

Direct observation of light-driven, concerted electron–proton transfer

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The phenols 4-methylphenol, 4-methoxyphenol, and *N*-acetyl-tyrosine form hydrogen-bonded adducts with *N*-methyl-4, 4'-bipyridinium cation (MQ⁺) in aqueous solution as evidenced by the appearance of low-energy, low-absorptivity features in UV-visible spectra. They are assigned to the known examples of optically induced, concerted electron–proton transfer, photoEPT. The results of ultrafast transient absorption measurements on the assembly MeOPhO–H–MQ⁺ are consistent with concerted EPT by the instantaneous appearance of spectral features for MeOPhO–H–MQ⁺ in the transient spectra at the first observation time of 0.1 ps. The transient decays to MeOPhO–H–MQ⁺ in 2.5 ps, accompanied by the appearance of oscillations in the decay traces with a period of ~1 ps, consistent with a vibrational coherence and relaxation from a higher $\nu(\text{N-H})$ vibrational level or levels on the timescale for back EPT.

light driven | electron | proton | transfer | photoEPT

Proton-coupled electron transfer (PCET) reactions, in which both electrons and protons are transferred, play an important role in redox processes in chemistry and biology with examples in water oxidation (1–4), CO₂ reduction (5), mitochondrial respiration (6), and conversion of nucleotides to 2'-deoxynucleotides (7, 8). Mechanistically, PCET occurs by stepwise, electron transfer followed by proton transfer (ET-PT) (9–13) or proton transfer followed by electron transfer (PT-ET), or concerted pathways (EPT) with concerted transfer in a single step. Although more complex microscopically, EPT can offer a significant advantage in avoiding high-energy intermediates (14, 15).

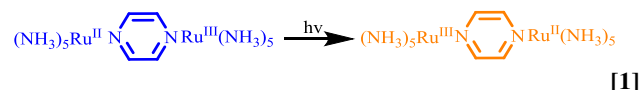
Light driven, photochemical EPT (photoEPT) has been reported (16–18), by Westlake et al. (18) for amine adducts with 4-nitro-4'-biphenylphenol, Scheme 1. In these adducts, intramolecular charge transfer (ICT) excitation is accompanied by proton transfer to an H-bonded base, Scheme 1, as shown by ultrafast and coherent Raman measurements.

Although seemingly a breakdown of the Franck–Condon principle, the appearance of optically induced electron–proton transfer was rationalized by noting that optical excitation and associated changes in electronic structure result instantaneously in a spatially fixed proton in the vibrational force field of the electronic excited state. Subsequent theoretical analysis by Hammes-Schiffer and coworkers (19, 20) supported this conclusion and the coexistence of distinct spectroscopic states, one a conventional ICT state, with excitation followed by proton transfer (photoET-PT), and a concerted photoEPT state.

An important, if largely unrecognized, role for photoEPT could exist and play a role broadly, for example, in DNA photodamage (21, 22) or in forming reactive oxygen intermediates (ROS) (23). Nonetheless, reports of photoEPT and its role in excited state reactivity in chemistry and biology are rare (17–20, 24, 25).

In electron transfer, a significant advance came from the appearance and analysis of low-energy intervalence transfer (IT) (26) absorption bands in mixed-valence complexes (27), Eq. 1, and from an analysis by Hush (28). In appropriate limits, the

Hush treatment provides quantitative relationships between absorption band energies, widths, and oscillator strengths. Analysis of IT absorption bands provides intramolecular and medium reorganization energies and electronic matrix elements arising from donor–acceptor wave function mixing:



In gaining further experimental insight into photoEPT, the direct observation of an optical transition or transitions analogous to a mixed valence IT band would be an important step forward. It would enable further characterization of the coupled electron/proton transfer process by using absorption band properties to assess barriers and the extent of electronic coupling. Given the expected relatively weak electronic coupling between donor and acceptor across a linking H bond as in Eq. 1, absorptivities for these transitions are expected to be low, making direct observation of a photoEPT transition difficult experimentally.

We report observation of photoEPT absorptions, here in H-bonded complexes between *N*-methyl-4,4'-bipyridinium cation (MQ⁺) and the biologically relevant donor tyrosine (TyrOH) and the phenols 4-methylphenol (*p*-MePhOH) and 4-methoxyphenol (*p*-MeOPhOH). Structures are shown in Chart 1.

