Remote control of SMM behaviour via DTE ligands

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Complete List of Authors:	Goulven, Cosquer; Tohoku University, Chemistry; Japan Science and Technology (JST), Core Research for Evolutional Science and Technology (CREST) Breedlove, Brian; Tohoku University, Chemistry; Japan Science and Technology (JST), Core Research for Evolutional Science and Technology (CREST) Yamashita, Masahiro; Tohoku University, Chemistry; Japan Science and Technology (JST), Core Research for Evolutional Science and Technology (CREST)

Remote control of SMM behaviour via DTE ligands

Goulven Cosquer,[a, b] Brian K. Breedlove [a, b] and Masahiro Yamashita* [a, b]

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Chemists and physicists are continuously working to understand the mechanisms controlling molecular magnetism, especially single-molecule magnetism, to improve the magnetic properties, such as the blocking temperature. With the current research focused on preparing molecular devices, methods to control the components of the devices are necessary. Extensive research has shown that stimuli, such as light, electric current, etc., can be used to change the properties of the molecules making up the devices. Bis(carboxylato)dithienylethene (DTE) derivatives can be photo-isomerized between open and closed forms, i.e., unconjugated and π-conjugated forms, and because of the carboxylate groups, it can be used to link 3*d* and/or 4*f* metal ions. Herein the use of DTE ligands to remotely control the magnetic properties of single-molecule magnets is discussed.

Introduction

Single-molecule magnets (SMMs), which were first discovered about 21 years ago,[1] keep their magnetisation without an external magnetic field below their blocking temperature (T_B), which depends on the height of the energy barrier separating the two magnetic ground states (Δ). The higher Δ is, the higher T_B is. Δ arises from the spin anisotropy of the complexes, and a higher spin value causes a higher Δ. Spin anisotropy occurs due to the magnetic interactions between magnetic ions and the geometric arrangement of the ions. To increase T_B of 3*d* metal SMMs, three strategies have been applied. The first strategy involves increasing the number of the magnetic centers. However, the boundary between SMM and bulk magnet behaviours is quickly reached. The second strategy is to increase interactions between the ions by decreasing the distance between them or by modifying the bridging ligands. The last strategy is to increase the spin value of the magnetic ions. However, for single 3*d* metal ions, the limit is S = 5/2.

To overcome this limit, lanthanide complexes have been investigated. Holmium ions have the highest spin value ($m_J = 8$).[2, 3] In addition, lanthanide ions have inherent anisotropic behaviour,[4] which has given rise to a new class of SMMs called single-ion magnets (SIMs),[5] where magnetic properties are not due to interaction between ions, unlike SMMs. However, due to shielding of 4*f* electrons by 5*s*, 5*p* and 6*s* electrons, lanthanide ions cannot strongly couple to other ions. By combining 3*d* and 4*f* ions, it is possible to obtain high anisotropy with strong magnetic interactions and a high m_J, which would increase Δ.[6–12] Moreover, the splitting of the m_J levels of the lanthanide ions, which controls the anisotropy and magnetic properties of lanthanide ions, is sensitive to the crystal field.

Until recently, research has mainly focused on increasing T_B in order to obtain a room *T* memory storage device. However, this goal has yet to be reached because of the number of possible magnetic relaxation mechanisms, which cause a small effective Δ (Δ_{eff}) compared to the theoretical Δ. More recently, researchers have been investigating the use of SMMs in spintronics, which exploit the spin of the electron, its magnetic moment, and its electronic charge.[13–15] SMMs, which exhibit slow relaxation of their magnetisation, meaning electrons can be polarised, are better than conventional spintronic materials based on ferromagnetic multilayer thin films because SMMs are coordination complexes with properties that can be tuned by modifying the crystal field or by applying external stimuli.

Methods for tuning SMM properties.

In the case of lanthanide-based SMMs, their magnetic properties can be modified by removing the solvent molecules present in the crystal lattice or coordinated to the lanthanide ions, such as water or organic solvents, like methanol.[16–19] In some cases, the desorption process is reversible. Since the solvent molecules are directly coordinated to the lanthanide ions or trapped in the crystal lattice interacting through hydrogen bonding with the coordination sphere of the ion, when they are removed, the coordination sphere is modified. In other words, the energy splitting of the m_J levels changes. In addition, solvent loss can change Δ by an order of magnitude and has an effect on the relaxation mechanism (Fig. 1).

