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Using internal strain and mass to modulate Dy...Dy coupling and relaxation of magnetization in heterobimetallic metallofullerenes DyM2N@C80 and Dy₂MN@C₈₀ (M = Sc, Y, La, Lu)†

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Endohedral clusters inside metallofullerenes experience considerable inner strain when the size of the hosting cage is comparably small. This strain can be tuned in mixed-metal metallofullerenes by combining metals of different sizes. Here we demonstrate that the internal strain and mass can be used as variables to control Dy...Dy coupling and relaxation of magnetization in Dy-metallofullerenes. Mixed-metal nitride clusterfullerenes $Dy_xY_{3-x}N@I_h-C_{80}$ (x = 0-3) and $Dy_2LaN@I_h-C_{80}$ combining Dy with diamagnetic rare-earth elements, Y and La, were synthesized and characterized by single-crystal X-ray diffraction, SQUID magnetometry, ab initio calculations, and spectroscopic techniques. DyxY3-xN clusters showed a planar structure, but the slightly larger size of Dy^{3+} in comparison with that of Y^{3+} resulted in increased elongation of the nitrogen thermal ellipsoid, showing enhancement of the out-of-plane vibrational amplitude. When Dy was combined with larger La, the Dy₂LaN cluster appeared strongly pyramidal with the distance between two nitrogen sites of 1.15(1) Å, whereas DyLa₂N@C₈₀ could not be obtained in a separable yield. Magnetic studies revealed that the relaxation of magnetization and blocking temperature of magnetization in the DyM₂N@C₈₀ series (M = Sc, Y, Lu) correlated with the mass of M, with DySc₂N@C₈₀ showing the fastest and DyLu₂N@C₈₀ the slowest relaxation. Ab initio calculations predicted very similar g-tensors for Dy^{3+} ground state pseudospin in all studied $DyM_2N@C_{80}$ molecules, suggesting that the variation in relaxation is caused by different vibrational spectra of these compounds. In the Dy₂MN@C₈₀ series (M = Sc, Y, La, Lu), the magnetic and hysteretic behavior was found to correlate with Dy...Dy coupling, which in turn appears to depend on the size of M^{3+} . Across the Dy₂MN@C₈₀ series, the energy difference between ferromagnetic and antiferromagnetic states changes from 5.6 cm⁻¹ in Dy₂ScN@C₈₀ to $3.0~\text{cm}^{-1}$ in Dy₂LuN@C₈₀, $1.0~\text{cm}^{-1}$ in Dy₂YN@C₈₀, and $-0.8~\text{cm}^{-1}$ in Dy₂LaN@C₈₀. The coupling of Dy ions suppresses the zero-field quantum tunnelling of magnetization but opens new relaxation channels, making the relaxation rate dependent on the coupling strengths. $DyY_2N@C_{80}$ and $Dy_2YN@C_{80}$ were found to be non-luminescent, while the luminescence reported for DyY2N@C80 was caused by traces of $Y_3N@C_{80}$ and $Y_2ScN@C_{80}$.

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Introduction

Nitride clusterfullerenes with the molecular composition M₃N@C_{2n} is one of the most versatile classes of endohedral metallofullerenes (EMFs). 1-6 The cage size ranges from C₆₈ to C_{98} and even larger; however the highly symmetric I_h - C_{80} fullerene is usually most abundantly produced in the synthesis. The M₃N cluster has a triangular shape with a nitride ion in its center and three M(III) rare-earth metals located at the apexes of the triangle. Of particular interest is the possibility to combine two or even three different metals in the M3N cluster in the arc-discharge process and the ability of chromato-

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graphic techniques to separate mixtures of such heterometallic (mixed-metal) EMFs into individual components. 7-20 When specific interactions between metal ions are important, the mixed-metal approach provides the possibility to study such interactions by systematically varying the composition of the M₂N cluster. For instance, the magnetic properties of EMFs depend on the dipolar and exchange interactions between endohedral lanthanide ions, ^{21,22} and these interactions can be addressed by changing the number and type of magnetic ions in the heterobimetallic $M'_xM''_{3-x}N@C_{80}$ system (x = 0-3, M' and M" are different rare-earth metals, including non-magnetic Sc, Y, La, or Lu, and magnetic 4f lanthanides). 22-31 Such a precise composition control in a virtually identical chemical environment is quite unique and rarely available for heterometallic systems in lanthanide chemistry. 32-38

In this work, we employ the M'xM"3-xN@C80 platform to study the influence of the internal strain on the static and dynamic magnetic properties of Dy-containing nitride clusterfullerenes. The use of external stimuli to modulate the properties of single molecule magnets has attracted significant attention as it opens the way for multifunctional magnetic systems.^{39,40} Mechanical pressure was found to change both the ligand field and magnetic interactions in several transition-metal single-molecule magnets (SMMs), 41-48 but the studies of pressure-induced variations in the SMM behavior remain very scarce for lanthanide SMMs. 49-52 One of the main effects of mechanical pressure on molecular systems is the internal strain, which not necessarily requires the use of external pressure as it can be addressed by a judicious molecular design. Endohedral fullerenes provide an opportunity to engineer the internal strain through varying the size of the endohedral cluster. A fullerene cage is rather rigid and its size is usually not changed much when the internal species are varied. As a result, the endohedral M₃N cluster experiences a strain of different magnitude depending on the size of constituting metals.⁵³ This strain can be attested for via variation of different structural and physicochemical properties. For instance, the C₈₀-I_h fullerene cage is the most preferred for the metal-nitride cluster, and M₃N@I_h-C₈₀ species are usually obtained with the highest yield among other cages, but when the metal ions are too large, the yield of EMFs decreases and the M₃N cluster changes its geometry from planar to pyramidal (M = Tb, Gd). 54,55 With a further increase of the metal size, the distribution shifts from C₈₀ to larger cages, and for La and Ce, M₃N@C₈₀ is not formed at all. ⁵⁶⁻⁵⁸ Likewise, the preferable fullerene cage isomers can be changed depending on the size and shape of the endohedral cluster. 9,59-61 The size of the cluster and the associated internal strain were also shown to influence NMR and vibrational spectroscopic properties, 7,13,62 dynamics of the M₃N cluster inside the cage, 63,64 preferable cycloaddition sites, 65-68 and even electrochemical potentials of endohedral Ce(IV/III)^{14,15} and Ti(IV/III)^{69,70} redox couples. An earlier study demonstrated that the replacement of Sc by Lu in both DySc₂N@C₈₀ and Dy₂ScN@C₈₀ metallofullerenes resulted in the noticeable variation of their dynamic magnetic properties and Dy...Dy coupling.24 The exact reasons why diamagnetic metals can influence the magnetic behavior of Dy remained unclear as both the mass and size of the diamagnetic ion could play a certain role. Here we extend the DyM2N@C80 and Dy2MN@C80 series with further diamagnetic rare-earth metals, Y and La, and analyze the changes in internal strain and its relationship with magnetic properties when the size of the diamagnetic metal M is varied from Sc to La. Thanks to the different variations of the ionic radius and atomic mass in the Sc3+-Y3+-La3+-Lu3+ series, we could distinguish two factors playing the main roles in the relaxation of magnetization of nitride clusterfullerenes, that is, the mass of M in the DyM2N@C80 series and the size-related strain in the Dy₂MN@C₈₀ series.

Synthesis and separation

Nitride clusterfullerenes were synthesized using a previously developed approach.⁷¹ Dy-Sc and Dy-Lu nitride clusterfullerenes were obtained by us earlier, 13,24,71,72 and in this work the synthesis was performed for Dy-Y and Dy-La systems. A mixture of M_2O_3 (M = Y or La), Dy_2O_3 , guanidinium thiocyanate and graphite powder with a molar ratio of 1:1:5:15 was filled in core-drilled graphite rods. The rods were evaporated by the direct current arc-discharge process in the chamber filled with He as a cooling gas (180 mbar). The produced soot was washed with acetone for 2 hours to remove the polyaromatic hydrocarbons, and then Soxhlet extracted with CS₂ overnight to dissolve the fullerenes. The CS₂ extract was separated by high-performance liquid chromatography (HPLC).

