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Introduction

To date, a number of endohedral fullerene compounds with rare-earth metals are known to exhibit the properties of singlemolecule magnets (SMMs).1-39 Almost exclusively, they are metallo- or clusterfullerenes with one or two dysprosium atoms, such as DySc₂N@C₈₀-I_h, the first compound where SMM properties have been discovered,⁵ while molecules with three dysprosium atoms can exhibit magnetic frustration.^{7,40} In general, the SMM systems may be of great value to modern technology as materials for high-capacity data storage, or as prototypical magnetic qubits.⁴¹ In this regard, the endohedral SMM compounds are of particular interest due to the shielding effect of the carbon cage that protects the entrapped magnetic species from chemical degradation, as well as from other intermolecular interactions that could speed up unwanted magnetic relaxation. Further developments in this field can be associated with the exohedral functionalization of endohedral SMMs.^{14,29,42} Exohedral groups can affect the electronic properties of the molecule including the ground electronic state. Thus, in the above cited works, a single monovalent addend "substitutes" one of the electrons transferred to the

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We present a quantum-chemical study of the effect of exohedral functionalization with a CF_2 group on the lowest electronic states and the zero-field splitting pattern in a potential single-molecule magnet (SMM) compound $DySc_2N@C_{80}(CF_2)$. Multiconfiguration perturbational methodology is applied to various spin states of the endohedral compound, comparing different active spaces and state-averaging schemes in order to check for the possible involvement of orbitals other than 4f-Dy in the nondynamical electronic correlation and to suggest the most appropriate computational parameters. Combining the spin-orbit coupling calculations with perturbational corrections, we demonstrate that the interactions within the endohedral cluster and with the fullerene cage exert only a small effect on the non-relativistic approximation to the electronic states of the Dy^{3+} ion, yet they are significant enough to alter the parameters of zero-field splitting depending on the orientation of the $DySc_2N$ cluster inside the fullerene cage.

carbon cage returning it to the endohedral moiety. Another possible effect is the orienting influence on the endohedral atoms and hampering of their rearrangements inside the carbon cage.^{43,44} In addition, exohedral functionalization can be used to tune the solubility of the endohedral molecules, link them to the desired substrates, *etc.*

The easiest accessible endohedral compounds belong to the trimetallic nitride M₃N@C₈₀ family where M is typically a scandium or a lanthanide atom in a +3 oxidation state, the formal charge of the M_3N cluster being +6, and the I_h cage of C₈₀ conveniently accommodates 6 extra electrons into its fourfold-degenerate doubly occupied frontier level (the D_{5h} cage of C_{80} is also possible).⁴⁵ To date, several exohedral derivatives of these compounds have been obtained.46 Among them is $Sc_3N(OC_{80}(CF_2))$ that can be produced in a rather simple carbene addition (more exactly, according to the quantum-chemical findings, nucleophilic addition - intramolecular substitution) reaction with metal difluorochloroacetates.44 The reaction is rather universal, being applicable to other related endohedral compounds like Sc₃N@C₇₈.⁴⁷ It likely proceeds with kinetically controlled regioselectivity. Computations indicate that one of the endohedral metal atoms of the Sc₃N cluster tends to be oriented towards the CF₂ group, which is probably due to a combination of two factors. Firstly, bond opening in the carbon cage upon CF_2 insertion provides more space for the atom in its vicinity. Secondly, the bridgehead atoms that are linked to the electron deficient carbon end of the CF2 dipole are negatively charged and thus attract the positively charged metal atoms.

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In the present paper, we report a computational study of the spin-orbit coupling effects and, accordingly, of the potential SMM properties in two conformers of DySc₂N@C₈₀(CF₂). We compare various possible spin states and different selections of active spaces in the framework of a multiconfiguration description of the said states. The complete or restricted active space self-consistent field or configuration interaction (CASSCF/RASSCF or CASCI/RASCI) is inevitably required to describe the nondynamic electronic correlation effects in the 4f-shell. Previously, it has been applied to a number of endohedral SMM systems.^{2,12-15,18-21,27,37-40,42,48-51} However, the prohibitively large size of endohedral metallofullerenes often prevents complementary analysis of the dynamic correlation effects via, e.g., a perturbation treatment. A good exception can be found in ref. 50 where the XMS-CASPT2 multistate perturbation theory on top of CASSCF has been applied to anionic digadolinium endohedral systems. In addition, many works are restricted to just the minimum necessary active space based on the 4f-shell of the lanthanide atom(s). Apart from understanding the effect of chemical functionalization, the present study was also aimed at analyzing how important the effects of dynamic correlation and the nondynamic correlation effects outside the f-shell may be for the prediction of magnetic properties of the endohedral compounds.

