



A Hybrid Organic-Inorganic Molecular Daisy Chain

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Complete List of Authors:	Fernandez, Antonio; University of Manchester, Chemistry Moreno Pineda, Eufemio; University of Manchester, School of Chemistry Soria, Jesus; University of Manchester, Chemistry McInnes, Eric; University of Manchester, School of Chemistry Timco, Grigore; The Lewis Magnetism Laboratory, School of Chemistry, The University of Manchester, ; University of Manchester, School of Chemistry Winpenny, R; The University of Manchester, Department of Chemistry

COMMUNICATION

A Hybrid Organic-Inorganic Molecular Daisy Chain

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Antonio Fernandez, Eufemio Moreno Pineda[§], Jesús Ferrando-Soria, Eric J. L. McInnes, Grigore A. Timco and Richard E. P. Winpenny*

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A hybrid organic-inorganic molecular daisy chain has been synthesised in one pot reaction. The molecule contains two {Cr₆Zn₂} rings linked through an organic molecule that acts as both template and ligand. Magnetic and spectroscopic data reveal the magnetic complexity of the daisy chain, which can be casted to two magnetic isomers through comparison of experimental and simulated data for Cr(III) chains.

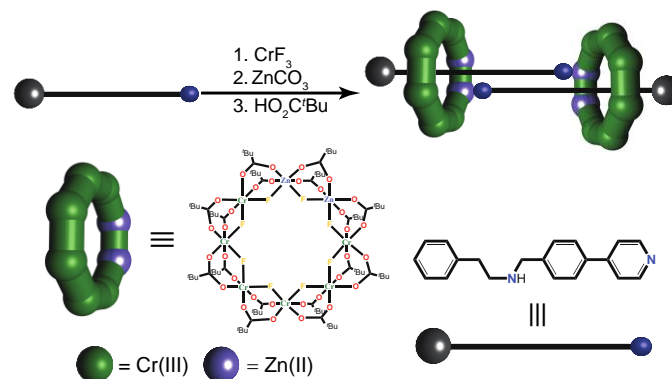
Hybrid organic–inorganic materials that combine features of both chemistries have been developed in recent years, where the combination of the physical properties associated with inorganic systems, such as the magnetic or spectroscopic properties, with those associated with organic systems, i.e. dynamism and/or molecular recognition, seems in principle an attractive goal. In the field of metal-organic frameworks¹ examples of organic-inorganic materials can be found, as well as in coordination polymers and interlocked systems in supramolecular chemistry.²

One particular type of supramolecular hybrid materials are the organic-inorganic rotaxanes, where inorganic and organic structural units are interconnected mechanically at the molecular level.³ In these systems the inorganic part is formed by {Cr₇M} molecular nanomagnets,⁴ which are excellent subjects for studies of fundamental physics, such as quantum tunnelling of total spin,⁵ and possible long term applications as qubits for quantum information processing (QIP).^{6,7}

A step forward in terms of complexity and sophistication, beyond rotaxanes, are the molecular daisy chains.⁸ This term was first coined by Stoddart⁹ more than a decade ago, for

systems formed by a linear thread and a threadable macrocycle, which are covalently bound. Introduction of a stopper unit prevents dethreading of these supramolecularly assembled chains and therefore converts the supramolecular binding into a mechanical bond, leading to mechanically interlocked system. The molecular daisy chains reported so far are mainly organic based on cyclodextrins,¹⁰ crown ethers or cucurbit[6]uril¹¹ as macrocyclic components, where the driving force for the interlocked system formation is the host-guest supramolecular interaction, with only a few examples of anions or metals used as templates.¹² Potential applications for daisy chains range from drug delivery systems, switches, molecular motors to machines, as well as nanovalves and molecular actuators.¹³

Here we report the first hybrid organic-inorganic molecular daisy chain (Scheme 1). The inorganic part consists of a {Cr₆Zn₂} ring, with a metal core reminiscent of {Cr₇M} wheels.⁴



Scheme 1. Schematic description of the formation of the daisy chain (1), involving the organic axle (L) and the inorganic wheel ({Cr₆Zn₂}).