Fig. 1a and b show typical HPLC profiles of the extracts obtained in the Dy-Y and Dy-La EMF syntheses. The use of the organic nitrogen source suppresses the formation of empty fullerenes, and nitride clusterfullerenes become the main fullerene products.⁷³ The most abundant fraction in the Dy-Y system is the $Dy_xY_{3-x}N@I_h$ -C₈₀ mixture. According to massspectrometry analysis (Fig. 1c) and recycling HPLC (Fig. 1a), it contains components with all x from 0 to 3. This agrees with the similarity of the ionic radii of Dy3+ and Y3+, which largely determines the probability of the EMF formation with a given cage size. The metals with substantially different ionic radii give a strong variation of the composition in the mixed-metal EMF synthesis, 13 and the Dy-La system is a good example of this behaviour. The overall yield of Dy-La EMFs is considerably lower than that of Dy-Y EMFs, and the main HPLC fraction is Dy₃N@I_h-C₈₀ (Fig. 1b). Dy₂LaN@C₈₀ is found in the adjacent fraction with much lower abundance, whereas DyLa2N@C80 and La₃N@C₈₀ were not formed at all, at least in the amounts detectable by LDI-TOF MS. Apparently, the La³⁺ ion is too large, and the formation of La₂MN@C₈₀ was not detected even in the La-Sc system, with rather small Sc3+ ions.74,75 As to La₃N-clusterfullerenes, the smallest cage able to accommodate the La₃N cluster is C₈₈.⁵⁷

Individual target compounds were obtained by subjecting the respective fractions to recycling HPLC (Fig. 1a and b). The

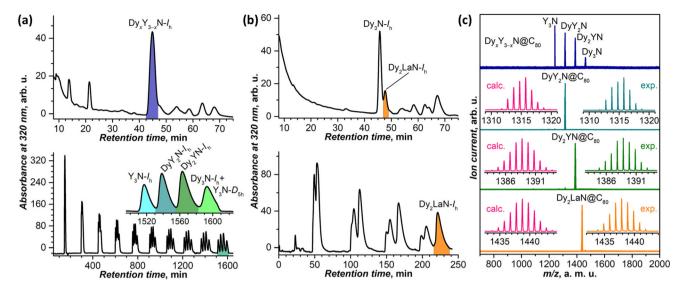


Fig. 1 (a) HPLC of the raw Dy-Y EMF extract, highlighting the main fraction (top) and recycling HPLC of this fraction giving individual compounds (bottom, the inset shows an enlarged 10th cycle). (b) HPLC of the raw Dy-La EMF extract, highlighting the fraction with the target compound (top) and recycling HPLC of this fraction giving individual Dy₂LaN@C₈₀ (bottom). (c) LDI mass spectra (positive ion mode) of a Y-Dy mixture and purified DyY₂N@C₈₀, Dy₂YN@C₈₀, and Dy₂LaN@C₈₀; insets show experimental and calculated isotopic patterns. Experimental conditions for linear HPLC: linear combination of two 10 \times 250 mm Buckyprep columns; flow rate: 5 mL min⁻¹; injection volume: 4.5 mL; toluene as eluent; and 40 °C. Recycling HPLC: 10 x 250 mm Buckyprep (a) or Buckyprep-D (b) columns; flow rate: 1.0 mL min⁻¹; injection volume: 4.5 mL; and toluene as eluent.

Dy_xY_{3-x}N@I_h-C₈₀ mixture is well resolved after 10 cycles, allowing collection of pure Y₃N@I_h-C₈₀, DyY₂N@I_h-C₈₀, and Dy₂YN@I_h-C₈₀ in subsequent cycles, whereas Dy₃N@I_h-C₈₀ still has an admixture of another isomer of Y₃N@C₈₀ with a D_{5h} cage, which has longer elution time than the Ih isomer. Dy₂LaN@I_h-C₈₀ could be obtained after 4 cycles, the main admixtures being the tail of Dy₃N@I_h-C₈₀ from the preceding fraction and sulphide clusterfullerene Dy₂S@C₈₂ formed due to the presence of sulfur in the nitrogen source.⁷⁶ The purity of isolated Dy-Y and Dy-La nitride clusterfullerenes was evaluated by laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF MS) as shown in Fig. 1c. UV-vis-NIR and FT-IR absorption spectra of DyY2N@C80, Dy2YN@C80, and Dy₂LaN@C₈₀ (Fig. S1 and S2†) exhibit the characteristic pattern of $M_3N@I_h$ - C_{80} EMFs.

Single-crystal X-ray diffraction

Molecular structures of $Dy_xY_{3-x}N@I_h-C_{80}$ (x = 0-3) and Dy₂LaN@I_h-C₈₀ were studied by single-crystal X-ray diffraction (SC-XRD). Crystals were obtained by co-crystallization of fullerenes with nickel(II) octaethylporphyrin (NiOEP). For this, benzene or CS2 solutions of EMFs were layered with NiOEP solution in benzene in glass tubes and left to diffuse over 2-4 weeks, resulting in the formation of black block crystals on the walls. X-ray diffraction data collection was carried out at the BESSY storage ring (BL14.2, Berlin-Adlershof, Germany).⁷⁷ XDSAPP2.0 suite was employed for data processing. 78,79 The structure was solved by direct methods and refined using SHELXL-2018.80 Hydrogen atoms were added geometrically

and refined with a riding model. The crystal data are presented in Tables S1 and S2.†

$$Dy_xY_{3-x}N@I_h-C_{80}$$
 (x = 0-3)

M₃N@C₈₀ molecules usually co-crystallize with NiOEP in one of the three space groups, C2/c with 8 molecules, C2/m with 4 molecules, and $P\bar{1}$ with 2 molecules in the unit cell (Table S3†). C2/c is found in this work for Y₃N@C₈₀, DyY₂N@C₈₀, and Dy₃N@C₈₀. Their asymmetric unit contains one intact NiOEP molecule, one intact fullerene, one intact solvent benzene, and two halves of solvent benzene. $Dy_2YN@C_{80}$ crystallized in the $P\bar{1}$ space group, and its asymmetric unit contains one intact NiOEP molecule, one intact fullerene, and two intact solvent benzene molecules. The fullerene cage is ordered and unambiguously assigned to the $I_h(7)$ isomer in all four crystals, and the symmetry notation of $I_h(7)$ - C_{80} will be omitted hereafter. The packing in the crystals, with one fullerene molecule supported by one NiOEP molecule, is also typical of EMF·NiOEP co-crystals.72 An identical orientation of the fullerene cage versus NiOEP is found in all three crystals with the C2/c space group, whereas the cage orientation of Dy₂YN@C₈₀ is somewhat different (Fig. 2).

