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Functionalized Hydrophobic and Hydrophilic Self-Assembled Supramolecular Rectangles

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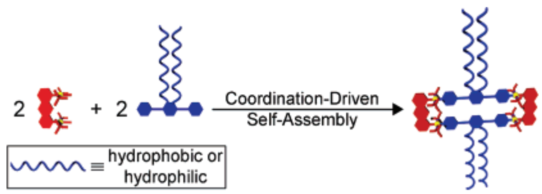
Received November 5, 2007



The synthesis of six new, functionalized 180° pyridyl donor ligands and their coordination-driven self-assembly into supramolecular rectangles is reported. Three of the new donors have been functionalized with hydrophobic straight chain alkane units (C_6, C_{12}, and C_{18}) while the remaining three have been functionalized with derivatized di-, tetra-, and hexaethylene glycol hydrophilic units (DEG, TEG, and HEG, respectively). The resulting self-assembled hydrophobic and hydrophilic supramolecular rectangles have been fully characterized by multinuclear NMR and electrospray ionization mass spectrometry. Molecular force field modeling suggests that the functionalized rectangles range in size from roughly 3.0×2.9 to 3.0×6.0 nm^2 in size.

Introduction

Self-assembly[1] is a process ubiquitous throughout nature and can account for much of the elegant and complex functionality of biological systems. Over the past few decades, synthetic chemists have developed various means of achieving abiological self-assembly[2] that have both furthered our understanding of the self-assembly process itself and also opened the door to a variety of molecular structures that would have otherwise proven especially difficult to prepare. Recently, self-assembly has been shown to play an important role in the development of molecular materials and in the "bottom-up" approach[3] to nanofabrication.

Coordination-driven transition-metal-mediated self-assembly involving dative metal−ligand bonding[4,5] has become a widely employed, robust means of preparing supramolecular polygons and polyhedra with promising electronic, catalytic, photophysical, and/or redox properties.[6] While early examples of such self-assembled metal−organic structures exhibited little functionality, there has recently been a drive to incorporate many different functional moieties into their component building blocks. These functionalized building blocks are then brought together and precisely positioned upon spontaneous self-assembly with appropriately designed complementary components. This process has been utilized to prepare, for example, discrete supramolecular metal−organic assemblies functionalized with dendrimers,[7] crown ethers,[8] carboranes,[9] optical sensors,[10] saccharides,[11] photoactive perylene diimides[12] and azobenzenes,[13] and polymerizable methyl methacrylate units[14] that have been distributed on their periphery,[7−8,11] within building blocks,[9−10,12] and also, in some cases, within interior cavities.[13−15]

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10.1021/jo702380b CCC: $40.75
Published on Web 02/02/2008

Building upon molecular self-assembly, self-organization[2f,16] is a process by which molecules, often structures such as dual-character block copolymers[17] and the like, are able to arrange into well-defined configurations in different media. Self-organization can take place: on surfaces, leading to well-ordered self-assembled monolayers;[18] in solution, giving rise to mycelles,[19] vesicles,[20] cylinders,[21] spheres,[22] etc.; and, using Langmuir–Blodgett techniques, at the air–water interface.[23] There have only recently been examples where both self-assembly and self-organization involving metallacycles have been utilized, with the combination allowing for relatively facile and spontaneous formation of arrays and assemblies of great complexity. Lu et at., for example, have prepared[6g,h] alkoxy-bridged Re(I) supramolecular rectangles that contain long alkyl chains (C_4H_9, C_8H_{17}, and $C_{12}H_{25}$). The presence of these hydrophobic substituents induces the supramolecular rectangles to aggregate in solution upon increasing the water content in the solvent medium, leading to enhanced luminescence[6g] and the ability of the rectangles to act as probes for photoluminescence quenching.[6h] Recent studies performed by our group, in collaboration with Wan et al., have demonstrated[24] higher order assembly in the self-organization of supramolecular polyhedra and polygons on Au(111) and/or HOPG surfaces. With these recent advances in mind, we have endeavored to endow a known[25] supramolecular metallacycle with both hydrophobic as well as hydrophilic functionalities of varying length. Such structures may then be able to undergo higher order self-organization in a variety of ways, resulting in control over the arrangement and distribution of these very important metallacycles.

Results and Discussion

Synthesis of the 180° Functionalized Donors. New linear hydrophobic and hydrophilic donor units of varying size were synthesized according to a divergent approach utilizing 3,6-diiodobenzene-1,2-diol[26] (**1**) as their core, as shown in Scheme 1. Hydrophobic 3,6-diiodobenzenes **2**–**4** were prepared by deprotonation of diol **1** and subsequent nucleophilic attack on 1-bromohexane, 1-bromododecane, and 1-bromooctadecane, respectively, in 85–96% yield. Related hydrophilic analogues **5**–**7** were similarly prepared through a reaction of **1** with monomethylated and bromo-terminated derivatives of diethylene glycol, tetraethylene glycol, and hexaethylene glycol, respectively, in 91–98% yield. Sonogashira coupling (Scheme 2) of hydrophobic and hydrophilic diiodibenzenes with 4-ethynylpyridine using $Pd(PPh_3)_2Cl_2$ afforded the desired linear hydrophobic donors [C_6 (**8**), C_{12} (**9**), and C_{18} (**10**)] and hydrophilic donors [DEG (**11**), TEG (**12**), and HEG (**13**)] in good yield (88–98%).

Self-Assembly and NMR Studies. With this series of new functionalized linear donors at hand, the self-assembly of hydrophobic supramolecular rectangles was performed. Heating donors **8**–**10** with the molecular "clip"[25] (Scheme 3a) in a 1:1 stoichiometric ratio in a 1.7:1 (v/v) solution of CD_3COCD_3/D_2O at 55–60 °C for 18 h gave homogeneous orange solutions. Preliminary analysis of the reaction mixtures with $^{31}P\{^1H\}$ NMR showed the presence of one sharp singlet, indicating the formation of descrete, highly symmetric supramolecular rectangles. The rectangles were isolated (95–98% yield) following counterion exchange of the nitrate anions to hexafluorophosphate anions to increase the stability[26] of the supramolecular complexes. Multinuclear NMR (^1H and ^{31}P) analysis of supramolecular rectangles **14**–**16** was performed and revealed similar characteristics in each case. Figure 1 displays, as a representative case, the partial (aromatic region) ^1H NMR spectra for the molecular clip, C_{18} donor **10**, and hydrophobic supramolecular

