

# Supramolecular porphyrinic prisms: coordinative assembly and solution phase X-ray structural characterization†

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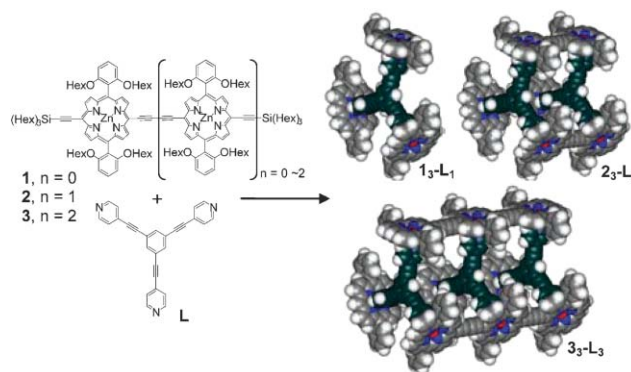
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Supramolecular porphyrin prisms have been obtained *via* coordinative self-assembly and characterized by <sup>1</sup>H NMR, PFG NMR, electronic absorption spectroscopy and synchrotron-based measurements of solution phase X-ray scattering and diffraction.

Highly conjugated porphyrin dimers, trimers, and larger oligomers are often much broader blue absorbers and much stronger red absorbers than simple monomers such as tetraphenylporphyrin.<sup>1</sup> The striking spectral enhancements, which are due in part to symmetry reduction and unidirectional electronic delocalization, make the oligomers potentially very attractive as light harvesters for energy conversion schemes. This is especially true if conjugation is introduced in ways that simultaneously sustain reasonably long (*ca.* ns) singlet excited-state lifetimes and inhibit access to chemically unstable (in the presence of O<sub>2</sub>) triplet excited states. *Meso*-connected ethynyl and butadiynyl groups are two examples of conjugating linkages meeting these requirements.<sup>2</sup>

For certain purposes, such as photo-electrode sensitization, it may be desirable to further organize porphyrins into higher-order structures. Such structures are potentially useful for minimizing chromophore aggregation, controlling chromophore spacing, and facilitating chromophore immobilization (*e.g.* by allowing for redundant surface attachment and by enabling control of orientation).<sup>3</sup> They also can be useful for fundamental photo-physical investigations.<sup>4</sup> Herein we report on the formation of well defined prism-shaped assemblies featuring three, six, or nine porphyrins and comprising, respectively, triplicate sets of porphyrin monomers (**1**), dimers (**2**), or trimers (**3**). We also report on the *in situ* X-ray structural characterization of the prisms *via* both scattering (overall assembly size) and diffraction (intra-assembly atom–atom spacing).

As illustrated in Scheme 1 the prisms form *via* reversible coordination of triethynylpyridylbenzene (**L**) by porphyrinic Zn(II) sites. (For simplicity, solubilizing groups are omitted from the prisms.) Shown in Fig. 1 are a series of electronic absorption spectra for the



Scheme 1

addition of **L** (essentially nonabsorbing) to **3** in CH<sub>2</sub>Cl<sub>2</sub> as solvent. The observed binding stoichiometry (inset) is consistent with the formation of the proposed prism, **3**<sub>3</sub>-**L**<sub>3</sub>. The observed isosbestic behavior points to all-or-nothing prism formation, while the resistance to spectral change beyond the 3 : 3 stoichiometry illustrates the stability of the putative prism. A similar titration of **2** reaches an end point with ~0.67 equivalents of **L**, consistent with the formation of **2**<sub>3</sub>-**L**<sub>2</sub>. All-or-nothing prism formation is again indicated, but excess **L** causes further spectral changes, implying further ligation and break-up of the prism (see ESI†). For both **2** and **3**, prism formation is characterized by broadening in the porphyrin Soret region and intensification and red-shifting in the Q-band region beyond 700 nm. Similar effects have been noted previously by Taylor and Anderson in their studies of the

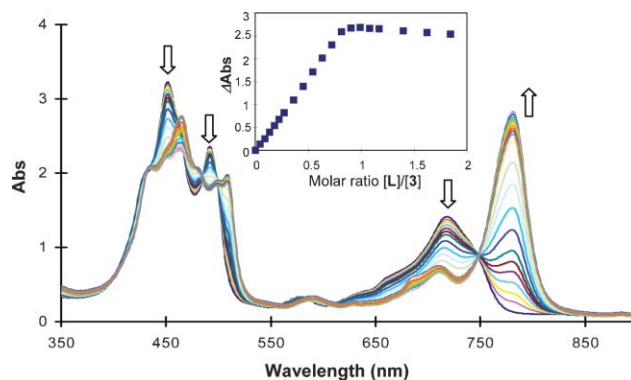


Fig. 1 Spectrophotometric titration of trimer **3** (conc. =  $2.0 \times 10^{-5}$  M) with trigonal ligand **L** in dichloromethane as solvent. Inset: absorbance change at 780 nm, showing stoichiometric coordination of **L** and illustrating resistance of prism to fragmentation by excess **L**.

