# PCCP



View Article Online **PAPER** 



Cite this: Phys. Chem. Chem. Phys., 2025, 27, 17759

# 2,4,6-Triphenyl-1,3,5-triazine functionalized fac-tris(2-phenylpyridine)Ir(III) complexes with polarity sensitive T<sub>1</sub> state properties†

Peter I. Djurovich, D Kelly K. Biv, Ruben Mirzoyan and Mark E. Thompson D\*

Here, we report the synthesis and study of three Ir(III) complexes, which are derivatives of fac-Ir(ppy)<sub>3</sub> (Hppy - 2-phenylpyridine). In these derivatives, the third position of the pyridine ring of one of the ppy ligands is functionalized with a tolyl (Ir-tol) or triphenyl triazine group (Ir-meta and Ir-para). Ir-meta has a 3-(3,5-diphenyl-2,4,6-triazinyl)phenyl group on the ppy pyridyl ligand, giving a meta disposition of the triazine to the ppy ligand, and Ir-para has a 4-(3,5-diphenyl-2,4,6-triazinyl)phenyl group bound to the ppy ligand, placing the triazine moiety para to the ppy ligand. The complex Ir-tol shows electrochemical properties and phosphorescence characteristics nearly identical to the unfunctionalized fac-Ir(ppy)3. Complexes Ir-meta and Ir-para show reduction potentials that are anodically shifted from those of Ir-tol by ca. 0.6 V, consistent with the reduction centered on the triazine moiety. In non-polar media, the lowest triplet state  $(T_1)$  of **Ir-meta** and **Ir-para** has mixed metal-to-ligand charge transfer (MLCT) and ligand centered (LC) character localized on the Ir-ppy moiety of the functionalized ligand. With an increase in solvent polarity, i.e.  $CH_2Cl_2$  and dimethyl sulfoxide (DMSO), the  $T_1$  state of these complexes gains character of intraligand charge transfer (ILCT) from Ir-ppy to the triazine moiety of the functionalized ligand. This change in excited state character is accompanied by a distortion in the molecular geometry towards planarization of the acceptor and donor units. Such polarity-controlled modulation of T<sub>1</sub> state character is observed using transient absorption (TA) spectroscopy and is found to markedly affect the photoluminescence properties of the complexes.

Received 18th March 2025, Accepted 21st July 2025

DOI: 10.1039/d5cp01062d

rsc.li/pccp

#### Introduction

The photophysical properties of the complex of Ir(III) ions with three cyclometalated 2-phenylpyridine (ppy) ligands in a facial configuration (fac-Ir(ppy)3: Ir-ppy), first reported by Watts and co-workers, have been thoroughly investigated, due in large part to its high phosphorescence efficiency and comparatively short triplet lifetime. 2-9 These properties arise due to the role of the d<sup>6</sup> iridium(III) cation in the electronic structure of the complex, leading to several highest occupied molecular orbitals (HOMOs) of the complex possessing significant iridium 5dorbital character. Hence, with several lowest unoccupied MOs (LUMOs) representing  $\pi^*$  orbitals on the **ppy** ligands, the lowest excited states of Ir-ppy show significant metal-to-ligand charge transfer (MLCT) character. Spin multiplicity of the excited states is strongly affected by spin-orbit coupling (SOC) induced

Department of Chemistry, University of Southern California, Los Angeles, California 90089, USA. E-mail: met@usc.edu

† Electronic supplementary information (ESI) available: Synthetic details and characterization of the complexes, and additional electrothermal data and photophysical data. See DOI: https://doi.org/10.1039/d5cp01062d

by the iridium center ( $\zeta = 3909 \text{ cm}^{-1}$ ), <sup>10</sup> which activates the otherwise spin-forbidden intersystem crossing (ISC) and phosphorescence. Indeed, ISC  $(S_1 \rightarrow T_1)$  of **Ir-ppy** is fast with a time constant of  $\tau_{\rm ISC} \approx 100$  fs. The  $T_1 \rightarrow S_0$  phosphorescence of Ir-ppy is intense and characterized with a decay time constant of  $\tau = 1.5-2 \, \mu s_1^{7,9}$  which is widely regarded as a benchmark value among mononuclear Ir(III) complexes, with only a few faster monometallic phosphorescing complexes. 11,12 Efficient population of the lowest triplet state and efficient phosphorescence have opened numerous applications for Ir-ppy and analogous organometallic iridium complexes, for instance, application in organic light emitting diodes, 3,13-17 cellular imaging<sup>18-21</sup> and photodynamic therapy,<sup>22-24</sup> photo-redox catalysis<sup>25-27</sup> and sensing.<sup>20,22,28</sup> The properties of these Irbased materials are heavily influenced by the choice of the coordinated ligands. 27,29,30 One way to modulate photophysical properties is based on the localization of the triplet state in a heteroleptic complex, such that excitation can involve different ligands, but the excited molecule relaxes into the excited state involving the lowest energy ligand or the MLCT state.31-36 Homoleptic complexes like Ir-ppy also tend to have their excited states localized on a single ligand, due to small energy

**Paper PCCP** 

differences between the otherwise identical ligands in the relaxed triplet state.37,38 In most heteroleptic complexes, the ligands that make up the complex are quite dissimilar, such that the energy difference between MLCT or mixed ligand-MLCT states involving the different ligands is substantially different; however, the nature of the excitation is quite similar. Here we present a set of derivatives of Ir-ppy, in which one of the ppy ligands is functionalized with a 2,4,6-triphenyl-1,3,5triazine acceptor. In these heteroleptic complexes, the triplet excited state could be either MLCT, similar to the one that involves the other ppy ligands, or an intraligand charge transfer (ICT) transition, involving the triazine-ppy ligand. The strong SOC of the Ir(III) center is maintained in the lowest excited states. Control of the character of the T<sub>1</sub> state, namely, the extent of charge transfer to the triazine acceptor, is controlled via the medium polarity which markedly affects the energy of the ICT state.

### Results and discussion

#### **Synthesis**

Ir(III) complexes were synthesized using a multistep process, starting from a dichloro-bridged dimer [i.e. (ppy)<sub>2</sub>Ir(μ-Cl)<sub>2</sub>Ir(ppy)<sub>2</sub>],<sup>39</sup> which reacted with 3-bromo-2-phenylpyridine in a 2-methoxyethanol:water mixture (4:1) in the presence of silver triflate to afford the tris-cyclometalated complex Ir-Br (Scheme 1). As reported by Dedeian et al.,8 the reaction conditions utilized in the synthesis of Ir-Br (including water as a protic and coordinating solvent) afford the thermodynamically favored facial (fac) configuration of the ligands, rather than the meridional (mer) isomer. Notably, Watts and co-authors also mentioned a facile formation of the fac-isomer of Ir-ppy when the H-ppy ligand precursor reacts with the hydrated form of IrCl<sub>3</sub>. The final products (Ir-tol, Ir-meta and Ir-para) were obtained via Suzuki coupling (Scheme 1).40 These complexes are assigned as fac-isomers owing to their high photoluminescence efficiencies in toluene solution (vide infra), a property not characteristic of mer-isomers, which show efficient nonradiative decay due to photo-isomerization.<sup>5,41</sup> While all three complexes are soluble in toluene and dichloromethane, the Ir-meta and Ir-para complexes, especially the latter, are much less soluble in dimethyl sulfoxide (DMSO). It is also noteworthy that the <sup>1</sup>H NMR spectra of **Ir-tol** and **Ir-para** in DMSO-d<sub>6</sub> display broadened resonances for the pendant phenylene group indicative of slow dynamic

exchange of the phenylenes caused by rotation around the bond linked to the pyridyl ligand (Fig. S2 and S4, ESI†).

