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Construction of Endo-Functionalized Two Dimensional Metallacycles via Coordination-Driven Self-Assembly

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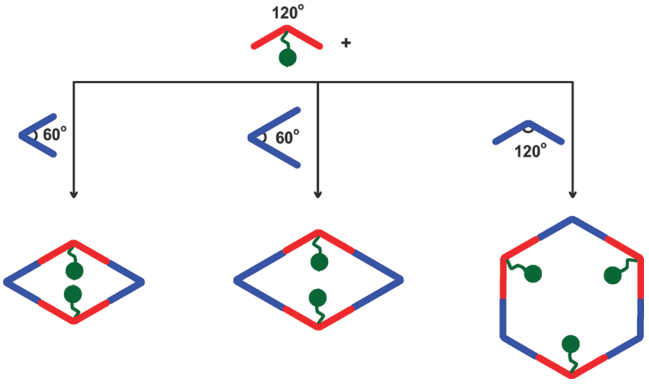

The synthesis of three endofunctionalized two-dimensional supramolecular metallacycles including two [2 + 2] rhomboids (**5** and **6**) and a [3 + 3] hexagon (**7**) is reported. The resulting self-assembled supramolecular structures, containing several nitrobenzyl moieties at their interior surface, have been fully characterized by multinuclear NMR (^{31}P and ^{1}H) and electrospray ionization mass spectrometry. A significant C−H···O hydrogen bonding between the nitrobenzyl acceptor and the edge molecules of the supramolecular architecture is observed in the small rhomboid **5** and this interaction gradually decreases upon the enlargement of the resulting polygonal structures from a small rhomboid **5** through a large rhomboid **6** to a hexagon **7**. Molecular modeling with the MMFF force field gives a possible conformation of each self-assembly in different solvents and shows that the hydrophilic nitrobenzyl moiety prefers to be buried in the cavity of the resulting polygonal structures in nonpolar solvents, thus forming hydrogen bonds with the peripheral component building units.

Introduction

Metallosupramolecular chemistry has been a remarkable research area in the realm of supramolecular chemistry since the 1980s.[1] Over the past few decades, metal-directed self-assembly has proven to be a powerful tool in the synthesis of well-defined multimetallic architectures with increasing structural complexity based on metal−ligand interactions.[2] These architectures were spontaneously generated by simply mixing appropriately designed complementary building units (acceptor and donor) in a suitable solvent. The shape of the donor and acceptor building blocks is dominated by the turning angle formed between the bonding sites of the individual components. With the further introduction of various functional moieties on the tectons, a wealth of decorated supramolecular polygons and polyhedra can be potentially employed as precursors of electronic,[3]

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catalytic,[2i,4] and photophysical materials[5] and used for molecular recognition and encapsulation.[2g,6]

To date, three methods have been successfully employed to incorporate functionalities into supramolecular metal−organic assemblies. First, the functional moieties can be incorporated into the edge or corner of a building block. In this way, numerous functional moieties including porphyrin,[7] diazacrown ether,[8] cavitand,[9] carborane,[10] and chiral metallocorners[7b,11] have been introduced into the supramolecular architectures. Furthermore, covalently grafting a functional moiety on the exterior surface of an angle-directed building block has resulted in a large number of discrete supramolecular metal-organic assemblies peripherally functionalized with dendrimers,[12] ferrocene,[3d,13] crown ethers, and pseudorotaxanes.[14] Lastly, the interior surface of self-assembled suprastructures can also be decorated via covalent attachment of a functional moiety on the concave side of a directional building block. Fujita and co-workers have synthesized a variety of three-dimensional endofunctionalized $M_{12}L_{24}$ cuboctahedra, which are interiorly decorated by oligo(ethylene oxide) chains,[15] azobenzene units,[16] perfluoroalkyl chains,[17] and polymerizable methyl methacrylate units.[18] However, the synthesis of endofunctionalized two-dimensional metallacyclic complexes has not been reported up to now. Herein we report the synthesis of two [2 + 2] rhomboids and a hexagon with endofunctionalized architectures via coordination-driven self-assembly between di-Pt(II) acceptors and an endofunctionalized bipyridyl donor ligand.

