

## Supporting Information for

# Self-Assembly of a Hexagonal Supramolecular Light-Harvesting Array from Chlorophyll Trefoil Building Blocks

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**Optical Spectroscopy.** Steady-state absorption spectroscopy was performed using a Shimadzu 1601 UV/Vis spectrophotometer. A single-photon-counting fluorimeter (Photon Technology International) was used for emission experiments. Measurements were performed at room temperature in a 1 cm quartz cuvette with excitation/emission geometries at right angles. All solvents were spectroscopic grade and used as is, except for tetrahydrofuran (THF), which was further purified by passing it twice through alumina (GlassContour) immediately prior to use.

Femtosecond transient absorption (fsTA) measurements were made using a Ti:sapphire laser system detailed previously.<sup>1, 2</sup> The instrument response function (IRF) for the pump-probe experiments was 180 fs. Typically 5 s of averaging was used to obtain the transient spectrum at a given delay time. Samples were photoexcited with 655 nm or 416 nm, 130 fs, 0.25-1.00  $\mu$ J laser pulses focused to a 200  $\mu$ m spot in a 2 mm pathlength quartz cuvette. The optical density at the pump wavelength was kept between 0.5-0.7. Analysis of the kinetic data was performed at multiple wavelengths using a Levenberg-Marquardt nonlinear least-squares fit to a general sum-of-exponentials function convoluted with a Gaussian instrument response function.

**SAXS/WAXS.** The coordination structure for was investigated using small- and wide angle X-ray scattering (SAXS/WAXS) measurements under solution sample concentrations at  $10^{-6}$  M in toluene. A high-flux synchrotron source (Advanced Photon Source at Argonne National

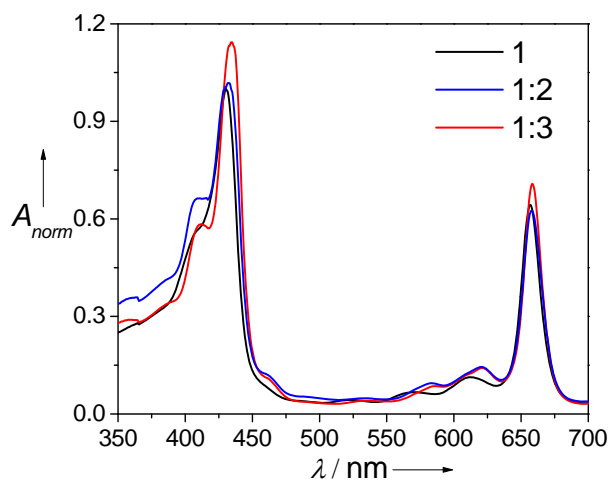
Laboratory) was used to obtain scattering patterns over the  $q$  region,  $0.01 \text{ \AA}^{-1} < q < 1.9 \text{ \AA}^{-1}$  (Figure S2). In the low-resolution scattering region  $q < 0.2 \text{ \AA}^{-1}$ , a Guinier relationship (eq. 1) was applied to the scattering data. The Guinier fit to the **1:3<sub>3</sub>** compound over a range of  $0.005 \text{ \AA}^{-2} < q^2 < 0.010 \text{ \AA}^{-2}$  (Figure S3) shows an essentially linear region. A least-squares fit to this region reveals a  $R_g$  of 13.4  $\text{\AA}$ .

The monodispersity of **1:3<sub>3</sub>** in solution allows an analysis of atomic pair distribution functions (PDFs) by directly comparing reciprocal-space scattering patterns and real-space molecular models. The experimental PDF was obtained using the X-ray scattering fitting program GNOM<sup>4</sup> and model PDFs were generated in the same method from MM+ geometry optimized models.<sup>5</sup> Figure S4 shows the **1:3<sub>3</sub>** experimental PDF overlaid with the best-fit monomer model structure with quinuclidines coordinated to each Zn metal center.