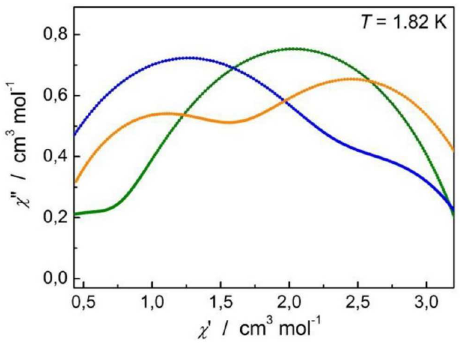


Fig. 1 A comparison of the best fits of the Cole−Cole plots generated by using the Debye model for initial (orange), dry (blue), and rehydrated (olive) Dy SIMs at 1.82 K. Reproduced from Ref [17]

Solvation and desolvation are not the only methods for altering the SMM properties. For instance, theoretical calculations have shown that changing the orientation of water molecules coordinated to dysprosium ions has an effect.[20] Rotating the hydrogen atoms of the water molecules by 90° around the coordination axis causes the anisotropy axis to rotate and reduces Δ by 80%. Another way to switch off the SIM properties of lanthanide complexes is to protonate a chelating ligand coordinated to a lanthanide ion.[21, 22] On the another hand, a crescent-shaped electron-withdrawing ligand coordinated to the lanthanide ion causes an increase in Δ.[23] However, this approach does not involve tuning of the SMM properties because it involves ligand substitution. All of these methods require substantial chemical changes to tune the properties and, thus, cannot be used in functional devices. SMM properties can also be modified by changing the electronic configuration of the complexes by using a redox active ligand. The crystal field around lanthanide ions depends on the oxidation state of the ligand, and thus, if it is changed, the SMM behaviour will also be affected.[24]

The most promising approach to obtain a functional switching SMM device appear to employ a photo-switcher. Several examples use spin crossover processes, which change the electronic configuration of the SMM and, therefore, change the anisotropy and the spin value. However, it can be use only with some 3*d* elements with appropriated coordination geometries and strength of crystal fields.[25, 26] Changing the interactions between SMMs, instead of changing the SMMs themselves, is another method for tuning the magnetic properties. For this, a photochromic bridging ligand, like bis(carboxylato)dithienylethene (DTE), can be used (Fig. 2). The open form of DTE (DTE-o) is not conjugated, meaning that there is no electronic communication between its extremities. Irradiating DTE-o with UV light generates the closed form (DTE-c), which is conjugated, meaning that electronic communication can occur. Irradiation with visible light regenerates DTE-o. Besides electronic communication, the cyclisation and decyclisation processes of DTE drastically change the geometry of the ligand. In other words the angle between the thiophene rings changes from abouts 45° in DTE-o to 0° in DTE-c, and the distance between the carbon of carboxilato group decrease almost 10% during the cyclisation of the DTE. These modifications restrain the SMM complexes and, thus, change their crystal field. In addition, a photochromic bridging ligand can be used with any magnetic ion.

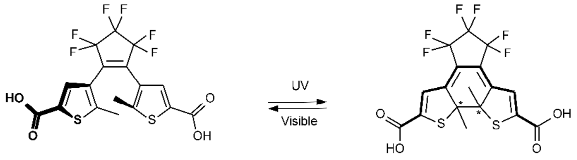


Fig. 2 Photochromic DTE ligand with two carboxyl groups in the open and closed form.

for [Mn4]DTE projected along the b axis. The hydrogen atoms and the water molecules of crystallization are omitted for clarity. Adapted from Ref 30

After irradiation with visible light for 3 h, the maximum ratio of DTE-c to DTE-o was 100%. Clear differences in the dc and *M* vs *H* data at 0.5 K were seen after irradiation with visible light (Fig. 4). In the plots for the irradiated samples, weak hysteresis was observed without coercivity and with intermolecular interactions among the $[Mn_4]$ clusters. The Δ value for the irradiated complex was 46.7 K, which is significantly larger than the theoretical value calculated for $[Mn_4]$DTE-c, and was attributed to an intercluster relaxation process. The magnetic data show that the irradiation with visible light indirectly enhances the $[Mn_4]$ intercluster interactions. In other words, the SMM properties can be remotely controlled using the DTE ligand.

