

# Electrochemistry of hydrogen-bonding systems

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Received: 30 September 2006 / Revised: 15 October 2006 / Accepted: 9 November 2006 / Published online: 28 April 2007  
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**Abstract** Hydrogen bonding is one of the most important intermolecular forces in molecular self-assembly or non-covalent synthesis. It is now possible to prepare rather large supramolecular assemblies (>1,000 Da) held together by hydrogen bonds between their molecular building blocks. From the standpoint of electrochemistry, this opens up interesting research avenues. This manuscript reviews recent results—mostly from the authors' own group—on the electrochemistry of systems in which hydrogen bonding plays a crucial role. First, we explore the encapsulation of redox-active centers inside large hydrogen-bonded assemblies and its effects on the kinetics and thermodynamics of the electron transfer reactions of the encapsulated center. Second, we survey the use of electrochemistry to modulate the strength of hydrogen bonding between complementary partners. In this regard, the association and dissociation of dimeric calixarene molecular capsules can be fully controlled by the oxidation state of ferrocenyl centers located nearby the hydrogen-bonding sites. Finally, we also present very recent and intriguing results on the strong electronic coupling between two equivalent ferrocenyl centers held together by four hydrogen bonds in a non-covalent dimer.

**Keywords** Hydrogen bonding · Electrochemistry · Voltammetry · Self-assembly

## Introduction

The quick development of supramolecular chemistry during the last 20–30 years has opened the way to molecular self-assembly as one of the key methods to prepare structures in condensed phases. Molecular self-assembly or non-covalent synthesis relies on a large number of rather weak interactions ( $1\text{--}20\text{ kcal mol}^{-1}$ ) to hold together the relevant building blocks (molecules or ions). Taking a clue from biological systems, supramolecular chemists use hydrogen bonding as one of the most important cohesive forces [1]. A hydrogen bond is formed by the interaction between a strongly polar X–H bond with another electronegative atom, Y, which bears lone electron pairs. The hydrogen bond can be visualized simplistically as the result of ‘sharing’ the hydrogen atom, with a partial positive charge, by the two electronegative atoms X and Y. The X–H component of the hydrogen bond is referred to as proton donor (D), and the Y component is the proton acceptor (A). The role of X is typically played by N, O, or F, and Y is most commonly N or O, but many other variations are known or have been proposed [2]. The strength of a single hydrogen bond is usually just a few kilocalories per mole, but it can increase if the electronegative atoms bear suitable charges [2]. A hydrogen bond is usually weaker than most covalent bonds but stronger than other non-covalent interactions, such as dipole–dipole or van der Waals forces. Hydrogen bonds usually show a strong preference for linear geometries, and they can enforce specific orientations (directionality) for the approach of two complementary building blocks. Their low bond enthalpies lead to reversible bond formation, which facilitates the assembly of complicated structures, as the correction of mistakes is possible.

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In the solution phase, hydrogen bonding is most often detected by  $^1\text{H}$  nuclear magnetic resonance (NMR) or Fourier transform infrared (FT-IR) spectroscopies [1, 2]. However, one of the key ideas in this review article is to demonstrate that, in some cases, hydrogen bonding can be detected using electrochemical techniques. By the same token, the strength of hydrogen bonding can be strongly affected by the oxidation state of suitable electro-active groups located in the proximity of the interacting X–H or Y groups.

