Selective arc-discharge synthesis of Dy2S-clusterfullerenes and their isomer-dependent single molecule magnetism

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Abstract: A method for the selective synthesis of sulfide clusterfullerenes Dy2S@C2n is developed. Addition of methane to the reactive atmosphere reduces the formation of empty fullerenes in the arc-discharge synthesis, whereas the use of Dy2S3 as a source of metal and sulfur affords sulfide clusterfullerenes as the main fullerene products along with smaller amounts of carbide clusterfullerenes. Two isomers of Dy2S@C82 with Cs(6) and C3v(8) cage symmetry, Dy2S@C72-Cs(10528), and a carbide clusterfullerene Dy2C2@C82-Cs(6) were isolated. The molecular structure of both Dy2S@C82 isomers was elucidated by single-crystal X-ray diffraction. SQUID magnetometry demonstrates that all of these clusterfullerenes exhibit hysteresis of magnetization, with Dy2S@C82-Cs(8) being the strongest single molecule magnet in the series. DC- and AC-susceptibility measurements were used to determine magnetization relaxation times in the temperature range from 1.6 K to 70 K. Unprecedented magnetization relaxation dynamics with three consequent Orbach processes and energy barriers of 10.5, 48, and 123 K are determined for Dy2S@C82-C3v(8). Dy2S@C82-Cs(6) exhibits faster relaxation of magnetization with two barriers of 15.2 and 523 K. Ab initio calculations were used to interpret experimental data and compare the Dy-sulfide clusterfullerenes to other Dy-clusterfullerenes. The smallest and largest barriers are ascribed to the exchange/dipolar barrier and relaxation via crystal-field states, respectively, whereas an intermediate energy barrier of 48 K in Dy2S@C82-C3v(8) is assigned to the local phonon mode, corresponding to the librational motion of the Dy2S cluster inside the carbon cage.

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Selective arc-discharge synthesis of Dy₂S-clusterfullerenes and their isomer-dependent single molecule magnetism†

Chia-Hsiang Chen,‡a Denis S. Krylov,‡a Stanislav M. Avdoshenko,‡a Fupin Liu,‡a Lukas Spree,‡a Ravi Yadav,a Antonis Alvertis,a Liviu Hozoi,a Konstantin Nenkov,a Aram Kostanyan,b Thomas Greber,b Anja U. B. Wolterb and Alexey A. Popov‡a

A method for the selective synthesis of sulfide clusterfullerenes Dy₂S@C₈₂ is developed. Addition of methane to the reactive atmosphere reduces the formation of empty fullerenes in the arc-discharge synthesis, whereas the use of Dy₂S₂ as a source of metal and sulfur affords sulfide clusterfullerenes as the main fullerene products along with smaller amounts of carbide clusterfullerenes. Two isomers of Dy₂S@C₈₂ with C₁(6) and C₅v(8) cage symmetry, Dy₂S@C₇₂−C₅v(10528), and a carbide clusterfullerene Dy₂C₂@C₈₂−C₅v(6) were isolated. The molecular structure of both Dy₂S@C₈₂ isomers was elucidated by single-crystal X-ray diffraction. SQUID magnetometry demonstrates that all of these clusterfullerenes exhibit hysteresis of magnetization, with Dy₂S@C₈₂−C₅v(8) being the strongest single molecule magnet in the series. DC- and AC-susceptibility measurements were used to determine magnetization relaxation times in the temperature range from 1.6 K to 70 K. Unprecedented magnetization relaxation dynamics with three consequent Orbach processes and energy barriers of 10.5, 48, and 1232 K are determined for the Dy₂S@C₈₂−C₅v(8) isomer. The molecular structure of the Dy₂C₂@C₈₂−C₅v(6) clusterfullerene is assigned to the local phonon mode, corresponding to the librational motion of the Dy₂S cluster inside the carbon cage.

Introduction

The discovery of single molecule magnetism in the Mn₁₂ complex in 1993 (ref. 1) initiated an on-going chase for molecule with a high blocking temperature and large relaxation barrier of magnetization. Lanthanides entered the field in 2003 with the report on the slow relaxation of magnetization in their double-decker complexes, and hundreds of lanthanide-SMMs have been described since that time. Quantum tunneling of magnetization (QTM) is one of the most important mechanisms of losing the spin information by single-ion lanthanide SMMs at zero field. One of the ways to improve the situation is to increase the local symmetry of the crystal field acting on the lanthanide ion, and some of the best single-ion Dy-SMM have been obtained following this strategy. Another approach is to combine two or more lanthanide ions in one molecule, or combine lanthanides with transition metals in 3d–4f complexes. Exchange and dipolar coupling in polynuclear complexes create a manifold of additional states and an additional barrier to relaxation, thus preventing QTM. Therefore, single-ion anisotropy and inter-lanthanide interactions are the two key ingredients in improving the SMM properties.

Endohedral metallofullerenes (EMFs), and in particular clusterfullerenes, combining lanthanides and non-metal ions in endohedral species, provide a convenient platform for creating SMMs. The presence of negatively charged non-metal ions (such as a nitride ion N³⁻ in the nitride clusterfullerene M₃N@C₈₀) close to the lanthanide ions leads to the large magnetic anisotropy of the latter, whereas the possibility of varying the composition of the endohedral cluster by combining lanthanides with scandium or other diamagnetic analogs allows tuning the intracluster interactions. Both parameters can change strongly with variation of the central (non-metal) atom in clusterfullerenes. EMFs emerged as a new class of SMMs in 2012, when the nitride clusterfullerene DySc₂N@C₈₀ was shown to exhibit a hysteresis of magnetization

‡ These authors contributed equally.

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with zero-field quantum tunneling of magnetization. Subsequent studies have shown that SMM behavior of Dy-Sc nitride clusterfullerenes strongly depends on the endohedral cluster composition, with Dy2ScN@C80 being a better SMM than DySc2N@C80 and much better than Dy3N@C80. The superior SMM properties of Dy2ScN@C80 are explained by the ferromagnetic exchange and dipolar coupling of Dy ions, which lead to the exchange/dipolar barrier of 10.5 K and suppress zero-field QTM. At higher temperatures, the relaxation of the magnetization in Dy2ScN@C80 proceeds via the Orbach mechanism with a high barrier of 1735 K, corresponding to the fifth Kramers doublet of the Dy3+ ion. The long magnetization relaxation time of Dy2ScN@C80 was partially preserved even on a metallic substrate. HoSc2N@C80 was also found to be a SMM, albeit with much faster relaxation than in the Dy analog. Other types of clusterfullerenes were also tested for SMM behavior. Ti-carbide Dy2TiC@C80 was found to exhibit hysteresis similar to Dy2ScN@C80 albeit with a lower blocking temperature. At the same time, addition of one more carbon atom to the cluster, such as in Dy2TiC@C80, led to substantially worsened SMM properties. Field-induced SMM behavior was also demonstrated for cyano-clusterfullerenes with single metal atoms, TbNC@C82 (ref. 43) and TbNC@C76. As Tb31 and Ho32 are non-Kramers ions, the corresponding EMFs exhibit much faster relaxation of magnetization, and hence better EMF-SMMs are to be looked for among Dy-EMFs.

In this work we focus on Dy-based sulfide clusterfullerenes of the formula Dy2Sx@C2n to study how Dy-S bonding and interlanthanide coupling via the sulfide bridge affect the SMM properties. The first synthesis of the sulfide clusterfullerene Sc2S@C82 was reported in 2010. In that work, guanidinium thiocyanate was used as a source of nitrogen in the synthesis of nitride clusterfullerenes, and the sulfide was obtained as a by-product with much lower relative yield. Echegoyen et al. used the addition of SO2 gas to the reactor atmosphere and obtained a family of Sc2Sx@C82 EMFs with 2n ranging from 70 to 100 according to mass-spectrometry. In SO2-assisted synthesis, empty fullerenes are the main fullerene products. Thus, both synthetic routes to sulfide clusterfullerenes led to other types of fullerenes (nitride clusterfullerenes or empty fullerenes) as the main products. Isolation of sulfide clusterfullerenes then required tedious multistep chromatographic separation. The principal possibility to obtain non-Sc M2S@C82 clusterfullerenes was also demonstrated in 2010, but the isolated amounts were very small.