Analysis of all reported M₃N@I_h-C₈₀·NiOEP crystal structures (see Table S3 in the ESI†) shows that unless the M3N cluster is severely disordered, it usually has two M3N sites, of which the major one has an occupancy of 0.7-0.9. The two sites share a common nitrogen position and are related by a rotation of 10-20° around an axis located nearly perpendicular to their M₃N planes so that the two sites appear roughly in one plane. This common pattern was found earlier for Gd₃N,⁵⁴ Dy₃N, ⁶² Ho₃N, ⁸¹ Er₃N, ⁸¹ Tm₃N, ⁸² Lu₃N, ⁶⁴ DyEr₂N, ¹³ and

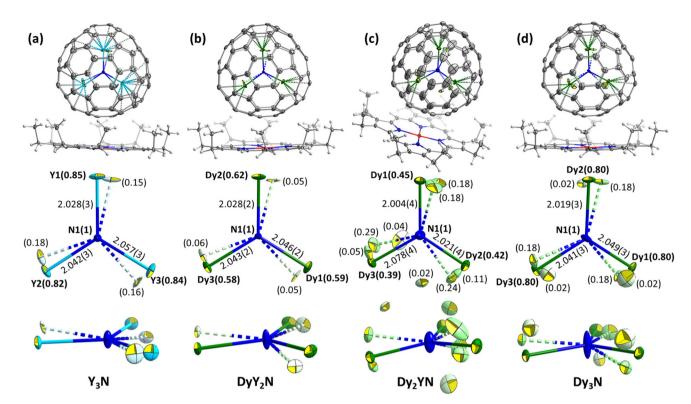


Fig. 2 Molecular structures in $M_3N@I_n$ - C_{80} - $NiOEP\cdot 2C_6H_6$ single crystals: $M_3N = Y_3N$ (a), DyY_2N (b), Dy_2YN (c), and Dy_3N (d). Top row: M₃N@C₈₀·NiOEP fragments; middle row: the structures of M₃N clusters with metal cite occupancies and bond lengths in Å for main sites; bottom row: different views of the M₃N clusters highlighting the shape of the nitrogen thermal ellipsoid. The displacement parameters are shown at the 30% probability, M-N bonds are shown as solid lines for the main site and as dotted lines for the site with the second highest occupancy. Color code: blue for nitrogen, cyan for yttrium, green for dysprosium sites with high occupancy and pale green for low-occupancy sites.

DyGd₂N, ¹³ and in this work for Y₃N, DyY₂N and Dy₃N (Fig. 2a, b and d). Dy₂YN shows a higher degree of disorder in the cluster (Fig. 2c).

The ionic radii of Y^{3+} (0.90 Å) and Dy^{3+} (0.91 Å) are rather similar, and it is therefore hard to expect that these metals will have different positions in Y₂DyN@C₈₀ and YDy₂N@C₈₀. The more plausible scenario is the uniform distribution of Y and Dy in all three positions in the M₃N cluster. Indeed, we could not differentiate between Dy and Y in the crystal structures of these fullerenes, and decided to apply free occupancy refinement on all possible metal positions with the relatively heavier Dy to identify the metal positions of DyY2 and Dy2Y. Since Y has fewer electrons than Dy, the maximal total occupancy of such "Dy³⁺" sites should be 0.68 in DyY₂N and 0.84 in Dy₂YN. Despite the similarity of ionic radii, the influence of the metal size on the cluster is still discernible. With the stepwise replacement of Y³⁺ with Dy³⁺, the shape of the nitrogen thermal ellipsoid gradually elongates in the direction perpendicular to the M₃ plane. This points to the increasing amplitude of the out-of-plane nitrogen vibration, which is associated with the trend towards M₃N pyramidalization with the increasing radius of M³⁺. At the threshold between the planar and pyramidal clusters, the amplitude is the highest as shown in ref. 13, and this is the reason for a particular strong ellipsoid elongation found in Dy₃N here and also in an earlier report⁶² (our new structure has different Dy₃N site occupancies but otherwise is very similar). We therefore refined the data with one position of N and the elongated ellipsoid, rather than splitting the nitrogen into two sites.

For Y₃N@C₈₀, a slightly pyramidal Y₃N cluster with a displacement of nitrogen from the Y₃ plane by 0.129(6) Å was reported in the pyrrolidine adduct,83 while a planar Y3N cluster was found in a phenyl-C81-butyric acid methyl ester derivative.⁸⁴ In the co-crystal of pristine Y₃N@C₈₀ with NiOEP reported here for the first time, the Y₃N cluster is planar.

Dy₂LaN@I_h-C₈₀

Dy₂LaN@C₈₀ also co-crystallized with NiOEP in the C2/c space group. The asymmetric unit contains one intact NiOEP molecule, one intact fullerene with two overlapping orientations, one intact solvent benzene, and two halves of solvent benzene. The fullerene cage is disordered between two orientations (site occupancy ratio of 0.61:0.39) as shown in Fig. 4a and S3,† which are correlated with a mirror plane passing through N-Ni-N bonds and perpendicular to the NiOEP molecule.

The Dy₂LaN cluster has considerable disorder with four metal sites (Fig. 4b), which hampers the reliable differentiation between Dy and La. We applied free occupancy refineResearch Article

ment with the heavier Dy to identify the metal positions of Dy₂La. Note that for La uniformly distributed between three sites, the site occupancy of such "Dy" should be 0.94. The Dy₂LaN cluster is pyramidal and has two nitrogen sites (N1A/N1B with occupancies of 0.70/0.30), which is common for the M₃N cluster in M₃N@C₈₀ molecules with large metals, such as DyGd₂N,¹³ CeLu₂N,⁸⁵ Tb₃N,⁵⁵ or Gd₃N.⁵⁴ The Dy₂LaN cluster has the highest sum of ionic radii of three M3+ ions among all M3N@C80 molecules studied by SC-XRD and shows the highest pyramidalization with an N1A/N1B out of M3-plane displacement of 0.619(4)/0.530(9) Å determined for Dy1A/ Dy2A/Dy3A sites with the largest occupancy, and an N1A···N1B distance of 1.15(1) Å. This can be compared to 0.522(8)/0.46(2) Å in Gd_3N (N···N distance: 0.991 Å), 54 0.46(2)/0.45(2) Å in $DyGd_2N$ (0.91(3) Å), ¹³ 0.453(4)/0.405(7) Å in Tb_3N (0.858(8) \mathring{A}), ⁵⁵ and 0.349(8)/0.325(8) \mathring{A} in CeLu₂N (0.685(9) \mathring{A}). ⁸⁵ The M-N1A distances in the most abundant sites of Dy₂LaN are 2.095(4) (Dy1A), 2.082(3) (Dy2A), and 2.118(5) Å (Dy3A). For comparison, DFT predicts the Dy-N and La-N bonds in $Dy_2LaN@C_{80}$ to be 2.072 Å and 2.156 Å long, and the lack of a clear differentiation between Dy-N and La-N bond lengths in the crystal structure indicates that La is equally distributed between all metal positions. The same conclusion can also be made based on the occupancies of metal sites in Fig. 4b.

NiOEP has a considerable influence on the position of metal atoms inside the fullerene. In a vast majority of M₃N@C₈₀·NiOEP co-crystals, two metal atoms of the M₃N cluster are located above the N-Ni-N bonds. 63,64,81,86,87 The recently reported Tb2@C80(CF3) co-crystallized with NiOEP also shows such a tendency.88 This effect seems to have an electrostatic nature as endohedral metals tend to be located close to negatively charged nitrogens of the porphyrin,87 and this alignment was observed in the absence of Ni, when the LaSc₂N@C₈₀ fullerene was co-crystallized with H₂OEP.⁷⁵ Fig. 3 and S4† show that this pattern is also realized in $\mathrm{Dy}_{x}\mathrm{Y}_{3-x}\mathrm{N}@I_{\mathrm{h}}\mathrm{-C}_{80}$ (x=0-3) and $\mathrm{Dy}_{2}\mathrm{LaN}@I_{\mathrm{h}}\mathrm{-C}_{80}$. Even when the metals are disordered, the sites with the highest occupancy are located above NiOEP nitrogens.

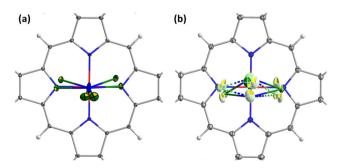


Fig. 3 Orientation of endohedral DyY2N and Dy2LaN clusters with respect to NiOEP as representative examples of M₃N@C₈₀·NiOEP single crystals. Fullerene cage, C₂H₅ groups of NiOEP, and the solvent molecules are omitted for clarity. The displacement parameters are shown at a 30% probability. Color code: grey for carbon, blue for nitrogen, white for hydrogen, red for nickel, and green for metals in M₃N clusters.