#### Electrochemical analysis

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) electrochemical measurements were conducted for Irtol, Ir-meta and Ir-para in anhydrous N,N-dimethylformamide (DMF), using an internal ferrocenium/ferrocene couple as the reference potential. The obtained voltammograms and DPV curves are shown in Fig. S5 (ESI†), and pertinent data are collected in Table S1 (ESI†). The first oxidation and reduction waves of **Ir-tol** appear at  $E_{\rm ox}$  = 0.33 V and  $E_{\rm red}$  = -2.65 V. These values are close to those reported for Ir-ppy under the same conditions ( $E_{ox} = 0.31 \text{ V}$  and  $E_{red} = -2.7 \text{ V}$ ).<sup>5,8</sup> In the case of Ir-meta the first oxidation and reduction potentials appear at  $E_{\rm ox}$  = 0.31 V and  $E_{\rm red}$  = -2.05 V, respectively. The oxidation potential is close to the value reported for Ir-ppy, whereas the reduction potential shows a significant anodic shift. The data suggest a similar make-up for the HOMOs of Ir-meta, and Ir-ppy, but very different LUMOs. The reduction of Ir-meta likely takes place at the triazine moiety. Indeed, the CV and DPV measurements for 2,4,6-triphenyl-1,3,5-triazine give a reduction potential of -2.07 V under the same conditions (see Fig. S5, ESI†). Hence, we conclude that the LUMO of **Ir-meta** is localized on the 2,4,6-triphenyl-1,3,5-triazine unit. In the case of Ir-para, the first oxidation and reduction reactions occur at  $E_{ox}$  = 0.35 V and  $E_{red}$  = -2.00 V, respectively. These potentials are anodically shifted by ca. 0.05 V compared to those measured for Ir-meta, indicative of a slightly stronger electronic influence of the 1,3,5-triazine unit in Ir-para.

#### Steady-state spectroscopy

Optical spectroscopic measurements of Ir-tol, Ir-meta and Ir-para were conducted in three different solvents: toluene, dichloromethane and dimethyl sulfoxide (DMSO) at a concentration of  $\approx 10^{-5}$  M. The steady-state absorption and emission spectra are shown in Fig. 1, and pertinent data of photoluminescence characteristics are given in Table 1. The UV-visible absorption spectra of all three complexes in toluene are reminiscent of those of Ir-ppy<sup>7,9</sup> (see Fig. S6, ESI†). The low energy bands display features with moderate intensity ( $\varepsilon_{\rm max}$  = 1.5  $\times$ 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) bearing relatively strong metal-to-ligand charge transfer (MLCT, d  $\rightarrow \pi^*$ ) character admixed with ligand centered (LC,  $\pi \to \pi^*$ ) transitions. <sup>42</sup> The absorption spectra of the

Scheme 1 Synthetic route to Ir-tol, Ir-meta and Ir-para,  $\phi_2$ trz = 3,5-diphenyltriazine

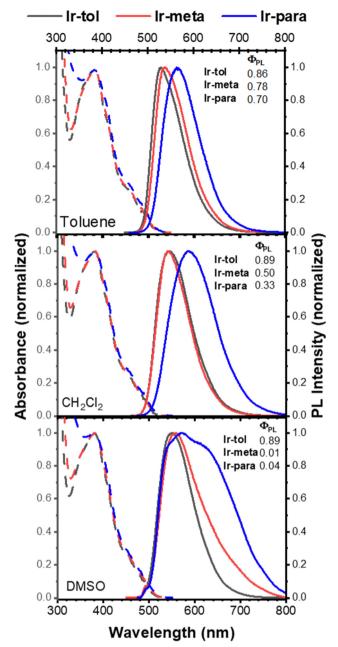


Fig. 1 Absorption (dashed) and emission (solid) spectra of Ir-tol (black), Ir-meta (red) and Ir-para (blue) at room temperature in toluene, CH<sub>2</sub>Cl<sub>2</sub> and DMSO. Photoluminescence (PL) spectra were recorded in deoxygenated solvents. All samples were excited at 380 nm.

three Ir-based complexes are weakly perturbed regardless of the solvent polarity and thus nearly indistinguishable for all solutions (Fig. 1).

The photoluminescence spectrum of Ir-tol in toluene peaks at 529 nm, with an efficiency of  $\Phi_{\rm PL}$  = 0.86 and a decay time of  $\tau$  = 1.47 µs at room temperature in deoxygenated solution (Table 1). The emission is effectively quenched by  $O_2$  when the sample is exposed to the air ( $\Phi_{PL}$  = 0.02 and  $\tau$  = 35 ns). The emission efficiency and decay time constant for Ir-tol are similar to those for Ir-ppy under the same conditions<sup>7</sup> and

Table 1 A summary of the key photophysical properties of complexes Irtol, Ir-meta and Ir-para. Emission was measured for dilute, deoxygenated solutions ( $\approx 10^{-5}$  M) at room temperature

Compound	Solvent	$\lambda_{\max}^{a}$ (nm)	$\Phi_{ m PL}$	$\tau^b$ (µs)	$k_{\rm r}^{\ c} \ (10^5 \ { m s}^{-1})$	$k_{\rm nr}^{\ c} (10^5 { m s}^{-1})$
Ir-tol	Toluene	529	0.86	1.47	5.9	0.95
	$CH_2Cl_2$	544	0.89	1.67	5.3	0.65
	DMSO	549	0.89	1.51	5.3	0.73
Ir-meta	Toluene	536	0.78	1.48	5.3	1.5
	$CH_2Cl_2$	544	0.50	1.00	5.0	5.0
	DMSO	558	0.01	0.059 (93%)	_	_
				1.25 (7%)		
Ir-para	Toluene	563	0.70	2.20	3.2	1.4
•	$CH_2Cl_2$	585	0.33	0.57	5.8	11.8
	DMSO	573	0.04	0.029 (89%)	_	_
		615(sh)		0.77 (11%)		

<sup>&</sup>lt;sup>a</sup> Samples were excited at 380 nm. <sup>b</sup> Samples were excited at 405 nm (1 ns laser pulse) and were well fit with a single exponential decay unless listed otherwise. <sup>c</sup> The radiative rates are calculated as  $k_r = \Phi_{PL}/\tau$ ; the non-radiative decay rates are calculated as  $k_{\rm nr}$  =  $(1 - \Phi_{\rm PL})/\tau$ .

consistent with T₁ → S₀ phosphorescence having a lowest excited state with significant <sup>3</sup>MLCT character. <sup>14,43</sup> A red-shift in the emission maximum for Ir-tol compared to that for Ir-ppy  $(\lambda_{\text{max}} = 510 \text{ nm}, \text{ see Fig. S6, ESI}^{\dagger})$  suggests that the emitting triplet state of Ir-tol is localized on the tolyl functionalized ppy ligand. The emission maximum of Ir-tol undergoes a bathochromic shift in polar  $CH_2Cl_2$  ( $\lambda_{max} = 544$  nm) and DMSO  $(\lambda_{\text{max}} = 549 \text{ nm})$ . Nevertheless, the photoluminescence efficiency and decay time constants remain comparable to those in toluene ( $\Phi_{PL}$  = 0.89 and  $\tau$  = 1.67  $\mu s$  in  $CH_2Cl_2$  and  $\Phi_{PL}$  = 0.89 and  $\tau = 1.51 \mu s$  in DMSO).

