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Construction of Functionalized Metallosupramolecular Tetragonal Prisms via Multicomponent Coordination-Driven Self-Assembly

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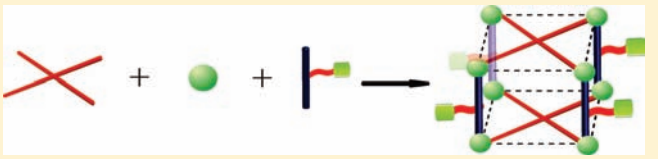
Supporting Information

ABSTRACT: A new approach for the construction of functionalized metallosupramolecular tetragonal prisms via multicomponent, coordination-driven, template-free self-assembly is described. The combination of tetra-(4-pyridylphenyl)ethylene, a 90° Pt(II) acceptor, and ditopic bipyridine or carboxylate ligands functionalized with hydroxyl or amine groups, hydrophobic alkyl chains, or electrochemically active ferrocene, yields a suite of seven self-assembled tetragonal prisms under mild conditions. These three-dimensional metallosupramolecules were characterized by multinuclear NMR (^{31}P and ^{1}H) and mass spectrometry. Their shapes and sizes were established using Merck Molecular Force Field (MMFF) simulations. In addition, their approximate sizes were further supported by pulsed-field-gradient spin−echo (PGSE) NMR experiments.



INTRODUCTION

Multicomponent self-assembly is a ubiquitous phenomenon in biological systems. Nature has demonstrated an extraordinary ability to assemble two-dimensional (2-D) and three-dimensional (3-D) supramolecular nanoarchitectures from multiple subunits to effect biological functions.[1] For example, the capsids of *Tomato Bushy Stunt Virus* are assembled from three protein subunits and serve the role of nucleic acid storage.[2] Apoferritin is a globular protein composed of 24 components to store and keep intracellular iron in a soluble and nontoxic form.[3] One strategy to mimic biological processes and to develop new biomimetic materials is the synthesis of functionalized supramolecular nanoscale structures with well-defined shapes and sizes, accessible through efficient and predictable multicomponent self-assembly.[4]

In the past two decades, coordination-driven self-assembly has emerged as a powerful tool to construct abiological structures, enabling an efficient route which parallels natural pathways. The rational design of discrete polygons and polyhedra has been achieved by utilizing molecular subunits encoded with specific chemical and geometric information.[5] In addition, by conjugating chemical functionalities to individual building blocks prior to self-assembly, functionalized supramolecular nanoarchitectures with predetermined sizes and shapes can be realized.[6] Despite the efficiency of preparing abiological structures via coordination-driven self-assembly, most reports are limited to a single metal acceptor and a single, electron-rich donor.[5,6] The self-assembly of three or more components is plagued with the formation of entropically favored, disordered oligomers, and/or dynamic mixtures.[7] Therefore, efficient methods to self-assemble discrete supramolecular structures with controllable size and shapes from more than two distinct tectons remain underdeveloped.

Recently, an interest in multicomponent coordination-driven self-assembly with an emphasis on constructing discrete supramolecular structures has emerged.[8−12] For example, by employing sterically demanding tectons in the presence of aromatic templates, Fujita et al. have designed multicomponent self-assembled trigonal prisms which are competent for host−guest chemistry.[9] Severin et al. have described the preparation of macrocycles and cages based on metal−ligand interactions and reversible covalent reactions.[10] Stoddart et al. have developed multicomponent self-assemblies of Borromean rings using complementary imine bond formation and metal−ligand coordination.[11] We have previously demonstrated that discrete metallosupramolecular macrocycles and tetragonal prisms can be obtained by controlling the size, shape, and ratio of the multiple subunits used in self-assembly.[12] More recently, we and others have found that three-component systems composed of square planar platinum(II) or palladium(II) centers, pyridine, and anionic carboxylate donors can self-assemble into multicomponent supramolecular rectangles and prisms with high efficiency.[13] The isolation of discrete self-assemblies without deleterious side product formation was ascribed to the favorable energetics associated with heteroligated Pt or Pd centers containing one carboxylate and one pyridine ligand. Despite these emerging strategies, which allow the use of multiple building blocks, reports of multicomponent coordination-driven self-assemblies using functionalized tectons are rare. The attachment of specific chemical functionalities to metallosupramolecules is necessary to enable applications in supramolecular catalysis, chemical sensing, and host−guest chemistry, therefore motivating the development of novel routes to functionalized aseemblies.[6]

We report herein the formation and characterization of 3-D tetragonal prisms arising from template-free, multicomponent coordination-driven self-assembly. As shown in Scheme 1, the

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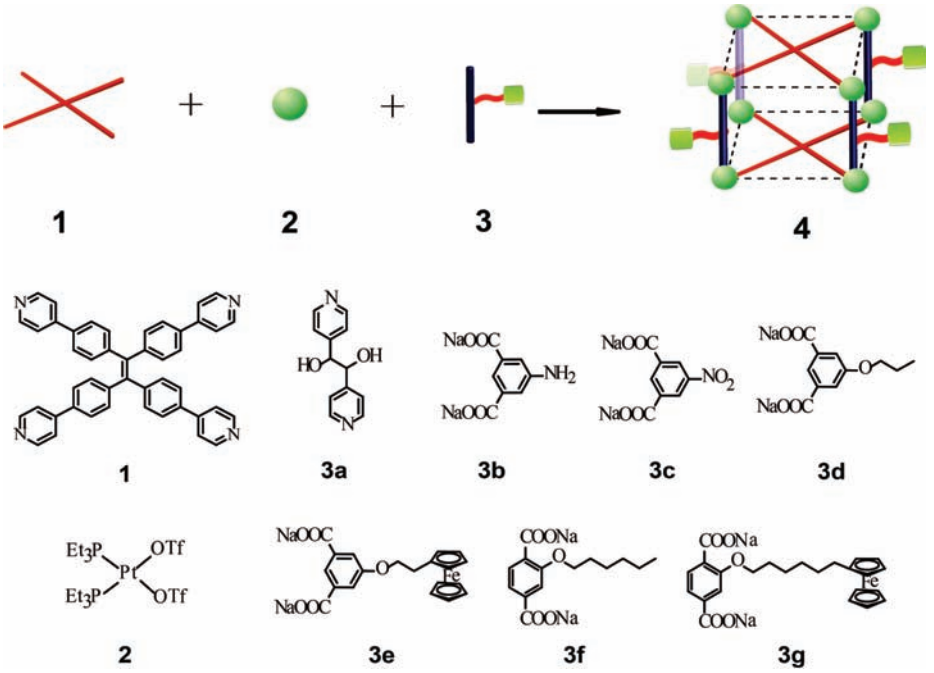
Scheme 1. Multicomponent Coordination-Driven Self-Assembly of Functionalized Tetragonal Prismatic Cages



