BEST PERFORMING PENTAGONAL BIPYRAMIDAL AND SANDWICHED Dy(III) BASED SINGLE-ION MAGNETS

Abstract

The field of single-molecular magnetism has received huge attention as they can be potential applicants in data storage devices, quantum computers etc. Initially, polynuclear clusters based on anisotropic paramagnetic centers are on focus which slowly shifted towards mononuclear complexes, especially towards trivalent lanthanides, taking the advantages of large inherent magnetic anisotropy associated with them. In this chapter, the best performing single-ion magnets (SIMs) with popular pentagonal bipyramidal and sandwiched-shaped ligand field are discussed along with the basics of the single-molecule magnets (SMMs).

Keywords: Molecular magnets, magnetic anisotropy, coordination compounds, ligand field.

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I. INTRODUCTION

We are living in an era of technology, highly dependent on digital data. In the olden days, data is being stored in the form of printed books, documents, photos etc. However, the advancement of the technology, most of the information are being stored in digital form. “Data is the new oil” is possibly one of the most popular catchphrases which highlights the importance of data in this era. This is reflected on the exponential increase of digital data every year. Nearly 44 zettabyte of data was generated in 2020 itself, contributed through different sources such as social media sites, financial institutions, medical facilities, shopping platforms, automakers, and many other activities online. It has been expected that the amount of data generated each day will reach 463 exabytes globally, by 2025. The first-generation data storage devices are floppy disk, which could store small data in electronic form, despite of its bigger size. With the advancement of this technology, different technically advanced data storage devices have been designed and now a days we can store the data of 1TB in a small device, as small as a cap of a pen. The data are being saved in binary language (1 and 0) where nano sized ferromagnetic and ferrimagnetic alloys are used in generating magnetic domain. These compounds can save the data in below Curie temperature (T_c) by holding their magnetisation. In case of common paramagnets, the spins are randomly oriented due to the thermal energy. But on the application of a suitable external magnetic field, these spins can be oriented into one particular direction. On removing the external magnetic field, these aligned spins require energy to get randomised. If the temperature is low enough, these spins doesn’t have enough thermal energy to flip. The temperature up to which the magnetisation can be hold is called blocking temperature (T_B). Thus, below this temperature, the system can behave as magnet. However, above T_B, the system has enough thermal energy to flip the spin and hence the magnetisation of spin ceases. The energy requires to flip the spin from one orientation (up) to opposite orientation (down) is termed as energy of spin reversal, U_{eff}. This up(1)-down(0) strategy is used to save the data in an data storage device. The amount of data that can be stored within a particular space depends on the size of the nanoparticles. It is to be noted that apart from size of the data storage capacity, other important factors such as the anisotropy, activation energy and blocking temperature associated with the device also depend on size of the nanoparticles. On reducing the size of the nanoparticles below a range, the memory effect of the system collapse. Thus, designing a high-density data storage device using nano sized samples cannot be effective enough after a certain limit. This problem can be overcome if the dimension of the binary language (1 and 0) becomes smaller than conventional nanomaterials.

II. SINGLE-MOLECULE MAGNETISM

In 1993, Sessoli and co-workers have reported that a dodecanuclear mixed-valent (Mn^{III}/Mn^{IV}) cluster, $[Mn^{III}_8Mn^{IV}_4O_{12}(OAc)_{16}(H_2O)_4]$, can hold its magnetisation below a certain temperature.[1] This work opened up a new research field known as single-molecule magnetism, which deals with the designing of molecules that can behave as magnets which can be potential applicants in designing high-density data storage device. These molecules have much smaller dimension (few angstroms) than nano-sized systems, reducing the size of the data storage device to large extent.

Thus, *single-molecule magnets* (SMMs) are molecules that can retain their magnetisation for a longer period of time in absence of any external magnetic field below the blocking temperature. To be an SMM, the molecule must possess strong magnetic anisotropy as well as a bistable spin state.[2-5] Such molecules can be potential applicants in (a) designing high-density data storage devices[6-8]**,** (b) molecular spintronics [9-11]**,** (c) quantum computing devices[12-15] and so on.

III. DEVELOPMENT OF SMMS

After the discovery of the slow relaxation of magnetisation behaviour of Mn_{12} clusters, numerous numbers of transition metal-based polynuclear clusters are being reported, with special emphasis on Mn^{3+} ion, as it possesses considerable amount of magnetic anisotropy originated from Jahn-Teller distortion.[16-19] The magnetic relaxations of transition metal based SMMs arise from large spin ground state (S) and uniaxial magnetic anisotropy or zero field splitting parameters (D). The energy barrier of spin reversal (U_{eff}) which separates the two spin states ($+M_s$ and $-M_s$) can described as $U_{\mathrm{eff}} = |D| \cdot S^2$ (for integer spin) and $U_{\mathrm{eff}} = |D| \cdot (S^2 - \frac{1}{4})$ (for half integer spin).[20-23] From the primary observation it can be considered that increasing S can lead to very high Ueff for any cluster. Thus, initial attempts in designing high performing SMMs were concentrated on increasing S by the accumulation of paramagnetic metal ions using suitable bridging ligands producing large sized polynuclear clusters.[17, 18, 24, 25] But, the energy barriers of such clusters are not high as expected, some values are even surprisingly dwarf. There are several reasons associated with such observations, such as the magnetic anisotropy of the polynuclear cluster is highly sensitive to the alignment of the individual local anisotropy axes. The anisotropy can be drastically reduced if the local anisotropy axes of each of the ion centres are misaligned.[26] Apart from the alignment, without suitable magnetic interactions among the paramagnetic centres can lead to diminishing U_{eff}, for instance, the ferromagnetic coupling among the metals centres is favourable as it increases S, while antiferromagnetic interactions cancel the spins and hence it is undesirable. The antiferromagnetic coupling among spin centres are found to be more common in polynuclear clusters as compared to ferromagnetic interactions, diminishing the chance of producing clusters with higher U_{eff} values.[27-29] Later it has been observed that increasing S just by accumulating paramagnetic centres also results in very small values of D, since S and D are inversely proportional to each other.[17, 30] For instance, an Mn_{19} cluster consisting of twelve Mn(III) and seven Mn(II) ions has very large ground spin state with S = 83/2, but has no slow relaxation of magnetisation asD is negligibly small. On the other hand, an Mn_6 cluster with six Mn(III) ions with ground spin state S=12, has significant magnetic anisotropy with $D = -0.43\ \mathrm{cm}^{-1}$.[31] Adding all these factors, it has been observed that accumulation of paramagnetic ions is not necessarily productive enough.