The low selectivity of the arc-discharge synthesis is a serious obstacle when low-yield EMFs, such as sulfide clusterfullerenes, are the goal of the synthesis. It is therefore desirable to develop more selective approaches for the synthesis of clusterfullerenes. The first selective method for the synthesis of EMFs was developed by Dunsch and coworkers. The authors found that addition of NH3 gas to the arc-discharge reactor atmosphere dramatically reduced the yield of empty fullerenes but did not affect the formation of nitride clusterfullerenes. The latter could be thus obtained with a high degree of selectivity. High selectivity of nitride clusterfullerenes was also achieved with the use of solid nitrogen sources (such as guanidinium thiocyanate, inorganic salts, urea or using NOx vapor from NOx-generating solid reagents and air (known as the CAPTEAR approach). More recently, we have adapted a method for selective synthesis of carbide clusterfullerenes using methane as a reactive gas. Its influence on the arc-discharge is similar to that of NH3. Namely, hydrogen suppresses the formation of empty fullerenes, and carbide clusterfullerenes, especially Ti-carbide clusterfullerenes M2TiC@C80 and M2TiC2@C80 as well as Sc-carbide Sc2CH@C80 (ref. 54) and Sc2C2@C80 can be obtained with a high degree of selectivity.

In this work, we pursue two goals. First, we develop the procedure for the selective synthesis of sulfide clusterfullerenes and synthesize a new family of EMF-SMMs, Dy-based sulfide clusterfullerenes. Second, we perform a thorough analysis of the magnetic properties of the Dy-sulfide clusterfullerenes and demonstrate that they exhibit SMM behavior. Their unprecedented magnetization relaxation dynamics is analyzed as a function of temperature and the main relaxation pathways are revealed.

Results and discussion

Synthesis of clusterfullerenes

Selective synthesis of nitride and carbide clusterfullerenes was achieved via addition of hydrogen-containing compounds. Hydrogen suppresses the yield of empty fullerenes, and EMFs can be obtained with improved selectivity. To achieve a similar effect in the synthesis of sulfide clusterfullerenes, several combinations of dysprosium and sulfur sources were tested. In particular, we used (i) a mixture of Dy powder with elementary sulfur; (ii) a mixture of Dy powder with a solid organic sulfur compound, dibenzyl sulfide; (iii) Dy2S3 sulfide. The syntheses were performed in pure helium atmosphere (230 mbar), as well as with the addition of several mbar of methane. Mass-spectrometric analysis showed that all three strategies led to formation of Dy2S@C2n clusterfullerenes, albeit with quite a low yield. In all cases the presence of methane increased the relative yield of sulfide clusterfullerenes (as far as it could be decided based on laser-desorption ionization time-of-flight (LDI-TOF) mass-spectra; note that conclusions on the yield of EMFs based on LDI-TOF data should be treated with caution). The best results were obtained with the use of Dy2S3 as a simultaneous source of metal and sulfur, and this route was then further optimized by varying the amount of methane. Fig. 1 compares HPLC traces of Cs2 fullerene extracts obtained in the syntheses without methane and with 13 mbar and 20 mbar of CH4 (total pressure was kept at 250 mbar). In the absence of methane, empty fullerenes are formed in much larger amounts than EMFs, and the HPLC trace is very similar to that of a standard empty fullerene synthesis (not shown). Addition of 13 mbar CH4 to the reactor atmosphere immediately reduced the yield of empty fullerenes, and EMF peaks with retention times longer than 30 minutes can be well seen in the chromatogram. Their intensities are comparable to those of higher empty fullerenes (the yield of C60 and C70 is still considerably higher). In the presence of 20 mbar CH4, formation of empty...
fullerenes is suppressed almost completely, leaving only several well-established peaks marked with block letters (A–D). Mass-spectral analysis revealed that each peak corresponds to clusterfullerenes, including Dy2S@C72 (A), Dy3N@C80 (B), and two isomers of Dy2S@C82 (C and D). Mass-spectra of the fraction collected at longer retention times (37–45 min) also showed the presence of Dy2S@C78 and Dy2S@C86, but their amounts are too low for separation. Formation of the nitride clusterfullerene Dy3N@C80 seems to be inevitable even when only traces of nitrogen are present in the generator (earlier we observed the same effect in the synthesis of carbide clusterfullerenes43).

Mass-spectral analysis of the fractions C and D also showed that they contained certain amounts of carbide clusterfullerenes Dy2C2@C82. To obtain pure compounds, recycling HPLC was used at the second separation step (Fig. S1†). As a result of the chromatographic separation, pure Dy2S@C72, two isomers of Dy2S@C82, and one isomer of Dy2C@C82 were obtained. It should be noted that the use of methane suppresses the formation of empty fullerences and simplifies the separation of sulfide clusterfullerenes, but their overall yield remains quite low. The isolated amounts for each compound were less than 1 mg.

**Spectroscopic characterization and molecular structures**

Molecular structures of the isolated clusterfullerenes are first established with the use of UV-vis-NIR absorption spectroscopy. Due to multiple $\pi-\pi^*$ transitions, the absorption spectra of EMFs are very sensitive to the isomeric structure of the fullerene cage, which can be used for structure elucidation. Fig. 2 shows that Dy2S@C82-I and Dy2C@C82-I have very similar absorption spectra, which indicates that these two EMFs have the same carbon cage. This spectral pattern is in fact very characteristic for the EMFs with a C82-$C_4$ cage in the formal four-fold charged state, including ErS@C82$C_4$ (6),28 Sc2C2@C82$C_4$ (6),29 Sc2S@C82$C_4$ (6),30 and Y2C2@C82$C_4$ (6).31 Thus, we can reliably assign the cage isomer of isostructural Dy2S@C82 and Dy2C2@C82 molecules as C82-$C_4$(6). The absorption pattern of Dy2S@C82-II closely resembles that of EMFs with the C82-$C_3v$(8) cage in the four-fold charged state, such as sulfide clusterfullerenes ErS@C82$C_3v$(8)28 and Sc2S@C82$C_3v$(8),45,46 or the carbide clusterfullerene M2C2@C82$C_3v$(8).63,64 Note that the C82-$C_3v$(6) and C82-$C_3v$(8) cages are rather similar and are related via two Stone–Wales transformations (i.e. via the pseudo-rotation of two C–C bonds highlighted in red in Fig. 2 by 90°).

Possible orientations of the endohedral clusters in the Dy2S@C82 and Dy2S@C82 isomers are addressed with the use of DFT calculations (Fig. 2d–f). To avoid difficulties of treating the system with partially-filled 4f-shells at the DFT level, we used Y as a model of Dy in such calculations because of their close ionic radius. For Y2S@C82$C_4$ (6) and Y2S@C82$C_3v$(8), our calculations revealed one particular cluster orientation (identical for both carbide and sulfide clusters), which is at least 25 kJ mol$^{-1}$ lower in energy than all other configurations (Fig. 2d and e). For Y2S@C82$C_3v$(8), the calculations revealed several energy minima, all related via rotation of the cluster around the C3 axis of the carbon cage; the lowest-energy one is shown in Fig. 2f. DFT-based Born–Oppenheimer molecular dynamics (BOMD) simulations for Y2S@C82$C_4$ (6) at 300 and 450 K did not reveal reorientation of the cluster on the 100 ps time scale (Fig. 3a). These data indicate that the Dy2S cluster in Dy2S@C82$C_4$ (6) is probably fixed, or exhibits jump-like rotations with a low rate. Note that NMR studies of Sc2C2@C82$C_4$ (6) revealed that the rotation of the cluster became significant at the NMR time-scale only at temperatures above 370 K.39 For Y2S@C82$C_3v$(8), BOMD simulations show that at room temperature the cluster rotates around the C3 axis (Fig. 3b). A similar conclusion on the rotation of the Sc2S cluster was drawn earlier for Sc2S@C82$C_3v$(8).45

Assignment of the structure of Dy2S@C72 is based on the close similarity of its absorption spectrum (Fig. 4) to that of the non-IPR Sc2S@C72$C_3v$(10528) reported by Echeegoyen et al.46 DFT calculations of different cage isomers of Y2S@C72 also show that C72$C_3v$(10528) is the most energetically favorable cage isomer for Y2S@C72 (see ES†). The second most stable isomer, Y2S@C72$C_3v$(10616), is 42 kJ mol$^{-1}$ less stable. Thus, based on the absorption spectra and DFT calculations, we assign the structure of isolated Dy2S@C72 to the non-IPR C72$C_3v$(10528) cage isomer. In this structure, the metal atoms are coordinated to adjacent pentagon pairs, and the cluster is tightly fixed inside the fullerene.

