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Intramolecular charge separation in a hydrogen bonded tyrosine–ruthenium(II)–naphthalene diimide triad†

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Long-lived charge-separated states in the ns to μs range were observed upon laser flash excitation of a donor–chromophore–acceptor triad based on tris(bipyridine) ruthenium(II) as photosensitizer, naphthalene diimide as acceptor, and a hydrogen bonded phenol as donor.

Studies of photo-induced electron transfer reactions in donor–photosensitizer–acceptor (D–P–A) assemblies have provided a deeper understanding of how nature converts solar energy into high-energy substances.[1–4] We have previously shown efficient charge separation in tris(bipyridine)ruthenium(II)–naphthalene diimide (NDI) dyads.[5] They proved to be stable and about 88% of the excited state energy was converted to the charge-separated (CS) state. Although the P^+–A^- state was short-lived (< 5 ns), a sufficiently fast donor could provide high yield of the D^+–P–A^- state. A variety of organic donors have earlier been linked to ruthenium(II) polypyridyl complexes,[6–12] and in particular, it has been shown that strongly hydrogen bonded phenols are rapid electron donors to photo-generated ruthenium(III).[11,12] We have therefore prepared the **dpaTyr–Ru–NDI** triad (dpaTyr is bis-2,6-(dipicolylaminomethyl)tyrosine ethyl ester), where the strongly hydrogen bonded tyrosine is linked to the Ru–NDI unit (Fig. 1).[13] The importance of hydrogen bonds for rapid tyrosine oxidation in acetonitrile has been previously addressed.[10–12]

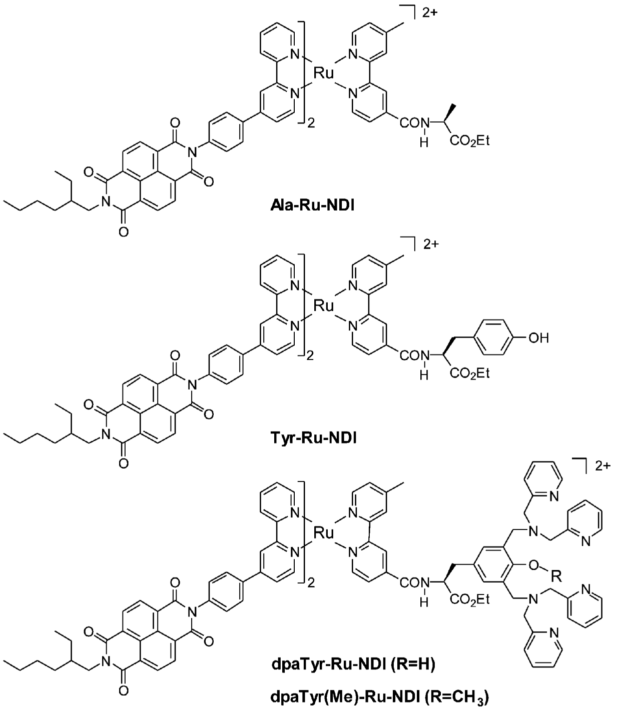

Fig. 1 Structures of complexes.

Here we report light-induced charge separation in the **dpaTyr–Ru–NDI** triad. In order to understand the processes involved in the charge separation, we have also prepared the reference complexes **dpaTyr(Me)–Ru–NDI** (methylated phenol), **Tyr–Ru–NDI**, and **Ala–Ru–NDI**.‡ The light-induced reactions in these complexes were studied by time-resolved absorption and emission, and the redox potentials of the various components were determined using cyclic and differential pulse voltammetry (CV and DPV).

The UV-Vis absorption spectrum of **dpaTyr–Ru–NDI** showed the MLCT band (λ_{max} = 465 nm, $\varepsilon = 2.4 \times 10^4$ M^{-1} cm^{-1}) of the ruthenium chromophore well separated from the $\pi \rightarrow \pi^*$ transitions of the naphthalene diimide units (378, 358, and 340 nm).

In CV and DPV, all complexes were adsorbed on the electrode at the first reduction at a potential similar to that of the first reversible NDI reduction in the related Ru–NDI dyads ($E_{1/2}$ = −0.97 V *vs.* Fc).[5] For **dpaTyr–Ru–NDI**, three irreversible oxidation peaks at +0.43 V, +0.58 V, and *ca.* +0.85 V are observed below the ruthenium oxidation at +0.88 V (Fig. 2). In contrast, **dpaTyr(Me)–Ru–NDI** shows two irreversible peaks at +0.62 and +0.70 V that are assigned to oxidations of the two amines, split by weak coulombic interactions. In **dpaTyr–Ru–NDI**, we thus assign the first oxidation to the hydrogen bonded phenol and the second oxidation to a non-hydrogen bonded amine.[14] The peak at *ca.* +0.85 V, may be due to an oxidation product.

