Synthesis of a Bis(pyridyl)-Substituted Perylene Diimide Ligand and Incorporation into a Supramolecular Rhomboid and Rectangle via Coordination Driven Self-Assembly

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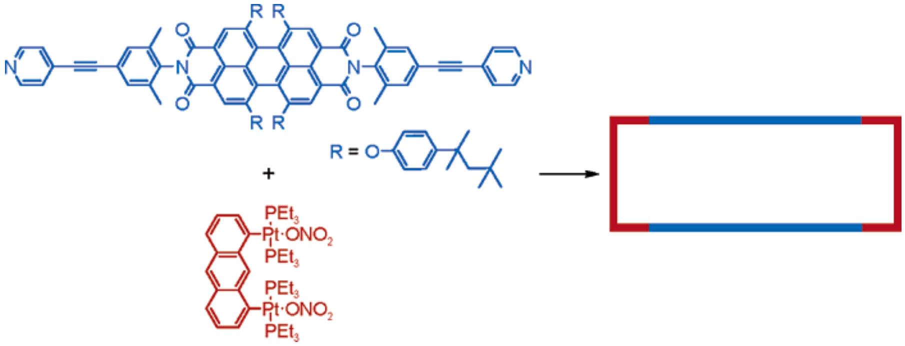

The synthesis of a bis(pyridyl)-substituted perylene diimide ligand and its incorporation into a supramolecular rhomboid and rectangle via platinum-mediated self-assembly is reported. Both ensembles are characterized by multinuclear NMR and electrospray ionization mass spectrometry. In addition, the UV/vis spectra of the ensembles exhibit displaced and enhanced absorptions relative to the starting ligand. Size estimations using MM2 simulations show the assemblies are almost 46 Å in length.

Introduction

Coordination-driven transition-metal-mediated self-assembly of discrete structures is now a well-established field.[1−8] However, many of the ensembles prepared to date were built from simple, fairly inert building blocks often aliphatic or aromatic in nature. Recent efforts have focused on incorporating functionality into the final assembly. For example, we recently reported[9] a supramolecular optical sensor capable of Ni(II), Cd(II), and Cr(III) uptake. Hupp and co-workers[10] have designed square- and loop-shaped macrocycles from salen-type components which interconvert upon Zn coordination. They have also prepared squares from Zn and Mn porphyrin ligands which served as epoxidation catalysts.[11]

This desire to incorporate functional ligands into supramolecular structures led us to investigate perylene diimide based dyes.[12] Their favorable physical and chemical properties have allowed them to be used as pigments in numerous industrial settings.[13] Other application-oriented areas include laser dyes and fluorescent light collectors,[14−17] semiconducting electronic materials,[18,19] organic field effect transistors,[20] and photovoltaics.[21]

