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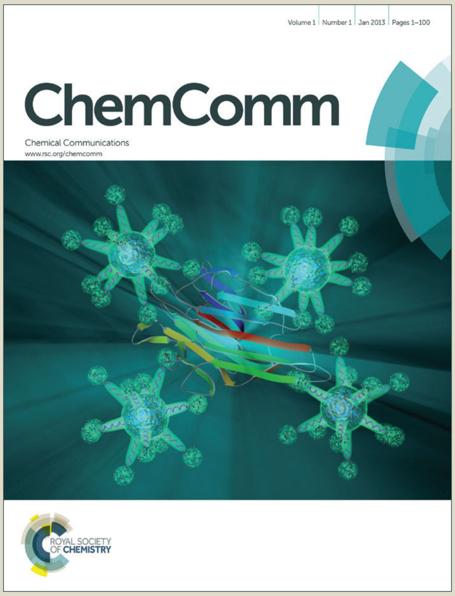

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Constructing supramolecular grids: from 4f square to 3d-4f grid

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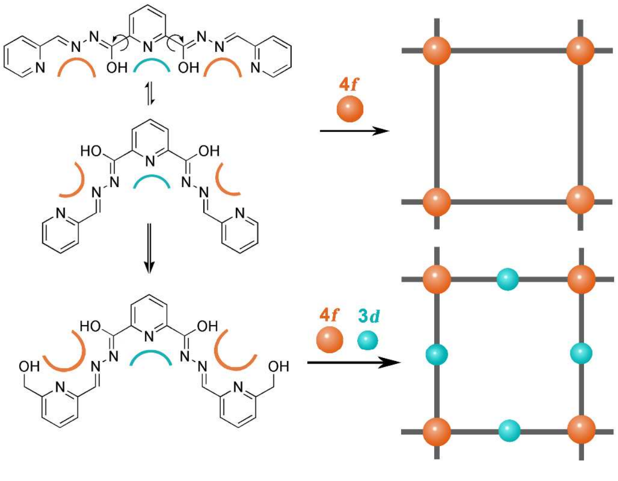
The first supramolecular 3d-4f grid was constructed using novel dihydrazone based ligands.

Within the field of supramolecular chemistry,[1] molecular architectures, such as rotaxanes,[2] catenanes,[3] knots,[4] helicates[5] and grids[6] have been undoubtedly flourished over the last three decades, or so, due to their interesting physicochemical properties and aesthetic beauties. In particular, metal based grids consist of both spin centers and stacking organic ligands expected to exhibit a wide variety of properties such as redox, magnetic, catalytic, photochemical and mechanical functions, especially the single-molecule magnet (SMM) behavior[7] which has attracted increasing attention recently.[8] Thus far examples of [n×n] (n = 2-5) transition metal grid-like complexes[9] constructed by the reactions of hydrazone ligands and transition metal salts have been prepared and structurally characterized. Particularly, the heterometallic grids[9g] and grid catenanes[10] reported recently have focalized our research interests on the constructions of grid-like molecules[11] that contain both 3d and 4f ions. To date, however, only several lanthanide grids were reported.[11b, 12]As for 3d-4f grid like compounds, no example has ever been reported due to the different characteristic coordination abilities of 3d and 4f ions.[12b, 13]

Recently, the attempts to construct lanthanide [n×n] grid structures with typical tritopic hydrazone ligands have been carried out by the group of Thompson.[14] However, linear trinuclear Ln^{III} complexes were obtained instead of grid-like molecule because of the larger ionic radii as well as the higher coordination number of lanthanide ions.[15] In order to construct larger 4f grids and put the frontiers to 3d-4f heterometallic grid-like compounds, we applied herein two new types of tritopic hydrazone ligands having small coordinative pocket in the middle to catch 3d ion and large pockets at both sides to accommodate 4f ions.

