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Chiral Molecular Ruby $[\text{Cr}(\text{dqp})_2]^{3+}$ with Long-Lived Circularly Polarized Luminescence

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ABSTRACT: The chiral resolution of a kinetically inert molecular ruby $[\text{Cr}(\text{dqp})_2]^{3+}$ (**1**, dqp = 2,6-di(quinolin-8-yl)pyridine) displaying strong dual light emission at room temperature has been achieved. The wrapped arrangement of the six-membered dqp chelating ligands around the Cr(III) provided non-planar helical conformations leading to the diastereoselective assembly of chiral bis-tridentate monometallic Cr(III)-helix. The *PP*-(+)- $[\text{Cr}(\text{dqp})_2]^{3+}$ and *MM*-(-)- $[\text{Cr}(\text{dqp})_2]^{3+}$ enantiomers could be separated and isolated by using cation-exchange chromatography and subsequent salt-metathesis with KPF₆. X-Ray crystallographic analysis based on Flack parameters assigned the absolute configurations of the two enantiomers. Circularly Polarized Luminescence (CPL) spectra showed two polarized emission bands within the NIR region corresponding to the characteristic metal-centered spin-flip $\text{Cr}({}^2\text{E} \rightarrow {}^4\text{A}_2)$ and $\text{Cr}({}^2\text{T}_1 \rightarrow {}^4\text{A}_2)$ transitions with exceptionally high dissymmetry factors, $|g_{\text{lum}}|$, of 0.2 and 0.1, respectively, which are comparable to those reported for rare-earth chiral complexes. Photophysical properties also revealed an extremely long excited-state lifetime of 1.2 ms and a high quantum yield of 5.2% at room temperature in water. These properties make $[\text{Cr}(\text{dqp})_2]^{3+}$ an ideal sensitizer for the preparation of enantiopure luminescent supramolecular energy-converting devices and also open up the possibility of using chiral Cr(III) chromophores for the construction of NIR-CPL materials and polarized photonic devices based on earth-abundant metals.

INTRODUCTION

Over the past few years, there has been a growing interest in Cr(III)-based coordination complexes because of their potential applications in solar cells,^{1,2} *in vivo* imaging and photodynamic therapy,³⁻⁵ sensing^{6,7}, (photo)redox catalysis^{1,8-10} and as light-conversion devices.¹¹⁻¹³ To date, these applications indeed exploit alternative complexes of lanthanides (4f) ions, or second (4d) and third (5d) row transition metal ions with organic dyes, because they favorably combine relatively long-lived emissive states with high to medium quantum yields.¹⁴⁻²² However, the latter systems also suffer from non-negligible drawbacks such as (i) the high costs of the rare-earth and rarest metals and (ii) the short nanosecond range lifetimes displayed by organic dyes taken separately. Thus, the design of alternative efficient long-lived emissive materials based on earth-abundant metals such as zinc, copper or chromium has become a major challenge to achieve.^{23,24} In this context, much attention has been paid to polypyridyl-Cr(III) complexes exhibiting strong and long-lived NIR emission arising from the lowest-lying metal-centered $\text{Cr}({}^2\text{T}_1)$ and $\text{Cr}({}^2\text{E})$ excited states. Remarkable advances involve the thorough investigation of pseudo-octahedral ter-bidentate Cr(III) complexes, such as $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{bpy})_3]^{3+}$, (phen = 1,10-phenanthroline, bpy = 2,2'-bipyridine), which display sharp emissions within the red to NIR region with lifetimes of several hundreds of μs .²⁵⁻²⁸ These archetypal complexes are chiral (D_3 symmetry with Δ and Λ isomers) and therefore intricate mixtures of diastereomers are formed when they are incorporated into

supramolecular architectures.²⁹ This shortcoming can severely hinder the molecular organization during the self-assembly, and, consequently, chiral resolution of the Cr(III) building blocks is critical. Interestingly, the closely-related centrosymmetric pseudo-octahedral bis-terdentate complex $[\text{Cr}(\text{tpy})_2]^{3+}$ (tpy = 2,2',6',2'' terpyridine) is achiral (D_{2d} symmetry) and allows in principle the preparation of isomerically pure linear supramolecular multicomponent assemblies. However, this complex exhibits a short excited-state $\text{Cr}({}^2\text{E})$ lifetime (140 ns) with a poor overall quantum yield which limit its uses.³⁰ It is worth noticing that chemical modification on tpy type ligands has recently been a strategy for chirality induction in related molecular systems such as Ru(II) and Fe(II) complexes.³¹ Inspired by the strategy employed by Hammarström and co-workers for improving the excited state lifetime of Ru(II)-polypyridine complexes and by McCusker and co-workers for the ligand design,³² Heinze and co-workers recently demonstrated that the coordination of two six-membered *N,N'*-dimethyl-*N,N'*-dipyridine-2-yl-pyridine-2,6-diamine chelate (ddpd, Scheme 1 left) to Cr(III) gave the pseudo-octahedral $[\text{Cr}(\text{ddpd})_2]^{3+}$ complex, which displayed an impressive lifetime (τ) of 889 μs and an overall quantum yield (Φ) of 11% in deaerated aqueous solution at room temperature.³³ The latter approach provides (i) less distorted excited states which limit non-radiative deactivation processes and therefore increase the excited state lifetimes,^{28,34} and (ii) strong ligand field preventing the operation of undesirable back-intersystem crossing $\text{Cr}({}^4\text{T}_2 \leftarrow {}^2\text{E}, {}^2\text{T}_1)$ (BISC), which is responsible for the low