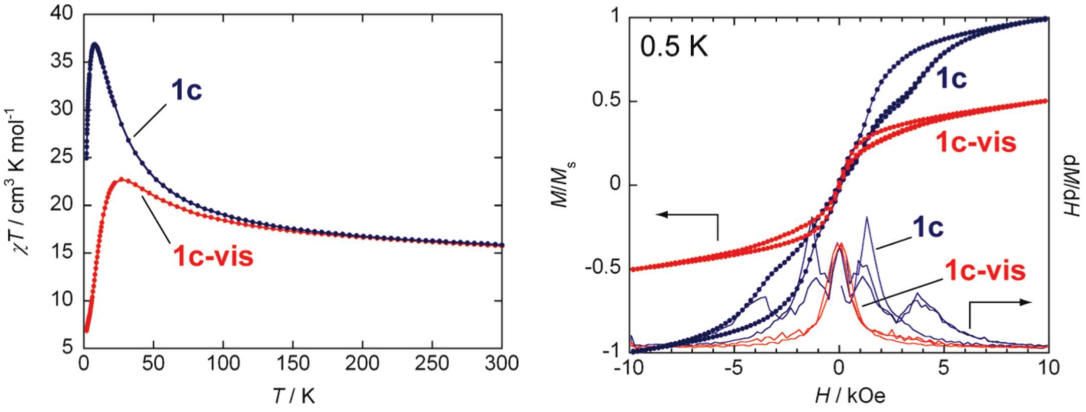


Fig. 4 (Left) T dependence of χT for [Mn$_4$]DTE before (blue) and after (red) irradiation. (right) Plots of M/M_s vs H and dM/dH vs H for [Mn$_4$]DTE before (blue) and after (red) irradiation. Adapted from ref 30

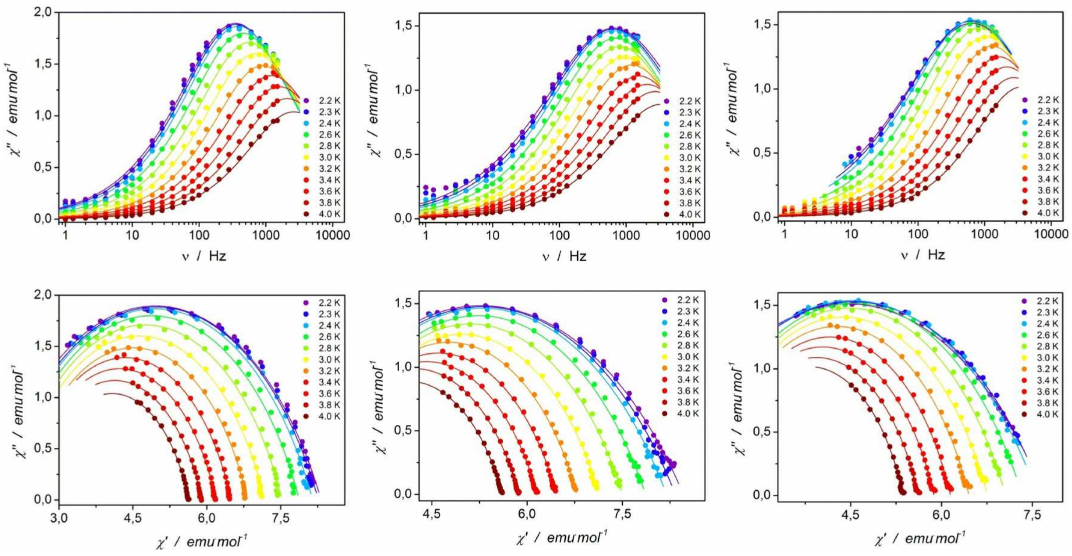


Fig. 5 (top) Frequency dependence of the out-of-phase ac magnetic susceptibility (χ") and (bottom) Cole-Cole plots for the complex with DTE-o (left), DTE-c (center), and re-opened DTE (right) in an applied H_{dc} of 1500 Oe (H_{ac} = 3 Oe). Solid lines were fitted using Debye model. Adapted from ref 35

DTE-4*f* Metal Ion Based SMMs.

