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Communication

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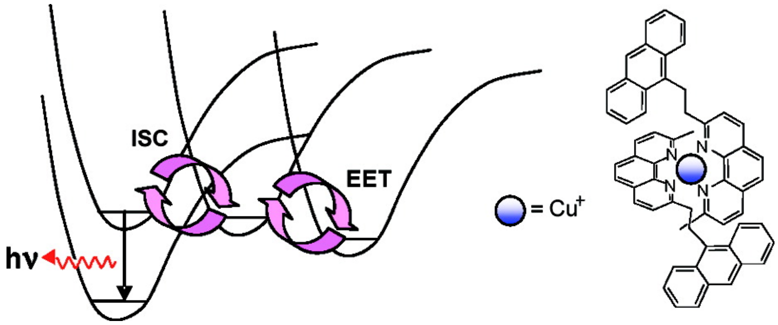

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COMMUNICATIONS

Equilibration between Three Different Excited States in a Bichromophoric Copper(I) Polypyridine Complex

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The efficient management of energy following light absorption is of utmost importance in natural photosynthetic assemblies as well as in artificial systems. Small supramolecular inorganic systems have proven successful in absorbing light energy and transferring it to a specific site, while reversible energy transfer processes in ruthenium(II) and osmium(II) polypyridine complexes have been reported to temporarily stock energy and prolong excited-state lifetimes.[1−3] We recently showed the intervention of reversible intramolecular energy transfer processes in enhancing the efficiency of photoinduced charge separation in rudimentary devices.[4] While coordination complexes based on transition metals and bidentate polypyridine ligands, notably $[Ru(bpy)_3]^{2+}$ complexes (bpy = 2,2′-bipyridine), typically present desirable redox and luminescence properties for diverse applications, complexes based on more abundant, less expensive copper(I) (for example, $[Cu(\mathbf{1})_2]^+$, **1** = 2,9-dimethyl-1,10-phenanthroline) have great potential for improvement.[5] Recent efforts to improve the luminescence properties of Cu(I)−phenanthroline complexes have largely been confined to steric congestion and rigidification around the metal center.[6]

In this paper, we report the unique excited-state equilibration between three different excited states in a structurally simple bichromophoric copper(I) complex ($[Cu(\mathbf{2})_2]^+$ in Figure 1) which constitutes a new strategy to greatly prolong luminescence lifetimes of copper complexes. This excited-state behavior was induced in a planned fashion due to the interplay of three different close-lying excited states. The three intervening lowest-lying quasi-isoenergetic excited states are the $^3(\pi-\pi^*)$ state localized on the appended anthracene and the ^{3}MLCT and ^{1}MLCT states localized on the central copper−phenanthroline unit, with the latter being responsible for the emission.

The lowest-lying ^{3}MLCT and ^{1}MLCT excited states are thermally accessible from one another in copper(I) complexes based on ligands such as 2,9-dimethyl-1,10-phenanthroline, **1**, where ΔE = ca. 1800 cm^{-1}.[7] Elaborating the complex with an appended chromophore presenting a sufficiently long-lived triplet excited state of similar energy was anticipated to introduce an ideal third excited state in terms of compatibility with a process of equilibration involving three different isoenergetic excited states. A combination of fast, reversible processes—intersystem crossing (ISC) and triplet−triplet energy transfer (EET)—was envisaged to offer an opportunity to study a process of double dynamic equilibration in a remarkably simple complex.

