<table>
<thead>
<tr>
<th>Title</th>
<th>A magnetic iron(III) switch with controlled and adjustable thermal response for solution processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Authors(s)</td>
<td>Gandolfi, Claudio; Morgan, Grace G.; Albrecht, Martin</td>
</tr>
<tr>
<td>Publication date</td>
<td>2012-02-27</td>
</tr>
<tr>
<td>Publication information</td>
<td>Dalton Transactions, 41 (13): 3726-3730</td>
</tr>
<tr>
<td>Publisher</td>
<td>RSC</td>
</tr>
<tr>
<td>Item record/more information</td>
<td><a href="http://hdl.handle.net/10197/3629">http://hdl.handle.net/10197/3629</a></td>
</tr>
<tr>
<td>Publisher's version (DOI)</td>
<td>10.1039/c2dt12037b</td>
</tr>
</tbody>
</table>
A magnetic iron(III) switch with controlled and adjustable thermal response for solution processing

Claudio Gandolfi, Grace G. Morgan and Martin Albrecht

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/c0xx00000x

Spin crossover requires cooperative behaviour of the metal centers in order to become useful for devices. While cooperativity is barely predictable in solids, we show here that solution processing and the covalent introduction of molecular recognition sites allows the spin crossover of iron(III) salen complexes to be rationally tuned. A simple correlation between the number of molecular recognition sites and the spin transition temperature enabled the fabrication of materials that are magnetically bistable at room temperature. The predictable behaviour relies on combining function (spin switching) and structure (supramolecular assembly) through covalent interactions in a single molecular building block.

Introduction

Molecular entities that possess two magnetically stable states are presumed to be the key component for the next generation of data storage and processing devices. While spin transition and thermal addressing of magnetic \textit{on} and \textit{off} states at the molecular level is not uncommon, the designed fabrication of spin-labile materials is often precluded by the complexity of the numerous and intricate inter- and intramolecular interactions that govern the spin crossover. As a consequence, the spin transition of the vast majority of spin-labile compounds is gradual and occurs over a broad (> 100 K) temperature range. An abrupt transition with hysteresis loop is, however, desired for device operations and requires the metal centers to interact cooperatively. Up to now, only few molecular systems are known that exhibit a strong cooperativity.  

Cooperativity typically results from a combination of intra- and intermolecular interactions such as hydrogen bonding, π-anion, or dipolar interactions, which are generally weak. Therefore, even minute changes for example in the crystallizing solvent have dramatic effects on the abruptness, and tailoring of materials for specific applications has been severely hampered. The empirical trends established thus far are typically specific for a single class of compounds only. Very recently, elegant work has demonstrated that the spin transition temperature can be controlled over a broad temperature range by the iodine content of a porous coordination polymer comprised of iron(II), pyrazine, and Pt(CN)$_4$ units.  

Previous approaches to overcome the severe limitations in tailoring spin transition have been based on supramolecular principles in an attempt to control the intermolecular organization of spin-labile systems. In particular the introduction of amphiphilic properties by charge balancing of cationic spin-labile iron triazole polymers with lipophilic counterions has afforded discrete nanoparticles with abrupt spin crossover, thus inducing an abrupt and hysteretic spin crossover in the solution phase. While the magnetic activity in these nanoparticles is strongly related to the spin crossover in analogous solid state Fe(trz)$_2$ materials (trz = 1,2,4-triazole derivative) and is governed by the same principles with low predictability, we considered that covalent bonding of the modular lipophilic chain to a spin-labile center may inherently link the magnetic function to structural aspects. This approach offers a methodology to induce spin crossover in the solution phase, where magnetic changes are generally only gradual due to the lack of cooperativity and the absence of intermolecular interactions between the active sites. Here we show that this approach provides a subtle control of the spin crossover via supramolecular principles.