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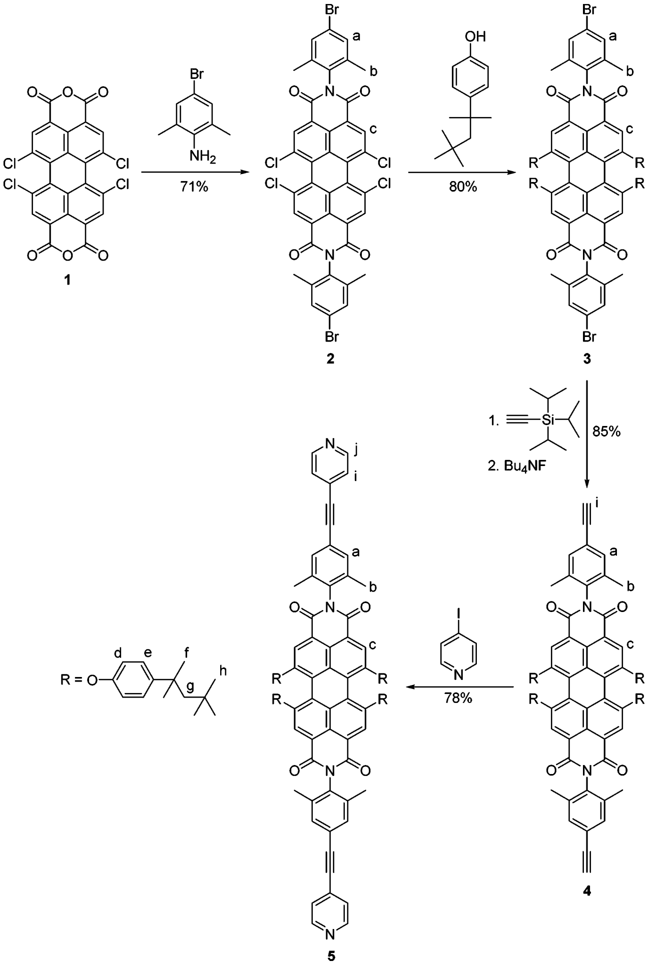
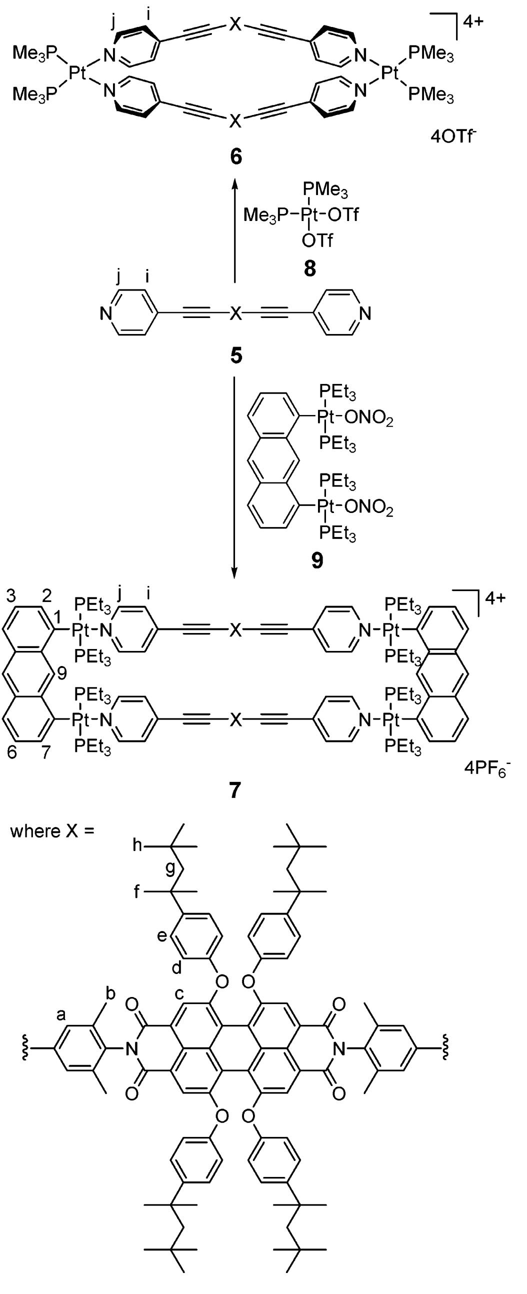
SCHEME 1. Synthesis of Perylene Diimide 5



SCHEME 2. Self-Assembly of Rhomboid 6 and Rectangle 7



Despite all this research, little is known about the incorporation of this class of compounds into larger supramolecular architectures. Würthner and co-workers[22–24] have reported several molecular squares containing simple perylene diimide precursors. Further investigation into these materials is highly warranted as it may reveal novel electronic and optical properties not present in the starting material. Herein, we report the synthesis of a new bis(pyridyl)-substituted perylene diimide ligand **5** and then describe its incorporation into a supramolecular rhomboid **6** and rectangle **7** via platinum-mediated self-assembly.

Results and Discussion

The synthesis of the perylene diimide **5** is shown in Scheme 1. In the first step, 1,6,7,12-tetrachloro-3,4,9,10-tetracarboxylic acid dianhydride **1** was imidated with 4-bromo-2,6-dimethylaniline in propionic acid to give **2** in 71% yield. Next, substitution of the chlorides with 4-(*tert*-octyl)phenol in 1-methyl-2-pyrrolidinone afforded **3** in 80% yield. Direct conversion of **3** to **5** with 4-ethynylpyridine was unsuccessful possibly due to the deactivating influence of the imide structure on the bromide. Instead, **3** was reacted with triisopropylsilylacetylene in the presence of Pd(II)/CuI catalysts and then the silyl group removed from the organic framework with tetrabutylammonium fluoride to give bis(acetylene) **4** in 85% yield. This species was coupled with 4-iodopyridine[25] in the final step to afford the desired ligand **5** in 78% yield.

