

Metallosupramolecular Tetragonal Prisms via Multicomponent Coordination-Driven Template Free Self-Assembly

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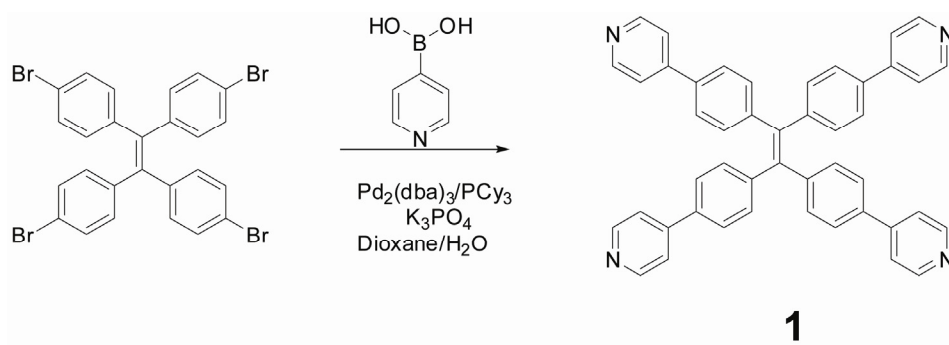
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Experimental Section

Methods and Materials: Tetra-(4-bromophenyl)ethylene was synthesized by McMurry coupling of 1, 4-bromophenone according to reported method,¹ the Suzuki coupling reaction between tetra-(4-bromophenyl)ethylene and pyridine 4-boronic acid afford donor **1**². Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a Varian Unity 300 spectrometer. The ¹H NMR chemical shifts are reported relative to residual solvent signals, and ³¹P{¹H} NMR resonances are referenced to an external unlocked sample of 85% H₃PO₄ (δ 0.0). Mass spectra for the tetragonal prism **4a** and **4b** were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system.

Synthesis of tetra-(4-pyridylphenyl)ethylene **1**:



To 50 mL schlenk bottle was added tetra-(4-bromo-phenyl)ethylene 161.0 mg (0.25 mmol), pyridine-4-boronic acid 246.0 mg(2.0 mmol), Pd₂(dba)₃ (40.0 mg) and PCy₃ (25.0) mg, then dioxane (8.0 mL) and K₃PO₄ aqueous solution(3.0 mmol) was added under nitrogen atmosphere at room temperature, the mixture solution was kept at 100 °C for 3 days. After cooling to room temperature, the reaction solution was

extracted with dichloromethane for three times, combine the organic phase and washed with water, dry with anhydrous magnesium sulfate and then subject to flash chromatography using(dichloromethane/ methanol, v : v = 10 : 1 as fluent). The product tetra-(4-pyridylphenyl)ethylene obtained as green-yellow solid. Yield: 40%. ^1H NMR (CDCl_3 , 300 MHz, 298 K): δ 8.65 (br, 8H, $\text{H}_\alpha\text{-Py}$), 7.45-7.50 (m, 20H, ArH), 7.22(br, 8H, $\text{H}_\beta\text{-Py}$); ^{13}C NMR (75 MHz, CDCl_3) δ 150.5, 147.6, 144.2, 140.9, 136.7, 132.4, 126.8, 121.5. HR-TOF-MS: Found, 641.2717 (M+H); Anal., 641.2705.

Synthesis of tetragonal prism 4a: The CD_2Cl_2 solution (0.6 mL) of Tetra-(4-pyridyl-phenyl)ethylene **1** (0.67 mg, 1.05 μmol) and 4, 4'- dipyridine **2a** (0.33 mg, 2.1 μmol) was added to the CD_3NO_2 solution of **3** (3.05 mg, 4.2 μmol) dropwisely, the mixture were kept at room temperature for 12 h and then transferred into NMR tubes for analysis or ESI-MS characterization. $^{31}\text{P}\{^1\text{H}\}$ NMR($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$, 2 : 1, 121.4MHz) δ = -0.7 ppm(^{195}Pt satellites, $^1\text{J}_{\text{Pt-P}}$: 3156 Hz); ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$, 2 : 1, 300 MHz, 298 K): δ = 8.93 (d, 16H, $\text{H}_\alpha\text{-Py}$ for donor **1**), 8.72 (d, 16H, $\text{H}_\alpha\text{-Py}$ for donor **2**), 8.05 (d, 16H, $\text{H}_\beta\text{-Py}$ for donor **2**), 7.73 (d, 16H, $\text{H}_\beta\text{-Py}$ for donor **1**), 7.10-7.40(dd, 32H, ArH), 1.36-1.37 (m, 96H, PCH_2CH_3), 1.10-1.20 (m, 144H, PCH_2CH_3); MS (ESI) for **4a** ($\text{C}_{244}\text{H}_{336}\text{F}_{48}\text{N}_{16}\text{O}_{48}\text{P}_{16}\text{Pt}_8\text{S}_{16}$): m/z: 1786.1 $[\text{M}-4\text{OTf}]^{4+}$; 1399.3 $[\text{M}-5\text{OTf}]^{5+}$.

