Transparent peer-review report

Synthesis and solid-state luminescence of 3-(pyridine-2-yl)-1,2,4-triazine-based Ir(III) complexes

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1st peer-review round

Reviewer #1 | major revision

In the article by Basim S.M. Al-Ghezi from the group of Grigory V. Zyryanov a series of new Ir complexes was successfully synthesized. Photophysical properties were characterized in powder and acetonitrile solutions in this work aiming at light-emitting applications. The MS contains good level of novelty and rather appealing for the broad circle of readers. Synthetic part is well-written. However, photophysical part of the article requires substantial attention. The authors are invited to revise their MS. Following issues should carefully be addressed in the revision:

a) Since luminescence both in solid and dissolved states is described, it is recommended to adjust the title of the article deleting solid-state. Synthesis and solid-state luminescence of 3-(pyridine-2-yl)-1,2,4-triazine-based Ir(III) complexes
b) Both Cyclometallated and Cyclometalated spellings are used in the text. Please revise.
c) Introduction. “Finally, cyclometalated iridium(III) complexes are of wide use in medicine as anticancer agents [13-19], in photody-namic therapy (PDT)[20], photothermal therapy (PTT)[21, 22], and photoactivated chemotherapy (PACT)[23].” No confirmation of wide use in medicine was found by the reviewer. Please revise. It is suggested to use “medicine applications”.
d) DCM:methanol = 1:1 mixture as a solvent. What is the reason of mixed solvent use? Did the authors try other compositions? Why not acetonitrile was used?
e) Similar type complex structures are well-investigated using XRD. Any XRD attempts were taken for these particular complexes? This would be of help to verify QCC results greatly. Please detalize.
f) “while the bands with the lowest energy originate from the MLCT state”. Please specify the WLs. Did the authors try to deconvolute spectral lines? Graphical image with π- π*, n-π* and MLCT contributions would greatly improve the understanding.
g) Please add section with description of QYs registration methodology.
h) What is the reason of Irpy2(L7) absorption substantial difference? The same for Irpy2(L8) emission in solid?
i) Is it possible to rank obtained complexes by brightness or any other parameters related to emission intensity both in solid state and solution?
j) Since the complexes have bimodal emission bands in solution, did the authors perform any attempts ratiometric luminescence thermometry? Just curious.

Reviewer #2 | minor revision

This manuscript is interesting for coordination chemistry community and could be accepted for publication. The topic is up to date and actual. The main question addressed by the research is new iridium complexes and its photo-physical properties. A series of novel iridium(III) complexes containing 5-N-(aryl)-amino- or 5-cycloamino-3-(pyridine-2-yl)-1,2,4-triazine ligands were obtained. These complexes exhibited red fluorescence in solution, as well as in a solid state. The subject addressed in this article is worthy of investigation. All parts of this manuscript are original and relevant for the field. This manuscript added some value to the coordination chemistry of iridium compounds. The information presented is new. All main questions posed were addressed and supported by the data. The methodology of research is appropriate. Tables and figures are fine. Quality of the data is fine. The conclusions supported by the data. The manuscript is good illustrated and interesting to read. I have only two suggestions for minor revision. First, it would be a good idea to cite following relevant references about other promising iridium complexes with interesting photo-physical properties in introduction: International Journal of Molecular Sciences 2023 24 (13), 10457; ChemistrySelect 2018 3 (42), 11875-11880; Macromolecular Rapid Communications 2024, 2400450, DOI: 10.1002/marc.202400450; Zeitschrift für Kristallographie-Crystalline Materials 2017 232 (12), 797-805. Second, some more detailed perspectives about the future research could be formulated in conclusions.

Reviewer #3 | accept at it is

Current manuscript deals with the synthesis of 1,2,4-triazine-based iridium(III) complexes and studying of their photophysical properties. Azahetrocycle-based iridium(III) complexes are of interest to due to their promising photophysical properties. Among such types of ligands 1,2,4-nriazine-based are very rare and reported only in a very few cases. The authors provided a very convenient method for the preparation of such complexes and studied their photophysical properties. These complexes exhibited red fluorescence, which suggests their application fir biovisualization and/or for OLED applications.

Owing high importance of Ir(iii) complexes based on N^N type ligands the manuscript can be accepted after the minor revision. The following issues need to be addressed:

1. The authors have to provide the pictures of 1H NMRs of the key complexes.
2. The English grammar needs to be checked/corrected.

Reviewer #4 | minor revision

The paper by Zyryanov et al. is devoted to the synthesis and study of the photophysical properties of iridium(III) complexes. New triazine ligands and eight new iridium complexes were synthesized. The obtained metal compounds show weak luminescence in the red region of the spectrum. The work can be useful for researchers working in the field of luminescent materials and can be accepted for publication after some corrections:

1. Throughout the paper the authors talk about fluorescence (abstract, spectra, table, discussion). However, no evidence for this mechanism is given. Furthermore, a significant Stokes shift could be an indication of phosphorescence. This is also supported by the '3MLCT state emission' postulated by the authors on page 4. Since luminescence properties are the main point of study in this paper, the authors need to understand these concepts.

