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# Dalton Transactions Editorial Office

Geneva, August 15, 2020

Concern: Submission of revised manuscript transferred from *Chem. Comm.* to *Dalton Trans.* (manuscript ID: CC-COM-07-2020-004934)

# Dear Dalton Transactions Editorial Office,

With this letter, we herein submit a revised manuscript entitled “Luminescent Polypyridyl Heteroleptic CrIII Complexes with High Quantum Yields and Long Excited State Lifetimes”. This manuscript was examined for publication in *Chem. Comm.* and the two contacted referees recommended transferring to Dalton Transaction after revision. We would like to thank the editor and the reviewers for their constructive comments. All referee comments and queries have been addressed in the revised version. The modifications in the manuscript are highlighted in yellow. Point by point replies to editor and reviewers comments are detailed on the following pages.

**Reviewer 1:**

First, we would like to thank reviewer 1 for his/her constructive comments and advices and for his/her extensive reading.

*1) Page 1, left column – “Earth crust”*

Authors reply: It has been corrected.  
  
*2) Page 1, right column – the section following Scheme 1 feels under-referenced. Similarly, the complex [Cr(ddpd)2]3+ is mentioned in a number of places without a literature citation? See, for example, page 3, left column (“related homoleptic…”) as well as page 4 “deuterium-free Cr(III) complexes…”*

Authors reply: Adapted references have been placed and/or added

4. S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger and K. Heinze, *Angew. Chem., Int. Ed.*, **2015**, *54*, 11572–11576.

11. L. A. Büldt and O. S. Wenger, *Chem. Sci.*, **2017**, *8*, 7359–7367.

33. C. Wang, S. Otto, M. Dorn, E. Kreidt, J. Lebon, L. Sršan, P. DiMartino-Fumo, M. Gerhards, U. Resch-Genger, M. Seitz and K. Heinze, *Angew. Chem. Int. Ed.*, **2018**, **57**, 1112–1116.

*3) Page 2, left column – “HCF3SO3” could rearrange to “CF3O2SOH” of “CF3SO3H” for consistency with “Cr-OSO2CF3” written just above*

Authors reply: The moiety {Cr-OSO2CF3} has been written that way to show bonding mode of the chromium cation with the triflate anion (through the oxygen atom). In all other cases when triflate exist as an unbound anion, it is written as CF3SO3-.

*4) Page 2, left column – “Reaction of the labile ligand intermediate with and” remove “and”*

Authors reply: “and” has been removed.

*5) Page 2, left column – “Seeking for longer lifetimes” remove “for”*

Authors reply: “for” has been removed.  
  
*6) Page 2, left column – “which makes it somehow safer and more environmentally-friendly.” This statement feels a bit too vague to be meaningful. I would recommend revising or removing.*

Authors reply: The sentence “It is worth highlighting that this synthetic method avoids the use strong acids and does not require large amounts of organic solvents which makes it somehow safer and more environmentally-friendly” has been removed.  
  
*7) Page 2, right column – “chlorine ions” replace with “chloride ions”*

Authors reply: “chlorine ions” has been replaced with “chloride ions”.

**Reviewer 2:**

We would also like to thank reviewer 2 for his/her extensive reading and his/her detailed analysis, corrections and suggestions.

*1) Page 1: “non-emissive Cr(4T2) state” is misleading as this state can be emissive in several chromium complexes.*

Authors reply: We agree that we were too much focused on strong-field Cr(III) complexes when writing this sentence. Therefore, “non emissive” has been removed..

*2) Page 2: “does not require large amounts of organic solvents, which makes it somehow safer and more environmentally-friendly”. This argument is rather weird as 3.5 equiv. of silver salt are required instead. As green chemistry is not the focus of this study, this statement can safely be omitted*.

Authors reply: The sentence “It is worth highlighting that this synthetic method avoids the use strong acids and does not require large amounts of organic solvents which makes it somehow safer and more environmentally-friendly” has been removed.

*3) “mer-[Cr(dqp)(O3SCF3)3] intermediate characterized by ESI-MS”: ESI MS does not allow for determination of the configuration (fac, mer).*

Authors reply: We absolutely agree. To avoid confusion, we have removed mer-.

*4)  Nomenclature of complexes: please use an alphabetical order of ligands in the heteroleptic complexes.*

Authors reply: We were not aware that the official nomenclature required alphabetical order for quoting the different ligands in a metallic complexes. To follow this rule, we have replaced seven times [Cr(dqp)(ddpp)]3+ with [Cr(ddpd)(dqp)]3+ in the main text, and seven times in the SI. We however maintain [Cr(tpy)Cl3], [Cr(ddpd)Cl3] and [Cr(dqp)Cl3] (instead of [CrCl3(tpy)], [CrCl3(ddpd)] and [CrCl3(dqp)] because this formulation highlights the choice of the tridentate binding unit as being the most important information.

