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Efficient Electronic Communication between Two Identical Ferrocene Centers in a Hydrogen-Bonded Dimer

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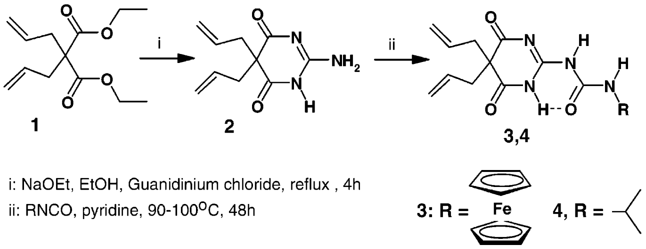
Efficient electronic communication between two equivalent redox centers requires tethering structures that support extensive electron delocalization.[1] In general terms, the extent of electronic coupling between the redox centers usually decreases quickly as the distance between them increases.[2] Knowledge of the structural features that favor electron delocalization is not only important from a fundamental point of view but also relevant for the preparation of molecules with potential applications as components in novel molecular electronic devices.[3,4] A considerable body of work has been devoted to the investigation of connecting structures with various types of unsaturated linkages,[2,3] and more recently, interesting results have been reported with tethers containing metal−metal bridges.[5] To the best of our knowledge, linkage structures assembled via noncovalent bonds have been pursued only in a few limited cases.[6−9] In this work, we report the preparation and properties of a ferrocene derivative that contains a quadruple hydrogen bonding motif (donor−donor−acceptor−acceptor, DDAA) similar to the well-known Meijer's ureidopyrimidine residue,[10] but modified to prevent keto−enol tautomerism, as described by Sanjayan and coworkers.[11] This ferrocene derivative (see Scheme 1 for structures) is designed to self-recognize, forming highly stable hydrogen-bonded dimers that contain two identical ferrocene centers. Surprisingly, the extent of electronic communication between the ferrocene centers, separated by more than 10 Å in the dimer, was found to be remarkably large.

Condensation of diester **1** with guanidinium chloride yielded amine **2**,[11] which was reacted with the corresponding isocyanate to give the ferrocene derivative (**3**) or a redox inactive, isopropyl derivative (**4**, see Scheme 1). Both compounds **3** and **4** are expected to form hydrogen-bonded complexes with themselves or any other compounds containing similar DDAA hydrogen bonding motifs.[10−12] The ^{1}H NMR spectrum of compound **3** in $CDCl_3$ verifies this hypothesis, as three hydrogen-bonded NH amide peaks are clearly visible in the spectrum (Figure 1) at 10.5, 11.5, and 12.8 ppm. Similar results were obtained with compound **4**. Quantitative dimerization was observed upon dilution to concentrations as low as 10 μM, which is consistent with a high equilibrium constant ($K_{\text{dim}} > 10^6$ M^{-1}) for the dimerization process.[12] Dimer formation was also evident in the FAB mass spectrum of **3** (see Supporting Information). ^{1}H NMR spectra obtained in CD_2Cl_2 were similar, revealing that the dimers are sufficiently stable to withstand the moderate increase in solvent polarity experienced in going from $CDCl_3$ to CD_2Cl_2. However, the spectrum of **3** in CD_3CN solution does not show the hydrogen-bonded NH resonances and corresponds to the monomer (Supporting Information), as anticipated from the greater polarity of this solvent, which effectively disrupts the hydrogen bonding interactions.

