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New luminescent and redox-active homometallic dinuclear iridium(III), ruthenium(II) and osmium(II) complexes prepared by metal-catalyzed coupling reactions†

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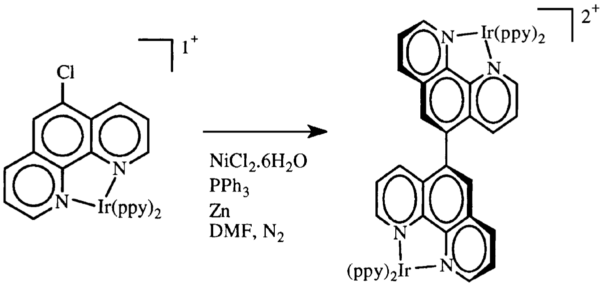
Four new homometallic dinuclear Ir^{III}, Ru^{II} and Os^{II} complexes are prepared and their luminescence properties and redox behavior are reported; the bis-phenathroline bridging ligand is found to isolate the two components of each dinuclear system because of its unusual nonplanar structure.

Luminescent and redox-active multinuclear metal complexes are extensively investigated because of their interest in the design of novel systems for photochemical energy conversion and for the elaboration of optical information at the molecular level.[1] Beside standardized synthetic methods like the so-called 'complexes as ligands and complexes as metals' approach,[2] metal-catalyzed coupling reactions involving suitable metal precursors are attracting an increasing attention due to the relatively high yields of these reactions and the unambiguity of the products obtained.[3]

In this paper we demonstrate the feasibility of the application of the coupling reaction to suitable Os^{II} polypyridine and Ir^{III} cyclometallated precursors, by the preparation of new luminescent and redox-active homometallic dinuclear Os^{II} and Ir^{III} compounds, and report the absorption spectra, luminescence properties and redox behavior of these new compounds. To the best of our knowledge, it is the first time that this synthetic approach has been applied to luminescent Os^{II} and Ir^{III} complexes. For the sake of completeness, an analogous Ru^{II} polypyridine complex was also prepared and its absorption spectrum, luminescence properties and redox behavior studied. The new compounds synthesized were $[(ppy)_2Ir(phen–phen)Ir(ppy)_2]^{2+}$ (**1**; ppy is the monoanion of 2-phenylpyridine; phen–phen = 5,5′-bis(1,10-phenanthroline)), $[(bpy)_2Ru(phen–phen)Ru(bpy)_2]^{4+}$ (**2**; bpy = 2,2′-bipyridine); $[(bpy)_2Os(phen–phen)Os(bpy)_2]^{4+}$ (**3**) and $[(Me_2bpy)_2Os(phen–phen)Os(Me_2bpy)_2]^{4+}$ (**4**; Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine).‡

The only published procedure for the synthesis of the free bridging ligand phen–phen (5,5-bis(1,10-phenanthroline)) is based on Skraup reactions applied to a benzidine derivative,[4] however this procedure is both toxic and low yielding. The incorporation of coupling methodologies into the synthesis would avoid both, although previous attempts involving copper coupling reactions on 5-bromo-1,10-phenanthroline have failed.[4] We attempted to apply nickel coupling reactions to 5-chloro-1,10-phenanthroline (Cl–phen) to form the free ligand, but this method failed, possibly due to the destabilisation of the nickel tetrakis(triphenylphosphine) catalyst involved in the reaction. However, upon complexation with $Ru(bpy)_2Cl_2$ to yield the new $[Ru(bpy)_2(Cl–phen)]^{2+}$ complex, the phenanthroline moieties couple together in a good yield, 65%, to form the homometallic dimer **2**. Preparation of the new compounds $[Os(bpy)_2(Cl–phen)]^{2+}$, $[Os(Me_2bpy)_2(Cl–phen)]^{2+}$ and $[Ir(ppy)_2(Cl–phen)]^{+}$ by standard literature procedures[5] afforded us suitable precursors to synthesise osmium and iridium homometallic dinuclear compounds by the same coupling reaction. This method yielded the desired compounds **1**, **3**, and **4** (Scheme 1) without particular problems and with comparable yields with respect to the Ru^{II} dimer.



Scheme 1

Each of the four dinuclear compounds exhibits a reversible two-electron oxidation process in acetonitrile solution (Table 1), which can be assigned to simultaneous one-electron oxidation involving the identical metal centres. As expected and in agreement with the above assignment, the osmium species are oxidized at less positive potentials than the ruthenium species. The Ir-centred oxidation process occurs at a typical potential for Ir^{III} cyclometallated species;[5b,6] its reversibility also suggests that an $Ir–C^-$ σ-bond orbital, sometimes playing the role of the donor orbital in the oxidation process,[6] is not involved in such a process in **1**. The coincidence of the two metal-centred oxidation processes in all the complexes indicates that the metal–metal electronic interaction across the phen–phen briding ligand is weak.