Computational methods

The computations were carried out with the use of the Firefly v 8.2 package⁵² partly based on the GAMESS(US) software⁵³ and the GAMESS(US) package itself. We use the Def2-TZVP basis set for the DySc₂N cluster and a more modest Def2-SVP set for the $C_{80}CF_2$ cage.⁵⁴ Two conformers were selected: one with the Dy atom against the CF_2 group and the other – with a Sc atom in that position. The geometry is optimized at the DFT level with the PBE0⁵⁵ exchange–correlation functional.

To compute the lowest electronic states with the spin-orbit effects taken into account, the following strategy is adopted. Initially, a set of lowest electronic states of a selected spin multiplicity is computed with a non-relativistic Hamiltonian at the XMCQDPT2 multi-configuration quasi-degenerate perturbation theory⁵⁶ on top of the state-averaged CASSCF calculation. The CASSCF active space includes the f-shell of the dysprosium atom and, in some cases, a group of other orbitals depending on the spin multiplicity considered. The exact details regarding the active space, the state averaging, and the XMCQDPT2 model space are given in the Discussion section. Then, spin-orbit coupling (SOC) corrections to the CASSCF Hamiltonian are computed. Finally, the transformation that couples the model space CASSCF states to the zerothorder XMCQDPT2 states is applied to the spin-orbit corrections to transform them into the desired XMCQDPT2 basis, and the thus corrected XMCQDPT2 Hamiltonian is rediagonalized. More specifically, the block of the matrix of spin-orbit corrections between the sets of CASSCF states of spins S_i and S_i has the structure

$$H_{S_{i}S_{j}}^{\text{SOC}} = \begin{pmatrix} H_{(-S_{i})(-S_{j})} & H_{(-S_{i})(-S_{j}+1)} & \cdots & H_{(-S_{i})S_{j}} \\ H_{(-S_{i}+1)(-S_{j})} & H_{(-S_{i}+1)(-S_{j}+1)} & \cdots & H_{(-S_{i}+1)S_{j}} \\ \vdots & \vdots & \ddots & \vdots \\ H_{S_{i}(-S_{j})} & H_{S_{i}(-S_{j}+1)} & \cdots & H_{S_{i}S_{j}} \end{pmatrix}$$
(1)

Its blocks correspond to the respective pairs of spin projections. If we denote as U(S) the orthogonal transformation in the XMCQDPT2 model space from the basis of CASSCF states of spin *S* to the basis of zeroth-order XMCQDPT2 states, which transformation being the same for all combinations of spin projections, we rotate the spin–orbit matrix to the new basis according to

$$H_{S_iS_j}^{\text{SOC-PT}} = \left(U(S_i)^+ \times I_{2S_i+1} \right) H_{S_iS_j}^{\text{SOC}} \left(U(S_j) \times I_{2S_j+1} \right), \qquad (2)$$

where I_{2S+1} is the identity matrix of the respective dimension. Addition of the diagonal spinless QDPT Hamiltonian with the same diagonal blocks $H^{\text{QDPT}}(S)$ for each spin projection of the given spin state affords:

$$H_{S_iS_j}^{\text{QDPT+SOC}} = H_{S_iS_j}^{\text{SOC/QDPT}} + \delta_{ij}H^{\text{QDPT}}(S_i) \times I_{2S_i+1}.$$
 (3)

The matrix consisting of the blocks according to eqn (3) is eventually subjected to diagonalization. A dedicated script has been written to extract the required data from the Firefly and GAMESS(US) outputs and effect the desired diagonalization.

Hereinafter, K-state averaged CASSCF calculations with an (N*e*,M*o*) active space will be denoted with SA(K)-CASSCF(N,M) and the respective XMCQDPT2 calculations on top of them – as SA(K)-XMCQDPT2(N,M).