Since the energy level splitting of the lanthanide ions are more sensitive to the crystal field than those of transition metal ions are, changing the conjugation of the bridging DTE should have a big effect on the magnetic behaviours of lanthanide SMMs. In the case of Dy ions, a two-dimensional coordination polymer, where two Dy ions are bridged together by carboxylato groups of three DTE-o to form a Dy dimer, has been reported.[38] The coordination spheres of the two ions have capped distorted square anti-prism geometries with two chelating carboxylato groups and three monodentate ones. The coordination spheres are completed by two coordinated solvent molecules. The C-C distance of about 3.6 Å between the two reacting carbon atoms of the DTE ligands is within the limit for the photocyclisation reaction to occur.

Plots of $\chi_M T$ vs. T for the complex with DTE-o remained constant around the expected value of 28 cm^3 K mol^{-1} for two isolated Dy ions down to 70 K and then decreased to 22.5 cm^3 K mol^{-1} at 1.8 K, indicating that thermal depopulation of the m_J levels and/or antiferromagnetic interactions occurred within the Dy$_2$ core of the complex. Similar $\chi_M T$ vs. T plots were observed after UV irradiation to form DTE-c and after visible irradiation to return to DTE-o. The H dependences of M for the complex with the open, closed and re-opened forms of DTE at 1.8 K are similar. In other words, M increased rapidly with an increase in H up to 0.7 T and then gradually increased without saturating up to 7 T, which confirms the presence of antiferromagnetic interactions in the Dy dimer.

In a zero H_{dc}, no maxima in the out-of-phase magnetic susceptibility (χ") were observed, whereas in an external H of 1500 Oe, a single frequency-dependent maximum was observed (Fig. 5). In the T range of 3.2–4.2 K, the Δ value for the complex with DTE-o was 14.2 K, and it corresponds to a thermal relaxation process (Fig. 6). In addition, the pre-exponential factor (τ_0) obtained from fitting the Arrhenius law was reported to be 1.90 × 10^{-8} s, and under 2.2 K, a quantum tunnelling relaxation process occurs with $\tau \approx$

0.466 ms.

After UV irradiation of the complex to cyclise DTE, Δ did not change at 14.7 K in an external H_{dc} of 1500 Oe, and $\tau_0 = 7.25 \times 10^{-9}$ s, which is comparable with that for the complex with DTE-o. The τ for the quantum tunnelling process of 0.1248 s is a factor of four less than that for the complex with DTE-o. This difference is attributed to the photochromic ring-closing of the DTE ligand, which leads to conjugation in the ligand and provides additional pathways for quantum relaxation.

For the re-opened complex, the parameters are similar to those for the complex with DTE-c, suggesting that photo-control of SMM behaviour is irreversible probably because of a loss of crystallinity during photo-cyclisation.

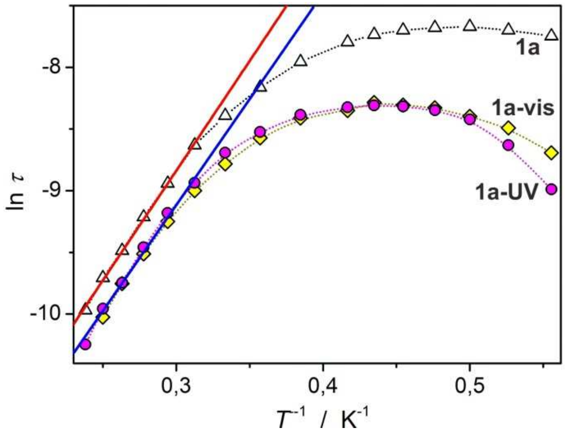


Fig. 6 Arrhenius plots for the complex with DTE-o (white triangles), with DTE-c (magenta circles) and with re-opened DTE (yellow diamonds). Solid lines were fitted using an Arrhenius law. Dotted lines are guides for the eye. Ref 35

DTE-3*d*-4*f* Mixed Metal SMMs

To improve the properties of SMMs, research has been done to combine the anisotropy of the 4*f* ions and the magnetic exchange properties of 3*d* ions. Two complexes with 1,3-bis((3-methoxysalicylidene)amino)propane (L) coordinated to Cu^{II} and Tb^{III} ions along with the DTE ligand, [CuTb(L)], have been reported to be SMMs.[36–40]

Using DTE-c, a ladder-type coordination polymer with a [CuTb(L)] moiety at each node was obtained (Fig. 7).[41] Two DTEs connect the nodes together. The distance between nodes of the ladder was determined to be ~15 Å, which is long enough to avoid direct interaction between the nodes, whereas the shortest Cu-Cu distance was 6.805(3) Å between neighbouring ladders.

