JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Fine-Tuning the Single-Molecule Magnet Properties of a [Dy(III)-Radical]$_2$ Pair

Elisabeth M. Fatila,[†] Mathieu Rouzières,[‡,⊥] Michael C. Jennings,[∥] Alan J. Lough,[§] Rodolphe Clérac,*[,‡,⊥] and Kathryn E. Preuss*[,†]

[†]Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada
[‡]CNRS, CRPP, UPR 8641, F-33600 Pessac, France
[⊥]Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France
[∥]FreeLance Crystallography, 185 Chelsea Avenue, London, Ontario N6J 3J5, Canada
[§]Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

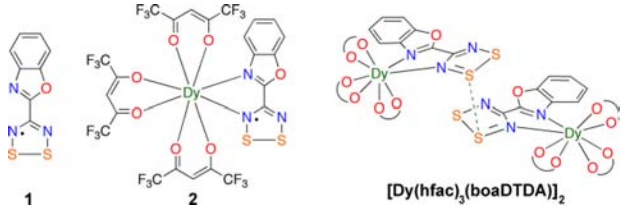
Ⓢ *Supporting Information*

ABSTRACT: A supramolecular species composed of a pair of nonequivalent Dy(III)−radical complexes exhibits single-molecule magnet (SMM) properties. The weak effective antiferromagnetic coupling between the Dy(III) ions can be compensated by application of a small (700 Oe) dc field, revealing the relaxation mode of the two distinct SMMs. These unique results illustrate how the dynamics of a supramolecular [Dy-Radical]$_2$ SMM can be fine-tuned by the exchange-bias and an applied magnetic field.

Single-molecule magnets (SMMs) are paramagnetic molecular species that exhibit slow dynamics of their magnetization.[1,2] To retain magnetization in zero field requires uniaxial magnetoanisotropy, i.e., a directional preference for the magnetic moment and an energy barrier that hinders randomization of its direction. Most SMMs are subject to quantum phenomena such as quantum tunneling of the magnetization (i.e., relaxation through the barrier).[3] From an application standpoint, SMMs have quantum bit (qubit) properties,[4] and a system with weak electronic coupling between two SMMs is a possible model for a 2-qubit quantum gate.[5] Large uniaxial anisotropy and high spin make select Ln(III) ions, such as Dy(III), ideal for SMM design.[2,6,7] The anisotropy in Dy(III) arises primarily from unquenched orbital momentum of the ion, but it may be modified by the ligand field.[8] The radial probability density of 4f orbitals tends to make electronic interactions between Dy(III) ions weak. This poses an obstacle for increasing the "height" of the thermal relaxation barrier by coupling multiple ions, but it may be a benefit for device design.

Several SMM species containing two Dy(III) ions have recently been reported.[7,9] Those in which the two Dy(III) ions are related by symmetry exhibit SMM behavior apparently as a single-molecule entity,[10] i.e., only one set of thermal-plus-quantum relaxation modes is observed. Those [Dy$_2$] species in which the two Dy(III) ions are not symmetry-related present more varied behavior. When the two inequivalent ions exhibit a single set of thermal-plus-quantum relaxation modes at low temperature, this may be the result of ferromagnetic coupling,[11] of undetermined but obviously weak interactions,[12] or of no interactions between ions.[13] When the species exhibits two different sets of SMM relaxation modes, indicative of two independent sources of SMM behavior in the single molecule, it is concluded that there is very weak or no coupling between the two unique Dy(III) ions.[14] Herein, we report a supramolecular species containing two Dy(III) ions, unrelated by symmetry, that are weakly antiferromagnetically (AF) coupled, allowing fine-tuning of the magnetization dynamics (Scheme 1).