The  $T_1 \rightarrow S_0$  phosphorescence of **Ir-meta** in toluene solution  $(\lambda_{\rm max} = 536 \text{ nm}, \Phi_{\rm PL} = 0.78 \text{ and } \tau = 1.48 \text{ µs})$  is similar to that of Ir-tol. Apparently, the 2,4,6-triphenyl-1,3,5-triazine substituent of Ir-meta exerts a minimal effect on the energy and character of the emitting T<sub>1</sub> state in this solvent. However, in polar  $CH_2Cl_2$ , luminescence efficiency decreases ( $\lambda_{max} = 544$  nm and  $\Phi_{PL}$  = 50%) along with a decrease of the decay time constant ( $\tau = 1.0 \mu s$ ). The radiative decay rate ( $k_r$ ) of **Ir-meta** is nearly constant in both solvents, so the decrease in emission efficiency in CH2Cl2 is primarily due to enhanced non-radiative decay  $(k_{\rm pr})$  (Table 1). In more polar DMSO, the spectrum peaks at 558 nm and broadens with the emission tail extending to lower energy (Fig. 1). The photoluminescence efficiency of **Ir-meta** also decreases precipitously ( $\Phi_{PL}$  = 1%). The emission decay curve in DMSO ( $\lambda_{det}$  = 560 nm) is biexponential, with two components having distinct decay time constants  $(\tau)$  and corresponding intensity fractions  $(f_i)$  ( $\tau_1 = 59$  ns,  $f_1 = 0.93$  and  $\tau_2 = 1.25 \text{ } \mu\text{s}, f_2 = 0.07; \text{ Fig. 2}.$ 

The photophysical behavior of Ir-para is similar to that of Ir-meta. Photoluminescence from Ir-para in toluene solution is intense and red-shifted ( $\lambda_{\rm max}$  = 563 nm,  $\Phi_{\rm PL}$  = 70% and  $\tau$  = 2.2 μs), consistent with emission having <sup>3</sup>MLCT character. In polar CH<sub>2</sub>Cl<sub>2</sub>, photoluminescence of Ir-para bathochromically shifts ( $\lambda_{max}$  = 585 nm) and the emission efficiency and decay time constant substantially decrease ( $\Phi_{PL}$  = 33% and  $\tau = 0.57 \,\mu\text{s}$ ), a change principally due to an increase in the rate

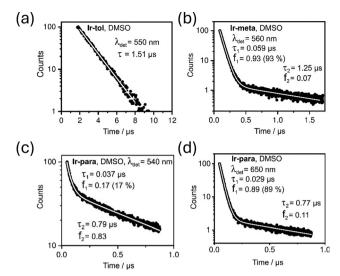


Fig. 2 Emission decay curves of deoxygenated DMSO solution samples excited at 405 nm (laser pulse = 1 ns) of (a) Ir-tol, (b) Ir-meta and (c) and (d) **Ir-para**. The fractional intensities are found as  $f_1 = \alpha_1 \tau_1/(\alpha_1 \tau_1 + \alpha_2 \tau_2)$  and  $f_2 =$  $\alpha_2\tau_2/(\alpha_1\tau_1+\alpha_2\tau_2)$ , where  $\alpha_1$  and  $\alpha_2$  are amplitudes corresponding to  $\tau_1$  and  $\tau_2$ , respectively.<sup>4</sup>

for non-radiative decay. In more polar DMSO, the photoluminescence spectrum of **Ir**-para displays a broad manifold ( $\lambda_{\text{max}}$  = 573 nm with shoulders at 540 and ca. 615 nm) that has a low efficiency ( $\Phi_{PL}$  = 4%). The luminescence lineshape indicates the presence of at least two weakly emissive species, one at high energy corresponding to the 3MLCT transition and another at lower energy. The emission decay curve measured at  $\lambda_{det}$  = 540 nm in DMSO has two components with distinct time constants and corresponding intensity fractions ( $\tau_1 = 37$  ns,  $f_1 = 0.17$  and  $\tau_2 = 0.79$  µs with  $f_2 = 0.83$ ) (Fig. 2). Detection at 650 nm gives similar decay constants with lower weighting for the long-lived component ( $\tau_1 = 29 \text{ ns}$ ,  $f_1 = 0.89 \text{ and } \tau_2 = 0.77 \text{ }\mu\text{s}$ ,  $f_2 = 0.11$ ) (Fig. 2).

The luminescence properties of Ir-meta and Ir-para in polar media provide evidence for the presence of additional low energy excited states. The redox potentials for the complexes would place an ILCT state at ca. 2.36 eV (525 nm), an energy not far from that of the <sup>3</sup>MLCT state. Judged by the radiative decay times, the fast component in the excited state decays from Ir-meta and Ir-para can be assigned to a state with <sup>3</sup>MLCT character. This state non-radiatively decays in polar solvents to either a dark ILCT state or a ground state at a rate much higher than the  $\sim 1$  µs radiative decay. Therefore, the nature of the slow decay component could be either due to ligand-based phosphorescence or thermal promotion to the bright <sup>3</sup>MLCT from the long-lived dark state.

#### Transient absorption spectroscopy and spectro-electrochemical studies

While the solvatochromic shift in emission energy between toluene, CH2Cl2 and DMSO is similar for the three complexes, the solvent dependence of the photoluminescence efficiency for Ir-meta and Ir-para differs markedly from that of Ir-tol.

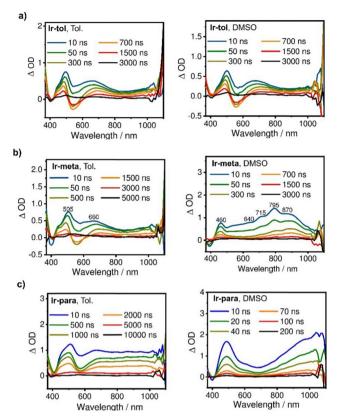


Fig. 3 TA spectra measured for (a) Ir-tol, (b) Ir-meta, and (c) Ir-para in toluene (Tol.) and DMSO.

