

## New Phosphorescent Cyclometalated Iridium(III) Complexes with Diphenyl-1,3-oxazolic and 2-(3-Thienyl)pyridine Ligands for LED Applications

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### Abstract

We report four new phosphorescent iridium(III) complexes with 2,4-diphenyl-1,3-oxazole [ $\text{Ir}(\text{24dpo})_3$ ], 2,5-diphenyl-1,3-oxazole [ $\text{Ir}(\text{25dpo})_3$ ], 2-(3-thienyl)pyridine [ $\text{Ir}(\text{3thpy})_3$ ] and [ $\text{Ir}(\text{3thpy})_2(\text{acac})$ ]. Three of them demonstrate good photophysical properties to be used as dopants to organic polymer matrix or to be used "as is" without a host matrix to fabricate OLEDs. Green and yellow light emission was observed for the photoluminescence: 569/525, 549/498 nm and 557,604/533 (solid state/ $\text{CH}_2\text{Cl}_2$  solution) for  $\text{Ir}(\text{24dpo})_3$ ,  $\text{Ir}(\text{3thpy})_3$  and  $\text{Ir}(\text{3thpy})_2\text{acac}$  respectively. Room temperature luminescent lifetimes are 2.5 and 1.8  $\mu\text{s}$  and quantum efficiencies 37 and 53% for  $\text{Ir}(\text{24dpo})_3$  and  $\text{Ir}(\text{3thpy})_3$ . The complexes are stable in air and sublimable at low pressure without considerable decomposition. Comparison of physico-chemical properties of the reported iridium(III) cyclometalated compounds with that known from literature is carried out.

### 1. Introduction

Complexes of iridium(III) with cyclometalating ligands (abbreviated hereafter as  $\text{C}^{\wedge}\text{N}$ ) such as  $\text{Ir}(\text{ppy})_3$  (ppy=2-phenylpyridine) and related compounds have high phosphorescent efficiency and microsecond lifetime, which make them efficient phosphor dopants in polymeric matrixes for OLEDs applications.<sup>1-3</sup> The photochemical and photocatalytic properties of the  $d^6$  configuration  $\text{Ir}^{3+}$  complexes are mainly determined by the lowest-energy excited states.<sup>4</sup> The  $\sigma$ -donor and  $\pi$ -acceptor properties of the ligands give rise to the low-lying metal to ligand charge-transfer (MLCT) states. The tris-cyclometalated complexes with a maximum number

of coordinating C atoms are most perspective. However, mainly bis-cyclometalated iridium complexes,  $\text{C}^{\wedge}\text{N}_2\text{Ir}(\text{acac})$  (acac=acetylacetonate), are investigated for LED applications due to the fact that they can be synthesized more easily than tris-complexes.<sup>5-7</sup> In this work, the preparation of highly phosphorescent iridium tris-cyclometalated complexes was aimed for. Reported here are results of a study of the tris-cyclometalated complexes: green color emitting  $\text{Ir}(\text{24dpo})_3$  (1),  $\text{Ir}(\text{3thpy})_3$  (2) and yellow emitting  $\text{Ir}(\text{25dpo})_3$  (3) (Fig.1).

