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Bidirectional Electron Transfer in Molecular Tetrads

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Numerous molecular-scale arrays have been built and examined as means by which to better understand the details of light-induced electron transfer between well-defined cofactors.[1] Such multicomponent systems, covering dyads, triads, tetrads, pentads, etc., have been highly successful as bioinspired mimics and as vehicles for cascade effects leading to unusually long-lived, charge-separated states.[2] As a general rule, the temporal isolation of the charge-separated state increases with increasing number of linear electron-transfer steps, each propelled by a modest thermodynamic driving force.[3] Within the field, the notion of two-color systems has been developed[4] wherein a common electron-transfer process can be driven by selective illumination of either of two different chromophores. Related strategies have emerged for through-bond electron exchange along linear arrays.[5] In seeking to extend the scope of such rational molecular architectures, we have developed a new type of array in which the direction of electron transfer can be alternated by selection of the illumination frequency. The products are chemically identical but differ with respect to both kinetic and magnetic properties.

Figure 1. Molecular formula of the target compound QPRQ.

The target compound, hereafter abbreviated as QPRQ, has a benzo-1,4-quinone residue (BQ_1) covalently attached to one of the meso positions of a zinc(II) 5,10,15,20-tetraphenylporphyrin (ZnP) (Figure 1). This is a tried and tested protocol that has formed the basis of a multitude of artificial photosynthetic models.[6] In the present work, ZnP is attached via the opposite meso site to a ruthenium(II) bis(2,2′:6′,2″-terpyridine) complex (RuTpy), which is also a popular module for constructing light-activated electron-transfer systems.[7] The opposite side of the RuTpy complex is linked covalently to a second BQ moiety (BQ_2) to complete the tetrad. A key feature of this linear array is the ethynylnaphthalene unit (NAP)[8] interposed between RuTpy and the appended BQ_2 terminal. Indeed, NAP introduces asymmetry into the metal complex and ensures that charge transfer occurs selectively to that terpyridine ligand under illumination. This is the most important part of the design protocol, at least in terms of directed electron transfer.

In tetrahydrofuran (THF) at room temperature, QPRQ displays the range of absorption transitions expected for ZnP and RuTpy (see the Supporting Information). Thus, illumination at 550 nm results in preferential (i.e., >90%) excitation into the first excited singlet (S_1) state resident on the ZnP unit. Weak fluorescence can be observed that is characteristic of the S_1 state, although its quantum yield and lifetime are greatly reduced relative to isolated ZnP.[9] Thus, the fluorescence lifetime is only 55 ± 5 ps, which can be compared to the value of 2.4 ns for the reference ZnP compound. Laser flash photolysis studies indicate that the ZnP π-radical cation evolves during decay of the S_1 state and that the ground-state system is restored with a lifetime of 105 ± 8 ps (Figure 2). Consequently, and on the basis of the many ZnP−BQ molecular dyads that have been reported,[6] attenuation of the S_1 fluorescence can be attributed to light-induced electron transfer from ZnP to BQ_1 and is followed by intramolecular charge recombination. The flash photolysis records contain no indication that the nearby RuTpy unit enters into the transient chemistry. Cyclic voltammetry in THF, used with electrostatic corrections, shows that the driving force for light-induced charge separation (CS) is ∼0.68 eV, while that for subsequent charge recombination (CR) is ∼1.36 eV. The ZnP triplet state is not populated during CR and under these conditions lies above the charge-separated state by ∼0.22 eV. It is perhaps worth stressing that the π-radical anion of BQ_1 cannot be resolved by optical means because of its relatively weak spectral signature, which is hidden underneath the more intense features of ZnP.

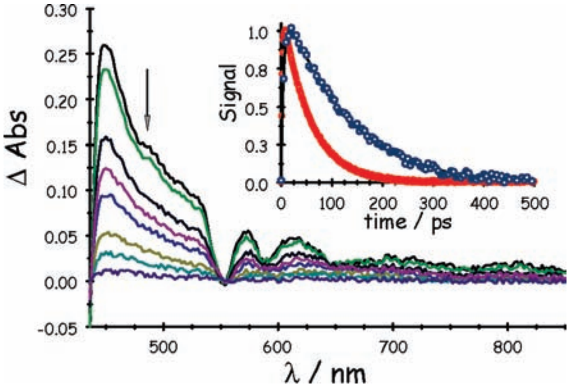

Figure 2. Transient differential absorption spectra recorded at delay times of 10, 30, 60, 80, 100, 150, 200, and 300 ps after excitation of QPRQ at 550 nm. Excitation forms the ZnP S_1 state, which evolves into the ion pair. The inset shows decay profiles for stimulated fluorescence (red) and absorbance at 586 nm (blue).

