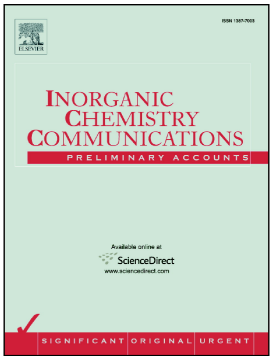

# Unique magnetic behaviour of coexistence of single ion magnet and spin crossover

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# Unique magnetic behaviour of coexistence of single ion magnet and spin crossover

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## Abstract

Herein, we report a highly rare magnetic phenomenon that is composed of both single ion magnet and spin crossover. To our knowledge, the current single ion magnet exists in a unique manner as it should be the first one only coordinated by carboxylate ligands plus water molecule.

**Keywords:** magnetic properties; single ion magnet; spin crossover; dual function

## 1. Introduction

In the light of functionality, selecting functional module for bottom-up molecule design should be one of rational choices in coordination chemistry, as this will gain more chance to maintain the functionality from the pre-designed functional module**[1-6]**.This, often, requires us to focus our attentions on some familiar and easy-preparing functional modules like that of paddle-wheel units $\{M_2(O_2C)_4\}$ (M=Cu, Ni, Zn, Co, Mo)**[7]**, trigonal $\{M_3(\mu_3\text{-}O)(O_2C)_6\}$ clusters (M=Sc, Cr, Fe, Ni, Al, In)**[8]**, 1D $\{M(O_2C)_2\}$n rods (M=Mg, Zn, Co, Ni, Fe, Cu, Mn)**[9]**, all of which contain open metal site and have been extensively utilized for constructing various metal-organic frameworks (MOFs) aiming at in the applications of gas storage, separation, heat transfer, catalysis, sensing, magnet and biomedicine. During the assembly process of functional molecules, especially different functional molecules, maintaining the predesigned functionalities for each other in the finally resulted materials is still a great challenge, as there, in nature, exists two contrary processes, isolation and coexistence of different functional modules**[10-13]**. Thereby, establishing certain balance between them will be crucial for the purpose. For example, for magnetic purpose, a large number of 3d-4f magnetic compounds have been prepared**[14-17]**. However, as we know, the famous performance for 3d metal like that of Co(II), Fe(II) should be spin crossover**[18-19]**, which is never maintained in these 3d-4f magnetic compounds.

Herein, we show how coordination competition and preference can be used to trace the balance of isolation and coexistence processes of difference functional modules and further to assembly of various functional modules in single crystal.

One effective approach of N-,O-donor mixed ligands ever have been extensively employed to produce 3d-4f magnetic compounds, mainly dependent on the coordination preference of them, where 3d metal ions prefer to attract N-donor ligands, by contrast, 4f metal ions is sensitive to O-donor ligands**[20]**. On the other hand, one key to maintain the $[CoN_6]^{2+}$ spin-crossover (SCO) function could be facile by employing two tridentate terpyridine ligands to play chelating effect on Co(II) ion**[19]**. In this regard, to isolate and coexist of both 3d SCO and 4f slow magnetism relaxation, it is proposed here that we first assembly $[Co(4\text{-}Br\text{-}PH\text{-}terpy)_2]^{2+}$ segment as cationic template and spin-crossover (SCO) functional module, then via charge balance the Dy(III)-carboxylate segment would be in situ generated and expected to make a contribution of slow magnetism relaxation. As expected, we obtained compound 1, namely

$[Co(4\text{-}Br\text{-}PH\text{-}terpy)_2][Dy(PHCOO)_4\cdot H_2O]_2$(4-Br-PH-terpy=4'-(4-bromophenyl)-2,2':6',2"-terpyridine) and found that the 3d SCO and 4f slow magnetism relaxation can be not only well maintained but also coexist.

## 2. Experimental detail

### 2.1 Materials and General Methods

Reagents and solvents were commercially available (Alfa) and were used without further purification. X-ray powder diffraction were collected by a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kα, (λ = 1.5406Å). The simulated powder patterns were calculated by Mercury 1.4 which can be obtained freely from the Cambridge Crystallographic Data Centre (CCDC). The purity of the bulk samples were determined by element analysis (EA) and powder X-ray diffraction (PXRD) researches.

