COMMUNICATION

Ytterbium can relax slowly too: a field-induced Yb$_2$ single-molecule magnet†

Po-Heng Lin,$^a$ Wen-Bin Sun,$^{a,b}$ Yong-Mei Tian,$^b$ Peng-Fei Yan,$^{a,b}$ Liviu Ungur,$^c$ Liviu F. Chibotaru$^{a,c}$ and Muralee Murugesu$^{a{*}}$

Received 25th July 2012, Accepted 15th August 2012
DOI: 10.1039/c2dt31677c

An unusual dinuclear Yb$_2$ complex isolated using a mixed ligand strategy leads to field-induced SMM behaviour. Low magnetic axiality and a large tunnelling gap lead to significant quantum tunnelling of the magnetisation, which was reduced under an applied static optimum field of 1600 Oe.

Since the discovery of lanthanide single-molecule magnets (SMMs) in 2003,$^1$ researchers have actively been searching for new lanthanide based SMMs. This is mainly due to the fact that lanthanide SMMs clearly surpassed energy barriers displayed by transition metal systems.$^2$ In lanthanide systems, a large intrinsic magnetic anisotropy contribution leads to magnet-like behaviour of slow relaxation of the magnetisation at low temperatures. Thus, recent research has led to the discovery of molecular complexes with Tb$^{III}$, Dy$^{III}$, Ho$^{III}$, Er$^{III}$, Tm$^{III}$, and Yb$^{III}$ to behave as SMMs. Among these ions Dy$^{III}$ has so far been the most prolific in this quest. However, larger energy barriers must be achieved to move towards application of these materials in technologies such as memory storage. Towards this goal other systems need to be investigated; new ligand design and new metal ions are obvious strategies to pursue.

Recently, Long and co-workers predicted that Yb$^{III}$ ions could also lead to SMM behaviour if an appropriate ligand system is employed.$^2c$ Although the Yb$^{III}$ ion is highly anisotropic, only two single-ion magnets have been reported so far.$^7$ No larger polynuclear complexes have been reported to date. In order to create polynuclear Yb based SMMs we need to develop a specific synthetic strategy where magnetic anisotropy of the Yb$^{III}$ ion will be enhanced through an appropriate ligand system.

As a proof of concept we have synthesised the Yb$^{III}$ analogue of our recently reported Dy$^{III}$ complex and studied its magnetic properties.$^5$ The reported complex exhibits slow relaxation of the magnetisation under an applied dc field. To our knowledge this field-induced SMM behaviour for a polynuclear Yb$^{III}$ complex has never been reported.

Our synthetic approach relies on the employment of a mixed ligand strategy where the presence of salen type ligand L (Scheme S1, ESI†) is ideal for coordination of metal ions as well as promoting magnetic interaction through phenoxide bridges. The use of Yb(acac)$_3$ as the synthetic precursor leads to coordination of acac$^-$ ligands to complete the coordination sphere of the lanthanide ions. We have recently reported the synthesis of a [Dy$_2$L$_2$(acac)$_2$(H$_2$O)] analogue, thus by following the same synthetic procedure [Yb$_2$L$_2$(acac)$_2$(H$_2$O)]·2CH$_2$Cl$_2$, 1, was isolated.$^8$

Complex 1 crystallises in the monoclinic $P2_1/n$ space group where the molecular structure is shown in Fig. 1 and S1.$^f$ The structure is composed of two Yb$^{III}$ ions located slightly out of the N$_2$O$_2$ coordination pocket of two L$^2$ ligands as the Yb$^{III}$ ions are larger than transition metal ions. Two acac$^-$ ligands and one H$_2$O molecule complete the coordination environment of the lanthanide ions. The Yb1 atom is in an octacoordinate distorted square antiprism geometry whereas Yb2 displays a heptacoordinate distorted capped trigonal prism. The intramolecular Yb1⋯Yb2 distance of 3.79 Å and the average Yb⋯O–Yb angle

![Fig. 1](image-url)

Fig. 1 Molecular structure of [Yb$_2$L$_2$(acac)$_2$(H$_2$O)], 1. Yb1 (right) is in a distorted square antiprism environment, Yb2 (left) is in a distorted capped trigonal prism environment. Colour code: Yb (purple), O (red), N (blue), C (grey), H (white). Orientation of the main anisotropy axes in the ground Kramers doublet is given in dashed lines.

$^a$Department of Chemistry, University of Ottawa, 10 Marie-Curie, Ottawa, ON, Canada, K1N 6N5. E-mail: m.murugesu@uottawa.ca
$^b$Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, No. 74, Xuefu Road, Nangang District, Harbin 150080, P.R. China. E-mail: wenbinsun@yahoo.cn
$^c$Division of Quantum and Physical Chemistry and INP AC, Celestijnenlaan, 200F, 3001 Leuven, Belgium
†Electronic supplementary information (ESI) available: Additional structural, magnetic computational data can be found there. CCDC 830606. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31677c
of 111.2° are similar to those of the recently reported isostructural Dy₂ complex. Additionally, complex I also reveals 5.94 Å as the closest intermolecular Yb2–Yb2 distance (Fig. S2†).

