Field-induced single-molecule magnet behavior in a Dy-based coordination polymer

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Abstract – A new mononuclear dysprosium-based coordination polymer \{Dy-CP\} is investigated for the magnetic properties. DC susceptibility of the Dy-CP does not exhibit any long-range ordering down to 1.8 K and the negative value of the Curie constant (\(\sim -4\) K) indicate the dominance of antiferromagnetic interactions between the Dy (III) spins. AC susceptibility of the Dy-CP exhibits absence of single molecular magnet (SMM) behavior at zero field and shows signal of quantum tunneling magnetization (QTM) below 8 K. However, on the superimposition of a DC field (3 kOe), a frequency-dependent relaxation peak emerged at \(T_f = 5\) K and the QTM signal is suppressed at higher fields. The intermediate value of \(p = 0.1\) reflects the formation of superparamagnetic state. The magnetic susceptibility analysis (Arrhenius fit) yields characteristics pre-relaxation factor \(\tau_o = 1.40 \times 10^{-12}\) s and energy barrier \(\Delta E/k_B = 9.3\) K, indicating the slow spin relaxation. The Cole-Cole fit shows further evidence for the single ion spin relaxation. Thus, the magnetic measurements support the SMM behavior in the Dy-CP under the application of DC magnetic field.

Introduction. – The study of single-molecule magnets (SMMs) has received considerable attention due to their potential applications in quantum computing devices, large data storage and spintronics [1–5]. In particular, the lanthanide-based coordination polymer molecules are found to be very fascinating candidates for the SMMs, due to their slow magnetic relaxation and large magnetic anisotropy, owing to unquenched orbital angular momentum (L), high spin angular momentum (S) and large total angular momentum (J) values of the lanthanide ions [6–10]. The researchers have studied the luminescent nature of SMMs and highlighted the correlation between magnetic and optical properties [11–13]. The interactions in the SMMs are attained by the overlap of the bridging ligand orbital and the 4f orbitals of the rare-earth ions. Therefore, ligand designing is one of the essential components to achieve such interactions. Dy is one of the most used elements for synthesizing SMMs because of the possibility of magnetic data storage in a single molecule at a temperature exceeding the liquid-nitrogen temperature [10,14,15].

The SMMs exhibit quantum tunneling magnetization (QTM) through the spin-reversal barrier via degenerate energy levels [16]. Though the spin relaxation mechanism is well known for transition-metal–based SMMs, it is still to be understood completely for polynuclear-lanthanide–based SMM systems. This is mainly because of the combined effect of several factors, such as high tunneling rates, weak magnetic interactions between the 4f ions and large magnetic anisotropy [17–20]. Therefore, understanding of the origin of spin relaxation observed in polynuclear-4f-based SMMs remains an interesting challenge.

In this article we have presented the low-temperature magnetic properties of the Dy-based coordination polymer \(C_{11}H_{18}DyN_3O_9\) (Dy-CP). The details of the compound synthesis and basic characteristic were already reported by Bandhana et al. [21]. Temperature– and magnetic-field–dependent DC magnetization and AC susceptibility measurements have been performed using the Magnetic Property Measurement System (MPMS), from Quantum Design, USA in the temperature range from 1.8 to 300 K.

In Dy-CP, two Dy (III) ions interact via two carboxylate oxygen atoms with distorted tricapped triangular prismatic geometry [21]. The magnetic site Dy coordinated directly only with the oxygen ion. The asymmetry in the structure strongly affects the coordination of Dy with anionic donor (Dy-Ox) and Dy-Dy intermolecular distance. The separation of Dy with all donor ligands
varies between 2.26 and 2.52 Å. The coordination geometry of the Dy site is different from 1) [Dy(OPCy3)2(H2O)]3+, 2) [Dy(OPBu)3(NH4Pr)2(H2O)]53+, 3) [Dy(bbpen)Br]; (bbpen = N,N’-bis(2-hydroxybenzyl)-N,N’-bis(2-methylpyridyl) ethylenediamine) and 4) [Dy(O2Bu)2(Py)3][BPh4] which leads to the small energy barrier of magnetic relaxation [22–25]. These systems exhibit large barrier of magnetic relaxation due to the desired disposition of the anionic and neutral donor where the anionic donor occupies the axial site and possesses strong axial ligand field. It has been found that the large energy barrier can be achieved in the complexes having high local symmetry and desired disposition of anionic and neutral site. The other complexes 

\[ \text{[Ln(Li)_2(HOCH_2CH_2OH)]_n} \] and 

\[ \text{([NH_2(CH_3)_2]_2[NiDy_2(HCOO)_2(abtc)]_n)} \] exhibit low energy barrier similar to Dy-CP [26,27]. Additionally, these systems exhibit small Dy-Dy separation compared to the compounds 1)–4) which exhibits large Dy-Dy intermolecular distance between 8 and 10 Å whereas in distortion modifies the distancing.