2. I see no need to give the energies in Hartree units in the text. It is sufficient to give the stabilization energy in kilocalories.

3. For which of the compounds did the authors use 19F NMR spectroscopy, as indicated in the experimental part of the paper?

4. In Part 4 (Limitations), the authors provide a rather obvious conclusion that the introduction of triazine reduces the luminescent properties. I would like to see some deeper analysis - what properties of triazine lead to this?

5. The conclusion on the effect of secondary and tertiary amines on luminescence properties in Part 5 (Conclusions) does not follow in any way from the material presented in the discussion. Compounds of a different type are not described in the article and no comparative analysis with similar compounds is provided.

Reviewer #5 | minor revision

The article is devoted to a relevant topic – the development of iridium complexes synthesis and studying their photophysical properties. Taking into account that iridium derivatives are the basis for a wide range of practically useful materials and have biological activity, the synthesis of new representatives of these compounds and the study of their properties are urgent tasks.

In the work, using the previous developments of the team of authors, a number of new ligands were synthesized - amino-substituted pyridin-2-yl-1,2,4-triazines, and on their basis new iridium (III) complexes were obtained, the structure of which was studied by physicochemical methods and quantum-chemical calculations. It is important that in addition to the synthesis, the work presents data on the photophysical properties of new complex compounds.

Considering the significance of the topic, the volume and novelty of the results obtained, a fairly good interdisciplinary level of the studies, the article can be recommended for publication. However, revision is required due to the careless design of the text and results. The comments related to the design can be formulated as follows.

1. The numbering of references should be put in order. Reference [11] is missing in the text. References [8] through [30] are numbered incorrectly. For example, judging by the content of the references, reference [9] in the text corresponds to reference number [8] in the list of ref. Reference [10] in the text should correspond to source [9] in the list of references, etc. up to reference [30] there are discrepancies of one or two positions.
2. The design of the experimental section should be improved:
- It is indicated that 19F NMR was recorded, however, the synthesized compounds do not contain fluorine.
- It is indicated that NMR spectra were recorded in deuterated acetonitrile, however, for specification of ligands L1 and L3 spectra, it is written that the spectra were obtained in CDCl3 and DMSO-d6, respectively.
- When describing the spectrum of the Irppy2L5 complex, two signals of pyrrolidine fragment are presented, each with an intensity of 2H, i.e. 4 protons in total. However, the pyrrolidine fragment contains 8 protons. That is, either some signals are not given, or the intensity is indicated incorrectly. In addition, a signal of 5.96 ppm triplet with a huge constant J = 32 Hz is given. Is there a typo here for value of J? If not, then such a value of J should be commented on in the discussion of the results.
- When describing the spectra of the Irppy2L7 complex, signals of the thiomorpholine fragment are given, however, the compound itself contains morpholine substituents, not thiomorpholine ones.
- The name of the substituent "Thiomorpholine" when describing the spectra of the Irppy2L8 complex is better written with the letter "o", it is written with an "a": "Thiamorpholine".

- The values of spin-spin coupling constants J should be checked. For the Irppy2L1, Irppy2L2, Irppy2L5, Irppy2L4, Irppy2L6 complexes, all the given values of J are equal to 8 Hz or 1 Hz. This may be due to the fact that these complexes contain similar structural fragments. However, the Irppy2L5, Irppy2L7, Irppy2L68 complexes contain the similar fragments, but the given J are of other values. Are there any typos in the written values of J?

3. When depicting the structure of the Irppy2(L1-L8) complexes in general form in Scheme 1, it would be better to indicate the positive charge of the cationic part of the complex and the negative charge of the chlorine counterion.
4. The second sentence in section "5. Conclusions" should be verified. Apparently, a preposition is missing.
5. In reference number [27] in the list of references it seems that it should say “albumin” and not “alnumin”.

Reviewer #6 | major revision

The manuscript “Synthesis and solid-state luminescence of 3-(pyridine-2-yl)-1,2,4-triazine-based Ir(III) complexes” by I.S. Kovalev, G.V. Zyryanov and co-workers describes the synthesis and luminescent properties of cyclometalated Ir(III) complexes with N,N-donor ligands. The study describes the synthesis of 8 new N,N-donor ligands and 8 new Ir(III) complexes based on them. Despite of the obtained complexes display low intensive luminescence, the study presents interesting results, which can be useful for further design of Ir(III) luminescent compounds for various applications. Therefore, the manuscript can be accepted for the publishing in Chimica Techno Acta after major revision. There are several points, which should be corrected and improved before accept:

1. Complexes 1-8 demonstrate similar emission band maxima in solution, but in the solid state some shifting of the maxima of the emission bands can be found. What is the reason for such photophysical behavior of complexes?
2. Authors describes the DFT quantum chemical calculations for the structures, but the most discussion belongs to the energies of optimized structures of complexes. In the case of luminescence, the studies of the HOMO/LUMO distribution and the gap between them is more informative. I can suggest, to use the optimized structures for the calculations of the frontier orbitals at least for the S0 state and support the discussion of the origin of transitions in UV and luminescent spectra by these computations. That will be also helpful for understanding of the role of triazine ligands in the luminescent transitions.
3. “The absolute quantum yield values in MeCN were < 0.1 % in all cases due to low emission intensity.” – it is not a reason for the low quantum yield. The low intensity

of emission is a consequence of the low quantum yield. Was the quantum yield measured for solutions of complexes or for the solid state? If it was measured in solutions, then is it possible that the quenching of luminescence is occurred due to the formation of exciplex with solvent molecules in the excited states?

4. Due to the discussion of photophysical properties of complexes in current form is not supported by calculations or any experiments establishing the origin of the emission and reasons of luminescence quenching, the comparison of the results presented in Photophysical part of the manuscript with literature data for relevant Ir(III) complexes is required. Possibly, the literature data will be helpful for the answering on the questions above.

5. Along with the manuscript authors use term "fluorescence" (e.g. "fluorescence emission spectra", "fluorescence emission band" and etc.), but according their statement of 3MLCT origin of emission it is not fluorescence, but phosphorescence. I recommend to remove word "fluorescence" in the discussion and in the captions for the figures 4 and 5, and keep only "emission":

Instead of "Fluorescence emission spectra showed several emission bands..." write "Emission spectra showed several emission bands..." or "Luminescence spectra showed several emission bands..."

Instead of "For all the complexes the fluorescence emission band ended beyond..." write "For all the complexes the emission band ended beyond..."

In Tanble 1 "λfl" should be "λem"

Caption "Fig. 4. – UV/Vis (A) and fluorescence emission (B) spectra of Irppy2(L1-L8) complexes in MeCN solution" should be "Fig. 4. – UV/Vis (A) and emission (B) spectra of Irppy2(L1-L8) complexes in MeCN solution"

Caption "Fig. 5. – Fluorescence emission spectra of Irppy2(L1-L8) complexes in powder at r.t." should be "Fig. 5. – Emission spectra of Irppy2(L1-L8) complexes in powder at r.t.". Please, check also the bold style for "Irppy2(L1-L8)" in this caption

In limitations "...very low fluorescence quantum yields..." should be written as "...very low photoluminescent quantum yields..."

6. In table 1 authors missed the emission band maximum for complex 8. Why? According the emission spectrum of this complex the maximum should be at ca. 790-800 nm.

7. In table 1, please, indicate what columns of emission bands maxima belongs to solutions and to solid-state.

8. Please, include to the experimental section a short description of the methods used for computations with the corresponding references.

9. Conclusions. "All the synthesized complexes demonstrated solid-state luminescence due to the presence of secondary and tertiary amine moieties at the C(5) position of 1,2,4-triazine core." – I'm not sure that it is the correct conclusion.

As it was mentioned in the discussion the luminescence of complexes arising from 3MLCT transition, therefore the main requirement for the luminescence is the presence of electron-rich system (which is heteroaromatic moiety in this case) and heavy atom, which can be formally "oxidized" in the excited states due to charge transfer from the metal center to ligand. I suggest to write this part conclusions as follow "All the synthesized complexes demonstrated luminescence in the solid-state and in solution. It was found that the emission band maxima of complexes depends on the substituent at secondary and tertiary amine moieties at the C(5) position of 1,2,4-triazine core. "

Reviewer #7 | major revision

The article is devoted to the synthesis of eight complexes of iridium(III) with 3-(pyridin-2-yl)-1,2,4-triazines. The compounds were obtained in high yields and have been characterized by 1H NMR spectroscopy and ESI mass spectrometry. The structures of two complexes were optimized by DFT. Due to the lack of imaginary vibrational frequencies, the most energetically favorable structures of iridium(III) complexes were assumed. The obtained compounds were investigated by UV-Vis and fluorescence spectroscopy in deoxygenated acetonitrile solution. The quantum yield of all obtained iridium(III) complexes was less than 0.1 %.

There are a number of serious deficiencies and questions in the article, which can reduce the scientific value of this study. These include:

1) Absence of images of 1H NMR spectra, only their textual descriptions are given.

2) The work lacks data on 13C NMR, IR spectroscopy, elemental analysis of the obtained complexes. It would also be a good idea to add X-ray structural analysis to confirm the structure. DFT calculation is an excellent theoretical complement to the experiment, but can hardly fully replace the direct method of investigation.