The self-assembly of rhomboid **6** and rectangle **7** is shown in Scheme 2. Rhomboid **6** was easily prepared by

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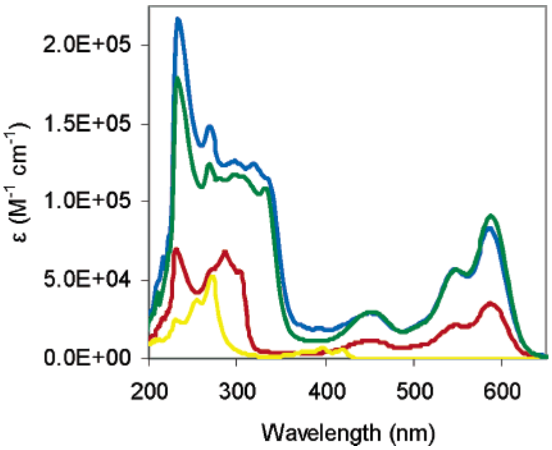

FIGURE 1. UV/vis spectra of **5** (red), **6** (green), **7** (blue), and **9** (yellow) in CH_2Cl_2.

combining ligand **5** with *cis*-$(PMe_3)_2Pt(OTf)_2$ **8** in a 1:1 ratio in acetone-d_6 at room temperature. After 20 h, the $^{31}P\{^1H\}$ NMR spectrum displayed a sharp singlet near −28 ppm due to **6** shifted approximately 8 ppm upfield relative to **8**. This is consistent with back-donation from the platinum atoms. The ^{195}Pt satellites flanking this peak were significantly broadened into the baseline. They were identified by close examination of the integration trace. The ^1H spectrum was also quite simple owing to the highly symmetrical nature of **6**. A broadened singlet for the α-pyridyl hydrogens at 9.25 ppm was shifted 0.6 ppm downfield relative to **5** because of the loss of electron density which occurs upon coordination. A few minor (<5%) byproducts were also formed. Evidence for the 2 + 2 stoichiometry was provided by electrospray ionization mass spectrometry (ESIMS). Isotopically resolved peaks centered at *m/z* 1359.9 and 982.8 were assigned to $[\mathbf{6}-3OTf^-]^{3+}$ and $[\mathbf{6}-4OTf^-]^{4+}$, respectively. Both are in good agreement with their theoretical distributions.

Formation of rectangle **7** required heating an aqueous acetone-d_6 solution of **5** and clip **9** for 120 h. The product was isolated as the hexafluorophosphate salt after anion exchange with KPF_6. In the $^{31}P\{^1H\}$ spectrum **7** gave rise to a singlet near 9 ppm with concomitant ^{195}Pt satellites. A smaller (~13%) unidentified species was present near 6 ppm. Inequivalent α- and *β*-pyridine hydrogens were obvious in the ^1H spectrum, in line with other related rectangles.[26] In the ESI mass spectrum of the nitrate salt partially resolved signals for $[\mathbf{7}-3NO_3^-]^{3+}$ *m/z* 1791.9 and $[\mathbf{7}-4NO_3^-]^{4+}$ *m/z* 1328.5 (base peak) added support to the structure.

The UV/vis spectra of assemblies **6**, **7** and starting materials **5**, **9** in CH_2Cl_2 are shown in Figure 1. In the visible range, perylene diimide based bands at 452, 548, and 588 nm of **5** experience a very small shift in wavelength (<5 nm) and an increase in absorption intensity upon incorporation into assemblies **6**, **7**. Würthner and co-workers have reported similar behavior in their molecular squares.[22,23] More pronounced changes were observed in the UV region. Specifically, $\pi-\pi^*$ transitions of **5** at 288 and 304 nm are red-shifted in **6**, **7** by about 30 nm as electronic reorganization near the metal sites occurs upon macrocycle formation. These bands, including an anthracene-based absorption at 268 nm, also increase in intensity in **6**, **7**. We have documented this behavior previously in some of our simpler supramolecular systems.[26,27]