quantum yields of most pseudo-octahedral Cr(III) complexes.³⁵ The deuterated version of this compound resulted in a further enhancement by factors of two and three of the lifetime and quantum yield, respectively.³⁶ A problem however arises because the *P* or *M* helical wrapping of the bound fused 6-membered chelate rings in $[\text{Cr}(\text{ddpd})_2]^{3+}$ (Scheme 1) restores chiral properties with the formation of three conceivable diastereomers: $[\text{Cr}(\text{M-ddpd})_2]^{3+}$, $[\text{Cr}(\text{P-ddpd})_2]^{3+}$ (i.e. an enantiomeric pair) and $[\text{Cr}(\text{M-ddpd})(\text{P-ddpd})]^{3+}$. The next obvious target is to either selectively induce the formation of one specific isomer, or to separate the various isomers obtained with these bis-terdentate Cr(III) complexes in order to implement chiroptical properties within the millisecond range. Accordingly, Cr(III)-polypyridyl complexes might act as sensitizers in diastereomerically pure supramolecular lanthanides-based energy converting devices.^{11,37–39} Major activity in this field is currently focused on the development of chiral materials including lanthanides metal complexes⁴⁰ and/or organic dyes⁴¹ (for instance helicene-type) showing Circularly-Polarized Luminescence (CPL),⁴² which represent the differential spontaneous emission of left and right circularly polarized light by luminescent systems. Within this context, metal-based CPL compounds have been described.⁴³ Nevertheless the use of first row metals is rare and mainly restricted to Zn(II) complexes and ligand-based emission.⁴⁴ Hence, chiral Cr(III) complexes have only been barely explored,⁴⁵ despite their advantageous characteristics (earth abundance, metal-based long excited state lifetimes, narrow emission bands, large energy gap between absorption and emission), which make them ideal candidates for the development of cheap emissive chiral materials. In addition the d-d spin flip emission is promising to favor important dissymmetry factor (g_{lum}) compared to MLCT transitions. To address this point, we report herein the synthesis of the pseudo-octahedral and kinetically inert $[\text{Cr}(\text{dqp})_2]^{3+}$ complex, (dqp = 2,6-di(quinolin-8-yl)pyridine, Figure 1), in which the two fused 6-membered chelate rings fulfill the aforementioned electronic and structural requirements for inducing favorable excited-state properties (long $\text{Cr}^{2\text{E}}$ lifetime and high quantum yield). Additionally, the twisted arrangement of the tridentate dqp ligands around the Cr(III) gets rid of the inversion center in the pair of $[\text{Cr}(\text{M-dqp})_2]^{3+}/[\text{Cr}(\text{P-dqp})_2]^{3+}$ chiral enantiomers (D_2 symmetry) whereas non-chirality is retained in the alternative S_4 -symmetrical $[\text{Cr}(\text{M-dqp})(\text{P-dqp})]^{3+}$ complex. Since the use of these Cr(III) complexes in the construction of enantiopure supramolecular assemblies and chiroptical materials require isolated enantiomeric building blocks, the thorough separation, resolution and chiro-optical characterization of $[\text{Cr}(\text{dqp})_2]^{3+}$ were achieved.

RESULTS AND DISCUSSION

Synthesis and structure of $\text{rac-}[\text{Cr}(\text{dqp})_2]^{3+}$ (**1**)

In order to overcome the reactivity problems associated with the kinetic inertness of Cr(III) salts, the homoleptic complex $[\text{Cr}(\text{dqp})_2]^{3+}$ (**1**) was readily obtained by the reaction of the labile precursor $\text{Cr}(\text{SO}_3\text{CF}_3)_2$ ¹² with 2,6-di(quinolin-8-yl)pyridyl (dqp)⁴⁶ followed by air oxidation affording $\text{rac-}[\text{Cr}(\text{dqp})_2]^{3+}$ with 60 % yield (Figure 1;

Figures S1-S3 and Appendix 1 in the Supporting Information). In agreement with the observed non-innocent redox behavior of the coordinated polypyridyl ligands in related Cr(III) complexes,⁴⁷ cyclic voltammetric (CV) studies showed two reversible waves located at $E_{1/2} = -770$ mV vs Fc^+/Fc and $E_{1/2} = -1245$ mV vs Fc^+/Fc , which were assigned to the successive reductions of the two coordinated ligands (Figure S3). Slow evaporation of a concentrated acetonitrile solution afforded single-crystals suitable for X-Ray diffraction. **1** crystallized in the triclinic phase (*P*-1, *Z*=2, Tables S1-S3). The unit cell contained the two enantiomeric PP - $[\text{Cr}(\text{dqp})_2]^{3+}$ and MM - $[\text{Cr}(\text{dqp})_2]^{3+}$ cations in racemic proportions and six triflate anions (Figure S4). The two tridentate ligands coordinate in a meridional fashion to the central Cr(III) ion with a twisted arrangement of the two organic strands along the pseudo- C_2 axis of the molecule (dihedral angles of ca. 36° and 44° between the central pyridine ring and the appended quinoline rings within each ligand, see Figure 1 and Table S3).

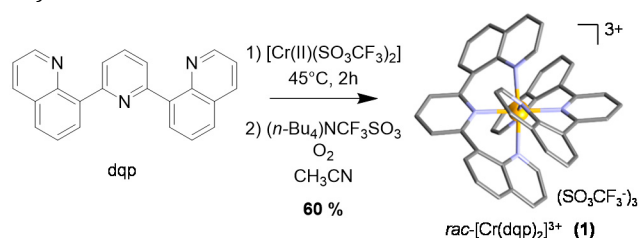
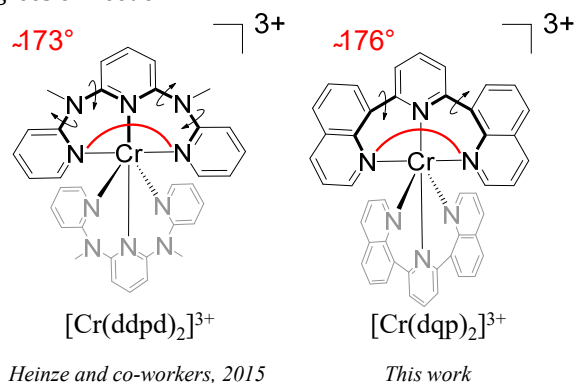


Figure 1. Synthesis of complex $\text{rac-}[\text{Cr}(\text{dqp})_2]^{3+}$ showing the D_2 -symmetrical MM - $[\text{Cr}(\text{dqp})_2]^{3+}$ cation in the crystal structure of its racemic form. Color codes: Cr (orange), N (blue), C (gray).

