Light- and pH-driven electron transfer in the pyranine–methylviologen system

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Abstract

A face-to-face electrostatic complex is formed in alkaline solution by pairing the trisodium salt of 8-hydroxy-1,3,6-pyrenetrisulfonic acid pyranine tsPyOH,3Na+, an anionic donor, with the dichloride salt of methyl viologen MV2Cl-, a cationic acceptor. The donor displays dual properties: it can be photoionized or can transfer an electron to the acceptor. It is shown that light absorption by the self-assembled complex leads to the formation of a particularly short-lived species (3.7 ps) assigned to a singlet excited state which relaxes to the ground state via a charge-transfer state. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Among the donor–acceptor systems available in the literature, the photophysical properties of self-assembled and ionic systems are much less explored, in particular in solutions [1–4] where the thermodynamics of formation of the complexes are dependent on many parameters such as the nature of the solvent, ionic strength, pH, temperature, and on aggregation problems [5]. We are interested in model systems where the donor can display dual properties. For instance, it can transfer a proton to the solvent and/or an electron to an acceptor. Such transfer processes can be controlled by light absorption and pH variation. Other interesting dual properties are the ability to transfer an electron to the donor or to be photoionized. In the last case, the resulting electron can either be transferred to the donor moiety or to the solvent and become a solvated electron. This should generate systems in which the competitive electron-transfer (ET) processes can be selected with the choice of the excitation wavelength. Such competitive processes, H+ versus e− transfer and photoionization versus e− transfer, frequently occur in biological systems, i.e. when drug molecules are intercalated in ADN and interact with the base units [6–8].

To this end, we have begun studying complexes formed by coupling a donor, pyranine (tsPyOH), a trisodium salt of the 8-hydroxy-1,3,6-pyrenetrisulfonic acid with an acceptor, the dichloride salt of methyl viologen. Pyranine displays the required properties. In acidic or neutral aqueous media, the
excited pyranine efficiently transfers a proton to the solvent [9,10], while in alkaline media at pH > 8, the excited pyranine anion can be photoionized [11].

We presently report our preliminary study of the model system, tsPyO\(^-\)/MV\(^{2+}\), in which the ET processes to the solvent (photoionization) and to the acceptor are in competition. The work is divided into three main sections. Section 2 describes the equipment and experimental conditions. In Section 3, we report the formation of the mixed complexes of pyranine and methylviologen in alkaline medium and the relaxation processes following the excitation of the pyranine anion in its monomeric form and in the mixed complex.

2. Experimental

2.1. Chemicals

Trisodium, 8-hydroxy-1,3,6-pyrenetrisulfonic acid Laser Grade commercial name: pyranine, or tsPyOH from Kodak and 1,1 dimethyl-4,4’-bipyridinium dichloride (methyl viologen or MV\(^{2+}\)) from Aldrich were used without further purification. Water was purified by Milli-ro and Milli-Q systems of Millipore to a resistivity > 18 MΩ cm\(^{-1}\). Alkaline solutions were prepared by adding sodium hydroxide from Fluka and the pH values are measured at 22°C with a Tacussel–Minisis 8000 pH meter.

2.2. Electrochemistry

Cyclic voltammetry was used for the determination of the oxidation potential of the donor in alkaline media and the reduction potential of the acceptor. All the solutions were saturated with argon and contained 0.1 M of NaCl. The concentrations of pyranine and methylviologen were kept constant (10\(^{-3}\) M) in all experiments. The glassy and platinum electrodes were used as working and counter electrodes, respectively. The saturated calomel electrode (SCE) served as the reference electrode.

2.3. Steady-state absorption and fluorimetry

The UV-VIS spectra of the compounds were recorded with a Varian Cary 3E. Fluorescence spectra were recorded with a SPEX fluorimeter and corrected for the monochromator and photomultiplier response over the 300–750 nm domain. When concentrated solutions are needed, i.e. for the fluorimetric titration, a thin cell of 1 mm and the front face configuration were used to avoid spectral distortions due to the inner-filter effect and emission re-absorption.

