CHAPTER 4

Studies of Spectroelectrochemistry and Photochemistry of bridged Os Dimer [(Phen)$_2$Os(tatpp)Os(Phen)$_2$][PF$_6$]$_4$
1 - Introduction

Nature uses multiple chromophoric assemblies (light harvesting complexes) to capture sunlight and transfer the energy/electrons into the photosynthetic reaction centres of green plants and bacteria. One can mimic the functional properties of such natural systems, if one could develop a viable design strategy for the construction of well-defined polymeric multichromophoric arrays. Osmium-polypyridyl complexes are one of the most widely studied chromophores for molecular light-to-chemical energy conversion because of their favorable photophysical properties and chemical stability. Schlike and coworkers have shown that in homodinuclear complexes of osmium, the fluorescence of the oligophenylenespacer is quenched by energy transfer to the metal-based units, which exhibit the absorption spectra and excited state properties of the corresponding [Os(bpy)]

We are recently interested to report that the dinuclear Os(II) complexes E and F (Fig-1) were capable of reversibly storing a maximum of two or four electrons, respectively, upon visible light irradiation in the acetonitrile and in the presence of sacrificial reductant agents. In both complexes, it was proposed that the central part of the bridging ligand plays both the role of the electron acceptor subunit for the photoinduced charge-separation process and the role of the multielectron storage unit. Reduction of the tatpp bridging ligand in E was observed directly using transient spectroscopy and, remarkably, showed that the charge-separated intermediate had a life time of 2.3 μs in dichloromethane.

In this paper we report on the reduction behavior of E. Importantly, we show that the photochemical ability of E to undergo two sequential one-electron reductions (to form
the singly reduced $E^-$ and the doubly reduced $E^{2-}$ is maintained in mixed water-acetonitrile solutions under basic conditions. The photochemical activity of $E$ in aqueous media considerably expands its potential use towards a number of important substrates, including water, and its environmental adaptability. The absorption spectra of the two reduced species, $E^-$ and $E^{2-}$, were found to depend on the solution pH, indicative of protonation(s) at the central reduced sites. To determine the identity of these solution species, we first undertook an extensive analysis of the absorption spectra of the redox and protonation isomers of $E$ as generated by chemical, spectroelectrochemical and photochemical means in both dry acetonitrile solution and mixed water-acetonitrile solutions. The notation used in Fig-1 will be used to identify these isomers, which are related by one-electron reduction/oxidation vertically and by protonation/deprotonation horizontally. It is important to realize that $E$ itself is a large metal complex carrying an over all 4+ charge from the two Os(I) ions coordinated to the tatpp bridging ligand. We note that many of the isomers can exist in multiple tautomeric forms, and we look necessary data to distinguish between them. The tautomers shown reflect our current best guess which is based, in part, on a comparison with the tautomers established for various redox isomers of tetraazapentacene$^{13}$.

2 - Experimental Section

(a) Materials

Cobaltacene (Alfa), trifluoroacetic acid (Alfa), and sodium borohydride(Aldrich) were used as received. Acetonitrile (Aldrich, 99.93+%, HPLC grade) was kept over molecular sieves (3Å) and passed through a column packed with neutral chromatographic alumina just before use. The complex $E$ was prepared on the similar lines as described$^{16}$ for ruthenium analogue. All redox and protonation titrations were carried out in a nitrogen atmosphere glove box. Stock solutions of $E$ (1.09×10$^{-4}$M), Co(Cp)$_2$(0.011M), and trifluoroacetic acid (TFA) (0.013M) were prepared in thoroughly degassed acetonitrile. $E^-$ and $E^{2-}$ were
Fig. 1 Structural drawing of the complexes E & Q and the related redox and protonation isomers for E. The structures of the related DPPZ and TPPHZ ligands are also shown.

\[ \bullet = [\text{Os(phen)}]^{2+} \]
generated by stochiometric addition of TFA to solutions of E and E⁺. Reduction with sodium borohydride (0.5M in diethoxy ether) were done using a 10 fold molar excess of reductant to E in 20% water-acetonitrile.

