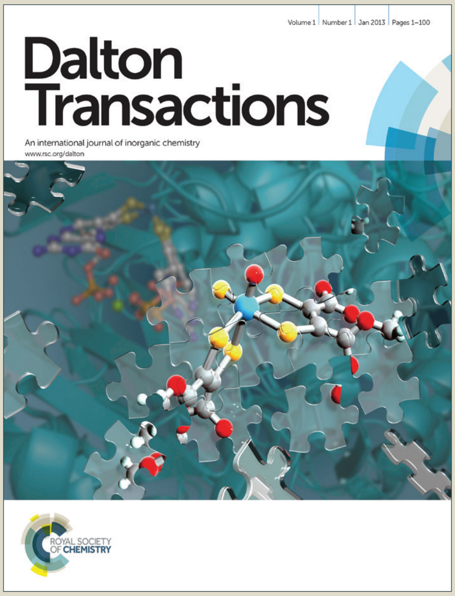
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Exploiting verdazyl radical to assemble 2p-3d-4f one-dimensional chains

Chao Wang,[a] Shuang-Yan Lin,[a,b] Wei Shi,[c] Peng Cheng[c] and Jinkui Tang*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A series of one dimensional chain complexes $[Ln(hfac)_3]_2{\cdot}[Cu(hfac)_2]_2{\cdot}4(3pyvd){\cdot}n\text{-}C_7H_{16}$ (Ln = Gd(**1**), Tb(**2**), Dy(**3**)) containing 2p, 3d and 4f spin carriers have been successfully synthesized and magnetically characterized where the verdazyl radicals represent the bridge linking copper(II) and lanthanide(III) ions. Rough estimation of magnetic behaviors of complex **1** revealed that the coupling between Gd(III) ion and radical is weak ferromagnetic, while alternating-current susceptibilities of complexes **2** and **3** suggest no slow magnetic relaxations exist at low temperature.

Introduction

One-dimensional chain complexes constructed from radicals and paramagnetic metal ions have attracted plenty of attention due to their unique magnetic properties.[1] In 2001, Gatteschi and co-workers first synthesized and investigated the milestone complex $[Co(hfac)_2(NITPhOMe)]$ (hfac = hexafluoroacetylacetonate and NITPhOMe = 2,4'-methoxyphenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) and found slow magnetic relaxation in this nanowire.[2] Hence, the Glauber conjecture has been demonstrated unambiguously fifty years after it was posed. Since then, more and more efforts were devoted into this area,[3] and a few complexes containing various kinds of radicals were characterized magnetically at low temperature in order to obtain so-called single-chain magnet (SCM).[4] In 2006, H. Miyasaka's group used TCNQ$^-$ (TCNQ$^-$ = 7,7,8,8-tetracyanoquinodimethane) as bridging ligands to link Mn^{III}_2 moieties together, and observed hysteresis loops obviously at the temperature as high as 4.0 K.[5] At the same year, Gatteschi's group employed a series of lanthanide(III) ions to construct a whole family of SCMs,[6] mainly owing to the strong Ising anisotropy of the magnetic centers. Among radical-3d transition metal complexes, strong magnetic interactions caused by significant orbital overlap are mostly responsible for the unusual magnetic properties observed.[7] While in 2p-4f complexes, the foremost reason is large anisotropies of lanthanide(III) ions. Thus, it seems interesting to combine both advantages through the strategy of constructing one-dimensional chains containing 2p, 3d and 4f spin carriers. Indeed, these complexes, achieved by the methods of molecular engineering, have been or expected to show more versatile structure and properties.[8]

In this regard, the selection of radical is essential for the molecular engineering. Firstly, it should be robust enough to undergo solvent reflux and column purification, and be easily modified to induce some functional groups.[9] Secondly, it should show coordination ability towards transition metal ions and lanthanide(III) ions. More importantly, this radical, chosen as appealing building blocks, must have two or more coordination sites and show different coordination abilities towards different sorts of metal ions in order to avoid forming uniform complex. Therefore, isopropyl substituted verdazyl radical,[10] especially its 3-pyridyl derivative 3pyvd (3pyvd = 1,5-diisopropyl-3-pyridin-3-yl-6-oxoverdazyl, shown in Fig. 1), which has been first systematically synthesized by Brook's group,[9d] rushes into our mind. Considering the oxophilic character of lanthanide(III) ions and the nitrophilic origin of copper(II) ion, one-dimensional chains could probably be formed by adding the 3pyvd to the mixture of lanthanide(III) ions and Cu(II) ions through the approach of self-assembly.

