

Light-Harvesting Arrays with Coumarin Donors and MLCT Acceptors

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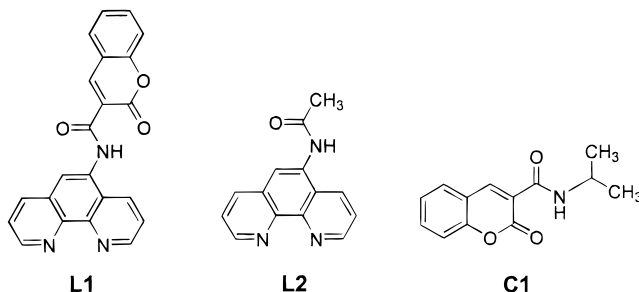
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Natural photosynthetic processes convert sunlight into chemical energy by utilizing light-harvesting complexes that efficiently capture and funnel photonic energy to the reaction centers.¹ The light-harvesting antenna systems contain a large number (hundreds) of chromophores which remarkably avoid non energy transfer quenching processes by providing a properly channeled energy gradient.^{1,2} The naturally occurring antenna assemblies have served as a paradigm for the design of many artificial light-harvesting complexes based on photon-driven energy transfer processes.^{2–11} There exist a comprehensive number of such artificial systems; however, we are primarily concerned about those constructed from inorganic transition metal complexes that display metal-to-ligand charge transfer (MLCT) excited states.^{6,9–11}

We describe a light-harvesting strategy which implements organic donor molecules covalently linked to the ligand periphery of Ru(II) inorganic acceptor compounds that possess MLCT excited states. The pendant organic chromophores act as light-harvesting antennae designed to collect and funnel the photonic energy to the inorganic core. The central Ru(II) MLCT complex then displays long-lived sensitized luminescence resulting from excitation of the organic antennae. In these studies, we use fluorescent coumarin dyes (donors) covalently linked through an amide spacer to the diimine ligands of Ru(II) complexes (acceptors). Irrespective of excitation wavelength, MLCT excited states are produced directly (visible excitation) or are sensitized through the peripheral coumarin antenna units (UV excitation).

All compounds relevant to this discussion were synthesized and characterized as described in the Supporting Information. L1 contains a single coumarin dye and serves as the energy transfer donor when chelated to Ru(II) complexes, whereas L2 serves as a model for the amide linkage. A compound representing the coumarin moiety containing an amide linkage (C1) was also synthesized to model the photophysical properties of the energy transfer donor in the absence of acceptor. Four Ru(II) compounds



were studied: $[\text{Ru}(\text{bpy})_2(\text{L1})](\text{PF}_6)_2$, $[\text{Ru}(\text{L1})_3](\text{PF}_6)_2$, $[\text{Ru}(\text{bpy})_2(\text{L2})](\text{PF}_6)_2$, and $[\text{Ru}(\text{L2})_3](\text{PF}_6)_2$. The first two complexes are a donor–acceptor dyad and tetrad, respectively, and the last two complexes are models, which contain the acceptor in the absence of donor.

