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Hierarchical organization of a robust porphyrin cage self-assembled by hydrogen bonds

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Abstract

Porphyrins appended with four rigid hydrogen bonding motifs on the meso positions were synthesized and self-assembled into a cofacial cage with four complementary bis(decyl)melamine units in dry solvents. The hydrocarbon chains on the melamine mediate the formation of nanofilms on surfaces as the solvent slowly evaporates.

Self-assembly and self-organization of porphyrinoids¹ continue to produce functional materials with applications ranging from electronics² to catalysis.³ Both coordination bonds and H-bonds can mediate formation of supramolecular porphyrinic materials. Porphyrinoids appended with H-bond motifs can assemble into diverse arrangements such as rosettes, squares, tapes, and nanoparticles for materials for solar energy harvesting, photonic devices, sensors, catalysts, and understanding biological electron transport.^{4–6} In addition to directing supramolecular architectures, the functional groups on the macrocycle and mode of assembly can modulate photophysical and chemical properties of chromophoric arrays. Responsive H-bond materials, whereby the supramolecular structure can be modulated by environmental conditions such as temperature or solvent, can find applications as catalytic hosts for specific guests, or control of electronic communication between subunits.⁷ While functional materials of porphyrins self-assembled by hydrogen bonding have demonstrated utility,⁵ porphyrins bearing hydrogen bonding motifs rigidly attached can be difficult to synthesize.⁴

Herein we report the synthesis of porphyrins possessing four rigid uracylic hydrogen bonding units on the meso positions (Scheme 1) and characterization of the self-assembly of these subunits into robust cage structures mediated by complementary 2,4-di(n-decylamino)-6-amino-1,3,5-triazine, bis(decyl)melamine, units. Two notable features are: the porphyrins are made in one step, and the supramolecular dynamics are significantly reduced because all four meso positions participate in the assembly instead of two.^{4–6} The free base and zinc complexes of two different macrocycles are used to form the cages (Scheme 2), where interconversion of the atropisomers of the uracylporphyrins is required. NMR, light scattering, and photophysical properties in solution indicate formation of the cages, and atomic force microscopy (AFM) elucidates the self-organization of the materials cast onto mica.

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Uracylporphyrin 1b and N-alkyluracyl porphyrin 2b are synthesized from 5-formyl-6-methyluracil⁸ and 1-ethoxy-methyl-5-formyl-6-methyluracil^{6,7,9} using Adler conditions with Zn(OAc)₂ (Scheme 1).^w N-alkylation of the uracil inhibits tautomerization at this position, diminishes unproductive H-bond formation, and improves solubility. Thus, we focus on these porphyrins herein. The free bases, 1a and 2a, are formed by demetalation reactions. The bis(decyl)melamine was prepared similarly to previous reports.¹⁰

For 2b the free energy barrier for atropisomer interconversion was determined by a van't Hoff plot (ln K versus 1/T) and the DG[‡] was found to be about 123 kJ mol⁻¹ in CD₃OD. This is consistent with earlier results, which proposed the increased rigidity of the macrocycle when complexed to a metal ion raises the rotational barrier by about 20 kJ/mol.¹¹ Therefore, the DG[‡] for 2a is estimated to be about 103 kJ mol⁻¹. Similar DG[‡] values for atropisomerization of 1a and 1b are expected. The porphyrins are poorly soluble in dry THF-d₈ but slowly become more soluble upon addition of the melamine and heating between 40–50 °C for greater than four days for 1a and 1b and two days for 2a and 2b. The formation of the cage removes the a⁴ atropisomer from the equilibrating solution thereby increasing the yield of the cage.¹² The self-assembled cage is characterized by the NMR chemical shifts of the uracil and melamine NH protons of the H-bonds (Table 1), and only one resonance, instead of six, for the uracyl methyl group indicating one atropisomer is present.¹

Diffusion ordered spectroscopy (DOSY) allows the molecular weights of the assemblies to be determined.^{6,7,13} For DOSY experiments, the normalized diffusion coefficient (D_{norm}) was measured as the ratio of the observed value (D_{obs}) to D_{b-CD}, where D_{b-CD} is the diffusion coefficient for the internal standard, heptakis(2,3,6-tri-O-methyl)-b-cyclodextrin (b-CD). The molecular weight could be calibrated by D_{norm} of a series of polystyrene standards (Fig. 1). The value of D_{norm} for Por 1b + melamine was 0.64, which indicates a 1b cage with a m of 3360 (calculated 3295), and D_{norm} for Por 2b + melamine was 0.60 which indicates the formation of a cage with a m of 3820 (calculated 3717).

The photophysical properties correlate with the NMR results.^{14w} UV-visible spectra of the 2a and 2b (Fig. 2) cages (38 mM–42 mM in porphyrin) with bis(decyl)melamine in dry THF were recorded over several days without heating. Heating at 45–47 °C for 2 days causes an increase in the UV-visible band intensities, indicating increased solubility and a shift in the equilibrium towards formation of the a⁴ atropisomer and the cages (Fig. 2). The emission spectra of the 2a and 2b cage solutions, exciting in the Soret or Q bands, are in agreement with the UV-visible results. An initial small decrease in the fluorescence intensity due to porphyrin aggregation is followed by an increase upon formation of the more soluble cages (Fig. 2). For the 1a and 1b the porphyrin Soret bands near 420 nm red shift by about 4 nm with a small decrease in intensity, indicating the formation of amorphous aggregates.

