Construction of Hexagonal Prisms of Variable Size via Coordination-Driven Multicomponent Self-Assembly

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Experimental Section

Methods and Material: Hexadentate ligand **1**[1,2] and platinum triflate **2**[3] were synthesized according to published literature procedures. The free acids of ligands **3b**, **3c**, and **3d** were purchased from Aldrich and TCI companies. They were then dissolved in an aqueous solution containing 2 equiv. of the sodium hydroxide. Evaporation of the solvent afforded a quantitative recovery of **3b**, **3c** and **3d**. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a Varian Unity 300 spectrometer. The ^{1}H NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an external unlock sample of 85% H_3PO_4 (δ 0.0). Mass spectra for **4a–d** were determined on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system.

General Procedure for the Self-Assembly. Hexadentate donors **1** (2 equiv), donors **3a**–**d** (6 equiv) and organoplatinum acceptor **2** (12 equiv) were placed in one glass vial. To the vial containing acceptors and donors was added 1 mL acetone aqueous solution (*v/v* 9:1). The vial was sealed with Teflon tape, and the resulting suspension was stirred at 50-56 ^{o}C for 6 h, after which the clear solution had formed. The OTf^- counterions were exchanged for PF_6^- using an aqueous solution of KPF_6 to precipitate the product, which was collected and washed with excess water and then dried in vacuum.

Supramolecular hexagonal prism 4a. Yield 93%. MS (ESI) calcd for $[M - 4PF_6]^{4+}$ *m/z* 2751.3, found 2751.2; calcd for $[M - 5PF_6]^{5+}$ *m/z* 2171.5, found 2171.5. ^{1}H NMR (Acetone-d_6, 300 MHz): δ 9.22 (s, 24H, H_α-Py for donor **1**), 8.93 (s, 24H, H_α-Py for donor **3a**), 8.14 (d, J = 6.0 Hz, 24H, H_β-Py for donor **3a**), 7.81 (d, J = 6.0 Hz, 24H, H_β-Py for donor **1**), 7.46 (d, J = 9.0 Hz, 24H, ArH), 7.17 (d, J = 9.0 Hz, 24H, ArH), 1.92-1.84 (m, 144H, PCH_2CH_3), 1.37-1.21 (m, 216H, PCH_2CH_3); ^{31}P {^{1}H} NMR (Acetone-d_6 , 121.4 MHz): δ 0.85 (dd, ^{2}Jp-p = 20.68 Hz, ^{195}Pt satellites, $^{1}J_{Pt\text{-}P}$ = 3081 Hz); Anal. Calcd for $C_{348}H_{504}F_{144}N_{24}P_{48}Pt_{12}$: C, 36.07; H, 4.38; N, 2.90. Found: C, 36.25; H, 4.56; N, 2.90.

Supramolecular hexagonal prism 4b. Yield 96%. MS (ESI) calcd for $[M - 4PF_6]^{4+}$

m/z 2328.3, found 2328.3; calcd for $[M - 5PF_6]^{5+}$ *m/z* 1834.1, found 1834.0. ^{1}H NMR (Acetone-d_6, 300 MHz): δ 8.76 (s, 24H, H_α-Py for donor **1**), 7.80 (d, J = 6.0 Hz, 24H, H_{phenyl} for donor **3b**), 7.57 (s, 24H, H_β-Py for donor **1**), 7.50 (d, J = 9.0 Hz, 24H, H_{phenyl} for donor **1**), 7.20 (d, J = 6.0 Hz, 24H, H_{phenyl} for donor **1**), 1.92-1.77 (m, 144H, PCH_2CH_3), 1.35-1.14(m, 216H, PCH_2CH_3); ^{31}P {^{1}H} NMR (Acetone-d_6, 121.4 MHz): δ 6.19 (d, $^2J_{P\text{-}P}$ = 21.85 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3228 Hz), 1.06 (d, $^2J_{P\text{-}P}$ = 21.85 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3403 Hz); Anal. Calcd for $C_{336}H_{480}F_{72}N_{12}O_{24}P_{36}Pt_{12}$: C, 40.78; H, 4.89; N, 1.70. Found: C, 40.49; H, 5.02; N, 1.80.

