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Phosphorescent biaryl platinum(IV) complexes obtained through double metalation of dibenzoiodolium ions†

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The first series of neutral, tris-chelate, phosphorecent Pt(IV) complexes is reported, which combine two cyclometalated 2-arylpyridine ligands and a dimetalated biaryl. The introduction of biaryl ligands is achieved under mild conditions through the oxidative addition of dibenzoiodolium ions to Pt(II) precursors to give Pt(IV) intermediates with a singly metalated 2-(2-iodoaryl)aryl ligand, followed by the reductive metalation of the C–I bond. The modulation of emission characteristics via derivatization of both types of ligands is demonstrated.

Dimetalated biaryls are highly electron donating ligands that have been pursued for the design of brightly emissive transition metal complexes because they can induce a strong ligand field, resulting in enhanced stabilities and emission quantum yields.[1] However, the number of luminescent biaryl complexes is quite limited, which has been attributed to synthetic difficulties.[1a] The most common syntheses make use of transmetalation reactions from dilithiated biaryls[1b,e] or dibenzostannol derivatives,[2] or involve the oxidative addition of biphenylene to low-valent metal precursors.[3] Several methods in which the two metalations are accomplished at different steps have also been employed.[1a,4]

Although a few Pt(IV) biaryl complexes have been reported,[4a,5] their photophysical properties were not investigated. We have previously shown that Pt(IV) complexes with cyclometalated 2-arylpyridines (C^N) may exhibit long-lived emissions from triplet ligand-centred excited states (^{3}LC) with little metal-to-ligand charge-transfer (MLCT) character.[6] To reach significant quantum efficiencies, these compounds require the presence of at least two strong σ-donor atoms from the ligands, which increase the energies of nonemissive ligand-to-metal charge-transfer (LMCT) states, thereby reducing the nonradiative deactivation often caused by the thermal population of such states. Thus, the most efficient Pt(IV) emitters are either cationic tris-cyclometalated complexes *fac*-[Pt(C^N)$_3$]$^+$ [6a] or neutral bis-cyclometalated derivatives that incorporate a strong-field supporting ligand, such as methyl,[7,8] aryl,[9] or *N*-heterocyclic carbene.[10] Additionally, their emissive characteristics can be altered by modulating the MLCT admixture into the excited state, which accelerates the radiative decay because of the spin-orbit coupling effects induced by the metal.[11] Increased MLCT admixtures and faster radiative decay rates are attained in neutral derivatives with respect to cationic ones,[8,12] and can also be augmented by strengthening π donation from the ligands.[9]
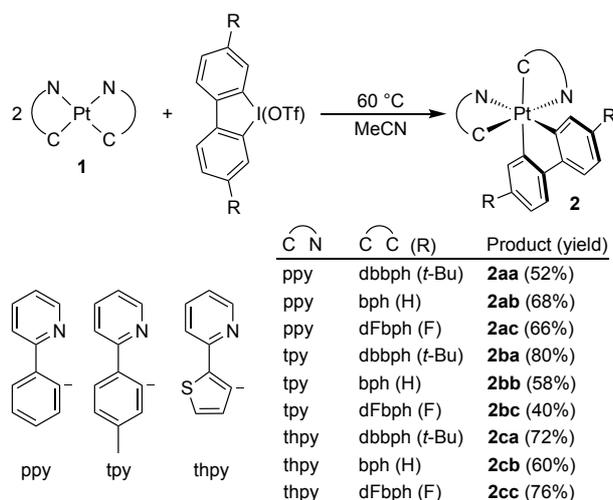
In view of their electronic properties, we expected biaryl ligands to be suitable for the development of efficient Pt(IV) emitters. In addition, thanks to their dianionic character, they offer the possibility to obtain uncharged Pt(IV) complexes with a robust, tris-chelate structure by adding two cyclometalated C^N ligands. In fact, neutral M(IV) complexes (M = Os, Pd, Pt) containing one dimetalated biaryl and two C^N ligands have been postulated in the patent literature as suitable dopants for organic light-emitting devices (OLEDs), although their structure and emission properties have not been demonstrated.[13] Herein, we present a novel method for the introduction of biaryl ligands, which employs dibenzoiodolium ions (cyclic diaryliodoniums) as precursors and has allowed the synthesis of phosphorescent complexes of the type [Pt(C^N)$_2$(C^C)], representing the first structural and photophysical characterization of neutral, tris-chelate Pt(IV) emitters.