Synthesis of tetragonal prism 4b: The CD_2Cl_2 solution (0.6 mL) of Tetra-(4-pyridyl-phenyl)ethylene **1** (0.87 mg, 1.35 μmol) and *trans*-1, 2-Di(4-pyridyl)ethylene **2b** (0.51 mg, 2.7 μmol) was added to the CD_3NO_2 solution of **3** (3.96 mg, 5.4 μmol) dropwisely, the mixture were kept at room temperature for 12 h and then transferred into NMR

tubes for analysis or ESI-MS characterization. $^{31}\text{P}\{^1\text{H}\}$ NMR($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$, 2 : 1, 121.4MHz) $\delta = -0.6$ ppm (^{195}Pt satellites, $^1J_{\text{Pt-P}}$: 3071 Hz); ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$, 300 MHz, 298 K): δ 8.77 (d, 16H, $\text{H}_\alpha\text{-Py}$ for donor **1**), 8.70 (d, 16H, $\text{H}_\alpha\text{-Py}$ for donor **2**), 7.69 (d, 16H, $\text{H}_\beta\text{-Py}$ for donor **2b**), 7.67 (d, 16H, $\text{H}_\beta\text{-Py}$ for donor **1**), 7.10-7.15, 7.40-7.49 (dd, 32H, ArH), 7.30(s, 8H, for the ethylene at donor **2b**), 1.36-1.37 (m, 96H, PCH_2CH_3), 1.10-1.20 (m, 144H, PCH_2CH_3); MS (ESI) for **4b** ($\text{C}_{252}\text{H}_{344}\text{F}_{48}\text{N}_{16}\text{O}_{48}\text{P}_{16}\text{Pt}_8\text{S}_{16}$): m/z: 1420.1 $[\text{M}-5\text{OTf}]^{5+}$.

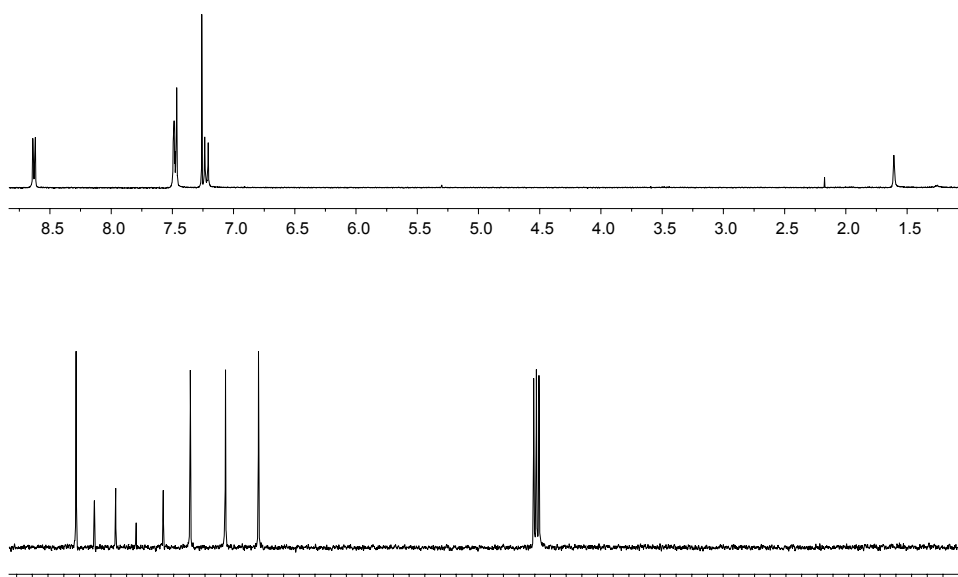


Figure S1 ^1H NMR(CDCl_3 , 300 MHz, 298 K) and ^{13}C NMR (CDCl_3 , 75 MHz, 298 K) of donor **1**

