

Identification of Lanthanide(III) Luminophores in Magnetic Circularly Polarized Luminescence Using Raman Optical Activity Instrumentation

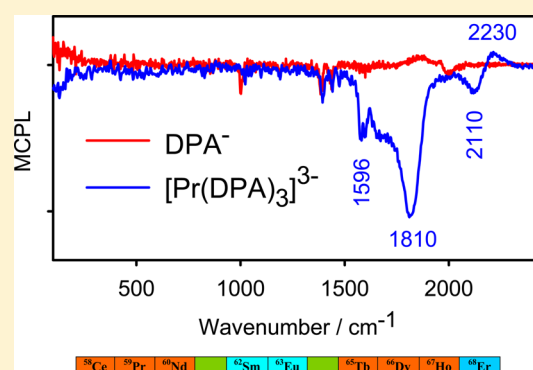
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S Supporting Information

ABSTRACT: Luminescence of lanthanide(III) ions sensitively reflects atomic environment. However, the signal may be weak and covered by Raman scattering. In the present study magnetic circularly polarized luminescence (MCPL) is explored as a more sensitive tool to recognize the lanthanide signal and assign underlying electronic transitions. MCPL spectra of the $\text{Na}_3[\text{Ln}(\text{DPA})_3]$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Ho}, \text{and Er}$) complexes were recorded on a Raman optical activity (ROA) instrument. The ROA spectrometer equipped with the 532 nm laser excitation sensitively detects differences in scattering of left- and right-circularly polarized light caused by the magnetic field. Weak bands sometimes invisible in unpolarized measurement could be detected as MCPL. Observed transitions were assigned with the aid of the ligand-field theory. MCPL also reflects the environment: chloride and nitrate salts (LnCl_3 and $\text{Ln}(\text{NO}_3)_3$) provide a different signal than the complex; for Nd^{III} the signal responds to distribution of chloride and nitrate ions around the metal. The MCPL technique thus appears useful for identification and assignment of lanthanide transitions and increases the potential of fluorescent probes for applications in analytical chemistry and imaging.



Lanthanide luminescence very much depends on the molecular environment, and as such can be used to study their properties, detect particular molecules or to label them for imaging of living cells. Advanced applications involve biomedical diagnosis and cancer therapy.^{1–6} Even more structure-sensitive is the circularly polarized luminescence (CPL), entirely caused by asymmetry of lanthanide ligands or interacting groups from the neighborhood.^{7–10}

Previously, we used the Raman optical activity (ROA) spectrometer to detect lanthanide CPL and showed that this technique is usable both for large dissymmetry factors (ratios of CPL to total luminescence)¹¹ as well as small signals caused by interaction of achiral lanthanide probes with sugars and amino acids.^{12,13} The strong laser radiation makes observable spectral features that may not be noticeable on more conventional CPL instruments.

However, lanthanide CPL is limited to chiral systems only. In the present study we use ROA spectrometer^{14–16} equipped with a permanent magnet and systematically explore a series of achiral lanthanide complexes and their salts. Indeed, it can be shown that while the total luminescence (TL) is often hidden in the Raman background, the magnetic circularly polarized luminescence (MCPL) is better detectable and very characteristic for a particular metal. As MCPL bands can be both positive and negative, they also provide a larger variety of spectral

features that can serve as structural markers of lanthanide environment.

We find this systematic “mapping” of lanthanide fluorescent probes also important because of the inability of contemporary quantum chemistry to treat lanthanides efficiently, that is, in this context, to provide a reliable link between the structure and CPL spectrum. The difficulty lies in the relativistic effects indispensable for lanthanide description and amazing complexity of (often high-spin) lanthanide electronic states as discussed in many previous works.^{17–21} In fact, lanthanide (and actinide) computational chemistry developed into self-standing field.²² Fortunately, many lanthanide properties can also be described by the computationally less demanding crystal field theory (CFT) partially based on empirical parameters.^{23–25} As shown below, CFT allowed us to assign the MCPL spectral bands and model bands intensities in a qualitative way.

METHODS

Primarily, complexes of lanthanide(III) with dipicolinate (DPA) are explored, because water-soluble DPA and similar ligands are convenient tools to convey the metal labels to the

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destination in a biologically relevant environments.²⁶ In addition, some chloride or nitrate salts are investigated.