Diaryliodonium ions, Ar$_2$I$^+$, have been shown to transfer an aryl cation to M(II) precursors (M = Pd, Pt) to give M(IV) aryl complexes.[9,14] Based on these precedents, we envisaged that dibenzoiodolium species could be employed to introduce a η^1-biaryl ligand into the coordination sphere of Pt(IV) via oxidative addition to *cis*-[Pt(C^N)$_2$] precursors (**1**). A second metalation

Scheme 1. Synthesis of complexes **2**.

C^N	C^C (R)	Product (yield)
ppy	dbbph (*t*-Bu)	**2aa** (52%)
ppy	bph (H)	**2ab** (68%)
ppy	dFbph (F)	**2ac** (66%)
tpy	dbbph (*t*-Bu)	**2ba** (80%)
tpy	bph (H)	**2bb** (58%)
tpy	dFbph (F)	**2bc** (40%)
thpy	dbbph (*t*-Bu)	**2ca** (72%)
thpy	bph (H)	**2cb** (60%)
thpy	dFbph (F)	**2cc** (76%)

would then be needed to obtain biaryl complexes. However, an initial exploration of the reactions between complexes **1** and dibenzoiodolium salts in 1:1 molar ratio in MeCN showed that the target complexes [Pt(C^N)$_2$(C^C)] (**2**) were already produced upon heating at 60 °C , resulting from a double metalation of the dibenzoiodolium ion. Subsequent experiments showed that the optimal conditions were a 2:1 molar ratio (**1**:dibenzoiodolium; Scheme 1). Isolated yields ranged from 40 to 80% with respect to the dibenzoiodolium salt after purification. Up to four resonances flanked by Pt satellites arising from inequivalent aromatic protons ortho to the metalated carbons can be discerned in the ^{1}H NMR spectra, and another two from the protons ortho to the nitrogens, all of which are strongly shielded by the diamagnetic current of orthogonal rings (Table S2, ESI†). This is consistent with an unsymmetrical arrangement of cyclometalated C^N ligands, which is typically brought about by oxidative additions on *cis*-[Pt(C^N)$_2$] complexes.[9,15,16] Further confirmation of this ligand disposition was provided by the crystal structure of **2ba** (Fig. 1). As expected, one of the metalated carbons of the biaryl ligand is trans to the metalated carbon of a tpy ligand, resulting in relatively long Pt–C bond distances [2.077(3), 2.075(3) Å] due to the strong trans influence of aryl carbons, while the Pt–C bonds trans to nitrogen atoms are shorter [2.006(3), 2.027(3) Å].
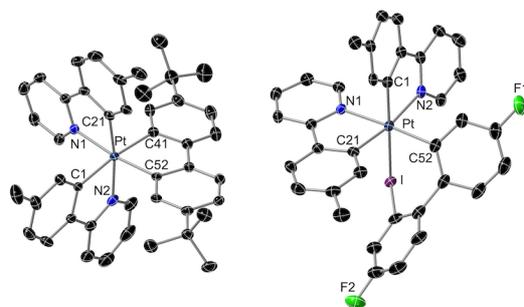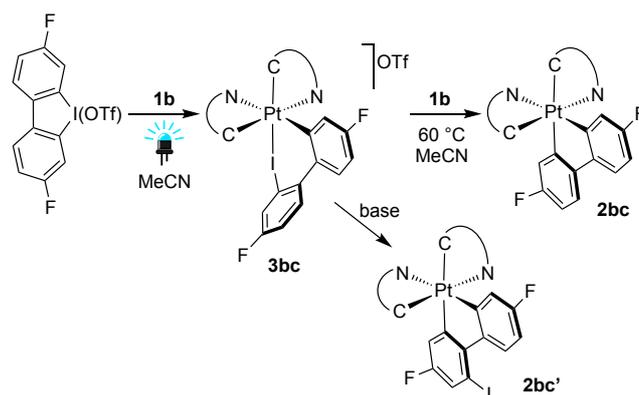

Fig. 1. Crystal structures of **2ba**·0.5CH$_2$Cl$_2$ (left) and **3bc**·Et$_2$O (right) (thermal ellipsoids at 50% probability). Hydrogen atoms, solvent molecules and the triflate anion of **3bc** are omitted.