For the ladder complex, $\chi_M T$ increased from 24.06 emu K mol^{-1} to 26.55 emu K mol^{-1} in the T range of 300–5 K due to weak ferromagnetic interactions in the [CuTb(L)] nodes. Then $\chi_M T$ decreased to 24.51 emu K mol^{-1} at 1.8 K due to anti-ferromagnetic interactions between [CuTb(L)] nodes or depopulation of the m_J levels of the Tb ion. After irradiation with visible light, no significant changes were observed in the thermal evolution of $\chi_M T$.

The ladder complex exhibited SMM behaviour. However, a maximum in the χ” signal with Δ = 22.04 K was only observed in an external H_{dc} of 1 kOe. After irradiation with visible light, τ decreased (Fig. 9), but Δ (23.94 K) barely changed in external H_{dc} of 1 kOe (Table 1), which indicates that the form of the DTE ligand has little effect on the anisotropy and interactions between the two ions of the [CuTb(L)] nodes, meaning that the magnetic properties are not affected.

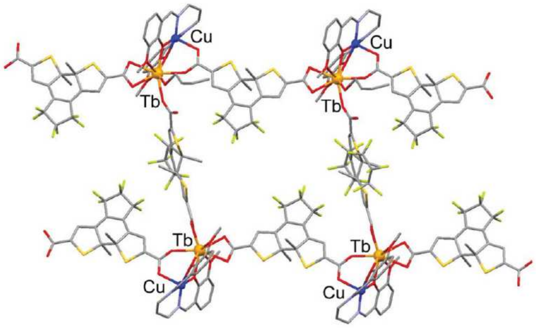


Fig. 7 Packing of the ladder complex. Ref 41

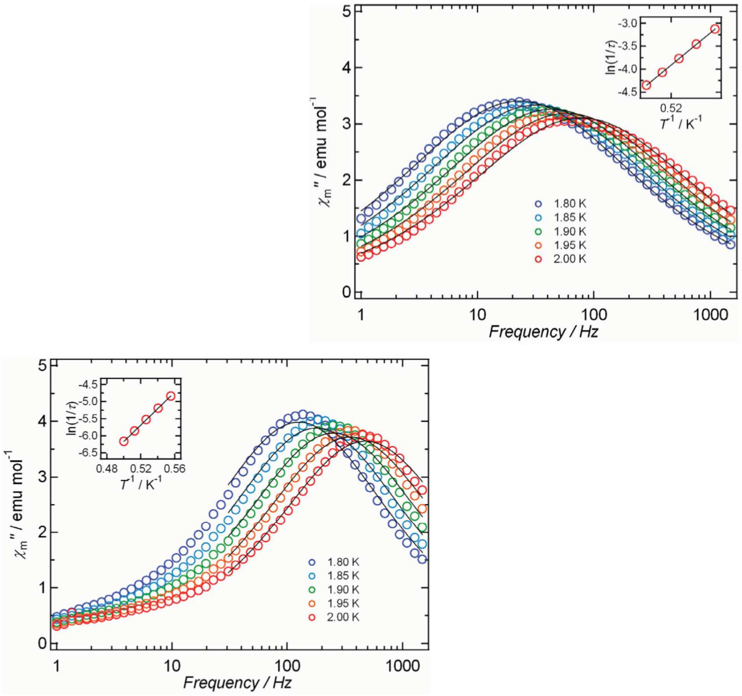


Fig. 9 χ'' for the ladder complex, before (top) and after (bottom) irradiation by visible light, under a 1 kOe external dc field and a 3 Oe ac field. Inset is the Arrhenius plot of relaxation time. Adapted from ref 41

The second complex is a discrete ring-like complex composed of two [CuTb(L)] moieties bridged by two DTE-o ligands (Fig. 10). Like the ladder complex, the Cu ion is coordinated by four atoms from L and one oxygen atom from a carboxylato group of the DTE bridge. The Tb ion is coordinated by four oxygen atoms of L, three oxygen atoms from the carboxylato groups of DTE, and two oxygen atoms from a nitrate ion. For each DTE, one carboxylato group coordinates to the Tb ion in a bidentate mode, and the second one bridges the Cu and Tb ions in a monodentate mode. The shortest intramolecular M-M distance between [CuTb(L)] units was determined to be 14.210(2) Å, and the shortest intermolecular distance was 6.767(1) Å.

