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Enhanced photooxidation sensitizers: the first examples of cyclometalated pyrene complexes of iridium(III)[†]

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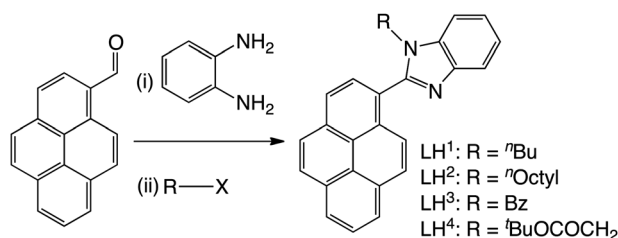
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The iridium(III) cyclometalation of alkylated pyrene–benzimidazole ligands proceeds in an unprecedented manner. The resultant complexes display remarkably enhanced photooxidation capabilities using 1,5-dihydroxynaphthalene as a substrate.

The utility of organic singlet oxygen (¹O₂) photosensitizers such as porphyrins, phthalocyanines, fullerenes and biologically relevant molecules has been well established.¹ Porphyrins, in particular, have attracted attention through their use in photodynamic therapy (PDT) and potential in cancer treatment,² and efforts remain regarding targeting of agents to specific tissue locale. Beyond PDT, photosensitized oxidation can be applied to oxidative transformations in organic chemistry and catalysis,³ as well as applied avenues such as water disinfection⁴ and hydrogen production.⁵ General challenges remain regarding the optimum characteristics of ¹O₂ photosensitizers, with the highly planarised organic systems suffering from aggregation in solution and compromised ¹O₂ quantum yields,⁶ for alternative agents maximal exploitation of the visible wavelengths is also a key challenge.

Very recently cyclometalated iridium(III) complexes have emerged as an alternative class of ¹O₂ photosensitizer.⁷ The heavy iridium atom facilitates efficient formation of triplet excited states localized on the complex, and it is these that transfer energy to the triplet ground state of oxygen (³O₂) yielding ¹O₂. The additional benefits of this class of photosensitizer are the synthetic variants that are achievable *via* stepwise addition of ligands to the iridium centre, potentially allowing control of key physical properties and functionality.

In this context, we describe a previously unreported class of iridium complex incorporating cyclometalated pyrene units,



Scheme 1 Reaction conditions for the synthesis of the pyrenyl ligands. (i) heat, PhNO₂; (ii) heat, 3-pentanone, 50% NaOH, NPr₄I.

additionally revealing the first structurally characterised cyclometalated chelate ring at iridium that is not an orthometalation. The incorporation of cyclometalated polyaromatic chromophores should improve the visible light absorption characteristics *versus* benchmark complexes such as [Ir(ppy)₂(bpy)]⁺ and [Ir(ppy)₂(acac)] and secondly, spin orbit coupling should facilitate the generation of triplet pyrene (³pyr*) excited states, which in turn are very sensitive to dissolved oxygen. From the results reported herein, these new compounds appear to be extremely effective ¹O₂ photosensitizers, as probed through a variety of studies utilising the ¹O₂ scavenger 1,5-dihydroxynaphthalene (1,5-DHN).

The synthesis of the ligands (Scheme 1) was achieved in two steps: condensation of 1-pyrenecarboxaldehyde with 1,2-diaminobenzene gave the benzimidazole intermediate⁸ and subsequent *N*-alkylation (using phase transfer conditions) gave a variety of species (LH^{1–4}) adorned with varying (R) side groups. The choice of alkylating group was determined to address issues of solubility and influences upon subsequent photooxidation performance. The iridium complexes were synthesised from IrCl₃·xH₂O based on the Nonoyama method that we have used previously,⁹ wherein the chloro-bridged, cyclometalated dimer [(L)₂Ir(μ-Cl)₂Ir(L)₂] was firstly isolated; subsequent reaction with 2,2'-bipyridine yielded the mixed-ligand cationic species, [Ir(L)₂(bpy)](PF₆). However, in the reactions with ligands *N*-functionalised with *n*-octyl (L²) and *tert*-butyl acetate (L⁴) groups, the predominant product from the reaction with IrCl₃·xH₂O was the charge-neutral tris-cyclometalated complex [Ir(L)₃]. This observation may be attributed to the relatively good solubility of the intermediate dimer species in these two cases. In contrast, the tris-cyclometalated complex of L³ was best obtained in two steps; abstraction of the

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bridging chlorides of the dimer precursor with AgNO_3 facilitated chelation of the third cyclometalating ligand, giving $[\text{Ir}(\text{L})_3]$.

