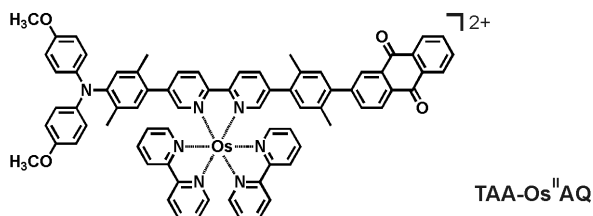


Large increase of the lifetime of a charge-separated state in a molecular triad induced by hydrogen-bonding solvent

Jihane Hankache and Oliver S. Wenger*^[a]

In the bacterial photosynthetic reaction center quinones act as primary (Q_A) and secondary (Q_B) electron acceptors.^[1] Q_A and Q_B are both hydrogen-bonded to amino acid side-chains, and a difference in hydrogen bonding is important for electron transfer from Q_A to Q_B .^[2] There have been numerous investigations of photoinduced electron transfer in artificial systems with quinone acceptors,^[3] but the influence of hydrogen-bonding on charge-recombination kinetics has received very limited attention.^[4] In donor-bridge-acceptor systems, hydrogen-bonds have so far been used mainly as structural scaffolds to provide a connection between two redox partners.^[3a] We attempted to explore whether charge-separated states could be stabilized kinetically by hydrogen-bond donating solvents. It is well known that the dielectric constant of a solvent affects electron transfer rates,^[5] but our present study focuses specifically on the hydrogen-bond donor property of the solvent.



Scheme 1. The molecular triad investigated in this work.

The molecule of central interest in this work is the triad shown in Scheme 1. It is comprised of a triarylamine (TAA) donor, an $\text{Os}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) photosensitizer ("Os^{II}"), and a 9,10-anthraquinone (AQ) acceptor. Our triad structurally resembles bis(terpyridine) triads,^[6] while functionally it is closer to previously investigated phenothiazine- $\text{Ru}(\text{bpy})_3^{2+}$ -anthraquinone triads.^[7] We had previously reported on long-lived charge-separation after photoexcitation of an analogous ruthenium(II) triad,^[8] and we had also described the synthesis of the rigid rod-like triarylamine-bipyridine-anthraquinone ligand which was now reacted with $\text{Os}(\text{bpy})_2\text{Cl}_2$. The change in metal is

trivial, but the important new finding is that hydrogen bonds between hexafluoroisopropanol (HFIP) and the quinone unit of the TAA-Os^{II}-AQ triad leads to a substantial thermodynamic and kinetic stabilization of the charge-separated state which is produced after photoexcitation of the metal complex.

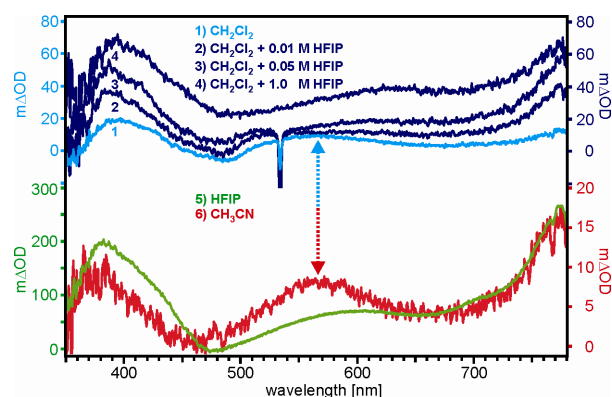


Figure 1. Transient absorption spectra obtained from $\sim 10^{-5}$ M solutions of TAA-Os^{II}-AQ after photoexcitation at 532 nm with 10-ns laser pulses. Detection occurred in a time window of 200 ns immediately after the excitation pulse. The sudden drop in ΔOD at 532 nm (light blue and dark blue traces) is an artifact caused by the excitation source.

The light blue trace in Figure 1 is the transient absorption spectrum detected in a 200-ns time window after 532-nm excitation of a $\sim 10^{-5}$ M solution of TAA-Os^{II}-AQ in de-aerated CH_2Cl_2 . Excitation occurs into a metal-to-ligand charge transfer (MLCT) absorption of the osmium complex (Figure S1 in the Supporting Information). Three absorption bands with maxima at 395 nm, 570 nm, and near 780 nm are observed. Spectroelectrochemical investigations of the individual molecular components of the triad from Scheme 1 demonstrate that the bands at 395 nm and 570 nm are caused by reduced anthraquinone (AQ^-) while the band in the red spectral range is due to oxidized triarylamine (TAA^+), see Figure S2 in the Supporting Information.^[8] Thus, transient absorption spectroscopy provides clear evidence for a charge-separated state of the type $\text{TAA}^+-\text{Os}^{\text{II}}-\text{AQ}^-$. Upon addition of HFIP to the CH_2Cl_2 solution of the triad, significant changes occur in the transient absorption spectra (dark blue traces in Figure 1). One of the key observations is that higher ΔOD values are detected when HFIP is present. As will be seen below, this is because the lifetime of the