In the present work, we describe the preparations of two novel 4f grids, $[Dy_4L_4(H_2O)_{12}]\cdot(CF_3SO_3)_4\cdot12H_2O$ (**1**), $[Dy_4(H_2L)_4Cl_4(H_2O)_8]\cdot Cl_8$ (**2**) and the construction of a rare 3d-4f grid like molecule, $[Dy_4Cu_4(H_2L')_4Cl_8(H_2O)_4]\cdot Cl_4\cdot28H_2O$ (**3**), with four Cu^{II} ions on the edges and four Dy ions at the corners of the square, using tritopic hydrazone ligands. Magnetic studies reveal that compounds **1** and **2** display field induced single-molecule magnet behavior, while compound **3** shows single-molecule magnet behavior under zero applied dc field.



Scheme 1 Schematic drawing of the ligands H_2L, H_4L' and the configurations of complexes **1**-**2** (top right) and**3** (bottom right).

The reactions of H_2L and $DyCl_3\cdot6H_2O$ or $Dy(CF_3SO_3)_3\cdot6H_2O$ in 1:2 methanol/acetonitrile produces colorless crystals of **1**, $[Dy_4L_4(H_2O)_{12}]\cdot(CF_3SO_3)_4\cdot12H_2O$ and **2**, $[Dy_4(H_2L)_4Cl_4(H_2O)_8]\cdot Cl_8$, respectively. Single-crystal X-ray studies reveal that compound **1** crystallizes in tetragonal space group *I4(1)/amd* with *Z* = 4. A perspective view of the square shaped molecule (Fig. S1) shows that four ligands construct the edges of the grid and four Dy^{III} ions represent the corners joining the edges together by coordinating to the donor atoms on both sides of the ligands (Scheme 1 top). The coordinating geometry of each Dy^{III} center is accomplished by three water molecules. The positive charges are further balanced by four $CF_3SO_3^-$, which reside inside the square. Due to the large size of

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$CF_3SO_3^-$, the ligands are oblique to the plane of the grid with an angle of 65°. In contrast with compound **1**, compound **2** crystallizes in tetragonal space group *P4(2)/n* with $Z = 2$ and shows similar grid-like core structure, while with the replacement of $CF_3SO_3^-$ with Cl^-, the ligands are protonated, capturing Cl^- through hydrogen bonds (Fig. 1 left). Meanwhile, one of the water molecules coordinated to each Dy^{III} center is replaced by Cl^-. The positive charges are further balanced by four Cl^- around the Dy^{III} centers. The ligands H_2L are a little oblique to the plane of the grid with an angle of 77°.

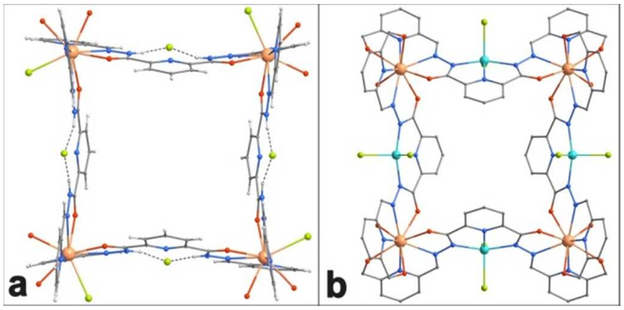

Fig. 1 Structures of **2** (a) and **3** (b) with orange, azure, green, blue, dark and red spheres representing Dy, Cu, Cl, N, C and O, respectively; solvents have been omitted for clarity.

From the perspective view of the configuration of ligand H_2L we can find that there are three coordinative pockets within the ligand; two of which at both sides can catch 4f ions, the other one in the middle is ideal for accommodating a 3d ion. Especially, the Cl^- situated in the N-N-N coordinative pocket through hydrogen bonds in **2** might be substituted by 3d ions (Scheme S1), constructing [2×2], even [3×3] 3d-4f grids by ligand H_2L.[14] Our initial approach has been to react ligand H_2L and 3d and 4f salts. Unfortunately, only pure 4f grids, instead of 3d-4f grids, have been isolated.