Results and Discussion

Synthesis of 120° Endo-Functionalized Donor Ligand. As shown in Scheme 1, the new endofunctionalized 120° donor ligand was synthesized by use of 4-hydroxy-3,5-diiodobenzoic acid as the starting material, which was protected as an ester and subsequently reacted with 4-nitrobenzyl bromide to produce the endofunctionalized diiodo complex. Sonogashira coupling of this diiodo complex with 4-ethynylpyridine in the presence of catalytic $Pd(PPh_3)_2Cl_2$ afforded the desired endofunctionalized 120° donor ligand **1** in a reasonable yield (63%).

Self-Assembly and NMR Studies. The endofunctionalized polygonal structures (**5**−**7**) were prepared by use of two different 60° phenanthrene (**2** and **3**) and a 120° ketone (**4**) di-Pt(II) ligand as acceptors and donor ligand **1** (Scheme 2).

The small self-assembled [2 + 2] rhomboid **5** was made by mixing the donor ligand **1** with acceptor **2** in a 1:1 ratio in CD_2Cl_2. The $^{31}P\{^1H\}$ NMR spectrum of **5** showed a single peak at 12.58 ppm with concomitant ^{195}Pt satellites, upfield shifted by roughly 6.5 ppm compared with the 60° phenanthrene acceptor ligand **2** (δ = 19.09 ppm) as a result of the coordination of the pyridine rings (Figure 1). This indicates that only one discrete supramolecular structure exists in the resulting solution. In the proton NMR spectrum of **5**, the α- and β-pyridyl hydrogen signals both experience significant downfield shifts compared with their chemical shifts in the precursor building block **1**, which are associated with the loss of electron density upon coordination by the nitrogen lone pair to the platinum metal centers (Figure 2). It is notable that the doublet peak at δ = 8.65 ppm corresponding to the α-protons of the pyridyl ring in **1** is split into a pair of doublets (α′ and α″) upon self-assembly. This is due to restricted rotation around the Pt−N coordination bond analogous to previous observations and reports.[19] On the other hand, the rather large chemical shift difference between the two pyridine α-protons ($\Delta\delta$ = 0.8 ppm) in **5** is much larger than the differences (approximately 0.2 ppm) in several previously reported rhomboid, triangle, and rectangle structures.[20] This may be due to the C−H···O hydrogen bonding between the oxygen atom of the endo nitro group and the α hydrogen atom of the pyridine ring. This is supported by

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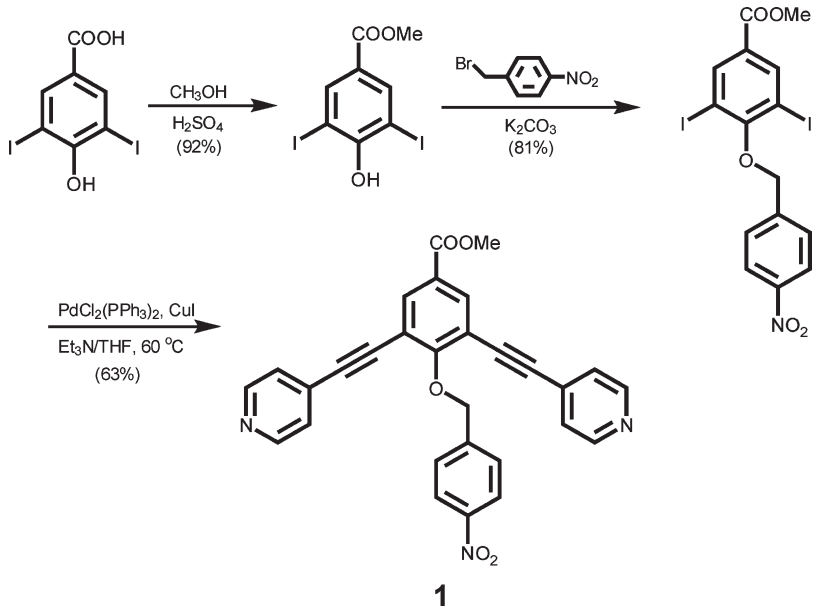
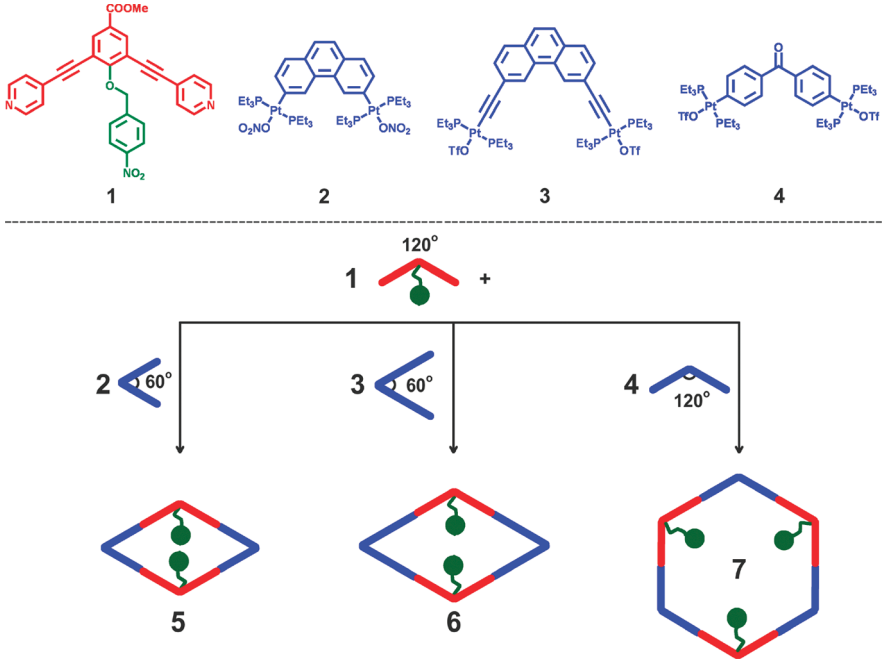
SCHEME 1. Synthesis of 120° Endo-Functionalized Donor Ligand 1