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charge-separated state is increasing. Another important observation is that the maximum of the absorption band which in pure CH_2Cl_2 is located at 570 nm shifts to longer wavelengths. In pure HFIP (green trace in Figure 1), the maximum of this band is at 605 nm. In pure CH_3CN (red trace in Figure 1), this absorption maximum is at nearly the same wavelength as in pure CH_2Cl_2 (vertical dotted arrow). The increase in dielectric constant (ϵ_s) between CH_2Cl_2 ($\epsilon_s = 8.93$) and CH_3CN ($\epsilon_s = 35.94$) is far greater than that between CH_2Cl_2 and HFIP ($\epsilon_s = 16.6$), hence the shift of the AQ⁻ absorption band maximum from 570 nm to 605 nm between CH_2Cl_2 and HFIP cannot be attributed to a change in dielectric constant of the solvent. HFIP is known to be a very strong hydrogen-bond donor,^[9] and therefore it appears plausible that the observed spectral shift is the result of a hydrogen-bonding interaction between HFIP and AQ⁻. In an attempt to support this hypothesis we performed spectro-electrochemical studies of AQ in CH_2Cl_2 in presence of HFIP (Figure S3 of the Supporting Information) but could only detect absorption bands that had been previously attributed to AQH₂ (i. e., twofold reduced and twofold protonated AQ).^[10] Thus, the spectro-electrochemistry experiment is inconclusive as far as the band shift observed upon photoinduced one-electron reduction of AQ is concerned.

What seems clear, however, is that the photoproduct observed in the green trace of Figure 1 is *not* the AQH₂ species that is detected in the spectro-electrochemistry experiment. The respective transient absorption spectrum (Figure 1) is missing the diagnostic very narrow and intense absorption peak of AQH₂ at 380 nm (Figure S3). Conversely, the spectro-electrochemical data is lacking a broad band around 620 nm which is only roughly a factor of 3 less intense than the band at 395 nm.^[16] We also note that in the spectro-electrochemical experiment *two*-electron reduction of AQ (coupled to twofold protonation by HFIP) is far more easy to perform than from a photoexcited state; our triads are present in dilute ($\sim 10^{-5}$ M) solution and can only efficiently perform *one*-electron redox chemistry.

Experimental evidence for hydrogen-bonding between HFIP and charge-neutral AQ comes from solution infrared spectroscopy (Figure S4 of the Supporting Information) and optical absorption spectroscopy (Figure S5 of the Supporting Information). We observe a shift of the CO stretching frequency of AQ in CH_2Cl_2 at 1678 cm^{-1} to lower energies upon addition of small amounts of HFIP (Figure S4), which is in line with prior IR studies focusing on the effect of hydrogen-bonding on CO stretching frequencies, see the Supporting Information for details. Optical absorption spectroscopy is less selective to hydrogen-bonding effects, but upon addition of HFIP to CH_2Cl_2 solutions of AQ we observe spectral band shifts that are consistent with the formation of hydrogen-bonded adducts between HFIP and AQ (Figure S5). Given the evidence for hydrogen-bonding between HFIP and charge-neutral AQ, it is to be expected that such hydrogen-bonds will become even stronger once AQ has been reduced.^[9,13]

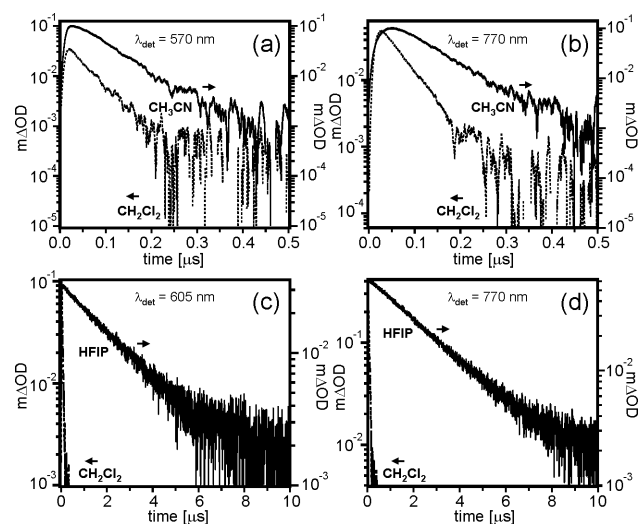


Figure 2. Temporal evolution of the transient absorption signals from Figure 1 at 570 nm and 605 nm (panels a, c) and 770 nm (panels b, d) after pulsed excitation at 532 nm (pulse width 10 ns) in different solvents: CH_2Cl_2 (blue traces), CH_3CN (red traces), HFIP (green traces).

