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A remarkably stable hydrogen-bonded porphyrin·iron(terpyridine) ion pair

Tyler B. Norsten, Kelly Chichak and Neil R. Branda*†

Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

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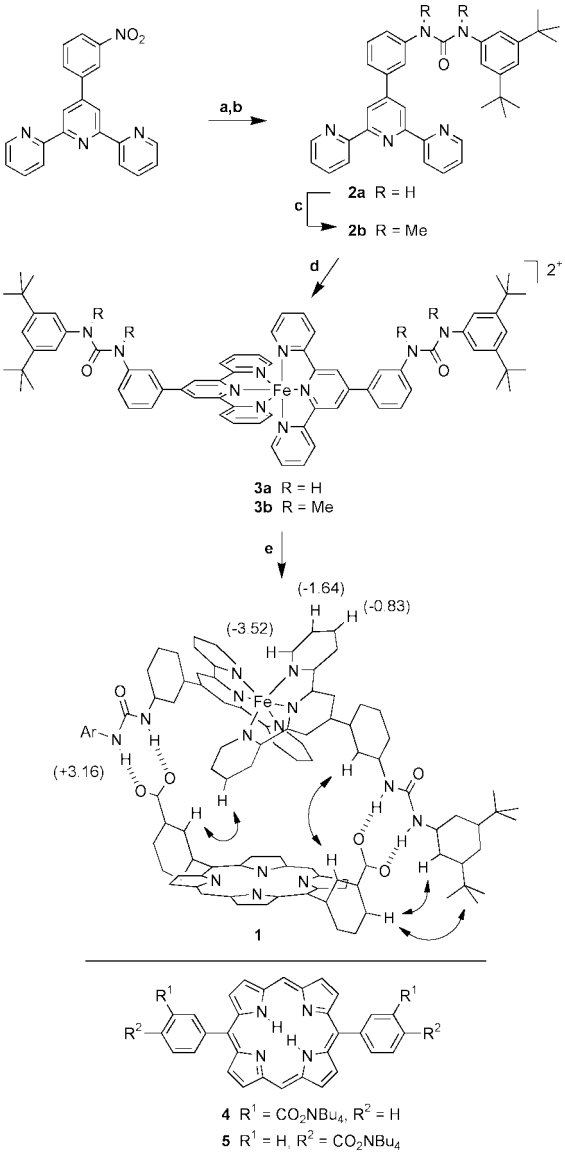
Even in highly competitive solvents such as DMSO, strong bimolecular association and subsequent fluorescence quenching result from the combination of hydrogen bonding and ion pairing between a porphyrinic bis(carboxylate) dianion and an iron(terpyridine) bis(urea).

In naturally occurring light harvesting systems, the relative orientation and proximity of the photoactive components play fundamental roles in the effective operation of the systems. These complex molecular devices rely primarily on non-covalent interactions to place the chromophores in optimal locations to facilitate beneficial electronic communication. Accordingly, significant efforts have been devoted to develop artificial multi-component photoactive arrays, with a particular emphasis on those involving porphyrins.[1–7] Because the photochemical characteristics are ultimately governed by the assemblies' topologies, their fabrication hinges on the tailoring of productive molecular recognition interactions such as coordination bonding,[2,3] ion pairing,[4] π–π stacking[5,6] and hydrogen bonding.[3,7] The hydrogen bond is a particularly serviceable driving force to align building blocks due to its directionality and its ease of tailoring. This is especially true when several hydrogen bonds are united into a multipoint recognition site. The utility of the hydrogen bond is diminished, however, in polar competitive solvents that can better solvate the hydrogen bonding surface. The implementation of cooperative or ionic hydrogen bonding motifs, where the hydrogen bond partners are of opposite charge, can often overcome these destructive solvation effects.[8] Strong complexation is especially critical in order to study energy/electron transfer processes at the low concentrations required by luminescence spectroscopy without having to add excessive quantities of quencher.