**Single-crystal X-ray diffraction**

The molecular structures of Dy2S@C82$C_4$ (6) and Dy2S@C82$C_3v$(8) are further corroborated by single-crystal X-ray diffraction of the cocystal Dy2S@C82$Ni^II$(OEP)·2C7H8 (Fig. 5), obtained by layering a toluene solution of NiII(OEP) (OEP = octaethylporphin) over a CS2 solution of the fullerene following the procedure developed in ref. 63. After the two solutions diffused together over a period of one month, small black crystals suitable for X-ray crystallographic study formed. X-ray diffraction data collection for the crystal was carried out at 100 K at the BESSY storage ring (BL14.3, Berlin-Adlershof, Germany)44 using a MAR225 CCD detector, $\lambda = 0.89429$ Å. Processing the
diffraction data was done with the XDSAPP2.0 suite. The structure was solved by direct methods and refined using all data (based on $F^2$) by SHELX 2016. Hydrogen atoms were located in a difference map, added geometrically, and refined with a riding model. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre with CCDC No. 1546957 and 1551313.†

The asymmetric unit cells of both crystals contain a half of the Ni$^{II}$(OEP) molecule and two halves of the C$_{82}$-C$_{8}$(6) or C$_{82}$-C$_{8}$v(8) cage. The fully ordered Ni$^{II}$(OEP) molecule is perpendicular to the crystal mirror plane, so the intact molecule was generated by combining the existing half-molecule with its mirror image. Complete fullerene cages in both crystals were generated by combining one of the halves of the fullerene cage with the mirror image of the other. Accordingly, the occupancies of the two cage orientations in both crystals are 0.50 and 0.50, respectively.

For Dy$_2$S@C$_{82}$-C$_{8}$v(8), two symmetry-related sulfur positions with 0.50/0.50 occupancies were refined. Dy is disordered over 9
sites with occupancies of $2 \times 0.35$ (Dy1), $2 \times 0.34$ (Dy2), $0.11$ (Dy3), $0.11$ (Dy4), $2 \times 0.09$ (Dy5), and $0.23$ (Dy6) (Dy1, Dy2, and Dy5 are located in general positions and their sites are duplicated by the crystallographic mirror plane, see ESI† for details).

For Dy$_2$S@C$_{82}$-C$_{3v}$(8), S is disordered over 3 sites with occupancies of $2 \times 0.31$ (S1) and $0.38$ (S2). Dy is disordered over 12 sites with occupancies of $0.25$ (Dy1), $0.38$ (Dy2), $2 \times 0.24$ (Dy3), $2 \times 0.18$ (Dy4), $2 \times 0.16$ (Dy5), $2 \times 0.04$ (Dy6), and $2 \times 0.07$ (Dy7) (S1, Dy3, Dy4, Dy5, Dy6, and Dy7 are located in general positions and their sites are duplicated by the crystallographic mirror plane, see ESI† for details). Two configurations of the cluster (Dy$_2$–S1–Dy4 shown in Fig. 5d, and Dy1–S1–Dy3) covering 61% of all Dy$_2$S sites have the same orientation of the cluster inside the cage as in the lowest energy conformer found by DFT (Fig. 2f). This configuration is also similar to the major site (60%) of the Sc$_2$S cluster in the co-crystal of Sc$_2$S@C$_{82}$-C$_{3v}$(8) with Ni$^{II}$(OEP).$^{67}$

**Magnetic properties of Dy-clusterfullerenes**

The isolation of two isomers of Dy$_2$S@C$_{82}$ and the isomer of the carbide Dy$_2$C$_2$@C$_{82}$ with the same carbon cage as one of the sulfide clusterfullerenes allows us to address the question of how the carbon cage and type of internal cluster affect the magnetic properties of EMFs. Fig. 6 shows magnetization curves for each sample measured in the temperature range from 1.8 to 5 K. Quite remarkable is the difference between the two isomers of Dy$_2$S@C$_{82}$. The C$_{3v}$ isomer exhibits narrow hysteresis at 1.8 K (coercive field 0.12 T), which closes at 3 K. The hysteresis of the C$_{3v}$ isomer is significantly broader at 1.8 K (coercive field 0.58 T, Fig. 6b), and the closing temperature is between 4 and 5 K. For Dy$_2$S@C$_{82}$-C$_{3v}$ we could also measure the blocking temperature $T_B = 4$ K as the temperature of the peak in the susceptibility of the zero-field-cooled (ZFC) sample (Fig. 6b); for other samples the $T_B$ values are near 2 K, which is too low to be reliably measured. Another SMM characteristic, the temperature at

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**Fig. 5** (a) Relative orientation of the Ni$^{II}$(OEP) and Dy$_2$S@C$_{82}$ molecules in the Dy$_2$S@C$_{82}$-C$_{3v}$($6$)-Ni$^{II}$(OEP)-2C$_7$H$_8$ cocrystal; only one orientation of the C$_{82}$-C$_{6}$($6$) cage together with the major site of the Dy$_2$S cluster are shown, solvent molecules are omitted for clarity; (b) major site of the Dy$_2$S cluster within the C$_{6}$($6$)-C$_{82}$ cage. Selected geometry parameters: Dy1–S1, 2.465(5) Å; Dy2–S1, 2.518(5) Å; Dy1–S1–Dy2, 98.3(2)$^\circ$. (c) Relative orientation of the Ni$^{II}$(OEP) and Dy$_2$S@C$_{82}$ molecules in the Dy$_2$S@C$_{82}$-C$_{3v}$($8$)-Ni$^{II}$(OEP)-2C$_7$H$_8$ cocrystal; only one orientation of the C$_{82}$-C$_{3v}$($8$) cage together with the major site of the Dy$_2$S cluster are shown, solvent molecules are omitted for clarity; (d) major site of the Dy$_2$S cluster within the C$_{82}$-C$_{3v}$($8$) cage. Selected geometry parameters: Dy2–S1, 2.437(11) Å; Dy4–S1, 2.511(9) Å; Dy2–S1–Dy4, 94.4(2)$^\circ$. Displacement parameters are shown at the 30% probability level.
which the relaxation time of magnetization is 100 s, is determined for Dy$_2$S@C$_{82}$-C$_{3v}$ to be $T_B \approx 2$ K.

The magnetization behavior of Dy$_2$C$_2$@C$_{82}$-C$_6$ is similar to that of the isostructural sulfide. The hysteresis is narrower but closes at a slightly higher temperature (Fig. 6c). Finally, Dy$_2$S@C$_{72}$ has the smallest opening of hysteresis among all studied samples (Fig. 6d). Thus, all four studied clusterfullerenes exhibited hysteresis of magnetization below 3 K and can be classified as single molecule magnets. Importantly, we observe considerably different SMM properties of sulfide clusterfullerenes with different fullerene cages.

