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Article

Heteroleptic Copper(I) Complexes Coupled with Methano[60]fullerene: Synthesis, Electrochemistry, and Photophysics

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Heteroleptic copper(I) complexes **CuPOP-F** and **CuFc-F** have been prepared from a fullerene-substituted phenanthroline ligand and bis[2-(diphenylphosphino)phenyl] ether (**POP**) and 1,1′-bis(diphenylphosphino)ferrocene (**dppFc**), respectively. Electrochemical studies indicate that some ground-state electronic interaction between the fullerene subunit and the metal-complexed moiety are present in both **CuPOP-F** and **CuFc-F**. Their photophysical properties have been investigated by steady state and time-resolved UV−vis−NIR luminescence spectroscopy and nanosecond laser flash photolysis in a CH_2Cl_2 solution and compared to those of the corresponding model copper(I) complexes **CuPOP** and **CuFc** and of the fullerene model compound **F**. Selective excitation of the methanofullerene moiety in **CuPOP-F** results in regular deactivation of the lowest singlet and triplet states, indicating no intercomponent interactions. Conversely, excitation of the copper(I)-complexed unit (405 nm, 40% selectivity) shows that the strongly luminescent triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state located at 2.40 eV is quenched by the carbon sphere with a rate constant of 1.6×10^8 s^{-1}. Details on the mechanism of photodynamic processes in **CuPOP-F** via transient absorption are hampered by the rather unfavorable partition of light excitation between the two chromophores. By determination of the yield of formation of the lowest fullerene triplet level through sensitized singlet oxygen luminescence in the NIR region, it is shown that the final sink of photoinduced processes is always the fullerene triplet. This can be populated via a two-step charge-separation charge-recombination process and a less favored ^{3}MLCT → $^3C_{60}$ triplet−triplet energy-transfer pathway. In **CuFc-F**, both of the photoexcited copper(I)-complexed and fullerene moieties are quenched by the presence of the ferrocene unit, most likely via ultrafast energy transfer.

Introduction

d^6 and d^{10} coordination compounds may possess low-lying metal-to-ligand charge-transfer (MLCT) excited states with marked reducing character; thus, they can be excellent partners for C_{60} fullerene electron acceptors in photoactive multicomponent hybrid systems.[1,2] In the search for the most appropriate electron/energy acceptors to be used in parallel with reducing coordination compounds, several criteria are usually met, which include reasonably long-lived excited-state lifetimes, good absorption in the UV−vis spectral region, photostability, and possibly photoluminescence. Accordingly, a large number of dyads in which fullerene is coupled with carefully chosen chromophores have been investigated over the years: porphyrin[3–8] and conjugated

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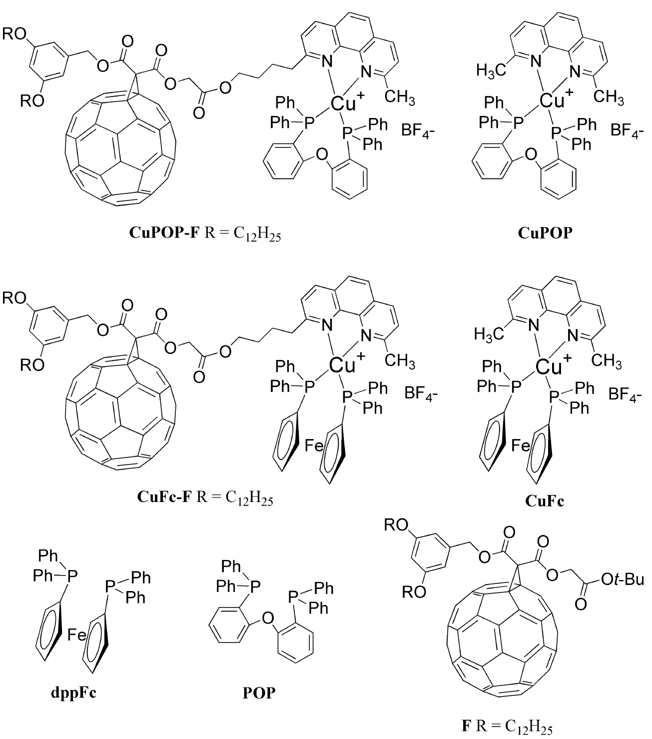
organic oligomer systems[9–15] are probably the most popular, whereas relatively less attention has been paid to hybrid systems with photoactive coordination compounds of ruthenium(II),[16–19] rhenium(I),[16] and copper(I).[20–24] In a ruthenium(II) system that we investigated previously, the energy of the lowest ^{3}MLCT level (2.4 eV) is higher lying than that of the fullerene singlet (1.8 eV) and triplet (1.5 eV), whereas the charge-separated state is intermediate (2.0 eV).[16] Upon excitation of the metal-complexed moiety, charge separation followed by charge recombination to the fullerene triplet is observed. Practically, because direct excitation of the fullerene moiety results in regular deactivation without intercomponent interactions, the fullerene triplet level is the final energy sink of the dyad, whatever the excitation wavelength.[16] The situation can be rather different in the case of copper(I) phenanthroline−fullerene hybrids. Copper(I) complexes are indeed stronger reducing agents than ruthenium(II) systems; thus, the charge-separated state can be the lowest in the energy diagram, originating a different pattern of photoinduced processes also finely depending on the fullerene cage functionalization [e.g., mono- vs bis(methanofullerenes)].[20]

In the past few years, there has been growing interest in heteroleptic copper(I) complexes with a phenanthroline and a phosphine-type ligand.[25] Some of them are strong green emitters from their lowest ^{3}MLCT* state[26–29] and are rather promising for the development of electroluminescent devices based on materials cheaper than traditional iridium(III) compounds.[30–33] Interestingly, the electronic and photophysical properties of these copper(I) complexes are more similar to ruthenium(II) polypyridine than to copper(I) bis(phenanthroline) analogues.[33] For instance, the energy of the excited state may exceed 2.40 eV, whereas a relatively high oxidation potential can render the charge-separated state in fullerene dyads almost isoenergetic to that obtainable with analogous ruthenium(II) polypyridyl/fullerene arrays.

