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A Unidirectional Energy Transfer Cascade Process in a Ruthenium Junction Self-Assembled by α- and β-Cyclodextrins

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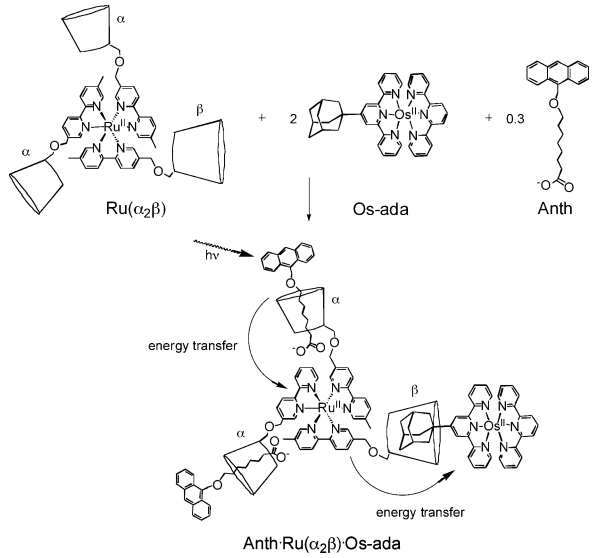
The supramolecular design of multicomponent systems that undergo photoinduced energy or electron transfer processes has been well recognized in view of its potential for development of nanosized molecular devices for solar energy conversion and components in photonic devices.[1] The introduction of transition metals in such systems is attractive due to their high stability, tunable redox, and excited-state properties that can lead to the design of molecular wires,[2] junctions,[3] and transistors.[4] The construction of multimetallic systems has been mostly based on the covalent linkage of the photoresponsive units. To overcome synthetic complexity and to access a library of dyads and triads, assembly based on cyclodextrin, CD, receptors has been used to form metal-containing donor−acceptor systems in water.[5] We have recently reported that the direction of photoinduced energy transfer can be switched *from* or *to* a Ru(II) center appended to a cyclodextrin by the choice of the metalloguest, Os(II) or Ir(III), bound in the CD cavity.[6] To further advance the function of the assembly to vectorially transfer energy in distinct steps, the selection of the direction of energy transport should be addressed by the spatial arrangement of the components. We report herein a self-assembled junction, formed by selective binding of three different photoactive components, in which a *unidirectional* two-step photoinduced energy transfer process takes place.

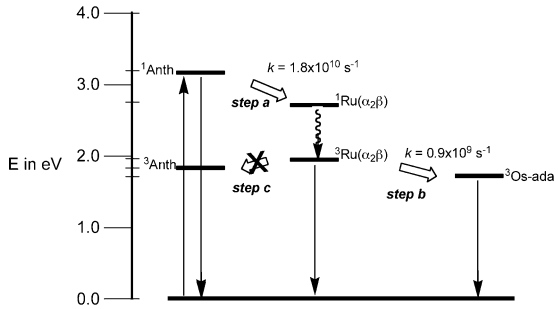
To introduce photoinduced directionality, α- and a β-CDs have been grafted onto a ruthenium core which can act as a junction by the selective binding of tailor-made photoactive guests. The complex $Ru(\alpha_2\beta)Cl_2$ has been prepared (Scheme 1), isolated by ion exchange chromatography, and fully characterized (Supporting Information). It shows typical absorption and emission spectra of ruthenium trisbipyridyl complexes, and in aqueous solution, it displays enhanced luminescence lifetimes (degassed 940 ns, aerated 690 ns) and quantum yield (0.039) compared to the parent compound $[Ru(5,5'\text{-dimethylbipyridine})_3]^{2+}$. Guest molecules **Anth** and **Os-ada** (Scheme 1) were designed with tails tailored for recognition of α- and β-CD, respectively, to assemble a triad of photoactive components, **Anth·Ru(α$_2$β)·Os-ada**. Anthracene can act as a singlet energy donor to Ru(II) by excitation in the 350−380 nm region, where the absorption cross section of the acceptor is minimum.[7] The Os(II) metalloguest has a ^{3}MLCT state at a lower energy than that of Ru(II) and can function as energy acceptor (Scheme 2). The flexibility of the system to "mix and match" the donor−acceptor components allows us also to study the dyad systems, **Anth·Ru(α$_2$β)** and **Ru(α$_2$β)·Os-ada**, to elucidate the processes occurring in the **Anth·Ru(α$_2$β)·Os-ada** triad.