Results and discussion

Complex 1a featuring a spin-labile iron(III) center in an N$_2$O$_2$ coordination sphere was functionalized with alkyl chains R of different length (Fig. 1). Solid samples of complexes 1 were spin-stable and did not undergo a crossover upon cooling to 30 K. Solutions of complexes 1 are red and display an absorbance maximum around 495 nm (CH$_2$Cl$_2$) which is diagnostic for an iron(III) high-spin (HS, S = 5/2) configuration. Upon cooling, all solutions change color to dark blue due to a new absorbance band at 650 nm, indicating a low-spin (LS, S = 1/2) species and thus a thermally induced spin crossover. In the solid state, in contrast, all alkyl-functionalized complexes 1b–g are spin stable and preserve the HS state between RT and 30 K. Monitoring of the extinction coefficients $\varepsilon_{500}$ and $\varepsilon_{650}$ at different temperatures allows the relative HS/LS ratio to be estimated. Accordingly, relatively large fractions of the complexes 1e–g undergo a spin crossover, whereas in solutions of 1a–d, a significant portion
remains in the HS configuration. Temperature-dependent analysis of the HS/LS distribution reveals the presence of an isosbestic point around 580 nm, thus identifying an equilibrium between HS and LS configurations.†

Fig. 1 Schematic representation of iron(III) sal-trien complexes functionalized with different lipophilic substituents R.

Fig. 2 Plot of the high-spin fraction of iron(III) sal-trien complexes, \( \gamma_{HS} \), as a function of temperature as determined by the diagnostic absorption at 650 nm (all complexes are 0.2 mM CH\(_2\)Cl\(_2\) solutions, except 1g at 0.04 mM; \( \gamma_{HS} \) is the molar fraction that is spin-crossover active). The behavior of complex 1b is identical to that of 1a and 1c and has been omitted for clarity.†

An apparent hysteresis was observed in the first cooling-heating cycle, but temperature-dependent UV-vis spectroscopy provided identical curves upon cooling and heating in subsequent cycles. The bistable window is dependent on the length of the alkylic chain and varies from 6 K (for 1e) to 14 and 17 K for solutions of complexes 1f and 1g, respectively. The remarkably large hysteresis of 1g covers the 273–290 K range (Fig. 3a), a window that is only marginally below room temperature (20 °C). While such properties may become particularly attractive for applications, for example for data storage, the robustness needs improvement. Currently, the hysteresis is only pertained during the first cooling-heating cycle and disappears in subsequent cycles. Moreover, the reversibility of the change in magnetization is affected with complex 1g. Repetitive cooling-heating cycles led to a decreased absorption for both the HS and LS states, indicating incomplete transitions upon recycling (Fig. 3b). In contrast, the spin crossover process of solutions containing complex 1f did not indicate any fatigue during three consecutive cycles (Fig. 3c).

A decrease of the spin transition temperature is induced upon lowering the concentration of the spin-labile species. A five-fold dilution of complex 1e or 1f from 0.2 mM to 0.04 mM reduced the spin transition temperature from 235 K to 226 K and from 253 K to 245 K, respectively. The molar extinction coefficient at 650 nm is not affected upon dilution, suggesting a complete spin change. The consistent lowering of the transition temperature by approximately 10 K demonstrates that the concentration constitutes a further handle to tailor the magnetic state of the complex at a given temperature, without compromising the sharp nature of the spin crossover.