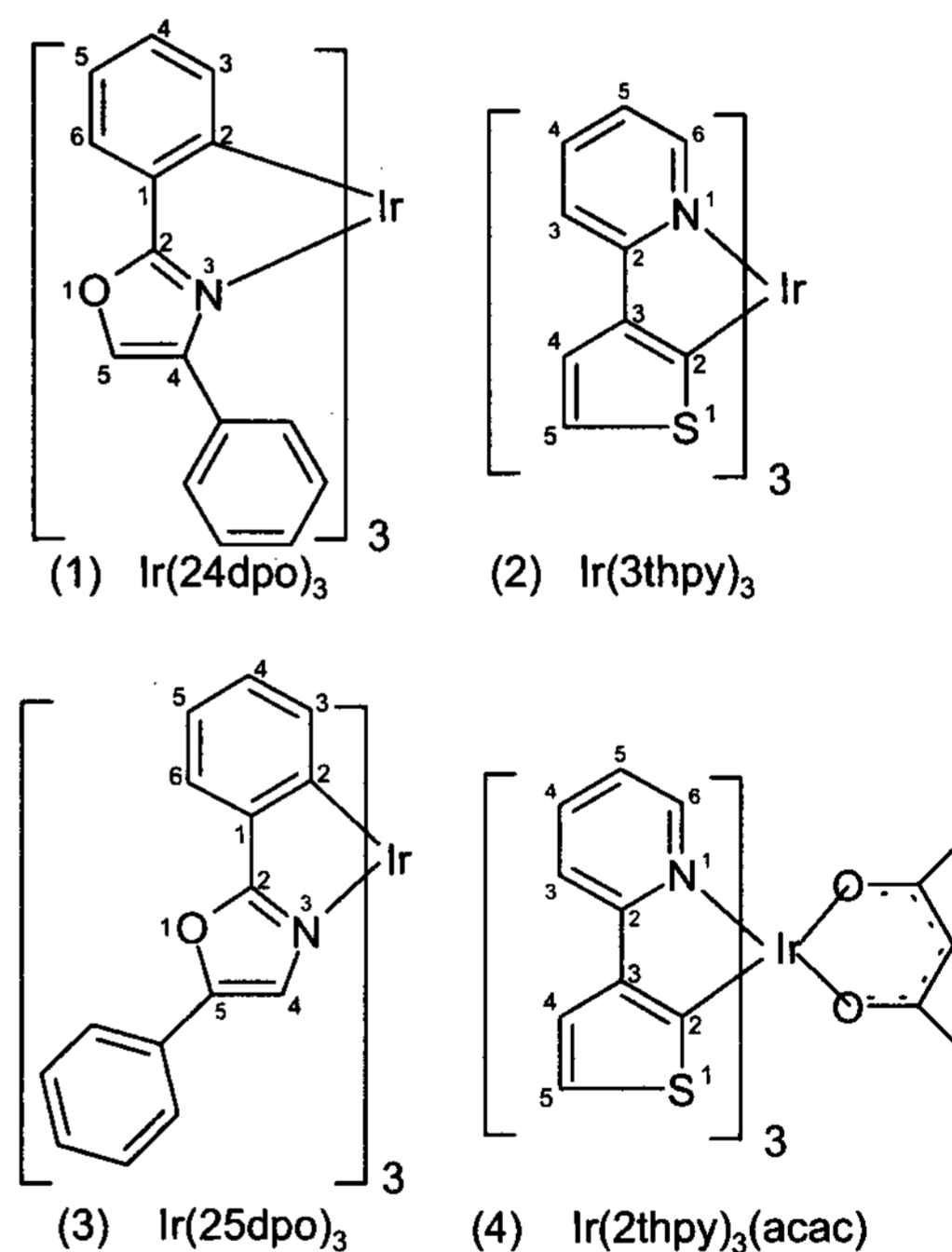


Figure 1. Studied iridium(III) complexes

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To draw comparisons with literature data on bis-complexes  $C^N_2Ir(acac)$ , we also studied  $Ir(3thpy)_2(acac)$  (**4**). Choice of these ligands was determined by the fact that they are isomeric to 2-(2-thienyl)pyridine (2thpy) and 2,5-diphenyl-1,3-oxazole (25dpo) ligands in iridium complexes  $Ir(2thpy)_3$ ,  $Ir(2thpy)_2(acac)$  and  $Ir(25dpo)_2(acac)$  already described in literature.<sup>4-5</sup>

## 2. Results and Discussion

### 2.1 General

Tris-cyclometalated complexes (**1**), (**2**), (**3**) of a general formula  $Ir(C^N)_3$  have been obtained from iridium chloride hydrate and 3,5 equivalents of a ligand by one step technique and identified by CHN analysis, <sup>1</sup>H NMR and mass spectrometry.