2.4. Time-resolved fluorescence

The fluorescence decay times were recorded using the Edingburg Instrument 199F time-correlated single-photon-counting system. The excitation source is a dye laser pumped with a frequency-doubled Nd:YAG (Quantronix, 76 MHz). With the rhodamine 6G dye, the excitation wavelength can be tuned from 560 to 620 over the visible and from 280 to 310 over the UV range.

2.5. Time-resolved absorption

The femtosecond time-resolved pump-and-probe set-up is composed of a commercial (Coherent/Continuum) Ti:Sa 20 Hz amplified laser system. To be able to excite the sample in the blue (293 nm) and probe the transients over a wide domain of the visible, the 790 nm beam was split into two beams and two continua of white light were generated through a 10 mm water cell. The first continuum was used as a probing source. From the second continuum, we selected the 586 nm with a filter 10 nm bandwidth and amplified it through a four-stage dye amplification system (Rhodamine 590 in methanol). The pulses were then compressed to a duration of 100 fs with a compression line (four prisms) and the output energy was 0.5 mJ. A 2 mm BBO non-linear crystal was used to generate the 293 nm excitation beam, the energy of which was kept around 40 μJ. The flowing sample cell used in the present experiments was made of fused silica (UV grade) and the optical pathlength was 2.0 mm.

3. Results and discussion

3.1. Optical properties of the ground-state complexes

The existence of two mixed complexes of stoichiometry 1/1 and 1/2 is demonstrated via titration method. Job’s method was successfully used in pre-
vious works to carry out the formation of ‘electrostatically’ linked mixed complexes of porphyrins and phthalocyanines [12]. This method relies on the fact that the optical density of a mixture of chromophores, which do not react with each other, is the sum of absorptions due to each chromophore separately. Correlatively, departures from additivity as the composition of the solution is continuously varied can be interpreted as evidence of the formation of a complex. The stoichiometry of the complex can be deduced from the composition at which the deviation from additivity is a maximum. In the tsPyO\(^-\)/MV\(^{2+}\) system, clear isobestic points at 294, 312, 357 and 466.5 nm, appeared during the titration of tsPyO\(^-\) by MV\(^{2+}\), revealing the existence of an equilibrium between two species. tsPyO\(^-\) forms, with MV\(^{2+}\), well defined and stable complexes corresponding to the tsPyO\(^-\)/MV\(^{2+}\) and MV\(^{2+}\)/tsPyO\(^-\) species. The spectra of the 1/1 complex and the corresponding monomers are displayed in Fig. 1.

Steady-state fluorimetry can also be used to determine the association constant of the 1/1 complex (see Fig. 2). The method is based on the assumption that neither the dimer nor the trimer fluoresce over the monomer emission domain [12]. Under such conditions, the detected fluorescence would be exclusively provided by the monomer species, in equilibrium with the complex. During the titration of the fluorescing tsPyO\(^-\) monomer by MV\(^{2+}\), the solution is excited at 466.5 nm, which correspond to an isobestic point of the absorption spectra (see Fig. 1), so that the number of absorbed photons is kept constant. The fluorescence area of the remaining tsPyO\(^-\) monomer, \(S_{\text{fluo}}\), is recorded as a function of the mole fraction of MV\(^{2+}\) added, \(x_{\text{MV}^{2+}}\) and the normalized fluorescence, \(S_{\text{fluo}}/S_{\text{fluo}}^0\), is plotted as a function of \(x_{\text{MV}^{2+}}\) (see Fig. 2). The association constant of the 1/1 complex, \(K_{\text{ass}}\), can be determined as follows:

\[
\text{tsPyO}^- + \text{MV}^{2+} \leftrightarrow \text{tsPyO}^-/\text{MV}^{2+}
\]

at equilibrium,

\[
K_{\text{ass}} = \frac{[\text{tsPyO}^-][\text{MV}^{2+}]}{[\text{tsPyO}^-]/\text{MV}^{2+}} = C_0 (1 - \alpha) (r - \alpha)
\]

with \(C_0\) being the starting concentration of [tsPyO\(^-\)] and the ratio \(r = [\text{MV}^{2+}]_0/[/\text{tsPyO}^-]_0\),

\[
\alpha = 0.5 \left[ B - \sqrt{B^2 - 4r} \right] \quad \text{with} \quad B = 1 + r + \frac{1}{K_{\text{ass}} C_0}.
\]

