Combined Experimental and Ab Initio Methods for Rationalization of Magneto-Luminescent Properties of YbIII Nanomagnets Embedded in Cyanido/Thiocyanidometallate-Based Crystals

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ABSTRACT: The ab initio calculations were correlated with magnetic and emission characteristics to understand the modulation of properties of NIR-emissive [YbIII(2,2′-bipyridine-1,1′-dioxide)4]3+ single-molecule magnets by cyanido/thiocyanidometallate counterions, [Ag(CN)2]− (1), [Au(SCN)2]− (2), [CdII(CN)4]2−/CdII(CN)2]3− (3), and [MIII(CN)6]3− [MIII = Co (4), Ir (5), Fe (6), Cr (7)]. Theoretical studies indicate easy-axis-type ground doublets for all YbIII centers. They differ in the magnetic axiality; however, transversal g-tensor components are always large enough to explain the lack of zero-dc-field relaxation. The excited doublets lie more than 120 cm−1 above the ground for all YbIII centers. It was confirmed by high-resolution emission spectra reproduced from the ab initio calculations that give reliable insight into energies and oscillator strengths of optical transitions. These findings indicate the dominance of Raman relaxation with the power n varying from 2.93(4) to 6.9(2) in the 4–3–5–1–2 series. This trend partially follows the magnetic axiality, being deeper correlated with the phonon modes schemes of (thio)cyanido matrices.

The development of lanthanides’ chemistry is driven by applications in life and technology.1,2 The latter is related to their emission originating from f–f electronic transitions.3 Lanthanide luminescent systems are promising for display devices, light-emitting diodes, optical communication, thermometry, sensing, and bioimaging.4–8 Their unique electronic properties related to spin–orbit coupling and crystal-field effects result also in strong magnetic anisotropy leading to the slow relaxation of magnetization.9,10 Resulting single-molecule magnets (SMMs) reveal magnetic hysteresis loop of a molecular origin arousing interest for data storage, quantum thermometry, and spintronics.11–13 The main issue is to take control over a large number of magnetic relaxation pathways.14 Among them, the Orbach process, quantum tunneling of magnetization (QTM), and Raman relaxation operate without the external field, while a direct process is recognized for field-induced SMMs. Strategies for the increased energy barrier of the Orbach process and eliminating QTM were broadly studied.15–17 In contrast, the two-phonon Raman relaxation is much harder to rationalize. Therefore, finding the means of doing so is of high interest in the field.18–20 Lately, the ideas of luminescent,21 conducting,22 or multifunctional SMMs23,24 have emerged, and the systems linking slow magnetic relaxation with porosity25,26 or photochromism27 were recognized. Lanthanide SMMs were lately applied in optical thermometry,28,29 while their emission spectra are usually used to perform magneto-optical correlations.30 The construction of such molecular materials may involve coordination chemistry.18–30 In this context, the application of cyanido metal complexes is efficient.31,32 These anionic moieties combined with d- and f-block metal ions resulted in coordination systems showing magnetic,33 optical,33 electric,34 and mechanical phenomena.35 They can enhance f-centered emission and induce their strong magnetic anisotropy.36–39 They also give information on how the exchange of d-block metal ions can affect the optical and magnetic properties of attached lanthanides.39,40,41 To better understand such modulation of emissive SMMs, we focused on supramolecular networks built of cationic LnIII complexes and noncovalently bonded cyanido moieties. We used 2,2′-bipyridine-1,1′-dioxide (2,2′-bpdo) ligands together with YbIII ions that exhibit NIR emission and magnetic relaxation, usually controlled by phonon-assisted Raman processes.42,43 We aimed to combine the ab initio calculations with experimental magnetic and luminescent characterizations to get insight into modifications of emissive [YbIII(2,2′-bpdo)4]3+ SMMs by the crystalization with (thio)cyanidometallate counterions. Herein, we report structures, magnetic and luminescent properties of the series of d–f YbIII.
cyanido/thiocyanido ionic crystals (1–7) showing magnetic relaxation and NIR emission governed by the d-block metal ions, which was rationalized by the combined approach based on experimental studies confronted with the ab initio calculations playing a key role in the elucidation of both magnetic anisotropies as well as emission patterns.

