Photochemical Energy Transduction in Helical Proline Arrays

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Molecular assemblies for photochemical energy conversion require a functional site for light absorption and others that donate or accept electrons.[1] We recently introduced the use of solid-phase peptide synthesis to prepare a 13-residue proline-II helix bearing a spatially ordered electron-transfer, donor/chromophore/acceptor array.[2] We report here a significant extension of this strategy to helices containing 21 or 27 proline residues. Their availability has allowed us to explore the effects of introducing a second chromophore, of increasing the distance between redox sites on back electron transfer, and of changing the helical form from proline-II to proline-I.

Figure 1 shows the structures of the original 13-residue redox triad, CH_2CO-Pro_3-Pra(PTZpn)-Pro_2-Pro($Ru^{II}b_2m)^{2+}$-$(Pro)_2$-Pra-(Anq)-Pro_3-NH_2 (**1**),[2] the 21-residue redox triad, CH_3CO-Pro_7-Pra(PTZpn)-Pro_2-Pra($Ru^{II}(p)m)^{2+}$-Pro_2-Pra(Anq)-Pro_7-NH_2 (**2**), the 27-residue redox tetrad CH_3CO-Pro_7-Pra(PTZpn)-Pro_2-Pra-($Ru^{II}(p)_2m^{2+}$)-Pro_5-Pra($Ru^{II}(p)_2m)^{2+}$-Pro_2-Pra(Anq)-Pro_7-NH_2 (**3**), and the amide-substituted chromophore Boc-Pra($Ru^{II}(p)_2m)^{2+}$-OH (**4**).[3,4,5] The redox sites of arrays **2** and **3** are joined by amide bonds to an oligoproline chain, which was assembled by the stepwise solid-phase method from Boc-Pro, Boc-Pro-Pro, and three derivatives of *cis-N^α-Boc*-4-amino-L-proline (Boc-Pra), namely, the PF_6^- salt of ruthenium complex **4**, the anthraquinone (Anq) derivative Boc-Pra(Anq),[2] and the phenothiazine (PTZ) derivative Boc-Pra(PTZpn).[2] After the desired assembly was prepared, it was cleaved from the methylbenzhydrylamine resin with bromotrimethylsilane, isolated by HPLC on butylsilica, and shown to be pure by analytical HPLC and from the expected mass of 3629 Da (**2**) or 5225 Da (**3**) by electrospray ionization mass spectroscopy. In cyclic voltammograms recorded in 0.1 M in tetra(1-butyl)ammoniumhexafluorophosphate (TBAH) in acetonitrile, waves vs SSCE appeared at 0.75 V (**2**) and 0.73 V (**3**) for the $PTZ^{+/0}$ couple, at 1.37 V (**2**) and 1.39 V (**3**) for the $Ru^{III/II}$ couple, at −0.90 V (**2**) and −0.92 V (**3**) for the $Anq^{0/-}$ couple, and at −1.11 V (**2**, **3**) for the $Ru(p)_2m^{2+/+}$ couple.

In triad **2** and tetrad **3**, the terminal oligoproline segments are Pro_7 instead of Pro_3 to provide nucleation sites[6] for interconversion between a proline-I helix[7] and a proline-II helix.[8] Arrays **2** and **3** were proline-II helices in water as shown by circular dichroism measurements in the π–π*/n–π* region (250–190 nm).[9] When dissolved in acetonitrile, proline-II helices were converted into proline-I helices within 12 h at 25 °C. The kinetics of these transformations are reported elsewhere.[10]

The use of amide-substituted bipyridine ligand (-p) at the chromophore in assemblies **2** and **3** rather than bpy in **1** decreases $\Delta G°$ for PTZ → Ru^{II}* reductive electron-transfer quenching from −0.1 to −0.3 eV. It also increases $\Delta G°$ for Ru^{II}* → Anq oxidative quenching from 0.0 to +0.1 eV.[11,12]