The organic thread acts as both a template and a ligand. At the centre is an alkylammonium group, used to template the formation of the eight member metallic ring. A phenyl-group acts as a stopper at one end of the thread, to prevent dethreading of

School of Chemistry and Photon Science Institute, The University of Manchester, Oxford Road, Manchester M13 9PL, UK. Fax: 44-161-275-1001; E-mail: richard.winpenny@manchester.ac.uk

[§] Current address: Institute of Nanotechnology, Karlsruhe Institute of Technology, D-76344, Eggenstein-Leopoldshafen, Germany.

[†] Electronic Supplementary Information (ESI) available: Synthetic method, crystallographic details, crystallographic figures and magnetic information.

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the template from the inorganic ring. The other end of the thread has a phenylpyridine that acts as a stopper and also as an *N*-donor ligand coordinating to a metal site in the second ring to form the interconnected rotaxane dimer.

The daisy chain was synthesised from the reaction between $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$, ZnCO_3 , pivalic acid ($\text{HO}_2\text{C}^t\text{Bu}$) and the thread ($L = N-[(1,1'-\text{biphenyl})-4\text{-ylmethyl}]-4\text{-phenylethane-1-amine}$) (7:2:18:1 molar ratio) resulting in a dimer with molecular formula $[\text{Cr}_6\text{Zn}_2(\mu\text{-F})_8(\text{O}_2\text{C}^t\text{Bu})_{15}(L)_2]$ (**1**) in good yield (35 %). While templating of such rings about ammonium cations is now well-known^[4] and the ability of the pyridine from the thread of a rotaxane to act as a ligand has been reported previously,^[14] both happening simultaneously is new. The mechanism of the self-assembly process is unclear, but previous work suggests formation of $\{\text{Cr}_5\}$ and $\{\text{Cr}_6\}$ chains H-bonded to *L* in an early step, followed by ring closure by addition of the divalent metal ions.¹⁷

The solid-state structure of **1** was determined on a single crystal grown from a saturated toluene solution (Figure 1). Each inorganic ring contains on average two Zn(II) and six Cr(III) ions, confirmed by elemental analysis; the metal ions in each ring are arranged in a regular octagon (Figure 1b), bridged on the inner edges by eight fluorides and on the outer edges by fifteen pivalates. The peripheral pivalates are arranged so that eight lie close to the plane of the eight metal centres, described as the equatorial sites, and the other seven alternate above and below the plane of the ring, described as axial sites.

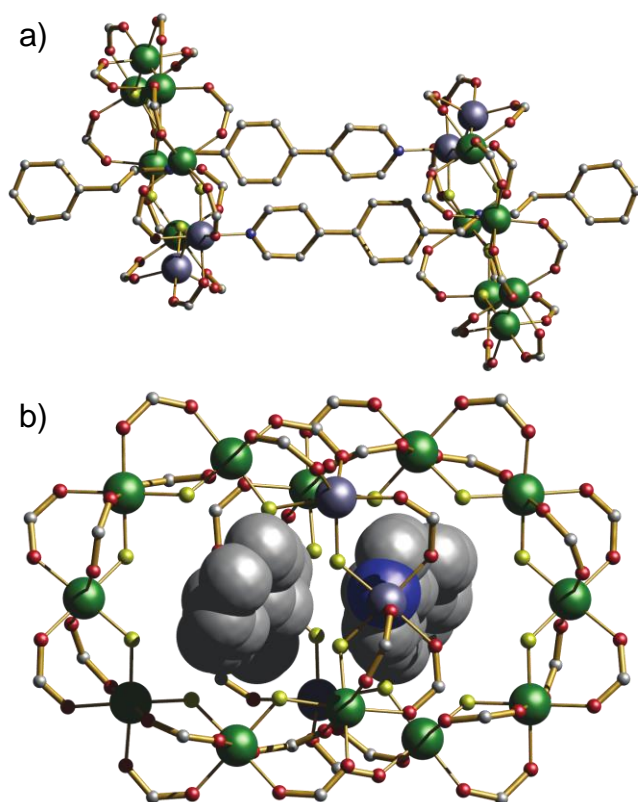


Figure 1. Crystal structure of **1** (ball and stick) viewed (a) in the plane of the $\{\text{Cr}_6\text{Zn}_2\}$ and (b) perpendicular to the plane of the $\{\text{Cr}_6\text{Zn}_2\}$. Colours: Cr, green; Zn, teal; F, yellow; O, red; C, grey; N, blue. H-atoms and ^tBu groups of pivalates omitted for clarity.

