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Supporting Information for

Supramolecular Porphyrinic Prisms: Coordinative Assembly and Solution-phase X-ray Structural Characterization

by

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Experimental Section.

Materials and General Procedures. All chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. Absorbance spectra were obtained using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Flash column chromatography was carried out with 230-400 mesh silica gel from Aldrich using the wet-packing method. NMR spectra were recorded on either a Mercury 400 (400.168 MHz for ^{1}H, and 100.622 MHz for ^{13}C) or an Inova 500 (499.773 MHz for ^{1}H, and 125.669 MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million downfield from tetramethylsilane with solvent resonances as internal standards. Electrospray mass spectra (ESI-MS) and high-resolution FAB mass spectra (FAB-HR) were obtained from the Analytical Services Laboratory at University of Illinois at Urbana-Champaign. 1,3,5-Triethylnylbenzene,[1] 2,6-Di(n-hexoxy)bezaldehyde and meso-(2,6-di(n-hexoxy)phenyl)dipyrromethane were synthesized according to the literature procedures.[2]

1,3,5-Triethynyl-4-pyridyl-benzene (L). To a solution of 1,3,5-triethynylbenzene (150 mg, 1 mmol) and 4-bromopyridineHCl (972 mg, 5 mmol) in triethylamine (50 mL) were added Pd(PPh3)4 (230 mg, 0.2 mmol) and CuI (10 mg, 0.05 mmol). The resulting mixture was refluxed for 2 days. The volatiles were removed under reduced pressure. The residue was dissolved in EtOAc and washed with sat NH_4Cl solution and H_2O. The organic layer was collected, dried over $MgSO_4$ and evaporated. The resulting crude product was purified by silica-gel chromatography (EtOAc/MeOH (9:1 v/v)) to afford pure 1,3,5-triethynyl-4-pyridyl-benzene (240 mg, 63% yield). ^{1}H NMR ($CDCl_3$): δ 8.66 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 6H), 7.78 (s, 3H), 7.47 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* 150.16, 135.41, 130.81, 125.72, 123.58, 91.64, 88.45. HR-MS (ESI) *m/z* 382.1327 (Calcd *m/z* 382.1344 for $[M+H]^+$).

[5,15-bis(ethynyl)-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (1a). Meso-(2,6-di(n-hexoxy)phenyl)dipyrromethane (2.1 g, 4.97 mmol), and trimethylsilanylpropanal (0.9 mL, 4.97 mmol) were dissolved in 800 mL of CH_2Cl_2 . The resulting solution was degassed for 5 min at 0 °C. $BF_3{\cdot}2Et_2O$ (125 μL) was added slowly and the reaction mixture was allowed to stir under N_2 atmosphere for 5 min. at 0 °C. 1.2 g of DDQ was then added to stop the reaction. After stirring for 30 min, 2 mL of pyridine was added. The precipitates were filtered off and the volatiles were removed under reduced pressure. The resulting residue was purified by silica-gel column chromatography (Hexane/dichloromethane (1:1 v/v)) to afford pure 5,15-bis[(trimethylsilanyl)ethynyl]-10,20-bis[2,6-di(n-hexoxy)phenyl]porphyrin which was further metallated with Zinc(II) acetate according to the literature procedure to afford [5,15-bis[(trimethylsilanyl)ethynyl]-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc.

400 mg of [5,15-bis[(trimethylsilanyl)ethynyl]-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc obtained from the above reaction was treated with TBAF (0.8 mL, 1 M in THF) in THF (28 mL) for 20 min. After workup, deep green crude product was purified by silica-gel column chromatography (Hexane/THF (7:3 v/v)) to afford 315 mg of [5,15-bis(ethynyl)-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (23% overall yield). ^{1}H NMR ($CDCl_3$): δ 9.63 (d, $^3J_{H\text{-}H}$ = 3.8 Hz, 4H), 8.88 (d, $^3J_{H\text{-}H}$ = 3.8 Hz, 4H), 7.69 (t, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 6.99 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H), 4.09 (s, 2H), 3.83 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 8H), 0.92 (m, 8 H), 0.50 (m, 16 H), 0.36 (m, 8 H), 0.23 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 12 H). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* 160.04,

151.98, 150.97, 132.12, 130.82, 129.97, 121.01, 115.15, 105.28, 98.63, 86.74, 82.80, 68.80, 31.02, 28.82, 25.09, 22.22, 13.73. HR-MS (EI) *m/z* 974.5965 (Calcd *m/z* 974.5962 for M^+).

