In Silico Molecular Engineering of Dysprosocenium-Based Complexes to Decouple Spin Energy Levels from Molecular Vibrations

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1

ABSTRACT. Molecular nanomagnets hold great promise for spintronics and quantum technologies, provided that their spin memory can be preserved above liquid-nitrogen temperatures. In the last few years, the magnetic hysteresis records observed for two related dysprosocenium-type complexes have highlighted the potential of molecular engineering to decouple vibrational excitations from spin states and, thereby, enhance magnetic memory. Herein, we study the spin-vibrational coupling in $[(Cp^{iPr5})Dy(Cp^*)]^+$ (Cp^{iPr5} = pentaisopropylcyclopentadienyl, Cp^* = pentamethylcyclopentadienyl), which currently holds the hysteresis record (80 K), by means of a computationally affordable methodology that combines first principles electronic structure calculations with a phenomenological ligand field model. Our analysis is in good agreement with the previously reported state-of-the-art *ab initio* calculations, with the advantage of drastically reducing the computation time. Then, we apply the proposed methodology to three alternative dysprosocenium-type complexes, extracting physical insights that demonstrate the usefulness of this strategy to efficiently engineer and screen magnetic molecules with the potential of retaining spin information at higher temperatures.

TOC GRAPHICS
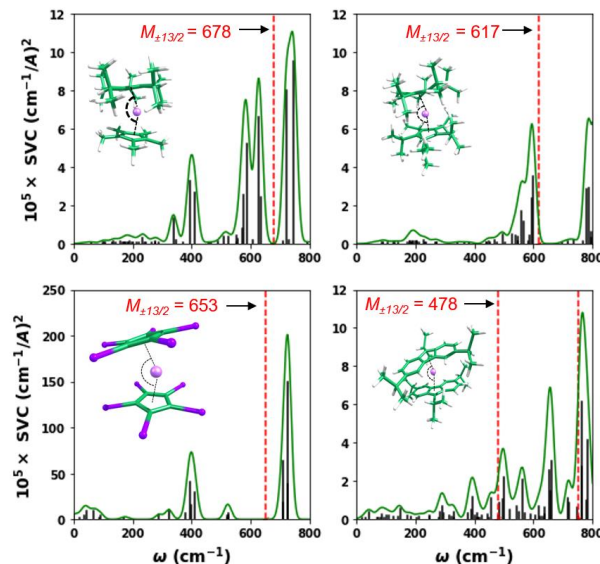
Since the discovery of slow relaxation of the magnetization and magnetic hysteresis in a bis(phthalocyaninato)-terbium complex in 2003,[1] lanthanide-based molecular nanomagnets have fascinated an interdisciplinary community of researchers because of their extraordinarily rich physical phenomena and potential applications in high-density magnetic memory storage, molecular spintronics and quantum computing.[2–5] This steadily rising interest has resulted in hundreds of reported coordination complexes that present magnetic bistability and an energy barrier for the magnetization reversal,[6–9] although their practical use is still a far dream due to the rapid loss of spin memory.

In order to improve the performance of these magnetic entities, commonly known as single-ion magnets (SIMs), the most pressing question is still fundamental in nature, namely: which are the chemical features that regulate the spin relaxation in these systems? While the effective energy barrier (U_{eff}) has progressively been enhanced during the last decade reaching values of *ca.* 2200