(**1**), (**2**) and (**4**) complexes are stable in air and can be sublimed at low pressure ( $5 \times 10^{-4}$  Torr, 270°C). They demonstrate higher storage stability (no changes in color and in properties with time) than  $Ir(ppy)_3$ , while  $Ir(25dpo)_3$  is well stored only under inert atmosphere.

### 2.2 Photophysical Properties

#### 2.2.1 Absorption Spectra

Intense absorption band of  $Ir(24dpo)_3$  and  $Ir(3thpy)_3$  appeared at 303 and 297 nm respectively (Table 1). These bands are typically assigned to the  $\pi - \pi^*$  transition of a ligand. Also several absorption peaks that could not be seen in the ligand spectrum appeared at lower energies. In iridium(III) cyclometalated complexes these bands ( $\lambda > 400$  nm) are used to be assigned to singlet and triplet metal-to-ligand charge

**Table 1. Photophysical data for cyclometalated iridium complexes**

Complex	Absorbance, $\lambda$ (nm)	Emission, $\lambda_{max}$ (nm)		Lifetime, <sup>a, b</sup> ( $\mu$ s) 298K	Quantum efficiency
		Powder	Solution		
$Ir(3thpy)_3$	297, 332, 375, 424	548, 590	498 <sup>c</sup>	1.8	0.53
$Ir(24dpo)_3$	297, 350, 392, 428	567	525 <sup>c</sup>	2.5	0.37
$Ir(25dpo)_3$			544, 590 <sup>c</sup>		
$Ir(3thpy)_2(acac)$		557, 604	533 <sup>c</sup>		
$Ir(ppy)_3$	289, 373, 450, 478	560	520 <sup>c</sup>	1.7	0.46
<sup>4</sup> $Ir(2thpy)_3$			545 <sup>d</sup>		
<sup>6</sup> $Ir(ppy)_2(acac)$	260, 345, 412, 460, 497		516 <sup>c</sup>	1.6	0.34
<sup>5</sup> $Ir(2thpy)_2(acac)$	302, 336, 387, 453		562 <sup>c</sup>	5.3	0.12
<sup>5</sup> $Ir(25dpo)_2(acac)$	297, 369, 420, 443		550 <sup>c</sup>	3.0	0.1

<sup>a</sup> The lifetimes and quantum efficiencies have error bars of  $\pm 10\%$ .