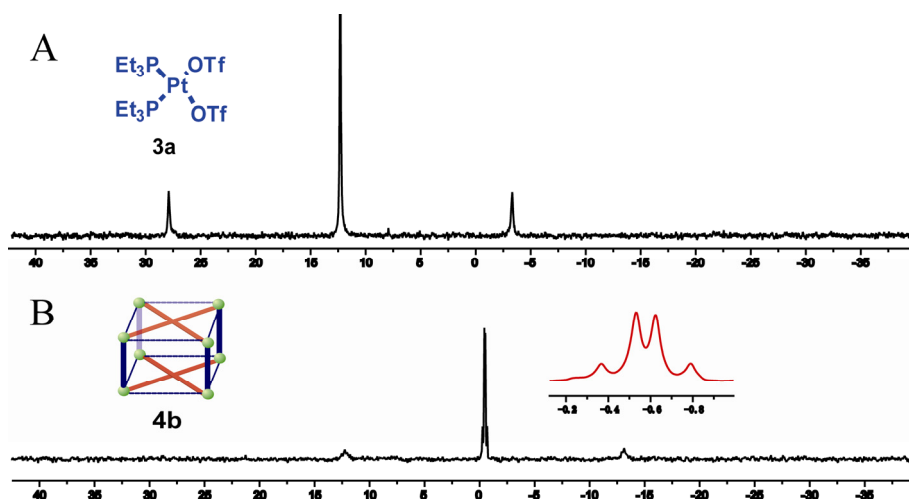


Figure S2 The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (121.4 MHz, 298K, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$ v : v = 2 : 1) of acceptor **3** (A) and tetragonal prism **4b** (B)