The triazine function strongly affects the non-radiative properties of the T<sub>1</sub> state in polar solvents, leading to a substantial decrease in  $\Phi_{PL}$ . The Ir complexes were thus investigated using nanosecond transient absorption (TA) spectroscopy in polar and nonpolar solvents to probe the nature of these excited state properties. The TA experiments were conducted with deoxygenated solutions in a 10 ns to 10 µs time range using a pump wavelength of 355 nm (1 ns pulse) and a probe spanning the 370-1100 nm spectral window (Fig. 3). The TA data were collected for all three complexes in toluene, CH<sub>2</sub>Cl<sub>2</sub> and DMSO. Partial decomposition was observed for the CH<sub>2</sub>Cl<sub>2</sub> samples over the course of data collection, so the analysis presented here will focus only on the toluene and DMSO samples. The spectra recorded in CH2Cl2 are given in the ESI.†

The TA spectrum of Ir-tol at 10 ns measured in toluene shows a positive band at ca. 505 nm with a shoulder at ca. 445 nm and a broad band centered at ca. 660 nm (Fig. 3a). The spectral feature centered at ca. 540 nm appearing as a bleach at long time delays is assigned to incomplete subtraction of the emission signal of the complex, a problem that occurs with highly luminescent materials. The transient absorption of Ir-meta in toluene (Fig. 3b) appears and develops in a comparable manner to that of Ir-tol. Such a close similarity of the TA features of the two complexes in toluene substantiates that the nature of the T<sub>1</sub> state for Ir-tol and Ir-meta is the same in this medium and thus assigned to have mixed MLCT/LC character. In contrast, the TA spectra obtained for Ir-para in

toluene differ in that the feature associated with emission centered at ca. 570 nm develops relatively fast in the first 500 ns but does not cross the zero-line of the optical density axis (likely due to its lower  $\Phi_{PL}$ ) and shows a broad absorption signal in the range of 700-1000 nm (Fig. 3c). Evidently, the latter broad signal is related to both the presence of the triazine function in the molecule and its para-position with respect to the pyridine ring of the functionalized ligand.

The TA spectra of the three compounds in DMSO in Fig. 3 differ significantly from each other. The spectra of Ir-tol in DMSO remain similar to that measured in toluene, indicating that the character of the T<sub>1</sub> state is preserved despite the large increase in solvent polarity. In contrast, the TA spectra of Irmeta in DMSO exhibit a positive band at ca. 460 nm and a band at ca. 795 nm, with shoulders at ca. 640 nm and 715 nm (Fig. 3b). The spectrum of Ir-para in DMSO appears distinct from that of Ir-meta and exhibits a positive band at ca. 500 nm and a broad band intensifying in the range of 800-1000 nm (Fig. 3c). The TA signals for the excited state of Ir-para also decay at a rate that is an order of magnitude faster than that of Ir-meta. Such a marked difference in the TA spectra of the Ir-meta and Ir-para in DMSO, compared to the spectra obtained for toluene solutions, suggests that the T1 state undergoes a significant change in character in polar media. The change could be associated with an increased contribution of charge transfer to the triphenyl-triazine acceptor to the T1 state in polar media.

To explore the nature of the ILCT states, we carried out spectro-electrochemical measurements with 2,4,6-triphenyl-1,3,5-triazine under an applied reducing potential (Fig. 4). The spectra thus obtained display bands at 345 nm, 640 nm, 715 nm and ca. 800 nm upon reduction. The bands appearing at 640 nm, 715 nm and 800 nm for the anionic form of 2,4,6triphenyl-1,3,5-triazine closely reproduce the bands at 640 nm, 715 nm and 795 nm observed in the TA spectra of Ir-meta

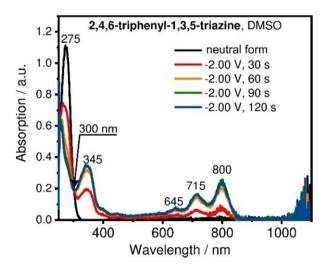


Fig. 4 Absorption spectra of 2,4,6-triphenyl-1,3,5-triazine, taken for the neutral form (black line) and upon reduction at  $-2\ V\ \emph{vs.}\ \mbox{Fc}^{0/1+}$  wave after the indicated amount of time.

in DMSO. Therefore, the strong contribution from the charge transfer state indicates that the T1 states of the triazine functionalized Ir complexes are more stabilized in polar DMSO. It is noted that in the case of Ir-para, the TA signals in DMSO do not reproduce the absorption signal of reduced 2,4,6-triphenyl-1,3,5-triazine as closely as observed for Ir-meta. This difference is consistent with the triazine moiety being more isolated from the ppy ligand in Ir-meta than in Ir-para. Conjugation to the pyridyl group of the ppy ligand in Ir-para leads to a less vibronic structure in the spectra of the reduced ligand (vide supra). The TA measurements collected using CH<sub>2</sub>Cl<sub>2</sub> solutions suffered from relatively fast sample degradation but agree qualitatively with the plots measured in DMSO (see the ESI†).

Since the overall emission quantum yields of Ir-meta and Ir-para in DMSO are low, the intensity for contributions of the two emission decay components obtained using timecorrelated single photon counting (TCSPC) measurements do not represent real concentrations of their associated species. To address this point, we analyzed the decay of the TA signal at wavelength slices corresponding to bands appearing in DMSO (Fig. S8, ESI†). The wavelength measured at 800 nm for Ir-meta was fit using a two-exponential function, giving decay time constants of 59 ns and 530 ns. The shorter time constant reproduces the value obtained using TCSPC measured for the fast decay component of Ir-meta in DMSO ( $\tau$  = 59 ns). The 1000 nm wavelength slice of TA data of Ir-para in DMSO is represented by a distinct mono-exponential component of TA signal decay with a time constant of 29 ns, which matches the time constant of the fast component of the TCSPC measured emission decay, discussed above.

These data correlate the TA absorption bands with the fast decay component of emission in DMSO, which we attribute to excited species with a MLCT dominant triplet state. With this being the case and the TA spectral features remaining unchanged throughout the experimental timeframe, we presume that the triplet state in polar solvents undergoes fast relaxation to a dark ILCT state with substantial triazine-based charge transfer character. The slow component of the TCSPC trace then comes from thermal promotion from the dark ILCT state to the bright MLCT state.

### Computational analysis and discussion

To gain further understanding of the photophysical properties of the complexes from the standpoint of molecular electronic structure, quantum-chemical calculations were performed using the Q-Chem package. 45 Density functional theory (DFT) at the B3LYP<sup>46</sup>/LACVP<sup>47</sup> level was utilized with effective core potentials (ECPs) for the Ir atoms. Excited states were calculated using the random phase approximation (RPA) method. 48–50 We assume that the triplet state of either of the three complexes is populated by ultrafast intersystem crossing after photoexcitation, similar to that found for Ir-ppy. 51,52 Therefore, since we are interested in understanding the  $T_1 \rightarrow S_0$  transition paths of these complexes, our discussion will primarily be focused on the  $T_1$  state properties.

The complexes in the ground electronic state are found to have slightly twisted geometry of the functionalized ligand with

the dihedral angles between coordinated phenyl and pyridyl rings (ppy fragment) being 12° in Ir-tol, 7° in Ir-meta and 16° in Ir-para, whereas dihedral angle in the unfunctionalized ppy ligands is ca. 1°. Also, in the functionalized ligand, the calculated dihedral angle between the coordinated pyridyl ring and the connected phenylene ring of triphenyltriazine, hereafter referred to as the  $\theta$ -angle, varies in complexes Ir-tol ( $\theta = 62^{\circ}$ ), **Ir-meta** ( $\theta = 71^{\circ}$ ) and **Ir-para** ( $\theta = 55^{\circ}$ ). These large dihedral angles are imposed by steric interactions with the nearby coordinated phenyl moiety of the ppy ligand.