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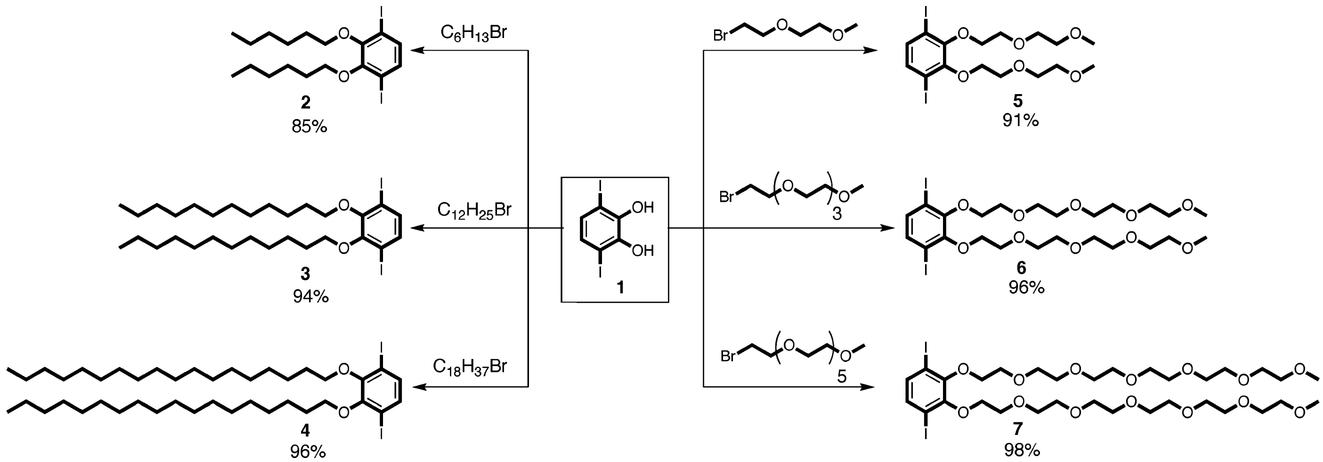
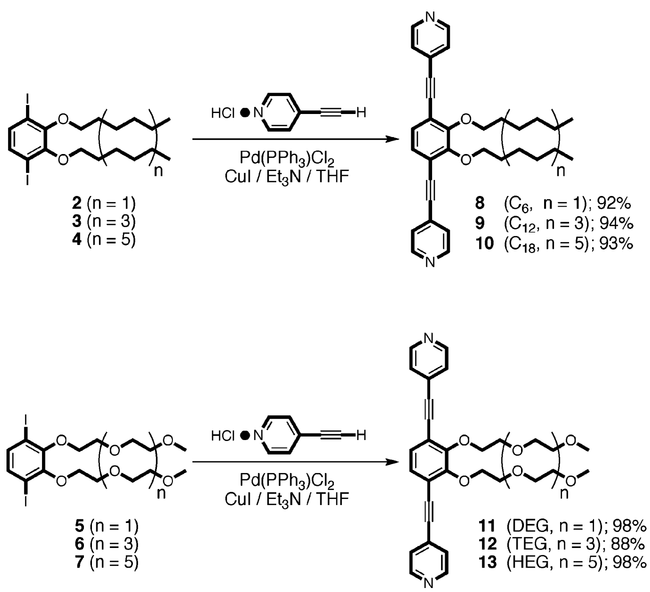
SCHEME 1. **Synthesis of Hydrophobic (2−4) and Hydrophilic (5−7) Diiodophenyl Derivatives**



SCHEME 2. **Sonogashira Coupling of Diiodophenyls 2−7 To Give New 180° Hydrophobic (8−10) and Hydrophilic (11−13) Donors**



rectangle **16**, along with the ^{31}P NMR spectra of **16** and the molecular clip. For each self-assembled rectangle, proton signals for the α- and β-pyridyl hydrogen atoms were shifted downfield by 0.5−0.54 (α-signals) and 0.71−0.79 ppm (β-signals) on account of the loss of electron density upon coordination. It was also observed by ^{1}H NMR studies that the α- and β-pyridyl hydrogen atoms of donors **8−10** were no longer equivalent following formation of hydrophobic rectangles. This result is consistent with previous studies involving similar rectangles[25,27] and indicates that free rotation of the donor pyridines is slow on the NMR time scale if not stopped altogether. Analysis of the ^{31}P {^{1}H} NMR spectra of hydrophobic rectangles **14−16** revealed a single, sharp peak at 8.58, 8.61, and 8.63 ppm, respectively, each upfield shifted from the molecular clip by nearly 6 ppm due to back-donation from the platinum atoms. Back-donation was also observed by the decrease in coupling of the flanking ^{195}Pt satellite peaks (ΔJ = 209 Hz for **14**, ΔJ = 199 Hz for **15**, ΔJ = 187 Hz for **16**).

Hydrophilic supramolecular rectangles **17−19** (Scheme 3b) were similarly prepared and analyzed. Heating donors **11−13** with the molecular clip in a 1:1 stoichiometric ratio in a 1.2:1 (v/v) CD_3COCD_3/D_2O solution at 55−60 °C for 18 h gave homogeneous orange solutions. Following counterion exchange to their hexafluorophosphate salts (96−97% isolated yield), multinuclear (^{1}H and ^{31}P) NMR spectroscopic studies indicated the presence of highly symmetric species. As with rectangles **14−16**, the α- and β-pyridyl hydrogen atoms of hydrophilic rectangles were downfield shifted relative to donors **11−13** by 0.5−0.6 and 0.72−0.83 ppm, respectively. Single, sharp peaks were observed in the ^{31}P {^{1}H} NMR spectra, shifted upfield by ∼6 ppm, and coupling of the ^{195}Pt stellite peaks was decreased by ΔJ = 209 Hz for **17**, ΔJ = 219 Hz for **18**, and ΔJ = 231 Hz for **19**.

Mass Spectrometric Analysis of Functionalized Rectangles. Further characterization of the hydrophobic and hydrophilic supramolecular rectangles was provided by electrospray ionization mass spectronometry (ESI-MS) studies, which are able to establish the molecularity of the self-assembled metallacycles. In the cases of the hydrophobic rectangles (Figure 2), peaks were found at m/z 1664.4, 1832.5, and 1285.5, corresponding to $[M - 2PF_6]^{2+}$of **14**, $[M - 2PF_6]^{2+}$ of **15**, and $[M - 3PF_6]^{3+}$ of **16**, where M represents the fully intact supramolecular assemblies. Their isotopic distributions are in excellent agreement with the theoretical distributions.

Well-resolved peaks for hydrophilic rectangles were observed (Figure 3) at m/z 1700.1, 1876.6, 2052.6 corresponding to $[M - 2PF_6]^{2+}$ of **17−19**, respectively. Again, their isotopic distributions are in excellent agreement with the theoretical distributions. These mass spectral results, together with the multinuclear NMR studies, confirm the self-assembly of both hydrophobic as well as hydrophilic supramolecular rectangles.