SCHEME 2. Molecular Structures of Donor (Red) and Acceptor (Blue) Building Blocks and Their Self-Assembly into [2 + 2] Rhomboids 5 and 6 and [3 + 3] Hexagon 7



the proton NMR comparison between the nitrobenzyl moiety in precursor ligand **1** and the product **5**, wherein the NMR signals attributed to the phenyl group of the nitrobenzyl moiety undergo a downfield shift by 0.11−0.18 ppm, indicating the loss of electron density upon hydrogen bonding.

Furthermore, the addition of a small amount of D_2O to the CD_2Cl_2 solution of **5** (CD_2Cl_2/D_2O = 50:1) to replace the C−H···O hydrogen bonding with the stronger O−H···O interaction between the water molecule and the nitrobenzyl moiety. As shown in Figure 2d, the α-protons (δ = 9.53 ppm) of the pyridine ring of self-assembled rhomboid **5** in CD_2Cl_2 experience a $\Delta\delta$ = 0.14 ppm upfield-shift upon the addition of D_2O, indicating that the C−H···O hydrogen bonding is indeed weakened. The signal of the β-pyridyl hydrogen of **5** in CD_2Cl_2 is split into two doublets with a chemical shift difference of 0.1 ppm (β' and β''). This may arise from the formation of hydrogen bonding between the β hydrogen atoms of the pyridine ring and the nitro-D_2O hydrogen bonding cluster.

The electrospray ionization mass spectrum (ESI-MS) of **5** exhibited two charge states at m/z = 3241.9 and 1039.4 corresponding to $[M - NO_3]^+$ and $[M - 3NO_3]^{3+}$ of the [2 + 2] rhomboid, respectively, which are in good agreement with their theoretical distributions (Figure 3a).

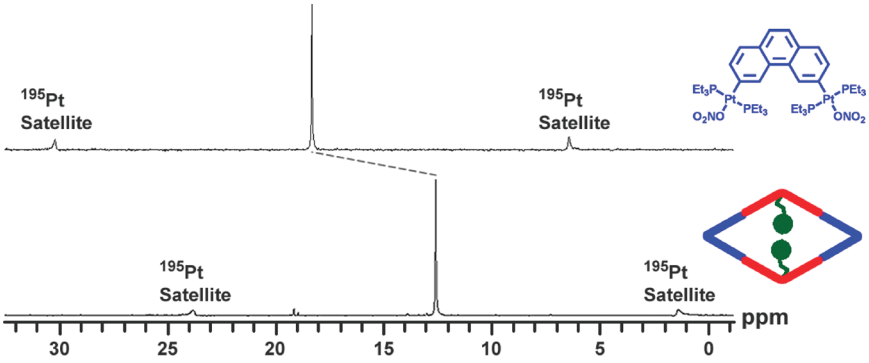


FIGURE 1. Comparison of the $^{31}P\{^{1}H\}$ NMR spectra (in CD_2Cl_2) of the 60° di-Pt(II) acceptor **2** and the self-assembled [2 + 2] rhomboid **5**.