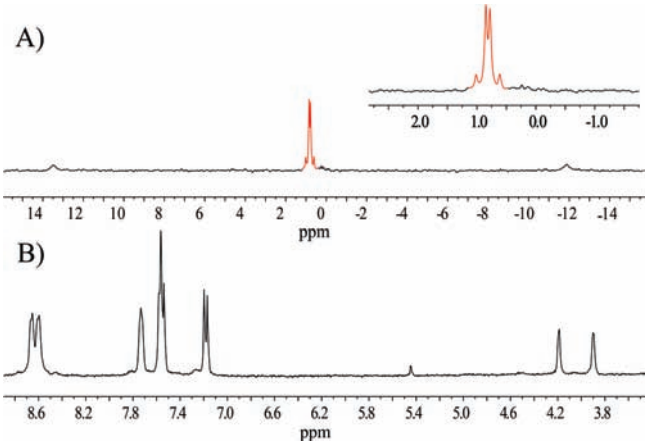


Figure 1. $^{31}P\{^{1}H\}$ NMR spectrum (A) and partial ^{1}H NMR spectrum (B; 300 MHz, 298 K) of **4a** recorded in acetonitrile-d_3.

combination of tetra-(4-pyridylphenyl)ethylene (**1**),[12b] *cis*-$(PEt_3)_2Pt^{II}(OTf)_2$ (**2**), and functionalized ditopic bipyridine or carboxylate ligands (**3a**−**3g**) in a ratio of 2:8:4 results in the formation of functionalized tetragonal prisms (**4a**−**4g**). Prisms **4** were characterized by multinuclear NMR and electron-spray ionization mass spectrometry (ESI-MS), supporting their assigned structures. Also, pulsed-field-gradient spin-echo (PGSE) NMR measurements and computational simulations were employed to predict the shapes and approximate sizes of the prisms.

RESULTS AND DISCUSSION

Tetragonal prism **4a** was prepared by mixing **1**, **2**, and ditopic 1,2-di(4-pyridyl)glycol (**3a**) in a 2:8:4 ratio in acetone/nitromethane (v:v = 2:1). After 12 h of stirring at room temperature, the reaction mixture appeared yellow. The well-defined NMR signals in both the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of **4a** support the formation of single, symmetric reaction product. The $^{31}P\{^{1}H\}$ NMR spectrum of **4a** displays two doublets, occurring at δ = 0.85 ppm and 0.78 ppm ($^{2}J_{P-P}$ = 20.2 Hz) as well as the expected ^{195}Pt satellites (Figure 1, A). These doublets are shifted upfield ($\Delta\delta$ = ∼ 4.2 ppm) relative to the singlet of the Pt starting material, **2**. The two doublets of **4a** indicate that the platinum centers each possess two distinct phosphorus environments and that all the Pt centers are themselves symmetry related. These observations are consistent with the assigned tetragonal prismatic structure of **4a**, as each platinum binds to both **1** and **3a**, breaking the symmetry of the phosphines.[12b,14] The ^{1}H NMR spectrum of **4a** displays sharp, clean signals for the pyridine protons, which exhibit typical downfield shifts relative to free pyridine ($\Delta\delta_{py\text{-}\alpha\text{-}H}$ = 0.20−0.30 ppm, $\Delta\delta_{py\text{-}\beta\text{-}H}$ = 0.40−0.50 ppm) associated with a loss of electron density upon binding (Figure 1B). Further support of the tetragonal prismatic structure of **4a** is given by ESI-MS. As shown in Figure 2, peaks centered at 1845.4, 1446.5, 1180.6, 848.3, and 515.8, corresponding to $[M - 4OTf]^{4+}$, $[M - 5OTf]^{5+}$, $[M - 6OTf]^{6+}$, $[M - 8OTf]^{8+}$, and $[M - 12OTf]^{12+}$, for **4a**, were observed. Furthermore, the peak arising from $[M - 4OTf]^{4+}$ was isotopically resolved and agreed well with its calculated theoretical distribution.

Functionalized tetragonal prisms **4b**−**4e** were prepared based on a recently reported strategy for the multicomponent self-assembly of 2-D and 3-D metallosupramolecules using a 90° Pt(II) acceptor with carboxylate and pyridine donors.[13] The general route involves mixing the tetratopic pyridine donor, **1**, Pt^{II} acceptor, **2**, and functionalized isophthalate derivatives (amino (**3b**), nitro (**3c**), *n*-propanyl (**3d**), or 3-ferrocenylpropanyl (**3e**)) in a 2:8:4 ratio in acetone/water (v:v = 8:1). In a typical synthesis, the solution is stirred for 4 h at 65 °C, after which the solvent is removed in vacuo and the resulting residue redissolved in neat nitromethane-d_3, followed by an additional 4 h of stirring at 65 °C. This route yielded prisms **4b**−**4e** in solution. $^{31}P\{^{1}H\}$