Our study shows evidences of strong anisotropy and the signal of QTM below 8 K. AC susceptibility measurements in the presence of applied DC magnetic field confirm the slow magnetic relaxation behavior from Cole-Cole and Arrhenius fit with low value of \( \alpha = 0.1 \) and energy barrier \( \Delta E/k_B \sim 93 \) K. These features put Dy-CP on the edge of the single-molecule magnets category for any reported Dy-based mononuclear SMMs.

**Results and discussions.** – The DC magnetic susceptibility \( (M/H) \) measurements of Dy-CP were performed under zero-field-cooled (ZFC) and field-cooled (FC) protocol in the presence of an applied field of 1 kOe and 3 kOe in the temperature range of 1.8–300 K. The temperature dependence of the DC magnetic susceptibility under 1 kOe (fig. 1) and 3 kOe field shows paramagnetic-like behavior with the complete overlapping of ZFC and FC curves, excluding the possibility of any type of short-range magnetic ordering in the compound. We have fitted \( 1/\chi_M vs. T \) curve using the Curie-Weiss equation (fig. 1(a)),

\[ \frac{1}{\chi} = (T + \Theta_{\text{CW}})/C; \]

where \( C = C_0g^2J(J + 1)/3, C_0 = N_A\mu_B^2/\kappa_b = 4.71 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1} \). We obtained \( \Theta_{\text{CW}} = -3.98 \) K, \( J \sim 15/2 \), and \( \mu_{\text{eff}} = 10.59 \) \( \mu_B \). The effective moment value is close to the theoretical value of 10.64 \( \mu_B \) for Dy (III) ions. These results confirm that the Dy (III) ions solely contribute to the total magnetization. The negative value of \( \Theta_{\text{CW}} \) points towards the antiferromagnetic exchange interaction between Dy (III) ions in this coordinated polymer compound. Figure 1(b) shows the DC magnetic susceptibility data (only ZFC) at 1 kOe and 3 kOe.

The complete overlap of magnetic susceptibility at both the fields indicates the absence of spin correlation with the application of magnetic field. The monotonic increase in the magnitude of DC susceptibility with decreasing temperature at 3 kOe without any observation of magnetic anomaly clearly indicates that the magnetic anomaly in AC susceptibility (discussed later) is not associated with any type of spin ordering.

Further to get the better understanding of the nature of interaction we have plotted \( \chi T/C \) vs. \( T \) in fig. 2. The magnitude of \( \chi T/C \) is used to classify the nature of the interaction between the magnetic ions [28]. If the systems exhibit ferromagnetic (FM) interactions then \( \chi T/C > 1 \) and in the case of antiferromagnets (AFM) \( \chi T/C < 1 \). There exists a paramagnetic boundary between FM and AFM interaction regimes for which \( \chi T/C \) is equal to 1. It was observed that the Dy-CP remains weakly antiferromagnetic throughout the investigated range with \( \chi T/C < 1 \). However, the presence of strong frustration...
Fig. 3: (a) and (b): temperature dependence of $\chi'$ and $\chi''$ at $H = 0$ Oe performed at various frequencies. (c) $\chi'$ vs. $T$ at $H = 3$ kOe between 13 Hz and 991 Hz. (d) Temperature dependence of $\chi'$ at $f = 131$ Hz performed at various DC applied fields. The insets of (b) and (c) represent the Cole-Cole plot and the Arrhenius fit using eqs. (2) and (3).

prevents the possibility of long-range ordering in the system.

The isothermal magnetizations $M$ vs. $H$ were performed at different temperatures (inset of fig. 2). At high temperature ($T = 300$ K), $M(H)$ is nearly a straight line, as is expected for the paramagnetic state. With the decrease in temperature, the curve develops a curvature, which is more pronounced at low temperatures. The $M(H)$ curve does not saturate up to the field of 70 kOe and points to the presence of strong magnetic anisotropy [29]. At lowest measured temperature ($T = 3$ K), its maximum unsaturated magnetization value of 5.48 N/β for Dy-CP is almost half of the expected value (10 N/β for each Dy (III) ion with $J = 15/2$ and $g = 4/3$) [30]. Furthermore, to confirm the presence of magnetic anisotropy we have plotted $M$ vs. $H/T$ at different temperatures. As seen from fig. 2(b), there is discernible deviation at higher $H/T$ value and all the curves do not superimpose on each other. This behavior indicates the presence of low-lying excited states and magnetic anisotropy in the compounds [29,30].

In order to understand the magnetic relaxation behavior, we have measured the dynamic magnetization (AC susceptibility) of the compound in the low temperature range 1.8–50 K, and the frequency range from 13 to 991 Hz, with the oscillation field of 3 Oe. At zero field, the real part of AC susceptibility ($\chi'$) exhibited frequency-independent behavior (fig. 3(a)). However the out-of-phase (imaginary) part of the AC susceptibility ($\chi''$) shows a discernible change in behavior below 8 K (fig. 3(b)). The peak value is not obtained above 1.8 K but the observation of a tail of peak below 8 K is an indicative of fast QTM which is attributed to spin-reversal barrier via degenerate energy levels [31–33]. Such behavior is commonly observed in lanthanides-based polymer systems [34–36]. The QTM in lanthanide systems is facilitated by the intermolecular interaction between lanthanide ions and poses a large energy barrier for magnetic tunneling [32,37]. On the other hand, in Dy (III) ions the spin-parity effect reduces the appearance of QTM [31,33,38]. The intensity of the tail increases at higher frequencies which demonstrates that QTM in
Dy-CP is consistent with other lanthanides SMMs which shows single-ion relaxation behavior [37].