Preparation of the Complex. $\text{Na}_3[\text{Ln}(\text{DPA})_3]$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Ho}, \text{and Er}$; DPA = dipicolinate = 2,6-pyridinedicarboxylate) complexes (Figure 1) were obtained

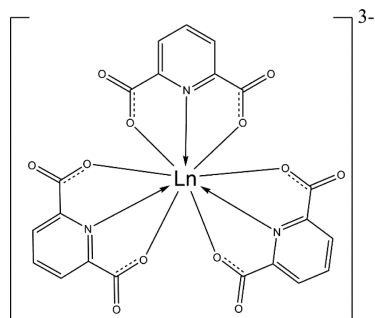


Figure 1. $[\text{Ln}(\text{DPA})_3]^{3-}$ complex studied, $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Ho}, \text{and Er}$; DPA = dipicolinate = 2,6-pyridinedicarboxylate.

from a mixture of lanthanide(III) chloride ($\text{Ce}, \text{Eu}, \text{Ho}, \text{Er}$) or nitrate ($\text{Pr}, \text{Nd}, \text{Sm}, \text{Tb}$) and pyridine-2,6-dicarboxylic acid solutions in a 1:3 molar ratio. Before that, commercial (Sigma-Aldrich) lanthanide salts were purified by crystallization. The pH value was adjusted to 7.0 by 1 M sodium carbonate solution.

MCPL Measurement. A scattered circularly polarized (SCP) ROA instrument¹⁶ (Biotools) equipped with magnetic cell based on four neodymium magnets²⁷ providing magnetic field of about 1.5 T was used for MCPL measurement. The laser power at the sample was 100–1000 mW. Spectra of 80 mg/mL of $\text{Na}_3[\text{Ln}(\text{DPA})_3]$ complexes and 150 mg/mL of $\text{LnCl}_3/\text{Ln}(\text{NO}_3)_3$, all in aqueous solutions, were measured at room temperature (20 °C). Both chloride and nitrate salts of neodymium were measured to estimate the influence of the Ln^{3+} environment on the spectra. Collection times varied from 1 to 20 h, depending on the intensity of the signal. TL and MCPL spectra were simultaneously recorded; TL may also be mixed with vibrational Raman bands, and MCPL may contain magnetic^{28,29} or natural vibrational ROA.^{11,13} Note also that sometimes luminescence is referred to as fluorescence; in the present study we consider these two terms equivalent. Because of high MCPL intensities, the ROA components were invisible, but the complexes exhibited different ratio of lanthanide TL and Raman intensities coming mostly from the DPA ion. The range of the spectrometer is limited to 535–610 nm and the spectra are reported in the wavenumber scale (shift from the 532 nm excitation, i.e., 100–2400 cm^{-1}) as is usual in Raman spectroscopy. Water baseline was subtracted from TL/Raman spectra. To eliminate artifacts, MCPL spectra are presented as averaged over two magnet orientations, $S_{\text{ave}} = (S_{\text{north}} - S_{\text{south}})/2$, that is, as idealized “north” orientation results. Raw spectra can be found in [Supporting Information](#).

Control measurements were performed at a similar home-made ROA instrument (located at the Palacký University), capable of measurement in multiple (SCP, and incident circular polarization, ICP) modulation schemes.³⁰

MCD Spectra. MCD and absorption spectra of $\text{Nd}(\text{NO}_3)_3$ aqueous solution (30 mg/mL) were measured at room temperature on a Jasco J-815 spectrometer equipped with a permanent magnet providing field of 1.5 T. The sample was contained in a rectangular quartz cell of 0.1 cm optical path

length. The spectra were recorded for both magnet orientations in the 180–850 nm range, using 0.5 nm resolution, 4 s response time, and a scanning speed of 20 nm/min. Three accumulations were averaged. Solvent spectra acquired at identical conditions were subtracted from those of the sample.

Theoretical Calculations. To get a good estimate of the structures, complex geometries were optimized by energy minimization using the Gaussian09³¹ program, the B3LYP³² functional, MWB28³³ pseudopotential and basis set for Ln, and the 6-31G(d,p) basis set for the other atoms. The conductor-like polarizable continuum solvent model (COSMO)³⁴ was applied. The optimized geometries were used within the crystal theory^{23,25} to calculate and assign observed transitions. The Lanthanide³⁵ program was adapted to provide also spectral intensities via a perturbational approach.^{36–38}

To briefly review the theory, within CFT, the free field ion Hamiltonian is given by

$$H = \sum_{k=2,4,6} F^k f_k + \xi_{4f} A_{\text{SO}} + \alpha L(L+1) + \beta G(G_2) + \gamma G(G_7) + \sum_{i=2,3,4,6,7,8} T^i t_i + \sum_{j=0,2,4} M^j m_j + \sum_{k=2,4,6} P^k p_k \quad (1)$$

where F^j are electron repulsion parameters, f_k is operator for angular part of the electrostatic interaction, ξ_{4f} is spin–orbit coupling constant, A_{SO} is angular part of the spin–orbit interaction, α , β , and γ are Trees configuration interaction parameters, L is the orbital quantum number, $G(G_2)$ and $G(G_7)$ are Casimir operators for the groups G_2 and G_7 , T^j is the three body configuration interaction parameters, t_i is the three particle operators, m_j and p_k are operators of magnetic correction, and M^j and P^j are magnetic interaction parameters. The parameters were taken from ref 25. The Lanthanide program has the advantage of working in basis set of products of one-electron functions,

