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Electron Transfer

Electron Transfer and Multi-Electron Accumulation in $ExBox^{4+}$**

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Abstract: *Molecules capable of accepting and storing multiple electrons are crucial components of artificial photosynthetic systems designed to drive catalysts, such as those used to reduce protons to hydrogen. $ExBox^{4+}$, a boxlike cyclophane comprising two π-electron-poor extended viologen units tethered at both ends by two p-xylylene linkers, has been shown previously to accept an electron through space from a photoexcited guest. Herein is an investigation of an alternate, through-bond intramolecular electron-transfer pathway involving $ExBox^{4+}$ using a combination of transient absorption and femtosecond stimulated Raman spectroscopy (FSRS). Upon photoexcitation of $ExBox^{4+}$, an electron is transferred from one of the p-xylylene linkers to one of the extended viologen units in ca. 240 ps and recombines in ca. 4 ns. A crystal structure of the doubly reduced species $ExBox^{2+}$ was obtained.*

Artificial photosynthetic reaction centers, capable of converting light into chemical energy, are highly desirable, yet complex alternative energy systems.[1] Significant progress[2] has been made in developing several aspects of these reaction centers, such as those relating to charge separation and transport in chromophore–catalyst dyads and the assembly of these components into large arrays. Another critical aspect of these arrays is the buildup of charge required for multi-electron processes,[3] for example, those involved in water splitting. This essential component must be 1) highly stable, 2) easily tailored, and 3) possess a wide range of accessible redox states.

Recently, we described the potential for a novel cyclophane,[4] for which we coined the name $ExBox^{4+}$, to function as a multi-electron acceptor in artificial photosynthetic systems.[5] $ExBox^{4+}$ (Figure 1) is a π-electron-poor, semi-

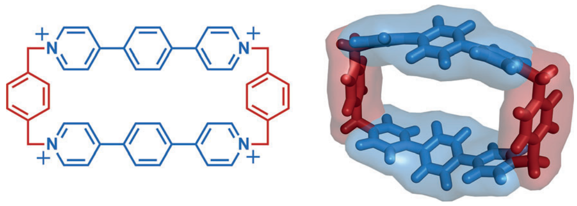

Figure 1. Structural formula of $ExBox^{4+}$ comprising two electron-rich *p*-Xy (red) and two electron-poor $ExBIPY^{2+}$ (blue) units.

rigid cyclophane comprising two 4,4′-phenylene-linked extended bipyridinium ($ExBIPY^{2+}$) units, tethered by two *p*-xylylene (*p*-Xy) linkers, leading to a box-like geometry.[6] In common with the well-characterized cyclobis(paraquat-*p*-phenylene)[7] ($CBPQT^{4+}$), $ExBox^{4+}$ 1) exists as a multicationic species, 2) has several accessible mixed-valence states, and 3) exhibits molecular recognition which aids in self-assembly with π-electron rich guests.[6] Although the *p*-Xy linkers within $CBPQT^{4+}$ can be modified covalently,[8] similar modifications have yet to be demonstrated in the case of $ExBox^{4+}$. However, $ExBox^{4+}$ provides a significant advantage over $CPBQT^{4+}$, with a cavity length of 15 Å, compared to that of 11 Å for $CBPQT^{4+}$. This increase in the cavity length allows $ExBox^{4+}$ to bind large polycyclic aromatic hydrocarbons (PAHs), several of which function as building blocks in artificial photosynthetic systems as chromophores and electron donors. In the case of complexed perylene, that is, $ExBox^{4+}\subset$perylene, photoexcitation results in the charge-separated state $ExBox^{3+}\subset$perylene^{+}.[5] This electron-transfer process, involving an acceptor with multiple accessible mixed-

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$xBox^{4+}$ = a boxlike cyclophane comprising two π-electron-poor extended viologen units tethered at both ends by two *p*-xylylene linkers.

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valence states, provides a promising system for accumulating electrons for artificial photosynthesis.

In this investigation, we report two advances in the potential application of $ExBox^{4+}$ in artificial photosynthesis. They are 1) through-bond electron transfer to the $ExBIPY^{2+}$ unit of $ExBox^{4+}$ and 2) confirmation in the solid state of the ability of $ExBox^{4+}$ to accept and stabilize two electrons. In addition to carrying out computational studies, we take advantage of a wide variety of experimental techniques, including femtosecond transient absorption (fsTA) and nanosecond transient absorption (nsTA) spectroscopies, femtosecond stimulated Raman spectroscopy (FSRS), and X-ray crystallography to highlight these two properties of $ExBox^{4+}$.