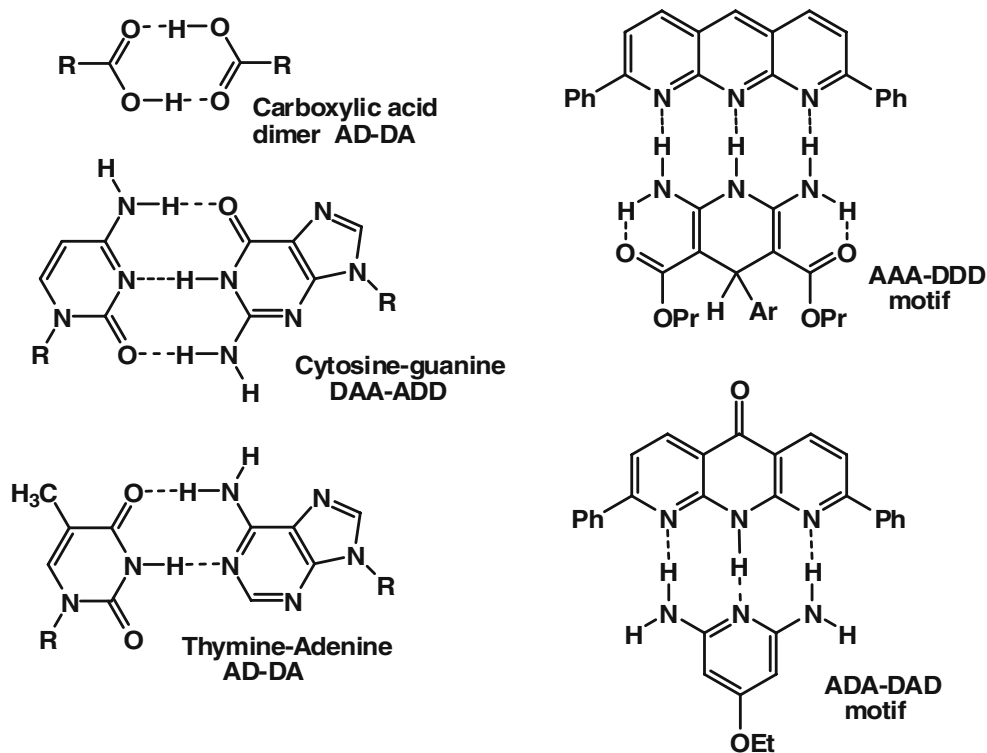
While many hydrogen bonds have been investigated, their rather small bond enthalpies require the combination of several hydrogen bonds to increase the binding affinity between any two building blocks. A few illustrative hydrogen-bonding motifs are shown in Fig. 1. On the top left corner of this figure, the dimer between two carboxylic acids is shown as a representative of many similar solid state dimers also formed by other functional groups, such as amides, imides, and ureas. As this kind of hydrogen-bonding motif (AD-DA) relies on just two hydrogen bonds, their association constants are rather low, and they are only important in the solid phase or in solution at relatively high monomer concentrations. As is well known, the cytosine–guanine and thymine–adenine base pairings constitute the fundamental recognition motifs for genetic information transfer. Notice that in the Watson–Crick scheme, three hydrogen bonds are present between cytosine and guanine, while only two hold together the thymine–adenine pair, which suggests that the former base pair is more stable than

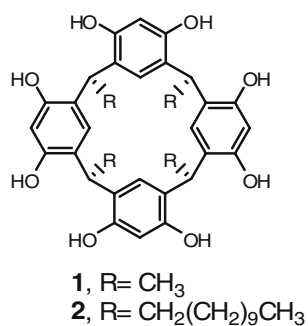
the latter. The two hydrogen-bonding motifs on the right side of the figure show two different synthetic motifs relying on three hydrogen bonds each. While the number of hydrogen bonds is the same, the AAA-DDD motif has a much higher equilibrium association constant ( $K > 10^5 \text{ M}^{-1}$  in  $\text{CDCl}_3$  solution) than the ADA-DAD motif ( $K = 80 \text{ M}^{-1}$  in  $\text{CDCl}_3$  solution) due to electrostatic secondary interactions, which favor hydrogen-bonding patterns that avoid alternating acceptors and donors [1].

### Encapsulation of redox-active centers inside hydrogen-bonded molecular capsules

The resorcinarenes are a well-known class of tetrameric macrocyclic octols that are easily prepared by the acid-catalyzed condensation of resorcinol in the presence of an aldehyde (see structures in Fig. 2). While their chemistry has been well developed for decades [3], MacGillivray and Atwood found, in 1997, that the simple resorcinarene **1** crystallizes forming fascinating hexameric molecular capsules [4]. Each capsule adopts a snug cube conformation with the 6 resorcinarene and 8 water molecules held together by a network of 60 hydrogen bonds. The internal volume estimated for each capsule is approx  $1,375 \text{ \AA}^3$ . This groundbreaking report attracted attention from several groups, and it was shown quickly that similar hexameric molecular capsules were formed by a number of resorcinarenes in the solution phase [5–9]. Due to its solubility in low

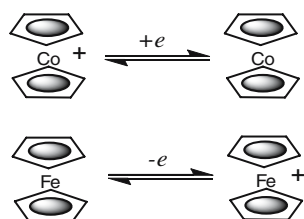
**Fig. 1** Examples of hydrogen-bonding motifs relying on two or three hydrogen bonds



