published by Ural Federal University
eISSN 2411-1414
chimicatechnoacta.ru

ARTICLE
2024, vol. 12(1), No. 12109
DOI: 10.15826/chimtech.2025.12.1.09

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

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Abstract

A series of novel iridium(III) complexes containing 5-N-(aryl)-amino- or 5-cycloamino-3-(pyridine-2-yl)-1,2,4-triazine ligands was obtained. These complexes exhibited red luminescence in solution as well as in the solid state. Based on the DFT studies it was suggested that N(2) atom of the 1,2,4-triazine core is preferable to N(4) one as the coordination site in the complexes of Ir(III).

Key findings

- Eight new iridium(III) complexes based on 6-phenyl-5-R-3-(pyridine-2-yl)-1,2,4-triazines were synthesized and characterized by spectroscopic techniques.
- Quantum chemical calculations of the Ir(III) coordination sites were performed revealing that N(2) atom of the 1,2,4-triazine core is preferable to N(4) one in the coordination of the Ir(III).
- The obtained iridium(III) complexes exhibited red luminescence both in solutions and in powder.

Accompanying information

Article history
Received: 01.11.24
Revised: 11.12.24
Accepted: 11.12.24
Available online: 18.12.24

Keywords
Iridium(III) complexes; 1,2,4-Triazines; luminescence; solid-state luminescence; DFT calculations

Funding
The work was supported by the Russian Science Foundation grant No. 23-23-00539.

Supplementary information
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Supplementary materials: READ

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1. Introduction

Cyclometallated iridium(III) complexes are of wide interest due to their promising photophysical properties [1], especially phosphorescence [2]. The bright luminescence of iridium(III) complexes arises from several factors: the lowest excited state is a mixture of metal-to-ligand charge transfer (MLCT) and ligand centered (LC) π–π* states, while the presence of a heavy iridium atom (heavy-atom effect) results in spin-orbit coupling (SOC) [3]. Large ligand field splitting (Δ_o) of *d*-electrons is achieved due to the presence of cyclometallated C–Ir bonds [3]. Therefore, iridium(III) complexes found wide applications in OLEDs [3, 4] and light-emitting electrochemical cells (LECs) [5, 6]. In synthetic organic chemistry iridium(III) complexes are of wide use as photocatalysts in visible-light driven reactions [7], C(sp^2)–H borylation reactions [8], C(sp^3)-H amidation reactions [9], CO_2 reduction [10], and light-driven water reduction [11]. Finally, cyclometallated iridium(III) complexes are of wide use in medical applications, namely, as anticancer agents [12–18], in photodynamic therapy (PDT) [19], photothermal therapy (PTT) [20, 21], and photoactivated chemotherapy (PACT) [22]. It is worth to mention that the fine tuning of photophysical and optical properties of such complexes is possible by varying the appropriate ligand environment, especially in case of an ancillary ligand [23, 24]. Thus, iridium(III) complexes can emit in the entire visible range from violet to red and even in the IR range [25, 26]. Among the plenty of Ir(III) ancillary ligands, the most widespread ones belong to N^N type (usually, 2,2'-bipyridine and 1,10-phenanthroline-bsed ligands are used) due to their commercial and synthetic availability, as well as their useful applications. Meanwhile, N^N type ligands based on derivatives and analogs of 3-(pyridine-2-yl)-1,2,4-triazines are less investigated despite promising practical

applicability of Ir(III) complexes with this type of ancillary ligands. Iridium(III) complexes containing 3-(pyridin-2-yl)-1,2,4-triazine core as ligand find applications as water-soluble phosphorescent turn-on sensors for human serum albumin [27], chemotherapy agents[28], and precursors for bioorthogonal reactions [29].

Keeping all that in mind, in the framework of this study we designed and investigated novel iridium(III) complexes based on 5-aminosubstituted 3-(pyridine-2-yl)-1,2,4-triazine ligands.

2. Experimental

Iridium dimer $[(ppy)_2IrCl]_2$ was purchased from Shanghai Macklin Biochemical Technology. 6-Phenyl-5-cyano-3-(pyridine-2-yl)-1,2,4-triazine was synthesized according to the literature [30]. 1,2,4-Triazine ligands **L2** [31] **L4** [32] and **L5**-**L8** [33] were synthesized as described in the literature. Acetonitrile from PanReac Applichem.