The fit of \(S_{\text{fluo}}/S_{\text{fluo}}^0 = 1 - \alpha\) (see Fig. 2) gives

\[
K_{\text{ass}} = (1.7 \pm 0.1) \times 10^5 \text{ M}^{-1}.
\]

The quality of the fit supports our assumption that the 1/1 complex is non-fluorescent. Further support will be given in Section 3.3.

The spectrum of the 1/1 (tsPyO\(^-\)/MV\(^{2+}\)) complex displays a new and very weak absorption band in the red, peaking at 640 nm (\( \varepsilon \sim 250 \text{ M}^{-1} \text{ cm}^{-1} \)) (see Fig. 3). A charge-transfer (CT) character be-
tween the donor and acceptor could induce such a CT transition. To be able to assign this band, we try to roughly estimate the energy of the CT transition from the redox potentials of the donor and acceptor in the complex.

The energy of the CT state, \(E_{\text{CT}}\), according to Marcus [13], can be approximated by:

\[
E_{\text{CT}} = E_{\text{ox}} - E_{\text{red}} + C + \lambda,
\]

where \(E_{\text{ox}}\) (0.42 V/SCE) and \(E_{\text{red}}\) (-0.65 V/SCE) are the half-wave potentials of monoelectronic oxidation of the donor tsPyO- and reduction of the acceptor MV2+, respectively [14].  

\(C\) is the Coulombic interaction between the reactant (tsPyO-/MV2+) and the product (tsPyO+/MV2+) and \(\lambda\), the total energy of re-organization after the charge transfer. With the hypothesis that the distance between the donor and acceptor does not change in the reactant and product, the Coulombic term, \(C\), can be expressed as follows:

\[
C = \frac{e^2}{4\pi\varepsilon_0} \frac{Q_D Q_A}{\varepsilon_\infty R} - \left(\frac{Q_D}{Q_D} + 1\right)\left(\frac{Q_A}{Q_A} - 1\right),
\]

where \(Q_D = (-4)\) is the total charge of the donor, tsPyO-, \(Q_A = (2)\) is the total charge of the acceptor, MV2+, before the charge transfer, \(\varepsilon_\infty\), the static dielectric constant of water [15] and \(R\), the distance separation between the donor and acceptor. \(R = 3\) Å for a close contact complex. We found \(C = -0.3\) eV.

The total re-organization energy, \(\lambda\), is the summation of two contributions \(\lambda_0\) and \(\lambda_1\):

\[
\lambda = \lambda_0 + \lambda_1.
\]

\(\lambda_0\) is the the re-organization energy of the solvent around the complex after the charge transfer and \(\lambda_1\) is the intramolecular re-organizational energy. The standard estimate for \(\lambda_0\) was obtained by Marcus by using a model in which reactants and products were modeled as spheres and the solvent as a dielectric continuum. It is expressed as:

\[
\lambda_0 = (\varepsilon)^3 \left[ (2a_D)^{-1} + (2a_A)^{-1} - (R)^{-1} \right],
\]

\[
\times \left[ (\varepsilon_{\text{opt}})^{-1} - (\varepsilon)^{-1} \right],
\]

where \(\varepsilon_{\text{opt}}\), is the optical dielectric constant of the solvent, \(a_D\) and \(a_A\) are the radius of the donor and acceptor, respectively and \(R\), the distance between them. Both pyranine and methylviologen have a flat shape and the solvent cavity fits better to an ellipsoidal cavity than to a spherical one. Lippert [16] demonstrated that the solvation of a point dipole placed in the center of an ellipsoidal cavity, whose large axis is \(b\), is identical with that of the same dipole in the center of a spherical cavity of radius \(a = 0.4b\). Here, \(a_D\) and \(a_A\) are taken to be equal to 3.2 Å which corresponds to 40% of the long axis of pyranine and methylviologen. We suppose a close contact of the two ions with \(R = 3\) Å.