[5-ethynyl-15-(tri-hexylsilanyl)ethynyl-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (1b) and [5,15-(tri-hexylsilanyl)ethynyl-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (1). A solution of **1a** (195 mg, 0.2 mmol) in THF (12 mL) was allowed to cool to -78°C and n-BuLi (1.6 M in hexane, 125 μL, 0.2 mmol) was added slowly. After the addition was completed, the reaction mixture was allowed to warm to room temperature. After the reaction mixture was again cooled to -78°C, trihexylsilylchloride (88 μL, 0.24 mmol) was added dropwise. After stirring for 15 min at -78°C, the reaction mixture was then allowed to stir for 6 h at RT. The volatiles were removed under reduced pressure and the residue was extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo to afford deep green oily product which was purified by silica-gel column chromatography (Hexane/THF (9:1 v/v)) to afford pure [5-ethynyl-15-(tri-hexylsilanyl)ethynyl-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc, **1b**, (120 mg, 46% yield) and pure [5,15-(tri-hexylsilanyl)ethynyl-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc, **1**, (61 mg, 22% yield).

[5-ethynyl-15-(tri-hexylsilanyl)ethynyl-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (1b). ^{1}H NMR ($CDCl_3$): δ 9.68 (m, 4H), 8.85 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H), 8.83 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H), 7.69 (t, $^3J_{H\text{-}H}$ = 7.9 Hz, 2H), 6.99 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 4H), 4.08 (s, 1H), 3.83 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 8H), 1.76 (m, 6H), 1.53 (m, 6H), 1.38 (m, 14 H), 1.00 (m, 6 H), 0.90 (m, 17 H), 0.53 (m, 14H), 0.40 (m, 8 H), 0.28 (m, 12 H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.17, 152.13, 150.99, 132.23, 132.01, 131.23, 130.89, 130.05, 123.40, 122.38, 121.12, 115.31, 109.23, 105.45, 100.76, 98.95, 98.55, 86.71, 82.81, 68.86, 33.61, 31.89, 30.98, 28.79, 25.05, 24.57, 22.92, 22.17, 14.40, 14.13, 13.67. HR-MS (EI) *m/z* 1255.7396 (Calcd *m/z* 1255.7353 for $[M+H]^+$).

[5,15-(tri-hexylsilanyl)ethynyl-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (1). ^{1}H NMR ($CDCl_3$): δ 9.61 (m, 4H), 8.23 (m, 4H), 7.68 (t, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H), 6.98 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 4H), 3.82 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 8 H), 1.75 (m, 12 H), 1.51 (m, 12 H), 1.38 (m, 20 H), 1.01

(m, 12 H), 0.91 (m, 26 H), 0.51 (m, 20 H), 0.39 (m, 8 H), 0.24 (m, 12 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 160.17, 152.08, 150.81, 131.86, 130.93, 129.94, 121.22, 115.16, 109.48, 105.39, 100.32, 98.57, 68.83, 33.62, 31.89, 31.00, 28.80, 25.06, 24.57, 22.93, 22.20, 14.41, 14.13. HR-MS (FAB) *m/z* 1537.0020 (Calcd *m/z* 1537.0018 for M^+).

[[5,5'-(1,3-butyne-1,4-biyl)bis[10,20-bis[2,6-bis[di(n-hexoxy)]phenyl]-15-[(trihexyl)ethynyl]porphinato]]]dizinc (2). A solution of **1b** (65 mg, 0.05 mmol) and TMEDA (0.58 mL) in CH_2Cl_2 (55mL) was bubbled with dry-air for 10 min. CuCl (384 mg) was added all at once and the reaction mixture was allowed to stir 30 min under dry-air. The reaction mixture was washed with water until all the CuCl was removed. The organic layer was collected, dried over $MgSO_4$ and the solvent was removed in vacuo. The dark residue was purified by silica-gel column chromatography (dichloromethane/Hexane (1:1.5 v/v)) to afford pure [[5,5'-(1,3-butyne-1,4-biyl)bis[10,20-bis[2,6-bis[di(n-hexoxy)]phenyl]-15-[(trihexyl)ethynyl]porphinato]]]dizinc (43 mg, 68%). ^{1}H NMR ($CDCl_3$): δ 9.84 (d, $^{3}J_{H-H}$ = 4.3 Hz, 4H), 9.61 (d, $^{3}J_{H-H}$ = 4.5 Hz, 4H), 8.93 (d, $^{3}J_{H-H}$ = 4.3 Hz, 4H), 8.84 (d, $^{3}J_{H-H}$ = 4.5 Hz, 4H), 7.71 (t, $^{3}J_{H-H}$ = 8.2 Hz, 4H), 7.02 (d, $^{3}J_{H-H}$ = 8.2 Hz, 8H), 3.87 (t, $^{3}J_{H-H}$ = 7.2 Hz, 16H), 1.77 (m, 12H), 1.54 (m, 12H), 1.39 (m, 28H), 0.99 (m, 28H), 0.91(m, 12H), 0.57(m, 34H), 0.44 (m, 16 H), 0.31 (m, 24 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 160.26, 153.02, 152.41, 151.28, 150.92, 132.74, 132.35, 131.41, 131.04, 130.25, 121.01, 116.13, 109.92, 105.38, 101.67, 99.31, 87.71, 82.16, 68.86, 33.64, 31.90, 31.09, 28.88, 25.14, 24.58, 23.89, 22.94, 22.29, 14.42, 13.80. MS (FAB): *m/z* 2507.9 (calculated *m/z* 2507.4 for M^+). Anal. calc. for $C_{156}H_{210}N_8O_8Si_2Zn_2$: C, 74.58; H, 8.43; N, 4.46%. Found: C, 74.44; H, 8.52; N, 4.49%.