Magnetic properties

Structure of the M₃N cluster and single-ion magnetic anisotropy of Dy3+

Confinement of the M₃N cluster inside the rigid fullerene cage results in a strain, which can be assessed through geometrical parameters of the cluster, such as the unusually short M-N bond lengths. For instance, the Dy-N bond length distribution in molecular compounds has a maximum near 2.5 Å, whereas Dy-N bonds in $M_3N@C_{80}$ are shorter than 2.1 Å (see Fig. 2 for examples from this work and ref. 13 for more details). This shortening has important consequences on magnetic properties since the negatively charged nitride ion (formal charge -3, Bader charge of $-1.7^{29,89}$) produces a strong uniaxial ligand field and hence leads to the large magnetic anisotropy of Dy³⁺.

The structural parameters of the M₃N cluster can be further adjusted by the variation of its composition, and in particular by combining metals of different sizes. For instance, Y3+ is larger than Sc^{3+} , and the Dy-N bond in DyY₂N@C₈₀ (Fig. 2b) is shorter than that in DySc₂N@C₈₀ (2.096(6) Å according to SC-XRD⁷²). Thus, combining Dy in M₃N with large metals might be considered as a strategy to shorten Dy-N bonds and thereby increase the magnetic anisotropy. However, this compression effect has its limits, and after a certain threshold, the M-N bonds will not be shortened anymore. Instead, the cluster changes its shape from planar to pyramidal with the nitride ion elevated above the metal plane. 13,54,55,81,85 Experimental examples for Dy-containing M₃N@C₈₀ characterized by SC-XRD are DyGd₂N@C₈₀ from ref. 13 and Dy₂LaN@C₈₀ described in this work (Fig. 4). As the ligand field is not purely an electrostatic phenomenon,90 the influence of this geometrical change on the magnetic anisotropy is a priori not clear. To better understand it, we performed a systematic ab initio computational study for a series of DyM2N@C80 and $Dy_2MN@C_{80}$ molecules. A combination of Dy $(R^{3+} = 0.912 \text{ Å})$ with Sc (0.745 Å), Lu (0.861 Å), Y (0.900 Å), Gd (0.938 Å), or La (1.032 Å) allows for a smooth variation of the cluster size. We used DFT-optimized structures from ref. 13 for this survey because not all SC-XRD structures are available, and the available ones often suffer from a significant degree of disorder, which prevents the analysis of a subtle variation of the M-N bond lengths (see Fig. 2 and 4). As the parameter describing the net size of metals in the M₃N cluster, the sum of their Shannon's ionic radii⁹¹ ($\sum R^{3+}$) is used.

Fig. 5a illustrates the bond shortening and cluster pyramidalization trends in DFT-optimized structures. The Dy-N bond length $(d_{D_{V-N}})$ decreases fast with the increase of $\sum R^{3+}$ from 2.4 Å (DySc₂N) to 2.7 Å (DyY₂N), but then the shortening of $d_{\mathrm{Dy-N}}$ stagnates and even reverses to a slight elongation in Dy₂LaN and DyLa₂N when $\sum R^{3+}$ exceeds 2.8 Å. In parallel, the cluster pyramidalization (h_N) starts to grow when $\sum R^{3+}$ exceeds 2.7 Å, and the growth continues all the way up to $h_{\rm N}$ = 0.82 Å in the hypothetical DyLa₂N@C₈₀ with a $\sum R^{3+}$ of 2.98 Å.

Single-ion magnetic anisotropy of Dy3+ ions was then studied ab initio at the CASSCF(9,7)/RASSI-SO level in

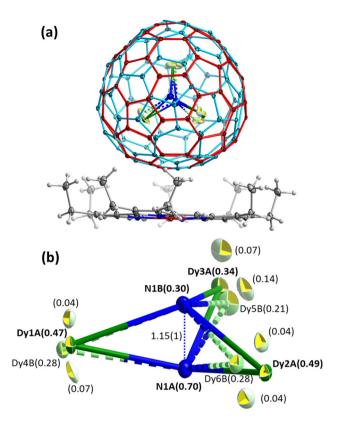


Fig. 4 (a) Fragment of Dy₂LaN@I_h-C₈₀·NiOEP crystals showing fullerene and porphyrin; solvent molecules are omitted for clarity; two orientations of the fullerene cage are shown in red (0.61) and cyan (0.39). (b) The structure of the Dy₂LaN cluster in the crystal showing all metal and nitrogen sites (site occupancies are listed in parentheses). Selected bond lengths: N1A-Dy1A, 2.095(4) Å; N1A-Dy2A, 2.082(3) Å; N1A-Dy3A, 2.118(6) Å; N1B-Dy1A, 2.042(8) Å; N1B-Dy2A, 2.136(7) Å; and N1B-Dy3A, 2.05(1) Å. M-N bonds are shown as solid lines for the main metal site and as dotted lines for the site with the second highest occupancy.

OpenMOLCAS. 92,93 The Dy atoms in M3N@C80 molecules were treated one at a time, while other magnetic ions (Dy and Gd) were replaced with Y. The results of ab initio computations are summarized in Fig. 5b-d, and full data are given in Tables S4-S6.† The ground magnetic state of Dy³⁺ in all studied molecules is the Kramers doublet (KD) with essentially a pure m_I = $\pm 15/2$ character. For the rigorous $m_I = \pm 15/2$ KD, the principal values of the pseudospin g-tensor should be (0, 0, 20). In $M_3N@C_{80}$ molecules, g_z values are spread between 19.78 and 19.88 without any obvious regularity except for a vague trend to decrease for larger metals, and in particular for DyLa₂N@C₈₀ (Fig. 5b). The transversal components, quantified as $g_{x,y} = \sqrt{(g_x^2 + g_y^2)/2}$, exhibit a more regular variation with $\sum R^{3+}$. The $g_{x,y}$ value increases with the size of metals and closely follows h_N dependence. In fact, there is a good linear correlation between $g_{x,y}$ and h_N (Fig. S5†). Since the transversal components of the ground-state g-tensors define the tunnelling gap and thus determine the efficiency of the quantum tunnelling of magnetization (QTM) in zero magnetic field, the cluster pyramidalization may be considered an important factor for the QTM. But in the DyM2N@C80 series, for which this kind of QTM is crucial, the strong cluster pyramidalization achieved only in the experimentally non-available $DyLa_2N@C_{80}$, whereas in $DyM_2N@C_{80}$ with Sc, Lu, and Y the cluster is nearly planar.

Fig. 5c compares the size of the ligand-field splitting in the studied molecules focusing on the energy of the first excited KD (KD2) and on the whole splitting of the ground-state ⁶H_{15/2} multiplet (which is equal to the energy of the eighth KD, KD8). Selected examples of the LF splitting in individual DyM₂N@C₈₀ and Dy₂MN@C₈₀ molecules are shown in Fig. 5d. Both the overall LF splitting and the KD2 energy increase with $\sum R^{3+}$, but in a different fashion. E(KD8) shows two distinct segments in its growth, which are related to the nature of the structural changes. While d_{Dv-N} decreases (that is, for $\sum R^{3+}$ 2.7 Å), the growth of E(KD8) is relatively fast, but beyond the cluster pyramidalization threshold, the growth of E(KD8) is slowed down. In contrast, E(KD2) grows continuously in the whole $\sum R^{3+}$ range, which can be well described by a quadratic function (Fig. 5c).

To summarize, our computations showed that the ground magnetic state of Dy3+ in M3N@C80 molecules is weakly affected by the size of the metals forming the cluster and the variation of the cluster geometry. The transversal components of the g-tensors do increase with the cluster pyramidalization, but there is a lack of experimentally available molecules, where this effect may have a pronounced influence on magnetic behavior. Ligand field splitting is more susceptible to the cluster shape variations. The total splitting can be indeed related to the Dy-N bond length, and therefore it experiences only marginal changes when the metal size increase leads to cluster pyramidalization. But the energy of the first excited KD appears to be sensitive to the size-dependent strain itself, irrespective of the changes in the cluster geometry it causes.

