

Self-assembled multiporphyrin arrays mediated by self-complementary quadruple hydrogen bond motifs†

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Discrete squares and tapes of porphyrins are self-assembled by self-complementary hydrogen bonding between diacetamidopyridyl recognition groups rigidly linked to the chromophore.

Porphyrins, and their cousins the phthalocyanines, have attracted considerable attention recently because of their potential use as components of nanometer scale photonic devices and materials.¹ The functionality of many, if not most, photonic devices,¹ including those found in nature,² strongly depends on the relative order of the chromophores throughout the entire material and on the mode of assembly. Supramolecular chemistry has been used as a stratagem to achieve the desired geometric order of porphyrin and other entities in both solids and in solution.³ Crystallization of porphyrins bearing H-bonding groups has yielded fascinating networks,^{3,4} and co-crystallization with other compounds has yielded interesting host-guest^{3,5} and magnetic⁵ materials. Yet consistently predicting long-range three-dimensional order in crystals remains elusive. Several discrete H-bond⁶ and metal ion⁷ assembled porphyrin systems in solution also have been reported. In order to better understand the role of non-covalent bonds in mediating electron and energy transfer in biological systems,² several non-coplanar or non-rigid supramolecular porphyrin-electron acceptor species have been studied.^{8,9} One of the primary goals of work reported herein is to understand the process of self-assembly and to reliably predict the structure of self-assembled porphyrin arrays in solution, as opposed to the solid state. We report the self-assembly of several rigid, co-planar multiporphyrin arrays and tapes by self-complementary H-bond motifs that exploit both the directionality of the recognition groups and the square-planar geometry of the porphyrin macrocycle to design predictable arrays in high yields. Though topologically similar to the square porphyrin arrays formed by coordination chemistry,^{3,7} the nature of the self-assembly linker has profound effects on the properties of the resultant array, *e.g.* porphyrin fluorescence.

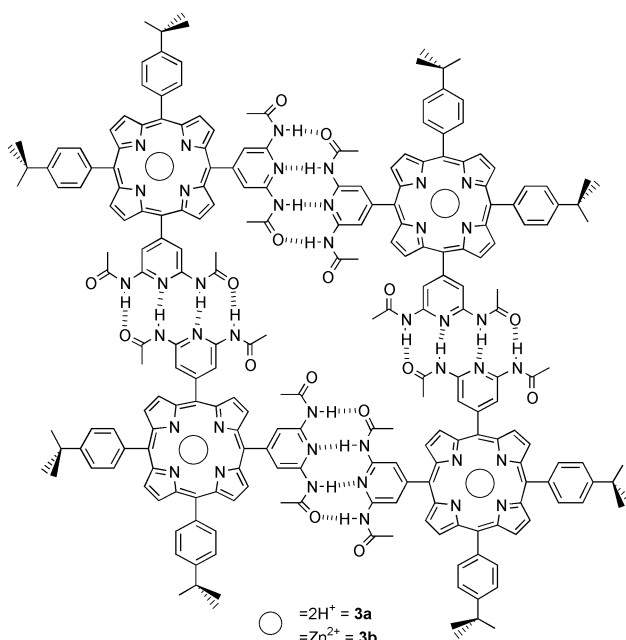
There are several ways in which 5-(3,5-diacetamido-4-pyridyl)-10,15,20-tris(4-*tert*-butylphenyl)porphyrin, **1a**,^{10†} may form a dimer by self-complementary hydrogen bonds.¹¹ The most stable is a linear, quadruple H-bonded system (graphical abstract), albeit this is weak compared to other H-bond systems. A variety of one- and two-dimensional porphyrin structures may be formed *via* this motif. In the present case we demonstrate this by the formation of linear dimers with the 5-substituted compound, linear trimers using a 2:1 stoichiometry of the 5- and the 5,15-substituted compounds **1a**, **2a**, respectively, and a linear tetramer using a 2:2 ratio of **1a** to **2a**.

If there are no dynamic processes occurring on the NMR¹² time scale, both the number of species self-assembling into the final structure, *n*, and the equilibrium constants, *K*, may be

determined by ¹H NMR experiments that monitor the chemical shift of suitable protons *vs.* the concentration of the self-complementary porphyrin.^{6,13} Noting the usual caveats and that these experiments do not yield structural information *per se*, fits of these curves for solutions of **1a**† indicate that the ultimate self-assembled product contains *ca.* 2 units (*K* = 160 dm³ mol⁻¹), consistent with the dimeric structure shown in the abstract, where *x* = 0. For the tapes these experiments and their fits show that *ca.* 3.2 units are in the final assembly when a 2:1 mixture of **1a** and **2a** is used to form the trimer (*K* = 110 dm⁶ mol⁻²), and about 4.1 units are present in the assembly of a 2:2 mixture of **1a** and **2a** (*K* = 70 dm⁹ mol⁻³). In the case of the linear tapes, there is no *a priori* reason that all of the self-assembled structures in the chloroform solution are the 2:1 trimers, and 2:2 tetramers, thus the NMR results are likely indicative of a mixture of dimers, trimers, tetramers, *etc.* substantially weighted toward the tape resulting from the starting stoichiometries by ΔG .†

The self-assembly of a square tetramer (Scheme 1) from only **3a** is also indicated by similar plots of concentration *vs.* amide NH chemical shifts.† Dramatic differences are observed in the plots for the linear tetramer *vs.* the closed-square tetramer.† For the square array, the rapid increase in the chemical shift at much lower concentrations indicates *K* (2400 dm⁹ mol⁻³) is much greater compared to the linear tetramer, and thus is a direct measure of the cooperative formation of a closed system with a more favorable ΔG . The fit yields *n* \approx 3.9 units of **3a**.