3) The stoichiometry of the complexes does not seem to be confirmed by anything other than ESI and 1H NMR. Wouldn't it be worth supplementing the work with UV or fluorescence titration to establish the stoichiometry by any convenient method, such as a Job's plot?

4) Figure 4 shows an anomalous spectrum of the L7 complex, which is not discussed in any particular way in the text of the paper. What is the reason for such a sharp drop of absorption to zero in a certain range of this spectrum? What is the main reason for the difference of this spectrum from all others, including the complex with ligand L8, which is close to it in structure?

5) What is the meaning of the obtained compounds if they have such a low quantum yield? Maybe authors should change the positioning of the work and shift the focus to the synthesis and characterization of new complexes?

6) Small errors in formatting and typos.

a. In the description of the 1H NMR spectra for the J value, the number of bonds through which spin-spin interaction occurs is not given.

b. Also, italicized spelling is used for J in some substances, but not in others.

c. In the conclusion, some words are written in 10 font instead of 9 font.

d. In the experimental part, the use of the 19F NMR method is indicated, although in the sense of the paper it is not needed and is not used anywhere.

e. Figures 1 and 3 are too bright, the colors are poorly combined with the white background.

In this form, the paper cannot be recommended for publication. The work requires a major revision and additions. Also, probably, it would be better to compile supplementary information as a separate file, in which the figures of spectra should be placed.

Editor's decision

Major revision.

Responses to the comments of Reviewer #1

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.

Comment a) Since luminescence both in solid and dissolved states is described it is recommended to adjust the title of the article deleting solid-state.
Synthesis and solid-state luminescence of
3-(pyridine-2-yl)-1,2,4-triazine-based Ir(III) complexes.

Response: Corrected

Comment b) Both Cyclometallated and Cyclometalated spellings are used in the text.
Please revise.

Response: Corrected

Comment c) Introduction. "Finally, cyclometalated iridium(III) complexes are of wide use in medicine as anticancer agents [13-19], in photody-namic therapy (PDT)[20], photothermal therapy (PTT)[21, 22], and photoactivated chemotherapy (PACT)[23]." No confirmation of wide use in medicine was found by the reviewer. Please revise. It is suggested to use "medicine applications".

Response: The sentence was corrected according to reviewer's suggestion.

Comment d) DCM:methanol = 1:1 mixture as a solvent. What is the reason of mixed
solvent use? Did the authors try other compositions? Why not acetonitrile
was used?

Response: Thank you for your question. We tested various DCM:methanol compositions and found that a 1:1 mixture gave the best results. Complexes precipitated from this mixture and were separated by simple filtration. As for acetonitrile: Synthesis of iridium complexes in its medium was unsuccessful.

Comment e) Similar type complex structures are well-investigated using XRD. Any XRD
attempts were taken for these particular complexes? This would be of help to verify QCC results greatly. Please detalize.

Response: Thank you for your comment. We have not found any descriptions of the crystal structures of iridium complexes containing an auxiliary 3-pyridyl-2-1,2,4-triazine ligand in the literature. Attempts to obtain a crystal suitable for XRD studies were unsuccessful.

Comment f) "while the bands with the lowest energy originate from the MLCT state". Please specify the WLs. Did the authors try to deconvolute spectral lines? Graphical image with π-π*, n-π* and MLCT contributions would greatly improve the understanding.

Response: Corrected

Comment g) Please add section with description of QYs registration methodology.

Response: Absolute quantum yields of luminescence were measured according to the reported procedure [Porrès, L., Holland, A., Pålsson, LO. et al. Absolute Measurements of Photoluminescence Quantum Yields of Solutions Using an Integrating Sphere. J Fluoresc 16, 267–273 (2006). https://doi.org/10.1007/s10895-005-0054-8]. The corresponding reference was inserted into the experimental section ([34])

h) What is the reason of Irpy2(L7) absorption substantial difference? The same for Irpy2(L8) emission in solid?

Response: Substantial difference in absorption and emission spectra of $Irppy_2L8$ could be explained by specific molecular packing in crystal form of the complex; the presence of a heavy sulfur atom could influence on bathochromic shift as well. Fluorescence emission of solution for the complex $Irppy_2L8$ is similar for the rest complexes. To reveal this, deep XRD studies will be performed, including PXRD studies. Absorption spectrum for Irpy$_2$L7 was remeasured and replaced by a new one.

Comment i) Is it possible to rank obtained complexes by brightness or any other parameters related to emission intensity both in solid state and solution?

Response: Solid-state luminescence could be observed by naked eye in case of every reported iridium complex, however it is impossible to rank them between each other because of the bias of a human eye. Due to low intensity of the complexes in solution, it is impossible to rank them as well.

Comment j) Since the complexes have bimodal emission bands in solution, did the authors perform any attempts ratiometric luminescence thermometry? Just curious.