Supramolecular hexagonal prism 4c. Yield 94%. MS (ESI) calcd for $[M - 5PF_6]^{5+}$ *m/z* 1924.7, found 1924.7. ^{1}H NMR (Acetone-d_6, 300 MHz): δ 8.96 (s, 24H, H_α-Py for donor **1**), 8.03 (d, J = 9.0 Hz, 24H, H_{phenyl} for donor **3c**), 7.71 (s, 48H, H_β-Py for donor **1** and H_{phenyl} for donor **3c**), 7.49 (d, J = 6.0 Hz, 12H, H_{phenyl} for donor **1**), 7.30 (d, J = 9.0 Hz, 12H, H_{phenyl} for donor **1**), 7.10 (d, J = 6.0 Hz, 12H, H_{phenyl} for donor **1**), 6.88 (d, J = 9.0 Hz, 12H, H_{phenyl} for donor **1**), 1.92-1.81 (m, 144H, PCH_2CH_3), 1.39-1.18 (m, 216H, PCH_2CH_3); ^{31}P {^{1}H} NMR (Acetone-d_6, 121.4 MHz): δ 6.73 (d, $^2J_{P\text{-}P}$ = 21.85 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3201 Hz), 1.10 (d, $^2J_{P\text{-}P}$ = 21.85 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3437 Hz); Anal. Calcd for $C_{372}H_{504}F_{72}N_{12}O_{24}P_{36}Pt_{12}$: C, 43.16; H, 4.91; N, 1.62. Found: C, 42.95; H, 5.04; N, 1.67.

Supramolecular hexagonal prism 4d. Yield 91%. MS (ESI) calcd for $[M - 5PF_6]^{5+}$ *m/z* 1958.4, found 1958.4; calcd for $[M - 6PF_6]^{6+}$ *m/z* 1607.9, found 1607.8. ^{1}H NMR (Acetone-d_6, 300 MHz): δ 8.95 (s, 24H, H_α-Py for donor **1**), 7.99-7.81 (m, 72H, H_β-Py for donor **1** and H_{phenyl} for donor **3d**), 7.63 (d, J = 9.0 Hz, 12H, H_{phenyl} for donor **1**), 7.36-7.28(m, 24H, H_{phenyl} for donor **1**), 7.01 (d, J = 9.0 Hz, 12H, H_{phenyl} for donor **1**), 1.89-1.76 (m, 144H, PCH_2CH_3), 1.33-1.21 (m, 216H, PCH_2CH_3); ^{31}P {^{1}H} NMR (Acetone-d_6, 121.4 MHz): δ 7.16 (d, $^2J_{P\text{-}P}$ = 21.85 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3170 Hz), 2.13 (d, $^2J_{P\text{-}P}$ = 21.85 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3388 Hz); Anal. Calcd for $C_{372}H_{504}F_{72}N_{24}O_{24}P_{36}Pt_{12}$: C, 42.47; H, 4.83; N, 3.20. Found: C, 42.14; H, 4.81; N, 3.13.