K, the temperature at which SIMs retain their magnetization (*i.e.*, blocking temperature (T_B)) has been substantially raised only very recently. The combination of an oblate lanthanide ion (squeezed along axial direction) with an axial ligand field has proven to be key to achieve higher U_{eff} values.[10] However, a high U_{eff} barrier does not guarantee a high T_B because of the vibronically-induced spin relaxation mechanisms –irrespective of the energy barrier– that can be active.[11–13] Indeed, the success of the dysprosocenium cation $[Dy(Cp^{ttt})_2]^+$, where Cp^{ttt} = $C_5H_2{}^tBu_3$-1,2,4 and $^tBu = C(CH_3)_3$, exhibiting magnetic hysteresis up to 60 K relies on the chemical design of an axial ligand framework that limits molecular vibrations.[14] Moreover, a thorough analysis of the spin-vibrational coupling revealed that the out-of-plane movement of the Cp-bonded hydrogen atoms played a crucial role for spin relaxation. Replacing these H atoms with the heavy isopropyl (iP_r) and methyl groups gave rise to the $[(Cp^{iPr5})DyCp^*]^+$ complex (Figure 1c) with the current T_B record of 80 K.[15] Almost simultaneously, a similar synthetic strategy resulted in $[Dy(Cp^{iPr5})_2]^+$ (Figure 1b) with T_B = 72 K, along with two other related dysprosocenium-type complexes with a similar behavior.[16]
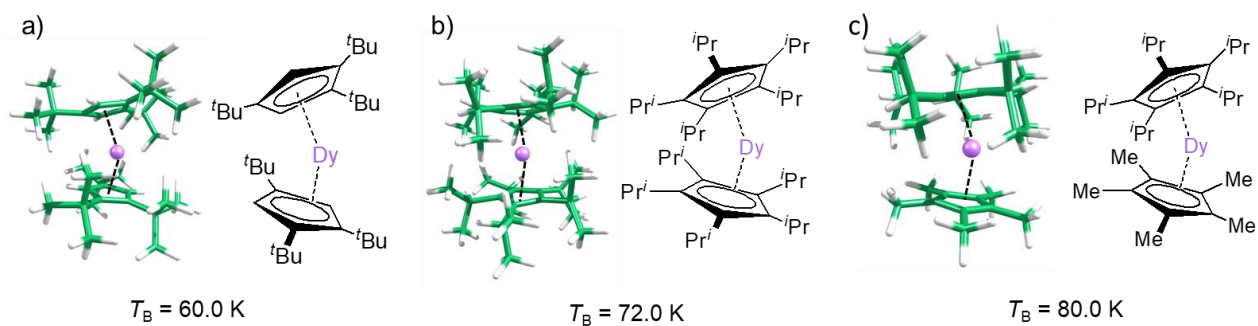

Figure 1. Chemical structures and blocking temperatures (T_B) of some related dysprosocenium SIMs: $[Dy(Cp^{ttt})_2]^+$ (a), $[Dy(Cp^{iPr5})_2]^+$ (b), and $[(Cp^{iPr5})DyCp^*]^+$ (c).

Based on these successful examples and the current theoretical understanding of spin-vibronic relaxation mechanisms, two ligand design principles seem to be drawn: (1) to avoid the resonances between the spin transitions involving different M_J states and the vibrational frequencies, and (2) to minimize the coupling between the M_J states and vibrational modes. A rational and practical path to achieve high-temperature operational SIMs is to design and explore spin relaxation in multiple candidate complexes by testing them *in silico* as an alternative to time-consuming synthetic efforts. In principle, high-level *ab initio* electronic structure calculations can be performed to predict spin-vibrational couplings.[14,15,17] Nevertheless, while these calculations can offer *a posteriori* advice of what to avoid in the subsequent experimental round of efforts, the high computational requirements make them impractical for an *a priori* screening of potential SIM candidates. Thus, a general predictive framework with feasible computational costs is an imperative necessity in order to guide the synthesis of new high-performing SIMs.

In this Letter, we demonstrate a computationally affordable scheme that combines electronic structure calculations and an effective electrostatic approach with the objective of identifying the key vibrational modes that are responsible for the spin relaxation. We apply our methodology to the prominent $[(Cp^{iPr5})DyCp^*]^+$ cationic complex and compare the coupling of spin energy levels and molecular vibrations with those reported by using *ab initio* multiconfigurational calculations. Finally, a series of synthetically viable dysprosocenium-type SIMs taking advantage of the predictive power of the employed approach is explored. The analysis of these derivatives can furthermore provide insights into general molecular engineering strategies for high-temperature SIMs.

