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.* (*38*), 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-Cl suggests that impurities in salts have little effect. The absence of blocking events from the water and TMA-Cl 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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38. Powell *et al.* observe oscillations from divalent ions precipitating at the pore mouth of a 2- to 6-nm Si nanopore (*28*). These oscillations are distinct from those observed in this work in that they are formed from an unstable (precipitating) system, which is difficult to sustain without reversible formation and dissolution of the precipitates.
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Materials and Methods
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Figs. S1 to S19
References

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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 (BIQ^{2+}) guest acceptor. In contrast, the addition of a tetraethylammonium cation, which binds more effectively than the BIQ^{2+} 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 O_2-evolving complex of photosystem II, Ca^{2+} 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 Ca^{2+}, 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 effect 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: **1**) donor (*9*) and a dicationic bisimidazolium quinone (BIQ^{2+}, **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 C_{60}, 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 $CDCl_3$ 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

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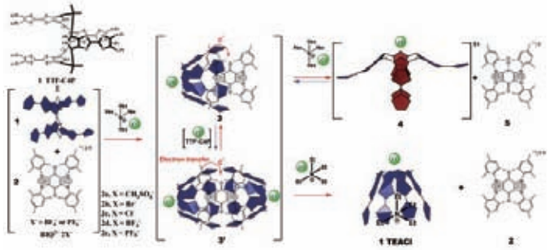
Electron transfer is one of the most fundamental chemical reactions in biological systems. Reversible electron-transfer processes play a key role in biological energy conversion. Often these events are controlled by external cofactors, including small ions, that either favor charge separation or recombination. For instance, in the O_2 evolving complex of Photosystem-II, Ca^{2+} 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 Ca^{2+} 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 tetrathiafulvene calix[4]pyrrole (TTF-C4P: **1**) donor and a dicationic bisimidazolium quinone (BIQ^{2+}: **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).

BIQ^{2+} (**2**) was chosen as the redox partner for **1** for several reasons. First, BIQ^{2+} 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., $[TTF\text{-}C4P]^{\bullet+}$ and $BIQ^{\bullet+}$ (**4** and **5** in Scheme 1). Finally, in combination with TTF-C4P, BIQ^{2+} 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 BIQ^{2+} salts **2**, and their proposed ion-mediated electron transfer reactions.

Five specific salts of BIQ^{2+}, **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^- = $MeSO_4^-$, Br^-, Cl^-) and those that do not (X^- = BF_4^-, and PF_6^-). As expected, these species react very differently with TTF-C4P. For instance, adding increasing amounts of $BIQ^{2+}2X^-$ (X^- = $MeSO_4^-$, 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 $MeSO_4^-$, Br^-, or Cl^-.