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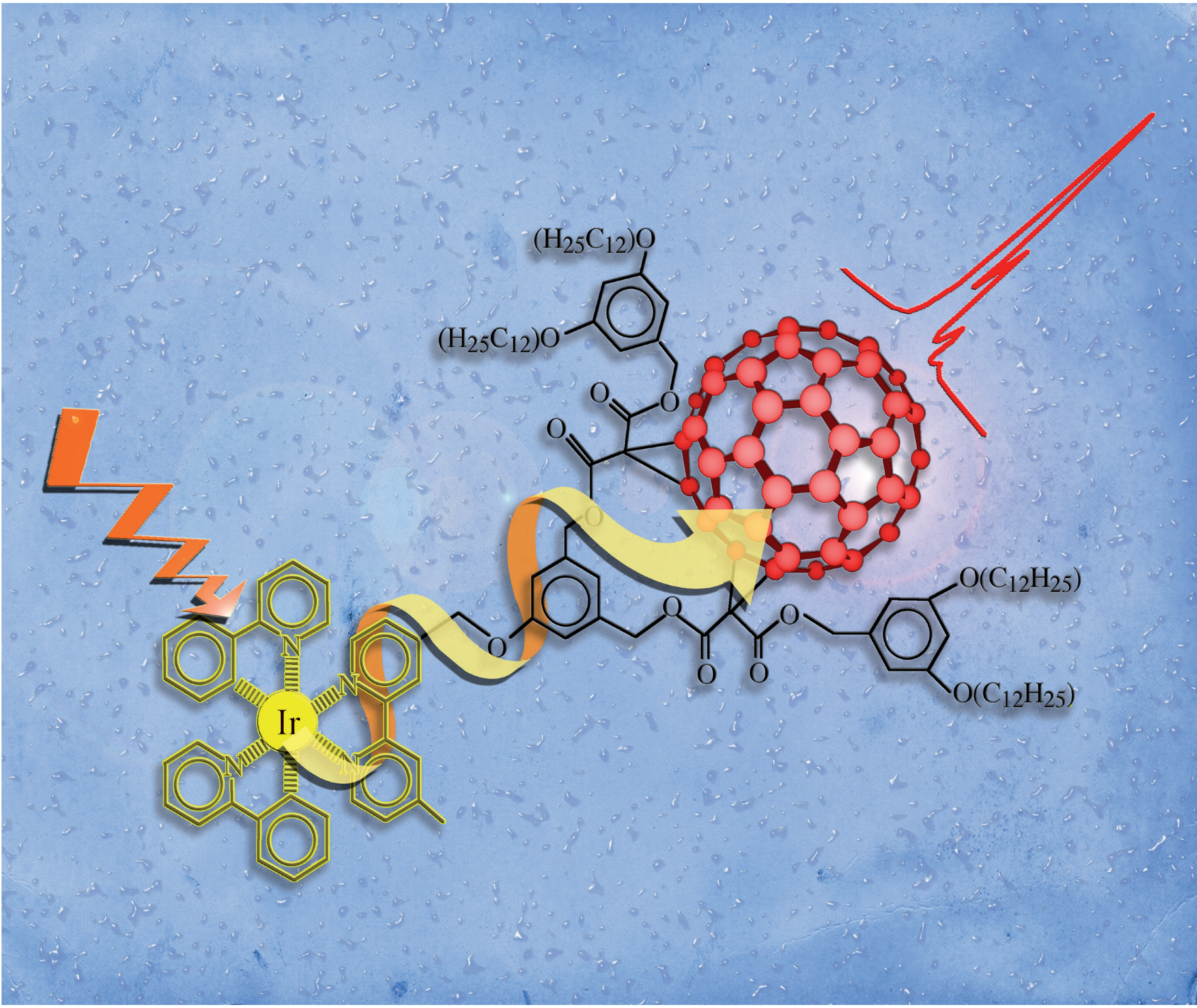

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A luminescent multicomponent species made of fullerene and Ir(III) cyclometallated subunits†

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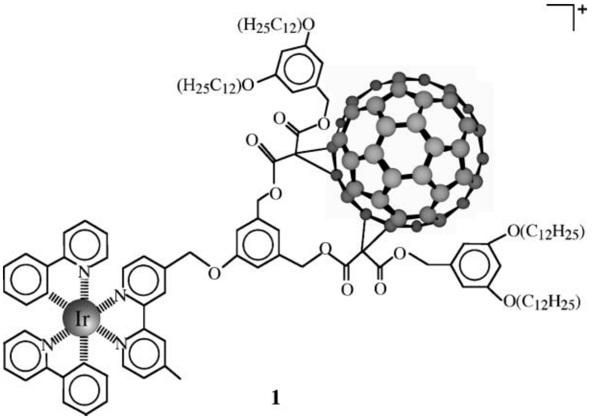
The first system containing a luminescent Ir(III) cyclometallated species and a functionalized C_{60} unit has been prepared; triplet–triplet energy transfer from the Ir-based MLCT state to the C_{60} triplet state occurs, leading to phosphorescence (lifetime, 4.8 ms) of the derivatized-C_{60} at 77 K.