We describe here the synthesis and characterization of the novel non-covalently bound porphyrinic assembly **1**. The building blocks were designed to harness the beneficial recognition attributes of both ion pairing and hydrogen bonding interactions. The first interaction is provided by the attraction between the Fe^{2+} dication complex **3a** and the porphyrinic bis(carboxylate) dianion **4**. The carboxylate groups on the porphyrin serve dual roles in that they also act as charged hydrogen bond acceptors for the neutral bidentate urea hydrogen bond donors on the iron(terpyridine) fragment. The result is the self-assembly of neutral complex **1**, which retains both its structural integrity and topology even at low concentrations in polar solvents such as DMSO.

Assembly **1** was prepared by mixing an equimolar mixture of building blocks **3a** and **4** in methanol (Scheme 1). The neutral complex precipitated from the solution and was easily isolated in high purity and in nearly quantitative yield. Owing to the charges balancing in the final complex, 2 equivalents of $[Bu_4N][BF_4]$ were produced in the reaction and were washed away during the filtration. The integration of signals in the ^1H NMR spectrum of the isolated solid supports the claim that the 1:1 complex is the product of the self-assembly process. Electrospray mass spectrometry confirmed this claim as peaks at *m*/*z* 1738.7 and 880.3 corresponding to $[M + Na]^+$ and $[M + 2Na]^{2+}$, respectively, were observed.

Assembly **1** is freely soluble in highly polar solvents such as DMSO and DMF, but is only sparingly soluble in all other common organic solvents. GCOSY and T-ROESY experiments aided in assigning the protons of complex **1**. The complex



Scheme 1 *Reagents and conditions*: (a) $SnCl_2·2H_2O$, EtOH; (b) triphosgene, CH_2Cl_2, then 3,5-di-*tert*-butylaniline, 78% for three steps; (c) NaH, CH_3I, DMF, 50 °C, 99%; (d) $Fe(H_2O)_6(BF_4)_2$, acetone, quantitative; (e) **4**, MeOH, 97%. The double bonds have been removed from structure **1** for clarity. Observed intermolecular nOe's (represented as arrows) and complex induced chemical shifts in the ^1H NMR spectrum (shown in parentheses) are highlighted.

† Current address: Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, B.C., Canada V5A 1S6. E-mail: nbranda@sfu.ca

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induced shift (CIS) values for complex **1** in the ^{1}H NMR spectrum in DMSO-d_6 and the observed intermolecular nuclear Overhauser enhancements (nOe's) are highlighted in Scheme 1. Both experiments support the proposed structure of **1**, where **3a** is straddling across the porphyrin macrocycle and is not lying to its side. The significant downfield shift ($\Delta\delta > 3$ in DMSO-d_6) observed for the urea N–H protons in assembly **1** is indicative of effective hydrogen bonding even in such a polar and competitive solvent. The role of the hydrogen bonds is also to steer the iron(terpyridine) fragment into a position where it lies directly over the porphyrin plane. This guidance is successful as diagnosed by the upfield shifts observed for the hydrogen atoms of **3a** lying directly over the porphyrin plane and within the shielding region of the macrocycle ($\Delta\delta$ are as large as -3.52). The signals for the four hydrogen atoms on the terminal pyridine ring of **3a** are unique in that they appear as broad peaks in the spectrum. We attribute this to the fact that **3a** can be thought of as a 'spit on a barbecue' in which the terpyridine can slowly rotate above the porphyrin ring. The terpyridine protons can, therefore, range in distance from 3.5 to 14.5 Å‡ from the plane of the macrocycle at any given moment affording a variety of possible conformers that can exist within the NMR time-scale. Variable temperature NMR experiments failed to alter the shape of these broadened signals.

