

Ion-Mediated Electron Transfer in a Supramolecular Donor-Acceptor Ensemble

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25. Alternative explanations for pore blocking are easily rejected. The possibility of ion clusters blocking the pores is unlikely because the diameter of such clusters measured by dynamic light scattering is ~500 nm, which is too large to block these pores. Precipitation of ions shown by Powell et al. (20), which might block the pore entrance, does not occur because of the high solubility product (K_{sp}) of NaCl, KCl, and LiCl. Impurities in the solution were ruled out, water alone does not cause pore blocking, and no blocking from the TMA-CI suggests that impurities in salts have little effect. The absence of blocking events from the water and TMA-CI removes the possibility of nanobubbles discussed by Smeets et al. (26) as well. Ag^+ and Cl^- dissolve from $Ag/AgCl$ electrodes with K_{sp} of 1.8×10^{-10} with $[Ag^+]$ about five orders of magnitude smaller than $[Na^+]$; therefore, their contribution to pore blocking is negligible. Once an ion blocks the pore, the ion must translocate to the other side, because the driving force of effluxing back to the solution is relatively weak compared with the high electric field across the blocker.

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Ion-Mediated Electron Transfer in a Supramolecular Donor-Acceptor Ensemble

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Ion binding often mediates electron transfer in biological systems as a cofactor strategy, either as a promoter or as an inhibitor. However, it has rarely, if ever, been exploited for that purpose in synthetic host-guest assemblies. We report here that strong binding of specific anions (chloride, bromide, and methylsulfate but not tetrafluoroborate or hexafluorophosphate) to a tetrathiafulvalene calix[4]pyrrole (TTF-C4P) donor enforces a host conformation that favors electron transfer to a bisimidazolium quinone (BIQ²⁺) guest acceptor. In contrast, the addition of a tetraethylammonium cation, which binds more effectively than the BIQ²⁺ guest in the TTF-C4P cavity, leads to back electron transfer, restoring the initial oxidation states of the donor and acceptor pair. The products of these processes were characterized via spectroscopy and x-ray crystallography.

Reversible electron-transfer (ET) processes play a key role in biological energy conversion. Often these events are controlled by external cofactors, including small ions, which favor either charge separation or recombination. For instance, in the O₂-evolving complex of photosystem II, Ca²⁺ and Cl⁻ are known to be essential activators for the fast turnover of water oxidation, whereas other ionic species can act as activators, inhibitors, or simple spectators (1–5). Redox-inactive metal ions, such as Ca²⁺, are known to control the reactivity of organic electron acceptors by binding to the one-electron reduced species involved, that is, radical anions of electron acceptors (6). Likewise, the key enzyme in respiration, cytochrome c oxidase, is a heme-copper oxidase with a positively charged protein surface that allows for the binding of a variety of anions with different affinities and stoichiometry (7). This recognition process has been reported to induce a redox-dependent structural change that affects the ET process (8). However, in spite of the pivotal role of ions as regulators of biological ET (1–8), anions and cations have rarely, if ever, been exploited to affect reversible ET processes in a simple donor-acceptor (D/A) ensemble.

Here, we report a supramolecular system, based on a tetrathiafulvalene calix[4]pyrrole (TTF-C4P) donor (9) and a dicationic bisimidazolium quinone (BIQ²⁺, 2) acceptor (10), wherein the judicious addition of anions or cations is used to control the direction of electron transfer. The ability to manipulate the ET process under simple thermal, as opposed to light-induced, conditions has allowed for the isolation and full characterization of both the stable radical products and the putative supramolecular intermediates.

TTF-C4P is an electron-rich calix[4]pyrrole (9, 11–13), a class of fluxional tetrapyrrolic macrocycles that are known to bind selected anions well in organic solvents (11). As a general rule, anion binding to calix[4]pyrroles induces a change from the so-called 1,3-alternate (Fig. 1 left) to the cone conformation (Fig. 1 center) because of concerted hydrogen bonding interactions. In the particular case of 1, large electron-deficient species, such as C₆₀, can be bound by the anion-induced bowl-like cone conformation (12, 13). As is true for other calix[4]pyrroles (14), within-the-bowl binding of small cations is also seen; this has been established explicitly in the case of tetraethylammonium chloride (TEACl) by proton nuclear magnetic resonance spectroscopy in CDCl₃ as well as by x-ray diffraction analysis (figs. S1 and S6).

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The following is a comment on the published paper shown on the preceding page.

