

Thermometry

Toward Magneto-Optical Cryogenic Thermometers with High Sensitivity: A Magnetic Circular Dichroism Based Thermometric Approach

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Abstract: Remote temperature probing at the cryogenic range is of utmost importance for the advancement of future quantum technologies. Despite the notable achievements in luminescent thermometers, accurately measuring temperatures below 10 K remains a challenging endeavor. In this study, we propose a novel magneto-optical thermometric approach based on the magnetic-circular dichroism (MCD) technique, which offers unprecedented capabilities for meticulous temperature variation analysis at cryogenic temperatures. The inherent temperature sensitivity of the MCD C -term, in conjunction with both positive and negative signals, enables highly sensitive magneto-optical temperature probing. Additionally, a groundbreaking relative thermal sensitivity value of 95.3 % K⁻¹ at 2.54 K can be achieved using a mononuclear lanthanide complex, [Ho(acac)₃(phen)], in the presence of a 0.25 T applied magnetic field and using a combination of multiparametric thermal read-out with multiple regression. These results unequivocally demonstrate the viability and effectiveness of our methodology for cryogenic temperature sensing.

Temperature is a vital parameter that requires close monitoring across various fields.^[1–3] Its criticality extends to numerous processes, including biological procedures, chemical reactions, and the successful implementation of a wide range of technologies. The significance of monitoring temperature becomes increasingly crucial in cutting-edge technologies such as superconductors, spintronics, quantum information processing, and quantum magneto-optical memories. In these domains, temperature assumes a critical role in information retention, particularly at ultra-low temperatures below 10 K.^[4–6] This importance is exceptionally

accentuated in the current era where quantum computers are becoming a reality, facilitated by the use of dilution refrigerators that can achieve temperatures approaching absolute zero. Therefore, accurate temperature monitoring is critical to maintain the property of a material (e.g., quantum state, superconducting state), optimize performance, and prevent any deviation that may lead to the loss of its highly sought-after property.^[4–6]

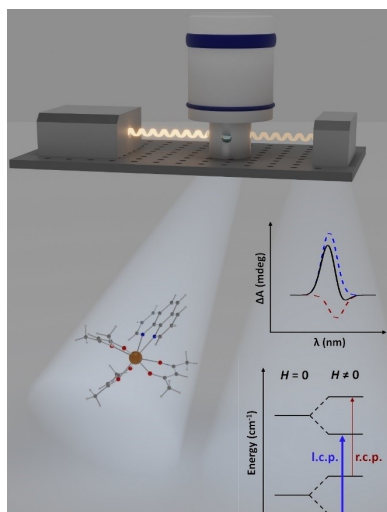
In recent years, luminescence thermometry has been successfully demonstrated as a highly sensitive remote technique to probe temperature.^[1–3] Several concepts have been employed to target different probing strategies, such as band-shift,^[7–9] lifetime,^[10–12] energy-transfer-based ratiometric thermometry,^[13–25] and single-band,^[26–38] each approach having its own advantages/disadvantages. In the presented context, bifunctional compounds acting as Single-Molecule Magnet (SMM) and Stark-sublevel ratiometric luminescent thermometers have been demonstrated as potential candidates for magnetic memory storage devices with real-time temperature sensing.^[26–38]

Nevertheless, despite the demonstrated success of different approaches, implementing luminescence thermometry at very low temperatures (<10 K) remains a difficult task. Most temperature-dependent processes that favor temperature-related spectral changes, such as energy-transfer (ET), hot bands population, and quenching pathways, are inefficient at such low temperatures.^[20–38] Another potential limitation in luminescence thermometry with molecular complexes is the choice of ligands with adequate energy-level position to promote an effective ET to the metal center and act as an efficient luminescent material. Therefore, not all complexes can be used as luminescent thermometers, and even in the context of high-performing SMMs, systems containing large and strongly luminescent counterions and/or radical-based systems are not suitable for luminescence thermometry.

To overcome these issues and open new avenues for temperature probing at low temperatures, we introduce a new concept based on magnetic circular dichroism (MCD) magneto-optical thermometry. MCD spectroscopy is a technique that relies on the differential absorption (ΔA) of left and right circularly polarized light (lcp and rcp, respectively) components induced by a magnetic field oriented parallel (positive H) or antiparallel (negative H) to the direction of the light propagation.^[39–55] The ΔA signal results from the Zeeman effect (magnetic perturbation) of the states involved in the optical transitions (Scheme 1).