^{1}H NMR spectroscopy data were obtained using a Bruker DRX-400 spectrometer with CD_3CN as a solvent. Chemical shifts were referenced in accordance to the CD_3CN residual proton resonance (1.94 ppm, δ-scale). ^{1}H NMR spectra were recorded for L1 and L3 in $CDCl_3$ and DMSO-d_6, respectively. Mass spectrometry data were acquired using an Agilent 6545 Q-TOF LC-MS with electrospray ionization. UV/Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer, and luminescence emission spectra (in solution and in powder) were recorded on a Horiba FluoroMax-4 spectrofluorometer by using quartz cells with a 1 cm path length at room temperature. Absolute quantum yields of luminescence were measured in an integrating sphere Quanta-ϕ of the Horiba FluoroMax 4 at room temperature [34]. IR spectra were measured on a LUMOS-Bruker IR-Fourier spectrometer in potassium bromide tablets.

2.1. Computational Details

The density functional theory (DFT) calculations were carried out at the PM3/B3LYP/def2-TZVP level of DFT theory with RIJCOSX approximation and D3BJ correction using ORCA 6.0 QC package [35]. The Chemcraft program (http://www.chemcraftprog.com/) was used for visualization.

2.2. General method for the synthesis of 5-arylamino-1,2,4-triazines

A mixture of corresponding 5-cyano-1,2,4-triazine (0.5 mmol) and amine (0.5 mmol) was stirred at 150 °C for 10 h under argon atmosphere. Then the resulting mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and impregnated on SiO_2 by means of evaporation at room temperature. The target product was isolated by flash chromatography using DCM:EtOAc (9:1) mixture as an eluent.

2.2.1. *N*-(2-Methylphenyl)-6-phenyl-3-(pyridine-2-yl)-1,2,4-triazine-5-amine (L1)

Yield 89%. m.p. 148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (*s*, 3H, Me), 7.11–7.37 (*m*, 4H, NH, 2-Methylphenyl), 7.40–7.48 (*m*, 1H, H-5 (Py)), 7.57–7.69 (*m*, 3H, Ph), 7.80–7.91 (*m*, 3H, Ph, H-4 (Py)), 8.18–8.24 (*m*, 1H, 2-Methylphenyl), 8.43 (*dd*, ^3J = 7.7, ^4J = 1.0 Hz, 1H, H-3 (Py)), 8.88 (*dd*, ^3J = 4.8, ^4J = 2.0 Hz, 1H, H-6 (Py)). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.8, 153.6, 151.9, 149.6, 147.8, 136.9, 136.1, 134.1, 133.8, 130.3, 129.7, 128.9 (2C), 128.6 (2C), 126.4, 126.2, 126.0, 125.0, 123.3, 18.2. ESI-MS, *m*/*z*: calcd 340.15 $(M + H)^+$; found 340.15. Anal. calcd for $C_{21}H_{17}N_5$: C 74.32, H 5.05, N 20.63%; found: C 74.27, H 4.99, N 20.55%. IR (KBr), ν, cm^{-1}: 3058 (CH(arom)), 1444 (N–H).

2.2.2. *N*-(4-Methoxyphenyl)-6-phenyl-3-(pyridine-2-yl)-1,2,4-triazine-5-amine (L3)

Yield 95%. m.p. oil. ^{1}H NMR (400 MHz, DMSO-d_6):: δ 3.85 (*s,* 3H, OMe), 6.93-6.99 (*m*, 2H, 4-methoxyphenyl), 7.22 (*brs*, 1H, NH), 7.41-7.47 (*m*, 1H, H-5 (Py)), 7.57–7.68 (*m*, 5H, Ph, 4-methoxyphenyl), 7.79–7.85 (*m*, 2H, Ph), 7.88 (*ddd*, ^3J = 7.7, 7.7, ^4J = 2.0 Hz, 1H, H-4 (Py)), 8.48 (*dd*, ^3J = 7.7, ^4J=1.0 Hz, 1H, H-3 (Py)), 8.88 (*dd*, ^3J = 4.8, ^4J = 2.0 Hz, 1H, H-6 (Py)). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.0, 156.6, 154.1, 151.8, 150.2, 148.6, 137.5, 134.4, 131.1, 130.2, 129.4 (2C), 129.1 (2C), 125.6 (2C), 125.0, 123.9, 114.1 (2C), 55.7. ESI-MS, *m*/*z*: calcd 356.15 $(M + H)^+$; found 356.15. Anal. calcd for $C_{21}H_{17}N_5O$: C 70.97, H 4.82 %; found: C 70.92, H 4.77 %. IR (KBr), ν, cm^{-1}: 3058 (CH(arom)), 2835 (O–CH_3), 1445 (N–H).

