The elusive phosphorescence of pyrromethene–BF_2 dyes revealed in new multicomponent species containing Ru(II)–terpyridine subunits

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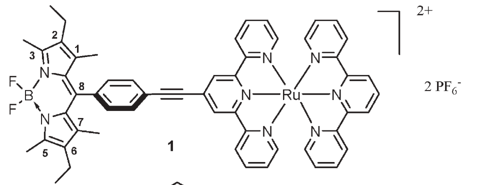
The triplet emitting state of an indacene at 774 nm (of 50 ms life-time) was observed for the first time in new ruthenium(II) complexes based on bipartite ligands carrying one or two indacene subunits linked *via* phenylethynyl connectors to terpyridine fragments.

Multichromophoric species are quite interesting from several viewpoints. For example, they can exhibit photoinduced intercomponent electron and/or energy transfer processes, possibly leading to valuable functions such as charge separation and/or energy migration.[1] The study of such types of processes and functions continues to be fruitful in terms of both fundamental knowledge (*e.g.*, for experimental verification of electron and energy transfer theories) and applicative reasons (*e.g.*, for the development of synthetic systems for artificial photosynthesis).



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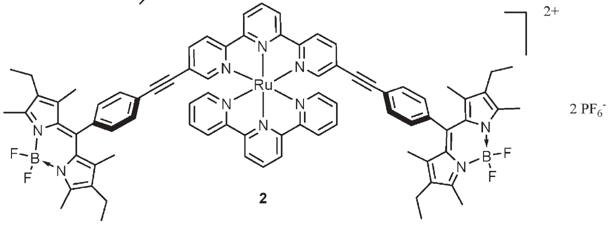

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Two classes of well-known luminescent species are the pyrromethene–BF_2 dyes (singlet emitters) and the Ru(II) polypyridine complexes (triplet emitters). The latter ones exhibit relatively intense and long-lived triplet metal-to-ligand charge-transfer (MLCT) emission,[2] whereas the former ones (sometimes called *bodipy* for 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene dyes) are strongly fluorescent and find applications in the field of opto-electronic switching and laser dyes.[3] In multicomponent species made of subunits belonging to such classes of compounds, interesting photoinduced intercomponent processes could therefore be expected, in particular if some internal barrier prevents the system from being coplanar.[4] These considerations prompted us to synthesize two novel multichromophoric compounds, **1** and **2**, in which one Ru(II) polypyridine subunit is interfaced with one and two bodipy subunits, respectively.

In order to avoid complete conjugation between both chromophoric centers we designed a bodipy constructed from kryptopyrrole and carrying a phenyl substitutent linked to the indacene core. From steric considerations the presence of the methyl in the 1,7-substitution positions and the phenyl ring in the 8-position will force the fragments to be orthogonal, disrupting the communication while maintaining the electronic properties of the individual units. The use of alkyne linkers is motivated by synthetic reasons (easy Pd(0) promoted cross-coupling protocols) and the substitution positions on the terpy fragment by electronic and steric considerations.[5]

The free ligands **L1** and **L2** containing a terpy subunit (terpy = 2,2′:6′,2″-terpyridine) covalently-linked to bodipy chromophores were constructed *via* a Sonogashira protocol,[6] and allowed to react with *cis*-Cl-[Ru(terpy)(DMSO)Cl_2][7] in refluxing methanol under anhydrous and anaerobic conditions. To ensure a good yield, the metal precursor was firstly dehalogenated with $AgBF_4$ (2.2 equiv.). All complexes were isolated as the hexafluorophosphate salts. Their molecular structures were unambiguously assigned by NMR, FT-IR, electrospray mass spectroscopy, and elemental analysis. Details on synthesis and characterization will be published elsewhere.†

The new compounds exhibit quite intense absorption in the visible region in acetonitrile solution (Table 1, Fig. 1), dominated by a sharp band with a maximum at 523 nm and by a broader band of lower intensity with a maximum (or shoulder) between 450 and 500 nm (ε of the band maxima in the range 1×10^4–2×10^5 M^{-1} cm^{-1}). Intense absorption bands are also present in the UV region (ε in the range 1×10^4–1×10^5 M^{-1} cm^{-1}). The sharp band with a maximum at 523 nm is assigned to spin-allowed π–π* transitions involving the pyrromethene–BF_2 dyes.[9] Such transitions also contribute to the shoulder on the blue side of the main band, which receives a significant contribution from spin-allowed MLCT transitions involving the metal-based subunits. For the UV absorption, the bands within the 270–300 nm range should receive a dominant contribution from π–π* transitions involving the polypyridine moieties.[2a]