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Scheme 1. Schematic representation of the experimental setup. The sample, $[\text{Ln}(\text{acac})_3(\text{phen})]$, is located inside of the magneto-optical cryostat (crystalline structure of the complexes represented in the scheme). The light from the spectrometer reaches the sample and is detected by the detectors. The lcp and rcp (left and right circularly polarized light) components were detected and the differential absorption signal generated via the expression $\Delta A = \text{lcp} - \text{rcp}$.

As an absorption-based technique, the lanthanide sharp bands are expected to be observed; also, due to the stronger spin-orbit coupling, another advantage is that f - f transitions will be much stronger than ligand bands, allowing the temperature probing with molecular compounds where luminescent processes are not observed. Additionally, dual signalled bands (i.e., positive and negative signals) permit the implementation of simple thermometric strategies based on the band difference, which does not require extensive post-treatment of the data for obtaining the temperature. Although it is not the focus of this work to describe theoretical aspects of the MCD spectroscopy in-depth, a concise discussion is presented in the ESI. For a more comprehensive exploration of the theoretical aspects, interested readers are encouraged to refer to the listed reference.^[39–41]

To target the first demonstration of the potential of MCD-based magneto-optical thermometers, we opt for simplicity in terms of synthetic procedures. Herein we studied three isostructural mononuclear complexes, $[\text{Ln}(\text{acac})_3(\text{phen})]$, where Ln stands for Nd^{III} , Dy^{III} , and Ho^{III} (Scheme 1, Figures S2–S4). Solid-state MCD spectra were obtained at 1.55 K under various applied magnetic fields (0.25 T to 7 T; Figure 1). Characteristic bands due to f - f absorptions are noticed for all three compounds. These MCD bands arise from the specific ground states (Nd^{III} : $^4\text{I}_{9/2}$; Dy^{III} : $^6\text{H}_{15/2}$; Ho^{III} : $^5\text{I}_8$) to different excited f states. Also, mirror-image is observed when applying a magnetic field antiparallel to the light direction (negative H). Aiming to understand each compound contribution, we selected the most intense bands for the MCD analysis (Figure S5–S7 and Table S1). Investigation of the field dependence of the selected MCD bands reveals that each band presents a

unique profile (Figure S8). These differences are related to distinct polarizations of different electronic transitions.^[56–58] For Nd^{III} and Dy^{III} complexes (Figure S8), some bands exhibit complete saturation at distinct fields. In contrast, other transitions display a decrease in the signal after reaching saturation. It should be noted that this decrease occurs for highly mixed transitions in which the combination of levels and sublevels in close proximity can result in crossing on the Zeeman sublevels at high fields (see Figure S9 for a hypothetical example). As a result, the differential absorption (ΔA) of lcp and rcp components are perturbed, changing the direction of ΔA . For the Ho^{III} complex (Figure S8), the selected transitions do not reach saturation.

As discussed in the theoretical aspects section (see ESI), the temperature-dependent C -term dominates the MCD spectra of lanthanide compounds. The temperature effect on the C -term for an lcp-dominated transition band is shown in Scheme 2. Increasing the temperature increases the upper Zeeman sublevel population, resulting in a global decrease of the MCD signal. Consequently, lcp and rcp-dominated transitions will behave similarly but decrease in opposite directions. Thus, by taking advantage of the difference between a lcp and a rcp dominated transition band, we can implement a highly sensitive thermometric parameter (Δ) for probing the temperature. It should be noted that by taking the transition band difference, we are implementing a simple yet elegant thermometric parameter that does not require extensive post-treatment of the data or complicated functions for Δ determination. Based on this temperature effect on the MCD C -term, we analyzed the variable-temperature (VT) MCD spectra for the synthesized complexes with an applied magnetic field of 0.25 T.

VT-MCD spectra for Nd^{III} and Dy^{III} compounds are shown in Figure 2a and 2b, respectively. As detailed in Table S1, we selected two bands for Nd^{III} and three for Dy^{III} . As previously mentioned, lcp (positive signal) and rcp (negative signal) dominated transition bands dramatically decrease when temperature increases. By taking the difference between the integrated area of a lcp and a rcp dominated transition band, we obtained the temperature dependence of Δ (Figure 2c for Nd^{III} , Figure 2d for Dy^{III}), i.e., $\Delta = I_{\text{lcp}} - I_{\text{rcp}}$. A sigmoidal logistic function (eq. 1) was used to fit the Δ parameters. It should be noted that this equation has no physical meaning, but it is only used to provide a fit.