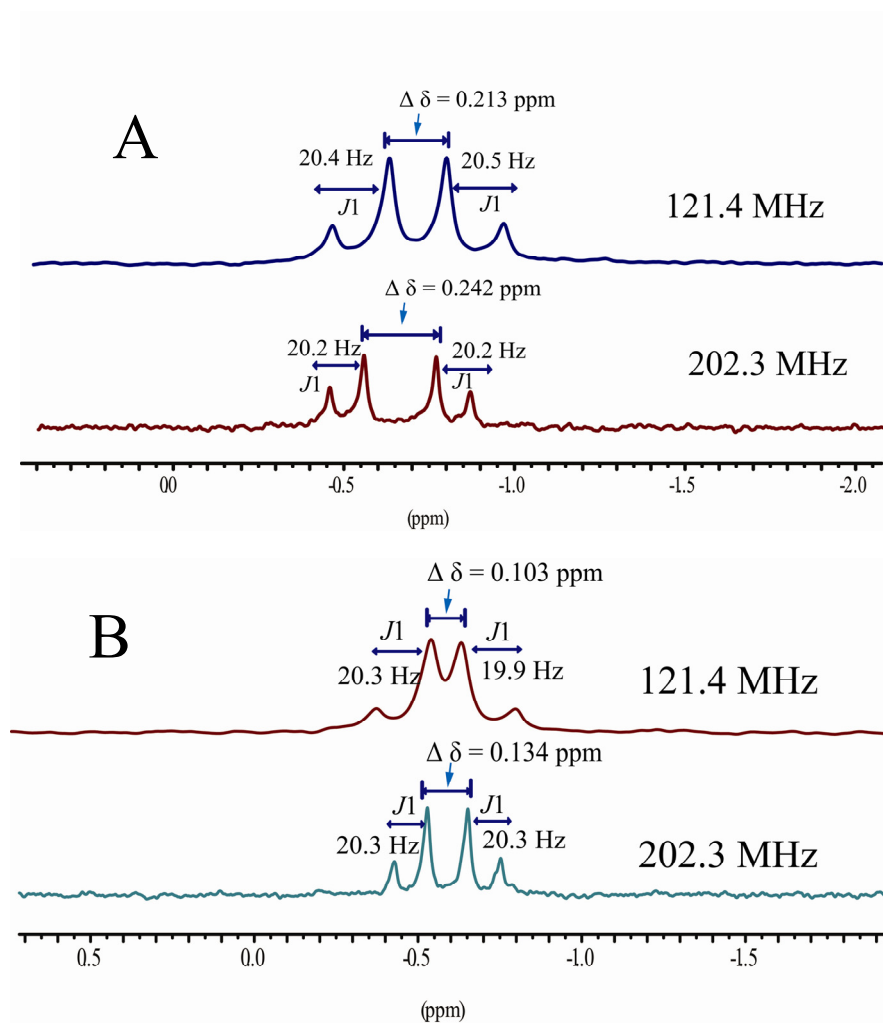


Figure S3 Strength-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (299K, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$ v : v = 2 : 1) of **4a** (A) and **4b**(B). *up*: 121.4 MHz; *down*: 202.3 MHz

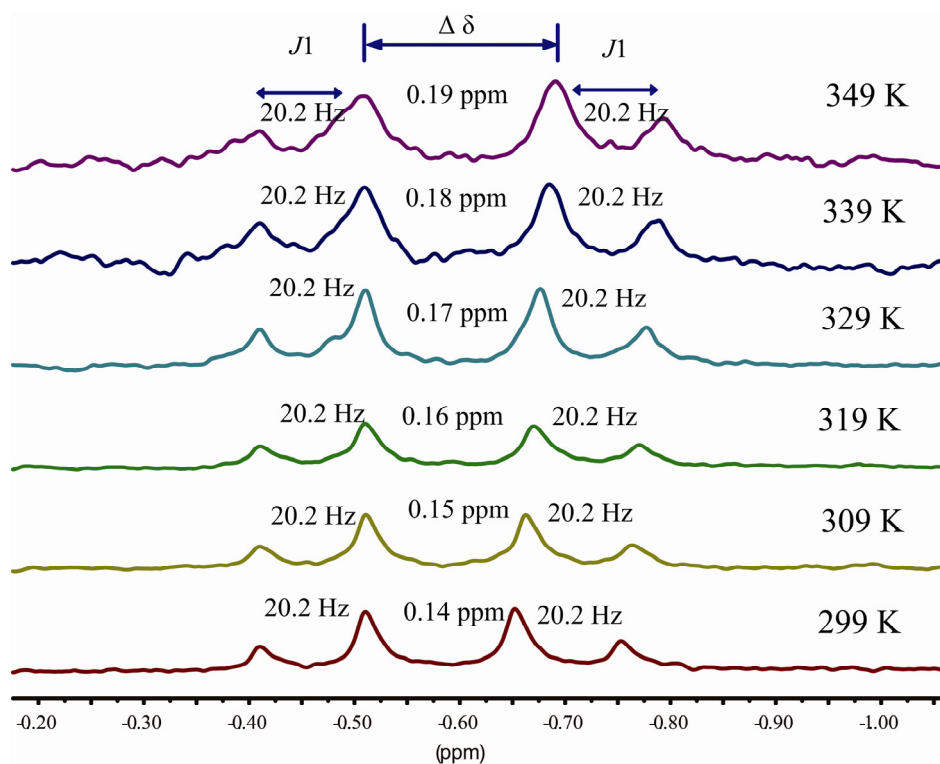


Figure S4 Temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (202.3 MHz, 299K, CD_3CN)