**Dynamics of the relaxation of magnetization**

To study the dynamics of the relaxation of magnetization at temperatures up to 60–70 K, we performed AC-susceptibility measurements for Dy$_2$C$_2$@C$_{82}$ and the two isomers of Dy$_2$S@C$_{82}$ (the amount of isolated Dy$_2$S@C$_{72}$ was not sufficient for such measurements). Characteristic temperature-dependent peaks in the out-of-phase susceptibility were found for all samples. As an example, Fig. 7 shows $\chi''$ susceptibility for Dy$_2$S@C$_{82}$-C$_6$, analogous data for other compounds are available in the ESI.$^\dagger$ Magnetization relaxation times $\tau$ shorter than 10 s were determined from the AC-data using a generalized Debye model (see Cole–Cole plots in the ESI.$^\dagger$). The longer $\tau$ values at the lowest temperatures were determined directly by measuring the relaxation of magnetization in a DC mode.

Fig. 8 shows the plots of magnetization relaxation times of Dy$_2$S@C$_{82}$-C$_6$, Dy$_2$C$_2$@C$_{82}$-C$_6$, and Dy$_2$S@C$_{82}$-C$_{3v}$ as a function of reciprocal temperature. The two isomers of Dy$_2$S@C$_{82}$ exhibit

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**Fig. 6** Magnetization curves for (a) Dy$_2$S@C$_{82}$-C$_6$(6), (b) Dy$_2$S@C$_{82}$-C$_{3v}$(8), (c) Dy$_2$C$_2$@C$_{82}$-C$_6$(6), and (d) Dy$_2$S@C$_{82}$-C$_{3v}$(10528) measured at $T = 1.8$–5 K with the magnetic field sweep rate of 8.33 mT s$^{-1}$. The inset in each panel zooms into the region near zero-field. In (b), determination of the blocking temperature of Dy$_2$S@C$_{82}$-C$_{3v}$(8) as the peak in the susceptibility of the zero-field-cooled (ZFC) sample is also shown (magnetic field 0.2 T, temperature sweep rate 5 K min$^{-1}$).

**Fig. 7** $\chi''$ of Dy$_2$S@C$_{82}$-C$_6$ measured at different temperatures as a function of AC frequency. Dots are experimental points, lines are results of the fit with a generalized Debye model.
strikingly different relaxation dynamics, which in both cases can be described as a combination of Orbach relaxation processes via two or three thermal barriers. The relaxation rate for the Orbach relaxation mechanism is the exponential function of the reciprocal temperature and the energy of an excited state, which defines the effective relaxation barrier \( T_{\text{eff}} \):

\[
\tau_{\text{Orbach}}^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/T)
\]  

(1)

In the log(\(\tau\)) vs. 1/\(T\) coordinates, relaxation via the Orbach mechanism appears as a straight line. A combination of several Orbach relaxation processes and relaxation via the Raman mechanism would then be described by the equation:

\[
\tau^{-1} = \sum_i \tau_0^{-1}_i \exp(-U_{\text{eff}}^{i}/T) + AT^n
\]  

(2)

where index \(i\) runs through all processes, and the term \(AT^n\) describes the rate of the relaxation via a Raman mechanism.

Table 1 lists \(U_{\text{eff}}^{i}\), \(\tau_0^{i}\), and other parameters determined by fitting experimental relaxation times by eqn (2). For Dy2S@C82-C3v, the best fit is obtained with three Orbach processes. For Dy2C2@C82-C4v, the limited set of data allowed only fitting with a single Orbach process. For Dy2S@C82-C3v, equally good fits were obtained with either three Orbach processes, or two Orbach processes and a Raman relaxation (see ESI†). Observation of several Orbach relaxation pathways is rather unusual but not unimaginable. Two linear regimes in the temperature dependence of relaxation rates have been observed for several 3d-4f SMMs. In these complexes, the low-temperature process corresponds to the relaxation via exchange excited states, whereas the higher-energy barrier is due to the Orbach relaxation via the crystal-field excited state of the lanthanide ions.21,68,69

At the lowest accessible temperatures (1.6–5 K), all three Dy-EMFs exhibit a linear regime with a relatively small barrier, \(U_{1}^{\text{eff}}\), presumably corresponding to the energy difference between the states with ferromagnetically and antiferromagnetically coupled Dy ions (it has contributions from both dipolar and exchange interactions, see more detailed discussion below). Magnetization relaxation pathways proceeding through excited “exchange states” are well documented for 3d-4f complexes, albeit usually with much shorter \(\tau_0\) values than those observed in EMFs.20,21,23,68–71 In Dy2S@C82-C3v, the \(U_{1}^{\text{eff}}\) barrier amounts to 6.5 K versus 15.2 K in Dy2S@C82-C4v and 17.4 K in Dy2C2@C82-C4v. At the same time, Dy2S@C82-C3v has the longest attempt time \(\tau_0\) of 3.6 s, which is 3–4 orders of magnitude longer than that of the EMFs with the \(C_3\) cage isomer (2.9 ms in Dy2S@C82-C3 and 0.5 ms in Dy2C2@C82-C3). Thus, due to the smaller barrier, the \(C_3\) isomer has a moderate inclination in log(\(\tau\)) vs. 1/\(T\) and hence smaller variation of the relaxation rate with temperature, whereas its much longer \(\tau_0\) value leads to the considerably longer magnetization relaxation times. The difference between the two isomers of Dy2S@C82 reaches two orders of magnitude near 5 K. In due turn, the magnetization of Dy2C2@C82-C4 relaxes ca. two times faster than that of the isostructural Dy2S@C82-C4, showing that the acetylide \(C_2^{-}\) central unit in the Dy2C2 cluster is inferior for the SMM properties compared to the sulfide ion \(S^{2-}\) in the Dy2S cluster within the same fullerene cage. This finding agrees with our earlier study of Dy2TiC@C80 and Dy2TiC2@C80, which also showed that the single carbide ion in the endohedral cluster leads to much better SMMs than the \(C_2\) unit.42 The best EMF-SMM molecule so far is the nitride clusterfullerene Dy2SeN@C803. It also has a \(U_{2}^{\text{eff}}\) barrier of 10.5 K and a long \(\tau_0\) value of 12 s (see Table 1).28 Thus, the comparison between sulfide, carbide, and nitride clusterfullerenes with two Dy atoms shows that their magnetization relaxation dynamics at low temperatures is determined by the Orbach process with the “exchange” barrier. The height of the barrier appears to be less important than the attempt time, which varies by several orders of magnitude between the EMFs. The best SMM in the series is not the EMF with the largest exchange barrier, but the molecule with the longest \(\tau_0\) value.

Above 5 K, the magnetization relaxation mechanisms for the \(C_{3v}\) and \(C_4\) isomers become significantly different. Between 5
Table 1  Parameters of Orbach and Raman relaxation processes in Dy-EMFs and the temperature range where these processes play the main role in the relaxation of the magnetization

