Pisa, 30th August 2024

Dear Prof. Gabbaï,

We are submitting a revised version of our manuscript ***Magnetic circularly polarized luminescence from spin flip transitions in a molecular Ruby***

We thank the referees for their comments and their overall positive assessment of our work. We believe we have improved the manuscript by clarifying a few points and improving our data analysis.

We attach in the following a point-by-point reply to all referees’ comments.

We hope that now the manuscript can be considered acceptable for publication in *Chemical Science*.

Yours sincerely



**Referee: 1**

Comments:  
It is obviously a brilliant work in photophysical properties of transition metal complexes. Responsiveness of transition metal complexes towards magnetic field is one of the important topics in inorganic chemistry. The salient feature of the current submission are on the data analysis on the magnetic CPL (MCPL) and magnetic CD (MCD) obtained with a spin-flip and phosphorescent Cr(III) complexes. I am not working on the MCPL/MCD spectroscopy, and hence my comments could be general. I suggest the following minor revisions:

(1)     The abstract of the current submission is too general and is lack of results and conclusion. The readers cannot grasp the most important data from the abstract.

We have rewritten the abstract to make it clearer and more specific.

(2)     Throughout the main text including the figure captions, the reader cannot find how these important MCPL/MCD data were measured. For example, the authors did NOT provide in the main text the information of the solvent used for measurement. The authors failed to provide how the applied magnetic field was continuously tuned from -1.5 T to +1.5 T.

We thank the reviewer for pointing this out. We now have added this information in the captions of Fig. 2 and 3, and in the text at the beginning of the Results section: “Optical and magneto-optical studies reported here were performed on deareated acetonitrile solutions of the racemic compound ([Cr(dqp)2](PF6)3).”

The MCPL measurements were reported at constant magnetic field (0.4 T), as our MCPL setup employs a permanent magnet, as specified in the experimental part in the supporting information file. Positive and negative field CPL spectra were acquired by simply reversing the magnet. We have explicitated this in the main text.

In MCD characterization we also performed spectra at different fields, as well as MCD vs field plots. Indeed, MCD setup is equipped with an electromagnet, which is made of two coils and two perforated iron cylinders at a distance of about 5 mm. The sample is placed between the two iron cylinders, where the magnetic field is concentrated. The electromagnet is able to vary the applied field in the range +/- 1.4 T, by changing the current passing in the coils. We have now added this information in the experimental part related to MCD, in the supporting information file: “MCD vs field plots in the +1.4/-1.4 T range were also acquired by regulating the current passing in the coils of the electromagnet. The strength of the magnetic field was measured with a Hall probe.”

(3)     To my knowledge, the MCPL/MCD should be in strict mirror images for an achiral or racemic system under applied S(+) and S(-) magnetic field (BTW, the authors should explain a little more how to define S(+) and S(-)). The authors provided semi-difference MCPL field, aiming to eliminate all the magnetic-independent contributions, such as baseline effects and possible artefact signals due to photoselection. I understand this is possibly a general method for data curation, but the authors should elaborate here to the readers not familiar with the MCPL technique, such as me.

For what concerns the definitions of positive and negative fields, we refer to the standard convention used in MCD spectroscopy, which we know added in the manuscript text: “Positive and negative fields are here defined as parallel and anti-parallel to the k-vector, i.e. the propagating direction of light.”

Regarding the elimination of artifacts in MCPL and MCD, it is routinely done by making the semidifference between the signal with positive and negative fields. In this way all the contributions (artefacts) that do not depend on the magnetic field are eliminated in the subtraction. This is a peculiar advantage of magneto-optical techniques, where the signal reverses its sign by reversing the magnetic field. Baseline subtraction is particularly important in MCPL, where the signal is only arising from the sample, thus a blank cuvette would not give any signal. As typical MCPL signal is at least 1 order of magnitude lower than CPL, it is particularly important to clean the signal through the semi-difference between the two fields, as non-perfect alignment of the optical components can give an apparent CPL signals which should have to be subtracted.