Scheme 1. Ligand 1, Complex 2, and Supramolecular Species



Reaction of neutral radical ligand 4-(benzoxazol-2′-yl)-1,2,3,5-dithiadiazolyl **1** (boaDTDA)[15] with Dy(hfac)$_3$(DME)[16] forms the 8-coordinate Dy(hfac)$_3$(boaDTDA) complex **2** (DME = 1,2-dimethoxyethane; hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato; Figure 1a). Removal of the solvent and sublimation of the solid residue at 110 °C generates high-

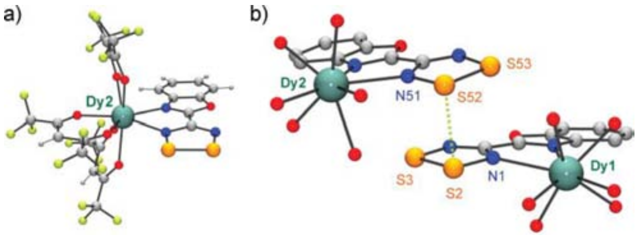


Figure 1. (a) One of two unique molecules of **2**. (b) [Dy(hfac)$_3$(boaDTDA)]$_2$ pair showing the S2···S52 contact. Only O atoms of hfac are shown; H atoms omitted.

Received: April 16, 2013
Published: June 19, 2013

purity, dark purple crystals, suitable for X-ray diffraction, on a preparative scale. Complex **2** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains two unique Dy(hfac)$_3$(boaDTDA) molecules that form [Dy(hfac)$_3$(boaDTDA)]$_2$ pairs associated via a *twisted-cofacial*[17] interaction with a close S2···S52 contact (2.901(4) Å; Figure 1b). Pairwise interactions of this nature are common for DTDA radicals[18] and result in strong AF coupling between the DTDA radical spins. The [DTDA]$_2$ unit can usually be considered diamagnetic below room temperature.[19] Similarly associated transition metal complexes of DTDA ligands show weak AF coupling between the metal ions through the [DTDA]$_2$ couple.[20]

The two Dy(III) ions in the [Dy(hfac)$_3$(boaDTDA)]$_2$ pair are both 8-coordinate by six O atoms (hfac ligands) and two N atoms (ligand **1**). However, the coordination environment of Dy1 is roughly square antiprismatic, whereas that of Dy2 is dodecahedral (Figure S1). The shortest through-space distance between any Dy1 and Dy2 is within the supramolecular pair (8.263(7) Å). The next closest distance is >2 Å longer. Thus, significant Dy1−Dy2 magnetic interactions likely occur within the supramolecular pair.

The magnetic properties of **2** were measured at an applied dc field of 1000 Oe. The χT product per complex at 270 K is 13.9 cm^3 K mol^{-1} (Figure 2), in good agreement with the expected value for an isolated Dy(III) metal ion ($S = 5/2$, $L = 5$, $^6H_{15/2}$, $g = 4/3$; $C = 14.17$ cm^3 K mol^{-1}). As anticipated, there is no apparent magnetic contribution from the radicals, which form effectively diamagnetic [boaDTDA]$_2$ ligand units. Lowering the temperature, the χT product decreases to a minimum value of 12.1 cm^3 K mol^{-1} at 1.8 K. This thermal behavior is mainly attributable to the inherent magnetism of the Dy(III) metal ion, specifically the thermal depopulation of the Stark sublevels of the $^6H_{15/2}$ state.[21] Weak coupling between the two Dy(III) ions cannot be readily extracted from these data due to the intrinsic magnetic properties of the Dy(III) ions. The field dependence of the magnetization below 8 K (Figure S2 and inset of Figure 2) reveals a relatively rapid increase of the magnetization at low fields followed by a slow linear increase at high fields without a clear complete saturation up to 7 T ($M = 6.07$ μ_B at 1.8 K). The high-field linear variation of the magnetization suggests the presence of significant magnetic anisotropy as expected for Dy(III) ions. This is supported by the observation that, while plotting the M vs H/T at different fields (inset Figure 2), the curves are not all superimposed on a single master-curve. It is worth noting that no hysteresis on the M vs H data (Figure S2) has been observed above 1.8 K (at 100−200 Oe/min). As often observed in lanthanide-based complexes, the interesting magnetic dynamics of these molecular systems can be hidden in static M vs H measurements that are not fast enough to probe the relaxation of the magnetization. Therefore, ac measurements were performed to test possible SMM properties of **2**.