2.3. Method for the synthesis of $Irppy_2$(L1-L6) complexes

A mixture of $[(ppy)_2IrCl]_2$ (50 mg, 0.047 mmol, 1 eq) and a corresponding ligand L (0.09 mmol, 2 eq) was refluxed in 30 ml of a DCM:methanol mixture (1:1) under argon for 20 h. Then the reaction mixture was concentrated in vacuo and the resulting powder was recrystallized from DCM:acetonitrile mixture (1:1).

2.3.1. $Irppy_2L1$

Red crystals. Yield 69 mg (0.08 mol, 88%). NMR ^{1}H (CD_3CN, δ, ppm): 2.28 (*s*, 3H, Me), 6.19 (*d*, *J* = 8.0 Hz, 1H, ppy), 6.30 (*d*, ^3J = 8.0 Hz, 1H, ppy), 6.76 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, ppy), 6.85–6.92 (*m*, 2H, ppy), 6.99–7.07 (*m*, 2H, ppy), 7.11–7.16 (*m*, 1H, H-6(Py)), 7.30–7.35 (m, 2H, ppy), 7.36–7.41 (*m*, 1H, ppy), 7.46–7.62 (*m*, 8H, Ph, ppy), 7.67–7.71 (*m*, 1H, ppy), 7.76–7.89 (*m*, 4H, ppy), 8.00–8.08 (*m*, 3H, ppy), 8.15–8.18 (*m*, 1H, ppy), 8.21 (*d*, ^3J = 8.0 Hz, 1H, ppy), 8.27 (*s*, NH). ESI-MS, *m*/*z*: calcd. 840.24 $(M + H)^+$; found 840.2431.

2.3.2. $Irppy_2L2$

Red crystals. Yield 76 mg (0.09 mol, 91%). NMR ^{1}H (CD_3CN, δ, ppm): 3.81 (*s*, 3H, MeO), 6.19 (*d*, ^3J = 8.0 Hz, 1H, ppy), 6.32 (*d*, ^3J = 8.0 Hz, 1H, ppy), 6.77 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, ppy), 6.87–6.95 (*m*, 2H, ppy),

 DOI: 10.15826/chimtech.2025.12.1.09

7.02–7.20 (*m*, 6H, Ph), 7.28 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, ppy), 7.54–7.57 (*m*, 3H, Ph), 7.63–7.66 (*m*, 2H, ppy), 7.79–7.90 (*m*, 4, ppy), 7.97–7.09 (*m*, 4H, ppy), 8.14 (*d*, *J* = 8.0 Hz, 1H, H-3(Py)), 8.20 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, H-4(Py)), 8.42 (*d*, ^3J = 8.0 Hz, 1H, H-5(Py)), 8.59 (*s*, 1H, NH), 8.67 (*d*, ^3J = 4.0 Hz, 1H, ppy), ESI-MS, *m*/*z*: calcd. 856.24 $(M + H)^+$; found 856.2415.

2.3.3. Irppy$_2$L3

Red crystals. Yield 78 mg (0.09 mol, 92%). NMR ^{1}H (CD_3CN, δ, ppm): 3.82 (*s*, 3H, MeO), 6.17 (*d*, *J* = 8.0 Hz, 1H, ppy), 6.30 (*d*, ^3J = 8.0 Hz, 1H, ppy), 6.75 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, ppy), 6.84–6.93 (*m*, 2H, ppy), 7.00–7.16 (*m*, 6H, Ph), 7.27 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, ppy), 7.53–7.56 (*m*, 3H, Ph), 7.61–7.64 (*m*, 2H, ppy), 7.78–7.84 (*m*, 4H, ppy), 7.94–7.05 (*m*, 4H, ppy), 8.16 (*d*, *J* = 8.0 Hz, 1H, H-3(Py)), 8.19 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, H-4(Py)), 8.44 (*d*, *J* = 8.0 Hz, 1H, H-5(Py)), 8.75 (*s*, 1H, NH), ESI-MS, *m*/*z*: calcd. 856.24 $(M + H)^+$; found 856.2415.

