Nanostructures

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Template Assembly of Spin Crossover One-Dimensional Nanowires**

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Spin crossover[1] (SCO) is an important example of molecular switching,[2] which can be realized by a wide variety of external stimuli.[3–6] Many applications have been explored, including sensor[7] and display[8] technologies, and data storage.[9] Much effort has been expended to develop the assembly of SCO complexes in materials and impressive results have been achieved with monodisperse nanoparticles,[10] nanocrystals,[11] thin films,[12] micro- and nanopatterned media,[13] Langmuir–Blodgett (LB) films,[14] and hysteretic soft-media assemblies.[15] Progress in this area was recently reviewed by Bousseksou et al., and the link between size morphology and switching characteristics was also examined.[16] However a striking absence from this list is the 1D nanowire. Magnetic nanowires[17] have been cited by the magnetic recording industry as being important in overcoming difficulties in domain wall motion,[18] and reliable thin-film etching[18b,19] and template-assisted electrodeposition[20] routes to nanowires of magnetic metals have been established. However, preparation of nanowires of functional molecules by such methods is not possible, and wet chemistry routes are better employed. Melt-assisted template assembly methods have been effective for polymers[21] and in favorable cases, nanowires of functional polymers show novel optical properties, including wave guiding[22] and lasing.[23] These nanowires are prepared by adding molten polymer to a nanoporous template, such as anodic aluminum oxide (AAO), followed by acidic or basic template dissolution. Preparation of polymer nanowires is also possible by using solution-assisted template wetting,[24] and this method can be extended to include small molecules,[25] but the acidic or basic treatment means that it is less suitable for fragile small molecules that would not survive dissolution of the template. However, by appropriate modification, insolubility in acids or bases may be conferred on functional small molecules such as mononuclear SCO complexes. To this end, we have investigated the potential of alkylated derivatives[26] of Wilson's [Fe(sal_2-trien)][27] complex, where sal_2trien is the hexadentate N_4O_2 bisimino ligand formed by condensation of salicylaldehyde with N^1,N^2-bis(2-aminoethyl)-1,2-ethanediamine, to form nanowires by template assembly in nanoporous AAO, and describe herein the first reported SCO nanowires formed from $[Fe^{III}L](BF_4)_{0.8}Br_{0.2}$ (**1**).

Alkylated ligand L was prepared by substitution of the amines on sal_2trien with 1-bromododecane,[28] and crystallization in the presence of $Fe(BF_4)_2{\cdot}6H_2O$ produced the mixed anion salt **1** with some bromide remaining from the ligand synthesis. Structural analysis of rod-shaped crystals of **1** showed packing by intercalation of the ligand C_{12} chains (Figure 1), and close association of the coordination centers

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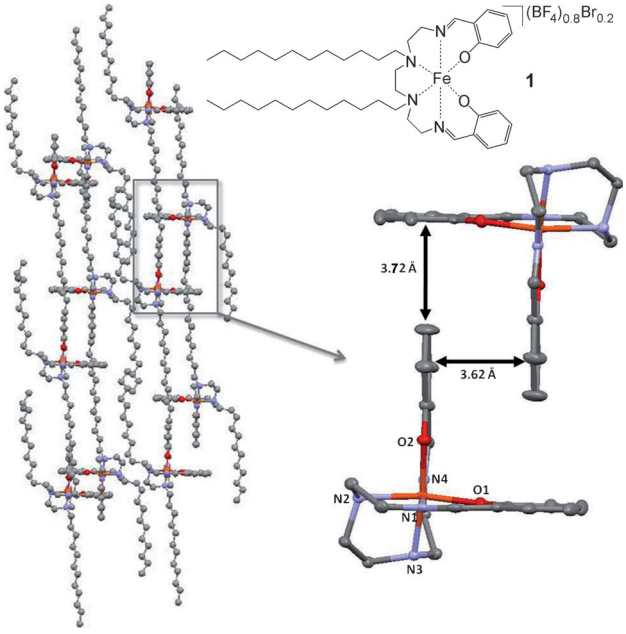