Arrays **2** and **3** have characteristic Ru^{II} → p*(p,m) metal-to-ligand charge-transfer (MLCT) absorption bands in acetonitrile centered at 464 nm. Emission from **4** occurs at 642 nm with emission quantum yield $\Phi_{em} = 0.13 \pm 0.01$ and lifetime $\tau = 1460$ ns ($k = 6.8 \times 10^5$ s^{-1}) with 642 nm monitoring in deaerated acetonitrile at room temperature. Compared to **4**, emission from **2** ($\Phi_{em} = 0.014 \pm 0.010$, $\tau = 30 \pm 10$ ns, k ∼3.0 × 10^7 s^{-1})[13] is >90% quenched. It is 60% quenched in **3** ($\Phi_{em} = 0.048 \pm 0.005$). The decay kinetics for **3** were nonexponential. By stripping analysis, there are two components: one with $\tau_1 \approx 50$ ns ($k_1 \approx 2 \times 10^7$ s^{-1}) and the other with $\tau_2 = 1120$ ns ($k_2 = 0.89 \times 10^6$ s^{-1}).

Nanosecond laser flash photolysis of **2** and **3** with absorbance monitoring in deaerated acetontrile revealed characteristic absorption features for the p$^-$ radical anion at 375 nm, PTZ$^+$ at 520 nm, and Anq$^-$ at 590 nm. Similar features were observed for **1** and ascribed to formation of the redox-separated state, CH_3CO-Pro_3-Pra(PTZ$^+$pn)-Pro_2-Pra($Ru^{II}(b)_2m)^{2+}$-Pro_2-Pra(Anq$^-$)-Pro_3-NH_2.[2] Decay of the analogous states for the proline-I forms of **2** and **3**, which occurs by Anq$^-$ →PTZ$^+$ back electron transfer, was followed by absorption monitoring at 520 and 590 nm. This gave $k_{ET} = 4.8 \times 10^6$ s^{-1} ($\tau = 208$ ns) for **2** and 5.0×10^5 s^{-1} for **3** ($\tau = 2000$ ns) independent of concentration in the range of 10^{-4}–10^{-5} M. Back electron transfer for **3** was nearly temperature independent in partially deaerated CH$_3$CN with $k(5 °C) = 7.1 \times 10^5$ s^{-1} and $k(40 °C) = 7.9 \times 10^5$ s^{-1}.

The sequence of events occuring after MLCT excitation is illustrated for **2** in Figure 2. Given the energetics, the first step is probably PTZ → Ru^{II}* electron transfer, which, from the emission lifetime measurements, occurs on a time scale of ∼30 ns. Given the time limitations of the apparatus used, we were unable to resolve the initial quenching events by transient absorption measurements for either **2** or **3**.

The available evidence points to back electron transfer proceeding through bonds of the oligoproline chain rather than

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(3) The PF_6^- salt of **4** was prepared as follows. Ligand 2,2′-bipyridine-4,4′-dicarboxylic acid bis(pyrrolidine amide) (p) was prepared from the corresponding bis(acid chloride) and pyrrolidine. Reaction of RuCl$_3$ with ligand p (1.9 equiv) in the presence of LiCl and triethylamine in DMF at reflux furnished dark purple complex Ru(p)$_2$Cl$_2$. Coupling of the benzotriazole ester of 4′-methyl-2,2′-bipyridine-4-carboxylic acid[4] (m) with the 4-amino group of *cis-N^α-Boc*-4-amino-L-proline methyl ester[5] (Boc-Pra-OCH$_3$) in the presence of 4-(dimethylamino)pyridine (0.1 equiv) afforded Boc-Pra(m)-OCH$_3$. Hydrolysis[4] of this ester with LiOH gave the free acid (Boc-Pra(m)-OH), which on heating with freshly prepared Ru(p)$_2$Cl$_2$ in refluxing methanol formed red chromophore **4** (see the Supporting Information).

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(7) The proline-I helix is a right-handed helix with all *cis*-amide bonds, 3.3 residues per turn, and 1.9 Å axial distance per residue. See: Traub, W.; Shmueli, U. *Nature* **1963**, *198*, 1165.

(8) The proline-II helix is a left-handed helix with all *trans*-amide bonds, 3.0 residues per turn, and 3.1 Å axial distance per residue. See: Cowan, P. M.; McGavin, S. *Nature* **1955**, *176*, 501.