From chemical considerations the five-coordinate metal site within each ring is likely to be Zn(II). The location of the second Zn(II) site in each ring is not so easily determined. To understand the problem, we number the metal sites with the five-coordinate Zn(II) site as 1. Two alternative isomers need to be considered: where the Zn ions are at 1,2- (**A**) or 1,3- (**B**) in the structure (Figure 2). Six of the six-coordinate sites have average distances between 1.93367(9) – 1.96567(8) Å, consistent with Cr(III) ions.⁴ The 3-site has bond lengths averaging 2.014 ± 0.040 Å; this is closer to the average that would be expected for a six-coordinate Zn^{II} site (ca. 2.09 Å) but a little short. Refinement of the structure as exclusively isomer **B** gives a respectable *R*-factor, but the anisotropic displacement parameters for the 2- or 3-metal sites are not ideal (too large for the 3-site as 100% Zn, too small for the 2-site as exclusively Cr); an ordered structure does not fit with magnetic data (see below). Based on the magnetic data (we fixed the site occupancies so that isomer **A** is present 30% and isomer **B** 70%). This leads to better anisotropic displacement parameters. Similar partial disorder of the divalent metal site in $\{\text{Cr}_7\text{M}\}$ rings has been discussed recently.^{4e} The compound can be recrystallized successfully from non-coordinating solvents (toluene, CH_2Cl_2 , Et_2O , THF), but attempts to characterise compound **1** in solution were unsuccessful; NMR spectroscopy does not work due to the paramagnetism of the sample, while the mass of the entire daisy-chain takes the sample outside the window we can reach by electro-spray mass spectrometry.

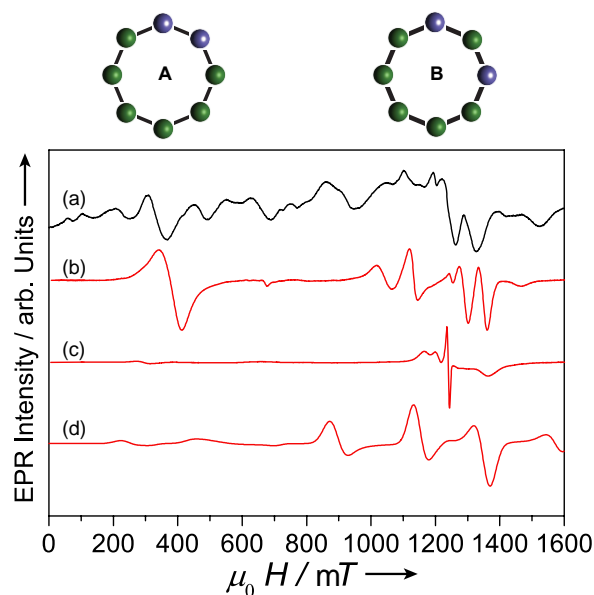


Figure 2. (Top) Representation of two possible isomers of **1**; (Bottom) Q-band EPR of **1** at 5 K (a) and comparison with experimental data for: (b) $\{\text{Cr}_6\}$ chain; (c) $\{\text{Cr}_5\}$ chains; and (d) a calculated spectrum for a single Cr(III) ion using the parameters described in the text.

The magnetic behaviour is only consistent with a mixture of isomers within the rings. Isomer **A** contains a single $\{\text{Cr}_6\}$ chain, which will have a diamagnetic ground state due to nearest neighbour anti-ferromagnetic exchange. In isomer **B** the Zn(II) there is an isolated Cr(III) ion, and a $\{\text{Cr}_5\}$ chain; each will have

an $S = 3/2$ spin ground state. The presence of isomers **A** and **B** can be probed through electron paramagnetic resonance (EPR) spectroscopy. Data collected at Q-band frequency at 5 K shows a rich EPR spectrum, which contains more features than could be expected from a single isomer.

It is not possible to simulate the spectrum, however it can be compared to experimental data for isolated $\{\text{Cr}_5\}$ and $\{\text{Cr}_6\}$ chains.^{14,15} This allows us to assign major features ca. 330, 1150, 1300 and 1380 G to a $\{\text{Cr}_6\}$ containing isomer (Figure 2b; the features arise from the $S = 1$ and 2 excited states of a $\{\text{Cr}_6\}$ chain). A $\{\text{Cr}_6\}$ chain suggests isomer **A** is present. One feature at ca. 1250 G appears to come from a $\{\text{Cr}_5\}$ chain (Figure 2c); it is due to the $S = 1/2$ first excited state of the $\{\text{Cr}_5\}$ and is sharper in the isolated chain. The other features from a $\{\text{Cr}_5\}$ chain are due to the ground $S = 3/2$ state and lie in the same region as features from the $\{\text{Cr}_6\}$ chain.