Figure 1. Molecular structure of **1**, and structure of **1** at 100 K showing intercalation of C_{12} ligand chains and π–π interactions between phenolate rings. Hydrogen atoms and counterions omitted for clarity.

by complementary π–π stacking and edge-to-face interactions.[29] All six bond lengths in the immediate coordination sphere increase by 0.1–0.2 Å on warming (Table S1 in the Supporting Information), as expected for SCO Fe^{III} ions. The intercalated nature of the alkyl chain packing, which results in a molecule length of approximately 3 nm, may assist in nanorod growth in an appropriate template, and nanowires of **1** could indeed be prepared by addition of a solution of the complex in chloroform to a 200 nm pore AAO template (Figure 2).

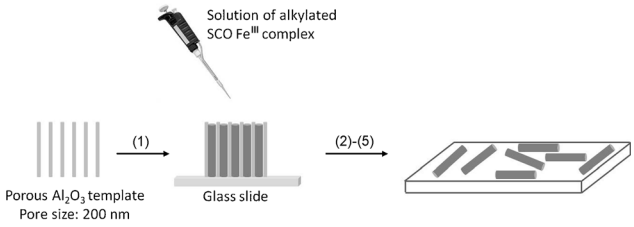

Figure 2. Wetting and dissolution for nanowire preparation. 1) Template wetting of AAO template with a solution of **1** in chloroform; 2) surface polishing of filled template; 3) dissolution of template in 0.6 M H_3PO_4; 4) centrifugation and washing; 5) suspension of nanowires in deionized water and deposition on a glass slide.

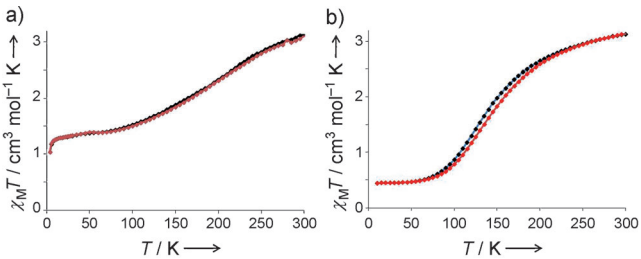

Figure 3. Plots of $\chi_m T$ vs. T for a) templated nanowire sample and b) the bulk powder of **1**. Full details of both measurements given in Supporting Information.

SQUID measurements on the templated material confirmed that SCO persisted in the nanoassembly (Figure 3a) although the profile is less complete than for the bulk powder (Figure 3b). Size effects on the thermal switching profile of nano-objects comprising SCO complexes has emerged as an important aspect of the phenomenon,[16] particularly in modulation of hysteresis width. We have shown that assembly into nanorods affects the degree of high-spin–low-spin (HS–LS) switching in **1**.

The nanowires were released from the template by dissolution in 0.6 M phosphoric acid. Attempted dissolution in basic solution resulted in precipitation of the metal hydroxide, and attempts to extract shorter-chain alkylated SCO complexes with acidic solutions sometimes resulted in dissolution of the entire assembly, although nanowire preparation was successful in several cases and will be reported elsewhere. The nanowires were isolated by centrifugation, aqueous washing of the residue, and deposition on a glass slide, where a mesh of nanowires was observable by optical microscopy (Figures S2 and S3 in the Supporting Information).