Multicomponent supramolecular architectures containing fullerene subunits have been extensively investigated, in particular for purposes related to solar energy conversion.[1] Fullerenes are indeed very good electron acceptors, and C_{60}-based donor–acceptor systems can give rise to long-lived charge-separated states, taking advantage of the small intrinsic reorganization energy of the fullerene subunit.[2] The above considerations prompted the preparation of several systems combining C_{60} with photo-active Ru(II),[3,4] Re(I),[4,5] and Cu(I)[6] polypyridine complexes, and their photophysical properties have proven to be very rich.[7]

Owing to the outstanding photophysical properties of Ir(III) cyclometallated compounds,[8] we have decided to prepare a fullerene-substituted Ir(III) complex as the first member of a new class of multicomponent photoactive compounds. Here we report the synthesis, the spectroscopic, redox, and luminescence properties of compound **1** resulting from the coordination of a fullerene-functionalized bipyridine ligand to an Ir(III)$(ppy)_2$ (ppy = mono-anion of 2-phenylpyridine) moiety. It is worth noting that η^2-C_{60} Ir complexes have already been reported,[9] but this is the first time that a potentially luminescent Ir(III) subunit has been connected to a fullerene moiety. Interestingly, **1** exhibits fullerene-based millisecond phosphorescence at 77 K in rigid matrix.[10]

Compound **1** has been prepared in a good yield (60%) by reacting $[(ppy)_2Ir(\mu\text{-}Cl)]_2$[11] with the fullerene-functionalized bpy (2,2′-bipyridine) ligand (**L**,[12] shown in the structural formula of **1**) in a refluxing dichloromethane–methanol 2 : 1 (v/v) mixture, and then purified as a PF_6^- salt. Details are given in the supplementary information.



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The absorption spectrum of **1** (see ESI) contains the characteristic features of both components, $[Ir(ppy)_2(bpy)]^+$ and C_{60}. A maximum at 260 nm is assigned to spin-allowed ligand-centered (LC) transitions involving ppy and fullerene. A shoulder at about 300 nm is mainly assigned to LC transitions involving bpy. At energy lower than 350 nm, contributions from spin-allowed metal-to-ligand charge-transfer (MLCT) transitions are seen. The spectrum extends towards the red and at wavelength longer than 450 nm fullerene absorption dominates, with contributions from spin-forbidden MLCT transitions.

Cyclic and differential pulse voltammetry showed that **1** undergoes several reversible processes (Table 1, Fig. 1). On oxidation, a single, mono-electronic reversible process is found, which is assigned to metal-centered oxidation, on the basis of the comparison with the model compound $[Ir(ppy)_2(bpy)]^+$.[11] On reduction, five reversible processes are present at potentials less negative than −1.80 V *vs.* SCE. The first three processes are assigned to successive one-electron reductions of the C_{60} subunit.[6] The fourth and fifth processes, partly overlapping (see Fig. 1), include the fourth one-electron reduction of fullerene as well as the bpy-based reduction, which is shifted to more negative potentials compared to the same process in $[Ir(ppy)_2(bpy)]^+$ because of the presence of the formerly reduced fullerene.

Table 1 Redox data of **1** and $[Ir(ppy)_2(bpy)]^+$, used as a model species[a]

	$E_{1/2}$(ox)	$E_{1/2}$(red)
1	+1.23	−0:68; −0.98; −1.19; −1.48; −1.60
$[Ir(ppy)_2(bpy)]^+$	+1.26	−1.37

[a] In acetonitrile, *vs.* SCE.

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† Electronic supplementary information (ESI) available: Synthesis and absorption spectrum of **1**, calculated driving forces of quenching processes. See DOI: 10.1039/b705296k

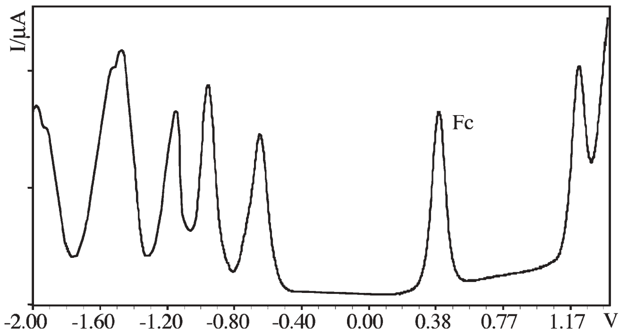


Fig. 1 Differential pulse voltammogram of **1** in acetonitrile. Fc is ferrocene, used as an internal reference. Scan rate, 10 mV s^{-1}.