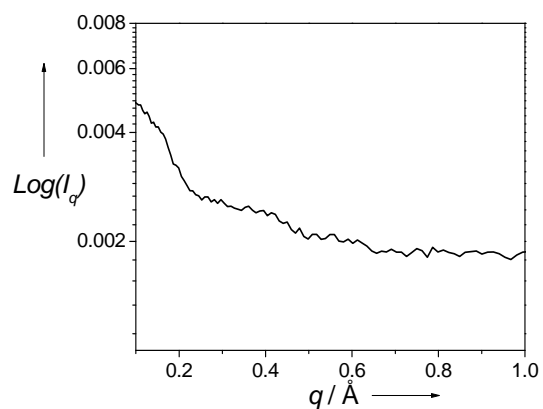
**Equilibrium Constant.** The equilibrium constant for the self-assembly of trefoil **1** with DABCO (**2**) was determined from the spectrophotometric titration of **1** ( $[1] = 8.22 \times 10^{-5} \text{ M}$ ) with **2** in toluene (Figure S7). Two isosbestic points were observed during the titration process indicative of the presence of three species (Figure S8). The titration data fit using multivariate factor analysis (SPECFIT V3.0)<sup>3</sup> and yielded stability constants of  $K = 3.24 \times 10^{12} \text{ M}^{-5}$  for the formation **1<sub>3</sub>:2<sub>3</sub>**, and  $K = 2.6 \times 10^4 \text{ M}^{-3}$  for the formation of the fully saturated **1:2<sub>3</sub>** complex..

## References

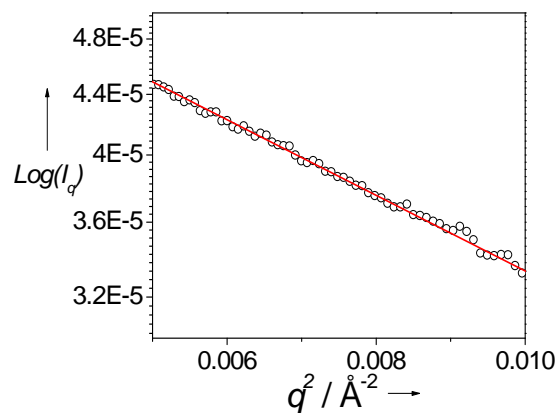
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2. Lukas, A. S.; Miller, S. E.; Wasielewski, M. R., *J. Phys. Chem. B* **2000**, *104*, 931-940.
3. SPECFIT, 3.0; Spectra Software Associates: Marlborough, MA, 2006.
4. Svergun, D. I., *J. Appl. Cryst.* **1992**, *25*, 495-503.
5. *Hyperchem*, Hypercube Inc.: 1115 NW 4th Street, Florida 32601, USA, 1994.



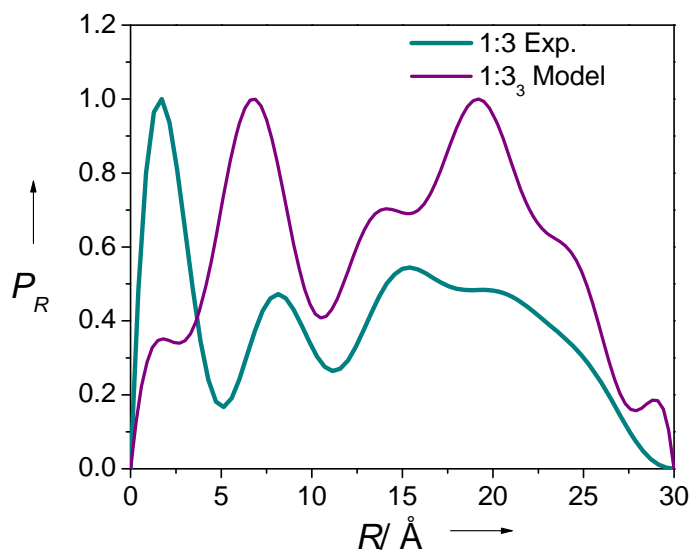
**Figure S1.** Structures of molecules and UV-vis spectra of **1** alone and **1** after titration with **2** and **3**.