Both compounds undergo two reversible oxidation processes in acetonitrile solution (Table 1). In both cases, the one at the less positive potential is assigned to the bodipy moieties, and the next one to metal-centered processes. This attribution is based on the redox data of the free bodipy ligands, which undergo oxidation processes (monoelectronic for the ligand of **1** and bielectronic for

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Table 1 Absorption, luminescence, and redox data in acetonitrile room temperature, unless otherwise stated. Some data[8] for **L1** and **L2** (uncomplexed bodipy–terpy ligands) are given for comparison

	Absorption	Luminescence[b]	Redox data[c]	
	λ/nm[a] (ε/M^{-1} cm^{-1})	λ/nm[a] (τ)	$E_{1/2}$(ox)	$E_{1/2}$(red)
1	523 (66 100)	536 (5 ns) 774 (50 ms)	+0.99 +1.44	−1.14 −1.36 −1.55
2	523 (89 600)	540 (4 ns) 774 (50 ms)	+0.99 [2] +1.44	−1.06 −1.33 [2] −1.48
L1	527	536 (7 ns)	+1.08	−1.35
L2	527	535 (6 ns)	+1.00 [2]	−1.37 [2]

[a] Lowest-energy maximum. [b] In butyronitrile matrix at 77 K. [c] Electrolyte 0.1 M TBAPF$_6$–anhydrous CH$_3$CN under nitrogen, at 1.5 mM, at rt. All potentials (±10 mV) are reported in volts *vs.* a Pt^0 pseudo reference electrode and using Fc$^+$/Fc as internal reference. Under these experimental conditions the Fc$^+$/Fc couple is quoted at 0.38 V (ΔE_p = 70 mV) *versus* the SCE electrode. The numbers in brackets refer to the number of exchanged electrons. When not specified, the process involves one electron.

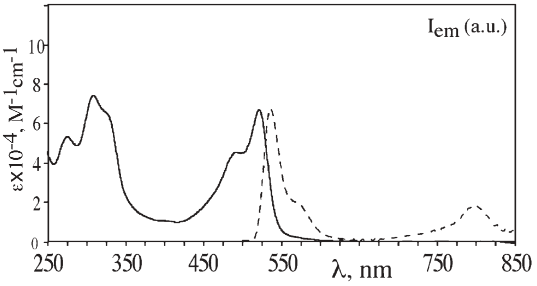


Fig. 1 Room temperature absorption (acetonitrile solution, solid line) and 77 K luminescence (butyronitrile matrix, dashed line) spectra of **1**.

the ligand used in **2**) within the range +1.00 and +1.10 V *vs.* SCE.[8] For **2**, the first oxidation integrates for two electrons, in agreement with the attribution. On reduction, a series of three reversible processes are seen in differential pulse voltammetry. The ones occurring at −1.36 and −1.33 V *vs.* SCE in **1** and **2**, respectively, can be assigned to the bodipy subunit(s) (in free bodipy ligands, reduction takes place at about −1.36 V[8]), whereas the other processes are terpy-centered. In particular, the first reduction at −1.14 and −1.06 V for **1** and **2**, respectively, is likely to be due to the reduction of the ethynyl substituted terpy ligands. The sequence of potentials is in keeping with the increase of electron-withdrawing groups on the ligand. As for the oxidation, the bielectronic nature of the second reduction of **2** was quite useful to identify the bodipy-based reduction processes.

At room temperature, in spite of the intense fluorescence exhibited by the free ligand **L1** and **L2** (Φ = 0.7 and 0.9, respectively[8]), neither **1** or **2** exhibit luminescence, independent of excitation wavelength. However, nanosecond transient absorption spectroscopy indicates that a non-emissive excited state having a relatively long lifetime (8 μs and 30 μs for **1** and **2**, respectively) is present after the ns laser pulse for both compounds (Fig. 2). From its spectral signature, common to both **1** and **2** (bleaching of the 530 nm absorption, weak absorption in the 550–700 nm region), and lifetimes, such a state is proposed to be the lowest-lying bodipy-centered triplet state, which is indeed expected to be the lowest excited state of the multichromophoric species.