*5) “pure racemic mer-PP/MM mixtures are obtained for 2 and 3 with no trace of either complexes with fac conformations or achiral PM diastereomers”: How did you confirm the absence of other isomers (fac, PM) in the bulk material? N.b. mer or fac denotes configurational not conformational isomers.*

Authors reply: In our mind, the numbering **2** and **3** referred to the crystal structures solved by X-ray diffraction. This is now clearly stated in the text on page 3, left column.*’’Pure racemic mer-PP/MM mixtures are observed in the crystal structures of* ***2*** *and* ***3*** *with no trace of either complexes with fac configuration or achiral PM diastereomers*’’.

*fac* conformation has been changed by *fac* configuration.

*6) Figure 2: The wavelength and wavenumber scales do not match (e.g. 20000 cm-1 corresponds to 500 nm). Where do the red and yellow arrows point to?*

Authors reply: We check our relationship which is indeed correct in the original picture. After careful consideration of this remark, we suppose that the referee would like to read round numbers on both scales. The figures have been adapted to follow this recommendation.

Concerning the second point: The red and yellow arrows in Figure 2a point to the ligand centered Cr(4T2 → 4A2) transition from which the ligand field splitting have been estimated. For helping readers: “*the orange, red and blue arrows point to the Cr(4T2 → 4A2) transition for each complex”* has been added in the caption of Figure 2a.

*7) Please crosscheck all numerical data given in the text and in the Figures.*

Authors reply. Done. Some minor inconsistencies could be detected at this occasion. Thank you.

*8) Page 3: On which basis were the spin-forbidden bands assigned as pi-pi, MC and MLCT? Simple analogy arguments might be misleading due to the very different ligand characters.*

Authors reply: Concerning the ligand-based bands pi-pi and LMCT (we did not assigned any MLCT in this work): we basically assume that the position of the ligands-based transitions are comparable with other related ligands and complexes as far as they belong to the family of polypyridyl ligands. See for example the references: J. C. Barbour, A. J. I. Kim, E. DeVries, S. E. Shaner and B. M. Lovaasen, Inorg. Chem., 2017, **56**, 8212–8222. D. Zare, B. Doistau, H. Nozary, C. Besnard, L. Guénée, Y. Suffren, A.-L. Pelé, A. Hauser and C. Piguet, *Dalton Trans.*, 2017, **46**, 8992–9009. More insight into the electronic origin those transitions will require theoretical calculations which are out of the scope of this synthetic work. Moreover, we are aware of the difficulties of making calculation on spin-forbidden transitions. Concerning the MC ligand transitions: according to the Tanabe-Sugano diagram for a d3 electronic configuration in the case of a large ligand field splitting, the Cr(2T1) and the Cr(2E) are low lying excited states with the Cr(2E) the lowest in energy. Thus, the transitions observed at lower energies can be assigned to the Cr(2T1←4A2) and two transitions for Cr(2E←4A2) (Figure 2b).

*9) Please use consistent descriptors, e.g. (6-6)+(5-5) or 6-6+5+5.*

Authors reply: the descriptors (6-6)+(5-5) and (6-6)+(5-5) have been selected and systematically used.

*10) Figure 2b: The number of transitions below the brackets does not match the description in the text (3+2).*

Authors reply: The pattern 3+2 is indeed observed for complexes **1** and **2**. However, the closer similitude of the bound ligands in complex **3** did not allow to observe a complete resolved splitting for 3. This is now clearly stated in the text on page 3, right column. ‘’*...energies as observed for [Cr(dqp)(tpy)]3+ and [Cr(ddpd)(dqp)]3+. For [Cr(dqp)(dqpOMe)]3+ (****3****), the two bound ligands are so similar that the splitting is reduced to such an extent that two bands are indeed observed for Cr(2E→4A2), but only one broad unsymmetrical band is detected for Cr(2T1→4A2) (Figure 2b, yellow trace)*’’.

*11) Which maxima were used for the calculation of the ligand field splitting of the complexes?*

Authors reply: The maxima occur at 472 nm (**1**), 415 nm (**2**) and 409 nm (**3**). Those values, taken from Table S13, have been included in the main text. The pseudo-octahedral ligand field values (Δ) were extracted from these maxima.

*12)  Figure 3: please add “deaerated” or “aerated” to the caption.*

Authors reply: deaerated has been added in Figure 3.