1. **Advances of Single-Ion Magnets (SIMs). :** As the clusters are not effective enough in the field of molecular magnetism in achieving higher U_{eff} and significant T_B, gradually field is shifted towards mononuclear complexes with the central metal ion has significant inherent magnetic anisotropy.[26] In 2003, Ishikawa and co-workers discovered that two

double-decker mononuclear complexes based on Tb(III) and Dy(III) ions, $[Pc_2Ln][TBA]$ (where Pc^{2-} is the dianion of phthalocyanine and $TBA^+ = N(C_4H_9)_4{}^+$) can hold their magnetisations.[32] This observation shows that even single ion based complexes can hold their magnetisations. Such mononuclear molecules which can hold their magnetisation in absence of an external magnetic field for a longer period of time are known as *single-ion magnets (SIMs)*. After this observation, the field of molecular magnetism has gradually shifted its attention from polynuclear clusters to the mononuclear complexes. With the advancement of this field, it has been observed that mononuclear complexes are better candidate over polynuclear molecules in achieving higher barrier height and blocking temperature.[33, 34]

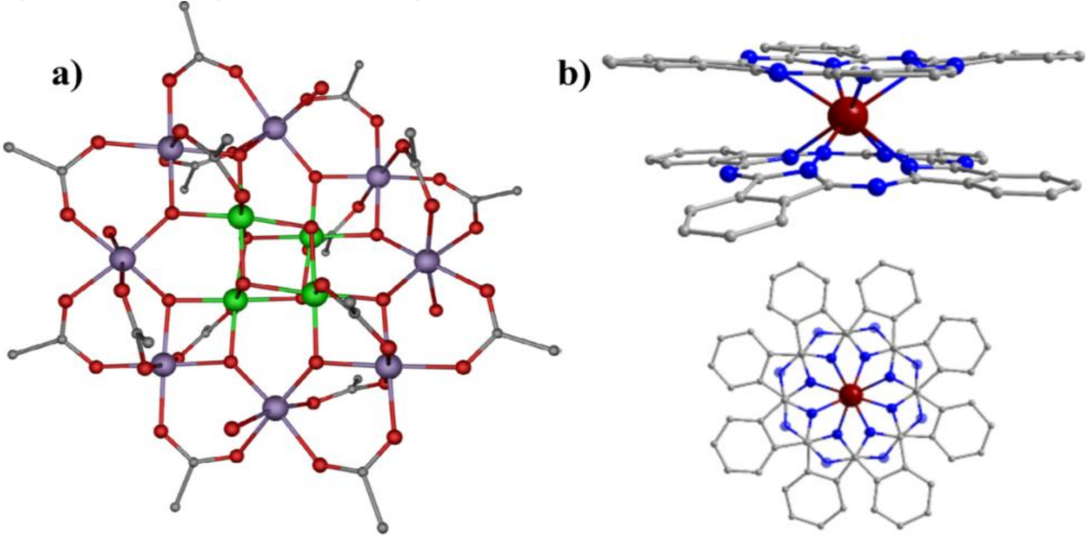

Figure 1: (a) Structure of dodecanuclear mixed valent Mn^{III}/Mn^{IV} cluster, which is consists of four Mn^{IV} centres (shown in green) and eight Mn^{III} centres (shown in purple).[1] (b) Structure of $[Pc_2Ln]^-$ ion, Ln: Tb(III) and Dy(III), where two Pc^{2-} ligands sandwiches the Ln(III) centre.[32]

The recent investigations show that SIMs based on lanthanide(III) ions, especially Dy^{III}, and in some special cases of Co(II) ions, possess higher barrier height, U_{eff} and and high blocking temperature, T_B as compared to other less anisotropic transition metal ions based SIMs.

In the field of molecular magnetism, Ln(III) ions are occupying special position due to their intrinsic single-ion anisotropy, considerable unquenched orbital angular momentum and large spin–orbit coupling in the ground state.[35, 36] The intrinsic single-ion anisotropy originates from the high anisotropic electronic charge distribution of 4f orbitals.