**Fig. 2** Resorcinarene structures

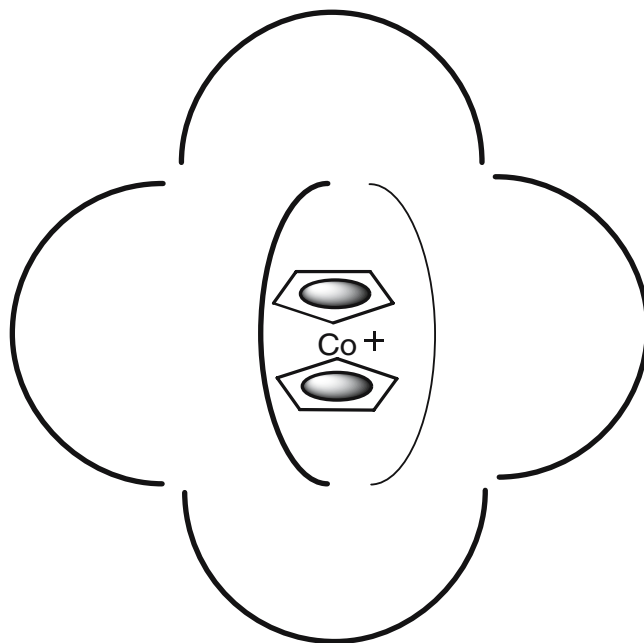
polarity solvents, resorcinarene **2** has been utilized extensively as the monomer for hexameric capsule formation in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> solution. As **2**<sub>6</sub> is quite effective at trapping alkylammonium cations, we decided to investigate the encapsulation of the redox-active cobaltocenium [10], an 18-electron organometallic complex of Co(III) sandwiched between two cyclopentadienyl anions, which undergoes fast one-electron reduction to the neutral cobaltocene [its Co(II) analogue, see Fig. 3].

NMR spectroscopic data in CD<sub>2</sub>Cl<sub>2</sub> solution verified the encapsulation of cobaltocenium inside a capsule composed of six molecules of resorcinarene **2**. From NMR diffusion coefficient measurements, we concluded that the resorcinarene molecular capsules were preformed in CD<sub>2</sub>Cl<sub>2</sub> solution, in the absence of cobaltocenium or any other cationic species [11]. Similar results in CDCl<sub>3</sub> solution have been reported by Avram and Cohen [8, 9]. It is now clear that cationic species are not required to ‘seed’ the formation of the capsules. The voltammetric behavior of cobaltocenium (as its hexafluorophosphate salt) in CH<sub>2</sub>Cl<sub>2</sub> solution is reversible, and the corresponding half-wave potential ( $E_{1/2}$ ) for the cobaltocenium/cobaltocene redox couple was found to be  $-1.06$  V vs Ag<sup>+</sup>/Ag. In the presence of six equivalents of resorcinarene **2**, this voltammetric wave disappears completely, and only the charging current baseline is observed in the potential range 0 to  $-1.6$  V [11]. What factors could be responsible for the disappearance of the voltammetric response due to cobaltocenium reduction? To discard the passivation of the electrode surface by a layer of organic molecules, we carried out voltammetric experiments using two electro-active species: cobaltocenium and decamethylferrocene [12]. The latter compound is considerably larger than the former (or ferrocene) due to the five methyl groups decorating the periphery of each of the

**Fig. 3** Cobaltocenium (top left), ferrocene (bottom left), and their most accessible electron transfer partners

cyclopentadienyl rings of the compound. In the absence of host **2**, both reversible redox couples were observed in the cyclic voltammogram as anticipated. However, upon addition of six equivalents of **2**, the wave corresponding to cobaltocenium disappears, while the wave corresponding to the reversible oxidation of decamethylferrocene remains essentially unchanged. Clearly, this finding reveals that the electrode surface is not passivated by the addition of host **2**.