We have expanded the text to better explain this concept: “Baseline effects and possible artefact signals due to photoselection, cause some deviation from the mirror image relationship expected for spectra obtained under opposite magnetic field, especially in the case of small signals (Figure S3a). The data treated according to Eq. 2 ensures that such artefacts, which are magnetic field-independent, are eliminated and only the true MCPL is recovered”

**Referee: 2**

Comments:  
In this manuscript, the authors investigated magnetic circularly polarized luminescence (MCPL) of [Cr(dqp2]3+. The electronic structures of this complex were characterized by the UV-vis, magnetic circular dichroism (MCD), MCPL, and high-frequency and -field EPR (HFEPR) spectroscopy. The MCD and MCPL spectra were quantitatively analyzed by a band deconvolution method, and the HFEPR spectra were analyzed based on spin-Hamiltonian of the quartet state. The precise analyses are plausible and useful, and therefore, this manuscript seems to be publishable. However, before accepting this manuscript, the authors should address the following points.

1, The authors described “This confirms that magneto-optical techniques are excellent tools to study SF transitions.”, but the previous papers related to the MCD of SF transitions (ex. European Journal of Inorganic Chemistry, 2017, 5103-5107, 2017. Journal of Physical Chemistry Letters, 11, 9828-9833, 2020.) were not cited. The authors should cite them to clearly show the positioning of this research.

In the introduction, we have added a sentence related to the previous MCD studies mentioned by the reviewer: “MCD was also used to study far red/near infrared (NIR) transitions in the case of Ir or Pt complexes,67,68 where their observation through emission, and thus MCPL, is challenging. On the other hand, emissive Cr(III) compounds are potentially a more suitable platform to address metal transitions through MCPL.” The suggested references have been added as well (new refs 67 and 68).

2, In Table S1, the authors analyzed the 4A2→4T2 transitions using the UV-vis and MCD spectroscopy. Firstly, the peaks 1-3 should be explained using zero field splitting and Zeeman splitting like Figure 4 for the general readers. The second is the notation. Does the δ value mean the 1/2 ZFS? What is the meaning of w = peak width? Full Width at Half Maximum? The authors should clarify the notations.

It is true that the fine structure of the ground level due to Zeeman splitting and ZFS splitting play a role in determining the whole shape of the MCD spectrum, which is probably given by C and B terms and possibly higher energy transitions overlapping. As it is not possible here to disentangle all the contributions, the analysis is merely phenomenological, as we do not make assumptions on the origin of the MCD signals, rather we are only interested in the energy barycenters of the 3 4A2→4T2 transitions. We have tried to make the nature of the analysis clearer. Note that we closely followed the method proposed by van Slaageren et al. reported in a few works for similar complexes (e.g. 10.1039/C9CP00745H, 10.1002/chem.202202898).

We confirm that w is the full width at half maximum of the peak, and we corrected this in the caption of Figure S1, where it is now called σ for consistency. We removed the δ notation, and we corrected a missing “2” factor to describe the full ZFS.

The third is the “Standard Error”. The Standard Error (3112 cm-1) of the energy of peak 1 seems to be much larger than those of peaks 2 and 3, and therefore, it seems to be inappropriate for the detailed analyses. The authors should check them carefully.

We agree that the fitting of peak 1 is affected by a significant error. However, the obtained energies give comparable results in terms of D and E values with respect to HFEPR analysis, which make us confident that the results are reliable.

We have clarified in the text that these results are however approximate and affected by a large error.

3, The authors measured the HFEPR spectra of a polycrystalline sample or a pellet sample, and described “a single crystal oriented with the z-axis of the ZFS tensor parallel to the magnetic field B0”. The review think it is better to investigate the frozen solution of [Cr(dqp)2]3+ as a randomly oriented sample. The authors should examine it.

It is true that a frozen solution can provide a random distribution of molecules relative to the field, but so does a pellet. The main advantage of a solution over a pellet is that it provides magnetic dilution. However, our spectra do not show a need for magnetic dilution as the resonances are crisp and narrow, and show little or no sign of magnetic interactions between the spins. A frozen solution experiment has also drawbacks: (a) the solvent heavily absorbs sub-THz waves reducing the S/N ratio, (b) the solvent needs to form a good low-temperature glass, and (c) most importantly, one needs to achieve sufficient concentration to observe a spectrum. This concentration limit differs from one transition ion to another, but a good guess for Cr(III) in our spectrometer would be at least 10 - 50 mM.