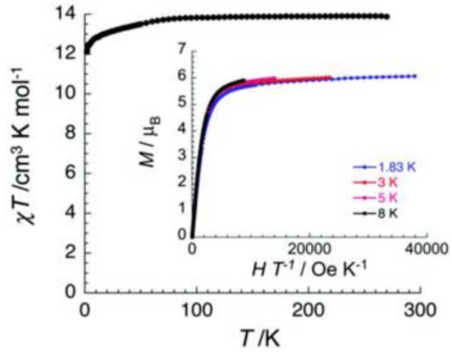


Figure 2. Temperature dependence of χT at 1000 Oe; χ is defined as molar magnetic susceptibility equal to M/H per mole of **2**. Inset: M vs H/T data for **2** (100−200 Oe min^{-1}).

In zero dc field, the appearance of an out-of-phase signal in the ac susceptibility clearly demonstrates slow relaxation of the magnetization at temperatures below 23 K (Figure 3). Plots of in-phase (χ') and out-of-phase (χ'') ac susceptibility in zero dc field as a function of frequency at various temperatures (1.82−25 K; Figure 3), and the resulting Cole−Cole plot (Figure S3), reveal shape- and frequency-dependent features typical of SMM behavior. It is worth highlighting that a single relaxation mode in the frequency dependence of the ac susceptibility (Figure 3, right) is observed, and this is further confirmed by the extrapolation to zero at high frequencies of χ' (i.e., the whole magnetization is blocked at high frequency). From these data, the temperature dependence of the relaxation time, τ, can be deduced (inset Figure 3). Below 5 K, τ is temperature independent, as expected in a regime dominated by the quantum tunneling of the magnetization (QTM), with a characteristic time: $\tau_{QTM} = 1.4 \times 10^{-4}$ s. Above 5 K, the relaxation time becomes progressively thermally activated, and above 15 K the energy barrier of the thermally activated regime (Δ_{eff}/k_B) can be determined as roughly 102 K with the pre-exponential factor of the Arrhenius law $\tau_0 = 7.3 \times 10^{-8}$ s.

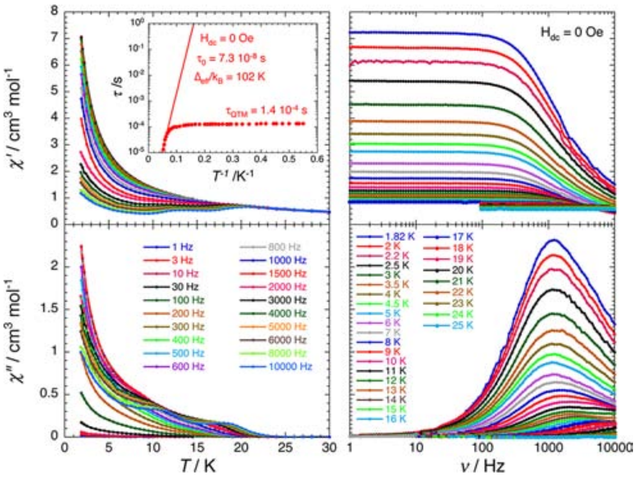


Figure 3. Temperature (left) and frequency (right) dependence of the real (χ', top) and imaginary (χ'', bottom) parts of the ac susceptibility, between 1 and 10000 Hz and between 1.8 and 30 K, respectively, for **2** in zero dc field. Solid lines are visual guides. Inset: τ vs T^{-1} plot for **2** in zero dc field. Solid line is the best fit to the Arrhenius law.