MQ⁺ is transparent in the visible spectrum whereas the spectrum of the reduced form of its dimethylated analog, methyl viologen (MV^{•+}), includes a characteristic intense $\pi \rightarrow \pi^*$

Significance

Concerted proton-coupled electron transfer (EPT) reactions in which both electrons and protons transfer in tandem are at the heart of many chemical and biological conversions including photosystem II. We report here the direct observation of absorption bands arising from photoEPT transitions, in this case, in H-bonded complexes between *N*-methyl-4,4'-bipyridinium cation and biologically relevant donors including tyrosine. The importance of these observations follows from the earlier experimental observations by Taube and coworkers on intervalence transfer in mixed-valence complexes. The observation of these photoEPT transitions and the appearance of reactive radical products also points to a possible, if inefficient, role in DNA photodamage and, possibly, in the formation of reactive oxygen intermediates.

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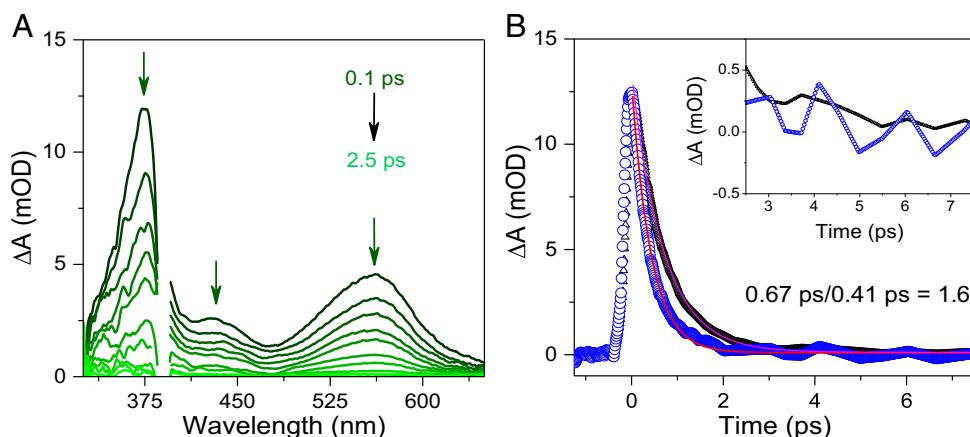


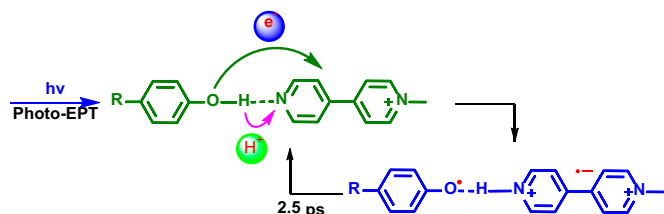
Fig. 2. (A) Transient absorption difference spectra at different delay times from 0.10 ps to 2.5 ps following ultrafast excitation (at 388 nm, and the pump pulse energy was 25 nJ per pulse) of a 25-mM solution of *p*-MeOPhOH with 25 mM added MQ⁺ in a 50-mM Tris buffer, pH = pD = 8.5, I = 0.8 M NaCl at T = 25 °C. (B) Absorption-time decay traces at $\lambda_{\max} \sim 560$ nm corresponding to the decay of HMQ* by back electron transfer following pulsed excitation at 388 nm with 25 mM *p*-MeOPhOH and 25 mM MQ⁺ (blue) in H₂O and D₂O (black). Inset shows the traces magnified from ~ 2.5 –7.5 ps.