Response: We did not perform this technique for the study. However, we are thankful for the Reviewer for advising to provide it in future for our investigations.

Responses to the comments of Reviewer #2

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.

Comment 1 First, it would be a good idea to cite following relevant references about other
promising iridium complexes with interesting photo-physical properties in introduction: International Journal of Molecular Sciences 2023 24 (13), 10457; ChemistrySelect 2018 3 (42), 11875-11880; Macromolecular Rapid Communications 2024, 2400450, DOI: 10.1002/marc.202400450; Zeitschrift für Kristallographie-Crystalline Materials 2017 232 (12), 797-805.

Iridium(III)-Incorporating Self-Healing Polysiloxanes as Materials for Light-Emitting Oxygen Sensors - Parshina - 2024 - Macromolecular Rapid Communications - Wiley Online Library

Cyclometalated Iridium(III) Complexes Featuring Disubstituted Cyanamides - Kinzhalov - 2018 - ChemistrySelect - Wiley Online Library

Iridium Complexes with BIAN-Type Ligands: Synthesis, Structure and Redox Chemistry

Response: These references were added to the reference list

Comment 2 Second, some more detailed perspectives about the future research could be formulated in conclusions.

Response: The conclusion was revised in accordance with the reviewer's comments.

Responses to the comments of Reviewer #3

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.

Comment 1. The authors have to provide the pictures of 1H NMRs of the key complexes.

Response: NMR spectra of key complexes have been added to Supporting Info.

2. The English grammar needs to be checked/corrected

Response: Thank you for your valuable comment. A thorough grammar check has been carried out.

Responses to the comments of Reviewer #4

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.

Comment 1. Throughout the paper the authors talk about fluorescence (abstract, spectra, table, discussion). However, no evidence for this mechanism is given. Furthermore, a significant Stokes shift could be an indication of phosphorescence. This is also supported by the '3MLCT state emission' postulated by the authors on page 4. Since luminescence properties are the main point of study in this paper, the authors need to understand these concepts.

Response: We are thankful to the Reviewer for the provided comments and critique. The presence of luminescence spectra and table data is the evidence of luminescence as a phenomenon for the reported complexes. We have just begun our research into the complexes of iridium with 3-(pyridine-2-yl)-1,2,4-triazine-based ligand and deep study of specific mechanism of luminescence (including potential phosphorescence) is in progress right now. The relevant results will be reported in future.

Comment 2. I see no need to give the energies in Hartree units in the text. It is sufficient to give the stabilization energy in kilocalories.

Response: Corrected

Comment 3. For which of the compounds did the authors use 19F NMR spectroscopy, as
indicated in the experimental part of the paper?

Response: Since this manuscript was previously part of a larger article and was later taken out into a separate article, the mention of ^{19}F NMR spectra was left by chance. Corrected.

Comment 4. In Part 4 (Limitations), the authors provide a rather obvious conclusion
that the introduction of triazine reduces the luminescent properties. I would like to see some deeper analysis - what properties of triazine lead to this?

Response: It is known that compounds with a 1,2,4-triazine framework rarely exhibit luminescent properties. Apparently, the presence of electron-acceptor 1,2,4-triazine core in the molecule leads to a strong intramolecular charge transfer (ICT), which causes nonradiative transitions and quenches the emission.

5. The conclusion on the effect of secondary and tertiary amines on luminescence properties in Part 5 (Conclusions) does not follow in any way from the material presented in the discussion. Compounds of a different type are not described in the article and no comparative analysis with similar compounds is provided.

Response: Presumably, the presence of the amino group leads to partial quenching of the intramolecular charge transfer in the ligand molecule, which has a positive effect on the luminescent properties of the entire complex.

Responses to the comments of Reviewer #5

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.

Comment 1. The numbering of references should be put in order. Reference [11] is missing in the text. References [8] through [30] are numbered incorrectly.
For example, judging by the content of the references, reference [9] in the text corresponds to reference number [8] in the list of ref. Reference [10] in the text should correspond to source [9] in the list of references, etc.
up to reference [30] there are discrepancies of one or two positions.

Response: The references were corrected

Comment 2.

a) The design of the experimental section should be improved:
- It is indicated that 19F NMR was recorded, however, the synthesized compounds do not contain fluorine.

Response: Since this manuscript was previously part of a larger article and was later taken out into a separate article, the mention of ^{19}F NMR spectra was left by chance. Response: Corrected.

b) - It is indicated that NMR spectra were recorded in deuterated acetonitrile,
however, for specification of ligands L1 and L3 spectra, it is written that
the spectra were obtained in CDCl3 and DMSO-d6, respectively.

