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# Dalton Transactions Editorial Office

Geneva, September 4, 2020

Concern: Submission of revised manuscript transferred from *Chem. Comm.* to *Dalton Trans.* (manuscript ID: DT-COM-08-2020-002872)

# 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 of the latter version, the referees recommended some minor revisions before publishing in *Dalton Transaction*. We would like to thank the editor and the reviewers for their constructive comments. All referees’ 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:**

*1) Comments to the Author*

*There are 4 Structures in this paper. We examined this file: 2015187-2015190. All four structures are based on outstanding diffraction data and have been determined and reported expertly.*

Authors reply: We thank reviewer 1 for his/her rewarding comment.

**Reviewer 2:**

*Comments to the Author  
I have only a few remarks, which the authors should address. Overall, this is a nice paper on novel chromium complexes and their optical properties.*

First, we would like to thank reviewer 2 for his/her recurrent constructive comments and advices and for his/her extensive reading.

*Page 1*

*1) The strong ligand field splitting induced by these ligands, together with the near to perfect octahedral geometry of the first coordination sphere (CrN6), is of crucial importance for restricting non-radiative pathways such as back intersystem crossing (BISC) Cr(2E/2T1->4T2) and potential energy surface crossing between the ground state and the low-lying excited states (Cr(2E/2T1)-Cr(4A2)) because both phenomena are detrimental to efficient photophysical properties. Furthermore, high-energy vibrations (N-H, C-H, O-H) arising from organic ligands or solvents are also considerable drawbacks promoting non-radiative pathways which shorten the lifetime of the spinflip excited states and reduce the luminescence quantum yields“*

*-> This paragraph sounds somewhat incoherent and could confuse the non-specialist reader. Please rephrase.*

Authors reply: The paragraph has been cut into three different sentences and significantly clarified for non-specialists.

The strong ligand field splitting induced by these ligands, together with the near to perfect octahedral geometry of the first coordination sphere (CrN6), is of crucial importance for restricting non-radiative pathways. In these conditions, back intersystem crossing (BISC) Cr(2E/2T1⭢4T2) and potential energy surface crossing between the ground state and the low-lying excited states (Cr(2E/2T1)-Cr(4A2)) are minimized.4,9 Moreover, high-energy vibrations (N-H, C-H, O-H) arising from organic ligands or solvents bound to CrIII should be avoided since they represent considerable drawbacks while promoting non-radiative pathways which shorten the lifetime of the spin-flip excited states and reduce the luminescence quantum yields.9

*2) „Firstly, the poor bite angles of the tpy ligand (~79°) reduce the ligand field strength (Scheme 1c), which leads to efficient BISC with the Cr(4T2) state“*

*Please add suitable reference for the tpy bite angle.*

Authors reply: The references (8) N. Serpone, M. A. Jamieson, M. S. Henry, M. Z. Hoffman, F. Bolletta and M. Maestri, J. Am. Chem. Soc., 1979, 101, 2907–2916 and (10) J. R. Jiménez, B. Doistau, C. Besnard and C. Piguet, Chem. Commun., 2018, 54, 13228–13231 have been specifically mentioned for supporting the standard chelate bite angles found in terpyridine ligands meridionally tri-coordinated to CrIII.

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*1) “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 …” should be specified by “… in the crystal”*

Authors reply: “in the crystal” has been added as requested.

*2) „further extended by Constable and co-workers for the synthesis of heteroleptic [Cr(triimine)2]3+,26 “*

*-> ref [26] is not a suitable reference for [Cr(triimine)2]3+ complexes but reports Cr(diimine)3 complexes.*

Authors reply: The appropriate reference: J. Schönle, E. C. Constable, C. E. Housecroft, A. Prescimone and J. A. Zampese, Polyhedron, 2015, 89, 182–188 has been included as reference 26.

*3) „Seeking longer lifetimes, the luminescent heteroleptic [Cr(ddpd)(tpy-R)]3+ (R = H, COOEt) complexes“*

*-> tpy-H is a somewhat misleading representation of terpyridine because of its similarity to protonated ligand, yet I think the reader will be able to understand what is meant. The position of the COOEt group is not made clear and this information should be added.*

Authors reply: To avoid confusion we have modified the sentence: the luminescent heteroleptic [Cr(ddpd)(tpy-R)]3+ (R = H, COOEt) complexes…“ has been replaced by “heteroleptic [Cr(ddpd)(tpy)]3+ complex and derivatives…”

*4) Please use a consistent representation: „5-5 membered chelates“ or „(5-5)-membered chelates“*

Authors reply: the notation (5-5)-membered chelates will be used in the whole text.

*Page 3*

*1) “the minor structural improvement in moving from ddpd to dqp ligand (the N(terminal)-N(central) distances featured by the bound dqp ligand is 1% longer than in ddpd, Figure S6)”*

*-> Why was the crystal structure of [Cr(ddpd)(dqp)]3+ used for this comparison in Figure S6 instead of the heteroleptic complexes [Cr(ddpd)(tpy)]3+ and [Cr(dqp)(tpy)]3+?*

Authors reply: There is no crucial reason. We just have selected these two complexes to make such a fine comparison because they are the most promising ones regarding their photophysical properties. In any case, the same feature is expected for [Cr(ddpd)(tpy)]3+ and [Cr(dqp)(tpy)]3+ complexes.