### 2.2 The synthesis of 4-Br-PH-terpy

The synthsis of this ligand is according to the reported method**[21]**. 4.49 mL (0.04 mol) 2-acetylpyridine, 2.81 g (0.02 mol) 4-bromobenzaldehyde were dissolved in 100 mL ethanol solution of KOH 3.08 g(0.055 mol) under stirring. Then 58 mL strong ammonia solution was added, the initially yellow solution immediately turned red-brown. The mixture was stirred for 24 h at room temperature, and the resulting yellow solid was collected by filtration subsequently washed with ethanol and water. The compound was purified by dissolving it in methanol, and slowly removing the methanol, colorless crystals suitable for X-ray diffraction were obtained. Yield 2.8 g (36%). The single crystal X-ray diffraction studies reveal that it was the organic molecule of 4-Br-PH-terpy. Elemental analysis (%) for 4-Br-PH-terpy ($C_{21}H_{14}N_3Br$): Calc. C/64.96; H/3.63; N/10.82; Exp.: C/65.12; H/3.65; N/10.86.

### 2.3 The synthesis of $[Co(4\text{-}Br\text{-}PH\text{-}terpy)_2][Dy(PHCOO)_4{\cdot}H_2O]_2$.

A mixture of $CoCl_2{\bullet}6H_2O$ 11.9mg (0.05 mmol) and 4'-(4-bromo phenyl)-2,2':6',2''-terpyridine 40.6mg (0.1 mmol) were added in 10 mL water, stirring for ten minutes after dissolving completely, then transferred to 25ml Teflon-lined stainless steel vessel. Subsequently $Dy_2O$ 318.65mg (0.05 mmol), PHCOOH 36mg (0.4 mmol) and $Na_2CO_3$ 21.2mg (0.2 mmol) were added. Finally, the mixture was heated at 180℃ for three days, after which the reaction system was cooled to room temperature. Red purple stick crystals were obtained. Yield 88% based on Co. Elemental analysis (%): Calc.: C/54.36, H/3.35, N/3.88. Exp.: C/54.44, H/3.25, N/3.75. The Y(III) replaced compound is synthesized as that used in synthesis of corresponding Dy(III) compound, except for the replacement of $Dy_2O_3$ by equal $Y_2O_3$. Yield 85% based on Co. Elemental analysis (%): Calc.: C/58.32, H/3.59, N/4.16. Found: C/58.74, H/3.54, N/4.15.

### 2.4 X-ray crystal structure determination.

Unit cell measurements and intensity data were collected at room temperature on a Bruker-AXS SMART Breeze CCD diffractometer using graphite monochromated MoKα radiation ($\lambda$=0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXL–97 program suite**[22]**. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

The X-ray crystallographic coordinates for structures reported in this study are deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 1007379 and 1402732 for compounds 1, and 1-Y. These data can be obtained free of charge (http://www.ccdc.cam.ac.uk/ data_request/cif ).

## 3. Results and Discussion

### 3.1 Structural descriptions.

Single X-ray diffraction reveals that 1 crystallizes in the monoclinic $P2_1/c$ space group and a ionic structure composed of one cationic [Co(4-Br-PH-terpy)$_2$]$^{2+}$ segment and two anionic [Dy(PHCOO)$_4$·H$_2$O]$^-$ segments (Fig. 1a). The asymmetric unit contains two crystallography-independent Dy(III) sites and one crystallography-independent Co(II) site. Both Dy1 and Dy2 are nine-coordinated by four chelated PHCOO$^-$ ligands plus one water molecules (O18 for Dy1 and O9 for Dy2), creating a tri-capped triprism, where for Dy1, O1, O2, O6, O4, O7, O18 atoms made the triprism and O3, O5, O8 act as capped atom, for Dy2, the corresponding is O9, O10, O12, O15, O16, O17 atoms and O11, O13, O14 (Fig. 1b). Notably, due to all PHCOO$^-$ ligands are chelate towards one Dy(III) site, then resulting in the single Dy(III) ion. To our knowledge, the combination of Dy(III) and PHCOO$^-$ ligands often produce 1D compounds, and only under the assistance of N-donor ligands, it could produce multi-nuclear compounds.1**[23]**, Thereby, the present structure of single Dy(III) ion is extremely rare, and maybe, providing a distinct type for Dy(III) single ion magnet constructed by PHCOO$^-$ ligands. The Co(II) site maintains the expected CoN6 coordination surrounding and shows a disordered octahedral geometry, where N1, N2, N3,N5 atoms form an irregular equatorial plane and N4, N6 offset from the axis with the angle of N4-Co1-N6/160.4° (Fig. 1c). Moreover, the overall 4-Br-PH-terpy ligand is not coplanar with dihedral angel of ca. 33.5° and 36.2° between phenyl and terpyridine. Furthermore, the hydrogen bond interactions between two [Dy(PHCOO)$_4$·H$_2$O]$^-$ units can create a supramolecular dinuclear structure (Fig. 1d).