Response: Corrected.

c) When describing the spectrum of the Irppy2L5 complex, two signals of pyrrolidine fragment are presented, each with an intensity of 2H, i.e. 4 protons in total. However, the pyrrolidine fragment contains 8 protons. That
is, either some signals are not given, or the intensity is indicated incorrectly. In addition, a signal of 5.96 ppm triplet with a huge constant
J = 32 Hz is given. Is there a typo here for value of J? If not, then such a
value of J should be commented on in the discussion of the results.

Response: Thank you for the detailed analysis of the NMR spectra description. Upon careful examination of the spectrum, it was found that the missing signals of the pyrrolidine fragment were found in the region of 1.75 ppm (2H, br. m) and 2.0 ppm (2H, br. m), partially hidden by the residual solvent signal (1.94 ppm). Such non-equivalence of signals is not observed in the case of the pipyridine, morpholine and thiomorpholine fragments. We cannot explain the reason for the hindered rotation and plan to study it in more detail, including XRD. Regarding the signal at 5.96 ppm: This is a signal of ammonium, an impurity. Corrected. The representative ^{1}H NMR spectra were placed into Supporting Info.

d) When describing the spectra of the Irppy2L7 complex, signals of the thiomorpholine fragment are given, however, the compound itself contains morpholine substituents, not thiomorpholine ones.

Response: Corrected.

e) The name of the substituent "Thiomorpholine" when describing the spectra of the Irppy2L8 complex is better written with the letter "o", it is written with an "a": "Thiamorpholine".

Response: Corrected.

f) The values of spin-spin coupling constants J should be checked. For the Irppy2L1, Irppy2L2, Irppy2L5, Irppy2L4, Irppy2L6 complexes, all the given values of J are equal to 8 Hz or 1 Hz. This may be due to the fact that these complexes contain similar structural fragments. However, the Irppy2L5, Irppy2L7, Irppy2L68 complexes contain the similar fragments, but the given J are of other values. Are there any typos in the written values of J?

Response: There were typos in description. Corrected.

Comment 3. When depicting the structure of the Irppy2(L1-L8) complexes in general form in Scheme 1, it would be better to indicate the positive charge of the cationic part of the complex and the negative charge of the chlorine counterion.

Response: Corrected.

Comment 4. The second sentence in section "5. Conclusions" should be verified. Apparently, a preposition is missing.

Response: Corrected.

Comment 5. In reference number [27] in the list of references it seems that it should say “albumin” and not “alnumin”.

Response: Corrected.

Responses to the comments of Reviewer #6

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.

Comment 1. Complexes 1-8 demonstrate similar emission band maxima in solution, but
in the solid state some shifting of the maxima of the emission bands can be found. What is the reason for such photophysical behavior of complexes?

Response: The presence of a strong bathochromic shift in the case of complex with ligand 8 (solid state emission) can be explained by the presence of a heavy sulfur atom in the molecule. We do not yet have a clear explanation for this fact, and this requires additional studies, including X-ray diffraction experiments.

Comment 2. Authors describes the DFT quantum chemical calculations for the structures, but the most discussion belongs to the energies of optimized structures of complexes. In the case of luminescence, the studies of the HOMO/LUMO distribution and the gap between them is more informative. I can suggest, to use the optimized structures for the calculations of the frontier orbitals at least for the S0 state and support the discussion of the origin of transitions in UV and luminescent spectra by these computations. That will be also helpful for understanding of the role of triazine ligands in the luminescent transitions.

Response: The article presents the primary data of photophysical tests of the complexes. A detailed analysis of the data obtained, including with the help of quantum-chemical calculations, will be the goal of our further work. As for the quantum-chemical calculations in the article itself, they were carried out with the purpose of studying the coordination of the triazine ligand with iridium(III). Since the data on coordination in the literature differs, we sought additional confirmation of our assumption about the type of coordination site.

Comment 3. “The absolute quantum yield values in MeCN were < 0.1 % in all cases due to low emission intensity.” – it is not a reason for the low quantum yield. The low intensity of emission is a consequence of the low quantum yield. Was the quantum yield measured for solutions of complexes or for the solid state? If it was measured in solutions, then is it possible that the quenching of luminescence is occurred due to the formation of exciplex with solvent molecules in the excited states?

Response: Indeed, low quantum yield of luminescence impact on low luminescence intensity; the manuscript was corrected. Quantum yields of luminescence were measured for solutions only. Quenching of luminescence may arise due to the presence of 1,2,4-triazine core which is strong electron-acceptor. Coordination with iridium atom could influence on electron density distribution of the entire complex requiring additional investigations. We are working on it right now.

Comment 4. Due to the discussion of photophysical properties of complexes in current
form is not supported by calculations or any experiments establishing the origin of the emission and reasons of luminescence quenching, the comparison of the results presented in Photophysical part of the manuscript with literature data for relevant Ir(III) complexes is required. Possibly, the literature data will be helpful for the answering on the questions above.