Chart 1



Herein we describe the synthesis and electrochemical and photophysical properties of a new hybrid system, **CuPOP-F**, made of a methanofullerene unit (**F**) linked to a green emitting and weakly reducing heteroleptic copper(I) complex (**CuPOP**; Chart 1). The pattern of photoinduced processes in the dyad is discussed in comparison to previously investigated hybrids with ruthenium(II) and copper(I) complexes and with an analogous complex (**CuFc-F**) bearing an electrochemically and photochemically active ferrocene center in place of the **POP** ligand.

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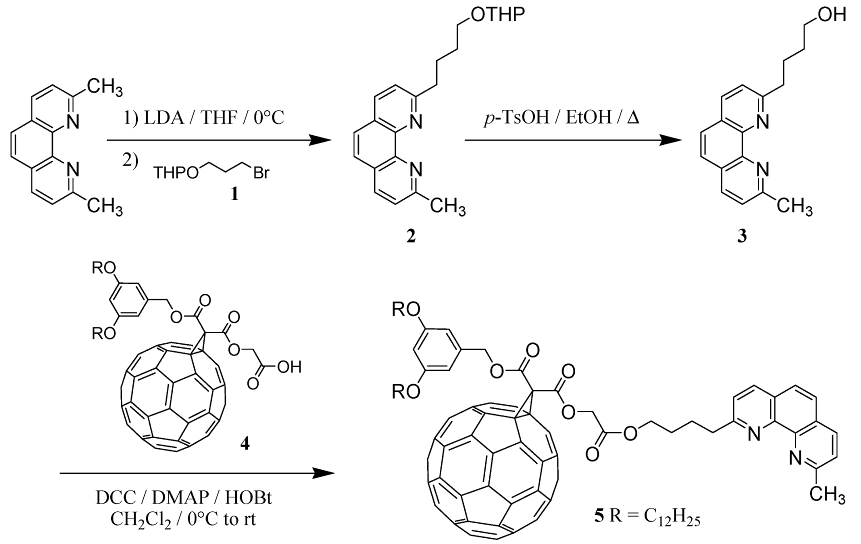
Scheme 1. Preparation of Ligand **5**



Synthesis

The preparation of fullerene-substituted phenanthroline ligand **5** is depicted in Scheme 1. Compound **2** was obtained from 2,9-dimethyl-1,10-phenanthroline by deprotonation of one of the methyl groups with lithium diisopropylamide (LDA) to generate the corresponding carbanionic species, followed by reaction with 4-(bromopropyl)tetrahydropyran-2-yl ether (**1**). Compound **2** was not isolated in a pure form and was used as received in the next step. The cleavage of the 3,4,5,6-tetrahydro-2*H*-pyranyl (THP) protecting group was achieved by treatment with *p*-toluenesulfonic acid (*p*-TsOH) in refluxing ethanol. Compound **3** was thus obtained in 50% yield (from 2,9-dimethyl-1,10-phenanthroline). Finally, the treatment of alcohol **3** with carboxylic acid **4** under esterification conditions [*N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), and 1-hydroxybenzotriazole (HOBt)] yielded ligand **5**. The corresponding complexes **CuPOP-F** and **CuFc-F** were obtained by the reaction of bis[2-(diphenylphosphino)phenyl] ether (**POP**) and 1,1′-bis(diphenylphosphino)ferrocene (**dppFc**), respectively, with stoichiometric quantities of **5** and [Cu(CH_3CN)$_4$]BF_4 in dichloromethane at 25 °C. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.

Electrochemical Properties

The electrochemical properties of **CuPOP-F** and **CuFc-F** were investigated by cyclic voltammetry (CV). For the sake of comparison, electrochemical measurements have also been carried out with model compounds **CuPOP**, **CuFc**, and **F**. All of the experiments were performed at room temperature in CH_2Cl_2 solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as the supporting electrolyte, with a platinum wire as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. Potential data for all of the compounds are collected in Table 1.

Table 1. Electrochemical Properties of **CuPOP-F**, **CuFc-F**, **CuPOP**, **CuFc**, and **F** Determined by CV on a Pt Working Electrode in CH_2Cl_2 + 0.1 M *n*-Bu_4NBF_4 Solutions at Room Temperature[a]

	reduction		oxidation	
	E_2	E_1	E_1	E_2
CuPOP		−1.75	+1.36	
CuFc		−1.75	+0.87	+1.68[b]
F	−0.89[c]	−0.51	+1.66[b]	
CuPOP-F	−0.86[c]	−0.45	+1.53	
CuFc-F	−0.86[c]	−0.46	+0.98	+1.68[b]

[a] Values for (E_{pa} + E_{pc})/2 in V vs SCE at a scan rate of 0.1 V s^{-1}. [b] Irreversible process, E_{pa} value reported. [c] Reversible for $V > 2$ V s^{-1}.