2.3.4. Irppy$_2$L4

Red crystals. Yield 74 mg (0.08 mol, 83%). NMR ^{1}H (CD_3CN, δ, ppm): 6.18 (*d*, *J* = 8.0 Hz, 1H, ppy), 6.31 (*d*, *J* = 8.0 Hz, 1H, ppy), 6.77 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, ppy), 6.87–6.94 (*m*, 2H, ppy), 7.01–7.13 (*m*, 7H, Ph, ppy), 7.15-7.21 (*m*, 1H, ppy), 7.39–7.45 (*m*, 3H, Ph, ppy), 7.47–7.74 (*m*, 8H, Ph, ppy), 7.78–7.89 (*m*, 4H, Ph, ppy), 7.96 (*d*, *J* = 8.0 Hz, 1H, H-5(Py)), 8.00–8.08 (*m*, 2H, ppy), 8.11–8.17 (*m*, 2H, ppy), 8.45–8.51 (*m*, 2H, ppy). ESI-MS, *m*/*z*: calcd. 918.25 $(M + H)^+$; found 918.2522.

2.3.5. Irppy$_2$L5

Red crystals. Yield 73 mg (0.08 mol, 83%). NMR ^{1}H (CD_3CN, δ, ppm): 2.79–2.94 (*m*, 2H, pyrrolidine-2-yl), 3.75–3.89 (*m*, 2H, pyrrolidine-2-yl), 6.18 (*dd*, ^3J = 8.0 Hz, ^4J = 0.7 Hz, ppy), 6.30 (*dd*, ^3J = 8.0 Hz, ^4J = 0.7 Hz, ppy), 6.77 (*ddd*, ^3J = 4.0 Hz, ^3J = 4.0 Hz, ^4J = 1.0 Hz, 1H, H-4(Py)), 6.89–6.92 (*m*, 2H, ppy), 7.01–7.06 (*m*, 2H, ppy), 7.07–7.10 (*m*, 1H, ppy), 7.24–7.26 (*m*, 2H, Ph), 7.37–7.40 (*m*, 2H, ppy), 7.44–7.47 (*m*, 1H, ppy), 7.57–7.60 (*m*, 1H, ppy), 7.63–7.65 (*m*, 1H, ppy), 7.68 (*dd*, ^3J = 8.0 Hz, ^3J = 4.0 Hz, 1H, ppy), 7.78–7.86 (*m*, 4H, Ph, ppy), 7.94–7.96 (*m*, 1H, ppy), 7.99 (*d*, 4.0 Hz, ppy), 8.03–8.06 (*m*, 2H, ppy), 8.16 (*ddd*, ^3J = 4.0 Hz, ^3J = 4.0 Hz, ^4J = 1.0 Hz, 1H, H-4(Py)), 8.69 (*d*, ^3J = 4.0 Hz, 1H, H-6(Py)). ESI-MS, *m*/*z*: calcd. 804.24 $(M + H)^+$; found 804.2432.

2.3.6. Irppy$_2$L6

Red crystals. Yield 70 mg (0.09 mol, 92%). NMR ^{1}H (CD_3CN, δ, ppm): 2.34 (s, 6H, Piperidin-1-yl), 3.55 (*s*, 4H, Piperidine-1-yl), 6.19 (*d*, *J* = 8.0 Hz, 1H, ppy), 6.31 (*d*, *J* = 8.0 Hz, 1H, ppy), 6.79 (*ddd*, ^3J = 8.0 Hz, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, ppy), 6.88–6.96 (*m*, 2H, ppy), 7.00–7.10 (*m*, 2H, ppy), 7.31–7.35 (*m*, 2H, ppy), 7.36–7.46 (*m*, 3H, ppy), 7.57–7.62 (*m*, 1H, ppy), 7.62–7.66 (*m*, 2H, Ph), 7.69 (*d*, ^3J = 8.0 Hz, 1H, ppy), 7.77–7.87 (*m*, 3H, Ph), 7.94-8.01 (*m*, 2H, ppy), 8.03–8.08 (*m*, 1H, H-4(Py)), 8.13–8.23 (*m*, 2H, H-3(Py), ppy), 8.68 (*d*, ^3J = 8.0 Hz, 1H, H-6(Py)). ESI-MS, *m*/*z*: calcd. 818.26 $(M + H)^+$; found 818.2617.