The strength of the binding between **3a** and **4** was too large to be accurately measured by ^{1}H NMR spectroscopy even in DMSO-d_6. Isothermal titration calorimetry (ITC) experiments in DMSO, however, indicated a binding stoichiometry of 1 : 1 for **3a** and **4** and an impressive value for the association constant (K_a) of $(2.47 \pm 0.44) \times 10^6$ M^{-1}. When the ITC experiments were repeated replacing **3a** with the *N*,*N*′-dimethylated analog **3b**, that can only associate through ion pairing, the heat released upon binding was so small that the association constant was impossible to estimate. The titration of **5** with **3a** also revealed a similar trend, despite the fact that the **3a**·**5** complex can be isolated as a solid in a similar fashion as for **1**. In this case, the hydrogen bonds are not suitably positioned to operate in unison and direct the formation of a strapped 1 : 1 complex. Although the ^{1}H NMR spectrum in DMSO-d_6 does reveal a 1 : 1 stoichiometry between **3a** and **5**, the signals for the urea N–H protons shift only 1 ppm downfield, and there is no observable shift of the signals corresponding to the C–H protons on the iron(terpyridine) fragment. This indicates that **3a** does not reside over the plane of **5** and the 1 : 1 complex should really be thought of as an aggregate $(\mathbf{3a}\cdot\mathbf{5})_n$. These experiments clearly highlight that ion pairing contributes to the association of **1**; however, the cooperative hydrogen bonds aid in aligning the building blocks into close proximity so that these ion pairing attractive forces can be maximized.

The relative positioning of **3a** and **4** within **1** has a significant impact on the photophysical behavior of the final assembly. Studies using steady-state fluorescence spectroscopy to monitor the changes in the emission intensities of DMSO solutions of **4** and **5** as the porphyrins were treated with aliquots of **3a** are shown in Fig. 1. The immediate quenching of the fluorescence of **4** is most likely a direct result of the straddling nature of the iron(terpyridine) fragment which positions the two chromophores into the most intimate arrangement possible and ensures maximum through-space communication. The fluorescence quenching of porphyrin **4** by **3a** is clearly a result of both strong bimolecular association and optimal spatial positioning of the two chromophores. The *N*,*N*′-dimethylated analog **3b**, on the other hand, only slightly quenched the fluorescence of **4** presumably in a dynamic, collision-based process. A similar low level of quenching was obtained when porphyrin **5** was titrated with **3a**. Despite the fact that both hydrogen bonding and ion pairing are present in the $(\mathbf{3a}\cdot\mathbf{5})_n$ polymolecular assembly, the terpyridine fragment cannot form a strapped arrangement, and any through-space communication between the chromophores is significantly reduced. Impressively, similar photophysical behavior of assembly **1** was observed in a 10% H_2O/MeCN solution attesting to the strength of the association between building blocks **3a** and **4** even in an aqueous environment.

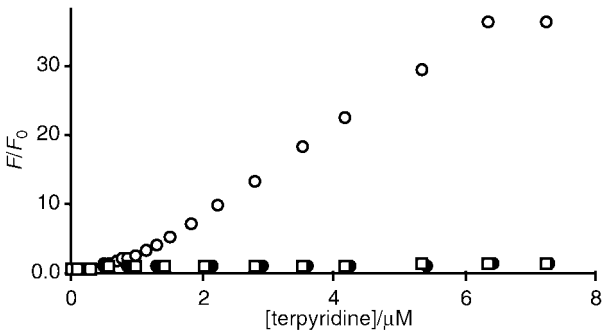

Fig. 1 Stern–Volmer quenching when a DMSO solution of **4** is titrated with **3a** (○), with **3b** (□), and when **5** is titrated with **3a** (●) (λ_{ex} = 415 nm, λ_{em} = 633 nm). Concentrations: [**4**] and [**5**] = 1.0×10^{-6} M, [**3a**] and [**3b**] = 2×10^{-5} M.

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‡ These distances were estimated from the lowest energy structure of assembly **1** using computer-assisted molecular modeling.

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