2. **Importance of a suitable ligand field:** As the 4f electrons are buried inside in the lanthanide ions, the crystal field splitting (CFS) in Ln(III) ions is much weaker than that in transition metal ions. This eventually leads to weaker interaction of the ligand field (LF) with the 4f electrons. Although the CFS in Ln(III) ions is small, the local symmetry around the metal centre plays vibrant rule on the single-ion magnetic behaviour of any molecule. J. Long and co-workers have demonstrated a strategy in designing an

appropriate ligand field around a given Ln(III) ion to enhance the anisotropy of the ion.[37] They explained that depending on the shape of 4f electron density, the ligand field should be designed. The overall shape of free-ion electron density in case of Ln(III) ions is either oblate (for Ce^{III}, Pr^{III}, Nd^{III}, Tb^{III}, Dy^{III}, and Ho^{III}) or prolate (for Pm^{III}, Sm^{III}, Er^{III}, Tm^{III}, and Yb^{III}). The intrinsic magnetic anisotropy associated with these ions can be enhanced by placing them in a suitable ligand field. The anisotropy of an oblate ion can be maximized by placing the ion in an axially stressed ligand field, i.e., in a field for which the electron density of the ligand is concentrated above and below the equatorial plane (xy plane). at this type of crystal field, the repulsion between the ligand and 4f electron charge cloud is minimum and hence the spin states with higher $+m_J$ and $-m_J$ values will be stabilized to highest extend, while smaller m_J states will have higher energy as the 4f electron cloud has highest repulsive interaction with the ligands. Alternatively, an equatorially stressed ligand field is the perfect choice for prolate shaped ions. Equatorially stressed implies a ligand field having strong equatorial ligands and weak/no axial ligand. This strategy of designing a suitable ligand field is found to be highly fruitful in designing single-ion magnets with high barrier height and blocking temperature from Ln(III) ions.

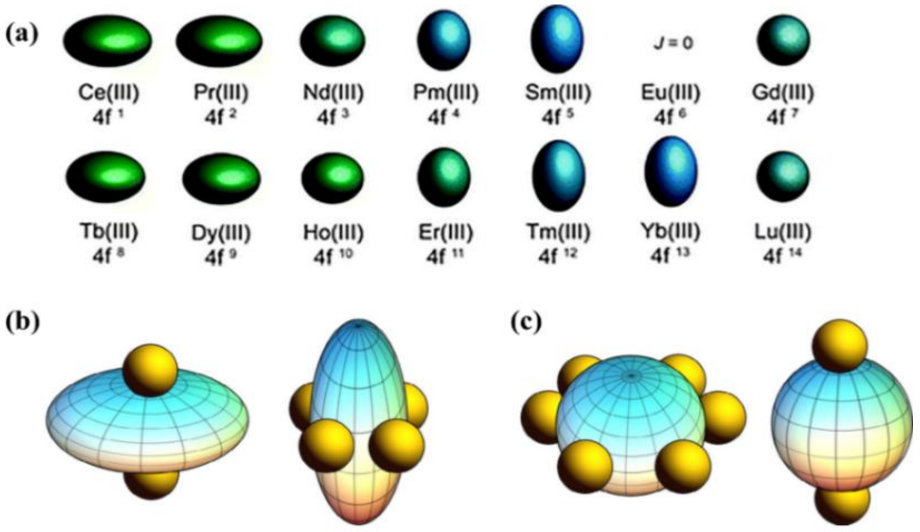

Figure 2: (a) Overall shape of free-ion electron density for Ln(III) ions; oblate, prolate and isotropic shaped ions are shown in different colours. Obtained from reference [37] (b-c) Pictorial representation of ligand field *w.r.t.* oblate and prolate Ln(III) ions to (b) enhance and (c) quench the magnetic anisotropy.

Different computational studies predict that the barrier height of spin reversal can be maximized for one or two coordinated perfectly linear Ln(III) based complexes. The U_{eff} can reach as high as 3000 K (figure 3a).[22, 38-42] It has also been suggested that the relaxation behaviour is highly sensitive towards different minute factors such as bond angles, metal-ligand distances etc.[39, 40] For example, for a two cordianted Dy(III) complex DyE_2, if the ligand field is perfectly linear (< E-Dy-E=180^o), the U_{eff} is estimated to be even higher than 2200 cm^{-1} which start reducing on deviating from the linearity, till as low as 100 cm^{-1} when the angle reduced to 90^o (figure 3b and 3c).[40]

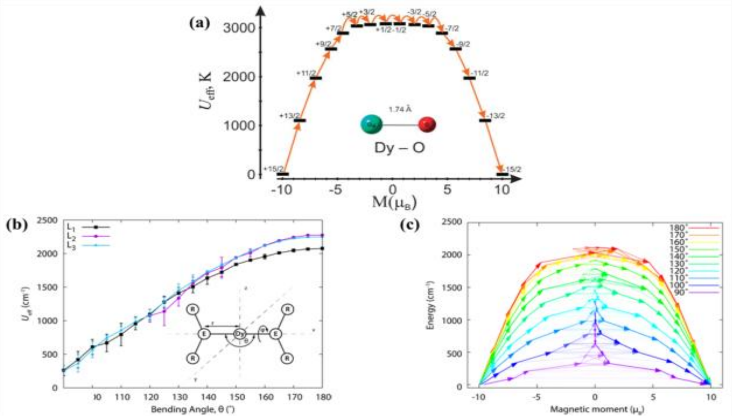

Figure 3: (a) Barrier for spin reversal in one coordinated $[DyO]^+$ ion at equilibrium geometry, obtained from reference [39]. (b) The variation of U_{eff} for a model two coordinated complex, $(DyER_2)_2$ as a function of the bending angle (<E-Dy-E) θ and the respective energy levels are shown in figure (c). Obtained from reference [40].