In the anodic region, model compound **F** presents an irreversible peak at ca. +1.7 V vs SCE, which can likely be attributed to the oxidation of the dialkyloxyphenyl unit.[34] In the cathodic region, compound **F** revealed the typical electrochemical response of methanofullerene derivatives,[35] and several reduction steps are seen. Whereas the first one is reversible, the second is irreversible at low scan rates, in accordance with observations on other C_{60} derivatives;[36] it becomes partially reversible upon an increase in the scan rate. The third wave gradually disappears when the second one becomes reversible, so that it probably implies a reduction of the product formed after the second reduction. For this reason, only the two first reduction potentials are listed in Table 1. Model compound **CuPOP** exhibits a one-electron-transfer process both in the cathodic and in the anodic region. As reported earlier,[37] the oxidation process can be assigned to the Cu^{II}/Cu^{I} redox couple and the reduction is centered on the phenanthroline ligand. Compound **CuFc** shows a one-electron-transfer process in the cathodic region at a potential value identical with that of **CuPOP** (−1.75 V vs SCE) and corresponding to the reduction of the phenanthroline ligand. In the anodic region,

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two processes are observed. The first is completely reversible, while the second one is irreversible whatever the scan rate is. The first oxidation process involves the ferrocene moiety and the second one the Cu^{II}/Cu^{I} redox couple.[37] The irreversibility of the second electron-transfer process reflects the instability of a copper(II) complex with an oxidized dppFc ligand, which is likely to undergo fast dissociation.[37] The cyclic voltammogram recorded for the hybrid compound **CuPOP-F** shows the characteristic electrochemical features of both **CuPOP** and **F**. The comparison of the $E_{1/2}$ potentials of **CuPOP-F** and **F** clearly shows that the two first reduction waves correspond to fullerene-centered reductions and the first oxidation process can be assigned to the Cu^{II}/Cu^{I} redox couple. Oxidation of the copper(I) center is more difficult in the case of **CuPOP-F** when compared to **CuPOP** ($\Delta E =$ 170 mV). This positive shift is explained, at least partially, by the presence of a longer alkyl substituent on the phenanthroline ligand, thus hindering the formation of a more flattened structure appropriate for the copper(II) oxidation state.[37] Similarly, the cyclic voltammogram of hybrid compound **CuFc-F** shows the typical electrochemical signatures of both **CuFc** and **F**. Clearly, the two first reductions are centered on the fullerene moiety and the first oxidation on the ferrocene subunit. Interestingly, in both **CuPOP-F** and **CuFc-F**, the two first fullerene-centered reduction potentials are shifted to more positive values by about 30−60 mV with respect to the corresponding fullerene model compound **F**. On the other hand, the ferrocene-centered oxidation potential is found to be more positive ($\Delta E = 110$ mV) when compared to **CuFc**. The latter observations indicate a small electronic interaction between the copper complex and the methanofullerene unit in both **CuPOP-F** and **CuFc-F**, suggesting that these compounds may adopt a folded conformation in which the two moieties are close to each other. This is in agreement with previous reports in which derivatives with a metal center and a fullerene unit, forced to be spatially close, behave similarly (more facile fullerene reduction, harder metal-centered oxidation).[21]

Photophysical Properties

CuPOP-F. The electronic absorption spectra of **CuPOP-F**, **CuPOP**, and **F** in CH_2Cl_2 are depicted in Figure 1. In the UV region above 300 nm, there is substantial superimposition of the bands of the two individual chromophores; furthermore, the MLCT absorption envelope of **CuPOP**, peaked at 380 nm, is also substantially overlapped to the profile of the carbon cage, hampering detailed investigations of photoinduced processes when the two moieties are combined (vide infra). The spectrum of the hybrid dyad matches well the profile obtained by summing the spectra of the model compounds **CuPOP** and **F**, except around 430 nm. Enhanced absorption in this region is often observed in fullerene multicomponent systems where the carbon sphere is in tight vicinity with other chromophore(s)[20] and ground-state donor−acceptor interactions at relatively high energy can be established. This is observed not only in hybrid systems encompassing fullerenes and copper(I) complexes[21] but also in fullerodendrimers[38–40] and host−guest adducts.[41]

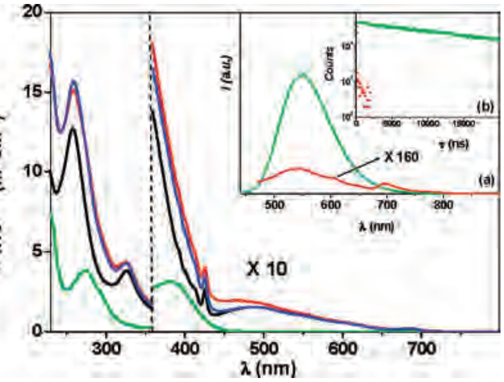

Figure 1. Absorption spectra of **CuPOP-F** (red), **CuPOP** (green), and **F** (black) in CH_2Cl_2 along with the profile obtained by the sum **CuPOP** + **F** (blue). For the sake of clarity, after 360 nm the spectra are multiplied by a factor of 10. Inset a: Emission spectra of **CuPOP** (green) and **CuPOP-F** (red; magnified by a factor of 160) in oxygen-free CH_2Cl_2 at 298 K; $\lambda_{exc} =$ 405 nm. Inset b: Emission decays of **CuPOP-F** (red) and **CuPOP** (green) at 550 nm; $\lambda_{exc} = 407$ nm, 298 K, oxygen-free CH_2Cl_2.

Both molecular subunits of **CuPOP-F** are luminescent. At 298 K, **CuPOP** exhibits strong green luminescence[26] in an oxygen-free CH_2Cl_2 solution ($\lambda_{max} = 562$ nm, $\tau = 4.6$ μs, and $\Phi_{em} = 0.09$),[37] which originates from deactivation of the lowest ^{3}MLCT state[29] and is blue-shifted in a 77 K CH_2Cl_2 matrix due to rigidochromism ($\lambda_{max} = 514$ nm and $\tau = 33$ μs).

