



## OPEN ACCESS

## EDITED BY

Fabio Piccinelli,  
University of Verona, Italy

## REVIEWED BY

Marco M. Allard,  
La Sierra University, United States  
Jatish Kumar,  
Indian Institute of Science Education and  
Research, India  
Yu-Wu Zhong,  
Chinese Academy of Sciences (CAS), China

## \*CORRESPONDENCE

Claude Piguet,  
✉ claude.piguet@unige.ch  
Juan-Ramón Jiménez,  
✉ jrjimenez@ugr.es

RECEIVED 30 July 2024

ACCEPTED 20 September 2024

PUBLISHED 09 October 2024

## CITATION

Poncet M, Besnard C, Guénée L, Jiménez J-R  
and Piguet C (2024) Tuning the circularly  
polarized luminescence in homoleptic and  
heteroleptic chiral Cr<sup>III</sup> complexes.  
*Front. Chem.* 12:1472943.  
doi: 10.3389/fchem.2024.1472943

## COPYRIGHT

© 2024 Poncet, Besnard, Guénée, Jiménez and  
Piguet. This is an open-access article distributed  
under the terms of the [Creative Commons  
Attribution License \(CC BY\)](#). The use,  
distribution or reproduction in other forums is  
permitted, provided the original author(s) and  
the copyright owner(s) are credited and that the  
original publication in this journal is cited, in  
accordance with accepted academic practice.  
No use, distribution or reproduction is  
permitted which does not comply with these  
terms.

# Tuning the circularly polarized luminescence in homoleptic and heteroleptic chiral Cr<sup>III</sup> complexes

Maxime Poncet<sup>1</sup>, Céline Besnard<sup>2</sup>, Laure Guénée<sup>2</sup>,  
Juan-Ramón Jiménez<sup>3\*</sup> and Claude Piguet<sup>1\*</sup><sup>1</sup>Department of Inorganic and Analytical Chemistry, University of Geneva, Geneva, Switzerland,<sup>2</sup>Laboratory of Crystallography, University of Geneva, Geneva, Switzerland, <sup>3</sup>Department of Inorganic Chemistry, University of Granada, Unidad de Excelencia de Química (UEQ), Granada, Spain

A series of highly emissive inert and chiral Cr<sup>III</sup> complexes displaying positive and negative circularly polarized luminescence (CPL) within the near-infrared (NIR) region at room temperature have been prepared and characterized to decipher the effect of ligand substitution on the photophysical properties, more specifically on the chiroptical properties. The helical homoleptic [Cr(dqp-R)<sub>2</sub>]<sup>3+</sup> (dqp = 2,6-di(quinolin-8-yl)pyridine; R = Ph, ≡-Ph, DMA, ≡-DMA (DMA = *N,N*-dimethylaniline)) and heteroleptic [Cr(dqp)(L)]<sup>3+</sup> (L = 4-methoxy-2,6-di(quinolin-8-yl)pyridine (dqp-OMe) or L = *N*<sup>2</sup>,*N*<sup>6</sup>-dimethyl-*N*<sup>2</sup>,*N*<sup>6</sup>-di(pyridin-2-yl)pyridine-2,6-diamine (ddpd)) molecular rubies were synthesized as racemic mixtures and then resolved and isolated into their respective pure *PP* and *MM* enantiomeric forms by chiral stationary phase HPLC. The corresponding enantiomers show two opposite polarized emission bands within the 700–780 nm range corresponding to the characteristic metal-centered Cr(<sup>2</sup>E' → <sup>4</sup>A<sub>2</sub>) and Cr(<sup>2</sup>T<sub>1</sub> → <sup>4</sup>A<sub>2</sub>) transitions with large *g*<sub>lum</sub> ranging from 0.14 to 0.20 for the former transition. In summary, this study reports the rational use of different ligands on Cr<sup>III</sup> and their effect on the chiroptical properties of the complexes.

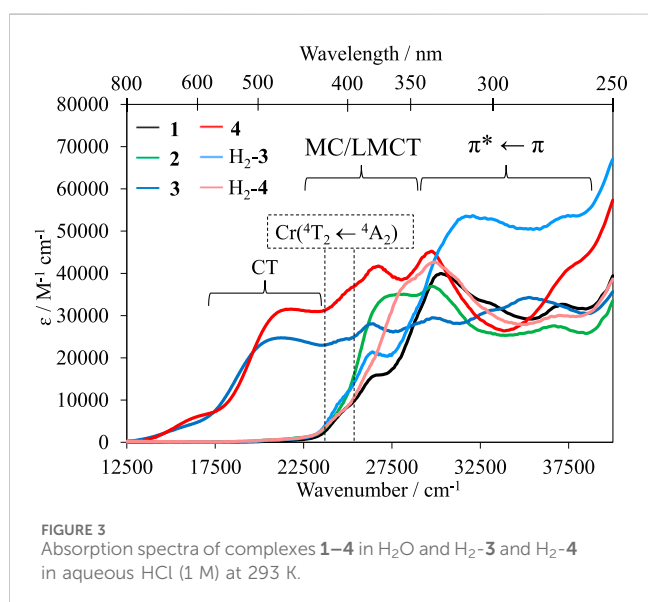
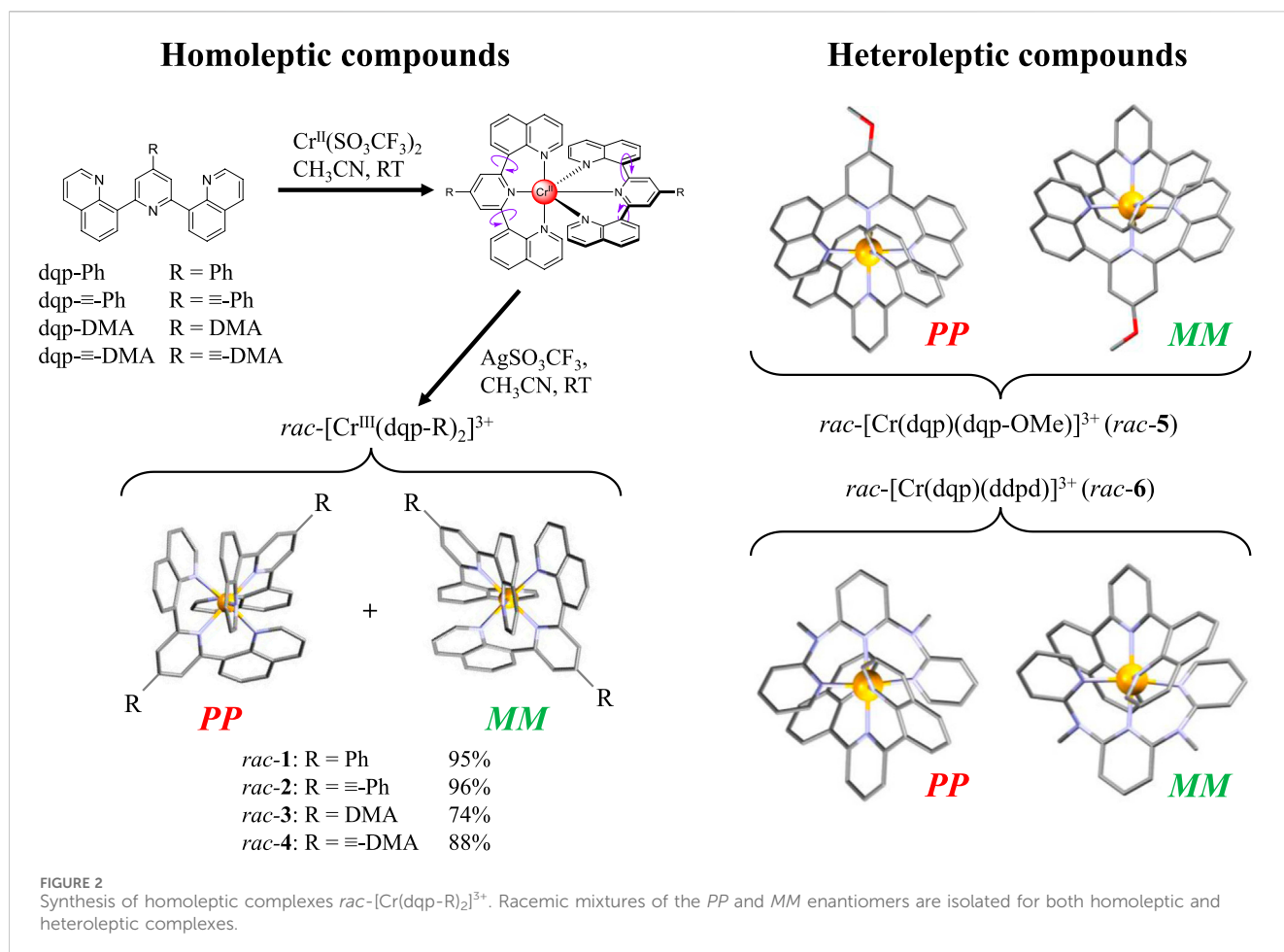
## KEYWORDS

chromium, chirality, emission, circularly polarized luminescence, circular dichroism, chiral HPLC

## 1 Introduction

Chiral chromophores displaying intense circularly polarized luminescence (CPL) signal and high CPL brightness (*B*<sub>CPL</sub>) are up-and-coming candidates for applications as molecular probes in biological systems (Carr et al., 2012; Staszak et al., 2019), in bio-imaging (Heffern et al., 2014), in light-emitting devices (e.g., CP-OLEDs) (Brandt et al., 2017; Zinna et al., 2017; Furlan et al., 2024), and in counterfeiting agents (e.g., security inks) (MacKenzie and Pal, 2021). The dissymmetry factor *g*<sub>lum</sub> is used to estimate the excess of emitted right- or left-circularly polarized light in an isotropic solution. It is deduced from *I*<sub>L</sub> and *I*<sub>R</sub>, which represent the emission intensities of left and right circularly polarized light, respectively (Equation 1 center, Richardson, 1979; Arrico et al., 2020). This parameter is directly related to the electric dipole ( $\vec{\mu}_{ij}$ ), the magnetic dipole ( $\vec{m}_{ij}$ ) transition moment, and the angle between these two vectors ( $\theta$ ) (Equation 1 right).