Solutions of complexes comprising short alkyl chains, viz. complexes 1b-d, display a gradual spin transition over approximately 80 K, which may not be complete at the lowest measured temperature of 170 K. Similar behavior has been reported for the unfunctionalized complex 1a. In sharp contrast, longer alkyl groups as in complexes 1e-g induce an abrupt HS to LS change that is essentially complete within a 10 K cooling range (Figure 2). Variation of the length of the alkyl chain provides a remarkably clear correlation between alkyl chain length and the spin crossover temperature \( T_{1/2} \), determined as the temperature where \( \gamma_{HS} = \gamma_{LS} = 0.5 \) (\( \gamma \) is the fraction of spin-crossover active molecules in a given spin state). While for complex 1e comprising C\(_{14}\) groups, the transition temperature is 235 K, \( T_{1/2} \) is raised to 253 K for 1f, and even closer to ambient temperature for 1g containing C\(_{30}\) tails (\( T_{1/2} = 273 \) K). The latter complex had to be measured at lower concentration (0.04 mM) due to its low solubility in CH\(_2\)Cl\(_2\). The correlation between chain length and spin crossover temperature brings changes of magnetization at room temperature within reach. With the compounds based on 1, however, further elevation of the spin transition temperature is prevented by the restricted solubility of complexes that are functionalized with longer alkyl chains. Nonetheless, this series is unique in allowing trends to be established in spin crossover behavior that correlate directly with the transition temperature. Variation of the length of the alkyl chain and the spin crossover temperature \( T_{1/2} \) is identical to that of 1a and 1c and has been omitted for clarity.†

The isosbestic points in the temperature-dependent UV–vis spectra suggest an equilibrium between high and low-spin species. Analysis of the temperature-dependence of this equilibrium for 1e using the van’t Hoff equation afforded the thermodynamic parameters for the LS to HS transition. Accordingly, \( \Delta H^\circ = 96.5(±1.1) \text{ kJ mol}^{-1} \) and \( \Delta S^\circ = 412(±5) \text{ J K}^{-1} \text{ mol}^{-1} \) in the 225–240 K temperature range (Fig. S7). For complexes 1f and 1g extraction of the thermodynamic data is restricted by the sharpness of the spin crossover (e.g. 4 K for 1g) and consequently by the limited amount of data points available for characterizing the crossover.‡
The hysteresis and the abrupt spin transition imply a cooperative action of the spin crossover-active molecules in solution. Cryogenic scanning electron microscopy (cryo-SEM) of frozen CH₂Cl₂ solutions of complexes 1c–1g indeed displayed a supramolecular organization of the complexes, presumably induced by intermolecular recognition due to the amphiphilic character of the complexes. All samples showed mutually interwoven fibers that are approximate 40±15 nm thick (Fig. 4).

However, remarkably different larger morphologies were observed dependent on the length of the alkyl chains. While micrometer-sized superstructures reminiscent of tertiary protein structures were identified for the complexes with abrupt spin transition, 1e–1g, no such motif was found with 1c. The spherical shape of these microsize motifs is most evident in solutions of 1c and 1e from CH₂Cl₂. Cryogenic scanning electron micrographs of representative sections of self-assembled species: (a) 1f from 2.5 mM solution and 0.5 mM (inset); (b) 1g from 0.5 mM solution; (c) 1e and (d) 1c from 5 mM solution in CH₂Cl₂. Cryogenic scanning electron micrographs of representative sections of self-assembled species: (a) 1f from 2.5 mM solution and 0.5 mM (inset); (b) 1g from 0.5 mM solution; (c) 1e and (d) 1c from 5 mM solution in CH₂Cl₂.

Fig. 4 Cooling-heating cycles for self-assembled complexes in solution. (a) Hysteresis of 1g around room temperature. (b) Magnetic response of complex 1g upon sequential cycling between 270 K and 298 K, revealing incomplete population of both the high- and the low-spin states in cycles 2 and 3. (c) Magnetic response of complex 1f during three cooling-heating cycles involving repetitive temperature changes between 230 K and 270 K.