*2) Figure 2: The wavenumbers where the blue, red and yellow arrows are pointing towards are inconsistent with the values for the ligand field splitting values given in the text („Thus, the Δ value is much lower for [Cr(dqp)(tpy)]3+ (1, 21186 cm-1) compared with 24096 cm-1 for [Cr(ddpd)(dqp)]3+ (2) and 24449 cm-1 for [Cr(dqp)(dqpOMe)]3+ (3).“)*

Authors reply: We have modified the position of the arrows. They are now pointed towards the right values; those given in the text: [Cr(dqp)(tpy)]3+ (1, 21186 cm-1) compared with 24096 cm-1 for [Cr(ddpd)(dqp)]3+ (2) and 24449 cm-1 for [Cr(dqp)(dqpOMe)]3+.

*3) Figure 2 caption: „Cr(4T2 → 4A2)“ represents an emission. Please correct. Please add a unit for the concentration in caption b).*

Authors reply: Both modifications have been made

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*1) Right column: Please add the % sign for all values (e.g. 0.9 and 3.4) to avoid confusion.*

Authors reply: the % sign has been added

*ESI*

*1) Figure S3: „H atoms are omitted for clarity“ is not correct.*

Authors reply: “H are omitted for clarity” has been removed from Figure S3”

*2) Table S9: This table shares the same caption as Table S5. Please correct.*

Authors reply: it has been corrected

*3) Table S14: According to ref. S8 p. 72 and ref. S9 p. 126 equation S3 should be E = 9B + 3C – 90(B²/Delta). Please clarify.*

Authors reply:

The referee made an error upon reading ref. S9 on p.126, because A.B.P. Lever, in the version of 1984, indeed wrote 50(*B*2/Delta). However, the referee points to an interesting problem that we were faced few years ago and which is summarized below.

At first sight, the energy of these levels can be roughly modeled by using the diagonal elements of the Tanabe-Sugano matrices assuming a pseudo-octahedral geometry for CrN6 chromophores (H. Witzke, Theoret. Chim. Acta, 1971, 20, 171-185). However, this level of approximation implies that the Cr(2E) and Cr(2T1) states are degenerate, which is clearly not the case in these complexes The additional consideration of configuration interaction between the states of the same multiplicity and symmetry, but from different strong field configuration led Jorgensen (C. K. Jorgensen, Adv. Chem. Phys., 1963, **5**, 33-146) to introduce second-order corrections  in eqs (1)-(3), which are derived from the off-diagonal elements of the Tanabe-Sugano matrices.

 (1)

 (2)

 (3)

Although Jorgensen fixed C/B = 4 for deriving eqs (1)-(3), there is no obvious reason for this assumption and a systematic and detailed ligand-field analysis of electronic spectra recorded for CrIII compounds revealed that 3 ≤ *C/B* ≤ 8. In his seminal textbook (A. B. P. Lever, Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier, Amsterdam-Oxford-New York-Tokyo, 1984, p. 126), Lever replaced eqn (3) with eqn (4).

 *(4)*

This transforms the modelling of the *E*(2T1)-*E*(2E) energy gap, for which Jorgensen’s approach predicts 66*B*2/** (eqn 3), to only 26*B*2/** (eqn 4). Compared with the theoretical set of exact energies computed by Ferguson(D. L. Wood, J. Ferguson, K. Knox, J. F. Dillon, *J. Chem. Phys*. **1963**, 39, 890-898. J. Ferguson, Prog. Inorg. Chem., 1970, 12, 159-293) by means of full Eisenstein’s matrices with B = 680 cm-1 and C= 2720 cm-1 (C/B = 4.0), the exact computed *E*(2T1)-*E*(2E) energy gap amounts to 630 cm-1 for ** = 19940 cm-1 in fair to good agreement with the prediction of the second-order correction 26*B*2/** = 603 cm-1 (eqn 4), but rather far from 1531 cm-1 obtained with eqn (3). We conclude that only a complete ligand-field treatment is capable of extracting reliable Racah parameters B and C for CrIII complexes, but eqn (4) seems superior to eqn (3) when a rough modeling of the energy of the lowest spin-flip 2E excited state is foreseen.

This approach has been described into details in 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, a reference added as S10 in the ESI and mentioned in Table S14.

*4) It’s true that the steady-state emission spectra were all recorded with 435 nm excitation, however the lifetimes were determined with 355 nm excitation.*

*Please provide excitation spectra to confirm that excitation at different wavelengths (namely the used 435 and 355 nm) gives the same results in the ESI if possible for all sample but at least for one representative example.*

Authors reply: The excitation spectra for compounds 2 and 3 have been added into the SI as Figure S11.

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