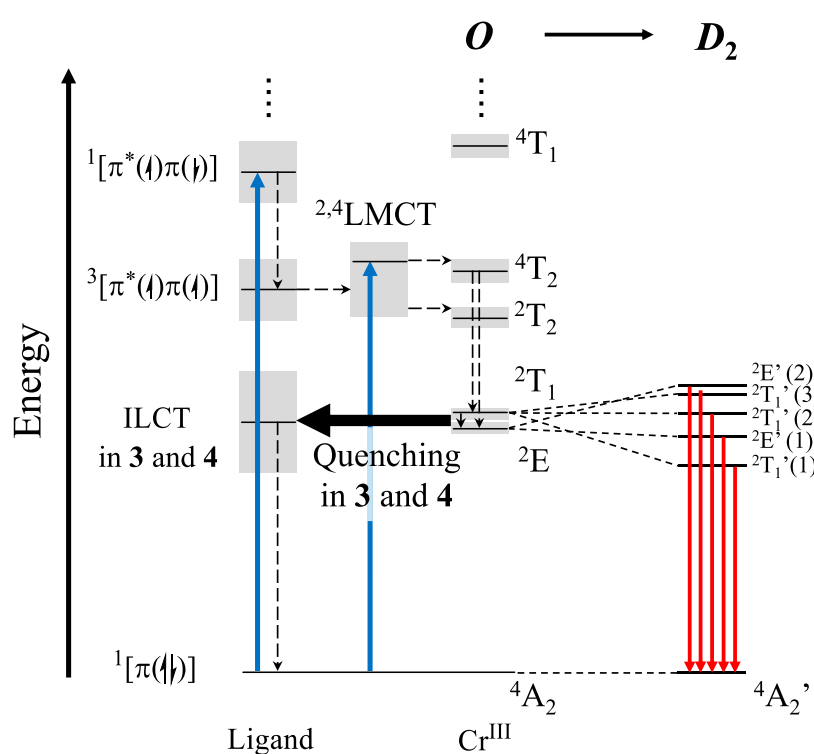




Appendix 1; Cantuel et al., 2002; Otto et al., 2015; Jimenez et al., 2019; Jiménez et al., 2020). The preparation of the homoleptic complexes  $[\text{Cr}(\text{dqp-R})_2]^{3+}$  is achieved by mixing one equivalent of  $\text{Cr}^{\text{II}}$  precursor and two equivalents of the corresponding ligands

$\text{dqp-R}$  ( $\text{dqp-Ph}$  for 1,  $\text{dqp-}\equiv\text{-Ph}$  for 2,  $\text{dqp-DMA}$  for 3, and  $\text{dqp-}\equiv\text{-DMA}$  for 4) under anaerobic conditions at room temperature. The formed  $\text{rac-}[\text{Cr}^{\text{II}}(\text{dqp-R})_2]^{2+}$  are oxidized to the kinetically inert  $\text{rac-}[\text{Cr}^{\text{III}}(\text{dqp-R})_2]^{3+}$  using  $\text{AgSO}_3\text{CF}_3$ , affording the desired complexes in good-to-excellent yields (74%–96%, Figure 2).

Single crystals suitable for X-ray diffraction analysis (Supplementary Tables S1–S13; Supplementary Figures S1–S7 in the Supplementary Material) were obtained through slow diffusion of diethyl ether into a concentrated methanol solution for 1, 2, 3 (with triflate counterions), and 4 (with chloride counterions). The  $\text{dqp}$  derivatives systematically adopt the thermodynamically more stable *meridional* binding around the kinetic labile  $\text{Cr}^{\text{II}}$  intermediate, leading to *meridional* arrangement in the final  $\text{Cr}^{\text{III}}$  complexes after oxidation. Under acidic conditions, the tertiary amine groups in 3 and 4 can be further protonated to yield  $[\text{Cr}(\text{dqp-DMAH})_2]^{5+}$  ( $\text{H}_2$ -3,  $\text{DMAH} = N,N$ -dimethylanilinium) and  $[\text{Cr}(\text{dqp-}\equiv\text{-DMAH})_2]^{5+}$  ( $\text{H}_2$ -4). Single crystals suitable for X-ray diffraction of both protonated complexes could also be successfully isolated by crystallization. The semi-flexible nature of the  $\text{dqp}$  backbone upon *mer* binding joined with the kinetic inertness of  $\text{Cr}^{\text{III}}$  results in the formation of racemic mixtures of helical *PP* and *MM* enantiomers of  $D_2$ -symmetry in the crystals (Figure 2). As previously reported, the two instances of intramolecular, interligand  $\pi$ -stacking between the aromatic quinolines produce stabilizing interactions compatible with the exclusive formation of



**FIGURE 4**  
Perrin–Jablonski diagram for a Cr<sup>III</sup> in *O* geometry. Excitation (blue arrows), internal conversion (dashed arrows), ILCT quenching in **3** and **4** (black arrow), and expected emission in a *D*<sub>2</sub> distorted geometry (red arrow) are represented. The splitting of the <sup>2</sup>T<sub>1</sub> and <sup>2</sup>E energy levels leads to five expected optically active energy levels in *D*<sub>2</sub> symmetry.

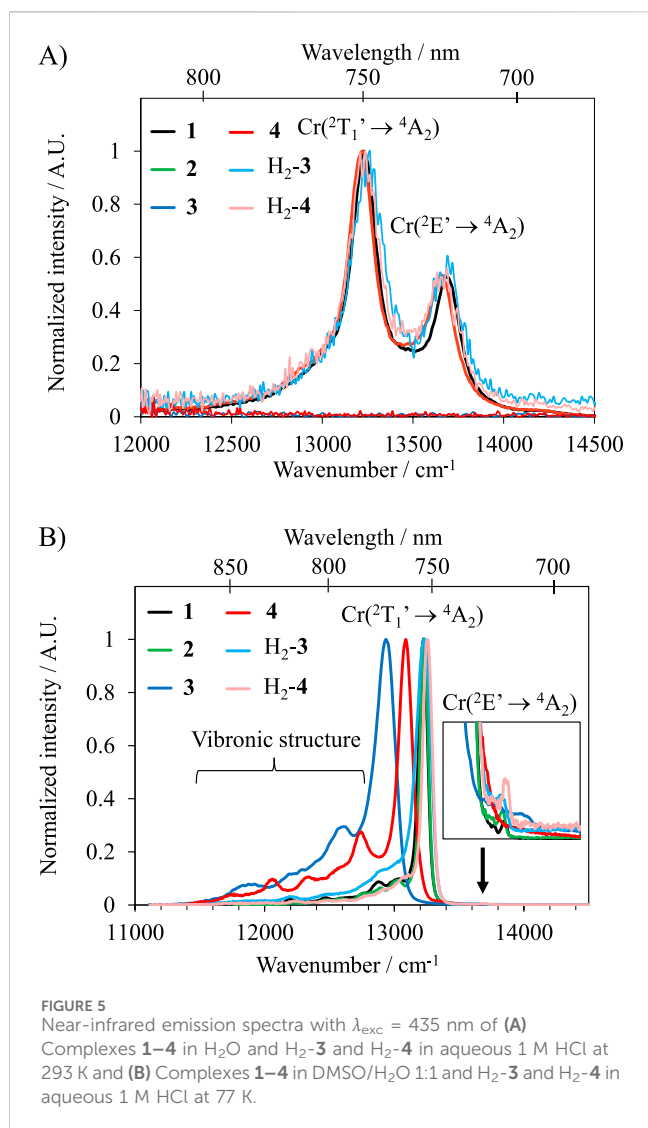
the *PP* and *MM* enantiomers (Jimenez et al., 2021). No meso *PM* complex could be observed, likely due to steric hindrance, as simulated in the parent [Cr(dqp)<sub>2</sub>]<sup>3+</sup> (Jimenez et al., 2021). To better appreciate the intramolecular interligand  $\pi$ -stacking, the interplanar angle is calculated as the angle between the mean plane of the 10 atoms of each quinoline (Supplementary Figures S8–S15). The closer the angle is to 0, the more parallel to each other the quinolines are. The calculated values for the complexes **1–5**, [H<sub>2</sub>-**3**] and [H<sub>2</sub>-**4**] lie within the 15.54°–16.68° range. In the heteroleptic complex [Cr(dqp)(ddpd)]<sup>3+</sup> (**6**), the corresponding quinoline–pyridine interplanar angle reaches 31.48°, far larger than in the other compounds, but yet smaller than the parent [Cr(ddpd)<sub>2</sub>]<sup>3+</sup> (46.52°) (Otto et al., 2015). The transoid bite angles N–Cr–N are in the 176.0(1)°–177.7(8)° range for the homoleptic complexes (**1–4**, H<sub>2</sub>-**3**, and H<sub>2</sub>-**4**) and in the 175.5(9)°–176.1(10)° range for the heteroleptic complexes (**5** and **6**). In addition, to evaluate the structural distortion with respect to a perfect octahedron, the following parameter  $\Sigma = \sum_{i=1}^{12} |90 - \varphi_i|$  is computed with  $\varphi_i$  being the cisoid bite angles N–Cr–N. The distortion in complexes **1–6**, H<sub>2</sub>-**3**, and H<sub>2</sub>-**4** ranges from 22.73° ≤  $\Sigma$  ≤ 31.49°, with the largest distortion in the heteroleptic complex **6**.