Table 2 Absorption and luminescence data, in acetonitrile unless otherwise stated. Emission maxima are corrected for detector response

	Absorption	Emission, 298 K		Emission, 77 K[a]	
	λ, nm (ε, M^{-1} cm^{-1})	λ, nm	τ, ns	λ, nm	τ
1	260 (90000) 310 (34000) 465 (3300)	606 700	5 1[b]	826	4.8 ms
$[Ir(ppy)_2(bpy)]^+$	465 (580)	590	340	532	5.2 μs

[a] In butyronitrile rigid matrix. [b] Contribution from the longer-lived component is also present.

The model species $[Ir(ppy)_2(bpy)]^+$ exhibits MLCT emission both at room temperature (r.t.) in fluid solution and at 77 K in rigid matrix.[11] Compound **1** exhibits a similar MLCT emission at r.t. but a quite different emission at 77 K (Table 2, Fig. 2). The r.t. emission of **1**, anyway, is very short-lived compared to the MLCT emission of the model compound. Moreover, a shoulder is present at about 700 nm, which cannot be assigned to the vibrational progression of the main emission band. On changing excitation wavelength, the ratio between the 606 nm main emission band and the emission feature at *ca.* 700 nm changes (it decreases moving excitation to the red, where C_{60} absorbs preferentially). The latter observation indicates that two independent emissions are present, as also suggested by the biphasic emission decay (Table 2). Fullerene derivatives are reported to exhibit fluorescence at about 700 nm, with a lifetime of 1 ns,[4,6] thus the short-lived emission at about 700 nm of **1** is safely assigned to fullerene-based fluorescence.

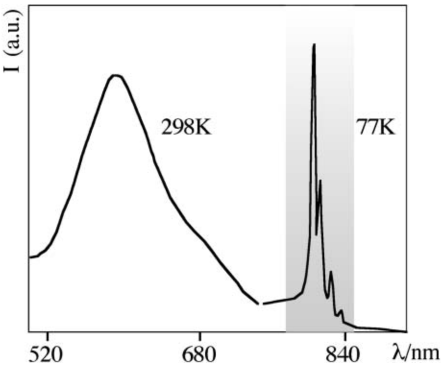


Fig. 2 Luminescence spectra of **1** in acetonitrile at 298 K (left) and in butyronitrile at 77 K (right). Excitation wavelength, 400 nm (cut-off filter at 450 nm).

The MLCT emission of **1** is clearly quenched (Table 2). Several thermodynamically allowed quenching processes are possible:

(i) energy transfer from the Ir-based ^{3}MLCT to fullerene, to produce the singlet state of C_{60} (driving force, −0.55 eV);[13]

(ii) energy transfer from the Ir-based ^{3}MLCT to fullerene, to produce the triplet state of C_{60} (driving force, −0.81 eV);

(iii) oxidative electron transfer from the Ir-based ^{3}MLCT to fullerene, to produce a charge-separated state (driving force, −0.40 eV).

Process (i) would be spin-forbidden, however the iridium complexes have strong spin–orbit coupling, so this mechanism cannot be totally ruled out on spin arguments. Process (ii) would be allowed according to the Dexter mechanism. Process (iii) is known to be quite fast in similar Ru(II)– and Re(I)–C_{60} species.[4] The rate constant k_q for the Ir-based MLCT quenching can be calculated by the usual equation $k_q = 1/\tau_1 - 1//\tau_0$, with τ_1 and τ_0 the lifetimes of the quenched and unquenched excited states, respectively.[14] The calculated quenching rate constant is 8.0×10^8 s^{-1}, a value which agrees with any quenching mechanism. At this stage we have no way to discriminate among the possibilities, however the charge-separated (cs) state would have an energy of 1.91 eV, and its deactivation to the ground state would be well inside the Marcus inverted region. As a consequence, direct decay from such a state to the ground state should be slow. Since back electron transfer to produce the fullerene triplet excited state is also allowed from the cs state (driving force, −0.41 eV), it is most likely that the final state of MLCT quenching is $^3C_{60}$ in any case. Figure 3 shows the energy level diagram and deactivation processes in **1**.