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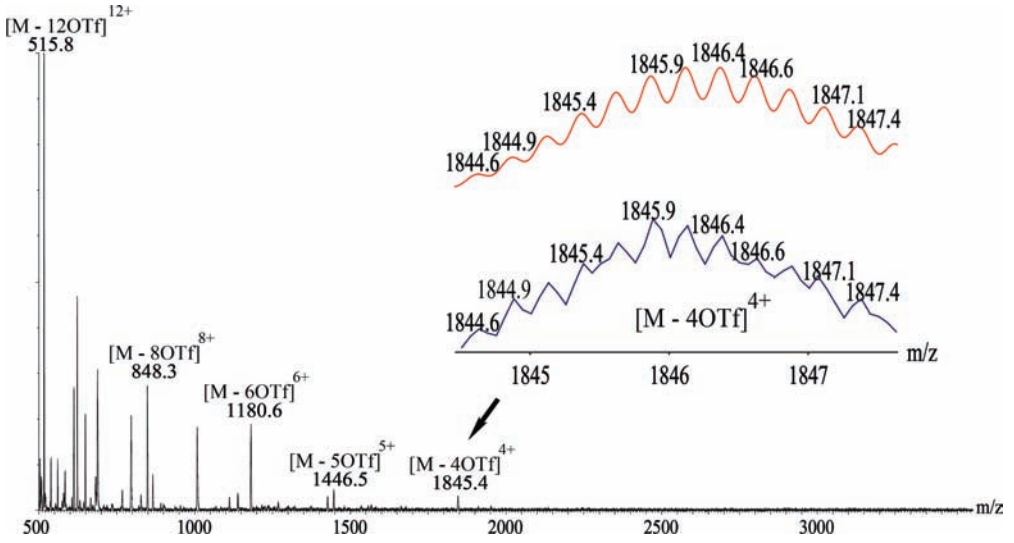

Figure 2. Full ESI-MS spectrum and isotopic resolved peak of $[M - 4OTf]^{4+}$ (calculated: *red*; experimental: *blue*) for tetragonal prism **4a**.

and ^{1}H NMR multinuclear analyses of the reaction mixtures indicated the formation of single, discrete self-assemblies with high symmetry. For example, the $^{31}P\{^{1}H\}$ NMR spectrum of **4b** displays two doublets with approximately equal intensities at δ = 6.95 and 1.01 ppm ($^{2}J_{P-P}$ = 21.9 Hz; Figure 3, A). The presence of doublets indicates distinct phosphorus environments, which would arise from the heteroligated platinum centers containing both pyridine and carboxylate ligands.[12,13] The doublet observed at 6.95 ppm is ascribed to the phosphines trans to carboxylates and displays a small shift relative to the resonance found in **2**. The doublet at 1.01 ppm is assigned to the phosphorus atoms trans to the pyridine ligands and is shifted nearly 6.5 ppm relative to that of **2**. Similarly to **4b**, self-assemblies **4c**−**4e** display two doublets with approximately equal intensities in their $^{31}P\{^{1}H\}$ NMR spectra, as shown in the Supporting Information, Figures S1−S3. In the ^{1}H NMR spectra of **4b**−**4e**, sharp signals corresponding to the coordinated pyridines were identified around δ = 7.73 and 8.66 ppm, with small downfield shifts relative to those of **1** ($\Delta\delta_{py\text{-}\alpha\text{-}H}$ = 0.20−0.30 ppm, $\Delta\delta_{py\text{-}\beta\text{-}H}$ = 0.30−0.40 ppm; Figure 3B and Supporting Information, Figures S1−S3). The sharp signals in both the $^{31}P\{^{1}H\}$ and the ^{1}H NMR spectra support the exclusive formation of single, functionalized tetragonal prisms as products, ruling out other possible assemblies and oligomers. ESI-MS provides further evidence for the tetragonal prismatic structures of **4b**−**4e**. As shown in Figure 4, peaks centered at 2063.5, 1510.6, 1178.6, and 680.7, corresponding to $[M - 3OTf]^{3+}$, $[M - 4OTf]^{4+}$, $[M - 5OTf]^{5+}$, and $[M - 8OTf]^{8+}$, for **4b**, were observed. Similarly to **4b**, the ESI-MS spectra of **4c**−**4e** display well-defined peaks arising from tetragonal prismatic structures, as shown in the Supporting Information, Figures S4−S6. All the peaks of $[M - 3OTf]^{3+}$ of **4b**−**4e** are isotopically resolved and in good agreement with their calculated theoretical distributions (Figure 4 and Supporting Information, Figures S4−S6).

To further demonstrate the construction of functionalized metallosupramolecules via the multicomponent self-assembly introduced above, asymmetric terephthalate ligands functionalized with *n*-hexyl (**3f**) and 6-ferrocenylhexyl (**3g**) were self-assembled with the tetratopic pyridine donor (**1**) and a Pt^{II} acceptor (**2**) to afford tetragonal prisms under similar synthetic

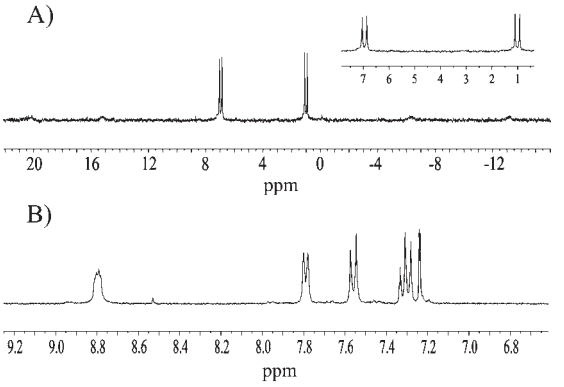

Figure 3. $^{31}P\{^{1}H\}$ NMR spectrum (A) and partial ^{1}H NMR spectrum (B; 300 MHz, 298 K) of **4c** recorded in nitromethane-d_3.