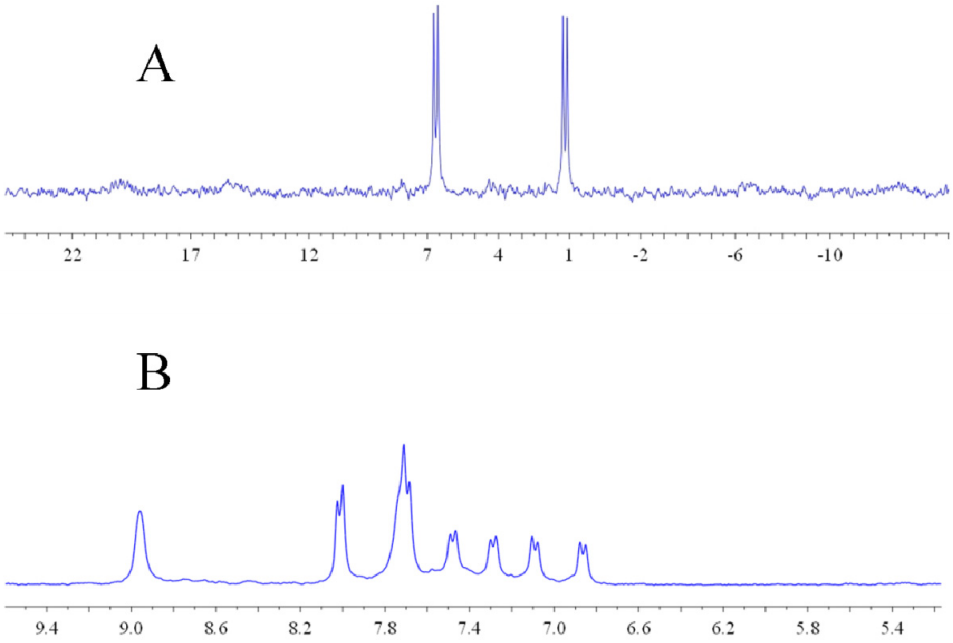

Figure S1. $^{31}P\{^{1}H\}$ (A) and partial ^{1}H NMR (B) spectra of self-assembled hexagonal prism **4c**.

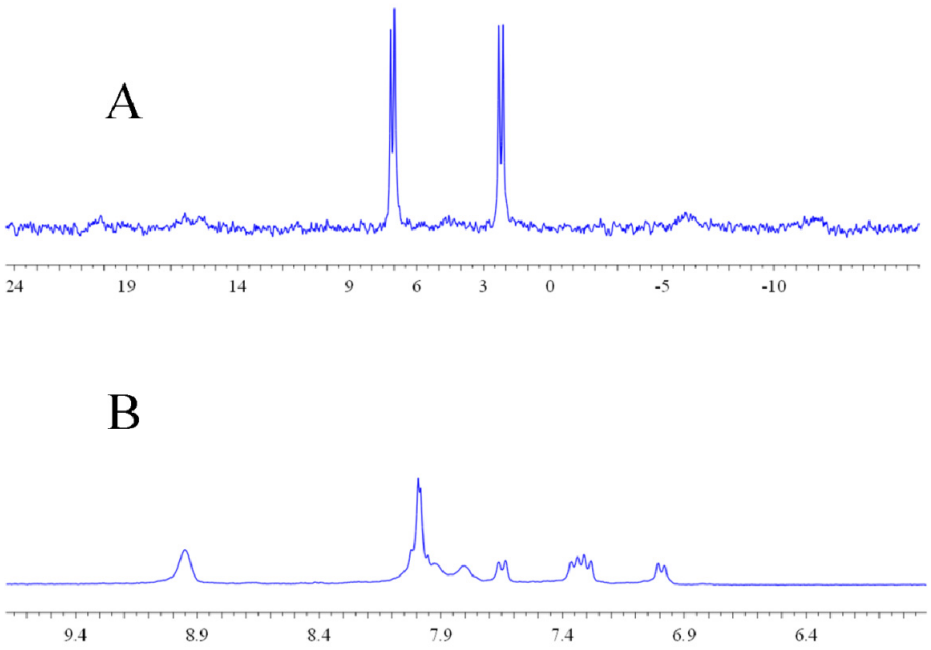

Figure S2. $^{31}P\{^{1}H\}$ (A) and partial ^{1}H NMR (B) spectra of self-assembled hexagonal prism **4d**.