The absorption spectra of the homoleptic complexes (**1–4**) were recorded in water at room temperature. Complexes H<sub>2</sub>-**3** and H<sub>2</sub>-**4** were recorded in acidic media (aqueous HCl 1 M) to ensure full protonation of the terminal tertiary amine (Figure 3).

The maxima observed within the 345–250 nm range (29,000–40,000 cm<sup>-1</sup>) are associated with  $\pi^* \leftarrow \pi$  transitions

located on the ligands. Ligand-to-metal charge transfers (LMCTs) are observed at lower energies from 435 nm to 345 nm (23,000–29,000 cm<sup>-1</sup>). Additionally, a shoulder is observed within the 420–400 nm range (23,800–25,000 cm<sup>-1</sup>), which has been assigned to the spin-allowed, parity-forbidden metal-centered (MC) Cr(<sup>4</sup>T<sub>2</sub> ← <sup>4</sup>A<sub>2</sub>) transition according to TD-DFT calculations performed on the parent [Cr(dqp)<sub>2</sub>]<sup>3+</sup> complex (Jimenez et al., 2019). Because  $\Delta = E(\text{Cr}(\text{}^4\text{T}_2 \leftarrow \text{}^4\text{A}_2))$  in octahedral complexes, the extracted energy values point to similar ligand-field splitting for all complexes within the 24,272–24,876 cm<sup>-1</sup> range (Supplementary Table S14). Complexes **3** and **4** display an additional intense broad absorption band in the visible range of the electromagnetic spectrum 800–435 nm (12,500–23,000 cm<sup>-1</sup>) assigned to the intraligand charge transfer (ILCT) from the terminal nitrogen of the aniline to the trivalent chromium center, as observed in related terpyridine-based complexes (Barbour et al., 2017). Ensuring full protonation using acidic conditions (aqueous 1 M HCl) removes the CT band in H<sub>2</sub>-**3** and H<sub>2</sub>-**4** (Figure 3). Moving down in energy and using an increased concentration of complexes, the spin-forbidden/parity-forbidden spin-flip (SF) transitions Cr(<sup>2</sup>T<sub>1</sub>, <sup>2</sup>E ← <sup>4</sup>A<sub>2</sub>) can be observed with low molar extinction coefficients ranging from 0.1 M<sup>-1</sup> cm<sup>-1</sup> to 0.6 M<sup>-1</sup> cm<sup>-1</sup>.

Because of the slightly distorted geometry going from *O*<sub>h</sub> to *D*<sub>2</sub>, a splitting of the two expected bands produces five distinct excited energy levels. The Cr(<sup>2</sup>T<sub>1</sub>) splits into three non-degenerated energy levels, and the Cr(<sup>2</sup>E) splits into two (Figure 4; Supplementary Figures S16–S19) (Jimenez et al., 2023). Recording the SF bands was impossible in complexes **3** and **4** because of the overlap with



the intense charge transfer absorption band in the visible region of the spectrum. Individual assignments of the absorption bands together with experimental radiative rate constants  $k_{\text{rad}}$ , radiative lifetimes  $\tau_{\text{rad}}$ , oscillator strengths  $f_{\text{exp}}$ , and dipole strengths  $D_{\text{exp}}$  are compiled in [Supplementary Table S14](#). From the absorption spectra and the calculated energies of the accessible excited levels, the ligand-field parameter  $\Delta$  and the Racah parameters  $B$  and  $C$  can be estimated using [Equations 3–6](#) ([Supplementary Table S15](#)) ([Jorgensen, 1963](#); [Witzke, 1971](#); [Chong et al., 2022](#)).

$$E(^4T_2) = \Delta. \quad (3)$$

$$E(^2T_1) = 9B + 3C - 24\left(\frac{B^2}{\Delta}\right). \quad (4)$$

$$E(^2E) = 9B + 3C - 50\left(\frac{B^2}{\Delta}\right). \quad (5)$$

$$E(^2T_2) = 15B + 5C - 176\left(\frac{B^2}{\Delta}\right). \quad (6)$$

$$E(^4T_1) = 1.5\Delta + 7.5B - 0.5\sqrt{(225B^2 + \Delta^2 - 18\Delta B)}. \quad (7)$$

For all studied complexes,  $B$  ranges from  $611\text{ cm}^{-1}$  to  $655\text{ cm}^{-1}$ , and  $C$  ranges from  $2,743\text{ cm}^{-1}$  to  $2,885\text{ cm}^{-1}$ , which implies a weak impact of the extension of the  $\pi$ -delocalized conjugated system contrariwise to a previously reported substitution of methoxy groups in the same position in the homoleptic  $[\text{Cr}(\text{dqp-Ome})_2]^{3+}$  ([Jimenez et al., 2021](#)). We note that for the  $[\text{Cr}(\text{dqp})_2]^{3+}$ , the ratio  $C/B$  equals 4.7, but the ratio is only 3.1 for  $[\text{Cr}(\text{dqp-Ome})_2]^{3+}$ . Typical values are in the range of 4.2–4.9 and are sometimes assumed to be 4.7 ([Adachi, 2024](#)).

Upon UV–VIS excitation ( $\lambda_{\text{exc}} = 350\text{–}435$  nm) at room temperature, the typical sharp NIR dual emissions (FWHM  $\approx 200\text{ cm}^{-1}$ ) observed in complexes **1** and **2** ([Figure 5A](#)) can be assigned to the radiative relaxation of the  $\text{Cr}(^2E)$  and  $\text{Cr}(^2T_1)$  excited state levels to the  $\text{Cr}(^4A_2)$  ground state level in approximate  $O$  symmetry ([Jimenez et al., 2019](#); [Jimenez et al., 2021](#)). The most intense band is attributed to the  $\text{Cr}(^2T_1' \rightarrow ^4A_2)$  SF transition (maxima  $13,227\text{ cm}^{-1}$  ( $756\text{ nm}$ ) in **1** and **2**) and the less intense to  $\text{Cr}(^2E' \rightarrow ^4A_2)$  (maxima at  $13,698\text{ cm}^{-1}$  ( $730\text{ nm}$ ) for **1** and  $13,661\text{ cm}^{-1}$  ( $732\text{ nm}$ ) for **2**). Contrariwise, the luminescence of complexes **3** and **4** is completely quenched, likely due to energy back transfer into the non-emissive CT levels ([Figure 4](#)). Upon protonation of the anilines ( $\text{H}_2\text{-3}$  and  $\text{H}_2\text{-4}$ ), a weak luminescence is retrieved with an overall photoluminescence quantum yield of  $\Phi_{\text{PL}} \leq 0.0011\%$  ([Supplementary Table S16](#); [Figure 5A](#)), in contrast to the non-luminescent terpyridine analog ([Barbour et al., 2017](#)).