As crystals suitable for X-ray structure determination could not be obtained, we optimized the geometry of **6** and **7** with the MM2 force-field simulation[28] (Figure 2). In **6**, the distance between the platinum atoms is 35.7 Å and the perylene diimide ligands are separated by 7.6 Å in the center of the cavity. One methyl group attached to each phenyl ring points into the interior. Given this, together with the bulky phenoxy substituents, the cavity appears to be rather inaccessible to anything but the smallest guest molecules. The rectangle **7** is almost 46 Å in length with a Pt−Pt distance similar to **6** (36.9 Å). However, its interior cavity is significantly wider (11.4 Å) and thus should be more amenable to guest inclusion. In both models the perylene diimide core is twisted out of planarity due to electrostatic repulsion between the oxygen nuclei of the phenoxy substituents.[29] Steric hindrance between the methyl-substituted phenyl rings and the imidate ring system results in these rings adopting an almost perpendicular arrangement to each other. Experimentally, we have observed no color change suggesting that any loss in conjugation must be minimal; however, **5** must exhibit a certain degree of flexibility in the closed assembly **6**.

In conclusion, the synthesis of a bis(pyridyl)-substituted perylene diimide ligand and its inclusion into two discrete supramolecules of nanoscopic dimensions via self-assembly with organoplatinum reagents has been described. They display new optical properties not present in either starting component.

Experimental Section

Methods and Materials. Organoplatinum compounds **8**[30] and **9**[26] were prepared as reported. 1,6,7,8-Tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride **1** was donated by BASF AG.[31]

***N,N′*-Bis-(2,6-dimethyl-4-bromophenyl)-1,6,7,8-tetrachloroperylene-3,4,9,10-tetracarboxdiimide 2.** 1,6,7,8-Tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride **1** (3.00 g, 5.66 mmol), 2,6-dimethyl-4-bromoaniline (11.3 g, 56.6 mmol), and propionic acid (50 mL) were stirred at 160 °C for 16 h. After the mixture was cooled to room temperature, water was added and the precipitate was filtered and washed with a mixture of methanol/water (1:1). Column chromatography (silica gel, CH_2Cl_2) gave the diimide **2** as an orange solid: yield 3.59 g, 71%; ^1H NMR ($C_2D_2Cl_4$, 300 MHz) δ 8.67 (s, 4H, H_c), 7.39 (s, 4H, H_a), 2.08 (s, 12H, H_b); ^{13}C NMR ($C_2D_2Cl_4$, 75 MHz) δ 161.7 (q), 138.4 (q), 136.0 (q), 133.8 (t), 132.6 (q), 132.0 (t), 131.8 (q), 129.4 (q), 124.1 (q), 123.4 (q), 123.1 (q), 18.2 (CH_3); MS (FD, 8 kV) *m/z* 894.2 (100) [M^+] (calcd for $C_{40}H_{20}Br_2Cl_4N_2O_4$ 894.22 g/mol), 447.3 (22) [$(M/2)^+$]; UV/vis ($CHCl_3$) λ_{max} (ϵ, M^{-1} cm^{-1}) 522 (42946), 488 (29832), 427 (11392). Anal. Calcd for $C_{40}H_{20}Br_2Cl_4N_2O_4$: C, 53.73; H, 2.25; N, 3.13. Found: C, 53.71; H, 2.26; N, 3.09.