Reversible Cation- and Anion-Controlled Electron Transfer Using a Supramolecular Donor-Acceptor Ensemble

FUKUZUMI Shunichi and OHKUBO Kei

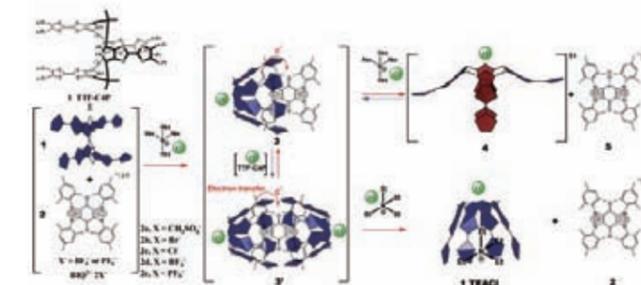
(Graduate School of Engineering)

Electron transfer is one of the most fundamental chemical reactions in biological systems. Reversible electron-transfer processes play a key role in biological energy conversion. Often these events are controlled by external cofactors, including small ions, that either favor charge separation or recombination. For instance, in the O₂ evolving complex of Photosystem-II, Ca²⁺ and Cl⁻ are known to be essential activators for the fast turnover of water oxidation, while other ionic species can act as activators, inhibitors, or simple bystanders [1,2]. Redox-inactive metal ions such as Ca²⁺ are known to control the redox reactivity of organic electron acceptors by binding to the one-electron reduced species involved, i.e., radical anions of electron acceptors [3]. The key enzyme in respiration, cytochrome c oxidase, is a heme-copper oxidase with a positively charged protein surface that allows for the binding of a variety of anions with different affinities and stoichiometry [4]. This recognition process has been reported to induce a redox-dependent structural change that affects the electron-transfer process [5]. However, in spite of the pivotal role of ions as regulators of biological electron transfer [1-5], we are unaware of any examples where anions and cations have been exploited to effect reversible electron transfer in a simple donor-acceptor (D/A) ensemble.

We developed a new supramolecular system, based on a tetrathiafulvalene calix[4]pyrrole (TTF-C4P: 1) donor and a dicationic bisimidazolium quinone (BIQ²⁺: 2) acceptor, where the judicious addition of anions or cations is used to control the direction of electron transfer. The ability to manipulate the electron transfer process under simple thermal, as opposed to light-induced, conditions has allowed for the isolation and full characterization of both the stable radical products and the putative supramolecular intermediates. This report is the first experimental study where external modulation of a strongly coupled donor-acceptor complex is used to control a reversible electron transfer process.

TTF-C4P (1) is an electron rich calix[4]pyrrole, a class of fluxional tetrapyrrolic macrocycles that are known to bind selected anions well in organic solvents. As a general rule, anion binding to calix[4]pyrroles induces a change from the so-called 1,3-alternate to the cone conformation. In the particular case of TTF-C4P, large electron deficient species, can be bound by the anion-induced “bowl-like” cone conformation. As is true for other calix[4]pyrroles, within-the-bowl binding of small cations is also seen; this has been established explicitly in the case of tetraethylammonium chloride (TEACl).

BIQ²⁺ (2) was chosen as the redox partner for 1 for several reasons. First, BIQ²⁺ is relatively large; as such, it was expected to be complexed by TTF-C4P but only when this latter receptor is in its anion-bound cone conformation. Second, the dicationic nature of 2 suggested to us that after putative electron transfer to give the capsule product 3, two cationic species would be produced that might diffuse apart to produce the individual radical species, i.e., [TTF-C4P]^{•+} and BIQ^{•+} (4 and 5 in Scheme 1). Finally, in combination with TTF-C4P, BIQ²⁺ as the acceptor was expected to provide a near isoergonic redox couple, allowing us to observe readily the effects of anions, cations, and conformational switching on a potentially reversible thermal electron-transfer process.



Scheme 1 Chemical structures of TTF-C4P 1 and BIQ²⁺ salts 2, and their proposed ion-mediated electron transfer reactions.

Five specific salts of BIQ²⁺, 2a–2e, were selected for study. These salts are identical except for the counter anion, X⁻. They encompass two subgroups, namely anions that bind well to TTF-C4P (X⁻ = MeSO₄⁻, Br⁻, Cl⁻) and those that do not (X⁻ = BF₄⁻, and PF₆⁻). As expected, these species react very differently with TTF-C4P. For instance, adding increasing amounts of BIQ²⁺2X⁻ (X⁻ = MeSO₄⁻, Br⁻, Cl⁻) salts into a chloroform solution of 1 held at a constant concentration resulted in the gradual emergence of absorption features centered at 751 nm and ca. 2000 nm, respectively, at the expense of the original TTF-C4P absorption band (λ_{max} = 329 nm) with a clear isosbestic point, λ_{iso} of 340 nm. Similar spectral changes were seen when THACl was added to a mixture of 1 and 2e (or 2d) (Fig. 1A), albeit not when 1 was mixed with 2e or 2d in the absence of MeSO₄⁻, Br⁻, or Cl⁻.