Incorporation of an inert dimethylene spacer allows the constituent chromophores in $[Cu(\mathbf{2})_2]^+$ to retain their individual characteristics, as shown by the electronic absorption spectra, which is essentially a summation of individual chromophore absorptions (see Supporting Information, Figure S1). The near-UV region is dominated by a band showing vibronic fine structure characteristic of anthracene (^1L_a transition), while MLCT absorption of the inorganic moiety dominates the visible spectral region. A slight decrease in the intensity of the MLCT absorption band of $[Cu(\mathbf{2})_2]^+$ with respect to $[Cu(\mathbf{1})_2]^+$ is consistent with the more encumbered primary coordination sphere on introducing the anthracene units.[8]

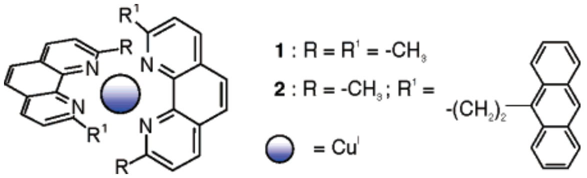

Figure 1. Complexes $[Cu(\mathbf{1})_2]PF_6$ and $[Cu(\mathbf{2})_2]PF_6$. (Only one of two possible enantiomers of $[Cu(\mathbf{2})_2]PF_6$ is shown.)

Steady-state emission spectra of $[Cu(\mathbf{1})_2]^+$ and $[Cu(\mathbf{2})_2]^+$ in degassed dichloromethane solution at room temperature show characteristic ^{1}MLCT fluorescence (λ_{max} = 710 and 712 nm, respectively) with similar quantum yields ($\phi_F = 0.04\%$), regardless of excitation wavelength (see Figure S2). The similarity of the quantum yields suggests that the slightly thermodynamically favorable photoinduced electron transfer reaction from Cu(I) to anthracene is inefficient (perhaps for kinetic reasons) and that anthracene-to-copper phenanthroline energy transfer (both singlet and triplet) is essentially quantitative.[9] However, the much greater oxygen sensitivity of the anthracene-appended complex with respect to the parent compound in air-equilibrated solution suggests that the excited-state lifetime is extended and thus more susceptible to a bimolecular quenching process. Emission of $[Cu(\mathbf{2})_2]^+$ at low temperature (77 K) results exclusively from the lowest-lying anthracene triplet state (14 450 cm^{-1}, see Figure S3).[10]

Ultrafast transient absorption spectroscopy was employed to follow the evolution of the excited complexes. Following excitation of the MLCT band of $[Cu(\mathbf{1})_2]^+$ at 400 nm, the Franck−Condon excited state rapidly populates the lowest-lying ^{1}MLCT state. Relatively slow intersystem crossing (15 ps), determined via time-resolved fluorescence and transient absorption spectroscopy, subsequently populates the ^{3}MLCT state in agreement with recent reports (see Figure S4).[11−13] In the case of $[Cu(\mathbf{2})_2]^+$, sequential processes of intersystem crossing (15 ps) and triplet−triplet energy transfer preside, as shown in Figure 2. Fast energy transfer is denoted by the grow-in of the characteristic anthracene $T_n \leftarrow T_1$ transition at 430 nm with a rate common with the decay of the ^{3}MLCT state (60 ps).[14,15] Following these processes, the spectrum shows almost exclusive localization of excitation energy on the anthracene subunit in the equilibrated system.

Nanosecond flash photolysis (Figure S5) shows that the absorption signature for the anthracene triplet state in $[Cu(\mathbf{2})_2]^+$ is persistent ($\tau = 1.2\ \mu s$), and that energy is predominantly localized

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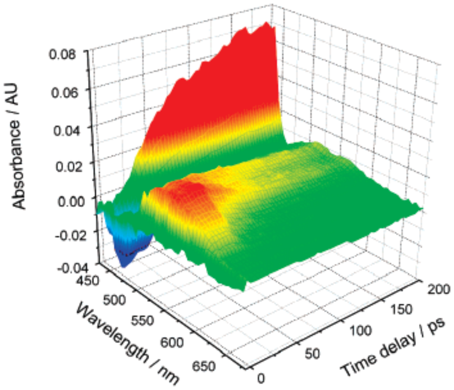

Figure 2. Transient absorption spectrum showing the approach to excited-state equilibrium via intersystem crossing (ISC) and triplet energy transfer (EET) following excitation at 400 nm. MLCT absorption is observed between 500 and 620 nm. Changes between 580 and 620 nm are indicative of ISC. Anthracene triplet-based absorption is seen at 430 nm.

