Electronic Coupling in Osmium-Porphyrin dimers

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Background: The extent of electronic coupling determines the ease with which an electron can be shared or transferred over long distances, either within a single molecule or across great distances between molecules. Understanding the factors affecting electronic coupling will allow us to create molecules capable of transferring charge over long distances, for example in molecular wires. It will also allow us to influence important biological electron transfer processes, such as photosynthesis.

Mixed valence dimers are ideal for studying intramolecular electron transfer and electronic coupling because they provide a framework that simplifies many of the parameters. The Hush formalism (Eqn. 1) provides a way to calculate

$$H_{DA} = \frac{2.05 \bullet 10^{-2}}{r}(\varepsilon_{max}\Delta\bar{\upsilon}_{1/2}\bar{\upsilon}_{max})^{1/2}$$

Eqn. 1

r is the distance between redox centers

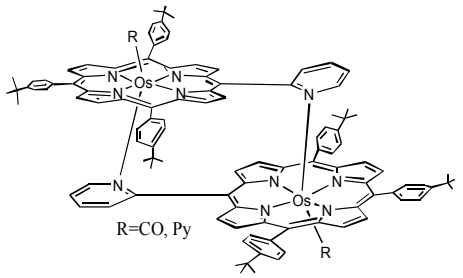
ε_{max} is the molar absorptivity of the intervalent charge transfer band

$\Delta v_{1/2}$ is the width of the IVCT at half height

v_{max} is the maximum wavelength of IVCT, see below

Once the coupling element is known, the rate of electron transfer can be calculated using Marcus theory.

The model system shown in Scheme 1 was developed because it is a small scale model of the special pair of cofacially oriented porphyrin rings found in photosystem I and because Fe and Ru analogs to the Os dimer have already been studied.



Scheme 1

Current work: The synthetic route for generating the dimer has been developed and the analogous monomers have been synthesized. The electronic properties of the monomers have been studied by electrochemical techniques and oxidative titrations performed while scanning over ultraviolet, visible, and near infrared wavelengths. For the dimers, the oxidative titration generates a mixed valence species and near infrared light will promote intramolecular electron transfer between the osmium centers. This electron transfer observed in the NIR is the intervalent charge transfer band (IVCT) of the Hush formalism. Making use of eqn 1, the degree of electronic coupling can be measured. The spectra of the dimers were compared to similar spectra of the corresponding monomers, which are not expected to undergo electron transfer.

Future work: The pyridine-capped dimer remains to be synthesized and characterized.

Acknowledgements:

National Science Foundation (CHE-RUI-0648597)