Magnetic hysteresis

We next turn to the experimental studies of the magnetic properties of DyY₂N@C₈₀, Dy₂YN@C₈₀, and Dy₂LaN@C₈₀ by SQUID magnetometry. DyY2N@C80 shows waist-restricted (butterfly) magnetic hysteresis with an abrupt drop of magnetization near zero field (Fig. 6a). This feature is caused by the quantum tunnelling of magnetization (QTM) and is typical of single-ion Dy SMMs. 27,30,94-98 The hysteresis remains open up to 8 K when measured at a sweep rate of 2.9 mT s^{-1} . Determination of the blocking temperature $T_{\rm B}$ from the zerofield cooled/in-field cooled (ZFC/FC) temperature dependence of magnetic susceptibility gives a value of 8.4 K (Fig. 6a). Similar characteristics of magnetic hysteresis were obtained for DyY₂N@C₈₀ in a recent report by Wang et al. 30

Magnetic hysteresis of Dy₂YN@C₈₀ remains open up to 5 K. Likewise, the hysteresis without distinct QTM features is measured for Dy₂LaN@C₈₀ up to 4 K (Fig. 7a). T_B values in Dy₂YN@C₈₀ and Dy₂LaN@C₈₀ are 4.7 and 3.3 K, respectively. The zero-field QTM feature in the hysteresis curves of both as is common for dinuclear **EMFs** is absent, EMF-SMMs. 22,24,99-101 The coupling of two magnetic moments Research Article

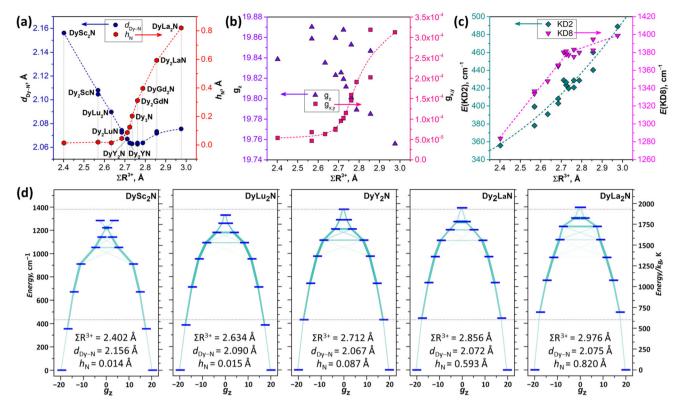


Fig. 5 (a) Dy-N bond lengths (d_{Dy-N}) and M₃N pyramid height (elevation of N above the plane of metal atoms, h_N) in DFT-optimized DyM₂N@C₈₀ and Dy₂MN@C₈₀ molecules (M = Sc, Lu, Y, La, Gd) plotted versus the sum of Shannon's ionic radii of metals in the M₃N cluster ($\sum R^{3+}$). (b) Components of the pseudospin g-tensor, g_z and g_{xy} (root mean square of g_x and g_y) for the Dy³⁺ ground state Kramers doublet (KD1) in the same set of molecules. (c) The energy of the first excited KD (KD2) and the total ligand-field splitting (KD8) in the same set of molecules. Dashed lines in (a) and (b) are a spline interpolation added to guide the eye; in (c), the dashed line for E(KD2) is a quadratic fit. (d) Dy3+ ligand-field splitting with transition probabilities in selected $M_3N@C_{80}$ molecules along with their $\sum R^{3+}$, d_{Dy-N} , and h_N parameters; dotted lines are guides to the eye and mark the KD2 and KD8 energies in DyY₂N@C₈₀. Ligand-field splitting and pseudospin g-tensor parameters used in (b-d) are computed ab initio at the CASSCF/RASSI-SO level using DFT-optimized molecular structures.

prevents an independent QTM-flip of one of the moments in zero field, 22 whereas the simultaneous flip of both moments is a rare-probability process detectable only at very low temperatures. 102

With the data from this work, we can compare hysteretic behaviour in complete sets of DyM2N@C80 and Dy2MN@C80 with the diamagnetic rare-earth M. Earlier we found that the T_B of DyLu₂N@C₈₀, 9.5 K, is higher than that of DySc₂N@C₈₀ by 2.6 K.²⁴ The value of 8.4 K determined here for DyY₂N@C₈₀ lies in between. Different from DySc₂N@C₈₀ and DyY₂N@C₈₀, DyLu2N@C80 showed some remanence and less efficient zerofield QTM. 24 Overall, the $T_{\rm B}$ in the DyM $_{2}$ N@C $_{80}$ series increases from Sc to Y to Lu and thus tends to correlate with the increase of the atomic mass rather than the ionic radius in this row (Fig. 8a).

A different situation is found in the binuclear Dy₂MN@C₈₀ series. Dy₂ScN@C₈₀ and Dy₂LuN@C₈₀ showed similar T_B and hysteresis closing temperatures of 8 K, but with a narrower hysteresis in Dy₂LuN@C₈₀.²⁴ The new data from this work reveal a decrease of the blocking temperature on going from Dy₂LuN to Dy₂YN to Dy₂LaN (Fig. 8b), as well as a decrease of the 2 K coercive field in the Dy₂MN series, Sc (0.70 T) > Lu (0.44 T) > Y

(0.28 T) > La (0.09 T). The latter effect is illustrated in Fig. 7b, which compares the hysteresis curves of four EMFs. Thus, the hysteretic behaviour in the Dy₂MN@C₈₀ series changes systematically with the M3+ size.

Importantly, when the metal M in DyM2N@C80 or Dy₂MN@C₈₀ is paramagnetic, the hysteretic behaviour is quite different from those of its diamagnetic analogs. At 1.8 K, Dy₃N@C₈₀ shows only a narrow hysteresis with fast QTM in zero field, which is caused by the multiply degenerate frustrated ground state.22 In Dy2GdN@C80, the presence of Gd accelerates the relaxation of magnetization when compared to Dy₂ScN@C₈₀ and Dy₂YN@C₈₀, so that only a very narrow hysteresis is open at 1.8 K.²³ In DyGd₂N@C₈₀, DyEr₂N@C₈₀, and Dy₂ErN@C₈₀, we could not find an open hysteresis down to 1.8 K (see Fig. S6† for magnetization curves; the synthesis is described in ref. 13).

Dy···Dy coupling in Dy₂MN@C₈₀

A considerable difference between the hysteresis curves of DyY₂N@C₈₀ and Dy₂YN@C₈₀ emphasizes that the interaction between the magnetic moments of Dy ions plays a crucial role in the static and dynamic magnetic behaviour, especially at

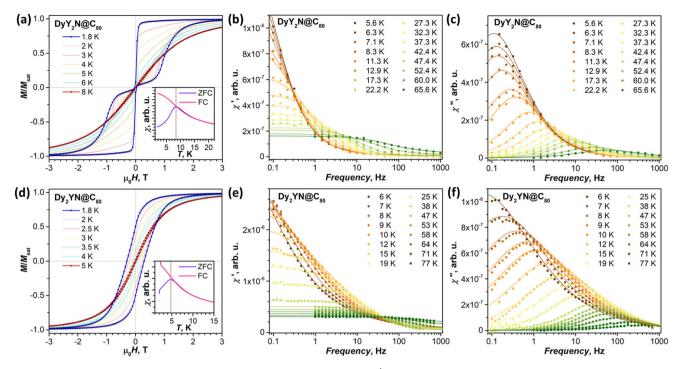


Fig. 6 (a) Magnetic hysteresis of DyY₂N@C₈₀ (magnetic field sweep rate: 2.9 mT s⁻¹); the inset shows determination of T_B from FC/ZFC measurements (temperature sweep rate: 5 K min⁻¹). (b and c) In-phase χ' (b) and out-of-phase χ'' (c) magnetic susceptibilities of DyY₂N@C₈₀ measured at different temperatures; dots are experimental values, lines are fitting with the generalized Debye model. (d) Magnetic hysteresis of Dy₂YN@C₈₀ (magnetic field sweep rate: 2.9 mT s⁻¹); the inset shows determination of T_R from FC/ZFC measurements. (e and f) In-phase χ' (e) and out-of-phase χ'' (f) magnetic susceptibilities of Dy₂YN@C₈₀ measured at different temperatures; dots are experimental values and lines are fitting with the generalized Debye model.