2.3.7. Irppy$_2$L7

Red crystals. Yield 66 mg (0.08 mol, 86%). NMR ^{1}H (CD_3CN, δ, ppm): 2.66 (*s*, 2H, morpholine-1-yl), 3.85 (*s*, 2H, morpholine-1-yl), 6.20 (*d*, ^3J = 8.0 Hz, 1H, ppy), 6.31 (*d*, ^3J = 8.0 Hz, ppy), 6.75–6.82 (*m*, 1H, ppy), 6.88–6.98 (*m*, 2H, ppy), 7.32–7.46 (*m*, 5H, ppy, Ph), 7.59–7.70 (*m*, 4H, ppy), 7.75–7.91 (*m*, 5H, ppy), 7.93–8.09 (*m*, 5H, ppy, Ph), 8.13–8.22 (*m*, 1H, H-3(Py)), 8.71 (*d*, ^3J = 8.0 Hz, 1H, H-6(Py)). ESI-MS, *m*/*z*: calcd. 836.02 $(M + H)^+$; found 836.0234

2.3.8. Irppy$_2$L8

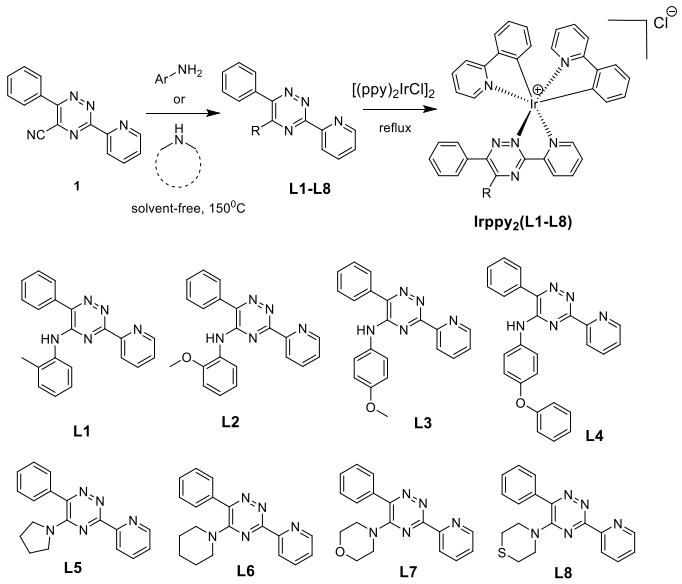
Red crystals. Yield 70 mg (0.08 mol, 86%). NMR ^{1}H (CD_3CN, δ, ppm): 2.72 (*s*, 2H, thiomorpholine-1-yl), 3.80 (*s*, 2H, thiomorpholine-1-yl), 6.19 (*d*, ^3J = 8.0 Hz, 1H, ppy), 6.31 (*d*, ^3J = 8.0 Hz, ppy), 6.76–6.83 (*m*, 1H, ppy), 6.88–6.96 (*m*, 2H, ppy), 7.33–7.47 (*m*, 5H, ppy, Ph), 7.58–7.71 (*m*, 4H, ppy), 7.76–7.90 (*m*, 5H, ppy), 7.94–8.10 (*m*, 5H, ppy, Ph), 8.14-8.22 (*m*, 1H, H-3(Py)), 8.70 (*d*, ^3J = 8.0 Hz, 1H, H-6(Py)). ESI-MS, *m*/*z*: calcd. 819.95 $(M + H)^+$; found 819.9528

3. Results and Discussions

3.1. Synthesis

We designed and synthesized **Irppy$_2$(L1-L8)** complexes, where **ppy** are archetypal 2-phenylpyridine ligands, and **L** is 6-phenyl-5-R-3-(pyridine-2-yl)-1,2,4-triazine ligands (Scheme 1). The choice of cyclic amines residues [31] or aniline derivatives [32] as R was due to a high electron-donating effect of these group which is favorable for the intense luminescence. These ligands were obtained by means of *ipso*-substitution of a C5-cyano group of the corresponding 5-cyano-1,2,4-triazines [31–33]. The target iridium complexes were obtained in excellent yields by means of a standard reaction between iridium dimer $[(ppy)_2IrCl]_2$ and 2 eq. of the corresponding 1,2,4-triazine ligands **L1–8** in DCM:methanol = 1:1 mixture as a solvent. Chloride anion was presented as a counterion in the complexes. The structures of the obtained complexes were confirmed by ^{1}H NMR spectroscopy and HRMS mass-spectrometry data.