*13)  Figure 3: the orange trace shows a small band at ca. 13500 cm-1. Is this an impurity (i.e. a homoleptic complex) or intrinsic to complex 3?*

Authors reply: We also pointed out this small band when doing the measurements. Different samples were measured among which the single crystals used for X-ray diffraction, and all showed the same band. This lets us think that this is intrinsic to the complex, perhaps a specific contribution of the vibrational structure in the ground state.

*14)  Figure 3 and corresponding text: The wavenumbers given in the text do not match the emission spectra (e.g. for 2: 752 nm).*

Authors reply: We thank the referee for this observation. Modifications have been made and now it is in the right way.

*15) Conclusion/title: “Ultimate optimization” and “Upgrading” appears somewhat exaggerated considering that the photophysical data achieved (quantum yields/lifetimes, see Table 1) are considerably lower than reported ones, not higher.*

Authors reply: Upgrading in the title has been removed and ultimate in the text has been also removed.

*16) Please provide the emission spectra at low temperature in the ESI for better comparison with the spectra at rt.*

Authors reply: The emission spectra at 77 K have been added to the SI (Figure S8).

*17) Please provide the emission spectra (excitation <= 435 nm) also in the visible spectral region to confirm absence/show presence of residual fluorescence in the ESI.*

Authors reply:

As requested, the emission spectra from 550 nm (excitation at 435 nm) have been recorded and added for [Cr(ddpd)(dqp)]3+ and [Cr(dqp)(dqpOMe)]3+ in the supporting information as Figure S10. For [Cr(dqp)(tpy)]3+, we did not have enough material to collect this additional data. Since it will require considerable efforts and time to synthesize a new batch of a complex of very limited interest, we hope that the two added spectra of the most pertinent complexes will be acceptable for the referee.

*18) Please provide excitation spectra to confirm that excitation at different wavelengths (e.g. the used 435 and 355 nm) gives the same results in the ESI.*

Authors reply: We did not record and discuss any excitation spectra. The steady-state emission spectra were systematically recorded upon excitation at 435 nm as mentioned in the text.

Typos/wording:  
*1)      Page 1: “These appealing long excited states lifetimes … “ –> “These appealing long lived excited states … “ or “**These appealing long excited state lifetimes … “*

Authors reply: It has been modified. “*These appealing long excited state lifetimes has been used*”

*2)      Page 1: “[Cr(III)N6]”: better use superscript for oxidation state “III” to avoid confusion.*

Authors reply: It has been modified. Cr(III) has been replaced by CrIII along the text

*3)      Page 1: “Back-InterSystem Crossing”: please check spelling.*

Authors reply: it has been modified. “back intersystem crossing”

*4)      Page 2: The statement “Reaction of the labile intermediate with and additional diimine or triimine ligand (L’) generates the corresponding heteroleptic [(L)Cr(L’)]3+ complex” is only correct for the tridentate ligands. And please correct “and” -> “an”.*

Authors reply: it has been modified. “*Reaction of the labile intermediate with additional triimine ligand (L’) generates the corresponding heteroleptic [(L)Cr(L’)]3+ complex*.”

*5)      Page 2: HCF3SO3 is not a very common formula for triflic acid. CF3SO3H might be more useful.*

Authors reply: it has been modified. CF3SO3H has been used.

*6)      Page 2: “Reaction of the labile intermediate with a additional diamine” -> “Reaction of the labile intermediate with an additional diamine”*

Authors reply: It has been modified.

*7)     Table 1: “ddpd” instead of “ddqp”.*

Authors reply: it has been modified.

8)     and several other typos in the text. Please re-read the text carefully.  
Authors reply: The text has been read carefully and typos identified and corrected as much as possible.

SI:  
*1) The salt Cr(CF3SO3)2 is mentioned but not used. Please remove.*

Authors reply: it has been removed.

*2) The complex CrCl3x3THF is used but no reference is given. Please add.*

Authors reply: The CrCl3x3THF has been purchased from a commercial supplier. This information has been added in the SI.

3) References to synthesis of dqp and ddpd were not given. Please add.

Authors reply: The reference for the synthesis of ddpd has been added in the SI: S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger and K. Heinze, *Angew. Chem., Int. Ed.*, 2015, **54**, 11572–11576. The dqp has been prepared by adapting the synthetic method employed in reference S2: M. Jäger, R.-J. Kumar, H. Görls H., J. Bergquist J. and O. Johansson. *Inorg. Chem*. 2009, **48**, 3228-3238

4) Elemental analyses are outside the 0.4% range in some cases. Please comment.