conditions as for **4b**−**4e**. $^{31}P\{^{1}H\}$ and ^{1}H NMR multinuclear analyses of the reaction mixtures indicated the formation of single, discrete self-assemblies with high symmetry. The $^{31}P\{^{1}H\}$ NMR spectra of **4f** and **4g** display four doublets with approximately equal intensities, corresponding to two sets of coupled phosphorus atoms, at δ = 6.79, 6.12, 1.28, and 1.21 ppm ($^{2}J_{P-P}$ = 21.4 Hz; Figure 5) for **4f**, 6.80, 6.10, 1.28, and 1.21 ppm for **4g** ($^{2}J_{P-P}$ = 21.4 Hz; Supporting Information, Figure S7). The presence of four doublets indicates distinct phosphorus environments, which is indicative of heteroligated coordination of pyridine and asymmetric carboxylate to each platinum center. The two doublets observed between 6.5 and 7.2 ppm are ascribed to the phosphines trans to carboxylates and display small shifts relative to **2**. Because the functionalized carboxylate linkers are asymmetric, two distinct Pt environments exist in these prisms and therefore two different phosphine environments trans to carboxylates are present. The other two doublets between 1.28 and 1.21 ppm are assigned to the phosphorus atoms trans to the pyridine ligands and are shifted nearly 6.5 ppm relative to **2**. The distinct phosphine environments trans to the pyridines also result from the asymmetry of the carboxylate linkers, which breaks the symmetry of the Pt centers.[13,14] In the ^{1}H NMR spectra of **4f** and **4g**, sharp signals corresponding to the

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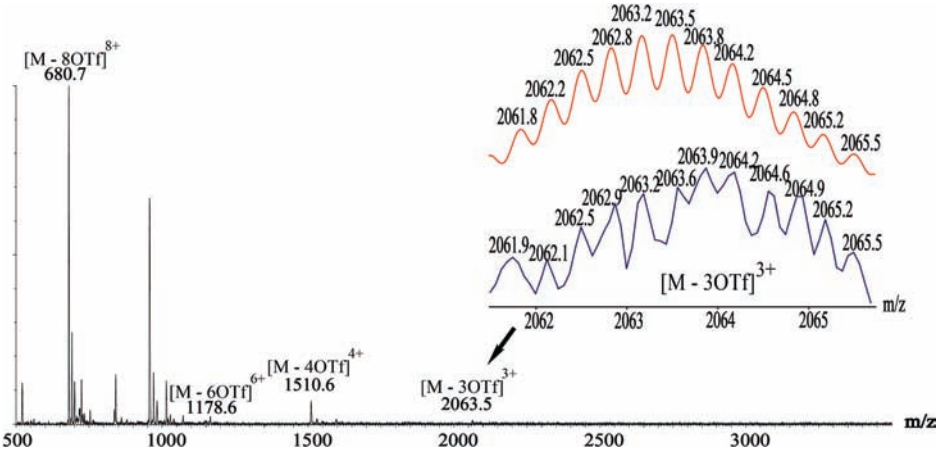

Figure 4. Full ESI-MS spectrum and isotopic resolved peak of $[M - 3OTf]^{3+}$ (calculated: *red*; experimental: *blue*) for tetragonal prism **4b**.

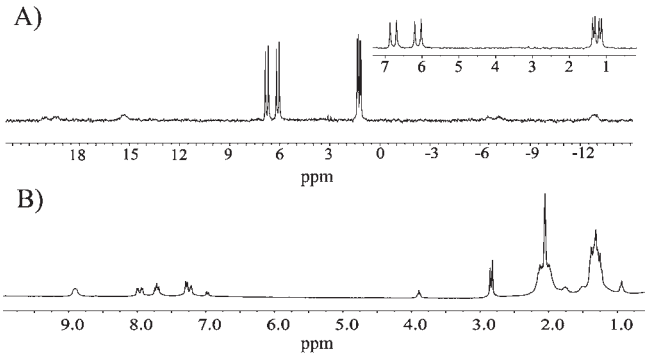

Figure 5. $^{31}P\{^1H\}$ NMR spectrum (*A*) and partial ^1H NMR spectrum (B; 300 MHz, 298 K) of **4f** recorded in acetone-d_6.

coordinated pyridines were identified around δ = 7.73 and 8.66 ppm with small downfield shifts relative to **1** ($\Delta\delta_{py\text{-}\alpha\text{-}H}$ = 0.20−0.30 ppm, $\Delta\delta_{py\text{-}\beta\text{-}H}$ = 0.30−0.40 ppm; Figure 5, and Supporting Information, Figure S7). ESI-MS also provides further evidence for the tetragonal prismatic structures of **4f** and **4g**. As shown in Figure 6 and Supporting Information, Figure S8, peaks corresponding to $[M - 3OTf]^{3+}$, $[M - 4OTf]^{4+}$, $[M - 5OTf]^{5+}$, $[M - 6OTf]^{6+}$, and $[M - 8OTf]^{8+}$ were observed for **4f** and **4g**. In addition, the peaks of $[M - 3OTf]^{3+}$ are isotopically resolved and in good agreement with their calculated theoretical distributions. The clean and well-defined signals in both the NMR and the MS spectra support the exclusive formation of functionalized tetragonal prisms as products.[15]

As attempts to grow single crystals of **4** suitable for X-ray crystallography have so far been unsuccessful, molecular force field simulations and PGSE NMR experiments were used to gain further structural information about **4**. Molecular dynamic simulations using the Merck Molecular Force Fields (MMFFs) were applied to independently equilibrate cages **4a**−**4g**, followed by energy minimizations of the resulting structures to full convergence. As shown in Figure 7 and Supporting Information, Figure S9, the computed structures of **4** are well-defined tetragonal prisms with diameters between 2.30 and 2.70 nm, which are comparable to the sizes determined by PGSE NMR measurements (**4a**: 2.32 ± 0.06 nm; **4b**: 2.48 ± 0.04 nm; **4c**: 2.84 ± 0.12 nm; **4d**: 2.12 ± 0.04 nm; **4e**: 2.26 ± 0.02 nm; **4f**: 2.21 ± 0.11 nm; **4g**: 2.43 ± 0.19 nm).