$$\Delta = \frac{A_1 - A_2}{1 + \left(\frac{x}{x_0}\right)^p} - A_2 \quad (1)$$

To evaluate the thermometric performance of these magneto-optical thermometers, we calculated the relative sensitivity (S_r) by applying equation 2^[1–3] on the fitted functions:

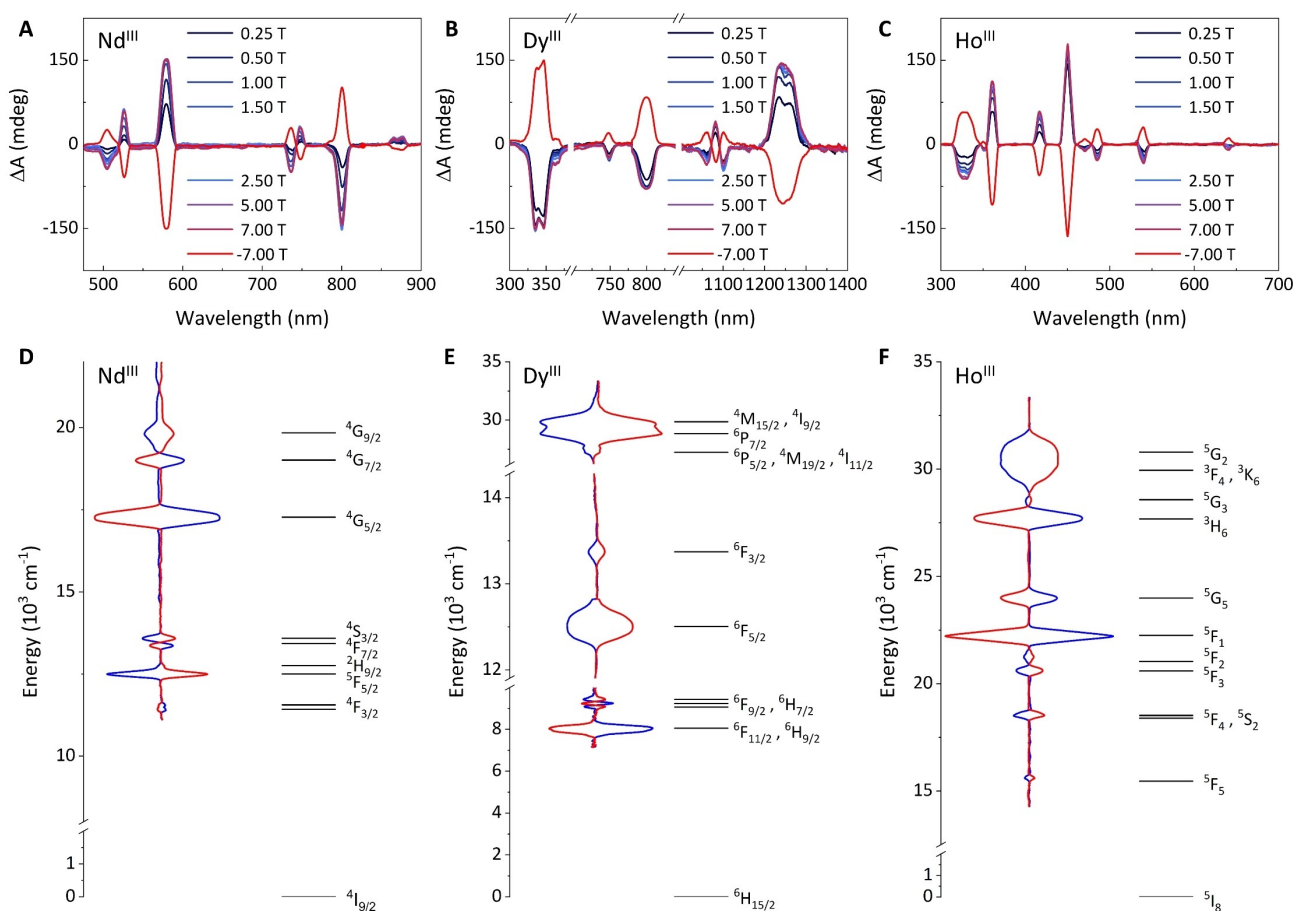


Figure 1. (A–C) MCD spectra obtained at 1.55 K under different applied magnetic field for (A) Nd^{III} , (B) Dy^{III} , and (C) Ho^{III} complexes. (D–F) Partial energy level diagram (D) Nd^{III} , (E) Dy^{III} , and (F) Ho^{III} complexes. The spectra depicted in the center is the +7 (blue line) and –7 T (red line) spectra from (A–C) converted to wavenumber units.