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formation of ladder structures from ditopic nitrogen donors and oligomeric Zn(II) porphyrins.<sup>2b</sup> These effects are consequences of porphyrin dimer or trimer planarization and the resulting enhancements of porphyrin–porphyrin electronic coupling.

A similarly quantitative titration for the formation of  $1_3\text{-L}$  was unattainable, reflecting prism instability at the low concentrations used for absorption measurements. This is consistent with the generally weak interaction of porphyrinic Zn(II) with pyridyl nitrogen atoms. The fact that prisms based on **2** and **3** do form at low concentrations, despite weak Zn–N bonding, is illustrative of beneficial pre-organization effects and the cumulative nature of assembly stabilization by metal–ligand interactions.

Prism formation was further examined by  $^1\text{H}$  NMR spectroscopy. Fig. 2 compares spectra for **L**, **2**, and  $2_3\text{-L}_2$  in toluene as solvent. Salient features are: (a) substantial upfield shifts of peaks for the phenyl,  $\beta$ -pyridyl, and especially,  $\alpha$ -pyridyl protons of **L**, evidencing the effects of large porphyrin ring currents,<sup>5</sup> and (b) single sets of signals for each of the three types of protons of ligated **L**. The second observation, while consistent with the formation of a highly symmetrical prism structure is also consistent with rapid exchange between bound and free versions of **L**. Additional spectra with excess **L** (not shown) showed progressive downfield shifts, consistent with rapid exchange between bound and free environments. Spectra for sub-stoichiometric amounts of **L**, on the other hand, showed full upfield shifts from the outset, consistent with the observation in Fig. S3 of the ESI of all-or-nothing  $2_3\text{-L}_2$  prism formation.

For  $1 + \text{L}$ , analysis of proton shifts indicates that  $\sim 93\%$  of the pyridyl nitrogens are ligated under stoichiometric conditions when  $[\text{I}] = 0.001 \text{ M}$ ;  $\sim 96\%$  are ligated (under stoichiometric conditions) when  $[\text{I}] = 0.01 \text{ M}$ .

Assembly sizes (hydrodynamic radii) were estimated from self-diffusion coefficients by using the Stokes–Einstein relation. The needed coefficients were obtained by the pulsed-field-gradient NMR method (see ESI).<sup>†6,7</sup> The values obtained were  $20 \pm 2$ ,  $35 \pm 2$ , and  $42 \pm 7 \text{ \AA}$ , respectively, for  $1_3\text{-L}$ ,  $2_3\text{-L}_2$ , and  $3_3\text{-L}_3$ . Importantly, identical values were obtained for porphyrin and linker protons, confirming in each case that the units comprised a common assembly.

Definitive evidence for prism formation was obtained from solution phase X-ray scattering measurements. These methods are emerging as a powerful means for structurally characterizing supramolecular assemblies, particularly those that cannot be studied by traditional crystallographic methods.<sup>8</sup> Small-angle X-ray scattering (SAXS) data were used to obtain measures of overall assembly size—specifically, electron-density-weighted radii of gyration ( $R_g$ ). The Guinier equation relates  $q$ -dependent (reciprocal-distance dependent) scattering intensities to  $R_g$ :

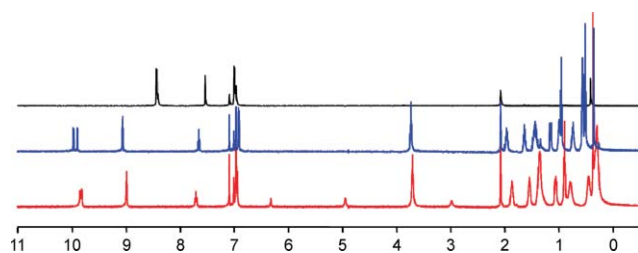


Fig. 2  $^1\text{H}$  NMR spectra of **L**, **2**, and  $2_3\text{-L}_2$  in toluene.