$$\chi_i = \{ |l m_{i1}\rangle |s z_{i1}\rangle |l m_{i2}\rangle |s z_{i2}\rangle \dots |l m_{in}\rangle |s z_{in}\rangle \} \quad (2)$$

where the brackets $\{\}$ denote antisymmetrized product, l is angular momentum ($l = 3$ for f -electrons), m_i is its projection, $s = 1/2$ is electronic spin, and z_i is its projection. This circumvents the relatively complicated algebra associated with the coupled representation based on total angular momenta.³⁹

The wave function is then obtained as $\Psi_A = \sum_i C_i^A \chi_i$, where the expansion coefficients C_i^A can be obtained as eigenvectors of the Hamiltonian matrix.

To obtain spectral intensities, the DPA ligand electrostatic potential V is added to the free-ion Hamiltonian (1) and treated as a perturbation. For example, the electric dipole moment matrix element for a transition between states A and B ($\alpha = x, y, \text{ or } z$) then becomes^{36–38}

$$\langle A | \mu_\alpha | B \rangle = \sum_{i,j} C_i^{A*} C_j^B \langle \chi_i | \mu_\alpha | \chi_j \rangle_{\text{eff}} \quad (3)$$

where the effective dipole moments

$$\langle \chi_i | \mu | \chi_j \rangle_{\text{eff}} = K \left(\sum_u \langle \chi_i | \mu | u \rangle \langle u | V | \chi_j \rangle + \sum_u \langle \chi_i | V^* | u \rangle \langle u | \mu | \chi_j \rangle \right)$$

K is a constant, and u denotes configurations where one f -electron is emitted to d -shell. $f \rightarrow g$ configurations were tried in test computations as well; these, however, did not bring any quality improvement and were not considered. MCPL intensities were calculated using a sum over state formula developed previously for magnetic circular dichroism.⁴⁰ The

potential V was calculated from nuclear charges and electron density obtained by the Gaussian calculation.

RESULTS AND DISCUSSION

Weak Luminophores' Spectra. From the practical point of view, we can divide the investigated metals into weakly and strongly emitting luminophores. As an example of the first group involving Ce, Pr, Nd, Tb, Dy and Ho, TL/Raman, and ROA/MCPL spectra of $\text{Na}_3[\text{Pr}(\text{DPA})_3]$ solution are plotted in Figure 2. The Raman trace is almost exclusively caused by the

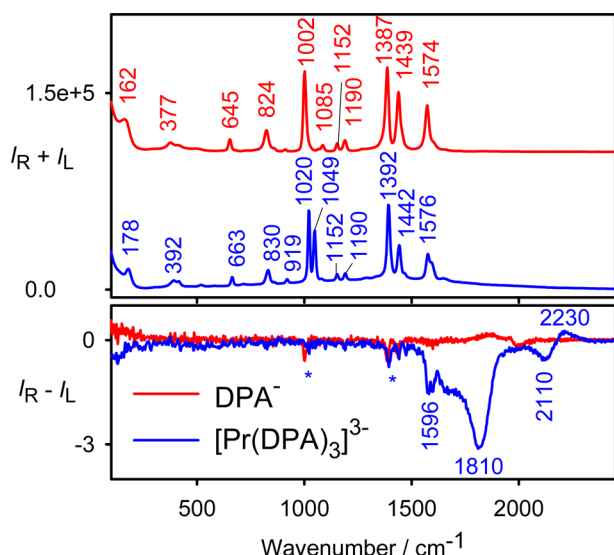


Figure 2. Total ($I_R + I_L$) and magnetic circularly polarized ($I_R - I_L$) luminescence spectra of Na_2DPA (red) and $\text{Na}_3[\text{Pr}(\text{DPA})_3]$ (blue) solutions. Asterisks (*) denote noise/artifact signal. The intensity scale was normalized to Na_2DPA Raman intensities.

DPA ligand, as can be seen on comparison with Raman spectrum of the Na_2DPA solution also plotted in Figure 2. In $\text{Na}_3[\text{Pr}(\text{DPA})_3]$, compared to Na_2DPA , most Raman bands undergo a minor shift only. The Raman band at 1049 cm^{-1} in the $\text{Na}_3[\text{Pr}(\text{DPA})_3]$ complex is from nitrate ion (Figure S4a). One can also observe an elevated baseline/background signal for the $\text{Na}_3[\text{Pr}(\text{DPA})_3]$ complex, most probably given by fluorescence of remaining impurities in the sample.