 DOI: 10.15826/chimtech.2025.12.1.09



Scheme 1 Synthesis of Ir(III) complexes.

3.2. Quantum chemical calculations

For 2-pyridyl-substituted 1,2,4-triazine ligands one may suggest two coordination sites for Ir(III) cation, namely, N2 atom [27–28] or, less commonly, N4 atom [29]. Therefore, in order to confirm the position of the coordination site of the 1,2,4-triazine moiety, quantum chemical calculations were carried out for the iridium(III) complex **Irppy₂L5** (Figure 1). The structures **Irppy₂L5_N4**, with N(4) atom in the 1,2,4-triazine moiety (as coordination site), and **Irppy₂L5_N2**, with N(2) atom in the 1,2,4-triazine moiety (as coordination site), were optimized. A frequency analysis revealed no imaginary frequencies, indicating that the actual minimum position on the potential energy surface (PES) of the atomic systems optimized structures was obtained.

As a result of the analysis of the total potential energies of the optimized structures, the advantage of the **Irppy₂L5_N2** structure over **Irppy₂L5_N4** was found to be −54.82 kJ/mol. This can be explained by steric hindrances arising as a result of the repulsion of the pyrrolidine-1-yl substituent at C(5) position of the 1,2,4-triazine core from the coordination center of the **Irppy₂L5_N4** structure. In the **Irppy₂L5_N2** structure, such hindrances are not observed, which leads to such a significant gain.

Nevertheless, for the complete proof of the energy gain of the atomic system of the 1,2,4-triazine-based iridium(III) complex with N(2) iridium(III) coordination, structures **Irppy₂L9** (with 6-phenyl-3-(pyridine-2-yl)-1,2,4-triazine, Figure 2) without the substituent at the the C(5) position of the 1,2,4-triazine were optimized (Figure 3). In this case there should be no steric effect. Indeed, the energy gain of **Irppy₂L9_N2** structure over **Irppy₂L9_N4** was revealed to be −8.73 kJ/mol. While this value is less than the one of structures **Irppy₂L5**, it is non-negligible.

Thus, based on quantum chemical calculations it was confirmed that the coordination of iridium(III) cation with N(2) atom of the 1,2,4-triazine core in 3-pyridine-2-yl-1,2,4-triazine complexes is more energetically favorable.

3.3. Photophysical studies

Photophysical properties of the synthesized Ir(III) complexes **Irppy₂(L1-L8)** were evaluated (Table 1, Figures 4–5, S1–S2). UV absorption and emission spectra were recorded in deoxygenated acetonitrile solutions with the concentration C = 10 μM. Thus, in UV spectra several absorption bands were observed. The bands with maxima around 248–297 nm correspond to the ligand-based π–π* transitions and the bands with maxima around 325–399 correspond to n–π* transitions, while the bands with the lowest energy originate from the MLCT state due to the presence of the heavy iridium atom. The last ones are characterized by a very low extinction coefficient values (*ca.* 800–2600 $M^{-1}\cdot cm^{-1}$). Emission spectra showed several emission bands: three narrow bands with low intensity around 400–500 nm as well as a broad band with maxima at 664–688 nm corresponding to the ^{3}MLCT-state emission. For all the complexes the emission band ended beyond the spectrofluorometer measurement range. The absolute quantum yield values in MeCN were < 0.1 % in all cases resulting in low emission intensity.

4. Limitations

For all the obtained iridium(III) complexes based on 6-phenyl-5-R-3-(pyridine-2-yl)-1,2,4-triazines, very low photoluminescence quantum yields (less than 0.1%) were observed. This might be associated with the influence of 1,2,4-triazine presented in these ligands.

5. Conclusions

In this work eight iridium(III) complexes based on 6-phenyl-5-R-3-(pyridine-2-yl)-1,2,4-triazine ligands have been successfully synthesized for the first time. Quantum chemical calculations were performed to estimate the possible Ir(III) coordination sites.