Later, we performed the AC susceptibility measurements in the presence of DC field. The AC susceptibility of Dy-CP measured under 3 kOe DC magnetic field is shown in fig. 3(c). As seen from the figure, we observed frequency dependence at low temperature with a clear peak near 5 K. The shift in the peak position with varying frequency indicates the presence of glassy state in the system [39]. For this we have calculated the Mydosh parameter $p$ by using the relation [33]

$$p = \frac{\Delta T_f}{T_f \Delta (\log f)},$$

where $T_f$ is the transition temperature at lowest measured frequency and $\Delta T_f$ is the difference between the transition temperature measured at the lowest and highest frequencies. By using the peak temperature, maximum and minimum frequency values, we obtained $p = 0.1$, as predicted for superparamagnet, which rejects the presence of the spin glass behaviour. Further, the frequency dependence of AC susceptibility data was analysed by the Cole-Cole plot using the equation [40, 41]

$$\chi(\omega) = \chi_S + \frac{\chi_T - \chi_S}{1 + (i\omega\tau)^{1-\alpha}},$$

where $\chi_T$ is the isothermal susceptibility and $\chi_S$ is the adiabatic susceptibility and $\alpha$ ranges between 0 $\leq$ $\alpha$ $\leq$ 1. The $\alpha = 0$ indicates no spread in the relaxation time and deviation from this value indicates wide distribution of relaxation time due to the formation of clusters [40–43]. To obtain $\alpha$, we did the fitting using the generalized Debye model equation (2) in the Cole-Cole plots of $\chi''$ vs. $\chi'$ for Dy-CP under 3 kOe applied DC field. We found the value of $\alpha$ $\sim$ 0.01 at 5 K. A very low value of $\alpha$ for Dy-CP corresponds to the narrow distribution of the relaxation time. For the relaxation time of Dy-CP, the frequency-dependent transition temperature in the range of 13–991 Hz is fitted with the Arrhenius equation [40]

$$\tau = \tau_0 \exp(\Delta E/k_B T).$$

The obtained energy barrier ($\Delta E/k_B$) of 93.4 K and pre-relaxation factor $\tau_0$ of $1.4 \times 10^{-12}$ s (inset of fig. 3(c)), are consistent with the previous reports on dysprosium-based SMMs and is large enough to put Dy-CP in the category of the single molecular magnets [44, 45]. However, our obtained energy barrier is small compared to the largest barrier seen for other Dy-based SMMs [22–25]. The Dy-based SMMs like [Dy(bbpen)Br; (bbpen = N,N′-bis(2-hydroxybenzyl)-N,N′-bis(2-methylpyridyl) ethylenediamine) and [Dy(O(Bu)2(py)2)][BF4]2, etc., exhibit large energy barrier of 1025 and 1815, respectively [24, 25]. In these systems, the negatively charged donor ligand occupies the axial site and leads to the highest barrier. Whereas the distorted tricapped triangular prismatic geometry of Dy-CP modifies the coordination geometry of Dy with anionic donor and gives rise to the small energy barrier to the magnetic relaxation.

Figure 3(d), shown for $f = 131$ Hz frequency, depicts the dependence of dynamic magnetization on the applied DC magnetic field more clearly. The AC susceptibility at zero field shows monotonous Curie-like behavior, and the application of DC field assists in arresting the spin dynamics at low temperatures leading to the peak shape anomaly, which broadens for higher fields. The interesting observation is the appearance of frequency-dependent peak at an applied DC field of 3 kOe, indicating SMM behavior (fig. 3(c)). A relaxation peak was observed below 8 K with a tail of QTM, which is now shifted to low temperatures on applying DC field. With further increase in the DC applied field $H > 5$ kOe, only a single relaxation peak is observed without the presence of a tail, confirming the complete suppression of QTM. Essentially, we found that QTM can be blocked with a suitable applied DC magnetic field. The application of the field lifts the degeneracy and prevents the tunneling of electrons from $+M_S$ state to $-M_S$ and results in the suppression of QTM.

Conclusion. – The magnetic properties of a Dy-based coordination polymer are studied. Reduced value of saturation magnetization indicates the presence of low-lying excitation and large anisotropy in the system. AC susceptibility shows paramagnetic-like features different from other members of SMMs group. Interestingly, the imaginary part of AC susceptibility shows the signature of QTM below 8 K which is further suppressed with the application of DC magnetic field due to the splitting of degenerate energy levels. Apart from this, field induces SMMs behavior in Dy-CP at $T = 5$ K, confirmed from the Arrhenius and Cole-Cole fit. Our work presents Dy-CP as an interesting candidate in SMMs class and can be further studied by advanced measurement techniques.

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