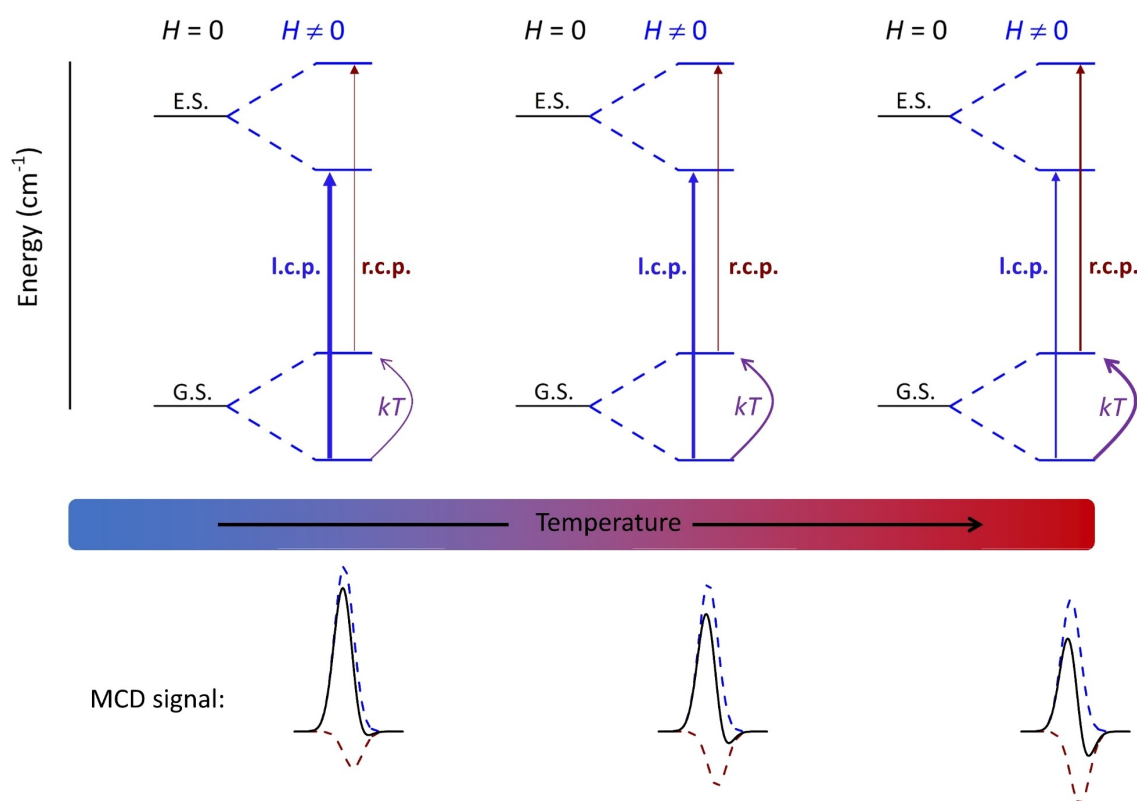
$$S_r(\%) = \left[\frac{\left(\frac{\partial \Delta}{\partial T} \right)}{\Delta} \right] \cdot 100 \quad (2)$$

The first term is the function's derivative, and the second term is the fitted Δ values. The maximum S_r values (S_m) obtained and the temperature of the maximum S_r value (T_m) for Nd^{III} and Dy^{III} complexes, respectively, are summarized in Tables S2 and S3. For the Nd^{III} complex, an unprecedented S_m value of $44.7\% \text{ K}^{-1}$ was observed at 2.38 K under a 0.25 T applied magnetic field, a value much higher than observed for any other optical thermometer operating at cryogenic ranges, thus representing the most sensitive thermometric implementation observed at cryogenic temperatures. The small energy gap between the Zeeman sublevels explains this high sensitivity value. Although slightly less sensitive, the Dy^{III} complex also presents remarkable values for S_m , with values of 37.7 (at 1.55 K) and $35.7\% \text{ K}^{-1}$ (at 1.76 K), depending on the band pair chosen for probing the temperature.