The excited-state dynamics of $ExBox^{4+}$, upon ultraviolet photoexcitation, span from the picosecond to the microsecond regimes. Following selective excitation of the $ExBIPY^{2+}$ chromophore in $ExBox^{4+}$ with a 330 nm, 150 fs pulse, the initial transient absorption spectrum is characterized by two strong absorptions at 490 and 1410 nm (Figure 2),

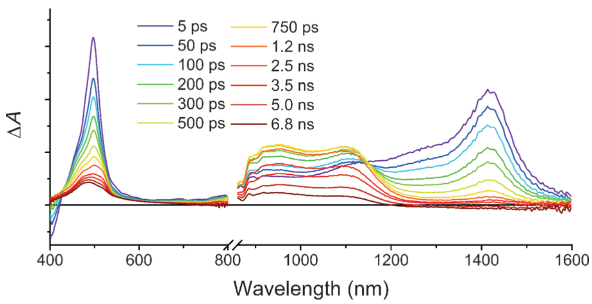

Figure 2. Combined visible and near-infrared femtosecond transient absorption spectra recorded in MeCN of $ExBox^{4+}$, exciting at $\lambda_{ex} = 330$ nm (0.6 μJ pulse^{-1}), highlighting the characteristic reduced $ExBIPY^{+}$ absorption from 900–1200 nm. Relative amplitudes on either side of the break are arbitrary.

which are assigned to $^{1}*ExBox^{4+}$ (see reference data given below). Both absorptions decay in $\tau = 223 \pm 11$ ps (84%) and 3.3 ± 1.3 ns (16%) (fit at $\lambda_{max} = 1410$ nm, see the Supporting Information), and are replaced by broad 900–1200 nm and much weaker 1410 nm absorptions that appear in $\tau = 263 \pm 24$ ps and decay with $\tau = 3.6 \pm 0.7$ ns (fit at $\lambda_{max} = 1100$ nm, see the Supporting Information). These absorptions correspond well to the absorption of $ExBIPY^{+}$ measured[7g] spectroelectrochemically in MeCN, but differ slightly in relative band intensities. Thus, the minor 3.3 ns (16%) component in the decay kinetics of $^{1}*(ExBox^{4+})$ at 1410 nm results from a small residual $ExBIPY^{+}$ absorption. Reduction of an $ExBIPY^{2+}$ unit can only occur in this case by oxidation of an adjacent, covalently-attached *p*-Xy linker by a through-bond pathway—differentiating it from the through-space pathway involved in host⊂guest charge transfer.[5]

To gain a better understanding of the photoexcited $ExBox^{4+}$, we investigated phenylene-extended methyl viologen[9] (MPV^{2+}) as a control in which the specific dynamics of a single $ExBIPY^{2+}$ unit can be studied separately from that of the cyclophane as a whole under the same conditions. Without any covalently attached electron donors, MPV^{2+} should only exhibit excited state relaxation. The $^{1}*(MPV^{2+})$ excited state decays in $\tau = 1.56 \pm 0.02$ ns (fit at $\lambda_{max} = 1458$ nm, see the Supporting Information), and the broad 900–1200 nm absorption band is absent. A small percentage of the transient spectrum at 480 nm persists past the experimental window (ca. 6 ns) and is characteristic of a long-lived triplet species formed by spin-orbit intersystem crossing[10] (SO-ISC) from the singlet excited state. The contour plots in Figure 3 A,B

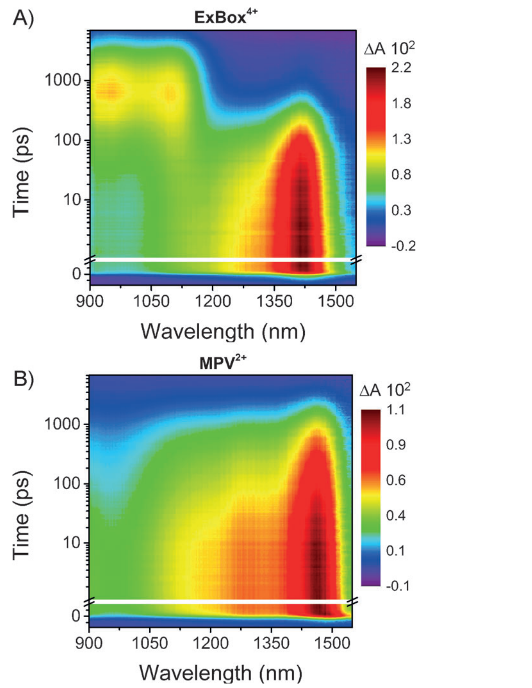

Figure 3. Contour plots of the NIR fsTA spectra recorded in MeCN of $ExBox^{4+}$ (A) and MPV^{2+} (B) ($\lambda_{ex} = 330$ nm), highlighting the lack of the intramolecular charge transfer (ICT) peak (900–1200 nm) in the spectra of MPV^{2+} after photoexcitation. This discrepancy is attributed to the presence of the *p*-Xy linkers in $ExBox^{4+}$.