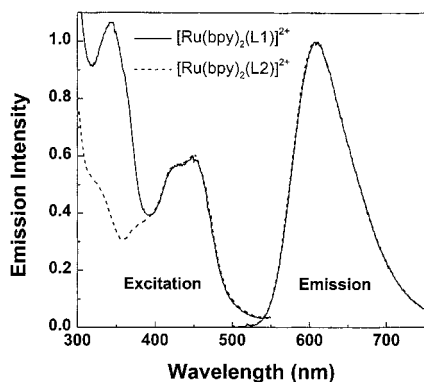
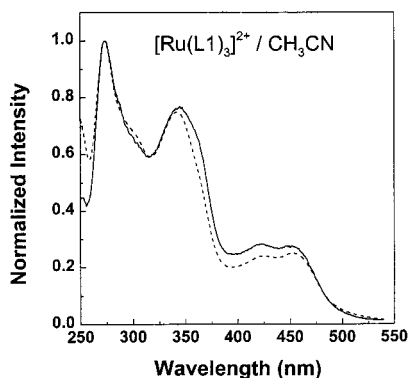
The spectroscopic and photophysical data for the compounds in this study are presented in Table 1. The electronic spectra of all complexes are provided in the Supporting Information. Figure 1 presents corrected excitation and uncorrected emission spectra for $[\text{Ru}(\text{bpy})_2(\text{L1})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{L2})]^{2+}$ in CH_3CN . In both cases, excitation at wavelengths between 300 and 550 nm results in the observation of only one visible emission band (Figure 1). The model complex, $[\text{Ru}(\text{bpy})_2(\text{L2})]^{2+}$, has a minimum luminescence yield when excited in the 325–400 nm wavelength range, whereas the dyad, $[\text{Ru}(\text{bpy})_2(\text{L1})]^{2+}$, exhibits sensitized emission from the coumarin chromophore that absorbs appreciably in that region. The excitation and UV–vis spectra of $[\text{Ru}(\text{L1})_3]^{2+}$ are compared in Figure 2. The excitation and absorption spectra of $[\text{Ru}(\text{L1})_3](\text{PF}_6)_2$ are almost completely superimposable, suggesting an energy transfer quantum yield near unity.^{5,11–13} The tetrad displays spectral features similar to those of the dyad, except that the absorption cross sections at all UV and visible wavelengths are increased. The coumarin band at 341 nm exhibits an extinction coefficient near $80\,000\ \text{M}^{-1}\ \text{cm}^{-1}$ as a result of additional light harvesting by multiple antenna units. In both the dyad and tetrad, the blue emission from the coumarin moiety is quenched to below detectable limits as measured with our single photon counting instrument. In order to obtain a quantitative measure of the energy transfer quantum efficiency, a direct comparison between the magnitude of the excitation spectrum and absorption spectrum can be made.^{5,12} Applying this treatment to the dyad and tetrad, the energy transfer efficiencies were calculated to be $94 \pm 5\%$ and $97 \pm 5\%$, respectively. At the close donor–acceptor distance encountered with the dyad and tetrad, either Forster (dipole–dipole) or Dexter (electron-exchange) energy transfer mechanisms are plausible.^{12,13} The Forster interaction is highly probable as a consequence of the large spectral overlap ($J = 4.14 \times 10^{-14}\ \text{M}^{-1}\ \text{cm}^3$) between the emission spectrum of the coumarin donor and the absorption spectrum of the Ru(II) complex. In the presented donor–acceptor systems, the Forster distance is calculated to be

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Table 1. Spectroscopic and Photophysical Data at 25 °C in CH₃CN

complex	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)	$\lambda_{\text{em max}}$, nm	τ , μs	Φ_r	k_r , s ⁻¹	k_{nr} , s ⁻¹
[Ru(bpy) ₂ (L1)] ²⁺	341 (30 000), 451 (16 000)	606	1.19 ± 0.07	0.087 ± 0.016	7.3 × 10 ⁴	7.7 × 10 ⁵
[Ru(L1) ₃] ²⁺	341 (78 700), 453 (26 100)	600	1.37 ± 0.07	0.100 ± 0.010	7.3 × 10 ⁴	6.6 × 10 ⁵
[Ru(bpy) ₂ (L2)] ²⁺	341 (7 000), 450 (14 000)	606	1.01 ± 0.04	0.074 ± 0.014	7.3 × 10 ⁴	9.2 × 10 ⁵
[Ru(L2) ₃] ²⁺	341 (14 000), 457 (18 000)	605	1.74 ± 0.08	0.080 ± 0.015	4.6 × 10 ⁴	5.3 × 10 ⁵
C1	294 (16 000)	426	328 ± 40 ps	0.020 ± 0.008	6.1 × 10 ⁷	3.0 × 10 ⁹

**Figure 1.** Corrected excitation and uncorrected emission spectra of [Ru(bpy)₂(L1)]²⁺ (solid lines) and [Ru(bpy)₂(L2)]²⁺ (dashed lines) in CH₃CN at 25 °C. The excitation spectra were detected at 600 nm.**Figure 2.** Absorption (solid line) and corrected excitation spectra (dashed line) of [Ru(L1)₃]²⁺ in CH₃CN, normalized to the maximum absorption peak at 275 nm. The excitation spectrum was detected at 600 nm.