The ligands and complexes were characterised by the usual spectroscopic and analytical methods (see ESI†) including ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and HR MS. An X-ray diffraction study was undertaken on $[\text{Ir}(\text{L}^3)_2(\text{bpy})](\text{PF}_6)$ and revealed a highly unusual coordination mode for the pyrenyl ligands: rather than the available (and ubiquitous for Ir^{III}) *ortho*-metalation (*i.e.* at position C2), the preference here is for metalation at position C10 resulting in the formation of a six-membered ring.¹⁰ This is the first structurally characterised example of such a coordination mode at iridium (Fig. 1). The distorted octahedral coordination sphere also revealed close pyrene–pyrene contacts (3.155–3.606 Å) apparently facilitated by a severe twist in the torsion angle between the imidazole and pyrene units (*i.e.* they are not co-planar). This very unusual binding mode allows accommodation of the highly bulky pyrene chromophores into the $\text{Ir}(\text{III})$ coordination sphere whilst promoting favourable intramolecular π – π interactions. Using this structural data, a single-point energy DFT calculation was obtained on $[\text{Ir}(\text{L}^3)_2(\text{bpy})]^+$ and revealed that the HOMO is localised on both pyrene units and $\text{Ir}(5d)$ whilst the LUMO is on the ancillary bipyridine (Fig. S2, ESI†).

Contrasting the optical properties with $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, revealed increased molar absorptivities throughout the UV and visible regions for the complexes described here (Tables S3 and S4, Fig. S3, ESI†). These enhanced absorption features

can clearly be attributed to the presence of cyclometalated pyrenyl chromophores, with both ^1IL (pyrene) and $^1\text{MLCT}$ transitions contributing (spin orbit mediated $^3\text{MLCT}$ transitions are also expected to contribute at longer wavelengths).¹¹ The emission properties of the free ligands are also included for completion (Table S3, ESI†) revealing structured, monomer-type fluorescence from the pyrene chromophores, which was insensitive to the nature of the substituent.¹² In comparison irradiation of aerated solutions of the complexes revealed bathochromically shifted emission profiles between 407–446 nm, with varying resolution of the vibronic definition (Fig. S4, ESI†); similar emission wavelengths were observed for the complexes in the solid state. The associated lifetimes were all <5 ns, suggestive of a fluorescent emitting state, presumably localized on the pyrene-derived chromophore. The spectral appearance suggests a monomer-type emission although (intramolecular) excimer fluorescence cannot be ruled out (*cf.* crystal structure). Somewhat unusually for $\text{Ir}(\text{III})$ complexes, the deoxygenated samples also showed identical emission profiles.

Analyses of the time-resolved transient difference absorption spectra (Table 1 and Fig. 2) for the four chosen complexes revealed the strong dependence of the triplet state lifetimes (τ_{T}) on dissolved oxygen, with lifetimes dramatically extended in deoxygenated *versus* air-equilibrated solvent; the τ_{T} values are significantly longer than that obtained for $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (0.34 μs). The nature of the substituent also influences τ_{T} , although the effects for a given substituent are reversed for neutral *versus* cationic variants.

Importantly, the iridium complexes each demonstrated excellent photostability, which is a key prerequisite for the feasibility of future applications of such species. The benchmark assessment of the photooxidation capability of the complexes was performed using 1,5-dihydroxynaphthalene (1,5-DHN),⁷ wherein the $^1\text{O}_2$ that is generated upon irradiation of the complex reacts with 1,5-DHN to give Juglone (Scheme S1, ESI†), the formation of which is easily traced using UV-vis spectroscopy (see ESI† for details). Four complexes were selected for assessment in this manner, and the data associated with the $^1\text{O}_2$ generation, kinetics and yields of Juglone are presented in Table 1 together with $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ for contextual comparison.

The results show that the new complexes show up to ten-fold larger rate constants compared to the model complex $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (Table 1). The kinetics associated with the photooxidation studies showed that reactions proceed *via* a

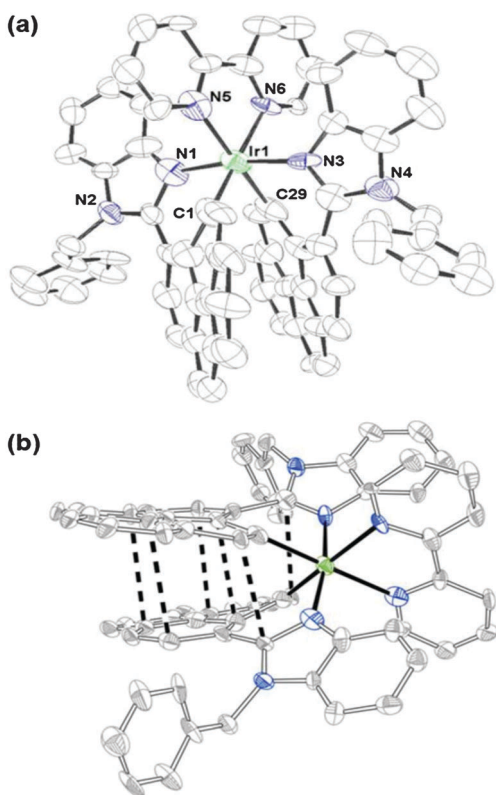


Fig. 1 Two views (a, b) of the X-ray crystal structure for $[\text{Ir}(\text{L}^3)_2(\text{bpy})](\text{PF}_6)$ revealing (b) the close intramolecular contacts of the cyclometalated pyrene units.

