky structure leads to the two S–Me groups at the ends of the axle floating above the surface. Conversely, in the case of **7**, the presence of a single S–Me end group at just one end of the axle, leads to convincing evidence of an Au–S bond. The results suggest that not only can we bind these hybrid rotaxanes to surfaces, but also that we should be able to chose the orientation of the rotaxane to the surface by choice of binding groups.

We thank the Royal Society for a Newton International Fellowship (to HR) and a Wolfson Merit Award (to REPW). This work was supported by the EPSRC(UK) and the EC through MolSPINQIP and through a Marie Curie IEF to AFL.

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