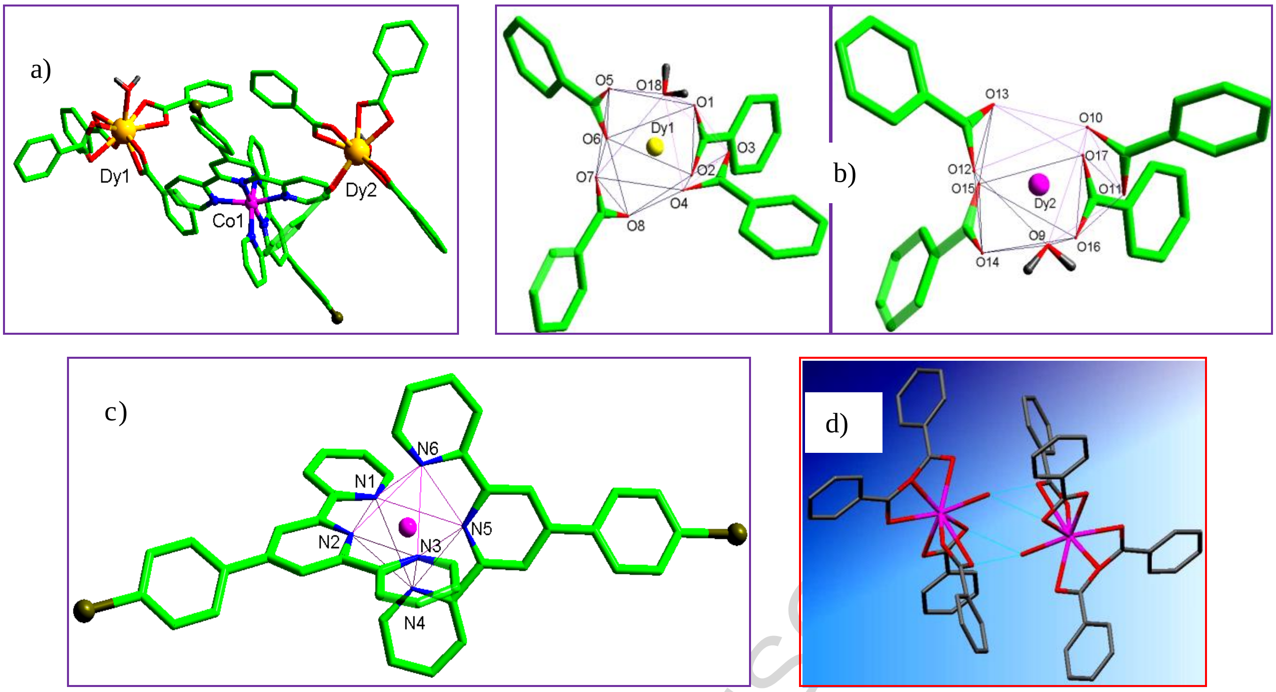

**Fig. 1.** The structure of 1: a) the coordination surrounding of Co(II) and Dy(III) ions; b) the geometry of Dy(III) ions; c) the geometry of Co(II) ion; d) the hydrogen bonds between two $[Dy(PHCOO)_4 \cdot H_2O]^-$ units.

To facilitate the next magnetic investigation, we also prepared Y(III)-replaced compound. However, interestingly, the Y(III)-replaced compound give the same space group and comparable parameter of unit cell as that observed in Dy(III) compound, but the resulted structure shows some difference in the aspect of anionic segment (Fig. 1a). As shown in Fig. 2a, we can find that Y1 site reserves the coordination and geometry feature like that of Dy1 site, whereas Y2 site becomes eight-coordinated finished only by $PHCOO^-$ ligands, giving a geometry of bi-capped triprism. This change directly results in the formation of binuclear structure for Y2 and Y2A (A: 1-x, 1-y, -z) and the coordination mode of two $PHCOO^-$ ligands become bridging.