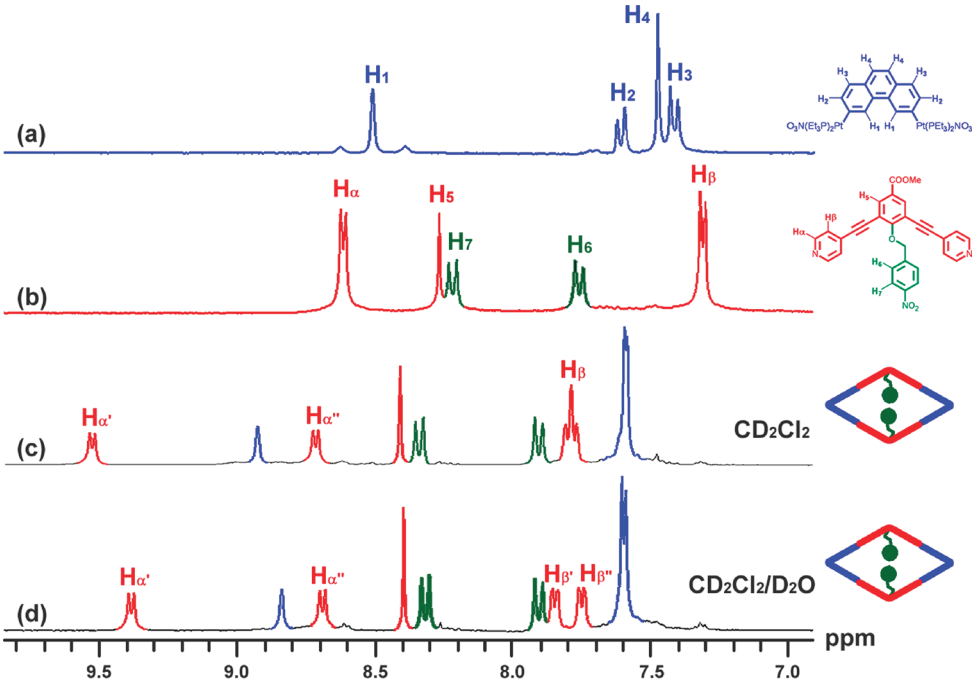


FIGURE 2. Comparison of representative ^{1}H NMR spectra of the aromatic portion of (a) the 60° di-Pt(II) acceptor **2** in CD_2Cl_2, (b) the 120° donor ligand **1** in CD_2Cl_2, (c) the self-assembled [2 + 2] rhomboid **5** in CD_2Cl_2, and (d) **5** in CD_2Cl_2/D_2O, displaying the characteristic shifts of proton signals associated with the donor and acceptor units upon coordination.

To further investigate the interaction between the encapsulated endonitrobenzyl group and self-assembled structures, we next utilized the larger 60° building block **3** to react with **1**. Mixing **1** and **3** in a 1:1 ratio in a mixed solvent of acetone-d_6 and CD_2Cl_2 yielded a homogeneous pale yellow solution of **6**. The $^{31}P\{^{1}H\}$ NMR spectrum showed the appearance of a doublet at $\delta = 16.98$ ppm with concomitant ^{195}Pt satellites (Figure 4a), likely due to the proximity of the endofunctionalized nitrobenzyl group to a PEt_3 group in rhomboid **6** which results in a different environment for the two phosphorus nuclei. The doublet corresponding to the α-protons of the pyridyl ring in precursor ligand **1** is split into a triplet upon the formation of the larger [2 + 2] rhomboid **6** (Figure 4b). Furthermore, four doublet signals corresponding to the hydrogen atoms of the nitrobenzyl group, in contrast to just two doublets in self-assembly **5**, are observed in the proton NMR spectrum of **6**, indicating that this nitrobenzyl group interacting with the peripheral edge of the rhomboid structure leads to nonequivalent environments for each of its hydrogen atoms. The formation of the [2 + 2] rhomboid structure in **6** is further confirmed by electrospray ionization mass spectrometry. As listed in Figure 3b, the peaks resulting from the rhomboid self-assembly minus triflate anions are found: $[\mathbf{6} - 2CF_3SO_3^-]^{2+}$ (m/z 1725.3) and $[\mathbf{6} - 3CF_3SO_3^-]^{3+}$ (m/z 1100.4). All observed peaks are isotopically resolved and in good agreement with their corresponding theoretical distributions.