Molecular Force Field Modeling. Attempts to grow single crystals of supramolecular rectangles **14−19** suitable for X-ray analysis have so far proven unsuccessful. Therefore, to gain a greater understanding of the size and shape of these functionalized metallacycles, molecular force field modeling investigations were performed. The structures of the supramolecular rectangles were each constructed within the input mode of the modeling program Maestro v.8.0.110.[28] A 1000 step Monte Carlo conformational search employing the MMFF force field[29] and a solvent model for octane[30] was performed to determine

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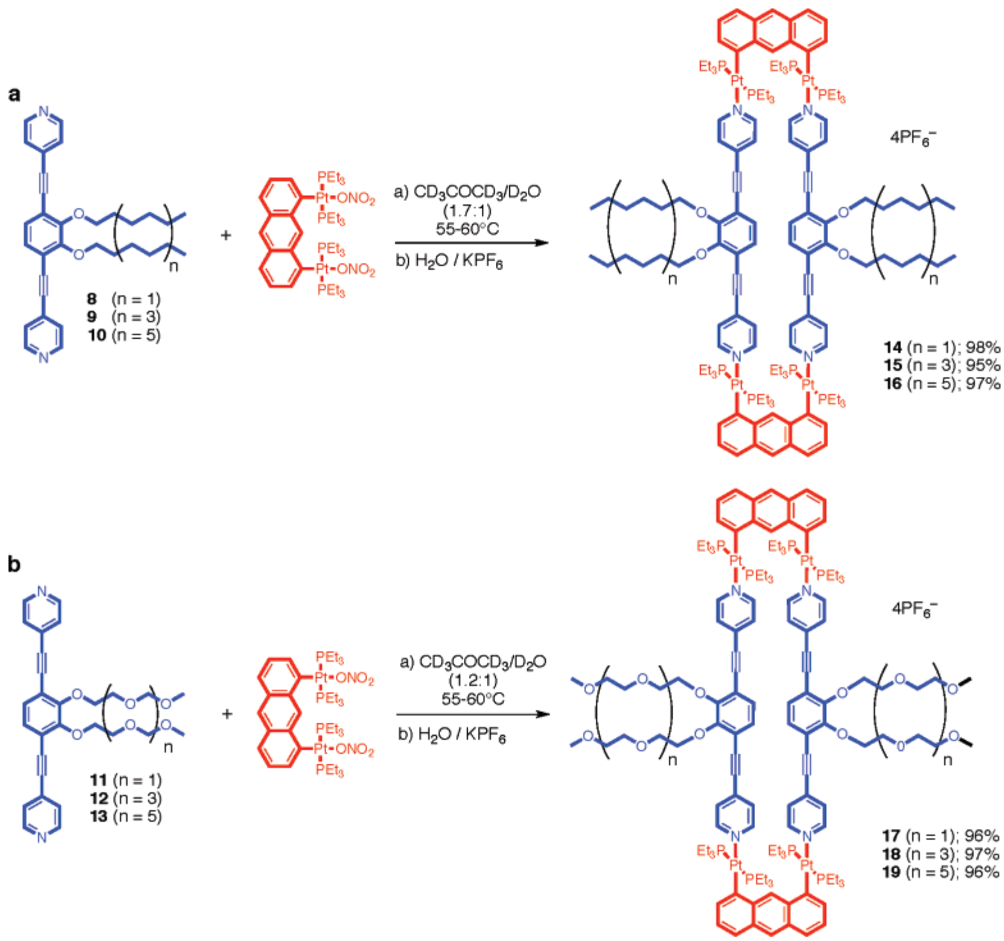
SCHEME 3. Coordination-Driven Self-Assembly of (a) Hydrophobic (14−16) and (b) Hydrophilic (17−19) Supramolecular Rectangles



the lowest energy conformation of each rectangle. In every case, the most favored conformer was predicted to be the one where the hydrophobic or hydrophilic "arms" of rectangles **14−19** intertwine or wrap around each other. This result is most prominently observed (Figure 4a) for rectangles **16** and **19**, which possess the longest chains (C_{18} and hexaethylene glycol, respectively). It is important to note, however, that torsional rotation about the many C−C and C−O bonds that make up the hydrophobic and hydrophilic arms requires very little energy and there are many similar conformations within only a few kilocalories per mole of the found global minimum.

To better gauge the differences in size across the series of rectangles, a second set of calculations was performed with their hydrophobic or hydrophilic arms fully elongated (MMFF force field, solvent model for octanol). These calculations reveal that the sizes of fully outstretched rectangles range from ~2.9 nm for **14** and **17**, to ~4.4 nm for **15** and **18**, up to ~5.9 nm for **16** and **19**, each with an anthracene−anthracene ($C_{10}-C_{10'}$)

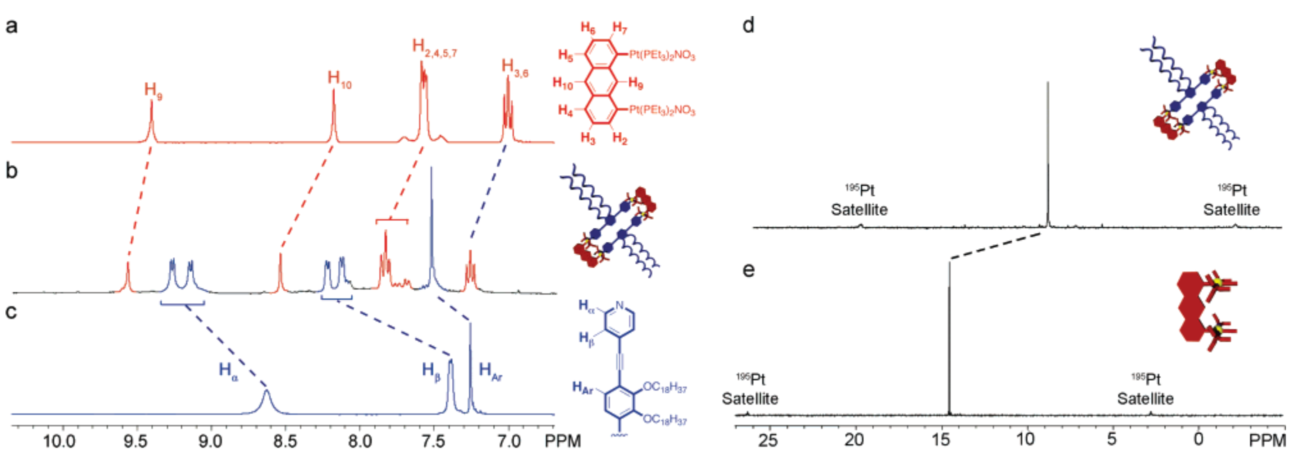


FIGURE 1. Representative ^{1}H NMR spectra (300 MHz, 298 K, CD_3COCD_3) of the aromatic portion of the (a) molecular clip, (b) hydrophobic molecular C_{18}Rectangle **16**, (c) and hydrophobic C_{18} donor **10** displaying the characteristic shifts of proton signals associated with the donor and acceptor units upon coordination as well as (d) the ^{31}P {^{1}H} NMR spectra of the self-assembled C_{18}Rectangle **16** and (e) molecular clip.