The selected valence molecular orbitals of Ir-tol, Ir-meta and Ir-para in their ground state geometries are shown in Fig. 5. The HOMO in all three compounds has a common electronic structure comprising an Ir  $d_{z^2}$  orbital and three phenyl  $\pi$ orbitals. The LUMO, LUMO+1 and LUMO+2 in Ir-tol are composed of the  $\pi^*$  orbital delocalized over the three cyclometalated phenyl-pyridine units. The negligible stabilization imparted by the p-tolyl substituent is likely a result of the relatively large dihedral angle between the arene and the pyridyl ligand. In both Ir-meta and Ir-para, the LUMO and LUMO+1 represent  $\pi^*$  orbitals on the triphenyltriazine moiety. These orbitals are near degenerate in Ir-meta as there is a node in the LUMO+1 at the carbon atom linking the meta-substituted phenylene group to the pyridyl ring, whereas the LUMO in Ir-para has bonding character between the carbon atoms linking the pyridyl ring with the para-substituted phenylene ring of the triphenyltriazine moiety. Thus, in contrast to Ir-meta, the populated LUMO of Ir-para can conjugate the triazine acceptor with the cyclometalated phenylpyridyl unit of the functionalized ligand, leading to enhanced stabilization relative to LUMO+1. The LUMO+2 in both Ir-meta and Ir-para is similar in energy and orbital composition to the LUMO of Ir-tol. The computational results support the conclusion based on the electrochemical data of a minor perturbation of the cyclometalated ppy ligand by the triazine acceptor in Ir-meta and relatively stronger electronic influence in the case of Ir-para.

The lowest triplet states of the complexes were investigated regarding their photoluminescent properties. Upon DFT geometry optimization, the T<sub>1</sub> state of Ir-tol in the gas phase finds a global minimum localized on the tolyl functionalized ligand with the  $T_1 \rightarrow S_0$  vertical excitation energy of 2.47 eV (502 nm). The electronic spin density of the T1 state for Ir-tol in the relaxed geometry demonstrates the mixed MLCT/LC character of the  $T_1$  state (Fig. 6). The localization of the relaxed  $T_1$  state on the functionalized ligand aligns with the rationale given above for the slight redshift of Ir-tol phosphorescence compared to that of Ir-ppy. The geometric distortions in the T<sub>1</sub> state are most reflected in shortening of the bond between the metalated phenyl and substituted pyridyl, as well as in the coordination bonds to the functionalized ligand (accommodating the excited state), and elongation of coordination bonds to the unfunctionalized ligands. Specifically, the calculated C<sub>Ph</sub>-C<sub>pvr</sub> bond length (1.42 Å) is 0.04 Å shorter than the corresponding bond lengths of the other ligands. Likewise, the Ir-C and Ir-N coordination bond lengths to the functionalized ligand in the relaxed T<sub>1</sub> state geometry are 1.99 Å and 2.13 Å, respectively,

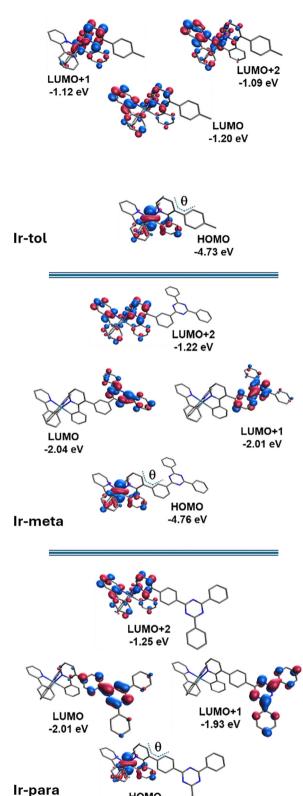


Fig. 5 Iso-surface contour plots (iso-value = 0.1) of valence molecular orbitals for Ir-tol, Ir-meta and Ir-para in ground state (S<sub>0</sub>) optimized (DFT) geometries. The dihedral angle between the pyridyl and phenylene rings of the functionalized ligand is indicated by  $\theta$ .

номо

-4.79 eV

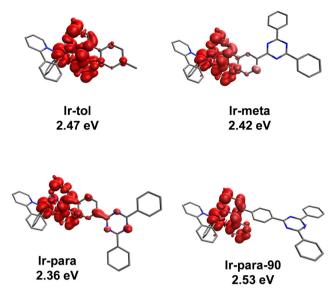


Fig. 6 Optimized geometries and iso-surface contour plots (iso-value = 0.02) of the spin density for the  $T_1$  state. The values for the  $T_1 \leftarrow S_0$  vertical excitation energy are given for each structure

whereas the distances are 2.04 Å and 2.19 Å, respectively, to the unfunctionalized ligands. A similar geometric reorganization pattern upon localization of the T1 state on a ligand was also calculated and discussed by Marian et al. for Ir-ppy. 38 Importantly, along with the changes in coordination bond lengths, the dihedral angle in the functionalized ligand decreased significantly ( $\theta = 47^{\circ}$ ) in  $T_1$  state geometry. The decrease in the dihedral angle allows spin density to extend onto the pendant p-tolyl ring. A corresponding localization on the substituted phenylpyridyl ligand occurs in the optimized T<sub>1</sub> geometry for Ir-meta and Ir-para where the dihedral angle decreased significantly in **Ir-meta** ( $\theta = 44^{\circ}$ ) and **Ir-para** ( $\theta =$ 39°) in  $T_1$  state geometry. The  $T_1 \rightarrow S_0$  vertical excitation energy for Ir-meta is 2.42 eV (513 nm), and for Ir-para, it is 2.36 eV (525 nm). When the dihedral angle for Ir-para is constrained to 90° (Ir-para-90), the spin density no longer extends onto the pendant triphenyltriazine and the  $T_1 \rightarrow S_0$  vertical excitation energy increases to 2.53 eV (489 nm).

The excited state properties of the complexes were further analyzed using TD-DFT calculations. The presence of local (MLCT) and long range (ILCT) (ppy-to-triazine) charge transfer transitions in Ir-meta and Ir-para made accurate modeling problematic, owing to the well-known difficulties for TD-DFT to account for CT transitions with a poor orbital overlap.<sup>53</sup> Standard TDDFT calculations provided consistent energies for the lowest MLCT transition (2.77 eV, 445 nm) for all three complexes; however, energies for the long range CT in Ir-meta and Ir-para were grossly underestimated, falling to 2.38 eV for the former and 2.43 eV for the latter complex. Application of coulomb attenuation methods (CAM) to the exchange increased the energy of the long-range CT state above that of the MLCT state. The energy of the lowest MLCT state also increased to around 3.10 eV for all the complexes. Nevertheless, the nature of the long-range CT in the T1 state can be best understood

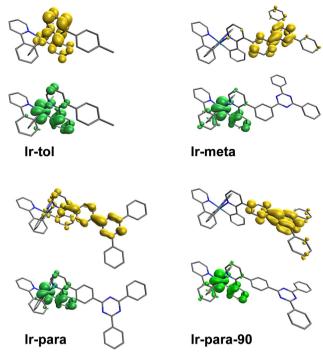


Fig. 7 Iso-surface contour plots (iso-value = 0.100) obtained for the NTOs of the  $T_1$  state for the Ir complexes in their  $S_0$  geometries. The hole is in green, and the electron is in yellow.

using natural transition orbitals (NTOs) obtained using calculations without CAM exchange and is thus shown in Fig. 7.