In order to probe the feasibility of lowering the relaxation probability via the quantum pathway, the ac susceptibility has been measured at 2.1 K at various applied dc fields (0−1600 Oe, Figure S4). As expected under small dc fields, which lift the zero-field degeneracy of the tunneling states, a second relaxation mode is observed at lower frequency corresponding to a relaxation mode dominated by the thermal energy barrier (Figure S4). From these data, the characteristic relaxation frequency as a function of applied dc field for the two relaxation modes (i.e., thermal and quantum relaxation modes) can be extracted (Figure S5). The probability of magnetization relaxation via the quantum tunneling appears to be minimized at roughly 700 Oe. Therefore, in order to probe the thermally activated regime of relaxation, the ac susceptibility has been measured using an applied dc field of 700 Oe. At this dc field, the in-phase and out-of-phase ac susceptibilities as a function of frequency at various temperatures (1.8−23 K; Figures 4 and S6) and as a function of temperature at various frequencies (0.1−10000 Hz; Figure 4) and the resulting Cole−Cole plot (Figure S7) are shown. Interestingly, these data highlight the presence of not one but two thermally activated relaxation modes of similar intensity. The characteristic time of both relaxation modes has been extracted and added to the Arrhenius plot (inset Figure 4). From these data, determination of the energy barrier of the thermally activated regime is possible using data above 9 K for the high-frequency mode and data above 6.5 K for the low-frequency mode. For both relaxations, Δ_{eff}/k_B is roughly 100 K, with a pre-exponential factor of the Arrhenius law $\tau_0 = 0.4 \times 10^{-8}$ s for the high-frequency mode and 9×10^{-8} s for the low-frequency mode. Below 9 and 6.5 K, the observed curvature of the τ vs $1/T$ plot indicates the presence of quantum effects, even at 700 Oe, influencing the magnetization relaxation. The quantum relaxation time for the high-frequency relaxation mode in 700 Oe dc field is roughly 10 s, which is, as expected under dc field, larger (indeed by 5 orders of magnitude) than the zero field value of 1.4×10^{-4} s.

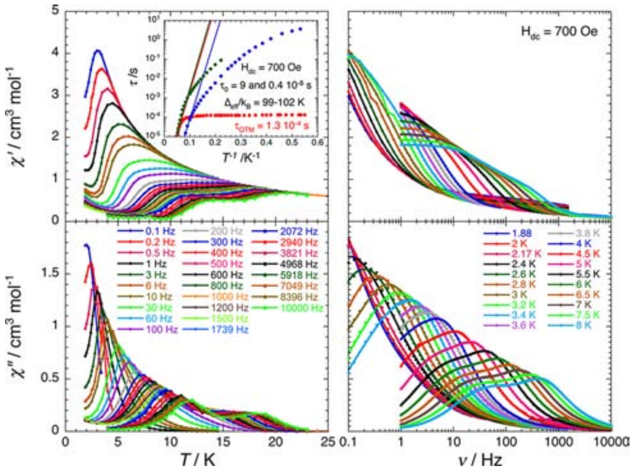


Figure 4. Temperature (left) and frequency (right) dependence of the real (χ', top) and imaginary (χ'', bottom) parts of the ac susceptibility, between 0.1 and 10000 Hz and between 1.8 and 8 K, respectively, for **2** in 700 Oe dc field. Solid lines are visual guides. Inset: τ vs T^{-1} plot for **2** in zero (red) and in 700 Oe dc field (green and blue). Solid lines are the best fit to the Arrhenius law discussed in the text.