Results and discussion

Electronic states and selection of active spaces in the nonrelativistic calculations

The two $DySc_2N@C_{80}(CF_2)$ conformers considered in our study are shown in Fig. 1. The CF₂ group is inserted into a [6,6]-bond of the I_h -C₈₀ cage as has been observed in the recently synthesized $Sc_3N@C_{80}(CF_2)$.⁴⁴ While there are a number of local minima with different orientations of the endohedral $DySc_2N$ cluster in the carbon cage, their energy differs very little, and



Fig. 1 Geometry of $DySc_2N@C_{80}(CF_2)$. Left: The Sc-CF₂ conformer; right: the Dy-CF₂ conformer.

the present two structures represent the two general cases: coordination of either a scandium atom or the dysprosium atom against the attachment site of the CF_2 addend. One can expect that the former type of coordination would leave the magnetic properties rather similar to those in the pristine $DySc_2N@C_{80}$ while the latter may introduce certain differences. The XMCQDPT2 ground state energy of the two conformers was found to be virtually indistinguishable within 0.02 eV.

The lowest electronic states of the Dy³⁺ ion with 4f⁹ configuration are known to have S = 5/2, the highest states of this sextet manifold overlapping with the lowest states of the quartet manifold.^{57,58} In our survey, we primarily focused on the sextet states of DySc₂N@C₈₀(CF₂) but also considered the states of the adjacent spin multiplicity, quartet and octet. For the sextet states, the basic CASSCF active space encompasses just the seven 4f-orbitals, and we used equal-weight averaging over all 21 possible states with 7 alpha- and two beta-electrons, *i.e.* SA(21)-CASSCF(9,7).

Constructing the sextet states of Dy^{3+} by the addition of two beta-electrons to a half-filled 4f-shell, one can find that the possible angular momenta are defined by the antisymmetric product

$$\{F \otimes F\} = P \oplus F \oplus H. \tag{4}$$

Although there is obvious symmetry lowering within $DySc_2N()$ $C_{80}(CF_2)$, it turns out that the extent of degeneracy lifting is rather moderate and is mostly due to the Dy–N interactions. In agreement with Hund's rule, the lower-energy states are characterized by the highest orbital momentum (⁶H states for an isolated ion), spanning some 0.2 eV in both conformations of the endohedral molecule at the XMCQDPT2 level. The ⁶F multiplet is found some 0.95 eV higher and spans just 0.05 eV, and the ⁶P states – *ca.* 4 eV higher. Hereinafter, we will keep referring to this Dy³⁺ term labelling.

It turns out that the inclusion of dynamic electron correlation *via* perturbation corrections actually does not affect very significantly the relative energy of the 21 states in question. The respective rotation matrix U(5/2) appears to be rather close to the identity matrix, and the magnitude of deviations between the CASSCF and XMCQDPT2 relative energy of the states is summarized in Table 1. A significant difference of 0.5 eV is obtained only for the ⁶P states that lie well above the ⁶H multiplet. In general, the separations between the multiplets show a reasonable order of magnitude compared both to the test calculations and to the experimental results (where the

 $\label{eq:table_formula} \begin{array}{ll} \mbox{Table 1} & \mbox{Relative SA(21)-CASSCF(9,7) and SA(21)-XMCQDPT2(9,7) energy} \\ (eV) of the lowest sextet states of DySc_2N@C_{80}(CF_2) in the non-relativistic calculation \end{array}$

	Sc atom against CF ₂		Dy atom against CF ₂	
State	CASSCF	XMCQDPT2	CASSCF	XMCQDPT2
⁶ H ⁶ F ⁶ P	$\begin{array}{c} 0.00{-}0.18\\ 1.04{-}1.09\\ 4.42{-}4.62\end{array}$	0.00-0.21 0.95-1.00 3.87-4.10	0.00-0.13 1.01-1.06 4.41-4.57	0.00-0.16 0.92-0.66 3.87-4.04

spin–orbit interactions lift much of the degeneracy) for a bare Dy^{3^+} ion. 59,60

We have also tested the effect of expansion of the active space on the sextet states through inclusion of other frontier orbitals. Upon inclusion of the lone pair of the nitrogen, the respective SA(21)-XMCQDPT2(11,8) calculation provides virtually homogeneous shift of all 21 states by just -0.05 to -0.06 eV, and the occupation number of the nitrogen orbital shows only marginal deviation from 2. Of the lowest vacant shells of dysprosium, the 6s- and 6p-states are spontaneously replaced with the 5d-states in the course of the CASSCF optimization. Inclusion of the said 5d-states of dysprosium, or of some vacant or occupied frontier orbitals of the carbon cage leaves the ⁶H and ⁶F multiplets essentially unchanged, with no population redistribution between the 4f-states of dysprosium and the newly added orbitals. At the CASSCF level, the states due to charge-transfer excitations between the dysprosium 4f-shell and the above non-4f orbitals emerge at least 4 eV above the ground state, *i.e.* only close to the 4f⁹ ⁶P multiplet or even higher. Note that in those calculations, various broader state averaging schemes were being employed in order to compare the 4f⁹ configurations and the other electronic configurations of dysprosium on a more balanced basis.