Further resolution was possible by SEM imaging of the mesh dispersed on an adhesive surface and covered with a thin layer of evaporated gold (Figure 4). The SEM images show long (5–10 μm) and flexible 1D structures with a range

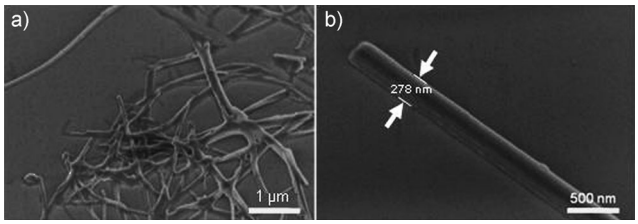

Figure 4. 2.0 kV SEM images of mesh of nanowires of **1** at a) 20000× magnification and b) 40000× magnification.

of diameters (Figure S9 in the Supporting Information), which are consistent with the morphology of previously reported AAO-templated nanowires where the pore size is known to vary.[23] Tapping-mode AFM was used to image individual wires (Figure S10 in the Supporting Information), and confirmed highly uniform structures along their length and height, consistent with the range of diameters observed by SEM ((80 ± 10) nm; Figure 5).

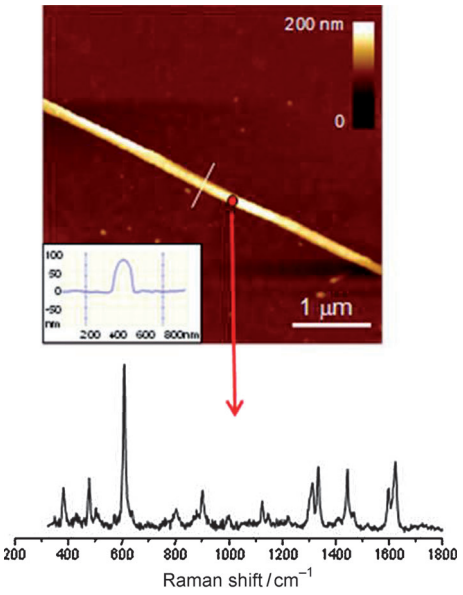

Figure 5. AFM topography of a single nanowire of **1** and Raman (532 nm) spectrum of this single nanowire at 293 K, confirming composition as HS **1**.

Comparison of the room-temperature Raman spectrum of a single spot on the nanowires (Figure 5) with that of the bulk powder (Figure S13 in the Supporting Information) confirmed that the nanowire comprised HS **1** at this temperature. The intense bands for the HS form are at 1626, 1600, 1446, 1336, and 1312 cm^{-1} and the most intense feature is at 612 cm^{-1}. Mapping at this frequency, within a 4.6 × 3.5 μm grid with a step size of 350 nm, shows regular intensity over an area corresponding to a nanowire, (Figure S14), thus con-

firming that the spectrum arises from a single wire and not from residual powder on the surface. The room-temperature spectrum of a mesh of wires matches that of the room-temperature AFM-coupled Raman single nanowire experiment (Figure 5), and bands at 1626, 1600, 1446, 1336, 1312 cm^{-1}, and 612 cm^{-1}, confirm the predominantly HS state. Upon cooling, a new band at 622 cm^{-1} starts to grow in by 148 K, (Figure 6) and indicates a change to the predominantly LS form, but less so than for the bulk powder