Scheme 1. Synthesis and Structures of Self-Recognizing Compounds **3** and **4**



i: NaOEt, EtOH, Guanidinium chloride, reflux , 4h
ii: RNCO, pyridine, 90-100°C, 48h

Voltammetric experiments with **3** in CH_2Cl_2 solution show two reversible oxidation waves (at 0.43 and 0.82 V vs Ag/AgCl) with similar current levels. Enriching the solvent mixture in acetonitrile leads to increased current levels for the first oxidation wave and decreased current levels for the second oxidation process at more positive potential (Figure 2). In CH_3CN solution, only one wave was observed for the oxidation of **3**. In other words, the presence of CH_3CN decreases the stability of the dimer, reducing its concentration and the current levels for the second oxidation process, which is characteristic of the dimer. However, a high level of acetonitrile (more than 80% v/v) is required for the complete disappearance of the second oxidation process, a reflection of the considerable stability of dimeric $\mathbf{3_2}$. These voltammetric results clearly reveal that the two equivalent ferrocene centers in the dimer undergo oxidation at very different half-wave potentials; that is, they exhibit a remarkable level of electronic communication.[13] This finding was further confirmed in another series of voltammetric experiments in which compound **3** (at fixed concentration) was titrated with increasing concentrations of redox inactive compound **4**. Again, increasing concentrations of **4** lead to decreased current levels for the second oxidation process, as the $\mathbf{3_2}$ species is gradually

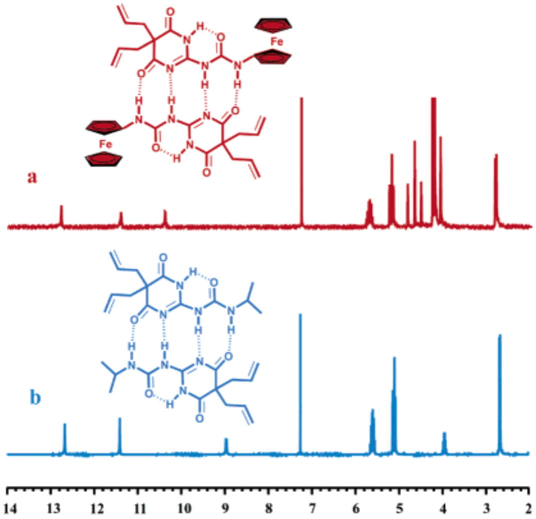


Figure 1. Partial ^{1}H NMR spectra (400 MHz) of compounds **3** and **4** in $CDCl_3$ solution. The proposed dimer structures are also shown.

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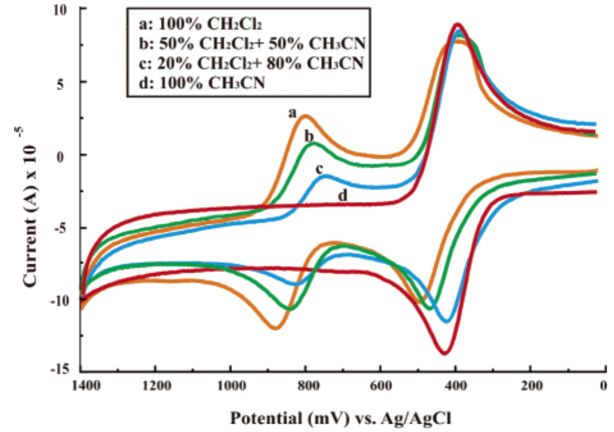

Figure 2. Cyclic voltammetric behavior on glassy carbon (0.071 cm^2) of 1.0 mM **3** in 0.2 M $TBAPF_6/CH_2Cl_2$ solution containing increasing proportions of CH_3CN. Scan rate: 0.1 $V{\cdot}s^{-1}$.

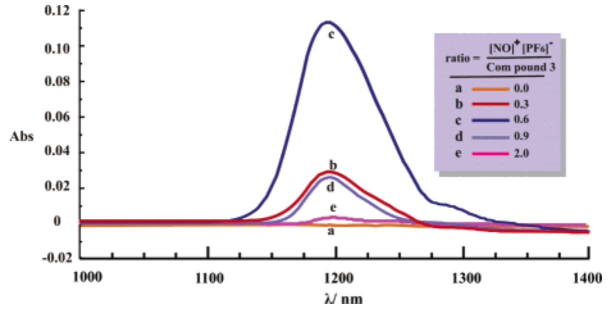

Figure 3. Intervalence charge-transfer band obtained with a 1.0 mM solution of **3** in 0.2 M $TBAPF_6/CH_2Cl_2$. Optical pathlength: 1.0 cm. Oxidant: $NOPF_6$.

replaced by the **3·4** heterodimer, which only contains a single ferrocenyl residue (see Supporting Information).