The disappearance of the cobaltocenium voltammetric wave is probably related to a substantial attenuation of the electrochemical kinetics of cobaltocenium reduction. Encapsulation of cobaltocenium inside a very large, closed assembly—formed by six resorcinarene molecules—must necessarily exert a strong effect on the kinetics of its one-electron reduction. Encapsulated cobaltocenium cannot approach the electrode surface as closely as free cobaltocenium to undergo heterogeneous electron transfer. In fact, cobaltocenium encapsulation inside **2**<sub>6</sub> increases considerably the distance between the outer Helmholtz plane (OHP) and the electrode surface, leading to a much weaker coupling of electronic density levels between the redox-active center and the electrode. A substantial slowdown in the kinetics of heterogeneous electron transfer must ensue, in agreement with the experimental observations. Given the size of the resorcinarene and its hexameric assembly, we estimate that, for encapsulated cobaltocenium, the OHP has to be at least 2 nm away from the electrode surface (Fig. 4). There are several precedents for this rationalization of the observed voltammetric data. Our group has reported a pronounced slowdown in the electrochemical kinetics for ferrocene oxidation upon encapsulation inside a hemi-carcerand [13],

**Fig. 4** Schematic drawing showing cobaltocenium encapsulated in the hydrogen-bonded assembly formed by six resorcinarene hosts

a host which can be roughly considered to be about one third of the size of the  $2_6$  capsule. In addition to this, our group [14] and others [15] have also observed the attenuation of electrochemical kinetics when redox centers are surrounded by covalently attached dendritic mass. Therefore, these kinetic encapsulation effects provide strong support to our interpretation.

In an attempt to better understand the mechanism for encapsulation of cobaltocenium inside  $2_6$ , we performed careful titrations of this redox-active cation with variable concentrations of host **2**. To our surprise, we quickly realized that only 2–3 equiv were necessary to fully shut down the electrochemical response of cobaltocenium. This result is in strong contrast to the NMR data, which clearly indicate a 6:1 (host/guest) stoichiometry for full encapsulation. There are two important differences between these two types of experiments. In the NMR experiments, solutions were prepared in pure, deuterated  $CD_2Cl_2$ , and the only solutes present are cobaltocenium hexafluorophosphate (approx 1 mM) and host **2** (0–8 mM). In the electrochemical experiments, solutions were prepared in un-deuterated  $CH_2Cl_2$  also containing 0.1 M tetradodecylammonium bromide as supporting electrolyte. The concentrations of cobaltocenium hexafluorophosphate and host **2** were similar to those used in the NMR experiments. It clearly became evident that the nature of the supporting electrolyte, especially the nature of its anion, was crucial to achieve encapsulation. The use as supporting electrolytes of tetraalkylammonium bromides and chlorides led to the observation of cobaltocenium encapsulation in voltammetric experiments, while the use of tetraalkylammonium perchlorates, hexafluorophosphates, or tetrafluoroborates led to no voltammetric evidence for the encapsulation [11, 12]. These observations strongly suggest that the cobaltocenium cation is trapped inside the assembly in the form of ion pairs, and larger anions may hinder the encapsulation. On the other hand, bromide and chloride are believed to participate in the network of hydrogen bonds holding together the resorcinarene molecules, probably assisting in the formation of aggregates smaller than the hexameric capsule. Mass spectrometric evidence for these bromide-containing assemblies has been reported by Schalley and coworkers [16]. In contrast to the anions, the nature of the cation has only a minor influence on the type of voltammetric behavior observed for cobaltocenium in the presence of resorcinarene hosts.

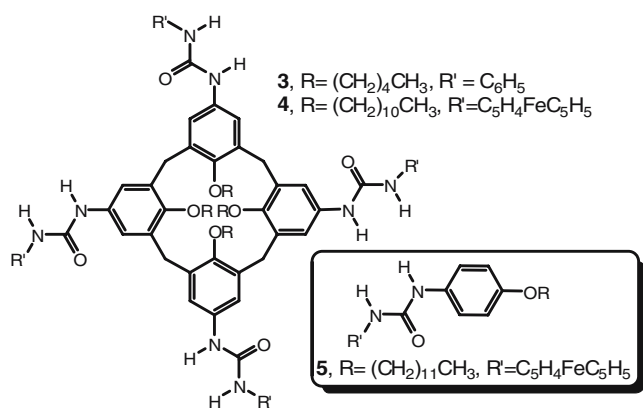
We also investigated the electrochemistry of ferrocene (Fig. 3) in the presence of host **2** and demonstrated that the positively charged, oxidized form (ferrocenium) is encapsulated by  $2_6$  [12]. The encapsulation of ferrocenium was affected by the nature of the supporting electrolyte anion in exactly the same ways that we have already discussed for encapsulation of cobaltocenium. In general terms, our

voltammetric and NMR spectroscopic data show how the incorporation of a redox-active cation inside a large, hydrogen-bonded assembly can basically nullify its voltammetric response due to electrochemical kinetic effects. Furthermore, our data also afford clear indications that the assembly of resorcinarenes in low polarity solutions is a very complicated process and that the hexameric molecular capsule first crystallized by MacGillivray and Atwood [4] is certainly associated to a Gibbs energy minimum, but the overall energetic landscape may be strongly affected by other system components, such as supporting electrolyte anions.