In rigid matrix at 77 K, only a weak structured emission, peaking at 826 nm, is present (Table 2, Fig. 2). From its energy and lifetime, it is attributed to fullerene phosphorescence. Phosphorescence of C_{60} is usually very difficult to observe: it has been detected only in the presence of an external heavy atom effect.[15] In fact, the phosphorescence process of C_{60} is both symmetry- and spin-forbidden and is induced by spin–orbit and vibronic interactions. As a consequence, this transition is extremely weak. Furthermore, if the symmetry remains I_h, the 0–0 band is often missing.[16] In a recent paper, the 0–0 vibrational band of the C_{60} phosphorescence has been identified at 786 nm in Xe matrix.[16] However, whereas phosphorescence of C_{60} is documented,[15] phosphorescence spectrum and lifetime from substituted fullerene are

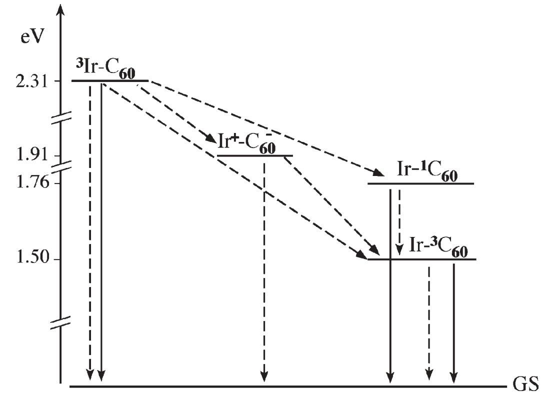
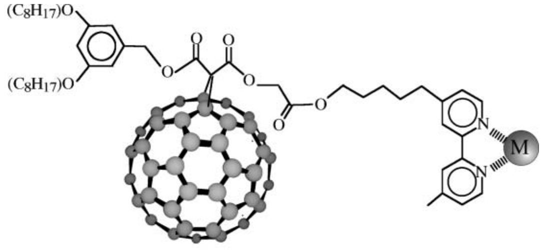


Fig. 3 Energy level scheme and decays of **1**. Solid and dashed lines indicate radiative and radiationless processes, respectively.

virtually unknown up to now.[10] In fact, derivatized C_{60} phosphorescence was not detected even in multicomponent C_{60}–metal complexes systems, including species containing heavy atoms like rhenium or ruthenium.[3–6] In **1**, an important role to make phosphorescence detectable is probably played by the presence of the heavy iridium ion. Moreover, symmetry is surely reduced, so the 826 nm emission maximum can be assigned to the 0–0 transition. Functionalization of C_{60} in **1** would also be taken into account for the red shift of the phosphorescence maximum compared to C_{60}, according to the suggestion that the triplet state level of C_{60} is modified by functionalization.[10]

Interestingly, the Ir-based MLCT emission is totally absent at 77 K. This suggests Dexter triplet–triplet energy transfer quenching as the dominant deactivation pathway for the ^{3}MLCT state, at least under these conditions. Actually, energy transfer rate constants are hardly affected by temperature and medium effects, while electron transfer rate constants are much more sensitive to such effects.[17] If Dexter energy transfer significantly contributes to the quenching mechanism even at r.t., the 77 K rate constant of the energy transfer process should be close to $8.0 \times 10^8\ s^{-1}$. On assuming that the 77 K intrinsic lifetime of the MLCT state of **1** is roughly identical to that of the model $[Ir(ppy)_2(bpy)]^+$, the energy transfer rate constant would exceed the MLCT radiative rate constant by more than three orders of magnitude, rationalizing the absence of detectable MLCT emission of **1** at 77 K.[18]



2:M = $Ru(bpy)_2^{2+}$ **3**:M = $Re(CO)_3Br$

Our suggestion of triplet–triplet Dexter energy transfer as the dominant mechanism for Ir-based MLCT quenching in **1** contrasts with the electron transfer quenching of MLCT emission proposed for related fullerene-substituted Ru(II)– and Re(I)–polypyridine complexes **2** and **3**.[4] In particular, for **2** (which exhibits driving forces to those of **1** for energy and electron transfer processes of −0.64 and −0.19 eV, respectively, that is less exergonic than those of **1**) MLCT quenching was ineffective at 77 K, indicating that the energy transfer pathway was extremely slow. However, significant differences between the systems can be found: linkage is very different (*e.g.* a pentylene spacer is present in the Ru species **2**, compared to the methylene present in **1**) and the acceptor ligand of the MLCT state is a peripheral bpy ligand for **2**, whereas it is the bpy ligand bearing the fullerene moiety in **1**. Both such differences lead to a much better electronic coupling between the energy transfer partner chromophores in **1**, which, together with better thermodynamic parameters, could allow for a much higher energy transfer rate constant.

In conclusion, the first multicomponent species (**1**) containing a luminescent Ir(III) subunit and a C_{60} moiety has been prepared. Absorption features and redox processes are evidenced and assigned to each component of the assembly. Intercomponent excited-state processes take place both at room temperature and at 77 K, where **1** displays phosphorescence from the C_{60} subunit.

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18 Note that such an assumption does not exclude the possibility that electron transfer can contribute to some extent to the quenching process at r.t.