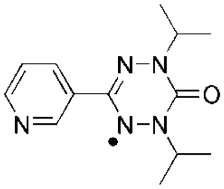


Fig. 1 Chemical structure of 3pyvd.

Experimental Section

General. All chemicals were commercial available and at least A.R. grade. The solvents were purified under standard methods and stored under inert atmosphere. 3pyvd,[9d] $Cu(hfac)_2{\cdot}2H_2O$ and $Ln(hfac)_3{\cdot}2H_2O$ (Ln = Gd, Tb, Dy)[6c] were synthesized according to the literature reported after slight modification. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 2400 analyzer. Fourier transform IR (FTIR) spectra were recorded with a Thermo Scientific Nicolet 6700 spectrophotometer with ATR module using the reflectance technique (4000-600 cm^{-1}). All magnetization data were collected on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. The variable-temperature magnetization was measured with an external magnetic field of 1000 Oe in the temperature range of 2.0-300 K using polycrystalline simples. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's constants.

Table 1 Crystallographic parameters of complexes **1**-**3**.

Compound name	**1**	**2**	**3**
Chemical formula	$C_{109}H_{98}Cu_2F_{60}Gd_2N_{20}O_{24}$	$C_{109}H_{98}Cu_2F_{60}N_{20}O_{24}Tb_2$	$C_{109}H_{98}Cu_2Dy_2F_{60}N_{20}O_{24}$
Formula Mass	3653.65	3656.99	3664.15
a/Å	16.8896(5)	16.7525(3)	16.9627(4)
b/Å	17.5155(5)	17.5540(3)	17.4217(3)
c/Å	25.1035(9)	24.9087(5)	25.2082(6)
α/°	90	90	90
β/°	92.938(3)	92.524(2)	92.590(2)
γ/°	90	90	90
Unit cell volume/Å^3	7416.6(4)	7317.9(2)	7441.9(3)
Temperature/K	173(2)	173(2)	173(2)
Space group	*P*21	*P*21	*P*21
No. of formula units per unit cell, *Z*	2	2	2
Absorption coefficient, μ/mm^{-1}	1.309	1.387	1.417
No. of reflections measured	45335	45203	41886
No. of independent reflections	29572	29509	27443
R_{int}	0.0498	0.0359	0.0406
Final R_1 values ($I > 2\sigma(I)$)	0.0654	0.0454	0.0618
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1536	0.0894	0.1449
Final R_1 values (all data)	0.0820	0.0533	0.0770
Final $wR(F^2)$ values (all data)	0.1713	0.0953	0.1585
Goodness of fit on F^2	1.034	1.034	1.018
Flack parameter	0.632(7)	0.644(7)	0.705(7)

Synthesis of di-*tert*-butyl 2,2'-carbonylbis-(2-isopropylhydrazinecarboxylate): With continuous stirring, 2.97 g bis(trichloromethyl)carbonate (triphosgene) in 15 mL dry toluene was slowly added to 150 mL dry toluene containing 10.3 g *tert*-butyl-2-isopropylhydrazinecarboxylate and 8.19 mL dry triethylamine under ice bath during two hours. When this addition was complete, the mixture was allowed to warm to room temperature and stirred for additional two hours and filtered. The filtrate was evaporated to dryness under reduced pressure to give crude product. Colorless crystals were obtained by recrystallization from hot *n*-heptane. Yield: 8.25 g. (74%) m. p. 176-178 °C.