<sup>b</sup> Degassed 2-methyltetrahydrofuran solution

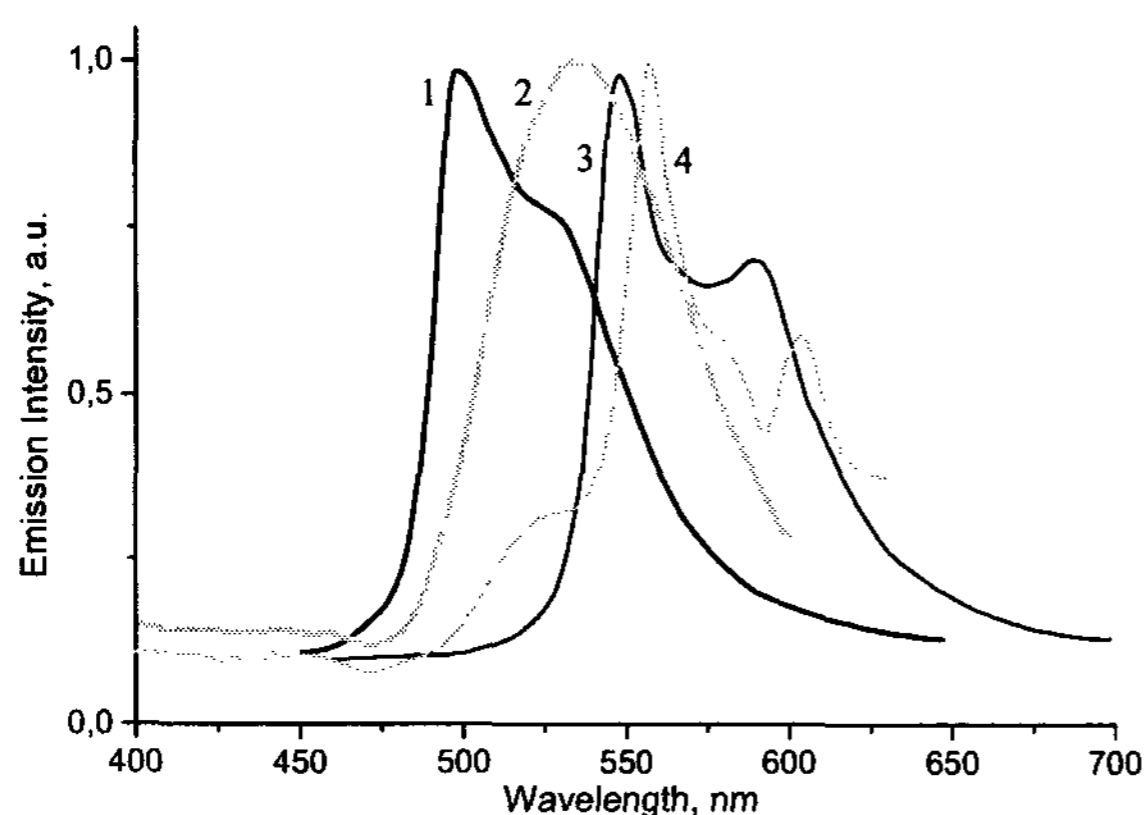
<sup>c</sup> Degassed  $CH_2Cl_2$  solution

<sup>d</sup> In polymethylmethacrylate at 300K

transfer (MLCT) transition, and the same assignment is likely here.<sup>4,6</sup> Due to strong mixing of metal and ligand orbitals occurring in cyclometalated complexes, bands in the range above 350 nm can be ascribed to an admixture of MLCT and ligand centered (LC)  $\pi-\pi^*$  transition. Since the general mechanism for mixing the states MLCT and  $\pi-\pi^*$  depends upon the energy separation of the states, different features in the absorption spectra are observed in these complexes.<sup>8</sup> Thus, absorbance spectra of the complexes are governed by the nature of the cyclometalating ligand which in turn determine emission spectra.

### 2.2.2 Emission Spectra

Luminescence spectra of the reported complexes are presented in Figs. 2,3. Solid state luminescence spectrum of Ir(24dpo)<sub>3</sub> and Ir(3thpy)<sub>3</sub> as well as Ir(ppy)<sub>3</sub>, is broader and red-shifted relative to the solution spectrum because of the close intermolecular contacts.