Reported compounds crystallize from the solutions containing Yb$^{3+}$ ions, 2,2′-bpdo ligands, and (thio)cyanido precursors, $[\text{AgI(CN)}_2]^{-}$ (1), $[\text{AuI(SCN)}_2]^{-}$ (2), $[\text{CdII(CN)}_4]^{2-}$/ $[\text{CdII}_2(CN)_7]^{3-}$ (3), and $[\text{MIII(CN)}_6]^{3-}$ [$\text{MIII} = \text{Co}$ (4), Ir (5), Fe (6), Cr (7)] (see Experimental section in Supporting Information (SI)). The samples of 1–7 were characterized by IR spectra, TG, elemental analyses, and X-ray diffraction methods (Figures S1–S8, Tables S1–S7). All compounds crystallize as supramolecular frameworks built of cationic $[\text{YbIII(2,2′-bpdo)}_4]^{3+}$ complexes separated by anionic (thio)-cyanido complexes and solvent (Figures 1 and S3–S7). The Yb$^{3+}$ units in 1–3 reveal the geometry of a square antiprism; however, the degree of distortion varies within the series, while the Yb$^{3+}$ centers in 4–7 adopt the intermediate geometry between a square antiprism and a dodecahedron (Table S7). The cyanido counterions are arranged through solvent-mediated hydrogen bonds (4–7); they form molecular aggregates based on metalophilic interactions (1, 2); or they in situ form $[\text{CdII}_2(CN)_7]^{3-}$ units accompanying $[\text{CdII(CN)}_4]^{2-}$ ions (3). The Yb$^{3+}$ complexes are arranged in a tubular manner.

Figure 1. Crystal structures of 1 (a), 2 (b), 3 (c), and 4–7 (d) including tubular arrangements of Yb$^{3+}$ complexes, the molecular building units, and detailed view of Yb$^{3+}$ coordination spheres.
All compounds were studied using direct- (dc) and alternate-current (ac) magnetic measurements (Figures 2 and S9−S22). At 300 K, for 1−5 with diamagnetic d-block metal complexes, the χM product lies in the range of 2.47−2.54 cm³ mol⁻¹ K expected for isolated Yb³⁺ ions (Figures S9−S10). For 6 and 7, the respective values of 2.84 and 4.34 cm³ mol⁻¹ K are enlarged because of the contributions from Fe³⁺ or Cr³⁺ centers, respectively. On cooling, the χM decreases for all cases due to the thermal depopulation of m_J levels within the ground multiplet. For 1−5, or even for 6 and 7, no distinct magnetic interactions are present. This claim is supported by M(H) curves at 1.8 K, showing a featureless increase of magnetization (M). At 50 kOe, the M values are in the 1.45−1.71 μB range for 1−5, while for 6 and 7, the values of 2.50 and 4.50 μB were found, respectively. The materials do not show a M(H) hysteresis loop even at 1.8 K owing to the moderate magnetic anisotropy of Yb³⁺. Compounds 1−7 were characterized by field-variable ac magnetic studies (Figures S11−S22). Without the dc field, none of them shows a notable signal in the χM″(ν) plots. When increasing the field, the appearance of the maxima occurs for 1−5. They are initially slightly shifted to lower frequencies, but higher fields facilitate magnetic relaxation. Such behavior is due to the quenching of QTM and the appearance of a direct relaxation. Optimal dc fields were selected to follow the T-dependences of relaxation times (Figures 2 and S11−S20). For 1−5, the maxima in the χM″(ν) plots appear in the narrow T-range, which implies the strong T-dependences of relaxation times. To extract their values, a generalized Debye model was used. Field- and T-dependences were simultaneously fitted using the eq 1:
Table 1. Best-Fit Parameters for Relaxation Processes (direct, QTM, and Raman) Fitted for the T-Dependences of the Relaxation Times in 1–5, Equation 1, in the Simultaneous Fitting of Both H- and T-Variable ac Magnetic Data, and the Parameters from the Linear Fitting of High T-Range Data, Equation 2

