Geometry Directed Self-Selection in the Coordination-Driven Self-Assembly of Irregular Supramolecular Polygons

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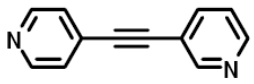
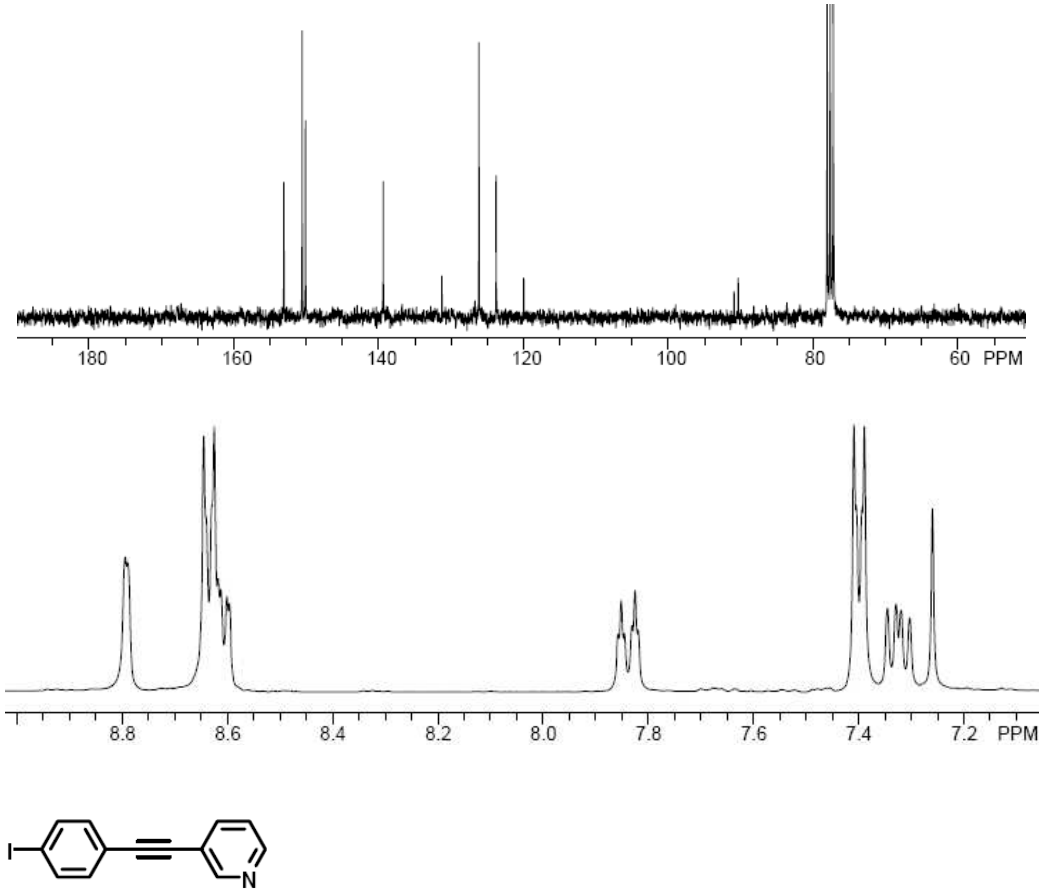
General Procedure for Sonogashira Coupling Reaction. A 50 mL Schlenk flask was charged with appropriate aryl halide, Ethynylpyridine, $Pd(PPh_3)_4$, and CuI, degassed, and back-filled three times with N_2(g). Dry THF (15 mL) and triethylamine (10 mL) were then introduced into the reaction via syringe. The reaction was allowed to stir at 60 °C for 16 h under N_2. The reaction mixture was partitioned between water (75 mL) and CH_2Cl_2 (50 mL). The organic layer was separated and extracted further with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The resulting brown residues were purified by column chromatography on silica gel.