The ROA/MCPL spectra (lower panel in Figure 2) are nearly zero for Na_2DPA (except for a noise), as can be expected, because vibrational magnetic Raman optical activity is normally observable for molecules exhibiting resonance effects only.^{27–29,41} Thus, for $\text{Na}_3[\text{Pr}(\text{DPA})_3]$ the spectrum is dominated by MCPL of the Pr^{3+} ion. On the basis of the CFT simulations (Figure S2) and available data in the literature (Table 1) the bands can be assigned to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} .⁴² Seemingly, the circular intensity difference, $\text{CID} = (I_R - I_L)/(I_R + I_L)$, usual in the ROA spectroscopy,⁴¹ or the dissymmetry factor, $g = 2(I_L - I_R)/(I_R + I_L)$ used more frequently for CPL measurements⁷ are quite low, $\text{CID} \sim 2 \times 10^{-5}$, if one compares extreme values of TL and MCPL intensities. However, TL praseodymium bands are hidden in the background signal and their intensity cannot be reliably determined. As shown below, typical CID for lanthanide MCPL bands may even approach 10^{-2} . With $I_R - I_L \sim 3$, the expected TL intensity for Pr^{3+} would be $\sim 3/10^{-2} = 300$, that is totally invisible in the $I_R + I_L$ scale of Figure 2 extending to $\sim 2 \times 10^5$.

MCPL spectra of all the Ce, Pr, Nd, Tb, Dy, and Ho representatives of the weak luminophores are plotted in Figure 3. Cerium, not possessing the 4f electrons, provides weakest signal partially hidden in the noise. Its MCPL bands centered at 300 , 360 , and 470 cm^{-1} come from the Laporte allowed decay of the lowest $^2\text{D}_{3/2}$ state ($4f^05d^1$) emission to the $^2\text{F}_{5/2}$ ground state ($4f^15d^0$).^{43–45} (Another transition $^2\text{D}_{3/2} \rightarrow ^2\text{F}_{7/2}$ is not observed at the DPA complex, but is observable in the CeCl_3 solution at 2174 cm^{-1} , Figure 5). MCPL spectra of the other five metals are stronger and most bands can be assigned to the known transitions, reproducible by the crystal field theory (Table 1).

Origin of the bands around 1025 and 1494 cm^{-1} accompanying the strong DPA Raman bands is somewhat unclear; most probably MCPL signal here is a combination of the true ligand signal (magnetic ROA enabled by the presence of the lanthanide ion) and instrumental artifacts accompanying strongly polarized Raman bands.^{46,47} However, nonzero signal was confirmed by independent measurements on both the ROA instruments.

Another feature that we are currently not able to fully explain is the relatively strong MCPL of Nd, Dy, and Ho at the lowest wavenumbers, below 200 cm^{-1} . Most probably, it is caused by a participation of vibrational Raman scattering of water^{48,49} (within the first hydration sphere for the salts) and the DPA ligand (for the complexes). The lanthanide provides electronic states and resonance with the laser excitation, which is necessary for the vibrational chiral signal to be observable.⁴¹

Spectra of Strong Luminophores. The remaining three lanthanides studied can be characterized as strong luminophores as their TL spectra are much stronger than (for Eu) or at least comparable (for Sm and Er) to the Raman signal of the DPA ligand. Their Raman/TL and MCPL spectra are plotted in Figure 4. TL bands of $[\text{Sm}(\text{DPA})_3]^{3-}$ are spread over most of the accessible spectral range and dominated by the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ (927 and 1119 cm^{-1}) and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (1731 , 1913 , 2001 , 2153 , 2242 , and 2327 cm^{-1}) Sm^{3+} transitions. Only the strongest Raman DPA bands can be recognized, such as symmetric breathing mode of the pyridine ring at $\sim 1020\text{ cm}^{-1}$, C–O stretch at $\sim 1394\text{ cm}^{-1}$, C–C ring stretch at $\sim 1444\text{ cm}^{-1}$ and the pyridine ring stretch at $\sim 1576\text{ cm}^{-1}$.^{50,51}

The TL and MCPL $[\text{Eu}(\text{DPA})_3]^{3-}$ spectra are consistent with those published in our recent study dedicated to interaction of this compound with amino acids.¹² The TL spectrum is entirely dominated by the europium 1864 and 1976 cm^{-1} $^5\text{D}_0 \rightarrow ^7\text{F}_1$ bands, which are accompanied by strong MCPL; however, weaker bands across the entire spectral region appear as well, such as the signal around 243 cm^{-1} ($^5\text{D}_1 \rightarrow ^7\text{F}_1$) and 900 cm^{-1} ($^5\text{D}_1 \rightarrow ^7\text{F}_2$) (cf. Table 1).