In this regard, particularly worth mentioning is a test of the sextet states of DySc₂N@C₈₀(CF₂) with the quintet 4f¹⁰ configuration of dysprosium due to a back charge transfer from the fullerene cage. The active space was expanded with the four highest occupied fullerene cage orbitals roughly related to the fourfold degenerate HOMO of the hexaanion of Ih-C80. In order to achieve a balanced description of the 4f⁹ and 4f¹⁰ states with their different orbital relaxation effects in the f-shell, we performed a CASSCF calculation with averaging over a total of 161 states: the 21 4f9 states and the 140 4f10 states due to a transfer of one beta-electron from any of the four fullerene orbitals. The weights were taken inversely proportional to the number of states in the said two subsets. In these calculations, the 4f¹⁰ states emerge at least 7 eV above the 4f⁹ ground state. While the 4f¹⁰ states may be further stabilized by relatively higher contribution of the dynamic correlation within the 4fshell, the XMCQDPT2 tests for the 21 sextet states in the Dy³⁺ ion and DySc₂N⁶⁺ cluster vs. the 35 quintet states in, respectively, Dy^{2+} and $DySc_2N^{5+}$ show that the magnitude of the effect is only about 3 eV. Thus, the estimated energy of the 4f¹⁰ sextet states of DySc₂N@C₈₀(CF₂) is at least 4 eV above the ground state. Unfortunately, direct application of XMCQDPT2 to the sets of states broadly averaged over different electronic configurations results in a considerably degraded description of all states. This is obviously due to a drastic impairment of the zeroth-order PT2 Hamiltonian when different occupations of the 4f-shell are being considered in the same calculation.

Obviously, should the active space be simultaneously expanded with both the occupied and unoccupied frontier orbitals of the carbon cage, relatively low-lying excitations within the fullerene cage would be expected some 1.5–2.0 eV above the ground state,^{59–61} somewhere between the ⁶F and ⁶P multiplets of Dy³⁺. However, in view of high degeneracy of

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Fig. 2 The fullerene cage vacant orbital that enters the expanded active spaces in $DySc_2N@C_{80}(CF_2)$. Left: The Sc-CF₂ conformer; right: the Dy-CF₂ conformer.

the frontier levels in $I_{\rm h}$ -C₈₀, a reliable calculation of this kind would be prohibitively expensive due to excessive size of the adequately selected active spaces. Furthermore, the abovedescribed investigation of the charge-transfer states suggests that the fullerene cage excitations would be essentially decoupled from the transitions within the f-shell, and it would be more or less safe to disregard them.

The lowest octet states in $DySc_2N(@C_{80}(CF_2))$ can, in general, either be due to triplet excitations within the fullerene subsystem, or due to a transfer of one 4f beta-electron to a vacant state of the fullerene cage, of the Dy^{3+} ion, or of the Sc^{3+} ions. In the latter case, that would likely be the 3d-states of scandium, which are known to determine the LUMO in, e.g., Sc₃N@C₈₀.⁶² Unfortunately, consideration of the triplet excitations in the fullerene subsystem would be as prohibitively expensive as in the case of the singlet excitations for the sextet states. Considering the excitations from the 4f-shell, irrespective of the type of starting extra vacant orbitals included in the active space, CASSCF optimization always tends to end up with the 5d-states of dysprosium plus one fullerene cage π -orbital localized against the Dy atom (Fig. 2). The latter π -orbital would even displace one of the 5d-orbitals from the active space whenever only the 5d-shell is added initially. In view of that, the active space for the octet calculations was selected as 7f + 5d + 1 π , and the respective SA(42)-CASSCF(9,13) and XMCQDPT2 calculations encompassed all electronic states due to the seven possible states of the remaining beta-electron within the 4fshell of dysprosium and the six possible states of the extra alpha-electron within the added 5d + 1π orbitals.