Table 1 Pseudo-first-order kinetics parameters, $^1\text{O}_2$ generation quantum efficiencies triplet excited state lifetimes (τ_{T}) and yields of Juglone for the photooxidations of 1,5-DHN using Ir complexes as sensitizers

Compound	$\tau_{\text{T}}^a/\mu\text{s}$	$k_{\text{obs}}^b/\text{min}^{-1}$	$v_i^b/\times 10^{-5}\text{M min}^{-1}$	Φ_{Δ}^c	Yield ^d (%)
$[\text{Ir}(\text{ppy})_2(\text{bpy})](\text{PF}_6)$	0.34	0.0026	0.052	0.97	26.7
$[\text{Ir}(\text{L}^1)_3]$	8.0	0.021	0.42	0.52	79.0
$[\text{Ir}(\text{L}^2)_3]$	15.0	0.015	0.30	0.43	75.5
$[\text{Ir}(\text{L}^1)_2(\text{bpy})](\text{PF}_6)$	13.3	0.021	0.42	0.86	97.8
$[\text{Ir}(\text{L}^3)_2(\text{bpy})](\text{PF}_6)$	3.9	0.035	0.70	0.80	99.2

^a Deoxygenated dichloromethane. ^b Initial rate of DHN consumption.

^c $^1\text{O}_2$ generation quantum yield determined using the value of TPP ($\Phi_{\Delta} = 0.65$) as a reference. ^d Yield of Juglone after reaction for 60 min.



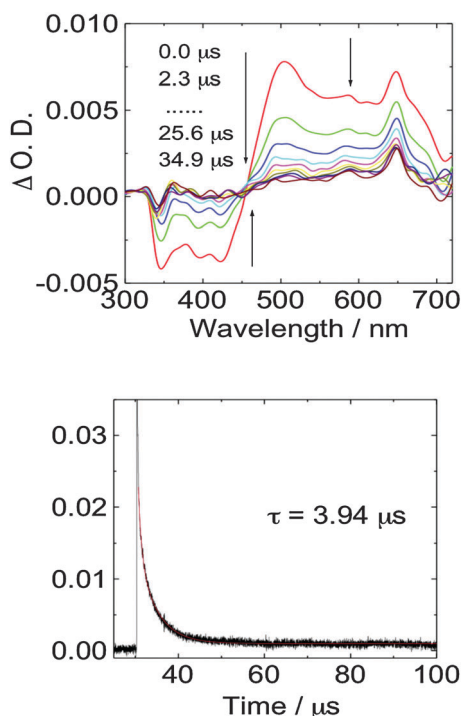


Fig. 2 Nanosecond time-resolved transient difference absorption spectra of (top) $[\text{Ir}(\text{L}^3)_2(\text{bpy})](\text{PF}_6)$ in de-aerated dichloromethane (2.0×10^{-5} M, 25°C). Arrows indicate the elapsed time after 355 nm laser flash. Bottom: fitted triplet state lifetime following the decay of the transients ($\lambda = 510$ nm) in deoxygenated dichloromethane (2.0×10^{-5} M, 25°C).

pseudo first-order rate constant in each case (see Fig. S5, ESI[†] for plot of $\ln(C_t/C_0)$ versus irradiation time). The $^1\text{O}_2$ quantum yields (Φ_Δ) of the complexes were determined (Table 1); generally the new complexes show smaller Φ_Δ values than the model complex $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ ($\Phi_\Delta = 0.98$). To some extent the Φ_Δ values can be regarded as an indication of the intersystem crossing (ISC) efficiency, and thus the observed Φ_Δ values are in broad agreement with the photophysical studies on the new complexes. The observation of fluorescence, instead of phosphorescence, suggests that the ISC efficiency is not 100% for this class of complex. However, the smaller Φ_Δ value is well compensated by the strong absorption of the complexes in the visible wavelength range.¹³ As a result, the DHN photooxidation efficiencies (Fig. S9, ESI[†]) of the new complexes are much higher than that of the reference complex, $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$.

Overall, the best performing complexes are the cationic variants, $[\text{Ir}(\text{L}^3)_2(\text{bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{L}^1)_2(\text{bpy})](\text{PF}_6)$, demonstrating comparable Φ_Δ (despite the measured differences in τ_T), with remarkable, near-quantitative, yields of Juglone after 60 min. As with the τ_T values, the results also show that the nature of the substituent can influence the photooxidation behaviour, however, there is no apparent advantage to forming charge-neutral tris-cyclometalated species incorporating three pyrenyl ligands.

The development of functional sensitizers for photooxidation processes is a key scientific challenge and it is apparent that cyclometalated iridium complexes possess much promise in this regard. It is now clear that through the control of the ligand architecture such species can be advantageously tuned to this purpose. Cyclometalation of the pyrene-based ligands described has yielded unusually coordinated species, and provided a series of complexes that demonstrate remarkably enhanced photooxidation characteristics when compared to $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$. The results show that the significantly tuned visible-light absorbing properties of the complexes are a key factor in their impressive photooxidation performance. Further work is currently underway to explore the broader utility and application of these highly performing $^1\text{O}_2$ generating complexes.

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