Computational Scheme and Validation. The proposed computational methodology to efficiently assess the spin-vibrational coupling (SVC) essentially consists of three steps. First, we perform high-level *ab initio* multiconfigurational calculations at a reference geometry (*e.g.*, crystal structure). This provides an accurate set of spin energy levels that are employed to parameterize a computationally inexpensive ligand field Hamiltonian within the Radial Effective Charge (REC) model,[18] implemented in the SIMPRE code.[19] This electrostatic approach has been shown to reliably reproduce the splitting of the ground *J* state of lanthanide ions in different complexes, as well as make useful predictions for similar compounds with small structural variations.[20] Second, we optimize the geometry and calculate the vibrational frequencies by means of density functional theory (DFT). This permits to generate a series of distorted molecular geometries along each normal mode. Finally, we compute the spin energy levels for all the distorted geometries using the REC model. This process, which is computationally very demanding when performed purely by means of *ab initio* multiconfigurational calculations,[14,15,21] is here computationally affordable and permits to obtain an SVC parameter that quantifies the average change in the Crystal Field Parameters (CFPs) by each vibrational mode. In particular, we define here SVC as the sum of the squares of the first derivatives of each CFP (in Iwahara−Chibotaru notation)[22,23] along the respective normal mode coordinate. Since CFPs are dependent on the reference frame, we adopt the convention of choosing the easy axis of magnetization as our *z* axis to facilitate comparison between different cases (see the Supporting Information for all technical details).

As a way of benchmarking our strategy, we apply the methodology proposed herein to the record-setting [(Cp^{iPr5})DyCp*]$^+$ complex (further abbreviated as Dy-5*) in order to check whether the reported conclusions can also be reproduced with our approach. The energies for the

ground J manifold for Dy-5*, which in the case of Dy^{3+} corresponds to the $^6H_{15/2}$ term, were firstly computed at the previously-reported crystal structure using the multistate complete active space second-order perturbation theory (MS-CASPT2) and, subsequently, fitted using the REC model (see the Supporting Information for further details, Section S2). The calculated ground multiplet energy levels, which are similar to the energies reported by Guo *et al.*[15] (Figure 2 and Table S3), are well reproduced using an effective charge of 0.08326 (in elemental charge units) and a radial displacement (D_r) of 1.3126 Å in the REC model. Additionally, the Landé *g*-factor of the full set of 8 Kramers doublets at MS-CASPT2 are also in good agreement with the previously-reported results (see Table S4). For the three levels of theory (Figure 2), the ground state is a well-isolated $M_J = \pm 15/2$ Kramers doublet with practically the same energy difference of around 675 cm^{-1} between the ground and first excited ($M_J = \pm 13/2$) doublets. The only significant discrepancies between the REC method employed in the present work and the XMS-CASPT2 calculations in ref. [15] appear in the highest energy region (above *ca.* 1500 cm^{-1}), which are not relevant for the SVC analysis (*vide supra*).
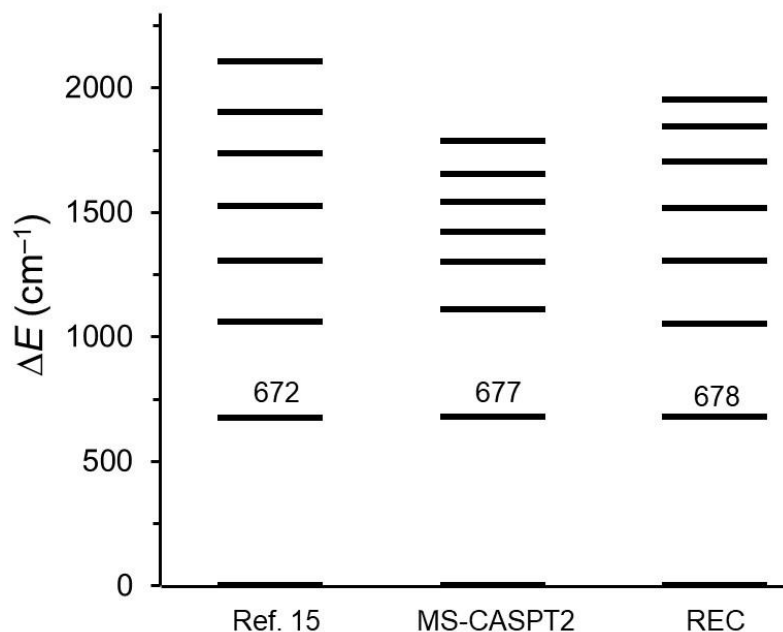
Figure 2. Energy spectra of Kramers doublets for the $^6H_{15/2}$ term of the Dy-5* complex predicted by Guo *et al.*,[15] by our MS-CASPT2 calculations and fitted by the REC model.