The $\chi_M T$ behaviour of the ring-like complex is similar to that of the ladder-like complex. $\chi_M T$ increased from 25.36 cm^3 K mol^{-1} at 300 K to 29.68 cm^3 K mol^{-1} at 1.8 K with a maximum of 29.68 cm^3 K mol^{-1} at 5 K. After irradiation with UV light to close the DTE ligand, the T dependence of $\chi_M T$ did not significantly change (Table 1). Like the ladder-like complex, in the ac magnetic measurements, a χ'' signal was observed without an external H_{dc}. However, a maximum was not observed. In an H_{dc} of 1 kOe, Δ was determined to be 23.76 K, which is similar to that for the ladder-like complex. Photo-cyclisation of the complex does not have an effect on the relaxation process.

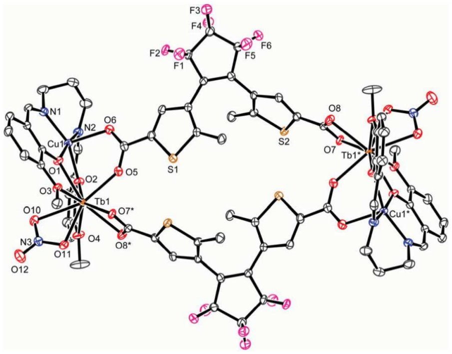


Fig. 10 ORTEP diagram of the ring-like complex. Ref 41

Table 1 Δ and τ_0 values at 0 Oe and 1 kOe fields for Cu-Tb dimer based ladder and ring-like complexes, before and after irradiation. Due to the absence of maximum of χ'' without external H_{dc}, the 0 Oe data are just estimations. Adapted from ref 41

		Δ	τ_0
0 Oe	Ladder-like complex	12.13	3.03×10^{-6}

	Ladder-like complex irradiated	13.46	5.27×10^{-7}
	Ring-like complex	14.91	2.39×10^{-7}
	Ring-like complex irradiated	8.44	9.30×10^{-6}
1 kOe	Ladder-like complex	22.04	2.11×10^{-7}
	Ladder-like complex irradiated	23.94	1.33×10^{-8}
	Ring-like complex	23.76	7.00×10^{-8}
	Ring-like complex irradiated	22.59	9.07×10^{-8}

Conclusions

DTE ligands can be used to control the magnetic properties of SMMs without chemical or electronic modification of the complex. Independent of the SMM being bridged by DTE, cyclization or ring opening of the ligand changes the relaxation parameters, albeit indirectly. For $3d$ ions, opening the DTE ligand changes the geometry of the bridge and, thus, increases the interactions between the bridged SMMs, which nearly doubles Δ of the SMMs. In the case of $4f$ ions, Δ is not affected, but the quantum relaxation process is when DTE is open or closed. When DTE is switch from the non-conjugated to the conjugated form, the quantum relaxation process becomes four times faster. There are two possible mechanisms for this acceleration. One involves a change in the energy splitting of the m_J levels upon rearrangement of the bridge, and the other involves the formation of a new and faster quantum pathway between neighbouring SMMs via the π-conjugation. On the other hand, heterometallic $3d$-$4f$ complexes, which were designed to combine the properties of the different ions, are insensitive to the form of DTE, the reason for which is not clearly understood at this time.

In order to develop criteria for controlling the magnetic properties of SMMs, more examples must be synthesised and studied in detail. Nevertheless, some lessons can be learned. The photo-cyclisation can be performed quantitatively in all cases, and the ratio of the open to closed forms depends on the penetration depth of the light during the process. For better light penetration, smaller crystals are needed, or it must be possible to perform the reaction in solution, which requires discrete molecules and not polymeric ones. However, since the carboxylato groups are strong ligands, which can easily substitute weaker ligands, bis(carboxylato)dithienylethene is not a good candidate for obtaining discrete molecules. In other words, depending on the ligands on the SMMs and the charge on the coordinated oxygen atom,[20] coordination polymers preferentially form when carboxylato-DTE is used as the bridging ligand. In the case of discrete complexes in solution, lanthanide SMMs are the most interesting due to their sensitivity to changes in the crystal field. Finally, calculations are necessary to fully understand the changes in SMMs after irradiation and to determine the relaxation mechanisms involved.