The assembly of the triad was performed by adding first **Os-ada** to **Ru(α$_2$β)** to ensure saturation of the β-CD cups since the adamantyl tail of the Os(II) guest can only bind to β-CD. It was followed by the addition of the **Anth** guest in a ratio that ensured that most of the **Anth** guest is bound to α-CD in order to avoid its participation in bimolecular processes. Control experiments showed that the binding of **Anth** to the β-CD cavity is negligible under the same experimental conditions. All photophysical studies were performed in degassed solutions.

Scheme 1. Aqueous Assembly of **Anth·Ru(α$_2$β)·Os-ada**; [**Ru(α$_2$β)**]= 6× 10−^{5} M



Scheme 2. A Simplified Energy Diagram of the Energy Cascade Process



To monitor the energy cascade process in **Anth·Ru(α$_2$β)·Os-ada**, the luminescence of **Os-ada** was monitored upon excitation of **Anth** at 360 nm. Comparison of isoabsorptive solutions of **Anth·Ru(α$_2$β)·Os-ada** and **Os-ada** indicates that the Os(II) luminescence is sensitized by 20% (Supporting Information). This has been derived by comparison of the **Anth·Ru(α$_2$β)·Os-ada** results with a model system with no CD recognition sites and hence absence of supramolecular assembly. These results demonstrate that there

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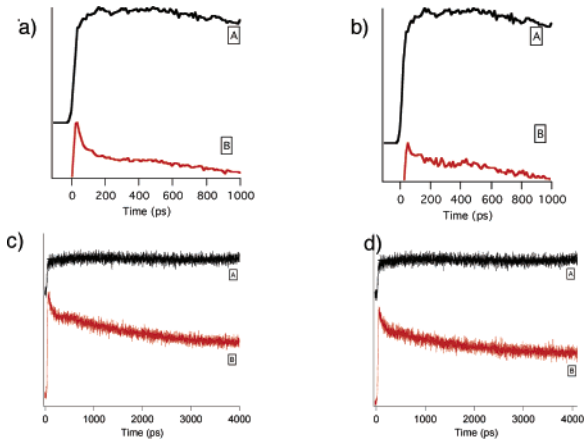

Figure 1. Time-resolved emission recorded at 400 nm (a, b) and 620 nm (c, d) of (a) **Anth** (black) and **Anth·Ru(α$_2$*β*)** (red); (b) **Anth** (black) and **Anth·Ru(α$_2$*β*)·Os-ada** (red); (c) **Ru(α$_2$*β*)** (black) and **Ru(α$_2$*β*)·Os-ada** (red); and (d) **Ru(α$_2$*β*)** (black) **Anth·Ru(α$_2$*β*)·Os-ada** (red); λ_{exc} = 350 nm, pulse-width = 20 ps fwhm.

is an energy transfer process in **Anth·Ru(α$_2$*β*)·Os-ada** which leads to the population of the **Os-ada**.

To unravel which excited states are involved in the process and elucidate the energy hopping mechanism in the assembly, time-resolved emission studies have been performed to monitor the decays of the excited states of all photoactive components. Solutions of **Anth** fluoresce with a lifetime of 3.5 ns (λ_{exc} = 350 nm). In the **Anth·Ru(α$_2$*β*)** dyad, excitation at 350 nm leads to a strong quenching of the **Anth** emission (Figure 1a). The dramatic reduction of the **Anth** excited-state lifetime, τ = 46 ps, is attributed to energy transfer from ^{1}**Anth** to ^{1}**Ru(α$_2$*β*)**. In the self-assembled triad **Anth·Ru(α$_2$*β*)·Os-ada**, the fluorescence of **Anth** is also strongly quenched, and its lifetime is shortened to 62 ps (Figure 1b). The similar quenching of **Anth** in the dyad and triad indicates that the presence of the **Os-ada** guest does not influence the energy transfer process from **Anth** to **Ru(α$_2$*β*)** (Scheme 2, *step a*). Following the energy cascade process in **Anth·Ru(α$_2$*β*)·Os-ada** upon excitation at 350 nm, the luminescence of **Ru(α$_2$*β*)** is monitored. A fast intersystem crossing from ^{1}MLCT of **Ru(α$_2$*β*)** leads to the population of the luminescent state of Ru^{II}, ^{3}MLCT, which is also strongly quenched and its lifetime is only 1.1 ns (τ = 940 ns for the unfilled **Ru(α$_2$*β*)** complex). This rate of quenching is the same as that observed in the dyad **Ru(α$_2$*β*)·Os-ada** (Figure 1c,d), which indicates that the presence of **Anth** does not affect the rate of quenching of **Ru(α$_2$*β*)**.