The electronic coupling matrix element (H_{DA}) was calculated by using Eq. 6 with $d = 7$ Å, the average of limiting values for d as described by the procedure in Curtis and Meyer (34):

$$H_{DA} = [(4.2 \times 10^{-4}) \times \epsilon_{\max} \times \Delta\bar{\nu}_{1/2} \times E_{\text{op}}]^{1/2} / d. \quad [6]$$

Values for the three adducts are listed in Table 1. Detailed interpretation of band properties by the classical Hush treatment may be inappropriate given the probable contribution to the absorption manifolds from the high-frequency $\nu(\text{O-H})/\nu(\text{N-H})$ transfer mode as evidenced by the large bandwidths and calculated reorganization energies ($\lambda \sim 22,000 \pm 1,000$ cm⁻¹) (Table 1). The reorganization energies are of similar magnitude ($\lambda \sim 9,000$ –21,000 cm⁻¹) to a related series of intramolecular amino-derivatized, 2,4-di-*tert*-phenyl analogs that undergo intramolecular thermally activated EPT (36). The ΔG° value for the tyrosine adduct from spectral fitting of ~ 1.1 eV (8,900 cm⁻¹) is comparable to ~ 1.4 eV (9,200 cm⁻¹) estimated from E° values for the TyrOH^{+/0} and MVH^{2+/+} couples and known pK_a values (37, 38).

The nature of the lower-energy absorption feature for the H-bonded adducts was investigated further by ultrafast transient absorption measurements by an apparatus and data analysis described earlier (39–41) and in *Supporting Information, Experimental, Ultrafast Transient Absorption Experiments*. Excitation (388 nm, 250 fs FWHM) into the low-energy absorption band for the *p*-MeOPhO-H—MQ⁺ adduct, at pH 8.5 in the aqueous Tris buffer, resulted in the time-resolved transient absorption difference spectra shown in Fig. 2A. At the observation time of 250 fs, positive absorption features appear at $\lambda_{\max} \sim 360$ nm, 440 nm, and 560 nm. The feature at 360 nm (27,800 cm⁻¹) is consistent with the simultaneous appearance of the phenoxyl radical



Scheme 2. Illustration of phenol-MQ⁺ photoEPT and the following back reaction.

(42, 43) and HMQ*⁺ (44), the feature at 440 nm (22,700 cm⁻¹) to the phenoxyl radical, and the broad feature at 560 nm (17,860 cm⁻¹) to the low-lying $\pi \rightarrow \pi^*$ absorption in HMQ* analogous to the absorption at 590 nm (16,950 cm⁻¹) MV*⁺ in MeCN (44).

The transient absorption features are consistent with excitation into the weak, low-energy absorption feature in the *p*-MeOPhO-H—MQ⁺ adduct resulting in the appearance of MeOPhO—H-MQ⁺. The transient features appear within 0.1 ps and decay within 2.5 ps without significant change in band position or shape. They are consistent with Scheme 2 and photoEPT excitation leading to concerted electron–proton transfer within the H-bonded complex.

In support of this assignment, careful examination of the transient absorption decay traces in H₂O in Fig. 2B provides clear evidence for a vibrational coherence (45–47). The oscillatory part of the decay from 2.5 ps to 7.5 ps is compared in H₂O and D₂O in Fig. 2B. The oscillations in H₂O appear with a period of ~ 1 ps consistent with a vibrational coherence that is sustained in picoseconds and vibrational relaxation from a higher $\nu(\text{N-H})$ vibrational level or levels on the timescale for back electron transfer (48).

From the time-resolved, single exponential decay traces at pH = pD = 8.5, $k_{D_2O} = 1.5 \times 10^{12}$ s⁻¹ for back EPT with deuteron transfer and $k_{H_2O} = 2.4 \times 10^{12}$ s⁻¹ for proton transfer, a kinetic isotope effect of $k_{H_2O}/k_{D_2O} = 1.6$. The results from these studies are important because they demonstrate an optical process that is analogous to IT in mixed-valence molecules. From the transient experiments, excitation into the underlying transition initiates photoEPT (Scheme 2). Although related transitions may exist, they are, no doubt, typically masked by higher absorptivity transitions and appear here as low-energy absorption features in H-bonded, donor–acceptor complexes. Assignment of the optical transition is consistent with the results of ultrafast transient absorption measurements. There is evidence for vibrational coupling following photoEPT excitation.

As expected, the underlying absorptions are of relatively low absorptivity consistent with weak electronic coupling between donor and acceptor in the H-bonded adducts. Nonetheless, the existence of the transitions, and the appearance of the high-energy, radical intermediates that they produce, could play a hidden role in low-efficiency, photochemical pathways both in biology and in photochemical energy conversion processes.

Methods

Detailed spectral data and analysis are included in *Supporting Information*.

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