At zero dc field, **2** exhibits SMM behavior with a single set of thermal-plus-quantum relaxation modes. Thus, the asymmetric $[Dy(hfac)_3(boaDTDA)]_2$ unit acts as a single supramolecular entity thanks to the weak, but efficient, magnetic coupling between the two Dy(III) magnetic centers. Upon application of a small dc field (700 Oe) to minimize the probability of the quantum relaxation pathway, two thermally activated relaxation modes are clearly revealed. The applied dc field compensates (at least partially) the weak AF interaction between the Dy(III) ions, and two unique thermal relaxation modes are observed. Each Dy(III) ion now acts as a quasi-independent molecular object with its own intrinsic SMM behavior. Put another way, the two inequivalent Dy(III) ions can be magnetically "decoupled" by application of a weak dc field, ergo they must be coupled weakly and antiferromagnetically in the absence of applied field.

The present interpretation of these unique results is supported by investigation of the Gd and Y analogues of **2**. Both species crystallize in the same morphology as **2** (Figures S8 and S10). The magnetic data for $Gd(hfac)_3(boaDTDA)$ **3** (Figure S9) are consistent with very weak AF interactions ($|J|/k_B < 0.01$ K) between the two $S = 7/2$ Gd(III) ions through the diamagnetic dimerized radical pair. Moreover, a 5% dilution of **2** in 95% diamagnetic $Y(hfac)_3(boaDTDA)$ **4** demonstrates magnetic behavior consistent with an admixture of "Dy1−Y2" and "Y1−Dy2" pairs (Figure S11). Two independent SMMs are apparent in zero dc field, and the characteristic time of their relaxation modes is comparable to those observed in **2** when the Dy(III) ions are decoupled in 700 Oe applied dc field (Figure S12).

While a similar "decoupling" field effect has been observed for single-chain magnets in 3D ordered antiferromagnetic phases,[22] this type of field effect has never before been reported for SMMs and provides unique evidence of weak AF coupling between the two Dy(III) ions. From a potential application standpoint, it is worth noting that because there are two inequivalent Dy(III) ions, each being a potential qubit, and these are weakly coupled to one another, the supramolecular $[Dy(hfac)_3(boaDTDA)]_2$ species represents a possible design for a CNOT quantum computing logic gate.[5] Future work will investigate this possibility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic and experimental details for **2**−**4** and a 5% dilution of **2** in **4**; Figures S1−S12; CIF for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

kpreuss@uoguelph.ca; clerac@crpp-bordeaux.cnrs.fr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Prof. Guillem Aromí provided useful and insightful comments. K.E.P. thanks NSERC (DG), the Canadian government (CRC Tier II), and U. Bordeaux (visiting professorship). E.M.F. thanks NSERC (CGS-D). R.C. and M.R. thank CNRS, U. Bordeaux, the Conseil Régional d'Aquitaine, and the ANR (NT09_469563, AC-MAGnets project).

■ REFERENCES

(1) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141−143. (b) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, 66−71. (c) Aromí, G.; Brechin, E. K. In *Structure and Bonding*; Winpenny, R. E., Ed.; Springer-Verlag: Berlin, 2006; Vol. *122*, pp 1−67. (d) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406−409. (e) Glaser, T. *Chem. Commun.* **2011**, *47*, 116−130.

(2) Katoh, K.; Isshiki, H.; Komeda, T.; Yamashita, M. *Coord. Chem. Rev.* **2011**, *255*, 2124−2148.

(3) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268−297.

(4) (a) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789−793. (b) Zhou, B.; Tao, R.; Shen, S.-Q.; Liang, J.-Q. *Phys. Rev. A* **2002**, *66*, 010301(R). (c) Leuenberger, M. N.; Meier, F.; Loss, D. *Monatsch. Chem.* **2003**, *134*, 217−233.

(5) Luis, F.; Repollés, A.; Martínez-Pérez, M. J.; Aguilà, D.; Roubeau, O.; Zueco, D.; Alonso, P. J.; Evangelisti, M.; Camón, A.; Sesé, J.; Barrios, L. A.; Aromí, G. *Phys. Rev. Lett.* **2011**, *107*, 1172031−1172035.

(6) (a) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.-y.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 8694−8695. (b) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *J. Am. Chem. Soc.* **2005**, *127*, 3650−3651.