Finally, monitoring of the **Os-ada** luminescent excited state showed that the state is populated with a rise time consistent with the **Ru(α$_2$*β*)** decay, and the rate agrees with our previous results for energy transfer between Ru(II) and Os(II) centers.[6] The **Os-ada** excited state emits at 720 nm with a lifetime of 130 ns. Independent experiments showed that the energy transfer from ^{3}**Ru(α$_2$*β*)** to ^{3}**Anth** (*step c*) is kinetically unfavorable since it is 3 orders of magnitude slower than the process from the ^{3}Ru to the ^{3}Os (*step b*), whereas the difference of the magnitude of ΔG of the two processes is small (0.1 eV). If we consider a Förster mechanism to be dominant, a comparison of the spectral overlap integrals allows us to conclude that *step b* is expected to be the preferred path. A calculation of the spectral overlap integral of the **Ru(α$_2$*β*)** emission and **Os-ada** absorption gives a J_F value of 6.6×10^{14} M^{-1} cm^{-1} nm^4. The J_F for **Ru(α$_2$*β*)** emission and **Anth** absorption is expected to be few orders of magnitude smaller from an estimation taking into account the minute extinction coefficient of the **Anth** triplet.[8] This is consistent with the rate for *step b* to be much larger than *step c*. However, we cannot exclude an exchange mechanism in the energy transfer process through the noncovalent interactions.[6] On the basis of the J_F for the **Ru(α$_2$*β*)·Os-ada** pair and assuming a distance of 17 Å, an energy transfer rate of 2×10^7 s^{-1} is estimated. The rate we observe (0.9×10^9 s^{-1}) is about 43 times faster than the rate expected on grounds of the Förster mechanism.

A final proof for the discussed cascade energy transfer mechanism came from subpicosecond time-resolved transient spectroscopy (Supporting Information). The transient spectra of the triad **Anth·Ru(α$_2$*β*)·Os-ada** were recorded at different delay times. The singlet excited state of the anthracene is populated (band at 590 nm) immediately after the laser pulse (0.2 ps). The fast decay is in agreement with the rate obtained from the time-resolved experiments and is a signature for the fast singlet energy transfer from **Anth** to **Ru(α$_2$*β*)**. The population of the ruthenium excited state is followed by the bleaching at 460 nm, which decays in about 1.1 ns forming the **Os-ada** excited state; its bleaching was monitored at 480 nm, which then decays to the ground state in a much longer time scale (τ = 130 ns). All the decay kinetics for the different processes correspond to the time-resolved emission data. The transient spectra do not reveal any other competitive process, such as photoinduced electron transfer (the radical cation of **Anth** has a very distinctive absorption at 700 nm) nor the population of **Anth** triplet excited state (at 420 nm).

We can conclude that upon excitation of the anthracene moiety in the supramolecular assembly a vectorial energy transfer cascade occurs with rates of 1.8×10^{10} s^{-1} (*step a*) and 0.9×10^9 s^{-1} (*step b*) via the excited state of the Ru(II), leading to the population of the lowest excited state localized on the **Os-ada**. Our directed self-assembly strategy based on judicious selection of host and guest components allows the construction of unidirectional wires of nanoscale dimensions.

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Supporting Information Available: Characterization data of compounds and steady-state emission spectra are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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