Response: Since the iridium complexes with 3-pyridin-2-yl-1,2,4-triazine ligands are not presented as luminescent in the literature, the presented article is the first example. Suitable references simply cannot be presented.

5. Along with the manuscript authors use term “fluorescence” (e.g. “fluorescence emission spectra”, “fluorescence emission band” and etc.), but according their statement of 3MLCT origin of emission it is not fluorescence, but phosphorescence. I recommend to remove word “fluorescence” in the discussion and in the captions for the figures 4 and 5, and keep only “emission”:
Instead of “Fluorescence emission spectra showed several emission bands...” write “Emission spectra showed several emission bands...” or “Luminescence spectra showed several emission bands...”
Instead of “For all the complexes the fluorescence emission band ended beyond...” write “For all the complexes the emission band ended beyond...”
In Tanble 1 “λfl” should be “λem”
Caption “Fig. 4. – UV/Vis (A) and fluorescence emission (B) spectra of Irppy2(L1-L8) complexes in MeCN solution” should be “Fig. 4. – UV/Vis (A) and emission (B) spectra of Irppy2(L1-L8) complexes in MeCN solution”
Caption “Fig. 5. – Fluorescence emission spectra of Irppy2(L1-L8) complexes in powder at r.t.” should be “Fig. 5. – Emission spectra of Irppy2(L1-L8) complexes in powder at r.t.”. Please, check also the bold style for “Irppy2(L1-L8)” in this caption
In limitations “...very low fluorescence quantum yields...” should be written as “...very low photoluminescent quantum yields...”

Response: We agree with the reviewer's comment. Corrected.

Comment 6. In table 1 authors missed the emission band maximum for complex 8. Why?
According the emission spectrum of this complex the maximum should be at ca. 790-800 nm.

Response: All the necessary updates were made. Maximum of emission for complex with ligand L8 was measured and added to the table (λem 793 nm)

Comment 7. In table 1, please, indicate what columns of emission bands maxima belongs to solutions and to solid-state.

Response: All the necessary updates were made

8. Please, include to the experimental section a short description of the methods used for computations with the corresponding references.

Response: All the necessary updates were made.

9. Conclusions. “All the synthesized complexes demonstrated solid-state luminescence due to the presence of secondary and tertiary amine moieties at the C(5) position of 1,2,4-triazine core.” – I’m not sure that it is the correct conclusion. As it was mentioned in the discussion the luminescence of complexes arising from 3MLCT transition, therefore the main requirement for the luminescence is the presence of electron-rich system (which is heteroaromatic moiety in this case) and heavy atom, which can be formally “oxidized” in the excited states due to charge transfer from the metal center to ligand. I suggest to write this part conclusions as follow “All the synthesized complexes demonstrated luminescence in the solid-state and in solution. It was found that the emission band maxima of complexes depends on the substituent at secondary and tertiary amine moieties at the C(5) position of 1,2,4-triazine core. ”

Response: All the necessary updates were made. Thank you for your comment.

Responses to the comments of Reviewer #7

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.

Comment 1. Absence of images of 1H NMR spectra, only their textual descriptions are
given.

Response: The representative ^{1}H NMR spectra were placed into Supporting Info.

Comment 2. The work lacks data on 13C NMR, IR spectroscopy, elemental analysis of
the obtained complexes. It would also be a good idea to add X-ray structural analysis to confirm the structure. DFT calculation is an excellent theoretical complement to the experiment, but can hardly fully replace the direct method of investigation.

Response: Due to the low solubility of the iridium complexes obtained, ^{13}C NMR and X-ray diffraction experiments are not possible.

Comment 3. The stoichiometry of the complexes does not seem to be confirmed by anything other than ESI and 1H NMR. Wouldn't it be worth supplementing the work with UV or fluorescence titration to establish the stoichiometry by any convenient method, such as a Job's plot?

Response: The reaction of the binuclear iridium complex with the triazine ligand is very slow and occurs with heating. UV or fluorescence titration experiments under such conditions are very difficult. Iridium complexes with a coordination number of metal cation is equals 6, in which three bidentate ligands are present, are widely discussed in the literature. This composition is also confirmed by high yields, which are possible only when the reagents react in stoichiometrically correct ratios. In our opinion, no additional research on this topic is necessary.

Comment 4. Figure 4 shows an anomalous spectrum of the L7 complex, which is not discussed in any particular way in the text of the paper. What is the reason for such a sharp drop of absorption to zero in a certain range of this spectrum? What is the main reason for the difference of this spectrum from all others, including the complex with ligand L8, which is close to it in structure?

Response: We are thankful for the Reviewer for pointing out for this anomaly. The absorption spectrum for the complex $Irppy_2L7$ was remeasured and the manuscript was updated.

Comment 5. What is the meaning of the obtained compounds if they have such a low quantum yield? Maybe authors should change the positioning of the work and shift the focus to the synthesis and characterization of new complexes?