The photophysical properties of methanofullerenes have been extensively investigated in the past.[23,42] **F** exhibits a weak and structured fluorescence band in CH_2Cl_2 at 298 K with the highest-energy feature peaked at 700 nm ($\tau = 1.5$ ns, $\Phi_{em} = 4.5 \times 10^{-4}$, CH_2Cl_2), also observable at 77 K ($\lambda_{max} = 706$ nm).[16]

In **CuPOP-F**, selective excitation of the fullerene moiety can be achieved above 520 nm, while the copper-complexed moiety can be excited at most with 40% selectivity at 405 nm. The fullerene-centered emission properties are substantially unaffected in **CuPOP-F** relative to **F**: the fluorescence quantum yields and lifetimes at $\lambda_{exc} > 520$ nm are identical for the two compounds (Figure 2, top panel). The fullerene triplet properties investigated at $\lambda_{exc} = 532$ nm are marginally affected in **CuPOP-F** compared to **F**: (i) the intense transient absorption features are peaked at 700 nm in both cases; (ii) the triplet lifetime of **CuPOP-F** is 18 μs, to be compared to 27 μs for **F** (oxygen-free CH_2Cl_2); (iii) **CuPOP-F** is a slightly weaker singlet-oxygen ($^1O_2$*) sensitizer than **F**, as is observable from the intensity of the senzitized $^1O_2$* luminescence in the NIR region (Figure 2, top panel).[16]

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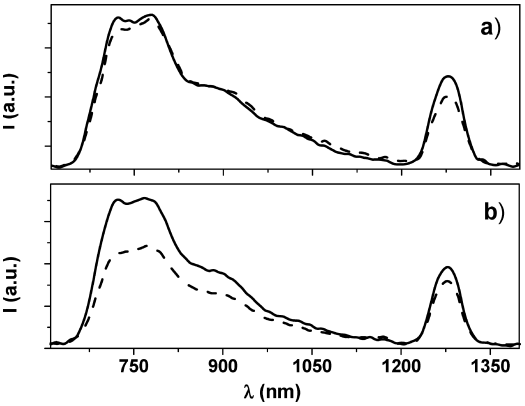

Figure 2. Vis−NIR emission spectra of **F** (full line) and **CuPOP-F** (dashed line) in CH_2Cl_2 at 298 K: (a) $\lambda_{exc} = 520$ nm (100% excitation on the **F** moiety); (b) $\lambda_{exc} = 405$ nm (light partitioning: 40% copper-complexed moiety; 60% fullerene moiety).

These observations indicate that no photoinduced processes occur upon excitation of the carbon sphere in **CuPOP-F**, and this is fully rationalized based on the energy level diagram (vide infra). The minor variations of the triplet properties of the dyad can be related to the specific chemical environment of the C_{60} moiety, in close vicinity to the copper(I) chromophore. It is well-known that, upon aggregation at the nano- and microscopic level, fullerenes may undergo variations of intersystem crossing efficiencies and triplet lifetimes.[43,44]

Upon excitation of **CuPOP-F** at 405 nm in oxygen-free CH_2Cl_2 (40% selectivity on the copper(I)-complexed moiety), a substantial decrease of the intense MLCT luminescence is detected when compared to **CuPOP** (Figure 1, inset). The measured emission quantum yields and lifetimes ($\lambda_{exc} = 407$ nm, laser diode) are 0.0003 and 6.1 ns, to be compared to 0.09 and 4600 ns for the reference system **CuPOP** under the same conditions. From lifetime data, it is possible to get the quenching rate constant for the MLCT excited state centered on the copper moiety of **CuPOP-F** ($^3Cu_{MLCT}$*), $k = 1.6 \times 10^8$ s^{-1}. An energy level diagram for **CuPOP-F** can be drawn where the energies of the copper-type moiety and of the methanofullerene fragments are estimated from 77 K emission spectra ($\lambda_{max} = 514$ nm; **CuPOP**) and literature data,[16] respectively (Figure 3). The charge-separated state energy (Cu^+F^-, 1.98 eV) is estimated from the first one-electron-oxidation and -reduction potentials of **CuPOP-F** (Table 1).[45]

With reference to Figure 3, quenching of the ^{3}MLCT excited state can occur, in principle, via (i) spin-forbidden (triplet−singlet) energy transfer to the fullerene lowest singlet level (Cu−^{1}F*); (ii) triplet−triplet energy transfer to Cu−^{3}F*; (iii) electron transfer to Cu^+F^-, followed by charge recombination back to the ground state or to Cu−^{3}F*. Hypothesis (i) can be ruled out because excitation of **CuPOP-F** at 405 nm, where 40% of the light is addressed to the copper-complexed chromophore, leads to a 40% decrease of the fullerene fluorescence intensity compared to what was recorded upon excitation above 520 nm, where only the fullerene chromophore absorbs (Figure 2, bottom panel). This clearly shows that transfer of the excitation energy from $^3Cu_{MLCT}$*−F to Cu−^{1}F* does not take place. Finding out if hypotheses (ii) and (iii) are the active mechanisms is very difficult because of the unfavorable distribution of the light absorption between the two chromophores. Nd:YAG laser lines at 266, 355, and 532 nm cannot be used to excite significantly the copper(I) moiety and carry out transient absorption studies. On the other hand, excitation at more favorable wavelengths, e.g., 400−410 nm (Ti:sapphire or 355-nm-fed OPO), does not give meaningful results because of the wide and intense singlet and triplet transient absorption signals of the directly excited fullerene moiety, which undergoes regular deactivation (see above).