Unfortunately, due to the larger size of the Ln(III) ions, synthesis of such low coordinated complexes are near to impossible. A number of attempts have been carried out to overcome this problem, mainly focusing on designing pseudo linear metallocene complexes.[43-49] Other than metallocene, when Ln(III) ions are present in any ligand field with higher order rotational symmetry, such as square antiprismatic (D_{4d}) [50, 51], pentagonal bipyramidal (D_{5h}) [52-59], hexagonal bipyramidal (D_{6h})[60, 61], they also behave as SIMs with significant U_{eff} and T_B.[62-68] Thus, construction of a compatible ligand field around the metal centre is most crucial step in designing SIMs.

3. **Mechanism of relaxation of magnetisation in smm**: In absence of an external magnetic field, both the ground state spin sublevels, *i.e.* $+m_s$ and $-m_s$, are equally populated as they are degenerate. On application of an external magnetic field, one of the two states gets stabilized and the other one gets destabilized. At this point all the spin centres occupy the stable spin state (say $-m_s$), aligning in one direction. Once the field is switched off, the spin states are degenerate again, but the $-m_s$ state is only populated, while $+m_s$ is still vacant. The spins have to get enough thermal energy to flip into the opposite spin. The thermal process of relaxation is popularly known as Orbach process. Apart from Orbach process, other relaxation processes such as Raman, direct and quantum tunnelling of magnetisation (QTM) are also present in the overall relaxation dynamics of SIMs. Depending on the metal ion, ligand field, and even external stimuli such as temperature, pressure, light etc., the weightage of the different relaxation processes varies. For example, Orbach process occurs at high temperature region, Raman and direct process are strong at moderate temperature, whereas, QTM occurs at low temperature region. It is worthwhile to mention that it is not necessary that each of these relaxation processes should be present in the relaxation dynamics. Except QTM, all other relaxation processes are function of temperature. The temperature dependence of relaxation time can be demonstrated as follows:

$$\tau^{-1} = \tau^{-1}_{QTM} + AT + CT^n + \tau_0^{-1}\exp(-U_{eff}/k_BT) \cdots\cdots\cdots\cdots \text{Equation 1}$$

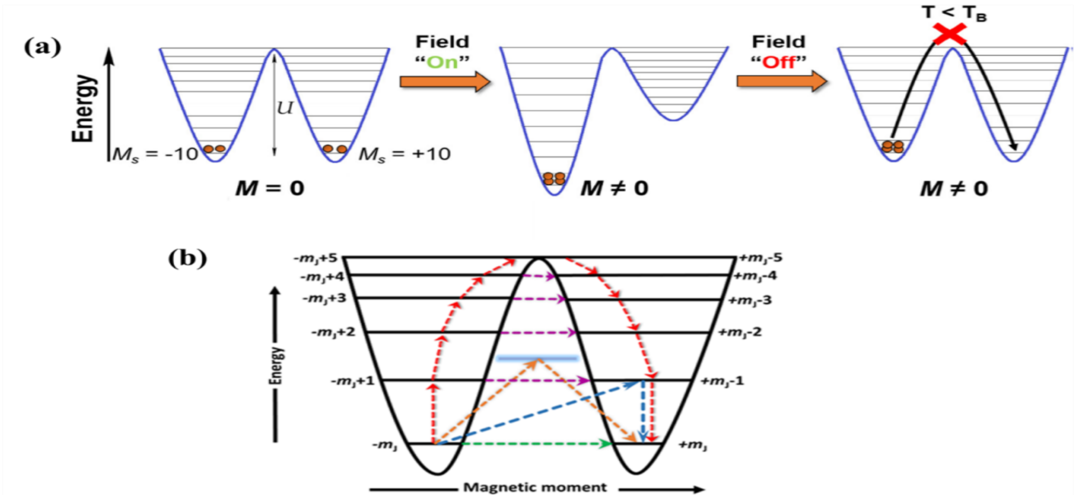

Figure 4: (a) Representation of the spin sublevels for molecules with bistable spin state in absence of an external magnetic field (left); on the application of an external magnetic field, -m$_s$ states are stabilized and all the molecules occupy this spin state (middle); once the field is switched off, the +m$_s$ and -m$_s$ states are degenerate and molecules have to possess U_{eff} amount of energy to relax their spin state. The figure is obtained from reference [69]. (b) Various possible pathways associated to relaxation of magnetisation for the magnetised molecules. The green arrow represents the ground state quantum tunnelling of magnetisation occurs in the ground state $+m_J$/$-m_J$ sublevels, while purple arrows represent QTM occurring at higher m_J sublevels known as thermally assisted quantum tunnelling of magnetisation (TA-QTM). The orange arrows represent Raman processes that occur via the formation of a virtual excited m_J state (showing in light blue). Thus, Raman process is a two-phonon phenomenon. The red and blue arrows represent the Orbach process at different energy sublevels. The figure is obtained from reference [70].

where, the first term ($\tau^{-1}{}_{QTM}$) represents the relaxation via quantum tunnelling of magnetization, while the second (AT) and third term (CT^n) represent the relaxation via direct and Raman process. The fourth term ($\tau_0^{-1}\exp(-U_{eff}/k_BT)$) in equation 1 represents the Orbach process, which determines the barrier height of spin reversal associated with a molecule, from linear fit to the high temperature region of lnτ vs 1/T plot. Different possible relaxation processes are shown in figure 4.