### Redox modulation of hydrogen-bonded assemblies

The idea of using redox conversions to modulate the stability of host–guest complexes is well established in the literature. Changing the oxidation state of a guest (or host) is an effective approach to modulate its binding affinity with suitable recognition partners because charge and electronic distribution both depend strongly on the selection of the oxidation state [17]. This general idea has been applied to the specific case of hydrogen-bonded assemblies. In 1997, Gupta and Linschitz [18] reported on the hydrogen-bonding interactions between quinones and various hydroxylic additives. Around the same time, Niemz and Rotello [19] started their extensive work on redox modulation of hydrogen-bonding interactions involving flavines. More recent work on this and related topics performed jointly by the groups of Cooke and Rotello [20] is also relevant. Smith and coworkers have investigated the electrochemical modulation of hydrogen-bonding interactions between *ortho*-quinones and ureas [21] and, later on, nitrobenzenes and ureas [22]. The group of Gonzalez has also contributed to this area, most recently reporting on the interactions of redox-active chloranil and several amides [23]. Finally, Leigh and coworkers have shown that the extent of hydrogen bonding between the wheel and one of the stopper components in a rotaxane molecular system can be controlled using redox conversions [24].

This important body of work led our research group to think about and design a system in which the self-assembly of a molecular capsule could be fully controlled using redox conversions. Our molecular design is based on the work of the groups of Rebek [25] and Böhmer [26], who demonstrated independently that tetraureido-calix[4]arenes form highly stable, dimeric molecular capsules in low polarity solvents, such as  $CDCl_3$ . A typical example of these self-recognizing calixarenes is **3** in Fig. 5. The two identical calixarenes approach head-to-head and establish a seam of hydrogen bonds formed between the ureas on both calixarene heads (upper rims). In the calixarene designed by our group (compound **4** in Fig. 5), each ureido group is



**Fig. 5** Structures of self-recognizing tetraureido-calix[4]arenes **3** and **4** and model compound **5**

terminated by a redox-active ferrocenyl group. We anticipated that the eight ferrocenyl groups (four on each calixarene) would be held spatially very close to one another in the dimeric molecular capsule. The expectation was that electrochemical oxidation should lead to strong electrostatic repulsions and capsule dissociation.

As we anticipated, **4** forms a very stable dimer in CDCl<sub>3</sub> solution, as evidenced in NMR spectroscopic experiments. The dimer has a very characteristic NMR spectrum, with two doublets (at 7.54 and 5.95 ppm) for the two calixarene aromatic protons, reflecting the two different microenvironments for these protons (near the NH or the carbonyl side of the ‘locked’ urea functional groups). The dimer exists in the presence of moderate proportions of CD<sub>3</sub>CN, but beyond 10% CD<sub>3</sub>CN, the NMR spectral patterns for the protons of **4** indicate that the dimeric molecular capsule **4**<sub>2</sub> dissociates, and **4** exists as the monomer in solution [27]. The cyclic voltammetric behavior of **4** in CHCl<sub>3</sub>/CH<sub>3</sub>CN (10:1) shows that the oxidation of all ferrocene centers takes place in a single voltammetric wave, which does not exhibit the shape expected for perfectly reversible behavior. Detailed analysis of this wave was hampered by its multi-electron character. To address the effect of oxidation on the integrity of the assembly, we resorted to IR spectroscopic and diffusion coefficient measurements. For instance, we monitored the urea C=O stretch (amide I) absorptions of compound **4**. Before oxidation, we observed a peak at 1,657 cm<sup>-1</sup> consistent with carbonyl involvement in hydrogen bonding. Full oxidation of **4** leads to extensive changes in this spectral region with peaks observed at 1,783 and 1,698 cm<sup>-1</sup>, suggesting that the carbonyl oxygens are no longer involved in hydrogen bonding [27]. Control experiments with the monomeric analogue **5** show a minor shift of the amide peak (from 1,678 before oxidation to 1,683 cm<sup>-1</sup> after oxidation) revealing that changes in electronic distribution associated with the oxidation cannot be responsible for the large frequency shifts observed in calixarene **4**.