low temperatures. To determine the sign and size of the Dy...Dy coupling, we employed the effective spin Hamiltonian (eqn (1)) successfully used earlier for other {Dy₂} EMFs: 24,99,100,102

$$\hat{H}_{\text{spin}} = \hat{H}_{\text{LF}_1} + \hat{H}_{\text{LF}_2} - 2j_{12}\hat{J}_1 \cdot \hat{J}_2 + \hat{H}_{\text{ZEE}}$$
 (1)

where \hat{H}_{LF_1} and \hat{H}_{LF_2} are ligand-field Hamiltonians of individual Dy³⁺ ions with parameters from ab initio calculations, Dy...Dy coupling is described by the bilinear product of total angular momentum operators of Dy ions $(\widehat{J_1} \text{ and } \widehat{J_2})$ scaled by the effective coupling constant j_{12} , and the interaction with the magnetic field is given in the Zeeman term \hat{H}_{ZEE} . In essence, the ligand-field terms split the ground-state multiplet of each Dy ion into 8 KDs, whereas the interaction term couples individual KDs of different ions. In the low-energy part of the spectrum, the Hamiltonian gives two quasi-doublets formed by coupling of the ground state KDs of two ions (KD1 and KD1') with ferromagnetic (FM) and antiferromagnetic (AFM) alignment of magnetic moments (Fig. S7†). The energy difference between the AFM and FM states is:

$$\Delta E_{\text{AFM-FM}} = 4J_{z1}J_{z2}j_{12}\cos(\alpha) = (g_{z1}/g_I)(g_{z2}/g_I)j_{12}\cos(\alpha) \approx 225j_{12}\cos(\alpha),$$
 (2)

where J_{z1} and J_{z2} are J_z projections in the ground state KDs of Dy^{3+} ions on individual quantization axes, α is the angle between their quantization axes, g_{z1} and g_{z2} are g_z components

of their pseudospin *g*-tensors, g_I is the Landé *g*-factor ($g_I = 4/3$ for the ⁶H_{15/2} multiplet of Dy³⁺), and the last approximate term is attributed to $J_{zi} \approx 15/2$. The middle part of the equation emphasizes the similarity of our approach to the method addressing the coupling of Dy moments based on the Lines model¹⁰³ and utilizing their ground state pseudospins as popularized by Chibotaru and Ungur et al. 104,105 When ligandfield parameters and the angle α are obtained by ab initio calculations, j_{12} is the only unknown parameter in eqn (1).

To determine j_{12} and thereby $\Delta E_{\text{AFM-FM}}$ for Dy₂YN@C₈₀ and Dy₂LaN@C₈₀, we measured their magnetization curves at different temperatures between 1.8 and 200 K and fitted them using the Hamiltonian (1) with j_{12} as a free parameter. The ab initio ligand-field splitting is already discussed above (Fig. 5 and Tables S4-S6†); the angles between the magnetic moments of 60.6° (Dy₂YN) and 63.0° (Dy₂LaN) were obtained from the same ab initio calculations and are approximately equal to the geometrical angle: $\alpha^{\circ} \approx 180 - \angle(\text{Dy-N-Dy})$. The fits performed employing the PHI code¹⁰⁶ with powder averaging gave the $\Delta E_{\text{AFM-FM}}$ values of 1.0 ± 0.1 cm⁻¹ (j_{12} = 0.009 ± 0.001 cm⁻¹) in Dy₂YN@C₈₀ and -0.8 ± 0.2 cm⁻¹ ($j_{12} = -0.008$ $\pm 0.002 \text{ cm}^{-1}$) in Dy₂LaN@C₈₀ (see Fig. S8 and S9[†] for comparison of experimental points and fitted curves). These values can be compared to $\Delta E_{AFM-FM} = 5.6 \text{ cm}^{-1} \text{ in Dy}_2ScN@C_{80}$ and $\Delta E_{AFM-FM} = 3.0 \text{ cm}^{-1} \text{ in } Dy_2LuN@C_{80}.^{24} \text{ Thus, we conclude}$ that the ΔE_{AFM-FM} value in the Dy₂MN@C₈₀ series systematically decreases and even changes its sign with the increase of

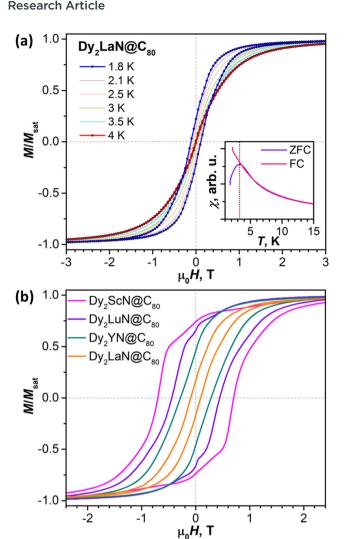


Fig. 7 (a) Magnetic hysteresis measurements for Dy₂LaN@C₈₀ (magnetic field sweep rate: 2.9 mT s⁻¹); the inset shows determination of T_B from FC/ZFC measurements. (b) Comparison of the magnetic hysteresis shape for $Dy_2MN@C_{80}$ EMFs (M = Sc, Lu, Y, La) at 2 K (2.1 K for La); magnetic field sweep rate: 2.9 mT s⁻¹ for all compounds.

the M^{3+} size. Furthermore, the contribution to $\Delta E_{\Delta EM-EM}$ from dipole-dipole interactions can be calculated using geometry parameters and α angles, giving similar values of $\Delta E_{\Delta EM-EM}^{dip} =$ 3.3-3.4 cm⁻¹ in all Dy₂MN@C₈₀ molecules. Therefore, the metal size dependence is mainly caused by the exchange contribution (likely Dy-N-Dy superexchange), which is ferromagnetic in Dy₂ScN@C₈₀ (ΔE_{AFM-FM}^{exch} = +2.3 cm⁻¹), but becomes progressively antiferromagnetic in other Dy₂MN@C₈₀ molecules with the increase of M (-0.3 cm⁻¹ for Lu, -2.4 cm⁻¹ for Y, and -4.2 cm⁻¹ for La). Interestingly, this systematic variation cannot be well correlated with the cluster geometrical parameters such as the Dy-N bond length (the values are similar for Dy₂LuN and Dy₂LaN), or the Dy-N-Dy angle (the values remain similar for all Dv₂MN), or the degree of cluster pyramidalization (Dy2ScN and Dy2LuN are just planar and Dy₂YN is nearly planar). Only the M³⁺ ionic radius appears to be a suitable parameter to correlate with $\Delta E_{\text{AFM-FM}}^{\text{exch}}$ (Fig. 8b).

Relaxation of magnetization

The magnetic hysteresis indicates that the studied EMFs feature single-molecule magnetic behaviour, which calls for a study of the relaxation of magnetization. Relaxation times, $\tau_{\rm M}$, were measured at different temperatures employing both DC and AC techniques. In the former, the samples were saturated at 7 Tesla, then the field was ramped at 70 mT s⁻¹ to 0 T or to 0.2 T, and then a decay of magnetization was measured and fitted with stretched exponential function. This technique allows reliable measurement of $\tau_{\rm M}$ not shorter than 50–100 s; the values longer than 104 s are also hard to determine since one would need to measure magnetization decay for a very long time. In AC measurements, the field was oscillated around 0 T with the amplitude of 5 Oe, giving in-phase and out-of-phase magnetic susceptibilities, χ' and χ'' . At each temperature, the frequency dependence of χ' and χ'' was measured and the curves were fitted with a generalized Debye model. Fig. 6(b, c, e and f) shows χ' and χ'' data for DyY₂N@C₈₀ and Dy₂YN@C₈₀. The values of relaxation times are listed in Tables S7 and S8 in the ESI.† The amount of synthesized

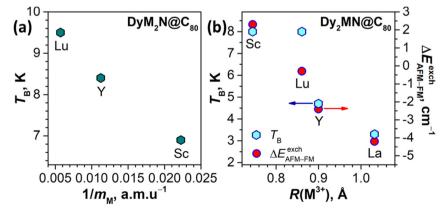


Fig. 8 (a) Correlation between reciprocal mass $1/m_M$ and blocking temperature T_B in the DyM₂N@C₈₀ series (M = Sc, Y, Lu). (b) Correlation between the ionic radius $R(M^{3+})$ and T_B (left scale, cyan hexagons) and $\Delta E_{RFM-FM}^{\rm exch}$ (right scale, red dots) in the Dy₂MN@C₈₀ series (M = Sc, Y, Lu, La).