| fitting type | parameter | 1       | 2       | 3       | 4       | 5       |
|--------------|-----------|---------|---------|---------|---------|---------|
| overall fitting of direct, QTM, and Raman relaxation processes (eq 1) | $A_{\text{dir}}/s^{-1}\text{K}^{-1}\text{Oe}^{-n}$ | $2.11(2)\times10^{-12}$ | $5.03(6)\times10^{-13}$ | $5(1)\times10^{-13}$ | $2.3(6)\times10^{-3}$ | $2.7(1)\times10^{-13}$ |
| $m$ | 4 (fixed) | 4 (fixed) | 4 (fixed) | 1.59(3) | 4 (fixed) |
| $B_1/s^{-1}$ | 497(14) | 2000 (fixed) | 2861(158) | 2365(115) | 190(8) |
| $B_2/\text{Oe}^2$ | $2.3(4)\times10^{-5}$ | $5(1)\times10^{-4}$ | $2.2(3)\times10^{-6}$ | $4.8(6)\times10^{-8}$ | $1.8(3)\times10^{-7}$ |
| $B_3/\text{Oe}^2$ | $1.1(1)\times10^{-5}$ | $1.0(4)\times10^{-7}$ | $−$ | $−$ | $−$ |
| $C_{\text{Raman}}/s^{-1}\text{K}^{-n}$ | 4.4(3) | 0.50(8) | 58(3) | 131(5) | 12.1(9) |
| $n$ | 4.92(5) | 6.9(2) | 3.43(5) | 2.93(4) | 4.06(6) |
| $U_{\text{dir}}/K$ | 20.6(5) | 22(1) | 10.2(5) | 9.4(5) | 18(1) |
| $\tau_0/s$ | $1.4(2)\times10^{-6}$ | $7(2)\times10^{-7}$ | $1.0(2)\times10^{-5}$ | $1.2(2)\times10^{-5}$ | $3(1)\times10^{-6}$ |
| Arrhenius dependence fitting (eq 2) | $\tau^{-1}(T) = \tau_0^{-1}\exp\left(-\frac{U_{\text{eff}}}{T}\right)$ |

where the first term corresponds to a direct process, the second to the QTM, while the last to the Raman relaxation. The term related to an Orbach process was excluded on the basis of the ab initio calculations and emission spectra (see below). However, for comparison, the formalism of an effective energy barrier ($U_{\text{eff}}$) was applied in the highest recorded T-regime:

$$
\tau^{-1}(T) = \tau_0^{-1}\exp\left(-\frac{U_{\text{eff}}}{T}\right)
$$

Final parameters of T-dependences of the relaxation times are gathered in Tables 1 and S8. In all cases, the power $n$ of Raman relaxation is lowered from the expected value of 9, which appears when not only acoustic but also optical phonons operate in spin–lattice relaxation.18–20,47,48 The best-fit parameters indicate the dominant role of the Raman relaxation. The power $n$ is the highest (6.79) for the [Au(SCN)$_2$]$^-$ based 2; it is followed by 1 built of [Ag((CN)$_2$)$_2$]$^-$ anions, $n = 4.92(5)$, and Ir$^{III}$-based 5, where $n = 4.06(6)$. Much smaller $n$ parameters of 3.43(5) and 2.93(4) were found for 3 and 4, involving Cd$^{II}$ and Co$^{II}$, respectively. The $C_{\text{Raman}}$ follow the opposite trend starting from 0.50(8) s$^{-1}$K$^{-n}$ for 2, and reaching 131(5) s$^{-1}$K$^{-9}$ in 4. As all compounds are built on [Yb(III)(2,2′-bpydo)]$^{13+}$ complexes, the variation in Raman relaxation can be primarily ascribed to the phonon modes of transition metal complexes. The increasing trend of the power $n$ in the series of 4–3–5–1–2 can be correlated with energies of key phonon modes.18–20,47,48 Their lowest energies giving the strongest T$^n$ dependence are offered by [Au(SCN)$_2$]$^-$ ions (2). Higher energies of key phonon modes were found for [Ag((CN)$_2$)$_2$]$^-$ ions (1) also forming supramolecular aggregates as [Au((SCN)$_2$)$_2$]$^-$, and for heavy [Ir$^{III}$(CN)$_6$]$^{3-}$ ions (5). Lighter Cd$^{II}$-cyanido units of 3 show much lower power $n$ while the lowest is detected for the lightest [Co$^{III}$(CN)$_6$]$^{3-}$ ions. The opposite trend of $C_{\text{Raman}}$ parameter suggests that the number of accessible phonons is the highest for [Co$^{III}$(CN)$_6$]$^{3-}$ while the lowest for [Au$^{III}$(SCN)$_2$]$^-$ ions. It is also important to mention that a relatively high value of 6.9(2) for 2 suggests that almost only acoustic phonons are involved in the relaxation while, for others, optical phonons contribute to the relaxation. In the latter case, the crucial role of optical phonons has to be caused by the significantly stronger spin-phonon coupling than for acoustic phonons as relaxation appears at the low T-range where optical phonon modes are not easily accessible.18–20,47,48 Materials with paramagnetic [M$^{III}$(CN)$_6$]$^{3-}$ ions reveal a $\chi_M''(\nu)$ signal, but it is only the onset of relaxation (6) or the low-frequency maxima of a dipolar origin (7) (Figures S21–S22). Compounds 1–7 exhibit solid-state NIR luminescence at 300 K (Figures 3 and S24–S25). The shape of the $^2$F$_{5/2}$ $\rightarrow$ $^2$F$_{7/2}$ band slightly varies because of subtle differences in the

**Figure 3.** Solid-state photoluminescence of 1–3 (a) and 4–7 (b), including the excitation and the emission spectra at the indicated wavelengths measured at room temperature.
Yb$^{III}$ complexes. The excitation spectra are divided into two ranges. Above ca. 900 nm, there is a band related to the direct $f$–$f$ excitation, while below ca. 500 nm all compounds reveal the excitation band caused by the energy transfer (ET) from 2,2′-bpdo ligand.\(^{39}\) Within 1–5, there are small differences in the structure of this band related to admixtures of ET from (thio)cyanidometallates. In 6, the intensity of the 2,2′-bpdo excitation is smaller than direct excitation as [Fe$^{III}$(CN)$_6$]$^{3-}$ ions harvest the energy from organic ligands.\(^{36}\) For the [Cr$^{III}$(CN)$_6$]$^{3-}$-based 7, the excitation spectrum shows an additional band at the edge of UV–vis ranges. It can be assigned to the Ce$^{III}$ $4T_{2g}$$\rightarrow$$4T_{5g}$ transition, thus the Ce$^{III}$-to-Yb$^{III}$ ET.\(^{56,37}\) After being cooled, the shapes of the excitation spectra barely change, with the only strong difference in 6 where 2,2′-bpdo-centered bands dominate at low-$T$. Pronounced differences are seen in the emission due to the partial disappearance of hot bands.