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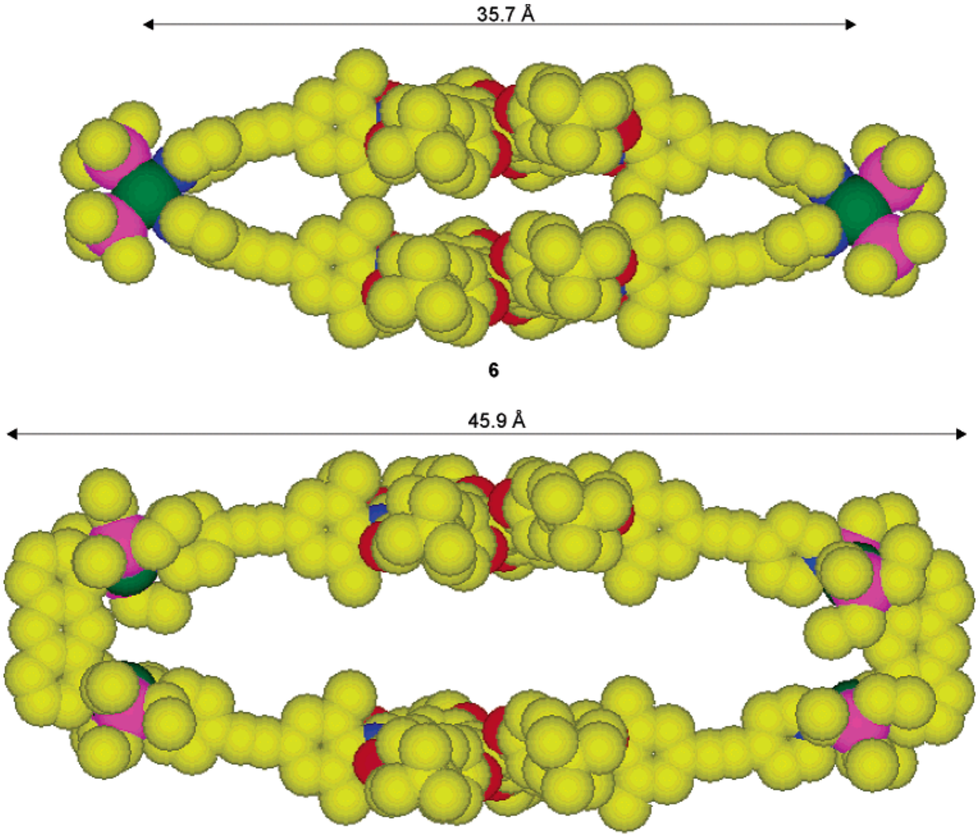

FIGURE 2. Space-filling models of **6** and **7** optimized with the MM2 force-field simulation.[28] Key: yellow = C, blue = N, red = O, pink = P, green = Pt. Hydrogens are omitted for clarity.

***N,N′*-Bis(2,6-dimethyl-4-bromophenyl)-1,6,7,8-tetra-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]perylene-3,4,9,10-tetracarboxdiimide 3.** A solution of **2** (1.50 g, 1.68 mmol), 4-(*tert*-octyl)phenol (3.46 g, 16.8 mmol), and K_2CO_3 (1.16 g, 8.39 mmol) in 1-methyl-2-pyrrolidinone (50 mL) was stirred at 90 °C for 16 h. After being cooled to room temperature, the reaction mixture was precipitated from a half-concentrated HCl solution. Vacuum filtration and column chromatography (silica gel, petroleum ether/CH_2Cl_2 3:2) gave **3** as a red solid: yield 2.11 g, 80%; mp 341.9 °C dec; ^{1}H NMR ($C_2D_2Cl_4$, 300 MHz) δ 8.09 (s, 4H, H_c), 7.29 (s, 4H, H_a), 7.21 (d, ^3J = 8.5 Hz, 8H, H_d), 6.84 (d, ^3J = 8.5 Hz, 8H, H_e), 2.01 (s, 12H, H_b), 1.64 (s, 8H, H_g), 1.27 (s, 24H, H_f), 0.68 (s, 36H, H_h); ^{13}C NMR ($C_2D_2Cl_4$, 125 MHz) δ 162.8 (q), 156.6 (q), 152.4 (q), 147.3 (q), 138.3 (q), 133.3 (q), 133.27 (q), 131.7 (t), 128.0 (t), 122.8 (q), 122.4 (q), 120.8 (q), 119.97 (q), 119.95 (t), 119.8 (t), 57.2 (q), 38.6 (q), 32.6 (CH_2), 32.2 (CH_3), 31.9 (CH_3), 18.2 (CH_3); MS (FD, 8 kV) *m/z* 1574.5 (100) [M^+] (calcd for $C_{96}H_{104}Br_2N_2O_8$ 1573.67 g/mol); UV/vis ($CHCl_3$) λ_{max} (ϵ, M^{-1} cm^{-1}) 592 (59959), 549 (34765), 453 (20476). Anal. Calcd for $C_{96}H_{104}Br_2N_2O_8$: C, 73.27; H, 6.66; N, 1.78. Found: C, 73.20; H, 6.74; N, 1.81.