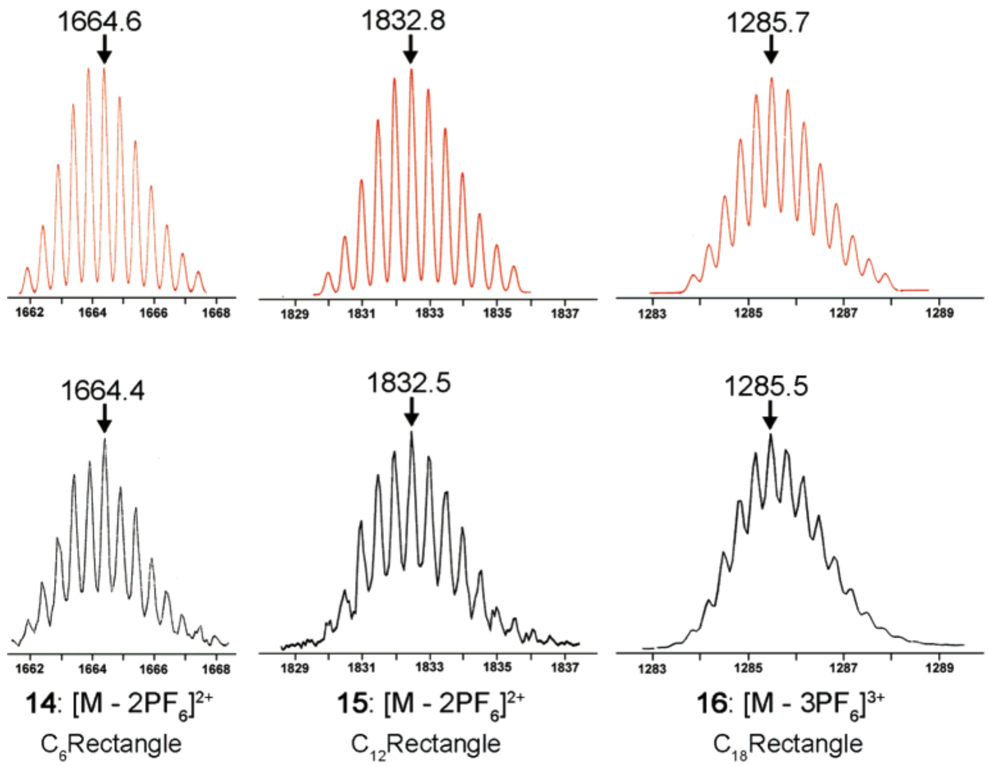


FIGURE 2. Theoretical (top, red) and experimental (bottom, black) ESI-MS results for hydrophobic rectangles **14**−**16**.

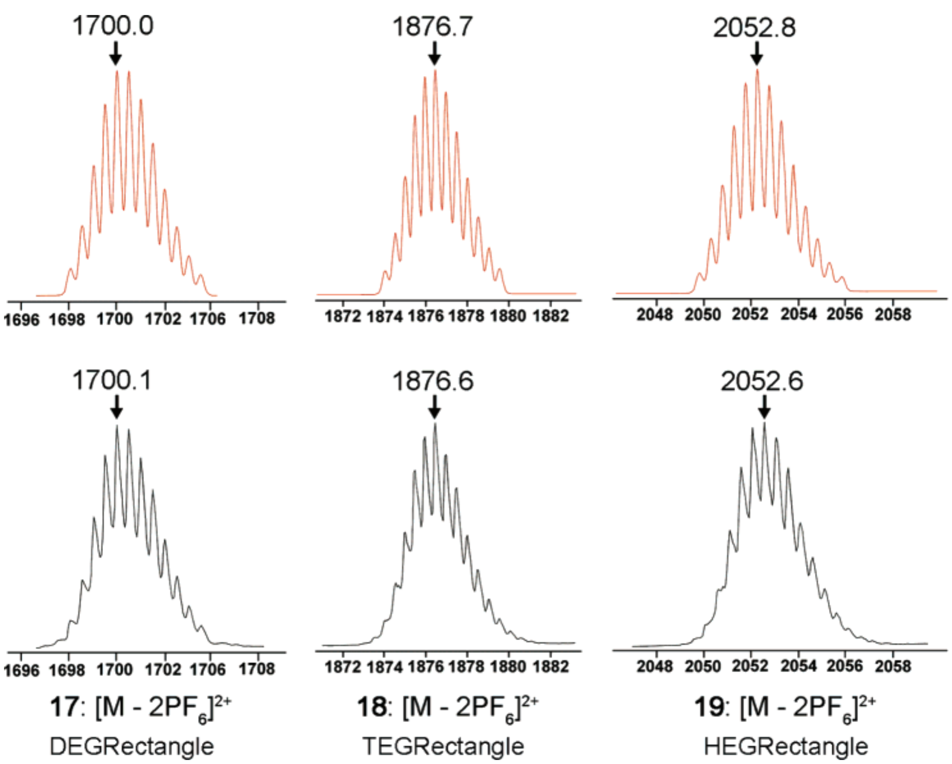


FIGURE 3. Theoretical (top, red) and experimental (bottom, black) ESI-MS results for hydrophilic rectangles **17**−**19**.

distance of roughly 2.9 nm. Representative examples of the longest fully outstretched rectangles, C_{18}Rectangle (**16**) and HEGRectangle (**19**), are shown in Figure 4b. Results for the shorter supramolecular rectangles can be found in the Supporting Information.