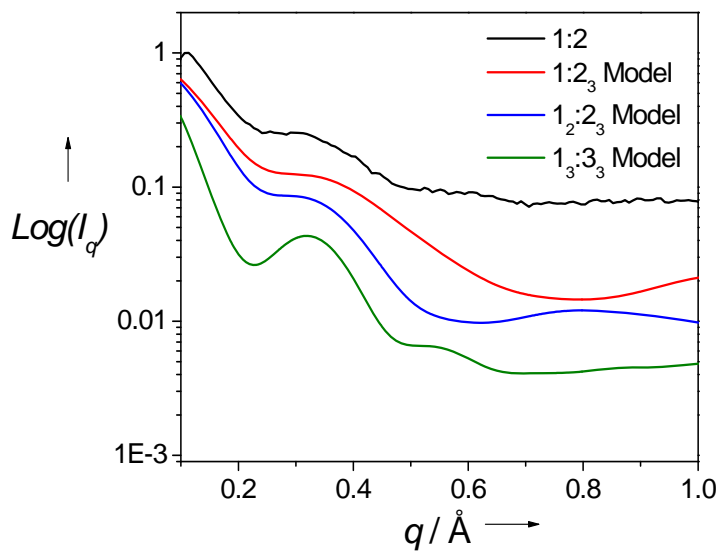
**Figure S2.** Scattering intensity,  $I(q)$ , for **1:3** vs. scattering length vector,  $q$ , data in toluene.



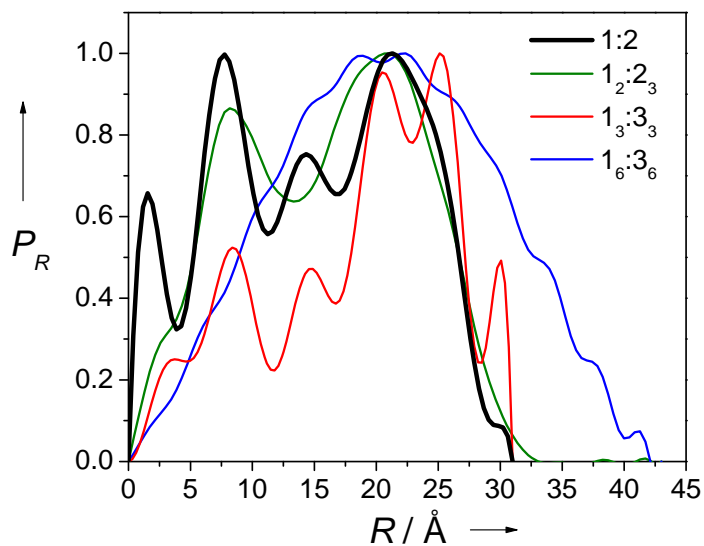
**Figure S3.** Experimental scattering intensity,  $I(q)$ , of **1:3** versus scattering length vector squared,  $q^2$ , data in toluene fit to a linear Guinier region.



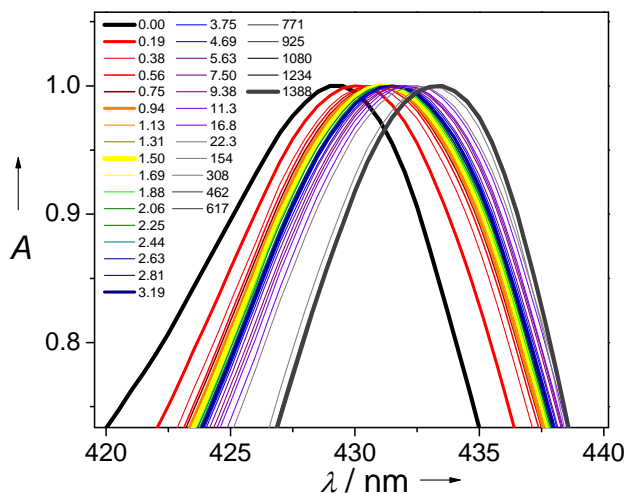
**Figure S4.** An overlay of the atomic pair-distribution function (PDF) for the experimental of **1:3** and the monomer (**1:3<sub>3</sub>**) MM+ modeled structure.