Conclusions

We have developed a magnetically switchable system based on alkyl-functionalized iron(III) sal₃-trien complexes, for which the transition temperature can be predictably modulated via supramolecular principles. While solution processing has generally been assumed to suppress spin crossover, the iron(III) sal₃-trien system exploits the dynamics of self-assembly in solution to induce cooperativity that is absent in the solid state. Specifically, the number of CH₂ units that are available as molecular recognition sites in solution are a key parameter to control the spin crossover temperature. These molecular recognition sites require a minimum distance to the polar spin labile site to be efficient for self-assembly. In our case, C₁₈ and longer units are appropriate, while C₁₂ units are too short. Tailoring of the spin crossover temperature is possible by adjusting the number of recognition sites per molecule or by variation of the molar concentration. This methodology has been used to fabricate a solution that is magnetically bistable around room temperature. Presumably, tailoring affects the self-assembly of the molecules and the type of tubular core-shell motif comprising alkyl groups as shells around the polar iron centers. The assembly in solution is likely dynamic, yet sufficiently ordered to constrain the conformation of the alkyl tails, thus imparting the intermolecular elastic strain required for cooperative spin crossover. An obvious advantage of the approach presented here is the covalent bonding between the molecular recognition sites and the magnetically labile metal center, which inherently connects structure and function. This methodology is applicable to a large diversity of magnetically bistable systems providing access to custom-tailored magnetically active solutions, which may become useful, for example for the fabrication of soft matter devices, for thermochromically triggered switches, and for early-stage detection of cancer tissue due to the temperature gradient between healthy and carcinogenic cells.

Experimental procedures
The syntheses of 1-bromotriacontane, 25 complexes 1a–e, 17,18 and 2e–i 19 were reported previously, all other reagents were commercially available and used as received. For synthesis, THF was dried by passage through a solvent purification column, all other reagents were commercially available and used as received. Flash chromatography was performed using silica gel 60 (63-200 mesh) or basic alox (0.05–0.15 mm, pH 9.5). All 1H and 13C (1H) NMR spectra were recorded at 25 °C on Bruker or Varian spectrometers and referenced to residual solvent 1H or 13C resonances (δ in ppm, J in Hz). Assignments are based either on distortionless enhancement of polarization transfer (DEPT) experiments. Melting points were determined using a Mettler Toledo TGA/SDTA 851 analyzer and are uncorrected. UV–vis measurements were performed on a Perkin Elmer Lambda 900 instrument in CH2Cl2 solution (0.2 or 0.04 mM). Low temperature absorbance experiments were carried out with an Oxford Instruments Optistat-DN cryostat connected to a temperature control unit. IR spectra were recorded on a Mattson 5000 FTIR instrument in CHCl3 solution. High resolution mass spectra and mass spectra were measured by electrospray ionization (ESI–MS) in CHCl3/MeOH on a Bruker 4.7 T BioAPEX II. Elemental analyses were performed at the ETH Zurich (Switzerland).

Synthesis of 4-(docosyloxy)salicylaldehyde.