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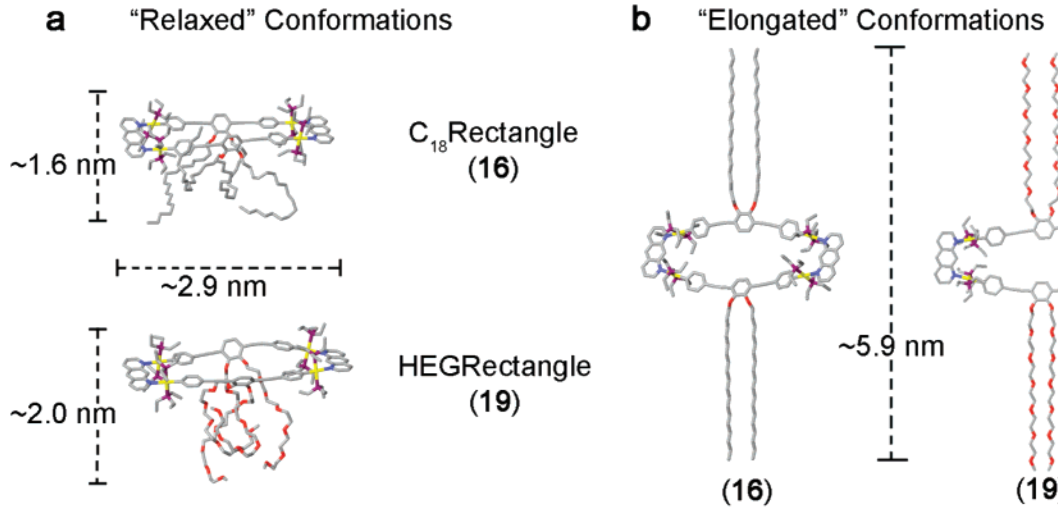

FIGURE 4. Computed global minimum ("Relaxed") (a) and fully stretched ("Elongated") (b) conformations of C_{18} hydrophobic and HEG hydrophilic supramolecular rectangles. Color scheme: C = gray, N = blue, O = red, P = purple, Pt = yellow. Hydrogen atoms are omitted for clarity.

Conclusion

A series of new hydrophobic and hydrophilic 180° donor compounds have been prepared and successfully utilized in the self-assembly of hydrophobic and hydrophilic supramolecular rectangles of varying sizes. Each rectangle is self-assembled in nearly quantitative yield despite the presence of long alkyl or polyethylene glycol chains present on the donor units. All six supramolecular rectangles have been characterized by multinuclear NMR and ESI mass spectronometry. These hydrophobic and hydrophilic rectangles represent an important addition to the now growing class of functionalized metallacyclic assemblies as their pendant chains will likely promote their self-organization in solution, at the air−water interface, and on a variety of surfaces. Such higher order assembly allows for greater control over the size, shape, orientation, and distribution of the underlying metallacycles in a variety of environments. Investigations along these lines are currently underway.

Experimental Section

General Procedure for Preparation of Hydrophobic Diiodides 2 and 4. To a solution of 3,6-diiodobenzene-2,3-diol (**1**[26]) (200 mg, 0.55 mmol) in anhydrous MeCN (15 mL) was added K_2CO_3 (380 mg, 2.75 mmol), 18Crown6 (catalytic), and the appropriate alkyl bromide (1-bromohexane, 456 mg, 2.75 mmol; 1-bromooctadecane, 920 mg, 2.75 mmol) and the mixture was allowed to reflux under N_2(g) for 18 h. The mixture was cooled, the solvent was evaporated, and the residue was partitioned between H_2O (150 mL) and hexanes (100 mL). The layers were separated and the aqueous layer was extracted with additional hexanes (4 × 60 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated to give an off-white residue. The residue was purified by column chromatography on silica gel (first with pure hexanes to remove excess alkyl bromide, followed by hexanes/CH_2Cl_2 95:2) to give the desired compounds as white solids.

2,3-Bis(hexyloxy)-1,4-diiodobenzene (2). Yield 494 mg (white solid), 85%. Mp 48−50 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (s, 2H), 3.98 (t, 4H, J = 6.6 Hz), 1.83 (pentet, 4H, J = 7.2 Hz), 1.49 (pentet, 4H, J = 7.2 Hz), 1.40−1.29 (m, 8H), 0.91 (t, 6H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 135.5, 93.7, 74.1, 31.9, 30.5, 30.4, 26.0, 22.9, 14.3. MS (LCMS) m/z 531.2 (M + H)$^+$. Anal. Calcd for $C_{18}H_{28}I_2O_2$: C, 40.77; H, 5.32. Found: C, 40.91; H, 5.33.

1,4-Diiodo-2,3-bis(octadecyloxy)benzene (4). Yield 460 mg (white solid), 96%. Mp 83−85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (s, 2H), 3.97 (t, 4H, J = 6.6 Hz), 1.82 (pentet, 4H, J = 6.9 Hz), 1.49 (pentet, 4H, J = 7.2 Hz), 1.41−1.17 (m, 36H), 0.88 (t, 6H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 135.5, 93.7, 74.1, 32.2, 30.5, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 29.9, 29.7, 29.6, 26.4, 22.9, 14.4. MS (LCMS) m/z 867.2 (M + H)$^+$. Anal. Calcd for $C_{42}H_{76}I_2O_2$: C, 58.19; H, 8.84. Found: C, 58.39; H, 8.87.

1-Bromo-2-(2-methoxyethoxy)ethane. To an acetone solution (100 mL) of 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate[31] (9.5 g, 35.0 mmol) was added LiBr (30 g, 0.35 mol) and the mixture was brought to reflux. After refluxing for 5 h, the solution was cooled and the solvent evaporated. The resulting residue was partitioned between H_2O (100 mL) and CH_2Cl_2 (100 mL) and the layers were separated. The aqueous layer was extracted further with CH_2Cl_2 (3 × 100 mL), the combined organic layers were dried ($MgSO_4$), filtered, and the solvent was evaporated to give the desired product as a pale yellow liquid. Yield 6.34 g, 99%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.80 (t, 2H, J = 6.6 Hz), 3.68−3.64 (m, 2H), 3.57−3.53 (m, 2H), 3.47 (t, 2H, J = 6.6 Hz), 3.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 58.9, 54.2, 31.8, 30.4, 29.3. Anal. Calcd for $C_5H_{11}BrO_2$: C, 32.81; H, 6.06. Found: C, 32.77; H, 6.04.

General Procedure for Preparation of Hydropilic Diiodides 5−7. To a solution of 3,6-diiodobenzene-2,3-diol (**1**) (300 mg, 0.83 mmol) in anhydrous MeCN (20 mL) was added K_2CO_3 (800 mg, 5.81 mmol), 18Crown6 (catalytic), and either 1-bromo-2-(2-methoxyethoxy)ethane (909 mg, 4.97 mmol), 13-bromo-2,5,8,11-tetraoxatridecane[32] (1.35 g, 4.97 mmol), or 19-bromo-2,5,8,11,14,-17-hexaoxanonadecane[33] (1.78 g, 4.97 mmol) and the respective mixtures were allowed to reflux under N_2(g) for 18 h. The mixtures were cooled, the solvent was evaporated, and the residues were partitioned between H_2O (150 mL) and CH_2Cl_2 (100 mL). The respective layers were separated and the aqueous layer was extracted with additional CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated to give, in each case, a yellow oil. The oils were purified by column chromatography on silica gel (CH_2Cl_2/MeOH 97:3) to give the desired compounds as yellow-orange oils.