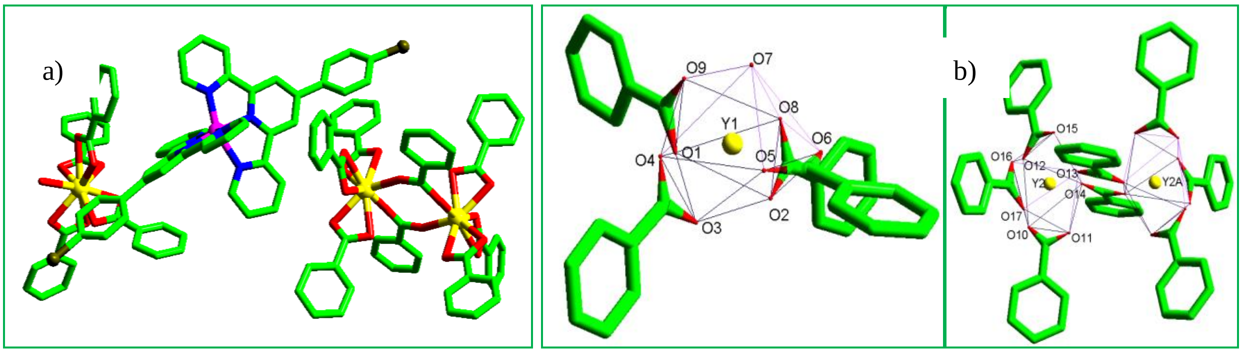

**Fig. 2.** The structure of Y(III) replaced compound: a) the coordination surrounding of Co(II) and Y(III) ions; b) the geometry of Y(III) ions.

### 3.2 Characterization of XRD.

It can be seen from the XRD image that the characteristic diffraction peaks of the materials we synthesized are consistent with the simulated diffraction peaks. There are no other hybrid peaks, which proves that the materials have been successfully synthesized and the purity is very high.

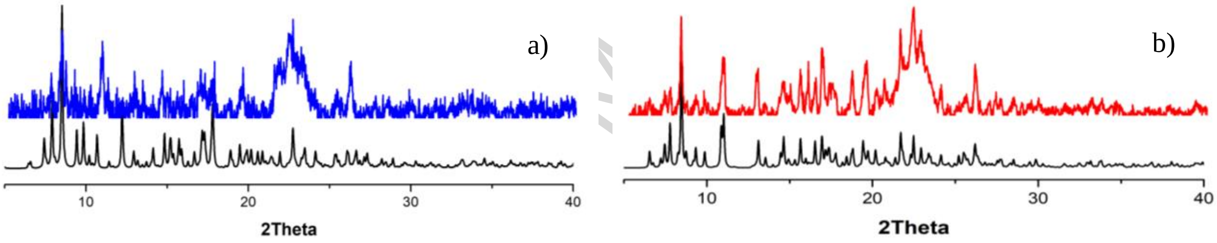

**Fig. 3.** a)The simulated XRD patterns/black from the single crystal data and the XRD patterns of the as-synthesized bulk crystals of **1**/blue; b)The simulated XRD patterns/black from the single crystal data and the XRD patterns of the as-synthesized bulk crystals of Y(III) replaced compound/red.

### 3.3 Magnetic Properties.

The magnetic properties of 1 is measured at 1000 Oe and 1.8-300K in the heating and cooling mode, giving no detectable hysteretic phenomenon (Fig. 4). The $\chi$MT value at 300K is 30.92 cm$^3$mol$^{-1}$K, bigger than the theoretical value (30.12 cm$^3$mol$^{-1}$K) of the sum (per Dy$_2$Co), mainly due to the spin-orbit coupling that often encountered for Dy(III) ions and high-spin octahedral Co(II) ions**[24]**. The low-temperature $\chi$MT products show rapid decrease as a result of significant magnetic anisotropy and/or anti-ferromagnetic interactions between Dy(III) ions, whereas the slow decrease below room temperature is derived from the depopulation of the spin-orbit coupling of octahedral Co(II) ion and/or Stark sublevels of Dy(III) ions**[24]**. Seen form these results, we can confirm that the Co(II) ions in 1 at room temperature is high-spin, and however, could not further confirm whether it is low-spin for Co(II) ions at low temperature, due to the presence of significant magnetic anisotropy for Dy(III) ions at low temperature. By contrast, this can be further attested by magnetic saturation at 2K. As shown in Fig. 4 (inset), the M value of 11.10 Nβ at 70000 Oe is close to the value of 11 of the sum (per $Dy_2Co$) with Co(II) in low-spin state (S=1/2), and smaller than the value of 13 of the sum (per $Dy_2Co$) with Co(II) in high-spin state (S=3/2), implying low-spin state for Co(II) ions at 2K. In this regard, and combining with the above discussion like that of high-spin state of Co(II) ions at room temperature, we can conclude spin crossover of Co(II) ions in 1.