(b) Instrumentation

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed using a PC-controlled potentiostat (CH Instruments< electrochemical analyser). Either glassy carbon (1.5) mm diameter disk or Au (1.0mm diameter disk) working electrodes from Cypress Systems were used. Immediately before use, the electrode were polished to mirror finish with wet alumina (Buehlar,0.05μm), folled by rinsing with Millipore Milli-Q water, dried, and stored in acetonitrile during the preparation of the electrochemical cell. A Pt wire and a premium 'noleak' Ag/AgCl reference electrode were used as counter and reference electrodes respectively, and potentials were quoted with respect to this reference. Experiments were conducted in dry acetonitrile (Aldrich,99.93+% HPLC grade) with 0.1M Nb₄⁺PF₆⁻ (Sigma) as supporting electrolytes, and in 20% water-acetonitrile mixtures at four selected pH values in the range 4-12. In these cases, the aqueous portion contained 0.1M NaH₂PO₄/0.1 M K₂HPO₄ buffer, and the pH of the water-acetonitrile solutions were deoxygenated by bubbling with Ar, and this atmosphere was maintained over the electrochemical solution throughout the course of experiment. The cell ohmic resistance was always compensated.

Spectroelectrochemical measurements were performed in tranmission mode. A quartz thin layer cell containing a gold mesh as working electrode¹⁵ was placed inside a 1-cm² path quartz cuvette containing ca 0.5 mL of E solution (2-10mm). The E solution filled the thin layer space where the gold mesh was located by capillary action¹⁶. The counter electrode were laterally located in the quartz cuvette and next to the capillary slit.

For the photochemical experiments, all solutions were sealed in a quartz or glass
cuvette with a rubber septum and degassed for 10 minutes with nitrogen or argon gas prior to irradiation. Typical solutions were 18 mm in M and 0.25 M triethylamine (TEA). The cuvette were immersed in a water bath (18 ± 2°C) and irradiated using a 100 W tungsten bulb with a 360 nm cutoff UV filter. The source-to-sample distance was nearly 3 cm, and the measured photon flux at the sample was 1.125 × 10^-6 lux. The progress of the photochemical reaction was maintained by periodically removing the cuvette from the water bath and recording the absorption spectra. For the 20% water-acetonitrile solutions, the pH of the solution was adjusted by adding acetic acid. The solution composition for electrochemical and photochemical reactions in 20% water-acetonitrile could not be made identical due to the requirement for NBu4PF6 in the electrochemical experiments and for TFA in the photochemical experiments and the occasional set of conditions where the water and acetonitrile components underwent phase separation.

3 - Results

(I) Chemical Reduction and Protonation: The singly (E^-) and doubly (E^-2) reduced forms of E were generated in situ via stoichiometric reductions with cobaltocene in acetonitrile, and their absorption spectra are shown in Fig 2a. Cobaltocene is a strong one-electron reducing agent (-1.0 V vs Ag/AgCl in acetonitrile) and thermodynamically capable of generating both E^- and E^-2. The cobaltacene ion produced is light yellow in color and add no appreciable absorption to the visible and near-IR portion (350-1000 nm) of the absorption spectra. Both E^- and E^-2 show new, strong ligand-centred (LC) band in the visible and near-IR portion of the spectrum. Formation of E^- yields two new absorptions in the near-IR at 860 nm (weak) and 970 nm (strong) which appear to be vibronic bands of the central reduced aromatic unit (tatpp radical anion) plus a partial bleaching of absorption at 325 nm. We also observe that the maximum of the 445 nm peak in M is blue shifted to 415

112
Figure 2. (a) Absorption spectra of $E$ (ca. 12 $\mu$M, solid line) after addition of 1.0 molar equiv of cobaltacene (dashed line, $E$) and 2.0 molar equiv of cobaltacene (dotted line, $E^2$) in dry degassed acetonitrile. (b) Absorption spectra of $E^2$ (ca. 12$\mu$M, dotted line) after addition of 1.0 molar equiv of TFA (dashed line, $HE$) and 2.0 molar equiv of TFA (solid line, $H_2E$) in dry degassed acetonitrile. (c) Absorption spectra of $E$ (ca. 12$\mu$M, dotted line) after addition of 1.0 equiv of TFA (solid line, $HE$) in dry, degassed acetonitrile. Spectrum of $E$ (dashed line) and $H_2E$ (dotted line) overlaid at same temperature.

Figure 3. Cyclic (a) and differential pulse (b) voltammograms of 0.03 mM $E$ in acetonitrile containing 0.1 M NBu$_4$PF$_6$. (a) potential scan rate = 50mV/s. (b) Pulse amplitude =0.05 V, step size= 0.004V, pulse duration =0.05 s, and pulse period =0.2s. The working electrode for both measurements was glassy carbon disk (1.5 mm diameter)
nm; however, a strong shoulder remains at 445 nm which is attributed to the Os-phen type MLCT. Addition of a second equivalent of IR peaks to give a strong band at 685 nm with a shoulder at 635 nm (see Fig 2a). This second reduction also results in the complete bleaching of the tatpp LC band at 325 and 445 nm.

