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Simultaneous hydrogen bonding and π-stacking interactions between flavin/porphyrin host–guest systems

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Dedicated to Harry Wasserman on the occasion of his 90th birthday

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ABSTRACT

In this Letter, we describe the formation of complexes between flavin and diamidopyridine functionalized porphyrin systems via hydrogen bonding and π-stacking interactions.

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Controlling the electron transfer process on a molecular scale is essential for designing molecular electronic devices including light harvesting systems, light-emitting diodes, and fiber optics.[1] Many biological electron transport systems provide design architectures for charge transfer and separation processes in artificial systems.[2] Especially in the photosynthesis process, energy and electron transfers occur very efficiently on a molecular scale.[3] These biological assemblies rely on the combination of molecular recognition and redox processes.[4] In these systems, enzymes possess redox-active core molecules, such as flavins, quinones, nicotinamides, and pterins, which use specific enzyme-cofactor interactions to control the redox activity of a given cofactor.[5] For example, molecular recognition elements, including hydrogen bonding, π-stacking, and electrostatic interactions, influence the oxidation and protonation states of the cofactor. Hence, understanding molecular recognition processes that govern electron transfer processes helps in the development of molecular electronic devices and model systems.[6]

Flavoenzymes catalyze a wide variety of biological processes such as redox transformations, signal transduction, and electron transfer.[7] These enzymes use cofactors (e.g., FMN or FAD) that bind to the active site of the apoenzyme through a series of noncovalent interactions. The interactions are responsible for fine-tuning the $FADH_2$–FAD redox cycle. In some flavoenzymes, flavin coenzymes coexist with metals, forming metalloflavoproteins, such as cytochrome c552 (*Chromatium vinosum*), cytochrome c553 (*Cholorobium thiosulfatophilum*), lactate dehydrogenase (aerobic yeast), yeast hemoglobin, (*Candida mycoderma*) and an oxygen binding flavohemoprotein (*Alcaligenos eutrophus*). Many model systems have been developed to study the interactions and mechanism of electron transfer between flavins and metals. However, these synthetic systems differ from biological systems because they primarily focus on covalent attachment to control the redox behavior.[8]

Herein, we report the use of molecular recognition to modulate the electrochemical behavior of flavin. In particular, two types of porphyrins[9] tethered to diaminopyridine (DAP) moieties have been used to probe the effect of porphyrin and metalloporphyrin (**3** and **4**, Scheme 1) units on flavin redox behavior. The synthesis of the flavin derivatives **1** and **2** used in this study has been described previously.[10] The synthesis of porphyrin systems **3** and **4** is described in the Supplementary data.

Complexation between flavins **1**–**2** and the porphyrins **3** and **4** was studied initially using ^{1}H NMR spectroscopy. These studies were carried out in a non-competitive solvent ($CDCl_3$), to permit the observation of specific hydrogen bonding interactions as well as to probe π–π stacking interactions. Addition of aliquots of guest porphyrin DAP to flavin resulted in a steady downfield shift of imide proton H(3) of flavin **1**, indicating the formation of a hydrogen bound complex (Fig. 1). Non-linear least-squares curve

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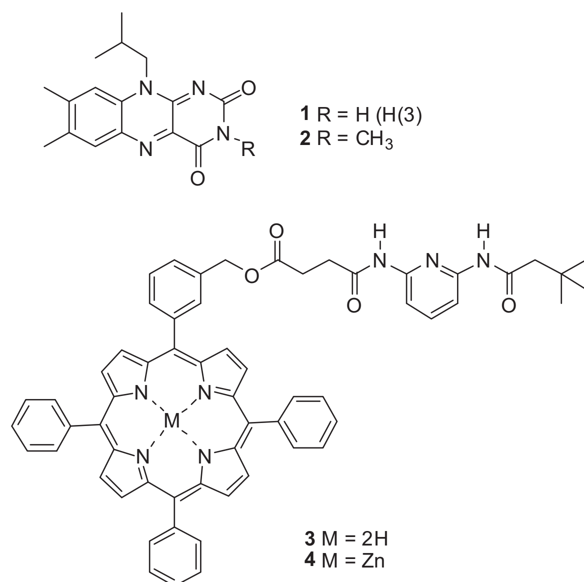

Scheme 1. Chemical structures of flavins and porphyrins used in this study.

fitting of the resulting shift values provided a binding constant of 2400 M^{-1}.[11]

Similarly, addition of aliquots of **4** to flavin **1** likewise produced a downfield shift of the imide proton H(3) of flavin **1**, indicating hydrogen bond formation with binding constant of 1500 M^{-1} (Fig. 1). In addition to the shift in the H(3), we also observed an upfield shift of aromatic protons in flavin **1**, suggesting that aromatic π–π stacking between the host and the guest is occurring. Non-linear least-squares curve fitting of the resulting shifts in the aromatic proton values provided the binding constants of 2200 and 1200 M^{-1} for **3** and **4**, respectively. As expected, derivative **2** did effect a shift in the aromatic protons, indicating the absence of intermolecular aromatic π–π stacking interactions. This study establishes that the flavin **1** undergoes hydrogen bonding mediated aromatic π–π stacking with **3** and **4**.[12]

With host–guest complexation established, we next studied the role the differing porphyrin moieties of **3** and **4** have on influencing flavin reduction potentials. The redox behaviors for the supramolecular complexes were determined in CH_2Cl_2 using cyclic voltammetry (CV). In particular, half-wave reduction potentials were obtained for **1** and **2** ($E_{1/2}$(unbound)) along with the corresponding potentials for **1** and **2** in the presence of **3** or **4** ($E_{1/2}$(bound)) (Table 1, Figure 2).

Figure 1. ^{1}H NMR titration curves for: (a) and (c) are imide proton shifts for **1** upon the addition of **3** and **4**, respectively; (b) and (d) aromatic proton shifts observed for flavin **1** upon addition of **3** or **4**, respectively.

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