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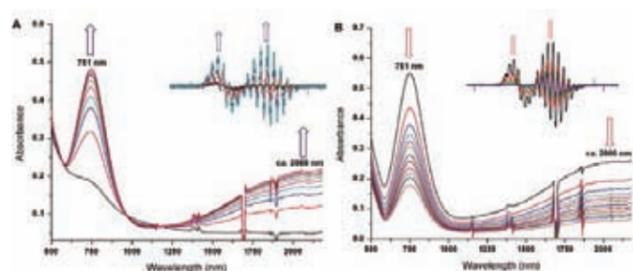


Fig. 1 A Spectroscopic changes observed when TTF-C4P, **1**, (30 μ M) is treated first with 1 molar equiv. of BIQ²⁺2PF₆⁻ and then with increasing quantities of THACl in CHCl₃ (up to 10 equivalents). The inset shows the EPR spectra of 1:1 mixture of TTF-C4P and BIQ²⁺2PF₆⁻ in CHCl₃ at r.t. and upon addition of THACl. B Cation induced reverse electron transfer seen upon the addition of up to 15 equiv. of TEACl to a 1:1 solution of TTF-C4P and BIQ²⁺2Cl⁻ in CHCl₃ (30 mM in each). Inset: EPR spectra of a 1:1 mixture of TTF-C4P and BIQ²⁺2Cl⁻ (1.1 \times 10⁻⁴ M in each) in CHCl₃ at r.t. upon addition up to 5 molar equiv. of TEACl.

ments, isolation and characterization of the radical salts, [TTF-C4P]^{•+}MeSO₄⁻ and [BIQ]^{•+}MeSO₄⁻. The signals at ca. 751 and ca. 2000 nm were ascribed to TTF^{•+} and [TTF]₂^{•+} radical cations derived from TTF-C4P. New spectral features at ca. 380 nm could also be assigned to the reduced radical BIQ^{•+} in this way.

Once produced, no further changes in these optical features were observed under ambient conditions. However, the deliberate addition of TEACl caused the intensity of the signals at ca. 751 and ca. 2000 nm to decrease and the peak at ca. 329 nm to be restored (Fig. 1B). These optical changes are thus fully consistent with the anion-induced formation of an electron transfer state consisting of BIQ^{•+} and [TTF-C4P]^{•+} and its subsequent cation-triggered reversal.

Electron paramagnetic resonance (EPR) spectroscopy confirmed that the underlying ET process was being “switched on” and “switched off” through the direct measurement of paramagnetic or radical species in solution via the addition of coordinating anions (e.g., Cl⁻) and small cations (i.e., TEA⁺), respectively (cf. insets to Fig. 1). There are two distinct radical signals corresponding to the radical cation of TTF-C4P, **1**, at $g = 2.0083$, and the reduced radical of BIQ²⁺, **2**, at $g = 2.0056$.

The same mixed EPR spectra, containing signals for both [TTF-C4P]^{•+} and BIQ^{•+}, were obtained when **1** was mixed with **2a**, **2b**, or **2c** in chloroform or when **1** was treated with **2d** or **2e** followed by THACl (see inset to Fig. 1A). On the other hand, the addition of two molar equiv. of TEACl, a chloride salt containing the small TEA⁺ cation that is known to bind within the calix[4]pyrrole “bowl” of TTF-C4P, to the 1:1 mixture of **1** and **2c** in chloroform at 298 K caused the EPR signals for both [TTF-C4P]^{•+} and BIQ^{•+}, to disappear nearly in their entirety (see inset to Fig. 1B).

Structural analysis of the third set of crystals revealed a supramolecular donor-acceptor assembly, wherein two anion-bound bowl-like TTF-C4P moieties tightly encapsulate a bis-imidazolium quinone guest in a 2:1 fashion (Fig. 2A). Based on the structural parameters, these capsule species are considered to be tightly coupled [TTF-C4P]^{•+}₂[BIQ^{•+}]₂X⁻ biradical systems (**1•3b** and **1•3c**; X = Br, Cl, respectively). This is the first time it has proved possible to isolate as a stable species a strongly coupled bimolecular radical ion pair involved in a bimolecular electron process prior to separation into the two radicals involved.

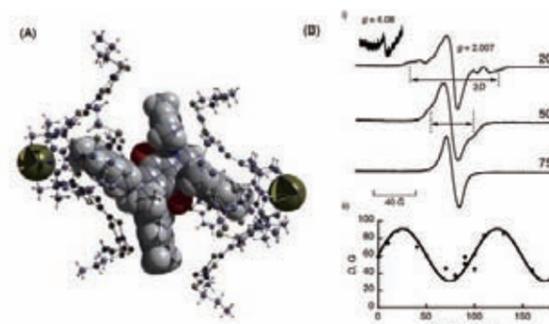


Fig. 2 (A) Single crystal X-ray structure of the supramolecular donor-acceptor complex of net stoichiometry [TTF-C4P]^{•+}₂[BIQ^{•+}]₂(Cl). (B) i) EPR spectra of a crystal of TTF-POMes recorded at different angles at 4 K. ii) The angle variation of the D value.