Synthesis of $[Gd(hfac)_3]_2\cdot[Cu(hfac)_2]_2\cdot4(3pyvd)\cdot n\text{-}C_7H_{16}$ (1): A mixture of $Gd(hfac)_3\cdot2H_2O$ (0.05 mmol, 41 mg) and $Cu(hfac)_2\cdot2H_2O$ (0.05 mmol, 25 mg) was suspended in 25 mL boiling *n*-heptane with stirring. After refluxing for about two hours, 24.8 mg (0.1 mmol) 3pyvd was added to this solution, and followed by 5 mL chloroform. And then, this solution was taken to mild reflux for another two hours and filtered after cooling to room temperature. The resulting brown solution was stored in refrigerator at 3°C and the greenish brown block-shaped single-crystals suitable for X-ray analysis were obtained after a few days. Yield: 22 mg (24.1%). Elemental analysis: calc(found)% complex **1**: C: 35.83(35.55) H: 2.70(2.61) N: 7.67(7.88). IR spectra of complex **1**: 3268(m), 3203(w), 3105(m), 2993(w), 1686(m), 1649(vs), 1612(w), 1561(m), 1536(m), 1508(m). 1475(w), 1391(w), 1369(w), 1350(w), 1314(w), 1253(vs), 1199(vs), 1139(vs), 1099(s), 952(w), 802(s), 742(m), 724(w), 681(w), 661(s), 588(m), 528(w).

Synthesis of $[Tb(hfac)_3]_2\cdot[Cu(hfac)_2]_2\cdot4(3pyvd)\cdot n\text{-}C_7H_{16}$ (2) and $[Dy(hfac)_3]_2\cdot[Cu(hfac)_2]_2\cdot4(3pyvd)\cdot n\text{-}C_7H_{16}$ (3): Complexes **2** and **3** were synthesized according to a similar process of complex **1**, using $Tb(hfac)_3\cdot2H_2O$ (**2**) and $Dy(hfac)_3\cdot2H_2O$ (**3**) as starting material instead of $Gd(hfac)_3\cdot2H_2O$. Elemental analysis: calc(found)% complex **2**: C: 35.88(35.49) H: 2.70(2.62) N: 7.67(7.82). complex **3**: C: 35.83(35.59) H: 2.70(2.59) N: 7.67(7.81). IR spectra of complex **2**: 3269(m), 3105(m), 2996(w), 1685(m), 1650(vs), 1613(w), 1561(m), 1532(m), 1509(m). 1473(w), 1391(w), 1368(w), 1350(w), 1314(w), 1255(vs), 1197(vs), 1138(vs), 1103(s), 948(w), 798(s), 741(m), 726(w), 682(w), 661(s), 584(m). IR spectra of complex **3**: 2984(w), 2942(w), 1650(vs), 1614(s), 1553(m), 1529(m), 1500(m), 1469(w), 1427(w), 1392(w), 1372(w), 1331(w), 1252(s), 1195(s), 1137(vs), 1101(m), 1054(w), 942(w), 796(m), 767(w), 741(w), 726(w), 698(w), 667(m), 583(m), 550(w), 529(w).

X-ray Crystallography: Single-crystal X-ray diffraction measurements of these three complexes were carried out on an Oxford Supernova diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) at 173(2) K. The structures were solved by direct methods and refined on F^2 with full-matrix least-squares techniques using SHELXL-13 programs. The locations of lanthanide and copper atoms were easily determined, oxygen, nitrogen, and carbon atoms were subsequently determined from the difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms. Most of the fluorine atoms in trifluoromethyl groups are severely disordered and were separated into two parts. The terminal carbon atoms of solvent molecule *n*-heptane in complex **3** is somewhat disordered, some restrained items are performed to bring this free solvent molecule into rational model. Crystallographic parameters of complexes **1**-**3** are listed in Table 1. CCDC 997126 (**1**), 997127 (**2**) and 997128 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis. In the previous reported synthetic strategies, the highly toxic reagent phosgene in toluene was adopted to give 2, 4-dialkyl substituted bis-hydrazide.[9d] In order to obtain large quantities of verdazyls to support our research of coordination, the avoidance of risky starting material as much as possible is required as synthetic advances. As discovered in 1987, a superior substitute of phosgene, bis(trichloromethyl)carbonate, which is convenient to store and weight, had been widely used in synthesis of unsymmetrical disubstituted ureas in the presence of nucleophilic agent.[11] Thus, triphosgene was employed in the synthesis of bis-hydrazide with triethylamine in carefully dried toluene. Thanks to the mild release of phosgene, which arisen by decomposition of triphosgene and intermediate, the reaction went smoothly, and the product yield was also significantly improved.