Upon changing the temperature, the Boltzmann distribution of the thermally equilibrated  $\text{Cr}(^2E')$  and  $\text{Cr}(^2T_1')$  levels is modified, and 77 K measurements result in a close to single emission assigned to  $\text{Cr}(^2T_1' \rightarrow ^4A_2)$  ([Figure 5B](#)). Interestingly, the total (**3** and **4**) and partial ( $\text{H}_2\text{-3}$  and  $\text{H}_2\text{-4}$ ) quenching pathways of the luminescence happening at 293 K vanish at 77 K, and strong luminescence is recovered ([Figure 5B](#)). For both  $\text{H}_2\text{-3}$  and  $\text{H}_2\text{-4}$  at 77 K, the main emission band is blue-shifted compared to the non-protonated **3** and **4** complexes. The room temperature  $\Phi_{\text{PL}}$  values determined in aerobic and anaerobic conditions ( $\text{CH}_3\text{CN}$ ,  $\lambda_{\text{exc}} = 435$  nm) are gathered in [Supplementary Table S16](#). The obtained values in oxygen-free solutions are 12.4%, making complexes **1** and **2** in the same range as the previously reported record-holding deuterium-free  $\text{Cr}^{\text{III}}$  complexes ([Jimenez et al., 2019](#); [Jimenez et al., 2021](#)). The origin of the high  $\Phi_{\text{PL}}$  observed is attributed to (i) the weak trigonal distortion forming the octahedral geometry, preventing the non-radiative deexcitation pathways ([Kitzmann et al., 2022](#)) and (ii) the strong LFS induced by the dq-p-type ligands, avoiding BISC to the  $\text{Cr}(^4T_2)$  excited state level ([Figure 1](#)).

Time-resolved experiments were conducted and displayed mono-exponential decays, resulting in  $\tau_{\text{Cr,obs}}^{^2E',^2T_1'} > 1$  ms in the deaerated solution at 293 K and up to 2.62(2) ms at 77 K (**2**, [Supplementary Table S16](#); [Supplementary Figures S20–S25](#)). Air-equilibrated experiments demonstrated the extreme dependence on dissolved dioxygen, as previously reported for  $\text{Cr}^{\text{III}}$  chromophores ( $\tau_{\text{Cr,obs}}^{^2E',^2T_1'} < 65\text{ }\mu\text{s}$ ) ([Kirk, 1999](#)). For more insight, the reader is referred to the in-depth analysis of the mechanism discussed by [Alazaly et al. \(2023\)](#).

Additionally, the rate of energy transfer from  $\text{Cr}(^2E'/^2T_1')$  to  $\text{O}_2$ ,  $k_{\text{q}}$ , can be estimated in **1** and **2** with the relationship  $k_{\text{q}} = 1/[\text{O}_2] \cdot (1/\tau_{\text{air}} - 1/\tau_{\text{Ar}})$  ([Burgin et al., 2022](#)), in which  $[\text{O}_2]$  is the oxygen concentration in the solvent at the experimental temperature

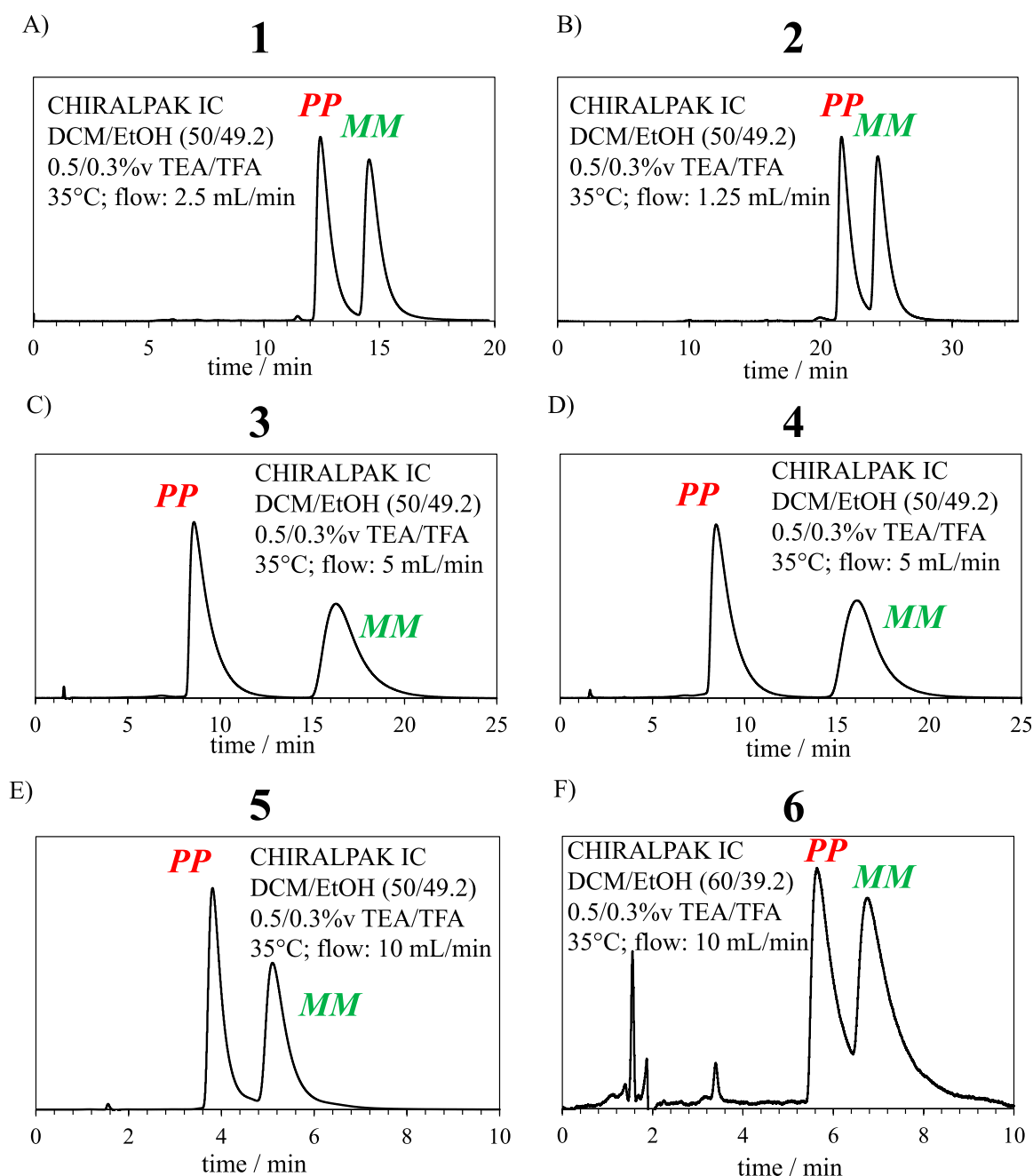


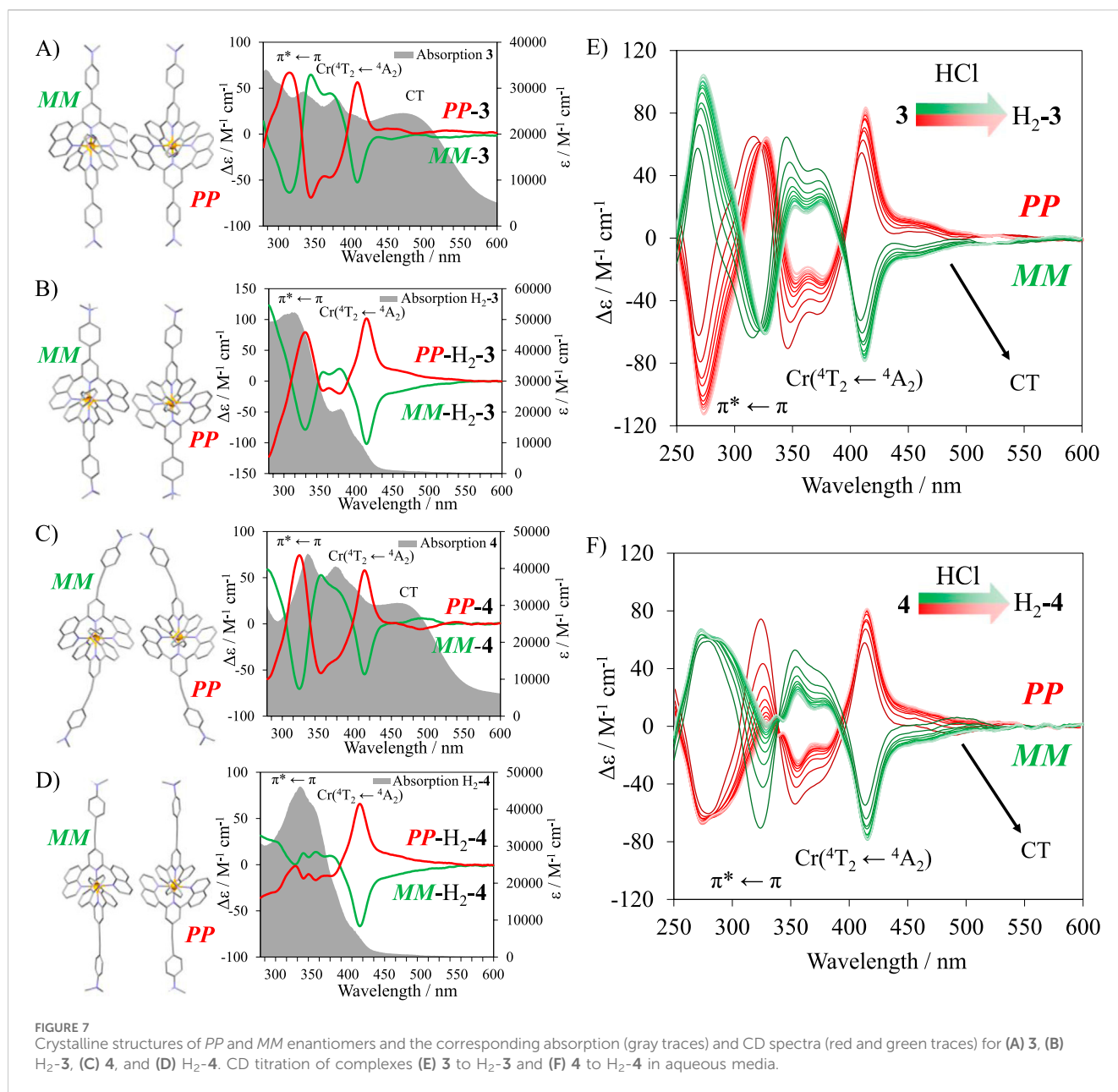
FIGURE 6  
CSP-HPLC conditions required for the enantiomeric resolution of complexes (A) 1, (B) 2, (C) 3, (D) 4, (E) 5, and (F) 6.