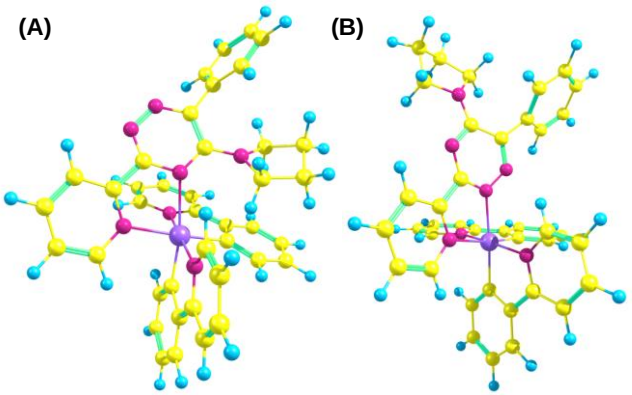


Figure 1 Optimized structures for the complexes Irppy₂L5_N4 (A) and Irppy₂L5_N2 (B).

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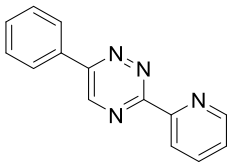
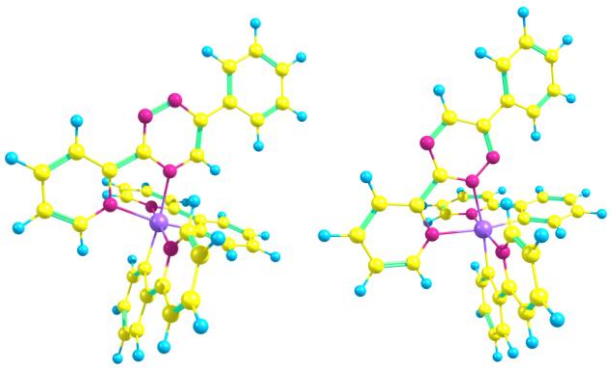


L9

Figure 2 Structure of the ligand **L9**.



(A) **(B)**

Figure 3 Optimized structures of the complexes **Irppy₂L9_N4** (**A**) and **Irppy₂L9_N2** (**B**).

Table 1 Photophysical properties of **Irppy₂(L1-L8)** complexes.

Ligand	λ_{ABS} (nm)	ε, ($M^{-1}\cdot cm^{-1}$)[a]	λ_{abs} (nm)[b]	λ_{em} (nm)[c]	Φ (%)[d]
L1	252, 342, 381sh, 467sh	800	398, 410, 422, 664	644	< 0.1
L2	255, 354, 492sh	2600	424, 439, 453, 688	677	< 0.1
L3	251, 287sh, 341, 506sh	1100	358, 369, 379, 409, 688	681	< 0.1
L4	249, 283sh, 345sh, 376sh, 498	1000	425, 439, 454, 677	708	< 0.1
L5	255, 339, 378sh, 503sh	900	428, 445, 459, 662	680	< 0.1
L6	250, 287sh, 341, 400sh, 506sh	900	474, 494, 511, 672	675	< 0.1
L7	253, 284, 342sh, 484sh	800	426, 438, 453, 473, 676	652	< 0.1
L8	266, 301, 388, 401sh, 489sh	1100	442, 452, 683	763	< 0.1

[a] for the most red-shifted bands;
[b] fluorescence spectra in acetonitrile solution;
[c] fluorescence spectra in powder;
[d] absolute quantum yields in acetonitrile solution.