Because of the different power of the concentration units it is difficult to directly compare the values of *K* for all but the linear and square tetramers. Additionally, the *K* values found by this data are about 4-fold weaker than those found by fluorescence



Scheme 1

† Electronic supplementary information (ESI) available: experimental details, NMR data and fits, van't Hoff plots, UV-VIS and fluorescence data, and ESI-MS spectrum for the self-assembled square species. See <http://www.rsc.org/suppdata/cc/b0/b008045o/>

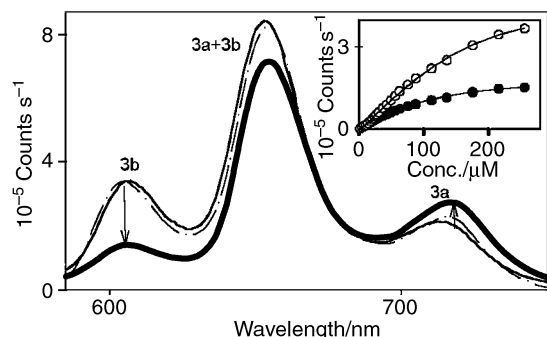


Fig. 1 Fluorescence emission spectra of a solution that is 140 μM in **3a** and 140 μM in **3b** in 2-methylTHF (—) and in ethanol (—) under identical experimental conditions. In ethanol where the H-bonding between the diacetamidopyridyl groups is minimal, the emission spectrum is nearly identical to the sum of the two components (---). Whereas in 2-methylTHF where H-bonding is significant, there is a substantial quenching of **3b** and enhanced emission from **3a**. The inset plots the emission intensity of **3b** at 610 nm vs. concentration in ethanol (○) and 2-methylTHF (●).

quenching experiments, indicating that dynamic processes are occurring during the NMR acquisition. To contrast the NMR data from all four systems, it may be more informative to compare the $C_{1/2}$ values, where this represents the concentration at the half maximum increase in the chemical shift. The $C_{1/2}$ value from the above NMR data for the closed tetrameric square, 0.8 mM, is a factor of *ca.* 10 less than the comparable open tetrameric tape, consistent with the calculated K values. Note that the linear systems have somewhat similar $C_{1/2}$ values: 8 mM, 5 mM and 9 mM for the dimer, trimer, and tetramer, respectively.^{†11} In toluene, where the H-bonds are expected to be stronger, similar results for n are obtained for all systems, but the $C_{1/2}$ values are *ca.* 4-fold lower for the linear assemblies and *ca.* 2-fold lower for the square.

In solvents with low H-bonding potential, the added thermodynamic stability of the closed, square tetramer, as opposed to an open-chain polymer with an average length of four units with enthalpically unfavorable 'unbonded' ends or entropically unfavorable higher order polymers, strongly argues in favor of the square structure when **3a** is the self-assembling species. Estimations of ΔG for these systems from the NMR concentration and temperature data⁸ show that the square tetramer ($\Delta G = -19.3 \text{ kJ mol}^{-1}$) is favored over the tetrameric tapes ($\Delta G = -10.5 \text{ kJ mol}^{-1}$) by *ca.* 8 kJ mol^{-1} . Van't Hoff plots[†] of the chemical shift vs. temperature are in qualitative agreement with the NMR equilibrium studies above.

As the concentration in chloroform, toluene, 2-methylTHF, and ethanol is increased from 1 μM to *ca.* 250 μM there is little change in the observed UV-VIS spectra, with < 1 nm shifts in the Q bands for both the free bases and the zinc complexes. This indicates very little electronic communication between the macrocycles in the self-assembled tapes and squares in the ground state. However, the relative emission is substantially diminished with increasing concentrations of **1a** or **3a** in chloroform, or 2-methylTHF, compared to ethanol.[†] This indicates that there is aggregation, which decreases the emission intensity by organization of the chromophores, and quenching of the excited state by energy transfer to neighboring subunits. Significant energy transfer among subunits is well demonstrated by the excitation and emission (Fig. 1) spectra of squares formed from a 1:1 mixture of the free base, **3a** and the zinc complex **3b** in 2-methylTHF. In solvents favoring H-bonding, excitation in the zinc porphyrin Q-band region at 557 nm where **3b** absorbs > 3 times **3a**, the self-complementary square emits predominantly from the free base at 720 nm, with concomitant quenching of **3b** at 610 nm. This direct observation of energy transfer is not observed in dilute solutions (< 10 μM) or in ethanol where the emission is essentially similar to the mathematical addition of the two individual spectra. The emission from **3b** (Fig. 1, inset) is substantially quenched as the concentration of the 1:1 mixture in 2-methylTHF increases, and to a much lesser extent in ethanol. The fluorescence lifetime,

determined by phase modulation, of **3a** is 10 ns and that of **3b** is 2 ns at 1 μM concentrations in air in chloroform. At 0.100 mM, **3a** exhibits two time constants 10 ns (80%) and 0.8 ns (20%). A 0.100 mM mixture of 1:1 **3a** and **3b** shows decays of 10 ns (50%), 1 ns (40%) and < 0.2 ns (10%). This is consistent with the notion of energy transfer from the singlet manifold, rather than the triplet manifold for the metallo self-assembled squares.⁷

The characterization of these supramolecular systems will serve as the basis for the characterization of future complex two- and three-dimensional arrays using various combinations of both H-bonding and metal ion coordinating porphyrins.⁹ The above data show that the self-complementary H-bonds afforded by the 3,5-diacetamido-4-pyridyl group are surprisingly effective in mediating the self-assembly of these photo- and electro-active species in solution. The solution phase chemistry, in turn, is vitally important for the understanding of how to direct the formation of solid state structures, and will help understanding of the resulting properties of the materials.

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