|                  | Dy$_2$C$_2$@C$_{60}$ | Dy$_2$S$_2$@C$_{82}$ $^b$ | Dy$_2$S@C$_{82}$ $^c$ | Dy$_2$S@C$_{82}$C$_3$ $^v$ | Dy$_2$ScN@C$_{60}$ $^d$ |
|------------------|----------------------|--------------------------|----------------------|--------------------------|----------------------|
| $U^\text{eff}_1$ | 17.4 ± 0.2           | 15.2 ± 0.3               | 18.0 ± 0.5           | 6.5 ± 0.5                | 10.7 ± 0.3           |
| $\tau_{01}$     | (5.2 ± 0.3) $\times$ 10$^{-4}$ | (2.9 ± 0.3) $\times$ 10$^{-3}$ | (1.6 ± 0.2) $\times$ 10$^{-3}$ | 3.6 ± 0.8                | 11.9 ± 1.5           |
| $T_{\text{range}}$ | 1.6–10               | 1.6–10                   | 1.8–15               | 1.6–4                    | 1.8–5                |
| $U^\text{eff}_2$ | 48 ± 1               | 61 ± 6                   | 48 ± 1               | 6.2 ± 0.6 $\times$ 10$^{-4}$ | 5–47                |
| $\tau_{02}$     | (7.8 ± 2.3) $\times$ 10$^{-5}$ | 15–35                  | (6.2 ± 0.6) $\times$ 10$^{-4}$ | 5–47                    | 48 ± 1               |
| $T_{\text{range}}$ | 48 ± 1               | 61 ± 6                   | 48 ± 1               | 6.2 ± 0.6 $\times$ 10$^{-4}$ | 5–47                |
| $A$              | (2.5 ± 0.6) $\times$ 10$^{-3}$ | 3.97 ± 0.08             | 3.6 ± 0.8             | 1.6–4                    | 1.8–5                |
| $n$              | ≤1.6, 20–43           | 48 ± 1                   | 61 ± 6               | 6.2 ± 0.6 $\times$ 10$^{-4}$ | 5–47                |
| $U^\text{eff}_3$ | 523 ± 35             | 696 ± 86                 | 1232 ± 160           | 1735 ± 21                | 63–76                |
| $\tau_{03}$     | (6.0 ± 4.4) $\times$ 10$^{-10}$ | (2.5 ± 4.3) $\times$ 10$^{-11}$ | (0.6 ± 1.5) $\times$ 10$^{-12}$ | (2.4 ± 0.8) $\times$ 10$^{-15}$ | 63–76                |
| $T_{\text{range}}$ | 40–53                | 47–53                    | 47–70               | 47–70                    | 47–70               |

$^a$ Effective barriers $U^\text{eff}$ are given in Kelvin, $\tau_{0i}$ values are given in seconds. $^b$ Modelling magnetization relaxation rate of Dy$_2$S$_2$@C$_{82}$ with two Orbach processes and an intermediate Raman process. $^c$ Modelling magnetization relaxation rate of Dy$_2$S@C$_{82}$ with two Orbach processes and an intermediate Raman process. $^d$ The highest temperature of the range is determined by the frequency and sensitivity limits of the PPMS system.

and 47 K, the magnetization relaxation of Dy$_2$S@C$_{82}$C$_3$ is driven by another Orbach process with $U^\text{eff}_2 = 48$ K and $\tau_{02} = 0.36$ ms. As will be discussed below in more detail, this barrier is too small to be assigned to one of the crystal-field (CF) states, and the $\tau_{02}$ value is likewise too long for the Orbach processes via CF states normally observed for Dy-SMMs. Above 47 K and up to the instrumental frequency limit at 70 K, the magnetization relaxation of Dy$_2$S@C$_{82}$C$_3$ is determined by the energy barrier of 1232 K and the corresponding $\tau_{03}$ value of 0.6 $\times$ 10$^{-12}$ s. Unfortunately, the measurements in this temperature range and frequencies, with the small amount of the available sample, are performed near the sensitivity limit of the PPMS system, which leads to large uncertainties in the determined values. Yet, there is no doubt that the barrier is rather high, but smaller than the barrier of the analogous relaxation process in Dy$_2$ScN@C$_{80}$, 1735 K. For comparison, the highest thermal relaxation process among lanthanide-only dimers, 721 K, was reported recently by Gao et al. for hydroxide-bridged five-coordinate Dy$_{III}$ dimer. The highest barrier among non-fullerene polynuclear Dy complexes is 888 K, whereas in single-ion Dy SMMs, the largest reported barrier is 1815 K.

For the C$_3$ isomers, the linear regime with the “exchange” barrier is operative up to ca. 10–15 K. Above ca. 45 K, Dy$_2$S@C$_{82}$C$_3$ exhibits a high-energy Orbach process with the parameters typical for the relaxation via a CF state, i.e. large $U^\text{eff}_3$ of several hundred K and a $\tau_{03}$ value in the range of 10$^{-10}$–10$^{-11}$ s. However, the relaxation dynamics between the temperature ranges of the two Orbach processes, i.e. 15–40 K, are not uniquely defined. Equally good fits were obtained for either an intermediate Orbach process ($U^\text{eff}_2 = 61$ K and $\tau_{02} = 0.08$ ms; see Fig. 8a) or for the Raman relaxation process ($A = 2.5$ ms K$^{-n}$ and $n = 3.97$, see Fig. S20$^d$). The choice of either an Orbach or Raman process also affects the parameters of other Orbach processes, especially the $U^\text{eff}_2$ and $\tau_{03}$ values (Table 1). The high energy Orbach process is observed at AC frequencies close to the frequency and sensitivity limits of the instrument, which significantly affects the accuracy of the fit and leads to large uncertainties for the $U^\text{eff}_2$ and $\tau_{03}$ values. It is very likely that the third linear regime for Dy$_2$S@C$_{82}$C$_3$ is not fully reached at accessible temperatures, and that the actual energy barrier for the relaxation via CF state is higher.

To summarize, although Dy$_2$S$_2$@C$_{82}$C$_3$ and Dy$_2$S@C$_{82}$C$_3$ have a similar structure of the encapsulated Dy$_2$S cluster, the differences in their fullerene cages have paramount effect on the magnetization relaxation dynamics. In the whole temperature range accessible for our measurements, relaxation times of the C$_3$ isomer are considerably longer than those of the C$_4$ isomer, from a factor of 5 to two orders of magnitude. The difference in the relaxation behavior of Dy$_2$S@C$_{82}$C$_3$ and Dy$_2$C$_2$@C$_{82}$C$_3$ is not as pronounced as between the isomers of Dy$_2$S@C$_{82}$, which shows that the influence of the cage isomerism may be stronger than the influence of the central atom(s) in the endohedral clusters.

Few SMMs with sulfur-ligated Dy have been reported so far, and all of them have substantially faster relaxation times and smaller relaxation barriers than in the Dy$_2$S@C$_{82}$ system reported in this work. In the EMF molecules, sulfur bears a substantially larger negative charge and the Dy–S sulfur distances are at the same time much shorter, which altogether leads to a stronger crystal field in sulfide clusterfullerenes.

**Effective spin Hamiltonian for di-nuclear Dy EMFs**

The system with two Dy centers with magnetic moments $J_{1,2}$ weakly coupled through exchange/dipolar interactions can be described by the following effective spin Hamiltonian:

$$H_{\text{tot}} = H_{\text{CF1}} + H_{\text{CF2}} - 2J_{1,2}I_1J_2$$

where the $H_{\text{CFi}}$ terms are single-ion crystal-field Hamiltonians, and the last term describes the exchange and dipolar interactions between the two Dy centers (rather unfortunately, both the exchange coupling and total magnetic moment of lanthanide are traditionally designated as $J$, so we use the small letter $j$ for the coupling and the capital $J$ for the momentum). In the spirit
of the Lines model, both exchange and dipolar interactions are modelled here by a single isotropic coupling parameter \( J_{12} \). We will first describe *ab initio* computations for the single-ion CF parameters in sulfide clusterfullerenes and compare them to other EMFs, then proceed to the discussion of the coupling parameter \( J_{12} \), and then comment on the spectrum of the total effective spin Hamiltonian.