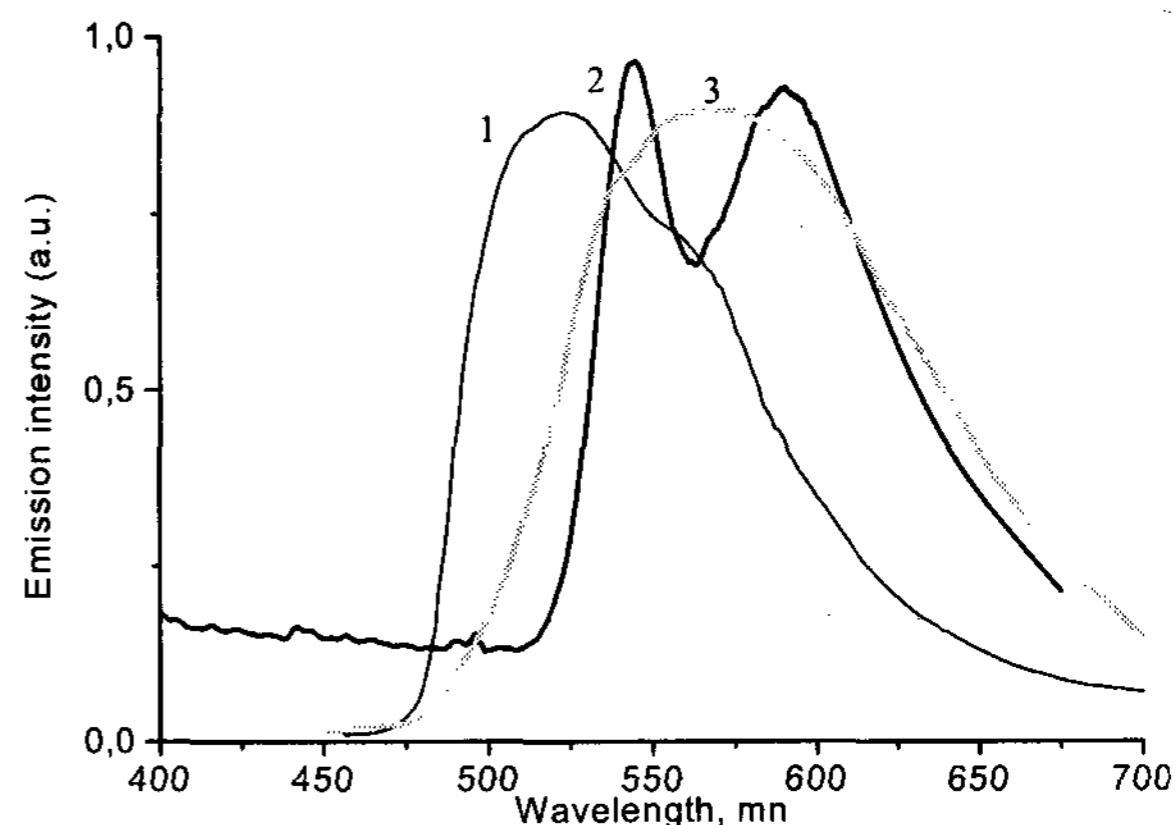


**Figure 2.** The emission spectra: 1-Ir(3thpy)<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution, 2-Ir(3thpy)<sub>2</sub>(acac)/CH<sub>2</sub>Cl<sub>2</sub> solution, 3-Ir(3thpy)<sub>3</sub>/solid state, 4-Ir(3thpy)<sub>2</sub>(acac)/solid state.

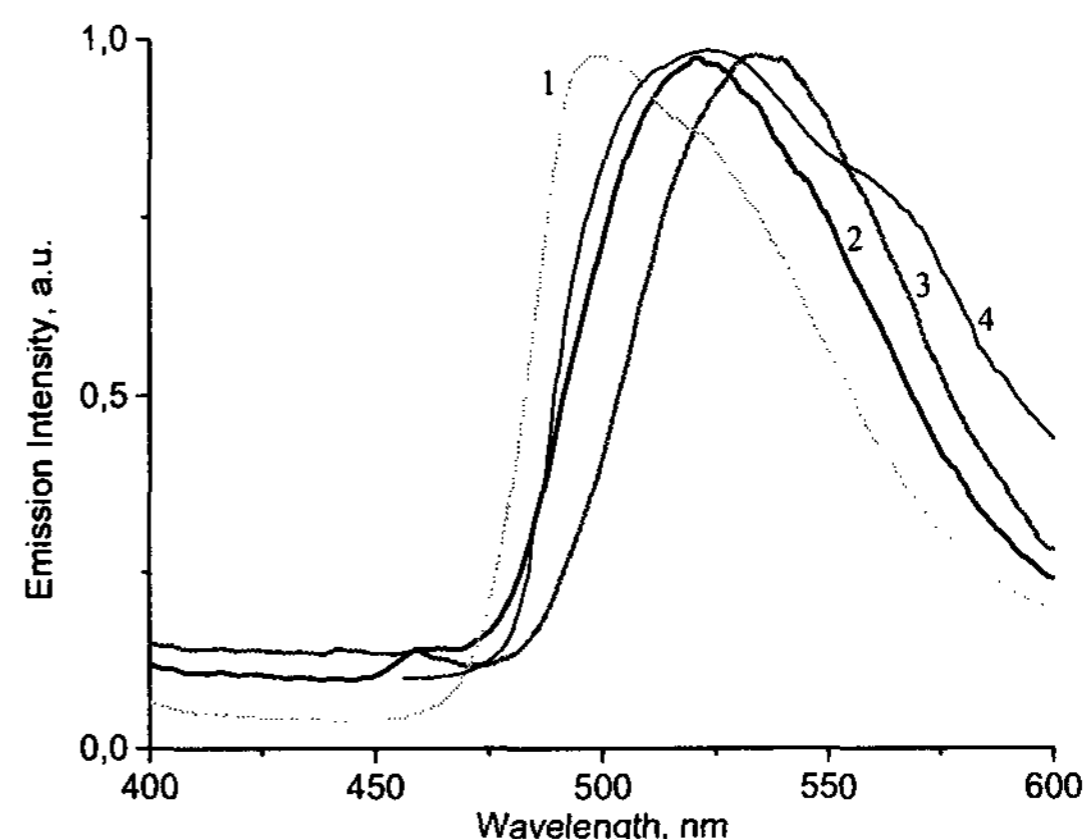
Comparison of spectroscopic properties of IrC<sup>N</sup><sub>3</sub> complexes revealed the following.