The SVC was computed for each vibrational mode following the methodology described in Section S3 of the Supporting Information. We calculated the CFPs at the equilibrium geometry and for each distortion of the coordination environment as a function of vibrational coordinate Q_n for each normal mode n. The variation of each CFP was fitted into a second-order polynomial and evaluated versus Q_n, allowing identifying which are the key vibrational modes that couple to the energy levels. Results are displayed in Figure 3. From 237 normal modes, only few vibrations below 1000 cm^{-1} have significant SVC values (Figure 3 and Table S10) and, therefore, contribute to vibronically-mediated magnetic relaxation. Among these, the normal modes at 625 and 635 cm^{-1}, which correspond to out-of-plane bending of the Cp moieties (see Figure S7), exhibit the largest SVC values of 6.63×10^5 and 2.45×10^5 cm^{-2} Å^{-2}, respectively. The other low-frequency vibrations (below 600 cm^{-1}) with relevant SVC values can be also

8

associated to motions in the Cp rings (Table S9 and Figure S8). Our relative SVC values are in good agreement with those reported by Guo et $al.;$[15] $i.e.,$ both computational schemes are predicting the largest SVC for the same vibrational modes, as well as similar vibrational frequencies (Figure 3, Figure S7,8 and Table S9). This agreement indicates that our new computational scheme can be used to efficiently identify the molecular vibrations responsible for magnetic relaxation in lanthanide-based SIMs.
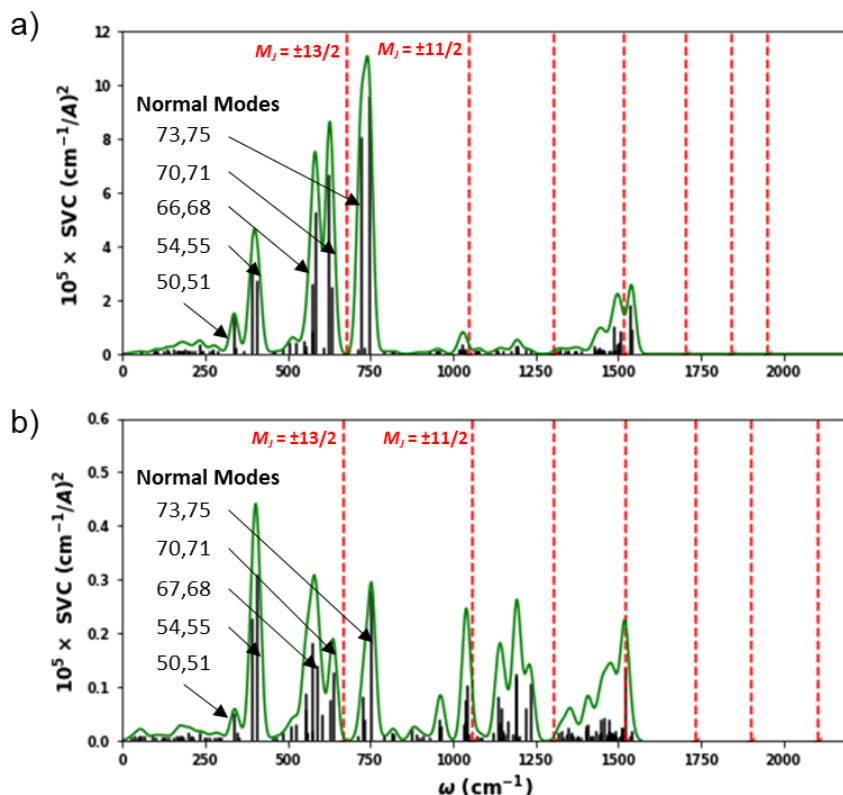

Figure 3. Spin-vibrational couplings (black lines) calculated for all normal modes of Dy-5* by using the REC model (a), and those reported by Guo et $al.$ (b). The energies of the exited M_J states (dashed red lines), convoluted SVCs represented by the finite-width Gaussian function (green line) with FWHM of 12 cm^{-1}.