The absorption spectra for protonated complexes $\text{HE}^+$ and $\text{H}_2\text{E}$, formed by addition of 1 and 2 equivalents of TFA to $\text{E}^{2-}$ respectively, are shown in Fig 2b. The most noticeable change upon formation of $\text{HE}^+$ is the appearance of a third band at 725 nm and a slight blue shift of a third band at 725 nm and a slight blue shift of the nearby bands to 655 and 608 nm (sh). Addition of the second proton gives $\text{H}_2\text{E}$ which has a broad, strong absorption centred at 580 nm. We note that the process is reversible and that stepwise deprotonations of $\text{H}_2\text{E}$ with NaOMe yielded the spectra for $\text{HE}^+$ and $\text{E}^{2-}$ respectively. $\text{H}_2\text{E}$ can also be prepared by reduction with excess NaBH$_4$ in acetonitrile and 5% acetic acid, and spectroscopic monitoring of this process shows no sign of any singly reduced intermediates. The UV-visible spectroscopic data for the complexes are gathered in Table 1.

Protonation of $\text{E}^{2-}$ with TFA presumably would yield $\text{HE}$; however, the resulting absorption spectrum, shown in Fig 2c, suggests that $\text{HE}$ may disproportionate as indicated in reaction 1, we observe two features in the spectrum of $\text{HE}$

$$2\text{E}^{2-} + 2\text{H}^+ \rightarrow 2\ "\text{HE}" \rightarrow \text{E} + \text{H}_2\text{E}$$

supporting this hypothesis: a strong, broad absorption characteristic of $\text{H}_2\text{E}$ at 580 nm, and the reappearance of some intensity to the bands at 445 and 325 nm characteristic of $\text{E}$. For comparison, the spectra of $\text{E}$ and $\text{H}_2\text{E}$ at the same molar concentrations are overlaid with that of $\text{HE}'$ is Fig 2c. The fact that the peak at 580 nm for $\text{HE}$ is one-half as intense as the same peak observed in a pure sample of $\text{H}_2\text{E}$ is particularly revealing. Also, a 1:1 mixture of $\text{E}$ and $\text{H}_2\text{E}$ gives the same spectrum as $\text{HE}$. So either these two do react to give $\text{HE}$, which coincidentally has a spectrum much like the sum of its components or the two do not
Table 1. Spectroscopic data of the Dimeric complexes in Deaerated acetonitrile.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption at 298K, $\lambda_{max}$, nm ($e,M^{-1}cm^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[(\text{phen})_2\text{Os(tatpp)Os(phen)}_2]^{4+}(E)$</td>
<td>325(72900), 425sh(42600), 445 (54300)</td>
</tr>
<tr>
<td>$[(\text{phen})_2\text{Os(tatpp)Os(phen)}_2]^{3+}(E^1)$</td>
<td>325sh(37600),415(54800),445sh(46100), 860(14100),970(35600)</td>
</tr>
<tr>
<td>$[(\text{phen})_2\text{Os(tatpp)}^2\text{Os(phen)}_2]^{2+}(E^2)$</td>
<td>430sh(40000)445(41900),635(25900),</td>
</tr>
<tr>
<td>685(55400)</td>
<td></td>
</tr>
<tr>
<td>$[(\text{phen})_2\text{Os(Htatpp)Os(phen)}_2]^{4+}(HE)$</td>
<td>418(43600),444sh(38000),608(27600),655(38000),725(43600)</td>
</tr>
<tr>
<td>$[(\text{phen})_2\text{Os(H_2tatpp)Os(phen)}_2]^{4+}(H_2E)$</td>
<td>580(37400),445(34100)</td>
</tr>
<tr>
<td>$[(\text{phen})_2\text{Os(tatpp)}^4\text{Os(phen)}_2]^{4+}(E^4)$</td>
<td>448(23400)</td>
</tr>
</tbody>
</table>
comproportionate and the resulting spectrum is simply that of the 1:1 mixture. The latter explanation seems far more reasonable, especially when one considers that a 400 nm blue shift of the peaks in the near-IR to give a new maximum at 580 nm upon a single protonation step is unlikely\textsuperscript{19,20}.