of **4a**

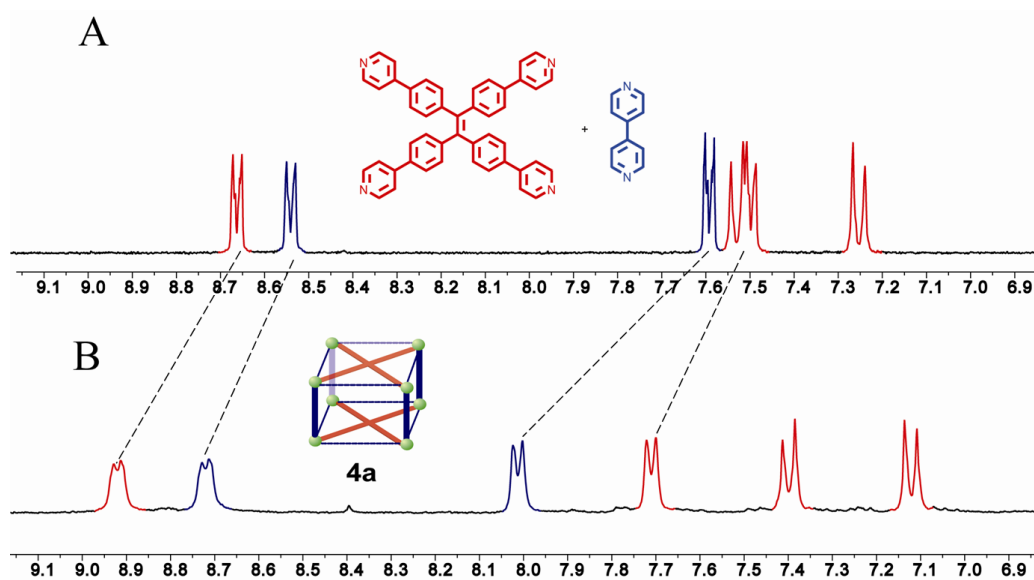


Figure S5 Partial ^1H NMR (300 MHz, 298 K) of donor **1** and **2a** mixture (A) and tetragonal prism **4a** (B) in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$ ($v : v = 2 : 1$)

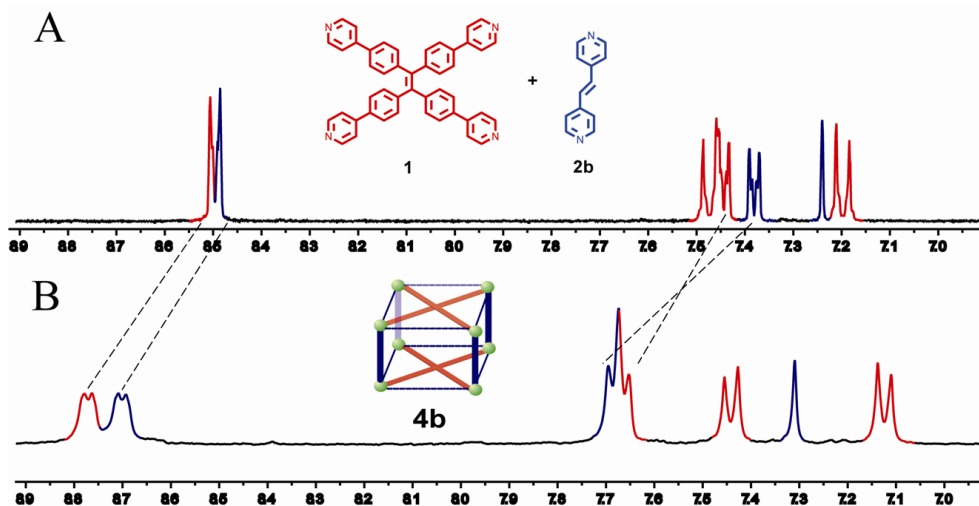


Figure S6 Partial ^1H NMR (300 MHz, 298 K) of donor **1** and **2b** mixture (A) and tetragonal prism **4b** (B) in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$ (v : v = 2 : 1)

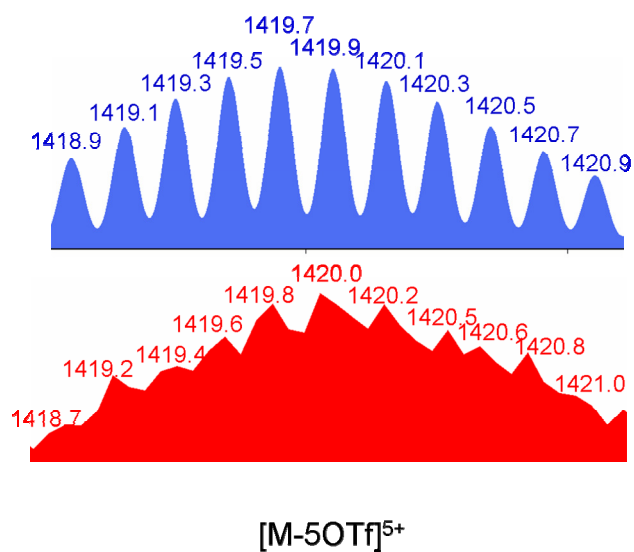


Figure S7 Theoretical (top, blue) and experimental (bottom, red) of ESI-MS results for tetragonal prism **4b**