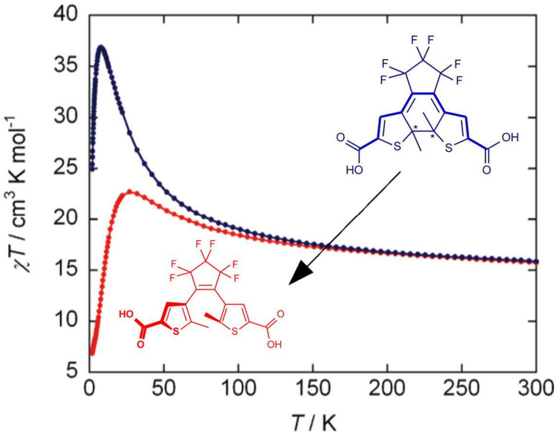
Notes and references

[a] *Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan*
[b] *Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology (JST), 4-1-8 Kawaguchi, Saitama 332-0012, Japan*

1 R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, Nature, 1993, 365, 141.
2 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei, D. Gatteschi, J. Am. Chem. Soc., 1985, 107, 8128.
3 O. Guillou, P. Bergerat, O. Kahn, E. Bakalbassis, K. Boubekeur, P. Batail, M. Guillot, Inorg. Chem., 1992, 31, 110.
4 C. Benelli, A. Caneschi, D. Gatteschi, R. Sessoli, Adv. Mater.,1992, 4, 504.
5 N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, J.Am. Chem. Soc., 2003, 125, 8694.
6 J. Rinck, G. Novitchi, W. van den Heuvel, L. Ungur, Y. Lan, W. Wernsdorfer, C. E. Anson, L. F. Chibotaru, A. K. Powell, Angew. Chem., Int. Ed., 2010, 49, 7583.
7 C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk, V. L. Pecoraro, Angew. Chem., Int. Ed., 2004, 43, 3912.
8 F. Pointillart, K. Bernot, R. Sessoli, D. Gatteschi, Chem.–Eur. J., 2007, 13, 1602.
9 V. Chandrasekhar, B. M. Pandian, J. J. Vittal, R. Clérac, Inorg. Chem., 2009, 48, 1148.
10 T. Yamaguchi, Y. Sunatsuki, H. Ishida, M. Kojima, H. Akashi, N. Re, N. Matsumoto, A. Pochaba, J. Mrozinski, Inorg. Chem., 2008, 47, 5736.
11 C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk, V. L. Pecoraro, Inorg. Chem., 2006, 45, 10022.
12 F. Pointillart, K. Bernot, R. Sessoli, D. Gatteschi, Inorg. Chem.,2010, 49, 4355.
13 J.-L. Liu, Y.-C. Chen, Y.-Z. Zheng, W.-Q. Lin, L. Ungur, W. Wernsdorfer, L. F. Chibotaru, M.-L. Tong, Chem. Sci., 2013, 4, 3310.
14 M. Ren, D. Pinkowicz, M. Yoon, K. Kim, L.-M. Zheng, B. K. Breedlove, M. Yamashita Inorg. Chem., 2013, 52, 8342.
15 Q. Zhou, F. Yang, B. Xin, G. Zeng, X. Zhou, K. Liu, D. Ma, G. Li, Z. Shi, S. Feng Chem. Commun., 2013, 49, 8244.
16 M. Ren, S.-S. Bao, N. Hoshino, T. Akutagawa, B. Wang, Y.-C. Ding, S. Wei, L.-M. Zheng, Chem.–Eur. J., 2013, 29, 9619.
17 G. Cucinotta, M. Perfetti, J. Luzon, M. Etienne, P. E. Car, A. Caneschi, G. Calvez, K. Bernot, R. Sessoli, Angew. Chem., Int. Ed., 2012, 51, 1606.
18 D. Tanaka, T. Inose, H. Tanaka, S. Lee, N. Ishikawa, T. Ogawa, Chem. Commun., 2012, 48, 7796.
19 G. Cosquer, F. Pointillart, S. Golhen, O. Cador, L. Ouahab, Chem.–Eur. J., 2013, 19, 7895.
20 F. Habib, G. Brunet, V. Vieru, I. Korobkov, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc., 2013, 135, 13242.
21 L. Norel, M. Feng, K. Bernot, T. Roisnel, T. Guizouarn, K. Costuas, S. Rigaut, Inorg. Chem. 2014, 53, 2361.
22 S. Mossin, B. L. Tran, D. Adhikari, M. Pink, F. W. Heinemann, J. Sutter, R. K. Szilagyi, K. Meyer, D. J. Mindiola, J. Am. Chem. Soc., 2012, 134, 13651.
23 X. Feng, C. Mathonière, I. R. Jeon, M. Rouzières, A. Ozarowski, M. L. Aubrey, M. I. Gonzalez, R. Clérac, J. R. Long, J. Am. Chem. Soc., 2013, 135, 15880.
24 C. Kachi-Terajima, H. Miyasaka, A. Saitoh, N. Shirakawa, M. Yamashita, R. Clérac, Inorg. Chem., 2007, 46, 5861.
25 J. Yoo, W. Wernsdorfer, E. C. Yang, M. Nakano, A. L. Rheingold, D. N. Hendrickson, Inorg. Chem., 2005, 44, 3377.
26 H. Hiraga, H. Miyasaka, K. Nakata, T. Kajiwara, S. Takaishi, Y. Oshima, H. Nojiri, M. Yamashita, Inorg. Chem., 2007, 46,9661.
27 M. Morimoto, H. Miyasaka, M. Yamashita, M. Irie, J. Am. Chem. Soc., 2009, 131, 9823.
28 R. B. Woodward, R. Hoffmann, The conservation of orbital symmetry; Verlag Chemie: Weinheim, 1970.