The Cr-N bond lengths are similar to those found in related polypyridyl Cr(III) complexes,^{30,33} and the N(terminal)-Cr-N(terminal) bite angles of $176.46(6)^\circ$ (Table S2) are close to those of a perfect octahedron (180°) and slightly larger than $173.56(8)^\circ$ reported for $[\text{Cr}(\text{ddpd})_2]^{3+}$ (Scheme 1).³³ A detailed geometrical analysis using $\Sigma = \sum_{i=1}^{12} |90 - \phi_i|$, where ϕ_i are the cisoid N–Cr–N bond angles, shows that $\Sigma = 29^\circ$ for $[\text{Cr}(\text{dqp})_2]^{3+}$ compared with $\Sigma = 36^\circ$ for $[\text{Cr}(\text{ddpd})_2]^{3+}$, a trend confirming a slightly larger distortion from ideal octahedral geometry for the latter complex. On one hand, the larger bite angles found in $[\text{Cr}(\text{dqp})_2]^{3+}$ further optimizes the metal-ligand orbital overlap and thus maximizes the ligand-field strength. On the other hand, the more rigid structure provided by the substitution of the methyl-amino pyridine groups attached at the 2,6-positions of the central pyridine in $[\text{Cr}(\text{ddpd})_2]^{3+}$ with two fused aromatic quinoline rings in $[\text{Cr}(\text{dqp})_2]^{3+}$ reduces the degree of freedom in both ligand and complex (Scheme 1). This may have a favorable effect in limiting non-radiative deactivation processes in the latter chromophore. Finally, as observed in its analogue $[\text{Ru}(\text{dqp})_2]^{2+,32}$ the extended aromatic quinoline rings of the homochiral twisted dqp ligands bound to Cr(III) pack on top of each other and produce some stabilizing intramolecular interstrand π -stacking interactions (distances between the centers of gravity of two adjacent quinoline units in the complex are approximately 3.5 Å, Figure S5), which may explain the high diastereoselectivity of the complexation reaction leading to the exclusive

formation of the enantiomeric PP -[Cr(dqp) $_2$] $^{3+}$ / MM -[Cr(dqp) $_2$] $^{3+}$ pair with no trace of the PM diastereomer.

Scheme 1. Molecular structures of molecular rubies highlighting N-Cr-N bite angles and the available rotational degrees of freedom.



Chiral resolution of rac -[Cr(dqp) $_2$] $^{3+}$ (**1**).

Enantiomeric resolution of closely-related pseudo-octahedral complexes have been reported for (i) helical non-covalent Cr(III) tripod receptors using cation-exchange chromatography,⁴⁸ (ii) bis-terdentate Cr(III) complexes using capillary electrophoresis (CE)⁴⁹ and (iii) analogous [Ru(dqp) $_2$] $^{2+}$ complexes with the help of auxiliary chiral TRISPHAT counter-anions.⁵⁰ Cation-exchange chromatography using SP Sephadex as stationary phase has been additionally proved to be efficient for the separation of polymetallic complexes.⁵¹ Rac -[Cr(dqp) $_2$] $^{3+}$ (**1**, 18 mg) was thus adsorbed onto a 90 cm length chromatography column charged with Sephadex SP-C25 ion-exchange resin and eluted with an aqueous solution of Na $_2$ Sb $_2$ [(+)-C $_4$ O $_6$ H $_2$] $_2$ 5H $_2$ O (0.15M). Two successive orange bands could be separated (fraction I and fraction II, Figure S8). Salt metathesis with KPF $_6$ finally led to the isolation of the two enantiomers (PP/MM)-[Cr(dqp) $_2$](PF $_6$) $_3$ in similar proportions. Single-crystals suitable for X-Ray diffraction could be obtained for fraction II by the slow evaporation of an acetone concentrated solution. The complex crystallized in the non-centrosymmetric orthorhombic Sohncke space group ($P2_12_12_1$, $Z=4$), confirming the chiral nature of the crystallized species. Since the dqp ligand does not possess stereogenic center, the chiral properties arises from the presence of chirality axis in the resulting complex. According to Cahn-Ingold-Prelog priority rules, crystals of fraction II contain the MM -[Cr(dqp) $_2$] $^{3+}$ enantiomer (left-handed helix, Flack parameter = 0.005(5), Figure S7). Structural features (angles and bond lengths) are gathered in Table S4-S6 and, as expected, they mirror those previously discussed for rac -[Cr(dqp) $_2$] $^{3+}$. Slight differences in the intermolecular interactions (i.e. packing) result from the substitution of CF $_3$ SO $_3^-$ with PF $_6^-$ counter-anions (Figure S6). The PP -[Cr(dqp) $_2$](PF $_6$) $_3$ enantiomer (fraction I) displays specific rotation $[\alpha]_D^{25} = +1730(40)$ deg·cm 3 ·mol $^{-1}$ ·dm $^{-1}$ and molar rotation $\varphi_{589}^{25} = +19964(100)$ deg·mol $^{-1}$ ·dm 2 which are opposed, within experimental uncertainties, to $[\alpha]_D^{25} = -1811(40)$ deg·cm 3 ·mol $^{-1}$ ·dm $^{-1}$ and $\varphi_{589}^{25} = -20898(100)$ deg·mol $^{-1}$ ·dm 2 measured for fraction II. These values are significantly higher than those reported for 3d/4f metal based-helicates,^{40,43,44,51} which confirms the strong helical