**Referee: 3**

Comments:  
The manuscript reports on the magneto-optical study of the Cr(III) complex, [Cr(dqp)2]3+, with quasi-octahedral coordination. This complex is chiral and well known for its circular-polarized photoluminescence (CPL), but the influence of magnetic field on CPL and spin-flip emission in such complexes has not been studied yet. The authors demonstrate clear magnetochiral response in luminescence and absorption spectra and reconstruct the structure of ground state levels based on these data. High-frequency EPR study is also performed to determine ZFS parameters and to demonstrate the reliability of the parameters determined from M-CPL measurements. I find the work to be well organized and performed, results will be of high interest to the broad audience, and the manuscript can be recommended for publication in Chem Sci. However, I have two questions, which the authors may consider in the revised version.

1.      First, in the emitting 2E state, the authors consider only the lowest-energy component. It is not very clear why they can ignore the higher-energy components. What is the size of the splitting? What could be thermal populations for that higher state at room temperature?

From the better resolved PL spectrum in Fig. S2, we see a weak band lying around 710 nm (approx. 14100 cm-1), which could be associate to the higher energy component of the 2E state (E is doubly degenerate). This component is well separated from the main 729 nm one and it is very weak in PL with non-significant associated MCPL. Therefore, it can be ignored in the MCPL analysis. We have clarified this better in the revised text.

2.      Second, the scheme in Figure 4 considers two non-interacting Kramers doublets in the ground 4A2 state. However, it is clear from the EPR data (Fig. 5) that there seems to be avoided crossing between the levels in the field of 0.4 T (used in MCPL measurements) and hence considerable mixing. The authors can compute this precisely since they have precise spin Hamiltonian parameters from HFEPR measurements. In the situation of mixing, I doubt that the simple rigid-shift approximation remains valid. I think the authors might analyze this situation more carefully.

We thank the referee for raising this important point. Prompted by this suggestion, we computed the mixing coefficients from EPR data. Indeed, considering for example *B0*|| *z*, we see that, while the outer levels have a rather well-defined character of +1/2 and -3/2 (highest and lowest one respectively), the inner ones are mixtures of -1/2 and +3/2. We have added two new tables (Table S3, S4) in the SI with the mixing coefficients at 0.4 T, as well as an expansion of the EPR levels at low field (Fig. S11).

This also prompted us to improve the analysis of the MCPL data. In the new analysis, we reduced the free parameters and underlying assumptions to explain the MCPL spectrum. Instead of leaving as free parameter the energies of the four ground state levels, in the analysis of MCPL we have now used HFEPR energy levels at 0.4 T (the new Fig. 4 reflects this change). In the new fitting (Fig. 2) only the asymmetry parameter dA is left free, while σ, areas and energy barycenter of the transitions are fitted according to usual rigid shift procedure.

To the best of our knowledge, there is no literature on the treatment of magnetooptical data in the presence of mixed levels. For this reason, we can only treat transitions between pure levels. We are aware that the mixing will affect the purely polarized character of the transitions, which is one of the requirements of the rigid shift approach. Despite this and despite having reduced the number of free parameters, the MCPL is still reasonably well reproduced (new Fig. 2). The overestimation of the simulation with respect to the experimental data may be explained by considering that the state mixing will somewhat reduce the intensity of the simulated MCPL spectrum. We have added these considerations in the revised text.A more quantitative treatment of the mixing in the MCPL data is beyond the scope of the present work, but we expect to expand on the problem in future works.

Note that the rigid shift requirement that the state splitting of the levels is much smaller than the linewidth is still respected.

Small remarks:

Page 3, the phrase “we followed the method proposed by van Slageren et al. (see ESI).72” I think, the reference number here should be 73, not 72

Table S1: peak width is denoted as σ in the table and w in the footnote

In the section “Analysis of MCPL data” in SI, reference to Figure S5 should be changed to Figure S6.

The first paragraph after eq. S13, correct “Table SX” to “Table S2”

Caption to Figure S8: “field dependence of the magnetization at 2 K (inset)”. “2 K” should be corrected to “2–7 K”.

We have corrected the mistakes. We thank the reviewer for noticing them.