If a $\{\text{Cr}_5\}$ chain is present, this must be isomer **B**, which also contains a single isolated Cr(III) ion (Figure 2d). A spectrum was calculated for an individual Cr(III) ion in this environment using parameters ($g = 1.98$ and an axial zero-field splitting parameter of $D = -0.34 \text{ cm}^{-1}$)¹⁸ obtained from previous studies of heterometallic rings through a variety of techniques.^{4b,14} This simulates most of the remaining features of the spectra (Figure 2d). Adding together the spectra calculated for each fragment involves assumptions about relative transition probabilities in the different isomers.

The other transitions observed in the experimental data, could be due to long-range exchange interaction, or other parameters (e.g. single ion rhombic anisotropy). Choosing which of these further parameters to include would be arbitrary at this stage. Attempts to fit the spectra using isomer **B** but with weak exchange interactions between the isolated Cr^{III} site and the $\{\text{Cr}_5\}$ chain were largely unsuccessful (Figure S5).

We have studied the magnetic susceptibility behaviour of polycrystalline samples of **1** in the temperature range 2 – 300 K under 1 kOe applied magnetic field (Figure 3). $\chi_M T$ of **1** (where χ_M is the molar magnetic susceptibility) at room temperature is $22.4 \text{ cm}^3 \text{ K mol}^{-1}$, which is quite close to $22.1 \text{ cm}^3 \text{ K mol}^{-1}$, which would be expected for twelve non-interacting Cr(III) ions ($g_{\text{Cr}} = 1.98$, $S = 3/2$). Upon cooling $\chi_M T$ decreases reaching a value of $4.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K, as a consequence of the antiferromagnetic interactions between the Cr(III) sites within each ring (Figure 3a).

The best measurement of the spin ground state comes from the molar magnetisation (M), which was studied at 2 and 4 K in the field range of 0 – 7 T (Figure 3b). The observed behaviour is not consistent with an ordered structure, i.e. with isomer **A**, a $\{\text{Cr}_6\}$ chain,¹⁴ nor with isomer **B**, containing a mixture of a $\{\text{Cr}_5\}$ chain and a single Cr(III) site (See Figure S4). To fit the magnetic data, both $\chi_M T(T)$ and $M(H)$ were calculated for isomers **A** and **B** using an isotropic Heisenberg Hamiltonian ($\hat{H} = \mu_B \sum_i g \vec{S}_i \vec{B} - 2 \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$); with $g = 1.98$ and $J = -5.8 \text{ cm}^{-1}$ as used previously for $\{\text{Cr}_7\text{Zn}\}$ rings.^{5a} To simulate the experimental data the contributions of each isomer **A** and **B** were weighted and added, with the only free parameter being the relative contribution of each isomer; this gave a 3:7 weighting values for isomer **A** to **B**.

The model assumes magnetic interactions between rings would be much weaker. Attempts to fit the $M(H)$ data to isomer **B**, but with a weak exchange interaction between the single chromium site and the $\{\text{Cr}_5\}$ chain produces a very poor agreement (Figure S4).