Dy2LaN@C80 was not sufficient for its studies by AC magnetometry.

DyY2N@C80. Due to the QTM, zero-field relaxation times in DyY₂N@C₈₀ are comparably short and can be measured only with the AC technique. But the low-temperature $\tau_{\rm M}$ values of 1-2 seconds are close to the frequency limits of the magnetometer, and thus the lowest accessible temperature was 5 K. The $\tau_{\rm M}$ values show a weak temperature dependence at 5–10 K, but then accelerate with the temperature increase. The $\tau_{\rm M}(T)$ dependence does not exhibit a linear Arrhenius behaviour, at least up to 60 K, at which temperature an onset of a new relaxation regime could be detected. The signal intensity at this temperature is already rather low, thus limiting the available range to T < 70 K. The whole dependence could be fitted by a combination of three mechanisms (solid blue line in Fig. 9):

$$\tau_{\text{M}}^{-1}(T) = \tau_{\text{QTM}}^{-1} + CT^n + \tau_0^{-1} \exp(-U^{\text{eff}}/T)$$
 (3)

The QTM regime with $\tau_{\rm QTM}$ = 2.2 \pm 0.1 s dominates below 7 K, the Raman regime with $C = (3.1 \pm 0.3) \times 10^{-3} \text{ s}^{-1} \text{ K}^{-n}$ and $n = 2.53 \pm 0.03$ has the main contribution up to 55 K, and the Orbach mechanism with an attempt time of τ_0 = (2.5 ± 1.8) × 10^{-9} s⁻¹ and an effective barrier of $U^{\text{eff}} = 929 \pm 47$ K outweighs the Raman process above 60 K. The Orbach mechanism involving excited ligand-field states is naturally expected for DyY₂N@C₈₀, and most probably it is its onset that we detect above 60 K. But since this process can only be attested by a few highest-temperature $\tau_{\rm M}$ points measured at the accuracy limits of our magnetometer, the reliability of the Ueff value does not seem sufficient for a discussion of particular KDs involved.

In the finite field of 0.2 T, applied to suppress the QTM, the relaxation times of DyY2N@C80 increased dramatically and

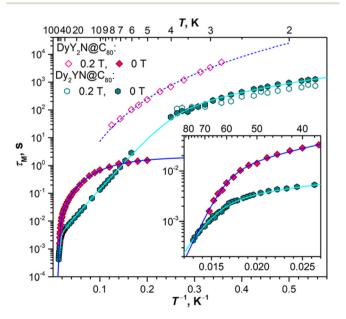


Fig. 9 Magnetization relaxation times of DyY2N@C80 and Dy2YN@C80 determined by DC and AC magnetometry (open points, at 0.2 T; filled points, at zero field). Lines are fits with relaxation mechanisms discussed in the text. The inset shows enlargement of the high-temperature part.

could be measured by the DC technique between 2.8 and 7 K. The values showed a steady decrease with temperature and could be well described by the Raman process with $C = (1.2 \pm$ $(0.1) \times 10^{-6} \text{ s}^{-1} \text{ K}^{-n}$ and $n = 5.05 \pm 0.08$ (dashed blue line in Fig. 9). An alternative fit with the Orbach mechanism gave τ_0 = $3.0 \pm 0.5 \text{ s}^{-1}$ and $U^{\text{eff}} = 21.3 \pm 0.6 \text{ K}$, similar to the values reported by Wang et al., 30 but the agreement with the experimental data is worse than that for the Raman mechanism. Note that the removal of the QTM part from eqn (2) and keeping the fitted zero-field parameters for Raman and Orbach mechanisms cannot produce the long relaxation times measured at 0.2 T, indicating that there may be more processes involved in the relaxation and that the mechanism identified at zero field as Raman should be also coupled to the OTM, despite its obvious temperature dependence. Whether the QTM shows unconventional temperature dependence, 72,107 or there may be another relaxation process, which evades detection by AC measurements due to its lower rate, is hard to determine at this moment.

Dy₂YN@C₈₀. For Dy₂YN@C₈₀, DC (below 4 K) and AC measurements (6-77 K) gave a consistent set of data, which could be described by a combination of the Raman process and two distinct Orbach regimes (cyan line in Fig. 9):

$$\tau_{\text{M}}^{-1}(T) = CT^{n} + \tau_{0,1}^{-1} \exp(-U_{1}^{\text{eff}}/T) + \tau_{0,2}^{-1} \exp(-U_{2}^{\text{eff}}/T)$$
(4)

The Raman mechanism with $C = (1.11 \pm 0.07) \times 10^{-4} \text{ s}^{-1}$ K^{-n} and $n = 3.34 \pm 0.06$ describes the low-T part (1.8-4 K) measured by DC magnetometry. The first Orbach regime with $\tau_{0,1} = (1.84 \pm 0.06) \times 10^{-3} \text{ s}^{-1}$ and a barrier of $U_1^{\text{eff}} = 43.8 \pm 0.3 \text{ K}$ is well established between 6 and 50 K, whereas the second Orbach regime with $\tau_{0,2} = (8 \pm 4) \times 10^{-8} \text{ s}^{-1}$ and a barrier of $U_2^{\rm eff}$ = 680 ± 40 K dominates above 60 K. Similar to the measurements for DyY2N@C80, the parameters of the high-T regime are determined with limited accuracy because of the low signal intensity at these temperatures near the sensitivity limits. Thus, we can hypothesize that this process corresponds to the relaxation via ligand-field excited states, but the precise determination of the involved states is hardly possible.

The Orbach regime with a barrier of 44 K (30 cm⁻¹) is quite remarkable. It cannot be assigned to ligand-field excited states since the latter have energies at least an order of magnitude higher (Fig. 5). Thus, U_1^{eff} most likely corresponds to a vibrational mode with a strong spin-phonon coupling. The Arrhenius behavior with the energy equal vibrational frequency was predicted for spin-lattice relaxation coupled to local or optical phonons already back in 1960s 108,109 and re-introduced in more recent theoretical studies. 110 The fullerene cages are rather rigid, and their vibrations occur above 200 cm⁻¹, but the endohedral clusters are composed of heavy atoms and have several modes at low frequencies. 24,62,101 In Dy₂YN@C₈₀, the lowest-frequency modes predicted by DFT in harmonic approximation for an isolated molecule are rotational motions (librations) of the cluster at 40.6, 41.1, and 48.3 cm⁻¹. A simple harmonic approximation is most probably not fully suitable for these modes; besides, such intramolecular vibrations can

strongly mix with lattice modes, ²⁴ which altogether would affect their frequencies and facilitate the momentum transfer.

Research Article

In the low-temperature range, the Raman process with a small exponent is only weakly affected by a magnetic field of 0.2 T, presumably via the direct mechanism. Note that the relaxation times of $\mathrm{Dy_2YN@C_{80}}$ at low temperatures are much longer than those in $\mathrm{DyY_2N@C_{80}}$ in zero field, but considerably shorter than the latter in a field of 0.2 T. Thus, the coupling of Dy moments quenches the zero-field QTM, but adds new relaxation pathways, which makes the relaxation of $\mathrm{Dy_2YN@C_{80}}$ faster once the QTM in $\mathrm{DyY_2N@C_{80}}$ is suppressed. The difference in relaxation times between mono- and dinuclear systems is considerable at higher temperatures as well and remains detectable even when the relaxation starts to be dominated by ligand-field excited states.