In the synthesis of the final products, the counter ion, hfac anion, was introduced to construct these infinite chains, mainly owing to its strong electron-withdrawing effect, which could enhance the coordination ability of radical itself. Meanwhile, to avoid the decomposition of radical, the nonpolar mixed solvent, *n*-heptane/chloroform, in which the metal-hfac salts are finely soluble, is employed as the best medium. Finally, the resulting mixture must be placed at approximate 3 °C to avoid quick crystallization, which usually leads to microcrystalline and poor diffraction data.

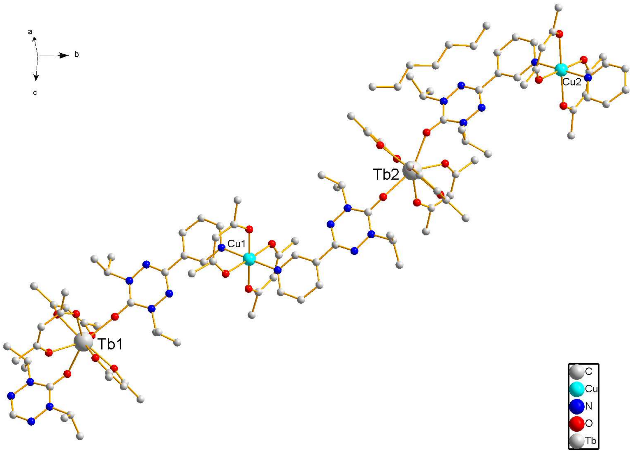


Fig. 2 Molecular structure of complex **2**, hydrogen atoms and disordered fluorine atoms are omitted for clarity.

Crystal Structure. Single-crystal X-ray diffraction reveals that all three complexes are isomorphous, and crystallize in monoclinic space group *P*21. As shown in Fig. 2, the asymmetric unit consists of two Ln(hfac)$_3$ units, two Cu(hfac)$_2$ units, four 3pyvd radicals and a *n*-heptane solvent molecule. In these complexes, take complex **2** for example, two Tb(III) ions and two Cu(II) ions are located in extremely similar coordination environments respectively, and 3pyvd radicals display as bis-monodentate bridging ligands connecting Tb(III) ions and Cu(II) ions together, forming the infinite one-dimensional chains. The Cu1(II) ion is six-coordinated in an axially elongated octahedron, the equatorial sites are occupied by two nitrogen atoms (N9, N10) from two pyridyl ring of verdazyl radicals and two oxygen atoms (O12, O14) from two separated hfac units with the bond lengths in the range of 1.999(6) to 2.049(5) Å. While another two oxygen atoms (O11, O13) in chelating hfac unit occupy the axial sites of this octahedral coordination sphere. The Tb(III) ion is eight-coordinated with six oxygen atoms coming from three chelating hfac ligands, and the coordination sphere of Tb(III) ion is completed by two oxygen atoms from verdazyl rings of the radical molecules. These Tb-O bond lengths are from the minimum 2.308(5) Å to the maximal 2.382(5) Å, which are comparable to the reported verdazyl coordinated lanthanide(III) complex.[3i] Within the verdazyl ring, the bond lengths of the adjacent nitrogen atoms are close to the 1.368(8) Å, which is the typical length of verdazyl ring in radical form.[10c] The verdazyl ring twists out of the pyridyl plane with the dihedral angle of 8.61°, indicating that these two rings are nearly coplanar to each other.[12] The nearest Cu···Cu distance within the chain is 21.386 Å, while the nearest Tb···Tb distance is 21.782 Å. Moreover, there also exist one *n*-heptane solvent molecule, which is somewhat disordered in complex **3**, filling in the interspace. Thus, each chain is well isolated.