The present results indicate that MCD-based magneto-optical thermometers have considerable potential to be implemented as cryogenic thermometers. The few examples of lanthanide optical thermometers operating at cryogenic

temperatures rely on lanthanide-lanthanide energy transfer (for example, Tb^{III} - Eu^{III}) or Stark-sublevel (M_J) population distribution approaches.^[20–38] Although both methods are successfully demonstrated, there is only a small margin of improvement for the sensitivity values. For the lanthanide-lanthanide energy-transfer system, several reports demonstrate how the sensitivity is tuned via metal distances and composition, suggesting that there is no margin to enhance the sensitivities at this temperature range substantially. For M_J -based luminescent thermometers, the relatively significant energetic difference between the lower and upper sublevels (tens to hundreds of wavenumbers) limits the sensitivities values yet has as an advantage the increase of the operational range. MCD-based magneto-optical thermometry, on the other hand, has the benefit of dealing with much smaller energy differences (see theoretical aspects section in the ESI) due to the small energy gap between Zeeman sublevels, facilitating the thermal population of the upper levels and consequently boosting up the sensitivities values.

Besides the outstanding results obtained with the Nd^{III} and Dy^{III} complexes, we also studied the magneto-optical thermometric performance of the Ho^{III} complex (Figure 3). For this complex, the presence of several bands with



Scheme 2. Temperature effect on MCD transitions. Increasing the temperature results in a higher population of the upper Zeeman sublevel by a factor of kT . In this example we can see the reduction of the lcp and enhancement of the rcp components, resulting in a global decrease of the MCD band intensity. In this scheme the enhancement of the rcp component and consequently, the band asymmetry is exaggerated in order to facilitate the understanding of the effect.

considerable intensities (three positive and three negative) possibilities the implementation of nine different thermometric parameters (Figure 3b) thus revealing another advantage of MCD based magneto-optical thermometers. The possibility of implementing other thermometric parameters in various spectral regions highlights this approach versatility. For the Ho^{III} complex, S_m values as high as $42.3\% \text{ K}^{-1}$ at 2.50 K can be obtained under a 0.25 T applied magnetic field (Table S4).

For all the previous results, we used an applied magnetic field of 0.25 T. Based on the theoretical aspects of MCD spectroscopy; it is easy to predict that increasing the magnetic field strength decreases the temperature sensitivity. Increasing the magnetic field results in the broader opening of the Zeeman sublevel gaps, enhancing the required energy to populate the upper Zeeman sublevel (Figure S10). Therefore, the sensitivities decrease, but the operational ranges are enhanced. To demonstrate how the performance is affected by different magnitude magnetic fields, we obtained the VT-MCD spectra for all three complexes under 0.5, 1.0, 1.5, and 5.0 T applied magnetic fields (Figure S11–S22, Tables S2–S4). It is evident from the presented data that the operational range is significantly stretched towards higher temperatures with the cost of a dramatic reduction of S_r .

Another important parameter for optical thermometers is the temperature uncertainty (δT). In this present work, as a proof-of-concept, we are demonstrating how to obtain the δT for the Ho^{III} complex with the minimum (0.25 T) and maximum (5.00 T) applied magnetic field (Figure S23, see ESI for the methodology). Under a 0.25 T magnetic field, in agreement with the highest S_r values, δT values close to 0.02 K are obtained. Nevertheless, upon the application of a 5.00 T magnetic field, discernible δT values well beyond 1 K come into play. This observation indicates the unsuitability of the presented approach for precise temperature sensing at higher magnetic fields. With that said, the possibility of implementing nine different thermometric parameters for the Ho^{III} complex allows us to overcome the low sensitivity and high uncertainty under higher applied magnetic fields while enhancing the accuracy of the temperature read-out.^[59] As such, we can adopt the multiparametric thermal read-out method in conjunction with a multiple regression approach, a novel technique introduced in recent work by Carlos and co-workers.^[60] In this approach, a multiple (linear or non-linear) regression can be applied to the different thermometric parameters, providing a self-calibrated read-out, and increasing the precision of temperature measurement. In this approach, the nine different thermometric parameters were used simultaneously to calculate S_r using equation 3:^[60]