Alternatively, a novel dihydrazone based ligand H_4L' with two larger O-N-N-O pockets at each sides which can stabilize the corners of the grid and a N-N-N pocket in the middle able to accommodate 3d ion (Scheme 1), was designed and applied in the construction of 3d-4f grid-like compounds. Just as what we expected, the reaction of H_4L' with $DyCl_3{\cdot}6H_2O$ and $CuCl_2{\cdot}2H_2O$ in the presence of triethylamine produces green block shaped crystal of **3**, $[Dy_4Cu_4(H_2L')_4Cl_8(H_2O)_4]{\cdot}Cl_4{\cdot}28H_2O$, with desired 3d-4f grid structure. Single-crystal X-ray studies reveal that compound **3** crystallizes in orthorhombic space group *Pmmn* with $Z = 2$. Akin to compounds **1** and **2**, four ligands in compound **3** serve as the edges and four Dy^{III} ions represent the corners (Scheme 1 right), which are locked by two O-N-N-O pockets. Meanwhile, the N-N-N pocket in each edge of the square binds a Cu^{II} ion, which is further stabilized by two coordinated Cl^-. The coordinating geometry of each Dy^{III} center is accomplished by one coordinated water molecule. Due to the steric hindrance of the coordinated water molecule, the ligands are a little oblique to the plane of the grid with an angle of 47.6°. The positive charges are further balanced by four Cl^- outside the grid.

All the Dy^{III} ions in these compounds are nine coordinated. The coordination geometry of Dy^{III} ion in each compound was calculated by *SHAPE* 2.1,[16] giving the departure parameters in Table S3. From these results, we can see that the Dy^{III} ions in compound **1** are proximal to tricapped trigonal prism (D_{3h}) coordinate geometry. Similarly, the smallest calculated parameter for compound **2** is also tricapped trigonal prism. While, the coordinate symmetry of Dy^{III} ion for compound **3** is more proximal to capped square antiprism (C_{4v}) rather than tricapped trigonal prism (D_{3h}), reflecting the structure change caused by the addition of external $-CH_2OH$ group on both sides of the hydrazone ligand. In compounds **1** and **2**, the N'-N-O and N-N'-N (N' represents the N atom from pyridyl) pockets are relative larger with N'···O and N···N distances of 4.42 and 4.44 Å, respectively. With the addition of $-CH_2OH$, the pockets in compound **3** get smaller with N'···O and N···N distances of 4.32 and 3.89 Å, respectively. As a result, the Dy···Dy distance in complex **3** approaches to 10.65 Å, which is shorter than the value of 11.04 and 11.17 Å for compounds **1** and **2**. The Dy^{III} ions in compounds **1** and **3** are in the same plane, while for compound **2**, the Dy^{III} ions are out of plane. In addition, the five coordinated Cu^{II} ions in compound **3** are slightly out of the Dy_4 plane with the distance of 0.49 Å. The Dy^{III} and Cu^{II} ions are bridged by N=N group with Dy···Cu distance of 5.3 Å, suggesting magnetic coupling could be probably engendered.

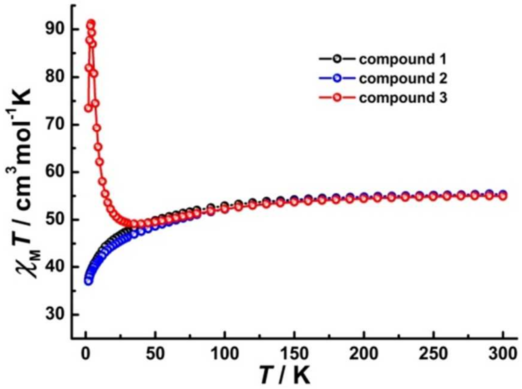

Fig. 2 Temperature dependence of $\chi_M T$ product at 1 kOe, between 2 and 300 K for **1** (black), **2** (blue) and **3** (red).