Table 1 Summary of Guinier analysis of free porphyrin monomer, dimer, and trimer species, and corresponding prism assemblies

		$R_g/\text{\AA}$
Monomer ( <b>1</b> )	Model	4.14
	Experiment	$4.12 \pm 0.22$
Prism ( $1_3\text{-L}$ )	Model	10.63
	Experiment	$10.37 \pm 0.16$
Dimer ( <b>2</b> )	Model	7.70
	Experiment	$7.68 \pm 0.14$
Prism ( $2_3\text{-L}_2$ )	Model	12.76
	Experiment	$12.87 \pm 0.21$
Trimer ( <b>3</b> )	Model	11.35
	Experiment	$11.38 \pm 0.24$
Prism ( $3_3\text{-L}_3$ )	Model	15.72
	Experiment	$15.73 \pm 4.21$

$$I(q) = I(0)\exp(-q^2R_g^2/3) \quad (1)$$

where  $I(0)$  is proportional to the electron-density-contrast weighted square of the number of electrons in the scattering object.<sup>9</sup> Table 1 compares modeled and experimental measured porphyrin panel and prism sizes. As expected, the scattering experiments return larger radii for prisms than component panels, with prism sizes increasing in the order  $1_3\text{-L} < 2_3\text{-L}_2 < 3_3\text{-L}_3$ . The observed close agreement between experiment and model provides compelling evidence for prism formation and rules out the formation of larger aggregates (Fig. 3). (Note also that the electron-density-weighted  $R_g$  values are also expected, and observed, to be smaller than the hydrodynamic radii for these systems.)

Wide-angle X-ray scattering (WAXS) was used to obtain information about interatomic spacings within assemblies. Measurements were made in the  $q$ -range from  $0.09$  to  $2.7 \text{ \AA}^{-1}$ , corresponding to a spatial resolution of  $2.4 \text{ \AA}$  ( $d = 2\pi/q$ ). These were then Fourier transformed into real space using the program GNOM.<sup>10</sup> Fig. 4 shows experimental and calculated pair-distribution plots for a representative prism and panel. Since scattering intensity scales as the product of the number of electrons comprising a scattering (diffracting) pair, the most intense peaks should be those for Zn–Zn pairs. The data, shown in Fig. 4, reveal an intense peak at  $13.5 \text{ \AA}$ , assignable to scattering by the pair of zinc atoms embedded in the porphyrin dimer. Additionally, however, the data reveal a second Zn–Zn interaction, unique to the prism, at  $18.5 \text{ \AA}$ . In all the prism assemblies, it is possible to detect the presence of the Zn–Zn scattering interactions which are unique

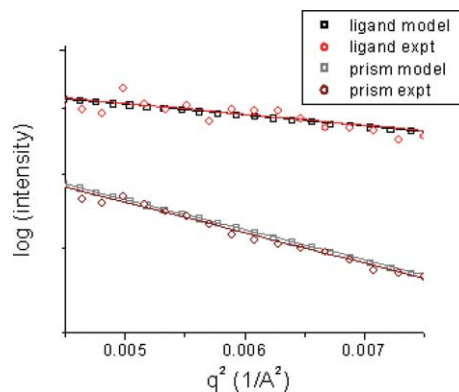
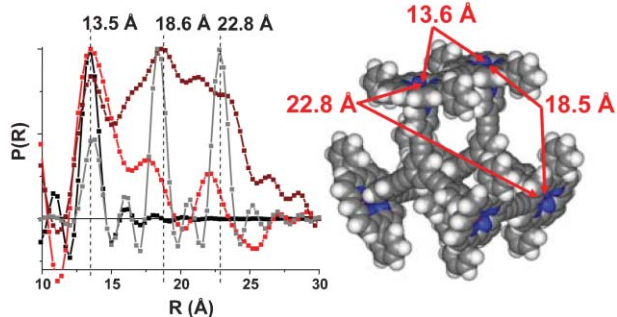


Fig. 3 Experimental and modelled Guinier plots for **2** (upper) and  $2_3\text{-L}_2$  (lower). Intensities are normalized by  $I_0$ .