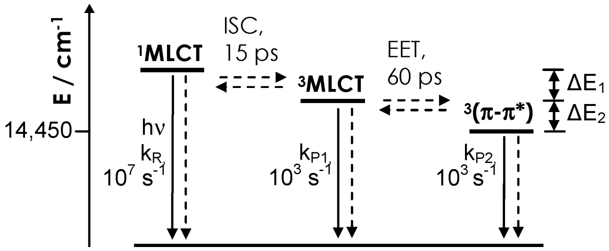

Figure 3. Jablonski diagram showing pertinent low-lying excited states and notably the interaction of the three lowest-lying excited states: k_{ISC}, $k_{\mathrm{EET}} > k_{\mathrm{R}} \gg k_{\mathrm{P1}}$, k_{P2}. $\Delta E_1 =$ ca. 1800 cm^{-1};[7] $\Delta E_2 =$ ca. 430 cm^{-1}.[15]

on the anthracene unit. This temporarily stored energy is funneled back to the emissive copper-containing unit. The similar quantum yields of $[\mathrm{Cu}(\mathbf{1})_2]^+$ and $[\mathrm{Cu}(\mathbf{2})_2]^+$ show that this process is highly efficient and highlights the role of the anthracene unit as an energy reservoir.

Time-resolved emission (Figure S6) further supports the idea of an excited-state equilibration, where energy is stocked on the anthracene and subsequently relayed to the emissive copper unit. Indeed, the MLCT emission has a luminescence lifetime of 1.2 μs, which corresponds to the rate of disparition of the anthracene triplet, and is ca. 15 times longer than the parent complex $[\mathrm{Cu}(\mathbf{1})_2]^+$ ($\tau =$ 70 ns). This represents the longest luminescence lifetime observed for a simple copper phenanthroline complex of this type. The strategy of introducing multiple isoenergetic excited states with different de-excitation kinetics represents an alternative and potentially complementary approach to improving the luminescence properties of copper phenanthroline complexes, which typically repose upon steric ligand confinement of the first coordination sphere.[6]

Pertinent photophysical events, with kinetic and energetic parameters consistent with the implementation of an excited-state equilibration between three excited states, are shown in the Jablonski diagram in Figure 3. In summary, following visible light absorption an ultrarapid relaxation (<100 fs) is followed by intersystem crossing (15 ps) and fast triplet−triplet energy transfer (60 ps), with the two latter processes being reversible due to the proximity of the excited states. The de-excitation of the equilibrated system can now be described by eq 1.

$$k_{\mathrm{eq}} = \alpha\left(\frac{1}{\tau_{1_{\mathrm{MLCT}}}}\right) + \beta\left(\frac{1}{\tau_{3_{\mathrm{MLCT}}}}\right) + \gamma\left(\frac{1}{\tau_{3_{(\pi-\pi^*)}}}\right) \qquad (1)$$

where α, β, and γ represent the fractional concentration of ^{1}MLCT, ^{3}MLCT, and $^3(\pi-\pi^*)$ states at equilibrium, respectively, and $\alpha + \beta + \gamma = 1$. In this case, $\gamma \gg \alpha, \beta$.

In conclusion, we have shown that a double dynamic equilibration involving three energetically close-lying excited states (of type ^{1}MLCT, ^{3}MLCT, and$^3(\pi-\pi^*)$) in anthracene-appended $[\mathrm{Cu}(\mathbf{2})_2]^+$ governs the observed photophysical parameters, most notably the excited-state lifetime, which is qualitatively predictable. Energy is temporarily stored on an organic auxiliary before being relayed with >90% efficiency to the emissive center. In principle, this strategy can be readily applied in the design of novel supramolecular systems for applications as sensors, artificial light-harvesting antenna systems, and charge separation devices.

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Supporting Information Available: Synthetic procedures, electronic absorption spectra, steady-state and time-resolved emission, transient absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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