Dynamic light scattering data reveals the hydrodynamic diameter of the initially formed aggregates of 2a, 2b, and for 2a–2b cages to be about 42 nm, and after heating the average particle size is between 7–9 nm. There is a broad distribution of sizes for the aggregates of 1a, 1b, and 1a–1b centered at about 40 nm. The cages are found to be about 9–13 nm in diameter. Assuming extended decyl groups, an estimation of the cage dimensions from Chem 3Dr is about 5.2 nm from terminal methyl to terminal methyl on opposite sides of the cage and about 2 nm perpendicular to the porphyrin planes.

A 1: 1 mixture of free base and Zn²⁺ macrocycles, cage 2a :2b, was also examined. At equilibrium, if the intermolecular forces that mediate the assembly are equivalent, there

^wElectronic supplementary information (ESI) available: Experimental, DOSY NMR and AFM data. See DOI: 10.1039/c1cc11553g

should be a 1 : 2: 1 mixture of cages 2a :2a, 2a :2b, and 2b :2b, respectively. The UV-visible spectra for this mixture shows similar trends as the above cages; the initial formation of amorphous aggregates and the more soluble cage after heating at 45–47 °C for a few days. The fluorescence spectra of cage 2a–2b evolve in a complex manner. Initially, in the aggregation stage of the self-assembly process, some energy transfer from the metalloporphyrins to the free bases is observed. The solution may contain more aggregates of the Zn²⁺ complexes because they are less soluble. After heating the solution, only a small amount of energy transfer is observed, which is consistent with separation of the porphyrins in the cage structure. Thus, after about three days UV-visible, fluorescence, and NMR indicate that the system has reached equilibrium.

Time correlated single photon counting experiments on these self-assembled cages were carried out in dry THF under N₂ at the same concentration used for the UV-visible studies, and 408 nm excitation (Table 2). Incomplete demetalation of the Zn²⁺ complexes to form the free bases results in some of the metalloporphyrin present in the samples of 1a and 2a. The lifetimes for 1a, 2a, 1b, 2b are somewhat shorter than standard tetraphenylporphyrin (TPP, 11 ns) and ZnTPP (2.7 ns) under similar conditions¹⁵ because of some aggregation. However, the solutions with the cages, with reduced aggregation, generally display lifetimes closer to those for other meso aryl porphyrins.

Since self-assembled materials must interact with surfaces when incorporated into devices, we examined the self-organization of the cages into films. The supramolecular cages were drop cast from 30–40 mM THF solutions onto freshly cleaved mica and imaged with AFM. For the 2a cage, a film corresponding to a single layer of the cage structures is observed (Fig. 3); estimated height = 2.8 nm.⁶ In this film, the self-assembled cage is hierarchically organized by interactions between the protruding hydrocarbon chains on the four bis(decyl)melamine units.¹⁶ Friction images show no indication of separation of the porphyrin and the melamine components. When the 2b cage is cast onto mica, somewhat thicker 12 nm films are observed, with root-mean-square roughness of about 4 nm. The three different cages resulting from the mixture of 2a and 2b, yield more complex patterns on the surface.^w This hierarchical self-organization into films is analogous to those observed for squares of porphyrins self-assembled by coordination chemistry.¹⁷

The synthesis of the porphyrins and aldehydes is straight forward. The cooperative self-assembly of the porphyrin cages mediated by four rigid meso uracil groups and the bis(decyl)melamine form a stiff cage robust enough to allow organization on surfaces driven by the long hydrocarbon chains into nm thick films on mica. Assembly, in this case, turns off electronic communication between chromophores.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. The five points on the curve are D_{norm} of polystyrene standards versus molecular weight, and the D_{norm} of the two cages to yield estimates of the molecular weights. (10 mM in THF-d₈)

Fig. 2. After initially decreasing due to aggregation, the intensity of the UV-visible and fluorescence spectra increase with time and heating as the amount of the self-assembled 2b cage increases.

Fig. 3. Contact mode AFM topography image of the 2a cage on mica (left) and height profile (right).

Scheme 1.

(i) Reflux 10 h in 10% nitrobenzene in acetic acid with 0.05 M $\text{Zn}(\text{OAc})_2$. The porphyrin is prepared as a mixture of the four atropisomers (a^4 , a^3b , a^2b^2 , $abab$) since the uracyl moieties are nominally orthogonal to the macrocycle plane.

Scheme 2.

Heating of two equivalents of one of the porphyrins in the presence of four equivalents of the H-bond complimentary bis(decyl)melamine (left) results in formation of the a^4 atropisomer and self-assembly of the cage in solution. The decyl groups mediate formation of monolayer films of the cage on surfaces (right).

Table 1

NMR

Compound	Uracyl NH	Melamine NH
Por 1b	11.5 ppm	na
Por 2b	12 ppm	na
Melamine	na	4.5–5 ppm
Por 1b cage	14 ppm	5.5–6.7 ppm
Por 2b cage	13.8 ppm	5.5–6.1 ppm

10 mM in THF-d₈.

Table 2

Fluorescence lifetimes of porphyrins and cages

Compound	t ₁ (ns)	t ₂ (ns)
1a	2.2 (19%) ^a	8.8 (81%)
1b	2.5	
2a	1.8 (5%) ^a	8.6 (95%)
2b	3.8	
1a cage	2.8 (20%)	10.2 (80%)
1b cage	2.9	
1a–1b cage mix.	3.1(58%)	8.6 (42%)
2a cage	3.6 (11%)	9.6 (89%)
2b cage	2.4	
2a–2b cage mix	3.5 (60%)	9.7 (40%)

^aSome metalloporphyrin present, 408 nm excitation, 200 ps instrument response time.