On the other hand, illumination of QPRQ in THF at 490 nm, where the RuTpy chromophore is the dominant (i.e., >95%) absorber, results in rapid formation of the metal-to-ligand charge-transfer (MLCT) triplet state localized on RuTpy (Figure 3).[9] In this species, the promoted electron is delocalized over the NAP-substituted terpyridine ligand and therefore poised for transfer to the adjacent BQ residue, BQ_2. Indeed, the lifetime of the MLCT triplet state is only 95 ± 12 ps, which is much shorter than the value of 415 ns recorded for the relevant reference compound[9] lacking both BQ and ZnP moieties. CR of the resultant ion pair occurs via first-order kinetics with a lifetime of 440 ± 25 ps (Figure

10.1021/ja908865k

3). From the cyclic voltammograms, the thermodynamic driving forces for CS and CR are 0.13 and 1.80 eV, respectively. The relatively slow rate of CR reflects the triplet character of the ion pair, the large amount of energy to be dissipated, and the extended separation distance. A control compound that has the precursor hydroquinol functions protected by benzyl groups (see the Supporting Information) does not show CS. Instead, triplet energy transfer occurs to form the T_1 state localized on ZnP,[10] for which the respective energy gap is 0.31 eV. This step is quite slow, with an MLCT triplet lifetime of 450 ± 25 ps, because of the prior localization of the promoted electron on the NAP-bearing terpyridine ligand. Triplet energy transfer competes poorly with CS when the BQ residue is in place.

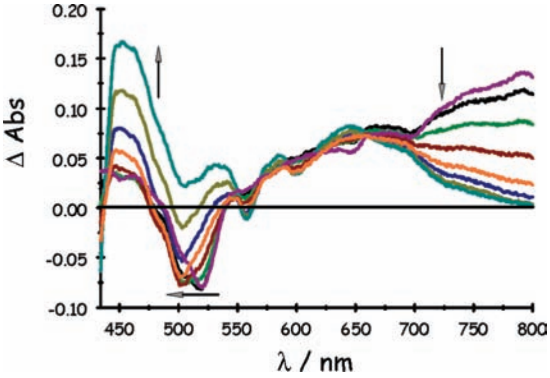

Figure 3. Transient differential absorption spectra recorded at delay times of 10, 40, 70, 120, 200, 300, 500, and 1,000 ps after excitation of QPRQ in THF with a subpicosecond laser pulse at 490 nm. Decay of the RuTpy T_1 state is most evident at ~800 nm, while the ZnP radical cation absorbs strongly at 460 nm.

Following excitation at 490 nm, the flash photolysis records indicate that the ZnP π-radical cation[11] is formed by way of hole transfer (HT) to ZnP from the oxidized form of RuTpy (Figures 3 and 4). This step is apparent from the growth of an absorption profile with prominent maxima at ~460 and 660 nm, in agreement with its assignment;[11] the RuTpy triplet absorbs strongly in the near-IR region, while the oxidized form of the metal complex can be recognized by way of the shift in the bleaching of the MLCT absorption band. There is a good driving force ($\Delta G^0 = -0.48$ eV) for this process. On the basis of measured molar absorption coefficients for the intermediate species involved in the overall reaction, it appears that the ZnP π-radical cation is formed with a quantum efficiency of ~60%. Since the triplet ion pair is generated with a quantum efficiency of >95%, it follows that HT competes reasonably well with the primary CR event. The lifetime of the secondary ion pair is extended to 4 ± 1 μs in THF at 295 K. This lifetime increases to 23 ± 3 μs at 180 K.

Thus, we have shown that excitation into the ZnP unit results in rapid electron transfer to BQ_1 to form in quantitative yield a singlet ion pair that lives for 105 ps. Conversely, excitation into the RuTpy complex gives a 60% yield of a triplet ion pair for which the redox products are more widely spaced and the electron is localized on BQ_2, not BQ_1. There is a 40 000-fold prolongation of the lifetime of the ion pair caused by a combination of spin factors, driving forces, and separation distances. Furthermore, the lifetime of the triplet ion pair increases by ~30% upon application of a strong (i.e., 30−50 mT) magnetic field under conditions where the corresponding singlet ion pair remains unaffected.

In conclusion, QPRQ displays bidirectional electron transfer along the molecular axis, with the direction and flux being determined by the wavelength of the incident light beam. Direct excitation of the Soret band of ZnP at 420 nm causes electron transfer in both directions as a result of the initial partition of the ZnP S_2 state into electron transfer to BQ_1 and energy transfer to RuTpy.

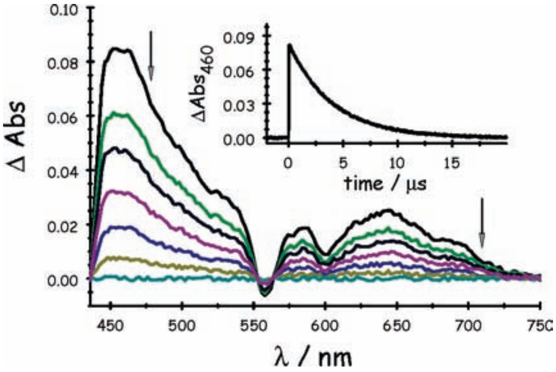

Figure 4. Transient differential absorption spectra recorded at delay times of 0, 0.08, 1.3, 2.2, 4.0, 5.6, and 8.4 μs after excitation of QPRQ in THF with a 4 ns laser pulse at 490 nm. The spectral changes relate to collapse of the triplet ion pair to the ground state. The inset shows a kinetic trace recorded at 460 nm.

Acknowledgment. Financial support was provided by EPSRC (EP/D032946/1) and Newcastle University.

Supporting Information Available: Brief experimental procedures, structural proofs, and spectroscopic data for QPRQ. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA908865K