(II) Cyclic Voltammetry and Spectroelectrochemistry of E

(A) In acetonitrile: The cyclic voltammogram for 0.03 mM E in 0.1 M NBu\textsubscript{4}PF\textsubscript{6} - acetonitrile solution in the potential region from 0.4 to -1.6 V is shown in the Fig 3. The voltammetric scan was started at 0.4 V and scanned in the negative direction down to -1.6 V. Three quasireversible tatpp-centred reductions are observed and are indicated as A\textsubscript{1}/C\textsubscript{1}, A\textsubscript{2}/C\textsubscript{2} and A\textsubscript{3}/C\textsubscript{3} in the voltammogram. These voltammetric peaks reflects two monoelectronic and one bielectronic processes with \(E_{1/2}\) potentials of -0.22, -0.71, and -1.28 V vs Ag/AgCl, respectively. Our earlier reported data were based on measurements made with 0.5 mM E solutions and are reproducible under these conditions. Only upon the dilution of the solution (0.03 mM E solutions and are reproducible under these conditions. Only upon the dilution of the solution (0.03 mM E in this work) do we observe the voltammogram presented in figure 3. DPV data (see Fig 3, inset) corroborate the information provided by the CV and show the A\textsubscript{3}/C\textsubscript{3} process to involve twice as many electrons as the other two. Not shown are an additional reduction process at ca., \(-1.92\) V, which is likely related to the reduction of the terminal phenanthroline ligands, and a bielectronic oxidative process at \(+1.36\) V corresponding to two weakly coupled Os\textsuperscript{2+/3+} centres.

Fig 4 shows how the absorption spectra of E evolve during a CV performed at 5 mV/s in 0.1 M NBu\textsubscript{4}PF\textsubscript{6} - acetonitrile solution and scanning in the potential window shown in Fig 3 starting at +0.4 V. The top three frames (Fig 4a-c) correspond to the negative-going scan, and the three frames at the bottom (Fig 4d-f) were obtained during the subsequent positive-going scan. The arrows in each frame indicate the evolution of the
Figure 4. Spectroelectrochemistry of 0.02 mM E in acetonitrile containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub> using a capillary slit cell. Spectra were collected during a cyclic potential scan at 5mV/s in the 0.4 to 1.6 V potential range. For the sake of clarity, only a selected subset of spectra is shown during a negative (a-e) and positive-going (d-f) potential scan direction.

Figure 5. Evolution as a function of bands peaking at 970 nm (E<sup>+</sup>: solid line) and at 685 nm (E<sup>-</sup>; dashed line). The Y-axis is presented as normalized absorbance, A/A<sub>max</sub>, for each band. Data were obtained from the spectra depicted in figure 4.
corresponding spectral peaks, and it is clearly seen that for those frames aligned vertically, virtually identical processes occur, only in opposite directions.

Describing each frame in detail, we can see that in Fig 4a, the first spectrum corresponds to E (bearing a dark yellow color) as the starting material with a sharp band at 445 nm and a small shoulder at 425 nm. During the first electroreduction process (voltammetric peak C1), the sharp band at 445 nm (which we now recognize as a signature peak for E) decreases as the expense of the development of three spectral peaks: a rather broad signature at 415 nm and a pair of sharper bands at 860 and 970 nm. This spectrum is virtually identical with that obtained by cobaltocene reduction of E to E (see fig 2a) and corroborates that the two processes yield the same product. Despite the large spectral changes (mostly in the near IR), we note that the solution does not undergo visible color change during this process and maintains a yellow hue through out this first process.

Fig 4b shows the spectral evolution encompassing voltammetric peak C₂, with a visible yellow to green transformation. Spectrally, we observe that the band pair at 860 and 970 nm is converted into another pair at 635 and 685 nm, respectively. Again, the agreement of cobaltocene reduction data is clear indicating that these latter peaks are associated with formation of E²⁻.

In the third potential region (Fig 4c) and encompassing the voltammetric peak C₃, all the spectral features from Fig 4b are seen to decrease significantly in intensity, bringing about a bleaching of the green solution color to a pale yellow hue. There is an almost complete disappearance of the band pair at 635 and 685 nm, leaving only a broad band at 445 nm of low intensity. The bands at 635 and 685 nm are likely to be associated with LC transition of the doubly reduced tatpp²⁻ ligands (in E²⁻). The fact that the two peaks are bleached upon an additional two-electron reduction (see Fig 4c) suggest that the tatpp-2 bridging ligand is reduced to tatpp-4. Such extensive reduction of the
tetraazapentacene framework would disrupt any extended conjugation across the tatpp ligand and could easily be expected to bleach any low energy LC transitions. This last redox process, reduction of E^2 to E^4 has never been observed in the photochemical process. As shown in the frames d,e and f of Fig 4, the three reductive processes are completely reversible, and all of the redox intermediate are seen to reappear and disappear in order until E is completely regenerated. The potential at which the various species appear and disappear in the spectroelectrochemical experiments can be correlated with the CV data by plotting the normalized intensity for the peak at 970 nm (E^-) and 685 nm (E^2-) as a function of the electrode potential, as shown in Fig 5. We observe that the peak associated with E^- reaches a maximum at ca -0.3 V (vs E_{1/2} E^{2-}) = -0.22 V in the CV data). The slightly more negative potentials for the spectroelectrochemical data is not unreasonable since not all the complex E is reduced at the E_{1/2}. As the potential increases more negatively, we observe the appearance of the peaks at 685nm (E^2-) at the expense of the 970nm peak, reaching a maximum at -1.0 V (vs -0.71V for the E_{1/2} for E^-). Finally a potential more negative than -1.0 V, the 685 nm peak begins to bleach, indicating formation of E^4 (E_{1/2} (E^{2-4}) = -1.28V. At -1.6 V, the scan is reversed and E^2- and then E^- are seen to reappear and disappear in order until E is regenerated at +0.4 V. The intensities of the 685 nm and 970 nm peaks are rather higher on the return (positive-going) scan, which indicates that the electroreduction processes continued forming E^4 even during the switch of the potential scan at -1.6 V, and thus providing a higher yield of E^2 and E^- during the positive-going scan.