22.7 Å,¹² assuming random donor–acceptor orientations ($k^2 = 2/3$). However, proper determination of the energy transfer mechanism is only possible by evaluating the distance dependence of energy transfer rates.^{12,13} Since the overall energy transfer quantum yields approach unity, nearly all of the energy absorbed by the coumarin antenna is funneled to the Ru(II) core and emitted as visible light.

The excited state lifetimes of [Ru(bpy)₂(L1)]²⁺ and [Ru(L1)₃]²⁺ in deaerated CH₃CN are single exponential as measured with 500 ps pulses from an N₂-pumped dye laser system. These lifetimes are 1190 ± 70 and 1390 ± 70 ns, respectively. Regardless of excitation wavelength (350–500 nm), the emission lifetimes measured at 600 ± 4 nm were the same within experimental error in each case. In an attempt to estimate the rate of energy transfer from the coumarin moiety to the Ru(II) complex, time-correlated single photon counting measurements were employed. With 341 nm excitation, no measurable rise time was observed for the MLCT-based emission at 605 nm for [Ru(bpy)₂(L1)]²⁺, indicating

that the intramolecular energy transfer rate is rapid, >10⁹ s⁻¹.^{9–11} This is not surprising since theory predicts a rate constant of energy transfer >10¹¹ s⁻¹, based on the lifetime of the donor and the high efficiency of energy transfer.^{12,13} We postulate that energy migration in the dyad and tetrad follow a pathway first suggested by Wilson and co-workers to explain the intramolecular quenching of singlet aromatic hydrocarbon fluorescence by Ru(II)–bipyridine complexes.¹¹ In our case, excitation of the coumarin unit(s) is followed by rapid singlet–singlet energy transfer to produce ¹MLCT excited states, which then intersystem crosses to generate ³MLCT excited states. Relaxation of the ³MLCT excited states to the ground state is accompanied by the characteristic long-lifetime emission found in this class of molecules.

The present work provides a strategy for the generation of light-harvesting arrays that display sensitized high quantum yield emission concomitant with long lifetimes. These organic–inorganic hybrids are superior to polynuclear light-harvesting arrays in that the absorption cross sections are optimized without negatively affecting the photophysical properties of the MLCT chromophore. This idea is clearly illustrated by the large quantum yields and lifetimes of emission for the dyad and tetrad. By comparison, many polynuclear complexes generally display sensitized emission lifetimes <100 ns and quantum yields substantially lower than 0.01.^{6,9,10} Importantly, the addition of multiple coumarin chromophores to the Ru(II) complex does not appear to increase the nonradiative decay rate. This suggests that further addition of coumarin light-harvesting chromophores may only have the effect of increasing the UV absorption cross sections without corrupting the Ru(II) photophysics.

The development of intramolecular energy transfer processes that occur along predetermined directions is important for the development of photochemical molecular devices.^{2–10} Presently, there are many examples of devices that absorb an optical signal, enable facile excited state energy migration, and emit an optical signal at a remote site.^{3,5–7} The compounds in the present study perform the same functions; however, the long-lifetime emission may also prove useful in biological systems requiring extrinsic luminescence probes¹⁴ and in lifetime-based chemical sensing.^{14,15} Optimization of molecular-level energy transfer processes within such complexes may lead to improved light-to-chemical energy conversion schemes and to enhanced photovoltaic cell operation based on dye sensitization.^{6–8,9b,16}

Supporting Information Available: Experimental details as well as the synthesis, characterization, and electronic spectra of each molecule. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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