4. **Axially stressed ligand field derived dy(iii) based sims:** Being an oblate, axially stressed ligand field is suitable for Dy(III) ion, specially, two coordinated linear Dy(III) complex can be the best choice. But, due to the larger ionic radii of all lanthanide(III) ions, synthesis of such low-coordinated complex is very difficult. Thus, an alternative strategy has been designed, by designing ligand field where strong donor atoms are placed in axial position (e.g. alkoxide, aryl oxide, phosphine oxide, carboxylate, cyclopentadienyl etc.) and weak donor ligands (e.g. water, pyridine etc.) are in equatorial positions. Such ligand field is called axially stressed ligand field, where the electron cloud of Dy(III) ion is least interacted with the ligand and hence the m_J states are highly stabilized producing higher energy barrier.

Ln(III) ions are oxophilic in nature, hence alkoxide (RO^-) and aryloxides (ArO^-) can behave as strong field ligand. Y. Z. Zheng and co-workers have reported a D_{5h}

molecule where two ^{t}BuO$^-$ (*tert*-butoxide ion) ligand coordinate to the Dy(III) centre through axial position, while five weakly coordinating pyridine ligands are present in the equatorial positions, producing $[Dy(O^tBu)_2(pyridine)_5][BPh_4]$ (**1**). The axial Dy-O bonds are (2.110 and 2.114 Å) much shorter than the equatorial Dy-N bonds (2.534-2.580 Å) and the O-Dy-O angle is nearly linear (178.91^o), which implies that Dy(III) ion is in an axially stressed ligand field. Alternating current susceptibility studies reveals that it possess χ" peak abpve 100 K, in absence of any external magnetic field. The energy barrier, U_{eff}, is estimated by fitting the lnτ vs 1/T plot at the higher temperature region using Arrhenius equation $[\tau^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/k_BT)]$ yielding U_{eff} = 1815 K (1261 cm^{-1}) and $\tau_0 = 1.170 \times 10^{-12}$ s. This is consistent with the computationally predicted U_{eff} =1755 K (1220 cm^{-1}). This value was the largest U_{eff} reported. The blocking temperature (T_B) was estimated by performing zero field cooled- field cooled experiment (ZFC-FC), obtained as T_B=14 K.

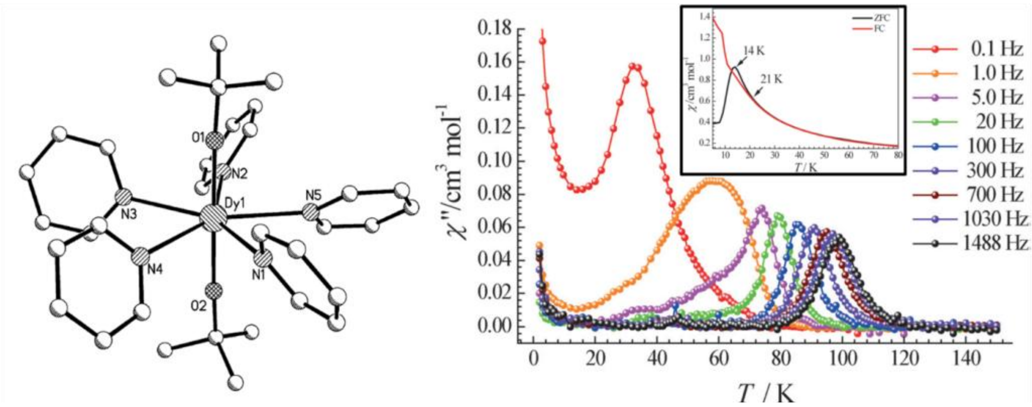

Figure 5: Molecular structure of the cationic part of 1 *i.e.* $[Dy(O^tBu)_2(pyridine)_5]$ $[BPh_4]$ (left). Its out-of-phase magnetic susceptibility in absence of any external magnetic field (right) and the ZFC-FC plot is shown in the inset. Figures are taken from reference [53]. D_{5h} symmetric P=O ligand-based SIMs.

P=O donor ligands are also popular in designing axially stressed D_{5h} symmetric Dy(III) based single-ion magnets. The advantage of these complexes over alkoxides is the stability of these complexes; these complexes are highly air stable due to stability of the Dy-O and P=O bonds. Thus, these molecules can be potential single-ion magnets for practical use. The extent of ligation of these P=O donor ligands is dependent on the three -R groups attached to the P atom: An electron donating -R group attached to the P atom increases the electron density on the P and hence O atom, enhancing the ligation capability towards the Dy(III) ion. Alternatively, an electron withdrawing -R group reduces the ligation capability. This imply that by incorporating proper substituents, the ligand field around the Dy(III) centre can be significantly modified. As Dy(III) ion is oblate shaped, a D_{5h} symmetric ligand field comprises of two R_3P=O axial ligands along with five weak donor ligands (e.g. H_2O) in the equatorial plane is suitable for it.