A proposed reaction scheme, following excitation of the ruthenium chromophore in acetonitrile for **dpaTyr–Ru–NDI**, is shown in Fig. 3. Time correlated single photon counting experiments on all four complexes showed efficient quenching of the ruthenium ^{3}MLCT excited state by the NDI moieties. The emission decay was biexponential with τ_1 = 27 ns (75%) and τ_2 = 7 ns (25%),[15] giving a quenching rate constant of $k_f = 3.7 \times 10^7$ s^{-1} for the major component. In analogy with similar Ru–NDI dyads,[5] we

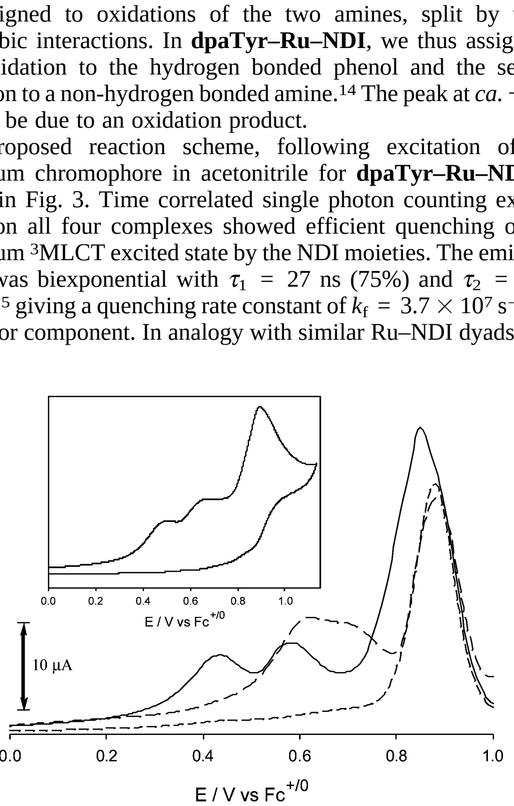

Fig. 2 DPV of **dpaTyr–Ru–NDI** (solid), **dpaTyr(Me)–Ru–NDI** (long dash), and **Ala–Ru–NDI** (short dash) in CH_3CN (1 mM, 0.1 M $TBAPF_6$). Inset: CV of **dpaTyr–Ru–NDI**.

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† Electronic supplementary information (ESI) available: experimental. See http://www.rsc.org/suppdata/cc/b3/b308101j/

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attribute the quenching to electron transfer to the NDI unit. In **Ala–Ru–NDI** and **Tyr–Ru–NDI**, the $\mathrm{NDI}^{\cdot-}$ signal was never detected by transient absorption which suggests a rapid charge recombination (Ru^{3+}–$\mathrm{NDI}^{\cdot-} \rightarrow \mathrm{Ru}^{2+}$–NDI, $k_b > 3.7 \times 10^7\ \mathrm{s}^{-1}$).

With **dpaTyr–Ru–NDI** and **dpaTyr(Me)–Ru–NDI**, however, a fraction of the reduced NDI moieties (474 nm, $\varepsilon \cong 2.3 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$)[16] was much more long-lived, suggesting that the CS state $(\mathrm{dpaTyr})^{\cdot+}$–$\mathrm{Ru}^{2+}$–$\mathrm{NDI}^{\cdot-}$ was formed (Fig. 4, upper inset). With **dpaTyr–Ru–NDI**, the charge separation yield was ~10%. The decay of the $\mathrm{NDI}^{\cdot-}$ signal was biexponential with $k_b = 3.3 \times 10^6\ \mathrm{s}^{-1}$ and $1.0 \times 10^5\ \mathrm{s}^{-1}$, both with equal amplitudes (Fig. 4, solid line). A third fraction, ~30% of the $\mathrm{NDI}^{\cdot-}$ signal, was very long-lived and was quenched by oxygen on the minute time scale. For **dpaTyr(Me)–Ru–NDI**, only the long-lived CS state was formed with a yield of ~5% of the initially excited molecules (Fig. 4, dotted line). This suggests an irreversible donor oxidation where a tertiary amine acts as electron donor. Since the initial $\mathrm{NDI}^{\cdot-}$ yield was significantly higher in **dpaTyr–Ru–NDI** than in **dpaTyr(Me)–Ru–NDI**, it can be assumed that both the amines and the hydrogen bonded tyrosine in **dpaTyr–Ru–NDI** can act as parallel donors with comparable rates. This is also indicated by the redox potentials which show that both functional groups should act as electron donors to photo-generated Ru(III). It was not possible to detect any transient signals from the oxidized donor in the CS states from **dpaTyr–Ru–NDI** and **dpaTyr(Me)–Ru–NDI**, since both the extinction coefficients and concentrations were small.[17]