The replacement of lanthanide(III) ions causes the bond lengths and angles of these three complexes vary a little. Due to the lanthanide contraction phenomena, the average bond length between the lanthanide(III) ions and the coordinated verdazyl oxygen atoms decrease from 2.339 Å in complex **1** to 2.328 Å in complex **3**.

As one can see, for verdazyl radical, it is the first time that three sorts of spin carriers were situated in single nanowires with unambiguous structures, this successful synthesis of hetero-tri-spin chains employing isopropyl substituted verdazyl radical have proven its coordination abilities to both transition metal via pyridyl nitrogen and lanthanide(III) ions through carbonyl oxygen. Due to readily modified substituents in verdazyl molecule, this system will provide us with the possibilities of more versatile structures as well as more novel properties in magnetism by introducing different functional groups.

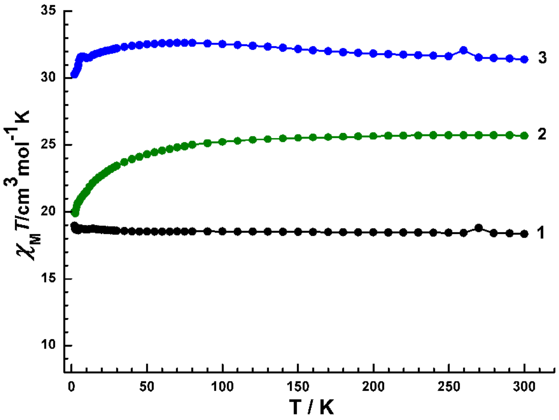


Fig. 3 $\chi_M T$ versus T curves for three complexes. The solid lines are guides for the eye.

Magnetic Properties. The magnetic properties of complexes **1-3** have been measured using polycrystalline samples under 1000 Oe *dc* field. The temperature dependence of the magnetic susceptibilities in the form of $\chi_M T$ versus T plots for all three complexes are shown in Fig. 3 and Fig. S1-S2. For complex **1**, the observed room-temperature $\chi_M T$ value is 18.40 cm^3 K mol^{-1}, which is slightly higher than the uncoupled system of two Gd(III) ions (f^7 electron configuration, g = 2.00, $\chi_M T$ = 7.875 cm^3 K mol^{-1}), two Cu(II) ions (d^9 electron configuration, g = 2.00, $\chi_M T$ = 0.375 cm^3 K mol^{-1}) and four verdazyl radicals (S = 1/2, g = 2.00, $\chi_M T$ = 0.375 cm^3 K mol^{-1}). As the temperature decrease, the $\chi_M T$ value gradually increases, and finally reaches a maximum of 18.96 cm^3 K mol^{-1} at 2.0 K. For complex **2**, the $\chi_M T$ value at room temperature is 25.70 cm^3 K mol^{-1}, which is a good agreement with two isolated Tb(III) ions (^{7}F$_6$, g = 3/2, $\chi_M T$ = 11.81 cm^3 K mol^{-1}), two Cu(II) ions (d^9 electron configuration, g = 2.00, $\chi_M T$ = 0.375 cm^3 K mol^{-1}) and four verdazyl radicals (S = 1/2, g = 2.00, $\chi_M T$ = 0.375 cm^3 K mol^{-1}). On cooling, the $\chi_M T$ value decreases smoothly, which could ascribe to the depopulation of Tb(III) m$_j$ sub-levels. But below 50 K, it begins to decrease more and more sharply and reaches a minimum of 18.98 cm^3 K mol^{-1} at 2.0 K. For complex **3**, at room temperature, the $\chi_M T$ value is 31.41 cm^3 K mol^{-1}, which is somewhat higher than the total value of uncorrelated paramagnetic ions (30.61 cm^3 K mol^{-1}, ^{6}H$_{15/2}$ for Dy(III) ion). The $\chi_M T$ value increases gradually and reaches a maximum at 75 K with a value of 32.64 cm^3 K mol^{-1}. Below 75 K, $\chi_M T$ begins to descend and reaches a minimum of 30.26 cm^3 K mol^{-1} at 2.0 K. The field dependence of M for three complexes was carried out at 1.9 K in the field range of 0-70 kOe (Fig. 4). At the highest field, the M value for complex **1** is 20.06 μ_B , which shows saturation value and agrees well with the theoretical one. While the M value for complex **2** and **3** are 16.75 μ_B and 17.88 μ_B, respectively, which are far from saturations ($^7F_6$ of Tb(III) and $^6H_{15/2}$ of Dy(III)). For complex **3**, the magnetization curve at different temperature are also measured (Fig. S3), three M versus H/T curves do not show coincidence at high field range, indicating the presence of magnetic anisotropy in Dy(III) ion.