Scheme 2. Formation of **3bc**, **2bc** and **2bc'**.

Additional experiments were carried out to identify intermediate species with a singly metalated biaryl and to elucidate the subsequent processes. For this, we employed precursor **1b** (C^N = tpy) and 3,7-difluorodibenzo-5-iodolium triflate, (dFbphI)OTf. Since no reaction took place at 25 °C and heating at 60 °C produced **2b**, we tried photochemical conditions, in the expectation that the highly photoreducing character of **1b**[9] would drive the desired reaction at 25 °C. Gratifyingly, irradiation with blue light (λ = 454 nm) for 4 h produced a clear solution containing the cationic complex [Pt(tpy)$_2$(dFbphI-κ^2*C,I*)]OTf (**3bc**; Scheme 2), which bears a *C,I* chelating 2-(4-fluoro-2-iodophenyl)-4-fluorophenyl ligand arising from the oxidative addition of the (dFbphI)OTf reagent. Its identity was established by an X-ray diffraction analysis, which revealed a *fac-C,C,C* configuration (Fig. 1).

Heating of a solution of **3bc** in MeCN at 60 °C for 24 h did not lead to any reaction. Since the metalation of the C–I bond would require a two-electron reduction, we hypothesized that the reductant could be precursor **1b**. In agreement with this hypothesis, the reaction of **3bc** with **1b** in 1:1 molar ratio at 60 °C in MeCN afforded **2bc** as the major product, as revealed by the ^{1}H NMR data of the crude reaction mixture. A small amount of [PtI(tpy)$_2$(CH$_2$CN)] was also identified, indicating that the reaction involves radical intermediates that can abstract a hydrogen atom from the solvent.[9] Therefore, **1b** provides the necessary electrons for the reductive metalation of the C–I bond, which is consistent with the 2:1 molar proportion (**1**:dibenzoiodolium) required for the optimal synthesis of complexes **2**. It is thus reasonable that complexes analogous to **3bc** form also under thermal conditions and are intermediates in the formation of **2**.

We also found that, in the presence of weak bases, complex **3bc** slowly transformed into [Pt(tpy)$_2$(dFbphI-κ^2*C,C*)] (**2bc'**; Scheme 2), which results from the electrophilic metalation of the ortho C–H bond of the 4-fluoro-2-iodophenyl moiety, demonstrating the dual reactivity of this group. Complex **2bc'** was obtained in good yield by reacting **3bc** with γ-picoline or Na$_2$CO$_3$ in MeCN at 50 °C. Its identity was confirmed by a single crystal X-ray diffraction analysis (Fig. 2).

Complexes **2** are highly stable under photoexcitation with UV light and most of them exhibit significant phosphorescent emissions in deaerated CH$_2$Cl$_2$ solution and poly(methyl
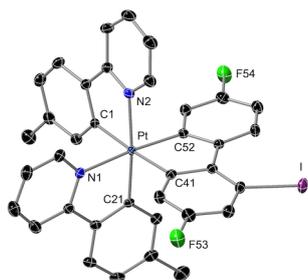
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Fig. 2. Crystal structure of **2bc'** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted.

methacrylate) (PMMA) matrices (2 wt%) at 298 K (Fig. 3, Table 1) and in frozen 2-methyltetrahydrofuran glasses at 77 K (ESI†). The emission energies, vibronic structure and long lifetimes are typical of primarily ^{3}LC excited states involving C^N ligands, as commonly found for bis- and tris-cyclometalated Pt(IV) complexes.[6–9] As an exception, **2aa** produces very weak emissions from ^{3}LC(ppy) and ^{3}LC(dbbph) states that can be discerned at 298 K, both in solution (Fig. 3) and in rigid PMMA matrix (Fig. S14, ESI†). The observed biexponential decays provide further support for a dual emission (see the ESI† for a detailed discussion). In contrast, the emissions observed at 77 K arise from ^{3}LC(C^N) states in all cases, suggesting that cyclometalated 2-arylpyridines are much better suited for radiative decay than biaryls in these systems.