CONCLUSION

We report here a facile route to functionalized metallosupramolecular tetragonal prisms via multicomponent, coordination-driven, template-free self-assembly. Functionalities were introduced onto 3-D nanostructures by utilizing premodified building blocks prior to self-assembly. The methodology developed in this paper extends the emerging strategy of simple, multicomponent self-assembly to allow the integration of specific functionalities onto supramolecules. As such, this chemistry is an important step in designing functional nanoscale architectures which can mimic natural systems.

EXPERIMENTAL SECTION

General Details. Ligands **3d**[16] and **3f**[17] were prepared according to reported procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. ^1H NMR chemical shifts are reported relative to residual proteo solvent signals, and $^{31}P\{^1H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Mass spectra for the self-assemblies were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. Molecular modeling of tetragonal prisms was performed using the program Maestro v 8.0.110 with MMFF methods. Platinum was modeled using the force field of carbon restrained to have a planar geometry and typical platinum−nitrogen, platinum−oxygen, and platinum−phosphorus bond lengths. For the models of **4e** and **4g**, ferrocenes were replaced with cyclopentadiene groups.

Synthesis of 3e. Dimethyl-5-hydroxyisophthalate (450.0 mg, 2.1 mmol) and potassium carbonate (0.8 g, 5.8 mmol) were mixed in 20.0 mL of anhydrous dimethylformamide (DMF) and stirred for 1 h under an atmosphere of nitrogen. A solution of 3-bromopropanylferrocene[18] (0.65 g, 2.1 mmol) in 1.0 mL of DMF was then added dropwise. The resulting solution was stirred at 60 °C for 24 h, quenched with water, and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (eluent: hexane/dichloromethane, v:v = 1:10) to afford dimethyl-3-ferrocenylpropanyloxyisophthalate as a reddish oil which was used, as isolated, in future steps. Yield: 43%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 8.27 (m, 1H, Ar-*H*), 7.76 (m, 2H, Ar-*H*), 4.05−4.15 (m, 11H, Fc and OCH_2), 3.95 (s, 6H, $COOCH_3$), 2.54 (m, 2H, CH_2CH_3), 2.02 (t, 2H, 6.0 Hz, CH_3).

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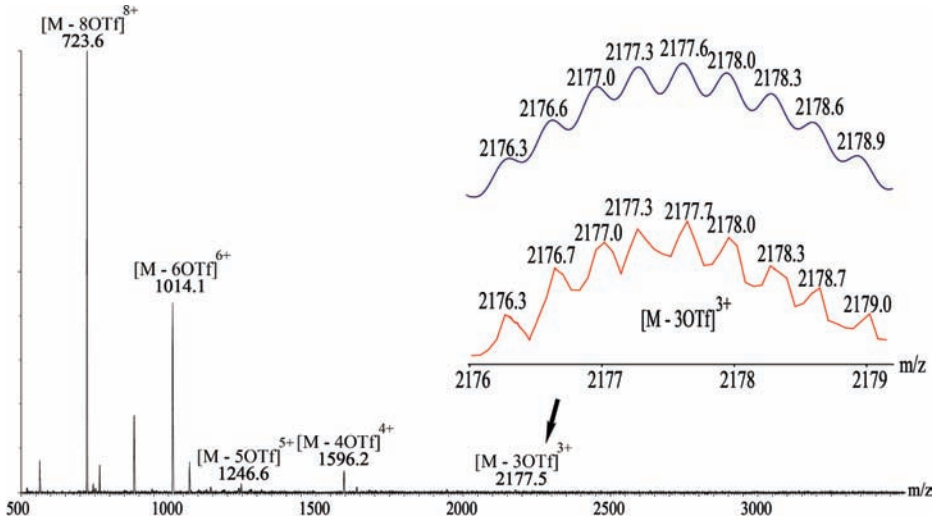

Figure 6. Full ESI-MS spectrum and isotopic resolved peak of $[M - 3OTf]^{3+}$ (calculated: *blue*; experimental: *red*) for tetragonal prism **4f**.

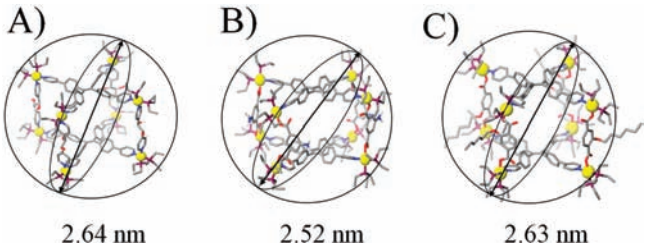

Figure 7. Molecular models of tetragonal prisms **4a** (A), **4b** (B), and **4f** (C).

To a solution of dimethyl-3-ferrocenylpropanyloxyisophthalate, 0.50 g (1.1 mmol) in 5.0 mL of methanol, was added 5.0 mL of aqueous NaOH (0.20 g, 5.0 mmol). The mixture was refluxed for 5 h, and the solvent removed under reduced pressure. The resulting aqueous solution was acidified with HCl to afford a yellow precipitate, 3-ferrocenepropanyloxyisophthalic acid. Yield: 82%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ = 8.08 (s, 1H, Ar-*H*), 7.65 (m, 2H, Ar-*H*), 4.05−4.13 (m, 11H, Fc and OCH_2), 2.47 (m, 2H, CH_2CH_3), 1.99 (t, 3H, 6.1 Hz, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): 167.4, 159.6, 133.6, 123.0, 119.7, 89.7, 69.0, 68.4, 67.6, 30.3, 26.1.