[[5,5'-(1,3-butyne-1,4-biyl)bis[10,20-bis[2,6-bis[di(n-hexoxy)]phenyl]]-15-[(trihexyl)ethynyl]-porphin-5-yl]-1,3-butadiynyl]-10,20-bis[2,6-bis[di(n-hexoxy)]phenyl]-porphinato]trizinc (3). A solution of **1b** (130 mg, 0.1 mmol), **1a** (24.5 mg, 0.025 mmol) and TMEDA (1.3 mL) in CH_2Cl_2 (380mL) was bubbled with dry-air for 10 min. CuCl (891 mg) was added all at once and the reaction mixture was allowed to stir 20 min under dry-air. The reaction mixture was washed with water until all the CuCl was removed. The organic layer was collected, dried over $MgSO_4$ and the solvent was removed in vacuo. The dark residue was purified by silica-gel column chromatography (chloroform/dichloromethane/Hexane (3:2:3 v/v)) to afford pure **3** (19 mg, 23 %) and pure **2** (25 mg, 39 %). ^{1}H NMR (CDCl$_3$): δ9.85 (d, $^3J_{\text{H-H}}$ = 4.3 Hz, 8H), 9.62 (d, $^3J_{\text{H-H}}$ = 4.3 Hz, 4H), 8.96 (d, $^3J_{\text{H-H}}$ = 4.3 Hz, 8H), 8.85 (d, $^3J_{\text{H-H}}$ = 4.3 Hz, 4H), 7.73 (t, $^3J_{\text{H-H}}$ = 8.2 Hz, 2H), 7.71 (t, $^3J_{\text{H-H}}$ = 7.9 Hz, 4H), 7.05 (d, $^3J_{\text{H-H}}$ = 8.2 Hz, 4H), 7.03 (d, $^3J_{\text{H-H}}$ = 7.9 Hz, 8H), 3.93 (t, $^3J_{\text{H-H}}$ = 6.7 Hz, 8 H), 3.88 (t, $^3J_{\text{H-H}}$ = 6.5 Hz, 16 H), 1.77 (m, 12H), 1.54 (m, 12H), 1.40 (m, 36H), 0.99 (m, 36H), 0.92 (m, 12H), 0.64 (m, 16 H), 0.57 (m, 26H), 0.51 (m, 8H), 0.45 (m, 16H), 0.40 (m, 12H), 0.32 (m, 24H). NMR (CDCl$_3$): δ160.16, 152.91, 152.29, 151.16, 151.01, 150.71, 132.70, 132.57, 132.21, 131.33, 131.07, 130.91, 130.11, 120.93, 120.81, 115.96, 105.43, 101.38, 99.85, 99.01, 97.29, 87.81, 87.49, 82.27, 81.85, 68.89, 33.63, 31.90, 31.13, 31.06, 28.91, 28.86, 25.20, 25.14, 24.59, 24.29, 22.94, 22.36, 22.27, 14.42, 13.85, 13.77. MS (FAB): *m/z* 3484.2 (calculated *m/z* 3484.9 for M$^+$). Anal. calc. for $C_{216}H_{276}N_{12}O_{12}Si_2Zn_3$: C, 74.44; H, 7.98; N, 4.82%. Found: C, 74.97; H, 7.85; N, 4.92%.