The static magnetic susceptibilities of compounds **1**-**3** (Fig. 2) were collected in the temperature range of 2-300 K under an applied magnetic field of 1000 Oe, and the magnetization (*M*) data were collected in the field range of 0-7 T below 5 K. The room temperature values of $\chi_M T$ are 55.17 and 55.29 $cm^3{\cdot}K{\cdot}mol^{-1}$ for **1** and **2**, respectively. These are close to the expected value of 14.17 $cm^3{\cdot}K{\cdot}mol^{-1}$ for each Dy^{III} ion indicating the free-ion approximation applies.[17] Upon cooling, the $\chi_M T$ values for both compounds decrease slowly down to 2 K reaching the values of 37.4 and 37.0 $cm^3{\cdot}K{\cdot}mol^{-1}$ for **1** and **2**, respectively. The slow decrease is indicative of Stark level splitting at the lanthanide ions in weak crystal field. The field-dependent magnetizations for compounds **1** and **2** are also in the same tendency (Fig. S5 and S6). The magnetizations rise abruptly at low fields and reach 21.41 and 20.51 μ_B at 7 T without saturation, suggesting the presence of magnetic anisotropy and/or considerable crystal-field effects. In the case of compound **3**, the room temperature $\chi_M T$ is 54.9 $cm^3{\cdot}K{\cdot}mol^{-1}$. With lowering the temperature, the $\chi_M T$ values increase sharply, after a slow decrease down to 30 K, reaching the maximal value of 91.2 $cm^3{\cdot}K{\cdot}mol^{-1}$, then decrease suddenly again and reach the minimal value of 73.5 $cm^3{\cdot}K{\cdot}mol^{-1}$ at 2.0 K. The increase of $\chi_M T$ values suggests that ferromagnetic coupling between Dy^{III} ions and Cu^{II} ions is operative, while the decrease is likely ascribed to the presence of magnetic anisotropy and/or intermolecular weak antiferromagnetic interactions. The field-dependent magnetizations for **3** (Fig. S7) rise abruptly at low fields and reach 22.2 μ_B at 7 T without saturation, suggesting the presence of magnetic anisotropy.

To investigate the SMM behavior of **1**-**3**, alternating-current (ac) magnetic susceptibility measurements were also performed under zero dc fields. No SMM behavior is observed above 1.9 K for **1** and **2** due to the absence of any frequency and temperature dependent out-of-phase (χ'') signals. However non-zero temperature-dependent χ' and χ'' signals were observed for both **1** and **2** upon the application of 700 and 500 Oe static dc field at low temperature (Fig. S8 and S9). Especially for compound **2**, the maximum peaks in the χ'' signal are observed below 2.3 K, indicative of the field induced SMM behavior. It is worth noting that temperature dependent peaks of χ' and χ'' signals are observed below 3.5 K for **3** in zero applied filed (Fig. S10). Frequency-dependent susceptibility measurements were also performed on compound **3**, showing frequent dependent χ'' signal under zero applied dc field in the frequency range of 1-1488 Hz (Fig. 3). As the temperature is lowered, the maximum peaks of χ'' signal shift toward lower frequency smoothly without frequency independent phase, suggesting that the quantum regime is absent in the operating temperatures of the magnetometer.

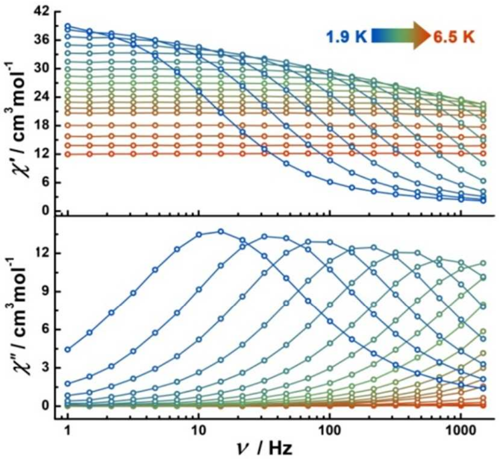

Fig. 3 Frequency-dependent magnetic susceptibilities for **3** at indicated temperatures, under zero dc field.