The corresponding sodium salt, **3e**, was isolated by neutralization of 3-ferrocenepropanyloxyisophthalic acid (111.3 mg) with 2 equiv of sodium bicarbonate (45.8 mg) in 3.0 mL of aqueous solution and subsequent precipitation with acetone to give a yellow solid.

Synthesis of 3g. Dimethyl-2-hydroxyterephthalate (630.0 mg, 3.0 mmol) and potassium carbonate (0.9 g, 6.9 mmol) were mixed in 20.0 mL of anhydrous DMF and stirred for 3 h under an atmosphere of nitrogen. A solution of 6-bromohexylferrocene[19] (1.24 g, 3.6 mmol) in 1.0 mL of DMF was then added dropwise. The resulting solution was stirred at 60 °C for 2 days, quenched with water and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (eluent: hexane/dichloromethane, v:v = 2:3) to afford dimethyl-6-ferrocenyl-hexyloxy-terephthalate as a reddish oil which was used, as isolated, in future steps. Yield: 43%. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.78 (d, 1H, Ar-*H*, 8.4 Hz), 7.63 (d, 1H, Ar-*H*, 8.4 Hz), 7.61 (s, 1H, Ar-*H*), 4.00−4.15 (m, 11H, Fc and OCH_2), 3.94, 3.91 (s, 6H, COOCH_3), 1.40−2.35 (m, 11H, alkyl chain).

To a solution of dimethyl-6-ferrocenylhexyloxyterephthalate, 0.47 g (1.0 mmol) in 5.0 mL of methanol, was added 5.0 mL of aqueous NaOH (0.36 g, 9.0 mmol). The mixture was refluxed for 5 h, and the solvent removed under reduced pressure. The resulting aqueous solution was acidified with HCl to afford a yellow precipitate, 6-ferrocenehexyloxyterephthalic acid. Yield: 82%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ = 7.54 (d, 1H, Ar-*H*, 8.4 Hz), 7.55 (d, 1H, Ar-*H*, 8.4 Hz), 7.52 (s, 1H, Ar-*H*), 4.03−4.10 (m, 11H, Fc and OCH_2), 1.35−2.28 (m, 11H, alkyl chain); ^{1}H NMR (DMSO-*d6*, 5 MHz, 298 K): 168.1, 167.5, 157.6, 135.2, 126.8, 121.6, 114.1, 89.8, 69.1, 68.9, 68.6, 67.6, 31.4, 29.8, 29.3, 29.2, 25.8.

The corresponding sodium salt, **3g**, was isolated by neutralization of 6-ferrocenehexyloxyterephthalic acid (102.2 mg) with 2 equiv of sodium bicarbonate (38.2 mg) in 3.0 mL of aqueous solution and subsequent precipitation with acetone to give a yellow solid.

Self-Assembly of Tetragonal Prism 4a. Tetra-(4-pyridylphenyl)ethylene **1** (1.04 mg, 1.62 μmol), $(PEt_3)_2Pt(OTf)_2$ (**2**) (4.72 mg, 6.49 μmol), and dipyridine ligand **3a** (0.70 mg, 3.24 μmol) were mixed in 0.9 mL of acetone/nitromethane (v:v = 2:1) and then stirred for 12 h at room temperature. After removing the solvent in vacuo, the resulting residue was washed with dichloromethane three times to afford **4a** as yellow solid. Yield: 41%. ^{31}P{^{1}H} NMR (acetonitrile-d_3, 121.4 MHz) δ = 0.85 (d, $^2J_{P-P}$ = 20.2 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: 3082.3 Hz), 0.78 (d, $^2J_{P-P}$ = 20.2 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: 3080.2 Hz); ^{1}H NMR (acetonitrile-d_3, 300 MHz, 298 K): δ = 8.67 (m, 16H, $H_{\alpha\text{-Py}}$ for donor **1**), 8.67 (m, 16H, H_{α}-Py for donor **3a**),7.75 (m, 16H, $H_{\beta\text{-Py}}$ for donor **1**), 7.58 (m, 16H, $H_{\beta\text{-Py}}$ for donor **3a**), 7.20−7.54 (d, 32H, Ar−H, 8.4 Hz), 4.19 (m, 8H, C*H*−OH), 3.90 (m, 8H, CH−O*H*), 1.84 (m, 96H, PCH_2CH_3), 1.23(m, 144H, PCH_2CH_3); MS (ESI) for **4a** ($C_{252}H_{352}F_{48}N_{16}O_{56}P_{16}Pt_8S_{16}$): *m/z*: 1845.6.2 $[M - 4OTf]^{4+}$; 1446.9 $[M - 5OTf]^{5+}$. Anal. Calcd for $C_{252}H_{352}F_{48}N_{16}O_{56}P_{16}Pt_8S_{16}$: C, 37.92; H, 4.44; N, 2.81; Found: C, 37.47; H, 4.50; N, 2.83.

General Procedure for the Self-Assembly of Tetragonal Prisms 4b−4g Using Functionalized Phthalate Ligands. Tetra-(4-pyridylphenyl)ethylene **1**, $(PEt_3)_2Pt(OTf)_2$ **2**, and phthalate derivatives **3b**−**3g** were mixed in 0.9 mL of acetone/H_2O (v:v = 8:1). The mixtures were stirred at 65 °C for 4 h, at which time the solvents were removed and the residues redissolved in nitromethane-d_6, followed by a further 4 h of stirring at 65 °C. Tetragonal prisms **4b**−**4g** were isolable as solids recrystallized from acetone/diethyl ether.