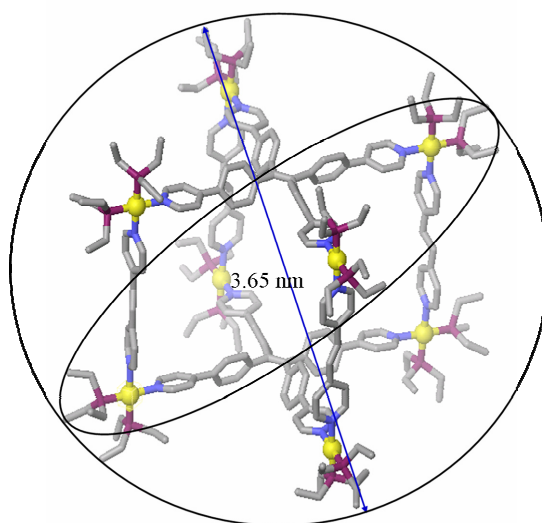


Figure S8 Molecular modeling of tetragonal prism **4b**

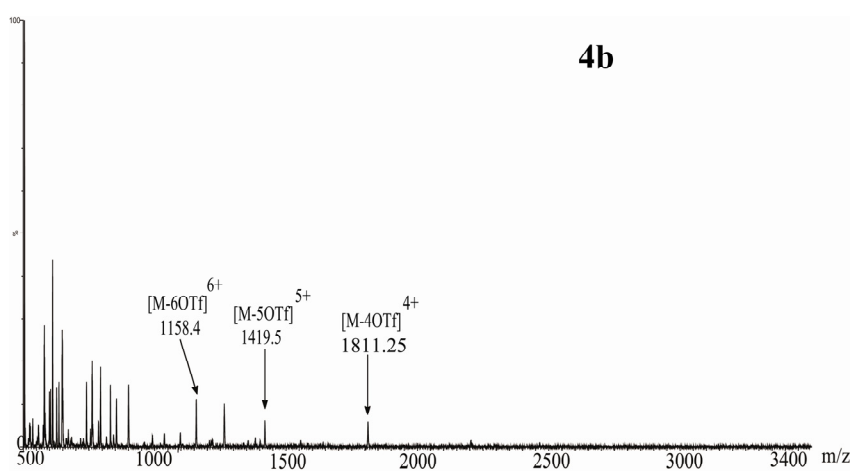
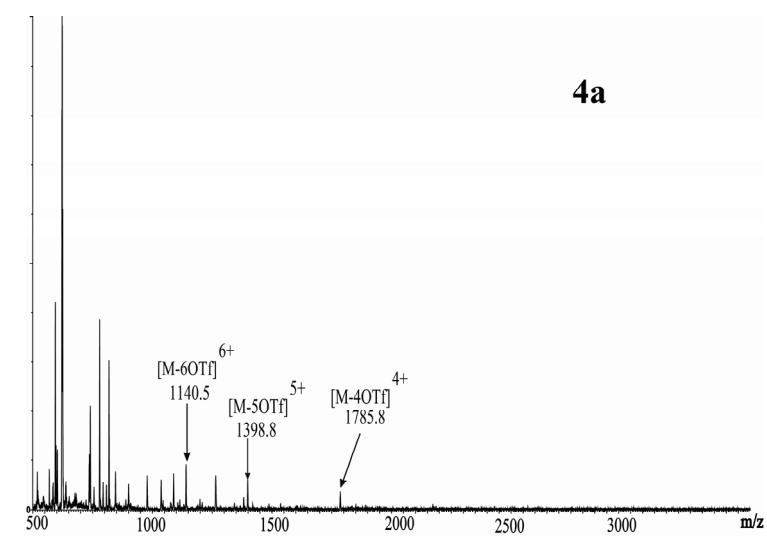


Figure S9 Low Resolution EST-MS of tetragonal prisms **4a** and **4b**

Table S1: Calculation of diffusion coefficient by PGSE measurement

Compound	Diffusion Coefficient ($10^{-6}\text{cm}^2/\text{s}$)
4a	(2.65 ± 0.12)
4b	(2.63 ± 0.12)

PGSE measurements were carried out in CD_3CN solvent at 298K. The ratio of the diffusion coefficient is proportional to the inverse of their radius of the molecule (Stokes-Einstein Equation).

Reference

1. Duan, X - F.; Zeng, J.; Lv, J - W.; Zhang, Z - B. *J. Org.Chem.* **2006**, *71*, 9873-9876.
2. Kudu, N.; Perseghini, M.; Fu, G. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 1282 – 1284.