***N,N′*-Bis(2,6-dimethyl-4-ethynylphenyl)-1,6,7,8-tetra-[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]perylene-3,4,9,10-tetracarboxdiimide 4.** A solution of **3** (1.02 g, 0.647 mmol), CuI (24.6 mg, 0.129 mmol), triphenylphosphine (34.0 mg, 0.129 mmol), and $Pd(PPh_3)_2Cl_2$ (45.4 mg, 0.647 mmol) in THF (6 mL) and triethylamine (12 mL) was heated to 80 °C. A solution of triisopropylsilylacetylene (0.272 g, 1.49 mmol) in THF (2 mL) was added via syringe, and the reaction mixture was stirred in the dark at 80 °C for 16 h in an argon atmosphere. After the mixture was cooled to room temperature, CH_2Cl_2 was added and the organic phase was washed with water, hydrochloric acid (2 N), a saturated solution of ammonium chloride, and water again. The organic phases were combined, dried with $MgSO_4$, and concentrated in vacuo. Column chromatography (silica gel, petroleum ether/CH_2Cl_2 3:2) gave the intermediate bis(silylacetylene)-substituted dye which was dissolved in dry THF (15 mL) and flushed with argon. Then a solution of $Bu_4NF{\cdot}3H_2O$ (355 mg, 1.13 mmol) in dry THF (2 mL) was added. The progress of the reaction was monitored by TLC (petroleum ether/CH_2Cl_2 7:3). After 2 h, water was added, and the mixture was extracted several times with CH_2Cl_2. The organic phases were combined and dried over $MgSO_4$ and then concentrated in vacuo. Column chromatography (silica gel, petroleum ether/CH_2Cl_2 7:3) gave **4** as a red solid: yield 0.807 g, 85%; ^{1}H NMR (CD_2Cl_2, 250 MHz) δ 8.13 (s, 4H, H_c), 7.35−7.32 (m, 12H, H_{a+d}), 6.93 (d, ^3J = 8.5 Hz, 8H, H_e), 3.14 (s, 2H, H_i), 2.06 (s, 12H, H_b), 1.74 (s, 8H, H_g), 1.36 (s, 24H, H_f), 0.76 (s, 36H, H_h); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 162.8 (q), 156.7 (q), 153.0 (q), 147.4 (q), 136.7 (q), 135.3 (q), 133.5 (q), 132.3 (t), 128.2 (t), 122.9 (q), 122.8 (q), 120.9 (q), 120.3 (q), 120.0 (t), 119.9 (t), 83.4 (q, ethynyl), 77.7 (CH, ethynyl), 57.3 (q), 38.7 (q), 32.7 (CH_2), 32.0 (CH_3), 31.7 (CH_3), 17.8 (CH_3); MS (FD, 8 kV) *m/z* 1463.4 (100) [M^+] (calcd for $C_{100}H_{106}N_2O_8$ 1463.92 g/mol); UV/vis ($CHCl_3$) λ_{max} (ϵ, M^{-1} cm^{-1}) 591 (52790), 549 (30461), 454 (17653).

Perylene Diimide 5. A solution of **4** (100 mg, 0.0685 mmol), CuI (3.25 mg, 17.1 μmol), triphenylphosphine (4.48 mg, 17.1 μmol), and $Pd(PPh_3)_2Cl_2$ (6.00 mg, 8.55 μmol) in THF (1 mL) and triethylamine (3 mL) was prepared. 4-Iodopyridine (35.0 mg, 0.171 mmol) was added, and the reaction mixture was stirred at room temperature in the dark in an argon atmosphere. After 2 days, CH_2Cl_2 and water were added to the reaction mixture and the organic phase was washed with water, hydrochloric acid (2 N), a saturated solution of ammonium chloride, and again with water. The organic phases were combined, dried with $MgSO_4$, and concentrated in vacuo. Column chromatography (silica gel, CH_2Cl_2/ethyl acetate 7:3) followed by recrystallization with methanol gave **5** as a red solid: yield 86.4 mg, 78%; ^{1}H NMR (CD_2Cl_2, 250 MHz) δ 8.59