The stability of the mixed valence species $(\mathbf{3_2})^+$ can be initially estimated from the equilibrium constant (K_c) for the comproportionation process:[2] $\mathbf{3_2} + (\mathbf{3_2})^{2+} \rightleftarrows 2(\mathbf{3_2})^+$, which is evaluated from the electrochemical potential data as $K_c = 3.9 \times 10^6$. The stability of $(\mathbf{3_2})^+$ in dichloromethane solution should allow the detection of an intervalence charge-transfer (IVCT) band in the near-IR spectral region.[2] Indeed, partial oxidation of a solution of **3** in 0.2 M $TBAPF_6/CH_2Cl_2$ gives rise to a new absorption band (Figure 3) at $\bar{\nu}_{max} = 8368$ cm^{-1} ($\lambda_{max} = 1195$ nm, $\epsilon_{max} = 240$ $M^{-1}{\cdot}cm^{-1}$). IVCT character is confirmed by the band's eventual disappearance upon further addition of oxidant. Furthermore, the band is in the anticipated spectral region, judging from previously reported IVCT transitions in other dinuclear ferrocene compounds with good levels of electronic coupling.[2,14] The application of the two-state, Hush model[15] to the spectrum of the mixed valence species $(\mathbf{3_2})^+$ predicts a half-height bandwidth ($\Delta\bar{\nu}_{1/2}$) of $[(2310)(8368)]^{1/2} = 4397$ cm^{-1}, which is considerably larger than the value determined experimentally ($\Delta\bar{\nu}_{1/2} = 560$ cm^{-1}). Since the Hush model can only be rigorously applied to weakly coupled mixed valence species,[15,16] the overestimation of $\Delta\bar{\nu}_{1/2}$ and the large K_c value both indicate that electronic coupling in this system is quite strong. In turn, this also suggests that the rate of thermal electron transfer between the two ferrocene centers is faster than the value calculated from the Hush model (2.5×10^8 s^{-1}).

These results are remarkable for various reasons. First, the extent of electronic communication, as estimated by the difference between the two observed half-wave potentials ($\Delta E_{1/2}$), is quite pronounced in dimer $\mathbf{3_2}$, particularly when considering that the edge-to-edge distance between the two ferrocene centers is at least 1.0 nm, as determined from molecular modeling computations (see minimized structure for the dimer in Supporting Information). In comparison, biferrocene shows a $\Delta E_{1/2}$ value in CH_2Cl_2 solution of 350 mV.[14] Bis(ferrocenyl)acetylene and *trans*-bis(ferrocenyl)ethylene exhibit $\Delta E_{1/2}$ values of only 130 and 120 mV, respectively, in the same medium.[2,14,17] A recent determination of $\Delta E_{1/2}$ in an organometallic compound containing two terminal ferrocenyl units connected through a $-C{\equiv}C{-}Ru_2{-}C{\equiv}C-$ tether yielded a value of 310 mV,[5] which was taken as a demonstration of the positive influence that the diruthenium bridge has on the extent of electronic coupling. All these $\Delta E_{1/2}$ values are smaller than that measured with our noncovalent dimer, which clearly illustrates the efficient electronic coupling between the two ferrocene nuclei in dimer $\mathbf{3_2}$.

To the best of our knowledge, this is the first example of a noncovalent mixed valence species, composed of two identical halves that are kept together by four hydrogen bonds. While further work is obviously needed to understand the electronic coupling between the ferrocene centers in $\mathbf{3_2}$, the data presented here suggest that hydrogen bonding may assist electron transport/delocalization in synthetic materials.

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Supporting Information Available: Additional experimental details and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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