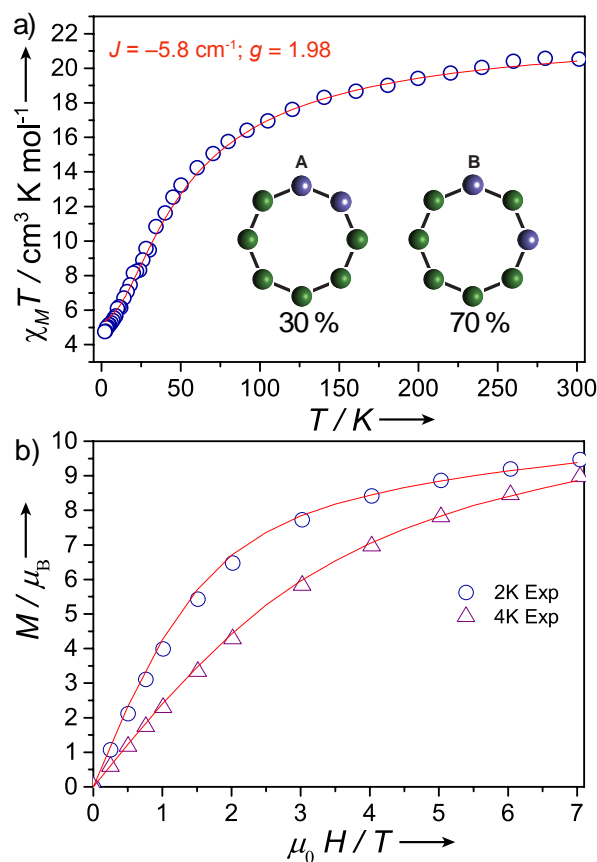


Figure 3. (a) Variation of $\chi_M T$ vs. T for **1** at 1 kOe from 2–300 K; (b) M vs. H for **1** from 0–7 T at 2 and 4 K and simulation with the model described in the text (solid lines).

In summary, a hybrid organic-inorganic daisy chain has been synthesised. The magnetic and spectroscopic properties of the system were studied through X-ray, SQUID and EPR techniques, and the best interpretation of this data requires presence of two isomers, **A** and **B**, in approximately 3:7 ratio. Extending the organic axle, including more quaternary amine stations, could be the next step towards mechanically controlled magnetic systems at molecular level. This could lead to a method to switch the interaction through distance between the magnetic units of the structures by external stimuli, bringing the possibility of connecting molecular motion with magnetism.

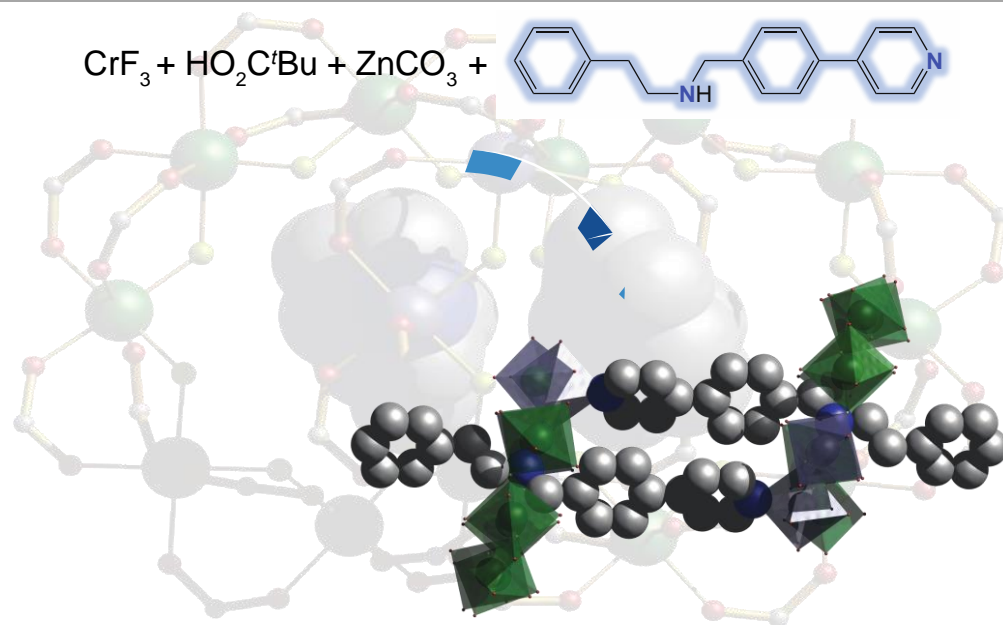
This work was supported by the EPSRC(UK), including for the National EPR Facility, the European Commission (Marie Curie Intra-European Fellowship to AF (300402) and JFS (622659)). EMP thanks the Panamanian agency SENACYT-IFARHU for funding. REPW thanks the Royal Society for a Wolfson Merit Award. We also thank EPSRC (UK) for funding an X-ray diffractometer (grant number EP/K039547/1).