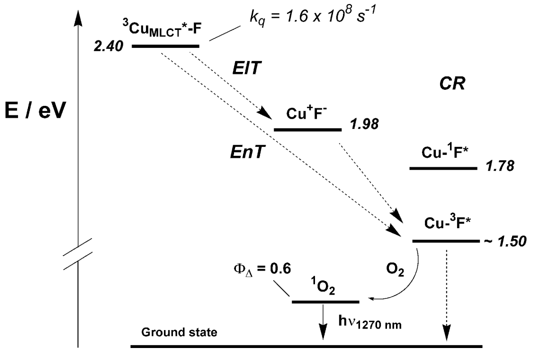

Figure 3. Schematic energy level diagram for **CuPOP-F**. The energy positions of the lowest excited states centered on each moiety are estimated from experimental (emission and electrochemical) and literature data. Cu^+F^- represents the charge-separated state obtained upon electron transfer from the metal-complexed moiety to the carbon sphere.

Because of the difficulty of studying in detail the photoinduced excited-state dynamics of **CuPOP-F** by means of transient absorption spectroscopy, a different approach was attempted aimed at determining the yield of formation of the lowest available excited level, i.e., the fullerene triplet (Figure 3). This value may provide some hints about excited-state intercomponent processes involving upper-lying levels, as was also pointed out previously in an analogous case of two dyads made of a methanofullerene chromophore coupled to a ruthenium(II) or rhenium(I) complex.[16] The approach is based on the fact that fullerene triplets are potent singlet-oxygen sensitizers[46] and the yields of triplet formation (Φ_T) are found to be identical with that of sensitization of $^1O_2$* (Φ_Δ) for C_{60},[47] its close[42] and open cage[48] derivatives, as well as for higher fullerenes like C_{70}[49] and C_{76}.[50] Therefore, the measure of Φ_Δ can be taken as an indirect evaluation of

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Φ_T for all fullerenes.[51] Φ_Δ, in its turn, is determined via the comparative method by measuring the intensity of the sensitized singlet-oxygen luminescence in the NIR region ($\lambda_{max} = 1268$ nm).[40,52,53]

Using as a reference C_{60} ($\Phi_\Delta = 1$), we have determined Φ_Δ of the reference fullerene compound **F** in CH_2Cl_2 as 0.8, in line with those of methanofullerenes investigated earlier.[16,42] Then, upon selective excitation of the carbon sphere ($\lambda_{exc} = 520$ nm; Figure 2a), we obtained $\Phi_\Delta = 0.6$ for **CuPOP-F**, a slightly lower value that might reflect specific interaction of the two chromophores as commented on above. Then, the same experiment was repeated under 405 nm excitation (Figure 2b), where a fraction of the incoming photons (40%) are absorbed by the copper(I) moiety of **CuPOP-F**.[54] Notably, despite the net loss of 40% of fullerene singlets (see the fluorescence signal around 700 nm), the intensity of the 1268 nm band of $^1O_2$* is slightly higher compared to the experiment made at $\lambda_{exc} = 520$ nm. Clearly, we have to rule out quantitative deactivation of Cu^+F^- to the ground state following $^3Cu_{MLCT}*{-}F \rightarrow Cu^+F^-$ electron transfer. In fact, under these conditions, a much lower 1268 nm emission signal should be found from the 60% excited fullerene moiety characterized by intrinsic $\Phi_\Delta = 0.60$, i.e., approximately 45% and not the measured (dashed line in Figure 2, bottom panel) 80% of the intensity of **F**. The measured singlet-oxygen luminescence intensity of **CuPOP-F** excited at $\lambda_{exc} = 405$ nm is compatible, within the experimental error, with quantitative population of the lowest fullerene triplet following excitation of the copper(I)-complexed moiety. Both direct ($^3Cu_{MLCT}*{-}F \rightarrow Cu{-}^3F*$) and stepwise ($^3Cu_{MLCT}*{-}F \rightarrow Cu^+F^- \rightarrow Cu{-}^3F*$) deactivations may be responsible for the observed trend (Figure 3). The first step in the latter process is substantially less exoergonic ($\Delta G_{CS}° = -0.42$ eV) than direct triplet energy transfer ($\Delta G_{EnT}° = -0.90$ eV), and its related free energy change is comparable to the value found at the maximum of the Marcus parabola in zinc(II) porphyrins/C_{60} molecular dyads.[55] Thus, the two-step route $^3Cu_{MLCT}*{-}F \rightarrow Cu^+F^- \rightarrow Cu{-}^3F*$ is likely to be kinetically more favored compared to the direct $^3Cu_{MLCT}*{-}F \rightarrow Cu{-}^3F*$ one, as suggested in the case of ruthenium(II) and rhenium(I) fullerene dyads having similar energy diagrams.[16]

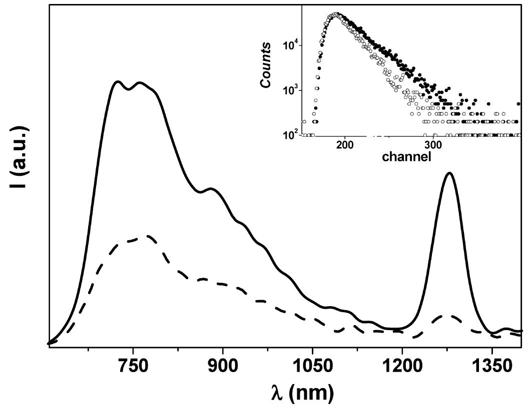

Figure 4. Emission spectra of **F** (full line) and **CuFc-F** (dashed line) at $\lambda_{exc} = 325$ nm. Inset: Fullerene fluorescence decay at 730 nm of **F** (full black circles) and **CuFc-F** (empty black circles). In the full gray circles is reported the decay profile of the excitation source, $\lambda_{exc} = 331$ nm. *x* axis: 1 channel = 51 ps; 298 K, CH_2Cl_2.