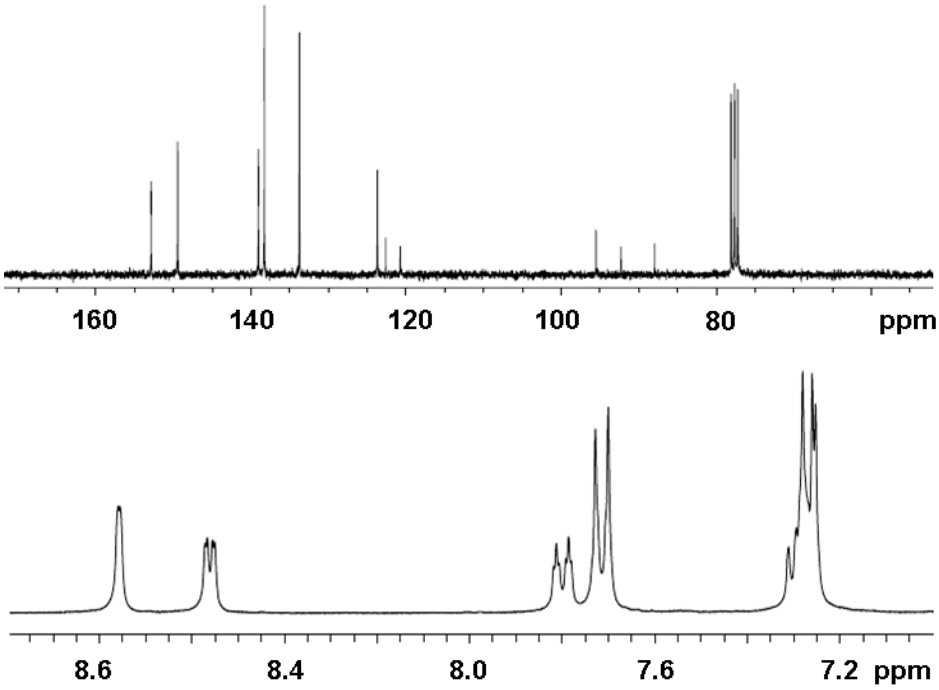
Unsymmetrical ligand 1a. Reaction scale: 4-Bromopyridine hydrochloride (368 mg, 1.89 mmol), 3-Ethynylpyridine (150 mg, 1.45 mmol), $Pd(PPh_3)_4$ (60 mg, 0.052 mmol), and CuI (10 mg, 0.052 mmol). Chromatography eluent: Acetone/CH_2Cl_2 (1:1). Yield: 150 mg (off white solid), 57.2 %. Mp 62–63 °C; ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.80 (d, 1H, *J*=1.2 Hz, H_2-3-Pyr), 8.64 (d, 2H, *J*=6.0 Hz, H_α-4-Pyr), 8.61 (dd, 1H, *J*=5.1, 1.5 Hz, H_6-3-Pyr), 7.83 (td, 1H, *J*=1.8, 8.1 Hz, H_4-3-Pyr), 7.40 (d, 2H, *J*=6.0 Hz, H_β-4-Pyr), 7.32 (dd, 1H, *J*=7.5, 5.1 Hz, H_5-3-Pyr). ^{13}C NMR ($CDCl_3$, 300MHz) δ 153.08, 150.56, 150.10, 150.60, 139.36, 131.26, 126.14, 123.78, 119.96, 90.92, 90.35 ppm. HRMS (ESI-TOF): m/z 181.0761 ($[M+H]^+$; calcd for $C_{12}H_9N_2$: 181.0766) Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.55. Found: C, 79.71; H, 4.43; N, 15.28.

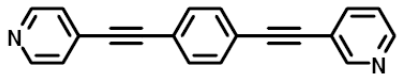
Figure S1. ^{13}C (top) and Partial ^{1}H (bottom) NMR spectra ($CDCl_3$, 300 MHz) recorded for **1a**