induction performed by the twisted dqp ligands. We therefore conclude that the first eluted fraction corresponds to PP -(+)-[Cr(dqp) $_2$] $^{3+}$ followed by MM -(-)-[Cr(dqp) $_2$] $^{3+}$ (Figure 2 and Figure S8). We were not able to detect traces of the third conceivable PM diastereomer, in agreement with the operation of an efficient diastereoselective induction accompanying the complexation process.

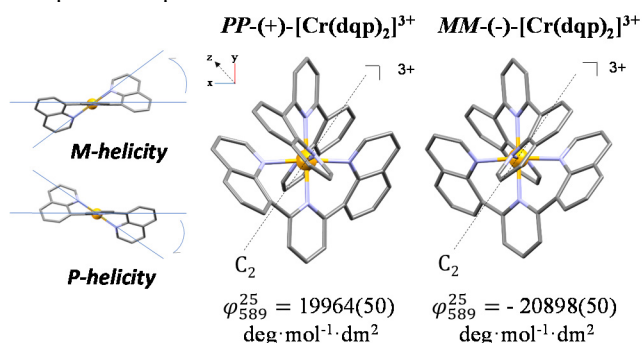


Figure 2. Crystal structures of the two enantiomers highlighting the molar rotations of the two different helices in acetonitrile.

Absorption and Emission properties of rac -[Cr(dqp) $_2$] $^{3+}$ (1**).** The absorption spectra of rac -**1** in water (Figure S9 and Table S7) show maxima between 280-350 nm ($\epsilon > 10^3$ M $^{-1}$ cm $^{-1}$), which can be attributed to standard intense $\pi^* \leftarrow \pi$ transitions, together with bands of lower intensities between 350-500 nm ($\epsilon < 10^3$ M $^{-1}$ cm $^{-1}$) assigned to mixed metal-centered and ligand-to-metal charge transfer (MC)/LMCT transitions. The weak transitions located at even lower energies (500-600 nm) are ascribed to the spin-forbidden $^3\pi^* \leftarrow \pi$ transitions.^{28,31} According to TD-DFT calculations, the shoulder at 401 nm (Figures S9 and S11, Table S7 and S10) can be ascribed to the spin-allowed Cr($^4T_2 \leftarrow ^4A_2$) transition, this in fair agreement with the expected stronger ligand-field strength in rac -**1** compared with [Cr(ddpd) $_2$] $^{3+}$ (430 nm).³³ The weak ($\epsilon < 1$ M $^{-1}$ cm $^{-1}$) spin-flip transitions Cr($^2E, ^2T_1 \leftarrow ^4A_2$) occurring in the red to near-infrared domain can be evidenced in concentrated aqueous solution (7.7 mM) (Figure 3 and Figure S10). The two absorption bands located on the high energy side (13758 and 14310 cm $^{-1}$) correspond to the splitting of the Cr(2T_1) state due to the drop in symmetry ($O \rightarrow D_2$).⁵² The low energy band (13354 cm $^{-1}$) can be thus assigned to the Cr($^2E \leftarrow ^4A_2$) transition.

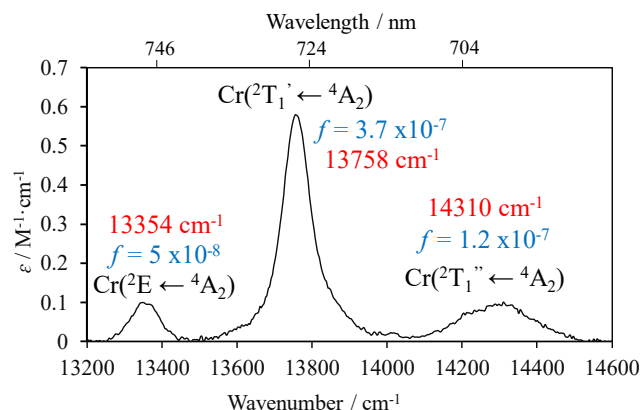


Figure 3. Absorption spectrum of complex *rac*-[Cr(dqp)₂]³⁺ in water at 293 K (*c* = 7.7 mM) highlighting the calculated values of the oscillator strengths f_{exp} for each spin-flip transition.

The associated experimental oscillator strengths, f_{exp} (eq. 1), are in the order of 10^{-7} , in agreement with previous data reported for related Cr(III) compounds,⁵³ but significantly smaller than 10^{-6} found in lanthanides complexes.⁵⁴ This is due to the double forbidden character (electric-dipole and spin) of the d-d spin-flip transitions in Cr(III), whereas the large spin-orbit coupling constant relaxes the spin limitation for 4f block cations.

$$f_{\text{exp}} = \frac{2303 mc^2}{N_a \pi e^2} \frac{1}{X} \int \epsilon(\tilde{\nu}) d\tilde{\nu} = 3.63 \times 10^{-9} \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (1)$$

In eq.1, m is the electron mass, c is the velocity of the light in vacuum, N_a is Avogadro's number, e is the electron charge, $X = (n^2 + 2)^2 / 9n$ is the local correction where n is the refractive index of the medium, $\tilde{\nu}$ is the wavenumber and ϵ is the molar absorption coefficient.

