Engineering a redox-active proton wire with protoncoupled electron transfer

Joshua Goings and Sharon Hammes-Schiffer PHYS: Tuesday, August 27, 2019,11:50 AM

Yale





"[We aim] to establish the fundamental principles needed for **efficient interconversion of electrical energy and chemical bonds** through precise control of electron and proton transfers."

experiment



- Emmanuel Odella
- Brian Wadsworth
- S. Jimena Mora
- Devens Gust
- Ana Moore
- Tom Moore
- Gary Moore

theory

Yale

- Josh Goings
- Mioy Huynh
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Can we understand how to design a redox-active proton wire?

theory

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PCET in Photosystem II



Bioinspired systems for PCET

Inspired by the Tyr/His redox relay in photosystem II, set out to create redox-active molecules to drive proton translocation.



photosystem II

benzimidazolephenol (BIP) constructs

In the simplest case, upon oxidation of the phenol, proton moves from the phenol to the benzimidazole. Process is reversible.

Phenol pK_a changes from around 10 to -2 upon oxidation.

Creating a proton relay with two proton transfers

One proton hop is good...how about more?



Oxidize, and monitor equilibrium between **E***n***PT** products (one Electron with *n* **P**roton Transfers) using IRSEC



Tuning E2PT/E1PT Equilibrium



basicity, so less of a "pull" on the protons

Odella, E.; *et al.* Controlling Proton-Coupled Electron Transfer in Bioinspired Artificial Photosynthetic Relays. *J. Am. Chem. Soc.* **2018**. https://doi.org/10.1021/jacs.8b09724.

 $-OCH_3$ point extrapolated to get K_{eq}

Can we extend the proton relay?

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Yes! By changing substituent to a cyclohexylimine.



Proton-Coupled Electron Transfer Drives Long-Range Proton Translocation in Bioinspired Systems

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Can we extend the proton relay?

Longer relays yield more opportunity for unproductive isomers

Strong basicity of **cyclohexylimine** substituent gives single isomer in nonpolar solvent; DFT calc's support thermodynamic stability



one benzimidazole

two benzimidazoles

three benzimidazoles

Synthesized three benzimidazole-phenol (BIP) products with hydrogen bonds aligned for proton transfer

Experimental characterization



IRSEC:

Peak @ 1660 cm⁻¹ shows protonated imine CN stretch

No peak @ 1556 cm⁻¹ shows lack of benzimidazolium ion

(except for **1**, which lacks cyclohexylimine) 60 mV reduction in E (V vs SCE) with each additional benzimidazole **Process is reversible**



Experimental + theoretical characterization



Theoretical characterization

Although the overall reaction is concerted on the electrochemical timescale, theory can decompose the contributions of individual steps in the thermodynamic cycle



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Proton transfer from oxidized phenol to first benzimidazole exoergic.
Subsequent transfers between benzimidazoles exoergic, but decreasing.
Final proton transfer to imine bit more favorable, due to basicity of imine.



Pushing protons forward

Further tune the electron donating/withdrawing nature of substituents?

Distort pi-conjugated framework supporting the Grotthuss-type hydrogen-bonded network?











Figures from Ana and Tom Moore.

Summary

- 1. Synthesized a series of molecules with increasing number of proton translocations upon oxidation
- 2. Spectroscopic and electrochemical evidence show complete, reversible PT, and a decrease in redox potential with additional benzimidazole linkers
- 3. Theoretical calculations validate the experimental interpretation, and give insight into the thermodynamic contributions of each proton transfer
- 4. Insights may guide future development of related molecules



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