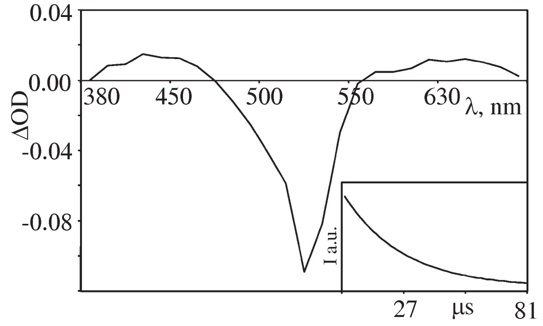
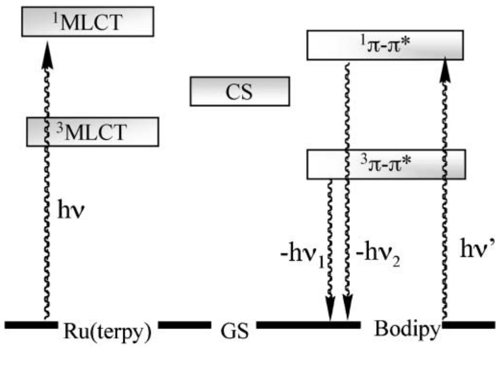


Fig. 2 Transient absorption spectrum of **2** in acetonitrile at room temperature. Excitation wavelength is 355 nm. The inset shows the transient decay recorded at 610 nm.

Apparently, ^{3}MLCT emission is quenched by down-hill energy transfer and the fluorescent $^1\pi$–π* bodipy level could be deactivated by intersystem crossing promoted by the presence of the heavy metal center. However, a charge-separated state (CS) produced by electron transfer from the singlet bodipy level to the metal complex is thermodynamically allowed (the driving force for the process is 0.17 and 0.25 eV for **1** and **2**, respectively)‡ and could contribute to the deactivation of the bodipy-centered $^1\pi$–π* state, ultimately leading to the bodipy $^3\pi$–π* state. Such photoinduced electron transfer processes have been postulated to explain the fluorescence quenching in some bodipy dyes.[10] Indeed, the charge-separated state would produce the lowest-lying $^3\pi$–π* state by recombination, favoured compared to recombination to the ground state since this latter process, having a driving force of about 1.95 eV, would be in the Marcus-inverted region. The role of the charge-separated state in the $^1\pi$–π* quenching process is supported by the fluorescence of **1** and **2** at 77 K (Table 1; see also later). In fact, the small driving force of the electron transfer process producing the charge-separated state would make the process inefficient at low temperature. Scheme 1 shows an energy level diagram depicting the relevant excited-state levels of **1** and **2**.§¶

One of the most interesting features of **1** and **2** is their luminescence behaviour at 77 K in a butyronitrile rigid matrix. In



Scheme 1 Excited state levels of the mixed Ru(terpy)–bodipy dyads. GS for ground state, CS for charge-separated state. Only radiative transitions are evidenced (see text).

this condition, both compounds exhibit two emissions (Fig. 1, Table 1). The one centered at about 540 nm is the typical bodipy $^{1}\pi$–π^* fluorescence, while the long-lived emission at about 770 nm cannot be due to the ^{3}MLCT emission, on the basis of the energy and lifetime (see Table 1; from model species, ^{3}MLCT would be expected at a wavelength shorter than 700 nm and with a lifetime in the microsecond timescale[2a,4,5]). The luminescence spectra are essentially independent of excitation wavelength, within the range 420–520 nm. The millisecond lifetime of the emission strongly indicates that its origin is an organic triplet state, so it can be safely assigned to the not-yet reported phosphorescence originating from the bodipy $^{3}\pi$–π^*. We propose that the phosphorescence of the bodipy in **1** and **2** is due to the presence of the heavy ruthenium metal which would allow intensity to be stolen from the spin-allowed radiative decay by enhanced spin–orbit coupling. In particular, it is probably the interaction between the bodipy $^{3}\pi$–π^* state and the closely-lying metal-based ^{3}MLCT level which provides a channel to enhance spin–orbit coupling in the present systems.

In short, the absorption spectra, redox behaviour, and luminescence properties of hybrid complexes **1** and **2** have been investigated. At room temperature, both MLCT phosphorescence from the metal-based subunits and bodipy-based fluorescence are quenched, also *via* population of an intercomponent, intermediate charge-separated state. At 77 K, besides the restored bodipy fluorescence as a consequence of failure of electron transfer quenching *via* the intermediate charge-separated state, the phosphorescence of the bodipy subunits is evidenced. To the best of our knowledge, this is the first time that the elusive phosphorescence of bodipy has been obtained, in spite of the many photophysical investigations performed so far. Enhanced spin–orbit coupling in the bodipy subunits, mainly induced by interaction with the low-lying metal-based MLCT triplet, is proposed to be responsible for such a result.