The calculated electronic configuration for the T<sub>1</sub> state shows that the electron hole is localized on the Ir atom and the metalated phenyl of the substituted ligand in all the complexes. The electron is localized on the phenylpyridyl ligand in Ir-tol, whereas the position shifts onto the phenyltriazine moiety in the other derivatives. There is minimal electron density on the pyridyl ring in Irmeta, whereas Ir-para has a noticeably larger contribution from the phenylpyridyl ligand. Electron density is absent on the phenylpyridyl ligand upon rotation of the phenylene group in Ir-para-90. The poor overlap between the hole and the electron in the CT state for Ir-meta effectively separates the charges onto the metalligand and the phenyltriazine. This decoupled electronic configuration will suppress the rate of charge separation and radiative decay as well as promote non-radiative deactivation of the excited state. A similar situation is present in Ir-para; however, the extent to which the hole and the electron are coupled will vary depending on the dihedral angle between the phenylene and pyridyl ligand. The acute angle in Ir-para allows for enhanced conjugation between the phenyltriazine and phenylpyridyl ligand, whereas the orthogonal orientation in Ir-para-90 leads to slow-but complete—charge separation analogous to that found in Ir-meta.

Calculations were carried out for the anionic forms of Irmeta and Ir-para to account for the difference in the TA spectra observed in these complexes in DMSO (Fig. 8). The spin density derived from these calculations can be used to evaluate the extent of electron localization in the long-range CT state. The dihedral angle in **Ir-meta** ( $\theta = 70^{\circ}$ ) remains close to the value in

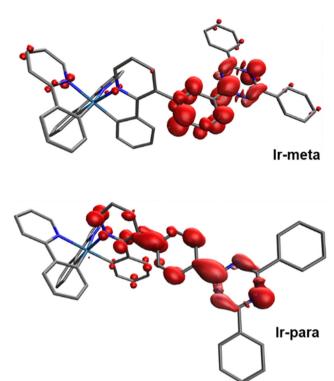


Fig. 8 Iso-surface contour plots (iso-value = 0.02) of the spin density for the anionic structures of Ir-meta and Ir-para.

the neutral S<sub>0</sub> state; however, the value in **Ir-para** ( $\theta = 40^{\circ}$ ) decreased significantly in the anionic geometry. The charge localization in Ir-meta is similar to that calculated for triphenyltriazine, whereas charge localization in Ir-para extends onto the pyridyl ligand. Therefore, the increase in delocalization for Ir-para likely is responsible for the bathochromic shift in the positive near-infrared band observed for the excited state in the TA spectra.

# Summary

We demonstrate a synthetic approach to tailoring transition metal complexes via on-complex ligand functionalization. In this work, the approach afforded novel complexes Ir-tol, Ir-meta and Ir-para and a simple method of introducing a triphenyl triazine acceptor group at a sterically encumbered position of a cyclometalated ligand is demonstrated using well-established cross-coupling protocols. The photoluminescence properties of Ir-tol are reminiscent of the unfunctionalized Ir-ppy with efficient phosphorescence stemming from the MLCT/LC character T<sub>1</sub> state under both non-polar toluene and polar DMSO solution conditions. The T1 state character and photoluminescence properties of both acceptor functionalized complexes Irmeta and Ir-para are sensitive to increased solvent polarity manifested by a marked decrease of phosphorescence efficiency. Analysis of electronic structures of the three complexes by computational methods, conducted with an eye on the TA data, suggests that the structurally relaxed T<sub>1</sub> state localizes primarily on the cyclometalated Ir-ppy part of the functionalized ligand.

With an increase in medium polarity, electron density in the T<sub>1</sub> state of Ir-meta and Ir-para extends onto the triphenyltriazine group and gains ILCT character, affording a larger dipole moment and additional stabilization due to the solvation energy. Extension of the T1 state localization onto the acceptor is concurrent with distortion of molecular geometry towards planarization of the functionalized ligand, which is more favorable in the case of **Ir-para**. The increasing involvement of the triazine acceptor in the T<sub>1</sub> state with the increase of solvent polarity is also manifested in the evolution of the nanosecond TA spectra where new red-shifted positive bands appear in DMSO solution. Indeed, conjugation of the pyridyl and phenylene rings in the T<sub>1</sub> state of Ir-para in DMSO results in more red shifted TA bands (800-1000 nm), whereas for Ir-meta, the TA bands appearing in DMSO solution (640-800 nm) are more reminiscent of the absorption spectrum of reduced 2,4,6triphenyl-1,3,5-triazine. Finally, the ILCT nature of the T<sub>1</sub> state for Ir-meta and Ir-para accounts for the decrease in phosphorescence efficiency in polar solvents. In polar solvents, the ILCT red shifts to fall lower in energy than the MLCT state, and thus the emission involves thermal promotion from the weakly emissive or dark ILCT state to the bright MLCT state.

## **Experimental**

The detailed syntheses of Ir-tol, Ir-meta, and Ir-para and their characterization are given in the ESI.† Electrochemical and photophysical measurements were carried out using anhydrous Supelco solvents. NMR spectra were taken with a Varian 400 MHz (<sup>1</sup>H) instrument. UV-visible absorption spectra were taken with an Agilent 4853 diode array spectrophotometer. Photoluminescence quantum yields were measured using a Hamamatsu C9920 integrating sphere system. Emission lifetimes were obtained using time correlated single photon counting (TCSPC). Emission lifetime and quantum yield measurements were conducted for samples deoxygenated by purging nitrogen gas through the sample solution. Steady-state emission spectra were obtained with a QuantaMaster model C-60SE spectrofluorometer of Photon Technology International. Transient absorption experiments were conducted with a Magnitude Envision instrument. Cyclic voltammetry and differential pulse voltammetry measurements were conducted using an EG&G Model 283 potentiostat/galvanostat with 0.1 M tetra-n-butylammonium hexafluorophosphate in N,N-dimethylformamide as an electrolyte under a nitrogen atmosphere. The working, counter, and pseudo-reference electrodes were composed of glassy carbon, platinum wire, and silver wire, respectively. The ferrocene redox couple was used as the internal references for all electrochemical measurements.

### Conflicts of interest

One of the authors, Thompson, has a financial interest in the Universal Display Corporation (UDC), one of the funding sources for this work.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Acknowledgements

The authors would like to thank Dr Marsel Z. Shafikov for his contributions to this work. He prepared the complexes, carried out much of the photophysical and electrochemical measurements and generated early drafts of the manuscript. We are disappointed that he chose to not be a coauthor of this study. The authors would like to acknowledge the Department of Energy, Office of Energy Efficiency and Renewable Energy, Award: EE0009688 (Shafikov, Biv), and the Universal Display Corporation (Djurovich, Thompson) for support. Funds were provided by the National Science Foundation (award: CHE-2018740) to acquire the X-ray diffractometer that was used to determine the crystal structures reported here. In addition, we thank the National Science Foundation (CHE-0840366) for the funds to acquire the NMR spectrometer used in our work.