Even though the orbital of Fig. 2 tends to displace even the 5d-orbitals of dysprosium, it shows any significant population only starting from the 33rd octet state of 42. Thus, the lowest octet states have the $4f^{8}5d^{1}$ configuration. At the XMCQDPT2 level, the calculated set of octet states spans the range of 4.3–6.4 eV above the lowest sextet states in both conformers of DySc₂N@C₈₀(CF₂). In an isolated Dy³⁺ ion, the 35 $4f^{8}5d^{1}$ states would have spatial symmetry according to

$$F \otimes D = P \oplus D \oplus F \oplus G \oplus H.$$
 (5)

In $DySc_2N@C_{80}(CF_2)$, all those octet multiplets show more pronounced dispersion in the energy scale than the three sextet multiplets, and their respective energy subranges nearly overlap. At the XMCQDPT2 level, the gap between the octet and the sextet states in $DySc_2N@C_{80}(CF_2)$ is, on average, some 0.5 eV lower than in the isolated Dy^{3+} .

Finally, the lowest quartet states in $DySc_2N@C_{80}(CF_2)$ can be, again, due to the poorly computationally accessible triplet excitations within the fullerene subsystem, or due to flipping one alpha-spin within the 4f-shell, or due to back charge transfer into the 4f-shell to give the $4f^{10}$ configuration of dysprosium. However, one cannot expect any strong exchange coupling between the endohedral cluster and the carbon cage, so the quartet states of the latter kind would be close in energy to the respective $4f^{10}$ sextet states considered above. In view of that, we decided to consider only the quartet states due to spin flipping within the 4f-shell.

Without the spin-orbit effects, there are 224 quartet states characterized by angular momenta from S up to M. According to the CASSCF calculations for an isolated ion, the lowest multiplets in the order of increasing energy are likely ⁴I, ⁴F, ⁴M, and ⁴G. Because of the costs of the perturbational treatment, we have considered only the said 48 lowest states at the SA(48)-XMCQDPT2(9,7) level. Their energy with respect to the lowest sextet state shows little difference between the conformers of DySc₂N@C₈₀(CF₂), falling in the range of 3.15-3.50 eV at the CASSCF level and 3.0-3.4 eV at the XMCQDPT2 level. Because of totally insignificant separation of the states, XMCQDPT2 shows here a much higher level of mixing of the CASSCF solutions, yet the energy range is reproduced quite well. According to the full SA(224)-CASSCF(9,7) calculation, the next quartet states emerge some 0.3 eV above the upper state of this group of 48.

In Table S3 of the ESI,[†] we summarize the relative energy estimates for various types of the above discussed electronic states of $DySc_2N@C_{80}(CF_2)$.

Spin-orbit coupling and zero-field splitting

The calculated spin–orbit coupling matrix elements appear, not surprisingly, to be rather high, reaching several tenths of an eV by absolute value. With such magnitude, one may expect not only the interactions within the sextet manifold but, perhaps, also between the different spin multiplicities. However, that did not happen to be the case.

With the spin–orbit effects taken into account, the ground state of Dy^{3+} becomes ${}^{6}H_{15/2}$, 57,58 which should give rise to eight Kramers doublets. The relative energy of these doublets was calculated for the two conformers of $DySc_2N@C_{80}(CF_2)$ both with just the 21 sextet states and with the additional 42 lowest octet states, 48 quartet states, or with the both octet and quartet sets. It turns out that the relative energy deviations from the sextet-only calculation remain within just 1%. Thus, unless the usually omitted states due to the excitations within the fullerene subsystem are actually of importance, the sextet-only treatment of the spin–orbit problem within the 4f-shell seems to be justified.