Synthesis and Characterization of 4b. Reaction scale: tetratopic ligand (**1**) (0.94 mg, 1.47 μmol), $(PEt_3)_2Pt(OTf)_2$ (**2**) (4.28 mg,

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5.87 μmol), and 5-aminoisophthalate (**3b**) (0.66 mg, 2.94 μmol). Yield: 82%. $^{31}P\{^1H\}$ NMR (nitromethane-d_3, 121.4 MHz) δ = 6.95 (d, $^2J_{P-P}$ = 21.6 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3220.7 Hz), 1.01 (d, $^2J_{P-P}$ = 21.5 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3428.3 Hz); ^{1}H NMR (nitromethane-d_3, 300 MHz, 298 K): δ = 8.79 (m, 16H, $H_{\alpha\text{-Py}}$ for donor **1**), 7.78 (m, 16H, $H_{\beta\text{-Py}}$ for donor **1**, Ar−H), 7.56 (m, 16H, Ar−H), 7.34 (m, 4H, Ar−H), 7.30 (m, 16H, Ar−H), 7.24 (m, 8H, Ar−H), 1.98 (m, 96H, PCH_2CH_3), 1.31 (m, 144H, PCH_2CH_3); MS (ESI) for **4b** ($C_{225}H_{324}F_{15}N_{12}O_{31}P_{16}Pt_8S_5$): *m*/*z*: 2063.2 $[M - 3OTf]^{3+}$. Anal. Calcd for $C_{228}H_{324}F_{24}N_{12}O_{40}P_{16}Pt_8S_8$: C, 41.23; H, 4.62; N, 2.53; Found: C, 40.52; H, 4.76; N, 2.51.

Synthesis and Characterization of 4c. Reaction scale: tetratopic ligand (**1**) (1.00 mg, 1.56 μmol), $(PEt_3)_2Pt(OTf)_2$ (**2**) (4.55 mg, 6.24 μmol), and 5-nitroisophthalate (**3c**) (0.80 mg, 3.12 μmol). Yield: 74%. $^{31}P\{^1H\}$ NMR(nitromethane-d_3, 121.4 MHz) δ = 6.71 (d, $^2J_{P-P}$ = 21.7 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3203.7 Hz), 1.35 (d, $^2J_{P-P}$ = 21.6 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3512.3 Hz); ^{1}H NMR (nitromethane-d_3, 300 MHz, 298 K): δ = 8.82 (m, 16H, $H_{\alpha\text{-Py}}$ for donor 1), 8.83 (m, 8H, Ar−H), 8.36 (m, 4H, Ar−H), 7.79 (m, 16H, $H_{\beta\text{-Py}}$ for donor **1**), 7.54 (m, 16 H, Ar−H), 7.26 (m, 16 H, Ar−H), 1.99 (m, 96H, PCH_2CH_3), 1.31 (m, 144H, PCH_2CH_3); MS (ESI) for **4c** ($C_{252}H_{316}F_{15}N_{12}O_{39}P_{16}Pt_8S_5$): *m*/*z*: 2104.5 $[M - 3OTf]^{3+}$. Anal. Calcd for $C_{228}H_{316}F_{24}N_{12}O_{48}P_{16}Pt_8S_8$: C, 40.5; H, 4.71; N, 2.49; Found: C, 39.60; H, 4.51; N, 2.42.

Synthesis and Characterization of 4d. Reaction scale: tetratopic ligand (**1**) (0.93 mg, 1.45 μmol), $(PEt_3)_2Pt(OTf)_2$ (**2**) (4.25 mg, 5.80 μmol), and 5-(3-propanyl)isophthalate (**3d**) (0.78 mg, 2.90 μmol). Yield: 86%. $^{31}P\{^1H\}$ NMR (acetonitrile-d_3, 121.4 MHz) δ = 6.71 (d, $^2J_{P-P}$ = 21.7 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3192.7 Hz), 1.17 (d, $^2J_{P-P}$ = 21.6 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3448.9 Hz); ^{1}H NMR (acetonitrile-d_3, 300 MHz, 298 K): δ = 8.67 (m, 16H, $H_{\alpha\text{-Py}}$ for donor **1**),7.70 (m, 16H, $H_{\beta\text{-Py}}$ for donor **1**), 7.52 (m, 16H, Ar−H), 7.39 (d, 8H, Ar−H), 7.20 (s, 16H, Ar−H), 3.92 (t, 8H, OCH_2, 5.4 Hz), 2.12 (m, 8H, alkyl), 1.79 (m, 96H, PCH_2CH_3), 1.18 (m, 144H, PCH_2CH_3); 1.01 (t, 12H, CH_3, 7.4 Hz); MS (ESI) for **4d** ($C_{237}H_{344}F_{15}N_8O_{35}P_{16}Pt_8S_5$): *m*/*z*: 2121.8[M − 3OTf]$^{3+}$. Anal. Calcd for $C_{272}H_{356}F_{24}N_{12}O_{68}P_{16}Pt_8S_8$: C, 42.30; H, 5.09; N, 1.64; Found: C, 41.84; H, 4.93; N, 1.68.

Synthesis and Characterization of 4e. Reaction scale: tetratopic ligand (**1**) (0.94 mg, 1.47 μmol), $(PEt_3)_2Pt(OTf)_2$ (**2**) (4.29 mg, 5.88 μmol), and 5-(3-Ferrocenylpropanyl)isophthalate (**3e**) (1.33 mg, 2.94 μmol). Yield: 65%. $^{31}P\{^1H\}$ NMR(acetonitrile-d_3, 121.4 MHz) δ = 6.72 (d, $^2J_{P-P}$ = 21.6 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3202.7 Hz), 1.19 (d, $^2J_{P-P}$ = 21.6 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3431.9 Hz); ^{1}H NMR (acetonitrile-d_3, 300 MHz, 298 K): δ = 8.70 (m, 16H, $H_{\alpha\text{-Py}}$ for donor **1**),7.72 (m, 16H, $H_{\beta\text{-Py}}$ for donor **1**), 7.53 (m, 20H, Ar−H), 7.45 (m, 8H, Ar−H), 7.25 (m, 16H, Ar−H), 4.08−4.16 (m, 45H, ferrocene), 4.05 (t, 8H, OCH_2, 5.4 Hz), 2.54 (m, 8H, CH_2-Fc); 1.89 (m, 104H, PCH_2CH_3, $OCH_2CH_2CH_2Fc$), 1.15 (m, 144H, PCH_2CH_3); MS (ESI) for **4e** ($C_{277}H_{376}F_{15}Fe_4N_8O_{35}P_{16}Pt_8S_5$): *m*/*z*: 2366.9[M − 3OTf]$^{3+}$. Anal. Calcd for $C_{280}H_{376}F_{24}Fe_4N_8O_{44}P_{16}Pt_8S_8$: C, 44.54; H, 5.02; N, 1.48; Found: C, 43.71; H, 4.92; N, 1.48.