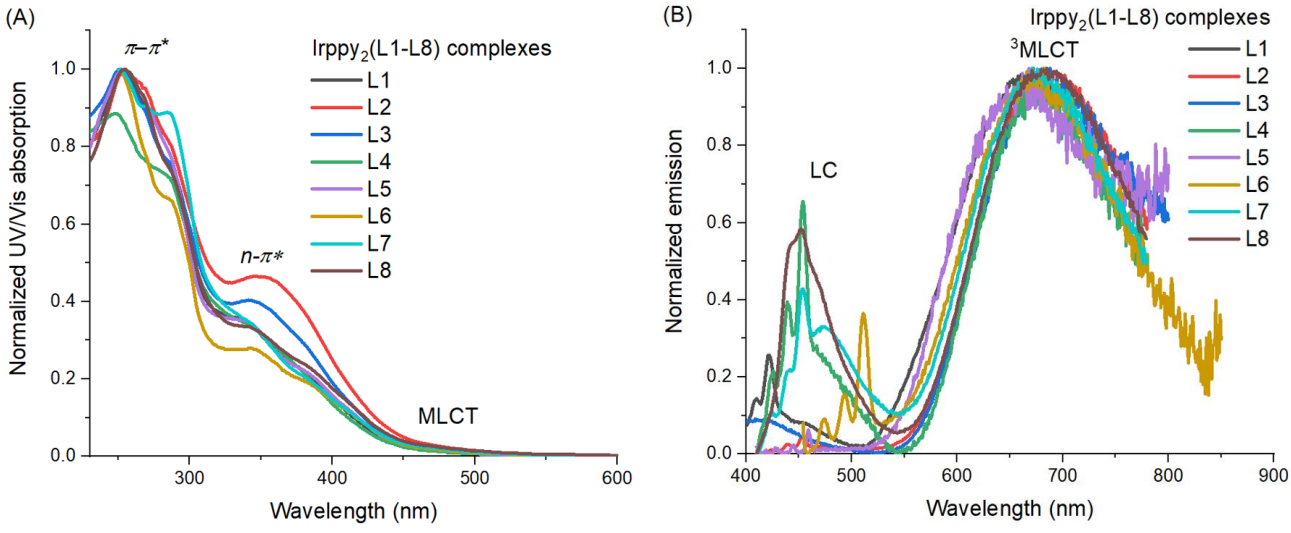


Figure 4 Absorption (A) and emission (B) spectra of **Irppy₂(L1–L8)** complexes in MeCN solution.

 DOI: 10.15826/chimtech.2025.12.1.09

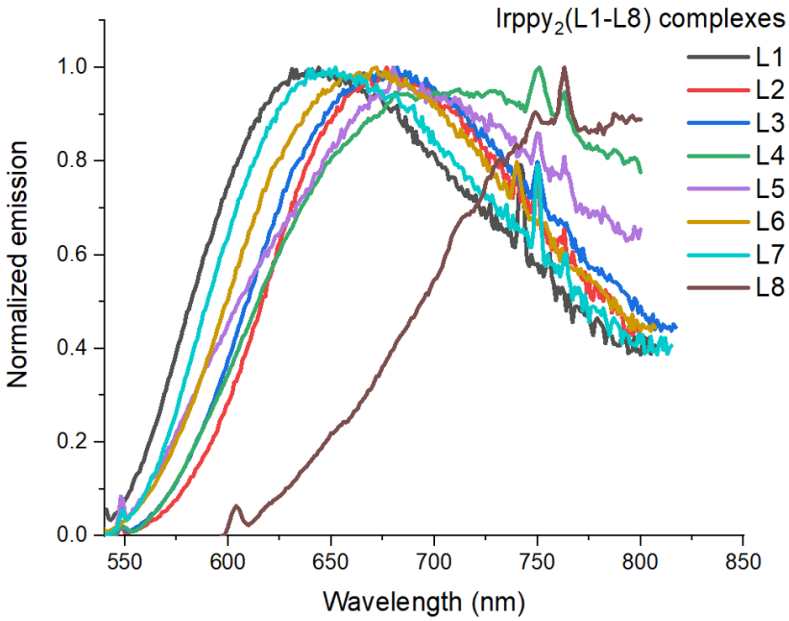


Figure 5 Emission spectra of **Irppy₂(L1–L8)** complexes in powder at r.t.

It was found that N(2) atom of the 1,2,4-triazine core is more preferable than N(4) one for the coordination of Ir(III). All eight iridium(III) complexes with an auxiliary 3-pyridin-2-yl-1,2,4-triazine ligands demonstrated red luminescence both in the solid state and in a solution. It was found that the emission band maxima of the complexes depend strongly on the nature of amine moieties at the C(5) position of the 1,2,4-triazine core. The search for complexes with the best photophysical properties is in progress.

Supplementary materials

Figures S1–5 Representative 1H NMR spectra of Irppy2(L1, L2 ,L4-6) complexes.

Acknowledgments

None.

Author contributions

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Conflict of interest

The authors declare no conflict of interest.

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