To a solution of 2,4-dihydroxybenzaldehyde (1.86 g, 13.2 mmol) in DMF (20 mL) was added NaHCO3 (1.11 g, 13.2 mmol). After 10 min stirring at RT, 1-bromodocosane (4.50 g, 11.0 mmol) in DMF/THF (1:4 v/v, 25 mL) was slowly added. The mixture was heated to 120 °C for 3 h under Ar. After cooling to RT, aqueous HCl (1 M, 100 mL) was added, and the mixture was stirred vigorously and then filtered. The residue was suspended in acetone (100 mL), filtered, washed again with acetone (100 mL), and then extracted with THF (4 × 50 mL). A brownish precipitate formed upon standing for 2 d at 4 °C, which was filtered off. The filtrate was concentrated to 50 mL and the formation of a precipitate was induced by addition of EtOH under stirring. The residue was filtered and dried in vacuo to give the title compound as a white solid (3.65 g, 74%). Purification by column chromatography (SiO2, hexane/THF 15:1) afforded a microanalytically pure white solid, M.p. 73 °C. 1H NMR (CDCl3, 360 MHz): δ 11.49 (s, 1H, OH), 9.70 (s, 1H, CHO), 7.41 (d, 1H, J = 8.6 Hz, C6H5), 6.52 (d, 1H, J = 8.6 Hz, C6H5), 6.41 (s, 1H, C6H5), 4.00 (t, 2H, J = 6.5 Hz, OCH2), 1.79 (m, 2H, OCH2CH2), 1.50–1.39 (m, 2H, OCH2CH2CH2), 1.39–1.13 (m, 52H, CH2), 0.88 (t, 3H, J = 6.4 Hz, Me). 13C [1H] NMR (CDCl3, 91 MHz): δ 194.3 (CHO), 166.5, 164.6 (CCH), 135.2 (CCH), 115.1 (CCH), 108.8 (CCH), 101.1 (CCH), 68.6 (OCH2), 32.0, 30.1–28.4, 26.1, 22.8 (all CH2), 14.3 (Me). HR–MS (EI): calecd for C28H28O3 [M + H+] m/z = 451.2092, found m/z = 451.2047. Anal. found (calcd) for C28H28O3: C 77.90 (77.97); H 11.48 (11.43). The mixture was heated to 120 °C for 3 h under Ar. After cooling to RT, aqueous HCl (1 M, 50 mL) was added and the mixture was stirred vigorously for 15 min and filtered and the residue was washed with water (3 × 50 mL) and acetone (50 mL) and then extracted with warm THF (4 × 50 mL). A brownish precipitate formed upon staying overnight at RT, which was filtered off. The filtrate was concentrated to 20 mL and warmed to obtain a clear solution, acetone was added dropwise to initiate precipitation. After stirring for 2 h at RT, the formed precipitate was collected by centrifugation. The slow precipitation was repeated three times and the residue dried in vacuo to give the title compound as a white solid (110 mg, 20%). Filtration of a warm solution of the title compound in THF over SiO2 gave microanalytically pure material. M.p. 83 °C. 1H NMR (CDCl3, 360 MHz): δ 11.48 (s, 1H, OH), 9.70 (s, 1H, CHO), 7.41 (d, 1H, J = 8.6 Hz, C6H5), 6.52 (d, 1H, J = 8.6 Hz, C6H5), 6.41 (s, 1H, C6H5), 4.00 (t, 2H, J = 6.5 Hz, OCH2), 1.79 (m, 2H, OCH2CH2), 1.50–1.39 (m, 2H, OCH2CH2CH2), 1.39–1.13 (m, 52H, CH2), 0.88 (t, 3H, J = 6.4 Hz, Me). 13C [1H] NMR (CDCl3, 91 MHz): δ 194.4 (CHO), 166.6, 164.7 (2 × CCH), 153.5 (CCH), 115.1 (CCH), 108.9 (CCH), 101.2 (CCH), 68.7 (OCH2), 32.1, 30.1–28.4, 26.1, 22.8 (all CH2), 14.3 (Me). HR–MS (ESI): calecd for C28H28O3 [M + H+] m/z = 557.4699, found m/z = 557.4690. Anal. found (calcd) for C28H28O3 (558.93): C 79.48 (79.51); H 12.19 (11.90).

Synthesis of complex 1f

Triethylenetetramine (43 mg, 0.30 mmol) was dissolved in EtOH (2 mL) and treated with a solution of 4-(docosyloxy)salicylaldehyde (264 mg, 0.59 mmol) in THF (10 mL). After 10 min, solid NaOMe (32 mg, 0.59 mmol) was added and the yellowish suspension was stirred for 10 min. An ethanolic solution of Fe(NO3)3 × 9H2O (120 mg, 0.30 mmol in 3 mL) was then added dropwise. The dark purple suspension was stirred for 30 min at RT and filtered over a short pad of silica. The product was eluted with warm EtOH/THF 2:1 (3 × 60 mL) and dried under reduced pressure. The residue was dissolved in CHCl3 (20 mL) and purified on a short pad of Al2O3 by consecutive elution with CHCl3 (150 mL) and warm EtOH/THF 2:1 (3 × 30 mL). After evaporation of the EtOH/THF fraction, the residue was redissolved in CH2Cl2 (20 mL) and centrifuged. The supernatant was evaporated under reduced pressure to give the analytically pure purple solid 1f (140 mg, 42%). M.p. 197 °C (decomp.). IR (CHCl3): 1600 cm–1 (C=N). UV–vis (CH2Cl2): λmax (ε) = 496 nm (4100 M–1 cm–1). HR–MS (ESI): calecd for C46H42Fe2O12 [M – NO3]– m/z = 1056.8027, found m/z = 1056.8026. Anal. found (calcd) for C46H42Fe2O12 (1119.47): C 68.40 (68.67); H 10.13 (10.08); N 5.97 (6.26).