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(12) From single-mode emission spectral fitting (Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 372), $E_o = 15\,800$ cm^{-1}, $\Delta\bar{\nu}_{1/2} = 1740$ cm^{-1}, $\hbar\omega = 1220$ cm^{-1}, and $S = 0.96$, from which the free energy of the excited state above the ground state is, $\Delta G_{ES}° = E_o + (\Delta\bar{\nu}_{1/2})^2/(16k_B T(\ln 2)) = 2.12$ eV for Ru(p)$_2$m^{2+}* in acetonitrile at 25 °C.

(13) There is also a small component of unquenched emission from **3** with $\tau \approx 1000$ ns, probably due to partial oxidation of PTZ to the *S*-oxide during workup.[2]
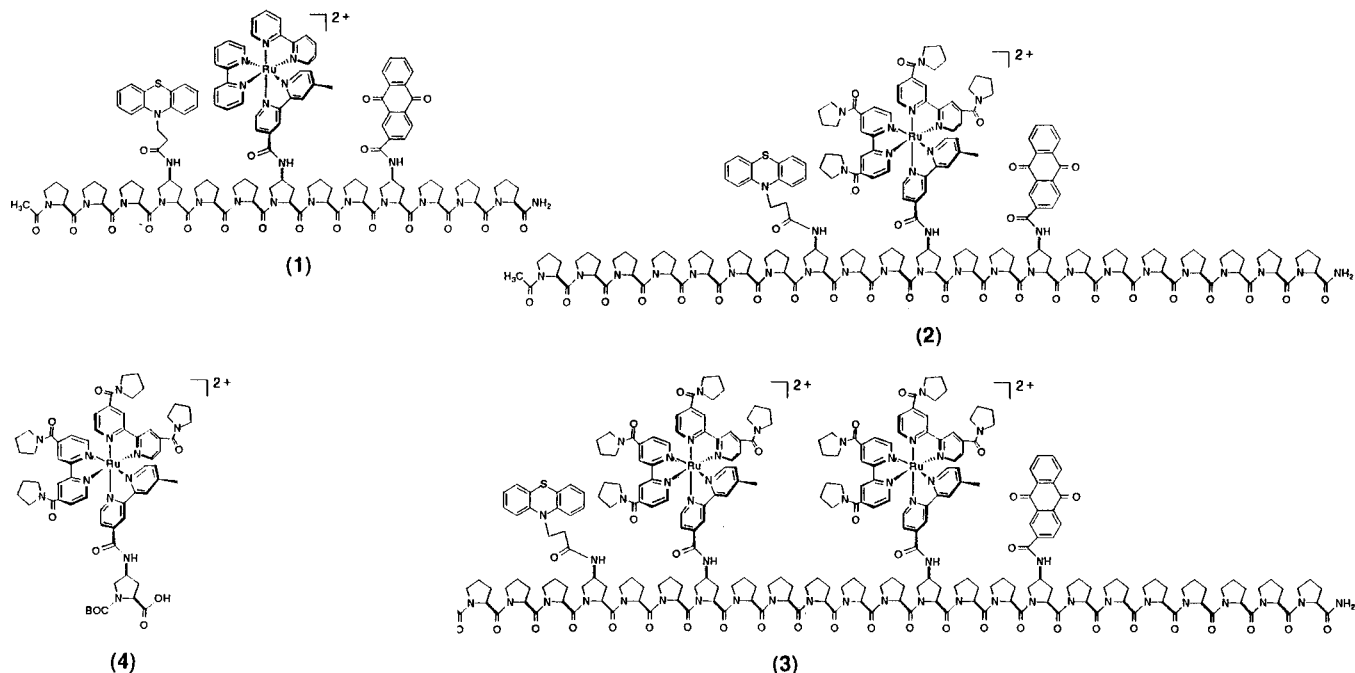
Figure 1. Structures of oligoproline arrays **1**−**3** and chromophore module **4**.
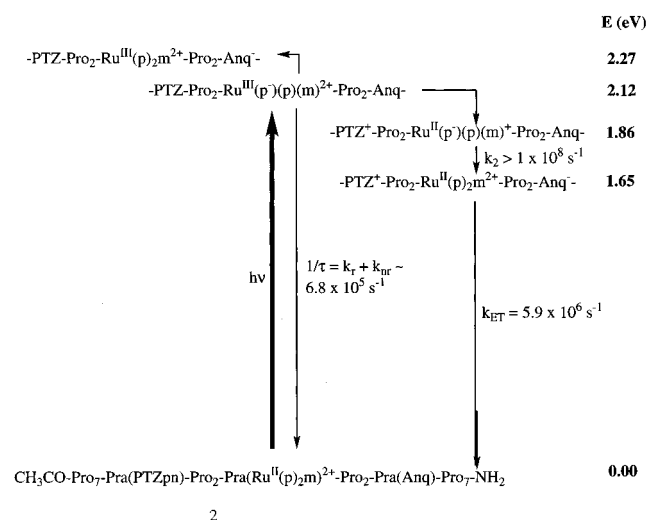