Figure 2 shows the temporal evolution of the transient absorption signals from Figure 1. In pure CH_2Cl_2 (dashed traces) the ΔOD at 550 nm (AQ⁻, Figure 2a) and 770 nm (TAA⁺, Figure 2b) decays with time constants of $\tau_{\text{CR}} = 44$ ns and 48 ns, respectively. These decay times are identical within experimental accuracy and reflect intramolecular charge recombination (CR) between AQ⁻ and TAA⁺. In pure CH_3CN (solid traces) the decays are not much slower: 74 ns is measured at 570 nm (Figure 2a), 80 ns at 770 nm (Figure 2b). By contrast, in pure HFIP (solid traces) $\tau_{\text{CR}} = 1800$ ns at 605 nm (Figure 2c) and $\tau_{\text{CR}} = 1980$ ns at 770 nm (Figure 2d). In order to better illustrate the increase in τ_{CR} between pure CH_2Cl_2 and HFIP, the decays of the transient absorption intensities at 570 nm and 770 nm in pure CH_2Cl_2 have been included into Figure 2c/2d (dashed traces). The observed strong increase of τ_{CR} cannot be reconciled with an increase in solvent dielectric constant because ϵ_s of HFIP (16.6) is much smaller than that of CH_3CN (35.94). It seems much more plausible that this lifetime increase is caused by hydrogen-bonding between HFIP and anthraquinone monoanion as illustrated in Figure 3a.

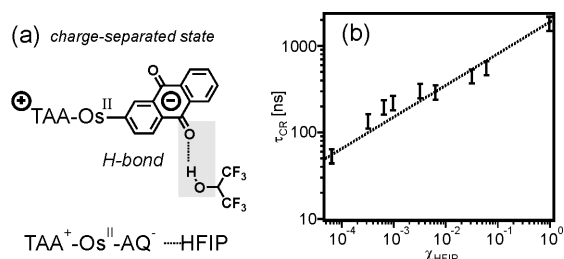


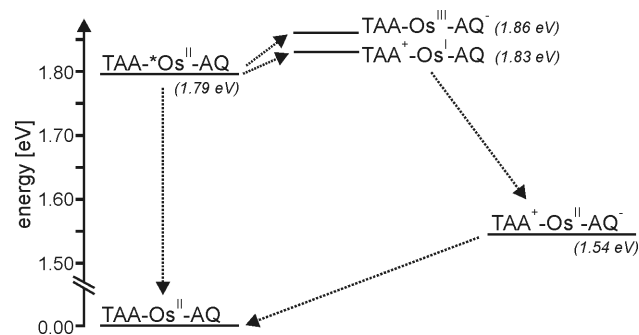
Figure 3. (a) Hydrogen-bonded adduct between HFIP and anthraquinone monoanion in the charge-separated state of the triad. (b) Correlation between the lifetime of the charge-separated state (τ_{CR}) and the molar fraction of HFIP in CH_2Cl_2 .

Figure 3b shows that there is a correlation between τ_{CR} and the molar fraction (χ_{HFIP}) of HFIP in CH_2Cl_2 , the respective raw data obtained from CH_2Cl_2 / HFIP mixtures is shown in Figure S6 of the Supporting Information. The physical origin of the log-log relation between τ_{CR} and χ_{HFIP} will require deeper discussion that is beyond the scope of this communication.

Table 1. Reduction potentials (E) for all relevant redox-active components of the molecular triad from Scheme 1 in Volts vs. the ferrocenium/ferrocene (Fc^+/Fc) couple in two different solvents. 0.1 M tetrabutylammonium hexafluorophosphate served as a supporting electrolyte.

redox couple	E [V], CH_2Cl_2	E [V], CH_3CN
Os(III/II)	+0.56	+0.48
TAA ⁺ /TAA	+0.24	+0.30
AQ/AQ ⁻	-1.30	-1.27
Os(II/I)	-1.59	-1.61