For $[\text{Er}(\text{DPA})_3]^{3-}$, TL of Er^{3+} occurs below 830 cm^{-1} and the intensity is comparable with the Raman DPA signal dominating above this limit. Most intense bands (350 , 430 , 603 , 665 , 725 cm^{-1}) were identified as the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ electronic transition. This transition also generates the strong MCPL “couplet” signal (positive at 328 cm^{-1} and negative at 362 cm^{-1}).

CID values obtained for selected bands of the strongly luminescent metals are listed in Table 2. We see that the magnetic field induces rather strong chirality in lanthanide ions, given that CIDs for natural ROA of typical organic molecules are about 10^{-4} . The most efficient “chirality transmitter” is the Er^{3+} ion with maximal CID of 4.6×10^{-2} .

Table 1. Observed Spectral Bands for $[\text{Ln}(\text{DPA})_3]^{3-}$ and Their Assignment

	Raman shift (cm^{-1})	corresponding wavelength (nm)		
		this work	literature values	transitions ^a
Ce	470, 360, 300	546, 542, 540	548, 547 ^{43–45}	$^2\text{D}_{3/2} \rightarrow ^2\text{F}_{5/2}$
Pr	2230, 2110, 1810	604, 599, 589	603, 602 ^{57,58}	$^1\text{D}_2 \rightarrow ^3\text{H}_4$
Nd	2246, 2170, 2042, 1913, 1772, 1746, 1648, 1608, 1498	604, 601, 597, 592, 587, 586, 583, 582, 578	602 ⁵⁹ 583 ⁵⁹	$^4\text{G}_{5/2} \rightarrow ^4\text{I}_{9/2}$ $^2\text{G}_{7/2} \rightarrow ^4\text{I}_{9/2}$
Sm	2353, 2327, 2293, 2242, 2153, 2114, 2011, 1978, 1913, 1887, 1731, 1692	608, 607, 606, 604, 603, 601, 599, 596, 595, 592, 591, 586, 585	597 ⁶⁰	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ $^4\text{F}_{3/2} \rightarrow ^6\text{H}_{9/2}$
	1188, 1142, 1119, 1062, 927	568, 566, 564, 564, 560	565 ⁶⁰	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ $^4\text{F}_{3/2} \rightarrow ^6\text{H}_{7/2}$
Eu	1976, 1864	594, 591	591 ⁶¹	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
	1655	583	583 ⁶¹	$^5\text{D}_0 \rightarrow ^7\text{F}_0$
	808–909	556–550	557 ⁶²	$^5\text{D}_1 \rightarrow ^7\text{F}_2$
	243	539	540 ²³	$^5\text{D}_1 \rightarrow ^7\text{F}_1$
Tb	1997, 1917, 1757, 1652, 1607, 1530, 1486, 1465	595, 592, 587, 583, 582, 579, 578, 577	580 ⁶³	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
	614, 527, 489, 410, 367, 328, 283, 261	550, 547, 546, 544, 543, 541, 540, 539	540 ⁶³	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
Dy	2001, 1875, 1652, 1576, 407, 325	595, 591, 583, 581, 544, 541	570 ⁶³ 540 ⁶³	$^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ $^4\text{I}_{15/2} \rightarrow ^6\text{H}_{13/2}$
Ho	1574, 1453, 1025, 838, 699, 665, 606, 565, 498, 466, 412, 283, 237, 175, 134	581, 577, 575, 557, 553, 552, 550, 548, 546, 545, 544, 540, 539, 537, 536	545 ⁶³	$^5\text{G}_5 \rightarrow ^5\text{I}_7$ $^5\text{S}_2 \rightarrow ^5\text{I}_8$
Er	741, 725, 685, 665, 617, 603, 539, 454, 430, 422, 362, 350, 328, 292	554, 553, 552, 551, 550, 550, 548, 545, 544, 544, 542, 542, 541, 540	545 ⁶³	$^2\text{G}_{9/2} \rightarrow ^4\text{I}_{13/2}$ $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$

^aAs obtained by CFT. Note that the spectroscopic symbols describe free-ion energy levels that are highly degenerate and split in nonsymmetric environment.