Notes and References

- ‡ Crystal data for **3** [$C_{95}H_{156}Cr_6F_8N_2O_{30}Zn_2$]: $M_r = 2400.95$, monoclinic, space group $P2_1/c$, $T = 270.1(2)$ K, $a = 23.6326(12)$, $b = 22.5386(11)$, $c = 37.8111(15)$ Å, $\beta = 126.954(3)$, $V = 16094.2(14)$ Å³, $Z = 4$, $\rho = 0.991$ g cm⁻³, total data = 22942, $R_1 = 0.0831$ for $I \geq 2\sigma(I)$ and $wR_2 = 0.2321$. The data was collected on an Agilent SuperNova CCD diffractometer with MoK α radiation ($\lambda = 0.71073$ Å), solved using SUPERFLIP^{16a}, and refined on F^2 using SHELX-14^{16b} in Olex2.^{16c}
- See for example: (a) R. Robson, *Dalton*. 2000, **21**, 3735; (b) Q. Li, W. Zhang, O. Š. Miljanić, C.-H. Sue, Y.-L. Zhao, L. Liu, C. B. Knobler, J. F. Stoddart and O. M. Yaghi, *Science*, 2009, **325**, 855; (c) H. Deng, M. A. Olson, J. F. Stoddart and O. M. Yaghi, *Nat. Chem.* 2010, **2**, 439; (d) S. J. Loeb, *Chem. Soc. Rev.* 2007, **36**, 226.
 - (a) H. Ogino, *J. Am. Chem. Soc.* 1981, **103**, 1303; (b) S. R. Batten and R. Robson, *Angew. Chem. Int. Edn.* 1998, **37**, 1460; (c) M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720; (d) S. J. Cantrill, K. S. Chichak, A. J. Peters and J. F. Stoddart, *Acc. Chem. Res.* 2005, **38**, 1; (e) J. D. Crowley, S. M. Goldup, A.-L. Lee, D. A. Leigh and R. T. McBurney, *Chem. Soc. Rev.* 2009, **38**, 1530; (f) T. K. Ronson, J. Fisher, L. P. Harding, P. J. Rizkallah, J. E. Warren and M. J. Hardie, *Nature Chem.* 2009, **1**, 212; (g) S. Kitagawa, R. Kitaura, and S.-I. Noro, *Angew. Chem. Int. Edn.* 2004, **43**, 2334.
 - (a) C.-F. Lee, D. A. Leigh, R. G. Pritchard, D. Schultz, S. J. Teat, G. A. Timco and R. E. P. Winpenny, *Nature*, 2009, **458**, 314; (b) B. Ballesteros, T. B. Faust, C.-F. Lee, D. A. Leigh, C. A. Muryn, R. G. Pritchard, D. Schultz, S. J. Teat, G. A. Timco and R. E. P. Winpenny, *J. Am. Chem. Soc.* 2010, **132**, 15435.
 - (a) M. Affronte, S. Carretta, G. A. Timco and R. E. P. Winpenny, *R. Chem. Commun.* 2007, **18**, 1789; (b) S. Piligkos, H. Weihe, E. Bill, F. Neese, H. El-Mkami, G. M. Smith, D. Collison, G. Rajaraman, G. A. Timco, R. E. P. Winpenny and E. J. L. McInnes, *Chem. Eur. J.* 2009, **15**, 3152; (c) G. F. S. Whitehead, F. Moro, G. A. Timco, W. Wernsdorfer, S. J. Teat and R. E. P. Winpenny, *Angew. Chem. Int. Ed.* 2013, **52**, 9932; (d) G. F. S. Whitehead, J. Ferrando-Soria, L. G. Christie, N. F. Chilton, G. A. Timco, F. Moro and R. E. P. Winpenny, *Chem. Sci.* 2014, **5**, 235; (e) F. K. Larsen, J. Overgaard, M. Christensen, G. J. McIntyre, G. Timco and R. E. P. Winpenny, *Acta Cryst. Sect. B.*, 2014, **70**, 932.
 - (a) G. A. Timco, E. J. L. McInnes and R. E. P. Winpenny, *Chem. Soc. Rev.* **2013**, **42**, 1796; (b) S. Carretta, P. Santini, G. Amoretti, T. Guidi, J. R. D. Copley, Y. Qiu, R. Caciuffo, G. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.* 2007, **98**, 167401.
 - (a) A. Ardavan, O. Rival, J. J. L. Morton, S. J. Blundell, A. M. Tyryshkin, G. A. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.* 2007, **98**, 057201; (b) C. J. Wedge, R. E. George, G. A. Timco, F. Tuna, S. Rigby, E. J. L. McInnes, R. E. P. Winpenny, S. J. Blundell and A. Ardavan, *Phys. Rev. Lett.* 2012, **108**, 107204.