(2.42 mM in  $\text{CH}_3\text{CN}$  at 293 K),  $\tau_{\text{air}}$  is the  $\text{Cr}(^2\text{E}'/^2\text{T}_1')$  lifetime under air-equilibrated conditions, and  $\tau_{\text{Ar}}$  is the respective lifetime under deaerated conditions. The obtained values of  $6.23 \cdot 10^6 \text{ s}^{-1}$  (1) and  $7.59 \cdot 10^6 \text{ s}^{-1}$  (2) demonstrate the effectiveness of  $\text{O}_2$  quenching (Supplementary Table S16).

The thermal equilibrium of the  $\text{Cr}(^2\text{T}_1')$  and  $\text{Cr}(^2\text{E}')$  levels was confirmed by the recording of identical excited state lifetimes at both maxima. The sensitization efficiency for transferring the energy from the ligand to the  $\text{Cr}(^2\text{E}'/^2\text{T}_1')$  excited state  $\eta_{\text{sens}}^{\text{L} \rightarrow \text{Cr}}$  is found to be above 71% (Supplementary Table S16). The measurement of certain photophysical properties in 3, 4,  $\text{H}_2$ -3,

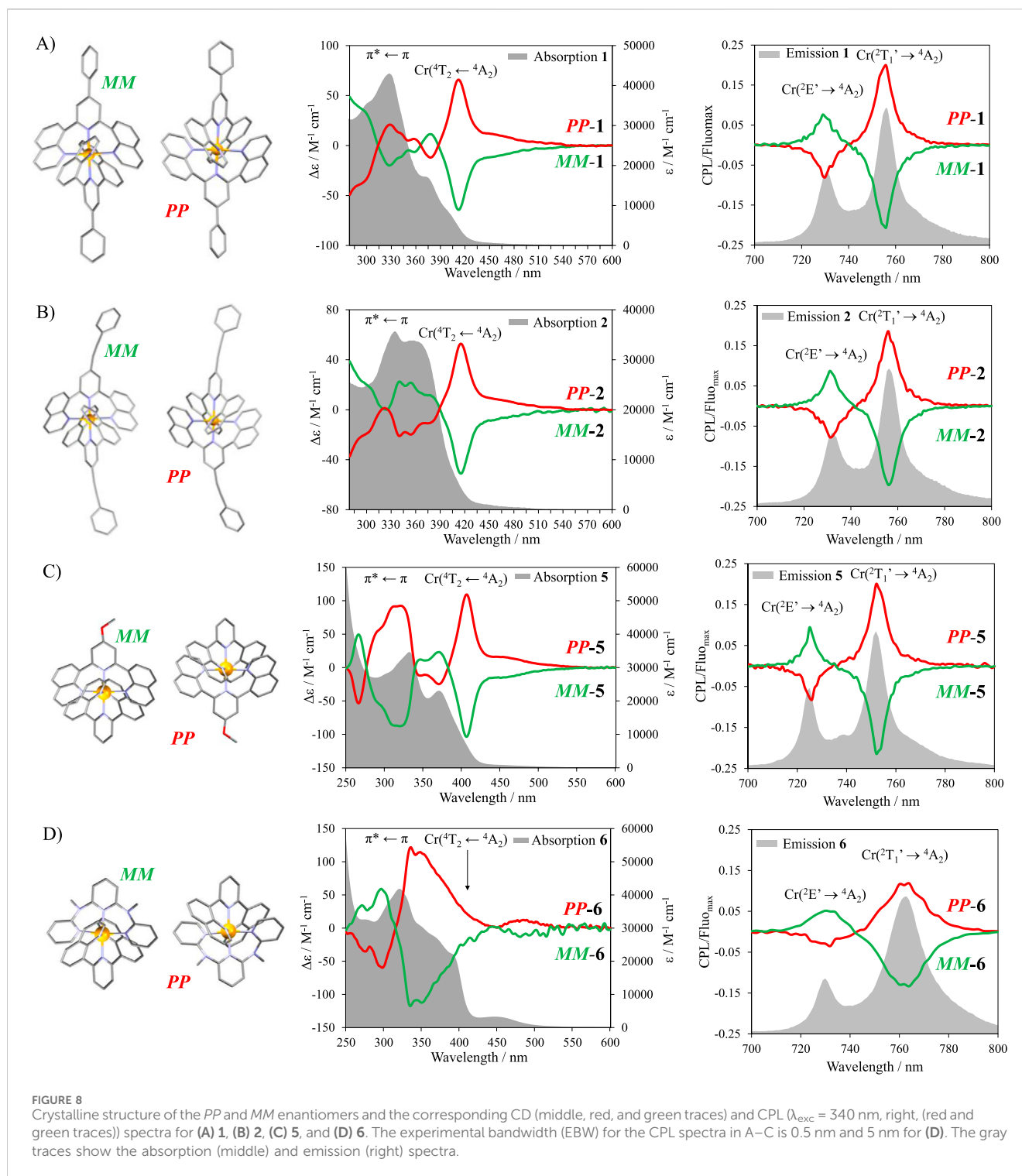
and  $\text{H}_2$ -4 was limited by (i) the weak emitted signals ( $\text{H}_2$ -3 and  $\text{H}_2$ -4) that prevented reliable measurements of the excited state lifetimes and (ii) the lack of emissive properties in 3 and 4. Nevertheless, the retrieval of the luminescence at 77 K allowed time-resolved measurements on all complexes. Excitation spectra were recorded in dilute solutions and closely match the absorption spectra of the corresponding compounds (Supplementary Figures S26–S29).

Chiral stationary phase high-performance liquid chromatography (CSP-HPLC) was proven to be effective, straightforward, and quick in the separation of the racemic



mixture of d-block complexes such as  $Ru^{III}$ ,  $Cr^{III}$ , and  $Co^{III}$  (Yoshida et al., 2013; Cortijo et al., 2017; Dee et al., 2019). Isocratic elution using a  $CH_2Cl_2/CH_3CH_2OH$ /triethylamine/trifluoroacetic acid 50/49.2/0.5/0.3 (v:v) mixture resulted in the separation of the complexes 1–6 (Figures 6A–F). For complexes 1, 2, and 5, the elutions of *MM* enantiomers tail and slightly overlap with the elution peaks of the *PP* enantiomers. As a result, a small amount of contamination was observed upon reinjection in the analytical column (Supplementary Figures S30–S32). Nevertheless, thorough integrations of the chromatogram reveal that  $\leq 0.5\%$  mol was present in the sample. Therefore, the chiroptical studies were carried out while considering these contaminations as negligible. The obtention of a mirror image of the circular dichroism (CD) and CPL signals confirmed the adequacy of the latter assumption. Note that the efficient separation of **3** and **4** would allow a larger scale separation.

The CD was recorded, and mirror images were systematically obtained for all complexes 1–6,  $H_2\text{-3}$ , and  $H_2\text{-4}$  (Figures 7, 8). The study of the analogous crystallized *MM*- $[Cr(dqp)_2]^{3+}$  in CD allowed the assignment of the measured complexes (Jimenez et al., 2019). In all complexes except for **6** (Figure 8D), a strong Cotton effect could be observed in the 410–430 nm range, corresponding to the MC  $Cr(^4T_2 \leftarrow ^4A_2)$  transition. The UV range is also dominated by considerable Cotton effect matching with  $\pi^* \leftarrow \pi$  transitions located on the ligands. Despite the significant absorption of the CT bands in complexes **3** and **4** ( $\epsilon = 25,000\text{--}32,000\text{ M}^{-1}\text{cm}^{-1}$ ), little to no Cotton effect was observed, confirming the low  $g_{abs}$  for these specific transitions (Figures 7A, C). Because **3** and **4** could be protonated in solution, their conversion to the respective protonated species  $H_2\text{-3}$  and  $H_2\text{-4}$  could be followed by CD upon successive addition of hydrochloric acid (0.05 M) in the aqueous solution (Figures 7E, F). The MC ligand-field



$\text{Cr}(^4\text{T}_2 \leftarrow ^4\text{A}_2)$  transition is less affected by the protonation of the ligands than the  $\pi^* \leftarrow \pi$  transitions, which display important changes in the 250–400 nm range.