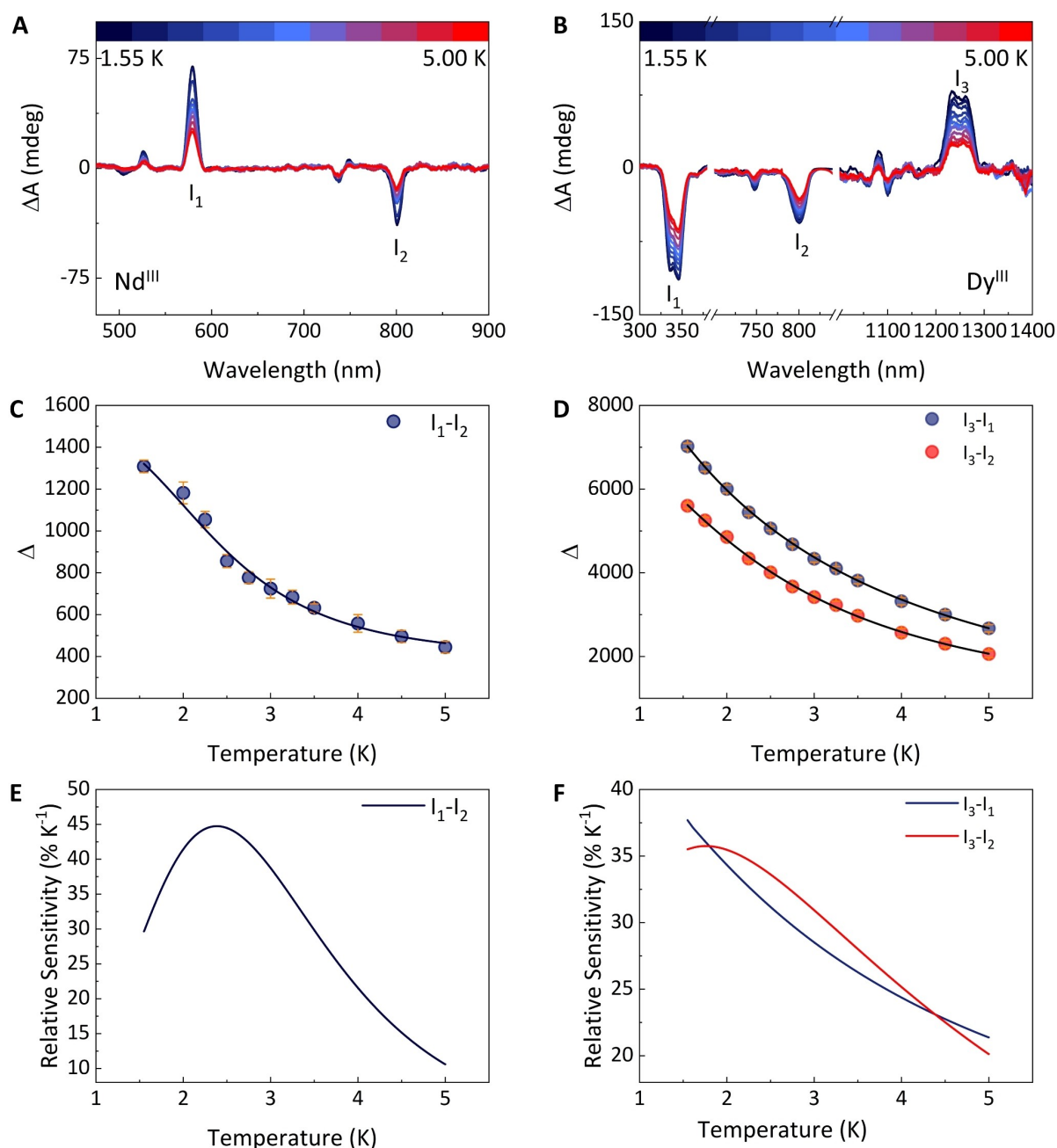


Figure 2. Variable-temperature MCD spectra for Nd^{III} and Dy^{III} complexes under a 0.25 T applied magnetic field. VT MCD spectra for (a) Nd^{III} and (b) Dy^{III} complexes. Temperature dependence of the Δ parameter for (c) Nd^{III} and (d) Dy^{III} complexes. Relative sensitivities calculated for (e) Nd^{III} and (f) Dy^{III} complexes.

$$S_r(\%) = \sqrt{\sum_{i=1}^n \left[\frac{\left(\frac{\partial \Delta}{\partial T} \right)}{\Delta} \right]^2} \cdot 100 \quad (3)$$

Similarly, we can also calculate the temperature uncertainty for this approach.^[60]

$$\delta T = \frac{1}{S_r} \sqrt{\sum_{i=1}^n \left(\frac{\delta I}{I} \right)^2} \quad (4)$$

As can be observed in Figures 4a and c, the combination of the nine thermometric approaches in the Ho^{III} complex via a multiple regression enhances the maximum S_r when applying a 0.25 T magnetic field to an unprecedentedly value of $95.3 \% \text{ K}^{-1}$, and reduces δT to approximately 0.008 K. Additionally, open up the possibility of magneto-optical thermal sensing with higher magnetic fields, increasing the