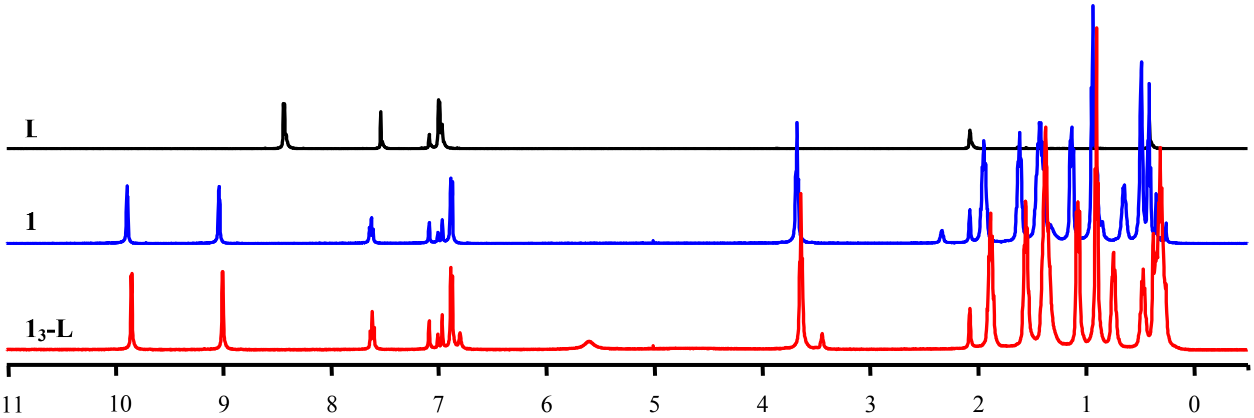


Fig. S1 ^{1}H NMR spectra of **L**, **1**, and **1_3-L** at 5.3 x 10^{-3}M.

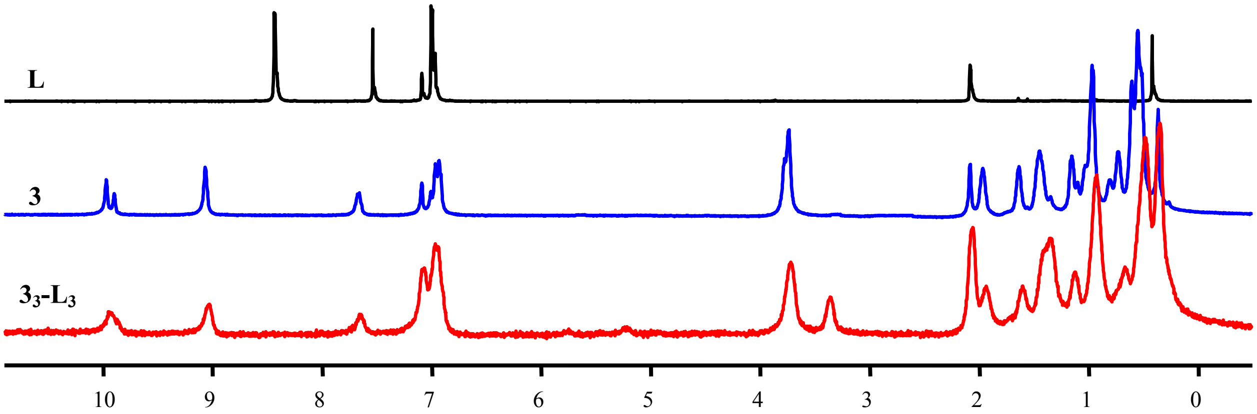


Fig. S2 ^{1}H NMR spectra of **L**, **3**, and **3_3-L$_3$** at 0.9 x 10^{-4}M.