**Fig. 4** Right: Simplified model of dimer prism assembly (minus solubilizing groups), illustrating metal–metal separation distances. Left: Experimental and modeled pair-distribution plots, obtained by transforming corresponding wide-angle scattering intensity versus  $q$  plots. Maroon trace: Experimental pair-distribution function (PDF) plot for  $2_3\text{-L}_2$ . Red trace: Experimental plot for free dimeric porphyrin panel (**2**). Black trace: Modeled PDF for free dimeric panel based on contributions only from Zn–Zn interactions. Gray trace: Modeled PDF for  $2_3\text{-L}_2$  based on contributions only from Zn–Zn interactions. The low amplitude oscillations in the calculated PDFs are Fourier transform truncation artifacts that are expected to contribute to the experimental plots as well.

to prism assembly and do not appear for the porphyrin panel alone. Additional peaks, including negative-going peaks clearly absent from the simplified modelling, are likely caused by solvent ordering that creates regions surrounding the porphyrinic assemblies of higher and lower electron density compared to bulk solvent. Further modelling of solvent ordering by the prisms and related assemblies is in progress.

In summary, highly chromophoric porphyrin prisms have been obtained *via* coordinative self-assembly and characterized *via*  $^1\text{H}$  NMR, PFG-NMR and electronic absorption spectroscopy. The largest of the prisms resists break up in the presence of excess linker ligand. Unequivocal evidence for prism formation in solution has been obtained from synchrotron-based measurements of X-ray scattering and diffraction.‡§¶

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## Notes and references

‡ Synthesis of porphyrin oligomers: Zinc porphyrin monomer, dimer, and trimer panel species were synthesized according to modified literature procedures.<sup>2b</sup> Briefly, a stepwise approach, entailing desilylation with TBAF followed by monoprotection with trihexylsilane and Cu mediated oxidative coupling, was used to synthesize the dimer and trimer from the monomer. For the monomer, trihexylsilane endgroups facilitate chromatographic separation of [5,15-bis(2,6-di-hexoxy)-10,20-(bis-ethynyl)porphyrinato]zinc (**1a**), [5,15-bis(2,6-di-hexoxy)-10-(ethynyl)-20-(trihexylsilyl-ethynyl)porphyrinato]zinc (**1b**), and [5,15-bis(2,6-di-hexoxy)-10,20-bis(trihexylsilylethynyl)porphyrinato]zinc (**1**). They also increase the solubilities of dimers, trimers and prisms. The trimeric zinc porphyrin (**3**) was prepared in reasonable yield by Glaser–Hey coupling<sup>11</sup> with CuCl in DCM, treating **1a** with **1b**. Dimeric porphyrin (**2**) was obtained by Glaser–Hey coupling of **1a** in DCM and as a side product during the synthesis of trimeric porphyrin. The oligomers (*i.e.* panel units) have been characterized by  $^1\text{H}$  and  $^{13}\text{C}\{\text{H}\}$

NMR, UV-Vis, and high-resolution mass spectrometry. The trigonal ligand, 1,3,5-triethylpyridylbenzene (**L**), was prepared in high yield by Sonogashira coupling of 1,3,5-triethylbenzene and 4-bromopyridine.<sup>12</sup> § Solution phase X-ray scattering measurements: The assembly solutions (prisms or panels in toluene) used in the SAXS measurements were diluted to sufficiently low concentrations such that monodisperse assemblies were obtained. Consequently, the concentration of  $3_3\text{-L}_3$  ( $7.6 \times 10^{-6}$  M) was substantially less than that of the other assemblies (monomer prism  $5.2 \times 10^{-4}$  M; dimer prism  $1.7 \times 10^{-4}$  M). This is reflected in the greater uncertainty for  $R_g$  for the trimer-based prism. Aggregation of assemblies was detected in more concentrated solutions as evidenced by nonlinearity of Guinier scattering plots (upward curvature in small  $q$  region).<sup>13</sup>

¶ PFG NMR measurements: All PFG NMR experiments were performed on a Varian Inova 400 spectrometer equipped with an ultra-shielded Doty PFG probe. The 13-interval PFG NMR pulse sequence with bipolar-gradient pair suggested by Cotts *et al.* was used to measure the self-diffusivity.<sup>14</sup> The resonance frequencies of  $^1\text{H}$  nuclei was 400.6 MHz and the corresponding  $\pi/2$  pulse widths were 19  $\mu\text{s}$ . The delays before and after gradient pulses varied between 400 and 500  $\mu\text{s}$ , depending on the width of the applied gradient pulse. Preliminary experiments indicated that the residual eddy current was negligible under these conditions. The gradient pulse widths ranged from 500 to 1250  $\mu\text{s}$ , and gradient intensities ranged from 5 to 250  $\text{G cm}^{-1}$ . Diffusion times between 600 and 800  $\mu\text{s}$  were used, with 16–64 scans on each of nine gradient intensities per sample. Prior to the acquisition of NMR signals, the adsorbed sample was equilibrated for at least 20 min at the desired temperature. The error in temperature was less than 0.1 K.

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