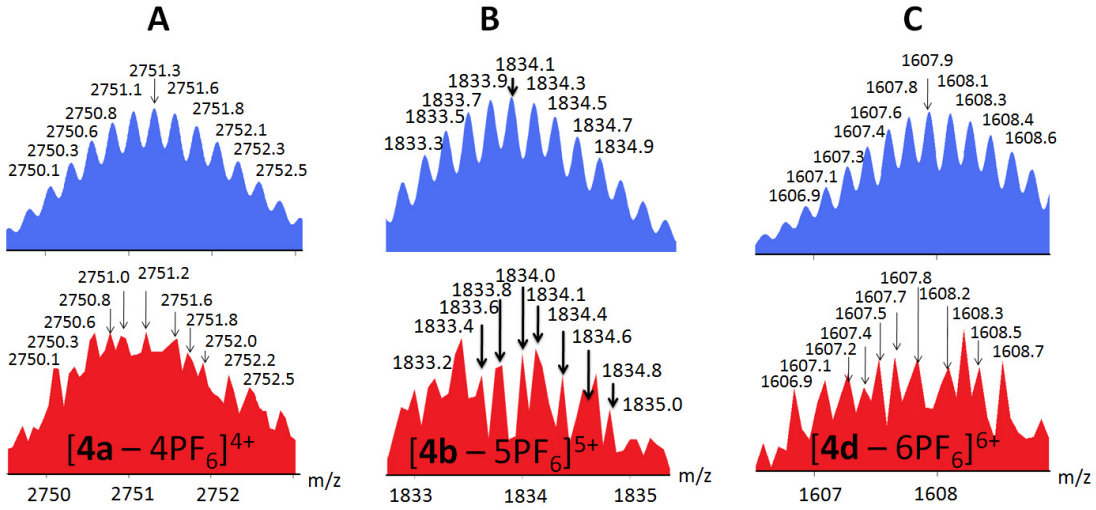

Figure S3. Theoretical (top, blue) and experimental (bottom, red) ESI-MS results for hexagonal prisms **4a** (A), **4b**(B), and **4d** (C).

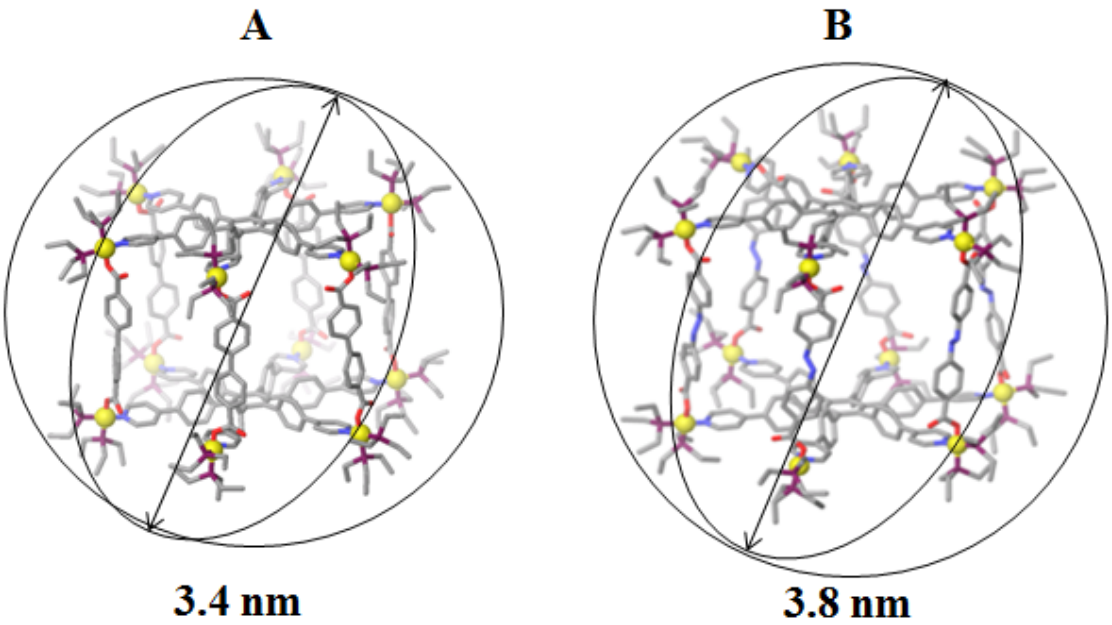

Figure S4. Molecular modeling of supramolecular hexagonal prisms **4c** (A) and **4d** (B).

References

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