At room temperature and upon excitation at 355 nm, *rac*-1 exhibits two sharp emission bands at 747 nm (13395 cm⁻¹) and 724 nm (13802 cm⁻¹) which correspond to the respective spin flip Cr(²E → ⁴A₂) and Cr(²T₁ → ⁴A₂) transitions. At 77 K, the thermally-driven population of the Cr(²T₁) excited state vanishes and only the narrow Cr(²E → ⁴A₂) phosphorescence can be recorded (Figure 4a). Compared with related complexes [Cr(ddpd)₂]³⁺, [Cr(ddpd)(tpy)]³⁺, [Cr(H₂tpda)₂]³⁺ (H₂tpda = 2,6-bis(2-pyridylamino)pyridine) and [Cr(tpy)₂]³⁺ the excited Cr(²E) state in [Cr(dqp)₂]³⁺ is blue shifted, by more than 400 cm⁻¹, while the excited Cr(²T₁) state of all these complexes are almost isoenergetic.^{30,33,52,55} Consequently, the Cr(²T₁/²E) energy gap is reduced by a factor two and amounts to only 420 cm⁻¹ in [Cr(dqp)₂]³⁺ (Figure 4b). Additionally, the emission bands in *rac*-1 are much narrower (full width at half height FWHH = 220 cm⁻¹) with respect to [Cr(ddpd)₂]³⁺, [Cr(tpy)₂]³⁺ (FWHH = ~ 400 cm⁻¹) and [Cr(H₂tpda)₂]³⁺ (FWHH = 350 cm⁻¹). This confirms minor geometry change between the ground Cr(⁴A₂) state and the excited Cr(²E), and Cr(²T₁) states (Figures S12 and Figure S13). Additionally, the excitation spectra recorded upon monitoring the emission bands at 747 nm and 724 nm (13395 cm⁻¹ and 13802 cm⁻¹ respectively) closely match the absorption spectrum, demonstrating the participation of $\pi\pi^*$, LMCT and LMCT/MC excited states for feeding the emissive Cr-centered doublet states (Figure 4c).

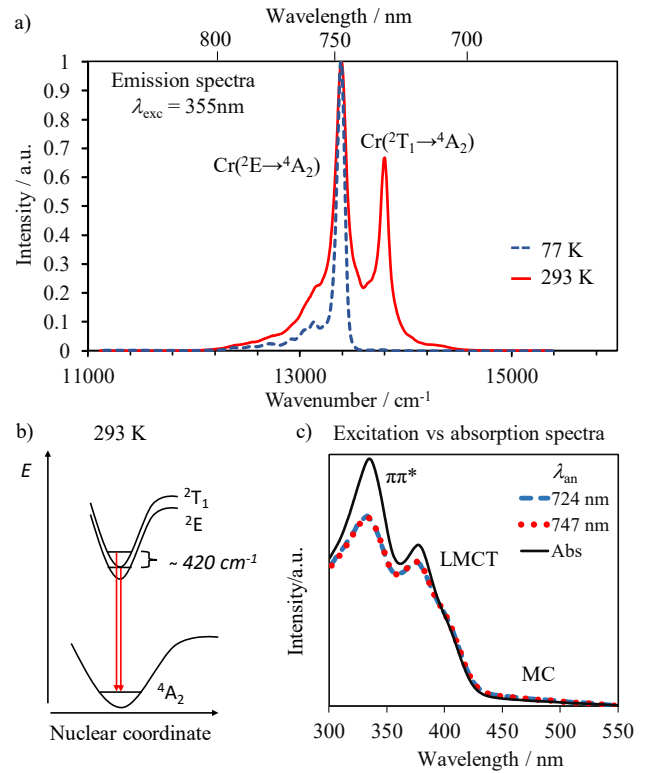


Figure 4. (a) Emission spectra of *rac*-[Cr(dqp)₂]³⁺ at 293 K (H₂O) and 77 K (H₂O/DMSO), (b) associated schematic energy diagram including the energy levels and (c) excitation spectra (λ_{an} = 724 nm dashed blue line and λ_{an} = 747 nm red dotted line) and absorption spectrum (black trace) (λ_{exc} = 355 nm).

Racah parameters B and C have been estimated with the help of eqs 2-4 (Table S8).⁵⁶

$$E(^4T_2) = \Delta \quad (2)$$

$$E(^2T_1) = 9B + 3C - 24(B^2/\Delta) \quad (3)$$

$$E(^2E) = 9B + 3C - 50(B^2/\Delta) \quad (4)$$

The concomitant increase of both ligand-field strength (Δ = 22883 to 24937 cm⁻¹) and nephelauxetic effects (B = 763 to 656 cm⁻¹) in going from [Cr(ddpd)₂]³⁺ to [Cr(dqp)₂]³⁺ combined with the predicted $E[\text{Cr}(^2\text{E})] - E[\text{Cr}(^2\text{T}_1)] = 26(B^2/\Delta)$ energy gap (eqs 3-4) explains the small separation between the two emissive spin-flip states in [Cr(dqp)₂]³⁺, a strong point for its potential use as molecular thermometer at low temperature.⁷

Table 1. Kinetic rate constants and emission quantum yields recorded for *rac*-[Cr(dqp)₂]³⁺ in water at 293 K.