With this hypothesis, we found for \(\lambda_0\) a value of 0.88 eV. \(\lambda_1\) is the total nuclear re-organization or intramolecular re-organizational energy given by:

\[
\lambda_1 = \sum_{l,n} \lambda_{l,n} = \frac{1}{2} \sum_l f_{n} (\Delta q_{e,n})^2.
\]

\(\lambda_1\) is the summation over the \(n\) coupled intramolecular vibrations. The contribution of the \(n\)th normal mode to the re-organization energy is given in terms of its force constant, \(f_{n}\), and the change in equilibrium positions between the reactants and products:

\[
\Delta q_{e,n} = q_{\text{product},e} - q_{\text{reactant},e}.
\]

To be able to properly account for \(\lambda_1\), the frequency and re-organization energy of each individual internal mode must be known. Such information is very scarce and often a single averaged high frequency is
chosen, i.e. 1500 cm\(^{-1}\), which is close to the frequencies of skeletal stretching vibrations of aromatic molecules [17,18]. Some rare calculations are, however, available in the literature. They are based on the experimental determination, by resonance Raman, of the vibration modes which are Franck-Condon active in the CT transition of donor coupled with an acceptor [17–22]. Myers et al. [17,18] found values of the total internal re-organization energy ranging from 0.29 to 0.43 eV for the system for hexamethylbenzene/tetracyanoethylene and dicyanoethylene-aza-adamante donor/acceptor compounds, respectively. Larsson et al. [22] performed calculations on a benzene and benzene anion system and found, by taking into consideration four vibrational modes, an internal re-organization around 0.2 eV. When ground state CTs are formed, which also emit in the excited state, Gould et al. [19–21] also proposed another method to determine the internal re-organisation energy, based on the analysis of the emission spectrum and excitation spectrum. Although it does not correspond to our present case, we note that the internal re-organization, \(\lambda_i\), obtained for various systems with substituted benzene as a donor and tetracyanoazobenzene or tetracyanoanthracene as acceptors, varies between 0.2 and 0.3 eV. These values are consistent with the ones obtained from the resonance Raman study. We note, from the various papers of the literature, that the averaged contribution of \(\lambda_i\) is no bigger than 0.3 eV, for aromatic systems. For our present system, if we took a value of \(\lambda_i\) equal to 0.3 eV, it would counterbalance the Coulombic interaction \(C\) (−0.3 eV), and therefore we would obtain from Eq. (1), \(E_{CT} = 1.95\) eV or 636 nm.

Although it is a rough estimation, the value found is very close to the energy of the maximum of the absorption spectrum of the complex 640 nm. We therefore tentatively attribute it to a CT band of the complex.

3.2. Decay pathway of the excited tsPyO\(^{-}\)

The lifetime of tsPyO\(^{-}\) in alkaline water is first measured via the time-resolved fluorescence technique. Monoexponential decays of the fluorescence are obtained over the fluorescence domain of tsPyO\(^{-}\) from 470 to 600 nm. The lifetime deduced from these decay kinetics is \(5.3 \pm 0.1\) ns and is attributed to the singlet excited-state lifetime. The corresponding quantum yield of fluorescence determined with steady-state fluorimetry is very high, \(0.99 \pm 0.05\). Thus, for the following transient absorption experiments which cover the time domain of 30 ps, the singlet excited state of tsPyO\(^{-}\) can be considered to be stable on this time scale.