In silico Molecular Engineering. Based on the nature of the key molecular vibrations responsible for the magnetic relaxation in Dy-5*, we explore a set of rational structural modifications to decouple the spin and vibration states and, thereby, mitigate the undesired fast magnetic relaxation. The three structural modifications (Figure 4) consist of: i) peripheral substitution of all the Cp rings by *i*Pr groups resulting in $[Dy(Cp^{iPr5})_2]^+$, ii) full functionalization of the Cp rings by iodine atoms instead of alkyl chains giving rise to the $[Dy(Cp^{I5})_2]^+$ complex, and, finally, iii) ligand π-extension with fluorene (FE) units partially substituted by terminal *i*Pr groups, as in $[Dy(FE^{iPr3})_2]^+$. While $[Dy(Cp^{iPr5})_2]^+$ has been experimentally studied,[16] the other two novel dysprosocenium-type complexes, $[Dy(Cp^{I5})_2]^+$ and $[Dy(FE^{iPr3})_2]^+$, have not been synthesized to the best of our knowledge. At least in the case of the periodinated complex (halogenated metallocenes), experimental evidence supports the possibility of its plausible synthesis.[24,25]

The three $[Dy(Cp^{iPr5})_2]^+$, $[Dy(Cp^{I5})_2]^+$, and $[Dy(FE^{iPr3})_2]^+$ complexes were initially optimized at the DFT level (Figure 4, Figure S9, S15 and S21). For these complexes, a deviation of the ligand-metal-ligand linearity with α(Cp–Dy–Cp) angles in the 150−162° range is found, in line with other experimentally characterized Dy-based complexes.[14–16] While detrimental to the linearity of the crystal field, this structural deviation is not completely preventable *a priori* by molecular design. Therefore, the chemical modification efforts need to be subtler and focus on the relation between the crystal field energy levels and the vibrational modes for a more effective design (*vide supra*). Interestingly, MS-CASPT2 calculations on the previously-optimized structures reproduce — in the case of $[Dy(Cp^{iPr5})_2]^+$— and predict — for $[Dy(Cp^{I5})_2]^+$ and $[Dy(FE^{iPr3})_2]^+$— a magnetic behavior that is qualitatively similar to that found for other known dysprosocenium complexes, both in terms of energies and wave functions as well as in the