$k_{\text{Cr,rad}}^a$ /s ⁻¹	$k_{\text{Cr,rad}}^{2T_1}$ /s ⁻¹	$k_{\text{Cr,nrad}}^{2E}$ /s ⁻¹	$k_{\text{Cr,nrad}}^{2T_1}$ /s ⁻¹	$\tau_{\text{Cr,rad}}^c$ /ms	$\tau_{\text{Cr,rad}}^{2T_1}$ /ms	$\tau_{\text{Cr,obs}}^{2E, 2T_1}$ /ms	Φ_{Cr}^{2E} /%	$\Phi_{\text{Cr}}^{2T_1}$ /%	Φ_{Cr}^L /%	Φ_{Cr}^L /%	$\eta_{\text{sens}}^{L \rightarrow \text{Cr}}$ /%
10(1)	35(3)	798(15)	823(15)	98(8)	29(2)	1.2(1)	1.2(1)	4.2(4)	5.2(4)	1.0(1)	96(7)

^a k_{rad} obtained from eq. 5. ^b $k_{\text{nrad}} = (1/\tau_{\text{obs}}) - k_{\text{rad}}$. ^c $\tau_{\text{rad}} = 1/k_{\text{rad}}$. ^d τ_{obs} from time-resolved experiments at 293K (deaerated solution). ^e Intrinsic quantum yield of the specified Cr level $\Phi_{\text{Cr}}^L = \tau_{\text{obs}}/\tau_{\text{rad}}$. ^{f,g} Overall quantum yield Φ_{Cr}^L determined by absolute method using an integration sphere (λ_{exc} = 410 nm) in /deaerated and /aerated solutions. ^h $\eta_{\text{sens}}^{L \rightarrow \text{Cr}} = \frac{\Phi_{\text{Cr}}^L}{\Phi_{\text{Cr}}^{2E} + \Phi_{\text{Cr}}^{2T_1}}$. Lifetime: estimated relative uncertainty $\pm 10\%$. Quantum yield: estimated relative uncertainty $\pm 10\%$

Room temperature overall luminescence quantum yields (Φ_{Cr}^L) determined for *rac*-[Cr(dqp)₂]³⁺ in diluted aqueous solution upon excitation at 410 nm amount to 5.2% (deaerated) and 1.0% (aerated) (Table 1). These values are among the highest so far reported^{2,33,55} and can be reasonably associated with the strong ligand field provided by the dqp ligand ($\Delta = 24937 \text{ cm}^{-1}$) which increases the energy gap between the Cr(²T₁,²E) and Cr(⁴T₂) levels, thus preventing back-intersystem crossing (BISC). Time-resolved experiments in deaerated aqueous solutions displayed mono-exponential decays yielding $\tau_{Cr,obs}^{2T_1} = \tau_{Cr,obs}^{2E} = 1.2 \text{ ms}$ at 293 K and $\tau_{Cr,obs}^{2E} = 3 \text{ ms}$ at 77 K (Figure S15-S17, Table S9). The identical room temperature lifetimes measured for the Cr^{III}(²E) and Cr^{III}(²T₁) levels together with similar excitation spectrum indicate thermal equilibrium of those states. The much longer low-temperature lifetime evidences the operation of efficient thermally-activated non-radiative deactivation processes operating in *rac*-[Cr(dqp)₂]³⁺. Even so, τ_{obs} at 293K remains in the millisecond regime which, to the best of our knowledge, currently represents the highest value reported for a Cr(III)-based complex bearing deuterium-free ligands. This enhancement in the lifetime compared to previous Cr(III) chromophores can be traced back to the only minor distortions from octahedral geometry, which avoids the pernicious ²E/⁴A₂ surface crossing due to the anharmonic potential misalignment that considerably reduces the excited state lifetime.^{28,34} In the solid state, the operation of efficient intermolecular energy transfers due to concentration-quenching mechanisms severely shorten the Cr(²T₁,²E) emission lifetimes and bi-exponential traces are observed in the phosphorescence decays as often observed for Cr(III) complexes (3.2 μ s and 0.6 μ s; Figure S14).^{28,52} The intrinsic radiative rate constant ($k_{rad} = 1/\tau_{rad}$) for the Cr(²E) and Cr(²T₁) excited states were experimentally determined by the integration of the Cr(²E,²T₁ ← ⁴A₂) transitions evidenced in the absorption spectrum (Figure 3), followed by the application of Einstein relationship (eq. 5), where c is the velocity of the light in vacuum, N_A is Avogrado's number, n is the refractive index of the medium, $\tilde{\nu}$ is the transition wavenumber, ϵ is the molar absorption coefficient, $(2S + 1)(2L + 1)$ is the degeneracy of the ground state and $(2S' + 1)(2L' + 1)$ represents the degeneracy of the excited state.

$$k_{rad} = 2303 \times \frac{8\pi c n^2 \tilde{\nu}^2 (2S + 1)(2L + 1)}{N_A (2S' + 1)(2L' + 1)} \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (5)$$

The computed values of $k_{Cr,rad}^{2E} = 10(1) \text{ s}^{-1}$ and $k_{Cr,rad}^{2T_1} = 35(3) \text{ s}^{-1}$ (Table 1) show that the Cr(²T₁) state is intrinsically three times more emissive than the Cr(²E) one, a prediction which seem to mismatch the observed relative emission intensity (Figure 4a). According that the steady-state emission I_{Cr} is given by the product of the normalized steady-state population of the excited level (N_{Cr}) with its radiative rate constant, the expected intensity ratio at 293 K is indeed given

by $\frac{I_{Cr}^{2E}}{I_{Cr}^{2T_1}} = \frac{N_{Cr}^{2E}}{N_{Cr}^{2T_1}} \times \frac{k_{Cr,rad}^{2E}}{k_{Cr,rad}^{2T_1}}$. Computation using Boltzmann

partition for modeling the population ratio between the two doublet excited states separated by an energy gap $\Delta E = 420$

cm^{-1} affords $\frac{I_{Cr}^{2E}}{I_{Cr}^{2T_1}} = \left(\frac{4}{6}\right) \times \exp\left(-\frac{\Delta E}{RT}\right) \times \left(\frac{10}{35}\right) = 1.54$, which

fairly matches the experimental ratio of 1.53 (Figure 4a) and corroborates thermal equilibration between ²E and ²T₁ states.