(7) Woodruff, D. N.; Winpenny, R. E. P.; Layfield, R. A. *Chem. Rev.* **2013**, DOI: 10.1021/cr400018q.

(8) (a) Chen, G. J.; Gao, C. Y.; Tian, J. L.; Tang, J.; Gu, W.; Liu, X.; Yan, S. P.; Liao, D. Z.; Cheng, P. *Dalton Trans.* **2011**, *40*, 5579−5583. (b) Murugesu, M. *Nature Chem.* **2012**, *4*, 347−348.

(9) Habib, F.; Murugesu, M. *Chem. Soc. Rev.* **2013**, *42*, 3278−3288.

(10) (a) Lin, P.-H.; Burchell, T. J.; Clérac, R.; Murugesu, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8848−8851. (b) Ma, Y.; Xu, G.-F.; Yang, X.; Li, L.-C.; Tang, J.; Yan, S.-P.; Cheng, P.; Liao, D.-Z. *Chem. Commun.* **2010**, *46*, 8264−8266. (c) Xu, G.-F.; Wang, Q.-L.; Gamez, P.; Ma, Y.; Clérac, R.; Tang, J.; Yan, S.-P.; Cheng, P.; Liao, D.-Z. *Chem. Commun.* **2010**, *46*, 1506−1508. (d) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. *Nature Chem.* **2011**, *3*, 538−542. (e) Long, J.; Habib, F.; Lin, P.-H.; Korobkov, I.; Enright, G.; Ungur, L.; Wernsdorfer, W.; Chibotaru, L. F.; Murugesu, M. *J. Am. Chem. Soc.* **2011**, *133*, 5319−5328. (f) Liang, L.; Peng, G.; Li, G.; Lan, Y.; Powell, A. K.; Deng, H. *Dalton Trans.* **2012**, *41*, 5816−5823. (g) Liu, R.; Zhang, C.; Li, L.; Liao, D.; Sutter, J.-P. *Dalton Trans.* **2012**, *41*, 12139−12144. (h) Lin, P.-H.; Korobkov, I.; Burchell, T. J.; Murugesu, M. *Dalton Trans.* **2012**, *41*, 13649−13655. (i) Zou, L.; Zhao, L.; Chen, P.; Guo, Y.-N.; Guo, Y.; Li, Y.-H.; Tang, J. *Dalton Trans.* **2012**, *41*, 2966−2971. (j) Nematirad, M.; Gee, W. J.; Langley, S. K.; Chilton, N. F.; Moubaraki, B.; Murray, K. S.; Batten, S. R. *Dalton Trans.* **2012**, *41*, 13711−13715. (k) Yi, X.; Bernot, K.; Pointillart, F.; Poneti, G.; Calvez, G.; Daiguebonne, C.; Guillou, O.; Sessoli, R. *Chem.—Eur. J.* **2012**, *18*, 11379−11387. (l) Tuna, F.; Smith, C. A.; Bodensteiner, M.; Ungur, L.; Chibotaru, L. F.; McInnes, E. J.; Winpenny, R. E.; Collison, D.; Layfield, R. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 6976−6980. (m) Habib, F.; Lin, P. H.; Long, J.; Korobkov, I.; Wernsdorfer, W.; Murugesu, M. *J. Am. Chem. Soc.* **2011**, *133*, 8830−8833.

(11) (a) Guo, Y.-N.; Xu, G.-F.; Wernsdorfer, W.; Ungur, L.; Guo, Y.; Tang, J.; Zhang, H.-J.; Chibotaru, L. F.; Powell, A. K. *J. Am. Chem. Soc.* **2011**, *133*, 11948−11951. (b) Bernot, K.; Pointillart, F.; Rosa, P.; Etienne, M.; Sessoli, R.; Gatteschi, D. *Chem. Commun.* **2010**, *46*, 6458−6460.

