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Luminescent cyclometallated Ir(III) complexes of conjugatable carboxy-functionalized ligands†

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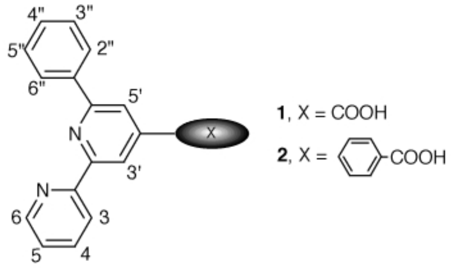
Novel bifunctional ligands based on a 6′-phenyl-2,2′-bipyridine moiety are synthesised and used to prepare iridium(III) complexes $[Ir(ppy)_2(L)]^+$ (ppy = 2-phenylpyridine anion; L = 1, 2, and 4) which have the potential to serve as luminescent probes.

Since the pioneering work by Meares *et al.*,[1] bifunctional chelates have been designed to accomplish many different functions. While the first component of the chelate is usually able to coordinate a metal ion, the second (and often remote) functional group must guarantee a potentially different performance such as conjugation with biomolecules, grafting on a solid support, or pH-dependent activity. Besides their early use in the delivery of radiometals,[1,2] bifunctional chelates have been also primary tools for the construction of tethered DNA intercalators,[3] metallo-dendrimers,[4] photosensitizers for solar cells,[5] pH sensors,[6] and self-assembling organometallic polymers[7] amongst others. Nevertheless, the incorporation of a functional metal complex into a biomolecule for analytical or therapeutic applications is still one of the major targets.[8]

Within the latter approach, the search for luminescent metal probes has already produced excellent examples of labeling *via* transition metal complexes. While most of the candidates for labeling experiments so far reported contained Ru(II) as the photoactive center,[9] we thought it would be of interest to investigate whether functionalized Ir(III) cyclometallated complexes could be a likely alternative.

The ligand 4′-(4-carboxyphenyl)-6′-phenyl-2,2′-bipyridine (**2**) recently proved capable of chelating an "$Ir(ppy)_2$" fragment (ppy = 2-phenylpyridine anion) by using two of the potentially available tridentate sites (*i.e.* the bipyridyl moiety) affording a strongly luminescent chromophore ($\Phi = 0.017$ in acetonitrile solution at room temperature).[10] Following this result, our next target molecules were ligands still bearing a 6′-phenyl-2,2′-bipyridine (hereafter pbpy) moiety on one side and a carboxyl function on the opposite side. We have therefore prepared two new bifunctional ligands where the COOH group is either directly bound to the pbpy fragment in the 4′ position (ligand **1**) or sitting at the end of a flexible spacer (ligand **4**, Scheme 1). In our opinion the series of ligands **1**, **2**[10] and **4** may then ensure a modulation of the chemical reactivity of the conjugatable function while keeping the coordinating ability of the pbpy fragment rather similar. We report here the synthesis of both the ligands and the corresponding series of $[Ir(ppy)_2(L)]^+$ complexes (L = **1**, **2**, and **4**), and on the photophysical properties of the Ir(III) derivatives.

In the preparation of ligand **1**,‡ 3-benzoylacrylic acid was converted directly into the final product by reaction with *N*-(2-pyridacyl)pyridinium iodide[11] in the presence of excess ammonium acetate.[12] Scheme 1 displays the synthetic procedure for ligand **4**.‡ Coupling of the protected 1-bromo-5-carboxypentane with the chalcone **I** afforded the intermediate **II**, which in turn was reacted with *N*-(2-pyridacyl)pyridinium iodide under Kröhnke conditions.[12] The final carboxylic acid **4** was obtained upon deprotection of the corresponding methyl ester **3** by a standard method.