Moreover, the hydrogen atom H9 bonded to the O9 atom hydrogen bonds to the phenoxide oxygen (O3) from the neighbouring molecule forming pairs of hydrogen bonded dinuclear units. It is noteworthy that the O9 atom is 2.33 Å away from its coordinated Yb2 ion and 4.12 Å away from the Yb2 from the neighbouring molecule (Fig. S3†).

The Near Infrared (NIR) fluorescence properties of I in the solid state and in CH₂Cl₂, CH₃CN and CH₃OH solutions were studied. Under the above conditions, the typical emission bands of Yb³⁺ assigned to the 2F₅/₂ → 2F₇/₂ transitions are all observed at 975 nm upon excitation at 390 nm. A slightly strong emission was observed in a CH₂Cl₂ solution (Fig. S4†). It is noteworthy that the solvent quenching effect of strong coordination of CH₃OH was not very obvious thanks to the strongly coordinating ability of CH₃OH. The free ligand H₂L does not exhibit NIR fluorescence under similar conditions. These observations are consistent with the NIR fluorescence of I in solution arising from the Yb³⁺ centre. Besides, the emission spectrum of Yb³⁺ ions in I reveals not only one sharp main component at 975 nm corresponding to the zero-phonon transition but also broader components at longer wavelengths (lower energy) at 1005 and 1028 nm, which were assigned to the inter-Stark 2F₅/₂ → 2F₇/₂ transitions.⁹

For I, its luminescent decay curves obtained from time-resolved luminescent experiments can be fitted with two exponentials, which is due to the different coordination geometries of the two Yb³⁺ ions (Fig. S5†). The decay times (μs) and amplitudes (%) were 2.47 μs (57.29%) and 10.38 μs (42.71%) and the intrinsic quantum yields (0.12% and 0.52%, respectively) of Yb³⁺ emission may be estimated by Φfl = τobs/τ0, where τobs is the observed emission lifetime and τ0 is the ‘neutral lifetime’, i.e. 2.0 ms for the Yb³⁺ ions.¹⁰ The value of the fluorescence lifetimes for I is comparable to those of dinuclear ZnLn Schiff base complexes and among the few examples of homo-nuclear lanthanide complexes with Schiff base ligands,¹⁰ which likely results from the quantity of accepting levels of the Yb³⁺ ion from the ligands.

Direct current (dc) susceptibility measurement of I (Fig. 2) indicates that the χT value of 5.47 cm³ K mol⁻¹ at 300 K is close to the theoretical value of 5.14 cm³ K mol⁻¹ for two non-interacting Yb³⁺ ions (2F₇/₂, J = 7/2, g = 8/7, χT free ion = 2.57 cm³ K mol⁻¹). Upon decrease of the temperature, the χT product decreases steadily reaching a minimum value of 3.12 cm³ K mol⁻¹ at 5 K followed by a slight increase at low temperature to reach 3.20 cm³ K mol⁻¹ at 2 K. The initial decrease of the χT product is most likely due to depopulation of the Stark sublevels and/or significant magnetic anisotropy present in Yb³⁺ systems. The final increase below 5 K indicates the presence of ferromagnetic interactions between the metal ions as previously seen for the Dy³⁺ analogue. Magnetisation measurements (Fig. 2 inset) at low fields indicate a linear increase of the magnetisation while at higher fields the curves increase slightly without complete saturation. Moreover, isotherm lines are observed to be close together without completely superimposing. This suggests the presence of a small amount of magnetic anisotropy in the system.

![Fig. 2 Temperature dependence of the χT product at 1000 Oe for complex I (with χ being the molar susceptibility per dinuclear complex defined as M/H). Inset: M vs. H data at various temperatures (1.9, 3, 5 and 8 K) are shown on a single M vs. H/T plot.](http://pubs.rsc.org/dms/pdf/dt)
magnetic. The lack of axial symmetry in the Yb environments results in strong relative rotation of the main magnetic axes in the four KDs on each Yb site, like it was seen in other low-symmetry Ln complexes and fragments.\textsuperscript{12} The obtained large transversal $g$ factors on Yb ions (low magnetic axiality) and the relatively large tunnelling gap in the ground exchange doublet (ca. 0.01 cm\textsuperscript{-1}, Table S4*) are the reason for strong quantum tunnelling of magnetisation and for the lack of slow relaxation in I without an applied dc field.

In conclusion, we were able to synthesize a Yb$_2$ complex where slow magnetic relaxation was observed under an applied static dc field. Such field-induced SMM behaviour is due to low magnetic axiality and the large tunnelling gap leads to significant quantum tunnelling of the magnetisation. Complex I represents the first example of a polynuclear Yb\textsuperscript{III} SMM reported to date. This promising result allows us to envision and tailor new SMMs based on Yb\textsuperscript{III} ions and potentially create high-energy barrier SMMs.

**Acknowledgements**

This work was financially supported by the NSFC of China (21102039 and 21072049) and Heilongjiang Province (10td03), NSERC-DG, CFI, ORF and ERA Canada.

**Notes and references**