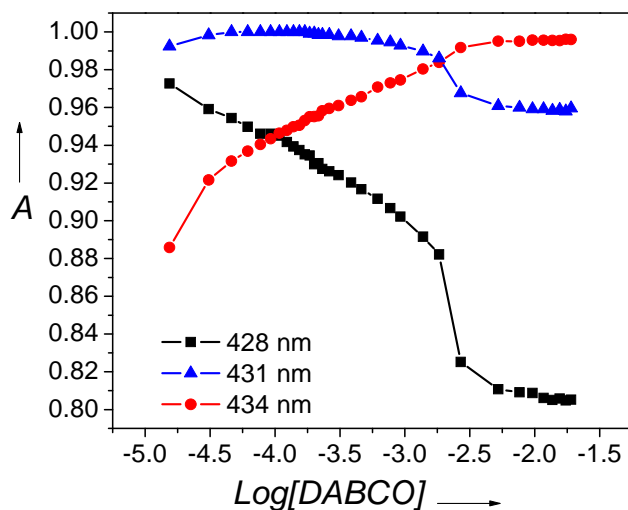
**Figure S5.** Scattering intensity,  $I(q)$ , versus scattering length vector,  $q$ , data for  $1_3:2_3$  and the corresponding model systems in toluene solution ( $0.1 \text{ \AA}^{-1} < q < 1 \text{ \AA}^{-1}$ ).



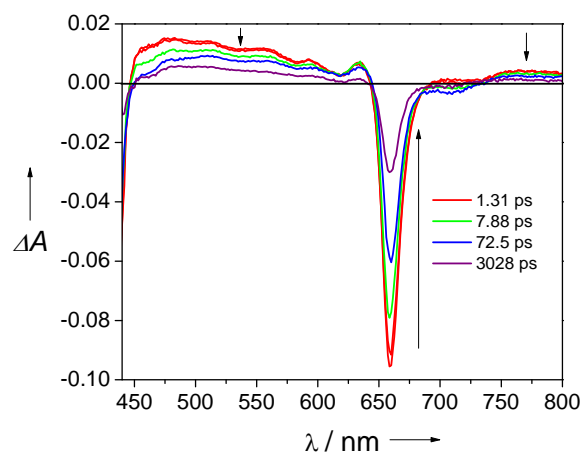
**Figure S6.** An overlay of the atomic pair-distribution function (PDF) for the experimental  $1:2$  and a variety of other MM+ modeled structures.



**Figure S7.** The normalized Soret band absorption spectra of the titration of **1** ( $[1] = 8.22 \times 10^{-5} \text{ M}$ ) with increasing equivalents of **2**.



**Figure S8.** UV-Vis titration data from the titration of **1** ( $[1] = 8.22 \times 10^{-5} \text{ M}$ ) with **2**. Changes in absorbance were monitored at three wavelengths 428 nm, 431 nm, and 434 nm, which correspond to the peak maximum of the three species believed to be present in solution: Trefoil (**1**), Trefoil<sub>3</sub>-DABCO<sub>3</sub> (**1**<sub>3</sub>:**2**<sub>3</sub>), and the fully DABCO saturated trefoil (**1**:**2**<sub>3</sub>), respectively.



**Figure S9.** Femtosecond transient absorption spectra of **1:3** in toluene excited at 416 nm.