Circularly polarized luminescence (CPL) measurements were recorded on each enantiomer of the emissive complexes **1**, **2**, **5**, and **6** (Figures 8A–D). The low photoluminescence quantum yield of **H**<sub>2</sub>-**3** and **H**<sub>2</sub>-**4** and the non-emissive character of **3** and **4** prevented CPL measurements. To ensure a correct determination of the dissymmetry factor, the highest resolution of the CPL spectra is

ensured with the smallest emission slit aperture settings available at the cost of the signal intensity (Sickinger et al., 2024). The experimental bandwidth (EBW) used in these experiments is 0.5 nm for **1**, **2**, and **5** and 5 nm for **6**. A better signal-to-noise ratio can be obtained by opening the slits (larger EBW), but the resolution of the spectra must be sacrificed, skewing the results and the value of  $g_{lum}$ . It is, therefore, more correct to measure the sample at the smallest slit aperture available and divide the CPL spectra by the maximum read value of the corresponding emission.



TABLE 1 CPL brightness ( $B_{CPL}$ ) calculation for each emissive transition in complexes 1, 2, 5, and 6.

Complex	$\epsilon/M^{-1}cm^{-1}$	$\phi_{PL}/\%$ <sup>(a)</sup>	${}^2T_1'/{}^2E'$ ratio		$ g_{lum} $	$B_{CPL}/M^{-1}cm^{-1}$
1	34,622 <sup>(b)</sup>	12.4	${}^2E'$	0.324	$8 \cdot 10^{-2}$	56
			${}^2T_1'$	0.676	$2 \cdot 10^{-1}$	290
2	36,118 <sup>(b)</sup>	12.4	${}^2E'$	0.333	$8 \cdot 10^{-2}$	60
			${}^2T_1'$	0.667	$2 \cdot 10^{-1}$	299
5	29,881 <sup>(b)</sup>	6.5	${}^2E'$	0.308	$8 \cdot 10^{-2}$	24
			${}^2T_1'$	0.692	$2 \cdot 10^{-1}$	134
6	32,684 <sup>(b)</sup>	6.0	${}^2E'$	0.181	$7 \cdot 10^{-2}$	14
			${}^2T_1'$	0.819	$1.4 \cdot 10^{-1}$	112
$[Cr(dqp)_2]^{3+}$ <sup>(c)</sup>	20,000 <sup>(d)</sup>	5.2	${}^2T_1'$	-	$2 \cdot 10^{-1}$	104
$[Cr(dqp-Br)_2]^{3+}$ <sup>(e)</sup>	10,591 <sup>(f)</sup>	14	${}^2T_1'$	-	$1.9 \cdot 10^{-1}$	140
$[Cr(dqp-OMe)_2]^{3+}$ <sup>(e)</sup>	5,000 <sup>(f)</sup>	17	${}^2T_1'$	-	$1.8 \cdot 10^{-1}$	76.5
$[Cr(dqp-\equiv)]^{3+}$ <sup>(e)</sup>	13,553 <sup>(f)</sup>	15	${}^2T_1'$	-	$1.7 \cdot 10^{-1}$	173
$[Cr(ddpd)_2]^{3+}$ <sup>(g)</sup>	30,000 <sup>(h)</sup>	11	${}^2T_1'$	-	$9.3 \cdot 10^{-2}$	153

<sup>a</sup>Deaerated conditions.

<sup>b</sup> $\lambda_{abs} = 340$  nm.

<sup>c</sup>Jimenez et al., 2019.

<sup>d</sup> $\lambda_{abs} = 370$  nm.

<sup>e</sup>Jimenez et al., 2021.

<sup>f</sup> $\lambda_{abs} = 405$  nm.

<sup>g</sup>Dee et al., 2019.

<sup>h</sup> $\lambda_{abs} = 300$  nm.

Under unpolarized excitation ( $\lambda_{exc} = 340$  nm), complexes 1, 2, 5, and 6 (Figures 8A–D) displayed strong circularly polarized emission within the 720–780 nm range. The dissymmetry factors  $|g_{lum}|$  obtained for the  $Cr({}^2E' \rightarrow {}^4A_2)$  transition reach 0.07–0.08 for all four complexes (Supplementary Figures S33–S36). Interestingly, for the  $Cr({}^2T_1' \rightarrow {}^4A_2)$  transition, complexes 1, 2, and 5 display  $|g_{lum}| = 0.20$ , whereas complex 6 reaches only  $|g_{lum}| = 0.14$ .

Putting these results in perspective with those of the previously reported homoleptic complexes of  $[Cr(ddpd)_2]^{3+}$  and  $[Cr(dqp-R)_2]^{3+}$  (R = H, Br, OMe, C $\equiv$ CH, Table 1) (Otto et al., 2015; Jimenez et al., 2019; Jimenez et al., 2021), a trend emerges for the  $Cr({}^2T_1' \rightarrow {}^4A_2)$  transitions. Indeed, all complexes containing two dqp-based ligands display the same dissymmetry factor of 0.2, whereas the more flexible  $[Cr(ddpd)_2]^{3+}$  culminated at 0.093 (Dee et al., 2019). By exploiting the chemical inertness of Cr<sup>III</sup>, one of each ligand could be implemented in the same complex to give the heteroleptic complex  $[Cr(dqp)(ddpd)]^{3+}$  (6), for which  $|g_{lum}| = 0.14$  corresponds to the average of the dissymmetry factors of the two parent homoleptic complexes. As an attempt to rationalize this result, a hypothetical “ligand dissymmetry factor”  $g_{lum}^L$  could be imagined for a given transition defined as Equation 8.

$$|g_{lum}^L| = \frac{\eta^L}{n} \cdot |g_{lum}^{total, homoleptic}|. \quad (8)$$

$\eta^L$  is the denticity of the ligand,  $n$  the number of available coordination sites around the metal center (6 for octahedral symmetry), and  $g_{lum}^{total, homoleptic}$  is the dissymmetry factor of the

corresponding homoleptic complex of a specific transition. Therefore, in the cases of  $[Cr(dqp)_2]^{3+}$  and  $[Cr(ddpd)_2]^{3+}$ , the following values are obtained:  $g_{lum}^{dqp} = 0.1$  and  $g_{lum}^{ddpd} = 0.0465$ . From these values, the dissymmetry factor of a heteroleptic complex could be estimated by applying Equation 9.

$$|g_{lum}^{total, heteroleptic}| = \sum |g_{lum}^L|. \quad (9)$$

For 2, one obtains  $g_{lum}^{dqp} + g_{lum}^{ddpd} = 0.1 + 0.0465 = 0.1465$ , which corresponds closely to the experimental value of 0.14, verifying the hypothesis. Unfortunately, the number of available compounds is limited; thus, to validate or invalidate the statement, more flexible tridentate ligands must be studied. As a general conclusion to the chiroptic luminescence, an extension of the organic  $\pi$ -delocalized electronic cloud in the *para* position of the pyridine does not influence the dissymmetry factor, while the implementation of ddpd ligands results in an attenuated  $g_{lum}$ . A plausible explanation for this observation is that the rigidification of the complex is key in the obtention of a large dissymmetry factor, and the rigidity must be maximized.

The  $B_{CPL}$  of the emissive complexes can be calculated using Equation 2. Because the  $g_{lum}$  values associated with the two observed emissions  $Cr({}^2T_1' \rightarrow {}^4A_2)$  and  $Cr({}^2E' \rightarrow {}^4A_2)$  are of opposite signs in the same enantiomer,  $B_{CPL}$  must be similarly split into two components. Accordingly, the  $\phi_{PL}$  must be split relative to the intensity of each band at the temperature measurement (293 K). The emission spectrum of the corresponding complex is approximated as two Gaussian curves, deconvoluted as such, and the ratio between them is calculated (idealized  $Cr({}^2T_1' \rightarrow {}^4A_2)$  and

$\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$  transitions, Supplementary Figures S37–S40). The calculated values of  $B_{\text{CPL}}$  are compiled in Table 1 and range from  $299 \text{ M}^{-1}\text{cm}^{-1}$  to  $122 \text{ M}^{-1}\text{cm}^{-1}$  for the  $\text{Cr}(^2\text{T}_1' \rightarrow ^4\text{A}_2)$  transition and  $60\text{--}14 \text{ M}^{-1}\text{cm}^{-1}$  for the  $\text{Cr}(^2\text{E}' \rightarrow ^4\text{A}_2)$  transition, which are among the highest reported values for CPL active compounds (Arrico et al., 2020). A higher  $B_{\text{CPL}}$  can be achieved by exciting the maxima of the absorption band to increase the value of  $\epsilon$  in the  $B_{\text{CPL}}$  calculation. The  $\phi_{\text{PL}}$  is considered invariant with the excitation wavelength.