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1,4-Diiodo-2,3-bis(2-(2-methoxyethoxy)ethoxy)benzene (5). Yield 430 mg (yellow oil), 91%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (s, 2H), 4.20 (t, 4H, J = 4.8 Hz), 3.86 (t, 4H, J = 4.8 Hz), 3.71 (t, 4H, J = 4.8 Hz), 3.56 (t, 4H, J = 4.8 Hz), 3.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.4, 135.7, 93.4, 72.8, 72.2, 70.8, 70.5, 59.3. MS (LCMS) m/z 567.0 (M + H)$^+$. Anal. Calcd for $C_{16}H_{24}I_2O_6$: C, 33.94; H, 4.27. Found: C, 34.04; H, 4.28.

13,13′-(3,6-Diiodo-1,2-phenylene)bis(oxy)bis(2,5,8,11-tetraoxatridecane) (6). Yield 594 mg (yellow oil), 96%. ^{1}H NMR ($CDCl_3$), 300 MHz) δ 7.25 (s, 2H), 4.18 (t, 4H, J = 4.8 Hz), 3.83 (t, 4H, J = 4.8 Hz), 3.73−3.59 (m, 16H), 3.53 (t, 4H, J = 4.8 Hz), 3.36 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.3, 135.6, 93.4, 72.7, 72.0, 70.8, 70.8, 70.8, 70.8, 70.7, 70.5, 59.2. MS (LCMS) m/z 742.9 (M + H)$^+$. Anal. Calcd for $C_{24}H_{40}I_2O_{10}$: C, 38.83; H, 5.43. Found: C, 38.94; H, 5.45.

19,19′-(3,6-Diiodo-1,2-phenylene)bis(oxy)bis(2,5,8,11,14,17-hexaoxanonadecane) (7). Yield 745 mg (orange oil), 98%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (s, 2H), 4.18 (t, 4H, J = 4.8 Hz), 3.84 (t, 4H, J = 4.8 Hz), 3.75−3.59 (m, 36H), 3.54 (t, 4H, J = 4.8 Hz), 3.37 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.3, 135.6, 93.4, 72.7, 72.1, 70.8, 70.8, 70.8, 70.8, 70.7, 70.7, 70.7, 70.7, 70.6, 70.5, 59.2. MS (LCMS) m/z 919.3 (M + H)$^+$. Anal. Calcd for $C_{32}H_{56}I_2O_{14}$: C, 41.84; H, 6.14. Found: C, 41.89; H, 6.15.

General Procedure for Preparation of Hydrophobic and Hydropilic Donors 8−13. A 100 mL Schlenk flask was charged with diiodide (**2**−**7**, 1.0 equiv), 4-bromopyridine hydrochloride (4.0 equiv), 10 mol % $Pd(PPh_3)_2Cl_2$, and 15 mol % CuI, degassed, and back-filled three times with N_2(g). Triethylamine (7 mL) and dry THF (7 mL) were then introduced into the reaction via syringe. The reaction was allowed to stir at room temperature for 36 h. The solvent was evaporated and the brown residue was partitioned between H_2O (75 mL) and CH_2Cl_2 (50 mL). The organic layer was separated and extracted further with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The resulting brown residues were purified by column chromatography on silica gel.

4,4′-(2,3-Bis(hexyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dipyridine (8). Reaction scale: **2** (180 mg, 0.34 mmol). Chromatography eluent CH_2Cl_2/Me_2CO (4:1). Yield 151 mg (brown oil), 92%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.69 (br, 4H), 7.47 (s, 4H), 7.25 (s, 2H), 4.16 (t, 4H, J = 6.3 Hz), 1.89−1.75 (m, 4H), 1.60−1.46 (m, 4H), 1.39−1.21 (m, 8H), 0.87 (t, 6H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 150.0, 131.3, 128.2, 125.6, 119.4, 92.4, 90.2, 74.8, 31.9, 30.6, 26.1, 22.9, 14.3. MS (LCMS) m/z 481.1 (M + H)$^+$. Anal. Calcd for $C_{32}H_{36}N_2O_2$: C, 79.96; H, 7.55; N, 5.83. Found: C, 79.69; H, 7.52; N, 5.81.

4,4′-(2,3-Bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dipyridine (9). Reaction scale: **3** (224 mg, 0.32 mmol). Chromatography eluent CH_2Cl_2/Me_2CO (8:1). Yield 194 mg (white solid), 94%. Mp 58−61 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.65 (br, 4H), 7.46 (d, 4H, J = 6.0 Hz), 7.24 (s, 2H), 4.16 (t, 4H, J = 6.6 Hz), 1.82 (pentet, 4H, J = 6.9 Hz), 1.52 (pentet, 4H, J = 6.9 Hz), 1.39−1.18 (m, 32H), 0.87 (t, 6H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 150.0, 131.4, 128.2, 125.6, 119.4, 92.4, 90.2, 74.8, 32.2, 30.7, 29.9, 29.9, 29.9, 29.9, 29.8, 29.6, 26.5, 22.9, 14.4. MS (LCMS) m/z 649.1 (M + H)$^+$. Anal. Calcd for $C_{44}H_{60}N_2O_2$: C, 81.43; H, 9.32; N, 4.32. Found: C, 81.33; H, 9.35; N, 4.31.

4,4′-(2,3-Bis(octadecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dipyridine (10). Reaction scale: **4** (175 mg, 0.2 mmol). Chromatography eluent CH_2Cl_2/MeOH (10:1). Yield 153 mg (white solid), 93%. Mp 78−79 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.64 (br, 4H), 7.39 (d. 4H, J = 6.0 Hz), 7.26 (s, 2H), 4.16 (t, 4H, J = 6.3 Hz), 1.82 (pentet, 4H, J = 6.9 Hz), 1.52 (pentet, 4H, J = 6.9 Hz), 1.41−1.14 (m, 48H), 0.87 (t, 6H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 150.0, 131.5, 128.2, 125.7, 119.4, 92.4, 90.2, 74.8, 32.2, 30.7, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 30.0, 29.9, 29.8, 29.6, 26.5, 22.3, 14.4. MS (LCMS) m/z 817.1 (M + H)$^+$. Anal. Calcd for $C_{56}H_{84}N_2O_2$: C, 82.30; H, 10.36; N, 3.43. Found: C, 82.01; H, 10.32; N, 3.42.