The associated intrinsic quantum yields ($\Phi_{Cr}^{Cr} = k_{Cr,rad} /$

$(k_{Cr,rad} + k_{Cr,nrad})$, Table 1) reach few percent, which reveals the detrimental contribution of non-radiative deactivation processes at room temperature. Interestingly, the overall quantum yield $\Phi_{Cr}^L = 5.2(4)\%$ recorded for *rac*-[Cr(dqp)₂]³⁺ at 293 K upon ligand excitation approaches the global intrinsic Cr-centered emission quantum yield $\Phi_{Cr}^{Cr} = \Phi_{Cr}^{Cr(2E)} + \Phi_{Cr}^{Cr(2T_1)} = 5.4(4)\%$. This implies a sensitization efficiency for funneling the energy from the ligand excited states onto the emissive Cr(III) excited levels which is close to be quantitative ($\eta_{sens}^{L \rightarrow Cr} = \Phi_{Cr}^{Cr} / \Phi_{Cr}^L = 96(9)\%$, Table 1). Please note that this yield is calculated for excitation at 355 nm, and might change upon excitation at different energy in line with the minor intensity discrepancy observed between absorption and excitation spectra (Figure 4c).

Circular dichroism (CD) and Circularly-Polarized Luminescence (CPL) of *PP*-[Cr(dqp)₂]³⁺ and *MM*-[Cr(dqp)₂]³⁺. The CD spectra of the *PP*-(+)-[Cr(dqp)₂]³⁺ and *MM*-(-)-[Cr(dqp)₂]³⁺ in acetonitrile (290-500 nm range) display mirror images, which indicates that enantiopure enantiomers were successfully isolated (Figure 5). The enantiomers show two main well-resolved transitions in the 290–350 and 350–500 nm ranges with strong Cotton effects at 318 nm and 414 nm. The three CD transitions within the 290–390 nm range are ascribed to ligand-centered transitions ($\pi^* \leftarrow \pi$) while those at lower energies (390-500 nm) are attributed to LMCT and metal-centered transitions. Unfortunately, the weak spin-forbidden Cr(²T₁,²E ← ⁴A₂) transitions escape detection as we could not record CD spectra for concentrated solutions. TD-DFT calculations based on the geometry obtained for the molecular structure of the *PP* enantiomer in the crystal structure of *rac*-[Cr(dqp)₂](SO₃CF₃)₃, allowed us to confirm that the strong positive Cotton effect at 318 and 414 nm are compatible with the *PP* helical configuration, and therefore the opposite negative Cotton effects characterize the *MM* helical configuration (Figure S18 and Table S10).

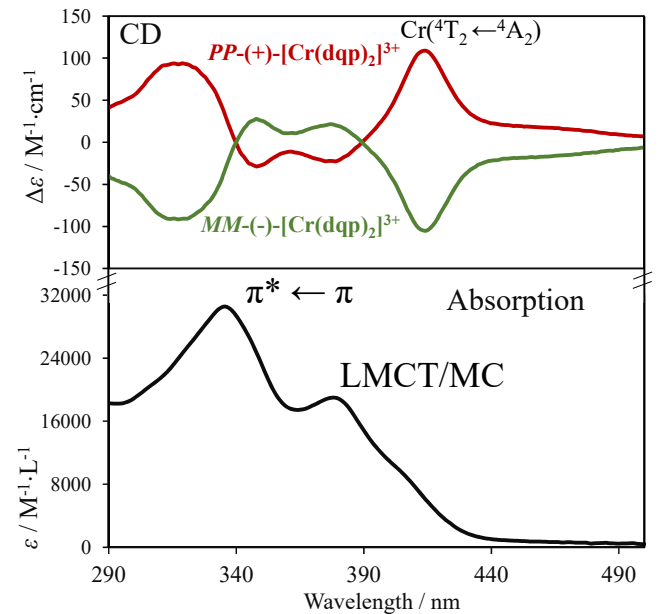


Figure 5. CD spectra of *PP*-(+)-[Cr(dqp)₂]³⁺ (red) and *MM*-(-)-[Cr(dqp)₂]³⁺ (green) (top) and associated absorption spectrum (bottom) in acetonitrile (5·10⁻⁴ M, 293 K).

The absorption dissymmetry factor, $g_{\text{abs}} = 2(\epsilon_{\text{L}} - \epsilon_{\text{R}})/(\epsilon_{\text{L}} + \epsilon_{\text{R}})$, where ϵ_{L} and ϵ_{R} are the molar absorption coefficient for left and right circularly polarized light, are in the order of 10^{-3} – 10^{-4} for the $\pi^* \leftarrow \pi$ transitions (Figure S19). These values are typical for pure organic molecules where the electronic transitions are electric-dipole (ED) allowed and magnetic-dipole (MD) forbidden. In contrast, due to the presence of magnetically-allowed metal-centered d-d transitions $\text{Cr}(^4\text{T}_2 \leftarrow ^4\text{A}_2)$ occurring at lower energy (390–500 nm), the g_{abs} is reinforced to reach values up to 0.012 (Figure S19). Interestingly, the CD spectra do not change over month periods, which confirms the well-known Cr(III) ligand exchange kinetic inertness and the resulting lack of racemization in solution at room temperature (Figure S20).