distribution of the Lande *g*-factors of the different Kramers doublets (see details in Table S15, S24 and S33).
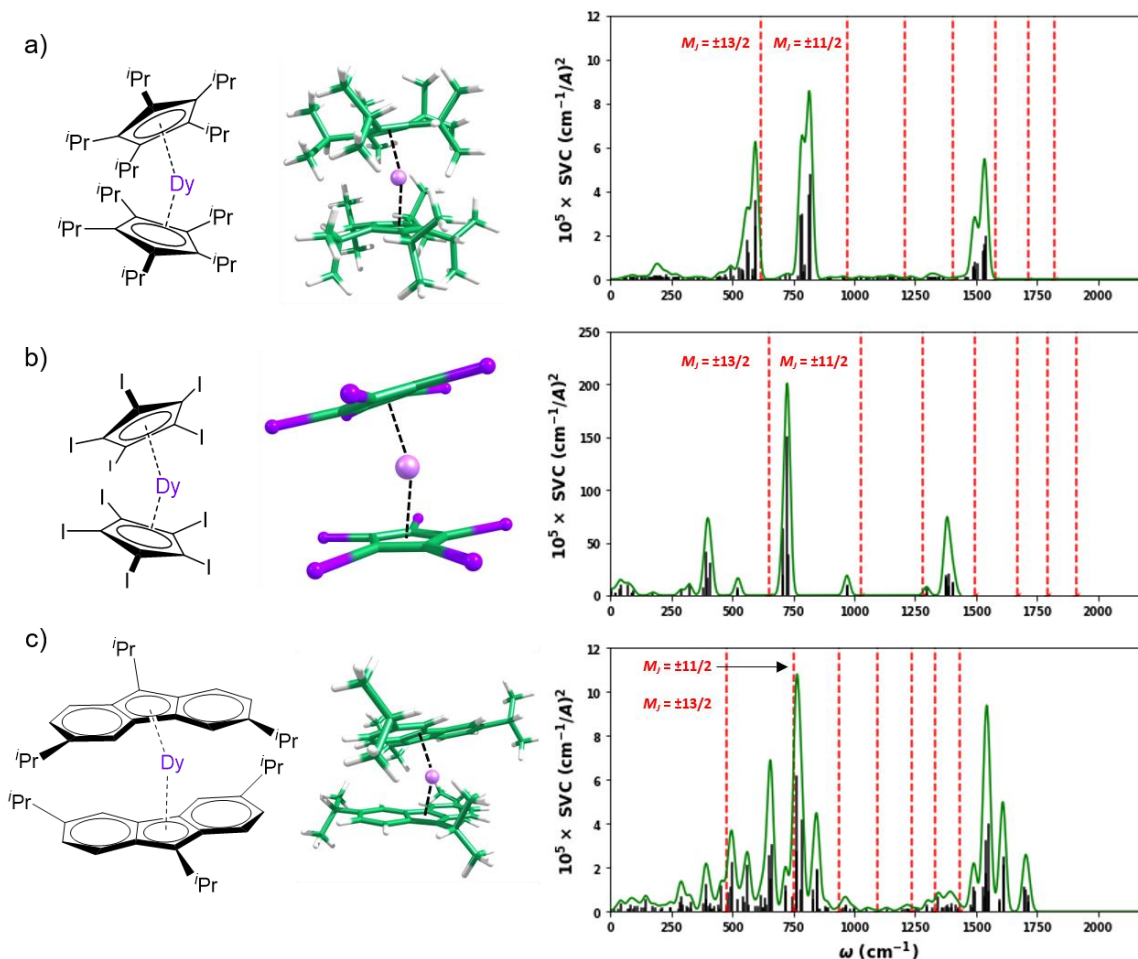

Figure 4. Spin energy levels (red) and spin-vibrational couplings (black) computed for $[Dy(Cp^{iPr5})_2]^+$ (a), $[Dy(Cp^{I5})_2]^+$ (b), and $[Dy(FE^{iPr3})_2]^+$ (c).

We can now turn our attention to the spin energy levels and the respective SVCs calculated for $[Dy(Cp^{iPr5})_2]^+$, $[Dy(Cp^{I5})_2]^+$, and $[Dy(FE^{iPr3})_2]^+$ by following the same computational protocol as for Dy-5* (Figure 4). The replacement of the methyl groups in one Cp ring by *i*Pr groups in $[Dy(Cp^{iPr5})_2]^+$, causes a narrowing energy gap (*ca.* 60 cm^{-1}) for the first two excited spin level