Ultrafast spectroscopic investigation to fully characterize the intercomponent processes is currently in progress.

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Notes and references

† Selected data for **1**: Isolated yield: 68%. ^{1}H NMR (d_6-acetone) : $\delta = 1.02$ (t, 6H, $^{3}J = 7.4$ Hz), 1.46 (s, 6H), 2.37 (q, 4H, $^{3}J = 7.4$ Hz), 2.53 (s, 6H), 7.34 (9 lines m, 4H), 7.64 (5 lines m, 2H), 7.77 (5 lines m, 4H), 7.97–8.11 (m, 6H), 8.60 (6 lines m, 1H), 8.79–8.95 (8 lines m, 4H). 9.08 (4 lines m, 2H), 9.25 (d, $J = 4.0$ Hz, 2H). IR (KBr) 2218 ($\nu_{C\equiv C}$), cm^{-1}. ES-MS (acetonitrile): *m*/*z* (%) = 1115.2 (100) $[M - PF_6]^+$. Anal. calc. for $C_{55}H_{47}BF_{14}N_8P_2Ru$: C, 52.44; H, 3.76; N, 8.89. Found: C, 52.63; H, 3.97; N, 9.02. Selected data for **2**: Isolated yield: 73%. ^{1}H NMR (d_6-acetone): $\delta = 0.96$ (t, 12H, $^{3}J = 7.4$ Hz), 1.30 (s, 12H), 2.33 (q, 8H, $^{3}J = 7.4$ Hz), 2.48 (s, 12H), 7.37 (td, 2H, $^{3}J = 6.0$ Hz, $^{4}J = 1.1$ Hz, 7.53 (AB sys, 8H, $J_{AB} = 8.4$ Hz, $\nu_0\delta = 87.9$ Hz), 7.77 (d, 2H, $^{3}J = 4.8$ Hz), 7.93 (d, 2H, $^{4}J = 1.4$ Hz), 8.10 (td, 2H, $^{3}J = 7.9$ Hz, $^{4}J = 1.4$ Hz), 8.23 (dd, 2H, $^{3}J = 8.4$ Hz, $^{4}J = 1.8$ Hz), 8.62 (td, 2H, $^{3}J = 8.2$ Hz, $^{4}J = 2.3$ Hz), 8.82 (d, 2H, $^{3}J = 8.1$ Hz), 8.88 (d, 2H, $^{3}J = 8.4$ Hz), 9.09 (d, 2H, $^{3}J = 8.4$ Hz), 9.14 (d, 2H, $^{3}J = 8.4$ Hz); IR (KBr): 2223 ($\nu_{C\equiv C}$) cm^{-1}. ES-MS (acetonitrile): 1517.3 (100) $[M - PF_6]^+$. Anal. calc. for $C_{80}H_{72}B_2F_{16}N_{10}P_2Ru$: C, 57.81; H, 4.37; N, 8.43. Found: C, 57.55; H, 4.53; N, 8.63.

‡ Driving force of the oxidative electron transfer process was calculated by the equation $\Delta G = e[{}^*E\text{ox(bodipy)} - E\text{red(Ru)}]$, in which $^*E$ox(bodipy) is the excited-state oxidation potential of the bodipy $^{1}\pi$–π^* level and *E*red(Ru) is first the reduction potential of the complexes. In its turn, $^*E$ox(bodipy) is approximate to *E*ox(bodipy) – *E*(00), with the first term being the first oxidation potential of the complexes (bodipy-centered) and the latter a potential which corresponds to the 77 K fluorescence energy of **1** and **2**. The work term is neglected.

§ The excited-state levels shown in Scheme 1 have been estimated as follows. ^{1}MLCT state: energy approximated from the spin-allowed MLCT bands in the absorption spectra of related compounds;[4,5,11] bodipy-centered $^{1}\pi$–π^* state: estimated from free ligand literature data[6] and the 77 K fluorescence spectra reported here; ^{3}MLCT states: emission energies of related complexes;[4,5,11] bodipy-centered $^{3}\pi$–π^* state: 77 K phosphorescence of **1** and **2**.

¶ In principle, bodipy fluorescence could be quenched *via* energy transfer to ^{3}MLCT. However, the Förster equation yields values lower than 1×10^6 s^{-1} for this process in **1** and **2**, mainly due to the negligible absorption of the metal subunits at $\lambda > 510$ nm, and these values cannot compete with intrinsic deactivation of the bodipy singlet state. The Dexter mechanism appears improbable as well.

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