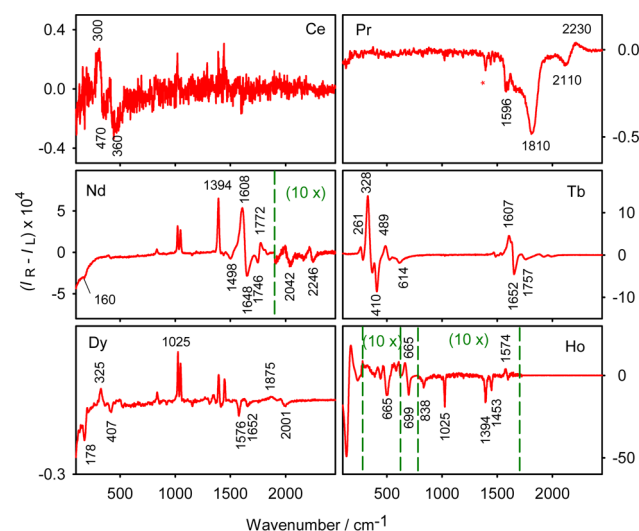


Figure 3. MCPL spectra of weakly luminescent $[\text{Ln}(\text{DPA})_3]$ complexes. Idealized ($S_{\text{ave}} = (S_{\text{north}} - S_{\text{south}})/2$) spectra divided by maximal Raman intensity are plotted. In the labeled parts the intensity was multiplied by 10 for better visibility.

Spectra obtained by the crystal field theory for Pr, Nd, Sm, Tb, Dy, Ho and Er are summarized in Figure S2. In addition to TL and MCPL, natural CPL was simulated as well, because the Δ -form of the complex is chiral. In solution, a fast $\Delta \leftrightarrow \Lambda$ equilibrium occurs and CPL is not observable.¹² For Ce^{3+} without 4f electrons our simplified approach was not possible. As pointed out above, the spectral intensities provided by CFT

without extensive fitting of simulation parameters are rather inaccurate and cannot be used to a band-to-band comparison with the experiment. Nevertheless, the simulations provided reasonable estimates of the energies allowing assigning the observed transitions. Calculated transition energies differ from the observed ones by 50–300 cm^{-1} . The simulated intensity patterns document the wealth of lanthanide transitions giving rise to the measurable MCPL intensities.

MCPL Spectra of Complexes versus Salts. The lanthanide ions have a strong affinity to water. Unlike for the relatively rigid Δ and Λ conformers in the DPA complexes, in chloride solutions the Ln^{3+} atoms are surrounded by a loosely structured hydration sphere, potentially containing some chloride atoms.^{52,53} As documented in Figure 5 for Ce, Tb, Ho, and Er, the hydration is reflected in the MCPL spectra as minor changes of frequencies and sometimes significant changes of intensities. As may be expected for the more dynamical hydrated ion, the chloride MCPL bands are in general broader than for DPA. For Ce, a new transition at 2174 cm^{-1} becomes visible. A large change also occurs for Er, where the MCPL spectrum of the hydrated ion flips sign within the region of largest intensity.

Another interesting possibility to monitor lanthanide neighborhood is documented in Figure 6. The NdCl_3 and $\text{Nd}(\text{NO}_3)_3$ spectra (also different from the DPA complex, compare to Figure 2) are plotted together with those of a NdCl_3 and KNO_3 mixture. As the spectra of the mixture are nearly the same as for $\text{Nd}(\text{NO}_3)_3$, we can conclude that Nd^{3+} has a higher affinity to the nitrate ions than to water and Cl^- molecules, and formation of a $[\text{Nd}(\text{NO}_3)_x]$ complex can be detected by MCPL.

Complementarity of Different Fluorescence Detection Modes. Measurements in different polarization modes⁵⁴

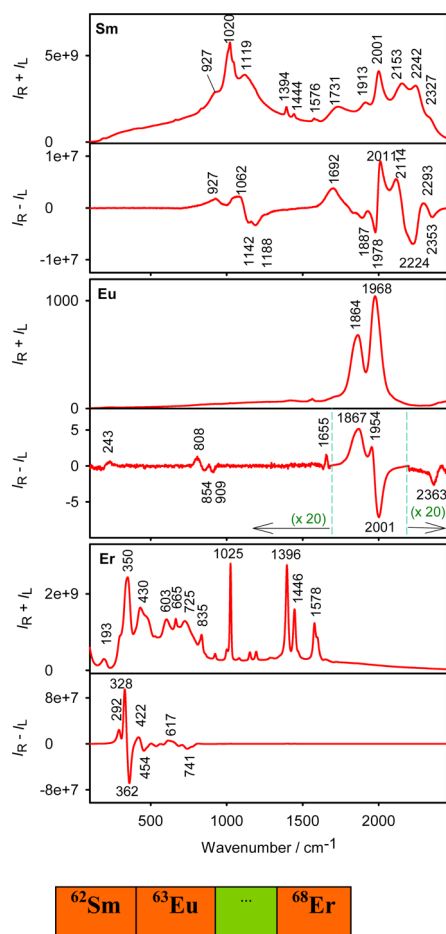


Figure 4. Experimental Raman/TL and MCPL spectra of DPA complexes of the strongly luminescent lanthanides.