### 3 Conclusion

A series of new chiral homoleptic and heteroleptic  $\text{Cr}^{\text{III}}$  chromophores with dqp-based ligands with *para* functionalization of the central pyridine have been synthesized and characterized. The addition of *N,N*-dimethylaniline to the complex resulted in a large increase in absorbance in the VIS region (CT) accompanied by quenching of the luminescence. Interestingly, weak luminescence is retrieved upon protonation of the aniline ( $\Phi_{\text{PL}} \leq 0.0011\%$ ). The highly luminescent complexes  $[\text{Cr}(\text{dqp-Ph})_2]^{3+}$  and  $[\text{Cr}(\text{dqp-}\equiv\text{-Ph})_2]^{3+}$  are promising candidates for use as chiral luminescent probes. Enantiomeric resolution of all six racemic complexes could be achieved by CSP-HPLC. Implementing *N,N*-dimethylaniline as a substituent to the complex resulted in a baseline separation of the two enantiomers, allowing a potential large-scale separation. Moreover, the evolution of the circular dichroism from the non-protonated to the protonated species in  $[\text{Cr}(\text{dqp-DMA})_2]^{3+}/[\text{Cr}(\text{dqp-DMAH})_2]^{5+}$  and  $[\text{Cr}(\text{dqp-}\equiv\text{-DMA})_2]^{3+}/[\text{Cr}(\text{dqp-}\equiv\text{-DMAH})_2]^{5+}$  could be followed. Near-perfect octahedral geometries are obtained with the help of the six-membered chelate rings, providing long excited state lifetime and high overall photoluminescence quantum yields at room temperature. Dual circularly polarized luminescence arises from the  $\text{Cr}(^2\text{T}_1')$  and  $\text{Cr}(^2\text{E}')$  excited level to the  $\text{Cr}(^4\text{A}_2)$  ground state within the 720–780 nm range. The observed  $|g_{\text{lum}}|$  for the emissive complexes amounts to 0.2 except for  $[\text{Cr}(\text{dqp})(\text{ddpd})]^{3+}$ , for which the  $|g_{\text{lum}}|$  was measured to be in between the two corresponding parent homoleptic complexes  $[\text{Cr}(\text{dqp})_2]^{3+}$  ( $|g_{\text{lum}}| = 0.2$ ) and  $[\text{Cr}(\text{ddpd})_2]^{3+}$  ( $|g_{\text{lum}}| = 0.093$ ). High  $B_{\text{CPL}}$  values, ranging from  $299 \text{ M}^{-1}\text{cm}^{-1}$  to  $122 \text{ M}^{-1}\text{cm}^{-1}$  for the  $\text{Cr}(^2\text{T}_1' \rightarrow ^4\text{A}_2)$  transition and  $60\text{--}14 \text{ M}^{-1}\text{cm}^{-1}$  for the  $\text{Cr}(^2\text{E}' \rightarrow ^4\text{A}_2)$  transition, were obtained, reaching the typical range of 4f-based chiral chromophores with the added value of the inertness and low cost of trivalent chromium.

### Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

### References

Adachi, S. (2024). Practical consideration on Racah parameter and Tanabe–Sugano diagram analyses for  $\text{Mn}^{4+}$  and  $\text{Cr}^{3+}$ -activated phosphors. *J. Luminescence* 273, 120628. doi:10.1016/j.jlumin.2024.120628

### Author contributions

MP: conceptualization, formal analysis, investigation, and writing—original draft. CB: formal analysis and writing—review and editing. LG: formal analysis and writing—review and editing. J-RJ: conceptualization, supervision, validation, and writing—review and editing. CP: conceptualization, funding acquisition, supervision, validation, and writing—review and editing.

### Funding

The author(s) declare that financial support was received for the research, authorship, and/or publication of this article. This work is supported through grants from the Swiss National Science Foundation (grant 200020\_207313). Financial support from the Swiss National Science Foundation is gratefully acknowledged. J-RJ acknowledges the funding received from the grant TED2021.129598A.I00 funded by MCIN/AEI/10.13039/501100011033 and by European Union NextGenerationEU/PRTR and is grateful to the Ministerio de Ciencia Innovación y Universidades for a Ramón y Cajal contract (grant RYC 2022-037255-I) funded by MCIN/AEI/10.13039/501100011033 and FSE+.

### Acknowledgments

K. L. Buchwalder is acknowledged for performing elemental analysis.

### Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

### Publisher's note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors, and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

### Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2024.1472943/full#supplementary-material>

Alazaly, A. M. M., Clarkson, G. J., Ward, M. D., and Abdel-Shafi, A. A. (2023). Mechanism of oxygen quenching of the excited states of heteroleptic chromium(III) phenanthroline derivatives. *Inorg. Chem.* 62, 16101–16113. doi:10.1021/acs.inorgchem.3c02343