When a different 120° building block **4** is employed to react with acceptor **1** in a 1:1 ratio in CD_2Cl_2, a [3 + 3] self-assembled hexagon **7** is generated. Only one sharp ^{31}P NMR peak at 13.6 ppm is observed for **7** (Figure S6 in Supporting Information), upfield shifted by almost 8.3 ppm, as compared with the starting acceptor ligand **4** ($\delta = 21.9$ ppm), as a result of the coordination of the pyridine moiety. In the NMR spectrum of **7**, the α- and β-proton NMR signals of the pyridine ring each display a downfield-shifted doublet, in contrast to a pair of doublets and a triplet in rhomboid structures **5** and **6**, respectively. Two discernible doublet

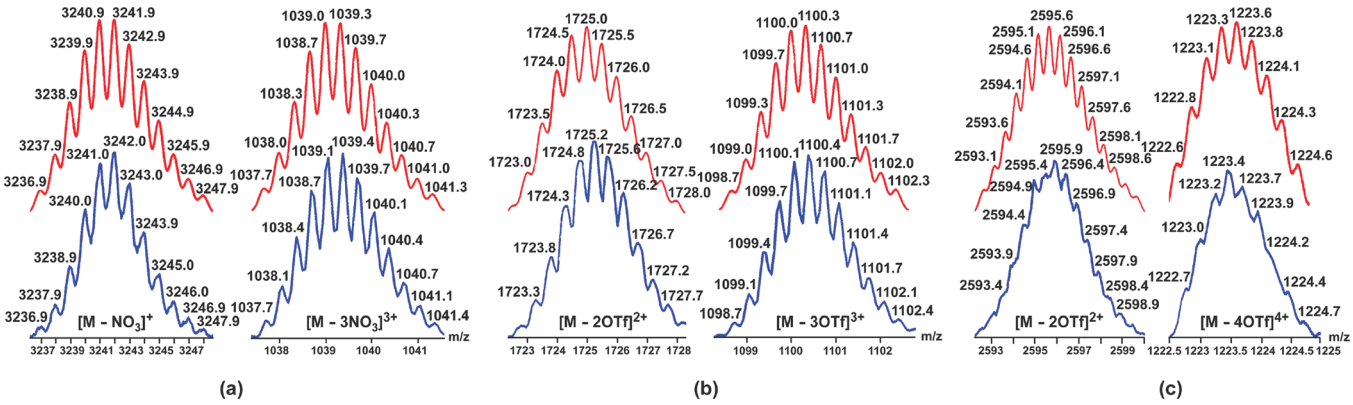


FIGURE 3. Theoretical (top, red) and experimental (bottom, blue) ESI-MS results for self-assembled (a) [2 + 2] rhomboid **5**, (b) [2 + 2] rhomboid **6**, and (c) [3 + 3] hexagon **7**.