The anomalously weak dual emission of **2aa** provides insight into the properties of the biaryl-centred excited state. Since the ^{3}LC(dbbph) emission has the lowest energy, only this state should be expected to be emissive according to Kasha's rule. The fact that also a similarly weak emission from ^{3}LC(ppy) state is observed indicates that direct deexcitation from this state competes effectively, implying that both internal conversion to and deexcitation from the ^{3}LC(dbbph) state are relatively slow. A similar behaviour has been observed for heteroleptic tris-cyclometalated Pt(IV) complexes.[16] Additionally, it is clear that deexcitation from the ^{3}LC(dbbph) state in **2aa** is mostly nonradiative. For the rest of ppy derivatives and all of the tpy ones, increasingly intense emissions from ^{3}LC(C^N) states are attained upon replacing the dbbph ligand with bph or dFbph. The opposite trend occurs for thpy derivatives, making **2ca** the most efficient emitter of the series (Φ = 0.21 in CH$_2$Cl$_2$ and 0.59
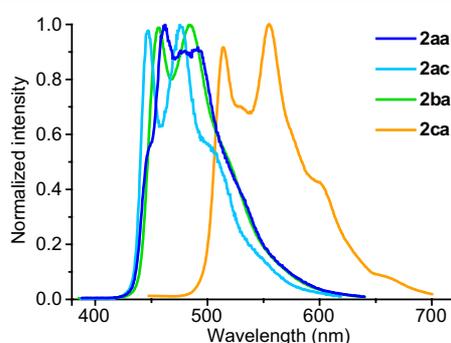

Fig. 3. Emission spectra of representative derivatives **2** in deaerated CH$_2$Cl$_2$ solution at 298 K.

Table 1 Emission data of complexes **2** at 298 K.

Comp.	Medium	$\lambda_{em}{}^a$/nm	Φ^b	τ^c/µs	$k_r{}^d \times 10^{-3}$ /s^{-1}	$k_{nr}{}^e \times 10^{-3}$ /s^{-1}
2aa	CH$_2$Cl$_2$	447	<0.01	5.1 (63 %)	–	–
				8.2 (37%)		
	PMMA	448	<0.01	88.3 (14%)	–	–
				235 (86%)		
2ab	CH$_2$Cl$_2$	452	0.075	36.7	2.0	25
	PMMA	452	0.29	152	1.9	4.7
2ac	CH$_2$Cl$_2$	448	0.13	56.6	2.2	15
	PMMA	448	0.44	195	2.2	2.8
2ba	CH$_2$Cl$_2$	456	0.052	22.5	2.3	42
	PMMA	457	0.40	215	1.9	2.8
2bb	CH$_2$Cl$_2$	453	0.12	36.2	3.3	24
	PMMA	454	0.41	140	2.9	4.2
2bc	CH$_2$Cl$_2$	453	0.15	50.8	2.9	17
	PMMA	452	0.56	201	2.8	2.2
2ca	CH$_2$Cl$_2$	514	0.21	83.6	2.5	9.4
	PMMA	513	0.59	248	2.4	1.6
2cb	CH$_2$Cl$_2$	514	0.16	76.8	2.1	11
	PMMA	513	0.41	162	2.5	3.6
2cc	CH$_2$Cl$_2$	514	0.091	57.3	1.6	16
	PMMA	513	0.42	291	1.4	2.0

^{a}Highest-energy emission peak. ^{b}Quantum yield. ^{c}Lifetime. ^{d}Radiative rate constant, $k_r = \Phi/\tau$. ^{e}Nonradiative rate constant, $k_{nr} = (1 - \Phi)/\tau$.