(d, $^3J = 5.4$ Hz, 4H, H_j), 8.14 (s, 4H, H_c), 7.45−7.42 (m, 8H, H_{a+i}), 7.34 (d, $^3J = 8.5$ Hz, 8H, H_d), 6.93 (d, $^3J = 8.5$ Hz, 8H, H_e), 2.10 (s, 12H, H_b), 1.74 (s, 8H, H_g), 1.36 (s, 24H, H_f), 0.76 (s, 36H, H_h); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 162.8 (q), 156.8 (q), 153.0 (q), 149.8 (t), 147.4 (q), 137.0 (q), 133.6 (q), 132.1 (t), 128.3 (t), 126.0 (t), 122.9 (q), 122.8 (q) 120.9 (q), 120.4 (q), 119.99 (q), 119.96 (t), 94.0 (q, ethynyl), 87.2 (q, ethynyl), 57.4 (q), 38.7 (q), 32.7 (CH_2), 32.0 (CH_3), 31.8 (CH_3), 17.9 (CH_3); MS (FD, 8 kV) *m/z* 1618.4 (100) [M$^+$] (calcd for $C_{110}H_{112}N_4O_8$ 1618.09 g/mol); UV/vis ($CHCl_3$) λ_{max} (ϵ, M^{-1} cm^{-1}) 592 (53508), 549 (30829), 454 (16872), 304 (80856), 288 (95810). Anal. Calcd for $C_{110}H_{112}N_4O_8$: C, 81.65; H, 6.98; N, 3.46. Found: C, 81.86; H, 7.07; N, 3.42.

Self-Assembly of Rhomboid 6. A red solution of perylene diimide **5** (5.6 mg, 3.4 μmol) in acetone-d_6 (0.5 mL) was added dropwise to a stirred solution of *cis*-$(PMe_3)_2Pt(OTf)_2$ **8** (2.2 mg, 3.4 μmol) in acetone-d_6 (0.5 mL). After being stirred at room temperature for 20 h, the reaction mixture was transferred to an NMR tube for analysis. The solution was removed under a gentle stream of N_2 gas to give the assembly **6** as a violet solid: yield 95%; ^{1}H NMR (acetone-d_6, 300 MHz) δ 9.25 (br s, 8H, H_j), 8.12 (s, 8H, H_c), 7.81 (d, $^3J = 6.6$ Hz, 8H, H_i), 7.43 (m, 24H, H_a and H_d), 7.03 (d, $^3J = 8.7$ Hz, 16H, H_e), 2.13 (s, 24H, H_b), 1.79 (m, 52H, PMe_3 and H_g), 1.38 (s, 48H, H_f), 0.77 (s, 72H, H_h); ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz) δ −27.8 (s, ^{195}Pt satellites $^1J_{Pt-P} = 3170$ Hz). Anal. Calcd for $C_{236}H_{260}F_{12}N_8O_{28}P_4Pt_2S_4$: C, 62.61; H, 5.79; N, 2.48. Found: C, 62.63; H, 6.05; N, 2.31.

Self-Assembly of Rectangle 7. Perylene diimide **5** (4.0 mg, 2.5 μmol) was added slowly to a stirred solution of clip **9** (2.9 mg, 2.5 μmol) in D_2O (0.1 mL) and acetone-d_6 (0.9 mL) in a 1-dram vial. The red mixture was immersed in an oil bath at 50 °C for 120 h during which time the NMR spectra simplified. The red suspension was filtered through a glass microfiber filter. The product **7** was precipitated as the hexafluorophosphate salt by addition of KPF_6. It was collected and washed with H_2O twice then dried in vacuo: yield 80%; ^{1}H NMR (acetone-d_6, 300 MHz) δ 9.50 (s, 2H, H_9), 9.22 (d, $^3J = 6.0$ Hz, 4H, H_j), 9.10 (d, $^3J = 6.0$ Hz, 4H, $H_{j'}$), 8.53 (s, 2H, H_{10}), 8.27−7.85 (m, 24H, H_i, $H_{2,4,5,7}$ and H_c), 7.48 (s, 8H, H_a), 7.36 (d, $^3J = 8.8$ Hz, 16H, H_d), 7.26 (t, $^3J = 7.6$ Hz, 4H, $H_{3,6}$), 6.88 (d, $^3J = 8.6$ Hz, 16H, H_e), 2.09 (s, 24H, H_b), 1.77 (s, 16H, H_g), 1.63 (br s, 48H, PCH_2), 1.37 (s, 48H, H_f), 1.01 (m, 72H, PCH_2CH_3), 0.77 (s, 72H, H_h); ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz) δ 8.96 (s, ^{195}Pt satellites $^1J_{Pt-P} = 2636$ Hz). Anal. Calcd for $C_{296}H_{360}F_{24}N_8O_{16}P_{12}Pt_4 \cdot 17H_2O$: C, 57.34; H, 6.40; N, 1.81. Found: C, 57.03; H, 6.10; N, 1.71.

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Supporting Information Available: NMR and mass spectral data for assemblies **6**, **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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