 - (a) F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.* 2005, **94**, 207208 (b) G. A. Timco, S. Carretta, F. Troiani, F. Tuna, R. G. Pritchard, E. J. L. McInnes, A. Ghirri, A. Candini, P. Santini, G. Amoretti, M. Affronte and R. E. P. Winpenny, *Nat. Nanotechnol.* 2009, **4**, 173.
 - (a) C. J. Bruns, M. Frascioni, J. Iehl, K. J. Hartlieb, S. Schneebeli, C. Cheng, S. I. Stupp and J. F. Stoddart, *J. Am. Chem. Soc.*, 2014, **136**, 4714; (b) J. Rotzler and M. Mayor, *Chem. Soc. Rev.* 2013, **42**, 44.
 - P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem. Int. Ed.* 1998, **37**, 1294.
 - (a) J. Watanabe, T. Ooya and N. Yui, *Chem. Lett.* 1998, **10**, 1031; (b) A. Harada, Y. Takashima and H. Yamaguchi, *Chem. Soc. Rev.* 2009, **38**, 875.
 - (a) H. Isobe, S. Sato and E. Nakamura, *Org. Lett.*, 2002, **4**, 1287; (b) S. Angelos, Y.-W. Yang, K. Pate, J. F. Stoddart and J. I. Zink, *Angew. Chem. Int. Ed.* 2008, **47**, 2222.
 - J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh and R. T. McBurney, *Angew. Chem. Int. Ed.* 2011, **50**, 9260.
 - (a) M. C. T. Fyfe and J. F. Stoddart, *Acc. Chem. Res.* 1997, **30**, 393; (b) J. P. Collin, C. Dietrich-Buchecker, P. Gavina, M. C. Jimenez-Molero and J. P. Sauvage, *Acc. Chem. Res.* 2001, **34**, 477; (c) C. A. Schalley, K. Beizai and F. Vogtle, *Acc. Chem. Res.* 2001, **34**, 465; (d) B. Champin, P. Mobian and J. P. Sauvage, *Acc. Chem. Res.* 2007, **36**, 358.
 - (a) S. T. Ochsenbein, F. Tuna, M. Rancan, R. S. G. Davies, C. A. Muryn, O. Waldmann, R. Bircher, A. Sieber, G. Carver, H. Mutka, F. Fernandez-Alonso, A. Podlesnyak, L. P. Engelhardt, G. A. Timco, H. U. Güdel and R. E. P. Winpenny, *Chem. Eur. J.* 2008, **14**, 5144; (b) M. L. Baker, A. Bianchi, S. Carretta, D. Collison, R. J. Docherty, E. J. L. McInnes, A. McRobbie, C. A. Muryn, H. Mutka, S. Piligkos, M. Rancan, P. Santini, G. A. Timco, P. L. W. Tregenna-Piggott, F. Tuna, H. U. Güdel and R. E. P. Winpenny, *Dalton Trans.* 2011, **40**, 2725.
 - A. B. Boer, D. Collison, C. A. Muryn, G. A. Timco, F. Tuna, and R. E. P. Winpenny, *Chem. Eur. J.* 2009, **15**, 13150.
 - (a) G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112; (b) O. V. Dolomanov, L. J. Bourhis, R. L. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339; (c) L. Palatinus, and G. Chapuis, *J. Appl. Cryst.* 2007, **40**, 786.
 - (a) A. McRobbie, A. R. Sarwar, S. Yeninas, H. Nowell, M. L. Baker, D. Allan, M. Luban, C. A. Muryn, R. G. Pritchard, R. Prozorov, G. A. Timco, F. Tuna, G. F. S. Whitehead and R. E. P. Winpenny, *Chem. Commun.*, 2011, **47**, 6251; (b) F. K. Larsen, J. Overgaard, S. Parsons, E. Rentschler, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *Angew. Chem. Int. Ed.* 2003, **42**, 5978.
 - S. Stoll and A. Schweiger *J. Magn. Reson.* 2006, **178**, 42.

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COMMUNICATION



Antonio Fernandez,
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Ferrando-Soria, Eric. J.
L. McInnes, Grigore
Timco and Richard E.
P. Winpenny*

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A hybrid daisy-chain has been made, involving an organic thread for an inorganic ring, where the organic thread for the ring also acts as a ligand for a second ring. The ring contains six chromium(III) and two zinc(II) ions, and two isomers of the rings are found in the daisy-chain.