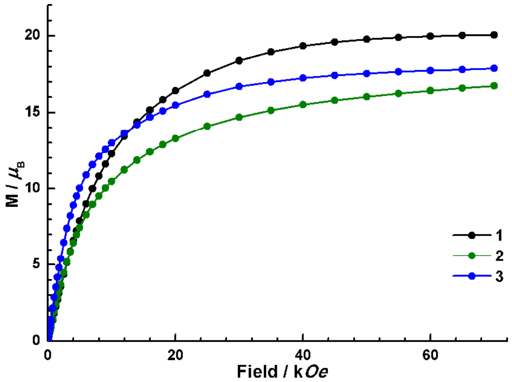


Fig. 4 Field dependence of magnetization curves of three complexes at 1.9 K. The solid lines are guides for the eye.

Due to the absence of angular momentum of Gd(III) ion, complex **1** provides possibility of quantitative analysis. In fact, there is no suitable model for such a complicated alternative chain containing all kinds of coupling parameters. However, considering that the nitrogen atom in pyridyl ring only carries very small spin densities, the magnetic coupling between the radical and Cu(II) ion should be very weak, and supposed to affect the $\chi_M T$ value at exceedingly low temperature. Therefore, this chain could be magnetically treated as a Gd(III) ion with two oxygen-coordinated radicals moiety and an isolated Cu(II) ion. Based on this approximation, the total susceptibilities (χ_t) could be roughly calculated as a sum of tri-spin fragment of Radical-Gd-Radical ($\chi_{R\text{-}Gd\text{-}R}$) and a constant χ_{Cu}, and the $\chi_{R\text{-}Gd\text{-}R}$ is originated from the spin Hamiltonian $\hat{H} = -2J(\hat{S}_{Gd}\hat{S}_{R1}+\hat{S}_{Gd}\hat{S}_{R2})+g_{Gd}\beta\hat{S}_{Gd}H+g_R\beta(\hat{S}_{R1}+\hat{S}_{R2})H+g_{Cu}\beta\hat{S}_{Cu}H$, where the coupling between two radicals is also negligible due to their commonly rather weak interactions and the parameter J stands for the magnetic coupling between Gd(III) ion and verdazyl radical through the coordinated carbonyl group. Assuming that, all spin carriers have the same g value ($g_{Gd} = g_R = g_{Cu} = g$), the best simulation (Fig. S1) performed in the temperature range of 16-300 K affords the parameters of $g = 2.03$, $J = 0.07(1)$ cm^{-1}.

Complexes **2** and **3**, containing anisotropic Tb(III) and Dy(III) ions were expected to be new series of SCMs, which is our original purpose to prepare and study such complexes. Thus, alternating-current susceptibilities were measured at low temperature range (Fig. S4-S5). With decreasing temperature, the in-phase susceptibilities of complexes **2** and **3** increased monotonically, however, unfortunately, no signal of imaginary components was observed even at the temperature as low as 2.0 K.