Two equal in composition but isomeric in nature diphenyloxazolic ligands form tris-cyclometalated iridium complexes with quite different properties.

Thus 25dpo complex (3) emits yellow color while 24dpo complex (1) has a more smoothed emission band in green range (Fig. 3).



**Figure 3.** The emission spectra: 1-Ir(24dpo)<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution, 2-Ir(25dpo)<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution, 3-Ir(24dpo)<sub>3</sub>/solid state.



**Figure 4.** The CH<sub>2</sub>Cl<sub>2</sub> solution emission spectra: 1-Ir(3thpy)<sub>3</sub>, 2-Ir(ppy)<sub>3</sub>, 3-Ir(3thpy)<sub>2</sub>(acac), 4-Ir(24dpo)<sub>3</sub>.

Emission band for 24dpo complex (1) nearly coincides with that for Ir(ppy)<sub>3</sub> (Fig.4).

As it shown in Table 1, complex with 3thpy (2) has the best luminescence quantum efficiency (53%) and lifetime higher than for Ir(ppy)<sub>3</sub>, whereas the compound (1) has a lower quantum efficiency (37%) but higher than Ir(ppy)<sub>2</sub>(acac).

It is interesting to note that another pair of complexes with isomeric thpy ligands (**2**) and  $\text{Ir}(\text{2thpy})_3^4$  have also different luminescent properties.

In discussing the 3thpy tris- and bis-cyclometalated complexes (**2**) and (**4**), it is informative to compare these complexes with formally similar  $\text{Ir}(\text{ppy})_3$  and  $\text{Ir}(\text{ppy})_2(\text{acac})$  complexes. Red shift of emission band for (**4**) relative to (**2**) is more larger than that for  $\text{Ir}(\text{ppy})_2(\text{acac})$  relative to  $\text{Ir}(\text{ppy})_3$ . These phenomena we believe is due to more prominent differences in structure of  $\text{IrC}^{\wedge}\text{N}_3$  and  $\text{C}^{\wedge}\text{N}_2\text{Ir}(\text{acac})$  complexes for 3thpy ligand.

### 3. Conclusion

Possibility of improvement of luminescent properties of iridium(III) cyclometalated complexes was demonstrated by variation of substituents at the position adjacent to ligand atoms bonded with metal. Photophysical properties of  $\text{Ir}(\text{24dpo})_3$ ,  $\text{Ir}(\text{3thpy})_3$  and  $\text{Ir}(\text{3thpy})_2\text{acac}$  complexes allows to use them both "as is" and as potential dopant to organic polymer matrix to fabricate high-performance green and yellow LED devices.

### 4. Acknowledgements

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### 5. References

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