When an electron-transfer process is slightly exoergonic at room temperature, it may become endoergonic (blocked) at 77 K.[16] In fact, the energy of a charge-separated state is expected to increase in a rigid matrix, where the effective solvent reorganization energy increases dramatically because the solvent molecules cannot reorient to stabilize the newly formed ions.[56] Consequently, for multicomponent arrays where the occurrence of photoinduced processes is conveniently signaled by luminescence quenching in solution, the lack of such quenching in a rigid matrix can be taken as evidence to support the electron-transfer mechanism in the fluid medium. Unlike the case of a methanofullerene dyad coupled with a ruthenium(II) complex, in which we observed recovery of the MLCT emission band of the latter at 77 K,[16] here the intense emission band of the copper(I) unit remains quenched in the low-temperature rigid matrix. However, this observation cannot rule out electron transfer in the fluid solution because a 0.45 eV difference between $^3Cu_{MLCT}$* and the charge-separated state (Figure 3) is likely to be too large to make the electron-transfer reaction endoergonic at 77 K, similarly to a methanofullerene dyad with a rhenium(I) complex, characterized by an energy gap between the MLCT and charge-separated states of 0.42 eV.[16] Accordingly, the $^3Cu_{MLCT}$* in **CuPOP-F** might undergo electron transfer also in a 77 K rigid matrix.

CuFc-F. The electronic absorption spectrum of **CuFc-F** in CH_2Cl_2 is practically identical to that of **CuPOP-F** because the ferrocene and **POP** fragments exhibit negligible absorption intensities compared to the other moieties of their dyad systems. In the reference complex **CuFc**, the potentially luminescent MLCT state(s) is (are) totally quenched by energy transfer to the ferrocene unit, as was already discussed.[37] Therefore, it is not surprising that the copper(I)-complexed moiety does not luminesce also in the dyad **CuFc-F**. Contrary to what is observed for **CuPOP-F**, in **CuFc-F** only partial quenching of the fullerene singlet state is observed ($\Phi = 0.00018$ and $\tau = 0.9$ ns; Figure 4) relative to **F**. A much stronger triplet quenching occurs: a vanishingly weak transient absorption signal is detected, with a lifetime comparable to that of **F**, which suggests the presence of trace amounts of free methanofullerene. Virtually no sensitized

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(54) The quantum yield of singlet-oxygen sensitization of **CuPOP** has also been measured and turns out to be 30%, i.e., substantially lower than that of the fullerene moiety. At any rate, this value has no consequences in the interpretation of our data because the copper-centered excited state responsible for photosensitization (^{3}MLCT) is completely quenched in **CuPOP-F**.

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singlet-oxygen luminescence is observed, confirming that a fullerene triplet is not generated (Figure 4).

Quenching of fullerene excited states in **CuFc-F** is clearly due to the presence of the ferrocene unit and, in principle, can occur via (i) singlet[57] and triplet[58] energy transfer to the lowest-lying ferrocene triplet electronic level (1.16 eV)[58] or (ii) ferrocene → fullerene electron transfer, generating the charge-separated state located at 1.45 eV according to the electrochemical data (Table 1). The latter process could be evidenced via transient absorption spectroscopy, through the detection of the fullerene radical anion in the NIR region. We found no evidence for this fingerprint down to a resolution of 10 ns, even via bimolecular quenching studies with ferrocene and **F**.[57] We have already discussed the elusive nature of the intimate mechanism of the quenching processes between ferrocene and fullerenes,[58] pointing out that the two mechanisms are also solvent- and distance-dependent.[57] Often, unambiguous rationalization of this process is hardly obtainable because of the lack of reliable spectroscopic fingerprints from the lowest ferrocene triplet,[59] and this becomes particularly challenging in the present case because of the tight vicinity of the donor−acceptor partners, which prompts ultrafast processes.

Conclusions

Two novel hybrid heteroleptic copper(I) complexes **CuPOP-F** and **CuFc-F** were prepared from a fullerene-substituted phenanthroline ligand and two bisphosphine ligands, namely, **POP** and **dppFc**, respectively. Ground-state electronic interaction between the closely spaced fullerene subunit and the metal-complexed moiety is evidenced with electrochemical studies in both cases. Photophysical studies indicate that no intercomponent interactions were observed upon excitation of the methanofullerene moiety in **CuPOP-F**, while excitation of the copper(I)-complexed unit (40% selectivity only) shows that the strongly luminescent ^{3}MLCT excited state at 2.40 eV is quenched by the fullerene moiety. The determination of the detailed mechanism(s) of photodynamic processes in **CuPOP-F** via transient absorption was hampered by the rather unfavorable partition of light excitation between the metal complex and the fullerene moiety. Nevertheless, by measurement of the yield of formation of the lowest fullerene triplet level through sensitized singlet-oxygen luminescence in the NIR region, it was unambiguously demonstrated that the final sink of the photoinduced processes is the fullerene triplet. In contrast, in **CuFc-F**, both the photoexcited copper(I)-complexed and fullerene moieties are quenched by the presence of the ferrocene unit, most likely via ultrafast energy transfer. This is in line with recent reports[57,58] having also shown that ferrocene, which, in principle, is an excellent electron donor in multicomponent arrays, is also indeed an outstanding energy acceptor, often promoting energy transfer rather than the most wanted electron transfer.

Experimental Section

General Procedures. All reagents were used as purchased from commercial sources without further purification. Compounds **4**,[60] **F**,[60] **CuPOP**,[37] and **CuFc**[37] were prepared according to previously reported procedures. All reactions were performed in standard glassware. Evaporation was done using a water aspirator and drying in vacuo at 10^{-2} Torr. Column chromatography: Merck silica gel 60, 40−63 μm (230−400 mesh). TLC: precoated glass sheets with silica gel 60 F_{254} (Merck), visualization by UV light. Melting points were determined on a Electrothermal Digital Melting Point apparatus and are uncorrected. IR spectra (cm^{-1}) were determined on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker ARX 300 spectrometer. Elemental analyses were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France).