Fig. 10 compares magnetization relaxation times in $DyM_2N@C_{80}$ and $Dy_2MN@C_{80}$ series. At low temperatures, all three mono-Dy EMFs show similar relaxation behaviour, including the very long relaxation in a field of 0.2 T and the fast temperature-independent QTM in zero field. The longest time both in zero field and in a finite field is found for

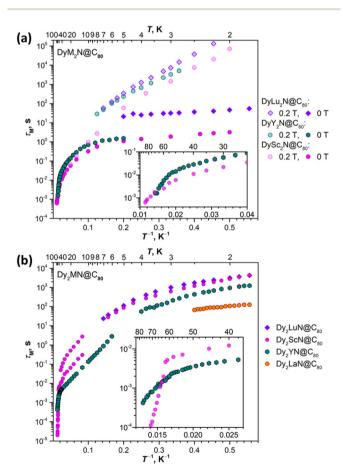


Fig. 10 Magnetization relaxation times of the $DyM_2N@C_{80}$ series (a; M = Sc, Lu, Y; field 0 T and 0.2 T) and $Dy_2MN@C_{80}$ series (b; M = Sc, Lu, Y, La; field 0 T). Insets show enlargement of high-temperature parts. The data for M = Sc are from ref. 72 ($DySc_2N$) and ref. 71 (Dy_2ScN), for M = Lu - from ref. 24.

DyLu₂N@C₈₀, followed by DyY₂N@C₈₀, and then DySc₂N@C₈₀. These data are in line with the row of $T_{\rm B}$ values for these EMFs. At higher temperatures, DyY₂N@C₈₀ and DySc₂N@C₈₀ both show a power-law temperature dependence, DySc₂N@C₈₀ being again somewhat faster. The data for DyLu₂N@C₈₀ in that temperature range are not available as the sample amount in ref. 24 was not sufficient for AC measurements.

The differences in relaxation rates in single-ion magnets can be either attributed to the different single-ion magnetic anisotropy or to the aforementioned spin-phonon interactions. As our computational study showed that the ground-state KD properties of Dy³⁺ are virtually identical (Fig. 5), it makes the differences in the spin-phonon coupling a primary factor. The correlation with the mass of M rather than its size is also a strong indication toward the phonon-based difference in relaxation rates in the DyM₂N@C₈₀ series. But the found sequence of relaxation rates (DySc₂N is faster than DyY₂N, and the latter is faster than DyLu₂N) is rather counter-intuitive. One could expect a reversed order of relaxation rates because heavier clusters have larger vibrational DOS at lower energies, which facilitates the spin-lattice relaxation at low temperature.

In the Dy₂MN@C₈₀ series, the rates determined at low temperature for Dy₂ScN and Dy₂LuN are very similar, while Dy₂YN and Dy₂LaN show progressively faster relaxation. The fast decrease of $\tau_{\rm M}$ falls in line with the decrease of the $\Delta E_{\rm AFM-FM}$ difference in this row and hence correlates with the size of M³+. At higher temperatures, the relaxation in Dy₂YN@C₈₀ remains faster than that in Dy₂ScN@C₈₀ until the switch to the Orbach regime νia single-ion LF-excitations. At that moment, Dy₂ScN@C₈₀ starts to show a faster relaxation as it also has a higher barrier and thus its relaxation accelerates faster with temperature. We conclude that while the relaxation of magnetization in Dy₂MN@C₈₀ is governed by a Dy···Dy coupled state, the $\Delta E_{\rm AFM-FM}$ value seems to be the main factor in play, and variations of the phonon DOS caused by a different mass of the M ion are less critical.

Photoluminescence of DyY2N@C80

Our earlier finding of thermally activated delayed fluorescence (TADF) in the series of $Y_xSc_{3-x}N@C_{80}$ EMFs $(x = 0-3)^{111,112}$ suggested that similar phenomena may be present in other M₃N@C₈₀ molecules. Indeed, TADF was recently reported in DyY₂N@C₈₀.³⁰ This result was very intriguing since the presence of Dy in the endohedral cluster was expected to increase the spin-orbit coupling and quench the fullerene-based radiative process. As ref. 30 lacked the characterization of the triplet state of DyY2N@C80 below 80 K, we decided to study the photoluminescence (PL) of DyY₂N@C₈₀ at helium temperatures. The measurements appeared complicated by a PL signal of the Y₃N@C₈₀ trace (which is also identifiable in ref. 30), and additional HPLC cycles were performed to minimize its contribution. After more thorough removal of Y₃N@C₈₀ (note that its content was already below the sensitivity of HPLC and MALDI-TOF and could only be assessed by PL measurements), we realized that the spectral features and PL lifetimes of purified DyY₂N@C₈₀ are virtually identical to those of Y₂ScN@C₈₀

(Fig. S10†). ¹¹¹ This surprising finding was then confirmed by LDI-TOF mass-spectrometry analysis, which revealed a small signal of $Y_2ScN@C_{80}$ when the measurements were performed with strongly increased laser power; under our standard LDI-TOF measurement conditions, this signal was not detectable (Fig. S11†). Based on these studies, we conclude that $DyY_2N@C_{80}$ is non-luminescent, whereas the PL signals that we and others³⁰ detected in $DyY_2N@C_{80}$ samples were caused by tiny traces of $Y_3N@C_{80}$ and $Y_2ScN@C_{80}$, which could not be detected by other techniques, but were still measurable in PL spectra. The contamination with $Y_2ScN@C_{80}$ is presumably caused by traces of Sc in the Y_2O_3 oxide used as the Y source in the arc-discharge synthesis. Analogous measurements for $Dy_2YN@C_{80}$ also did not show PL activity.

Conclusions

In this work, we reported the synthesis, isolation, and singlecrystal X-ray diffraction study of Dy2LaN@Ih-C80 and complete $Dy_xY_{3-x}N@I_h$ -C₈₀ series (x = 0-3). The M₃N cluster is found to be planar in all Dy_xY_{3-x}N EMFs, albeit with a systematic increase of the nitrogen out-of-plane amplitude from Y₃N to Dy₃N. The Dy₂LaN cluster is strongly pyramidal with a nitrogen out-of-plane displacement of 0.619(4)/0.530(9) Å. The studies of the magnetic properties of DyY2N@C80, Dy2YN@C80, and Dy₂LaN@C₈₀ revealed SMM behavior with magnetic hysteresis in all EMFs but with strongly metal-dependent parameters. Comparison of the relaxation behavior to other DyM2N@C80 and $Dy_2MN@C_{80}$ EMFs (M = Sc, Lu) and extended *ab initio* calculations revealed that the SMM properties in the DyM₂N@C₈₀ series can be correlated with the mass of M, whereas the variation of magnetic properties in the Dy2MN@C80 row correlates with the ionic radius of M3+. The mass dependence of spinlattice relaxation points to a clear connection with the phonon degrees of freedom, whereas the size dependence appears to be related to the variation of the Dy...Dy coupling. In particular, the energy of the exchange Dy...Dy interaction changes from a positive (ferromagnetic) value of +2.3 cm⁻¹ in Dy₂ScN@C₈₀ to an antiferromagnetic coupling of -4.2 cm⁻¹ in Dy₂LaN@C₈₀ with intermediate values of -0.3 cm⁻¹ in Dy₂LuN@C₈₀ and -2.4 cm⁻¹ in Dy₂YN@C₈₀. These magnetostructural correlations demonstrate that the variation of the endohedral cluster size and engineering of the inner strain in EMFs can be used as control parameters for tuning the static and dynamic magnetic properties.

Conflicts of interest

There are no conflicts to declare.

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