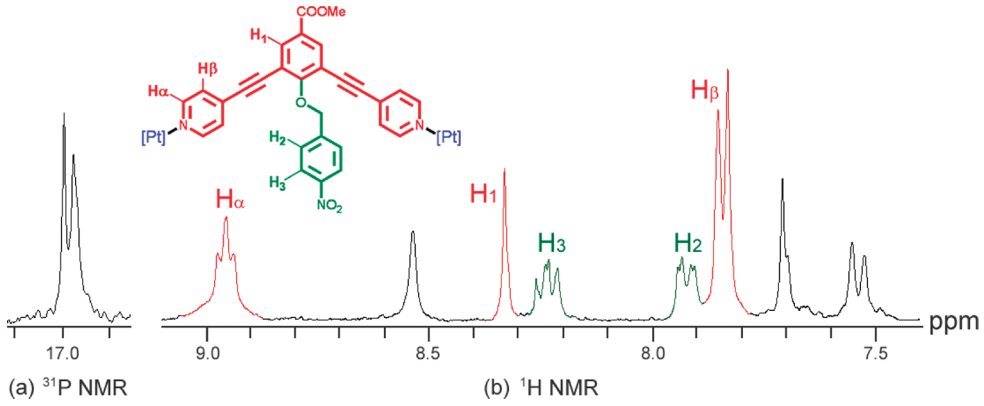


FIGURE 4. (a) ^{31}P NMR and (b) partial ^{1}H NMR spectra of self-assembled [2 + 2] rhomboid **6** in CD_2Cl_2.

signals for the nitrobenzyl moiety are observed as well, showing that this moiety hardly interacts with the peripheral building components upon the formation of the larger [3 + 3] hexagon. Well-resolved peaks for the [3 + 3] hexagon **7** were collected by ESI-MS at *m*/*z* 2595.9 and 1223.4, corresponding to $[M - 2OTf]^{2+}$ and $[M - 4OTf]^{4+}$, respectively (Figure 3c). Their isotopic distributions are also in good agreement with the theoretical distributions. These mass spectral results, together with the multinuclear NMR studies, confirm the self-assembly of the discrete supramolecular hexagon **7**.

Molecular Force Field Modeling. Our attempts to crystallize the above three polygonal structures have so far been unsuccessful. We have therefore used molecular force field simulations to investigate the structural details of the supramolecular architectures **5**−**7**. In the self-assembly **5**, modeling structures in different solvents display various conformations. As shown in Figure 5, the nitrobenzyl groups in the computed structures of **5** in the gas phase or in a nonpolar solvent such as $CHCl_3$ are along the edge like cavities of the self-assembled rhomboid because of the hydrophilic nature of the nitrobenzyl moiety. This conformation leads to the favorable formation of C−H···O hydrogen bonding in the [2 + 2] self-assembled rhomboid **5**. In contrast, the calculated results of **5** in polar solvents (octanol and water) show that the nitrobenzyl groups prefer to protrude into the center of the rhomboid structure, thus lowering the strength of the C−H···O hydrogen bonding

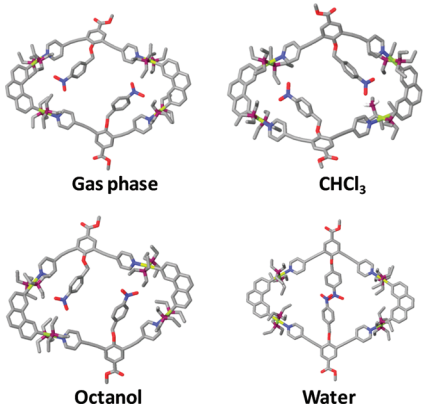


FIGURE 5. Computational models of [2 + 2] rhomboid **5** in different solvents.

between the α-hydrogen atoms of the pyridine ring and the nitrobenzyl group. Likewise, the calculated structures of **6** and **7** in $CHCl_3$ illustrate that the nitrobenzyl groups in each self-assembly cling to the edge of the resulting supramolecular architectures (Figure S7).

In conclusion, we have successfully prepared three endo-functionalized two-dimensional supramolecular architectures by the self-assembly of a new 120° dipyridyl donor ligand (**1**) with three different di-Pt(II) acceptors. The encapsulated nitrobenzyl groups are found to interact with the

edge of the resulting polygons, which are characterized by multinuclear NMR, ESI mass spectrometry, and molecular force field modeling.

Experimental Section

Methods and Materials. The organoplatinum acceptor ligands **2**, **3**, and **4** were synthesized according to the literature methods.[20a,21]

Preparation of Dipyridine Ligand 1. To a solution of 4-hydroxy-3,5-diiodobenzoic acid (2.0 g, 5.13 mmol) in methanol (100 mL) was added 10−15 drops of concentrated H_2SO_4. The solution was refluxed overnight. The mixture was cooled, and the solvent was evaporated. The residue was recrystallized twice from MeOH/H_2O to yield a white crystalline solid of methyl 4-hydroxy-3,5-diiodobenzoate (1.90 g, 91.7%). Mp over 250 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.36 (s, 2H), 6.12 (s, 1H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.2, 157.4, 141.1, 126.3, 81.8, 52.6. MS (EI) m/z 404.84 $(M + H)^+$. Anal. Calcd for $C_8H_6I_2O_3$: C, 23.79; H, 1.50. Found: C, 24.07; H, 1.66.