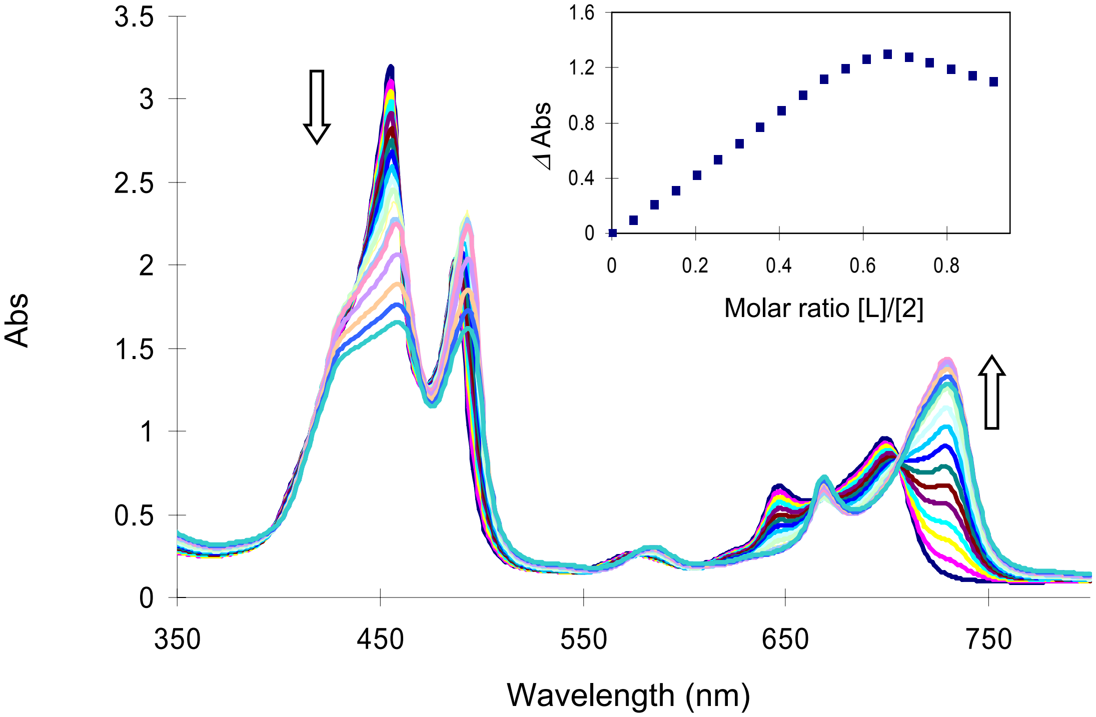


Fig. S3 Spectrophotometric titration of dimer **2** with trigonal ligand **L** in dichloromethane in the concentration of 1.8 x 10^{-5} M and titration curve at 729 nm. Arrows show change with absorption in the formation of $\mathbf{2_3 \cdot L_2}$.

Solution X-ray scattering experimental methods.

Solution X-ray scattering measurements were carried out at Beamline 12-BM-B at the Advanced Photon Source at Argonne National Laboratory. Detailed descriptions of procedures used for wide angle X-ray scattering measurements and coordinate-based analyses have been reported previously.[3-5] Briefly, a double-crystal Si(111) monochromator and a two-dimensional mosaic CCD detector were used in the data collection. The X-ray energy was set to 20 keV and the sample to detector distances where adjusted to obtain scattering in two different q-ranges: $0.03\ \text{Å}^{-1} < q < 0.84\ \text{Å}^{-1}$ and $0.1\ \text{Å}^{-1} < q < 2.6\ \text{Å}^{-1}$, where $q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of X-rays and 2θ is the scattering angle.

The sample solutions were prepared immediately prior to measurement. The solutions were injected into a capillary which was positioned in the beam path. The acquisition time for each sample was 100s or 240s, depending on the q-range and scattering intensity and 5 scans for each sample were averaged to obtain the overall scattering pattern. Checks for X-ray induced damage to samples were performed by comparing scattering patterns as a function of exposure time and by comparing scattering patterns from samples under static and flowed (50 x 10^{-6} L/min) conditions. In all cases the measured scattering patterns were found to be independent of X-ray exposure within the timeframes used in these experiments, presumably because of efficient scavenging and chemical quenching of radiation-produced free radicals. To obtain only the solute scattering intensity, a fraction of the blank solvent (toluene) was subtracted from the entire sample scattering intensity.

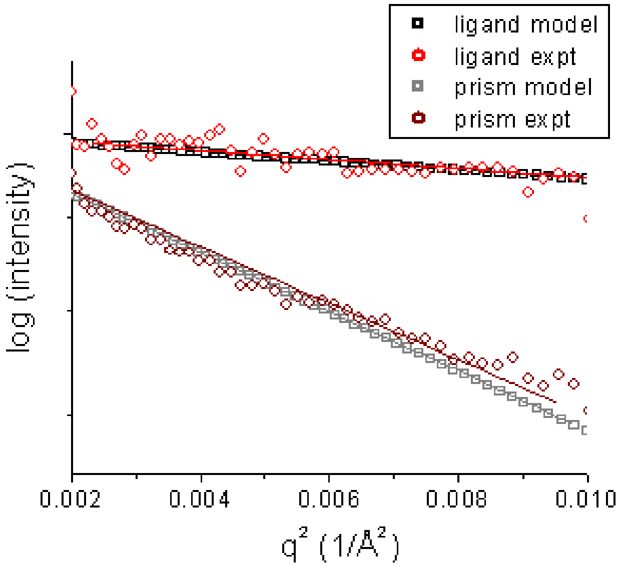


Fig. S4 Experiment and model Guinier plots for monomer ligand and prism. Intensity is normalized by I_o.