3-((4-iodophenyl)ethynyl)pyridine (1c). Reaction scale: 1,4-Diiodobenzene (1.44 g, 4.36 mmol), 3-Ethynylpyridine (150 mg, 1.45 mmol), $Pd(PPh_3)_4$ (60 mg, 0.052 mmol), and CuI (10 mg, 0.052 mmol). Chromatography eluent: CH_2Cl_2. Yield 150 mg (off white solid), 33.9 %. Mp 144–145 °C; ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.76 (d, 1H, *J*=1.2 Hz, H_2-3-Pyr), 8.51 (dd, 2H, *J*=4.8, 1.5 Hz, H_3-3-Pyr), 7.78 (td, 1H, *J*=7.8, 1.8 Hz, H_4-3-Pyr), 7.70 (d, J=8.4 Hz, $H_{\beta\text{-Phenylene}}$), 7.25 (m, 3H, $H_{\alpha\text{-Phenylene}}$, H_5-3-Pyr). ^{13}C NMR ($CDCl_3$, 300MHz) δ 152.86, 149.44, 139.03, 138.27, 133.74, 123.70, 122.63, 120.75, 95.50, 92.29, 87.94 ppm. HRMS (ESI-TOF): m/z 305.9789 ($[M+H]^+$; calcd for $C_{13}H_9NI$: 305.9780) Anal. Calcd for $C_{13}H_8NI$: C, 51.17; H, 2.64; N, 4.59. Found: C, 51.74; H, 2.66; N, 4.30.

Figure S2. ^{13}C (top) and Partial ^{1}H (bottom) NMR spectra ($CDCl_3$, 300 MHz) recorded for **3-((4-iodophenyl)ethynyl)pyridine (1c)**





Unsymmetrical ligand 1b. Reaction scale: **1c** (130 mg, 0.426 mmol), 4-Ethynylpyridine hydrochloride (71 mg, 0.509 mmol), $Pd(PPh_3)_4$ (40 mg, 0.035 mmol), and CuI (7 mg, 0.035 mmol). Chromatography eluent: Acetone/CH_2Cl_2 (1:1). Yield 50.0 mg (pale yellow solid), 41.9 %. Mp 183–184 °C; ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.78 (d, 1H, *J*=1.2 Hz, H_2-3-Pyr), 8.61 (d, 2H, *J*=6.0 Hz, H_α-4-Pyr), 8.56 (dd, 1H, *J*=4.8, 1.5 Hz, H_6-3-Pyr), (td, 1H, *J*=2.1, 7.8 Hz, H_4-3-Pyr), 7.55 (s, 4H, $H_{phenylene}$), 7.38 (d, 2H, *J*=6.3 Hz, H_β-4-Pyr), 7.26 (dd, 1H, *J*=7.8, 5.1 Hz, H_5-3-Pyr). ^{13}C NMR ($CDCl_3$, 300MHz) δ 152.94, 150.51, 149.94, 139.11, 132.53, 132.37, 131.71, 126.13, 123.98, 123.74, 123.04, 120.71, 93.93, 92.64, 89.24, 88.90. HRMS (ESI-TOF): m/z 281.1078 ($[M+H]^+$; calcd for $C_{20}H_{13}N_2$: 281.1079) Anal. Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.31; N, 9.99. Found: C, 84.31; H, 4.31; N, 9.56.

Figure S3. ^{13}C (a) and Partial ^{1}H (b) NMR spectra ($CDCl_3$, 300 MHz) recorded for **1b**