The mixture of 4-hydroxy-3,5-diiodobenzoate (0.808 g, 2 mmol), K_2CO_3 (2.36 g, 17 mmol), and 4-nitrobenzyl bromide (0.475 g, 2.2 mmol) in 30 mL of dry acetone was refluxed for 16 h and then filtered. The filtrate was evaporated to give a pale-yellow residue. The residue was purified by column chromatography on silica gel with a mixed solvent (ethyl acetate/hexane = 1:4) as eluent. The pale-yellow crystalline solid of methyl 3,5-diiodo-4-(4-nitrobenzyloxy)benzoate was obtained in a yield of 80.7% (0.87 g). Mp 104−106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.48 (s, 2H), 8.32 (d, 2H, J = 8.7 Hz), 7.82 (d, 2H, J = 8.7 Hz), 5.15 (s, 2H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.0, 160.7, 148.1, 143.2, 141.6, 130.1, 128.7, 124.0, 90.6, 73.0, 53.0. MS (EI) m/z 540.88 $(M + H)^+$. Anal. Calcd for $C_{15}H_{11}I_2NO_5$: C, 33.42; H, 2.06; N, 2.60. Found: C, 33.73; H, 2.33; N, 2.51.

A 100 mL Schlenk flask was charged with methyl 3,5-diiodo-4-(4-nitrobenzyloxy)benzoate (0.270 g, 0.5 mmol), 4-ethynylpyridine hydrochloride (0.280 g, 2 mmol), bis(triphenylphosphine) palladium(II) dichloride (90 mg, 0.13 mmol), and copper(I) iodide (25 mg, 0.13 mmol) under a stream of nitrogen. Freshly distilled triethylamine (10 mL) and tetrahydrofuran (15 mL) were added to the flask via syringe, and the reaction mixture was stirred overnight at 60 °C. The solvent was then evaporated, and the resulting residue was extracted with ethyl acetate over water. The organic phase was washed with brine and dried over anhydrous $MgSO_4$. Purification by silica gel column chromatography with eluent (ethyl acetate/methanol = 10:1) yields the pale yellow powder of methyl 4-(4-nitrobenzyloxy)-3,5-(bis(4-pyridyl)ethynyl)benzoate **1** (154 mg, 63%). Mp 157−160 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.65 (d, 4H, J = 6.0 Hz), 8.26 (s, 2H), 8.24 (d, 2H, J = 8.7 Hz), 7.74 (d, 2H, J = 8.4 Hz), 7.30 (d, 4H, J = 6.0 Hz), 5.57 (s, 2H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.8, 165.1, 150.3, 136.3, 130.6, 128.3, 126.7, 125.4, 124.0, 117.0, 92.6, 88.5, 74.6, 52.9. MS (EI) m/z 490.23 $(M + H)^+$. Anal. Calcd for $C_{29}H_{19}N_3O_5$: C, 71.16; H, 3.91; N, 8.58. Found: C, 70.82; H, 4.02; N, 8.45.

Self-Assembly of Rhomboid 5. The dipyridyl donor ligand methyl 4-(4-nitrobenzyloxy)-3,5-(bis(4-pyridyl)ethynyl)benzoate **1** (2.45 mg, 5.00 μmol) and the organoplatinum 60° acceptor **2** (5.82 mg, 5.00 μmol) were weighed accurately into a glass vial. To the vial was added 0.7 mL of CD_2Cl_2 solvent, and the reaction solution was then stirred at room temperature for 24 h to yield a homogeneous yellow solution. The solution was transferred into the NMR tube to collect ^{1}H and ^{31}P NMR spectra. Solid product was obtained by removing the solvent under vacuum. Yield: 96%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 9.53 (d, 4H, J = 5.7 Hz), 8.92 (s, 4H), 8.72 (d, 4H, J = 5.7 Hz), 8.41 (s, 4H), 8.35 (d, 4H, J = 8.7 Hz), 7.92 (d, 4H, J = 8.7 Hz), 7.81−7.77 (t, 8H, J = 5.7 Hz), 7.60 (m, 12H), 5.85 (s, 4H), 3.99 (s, 6H), 1.38 (m, 48H), 1.10−1.20 (m, 72H). ^{31}P $\{^1$H$\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 12.50 (s, $^1J_{Pt-P}$ = 2714.0 Hz). Anal. Calcd for $C_{134}H_{174}N_{10}O_{22}P_8Pt_4$: C, 48.70; H, 5.31; N, 4.24. Found: C, 48.89; H, 5.68; N, 4.39.