To evaluate the energy barrier of magnetic relaxation, the relaxation times were extracted from the maxima of the out-of-phase signals (Fig. S11). The τ *vs*. T^{-1} plot, showing smooth decrease, corroborates further the absence of quantum turning process that is probably suppressed by intramolecular Dy···Cu interactions. The plot was fitted using a reported method,[18] yielding effective energy barrier of U_{eff} = 32.2 K with a $\tau_0 = 8.1\times10^{-9}$ s (Fig. S12). The Cole-Cole plots of χ'' *vs*. χ' (Fig. S11) display semicircular profiles and are fitted well to a generalized Debye model.[19] The values of α parameter are in the range of 0.12-0.23, indicating a relatively narrow distribution of the relaxation times.

In conclusion, with the use of a novel dihydrazone based ligand we have successfully isolated two 4f grids **1**, **2** and one 3d-4f grid-like compound **3**, with the latter represents the first 3d-4f grid showing SMM behavior to our knowledge. Additionally, the ferromagnetic Dy···Cu coupling could be one of the efficient way to suppress the quantum turning effect[20] within this type of 3d-4f grids. Our work demonstrates that 3d-4f grids can be designed by dihydrazone based ligands and can be used to develop new magnetically coupled 3d-4f SMMs. Larger heterometallic compounds constructed by this type of ligands are underway in our laboratory.

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Notes and references

1 (a) J.-M. Lehn, *Chem. Soc. Rev.*, 2007, **36**, 151-160; (b) L. F. Lindoy, K.-M. Park and S. S. Lee, *Chem. Soc. Rev.*, 2013, **42**, 1713-1727.
2 (a) M. Xue, Y. Yang, X. Chi, X. Yan and F. Huang, *Chem. Rev.*, 2015, **115**, 7398-7501; (b) 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**, 314-318.
3 (a) G. Gil-Ramírez, D. A. Leigh and A. J. Stephens, *Angew. Chem. Int. Ed.*, 2015, **54**, 6110-6150; (b) N. H. Evans and P. D. Beer, *Chem. Soc. Rev.*, 2014, **43**, 4658-4683.
4 (a) J.-F. Ayme, J. E. Beves, C. J. Campbell, G. Gil-Ramírez, D. A. Leigh and A. J. Stephens, *J. Am. Chem. Soc.*, 2015, **137** 9812–9815; (b) G. Zhang, G. Gil-Ramírez, A. Markevicius, C. Browne, I. J. Vitorica-Yrezabal and D. A. Leigh, *J. Am. Chem. Soc.*, 2015, **137**, 10437–10442; (c) O. Lukin and F. Vögtle, *Angew. Chem. Int. Ed.*, 2005, **44**, 1456-1477; (d) R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434-5464; (e) J.-F. Ayme, J. E. Beves, C. J. Campbell and D. A. Leigh, *Chem. Soc. Rev.*, 2013, **42**, 1700-1712.
5 (a) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005-2062; (b) J.-C. G. Bünzli and C. Piguet, *Chem. Rev.*, 2002, **102**, 1897-1928.
6 (a) L. N. Dawe, K. V. Shuvaev and L. K. Thompson, *Chem. Soc. Rev.*, 2009, **38**, 2334-2359; (b) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J.-M. Lehn, *Angew. Chem. Int. Ed.*, 2004, **43**, 3644-3662; (c) J. G. Hardy, *Chem. Soc. Rev.*, 2013, **42**, 7881-7899.
7 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141-143.
8 (a) L. Sorace, C. Benelli and D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3092-3104; (b) J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078-2085; (c) D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, 2006; (d) P. Zhang and J. Tang, *Lanthanide Single Molecule Magnets*, Springer-Verlag, 2015.
9 (a) M. Steinert, B. Schneider, S. Dechert, S. Demeshko and F. Meyer, *Angew. Chem. Int. Ed.*, 2014, **53**, 6135-6139; (b) Y.-T. Wang, S.-T. Li, S.-Q. Wu, A.-L. Cui, D.-Z. Shen and H.-Z. Kou, *J. Am. Chem. Soc.*, 2013, **135**, 5942-5945; (c) B. Schneider, S. Demeshko, S. Dechert and F. Meyer, *Angew. Chem. Int. Ed.*, 2010, **49**, 9274-9277; (d) L. Zhao, C. J. Matthews, L. K. Thompson and S. L. Heath, *Chem. Commun.*, 2000, 265-266; (e) L. Zhao, Z. Xu, L. K. Thompson, S. L. Heath, D. O. Miller and M. Ohba, *Angew. Chem. Int. Ed.*, 2000, **39**, 3114-3117; (f) L. N. Dawe and L. K. Thompson, *Angew. Chem. Int. Ed.*, 2007, **46**, 7440-7444; (g) L. N. Dawe, K. V. Shuvaev and L. K. Thompson, *Inorg. Chem.*, 2009, **48**, 3323-3341.
10 (a) C. Giri, F. Topic, M. Cametti and K. Rissanen, *Chem. Sci.*, 2015, **6**, 5712-5718; (b) T. S. M. Abedin, L. K. Thompson and D. O. Miller, *Chem. Commun.*, 2005, 5512-5514.