Figure 2. Energy level diagram illustrating the sequence of events that occur upon metal-to-ligand charge transfer excitation of **2**.

through space:[14] (1) k_{ET} for **1** and **2** are the same within experimental error even though the through-space distance between the PTZ$^+$ and Anq$^-$ groups is ∼18.5 Å for the proline-II helix of **1** and 11.5 Å for the proline-I helix of **2** as measured as the distance between the C$^\gamma$ atoms of Pra(PTZpn) and Pra-(Anq). (There are 29 intervening covalent bonds between the N atom of the phenothiazine ring system and the C$^\gamma$ atoms of the anthraquinone ring system in either case.) (2) k_{ET} is comparable for **1** and **2** even though the chromophores (Ru(b)$_2$m)$^{2+}$ and (Ru(p)$_2$m)$^{2+}$ differ in their electronic and steric properties. (3) k_{ET} is the same for the proline-I (5.0 × 10^5 s^{-1}) and proline-II (4.9 × 10^5 s^{-1}) helical forms of **3** in acetonitrile even though the distance for through-space, back electron transfer down the proline helix differs by ∼14 Å.[15] (In either case, there are 47 intervening covalent bonds.) The measurements on the proline-II helix were

made before significant proline-II → proline-I conversion[10] had occurred (0.5 h) and after it was complete (36 h). (4) Back electron transfer by reversal of the electron-transfer chains, e.g., by Anq$^-$ → Ru(p)$_2$m^{2+} → PTZ$^+$ electron transfer for the redox-separated state of **2** in Figure 2, can be ruled out for **3**, since k_{ET} is nearly temperature independent.

The increase from 29 to 47 intervening covalent bonds decreases k_{ET} from 5.9 × 10^6 s^{-1} in **2** to 5.0 × 10^5 s^{-1} in **3**. Comparison of transient absorption changes at 520 nm reveals that the yield of redox-separated state for **3** is only ∼20% that of **2**.[16] Both the decreased yield for **3** and the relatively large fraction of unquenched emission can be attributed to inefficient quenching of Ru$_b^{II}$* by Anq and slow electron and energy transfer. Ru$_a^{II}$ and Ru$_b^{II}$ are separated by five proline spacers. Experiments currently in progress on oligoprolines without the donor or acceptor show that Ru^{II}* → Ru^{II} energy transfer is slow across five proline spacers but rapid across two.

These initial results illustrate the power of the oligoproline synthetic strategy to prepare functional assemblies in which spatial control of a redox array along an oligoproline helix can be used to control physical properties.

Supporting Information Available: Characterization of compound 4 (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(15) The axial distance between the γ-carbons of Pra(Anq) and Pra(PTZpn) is 37 Å for the proline-II helix of **3** and 23 Å for the proline-I helix of **3**.

(16) The relative yields were measured by comparing Δ*A* at 520 nm immediately after the laser pulse. At 520 nm, these measurements are free of complications from emitting impurities because there is an isobestic point between the ground and MLCT excited states. This is also a λ$_{max}$ for PTZ$^+$.