Self-Assembly of Rhomboid 6. To a 0.2 mL CD_2Cl_2 solution of the medium organoplatinum 60° acceptor **3** (4.243 mg, 3.06 μmol) in a vial was added a 0.2 mL CD_2Cl_2 solution of 4-(4-nitrobenzyloxy)-3,5-(bis(4-pyridyl)ethynyl)benzoate **1** (1.50 mg, 3.06 μmol). This process was repeated three times with acetone-d_6 instead of CD_2Cl_2 (3 × 0.15 mL) to complete transfer of the donor to the acceptor. The reaction mixture was stirred at ambient temperature for 3 h to produce a clear pale yellow solution. The solution was transferred into the NMR tube for ^{1}H and ^{31}P NMR spectra collection. The solid product was obtained by removing solvent under vacuum. Yield: 94%. ^{1}H NMR (CD_2Cl_2/acetone-d_6 = 1:1, 300 MHz): δ 8.95 (t, 8H, J = 5.7 Hz), 8.54 (s, 4H), 8.33 (s, 4H), 8.26 (m, 4H), 7.93 (quadruple, 4H), 7.83−7.85 (m, 12H), 7.71 (s, 4H), 7.55 (d, 4H, J = 8.1 Hz), 5.80 (s, 4H), 3.95 (d, 6H), 1.95−1.97 (m, 48H), 1.26−1.32 (m, 72H). ^{31}P $\{^1$H$\}$ NMR (CD_2Cl_2/acetone-d_6 = 1:1, 121.4 MHz): δ 16.98 (d, $^1J_{Pt-P}$ = 2324.2 Hz). Anal. Calcd for $C_{146}H_{174}F_{12}N_6O_{22}P_8Pt_4S_4$: C, 46.77; H, 4.68; N, 2.24. Found: C, 46.79; H, 4.92; N, 2.09.

Self-Assembly of Hexagon 7. The donor ligand 4-(4-nitrobenzyloxy)-3,5-(bis(4-pyridyl)ethynyl)benzoate **1** (2.45 mg, 5.00 μmol) and the 120° acceptor **4** (6.71 mg, 5.00 μmol) were added to separate glass vials. To the vials containing the donor was added 0.2 mL of CD_2Cl_2, and the resulting solution was transferred to the acceptor vial charged with 0.2 mL of CD_2Cl_2. This process was repeated thrice (3 × 0.15 mL) to ensure quantitative transfer of the donor to the acceptor. The reaction solution was then stirred at ambient temperature for 4 h to yield a homogeneous yellow solution. The solution was transferred into the NMR tube to collect ^{1}H and ^{31}P NMR spectra. Solid product was obtained by removing the solvent under vacuum pump. Yield: 95%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.73 (d, 12H, J = 5.1 Hz), 8.37 (s, 6H), 8.24 (d, 6H, J = 8.7 Hz), 7.90 (d, 6H, J = 8.7 Hz), 7.75 (d, 12H, J = 6.0 Hz), 7.58−7.52 (m, 24H), 5.79 (s, 6H), 3.97 (s, 9H), 1.37 (m, 72H), 1.10−1.21 (m, 108H). ^{31}P $\{^1$H$\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 13.62 (s, $^1J_{Pt-P}$ = 2641.9 Hz). Anal. Calcd for $C_{204}H_{261}F_{18}N_9O_{36}P_{12}Pt_6S_6$: C, 44.62; H, 4.79; N, 2.30. Found: C, 44.95; H, 5.13; N, 2.21.

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Supporting Information Available: Spectroscopic characterization of compound **1** and assemblies **5**, **6**, and **7**. Molecular modeling results of [2 + 2] rhomboid **6** and [3 + 3] hexagon **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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