### References

- 1 K. A. King, P. J. Spellane and R. J. Watts, Excited-State Properties of a Triply Ortho-Metalated iridium(III) Complex, J. Am. Chem. Soc., 1985, 107(5), 1431-1432, DOI: 10.1021/ ja00291a064.
- 2 K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson and R. J. Watts, A New Synthetic Route to the Preparation of a Series of Strong Photoreducing Agents: Fac-Tris-Ortho-Metalated Complexes of Iridium(III) with Substituted 2-Phenylpyridines, Inorg. Chem., 1991, 30(8), 1685-1687, DOI: 10.1021/ic00008a003.
- 3 M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, Very High-Efficiency Green Organic Light-Emitting Devices Based on Electrophosphorescence, Appl. Phys. Lett., 1999, 75(1), 4-6, DOI: 10.1063/1.124258.
- 4 K.-C. Tang, K. L. Liu and I. C. Chen, Rapid Intersystem Crossing in Highly Phosphorescent Iridium Complexes, Chem. Phys. Lett., 2004, 386(4-6), 437-441, DOI: 10.1016/ j.cplett.2004.01.098.
- 5 A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, Synthesis and Characterization of Facial and Meridional Tris-Cyclometalated Iridium(III) Complexes, J. Am. Chem. Soc., 2003, 125(24), 7377-7387, DOI: 10.1021/ja034537z.
- 6 W. J. Finkenzeller and H. Yersin, Emission of Ir(Ppy)3. Temperature Dependence, Decay Dynamics, and Magnetic Field Properties, Chem. Phys. Lett., 2003, 377(3-4), 299-305, DOI: 10.1016/S0009-2614(03)01142-4.
- 7 W. Holzer, A. Penzkofer and T. Tsuboi, Absorption and Emission Spectroscopic Characterization of Ir(Ppy)<sub>3</sub>, Chem. Phys., 2005, 308(1), 93-102, DOI: 10.1016/j.chemphys. 2004.07.051.

- 8 K. Dedeian, J. Shi, N. Shepherd, E. Forsythe and D. C. Morton, Photophysical and Electrochemical Properties of Heteroleptic Tris-Cyclometalated Iridium(III) Complexes, Inorg. Chem., 2005, 44(13), 4445-4447, DOI: 10.1021/ ic050324u.
- 9 T. Hofbeck and H. Yersin, The Triplet State of Fac-Ir(Ppv)<sub>3</sub>, Inorg. Chem., 2010, 49(20), 9290-9299, DOI: 10.1021/ ic100872w.
- 10 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, Handbook of Photochemistry, CRC Press, 3rd edn, 2006, vol. 633.
- 11 M. Z. Shafikov, A. V. Zaytsev, V. N. Kozhevnikov and R. Czerwieniec, Aligning Π-Extended Π-Deficient Ligands to Afford Submicrosecond Phosphorescence Radiative Decay Time of Mononuclear Ir(III) Complexes, Inorg. Chem., 2023, 62(2), 810-822, DOI: 10.1021/acs.inorgchem.2c03403.
- 12 R. M. Edkins, Y.-T. Hsu, M. A. Fox, D. Yufit, A. Beeby and R. J. Davidson, Divergent Approach for Tris-Heteroleptic Cyclometalated Iridium Complexes Using Triisopropylsilylethynyl-Substituted Synthons, Organometallics, 2022, 41(17), 2487-2493, DOI: 10.1021/acs.organomet.2c00292.
- 13 S. Kappaun, C. Slugovc and E. J. W. List, Phosphorescent Organic Light-Emitting Devices: Working Principle and Iridium Based Emitter Materials, Int. J. Mol. Sci., 2008, 9, 1527-1547.
- 14 H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck and T. Fischer, The Triplet State of Organo-Transition Metal Compounds. Triplet Harvesting and Singlet Harvesting for Efficient Oleds, Coord. Chem. Rev., 2011, 255(21-22), 2622-2652, DOI: 10.1016/j.ccr.2011.01.042.
- 15 E. Longhi and L. De Cola, in Iridium(III) Complexes for Oled Application, Iridium(III) in Optoelectronic and Photonics Applications, 2017, pp. 205-274.
- 16 J. Jayabharathi, V. Thanikachalam and S. Thilagavathy, Phosphorescent Organic Light-Emitting Devices: Iridium Based Emitter Materials - an Overview, Coord. Chem. Rev., 2023, 483, 215100, DOI: 10.1016/j.ccr.2023.215100.
- 17 G. Hong, X. Gan, C. Leonhardt, Z. Zhang, J. Seibert, J. M. Busch and S. Bräse, A Brief History of Oleds-Emitter Development and Industry Milestones, Adv. Mater., 2021, 33(9), 2005630, DOI: 10.1002/adma.202005630.
- 18 S. Meksawangwong, B. Gohil, W. Punyain, R. Pal and F. Kielar, Development of Tris-Cyclometalated Iridium Complexes for Cellular Imaging through Structural Modification, Inorg. Chim. Acta, 2020, 508, 119609, DOI: 10.1016/ j.ica.2020.119609.
- 19 K. K.-W. Lo and K. Y. Zhang, Iridium(III) Complexes as Therapeutic and Bioimaging Reagents for Cellular Applications, RSC Adv., 2012, 2(32), 12069-12083, DOI: 10.1039/ C2RA20967E.
- 20 S. Abbas, I.-U.-D. Din, A. Raheel and A. Tameez ud Din, Cyclometalated Iridium (III) Complexes: Recent Advances in Phosphorescence Bioimaging and Sensing Applications, Appl. Organomet. Chem., 2020, 34(3), e5413, DOI: 10.1002/ aoc.5413.
- 21 L. C.-C. Lee and K. K.-W. Lo, Shining New Light on Biological Systems: Luminescent Transition Metal Complexes

- for Bioimaging and Biosensing Applications, Chem. Rev., 2024, 124(15), 8825-9014, DOI: 10.1021/acs.chemrev. 3c00629.
- 22 A. Nakagawa, Y. Hisamatsu, S. Moromizato, M. Kohno and S. Aoki, Synthesis and Photochemical Properties of Ph Responsive Tris-Cyclometalated Iridium(III) Complexes That Contain a Pyridine Ring on the 2-Phenylpyridine Ligand, Inorg. Chem., 2014, 53(1), 409-422, DOI: 10.1021/ic402387b.
- 23 X.-D. Bi, R. Yang, Y.-C. Zhou, D. Chen, G.-K. Li, Y.-X. Guo, M.-F. Wang, D. Liu and F. Gao, Cyclometalated Iridium(III) Complexes as High-Sensitivity Two-Photon Excited Mitochondria Dyes and near-Infrared Photodynamic Therapy Agents, Inorg. Chem., 2020, 59(20), 14920-14931, DOI: 10.1021/acs.inorgchem.0c01509.
- 24 L. Zhang and D. Ding, Recent Advances of Transition Ir(III) Complexes as Photosensitizers for Improved Photodynamic Therapy, VIEW, 2021, 2(6), 20200179, DOI: 10.1002/VIW. 20200179.
- 25 T. M. Monos and C. R. J. Stephenson, Photoredox Catalysis of Iridium(III)-Based Photosensitizers, in Iridium(III) in Optoelectronic and Photonics Applications, ed. E. Zysman-Colman, John Wiley and Sons, Ltd., Sussex, England, 2017, pp. 541-581.
- 26 M. R. Schreier, X. Guo, B. Pfund, Y. Okamoto, T. R. Ward, C. Kerzig and O. S. Wenger, Water-Soluble Tris(Cyclometalated) Iridium(III) Complexes for Aqueous Electron and Energy Transfer Photochemistry, Acc. Chem. Res., 2022, 55(9), 1290-1300, DOI: 10.1021/acs.accounts.2c00075.
- 27 I. S. Alkhaibari, X. Zhang, J. Zhao, T. M. Stonelake, R. C. Knighton, P. N. Horton, S. J. Coles, N. J. Buurma, E. Richards and S. J. A. Pope, Tuning Excited State Character in Iridium(III) Photosensitizers and Its Influence on Tta-Uc, Inorg. Chem., 2024, 63(21), 9931–9940, DOI: 10.1021/acs.inorg chem.4c01003.
- 28 C. S. K. Mak, D. Pentlehner, M. Stich, O. S. Wolfbeis, W. K. Chan and H. Yersin, Exceptional Oxygen Sensing Capabilities and Triplet State Properties of Ir(Ppy-Nph<sub>2</sub>)<sub>3</sub>, Chem. Mater., 2009, 21(11), 2173-2175, DOI: 10.1021/ cm9003678.
- 29 J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau and M. E. Thompson, Synthetic Control of Excited-State Properties in Cyclometalated Ir(III) Complexes Using Ancillary Ligands, Inorg. Chem., 2005, 44(6), 1713-1727, DOI: 10.1021/ic048599h.
- 30 K. P. S. Zanoni, B. K. Kariyazaki, A. Ito, M. K. Brennaman, T. J. Meyer and N. Y. Murakami Iha, Blue-Green Iridium(III) Emitter and Comprehensive Photophysical Elucidation of Heteroleptic Cyclometalated Iridium(III) Complexes, Inorg. Chem., 2014, 53(8), 4089-4099, DOI: 10.1021/ic500070s.
- 31 K. Dedeian, J. M. Shi, N. Shepherd, E. Forsythe and D. C. Morton, Photophysical and Electrochemical Properties of Heteroleptic Tris-Cyclometalated Iridium(III) Complexes, Inorg. Chem., 2005, 44(13), 4445-4447.
- 32 W. Leslie, R. A. Poole, P. R. Murray, L. J. Yellowlees, A. Beeby and J. A. G. Williams, Near Infra-Red Luminescence from