Table 2. CID Values for Selected MCPL Bands in $[\text{Ln}(\text{DPA})_3]^3$ Measured at 1.5 T

Ln	wavenumber (cm^{-1})	CID
Sm	1692	2.0×10^{-3}
	1887	-8.7×10^{-4}
	1978	-1.5×10^{-3}
	2011	2.3×10^{-3}
	2114	1.9×10^{-3}
	2224	-2.1×10^{-3}
	2293	5.2×10^{-4}
Eu	2353	-1.4×10^{-3}
	1868	7.7×10^{-3}
	1954	3.3×10^{-3}
	2001	-9.0×10^{-3}
Er	292	2.8×10^{-2}
	328	4.6×10^{-2}
	362	-4.0×10^{-2}

of ROA spectrometer reveals interesting connection of MCPL to other spectroscopic techniques and energy transfer mechanisms within studied systems. A simplified scheme of the SCP and ICP data collection is plotted in Figure 7. Unlike Raman scattering, lanthanide fluorescence is rather slow¹³ and the absorption and emission of light are quasi-independent processes. For SCP, the polarization of the MCPL signal is then modulated by the E and G energy levels connected by the emitted radiation, which corresponds to differential absorption

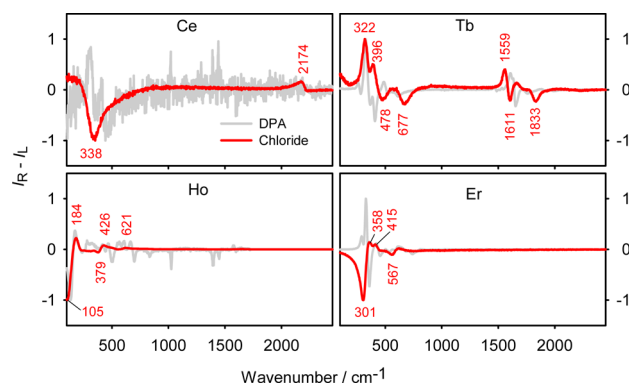


Figure 5. MCPL spectra of Ce, Tb, Ho, and Er chlorides. The spectra are normalized to the highest peak, spectra of DPA complexes are added as the gray line.

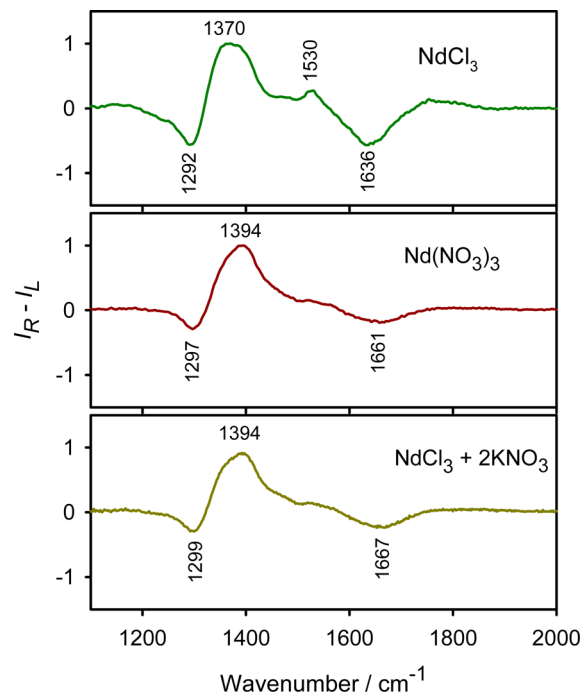


Figure 6. MCPL spectra of Nd chloride and nitrate, and a 1:2 mixture of NdCl_3 and KNO_3 .

of the $E \rightarrow G$ transition, that is, to magnetic circular dichroism (MCD). Because of the minimal geometry changes of lanthanide ion during excitation, the signal can also be related to the ground state ($G \rightarrow E$) MCD.

For ICP, circular dichroism of $G \rightarrow E'$ is measured as differential fluorescence of $E \rightarrow G$, which is known from 1970s as fluorescence detected circular dichroism (FD CD).^{54,55} First lanthanide (Eu) FD CD was recorded in 2005 using a variable liquid crystal circular polarizer.⁵⁶ As for MCD, the lanthanide $E \rightarrow G$ fluorescence is closely related to the $G \rightarrow E$ absorption. Some of these connections can be documented when the MCPL spectra are converted to the wavenumber scale and overlapped with absorption and MCD curves (Figure 8) for the investigated 578 nm ($^2G_{7/2} \rightarrow ^4I_{9/2}$) Nd^{3+} transition.