Compound 2. A 2 M solution of LDA in tetrahydrofuran (THF; 5.4 mL) was added slowly to a solution of 2,9-dimethyl-1,10-phenanthroline (3.73 g, 17.92 mmol) in anhydrous THF (70 mL) at 0 °C under argon. After 1 h, a solution of **1** (4.0 g, 17.92 mmol) in THF (25 mL) was added dropwise. The resulting mixture was stirred 2 h at 0 °C and then 15 h at room temperature. The solution was then poured into ice water (150 mL). The mixture was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated to yield **2** (6.0 g) as a pale-orange oil, which was used in the next step without purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (m, 4 H), 1.81 (m, 4 H), 1.99 (m, 2 H), 2.91 (s, 3 H), 3.23 (m, 2 H), 3.48 (m, 2 H), 3.83 (m, 2 H), 4.57 (br s, 1 H), 7.47 (m, 2 H), 7.66 (s, 2 H), 8.09 (m, 2 H).

Compound 3. A solution of **2** (6.0 g, 17.12 mmol) and *p*-TsOH (2.50 g, 17.92 mmol) in EtOH (400 mL) was refluxed for 4 h. The solvent was then evaporated. Column chromatography (Al_2O_3, CH_2Cl_2 containing 5% MeOH) yielded **3** (360 mg, 50% from 2,9-dimethyl-1,10-phenanthroline) as a colorless glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.77 (m, 2 H), 2.19 (m, 2 H), 2.92 (s, 3 H), 3.23 (t, $J = 6$ Hz, 2 H), 3.67 (t, $J = 5$ Hz, 2 H), 7.46 (d, $J = 8$ Hz, 1 H), 7.47 (d, $J = 8$ Hz, 1 H), 7.68 (s, 2 H), 8.09 (d, $J = 8$ Hz, 1 H), 8.12 (d, $J = 8$ Hz, 1 H). Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.45; H, 6.82; N, 10.88.

Compound 5. DCC (46 mg, 0.226 mmol) was added to a stirred solution of **4** (277 mg, 0.207 mmol), **3** (50 mg, 0.188 mmol), DMAP (9 mg, 0.075 mmol), and BtOH (catalytic amount) in CH_2Cl_2 (20 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h) and then stirred for 12 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2 containing 0.1% MeOH) yielded **1** (198 mg, 67%) as a dark-red glassy product. IR (KBr): 1746 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, $J = 6$ Hz, 6 H), 1.30 (m, 36 H), 1.72 (m, 4 H), 1.88 (m, 2 H), 2.04 (m, 2 H), 2.94 (s, 3 H), 3.24 (t, $J = 6$ Hz, 2 H), 3.87 (t, $J = 6$ Hz, 4 H), 4.33 (t, $J = 6$ Hz, 2 H), 4.97 (s, 2 H), 5.45 (s, 2 H), 6.38 (t, $J = 2$ Hz, 1 H), 6.59 (d, $J = 2$ Hz, 2 H), 7.47 (d, $J = 8$ Hz, 1 H), 7,53 (d, $J = 8$ Hz, 1 H), 7.69 (AB, $J = 9$ Hz, 2 H), 8.10 (d, $J = 8$ Hz, 1 H), 8.13 (d, $J = 8$ Hz, 1 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 14.1, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 39.0, 62.7, 65.8, 68.1, 69.1, 71.2, 101.7, 107.3, 122.3, 123.5, 125.5, 125.6, 126.9, 127.2, 136.2, 136.4, 136.6, 138.4, 139.8, 140.8, 140.9, 141.8, 141.9, 142.1, 142.2, 142.85, 142.9, 142.95, 143.8, 143.85, 144.4, 144.5, 144.6, 144.9, 145.0, 145.1, 145.2, 145.4, 145.5, 159.4, 160.5,

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162.2, 163.0, 163.05, 166.5. Anal. Calcd for $C_{113}H_{74}N_2O_8$: C, 85.48; H, 4.70; N, 1.76. Found: C, 85.19; H, 4.85; N, 1.70.

Compound CuPOP-F. $Cu(CH_3CN)_4BF_4$ (20 mg, 0.07 mmol) was added to a stirred solution of **POP** (40 mg, 0.07 mmol) in CH_2Cl_2 (10 mL). After 1 h, a solution of **5** (110 mg, 0.07 mmol) in CH_2Cl_2 (5 mL) was added. The resulting mixture was stirred for 2 h and evaporated. Gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **CuPOP-F** (113 mg, 71%) as a black glassy product. IR (KBr): 1746 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6 Hz, 6 H), 1.06 (m, 2 H), 1.24 (s, 36 H), 1.37 (m, 2 H), 1.72 (m, 4 H), 2.46 (s, 3 H), 2.86 (t, J = 6 Hz, 2 H), 3.88 (m, 6 H), 4.94 (s, 2 H), 5.48 (s, 2 H), 6.39 (t, J = 2 Hz, 1 H), 6.60 (d, J = 2 Hz, 2 H), 6.97 (m, 18 H), 7.20 (m, 8 H), 7.33 (m, 2 H), 7.62 (d, J = 8 Hz, 1 H), 7.72 (d, J = 8 Hz, 1 H), 7.87 (AB, J = 8 Hz, 2 H), 8.42 (d, J = 8 Hz, 1 H), 8.43 (d, J = 8 Hz, 1 H). $^{13}C\{^1H\}\{^{31}P\}$ NMR (75 MHz, $CDCl_3$): δ 14.1, 22.7, 24.5, 26.1, 27.3, 28.2, 29.3, 29.4, 29.5, 29.64, 29.65, 29.7, 31.9, 51.4, 62.6, 65.0, 68.2, 69.2, 71.3, 101.7, 107.5, 120.3, 123.5, 125.4, 125.8, 126.1, 126.4, 127.8, 128.2, 128.6, 128.65, 129.9, 130.1, 131.6, 132.3, 132.6, 133.1, 133.7, 136.6, 138.2, 138.4, 139.8, 140.9, 141.7, 141.9, 142.1, 142.2, 142.9, 142.95, 143.0, 143.8, 144.5, 144.6, 144.9, 145.2, 145.25, 158.2, 159.0, 160.5, 161.8, 163.0, 163.1, 166.4. FAB-MS: 2189.7 ([M − BF_4]; calcd for $C_{149}H_{102}N_2O_9P_2Cu$, 2189.95). Anal. Calcd for $C_{149}H_{102}N_2O_9P_2CuBF_4$: C, 78.60; H, 4.52; N, 1.23. Found: C, 78.32; H, 4.84; N, 1.19.