A room temperature reaction of **1** with $[Ir(ppy)_2Cl]_2$[13] (molar ratio 2:1) in CH_2Cl_2–MeOH followed by counterion exchange to PF_6^- gave the desired complex $[Ir(ppy)_2(\mathbf{1})]PF_6$ in high yield (ESI).† Reflux conditions were however necessary for the preparation of $[Ir(ppy)_2(\mathbf{4})]PF_6$.† For the latter species, it was also observed that occasionally a partial esterification of the carboxy group of **4** occurred (clearly shown by ^1H NMR spectroscopy), which was promoted by the solvent. Since the presence of methanol could not be avoided in the reaction mixture, a pure $[Ir(ppy)_2(\mathbf{4})]PF_6$ species was easily recovered upon subsequent hydrolysis under basic conditions. $[Ir(ppy)_2(\mathbf{1})]PF_6$ and $[Ir(ppy)_2(\mathbf{4})]PF_6$ are very soluble in chlorinated solvents and acetonitrile. In fact, it should be noted that $[Ir(ppy)_2(\mathbf{1})]PF_6$ is somewhat labile in acetonitrile solution, leading to partial dissociation of ligand **1**. Therefore this solvent could not be used for spectroscopic studies. Both $[Ir(ppy)_2(\mathbf{1})]PF_6$ and $[Ir(ppy)_2(\mathbf{4})]PF_6$ were fully characterized by analytical, spectrometric, and spectroscopic techniques.†

The absorption spectra of the PF_6^- salts of $[Ir(ppy)_2(\mathbf{1})]^+$, $[Ir(ppy)_2(\mathbf{2})]^+$, and $[Ir(ppy)_2(\mathbf{4})]^+$ in dichloromethane solution are characterized by intense spin-allowed ligand-centered (LC) bands with maxima in the 260–280 nm range and by moderately intense spin-allowed metal-to-ligand charge-transfer (MLCT) bands at lower wavelengths (Table 1). Spin-forbidden MLCT bands are also present in the visible region. Based on a comparison with literature data,[14] the lowest-energy MLCT transition is always assigned to the coordinated pbpy fragment. It is worth noting that the MLCT bands of $[Ir(ppy)_2(\mathbf{1})]^+$ are at significantly lower energy than the corresponding bands of $[Ir(ppy)_2(\mathbf{2})]^+$ and $[Ir(ppy)_2(\mathbf{4})]^+$. This may be explained considering that the electron withdrawing COOH group has a more significant effect on the electronic properties of the pbpy moiety in $[Ir(ppy)_2(\mathbf{1})]^+$ where it is directly linked to the polypyridine backbone, than in $[Ir(ppy)_2(\mathbf{2})]^+$ and $[Ir(ppy)_2(\mathbf{4})]^+$, in which

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† Electronic supplementry information (ESI) available: synthetic details and further characterization data for $[Ir(ppy)_2(\mathbf{1})]PF_6$ and $[Ir(ppy)_2(\mathbf{4})]PF_6$. See http://www.rsc.org/suppdata/dt/b0/b001670p/

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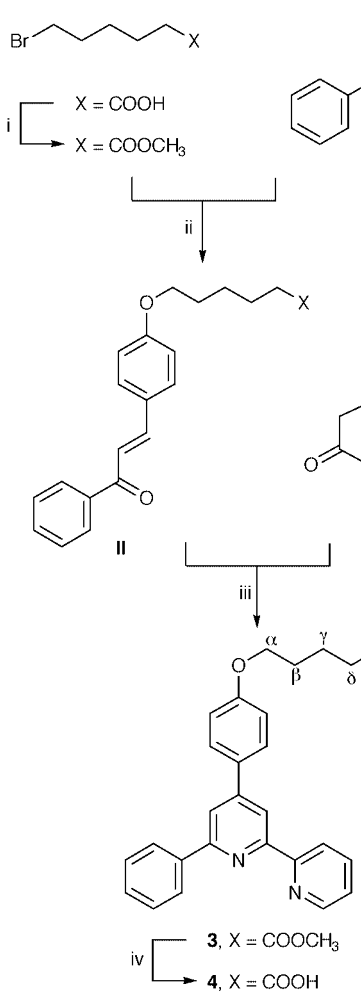

Scheme 1 Reagents and conditions: (i) MeOH (10 equiv.), H_2SO_4 (0.25 equiv.), reflux, 5 h, 92%. (ii) K_2CO_3 (5 equiv.), KI (0.1 equiv.), acetone, reflux, 5 h, 65%. (iii) NH_4OAc (10 equiv.), MeOH, reflux, 16 h, 63%. (iv) KOH (4.5 equiv.), THF–water (2 : 1, v/v), reflux, 4 h; the reaction mixture is then acidified with 2 N HCl (85%).

interposed subunits are present. As a consequence, the acceptor orbital of the MLCT transition is more stabilized in $[Ir(ppy)_2(\mathbf{1})]^+$ than in $[Ir(ppy)_2(\mathbf{2})]^+$ and $[Ir(ppy)_2(\mathbf{4})]^+$, and the corresponding absorption bands are displaced accordingly.