Fig. 4 displays the difference spectrum recorded at short time, \(t = 30\) ps. The photobleached band peaking at 520 nm corresponds to the stimulated emission of the singlet excited state of tsPyO\(^{-}\). Taking into account the shape of the steady-state fluorescence band of tsPyO\(^{-}\) (see Fig. 2), the absorption spectrum of the transient species was reconstructed (Fig. 4). It displays a very broad band peaking at 480 nm with a shoulder on the blue side around 450 nm. On the red side, over the 620–720 nm domain, a very weak and broad absorption (not shown) is also observed whose absorbance at 720 nm is 0.004. This last absorption is very reminiscent of the well-established absorbance of aqueous electrons, \(e_0\). These species could be generated from the photoinization of tsPyO\(^{-}\) as previously reported in a nanosecond time-resolved study by Gutman’s group [11] and also found by our group [25]. Their formation could be then correlated to the parent ion, the radical tsPyO\(^{+}\) whose absorbance is expected in

![Fig. 4. Differential absorption spectrum recorded after excitation of a 2×10\(^{-4}\) M aqueous solution of tsPyO\(^{-}\) at pH = 11. ( ) time = −10 ps, ( ) time = 30 ps. \(\lambda_{exc} = 293\) nm. (—) absorption spectrum reconstructed by subtracting the stimulated emission. Inset: kinetics recorded at 470 and 520 nm.](image-url)
the near UV domain [11,25]. The absorption band of tsPyO$^-$ is a narrow band peaking at 450 nm, which should be hidden in the broad absorption here observed. We therefore try to determine their contribution to the transient absorbance of Fig. 4. The concentration of $e_{aq}$ can be deduced from the well-established extinction coefficient of $e_{aq}$ in water [23]. It is only $2.1 \times 10^{-7}$ M, which corresponds to a very small yield of photoionization. Taking the extinction value determined for tsPyO$^-$ at $\phiH = 9$ ($\varepsilon_{450} = 43000 \pm 2000$ M$^{-1}$ cm$^{-1}$) [11,25], we calculate the correlated absorbance which is equal to $\sim 0.009$. This absorbance could explain the presence of a blue shoulder in the broad absorption of the reconstructed spectrum. This result does not contradict the nanosecond time-resolved data recorded by Gutman’s group [11] and our group which indicate that photoionization of the singlet excited state of tsPyO$^-$ can occur via the re-absorption of a second photon. In both nanosecond time-resolved experiments, a nanosecond laser with long pulse duration (15 ns) was used, thus allowing the long-lived $^1$S$\text{tsPyO}^-$ (5.3 $\pm$ 0.1 ns in alkaline water; this work and also Ref. [24]) to reabsorb a second photon. On this time scale, both groups observed correlated absorbances corresponding to aqueous electrons and radicals, peaking at 720 and 450 nm, respectively, but no broad and intense absorption over the intermediate wavelength domain. In the present experiment, the pulse duration of the exciting beam is $10^3$ times shorter, thus explaining the low yield of photoionization. In addition to the presence of aqueous electrons and radicals, we also observe a transient absorption peaking at 480 nm which was not seen in Gutman’s experiment and which is stable over the time window explored, from 0 to 30 ps. We therefore attribute this transient absorbing species to the singlet excited-state $^1$S$\text{tsPyO}^-$.