Synthesis and Characterization of 4f. Reaction scale: tetratopic ligand (**1**) (1.03 mg, 1.61 μmol), $(PEt_3)_2Pt(OTf)_2$ (**2**) (4.61 mg, 6.44 μmol), and 2-(6-hexyl)terephthalate (**3f**) (1.00 mg, 3.22 μmol). Yield: 74%. $^{31}P\{^1H\}$ NMR(acetone-d_6, 121.4 MHz) δ = 6.79 (d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3228.1 Hz), 6.12 (d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3221.9 Hz), 1.28 (d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3439.3 Hz), 1.21 (d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3445.3 Hz); ^{1}H NMR (acetone-d_6, 300 MHz, 298 K): δ = 8.92 (m, 16H, $H_{\alpha\text{-Py}}$ for donor 1),7.94−8.00 (m, 16H, $H_{\beta\text{-Py}}$ for donor **1**), 7.29−7.75 (m, 32H, Ar−H), 7.21 (s, 4H, Ar−H), 7.20 (d, 4H, 9.0 Hz), 6.96 (d, 4H, 9.0 Hz), 3.89 (t, 8H, OCH_2, 5.4 Hz), 2.13 (m, 44H, alkyl) 1.99 (m, 96H, PCH_2CH_3), 1.31 (m, 144H, PCH_2CH_3); MS (ESI) for **4f** ($C_{252}H_{368}F_{24}N_8O_{44}P_{16}Pt_8S_8$): *m*/*z*: 2177.7 $[M - 3OTf]^{3+}$. Anal. Calcd for $C_{252}H_{368}F_{24}N_8O_{44}P_{16}Pt_8S_8$: C, 43.35; H, 5.31; N, 1.60; Found: C, 42.71; H, 5.02; N, 1.62.

Synthesis and Characterization of 4g. Reaction scale: tetratopic ligand (**1**) (0.63 mg, 0.98 μmol), $(PEt_3)_2Pt(OTf)_2$ (**2**) (2.87 mg, 3.93 μmol), and 2-(6-Ferrocenylhexyl)terephthalate (**3g**) (0.97 mg, 1.97 μmol). Yield: 86%. $^{31}P\{^1H\}$ NMR (acetone-d_6, 121.4 MHz) δ = 6.80 (d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3215.9 Hz), 6.10 (d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3208.6.9 Hz), 1.28 (d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3419.3 Hz), 1.21(d, $^2J_{P-P}$ = 21.9 Hz, ^{195}Pt satellites, $^1J_{Pt-P}$: = 3410.3 Hz); ^{1}H NMR (acetone-d_6, 300 MHz, 298 K): δ = 8.91 (m, 16H, $H_{\alpha\text{-Py}}$ for donor **1**),7.93 (m, 16H, $H_{\beta\text{-Py}}$ for donor **1**), 7.27−7.72 (m, 16H, Ar−H), 7.23 (d, 4H, 9.0 Hz), 7.20 (s, 4H, Ar−H), 6.97 (d, 4H, 9.0 Hz), 4.05−4.10 (m, 45H, ferrocene), 3.89 (t, 8H, OCH_2, 5.4 Hz), 2.12 (m, 40H, alkyl), 1.99 (m, 96H, PCH_2CH_3), 1.32 (m, 144H, PCH_2CH_3); MS (ESI) for **4g** ($C_{292}H_{400}F_{24}Fe_4N_8O_{44}P_{16}Pt_8S_8$): *m*/*z*: 2422.8[M − 3OTf]$^{3+}$. Anal. Calcd for $C_{292}H_{400}F_{24}Fe_4N_8O_{44}P_{16}Pt_8S_8$: C, 45.44; H, 5.22; N, 1.45; Found: C, 44.71; H, 5.02; N, 1.44.

■ ASSOCIATED CONTENT

Supporting Information. $^{31}P\{^1H\}$ and ^{1}H NMR spectra, ESI-MS spectra; molecular modeling of **4c**−**4e**, **4 g**. ^{1}H NMR, ^{13}C NMR spectra of **3f** and **3g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The self-assembly of tetragonal prisms using asymmetric terephthalate derivatives may result in five possible isomers which differ by the relative orientations of the functional groups on the pillars. This is of consequence for **4f** and **4g** which may adopt the configurations show in the Supporting Information, Figure S10. ESI-MS data is, of course, unable to distinguish between these isomers because of their identical compositions. The $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of the reaction mixtures display sharp, well-resolved peaks which superficially suggests single product formation. However, the possibility exists that the spatial separation between pillars is too great to impart any significant changes in chemical shifts between isomers. Considered separately, each pillar has one Pt on the same side of the functionality and one more distant. Thus, the symmetry between isomers is only broken when considering the relative arrangement of a second functionality on a distant pillar, either 28 or 29 bonds away, depending on *up, up* or *up, down* orientations. As a result, the ESI-MS and NMR data are not sufficient to confidently support or rule out the formation of a single isomer over a product mixture.

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