Response: These complexes were synthesized as part of a search for iridium complexes with improved photophysical properties, including the ability to stain living cells. Although these hopes were not fulfilled, we believe that the results are worthy of publication.

Comment 6. Small errors in formatting and typos.

a) In the description of the 1H NMR spectra for the J value, the number of bonds through which spin-spin interaction occurs is not given.

Response: Corrected

b) Also, italicized spelling is used for J in some substances, but not in others.

Response: Corrected

c) In the conclusion, some words are written in 10 font instead of 9 font.

Response: Corrected

d) In the experimental part, the use of the 19F NMR method is indicated, although in the sense of the paper it is not needed and is not used anywhere.

Response: Since this manuscript was previously part of a larger article and was later taken out into a separate article, the mention of ^{19}F NMR spectra was left by chance. Corrected.

e) Figures 1 and 3 are too bright, the colors are poorly combined with the white background. In this form, the paper cannot be recommended for publication. The work requires a major revision and additions. Also, probably, it would be better to compile supplementary information as a separate file, in which the figures of spectra should be placed.

Response: Thank you for your valuable comments. ESI file have been compiled. We have tried to make all possible corrections to the manuscript to meet the requirements.

2nd peer-review round

Reviewer #1 | acceptance

All comments were addressed carefully. The manuscript can be recommended for acceptance.

Reviewer #2 | minor revision

The manuscript could be accepted for publication when authors will take into account all my comments.

Reviewer #3 | acceptance

Following the incorporation of the comments received, the manuscript has undergone substantial revision and is now suitable for publication in its current form.

Reviewer #4 | acceptance

The authors have done some work on the errors. The article can be accepted for publication.

Reviewer #5 | acceptance

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Reviewer #6 | acceptance

The authors have considered the issues raised by the reviewers and the manuscript is now acceptable for publication.

Reviewer #7 | major revision

The authors of this manuscript have made significant adjustments to their work, improving it considerably. However, there are still a few important issues that are crucial to address and whose addition could strengthen the work.

1) It follows from the experimental part that L1 and L3 are obtained for the first time in this work. For the new ligands L1, L3 there are no data on C13 NMR, IR and melting point (and some measurements are suitable for complexes too), which makes the description of the new compounds incomplete and inconclusive. As it may seem, if you were able to get 1H NMR spectra, you can get spectra by the signal accumulation method. If the solubility is negligible, it is probably worth using a different solvent, e.g., DMSO-d6. Anyway, you can characterize ligands L1, L3 if they are obtained for the first time.

2) The 1H NMR spectra have indeed been added to the SI. However, it is worth adding a mention of this in the “Supplementary information” section of the manuscript.

3) In the images of electronic absorption and excitation spectra on the ordinate axis it is better to replace commas with dots. It is also necessary to correct a number of typos, for example, “stronly”.

Unfortunately, I am forced to repeat the conclusion from the previous review. In this form, the paper cannot be recommended for publication. The work requires a revision and additions.

Editors’ comment

1) Please rewrite the abstract according to the guidelines from the template:
"We recommend the authors to adhere to the following structure, providing a brief description of each component: background, problems/gaps, purpose of the research, details/features of theoretical or experimental design, principal findings, major conclusions, and significance of the research for future investigations."
2) Images of several NMR and mass spectra of ligands and their iridium complexes mentioned in the manuscript text are missing in the Supplementary files. Please add all missing spectra.

Editor’s decision

Minor revision.

Responses to the comments of Reviewer #7

Thank you for carefully reading our manuscript and making insightful, critical, and constructive feedback.
Comment 1. It follows from the experimental part that L1 and L3 are obtained for the
first time in this work. For the new ligands L1, L3 there are no data on C13
NMR, IR and melting point (and some measurements are suitable for complexes
too), which makes the description of the new compounds incomplete and
inconclusive. As it may seem, if you were able to get 1H NMR spectra, you
can get spectra by the signal accumulation method. If the solubility is
negligible, it is probably worth using a different solvent, e.g. DMSO-d6.
Anyway, you can characterize ligands L1, L3 if they are obtained for the
first time.
Response: The description of the 13C NMR, FTIR spectra and physical properties were placed in an experimental part of the manuscript for new ligands L1, L3.
Comment 2. The 1H NMR spectra have indeed been added to the SI. However, it is worth
adding a mention of this in the “Supplementary information” section of
the manuscript.
Response: Mention of the presentation of 1H NMR spectra in ESI has been added to the relevant section.
Comment 3. In the images of electronic absorption and excitation spectra on the
ordinate axis it is better to replace commas with dots. It is also necessary

to correct a number of typos, for example, “stronly”.
Response: Corrected.

Responses to the comments of Editor

[1]

Final Editor’s decision

Accept.

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[1] The last comments of the Editor have not been addressed in the revised manuscript version.