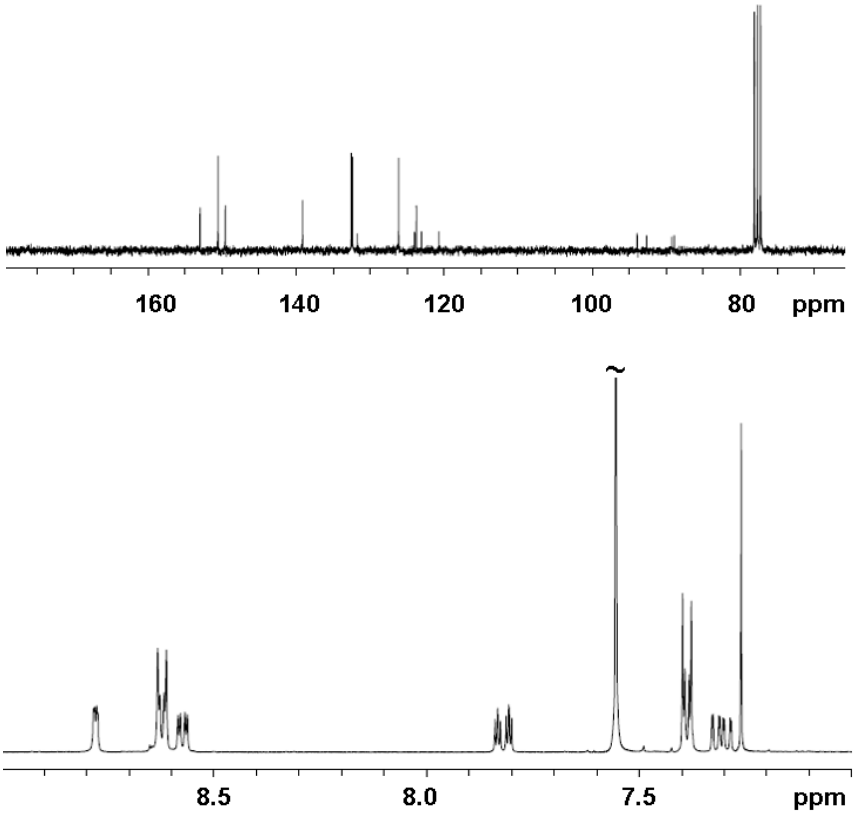


Figure S4. $^{31}P\{^{1}H\}$ (a) and ^{1}H NMR (b) spectra recorded for self-selection of **4b**.

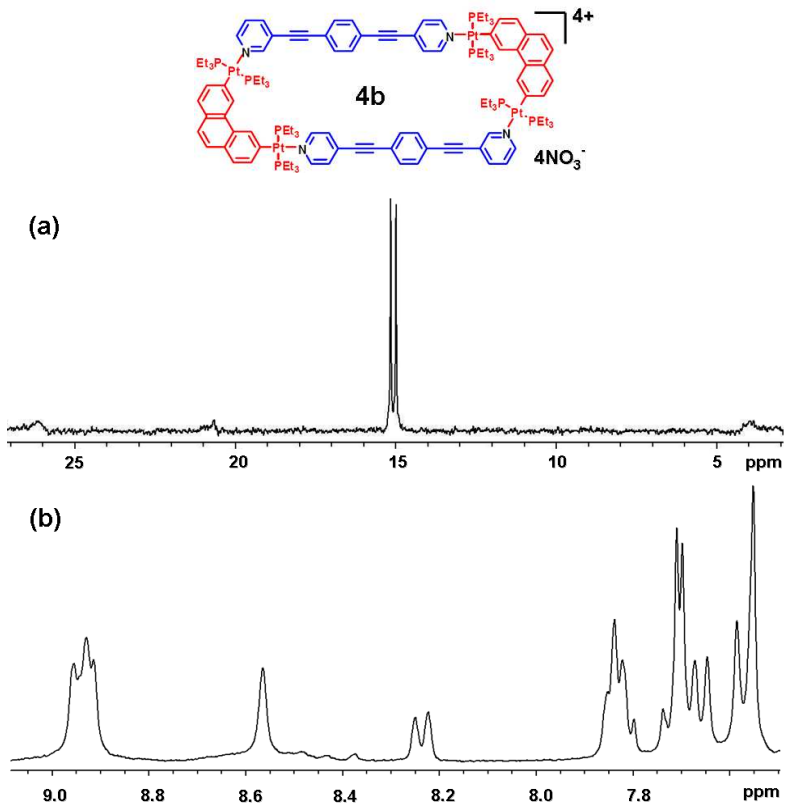


Figure S5. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra recorded for self-selection of **6b**.