Authors reply: Elemental analyses have been recalculated and are now in an accepted range.

5) Please consider using a consistent representation of triflate.

Authors reply: triflates anions are written as CF3SO3- along the SI.

6) Spectroscopic and analytical measurements: An excitation wavelength of 355 nm is given in the SI in contrast to the 435 nm denoted in Figure 3. Please clarify. (see also Figure S8)

Authors reply: On one hand, the 355 nm excitation is provided by a pulsed Nd-YAG laser that it is used when carrying out time resolved measurements for extracting the excited state lifetimes. On the other hand, the 435 nm excitation has been used for calculating the overall quantum yield through a comparative method using [Cr(ddpd)2]3+ as reference ( =12.1%; λexc = 435 nm). S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger and K. Heinze, *Angew. Chem., Int. Ed.*, 2015, **54**, 11572–11576.

7) X-Ray Crystallography: Cr(dqp)Cl3 is missing. Please add.

Authors reply: The X-ray data for Cr(dqp)Cl3 are provided in Table S1-S3 and Figure S2.

8) Please check the atom numbering in the crystal structures vs. the tables.

Authors reply: These values have been checked.

9) Figure S2: “Counter ions and H atoms are omitted for clarity.” is not correct.

Authors reply: it has been corrected.

10)  Table S15: Aerated and deaerated results are marked with footnotes. Please use different representations for aerated and deaerated results to make it clear which quantities were used in the equations. According to Footnote j the quantity η was calculated for aerated solutions. However, the results only match for deaerated solutions. It was not possible to reproduce the result for η for compound 1 using the data given in Table S15.

Authors reply: The reviewer is right. η has been calculated for deaerated solutions. This has been clarified in the footnote of Table S15. Moreover, the η values has been recalculated and we discovered that for 1 is 3% instead of 6%. Table S15 has been corrected accordingly. To clearly show which quantities were used to calculate the different parameters, the values obtained for aerated solutions are now written using italic fonts in Table S15.

Lack of literature citations

1)      Page 1, left col: MLCT quantum yields / lifetimes of polypyridyl ruthenium(II) complexes: citations missing.

Authors reply: The following references have been added: M. Abrahamsson, M. Jäger, T. Österman, L. Eriksson, P. Persson, H. C. Becker, O. Johansson and L. Hammarström, *J. Am. Chem. Soc.*, 2006, **128**, 12616–12617. M. Abrahamsson, H. C. Becker and L. Hammarström, *Dalton. Trans.*, 2017, **46**, 13314–13321.

2)     Scheme 1: citations missing for the respective data.

Authors reply: The following references have been placed: S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger and K. Heinze, *Angew. Chem., Int. Ed.*, 2015, **54**. J.-R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña and C. Piguet, *J. Am. Chem. Soc.*, 2019, **141**, 13244–13252. N. Serpone, M. A. Jamieson, M. S. Henry, M. Z. Hoffman, F. Bolletta and M. Maestri, *J. Am. Chem. Soc.*, 1979, **101**, 2907–2916.

3)     Section below Scheme 1 lacks citations of the statements given.

Authors reply: The following reference has been added: S. Otto, M. Dorn, C. Förster, M. Bauer, M. Seitz and K. Heinze, *Coord. Chem. Rev*., 2018, **359**, 102–111.

4)      “The Cr-N bond lengths 1.98(1)–2.1(1) Å compare well with those found in related complexes.” Please add suitable references.

Authors reply: Some references have been placed: J.-R. Jiménez, B. Doistau, C. Besnard and C. Piguet, *Chem. Commun.*, 2018, **54**, 13228–13231 has been placed. S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger and K. Heinze, *Angew. Chem., Int. Ed.*, 2015, **54**, 11572–11576. D. Zare, B. Doistau, H. Nozary, C. Besnard, L. Guénée, Y. Suffren, A.-L. Pelé, A. Hauser and C. Piguet, *Dalton Trans.*, 2017, **46**, 8992–9009.

5)      “…to the previously reported [Cr(ddpd)(tpy)]3+” Please add a pertinent citation.

Authors reply: The reference J.-R. Jiménez, B. Doistau, C. Besnard and C. Piguet, *Chem. Commun.*, 2018, **54**, 13228–13231 has been placed.

6)      The original citation for the derivation of the Racah parameters is missing.

Authors reply: The following references haven been added. 1. C. K. Jorgensen, *Adv. Chem. Phys.*, 1963, **5**, 33–146. 2. A. B. P. Lever, Inorganic Electronic Spectroscopy,Elsevier, Amsterdam, Oxford, New York, Tokyo, 2nd edn, 1984, p. 126.

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