Murugavel and co-workers have reported first D_{5h} symmetric P=O based Dy(III) SIM, $[DyL_2(H_2O)_5]\cdot I_3$, (**2**) L: ^{t}BuPO(NH^{i}Pr)$_2$, where Dy(III) ion is in an axially stressed ligand field. It shows slow relaxation of magnetisation upto nearly 40 K in absence of any external magnetic field. Best fitting of magnetic relaxation time (τ) using Arrhenius equation estimates the energy barrier of spin reversal as high as 651.0 K and the pre-exponential factor, $\tau_0 = 5.63 \times 10^{-12}$ s. The overall magnetisation relaxation dynamics is dominated by Orbach and Raman process. Hysteresis and ZFC-FC measurements were carried out on this compound to determine the blocking temperature (T_B). There is opening up of the hysteresis loop at 2 K with large coercivity of 1.5 T at a field sweep rate of 180 Oe/s. The opening of the loop can be observed up to 12 K. This value is further supported by the zero-field-cooled and field-cooled experiment, with a deviation of variable temperature ZFC magnetisation data from FC data at 12 K. However, the Er counterpart (**2Er**) doesn’t show any significant SIM behaviour in absence of an external magnetic field. In presence of an external field of 2000 Oe, though it behave as SIM, the U_{eff} value is very small (44 K). This is understandable as the axially stressed ligand field is unfavourable for prolate shaped ions.

For the last few years, a number of Dy(III) based D_{5h} symmetric single ion magnets are reported derived from P=O donor ligands. When the -R groups are changed, the slow relaxation behaviour also changes to different degree.[71] For example, when Cy_3PO is used as axial ligands in $[Dy(OPCy_3)_2(H_2O)_5]\cdot Br_3$, the barrier height is estimated as 543 K and T_B= 20 K.[52] The U_{eff} value is slightly reduced to 508 K and T_B=19 K when two of the three cyclohexyl groups are replaced by two phenyl groups.[72] The type of ions present in the lattice also places significant rules in the slow relaxation behaviour of such complexes. P=O donor ligand based D_{5h} symmetric single-ion magnets are not restricted only to Dy(III) ion, but this ligand field is extended to other oblate shaped Ln(III) ions such as Nd(III), Ho(III) etc. These ions also require strong axial ligands and weak or no equatorial ligands. The barrier heights in case of Nd(III) based D_{5h} symmetric SIMs generally lesser than Dy(III) analogues, as the inherent magnetic anisotropy is less in Nd(III) due to smaller value of S and L.

This ligand field is unfavourable for prolate shaped ions, such as Er(III), Yb(III). These ions need strong equatorial ligands, and weak or no axial ligands. Such strategy is found to be fruitful in designing prolate shaped trivalent lanthanide-based SIMs. J. Tang and co-workers have reported a Er(III) based D3h symmetric complex with no axial ligand, $Er[N(SiMe_3)_2]_3$ having barrier height of 122 K. On putting axial ligands such as THF, Cl etc., the value diminises to large extent. In case of Yb(III) also, using strong ligand such as Ph3PO in equatorial field can give produce to strong anisotropy, and hence larger barrier height.

Table 1 summarizes the best performing D_{5h} symmetric P=O donor Ln(III) based SIMs. It clearly shows that changing substituents on the ligand, the lattice ions as well as the type of Ln(III) ion used can lead to significant change in the SIM behaviour.

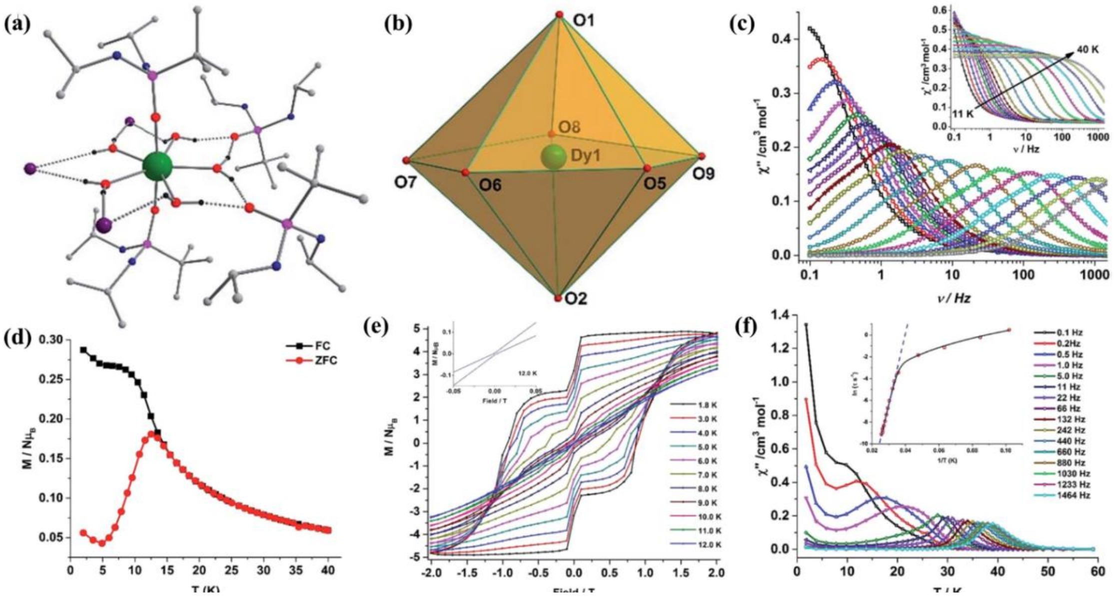

Figure 6: Molecular structure (a) and D_{5h} symmetric polyhedron around Dy(III) centre (b) in 2. Frequency dependent (c) and temperature dependent (f) out-of-phase magnetic susceptibility in absence of any external magnetic field. (d) Plot of variable temperature ZFC (red) and FC (black) magnetization. (e) Hysteresis plot of 1 at a sweep rate of 180 Oe/sec.