show the results of photoexcited $ExBox^{4+}$ and MPV^{2+} in the near-infrared (NIR) region, which allow for the direct assignment of the peaks at 490 and 1410 nm present in both $ExBox^{4+}$ and MPV^{2+} to their S_1 excited states, and the feature (Figure 3 A) from 900–1200 nm to the charge-shifted species ($ExBIPY^{+}$–p-Xy^{+}).

To corroborate these findings, femtosecond stimulated Raman spectroscopy (FSRS) was performed on $ExBox^{4+}$. FSRS offers a high degree of both temporal and spectral resolution and avoids much of the peak overlap observed in visible and NIR transient absorption experiments. Additionally, the Raman signatures[5] of the reduced species $ExBox^{3+}$ have already been characterized. In this investigation, $ExBox^{4+}$ was photoexcited with a 330 nm actinic pump pulse, followed by a 500 nm Raman pump pulse, on resonance with the strong excited-state absorption for both $ExBox^{4+}$ and MPV^{2+}. The FSRS spectra of $ExBox^{4+}$ exhibit several vibrational modes (see the Supporting Information), all of which decay with lifetimes in good agreement with the visible and NIR fsTA experiments. A single peak, centered around

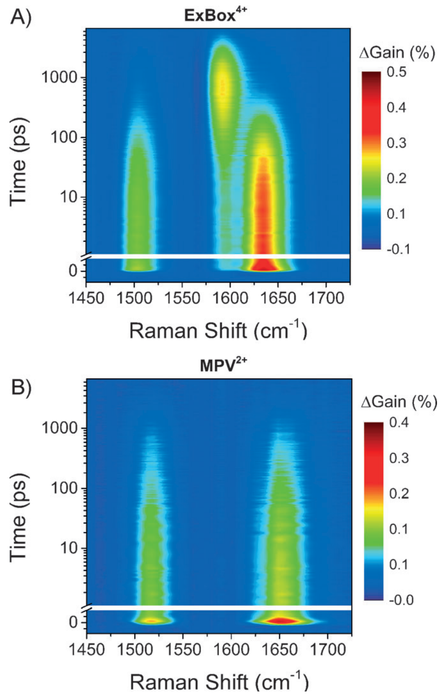

Figure 4. Contour plots of the FSRS spectra recorded in MeCN of $ExBox^{4+}$ (A) and MPV^{2+} (B) ($\lambda_{ex} = 330$ nm, $\lambda_{RP} = 500$ nm), highlighting the lack of the reduced $ExBIPY^{1+}$ peak at 1590 cm^{-1} in the spectra of MPV^{2+} after photoexcitation.

1590 cm^{-1} appears in $\tau = 310 \pm 10$ ps (fit at 1590 cm^{-1}, see Supporting Information), and is characteristic[5] of the quadrant stretches of $ExBox^{3+}$. FSRS performed on MPV^{2+} under the same conditions shows a similar set of peaks which decay in $\tau = 1.55 \pm 0.05$ ns (fit at 1650 cm^{-1}, see Supporting Information). The contour plots in Figure 4 A,B show the FSRS results of photoexcited $ExBox^{4+}$ and of MPV^{2+}. It is worth noting that the peak centered around 1590 cm^{-1} in the case of $ExBox^{4+}$ (Figure 4 A) is absent from the MPV^{2+} spectrum (Figure 4 B). Comparison of the fsTA and FSRS of $ExBox^{4+}$ with that of MPV^{2+} and previous results[5] on an $ExBox^{4+}$ host–guest complex suggests that the cyclophane undergoes intramolecular charge transfer (ICT) from one *p*-Xy linker to one $ExBIPY^{2+}$ unit with $\tau_{ICT} \approx 240$ ps, and subsequently recombines with $\tau_{CR} \approx 4$ ns.