(II) Electrochemistry and Spectroelectrochemistry

(B) In Aquous Medium: The reversibility of the electrochemical process is strongly affected by added water as shown in Fig 6. All redox processes (left to right: E^{4-2}, E^{2-}, E^-)
Figure 6. Effect of water on the cyclic voltammograms of E: (a) 0.5% water, (b) 10% water and (c) 20% water. These voltammograms were obtained at 50 mV/s with a glassy carbon disk (diameter = 1.5 mm) in 0.2 mM E in acetonitrile containing 0.1 M NBu$_4^+$PF$_6$. The solution were purged with argon for 30 min before recording the voltammograms.

Figure 7. Spectroelectrochemistry of E in 20% water-acetonitrile at pH 12 (a,b) and 9.5 (c,d). Frames a and c correspond to the first electoreduction process, and frames b and d to the second electoreduction process at the corresponding pH's. Spectra were collected during a cyclic potential scan at 5mV/s, but only those obtained during the negative-going potential scan are shown in this figure for the sake of clarity.
are still clearly observed upon addition of 0.5% water (Fig 6a); however the processes are noticeably less reversible \(E_{r-e} \) of the 99.8, 80.1 and 175mV for processes \(C_1/A_1, C_2/A_2, \text{and } C_3/A_3\) respectively), and the \(C_1\) peak begins to split. In a 10% water-acetonitrile solution (Fig 6b), all of the redox process are still discernible, but none are reversible, and at 20% water in acetonitrile (Fig 6c), the two peaks associated with \(E^{2+}\) and \(E^{0}\) couples are barely observed and have shifted to slightly more positive potentials. As the photochemical activity is still observed in 20% water-acetonitrile (vide infra) and the individual redox processes are still discernible in the CV, we choose to examine the spectroelectrochemistry of \(E\) in this mixture. The solution pH, as recorded by a standerred glass electrode, was varied in order to examine the range of species that could be formed in the presence of water.

Fig 7 compares spectroelectrochemical data at pH 12 and 9.5 as obtained during a potential scan from 0.4 to -1.6V. The columns of the left (Fig 7 a,c) show the initial one-electron reduction product, and the columns on the right (Fig 7b,d) show the disappearance of the one-electron product and the appearance of the doubly reduced product. at pH12 (Fig 7a,b), we can assign the one-electron reduction product as a mixture of mainly \(E^{2-}\) and some \(HE\). At pH 9.5 (fig 7c,d) unprotonated \(E^-\) is still the favored one-electron product, whereas \(HE\) is the dominant form of the doubly reduced product (as judged by the appearance of the 725 nm peak, see Fig 7d), with some \(E^{2-}\) still apparent as the 725 nm feature is not fully developed (see Fig 2b).

Contrasting with the previous spectroelectrochemical profiles, an interesting change in the absorption of the singly reduced product was observed at pH 7 (Fig 8a). Some \(E\) is initially formed, as indicated by the appearance of the 970 nm band, but peak quickly reaches a maximum at a value much less than that observed at higher pH (see Fig 7
a,c). As the band at 970 nm approaches its maximum value, a new broad peak at 580 nm begins to appear which is consistent with the appearance of this peak under potentials where only the single reduced product is formed at higher pH (see Fig 7 a,c) could be explained by protonation of E to HE and, once an appreciable concentration of the HE is generated, a disproportionation to \( \text{H}_2\text{E} \) and E (reaction 1). Any E formed in the disproportionation reaction would be immediately re-reduced by the electrode, and thus the \( \text{H}_2\text{E} \) is the only stable product obtainable under these conditions. As the electrode is biased more negatively, we eventually see the rapid appearance of the 580 nm peak associated with \( \text{H}_2\text{E} \) and the complete bleaching of the 325 nm peak associated with E (Fig 8b).