Synthesis of complex 1g

According to procedure 1f, triethylenetetramine (14 mg, 0.10 mmol) in EtOH (2 mL) was reacted with 4-(triacontyloxy)salicylaldehyde (110 mg, 0.20 mmol) in warm THF (16 mL), NaOMe (11 mg, 0.20 mmol) and ethanolic Fe(NO3)3 × 9H2O (40 mg, 0.10 mmol in 2 mL). The dark purple suspension was stirred for 30 min at 60 °C and filtered while warm. After cooling to RT the filtrate was centrifuged. The residue was redissolved in warm THF (70 mL), EtOH (70 mL) was added and a precipitate formed upon stirring at 0 °C for 30 min. After centrifugation the residue was separated, and dissolved
in warm THF. Upon standing at 0 °C for 30 min a precipitate formed which was collected by centrifugation, and redissolved in warm THF. After filtration through Celite, and evaporation of volatiles, $\text{1f}$ was obtained as a purple solid (58 mg, 47%). m.p. 196 °C (decomp.), IR (CHCl$_3$): 1604 cm$^{-1}$ (C=O). UV-vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (t) = 494 nm (4200 M$^{-1}$cm$^{-1}$). HR-MS (ESI, MeOH): calcd. for C$_{98}$H$_{82}$FeN$_{50}$O$_{35}$ [M – NO]$: m/z = 1281.0531$, found $m/z = 1281.0530$. Anal. found (calcd) for C$_{98}$H$_{82}$FeN$_{50}$O$_{35}$ (1343.90) $\times$ H$_2$O: C 70.82 (70.55); H 11.16 (10.81); N 5.21 (5.14).

**Procedure for the cryo-SEM measurements.** Images were acquired from 0.5–5 mM solutions in CH$_2$Cl$_2$ which were rapidly frozen using precooled liquid nitrogen. The sample was transferred onto the prechamber attached to a Philips XL30 FEG scanning electron microscope then sublimed at −95 °C under high vacuum for 15 min, cooled and sputter coated with platinum. The sample was moved onto the cryostat in the main chamber of the microscope and viewed at 3–20 kV using a secondary electron detector. A sample of a CH$_2$Cl$_2$ solution of $\text{1f}$ was further analysed by energy dispersive X-ray analysis at 20 kV and at 10 kV, revealing the presence of the elements Fe, C, N, and O constituting the complex.

**Acknowledgements**

We gratefully acknowledge financial support from ERA-net Chemistry, the Swiss National Science Foundation, the Alfred Wanner Foundation, and the European Research Council (StG 208561). We thank T. Bally (Univ. Fribourg) for sharing UV-vis spectroscopic facilities.

**Notes and references**

12. Complexes $\text{1g-e}$ were amorphous in the solid state; all our attempts to grow crystals of these complexes have failed.
For complexes 1a–d, thermodynamic data cannot be reliably determined since the spin transition is gradual and may not be complete at the lowest accessible temperature for CH$_2$Cl$_2$ solution.

For hysteretic spin crossover induced by N-functionalization of the sal₃trien ligand, see: P. N. Martinho, Y. Ortiz, B. J. Gildea, C. Gandolfi, G. McKerr, B. O’Hagan, M. Albrecht and G. G. Morgan, submitted for publication.


The number of methylene units controls the self-assembly and the sharp spin transition temperature of iron(III) complexes in solution, providing tailored magnetic spin switches.