The $ab$ initio calculations of a CASSCF/RASSI/SINGLE_ANISO type were performed on the structural models of 1–7 (Tables S9–S17, Figures 4–5, S23).\(^{15}\) The calculations were done using two basis sets (models S and L, Table S9). For Yb$^1$ center of 1, the active space was additionally enlarged to check the influence of increased orbital mixing (model L$^+$. The resulting energy splitting, the composition of the ground doublets, and pseudo-$g$-tensor components for calculated complexes are gathered in Tables S10–S16. The ground Kramers doublets for all computed Yb$^{III}$ centers were found to be an easy-axis type; however, the alignment of a magnetic easy axis (the $g_e$ component) varies in the 1(Yb1/Yb2)–2–4–5 series (Figure 4). This can be explained by the non-negligible structural differences between Yb centers crystallizing in various space groups with the distinguishable supramolecular environment of (thio)cyanido metal complexes. Moreover, the Yb complexes differ in the strength of magnetic axiality represented by the pseudo-$g$-tensor components. The strongest axiality of the highest $g_e$ and the lowest transversal components was found for the Yb$^1$ complex of 2, but even for this case, the $g_e$ and $g_\perp$ factors are above 0.15, which explains the lack of zero-dec-field magnetic relaxation. Weaker axiality is observed in Yb$^1$/Yb$^2$ centers of 1, and the weakest for Yb$^1$ units of isostructural 4 and 5. One can notice that the strength of the $T$-variation of Raman relaxation, represented by the power $n$, increases together with the increased magnetic axiality. However, this factor seems to play a supporting role as shown by 4 and 5 revealing almost identical ground states but very different Raman relaxation (Table 1). Thus, the correlation between the Raman process and the phonon modes scheme of the lattice, discussed above, plays a dominant role. The results of $ab$ initio calculations of the L model indicate that the first excited Kramers doublets for all calculated Yb centers lie more than 130 cm$^{-1}$ above the ground one, which excludes the Orbach relaxation process as such a high energy barrier cannot be used to reproduce the relaxation dynamics; for example, the effective energy barriers for the high $T$-range are smaller than 16 cm$^{-1}$ (22 K, Table 1). This confirms the supremacy of Raman relaxation in 1–5. There is no noticeable correlation between the energies of excited Kramers doublets and the parameters of Raman relaxation, for example, 2, showing the highest power $n$, exhibits the intermediate values of energy splitting. The quality of the calculations is documented by the dc magnetic curves (Figures S9–S10). Theoretical $\chi_M$*($T$) plots for 4 and 5 reveal noticeable discrepancies from the experiment, however, these differences are comparable with other reported cases of Yb$^{III}$ SMMs.\(^{24,42,44}\)

The results of the $ab$ initio calculations were used to rationalize the high-resolution emission spectra gathered at 80 K for 1, 2, 4, and 5. By taking advantage of the RASSI module of OpenMolcas, it is achievable to calculate transition moments between spin–orbit states obtained after diagonalization of AMFI spin–orbit Hamiltonian. From this, we can obtain oscillator strength for the transition from the energy state A to B which is represented by factors expressing the probability of emission, thus also emission band intensity. These factors are defined by eq 3:

$$f_{AB} = \frac{2m_J^2|\langle W|IB|H \rangle|^2}{3\hbar^2(E_B - E_A)}$$

where $E_A$ and $E_B$ are energies of state B and A, respectively, and $\langle W|IB|H \rangle$ is a transition moment between these two states. This method relies on two approximations. The first is the application of states taken from the state average multi-configurational calculations considering relativistic effects but done on the experimental geometry, not the geometry for an excited state. This can be justified by the small impact of changing geometry on the crystal field for well-screened 4f electrons. The second is the consideration of only electric-dipole transitions, but it is sufficient to explain intensities as shown by the Judd–Ofelt Theory of intensities (see discussion in the S1). In this approach, for A and B energy states which are exact solutions to the time-dependent Schrödinger equation with Hamiltonian, $H$, and for an arbitrary operator $W$, the eq 4 holds:

$$\langle W|IB|H \rangle = \frac{\langle W|H|A \rangle}{E_B - E_A}$$

Thus, there exists an arbitrary choice of the operator. To calculate dipole transition moment where operator $W$ is simply a vector of $(x,y,z)$ coordinates, we can also use $[W,H]$ which for nonrelativistic Hamiltonian is a velocity operator. These two approaches are identical as far as the used functions are exact solutions, but with the approximated functions in practical calculations, they differ. We found that the velocity gauge more correctly reproduces experimental spectra. The calculated cumulative strengths, which are obtained by the $2\times2$ summation over Kramers doublets of energy states $A$ and $B$ taken from the L/L$^+$ models are shown in Table S17. The obtained results were presented in the comparison with the experimental spectra which were repositioned to correspond to the relative energies from calculations (see Figures 5 and S26 with the comments in the captions). The $ab$ initio calculations with our approach well reproduce not only the energies but also relative intensities of emission bands. The latter can be now clearly assigned to the specific transitions between the doublets of the emissive and ground multiplets. This is particularly helpful for the detection of the 0–0 emission line and the separation of the hot bands, two issues that are critical for magneto-luminescence correlations in SMMs.\(^{21,23,24,26,30,42}\)