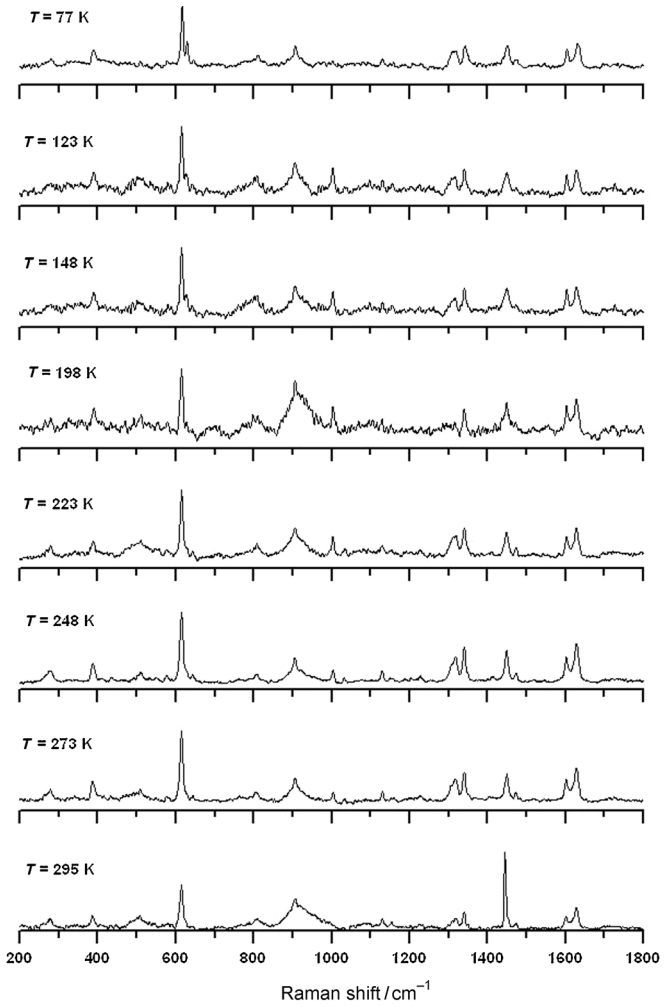

Figure 6. Variable-temperature Raman spectra (532 nm) on a mesh of nanowires of **1**. Growth of a new band at 622 cm^{-1} associated with the LS electronic state on cooling confirms the spin-state change.

(Figure S11). Both SQUID and Raman data therefore agree in confirming a SCO for the nanowires with a smaller LS fraction at low temperature in the nanowire sample compared with the bulk powder. This behavior shows that nanoassembly affects the thermal SCO profile of **1**, as previously observed with nanoparticles of Fe^{II} triazole[10b,d] and pyrazine[10c,13d,30] coordination polymers or SCO LB films.[14b] Modulation of the power settings on the laser did not alter the resulting spectra, thus suggesting that the nanowires are more thermally robust than the bulk powder. A laser power of 1.2 mW was routinely used, but increasing the power sequentially to 13.6 mW caused the powder sample to visibly char and the spectral quality to deteriorate, whereas the nanowires showed no degradation when irradiated at 532 nm at power settings of 1.20, 4.60, 7.50, 9.32, and 13.6 mW (Figure S15).

In conclusion, template methods have been successfully employed to prepare nanowires of a thermal SCO Fe^{III} complex, which shows retention of spin switching. The alkylated ligand design facilitated extraction of the wires from the template by ensuring that the complex was insoluble in the weak acid needed to dissolve the AAO. SQUID magnetometry on the templated sample and Raman spectroscopy on the isolated wires confirmed thermal SCO in the nanoassembly. When contained in the template, the nanowires are well-separated and ordered in a perpendicular arrangement in a robust matrix that should be easily handled and transferable onto a range of surfaces. Such surfaces could include a nanopatterned array of heaters, such as currently used in prototype heat-assisted magnetic recording (HAMR) devices.[31] In this way, the spin states of individual SCO nanowires, supported in an inert matrix, could be controlled by using existing industry procedures, that is, by employing techniques currently envisaged for heating nanorods of hard ferromagnets to lower the blocking temperature in "write" mode, to instead switch the spin state of a nanorod of a SCO paramagnetic material. Alternatively, isolation and manipulation of individual wires opens up the appealing prospect of electrical spin-state switching of individual rods, as has been demonstrated for single SCO molecules by Ruben,[32] for nanoparticles by Coronado,[33] and for nanoclusters by Grohmann,[13b] and their respective co-workers. By using this approach, it is possible to envisage that the magnetization versus field (M/H) data-storage paradigm could be replaced with electronic state versus electrical/thermal/optical perturbation with easy readout of the starting and resultant states. Our study of the assembly of thermal SCO complexes is ongoing, and a range of alkyl chain lengths and acid strengths are currently being investigated, in addition to variation of the nanowire dimensions by using templates of different diameter.

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