**Ab initio calculations of single-ion magnetic anisotropy in Dy-EMFs**

Single-point *ab initio* calculations discussed in this section were performed using a complete active space self-consistent field with spin–orbit interactions (CASSCF/SO-RASSI level of theory) as implemented in MOLCAS 8.0. In all systems, Dy\(^{3+} \) has a \(^{4}H_{15/2} \) ground state multiplet, resulting in eight low-lying Kramers doublets. The active space of the CASSCF calculations includes nine active electrons and seven active orbitals (e.g. CAS (9,7)). The single ion CF-parameters were then obtained with the use of the SINGLE_ANISO module\(^6\) and transferred to the PHI code\(^7\) for further pseudospin analysis of single ion as well total spin states. The crystal structures of EMFs often exhibit strong disorder of the cage and cluster positions, thus limiting the use of X-ray determined geometries for accurate analysis of the crystal field splitting. Besides, crystal structures are not always available. In this work, molecular geometries were optimized by DFT for Y analogs, and then one of the Y ions was replaced by Dy for the subsequent *ab initio* calculations. Table 2 lists the CF energy levels for each Dy ion in Dy\(_2\)S@C\(_{72}\), the two isomers of Dy\(_2\)S@C\(_{82}\) and Dy\(_2\)C\(_2\)@C\(_{82}\). The term “crystal field” is somewhat ambiguous here since *de facto* we discuss splitting of the \( j_l \) levels by the intramolecular interactions between the Dy ion and surrounding ions. The term “crystal field” is inherited in the field of SMMs from the earlier studies of lanthanide solids and broadly used in the literature, and we follow this convention.

| KD | Dy\(_2\)S@C\(_{72}\) | Dy\(_2\)S@C\(_{82}\) | Dy\(_2\)S@C\(_{82}\) | Dy\(_2\)C\(_2\)@C\(_{82}\) |
|----|-----------------|-----------------|-----------------|-----------------|
| 1  | 0               | 0               | 0               | 0               |
| 2  | 181             | 225             | 183             | 228             |
| 3  | 398             | 354             | 393             | 450             |
| 4  | 572             | 469             | 551             | 622             |
| 5  | 658             | 588             | 668             | 723             |
| 6  | 691             | 688             | 747             | 799             |
| 7  | 765             | 742             | 791             | 857             |
| 8  | 876             | 868             | 874             | 955             |

\(^d(Dy-X)^t\): \(2.456 \quad 2.313 \quad 2.329 \quad 2.484 \quad 2.506 \quad 2.509 \quad 2.486 \)

\(^\langle(Dy-X)^t\rangle\): 104.7

\(^a\) Energies are given in \(\text{cm}^{-1}\), the conversion factor of \(\text{cm}^{-1}\) to Kelvin units is 1.439. \(^8\) \(X\) is either a sulfide ion in sulfide clusterfullerenes or a center of the acetylide unit in Dy\(_2\)C\(_2\)@C\(_{82}\). The ground states of the Dy ions in all studied EMFs feature a highly anisotropic g-tensor with \(g_{zz}\) near 19.8–19.9 and vanishing small \(g_{xx}\) and \(g_{yy}\) components (see ESI for more details), which corresponds to the “pure” state with \(J_z = \pm 15/2\). The overall CF splitting (\(\Delta E_{1/2}\) hereafter) is in the range of 810–970 \(\text{cm}^{-1}\). The smallest energy difference between the ground and the first excited state, \(\Delta E_{1/2} = 181 \text{ cm}^{-1}\), is found in Dy\(_2\)S@C\(_{72}\) for all other EMFs the \(\Delta E_{1/2}\) energies are larger and reach 295 \(\text{cm}^{-1}\) for one of the Dy centers in Dy\(_2\)S@C\(_{82}\). These values are sufficiently high to conclude that the magnetic properties of these EMFs at liquid helium temperatures are determined solely by the ground state and intramolecular exchange/dipolar coupling between magnetic moments.

Although the central non-metal ion is the main “source” of magnetic anisotropy, the CF splitting in sulfide clusterfullerenes is not a simple function of the metal-sulfur distance. With a considerably smaller Dy–S distance, Dy\(_2\)S@C\(_{72}\) has the smallest \(\Delta E_{1/2}\) energy gap among the studied sulfide clusterfullerenes. Likewise, with almost identical Dy–S bond lengths and cluster geometry, the \(\Delta E_{1/2}\) values in Dy\(_2\)S@C\(_{82}\) are larger than those in Dy\(_2\)S@C\(_{82}\). Thus, despite the relatively small charges of individual carbon atoms, the fullerene cage (and in particular, the coordination mode of Dy ions to the nearby carbons) also plays a certain role, which may have a critical effect on the difference between the otherwise similar isomers.

The influence of the non-metal species on the magnetic anisotropy can be clearly seen from the comparison of Dy\(_2\)C\(_2\)@C\(_{82}\) and Dy\(_2\)S@C\(_{82}\). The Dy atoms in both molecules have virtually identical metal-cage coordination. Besides, the orientations of the anisotropy axes for each metal center are also very similar (along the Dy–S axes in Dy\(_2\)S@C\(_{82}\) and along the axes connecting Dy and the midpoint between the two carbons in Dy\(_2\)C\(_2\)@C\(_{82}\)). Finally, the acetylide unit and the sulfide ion have the same formal charge, –2. But in the Dy\(_2\)S cluster, the negative charge is localized on the single sulfur atom, whereas in the Dy\(_2\)C\(_2\) cluster the charge is shared between the two carbons. As a result, the CF splitting in the carbide clusterfullerene is systematically smaller than that in the sulfide clusterfullerene by 10%.

To place these results into a broader context, we performed *ab initio* calculations for Dy centers in other di-Dy clusterfullerenes known to exhibit SMM properties, including Dy\(_2\)ScN@C\(_{80}\)I\(_9\), Dy\(_2\)TiC@C\(_{80}\)I\(_9\) and Dy\(_2\)TiC@C\(_{80}\)I\(_9\). Also studied were hypothetical Dy\(_2\)C@C\(_{82}\)C\(_3\)(5), Dy\(_2\)C@C\(_{76}\)C\(_3\)(19138), and Dy\(_2\)O@C\(_{82}\)C\(_3\)(8), whose synthesis appears feasible based on the literature reports on analogous EMFs with other metals (such as cyano clusterfullerenes Tb\(_2\)NC@C\(_{76}\) (ref. 44) and three cage isomers of Tb\(_2\)NC@C\(_{82}\) (ref. 45–47) or oxide clusterfullerenes Sc\(_2\)O@C\(_{82}\) (80–82) Y\(_2\)O@C\(_{82}\) and Lu\(_2\)O@C\(_{82}\) (ref. 83)).

In clusterfullerenes with a single non-metal atom, the magnetic anisotropy axis is aligned along the bond connecting Dy to the central atom, sometimes with a slight deviation of a few grad (Fig. 9). In carbide clusterfullerenes with an acetylide unit, the anisotropy axis is directed towards the point between the two carbon atoms, whereas in clusterfullerenes with CN– ions the axis is directed towards more negatively charged...
Interestingly, although none of the relaxation processes described in the EMF-SMMs so far involve the first CF excited state, there is an empirical correlation between the strength of the EMF-SMM and the $\Delta E_{1-2}$ gap. Dy$_2$ScN@C$_{80}$-$I_h$ is the best EMF-SMM so far followed by Dy$_2$TiC@C$_{80}$-$I_h$, which is comparable to Dy$_2$S@C$_{2v}$-$C_{3v}$. Dy$_2$ScN@C$_{80}$ has a smaller $\Delta E_{1-2}$ energy than the $C_{3v}$ isomer and exhibits poorer SMM properties, and Dy$_2$C$_2$@C$_{82}$-$C_s$ is inferior to Dy$_2$S@C$_{2v}$-$C_s$. If this correlation holds for other EMFs, then the oxide clusterfullerene Dy$_2$O@C$_{2v}$-$C_{3v}$ may become a superior SMM than Dy$_2$ScN@C$_{80}$ as it has the largest $\Delta E_{1-2}$ and $\Delta E_{1-8}$ values ($430/448$ and $1358/1444$ cm$^{-1}$, respectively) in the whole group of computed EMFs. The reasons are the short Dy–O distances (2.041/2.029 Å) and rather large Dy–O–Dy angle of 134°. Even larger CF splitting was predicted recently in mixed-metal Dy–Sc and Dy–Lu oxide clusterfullerenes by Rajaraman et al. Thus, Dy-oxide clusterfullerenes seem to be a reasonable target for the SMM-EMF synthesis. Dy-cyano clusterfullerenes are expected to be comparable to sulfide clusterfullerenes in terms of the CF splitting. Flexible cluster geometry from almost linear in MNC@C$_{76}$ to triangular in MNC@C$_{82}$ leads to a large variation of the CF splitting (Fig. 9).