4,4′-(2,3-Bis(2-(2-methoxyethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dipyridine (11). Reaction scale: **5** (200 mg, 0.353 mmol). Chromatography eluent CH_2Cl_2/MeOH (96:4). Yield 181 mg (off white solid), 98%. Mp 56−59 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (d, 4H, J = 5.7 Hz), 7.41 (d, 4H, J = 5.7 Hz), 7.24 (s, 2H), 4.37 (t, 4H, J = 4.8 Hz), 3.88 (t, 4H, J = 4.8 Hz), 3.70 (t, 4H, J = 4.8 Hz), 3.52 (t, 4H, J = 4.8 Hz), 3.34 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.8, 150.4, 131.4, 128.3, 125.7, 119.3, 92.7, 89.9, 73.4, 72.2, 70.9, 70.8, 59.2. MS (LCMS) m/z 517.0 (M + H)$^+$. Anal. Calcd for $C_{30}H_{32}N_2O_6$: C, 69.75; H, 6.24; N, 5.42. Found: C, 69.52; H, 6.23; N, 5.41.

4,4′-(2,3-Bis(2,5,8,11-tetraoxatridecan-13-yloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dipyridine (12). Reaction scale: **6** (300 mg, 0.40 mmol). Chromatography eluent CH_2Cl_2/MeOH (95:5). Yield 246 mg (brown oil), 88%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.61 (br, 4H), 7.51 (s, 4H), 7.24 (s, 2H), 4.35 (t, 4H, J = 4.8 Hz), 3.86 (t, 4H, J = 4.8 Hz), 3.72−3.67 (m, 4H), 3.64−3.59 (m, 16H), 3.55−3.50 (m, 4H), 3.36 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.7, 149.9, 131.2, 128.2, 119.3, 92.7, 89.9, 73.4, 72.1, 70.8, 70.8, 70.8, 70.7, 70.7, 70.7, 59.1, 53.7. MS (LCMS) m/z 692.9 (M + H)$^+$. Anal. Calcd for $C_{38}H_{48}N_2O_{10}$: C, 65.88; H, 6.98; N, 4.04. Found: C, 65.67; H, 6.97; N, 4.03.

4,4′-(2,3-Bis(2,5,8,11,14,17-hexaoxanonadecan-19-yloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dipyridine (13). Reaction scale: **7** (340 mg, 0.37 mmol). Chromatography eluent CH_2Cl_2/MeOH (94:6). Yield 319 mg (orange oil), 98%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.57 (br, 4H), 7.51 (s, 4H), 7.24 (s, 2H), 4.35 (t, 4H, J = 4.8 Hz), 3.86 (t, 4H, J = 4.8 Hz), 3.72−3.60 (m, 4H), 3.65−3.57 (m, 32H), 3.56−3.51 (m, 4H), 3.36 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.7, 150.0, 131.2, 128.2, 125.6, 119.2, 92.6, 89.9, 73.3, 72.0, 70.8, 70.8, 70.8, 70.7, 70.0, 70.0, 70.0, 70.0, 70.0, 70.6, 59.1. MS (LCMS) m/z 868.9 (M + H)$^+$. Anal. Calcd for $C_{46}H_{64}N_2O_{14}$: C, 63.58; H, 7.42; N, 3.22. Found: C, 63.44; H, 7.39; N, 3.20.

General Procedure for Preparation of Hydrophobic Supramolecular Rectangles 14−16. Hydrophobic donors **8**−**10** (1.0 equiv) and the molecular clip[25] acceptor (1.0 equiv) were added to separate glass vials. To the vials containing donors was added 0.5 mL of a Me_2CO/H_2O (1.7:1) solution and the resulting suspension was transferred to the acceptor vial. This process was repeated (3 × 0.4 mL) to ensure quantitative transfer of the donor to the acceptor. The reaction solution was then stirred at 55 °C for 18 h, after which time a homogeneous orange solution had formed. The NO_3^- counterions were exchanged for PF_6^- using an H_2O solution of KPF_6. The product was washed several times with excess H_2O and the resulting solid collected.

C_6Rectangle (14). Reaction scale: clip (12.7 mg, 10.9 μmol), donor **8** (5.3 mg, 10.9 μmol). Yield 19 mg (orange solid), 98%. ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 9.55 (s, 2H, H_9), 9.19 (dd, 8H, J = 36.0, 5.7 Hz, H_α-Pyr), 8.53 (s, 2H, H_{10}), 8.18 (dd, 8H, J = 36.0, 5.7 Hz, H_β-Pyr), 7.88−7.78 (m, 8H, $H_{2,4,5,7}$), 7.53 (s, 4H, ArH), 7.27 (t, 4H, J = 8.1 Hz, $H_{3,6}$), 4.30 (t, 8H, J = 6.3 Hz, PhOCH_2), 1.98−1.84 (m, 8H, H_{alkane}), 1.76−1.51 (m, 56H, H_{alkane} and PCH_2-CH_3), 1.43−1.28 (m, 16H, H_{alkane}), 1.06−0.92 (m, 64H, PCH_2CH_3), 0.89 (t, 12H, J = 6.7 Hz, $-CH_3$). ^{31}P{^{1}H} NMR (CD_3COCD_3, 121.4 MHz) δ 8.58 (s, $^1J_{Pt-P}$ = 1325.6 Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 1664.6, found 1664.4.

C_{12}Rectangle (15). Reaction scale: clip (8.95 mg, 7.7 μmol), donor **9** (5 mg, 7.7 μmol). Yield 14.7 mg (orange solid), 95%. ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 9.55 (s, 2H, H_9), 9.19 (dd, 8H, J = 36.0, 5.7 Hz, H_α-Pyr), 8.53 (s, 2H, H_{10}), 8.19 (dd, 8H, J = 36.0, 5.7 Hz, H_β-Pyr), 7.90−7.80 (m, 8H, $H_{2,4,5,7}$), 7.54 (s, 4H, ArH), 7.27 (t, 4H, J = 8.1 Hz, $H_{3,6}$), 4.32 (t, 8H, J = 6.9 Hz, PhOCH_2), 2.01−1.87 (m, 8H, H_{alkane}), 1.77−1.53 (m, 56H, H_{alkane} and PCH_2-CH_3), 1.48−1.23 (m, 64H, H_{alkane}), 1.07−0.93 (m, 64H, PCH_2CH_3), 0.88 (t, 12H, J = 6.6 Hz, $-CH_3$). ^{31}P{^{1}H} NMR (CD_3COCD_3, 121.4 MHz) δ 8.61 (s, $^1J_{Pt-P}$ = 1330.7 Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 1832.8, found 1832.5.