As shown in the Fig 8c, the spectroelectrochemistry of E at pH 4 shows only the appearance of the doubly reduced product \( \text{H}_2\text{E} \) and no trace of the one-electron products E or HE. The clean isobestic points at 345, 380, and 490 nm show that E undergoes a concerted two-proton, two-electron reduction at this pH. Identical behavior is observed for the chemical reduction of E to \( \text{H}_2\text{E} \) with excess NaBH\(_4\) in 20% water-acetonitrile at pH 4.

(III) Photochemistry (in Acetonitrile)

Visible irradiation of E results in the appearance of two photoproducts, as shown in Fig 9a,b. Under these conditions, it is known that protons are generated in solution via these thermal decomposition of the coproduct, the TEA radical cation\(^21\), leading to uncertainty in the protonation state of the two products. We note that the first trace is for the spectrum of E without added TEA and the second trace with the added TEA already shows the formation of small amount of E even prior to irradiation. This represents either a small but reversible thermal reaction or a charge-transfer complex between the TEA and E. Higher concentration of TEA can lead to a complete thermal reduction of E to E but no further. We chose a concentration of 0.25 M TEA because here only a small amount of thermal reactivity
Figure 8. Spectroelectrochemistry of E in 20% water-acetonitrile at pH 7 (a,b) and pH 4 (c). The potential window was 0.4 to -1.6 V for pH 7 and 0.4 to -1.4 for pH 4. Other details as in Figure 7.

Figure 9. Evolution of the visible spectrum of 16µm E in deaerated acetonitrile containing 0.25 M TEA during photoirradiation: (a) 0-2 min and (b) 2-12 min.
is observed and the photochemical reaction still proceeds rapidly. Once \( E^- \) is fully formed, continued irradiation leads to the gradual disappearance of the \( E^- \) peaks and the appearance of three new bands at 725, 655, and 608 nm (Fig 10b), which are characteristics of the singly protonated, doubly reduced \( HE^- \). A comparison of the absorption data with those obtained by stoichiometric chemical reduction and protonation corroborates these assignments.

(IV) In Mixed Water-Acetonitrile

The photochemical activity of \( E \) is maintained when water is added to the system. Specifically, we examined the photochemistry of \( E \) in thoroughly degassed solutions of 20% water-acetonitrile at different pH values to mimic the spectroelectrochemical conditions. In general, the spectral obtained photochemically shown in Fig 10, closely match those obtained by electroreduction at similar pH; however, no photochemical activity was observed at pH 7 or below. At each of the three pH’s examined, two distinct photoproducts are observed sequentially and are clearly assignable to one-and two-electron reduced products. At pH 12 and 10 (Fig 10 a1, a2, b1, b2), the first photoproduct is \( E^- \). At pH 8, we observe an additional band at 580 nm during the first reduction we attribute to formation of \( H_2E^- \), presumably via the disproportionation of a small amount of \( HE^- \) generated from protonation of \( E^- \) at this pH. However, once all the \( E \) is consumed, we observe the complete conversion of the remaining \( E^- \) to \( H_2E^- \) (Fig 10 c2). The photochemical activity is not always as well behaved as the spectroelectrochemical data, as typified by the lack of clear isobestic points in the data collected at pH 12.

Discussion

We have identified seven distinct species of \( E \), depicted in Fig 1, that are interlinked by electron transfer and/or protonation/deprotonation process. Of these, only \( E^+ \) does not play a role in the photochemistry of \( E \), and only \( HE^- \) appears to be unstable with respect to disproportionation. Fortunately, all of these species show unique absorption spectra,
Figure 10. Evolution of the visible spectrum of 16μM E in deaerated 20% water-acetonitrile: pH 12 (a), and pH 10(b), and pH 8 (c). Frames numbered with a 1 correspond to the initial irradiation period (approximately 3-6 min long) and frames with a 2 correspond to the appearance of a distinct second photoproduct over the time period ranging from 3 to 15 min.

Figure 11. Qualitative molecular orbital energy diagram showing the important optical transitions and orbitals involved for related redox and protonation isomers of E.
summarised in table 1, which provide the common link between the titration, spectroelectrochemical, and the photochemical data.