Conclusions

In conclusion, we have adopted isopropyl substituted verdazyl radical in the design of 2p-3d-4f one dimensional chains. To our best knowledge, these are the first series of 2p-3d-4f chains based on verdazyl radical. These results have demonstrated that exploiting the coordination abilities of isopropyl substituted verdazyl radical to transition metal and lanthanide(III) ions is an efficient approach to produce system incorporating 2p, 3d and 4f spin carriers. This successful synthetic approach illustrated in this work may open up new opportunities to develop novel molecular magnetic materials based on versatile verdazyl radicals as the verdazyl derivatives, where some functional groups were introduced, could be appealing building blocks due to their coordination diversity.

Acknowledgment

We thank the National Natural Science Foundation of China (Grants 21371166, 21331003 and 21221061) for financial support.

Notes and references

[a] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China E-mail: tang@ciac.ac.cn*
[b] *University of Chinese Academy of Sciences, Beijing, 100049, P. R. China*
[c] *Department of Chemistry, Key Laboratory of Advanced Energy Material Chemistry (MOE), and Tianjin Co-Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, P. R. China.*

† Electronic Supplementary Information (ESI) available: additional magnetic data for complexes **1**, **2** and **3** are presented in **Fig. S1-S4**. Selected bond lengths and angles of complexes **1-3** are listed in **Tables S1-S3**, respectively. See DOI: 10.1039/b000000x/

1 I. Ratera and J. Veciana, *Chem. Soc. Rev.*, 2012, **41**, 303.
2 (a) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio and R. Sessoli, *J. Chem. Soc. Dalton Trans.* 2000, 3907;(b) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem.-Int. Ed.* 2001, **40,** 1760.
3 (a) N. Ishii, Y. Okamura, S. Chiba, T. Nogami and T. Ishida, *J. Am. Chem. Soc.* 2008, **130**, 24;(b) Y. Numata, K. Inoue, N. Baranov, M. Kurmoo and K. Kikuchi, *J. Am. Chem. Soc.* 2007, **129**, 9902;(c) R. Sessoli, *Angew. Chem.-Int. Ed.* 2008, **47**, 5508;(d) M. Balanda, M. Rams, S. K. Nayak, Z. Tomkowicz, W. Haase, K. Tomala and J. V. Yakhmi, *Phys. Rev. B* 2006, **74**, 224421;(e) L. Bogani, A. Caneschi, M. Fedi, D. Gatteschi,; Massi, M.; Novak, M. A. M. G. Pini, A. Rettori, R. Sessoli, and A. Vindigni, *Phys. Rev. Lett.* 2004, **92**, 207204;(f) R. Ishikawa, K. Katoh, B. K. Breedlove and M. Yamashita, *Inorg. Chem.* 2012, **51**, 9123;(g) N. shii, T. Ishida and T. Nogami, *Inorg. Chem.* 2006, **45**, 3837;(h) R. Liu, L. Li, X. Wang, P. Yang, C. Wang, D. Liao and J.-P. Sutter, *Chem. Commun.* 2010, **46**, 2566;(i) L. Norel, L.-M. Chamoreau, Y. Journaux, O. Oms, G. Chastanet and C. Train, *Chem. Commun.* 2009, 2381.
4 C. Coulon, H. Miyasaka and R. Clérac, In *Single-Molecule Magnets and Related Phenomena*; Winpenny, R., Ed.; Springer-Verlag Berlin: Berlin, 2006; Vol. **122**, p 163.
5 H. Miyasaka, T. Madanbashi, K. Sugimoto, Y. Nakazawa, W. Wernsdorfer, K.-i. Sugiura, M. Yamashita, C. Coulon, and R. Clérac, *Chem.–Eur. J.* 2006, **12**, 7028.
6 (a) L. Bogani, C. Sangregorio, R. Sessoli and D. Gatteschi, *Angew. Chem.-Int. Ed.* 2005, **44**, 5817;(b) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Am. Chem. Soc.* 2006, **128**, 7947;(c) K. Bernot, L. Bogani, R. Sessoli and D. Gatteschi, *Inorg. Chim. Acta* 2007, **360**, 3807.

