

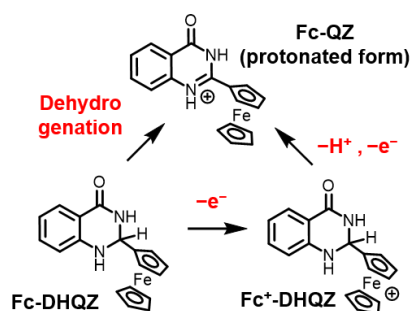
Structures and chemical properties of oxidized forms of ferrocene-substituted dihydroquinazolinone showing self-complementary hydrogen-bond interactions

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[Introduction] Hydrogen-bond (H-bond) pairs comprising electron donor and acceptor molecules have attracted attention because of correlated phenomena of electron transfer with proton transfer or H-bond vibration, which play important roles in biological activities or unique properties of materials.¹⁾ Among such pairs, self-complement H-bond dimers have been studied in terms of the mixed valency influenced by H-bond states.²⁾ However, a small number of examples of such H-bond dimers prevents further understanding of relationship between electron self-exchange reactions and proton displacements. Herein, I report that ferrocene-substituted dihydroquinazolinone (**Fc-DHQZ**) is a candidate for mixed valence H-bond dimers, where the charge distribution has an influence on the proton coordination.

[Results and discussion] **Fc-DHQZ** undergoes sequential oxidation reactions to afford its mono-oxidized (**Fc⁺-DHQZ**) and dehydrogenated (**Fc-QZ**) states (Scheme 1). These molecules form lactam-type H-bond dimers in their crystal structures, that of **Fc⁺-DHQZ** are shown in Figure 1. Contribution of *d*-orbitals to a spin distribution of **Fc⁺-DHQZ** was confirmed by magnetic susceptibility measurements and calculations. Electrochemical and optical studies indicate a base-catalyzed disproportionation of **Fc⁺-DHQZ** to **Fc-DHQZ** and **Fc-QZ** in its acetonitrile solution. In an acetonitrile–dichloromethane solvent system, the formation of a H-bond dimer comprising **Fc-DHQZ** and **Fc⁺-DHQZ** was investigated by measuring infrared and NMR spectroscopies. A spontaneous production of **Fc-QZ** in the mixed solution would stem from a deprotonation step of **Fc⁺-DHQZ**, which is a proton transfer from **Fc⁺-DHQZ** to **Fc-DHQZ** within the dimer.



Scheme 1. Sequential oxidation of **Fc-DHQZ**

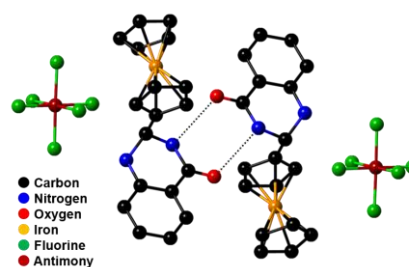


Figure 1. Ortep drawing of **Fc⁺-DHQZ**. Hydrogen atoms were omitted for clarity.

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