In an attempt to understand the underlying electronic reasons for the observed spectral changes, we examined the absorption spectra in detail. As is common to these types of complexes the absorption spectra of the species in Fig 1 in acetonitrile are dominated by every intense spin-allowed ligand-centred (LC) transitions in the UV and visible region and by intense spin allowed metal-to- ligand charge tranfer (MLCT) transitions in the visible. In particular, all the species show broad bands around 445 nm which are similar in energy and shape to the lowest-energy absorption band of \([\text{Os(phen)}_2]^{12}\) and can be assigned, in part, to the spin-allowed Os(\(d\pi\) \(\rightarrow\) phen(P\(^\ast\)) MLCT transition, which is responsible for the luminescent behavior of \([\text{Os(phen)}_2]^{12}\). These MLCT bands are constant throughout all the spectra and are not bleached upon reduction. From its structural shape and high molar extinction coefficient, it is clear that the band at 445 nm for \(E\) also recevies contributions from a LC (\(\pi-\pi^\ast\)) transition involving the tatpp ligand. The 445 nm band in \(E\) has a molar absorptivity of 56250 cm\(^{-1}\)M\(^{-1}\) compared to the anticipated molar absorptivity at 450 nm for two \([\text{Os(phen)}_2]^{12}\) MLCTs of 37000 cm\(^{-1}\)M\(^{-1}\). As the extinction coefficients for weakly coupled MLCTs are generally additives\(^{22}\), we can assign the extra molar absorptivity of ca 19250 cm\(^{-1}\)M\(^{-1}\) to a tatpp LC transition. A second LC band is observed at 325 nm and is assigned to a tatpp \(\pi-\pi^\ast\) transitions, as this peak is absent in \([\text{Os(phen)}_2]^{12}\).

Upon reduction, we observe the bleaching or movement of these LC transitions and see new LC bands that are characteristic of the reduced forms of the parent hydrocarbon, tetraazapentacene\(^{13}\). We note that the vibrational fine structure is seen as associated peaks or shoulders for the LC transitions in most of the complexes and that the energy difference between the first and second vibronic state is approximately constant at 1330 cm\(^{-1}\) for \(E\)
(445 and 425 nm), 1320 cm⁻¹ for E⁻¹ (860 and 970 nm), and 1242 cm⁻¹ for E⁻² (625 and 685 nm), as would be expected for aromatic ring breathing models. The slight decrease in vibrational energy upon going from E to E⁻¹ to E⁻² is consistent with reduction of the tetraazapentacene unit.

Fig 11 shows a MO energy level diagram in which we adopt a localized view of the electron distribution in which three tatpp-based orbitals, the HOMO⁻¹ (π), LUMO⁻¹ (π⁺), and LUMO⁻² (π⁺), and one-metal based orbital, the HOMO (dπ), play significant roles in the visible absorption spectra. As with related DPPZ and TPPHZ type complexes, we can attribute the various MOs as being largely localized on specific portions of the tatpp ligand and being "bipyridine-like" (π⁺) or tetraazapentacene-like (π and π⁺). For E (Fig 11), three of four possible transitions labelled LC₁, LC₂, and MLCT¹ would correspond to the peaks at 325 nm and two overlapping sharp and broad transitions at 445 nm, respectively. The overlap of the LC₀ and MLCT¹ transitions is apparent by the structured narrow peak (LC₀) and the latter the usual broad transition between 440 and 480 nm typically observed for Os (dπ) → bipyridine (π⁺) type transitions (MLCT). In this case, the π⁺ "bipyridine-like" acceptor orbital on tatpp is strongly coupled to the Os (dπ) orbitals and is the site initially populated upon MLCT. Importantly, the possible MLCT₀ transition Os (dπ) → tatpp (π⁺), is not observed, which is typical for this and related DPPZ and TPPHZ complexes and is related to the poor electronic coupling of the dπ and π⁺ orbitals.

Upon reduction to E⁻¹, the π⁺ orbitals is singly populated and a new transition, LC₂, becomes possible which we assign to a pair of vibronic peaks at 860 and 970 nm. The energy of the ν♭ band (≈10300 cm⁻¹) in E⁻¹ is reasonably close to the estimated energy difference between these two levels in LC₁-LC₀ ≈8300 cm⁻¹), considering the expected increase in →E between π⁺ and π⁺ upon reduction. Addition of a second electron to form E⁻² would fill the
π* orbital and lead to additional nuclear rearrangement to stabilize the π* at the expense of the π orbital. This would result in a further blue shift of the LC transition. There is a clear shift of the vibronic pair associated with LC from 860, 970 nm in E to 635, 685 nm in E², consistent with this interpretations. The fact that the first reduction leads to an apparent red shift of the 445 nm peak to 970 nm and the second reduction results in a blue shift to the 685 nm suggest that they are not the same type transition, as is suggested in our model with LC assigned to the 445 nm in E and LC assigned to the transitions at 970 and 685 nm in E and E² respectively. The bleaching of the 325 nm peak (LC) in E and E² is likely due to a blue shift outside our spectral window (<300 nm) and would be expected from the model in Fig 11.