7 A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, *Acc. Chem. Res.* 1989, **22**, 392.

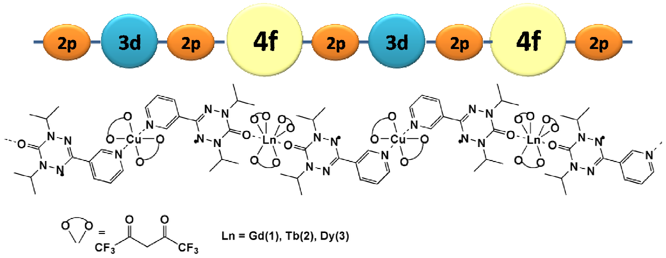
8 (a) M. Zhu, X. L. Mei, Y. Ma, L. C. Li, D. Z. Liao and J. -P. Sutter, *Chem. Commun.* 2014, **50**, 1906;(b) M. Zhu, Y. G. Li, Y. Ma, L. C. Li and D. Z. Liao, *Inorg. Chem.* 2013, **52**, 12326; (c) M. Zhu, P. Hu, Y. G. Li, X. F. Wang, L. C. Li, D. Z. Liao, V. M. L. Durga Prasad Goli, S. Ramasesha and J. -P. Sutter, *Chem, -Eur. J.* 2014, **41**, 13356.

9 (a) E. F. Ullman, L. Call and J. H. Osiecki, *J. Org. Chem.* 1970, **35**, 3623;(b) E. F. Ullman, J. H. Siecki, D. G. B. Boocock and R. Darcy, *J. Am. Chem. Soc.* 1972, **94**, 7049;(c) M. J. Plater, S. Kemp and E. Lattmann, *J. Chem. Soc. Perkin Trans. 1* 2000, 971;(d) E. C. Pare, D. J. R. Brook, A. Brieger, M. Badik and M. Schinke, *Org. Bio. Chem.* 2005, **3**, 4258.

10 (a) J. B. Gilroy, B. D. Koivisto, R. McDonald, M. J. Ferguson and R. G. Hicks, *J. Mater. Chem.* 2006, **16**, 2618;(b) D. J. R. Brook, C. J. Richardson, B. C. Haller, M. Hundley and G. T. Yee, *Chem. Commun.* 2010, **46**, 6590;(c) S. D. J. McKinnon, B. O. Patrick, A. B. P. Lever and R. G. Hicks, *Chem. Commun.* 2010, **46**, 773;(d) S. D. J. McKinnon, J. B. Gilroy, R. McDonald, B. O. Patrick and R. G. Hicks, *J. Mater. Chem.* 2011, **21**, 1523;(e) S. D. J. McKinnon, B. O. Patrick, A. B. P. Lever and R. G. Hicks, *J. Am. Chem. Soc.* 2011, **133**, 13587.

11 (a) F. Bigi, R. Maggi and G. Sartori, *Green Chem.* 2000, **2**, 140;(b) P. Majer and R. S. Randad, *J. Org. Chem.* 1994, **59**, 1937;(c) H. Eckert and B. Forster, *Angew. Chem. -Int. Ed.* 1987, **26**, 894;(d) C. L. Barr, P. A. Chase, R. G. Hicks, M. T. Lemaire and C. L. Stevens, *J. Org. Chem.* 1999, **64**, 8893.

12 R. G. Hicks, M. T. Lemaire, L. Ohrstrom, J. F. Richardson, L. K. Thompson and Z. Q. Xu, *J. Am. Chem. Soc.* 2001, **123**, 7154.



Exploiting the coordination abilities of isopropyl substituted verdazyl radical to transition metal and lanthanide(III) ions represents an efficient approach to produce system incorporating 2p, 3d and 4f spin carriers.