The reduction patterns of all the complexes (Table 1) show series of reversible two-electron reductions. The process at less negative potential occurs at similar potentials for all the complexes, and is therefore assigned to the reduction of the two phenanthroline halves of the phen–phen bridging ligand, which is the only polypyridine ligand common to all the species. The two-electron nature of this process suggests that the two phenanthroline halves of the bridge are reduced simultaneously, and indicates that these moieties are isolated from an electrochemical viewpoint. This result is quite surprising on considering the redox behavior of similar systems, such as the $[(bpy)_2Ru(bpy–bpy)Ru(bpy)_2]^{4+}$ complex (bpy–bpy = 4,4′-bis(2,2′-bipyridine)), in which only monoreduction of the

Table 1 Half-wave potentials in argon-purged acetonitrile solution, 298 K. All waves are bielectronic

Compound	$E_{1/2}$ (ox)/V *vs.* SCE	$E_{1/2}$ (red)/V *vs.* SCE
1	+1.28	−1.27; −1.89
2	+1.31	−1.26; −1.47; −1.78
3	+0.86	−1.26; −1.46; −1.77
4	+0.78	−1.23; −1.53

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† Electronic supplementary information (ESI) available: spectral data for **1**–**4**, cyclic voltammogram for **3** and absorption and emission spectra for **1**–**3**. See http://www.rsc.org/suppdata/cc/b0/b006456o/

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bridge occurs (at -1.10 V *vs.* SCE) before bpy-centred reductions take place;[7] that result suggested that in the bpy–bpy ligand the LUMO orbital in which reduction takes place extends over the two bipyridine halves of the bridging ligand (because the reduction is much easier than in isolated bpy), indicating that the reduced form of the bridging ligand is planar. However, planarity is forbidden in the case of the phen–phen bridging ligand used here, because of strong steric constraints. The absence of planarity is therefore suggested to be responsible for the electrochemical isolation of the two halves of phen–phen.[8] The successive two-electron reduction process of **1** occurs at a potential typical for ppy reduction in cyclometallated complexes[5b] and is attributed to simultaneous one-electron reduction of two ppy ligands coordinated to different metal centres. The second, bielectronic processes of **2** and **3** is attributed to simultaneous one-electron reduction of two bpy ligands coordinated to different metals and the third bielectronic process is assigned to one-electron reduction of the two remaining bpy ligands. The second bielectronic reduction of **4** is analogously assigned to simultaneous one-electron reduction of two $\mathrm{Me_2}$bpy ligands coordinated to different metals, slightly shifted to more negative potentials compared to that of **2** and **3** because the two methyl substituents make the ligand more difficult to reduce. The same reason probably moves the expected reduction of the other $\mathrm{Me_2}$bpy ligands out of the potential window investigated ($+2.00$ to -2.00 V *vs.* SCE).

The visible region of the absorption spectra of the $\mathrm{Ru^{II}}$ and $\mathrm{Os^{II}}$ complexes is dominated by moderately intense metal-to-ligand charge-transfer (MLCT) bands, whereas intense ligand-centred (LC) bands dominate the UV region (Table 2).[1a,9] In particular, by comparison among the various compounds and literature data,[9] the bands at about 285 nm can be assigned to spin-allowed bpy-centred transitions, the bands at about 270 nm are assigned to spin-allowed LC transitions involving the phen–phen bridge, the broad absorption features in the 400–500 nm region are attributed to spin-allowed MLCT transitions (with those involving the bridging ligand lower in energy than those involving the peripheral ligands), and the absorption bands at wavelengths longer than 500 nm to spin-forbidden MLCT transitions (such bands are particularly evident in the osmium-containing compounds due to enhanced spin–orbit coupling). For the $\mathrm{Ir^{III}}$ dinuclear complex **1** (Table 2), the UV region is also mainly dominated by LC spin-allowed transitions, with spin-allowed MLCT transitions contributing to the absorption spectrum at about 380 nm. The broad, weaker absorption feature in the 400–500 nm region is attributed to spin-forbidden MLCT transitions.[5b,6]

Table 2 Relevant spectroscopic and photophysical data in $\mathrm{CH_3CN}$ deaerated solutions at room temperature

Compound	Absorption $\lambda_{\max}$/nm (ε, $\mathrm{M^{-1}\ cm^{-1}}$)	Luminescence		
		$\lambda_{\max}$/nm	τ	ϕ
1	265 (108900) 374 (16500)	613	386 ns	0.123
2	284 (126800) 452 (34800)	617	1.3 μs	0.069
3	289 (130200) 432 (29900) 478 (30500)	743	222 ns	0.023
4	288 (118600) 485 (27700)	787	214 ns	0.0044

All the four new dinuclear complexes exhibit relatively intense room temperature luminescence (Table 2). In all the cases, on the basis of the luminescence energies, spectra, lifetimes and quantum yields, emission can be attributed to ^{3}MLCT levels. The redox data also suggest that for all the compounds the emitting ^{3}MLCT state involves the phen–phen bridging ligand. Differences among excited state energies in the various compounds are in line with redox and absorption data. The values calculated for the radiative and radiationless rate constants of the emitting excited state decay in **1**–**4** can be rationalized by considering the energy gap law[10] and the larger singlet character of the emitting level in the osmium and iridium complexes compared to the ruthenium one, which accelerate both the formally forbidden radiative and radiationless decay processes.

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Notes and references

‡ All the new complexes were isolated as their $\mathrm{PF_6}$ salts, and characterized by elemental analysis, UV-VIS spectra, mass spectra and, where possible, ^{1}H NMR. Relevant characterization data are reported as ESI. Details on the synthesis and on the equipment employed for spectroscopic and electrochemical experiments will be reported elsewhere.

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