11

doublets ($M_J = \pm 13/2$ and $\pm 11/2$) compared to Dy-5*, while for the higher M_J doublets similar energy gaps are found for both Dy-5* and [Dy(Cp^{iPr5})$_2$]$^+$ complexes (Figure 3, Figure 4a and Table S14). In terms of molecular vibrations and similarly to Dy-5*, only a few vibrations involving Cp motions present significant SVC values (Figure 4a and Figure S14). However, in [Dy(Cp^{iPr5})$_2$]$^+$, the vibrations at 593 and 597 cm^{-1} with SVC strengths of 2.38×10^5 and 3.52×10^5 cm^{-2} Å^{-2} are closer in resonance with the $M_J = \pm 13/2$ Kramers doublet (~25 cm^{-1}) than those active for Dy-5* with an energy separation of around 45 cm^{-1} (Figure 3). This SVC pattern, the crystal field splitting, and the orientation of g-factor for $^6H_{15/2}$ states can partially explain why [Dy(Cp^{iPr5})$_2$]$^+$ provides a T_B value (72 K) lower than that reported for Dy-5* (80 K). For [Dy(Cp^{I5})$_2$]$^+$ (Figure 4b), two interesting opposite effects occur; on one hand, the SVC values are much higher than those predicted for Dy-5* and [Dy(Cp^{iPr5})$_2$]$^+$, which would be detrimental for magnetic relaxation, but on the other hand the active molecular vibrations are off-resonance with respect to the spin energy levels. For instance, vibrations computed at 709 and 726 cm^{-1} with high SVCs are energetically separated from the $M_J = \pm 13/2$ Kramers doublet by 57 cm^{-1}. This later effect would limit the vibronically-induced magnetic relaxation. Finally, the π-extension of the ligands with fluorene units for [Dy(FE^{iPr3})$_2$]$^+$ has turned out to be a negative strategy since [Dy(FE^{iPr3})$_2$]$^+$ presents a dense non-negligible SVC spectra near in resonance to the spin energy levels which would promote an efficient magnetic relaxation. Among the three candidates, our outcomes therefore reveal that the [Dy(Cp^{I5})$_2$]$^+$ complex can be considered as a SIM candidate with the potential to show magnetic hysteresis at temperatures higher than 80K.

Here we are relying on a simplified computational approach that can nevertheless be employed as a qualitative guide tool. For our purposes, the relevant molecular vibrations are those that at the same time present: i) significant SVCs and ii) energies in the adequate window, namely in

near-resonance with allowed transitions between different M_J eigenstates. In the case of dysprosocenium SIMs, this tends to be in the 100−800 cm^{-1} energy window (see Tables S38), which in principle can promote transitions between subsequent spin energy levels at the same side of the barrier. Because the relatively-high energy gaps between M_J eigenstates, only local intramolecular vibrations are expected to hold enough energy to promote relaxation and long-wavelength phonons can be discarded. In fact, a recent theoretical study on sub-picosecond dynamics of spin energy levels by some of us demonstrated that long-wavelength phonons and low-frequency vibrations (below 10 cm^{-1}) do not modulate significantly the spin dynamics on a rather generic (no-symmetry, non-Kramer's) lanthanide-based complex.[26]

In summary, we have demonstrated a computationally efficient approach that combines *ab initio* and effective charge electrostatic calculations to identify the key molecular vibrations responsible for the magnetic relaxation in lanthanide-based single ion magnets and, thus, be able to establish some valuable structure-property guidelines for a more optimized rational design. Our efficient approximation has been successfully validated in the case of Dy-5*, which holds the record for magnetic hysteresis above liquid-nitrogen temperatures. Based on our validated results, we have *in silico* explored different chemically-viable dysprosocenium-type complexes to avoid vibrational-induced magnetic relaxation. Among the targeted compounds, $[Dy(Cp^{I5})_2]^+$ may be considered as a good candidate for a high-temperature operational SIM due to the absence of vibrational frequencies in resonance with the low-energy M_J Kramers doublet. From our outcomes, we can suggest some designing strategies for potential SIMs with high T_B: 1) the choose of molecules that are simple and rigid in the vicinity of the metal to provide sparse molecular vibrations in the low energy region (< 1000 cm^{-1} but especially < 500 cm^{-1}) and 2) the use of ligands that maximize ligand-field splitting to achieve energetically well-separated low-

lying spin energy levels, thereby minimizing energetic resonances between the available vibrations and the excitations required for barrier crossing (see Figure S27 and Tables S38-40). Although substituted cyclopentadienyl ligands currently fulfill these two requirements, there is surely room for improvement, either within these chemical families or in others.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:

Full theoretical and computational details; crystal field parameters, magnetic response properties, DFT-optimized geometries, vibrational frequencies, and spin-vibrational couplings, including Figures S1−S27 and Tables S1−S40.

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Notes

The authors declare no competing financial interests.

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ACKNOWLEDGMENTS

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