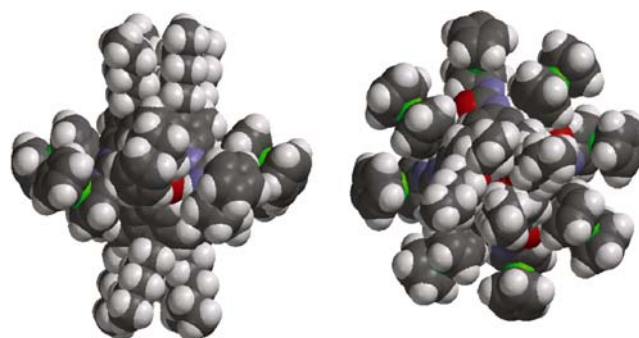
Diffusion coefficient ( $D_0$ ) measurements done using the pulse gradient stimulated echo (PGSE) NMR technique are also consistent with the breakup of the dimeric molecular capsule upon electron uptake from the ferrocenyl groups. We determined  $D_0$  values of  $3.8 \times 10^{-6}$  cm<sup>2</sup>/s for **4** before oxidation and  $7.5 \times 10^{-6}$  cm<sup>2</sup>/s upon full oxidation (**4**<sup>4+</sup>), which strongly support the oxidation-induced dissociation of the dimeric capsule assembly [27]. The process is, of course, reversible, i.e., dimerization is restored upon reduction in the ferrocenium centers in the oxidized **4**<sup>4+</sup>.

These results show that it is possible to design molecular systems in which self-assembly via hydrogen-bonding interactions can be turned ‘on’ and ‘off’ using redox conversions, leading to substantial structural changes on supramolecular assemblies, such as molecular capsules.

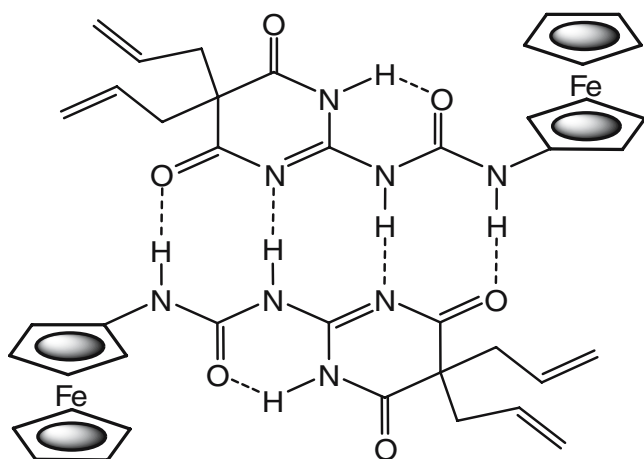
### Electronic coupling between hydrogen-bonded redox centers

In the dimeric assembly **4**<sub>2</sub> described above, eight ferrocene centers occupy very close spatial locations (see Fig. 6). Their proximity does not translate into any significant level of electronic communication, as they all get oxidized at similar potentials in voltammetric experiments. This is not entirely surprising, and similar results have been reported with dendrimers containing multiple equivalent redox centers crowding the surface of these macromolecules [28]. The literature contains a large body of work on compounds having two ferrocenyl centers separated by a linking spacer [29]. In these compounds, the degree of electronic coupling between the two ferrocene centers decays quickly as the separation distance increases. We were, thus, interested in learning what level of electronic coupling exists between ferrocene centers linked non-covalently through an appropriate array of hydrogen bonds.

With this idea in mind, we prepared compound **6** (Fig. 7) in which a ferrocene center is directly attached to a DDAA hydrogen-bonding array of the type first proposed by



**Fig. 6** Space filling models (*left* side view, *right* top view) of the **4**<sub>2</sub> molecular capsule. The minimized structure shown here was obtained with the PM3 semiempirical method



**Fig. 7** The dimeric assembly formed by self-recognition of ferrocenyl derivative **6**

Sanjayan and coworkers [30]. Compound **6** is expected to self-recognize, forming stable dimers in solvents of low polarity. This expectation was quickly confirmed by  $^1\text{H}$  NMR spectroscopic data obtained in  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$  solutions [31]. In fact, the  $\mathbf{6}_2$  dimer is highly stable, being the only species observed in solution at concentration levels as low as  $10\ \mu\text{M}$  **6**. Vapor pressure osmometric experiments also verified the quantitative dimerization of **6** in nonpolar solvents. The dimer was also detected in fast atom bombardment (FAB) mass spectrometric experiments. In more polar solvents, such as acetonitrile or dimethyl sulfoxide (DMSO), no dimerization takes place as the solvent molecules compete effectively for hydrogen-bonding donor and acceptor sites, preventing the assembly of the dimer.