Density functional theory (DFT) was utilized to gain a better understanding of the dynamics occurring upon photoexcitation of $ExBox^{4+}$ and MPV^{2+}. Their structures were both geometry optimized in the ground, singlet-excited, and triplet-excited state using DFT and TD-DFT (B3LYP, 6-31++G*). Normal mode analyses were performed on the singlet and triplet excited states of MPV^{2+}, as well as on the singly reduced MPV^{+} and oxidized *p*-Xy^{+}, to assist with the assignments of peaks observed in the FSRS spectra. Using the reduced MPV^{+} vibrations, the Raman peak of interest at 1590 cm^{-1} is assigned to quadrant stretches of the pyridinium units and *p*-phenylene linkers of the reduced $ExBIPY^{+}$ unit. A quadrant stretch of the oxidized *p*-Xy^{+} unit also contributes a shoulder at 1639 cm^{-1} to this peak, albeit of a much lower intensity. Singlet and triplet excited state $ExBox^{4+}$ and MPV^{2+} vibrations, along with the remaining charge-separated $ExBox^{4+}$ vibrations, are discussed in more detail in the Supporting Information.

The HOMO of $ExBox^{4+}$ is highly localized on the *p*-Xy linker, while the LUMO is delocalized across both $ExBIPY^{2+}$ units. These orbital localizations (see the Supporting Information) support the proposed charge transfer process, where an electron—in this case from a covalently attached *p*-Xy linker—is transferred to the delocalized LUMO of $ExBox^{4+}$. The nearly orthogonal orientation of the *p*-Xy linker/donor π systems relative to those of both $ExBIPY^{2+}$ acceptors results in decreased donor–acceptor electronic coupling, a feature which might explain the relatively slow electron-transfer rate, considering the short charge-separation distance from the *p*-Xy linker to $ExBIPY^{2+}$. Delocalization of the transferred electron across $ExBIPY^{+}$ would exacerbate this poor donor–acceptor overlap, resulting in recombination on a time scale of the order of nanoseconds.

The energy of the lowest-lying singlet state of $ExBox^{4+}$ has been shown[5] to be $E_S = 3.5$ eV. The ion pair energy of the intramolecular charge-transfer state was determined to be $\Delta G_{IP} = 2.61$ eV, using an expression (see the Supporting Information) developed by Weller,[11] and the difference between E_S and ΔG_{IP} gives the free energy for photoinduced charge separation, $\Delta G_{CS} = -0.89$ eV. A driving force of this magnitude is not surprising since the $ExBIPY^{2+}$ units undergoing reduction are similar to methyl viologen, which has been used extensively[12] as an electron acceptor. Using TD-DFT, the energy of the lowest-lying triplet was calculated to be $E_T = 1.98$ eV, a value which is energetically downhill from E_s. Additionally, E_T is lower in energy than ΔG_{IP}, providing favorable energetics which could allow for triplet formation from the charge-shifted species by spin-orbit, charge-transfer intersystem crossing (SOCT-ISC), a process which requires nearly orthogonal donor–acceptor orbitals as is the case for $ExBIPY^{+}$–*p*-Xy^{+}.[13]

To probe the small, long-lived triplet feature present in the fsTA spectra of both MPV^{2+} and $ExBox^{4+}$, nanosecond transient absorption (nsTA) spectroscopy was utilized. Representative spectra and kinetics of $ExBox^{4+}$, photoexcited at $\lambda_{ex} = 355$ nm (1.5 mJ $pulse^{-1}$) are provided in the Supporting Information. Under air-free conditions, nsTA showed that this 480 nm peak again persists beyond the experimental window (4.5 μs) in both systems. When the $ExBox^{4+}$ and MPV^{2+} solutions were exposed to air, the lifetime of this species fell to 1 μs and 600 ns, respectively. Accordingly, interaction with oxygen most likely accounts for the difference in rates between the air-free and oxygenated samples. Based on these results, this long-lived species is most likely a triplet state localized on the $ExBIPY^{2+}$ unit. The data for MPV^{2+} indicate that a small amount of spin-orbit-induced intersystem crossing occurs in competition with excited state decay to ground state. Moreover, the enhanced $^{3*}(ExBox^{4+})$ yield observed relative to that of $^{3*}(MPV^{2+})$ could be attributed to the availability of a second pathway, that is, SOCT-ISC, which occurs as a result of the return charge shift reaction that restores the $ExBox^{4+}$ ground state.