- Albano, G., Pescitelli, G., and Di Bari, L. (2020). Chiroptical properties in thin films of  $\pi$ -conjugated systems. *Chem. Rev.* 120, 10145–10243. doi:10.1021/acs.chemrev.0c00195
- Arrico, L., Di Bari, L., and Zinna, F. (2020). Quantifying the overall efficiency of circularly polarized emitters. *Chem. – A Eur. J.* 27, 2920–2934. doi:10.1002/chem.202002791
- Barbour, J. C., Kim, A. J. L., deVries, E., Shaner, S. E., and Lovaasen, B. M. (2017). Chromium(III) bis-aryletherpyridyl complexes with enhanced visible absorption via incorporation of intraligand charge-transfer transitions. *Inorg. Chem.* 56, 8212–8222. doi:10.1021/acs.inorgchem.7b00953
- Brandt, J. R., Salerno, F., and Fuchter, M. J. (2017). The added value of small-molecule chirality in technological applications. *Nat. Rev. Chem.* 1, 0045. doi:10.1038/s41570-017-0045
- Burgin, T. H., Glaser, F., and Wenger, O. S. (2022). Shedding light on the oxidizing properties of spin-flip excited states in a Cr(III) polypyridine complex and their use in photoredox catalysis. *J. Am. Chem. Soc.* 144, 14181–14194. doi:10.1021/jacs.2c04465
- Cantuel, M., Bernardinelli, G., Imbert, D., Bünzli, J.-C. G., Hopfgartner, G., and Piguet, C. (2002). A kinetically inert and optically active Cr(III) partner in thermodynamically self-assembled heterodimetallic non-covalent d-f podates. *J. Chem. Soc. Dalton Trans.*, 1929–1940. doi:10.1039/B200011C
- Carr, R., Evans, N. H., and Parker, D. (2012). Lanthanide complexes as chiral probes exploiting circularly polarized luminescence. *Chem. Soc. Rev.* 41, 7673–7686. doi:10.1039/C2CS35242G
- Cheng, Y., He, J., Zou, W., Chang, X., Yang, Q., and Lu, W. (2023). Circularly polarized near-infrared phosphorescence of chiral chromium(III) complexes. *Chem. Commun.* 59, 1781–1784. doi:10.1039/D2CC06548G
- Chong, J., Besnard, C., Cruz, C. M., Piguet, C., and Jimenez, J. R. (2022). Heteroleptic mer-[Cr(NNN)(CN)3] complexes: synthetic challenge, structural characterization and photophysical properties. *Dalton Trans.* 51, 4297–4309. doi:10.1039/d2dt00126h
- Cortijo, M., Viala, C., Reynaldo, T., Favereau, L., Fabing, I., Srebro-Hooper, M., et al. (2017). Synthesis, spectroelectrochemical behavior, and chiroptical switching of tris( $\beta$ -diketonato) complexes of ruthenium(III), chromium(III), and cobalt(III). *Inorg. Chem.* 56, 4555–4567. doi:10.1021/acs.inorgchem.6b03094
- Dee, C., Zinna, F., Kitzmann, W. R., Pescitelli, G., Heinze, K., Di Bari, L., et al. (2019). Strong circularly polarized luminescence of an octahedral chromium(III) complex. *Chem. Comm.* 55, 13078–13081. doi:10.1039/c9cc06909g
- Furlan, F., Moreno-Naranjo, J. M., Gasparini, N., Feldmann, S., Wade, J., and Fuchter, M. J. (2024). Chiral materials and mechanisms for circularly polarized light-emitting diodes. *Nat. Photonics* 18, 658–668. doi:10.1038/s41566-024-01408-z
- Gauthier, E. S., Abella, L., Hellou, N., Darquié, B., Caytan, E., Roisnel, T., et al. (2020). Long-lived circularly polarized phosphorescence in helicene-NHC rhenium(I) complexes: the influence of helicene, halogen, and stereochemistry on emission properties. *Angew. Chem. Int. Ed.* 59, 8394–8400. doi:10.1002/anie.202002387
- Hara, N., Okuda, K., Shizuma, M., Tajima, N., and Imai, Y. (2019). Control of circularly polarized luminescence using a suitable wired structure connecting a binaphthyl with two pyrenes. *ChemistrySelect* 4, 10209–10213. doi:10.1002/slct.201902176
- Heffern, M. C., Matosziuk, L. M., and Meade, T. J. (2014). Lanthanide probes for bioresponsive imaging. *Chem. Rev.* 114, 4496–4539. doi:10.1021/cr400477t
- Helm, L., and Merbach, A. E. (2005). Inorganic and bioinorganic solvent exchange mechanisms. *Chem. Rev.* 105, 1923–1960. doi:10.1021/cr030726o
- Homberg, A., Brun, E., Zinna, F., Pascal, S., Górecki, M., Monnier, L., et al. (2018). Combined reversible switching of ECD and quenching of CPL with chiral fluorescent macrocycles. *Chem. Sci.* 9, 7043–7052. doi:10.1039/C8SC02935K
- Jimenez, J. R., Doistau, B., Cruz, C. M., Besnard, C., Cuerva, J. M., Campana, A. G., et al. (2019). Chiral molecular ruby [Cr(dqp)2](3+) with long-lived circularly polarized luminescence. *J. Am. Chem. Soc.* 141, 13244–13252. doi:10.1021/jacs.9b06524
- Jimenez, J. R., Miguez-Lago, S., Poncet, M., Ye, Y. T., Ruiz, C. L., Cruz, C. M., et al. (2023). Eu-III functionalized silica nanoparticles encapsulating chiral Cr-III complexes with simultaneous unpolarized red and polarized NIR-I luminescence. *J. Mater. Chem. C* 11, 2582–2590. doi:10.1039/d2tc05344f
- Jiménez, J.-R., Poncet, M., Doistau, B., Besnard, C., and Piguet, C. (2020). Luminescent polypyridyl heteroleptic Cr(III) complexes with high quantum yields and long excited state lifetimes. *Dalton Trans.* 49, 13528–13532. doi:10.1039/D0DT02872J
- Jimenez, J. R., Poncet, M., Miguez-Lago, S., Grass, S., Lacour, J., Besnard, C., et al. (2021). Bright long-lived circularly polarized luminescence in chiral chromium(III) complexes. *Angew. Chem. Int. Ed.* 60, 10095–10102. doi:10.1002/anie.202101158
- Jorgensen, C. K. (1963). Spectroscopy of transition-group complexes. *Adv. Chem. Phys.* 5, 33–146. doi:10.1002/9780470143513.ch2
- Kirk, A. D. (1999). Photochemistry and photophysics of chromium(III) complexes. *Chem. Rev.* 99, 1607–1640. doi:10.1021/cr960111+
- Kitzmann, W. R., Ramanan, C., Naumann, R., and Heinze, K. (2022). Molecular ruby: exploring the excited state landscape. *Dalton Trans.* 51, 6519–6525. doi:10.1039/d2dt00569g
- Lunkley, J. L., Shirovani, D., Yamanari, K., Kaizaki, S., and Muller, G. (2008). Extraordinary circularly polarized luminescence activity exhibited by cesium tetrakis(3-heptafluoro-butylryl-(+)-camphorato) Eu(III) complexes in EtOH and CHCl3 solutions. *J. Am. Chem. Soc.* 130, 13814–13815. doi:10.1021/ja805681w
- MacKenzie, L. E., and Pal, R. (2021). Circularly polarized lanthanide luminescence for advanced security inks. *Nat. Rev. Chem.* 5, 109–124. doi:10.1038/s41570-020-00235-4
- Maiman, T. H. (1960). Stimulated optical radiation in ruby. *Nature* 187, 493–494. doi:10.1038/187493a0
- Mori, T. (2020). *Circularly polarized luminescence of isolated small organic molecules*. Singapore: Springer. doi:10.1007/978-981-15-2309-0
- Nagata, Y., and Mori, T. (2020). Irreverent nature of dissymmetry factor and quantum yield in circularly polarized luminescence of small organic molecules. *Front. Chem.* 8, 448. doi:10.3389/fchem.2020.00448
- Nakanishi, S., Nakabayashi, K., Mizusawa, T., Suzuki, N., Guo, S., Fujiki, M., et al. (2015). Cryptochiral binaphthyl-bipyrene luminophores linked with alkylene esters: intense circularly polarized luminescence, but ultraweak circular dichroism. *RSC Adv.* 6, 99172–99176. doi:10.1039/C6RA20342F
- Otto, S., Grabolle, M., Förster, C., Kreitner, C., Resh-Genger, U., and Heinze, K. (2015). [Cr(ddpd)2]3+: a molecular, water-soluble, highly NIR-emissive Ruby analogue. *Angew. Chem. Int. Ed.* 54, 11572–11576. doi:10.1002/anie.201504894
- Poncet, M., Benchohra, A., Jimenez, J. R., and Piguet, C. (2021). Chiral chromium(III) complexes as promising candidates for circularly polarized luminescence. *ChemPhotochem* 5, 880–892. doi:10.1002/cptc.202100146
- Reiné, P., Justicia, J., Morcillo, S. P., Abbate, S., Vaz, B., Ribagorda, M., et al. (2018). Pyrene-containing ortho-Oligo(phenylene)ethynylene foldamer as a ratiometric probe based on circularly polarized luminescence. *J. Org. Chem.* 83, 4455–4463. doi:10.1021/acs.joc.8b00162
- Richardson, F. S. (1979). Theory of optical activity in the ligand-field transitions of chiral transition metal complexes. *Chem. Rev.* 79, 17–42. doi:10.1021/cr60317a003
- Richens, D. T. (2005). Ligand substitution reactions at inorganic centers. *Chem. Rev.* 105, 1961–2002. doi:10.1021/cr030705u
- Saleh, N., Shen, C., and Crassous, J. (2014). Helicene-based transition metal complexes: synthesis, properties and applications. *Chem. Sci.* 5, 3680–3694. doi:10.1039/C4SC01404A
- Sang, Y., Han, J., Zhao, T., Duan, P., and Liu, M. (2020). Circularly polarized luminescence in nanoassemblies: generation, amplification, and application. *Adv. Mater.* 32, 1900110. doi:10.1002/adma.201900110
- Sato, S., Yoshii, A., Takahashi, S., Furumi, S., Takeuchi, M., and Isobe, H. (2017). Chiral intertwined spirals and magnetic transition dipole moments dictated by cylinder helicity. *Proc. Natl. Acad. Sci.* 114, 13097–13101. doi:10.1073/pnas.1717524114
- Sickinger, A., Baguenard, B., Bensalah-Ledoux, A., Guyot, Y., Guy, L., Pointillart, F., et al. (2024). Impact of the experimental bandwidth on circularly polarized luminescence measurements of lanthanide complexes: the case of erbium(III). *J. Mater. Chem. C* 12, 4253–4260. doi:10.1039/D3TC04717B
- Sinha, N., Jimenez, J. R., Pfund, B., Prescimone, A., Piguet, C., and Wenger, O. S. (2021). A near-infrared-II emissive chromium(III) complex. *Angew. Chem. Int. Ed.* 60, 23722–23728. doi:10.1002/anie.202106398
- Song, J., Xiao, H., Fang, L., Qu, L., Zhou, X., Xu, Z.-X., et al. (2022). Highly phosphorescent planar chirality by bridging two square-planar platinum(II) complexes: chirality induction and circularly polarized luminescence. *J. Am. Chem. Soc.* 144, 2233–2244. doi:10.1021/jacs.1c11699
- Staszak, K., Wieszczycka, K., Marturano, V., and Tylkowski, B. (2019). Lanthanides complexes – chiral sensing of biomolecules. *Coord. Chem. Rev.* 397, 76–90. doi:10.1016/j.ccr.2019.06.017
- Ward, M. D. (2010). Mechanisms of sensitization of lanthanide(III)-based luminescence in transition metal/lanthanide and anthracene/lanthanide dyads. *Coord. Chem. Rev.* 254, 2634–2642. doi:10.1016/j.ccr.2009.12.001
- Witzke, H. (1971). Semi-empirical evaluations of the Racah B and C parameters from the crystal field spectra of chromium(III) complexes. *Theor. Chim. Acta* 20, 171–185. doi:10.1007/BF00569263
- Yoshida, J., Watanabe, G., Kakizawa, K., Kawabata, Y., and Yuge, H. (2013). Tris( $\beta$ -diketonato) Ru(III) complexes as chiral dopants for nematic liquid crystals: the effect of the molecular structure on the helical twisting power. *Inorg. Chem.* 52, 11042–11050. doi:10.1021/ic401240f
- Yoshida, K., Kajiwara, M., Okazaki, Y., Véronique, L., Zinna, F., Sojic, N., et al. (2024). Modulation of circularly polarized luminescence by swelling of microgels functionalized with enantiopure [Ru(bpy)3]2+ luminophores. *Chem. Commun.* 60, 1743–1746. doi:10.1039/D3CC04391F
- Zinna, F., Pasini, M., Galeotti, F., Botta, C., Di Bari, L., and Giovannella, U. (2017). Design of lanthanide-based OLEDs with remarkable circularly polarized electroluminescence. *Adv. Funct. Mater.* 27, 1603719. doi:10.1002/adfm.201603719