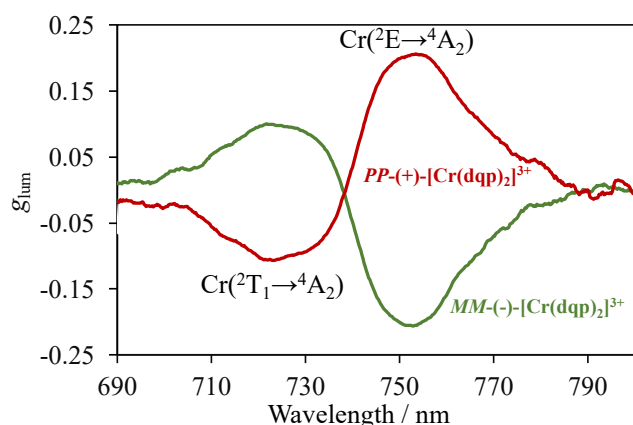


Figure 6. CPL spectra of $PP-(+)-[\text{Cr}(\text{dqp})_2]^{3+}$ (red) and $MM-(-)-[\text{Cr}(\text{dqp})_2]^{3+}$ (green) in deaerated acetonitrile solutions ($5 \cdot 10^{-5}$ M, $\lambda_{\text{exc}} = 390$ nm).

Upon non-polarized excitation at 390 nm ($5 \cdot 10^{-5}$ M in CH_3CN), $PP-(+)-[\text{Cr}(\text{dqp})_2]^{3+}$ and $MM-(-)-[\text{Cr}(\text{dqp})_2]^{3+}$ showed two circularly polarized emission bands at 749 and 728 nm corresponding to $\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$ and $\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$ transitions, respectively (Figure 6 and Figure S21). The degree of the CPL intensity is usually assessed in terms of the luminescent dissymmetry factor $g_{\text{lum}} = 2(I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$, where I_{L} and I_{R} represent the left and right circularly polarized emission intensities, respectively (with $-2 \leq g_{\text{lum}} \leq 2$). Interestingly the $\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$ and $\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$ emissions show g_{lum} of opposite signs for each enantiomer. Furthermore the $|g_{\text{lum}}|$ values in both deaerated (Figure 6), and aerated CH_3CN solutions (Figure S22) were found to be 0.2 and 0.1 for the respective $\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$ and $\text{Cr}(^2\text{T}_1 \rightarrow ^4\text{A}_2)$ transitions. The higher value displayed by the emission from $\text{Cr}(^2\text{E})$ regarding $\text{Cr}(^2\text{T}_1)$ is in line with the relative radiative rate constants ($k_{\text{Cr,rad}}^{^2\text{E}} < k_{\text{Cr,rad}}^{^2\text{T}_1}$), which mirror the more important electric dipole interdiction of the $\text{Cr}(^2\text{E} \rightarrow ^4\text{A}_2)$ transition. Interestingly, these impressive values are one or two order of magnitude higher than those found for molecular-helicenes⁴¹ or d block metal complexes.^{43,48} They are comparable with chiral lanthanide-based f $\rightarrow$ f intrashell transitions found for Eu-containing systems with chiral DOTA-based or BINAPO-based ligands.⁵⁷ The outstanding dissymmetry factor of $[\text{Cr}(\text{dqp})_2]^{3+}$ is the consequence of the

magnetically allowed and strongly electrically dipole forbidden nature of the d-d $\text{Cr}(^2\text{E}/^2\text{T}_1 \rightarrow ^4\text{A}_2)$ transitions, a trend which contrasts with the commonly described ligand-centered or charge transfer transitions displaying weak $|g_{\text{lum}}|$ values. While d-block CPL is currently dominated by weak dissymmetry factors collected for charge transfer emission of 4d and 5d metals⁴³ or for ligand-centered luminescence of Zn^{2+} complexes,⁴⁴ $[\text{Cr}(\text{dqp})_2]^{3+}$ competes with the strong CPL signals reported for lanthanide-based f-f transitions, thus making this earth abundant metal-based complex a good candidate for the replacement of rare earth in chiroptical applications.

CONCLUSION

The binding of the semi-rigid achiral bis-6-membered chelating dpq ligand around inert Cr(III) centers is highly stereoselective and leads to a pair of enantiomers $PP-(+)-[\text{Cr}(\text{dqp})_2]^{3+}$ and $MM-(-)-[\text{Cr}(\text{dqp})_2]^{3+}$. The very minor distortions from octahedral symmetry of the chromium chromophore provides a rare strong (5.2% quantum yield) and long-lived (1.2 ms) room temperature Cr(III)-centered dual phosphorescence in water. Chromatographic techniques succeeded in separating the two helical $PP-(+)-[\text{Cr}(\text{dqp})_2]^{3+}$ and $MM-(-)-[\text{Cr}(\text{dqp})_2]^{3+}$ enantiomers. Their circular dichroism (CD) and circularly polarized luminescence (CPL) spectra show mirror images supported by thorough TD-DFT theoretical calculations for the CD spectra. The impressive luminescent dissymmetry factors g_{lum} produced by the magnetic-dipole allowed, but electric-dipole forbidden d-d spin-flip transitions in $[\text{Cr}(\text{dqp})_2]^{3+}$ overpass by at least one order of magnitude those previously recorded for d-block complexes, which makes the latter complex comparable with rare earth centers. Since, the rich chemistry of Cr(III) polypyridyl complexes is compatible with the tuning of both emission energy and of g_{lum} through the control of the radiative constants, these enantiomeric Cr(III) complexes are promising candidates for working as chiral sensitizers in polarized light downshifting⁵⁸ and light-upconversion processes.⁵⁹ This study paves the way towards the incorporation of earth abundant near-infra-red CPL emitters into films or polarized photonic devices. Finally the magnitude of g_{lum} reaches the value required for the development of circularly polarized laser emission using solution dyes.⁶⁰

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge on the ACS publications website. Experimental details; Crystallographic data; absorption, emission spectra; list of transition bands; decay curves.

Accession Codes. CCDC 1920463–1920464 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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