We have established that electron transfer from the *p*-Xy linker of $ExBox^{4+}$ to an $ExBIPY^{2+}$ unit is possible, demonstrating that a second route for electron accumulation by $ExBox^{4+}$ exists. Compounds similar to $ExBox^{4+}$, such as $CBPQT^{4+}$, can be modified covalently[8] on the *p*-Xy linkers. Indeed, work is currently underway to functionalize the *p*-Xy linker of $ExBox^{4+}$ with a chromophoric electron donor, capable of electron transfer to $ExBox^{4+}$. This pathway could, in principle, function along with through-space electron transfer from an included guest.

Recent studies[5,6] have demonstrated the generation of doubly-reduced $ExBox^{2+}$ in solution by both chemical and electrochemical reduction. Unfortunately, on account of the overlapping one- and two-electron reduction potentials, electrochemically generated solutions consist of both $ExBox^{0}$ and $ExBox^{2+}$. While chemical reduction of $ExBox^{4+}$ with Zn dust avoids this issue, solutions are unstable for any useful period of time, and hence characterization is difficult. Single crystals, suitable for X-ray crystallography, of a mixture of $ExBox^{2+}$ and $ExBox^{4+}$ resulted from reduction of $ExBox^{4+}$ under inert conditions using 2.5 equivalents of cobaltocene. The crystallization, which was carried out inside an argon-filled glovebox at 0 °C, led to a mixture of oxidation states, as indicated by the presence and position of 3 PF_6^- counterions in the unit cell. The solid-state superstructure (Figure 5) con-

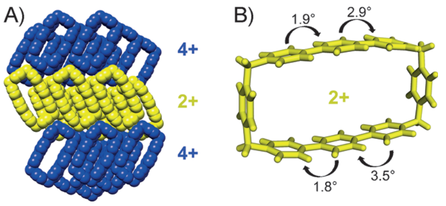

Figure 5. A) A space-filling representation of the crystal packing of the superstructure consisting of the mixed oxidation states, $ExBox^{4+}$ (blue) and $ExBox^{2+}$ (yellow). B) Stick representation of the crystal structure of $ExBox^{2+}$, containing two nearly planar $ExBIPY^{+}$ moieties. This solid-state structure provides confirmation that multi-electron transfer to $ExBox^{4+}$ is possible, and occurs by distribution along both ExBIPY units.

firms our previous observations[5] based on computational studies and resonance Raman experiments. The pyridinium-phenylene torsional angles within $ExBox^{2+}$ are significantly lower (1.8°–3.5°) than those (3.4°–20°) of $ExBox^{4+}$, confirming that both $ExBIPY^{2+}$ units become flattened in conjunction with the delocalization of unpaired electrons. This observation provides a clear indication that the stabilization of two electrons in $ExBox^{4+}$ is not only possible, but occurs in the expected fashion to distribute the radical electrons along both $ExBIPY^{2+}$ units.

In summary, a viologen-based cyclophane has been photoexcited and investigated on the pico- to the microsecond timescales. The results reported herein reveal a through-bond pathway for electron transfer to $ExBox^{4+}$ in addition to the already established through-space channel. Perusal of the solid-state structures of $ExBox^{4+}$ and $ExBox^{2+}$, with both redox states present in the single crystal, confirms that multiple electrons, when transferred to $ExBox^{4+}$, are distributed along both $ExBIPY^{2+}$ units which, in turn, become flattened and form semiquinoidal structures capable of stabilizing unpaired electrons. In the context of artificial photosynthesis, the next logical step towards utilizing $ExBox^{4+}$ will be to modify covalently one or both of the *p*-xylylene linkers with a simple chromophoric electron donor capable of reducing $ExBox^{4+}$ following photoexcitation. This cyclophane-based host should be able to bind a second, different electron donor forming a complex capable of both through-bond and through-space electron transfer to the cyclophane, by taking advantage of photoexcitation at multiple wavelengths during a single experiment.

Experimental Section

The details of the visible/near-infrared femtosecond transient absorption and femtosecond stimulated Raman spectroscopy experiments have been published elsewhere.[5] Both experiments utilize an ultraviolet (330 nm) femtosecond excitation pulse, derived from the second harmonic of the 660 nm output of an optical parametric amplifier. Nanosecond transient absorption experiments, also previously reported,[14] utilize the 355 nm frequency-tripled output of a Nd:YAG laser. Density functional theory (DFT) and time-dependent DFT (TD-DFT) were performed, using the B3LYP exchange-correlation functional with the 6-31++G* basis set, as implemented[15] in QChem 4.0.

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