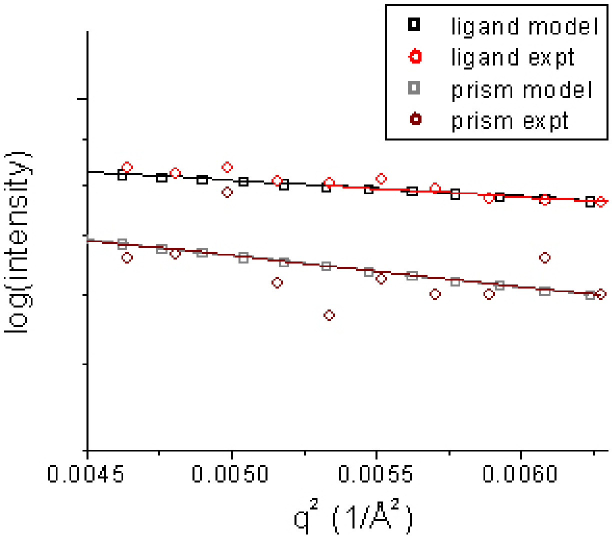


Fig. S5 Experiment and model Guinier plots for trimer ligand and prism. Intensity is normalized by I_o.

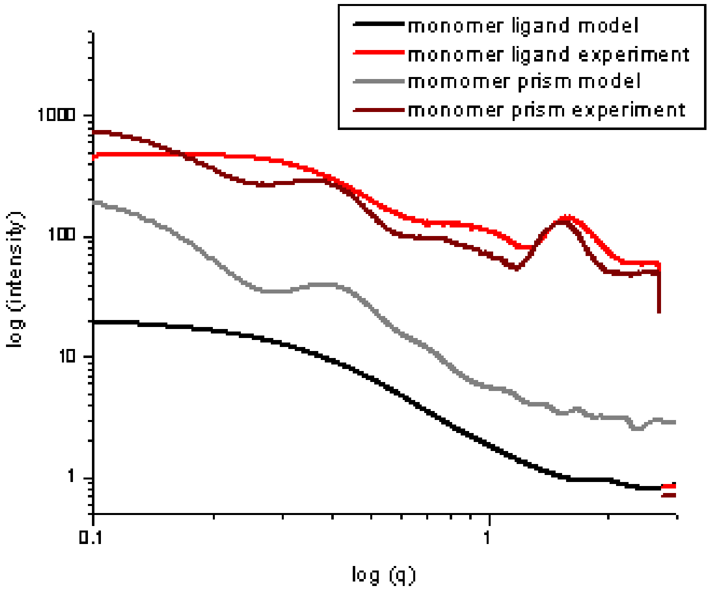


Fig. S6 Comparison of WAXS of monomer ligand and prism, experiment and model.

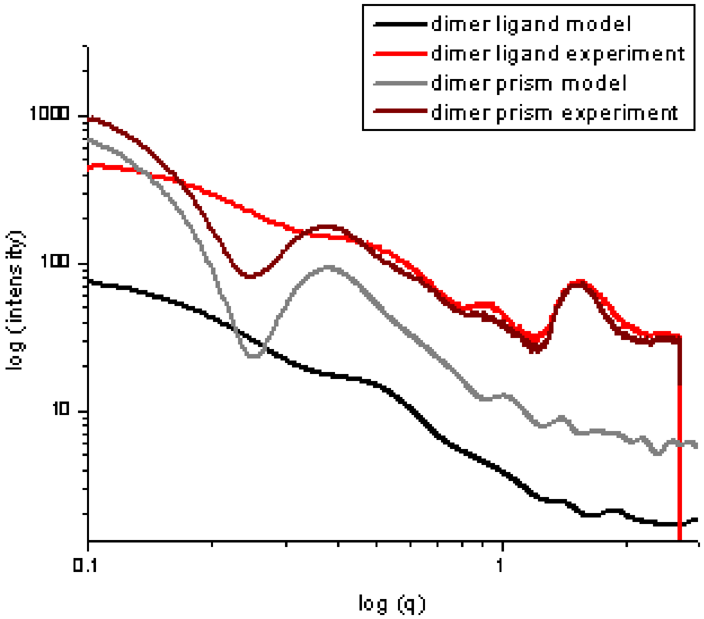


Fig. S7 Comparison of WAXS of dimer ligand and prism, experiment and model.