Cyclic voltammetry of compound **6** in  $\text{CH}_2\text{Cl}_2$  solution reveals two reversible oxidation waves, while only one wave is observed in  $\text{CH}_3\text{CN}$  solution [31]. We know that in the former solvent, compound **6** dimerizes quantitatively at millimolar concentration levels. Therefore, the observation of two anodic waves separated by 390 mV suggests a healthy (and surprising!) degree of electronic communication between the two equivalent ferrocene centers in dimer  $\mathbf{6}_2$ . In acetonitrile solution, **6** is present as the monomer, and electronic communication is obviously impossible, explaining the single oxidation wave. From the observed half-wave potential difference ( $\Delta E_{1/2}$ ) in  $\text{CH}_2\text{Cl}_2$  solution, the comproportionation equilibrium constant can be determined. In this case, the equilibrium expression is  $\mathbf{6}_2 + (\mathbf{6}_2)^{2+} = 2(\mathbf{6}_2)^+$  and  $K = 3.9 \times 10^6$ , suggesting that the hydrogen-bonded mixed valence species, in which just one of the ferrocene centers is oxidized, enjoys high stability. As a result of this observation, we set out to detect the inter-valence charge transfer (IVCT) spectroscopic band corresponding to the photo-induced electron transfer from the ferrocene to the ferrocenium center in the mixed valence dimer. Addition of the oxidant  $\text{NO}^+\text{PF}_6^-$  to a  $\text{CH}_2\text{Cl}_2$  solution of **6** leads to the

observation of the IVCT band at  $8,368\ \text{cm}^{-1}$  ( $\lambda_{\text{max}} = 1,195\ \text{nm}$ ). This band is not observed before the addition of oxidant and disappears after the addition of 1 equiv, reaching maximum intensity at approx 0.5 equiv of oxidant [31]. These findings are in clear agreement with the IVCT character of the band, confirming that it is a spectral feature of the mixed valence dimer  $(\mathbf{6}_2)^+$  and does not arise in either  $\mathbf{6}_2$  or  $(\mathbf{6}_2)^{2+}$ . Application of the Hush formalism [32] to the IVCT band of  $(\mathbf{6}_2)^+$  predicts a half-height bandwidth of  $4,397\ \text{cm}^{-1}$ , which is much larger than the experimentally measured value ( $560\ \text{cm}^{-1}$ ). This finding is also consistent with a strong level of electronic coupling between the two ferrocene centers in the  $\mathbf{6}_2$  non-covalent dimer.

To the best of our knowledge, partial oxidation of the  $\mathbf{6}_2$  dimer gives rise to the first example of a non-covalent mixed valence species,  $(\mathbf{6}_2)^+$ , composed of two identical halves kept together by four hydrogen bonds, which are parallel to one another and perpendicular to the main ferrocene–ferrocene axis. We are currently performing density functional calculations to provide a theoretical framework for the understanding of the surprisingly high degree of electronic coupling in our non-covalent dimer. The biological significance of these results cannot be underestimated, given the importance of hydrogen bonding in DNA and RNA structures, as well as the proposed influence that hydrogen-bonding patterns may have on the preferred pathways for electron transfer in proteins.

## Conclusions

In this short review article, we have summarized our work on the electrochemistry of hydrogen-bonded assemblies. The results described here clearly reveal that hydrogen-bonded assemblies offer fascinating possibilities from an electrochemical standpoint. For instance, encapsulation of redox centers may lead to the loss of their voltammetric response, a finding strongly reminiscent of the behavior of some redox proteins for which their buried redox centers are not directly addressable by electrodes. A second interesting result is that the stability of hydrogen-bonded assemblies may be modulated by electrochemical reactions. Finally, the interplay between hydrogen bonding and electron transfer is beautifully highlighted by the unexpected level of electronic coupling observed in the non-covalent ferrocene dimer  $\mathbf{6}_2$ , which opens up a number of interesting research avenues in search of a better fundamental understanding of how electron transfer and hydrogen-bonding phenomena affect each other.

**Acknowledgments** The authors are grateful to the US National Science Foundation and the Office of Naval Research for the generous support of this work.

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