11 (a) S. Xue, L. Zhao, Y.-N. Guo, X.-H. Chen and J. Tang, *Chem. Commun.*, 2012, **48**, 7031-7033; (b) S. Xue, L. Zhao, Y.-N. Guo and J. Tang, *Dalton Trans.*, 2012, **41**, 351-353.

12 (a) P.-H. Guo, J. Liu, Z.-H. Wu, H. Yan, Y.-C. Chen, J.-H. Jia and M.-L. Tong, *Inorg. Chem.*, 2015, **54**, 8087-8092; (b) L. K. Thompson and L. N. Dawe, *Coord. Chem. Rev.*, 2015, **289–290**, 13-31; (c) M. U. Anwar, L. K. Thompson, L. N. Dawe, F. Habib and M. Murugesu, *Chem. Commun.*, 2012, **48**, 4576-4578; (d) N. M. Randell, M. U. Anwar, M. W. Drover, L. N. Dawe and L. K. Thompson, *Inorg. Chem.*, 2013, **52**, 6731-6742; (e) S.-Q. Wu, Q.-W. Xie, G.-Y. An, X. Chen, C.-M. Liu, A.-L. Cui and H.-Z. Kou, *Dalton Trans.*, 2013, **42**, 4369-4372.

13 K. Liu, W. Shi and P. Cheng, *Coord. Chem. Rev.*, 2015, **289–290**, 74-122.

14 M. U. Anwar, S. S. Tandon, L. N. Dawe, F. Habib, M. Murugesu and L. K. Thompson, *Inorg. Chem.*, 2011, **51**, 1028-1034.

15 J. Rinck, Y. Lan, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2015, **54**, 3107-3117.

16 (a) S. Alvarez and M. Llunell, *J. Chem. Soc., Dalton Trans.*, 2000, 3288-3303; (b) D. Casanova, P. Alemany, J. M. Bofill and S. Alvarez, *Chem. Eur. J.*, 2003, **9**, 1281-1295.

17 O. Kahn, *Molecular magnetism*, VCH, 1993.

18 (a) E. Lucaccini, L. Sorace, M. Perfetti, J.-P. Costes and R. Sessoli, *Chem. Commun.*, 2014, **50**, 1648-1651; (b) M. Perfetti, E. Lucaccini, L. Sorace, J. P. Costes and R. Sessoli, *Inorg. Chem.*, 2015, **54**, 3090-3092.

19 (a) S. M. J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L.-C. Brunel, A. L. Rheingold, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 1999, **38**, 5329-5340; (b) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341-351.

20 (a) Y.-N. Guo, G.-F. Xu, W. Wernsdorfer, L. Ungur, Y. Guo, J. Tang, H.-J. Zhang, L. F. Chibotaru and AnnieK.Powell, *J. Am. Chem. Soc.*, 2011, **133**, 11948-11951; (b) F. Pointillart, K. Bernot, S. Golhen, B. Le Guennic, T. Guizouarn, L. Ouahab and O. Cador, *Angew. Chem. Int. Ed.*, 2015, **54**, 1504-1507.

Graphical Abstract

Novel supramolecular 4f and 3d-4f grids were constructed using dihydrazone based ligands, with the 3d-4f grid represents the first example of this type and shows SMM behavior.