CONCLUSIONS

We used the sensitive detection of circularly polarized luminescence enabled by the Raman optical activity spectrometer to investigate magnetic circularly polarized luminescence

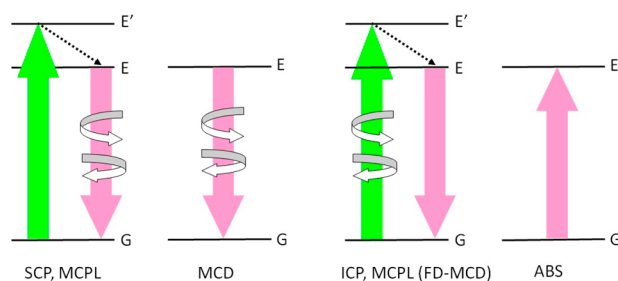


Figure 7. Two operational modes of the ROA spectrometer. In the SCP mode (left), the sample is irradiated by unpolarized radiation, and the intensity difference for the right- and left-circularly polarized emitted light is detected. MCPL from an excited electronic state E then approximately corresponds to magnetic circular dichroism (MCD) of transition $E \rightarrow G$. In the ICP mode (right) the sample is irradiated by right- and left-circularly polarized light, and the total intensity is detected. MCPL band of the transition $G \rightarrow E$ corresponds to the fluorescence-detected magnetic circular dichroism (FD MCD) of the $G \rightarrow E'$ transition. Because all the $4f$ states (G , E , and E') of Ln(III) ions have virtually the same geometries the FD MCD band shape is closely related to the $G \rightarrow E$ absorption.

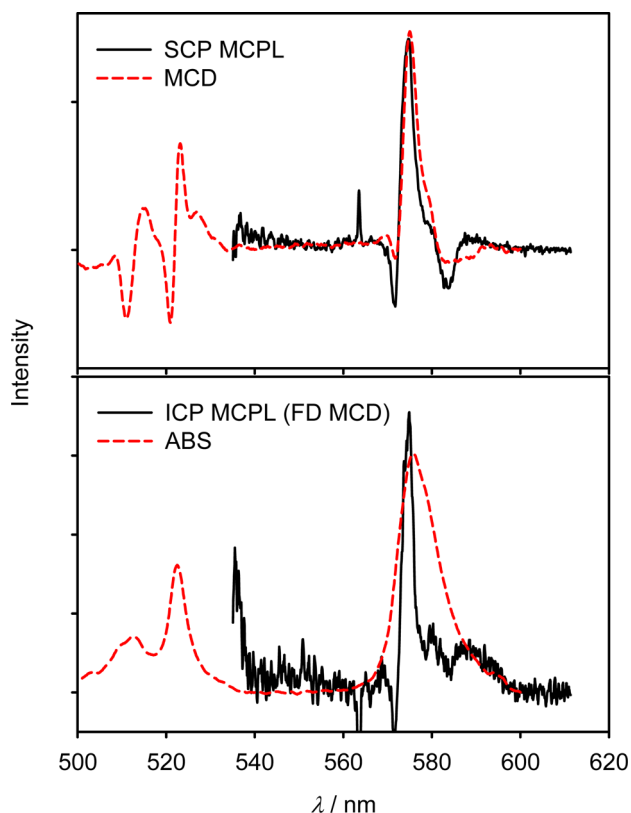


Figure 8. SCP MCPL and MCD (top) and ICP MCPL (FD MCD) and absorption (bottom) spectra of $\text{Nd}(\text{NO}_3)_3$. Intensity scales are arbitrary.

cence of a series of lanthanide complexes and salts. It turned out that MCPL spectra provided a very detailed view into lanthanide fluorescence and enabled to see transitions undetectable by total (unpolarized) fluorescence measurements.

For our series (except for Ce) the crystal field theory enabled us to assign most of the observed MCPL bands to Ln^{3+} transitions and the assignment was consistent with previous works. By comparing MCPL spectra of the DPA complex and

different salts, we also showed that the MCPL spectroscopy can be readily used to report on the lanthanide environment.

The variation of polarization modulations available in the latest generation of ROA spectrometers appeared to be useful for understanding of the origin of the signal. A simple model could be proposed to relate the MCPL spectra to MCD and FD MCD measurements. With the 532 nm laser excitation MCPL spectra could be detected approximately within the 535–610 nm range. This combination seems to be especially convenient for the lanthanide complexes; nevertheless, other excitations and instruments can make the method more universal in the future. For the lanthanides, the MCPL intensities were much stronger than natural or magnetic ROA and could be easily recognized, whereas total luminescence was, in some cases, hidden in the Raman signal.

From the point of view of analytical, bioimaging and similar applications, the strong luminescence of Sm, Eu, and Er is the most promising, nevertheless all lanthanides provide specific spectra reflecting their chemical neighborhood. Overall, we hope that in the future the technique will bring about new advances of the lanthanide labeling in analytical chemistry and imaging.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.analchem.7b00435](https://doi.org/10.1021/acs.analchem.7b00435).

Raw experimental spectra of lanthanide complexes and simulations (PDF).

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Notes

The authors declare no competing financial interest.

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