3.3 Decay pathway of the excited complex ($^1$S$\text{tsPyO}^-$/MV$^{2+}$)$^*$

Fig. 5 displays the difference spectrum recorded at short time (400 fs) and at 30 ps for the excited complex. At 30 ps, the difference spectrum is identical to the one established for the $^1$S$\text{tsPyO}^-$ monomer, which corresponds to the sum of the absorption of the singlet excited-state $^1$S$\text{tsPyO}^-$ peaking at 480 nm and the correlated fluorescence band. At short times, another transient species is formed which decays within 3.7 ps (Fig. 5). Its absorption maximum (491 nm) is slightly red-shifted as compared to the $^1$S$\text{tsPyO}^-$ monomer. We attribute this absorbing species to the singlet excited state, $^1$(tsPyO$^-$/MV$^{2+}$)$^*$, of the complex. As no stimulated fluorescence was detected for $^1$(tsPyO$^-$/MV$^{2+}$)$^*$, the decay channel must be non-radiative, in agreement with the steady-state experiments which predict that the 1/1 complex is non-fluorescent (cf. Section 3.1). The lifetime of $^1$(tsPyO$^-$/MV$^{2+}$)$^*$ is considerably shortened (3.7 ps) as compared to the $^1$S$\text{tsPyO}^-$ monomer (5.3 ns). This effect could be due to an intramolecular charge transfer from the donor tsPyO$^-$ to the acceptor MV$^{2+}$. Such short time constants were previously measured for systems composed of mixed complexes of metallated porphyrins and phthalocyanines bearing substituents with opposite charges [5]. They vary from 400 fs to 1.5 ps depending on the redox properties of the donor and acceptor, and the resulting CT states are long-lived, from 15 to 70 ps depending on the mixed complex [5]. In the present case, we do not observe the rise of any absorption which could correspond either to tsPyO$^-$ or to MV$^{2+}$. Such phenomenon is, however, possible if
(tsPyO/MV\(^{2+}\)) relaxes quickly to the ground state (tsPyO\(^{-}/\)MV\(^{2+}\)).

\[
S_1(\text{tsPyO}^-/\text{MV}^{2+} \rightarrow 3.7\text{ps} \rightarrow \text{CT}(\text{tsPyO}^-/\text{MV}^{2+}) \rightarrow 3.7\text{ps} \rightarrow (\text{tsPyO}^-/\text{MV}^{2+})]
\]

A fast relaxation process from the CT to ground state could be possible if the ground state of the complex possessed a CT character. This result supports our previous findings: in Section 3.2, the new transition band at 640 nm which appears in the absorption spectra is assigned to the S\(_1\) tsPyO\(^{-}\)MV complex. The mixed S\(_1\) complex, composed of the self-assembled pyranine and methylviologen displays in alkaline water a new and very weak absorption band peaking at 640 nm that we assigned to a CT band. As previous findings: in Section 3.2, the new transition band of the S\(_1\) tsPyO\(^{-}\) MV complex was tentatively assigned to the S\(_1\) → CT transition. The present data corroborate this assignment.

The long-lived species is assigned to the singlet excited state of S\(_1\) tsPyO\(^{-}\) monomer. With a concentration of 2 × 10\(^{-4}\) M of the two components, \(~18\%\) of tsPyO\(^{-}\) and MV\(^{2+}\) remain in their monomeric form in the solution and therefore tsPyO\(^{-}\) can be directly excited. In the mixed complex, the most efficient channel is therefore the decay of the singlet excited state of S\(_1\) (tsPyO\(^{-}/\)MV\(^{2+}\)) to the ground state via the CT (tsPyO\(^{-}/\)MV\(^{2+}\)) state.

4. Conclusion

The synergy of the multiple and complementary techniques and methods used in the present work, namely, spectrophotometric titrations, electrochemistry, steady-state and laser photolysis with femtosecond time resolution, allowed us to thoroughly investigate the properties of the pyranine monomer and its self-assembled complex with methylviologen.

The mixed 1/1 complex, composed of the self-assembled pyranine and methylviologen displays in alkaline water a new and very weak absorption band peaking a 640 nm that we assigned to a CT band. As a consequence, the photochemistry of the 1/1 complex is very fast: upon excitation, the singlet excited state of the 1/1 complex is formed within the pulse duration (100 fs) and disappears quickly back to the ground state via a CT state. The whole mechanism takes place within 3.7 ps. A very interesting aspect which we will also explore in the future is the applicability of such system as an intra-cavity saturable absorber for UV lasers: the complex absorbs over the whole near UV domain with high molar extinction coefficients and the very fast non-radiative decay of S\(_1\) (tsPyO\(^{-}/\)MV\(^{2+}\)) to the ground state would allow the generation of very short pulses.

References