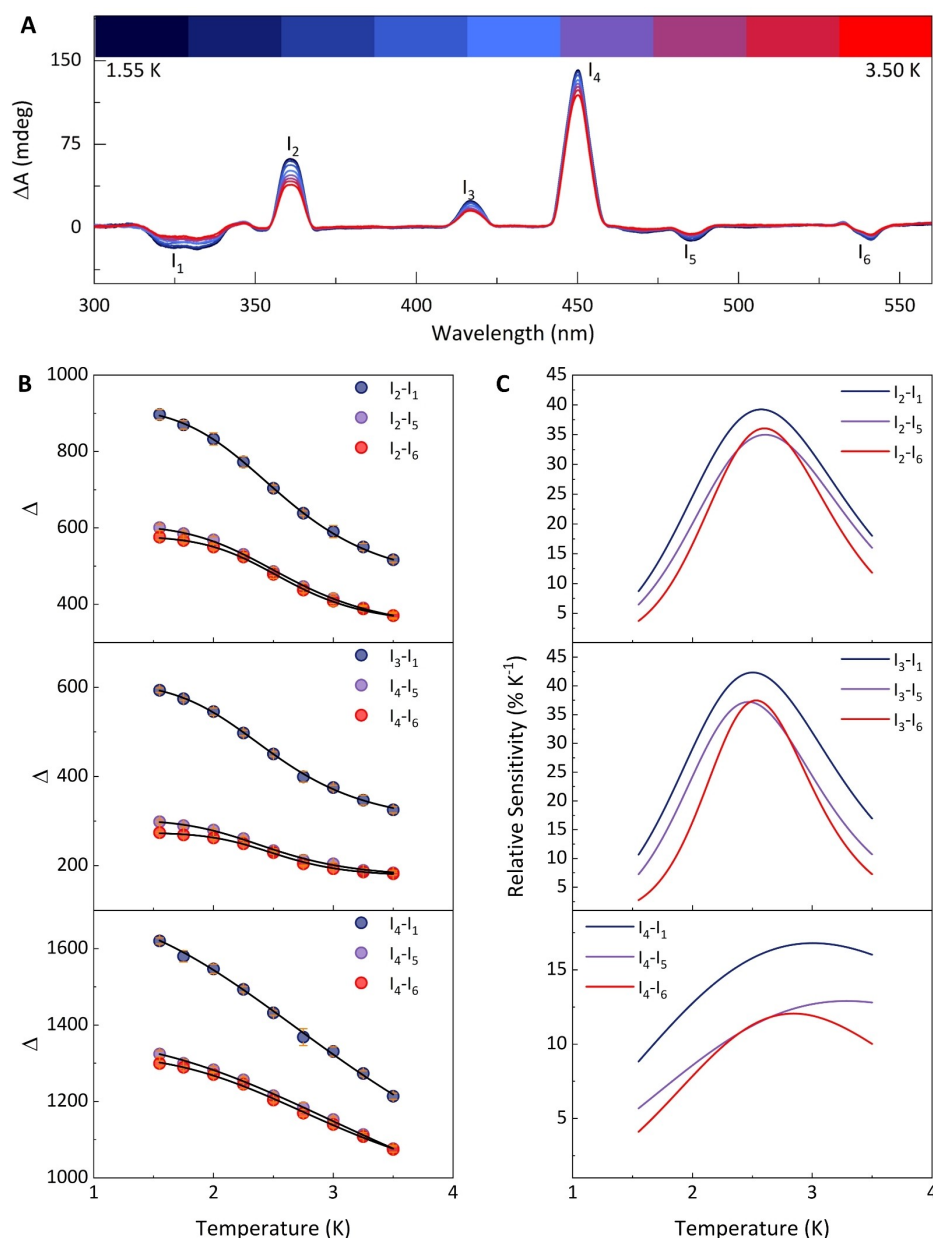


Figure 3. Variable-temperature MCD spectra for Ho^{III} complex under a 0.25 T applied magnetic field. (a) VT MCD spectra for Ho^{III} complex. (b) Temperature dependence of the different Δ parameters. (c) Relative sensitivities calculated for the different Δ parameters.

maximum S_r under a 5.00 T magnetic field to $3.6\% \text{ K}^{-1}$ and reducing δT to approximately 0.6 K, a remarkable performance enhancement when compared with the single parameter thermal sensing.