C_{18}Rectangle (16). Reaction scale: clip (7.1 mg, 6.1 μmol), donor **8** (5 mg, 6.1 μmol). Yield 12.8 mg (orange solid), 97%. ^{1}H

NMR (CD_3COCD_3, 300 MHz) δ 9.56 (s, 2H, H_9), 9.18 (dd, 8H, J = 36.0, 5.7 Hz, H_α-Pyr), 8.54 (s, 2H, H_{10}), 8.18 (dd, 8H, J = 36.0, 5.7 Hz, H_β-Pyr), 7.90−7.79 (m, 8H, $H_{2,4,5,7}$), 7.53 (s, 4H, ArH), 7.27 (t, 4H, J = 8.1 Hz, $H_{3,6}$), 4.32 (t, 8H, J = 6.9 Hz, PhOCH_2), 2.01−1.86 (m, 8H, H_{alkane}), 1.77−1.50 (m, 56H, H_{alkane} and PCH_2-CH_3), 1.46−1.19 (m, 112H, H_{alkane}), 1.07−0.91 (m, 64H, PCH_2CH_3), 0.87 (t, 12H, J = 6.3 Hz, $-CH_3$). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 121.4 MHz) δ 8.63 (s, $^1J_{Pt-P}$ = 1336.61 Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 2001.0, found 2000.7.

General Procedure for Preparation of Hydrophilic Supramolecular Rectangles 17−19. Hydrophilic donors **11**−**13** (1.0 equiv) and the molecular clip[25] acceptor (1.0 equiv) were added to separate glass vials. To the vials containing donors was added 0.5 mL of a Me_2CO/H_2O (1.2:1) solution and the resulting suspension was transferred to the acceptor vial. This process was repeated (3 × 0.4 mL) to ensure quantitative transfer of the donor to the acceptor. The reaction solution was then stirred at 55 °C for 18 h, after which time a homogeneous orange solution had formed. The NO_3^- counterions were exchanged for PF_6^- using an H_2O solution of KPF_6. The product was washed several times with excess H_2O and the resulting solid collected.

DEGRectangle (17). Reaction scale: clip (10.0 mg, 8.5 μmol), donor **11** (4.4 mg, 8.5 μmol). Yield 15 mg (orange solid), 96%. ^1H NMR (CD_3COCD_3, 300 MHz) δ 9.57 (s, 2H, H_9), 9.18 (dd, 8H, J = 24.9, 5.7 Hz, H_α-Pyr), 8.53 (s, 2H, H_{10}), 8.24 (dd, 8H, J = 24.9, 5.7 Hz, H_β-Pyr), 7.90−7.80 (m, 8H, $H_{2,4,5,7}$), 7.52 (s, 4H, ArH), 7.27 (t, 4H, J = 7.5 Hz, $H_{3,6}$), 4.56−4.46 (m, 8H, PhOCH_2), 3.98−3.89 (m, 8H, H_{glycol}), 3.72−3.64 (m, 8H, H_{glycol}), 3.55−3.49 (m, 8H, H_{glycol}), 3.30 (s, 12H, $-OCH_3$), 1.79−1.48 (m, 48H, PCH_2-CH_3), 1.13−0.86 (m, 64H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 121.4 MHz) δ 8.53 (s, $^1J_{Pt-P}$ = 1325.56 Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 1700.0, found 1700.1; calcd for $[M - 3PF_6]^{3+}$ m/z 1085.0, found 1085.0.

TEGRectangle (18). Reaction scale: clip (8.6 mg, 7.4 μmol), donor **12** (5.1 mg, 7.4 μmol). Yield 14.5 mg (orange solid), 97%. ^1H NMR (CD_3COCD_3, 300 MHz) δ 9.56 (s, 2H, H_9), 9.17 (dd, 8H, J = 24.9, 5.7 Hz, H_α-Pyr), 8.53 (s, 2H, H_{10}), 8.23 (dd, 8H, J = 24.9, 5.7 Hz, H_β-Pyr), 7.89−7.79 (m, 8H, $H_{2,4,5,7}$), 7.53 (s, 4H, ArH), 7.27 (t, 4H, J = 7.5 Hz, $H_{3,6}$), 4.56−4.46 (m, 8H, PhOCH_2), 4.01−3.91 (m, 8H, H_{glycol}), 3.76−3.54 (m, 40H, H_{glycol}), 3.51−3.43 (m, 8H, H_{glycol}), 3.27 (s, 12H, $-OCH_3$), 1.79−1.50 (m, 48H, PC$H_2$$CH_3$), 1.13−0.86 (m, 64H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_3-$COCD_3$, 121.4 MHz) δ 8.56 (s, $^1J_{Pt-P}$ = 1320.50 Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 1876.7, found 1876.6; calcd for $[M - 3PF_6]^{3+}$ m/z 1202.8, found 1202.7.

HEGRectangle (19). Reaction scale: clip (7.9 mg, 6.8 μmol), donor **8** (5.91 mg, 6.8 μmol). Yield 16.4 mg (orange solid), 96%. ^1H NMR (CD_3COCD_3, 300 MHz) δ 9.55 (s, 2H, H_9), 9.17 (dd, 8H, J = 24.9, 5.7 Hz, H_α-Pyr), 8.53 (s, 2H, H_{10}), 8.24 (dd, 8H, J = 24.9, 5.7 Hz, H_β-Pyr), 7.88−7.80 (m, 8H, $H_{2,4,5,7}$), 7.54 (s, 4H, ArH), 7.27 (t, 4H, J = 7.5 Hz, $H_{3,6}$), 4.56−4.47 (m, 8H, PhOCH_2), 4.01−3.92 (m, 8H, H_{glycol}), 3.79−3.51 (m, 72H, H_{glycol}), 3.49−3.43 (m, 8H, H_{glycol}), 3.27 (s, 12H, $-OCH_3$), 1.78−1.48 (m, 48H, PC$H_2$$CH_3$), 1.12−0.89 (m, 64H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_3-$COCD_3$, 121.4 MHz) δ 8.58 (s, $^1J_{Pt-P}$ = 1314.52 Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 2052.8, found 2052.6; calcd for $[M - 3PF_6]^{3+}$ m/z 1320.2, found 1320.1.

Acknowledgment. P.J.S. thanks the NIH (GM-057052) and the NSF (CHE-0306720) for financial support. B.H.N. thanks the NIH (GM-080820) for financial support. A.G. thanks the German Academic Exchange Service for financial support.

Supporting Information Available: Multinuclear NMR spectroscopic analysis of compounds **2**−**19** and full results obtained from molecular force field modeling studies. This material is available free of charge via the Internet at http://pubs.acs.org.

JO702380B