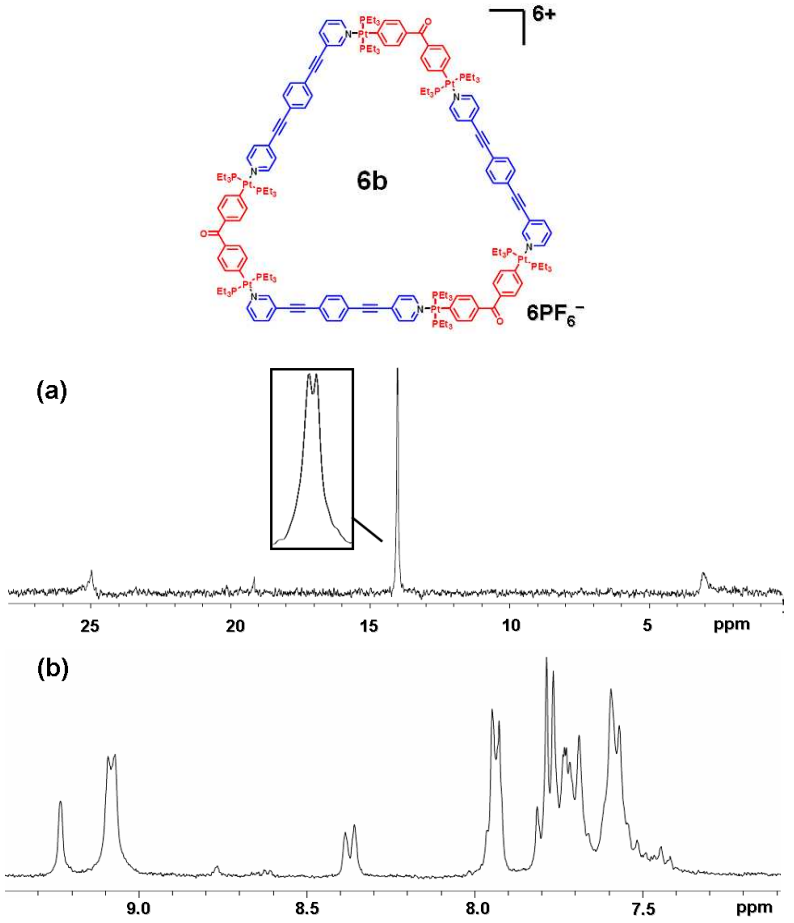


Figure S6. ESI-MS spectra recorded for self-selection of **4b**, **6a**, and **6b**.

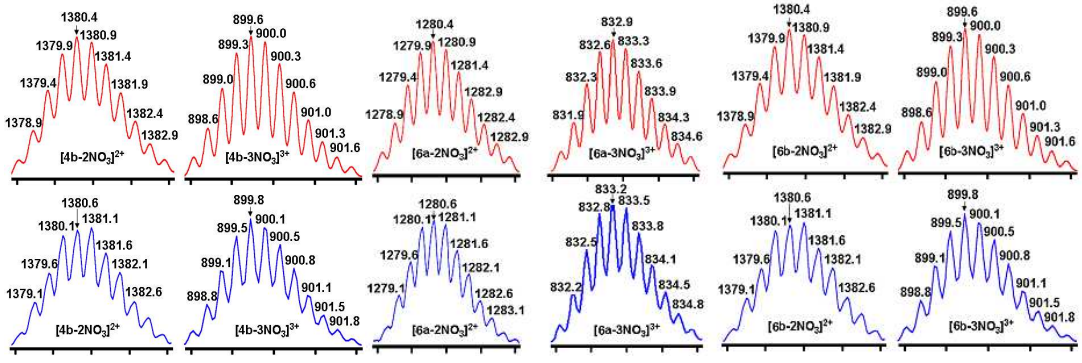


Table S1. X-ray crystallography data of **4a**.

Compound	**4a**
formula	C110 H172 Cl20 N8 O12 P8 Pt4
FW	3535.75
crystal system	triclinic
space group	$P\bar{1}$
a/Å	10.74550(10)
b/Å	18.3338(2)
c/Å	19.2355(2)
α/deg	78.1129(7)
β/deg	86.5602(7)
γ/deg	79.1068(6)
V/ Å^3	3640.55(6)
Z	1
D_c/g cm^{-3}	1.613
μ/mm^{-1}	4.339
$R_1{}^a$ ($I > 2\sigma$)	0.0481
$wR_2{}^b$ (all data)	0.1268
GOF	1.033