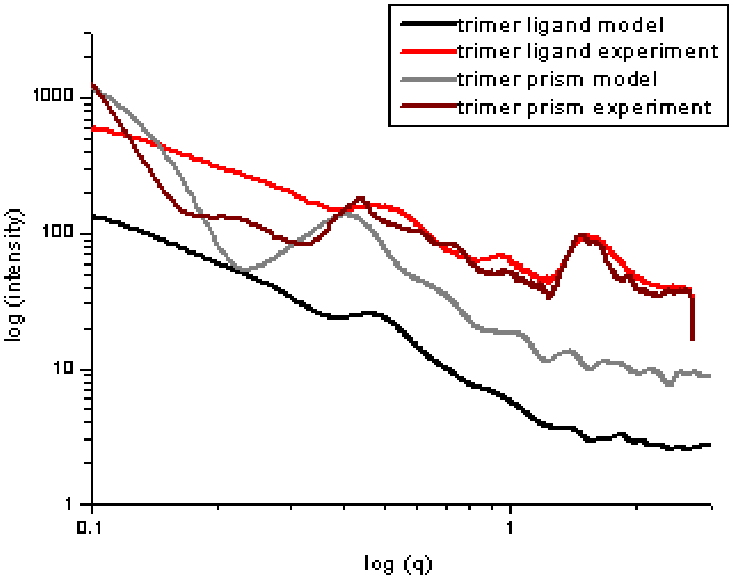
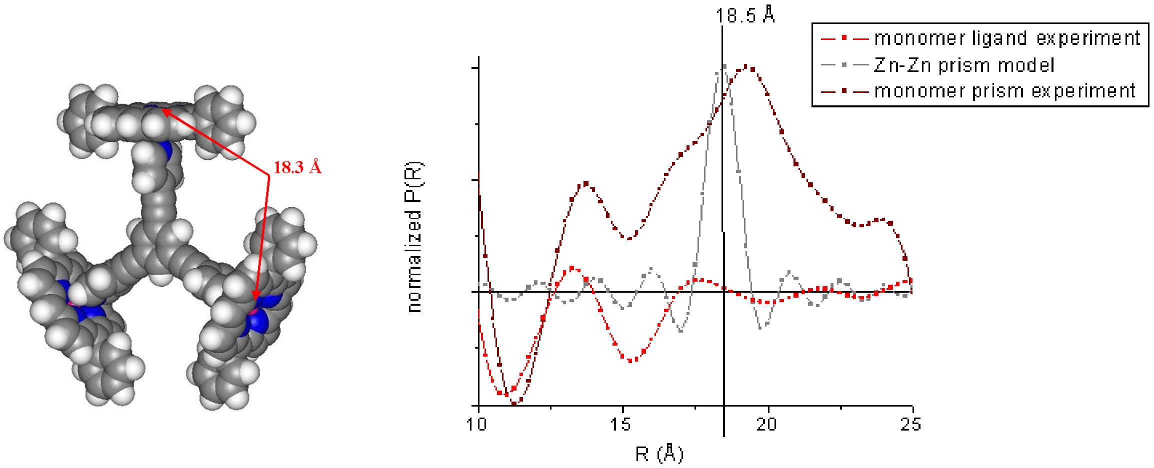
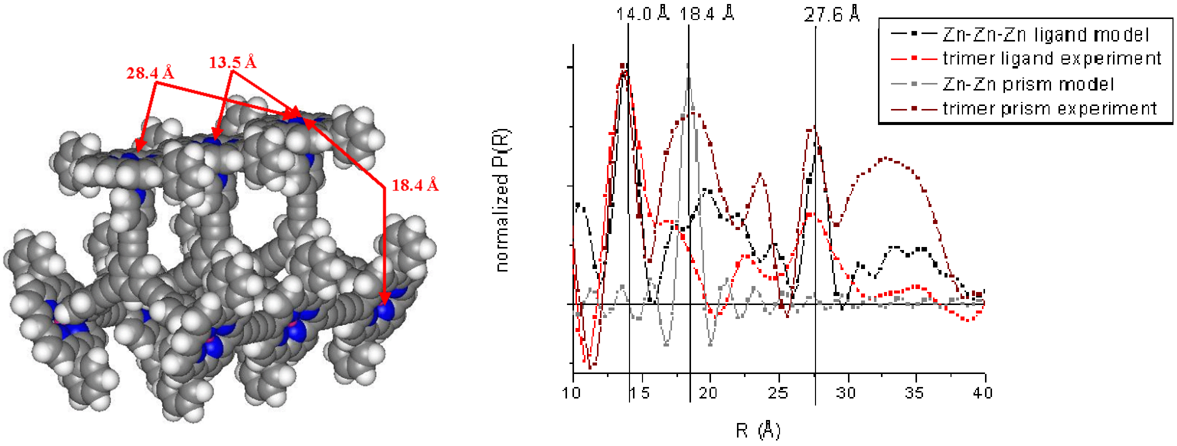


Fig. S8 Comparison of WAXS of trimer ligand and prism, experiment and model.



A **B**

Fig. S9 A) Model of monomer prism. Zn-Zn distance diagnostic of prism formation is indicated. B) PDF of monomer ligand and prism experiment as well as modeled Zn-Zn prism distance.



A **B**

Fig. S10 A) Model of trimer prism, indicating relevant Zn-Zn distances. B) PDF of trimer ligand and prism from experiment, intraligand Zn interactions and intraprism Zn interactions.