- Bis-Terpyridyl Iridium(III) Complexes Incorporating Electron-Rich Pendants, Polyhedron, 2004, 23(17), 2769-2777.
- 33 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, Highly Phosphorescent Bis-Cyclometalated Iridium Complexes: Synthesis, Photophysical Characterization, and Use in Organic Light Emitting Diodes, J. Am. Chem. Soc., 2001, 123(18), 4304-4312, DOI: 10.1021/ ja003693s.
- 34 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, Synthesis and Characterization of Phosphorescent Cyclometalated Iridium Complexes, Inorg. Chem., 2001, 40(7), 1704-1711.
- 35 T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard and M. E. Thompson, Temperature Dependence of Blue Phosphorescent Cyclometalated Ir(III) Complexes, J. Am. Chem. Soc., 2009, 131(28), 9813-9822, DOI: 10.1021/ja903317w.
- 36 R. J. Holmes, S. R. Forrest, Y. J. Tung, R. C. Kwong, J. J. Brown, S. Garon and M. E. Thompson, Blue Organic Electrophosphorescence Using Exothermic Host-Guest Energy Transfer, Appl. Phys. Lett., 2003, 82(15), 2422-2424, DOI: 10.1063/1.1568146.
- 37 A. F. Rausch, H. H. H. Homeier and H. Yersin, Organometallic Pt(Ii) and Ir(III) Triplet Emitters for Oled Applications and the Role of Spin-Orbit Coupling: A Study Based on High-Resolution Optical Spectroscopy, Top. Organomet. Chem., 2010, 29, 193-235, DOI: 10.1007/3418\_2009\_6.
- 38 M. Kleinschmidt, C. van Wüllen and C. M. Marian, Intersystem-Crossing and Phosphorescence Rates in Fac-Iriii(Ppy)3: A Theoretical Study Involving Multi-Reference Configuration Interaction Wavefunctions, J. Chem. Phys., 2015, 142(9), 094301, DOI: 10.1063/1.4913513.
- 39 M. Nonoyama, Benzo[H]Quinolin-10-Yl-N Iridium(III) Complexes, Bull. Chem. Soc. Jpn., 1974, 47(3), 767-768, DOI: 10.1246/bcsj.47.767.
- 40 A. Suzuki, Synthetic Studies Via the Cross-Coupling Reaction of Organoboron Derivatives with Organic Halides, Pure Appl. Chem., 1991, 63(3), 419, DOI: 10.1351/pac19916 3030419.
- 41 A. Yu. Gitlina, F. Fadaei-Tirani, A. Ruggi, C. Plaice and K. Severin, Acid-Base-Induced Fac → Mer Isomerization of Luminescent Iridium(III) Complexes, Chem. Sci., 2022, 13(35), 10370-10374, DOI: 10.1039/D2SC02808E.
- 42 T. Hofbeck and H. Yersin, The Triplet State of Fac-Ir(Ppy)<sub>3</sub>, Inorg. Chem., 2010, 49(20), 9290-9299, DOI: 10.1021/ ic100872w.
- 43 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, Synthesis and Characterization of Phosphorescent Cyclometalated Iridium Complexes, Inorg. Chem., 2001, **40**(7), 1704–1711, DOI: **10.1021/ic0008969**.
- 44 J. R. Lakowicz, in Measurement of Fluorescence Lifetimes, Principles of Fluorescence Spectroscopy, ed. J. R. Lakowicz, Springer US, Boston, MA, 1983, pp. 51-93.

- 45 Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit and J. Kussmann, et al., Advances in Molecular Quantum Chemistry Contained in the Q-Chem 4 Program Package, Mol. Phys., 2015, 113(2), 184-215, DOI: 10.1080/00268976. 2014.952696.
- 46 Y. Zhao and D. G. Truhlar, The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals, Theor. Chem. Acc., 2008, 120(1), 215-241, DOI: 10.1007/s00214-007-0310-x.
- 47 F. Weigend and R. Ahlrichs, Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy, Phys. Chem. Chem. Phys., 2005, 7(18), 3297-3305, DOI: 10.1039/b508541a.
- 48 D. Bohm and D. Pines, A Collective Description of Electron Interactions. I. Magnetic Interactions, Phys. Rev., 1951, 82(5), 625-634, DOI: 10.1103/PhysRev.82.625.

- 49 D. Pines and D. Bohm, A Collective Description of Electron Interactions: Ii. Collective Vs Individual Particle Aspects of the Interactions, Phys. Rev., 1952, 85(2), 338-353, DOI: 10.1103/PhysRev.85.338.
- 50 D. Bohm and D. Pines, A Collective Description of Electron Interactions: III. Coulomb Interactions in a Degenerate Electron Gas, Phys. Rev., 1953, 92(3), 609–625, DOI: 10.1103/ PhysRev.92.609.
- 51 G. J. Hedley, A. Ruseckas and I. D. W. Samuel, Ultrafast Luminescence in Ir(Ppy)<sub>3</sub>, Chem. Phys. Lett., 2008, 450(4), 292-296, DOI: 10.1016/j.cplett.2007.11.028.
- 52 G. J. Hedley, A. Ruseckas and I. D. W. Samuel, Ultrafast Intersystem Crossing in a Red Phosphorescent Iridium Complex, J. Phys. Chem. A, 2009, 113(1), 2-4, DOI: 10.1021/
- 53 M. J. Peach, P. Benfield, T. Helgaker and D. J. Tozer, Excitation Energies in Density Functional Theory: An Evaluation and a Diagnostic Test, J. Chem. Phys., 2008, 128(4), 044118, DOI: 10.1063/1.2831900.