Assuming protonation further stabilizes the new full π* orbital in E², we could expect that HE⁻ and H₂E should show a continued blue shift in the LC transitions. For H₂E, this is clearly seen by the appearance of the broad band at 580 nm at the expense of peaks at 635 and 685 nm. Upon protonation of E² to HE⁻, the vibronic pair at 630, 655 nm, which is smaller than that observed with H₂E as expected, and a new low energy transition at 725 nm is observed. The origin of this last transition is less clear, but it is clearly diagnostic of monoprotonation of E². While this model does not explain all the observed spectral changes, the gross change in the LC transitions seems adequately represented in this picture.

**Spectroelectrochemistry and Photoelectrochemistry**

Complex E is Photochemically active another way to view this process is as an intramolecular electron transfer between a weakly coupled "bipyridine like" unit and a central "tetraazapentacene like" unit. This view emphasizes that spatial separation of the electron-hole pair. As mentioned previously, the ³MLCT₀ state is poorly coupled with the Os dπ orbital, which apparently leads to long lived excited states and ultimately to a facile
reduction of the transient Os\(^{3+}\) centre by the sacrificial reductant. While reductive quenching of a photoexcited Os-bpy type chromophore is not unusual for a single reduction, the ability to repeat this process and doubly reduce the acceptor orbital is unprecedented. A similar situation with a different outcome is seen in the related dimer,\([(\text{bpy})_2\text{Os(bddpz)Os(bpy)}_2]\)^+ (where bddpz is the bridging bis DPPZ ligand, 1,1'-dipyrido[3,2-a:2’3’-c] phenazine), in which all the luminescent activity (as opposed to photochemical activity) is lost upon reduction to \([(\text{bpy})_2\text{Os(bddpz}^+\text{)}\text{Os(bpy)}_2]\)^-. In this case, the presumed mechanism of quenching is rapid intramolecular reduction of the excited [Os(III) bpy\(^{2-}\)] fragment by the bridging bddpz\(^{2-}\) radical anion. The observed reduction potential for the E\(^{2+}\) couple at -0.71 V suggests that the tatpp\(^{2-}\) ligand will still be the preferred site of charge injection, considering the reduction of the terminal phen ligand comes at far more negative potential (ca. -1.9 V). Protonation of the central tetraazapentacene nitrogens (formation of HE) would relieve some of the coulombic repulsion during the second charge injection, but does not appear to be an absolute necessity, as the second photochemical reduction occurs redialy in 20% water acetonitrile at pH 12 and yields mainly E\(^2\). Clearly the unusual electronic structure tatpp ligand in which the MLCT acceptor orbital (\(\pi^*\)) is not the ultimate site of electron storage is key to this behaviour. Currently, we are unsure if the loss of photochemical activity at pH 7.5 or below is due to deactivation of E or loss of free TEA through formation of triethylammonium ion. The observation of clean two-electron, two-protons reductions at lower pHs (by both chemical and electrochemical means) may signal a change in the reduction/protonation mechanisms involved and also highlights the ability of E to participate in concerted two-electron processes.

While the multielectron photoreduction of E in acetonitrile is intriguing and important, it is the retention of this multielectron photochemical activity in the presence of water that really shows promise from a practical standpoint. We observe two distinct photoproducts in water-acetonitrile (1.4, pH>7.5) solution whose
absorption spectra are virtually identical to those generated by sequential electroreduction under similar solvent conditions. Furthermore, a comparison of the absorption spectra with those obtained in acetonitrile clearly identify the photoproducts as one- and two-electron-reduced species.

Regardless of the detailed photophysics of $E$, we observe that it is possible to couple protonation with photoreduction, a feature that has been proposed as essential in most natural light-activated energy-storing processes$^{29,30}$. Most importantly, we can photochemically generate $H_2E$ at pH 8, which carries two protons and two electrons, or effectively one $H_2$ molecule, with in its structure.
References


2. (a) Dagani, R., The shape of things to come, *Chem Eng News* 1998 (b) Drain, C.M.


9. Chen, C-J. *In Comprehensive Supramolecular chemistry; Atwood, J.L., Davies, J.E.


    1999, 121, 4207.