Table 1: D_{5h}-symmetric P=O ligand derived Ln(III) based single-ion magnets along with their barrier heights (U_{eff}) and blocking temperature (T_B).(The Colours are given according to the variation of either lattice ions or the substituents)

Sl no.	Molecule: [Ln(OPR^{1}R^{2}R^3)$_2$(H$_2$O)$_5$].X$_3$						U_{eff} /K	T_B /K	Ref
	Ln	Complex	R^1	R^2	R^3	X			
1	**Dy**	**2**	- CMe$_3$	-NH^{i}Pr	-NH^{i}Pr	I	735	16	[71, 73]
2		**3**	- CMe$_3$	-NH^{i}Pr	-NH^{i}Pr	Br	640	14	[73]
3		**4**	- CMe$_3$	-NH^{i}Pr	-NH^{i}Pr	Cl	609	9	[73]
4		**5**	Cyclohexyl	Cyclohexyl	Cyclohexyl	Cl	472	11	[52]
5		**6**	Cyclohexyl	Cyclohexyl	Cyclohexyl	Br	543	20	[52]
6		**7**	Cyclohexyl	Cyclohexyl	Cyclohexyl	OTf	562	8.5	[74]
7		**8**	Cyclohexyl	Phenyl	Phenyl	Br	508	19	[72]
8		**9**	-NMe$_2$	-NMe$_2$	-NMe$_2$	Cl	460	6	[75]
9		**10**	-NMe$_2$	-NMe$_2$	-NMe$_2$	I	600	9	[75]
10	**Nd**	**11**	-CMe$_3$	-NH^{i}Pr	-NH^{i}Pr	I	~40	-	[54]
11		**12**	Cyclohexyl	Phenyl	Phenyl	I	-	-	[57]
12	**Ho**	**13**	Cyclohexyl	Phenyl	Phenyl	I	341	3	[76, 77]
13		**14**	-CMe$_3$	-NH^{i}Pr	-NH^{i}Pr	I	355	4	[78]
14		**15**	-NMe$_2$	-NMe$_2$	-NMe$_2$	Cl	290	-	[79]
15		**16**	-NMe$_2$	-NMe$_2$	-NMe$_2$	Br	320	-	[79]
16		**17**	Pyrrolidino	Pyrrolidino	Pyrrolidino	Cl	351	8	[80]
17		**18**	Pyrrolidino	Pyrrolidino	Pyrrolidino	Br	418	15	[80]

5. **Substituted cyclopentadienyl (cp) derived dy(iii) based sims :** Several single-ion magnets have been reported during the last two decades, specially, the development of Dy(III) based SIMs in the last decade. The molecules possess large effective barriers that stop them from the reversal of the magnetization. As mentioned above, two important criteria that determine whether a molecule is a good single-ion magnet or not are energy barrier and blocking temperature. It is not compulsory that a molecule with higher U_{eff} will possess higher blocking temperature. Thus, though the designing of SIMs with large U_{eff} is successful to large extent, but T_{B} is not being enhanced at the same pace. This is because the spins takes shortcuts in the barrier height through either ground state or excited states. As synthetically challenged two coordinated Dy(III) (symmetry $D_{\infty h}$) could be the perfect choice for SIM, recently a number of Ln(III) based metallocene, specially dysprocene, are reported as alternative molecules which also possess peudo-$D_{\infty h}$ symmetric ligand field around the Ln(III) centre. Substituted cyclopentadienyl (Cp) and to some extent cyclooctatetraene (COT) are the ligands that produces dysprocene with high T_{B}, even higher than liquid nitrogen temperature (80 K). In this class of compounds, the axial positions are occupied by Cp ligands in near to linear fashion and the equatorial positions are vacant, as the substituted Cp ligands provide enough steric hindrance that prevents other moieties to come to the vicinity of the metal centre.

D. Mills and co-workers and Layfield and co-workers have simultaneously reported a Dysprocene, $[(Cp^{ttt})_2Dy][B(C_6F_5)_4]$ (**19**), where Dy(III) ion sandwiched between two Cp^{ttt} rings where Cp^{ttt}: $C_5H_2(CMe_3)$-1,2,4. The opening up of hysteresis loop is observed up to 60 K and the energy barrier of spin reversal is as high as 1277 cm^{-1}. [45, 81] Table 2 and figure 7 lists the best performing Dy(III) SIMs derived from substituted Cp based ligands. On changing the substituents of the cyclopentadienyl rings, the SIM behaviour also changes drastically. For example, in place of Cp^{ttt} in **19** producing $[(Cp^{i}Pr_5)Dy(Cp^{*})][BH_4]$ (**20**), if one $Cp^{i}Pr_5$ and one $CpMe_5$ (Cp*) is used, the blocking temperature is enhanced by 20 K to 80 K, exceeding the liquid nitrogen temperature, which is the highest reported blocking temperature. Similarly, by replacing the H atom of $Cp^{i}Pr_4$ ring in $[Dy(Cp^{i}Pr_4)_2][B(C_6F_5)_4]$ (**23**) by different groups such as methyl (in **24**), ethyl (in **25**) and iso-propyl (in **26**), the T_{B} are enhanced from 17 cm^{-1} up to 62 cm^{-1}. Mills and co-workers have replaced one of the C atoms in each of the two Cp rings by P atoms producing $[Dy(Dtp)_2][Al(OC(CF_3)_3)_4]$ (**21**), and observed the T_{B} is 48 K. Thus, the modification of the Cp ring can lead to the experiencing higher blocking temperatures and energy barriers.