To evaluate the effect of dynamical correlation on CF splitting, a series of additional calculations were performed for simpler model systems, in which all cage carbon atoms were replaced by point charges corresponding to their formal charges in the respective EMFs. When 18 sextets and 15 quartets are used in the CASSCF computations, the model gives a reasonable agreement with full-molecule calculations at only a fraction of the computational cost. Subsequent multi-reference configuration interaction (MRCI) calculations were then performed with 18 sextets and 8 quartets using the Molpro code. MRCI calculations show that dynamic correlation increases the $\Delta E_{1-2}$ energy by ca. 10–15% (see ESI†). We can tentatively suggest that due to the lack of dynamical correlation, the CASSCF calculations for Dy-EMFs described above underestimate the CF splitting in a similar manner.

The strength of the molecular magnet is determined not only by the CF splitting, but also by the transition probabilities between the states with opposite spin, which are determined by transverse components ($g_{xx}$ and $g_{yy}$) of the $g$-tensor. Our calculations show that the nature of the central atom(s) and the cluster geometry strongly affect the transverse components of the $g$-tensor (see Tables S6–S15† for transition probabilities between single-ion states in all computed Dy-clusterfullerenes). The clusters with compact single non-metal atoms, such as oxide and nitride clusterfullerenes, have the smallest transverse components for several lowest excited states, which leads to the low transition probabilities. Our recent experimental study of the relaxation mechanism in Dy$_2$ScN@C$_{80}$-$I_h$ revealed that the Orbach relaxation process observed at high temperatures corresponds to the relaxation via the fifth Kramers doublet. On the other hand, the clusters with diatomic central units have a considerably higher transverse component of the $g$-tensor, which substantially increases transition probabilities for lower-energy KDs. For $C_3$ and CN central units, larger transverse components are observed already for the ground state (which

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may be another reason for the poorer SMM properties of carbide clusterfullerenes. Sulfide clusterfullerenes with relatively large sulfide ions are inferior to oxide and nitride clusterfullerenes, but are better than carbide and cyanoclusterfullerenes.

Exchange and dipolar interactions in Dy-EMFs

The low-temperature relaxation dynamics of all three EMF-SMMs with two Dy ions are determined by the exchange/dipolar barrier \( U_{12}^{\text{eff}} \). That is, due to the dipolar and exchange interactions between the Dy ions, the ground and the first excited state of the dinuclear system are the states in which Dy ions in their single-ion ground state \( (J_z = \pm 15/2) \) are coupled ferromagnetically and antiferromagnetically, respectively, and the Orbach process proceeds \( via \) the antiferromagnetic state. Knowing the \( U_{12}^{\text{eff}} \) values, the \( J_{12} \) coupling constants in eqn (2) can be computed by matching the lowest excited state energy (Table 3).

Dipolar contributions to \( U_{12}^{\text{eff}} \) energies (Table 3) are calculated straightforwardly using the equation:

\[
E^{\text{dip}}(\vec{\mu}_1, \vec{\mu}_2) = -\frac{\mu_0}{4\pi R_{12}} \left( \frac{1}{R_1} \cdot \vec{\mu}_1 - \frac{1}{R_2} \cdot \vec{\mu}_2 \right)
\]

(4)

where \( \vec{r}_i \) is the normal of the radius vector connecting two magnetic moments \( \mu_{-1} \) and \( \mu_{-2} \), and \( R_{12} \) is the distance between them. The angles between the moments are taken from \textit{ab initio} calculations. The \( \Delta E^{\text{dip}} \) values listed in Table 3 show that for all EMFs the dipolar contribution is in the range of 3–5 K. \( \Delta E^{\text{dip}} \) constitutes roughly a half of the \( U_{12}^{\text{eff}} \) barriers in Dy₂S₆@C₈₂−₅₃₃, and Dy₂S₆N@C₈₇, but is below 25% of that in Dy₂S₆@C₈₂−₆₃₃ and Dy₂C₂@C₈₂−C₃. From \( \Delta E^{\text{dip}} \), the dipolar contribution \( J_{12}^{\text{dip}} \) to the \( J_{12} \) constant in eqn (3) is computed by scaling with the factor of 15²coss, where \( c \) is the angle between the anisotropy axes of individual Dy ions.

The calculation of the exchange contribution to the coupling constant for Dy is not straightforward, and it is a common praxis to use Gd analogs to estimate \( J_{12}^{ex} \). For the latter, exchange coupling constants are computed using broken-symmetry approximation at the DFT level, and the different spin moments of Dy and Gd as well as non-colinearity of magnetic moments is accounted for by multiplying with the factor of 25/49 cos(a).²² The values calculated this way for Dy-EMFs (Table 3) are in reasonable agreement with experiment. Similar \( J_{12}^{ex} \) values are predicted for all other Dy-EMFs, showing that the extent of the exchange/dipolar coupling between the magnetic moment of Dy ions in clusterfullerenes is not dramatically changing with variation of the central atom(s). Remarkably, the \( J_{12}^{ex} \) value in Dy₂S₆@C₈₂−C₃ is predicted to be considerably smaller than that in the C₃ isomer.

Once the CF and coupling parameter in the spin Hamiltonian are known or estimated, the solution of eqn (3) allows simulation of the magnetization curves. Low-temperature experimental magnetization curves (Fig. 6 and S23†) have peculiarities at 1.5–2 T, whose presence is caused by exchange/dipolar interactions and hence can be used to verify the computational model. For Dy₂C₂@C₈₂−C₃ and Dy₂S₆@C₈₇C₃, the use of \( J_{12} \) parameters fitted to match the experimental \( U_{12}^{\text{eff}} \) values (0.175 and 0.220 cm⁻¹, respectively) leads to good agreement between simulated and experimental curves, confirming the assignment of \( U_{12}^{\text{eff}} \) to the exchange/dipolar barrier. However, for Dy₂S₆@C₈₂−C₃, the agreement with experiment is less satisfactory (Fig. S23†). To match the experimental magnetization curve, the \( J_{12} \) parameter should be increased from 0.104 cm⁻¹ to 0.18 cm⁻¹, which amounts to the calculated \( U_{12}^{\text{eff}} \) barrier of 11 K. The discrepancy between experimental and calculated \( U_{12}^{\text{eff}} \) is likely to be caused by the not-well defined geometry of the Dy₂S cluster as exchange parameters are very sensitive to the Dy-S-Dy angle, and for the C₃ isomer the cluster is not fixed in one position but is rather disordered between several dozen.

Orbach relaxation \textit{via} CF states

The large \( U_{12}^{\text{eff}} \) barriers of hundreds of K observed in both isomers of Dy₂S₆@C₈₂ are indicative of the relaxation \textit{via} CF states. It is usually assumed that in polynuclear systems, the Orbach mechanism involves CF states of the individual lanthanide ion. In Dy₂S₆@C₈₂−C₃, \textit{ab initio} CF splitting and transition probability calculations show that the barriers for the relaxation \textit{via} individual CF states of single Dy ions unperturbed by interaction with another Dy center may be expected in the range of up to 1000 K (corresponding to the fifth Kramer doublet), whereas the total CF splitting is exceeding 1300 K (Fig. 9). Within the limits of rather high experimental uncertainties, the experimental value is in line with this expectation. For Dy₂S₆@C₈₂−C₃, \textit{ab initio} calculations show that relaxation \textit{via} lower-energy Kramers doublets can also be efficient (see Table S6†). This expectation is also in line with the lower \( U_{12}^{\text{eff}} \) value observed for this compound experimentally (Table 1), but currently impossible higher-frequency AC measurements would be necessary to confirm the \( U_{12}^{\text{eff}} \) barrier in Dy₂S₆@C₈₂−C₃.