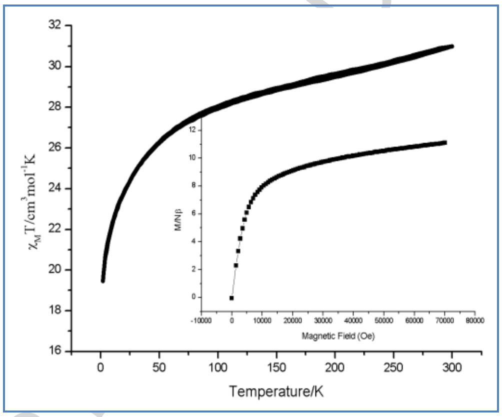

**Fig. 4.** The χMT vs. T plot of 1 and inset is the M vs. H plot of 1 at 2K.

Furthermore, to disclose molecule magnet property derived from Dy(III) ions, temperature-dependent ac magnetic susceptibility was employed. As shown in Fig. 5, it shows temperature-dependent out-of-phase (χ´´) component under zero dc field below 10K, suggesting the slow relaxation of the magnetization in 1**[25]**. But, the lack of peaks in the χ´´ signal prevents us to evaluate the relaxation energy barrier via the conventional Arrhenius plot method, mainly due to the existence of quantum tunnelling of the magnetization (QTM) at low temperature and zero dc field**[25]**. Then, another method, recently developed by Bartolomé el al, is applied, giving $U_{eff}=1.0\pm0.2$ K, $\tau_0=(3.97\pm0.2)\times10^{-6}$ s (Fig. 6)**[26]**. This suggests very small relaxation energy barrier due to strong quantum tunnelling.

Seen from the above results, we can conclude that compound 1 perform both spin crossover and single ion magnet. To further disclose the spin-crossover behaviour, the magnetic properties of Y(III) replaced compound was measured at 1000 Oe and 1.8-300K in the heating and cooling mode (Fig. 7). Similarly, no detectable hysteretic phenomenon was observed. Notably, the χMT value of 1.6 $cm^3mol^{-1}K$ at 300K is less than the expected value of 1.875 $cm^3mol^{-1}K$ for high-spin Co(II) ion, most likely, due to the onset of spin crossover at this temperature**[27]**. Below room temperature, the χMT value first decreases sharply until 150 K, and then gradually until 2K, giving the value of 0.38 $cm^3mol^{-1}K$ at 2K, suggesting a gradual, complete spin transitions from S=3/2 to S=1/2, with decreasing temperature. This is further convinced by the plots of magnetic saturation, which gives the saturation value of 0.91 Nβ at 70000 Oe and 2K, very close to the expected value of 1 Nβ for low-spin Co(II) ion.

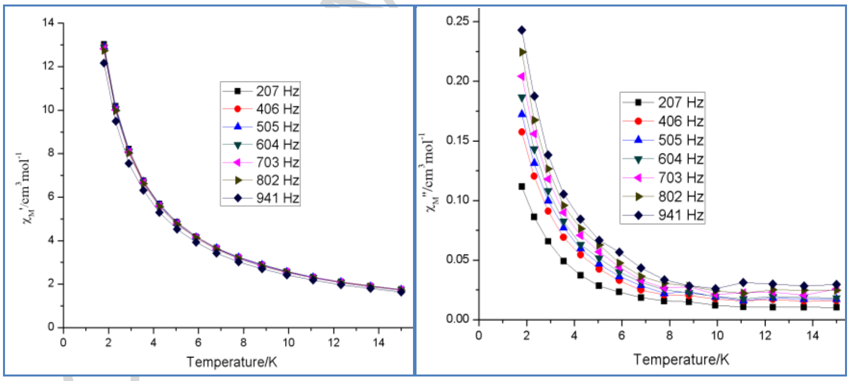

**Fig. 5.** Temperature dependence of the in-phase and out-of-phase (χ′′) components of the ac magnetic susceptibility data for 1 at ac=3 Oe, dc=0 Oe.