Table 1 summarizes the reduction potentials of all redox-active components of TAA-Os^{II}-AQ in pure CH_2Cl_2 and CH_3CN as determined by cyclic voltammetry (Figure S7 of the Supporting Information). The energy level diagram in Scheme 2 was established based on the CH_2Cl_2 data and based on an energy of 1.79 eV for the photoactive MLCT excited-state of the $\text{Os}(\text{bpy})_3^{2+}$ unit.^[11] We learn from this data that both oxidative and reductive quenching of the MLCT excited-state are weakly endergonic, but once this initial thermodynamic hurdle is taken, subsequent electron transfer to produce the fully charge-separated state with TAA⁺ and AQ⁻ is exergonic by roughly 0.3 eV. The TAA⁺-Os^{II}-AQ⁻ state is at nearly identical energies in CH_2Cl_2 (1.54 eV) and CH_3CN (1.57 eV), hence the observation of similar τ_{CR} values in these two solvents (~50 ns vs. ~80 ns, see above) is not surprising. However, in presence of HFIP the energy of the fully charge-separated state is expected to change: Prior electrochemical investigations demonstrated that addition of HFIP to CH_2Cl_2 solutions of various benzoquinones leads to substantial shifts in the reduction potentials of these compounds.^[9, 12] Cyclic voltammetry studies of TAA-Os^{II}-AQ in CH_2Cl_2 show that the wave associated with reduction of the AQ unit shifts positively when increasing the HFIP concentration, whereas all other redox couples remain virtually unaffected (Figure S8 in the Supporting Information). The highest HFIP concentration for which voltammograms of reasonable quality can still be measured is 4 mM (Figure S8),^[8] and at this point the shift of $E(\text{AQ}/\text{AQ}^-)$ amounts to 150 mV relative to the value in pure CH_2Cl_2 . Thus, already at 4 mM HFIP, the TAA⁺-Os^{II}-AQ⁻ state is thermodynamically stabilized by 0.15 eV with respect to pure CH_2Cl_2 . An extrapolation of the available CV data (Figure S9 of the Supporting Information) indicates that in pure HFIP the energetic stabilization provided by hydrogen-bonding will be on the order of 0.25 eV, but this only represents a rather crude estimate.



Scheme 2. Energy level diagram with all relevant photoexcited and charge-separated states in CH_2Cl_2 solution without HFIP.

Electron transfer rates (k_{ET}) are governed by the interplay of reaction free energy (ΔG) and reorganization energy (λ).^[5b] While charge-recombination in CH_2Cl_2 and CH_3CN is associated with a similar change in free energy ($\Delta G_{\text{CR}} = -1.54$ eV and -1.57 eV, respectively), ΔG_{CR} must be around -1.29 eV in HFIP. The hydrogen-bonds between HFIP and AQ are strengthened upon reduction of the AQ moiety,^[9, 13] hence proton motion is expected to contribute to the overall reorganization energy (λ) associated with electron transfer.^[14] The change in τ_{CR} between CH_2Cl_2 and HFIP is therefore most likely the result of the combined effect of significant changes in both ΔG_{CR} and λ . Specifically, what we mean is that while ΔG_{CR} increases from -1.54 eV to -1.29 eV when going from pure CH_2Cl_2 to pure HFIP (see above), the reorganization energy (λ) increases simultaneously. Prior investigations on related quinone systems demonstrated that hydrogen-bonding between alcohols and quinone anions can lead to a significant increase of λ .^[17] The precise change of λ (in eV) in our system cannot be determined from the available experimental data.^[18] However, even without having a precise number for the change in λ at hand, it appears reasonable to conclude that the experimentally observed increase in the lifetime of the fully charge-separated state from ~50 ns to ~2000 ns is caused by the combined effects of a increase in ΔG_{CR} (ΔG_{CR} becomes less negative) and an increase in λ . In other words, in HFIP there is less driving-force and a higher activation barrier than in CH_2Cl_2 , and this decelerates charge-recombination.

One would expect charge-separation rates to be affected by HFIP addition as well, but investigation of these processes requires higher temporal resolution than what was available for the current study. In the previously reported ruthenium triad the quantum yield for formation of the fully charge-separated state was found to be greater than 64 percent.^[8] For the osmium triad presented here, this quantum yield is yet to be determined based on the abovementioned measurements at higher temporal resolution. It is planned to address this issue in a more comprehensive paper (including a comparison of osmium, ruthenium and iridium triads) at a later stage.

In summary, we have demonstrated that the lifetime of a photo-generated charge-separated state can be increased from ~50 ns to ~2000 ns simply by changing from aprotic solvent to strongly hydrogen-bond donating HFIP. This principle for increasing lifetimes of charge-separated states should be applicable to many other molecular donor-bridge-acceptor systems with protonatable electron acceptors.