The luminescence spectra of $[Ir(ppy)_2(\mathbf{1})]^+$, $[Ir(ppy)_2(\mathbf{2})]^+$ and $[Ir(ppy)_2(\mathbf{4})]^+$ (Table 1, Fig. 1) can be safely assigned to triplet Ir→pbpy CT excited states.[14] Once again, the separation between the photoactive site and the COOH functional group is responsible for the differences among the complexes. The luminescence spectra of $[Ir(ppy)_2(\mathbf{1})]^+$ (both in solution at room temperature and in a rigid matrix at 77 K) are noticeably red shifted with respect to the other two complexes, as a consequence of the effect of the proximity between the acceptor orbital of the MLCT excited state and the electron withdrawing COOH group.

Although smaller, a similar difference exists between the emission spectra of $[Ir(ppy)_2(\mathbf{2})]^+$ and $[Ir(ppy)_2(\mathbf{4})]^+$. This can also be attributed to the electron withdrawing ability of the substituents of the pbpy acceptor ligand in the two complexes. Whereas the excited-state energy difference is fully rationalized, the difference among the luminescence lifetimes and quantum yields of the three complexes is not straightforward to explain. The energy gap law,[10,15] which states that the radiationless deactivations become faster on decreasing excited state energy, is not able to justify the data. Most likely the complexes are not strictly homogeneous as far as the deactivation processes are concerned, and further investigation is needed to fully clarify the photophysical data.

Table 1 Spectroscopic and photophysical data[a]

Compound	Absorption[b] λ_{max}/nm (ε/M^{-1} cm^{-1})	Luminescence, 298 K[b] λ_{max}/nm	τ/ns	Φ	77 K λ_{max}/nm	τ/μs
$[Ir(ppy)_2(\mathbf{1})]^+$	267 (38500) 378 (6300) 402 (4600) 515 (400)	735	392	9×10^{-4}	585[c]	3.9[c]
$[Ir(ppy)_2(\mathbf{2})]^+$	270 (55500) 292 (44600) 388 (7300) 480 (800)	640	249	0.044	565[d]	3.3[d]
$[Ir(ppy)_2(\mathbf{4})]^+$	273 (60200) 295 (46300) 385 (11200) 482 (800)	606	345	0.074	537[c]	3.7[c]

[a] Data for deoxygenated solutions. Absorption maxima (or shoulders) of the spin-allowed LC and MLCT bands are given. [b] In CH_2Cl_2. [c] In butyronitrile. [d] In MeOH–EtOH 4 : 1 (v/v).

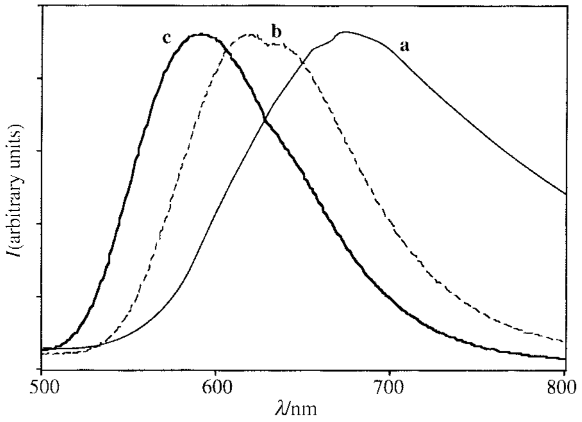

Fig. 1 Room temperature luminescence spectra of: (a) $[Ir(ppy)_2(\mathbf{1})]^+$, (b) $[Ir(ppy)_2(\mathbf{2})]^+$, and (c) $[Ir(ppy)_2(\mathbf{4})]^+$ in dichloromethane solution.

In summary, we have prepared two new functional Ir complexes that, together with the already available $[Ir(ppy)_2(\mathbf{2})]^+$ species, constitute a family of luminescent species bearing a COOH functionality at varying distance from the photoactive subunit. Modulation of the spectroscopic and photophysical properties of the complexes was clearly obtained. Because of the known reactivity of the carboxyl group, the reported species look promising candidates to be interfaced with suitable substrates for the generation of multicomponent systems featuring sensing properties triggered by light.

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Notes and references

‡ Synthetic details for the preparation of ligands **1** and **4** will be reported elsewhere. Both ligands were characterized by ^1H NMR analysis, melting point and elemental analysis.

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