29 (a) S. Nakamura, M. Irie, J. Org. Chem., 1988, 53, 6136; (b) K. Uchida, Y. Nakayama, M. Irie, Bull. Chem. Soc. Jpn., 1990, 63, 1311.
30 M. Irie, O. Miyatake, K. Uchida, J. Am. Chem. Soc., 1992, 114, 8715.
31 J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A. L. Maniero, L. C. Brunel, K. Awaga, H. Ishimoto, G. Christou, D. N. Hendrickson, Inorg. Chem., 2000, 39, 3615.
32 A. Yamaguchi, N. Kusumi, H. Ishimoto, H. Mitamura, T. Goto, N. Mori, M. Nakano, K. Awaga, J. Yoo, D. N. Hendrickson, G. Christou, J. Phys. Soc. Jpn., 2002, 71, 414.
33 E. C. Yang, N. Harden, W. Wernsdorfer, L. Zakharov, E. K. Brechin, A. L. Rheingold, G. Christou, D. N. Hendrickson, Polyhedron, 2003, 22, 1857.
34 H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K. Sugiura, M. Yamashita, R. Clérac, J. Am. Chem. Soc., 2006, 128, 3770.
35 D. Pinkowicz, M. Ren, L.-M. Zheng, S. Sato, M. Hasegawa, M. Morimoto, M. Irie, B. K. Breedlove, G. Cosquer, K. Katoh, M. Yamashita, Chem. Eur. J., 2014, 20, 12502.
36 J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, Inorg. Chem., 1996, 35, 2400.
37 J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, Inorg. Chem., 1997, 36, 3429.
38 J. P. Costes, F. Dahan, A. Dupuis, Inorg. Chem., 2000, 39, 165.
39 M. Sakamoto, K. Manseki, H. Okawa, Coord. Chem. Rev., 2001, 219–221, 379.
40 T. Kajiwara, M. Nakano, S. Takaishi, M. Yamashita, Inorg. Chem., 2008, 47, 8604.
41 T. Shiga, H. Miyasaka, M. Yamashita, M. Morimoto, M. Irie, Dalton Trans., 2011, 40, 2275.

Graphical and textual abstract



Herein the use of DTE ligands to remotely control the magnetic properties of single-molecule magnets is discussed.