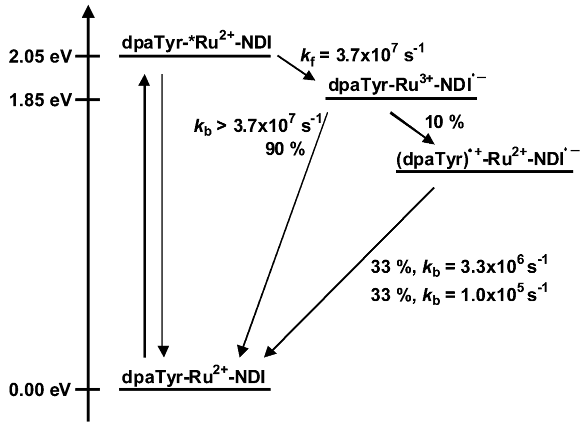

Fig. 3 Reaction scheme for **dpaTyr–Ru–NDI**. (A third fraction (~30%) of $(\mathrm{dpaTyr})^{\cdot+}$–$\mathrm{Ru}^{2+}$–$\mathrm{NDI}^{\cdot-}$ was very long-lived, see text.)

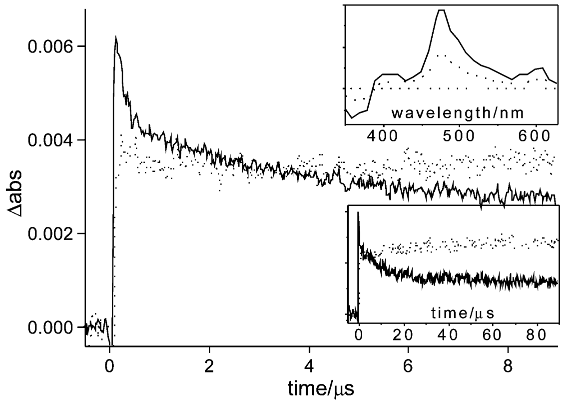

Fig. 4 Transient absorption traces probed at 474 nm for **dpaTyr–Ru–NDI** (solid line) and **dpaTyr(Me)–Ru–NDI** (dotted line). Lower inset: Corresponding traces at longer timescale. Upper inset: Transient absorption spectra for **dpaTyr–Ru–NDI** taken at 250 ns (solid line) and 10 μs (dotted line). Excitation at 455 nm.

The CS-state decay on the ns–μs time scale presumably involves the oxidized hydrogen bonded phenol, while amine oxidation is responsible for the irreversible fraction. The biexponential kinetics may reflect charge recombination in two different classes of isomers, one in which the dpaTyr and NDI units are spatially closer than in the other.

In summary, the present results show that the **dpaTyr–Ru–NDI** triad does form long-lived charge-separated states. Since electrochemical data suggest that the hydrogen bonded phenol and the tertiary amines are potential electron donors, the nature of the intermediates is not certain. However, it is clear that they are long-lived species containing the strongly reducing diimide anion radical. Since the goal of our work is to use this potential for further reactions, we feel that this is an important result.

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Notes and references

‡ The NMR and mass spectra of these molecules are consistent with their assigned structures. See ESI.

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13 In the NMR spectrum of **dpaTyr–Ru–NDI**, the phenolic proton is apparent at 11.0 ppm, indicating strong hydrogen bonding to the amines in the dpa moieties.
14 Similar potentials were observed for other hydrogen bonded phenols. In **Tyr–Ru–NDI**, the oxidation of the phenol was observed as a shoulder slightly above the $\mathrm{Ru}^{\mathrm{III/II}}$ redox couple.
15 All four complexes in this study showed very similar biexponential emission decay, while the decay for the corresponding Ru–NDI dyads and $[\mathrm{Ru}(4,4'\text{-Me-}2,2'\text{-bpy})(\mathrm{bpyPhNDI})_2]^{2+}$ was single exponential. This suggests that the biexponential kinetics may rather be due to different isomers of the complexes than due to conformational dynamics of the Ru–NDI unit.
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