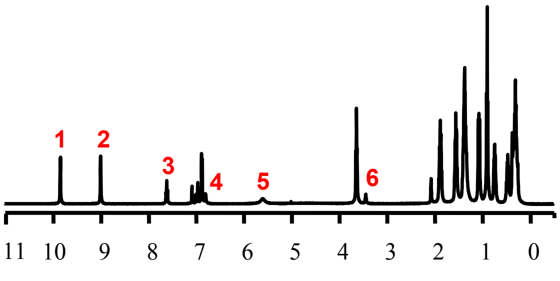
PFG-NMR measurements.

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 coefficient for self diffusion, D_s.[6] The resonance frequency for ^{1}H nuclei was 400.6 MHz and the corresponding $\pi/2$ pulse widths were 19 μs. The delays before and after gradient pulses varied between 400 and 500 μs, depending on the width of the applied gradient pulse. Initial experiments indicated that the residual eddy current was negligible under these conditions. The gradient pulse widths ranged from 500 to 1250 μs, and gradient intensities ranged from 5 to 250 Gauss/cm. Diffusion times between 600 and 800 μs were used, with 16 to 64 scans on each of nine gradient intensities per sample. Prior to the acquisition of NMR signals, the sample was equilibrated for at least 20 minutes at the desired temperature. The error in temperature was less than 0.2 K.

Measurments for monomer- and dimer-derived prisms were made at ambient temperature. Measurements for the trimer-derived prism were done at 39°C because of insufficient solubility at a lower temperature. The insensitivity of D_s values to the identity of the proton examined confirmed that assemblies rather than fragments were being monitored. The Stokes-Einstein equation:

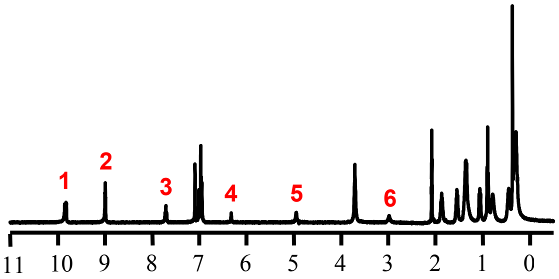
$$D_s = kT/6\pi\eta a$$

was used to estimate hydrodynamic radii, *a*. In the equation, *k* is Boltzmann's constant, T is the absolute temperature, and η is the temperature-dependent viscosity of the medium (toluene).



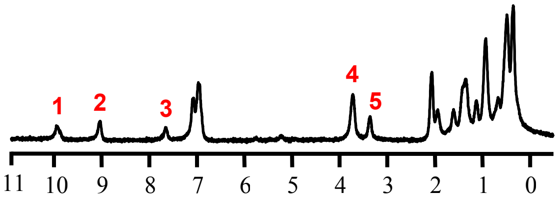
Peak Number	Self-Diffusivity (cm^2/sec)
1	1.93 X 10^{-6} ± 0.9 X 10^{-7}
2	1.90 X 10^{-6} ± 1.5 X 10^{-7}
3	1.80 X 10^{-6} ± 2.8 X 10^{-7}
4	2.08 X 10^{-6} ± 1.5 X 10^{-7}
5	1.91 X 10^{-6} ± 1.7 X 10^{-7}
6	2.02 X 10^{-6} ± 2.3 X 10^{-7}

Fig. S11 Peaks used for measuring self-diffusivity of **1_3-L** at 25°C.



Peak Number	Self-Diffusivity (cm^2/sec)
1	1.13 X 10^{-6} ± 0.7 X 10^{-7}
2	1.13 X 10^{-6} ± 0.3 X 10^{-7}
3	1.01 X 10^{-6} ± 0.6 X 10^{-7}
4	1.09 X 10^{-6} ± 1.1 X 10^{-7}
5	1.12 X 10^{-6} ± 0.9 X 10^{-7}
6	1.12 X 10^{-6} ± 0.7 X 10^{-7}

Fig. S12 Peaks used for measuring self-diffusivity of $\mathbf{2_3}$**-**$\mathbf{L_2}$ at 25°C.



Peak Number	Self-Diffusivity (cm^2/sec)
1	1.10 X 10^{-6} ± 1.4 X 10^{-7}
2	1.21 X 10^{-6} ± 1.8 X 10^{-7}
3	1.22 X 10^{-6} ± 2.5 X 10^{-7}
4	1.28 X 10^{-6} ± 2.9 X 10^{-7}
5	1.13 X 10^{-6} ± 1.9 X 10^{-7}

Fig. S13 Peaks used for measuring self-diffusivity of $\mathbf{3_3}$**-**$\mathbf{L_3}$ at 39°C.

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