(12) Layfield, R. A.; McDouall, J. J. W.; Sulway, S. A.; Tuna, F.; Collison, D.; Winpenny, R. E. *Chem.—Eur. J.* **2010**, *16*, 4442−4446.

(13) Pointillart, F.; Klementieva, S.; Kuropatov, V.; Le Gal, Y.; Golhen, S.; Cador, O.; Cherkasov, V.; Ouahab, L. *Chem. Commun.* **2012**, *48*, 714−716.

(14) (a) Guo, Y.-N.; Xu, G.-F.; Gamez, P.; Zhao, L.; Lin, S.-Y.; Deng, R.; Tang, J.; Zhang, H.-J. *J. Am. Chem. Soc.* **2010**, *132*, 8538−8539. (b) Lin, P.-H.; Sun, W.-B.; Yu, M.-F.; Li, G.-M.; Yan, P.-F.; Murugesu, M. *Chem. Commun.* **2011**, *47*, 10993−10995. (c) Li, X. L.; Chen, C. L.; Gao, Y. L.; Liu, C. M.; Feng, X. L.; Gui, Y. H.; Fang, S. M. *Chem.—Eur. J.* **2012**, *18*, 14632−14637. (d) Venugopal, A.; Tuna, F.; Spaniol, T. P.; Ungur, L.; Chibotaru, L. F.; Okuda, J.; Layfield, R. A. *Chem. Commun.* **2013**, *49*, 901−903.

(15) Fatila, E. M.; Goodreid, J.; Clérac, R.; Jennings, M.; Assoud, J.; Preuss, K. E. *Chem. Commun.* **2010**, *46*, 6569−6571.

(16) Fatila, E. M.; Hetherington, E. E.; Jennings, M.; Lough, A. J.; Preuss, K. E. *Dalton Trans.* **2012**, *41*, 1352−1362.

(17) Haynes, D. A. *Cryst. Eng. Commun.* **2011**, *13*, 4793.

(18) Rawson, J. M.; Banister, A. J.; Lavender, I. *Adv. Heterocycl. Chem.* **1995**, *62*, 137−247.

(19) (a) Shuvaev, K. V.; Decken, A.; Grein, F.; Abedin, T. S. M.; Thompson, L. K.; Passmore, J. *Dalton Trans.* **2008**, 4029−4037. (b) Alberola, A.; Carter, E.; Constantinides, C. P.; Eisler, D. J.; Murphy, D. M.; Rawson, J. M. *Chem. Commun.* **2011**, *47*, 2532−2534.

(20) (a) Britten, J.; Hearns, N. G. R.; Preuss, K. E.; Richardson, J. F.; Bin-Salamon, S. *Inorg. Chem.* **2007**, *46*, 3934−3945. (b) Hearns, N. G. R.; Clérac, R.; Jennings, M.; Preuss, K. E. *Dalton Trans.* **2009**, 3193−3203.

(21) (a) Kahn, M. L.; Sutter, J.-P.; Golhen, S.; Guionneau, P.; Ouahab, L.; Kahn, O.; Chasseau, D. *J. Am. Chem. Soc.* **2000**, *122*, 3413−3421. (b) Kahn, M. L.; Ballou, R.; Porcher, P.; Kahn, O.; Sutter, J.-P. *Chem.—Eur. J.* **2002**, *8*, 525−531.

(22) (a) Coulon, C.; Clérac, R.; Wernsdorfer, W.; Colin, T.; Miyasaka, H. *Phys. Rev. Lett.* **2009**, *102*, 167204(1−4). (b) Miyasaka, H.; Takayama, K.; Saitoh, A.; Furukawa, S.; Yamashita, M.; Clérac, R. *Chem.—Eur. J.* **2010**, *16*, 3656−3662. (c) Bhowmick, I.; Hillard, E. A.; Dechambenoit, P.; Coulon, C.; Harris, T. D.; Clérac, R. *Chem. Commun.* **2012**, *48*, 9717−9719.