The $ab$ initio calculations are even useful for the estimation of the energy of emissive multiplet, only slightly overestimating the related energies by less than 2%, being also appropriate for the determination of the detailed energy splitting of ground multiplets (Table S18). Then, we can undoubtedly determine the energy gaps between the two lowest-lying Kramers doublets which represent the energy barriers for a potential
Orbach magnetic relaxation ($\Delta E_{\text{Orbach}}$, Figures 5 and S26, Table S18). The related theoretically estimated energy gaps ($\Delta E_{\text{Orbach}}^{\text{ab initio}}$) are very close to the optically estimated values ($\Delta E_{\text{Orbach}}^{\text{exp}}$), and all of them, within the whole set of investigated Yb complexes, were found to be above 120 cm$^{-1}$. This confirms the lack of an Orbach relaxation in the accessible frequency range for the presented compounds which supports the conclusion of the dominant role of a Raman process. The optical estimation keeps the identical trend of the energy gaps in the 1–5 series as found from the ab initio calculations, for example, the highest $\Delta E_{\text{Orbach}}$ is ascribable to Yb2 centers of 1, confirming also that the energy schemes of doublets do not directly influence the efficiency of Raman relaxation as this trend does not follow those for the power $n$.

In conclusion, we present the methodology based on the ab initio calculations confronted with experimental magnetic and luminescent data that enables the deep investigation of physical properties of NIR-emissive [Yb$^{3+}$(2,2′-bpdo)]$_3$ nano-
magnets embedded in the crystal lattices with diverse cyanido/thiocyanidometallates. First, the ab initio calculations were used to determine the character of YbIII electronic ground states. They are of an easy-axis type with tunable magnetic axially within the series, but in all cases, the non-negligible transversal g-tensor components exist, explaining the lack of zero-dc-field magnetic relaxation. More importantly, the ab initio approach gave insight into the energy scheme both for the ground multiplet as well as for the emissive level. This leads to the successful reproduction of the emission spectra, including not only the energies of emission bands, which is typically explored,21,23,24,28,30,42 but also the bands’ intensities represented by the cumulative oscillator strengths proportional to transition moments computed using a velocity gauge. This is extremely helpful in the clear interpretation of emission patterns, in particular, in finding the 0−0 emission line and detecting the hot bands. As a result, we performed reliable magneto-luminescent correlations including the determination of energy gaps between two lowest-lying Kramers doublets. They, confronted with ac magnetic data, indicate that the SMM behavior in the whole series is dominated by the Raman relaxation. We observed the broad variation of the efficiency of Raman relaxation which is dependent on the (thio)cyanido counterion. This modulation partially follows the magnetic axially of the YbIII ground doublet which is related to subtle structural differences between lanthanide complexes induced by changing the crystal lattice by metal-based counterions. However, the main correlation exists between the T-dependence of a Raman process and the phonon modes scheme of the lattice. We found the increasing trend of the power n in the series with [Cd(CN)2]3−, [Ir(CN)2]3−, and [Au(SCN)2]− ions. This trend was assigned to the decreasing energies of the critical phonon modes, further correlated with the CN− to SCN− change, lighter-to-heavier metal substitution, and the formation of metallophilic aggregates. The C_Raman parameter reveals almost the opposite trend which suggests that the accessibility of key phonon modes can be governed by the opposite factors to those operating for their energies. Therefore, we show the great potential in using the ab initio calculations for the elucidation of magneto-luminescent properties of YbIII complexes with the particular attention given to the challenging task of the calculation of emission spectra. Our approach is a convenient tool for the discussion of SMM effects in luminescent complexes but can be extended for the investigation of advanced luminescent phenomena such as optical thermometry utilizing the T-dependence of hot emission bands.24,28 This research direction as well as the expansion of the methodology to other lanthanide ions with more complex energy level diagrams are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c02942.

Experimental section; basic characterization and detailed structural studies; complete dc and ac magnetic characteristics; details and expanded results of the ab initio calculations; additional luminescent characteristics (PDF)

X-ray data (CIF)

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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