The existence of a tightly coupled biradical “capsule” was further confirmed by low temperature (4 K) EPR analyses of a single crystal of the [TTF-C4P]^{•+}₂[BIQ^{•+}]₂Cl⁻ salt (Fig. 2B). Typical triplet signals were observed at $g = 4.08$ and 2.007 with zero-field splitting. The zero-field splitting parameter (D) observed when plotted against the angle of rotation for the single crystal, resulted in a sine curve which indicated the existence of an intramolecular radical ion pair.

On the basis the above findings, we propose that reversible, anion-induced electron transfer takes place in accord with Scheme 1. Specifically, the use of a BIQ²⁺ salt containing a coordinating anion or the addition of THACl to chloroform solutions of TTF-C4P and BIQ²⁺ salts with non-coordinating anions leads first to conformational “flipping” and stabilization of the calix[4]pyrrole cone conformation. This is followed by formation of a capsule-like donor acceptor complex, either **3** or **3'**, followed by fast electron transfer. The initial, within-the-capsule electron transfer is then followed by reversible separation of the two positively charged radical species in question. The net result is the formation of [TTF-C4P]^{•+} and BIQ^{•+} as electron transfer products under a reversible equilibrium process.

We have found that reversible electron transfer can be achieved using other electron acceptors. We thus believe that the ion-switched strategy reported herein may be generalized to provide working devices useful for light harvesting, ion sensing, energy storage, among other applications

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Design, Synthesis, and Electrochemistry of Room-Temperature Ionic Liquids Functionalized with Propylene Carbonate

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Communications

Ionic Liquids

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Design, Synthesis, and Electrochemistry of Room-Temperature Ionic Liquids Functionalized with Propylene Carbonate**

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Alkyl carbonates are often employed as solvents for the study of energy-storage devices (ESD), such as lithium secondary batteries (LSB) and electric double-layer capacitors. Some of these solvents, including propylene carbonate (PC) and diethyl carbonate, have already been put to practical use in modern electronics technology, such as in mobile phones and laptop computers. However, all of these organic solvents have potential safety drawbacks related to their flammable and volatile nature that can lead to explosions and/or fire accidents. Furthermore, lithium anodes with a high theoretical discharge capacity (3860 mAh g⁻¹) cannot be utilized in such solvents owing to dendritic lithium deposition during the charging cycle. However, room-temperature ionic liquids (RTILs)^[1-3] and RTIL-like solvents^[2-6] are expected to be a new class of solvents for next-generation rechargeable high-energy-density batteries because RTILs possess unique salt-like properties. Some of these properties, such as high electrochemical stability, negligible vapor pressure, and

resistance to combustion,^[1-3,7,8] are highly advantageous in electrochemical applications.^[1-3,7,8] Thus, we anticipated that chemically combining an appropriate carbonate and organic salt may remove some of the undesirable properties of alkyl carbonates and provide uniquely functionalized RTILs for ESDs, and particularly LSB systems (Figure 1).

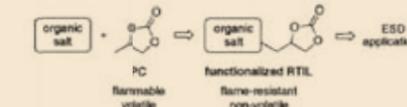


Figure 1. An organic salt (room-temperature ionic liquid; RTIL) attached to propylene carbonate (PC).

Many of common cations of organic salts (for example, imidazolium, pyridinium, ammonium, and phosphonium species) could be used for this ESD-oriented study; however, full-scale electrochemical and physicochemical measurement analysis often requires ten- to hundred-gram quantities of impurity-free samples, and a large-scale preparation of structurally complex organic salts is still synthetically challenging. Therefore, a readily accessible and generally inexpensive tetraalkylammonium salt (R₄N⁺X⁻), more specifically piperidinium salt **1**, seems to be a reasonable substructure to combine with a carbonate functionality (Figure 2).^[9]

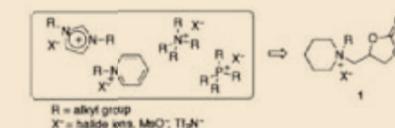


Figure 2. Common organic salts and piperidinium salt attached to PC (**1**).

Herein, we describe a novel RTIL containing a piperidinium cation with a PC moiety, which can form a solid electrolyte interphase (SEI) layer on the lithium deposit.^[10] A facile synthetic approach to **1** and the electrochemical properties of **1** as a solvent in a LSB system are also discussed.

The synthesis (Scheme 1) started from inexpensive, commercially available reagents, piperidine and epichlorohydrin, which afforded epoxypropylpiperidine **2** by using a modified Heywood-Phillips procedure.^[11] The TBAI-catalyzed cyclic

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