In Table 2 we provide the energy of the eight lowest Kramers doublets in the $DySc_2N@C_{80}(CF_2)$ conformer with the Sc atom against the CF_2 group *versus* the reference results for $DySc_2N@C_{80}$.⁴⁰ As one can see, the general character of zerofield splitting in the two compounds is highly similar, the

Table 2 Energy (cm⁻¹) of the eight lowest Kramers doublets in the DySc₂N@C₈₀(CF₂) conformer with the Sc atom against the CF₂ group. For comparison, the values for the pristine DySc₂N@C₈₀ from ref. 40 are given

Kramers	DySc ₂ N@C ₈₀	DySc ₂ N@C ₈₀ CF ₂		
doublet	$CASSCF + SOC^{40}$	CASSCF + SOC	XMCQDPT2 + SOC	
1	0	0	0	
2	415	411	493	
3	747	707	839	
4	1002	929	1091	
5	1158	1088	1270	
6	1256	1207	1405	
7	1334	1285	1500	
8	1465	1378	1604	



Fig. 3 The energy and spin projection (XMCQDPT2 + SOC) for the eight lowest Kramers doublets in $DySc_2N@C_{80}(CF_2)$. Left: The Sc-CF₂ conformer; right: the $Dy-CF_2$ conformer.

ground state Kramers doublet being a high-spin one (see Fig. 3 below). Thus, when a Dy atom is oriented against an unmodified portion of the wall of the fullerene cage, the remote changes in the molecular structures are of little importance, unless they strongly affect the distance to the nearest carbon atoms.³⁹ One can also see that the magnitude of the XMCQDPT2 corrections turns out to be moderate, though comparable to the magnitude of zero-field splitting. In addition, those corrections are inhomogeneous, generally increasing for higher Kramers doublets. Perhaps, such corrections for the dynamic correlation effects can often be omitted at the qualitative level, at least in the systems whose behavior is determined by a localized 4f-manifold.

However, comparing the two conformers, we see certain difference in the zero-field splitting (see also the ESI[†] for more details). The spin projection values for the calculated Kramers doublets are shown in Fig. 3. Compared against the conformer with the Dy atom sitting against the carbon cage wall, the conformer with the Dy atom against the CF₂ moiety shows weaker splitting, although in both cases the ground state is high-spin. Note that the splitting values found in the latter isomer are closer to those in the free $DySc_2N^{6+}$ cluster,⁴⁰ something we observe too in our test calculations.

There is a qualitative rationale behind the observed difference. In terms of the shape of its electron density distribution, Dy³⁺ belongs to the oblate type.⁶³ To maximize the anisotropy with an approximately axially symmetric ligand field, the ligands should preferably be placed closer to the axial direction rather than to the perpendicular equatorial plane and should be of donor nature. When the dysprosium atom is placed against the CF_2 addend it thus becomes oriented towards the positively charged carbon end of the CF_2 dipole. One can hypothesize that the acceptor effect of the said positively charged center results in a pronounced degradation of the anisotropy. In this regard, it would be particularly interesting to compare the CF_2 case against different functions such as donor CR_2 groups.

Another promising approach to tuning the zero-field splitting may involve the selection of different DyM_2N clusters (or clusters of other kind), as has been demonstrated recently.³⁹ By selecting the M atoms of greater size, one can affect the effective distance between the Dy atom and the carbon cage. Furthermore, in the case of the exohedrally functionalized molecules, larger M atoms may have increased affinity towards the functionalized region of the cage since it would typically be slightly buckled outwards and thus offer more space.

Conclusions

We see that the effect of exohedral functionalization on the SMM properties of endohedral fullerenes can be rather important, not only when a single monovalent addend forces one of the electrons transferred onto the fullerene cage back onto the endohedral moiety,^{14,29} but also in cases like the present one – when the electronic properties and structure of the fullerene cage change very little. This finding demonstrates a high potential of tunability of the magnetic properties of dysprosium endohedral fullerenes, even though it is always primarily the $DySc_2N^{6+}$ cluster that is responsible for them in the derivatives of $DySc_2N@C_{80}$. In view of that it would be most interesting to test other possible kinds of endohedral addends, in particular – with the emphasis on their donor/acceptor properties.

Fortunately, theoretical description of the lowest electronic states in the endohedral dysprosium compounds proves to be a less tricky problem than it could have been in such complex systems. Firstly, any influence of the electronic states other than the sextet ones seems to be quite negligible. Secondly, as follows from our testing of various active spaces, only those sexted states are important that are related to the 4f-shell of dysprosium. Furthermore, in $DySc_2N@C_{80}(CF_2)$, the effects of dynamic electronic correlation do not mix or reorder the lowest electronic states of interest and do not seem to affect the qualitative correctness of the CASSCF/SOC predictions. Yet we believe that, in view of the subtlety of the spin–orbit effects in question, the reliability of the computational predictions would benefit from perturbational corrections.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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