Table 2: High performing sandwiched Dy(III) based single-ion magnets along with their barrier heights (U_{eff}) and blocking temperature (T_{B})

Single-Ion magnet	U_{eff} /cm^{-1}	T_{B} /K	Reference
$[(Cp^{ttt})_2Dy][B(C_6F_5)_4]$ (**19**) Where $Cp^{ttt}=[C_5H_2\text{-}^{t}Bu_3\text{-}1,2,4]$	1277	60	[45, 81]
$[(Cp^{i}Pr_5)Dy(Cp^{*})][BH_4]$ (**20**)	1541	80	[44]
$[Dy(Dtp)_2][Al(OC(CF_3)_3)_4]$ (**21**) Where Dtp = $P(C^{t}BuCMe)_2)$	1223	48	[46]
$Tb(Cp^{i}Pr_5)_2$(**22**)	1205	52	[48]
$[Dy(Cp^{i}Pr_4)_2][B(C_6F_5)_4]$ (**23**)	1285	17	[49]
$[Dy(Cp^{i}Pr_4Me)_2][B(C_6F_5)_4]$ (**24**)	1468	62	[49]
$[Dy(Cp^{i}Pr_4Et)_2][B(C_6F_5)_4]$ (**25**)	1380	59	[49]
$[Dy(Cp^{i}Pr_5)_2][B(C_6F_5)_4]$ (**26**)	1334	56	[49]

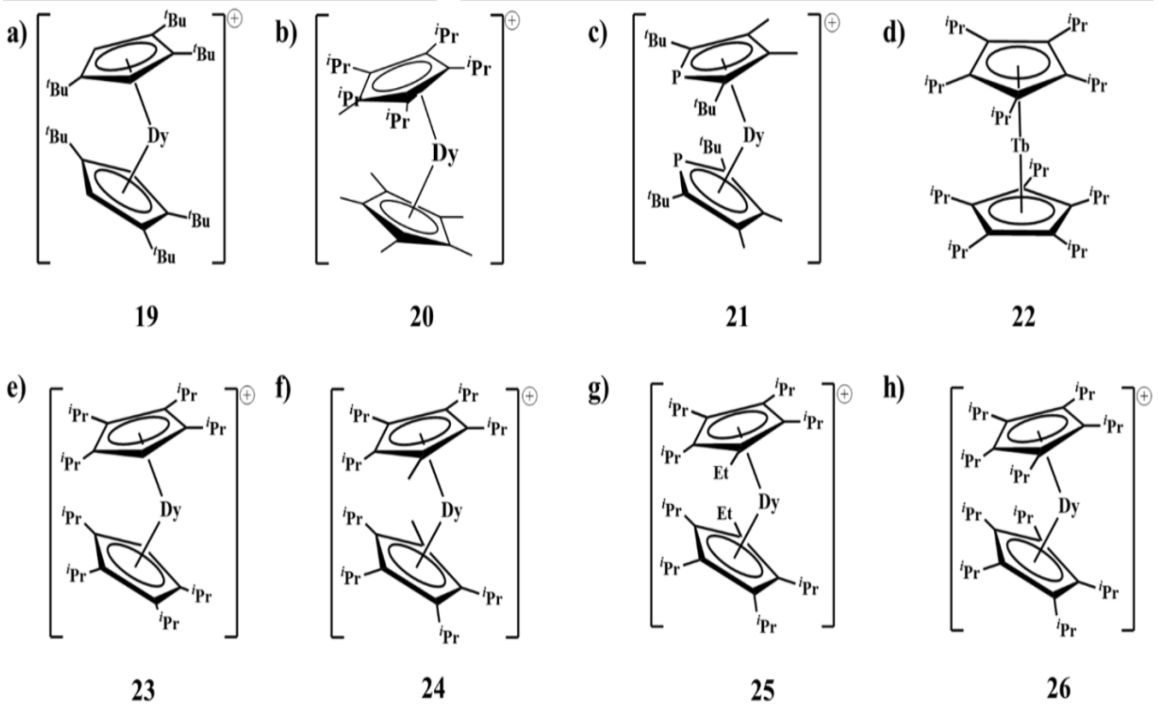

Figure 7: Molecular structures the cationic part of 19-26 (a-h). The counter anions are omitted for clarity. Molecule 20 possesses highest blocking temperature among all the single-molecule magnets.

IV. CONCLUSIONS

The exponential growth in the field of single-molecule magnets cites the importance of these compounds in this generation. Selection of the ion and designing a suitable ligand field for that ion is the most crucial step in developing a potential single-ion magnet. Trivalent lanthanides especially, Dy(III) ion is the most advantageous in designing single-ion magnets, taking the advantages of large inherent anisotropy and tuning the ligand field. This emerging field of research can minimize the size of the data storage devices to large extent in the near future.

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