In summary, herein, we demonstrate the implementation of magneto-optical thermometers via MCD spectroscopy for the first time. Despite being the first example, the obtained thermal relative sensitivities are among the highest ever observed for a lanthanide optical thermometer, suggesting that this technique possesses tremendous potential for magneto-optical temperature probing. For example, the Nd^{III} complex can reach a maximum relative sensitivity of $44.7\% \text{ K}^{-1}$ at 2.38 K under an applied magnetic field of 0.25 T, an unprecedented value at the cryogenic temperature

range. The high sensitivities arise from the nature of the MCD technique. The temperature-dependent C -term, in conjunction with positive and negative signals decreasing in different directions, results in an elegant and extremely sensitive approach to probe the temperature. Additionally, for complexes containing several transition bands, as for the Ho^{III} complex, it is possible to enhance the magneto-optical thermal sensing via a combination of multiparametric thermal read-out and multiple regression, positively impacting the accuracy of the temperature read-out. Applying this methodology yielded an unprecedented maximum relative sensitivity of $95.3\% \text{ K}^{-1}$ at 2.54 K under an applied magnetic field of 0.25 T.

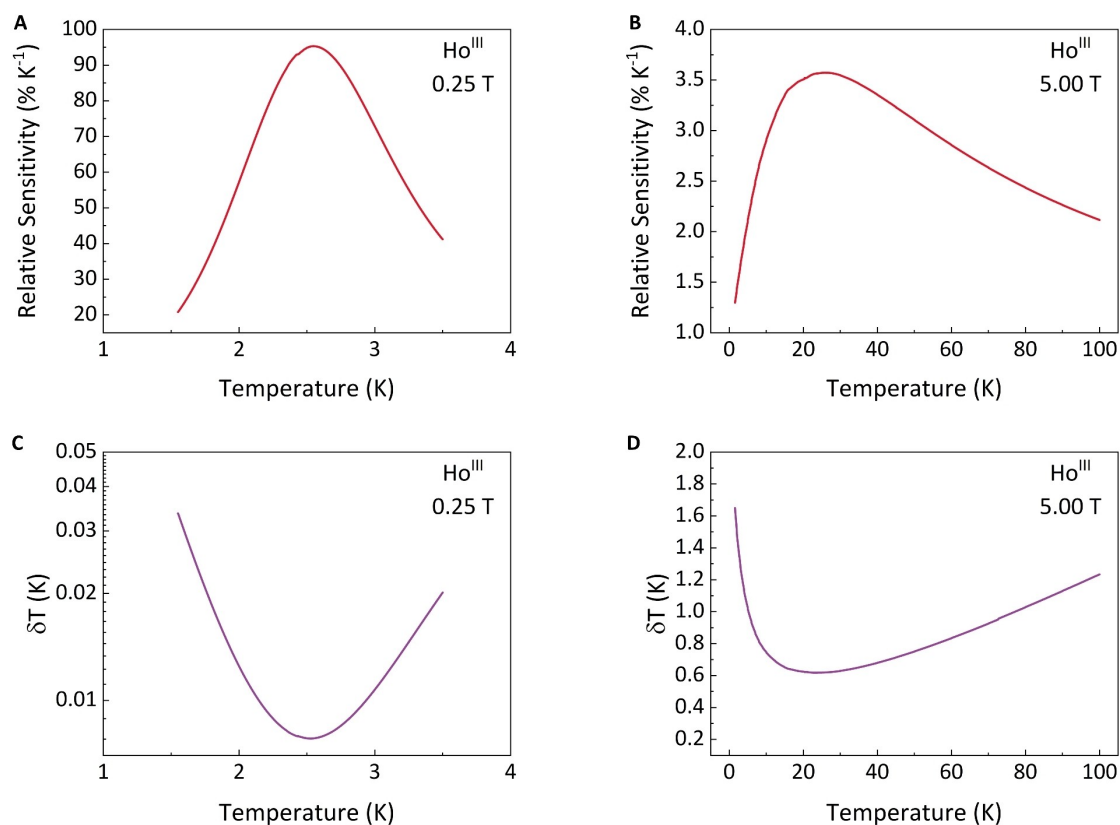


Figure 4. Relative sensitivities calculated for the Ho^{III} complex obtained via the combination of multiparametric thermal sensing and multiple regression under an applied magnetic field of (a) 0.25 T and (b) 5.00 T. Associated temperature uncertainties obtained under an applied magnetic field of (a) 0.25 T and (b) 5.00 T.

We foresee that MCD-based thermometry will enormously impact the field of bifunctional SMMs, opening the possibility to implement remote real-time probing of temperature for high-performance SMMs in which the luminescence is not operant. Such achievement can have an immense impact when aiming for multifunctional cryogenic materials for fields such as spintronics, quantum information processing, and magneto-optical memories.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Lanthanides • Magnetic Circular Dichroism • Magneto-Optical • Thermometry

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