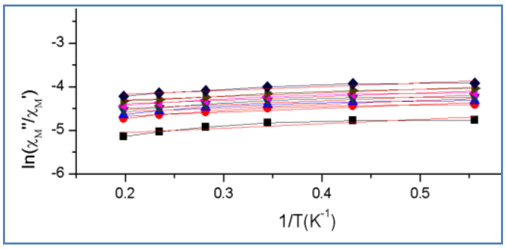

**Fig. 6.** Natural logarithm of the ratio of χ′′ to χ′ vs. 1/T for compound 1 derived from the above ac magnetic susceptibility data. The solid red line corresponds to a linear fit to the data.

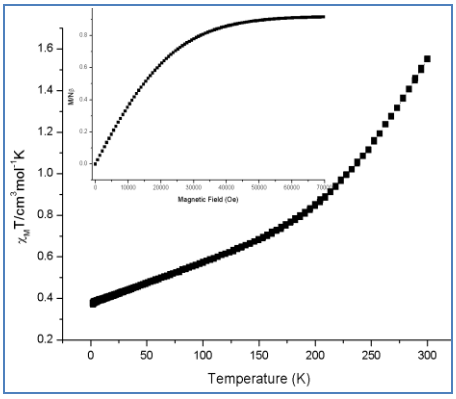

**Fig. 7.** The χMT vs. T plot of 1-Y and inset is the M vs. H plot of Y(III) replaced compound at 2K.

## Conclusions

In conclusion, taking advantage of coordination competition and preference, we have successfully isolated one novel [3d][4f] ionic compounds and achieved the maintenance, isolation, and coexistence of various functional modules. Corresponding to this is that the results provide a deep insight for understanding the coordination chemistry of 3d and 4f metal ions and a useful model for understanding the bottom-up assembly process of modules. To some extent, the synthesis approach used here would be an effective pathway towards the exploration of compounds with the coexistence of various magnetic functions. The results also suggest the diamagnetic ion replaced method is very effective to characterize this special magnetic phenomenon.

## Acknowledgements

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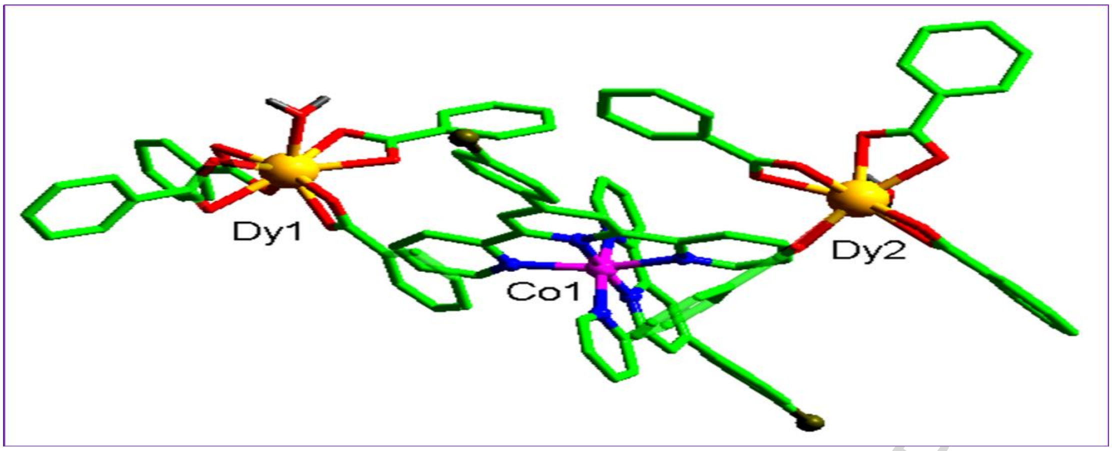

Graphical abstract

Highlights

In this work we launch a method to trace the balance of coordination competition and preference for maintenance, isolation, and coexistence of different functional modules.

Moreover, the current research results also show that this method can produce unique Dy(III)-carboxylate unit that could not be accessed via common method, thus generating multi-magnetic materials like that of SIM (single ion magnet)+SCO (spin crossover).