

Effect of oxidation state and coordination with Hg(II) on the electronic spectra of an anthraquinone-rhodamine sensor

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Quinones have long been studied as energy acceptors due to their role in photosynthetic energy transfer complexes.¹ Because of these energy acceptor properties, quinones are fluorescence quenchers. In contrast, hydroquinones do not quench fluorescence because energy transfer to hydroquinones is not as efficient.² The incorporation of a quinone into a rhodamine-based chemosensor allows for the selective modification of the emission intensity of the sensor based on the presence/absence of Hg(II) as well as on the oxidation state of the quinone moiety. In this study, a computational examination of the electronic transitions and through-space energy transfer processes lends insight into the experimental electronic spectra. Electronic transitions were calculated using DFT and TD-DFT based on a model optimized from single crystal x-ray diffraction (XRD) ion positions. DFT calculations were performed on gas phase models using VASP³ with the functional developed by Perdew, Burke, and Ernzerhof (PBE) in the basis of plane waves. TD-DFT calculations were performed in Gaussian 09⁴ with the B3LYP⁵ functional on the sensor in solution phase, which is simulated using a polarizable continuum model (PCM). Absorbance data was analyzed to locate electronic transitions of comparable energy localized on the anthraquinone moiety or the rhodamine moiety. These transitions were evaluated based on a dipole-dipole coupling mechanism to find the Förster resonance energy transfer coupling constant (V_{ij}), the square of which is approximately proportional to the rate of energy transfer between the donor and the acceptor.⁶ The calculated V_{ij} for the sensor in the absence of Hg(II) is significantly lower than in the presence of Hg(II), which correlates with the modest increase in emission when the cation is present (Figure 1). Coordination of Hg(II) to the sensor should result in significant fluorescence enhancement,⁷ but a corresponding increase in energy transfer to the quinone moiety accounts for the lower emission intensity in the coordinated sensor. Furthermore, the experimental addition of Hg(II) to the sensor in solution results in new absorbance peaks in the 500-600 nm range, which correlate with an absorbance peak that only occurs in the computed spectra of the sensor with Hg(II). Additional associations between computed electronic transitions and experimental absorption and emission spectra have also been explored.

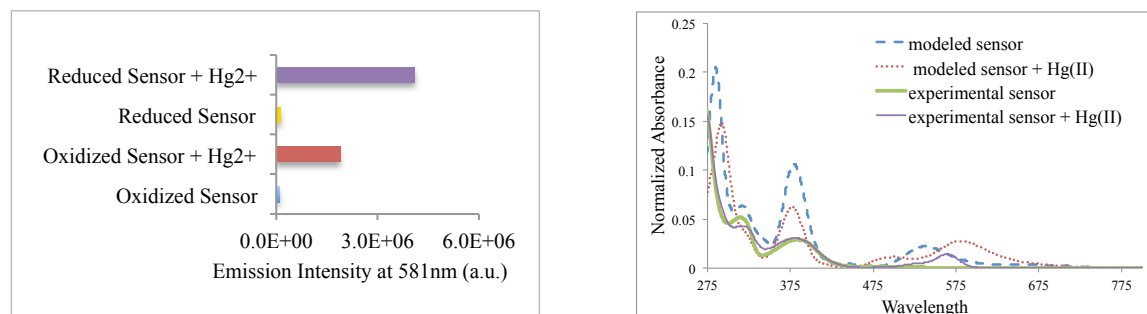


Figure 1. a) Emission intensity of anthraquinone-rhodamine sensor at 581nm with λ_{ex} = 558nm b) Theoretical and experimental absorbance in the presence/absence of Hg(II)

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