Intermediate barrier

The nature of the Orbach relaxation processes in Dy₂S₆@C₈₂ isomers with barriers of 50–60 K cannot be explained based on the energy spectrum of the Hamiltonian (3). The \( E_{12} \) values are clearly above the exchange/dipolar barrier and yet well below the energies of the CF-derived excited states. Besides, \( \tau_{02} \) values

| Table 3 | Exchange and dipolar coupling parameters in di-Dy EMFs |
|---------|-----------------------------------------------|
|         | \( U_{12}^{\text{eff}}, K \) | \( J_{12}^{\text{dip}}, \text{ cm}^{-1} \) | \( \Delta E^{\text{dip}}, \text{ cm}^{-1} \) | \( \Delta E^{\text{ex}}, \text{ cm}^{-1} \) | \( \Delta E^{\text{dia}}, \text{ cm}^{-1} \) |
| Dy₂S₆@C₈₂−C₃ | 78.8 | 3.4 | 0.051 | 0.013 |
| Dy₂S₆@C₈₂−C₇ | 15.2 | 0.220 | 77.6 | 3.6 | 0.051 | 0.136 |
| Dy₂S₆@C₈₂−C₆ | 6.5 | 0.140 | 78.9 | 3.7 | 0.059 | 0.063 |
| Dy₂S₆@C₈₂−C₅ | 17.4 | 0.175 | 71.8 | 3.8 | 0.025 | 0.108 |
| Dy₂S₆N@C₈₀ | 10.5 | 0.073 | 62.8 | 4.6 | 0.031 | 0.128 |
| Dy₂TIC@C₈₀ | 62.3 | 4.4 | 0.029 | 0.159 |
| Dy₂TIC@C₈₀ | 71.8 | 5.0 | 0.050 | 0.073 |
| Dy₂O@C₈₂−C₇ | 45.7 | 4.4 | 0.018 | 0.110 |

²² To compute exchange coupling constants, \( J_{12}^{ex} \) (Gd-Gd) values in Gd-EMF analogs were first computed using Orca code²² at the PBE0/TZV-DKH⁴⁶⁴⁶⁵ level within the broken-symmetry approximation, and then scaled by a factor of 25/49 cos(a)
are also much longer than would be expected for the relaxation through CF excited states.

Multiple studies of the electron spin-lattice relaxation times in salts of transition metals and lanthanides starting from the early 1960s and later on revealed that relaxation via the Raman mechanism in the presence of the so-called localized phonon of frequency \( \omega \) (usually associated with defects in those studies) can take an exponential form proportional to \( \exp(-\hbar\omega/k_B T) \).\(^{99-101}\) In other words, it can be described as an Orbach relaxation process with the energy barrier corresponding to the phonon excited state. Orbach relaxation processes with barriers corresponding to the frequencies of molecular vibrations were also observed in N@C\(_{60}\) (ref. 92) and other paramagnetic solids and host–guest systems.\(^{99-105}\) Very recently, Sanvito et al. studied the role of phonons in the under-barrier spin relaxation of SMMs and found that an anharmonic phonon with finite linewidth may result in the Arrhenius behavior with the barrier corresponding to a half of the phonon frequency.\(^{36}\)

To our knowledge, the possibility of Orbach relaxation via an excited phonon state has not been widely considered for SMMs. Usually, SMMs have rather high vibrational density of states in the low frequency range due to the presence of “floppy” fragments and side chains in the ligands. However, fullerene molecules are quite rigid, and their lowest frequencies vibrations occur above 200 cm\(^{-1}\). In EMFs, encapsulated clusters with heavy lanthanide atoms have few low-frequency vibrational modes due to frustrated rotations and translation as well as internal cluster vibrations. In the Raman spectra of Dy\(_2\)S@C\(_{82}\) isomers shown in Fig. 10a, the cage (above 220 cm\(^{-1}\)) and the cluster (between 50 and 160 cm\(^{-1}\)) vibrational features are well separated. The frequencies of \( \sim 40 \) cm\(^{-1}\) corresponding to \( \omega/2 \) values lie outside the accessible range of our spectrometer, but DFT computations show the presence of cluster vibrations in this frequency range, mainly of the librational character (in Dy\(_2\)S@C\(_{82}\)-\( C_{3v} \) such modes are predicted at 30, 39, and 48 cm\(^{-1}\)).

It is reasonable to suggest that the lowest-frequency librational mode may be responsible for the Orbach relaxation process with a barrier of 48 K (33 cm\(^{-1}\)). On the other hand, if following Sanvito et al. we suggest that the observed barrier corresponds to a half of the phonon frequency,\(^{36}\) then the relaxation of magnetization in Dy\(_2\)S@C\(_{82}\) may be induced by the mixed translation/deformation mode of the Dy\(_2\)S cluster with the calculated frequency of 62 cm\(^{-1}\) (Fig. 10b).

Thus, shielding of endohedral species by the carbon cage not only stabilizes the otherwise “improper” endohedral species (none of the clusters discussed in this work can exist outside the fullerene), but also isolates the Dy spin system from the lattice phonon bath, resulting in a kind of phonon bottlenecking at low temperatures. When the local vibrational modes gain certain thermal population, a new Orbach relaxation pathway is open and the rate of relaxation is accelerated. The sparse vibrational density of states in EMFs may be the reason for the long relaxation times that these molecules exhibit at low temperatures. Further studies of the low-frequency vibrational density of states as well as development of a rigorous theory of the spin-phonon relaxation in SMMs are required to confirm this hypothesis.

**Conclusions**

In this article, we report a new method for the selective synthesis of sulfide clusterfullerenes. We utilized the suppressing influence of hydrogen on the empty fullerene formation and performed arc-discharge synthesis in the presence of methane. Under optimized conditions, and with the use of dysprosium sulfide as a source of metal and sulfur, Dy\(_2\)S@C\(_{2n}\) clusterfullerenes could be synthesized with a high degree of selectivity, and molecular structures of the most abundant Dy-sulfide clusterfullerenes, Dy\(_2\)S@C\(_{82}\) (top) and Dy\(_2\)S@C\(_{82}\)-\( C_{3v} \) (bottom) compared to DFT-computed vibrational frequencies of individual molecules (black lines). (b) Atomic displacements of the two vibrations of the Dy\(_2\)S cluster in Dy\(_2\)S@C\(_{82}\)-\( C_{3v} \).

![Cluster modes vs. cage modes](image)

**Fig. 10** (a) Low-energy part of the Raman spectra of Dy\(_2\)S@C\(_{82}\)-\( C_{3v} \) (top) and Dy\(_2\)S@C\(_{82}\)-\( C_{3v} \) (bottom) compared to DFT-computed vibrational frequencies of individual molecules (black lines). (b) Atomic displacements of the two vibrations of the Dy\(_2\)S cluster in Dy\(_2\)S@C\(_{82}\)-\( C_{3v} \).
C_{6}(6) carbon cage, whereas among the two EMFs with the C_{6}2
C_{6}(6) fullerene cage, the sulfide clusterfullerene Dy_{2}S@C_{6}2
longer relaxation times than the carbide clusterfullerene
Dy_{2}C_{6}2@C_{6}2. Ab initio calculations for different types of clus-
terfullerenes showed that the clusters with a single non-metal
ion are more preferable for the better SMM performance than
the clusterfullerenes with diatomic non-metal units, and oxide
clusterfullerenes were found to have the highest crystal field
splitting.

Dynamic magnetic studies showed that the relaxation of
magnetization in Dy_{2}S@C_{6}2 isomers unprecedentedly involves
three Orbach processes operative at different temperatures.
Below 5–10 K, the dominant process is the relaxation via the
exchange/dipolar excited state with antiferromagnetic coupling
of Dy ions. At temperatures above 40–50 K, Orbach relaxation
via crystal-field excited states with relative energies exceeding
500 K is observed. The CF barriers in sulfide clusterfullerenes
are among the highest magnetization relaxation barriers
observed in dinuclear Dy-SMMs so far. For the intermediate
temperatures, we have discovered an unusual Orbach process,
whose energy barrier of 50 K corresponds to the intra-
molecular vibrations of the EMF molecules involving librational
motions of the endohedral cluster.

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