Compound CuFc-F. $Cu(CH_3CN)_4BF_4$ (40 mg, 0.13 mmol) was added to a stirred solution of **dppFc** (70 mg, 0.13 mmol) in CH_2Cl_2 (10 mL). After 1 h, a solution of **5** (200 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) was added. The resulting mixture was stirred for 2 h and evaporated. Gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **CuFc-F** (244 mg, 82%) as a black glassy product. IR (KBr): 1747 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6 Hz, 6 H), 1.25 (s, 36 H), 1.40 (m, 4 H), 1.73 (m, 4 H), 2.27 (s, 3 H), 2.68 (m, 2 H), 3.88 (t, J = 6 Hz, 4 H), 4.01 (t, J = 6 Hz, 2 H), 4.65 (s large, 4 H), 4.77 (s large, 4 H), 4.97 (s, 2 H), 5.49 (s, 2 H), 6.40 (t, J = 2 Hz, 1 H), 6.60 (d, J = 2 Hz, 2 H), 7.11 (m, 16), 7.31 (m, 4 H), 7.58 (d, J = 8 Hz, 1 H), 7.65 (d, J = 8 Hz, 1 H), 8.09 (AB, J = 8 Hz, 2 H), 8.55 (d, J = 8 Hz, 1 H), 8.58 (d, J = 8 Hz, 1 H). $^{13}C\{^1H\}\{^{31}P\}$ NMR (75 MHz, $CDCl_3$): δ 14.1, 22.7, 23.85, 23.9, 26.1, 27.5, 28.3, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 40.4, 62.7, 64.9, 68.2, 69.3, 71.3, 72.9, 74.2, 75.0, 101.7, 107.5, 123.5, 125.8, 126.7, 126.9, 128.3, 128.6, 128.8, 130.1, 132.1, 133.8, 136.6, 138.5, 138.7, 138.9, 139.8, 140.9, 141.7, 141.9, 142.1, 142.2, 142.7, 142.75, 142.9, 142.95, 143.0, 143.05, 143.8, 144.5, 144.55, 144.6, 144.7, 144.9, 145.2, 159.4, 160.5, 162.1, 163.0, 163.1, 166.4. FAB-MS: 2205.6 ([M − BF_4]; calcd for $C_{147}H_{102}N_2O_8P_2CuFe$, 2205.7). Anal. Calcd for $C_{147}H_{102}N_2O_8P_2CuFeBF_4$: C, 77.01; H, 4.48; N, 1.22. Found: C, 76.92; H, 4.60; N, 1.10.

Electrochemistry. The CV measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in an homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a SCE separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface. The working electrode was a platinum microdisk (0.5 mm diameter). The supporting electrolyte [n-Bu_4N][BF_4] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled over CaH_2 prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in compound and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling argon and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, Fc^+/Fc is observed at $+0.54 \pm 0.01$ V vs SCE.

Photophysics. Spectroscopic investigations were carried out in CH_2Cl_2 (Carlo Erba, spectrofluorimetric grade). Absorption spectra were recorded with a Perkin-Elmer λ40 spectrophotometer. Emission spectra were obtained with an Edinburgh FLS920 spectrometer (continuous 450 W xenon lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185−850 nm) or a Hamamatsu R5509-72 supercooled photomultiplier tube (193 K, 800−1700 nm range). Emission quantum yields were determined according to the approach described by Demas and Crosby[61] using [$Ru(bpy)_3Cl_2$] ($\Phi_{em} = 0.028$ in an air-equilibrated water solution)[62] as the standard. Emission lifetimes (10^{-10}−10^{-5} s time scale) were determined with the time-correlated single-photon-counting technique using (a) an Edinburgh FLS920 spectrometer equipped with a laser diode head as the excitation source (1 MHz repetition rate, $\lambda_{exc} = 407$ nm, 200 ps time resolution upon deconvolution) and a Hamamatsu R928 PMT as the detector (setup details are reported elsewhere)[7] and (b) an IBH spectrometer equipped with a nanoLed as the excitation source (50 kHz repetition rate, $\lambda_{exc} = 331$ or 560 nm, 200 ps time resolution upon deconvolution) and an Horiba TBX05 PMT as the detector; analysis of the luminescence decay profiles against time was accomplished by using the DAS6 software provided by the manufacturer. Transient absorption spectra and lifetimes were detected upon excitation at 532 nm (Nd:YAG laser); details on the apparatus have been already reported.[44] Experimental uncertainties are estimated to be 8% for lifetime determinations, 20% for emission quantum yields, 10% for relative emission intensities in the NIR, and 1 and 5 nm for absorption and emission peaks, respectively.

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