Experimental Section

The synthesis of the triarylamine-bipyridine-anthraquinone ligand corresponding to the rigid rod-like molecular axis of the TAA-Os^{II}-AQ triad has been previously reported.^[8] For complexation of this bidentate ligand to osmium(II), we did proceed as follows: The free ligand (30 mg, 0.037 mmol) was refluxed with Os(bpy)₂Cl₂ (21 mg, 0.037 mmol) in ethylene glycol (15 mL) overnight. After the reaction mixture had been cooled to room temperature, water was added. The desired complex was extracted from this solvent mixture with CH₂Cl₂, and the organic solvent was removed subsequently on a rotary evaporator. The crude product was subjected to column chromatography on silica gel (Machery Nagel, Silica Gel 60) using an eluent mixture comprised of 90% acetone, 9% water and 1% aqueous saturated KNO₃ solution (v:v:v). Acetone was evaporated from the desired chromatography fraction, and the complex was precipitated from the aqueous solution by adding a saturated solution of KPF₆ in water. The green solid was filtered, washed with de-ionized water and diethyl ether. Finally, it was dried under vacuum (42 mg, 72% yield). ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ [ppm] = 1.81 (s, 3 H, CH₃), 1.91 (s, 3 H, CH₃), 1.97 (s, 3 H, CH₃), 2.34 (s, 3 H, CH₃), 3.74 (s, 6 H, OCH₃), 6.77 (m, 8 H, amine), 6.99 (s, 1 H), 7.14 (s, 1 H), 7.16 (s, 1 H), 7.35 (m, 2 H), 7.46 (m, 3 H), 7.57 (m, 2 H), 7.67 (m, 2 H), 7.73 (m, 1 H), 7.82 (m, 6 H), 7.92 (m, 4H), 8.20 (m, 1 H), 8.30 (m, 3 H), 8.45 (m, 4 H), 8.59 (m, 2 H). ES-MS: m/z = 650.71 (calculated 650.71 for C₇₄H₅₉N₇O₄Os²⁺). Anal. Calcd. for C₇₄H₅₉N₇O₄OsP₂F₁₂ · 2 H₂O: C 54.64, H 3.90, N 6.03. Found: C 54.41, H 3.79, N 6.04.

NMR spectroscopy was performed on Bruker Avance DRX 300 and Bruker B-ACS-120 spectrometers. Electron ionization mass spectrometry (EI-MS) was made with a Finnigan MAT8200 instrument, and for elemental analysis a Vario EL III CHNS analyzer from Elementar was employed. Optical absorption spectra were recorded on a Cary 300 instrument from Varian. Transient absorption spectroscopy was performed using the second harmonic of a Quantel Brilliant b laser for excitation and an LP920-KS spectrometer from Edinburgh Instruments for detection. Prior to the time-resolved measurements, solutions were thoroughly deoxygenated by bubbling nitrogen gas through them.

Cyclic voltammetry was performed using a Versastat3-200 potentiostat from Princeton Applied Instruments, equipped with a glassy carbon disk electrode and a Pt wire as a counter electrode. A silver wire served as a quasi-reference electrode; ferrocene was added for internal voltage calibration. Only dry and deoxygenated solvents were used for electrochemistry. Spectro-electrochemical investigations occurred in the Cary 300 instrument using a commercially available optically transparent thin-layer (OTTLE) cell.^[15]

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Keywords: electron transfer • hydrogen bonding • proton transfer • kinetics • proton-coupled electron transfer

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- [18] Temperature-dependent investigations can potentially shed light on this issue, but this has to be the subject of a full paper that is to be published at a later stage.

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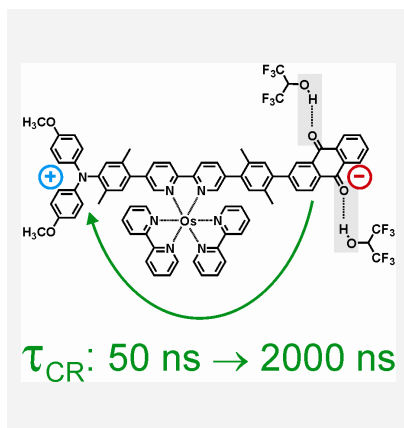
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Entry for the Table of Contents

Electron transfer

Jihane Hankache, Oliver S.
Wenger* Page – Page

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The lifetime of a charge-separated state increases from ~50 ns to ~2000 ns when changing the solvent from aprotic CH₂Cl₂ to the strong hydrogen-bond donor hexafluoroisopropanol.