in PMMA). This complex is also a significantly better emitter compared to cationic tris-cyclometalated Pt(IV) complexes bearing the thpy ligand [$\Phi \leq 0.07$ (solution) or 0.23 (PMMA)].[6b,16]

To understand the observed emissive properties, we examined the triplet excited states of the ppy and thpy complexes by means of DFT and TDDFT calculations (see the ESI† for details). The first three triplets correspond to LC excitations confined within each of the ligands. Their geometries could be successfully optimized in all cases and the calculated electronic energies with respect to the ground state are represented in Fig 4. The spin density distributions correspond to primarily π-π* transitions localized on the respective ligands, with a small metal orbital contribution that implies some MLCT character[6b,12] (Fig. S37, S38; ESI†). The increasing energy of the ^{3}LC(C^C) state in the sequence dbbph < bph < dFbph is clearly the major factor that can explain the observed differences within the subset of ppy complexes. The ^{3}LC(C^C) state has the lowest energy in **2aa**, which represents the most favourable case for the observation of a biaryl-based emission, whereas it lies above one of the ^{3}LC(C^N) states for **2ab** and **2bc**. Thermal equilibration between ^{3}LC(C^C) and ^{3}LC(C^N) states is expected to occur for all of the ppy derivatives because of their very similar energies, which should hinder emission due to the preferred nonradiative deactivation of ^{3}LC(C^C) states. This is consistent with the decreasing nonradiative decay rate constants (k_{nr}) and increasing quantum yields observed for the ppy complexes as the energies of the ^{3}LC(C^C) states increase. The effect is less pronounced in rigid
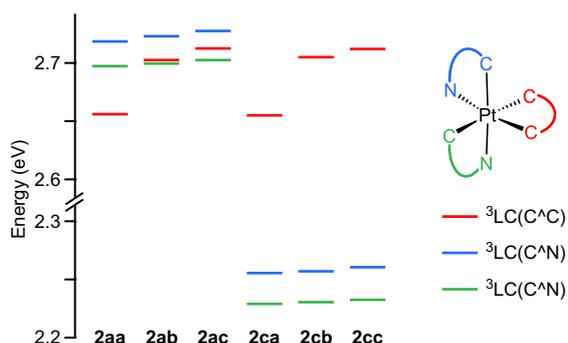
Fig. 4. Energy diagram showing the energies of the first three triplet excited states for the ppy and thpy derivatives with respect to the ground state (adiabatic energy differences).

PMMA matrix, where nonradiative deactivation is significantly reduced. A similar scenario is plausible for the tpy derivatives. In contrast, the impact of ^{3}LC(C^C) states on the luminescence of the thpy complexes appears to be irrelevant, reasonably because ^{3}LC(thpy) states lie at significantly lower energies.

The higher Φ values observed for **2ca** and **2cb** with respect to **2cc** can be mainly ascribed to their higher radiative rate constants (k_r), suggesting an increased MLCT admixture into the emissive state as a consequence of the stronger electron donating character of the dbbph and bph ligands relative to dFbph. Consistent with this, the calculated natural spin densities on the Pt atom (Table S25, ESI†) show that, for a given ^{3}LC(C^N) state, the metal orbital contribution to the excited state increases as the R substituent on the biaryl ligand becomes more electron donating. The effect is particularly relevant for thpy derivatives because metal-ligand orbital overlap in Pt(IV) complexes with this ligand is often very poor, leading to diminished MLCT contributions to the emissive state and lower k_r and Φ values compared with ppy or tpy complexes.[6b,16] The fact that **2ca** and **2cb** are much better emitters compared to cationic tris-cyclometalated Pt(IV) thpy complexes can also be ascribed to this electronic effect of the biaryl ligand.

In summary, we have demonstrated the synthesis of the first series of charge-neutral, tris-chelate Pt(IV) emitters by double metalation of dibenzoiodolium ions. The new compounds are particularly well suited for lower-energy emissions and offer the possibility to modulate the emission characteristics via derivatization of both the biaryl and 2-arylpyridine ligands.

Conflicts of interest

There are no conflicts to declare.

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