Electronic Supplementary Information

From supramolecular triangle to heteroleptic rhombus: a simple bridge can make a difference

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1. General Procedures

Chemicals were purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al2O3 (IB-F) or SiO2 (IB2-F); the separated products were visualized by UV light. Column chromatography was conducted using basic Al2O3, Brockman Activity I (60-325 mesh) or SiO2 (60-200 mesh) from Fisher Scientific. 1H and 13C NMR spectra were recorded on a Varian NMRS 500 spectrometer, using CDCl3 for ligands and CD3CN for complexes, except where noted. UV-vis spectra were recorded on a Cary 100 Bio Spectrophotometer EL 04113013. The photoluminescence spectra were measured on a Horiba Jobn Yvon Fluoromax-4 Spectrofluorometer using 5 nm slit for both excitation and absorption wavelength. Electrospray ionization (ESI) mass spectra (MS) were acquired with a Waters Synapt HDMS.
quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer, using solutions of ~0.3 mg sample in 1 mL of MeCN/MeOH (1:1, v/v). The Synapt Q/ToF instrument contains a travelling wave ion mobility (TWIM) device, in which ions drift under the influence of a traveling wave field against the flow of a carrier gas (N₂). This process disperses the ions based on their mass, charge, and shape (architecture). The separated ions travel through the transfer cell from which they are conveyed to the orthogonal ToF analyser for m/z measurement. The acquired data are typically displayed in 2-D plots of m/z ratio vs. the corresponding drift time through the IM cell. The TWIM MS experiments were performed under the following conditions: ESI capillary voltage, 1 kV; sample cone voltage, 8 V; extraction cone voltage, 3.2 V; desolvation gas flow, 800 L/h (N₂); trap collision energy (CE), 3 eV; transfer CE, 1 eV; trap gas flow, 1.5 mL/min (Ar); TWIM cell gas flow, 22.7 mL/min (N₂); sample flow rate, 5 μL/min; source temperature, 20 °C; desolvation temperature, 40 °C; TWIM wave height, 7.5 V; and TWIM wave velocity, 350 m/s. TWIM data analyses were conducted using the MassLynx 4.1 and DriftScope 2.1 programs provided by Waters.

2. Synthetic Procedure of Ligands and Complex.

1,2,3-Tris(methoxy)-4,6-bis[p-(4'-terpyridinyl)phenyl]benzene¹ (2), 1,2,3-tris(methoxy)-4,5,6-tris[p-(4'-terpyridinyl)phenyl]benzene¹ (3) and 4'-boronatophenyl-2,2':6',2''-terpyridine² were synthesized by literature procedures.

1,2-Bis(benzyloxy)-4,5-bis[p-(4'-terpyridinyl)phenyl]benzene (1). To a 3-necked round bottom flask, 1,2-bis(benzyloxy)-4,5-dibromobenzene (1.50 g, 3.35 mmol), 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (3.55 g, 10.1 mmol), Na₂CO₃ (7.10 g, 67.0 mmol), and a solvent mixture of water
(75 mL), toluene (75 mL), and Me$_3$COH (25 mL) were added. The system was freeze-pump-thawed (3×) and back-filled with nitrogen; and then PdCl$_2$(PPh$_3$)$_2$ (280 mg, 400 μmol) was added. The resultant suspension was refluxed for 48 h under nitrogen. After cooling to 25 °C, the aqueous layer was extracted with CHCl$_3$ (3×50 mL). The combined organic phase was dried (MgSO$_4$), and concentrated in vacuo to give a residue, which was purified by flash column chromatography (Al$_2$O$_3$), eluting with CHCl$_3$ to give 2, as a white solid: 1.95 g (64%); m.p. 219-221°C; $^1$H NMR (500 MHz, CDCl$_3$, ppm):

8.75 (s, 4H, tpy-H$^{3,5}$), 8.70 (d, $J = 5$ Hz, 4H, tpy-H$^{6,6'}$), 8.66 (d, $J = 8.0$ Hz, 4H, tpy-H$^{3,3'}$), 7.86 (dd, $J_1 = J_2 = 8$ Hz, 4H, tpy-H$^{A}$), 7.81 (d, $J = 7.5$ Hz, 4H, $^A$Ph-H), 7.54 (d, $J = 7.5$ Hz, 4H, $^C$Ph-H), 7.42 (dd, $J_1 = J_2 = 7.5$ Hz, 4H, $^C$Ph-H), 7.36 (t, $J = 7.5$ Hz, 2H, $^C$Ph-H), 7.33 (dd, $J_1 = J_2 = 5$ Hz, 4H, tpy-H$^{5,5'}$), 7.26 (d, $J = 7.5$ Hz, 4H, $^A$Ph-H), 7.13 (s, 2H, $^B$Ph-H), 5.29 (s, 4H, OCH$_2$Ph); $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): 156.46, 156.00, 150.01, 149.21, 148.72, 142.29, 137.44, 137.11, 136.52, 133.43, 130.65, 128.79, 128.14, 127.70, 127.23, 123.94, 121.59, 119.06, 117.72, 71.82; MALDI-ToF MS (m/z): Calcd. for [C$_6$H$_4$N$_6$O$_2$+H]: 905.36 Found: 905.38.

Zn Triangle 4a. To a solution of Zn(NO$_3$)$_2$·6H$_2$O (1.49 mg, 5.0 μmol) in MeOH (5 mL), a solution of ligand 1 (4.53 mg, 5.0 μmol) in CHCl$_3$ (1 mL) was added; the mixture was then stirred at 25 °C for 30 min. Excess NH$_4$PF$_6$ was added to afford a light-yellow precipitate, which was thoroughly washed by water to give the desired triangle 4a with PF$_6$ as counterion: 6.0 mg (95%); $^1$H NMR (500 MHz, CDCl$_3$, ppm):
MHz, CD$_3$CN, ppm): 8.95 (s, 12H, B$_{tpy-H^{3,5}}$), 8.69 (d, $J = 8.0$ Hz, 12H, B$_{tpy-H^{3,3''}}$), 8.11 (d, $J = 8.0$ Hz, 12H, A$_{Ph-H}$), 8.07 (dd, $J_1 = J_2 = 8.0$ Hz, 12H, B$_{tpy-H^{4,4''}}$), 7.81 (d, $J = 5.0$ Hz, 12H, B$_{tpy-H^{6,6''}}$), 7.59-7.54 (m, 24H, A$_{Ph-H}$, C$_{Ph-H}$), 7.47 (dd, $J_1 = J_2 = 7.5$ Hz, 12H, C$_{Ph-H}$), 7.41 (t, $J = 7.5$ Hz, 6H, C$_{Ph-H}$), 7.37-7.32 (m, 18H, B$_{tpy-H^{5,5''}}$, B$_{Ph-H}$), 5.35 (s, 12H, OCH$_2$Ph); $^{13}$C NMR (125 MHz, CD$_3$CN, ppm): 156.72, 150.81, 149.85, 148.98, 148.89, 145.13, 142.20, 138.31, 135.31, 133.42, 132.29, 129.67, 129.20, 128.92, 128.78, 128.54, 124.25, 122.34, 118.10, 72.10; ESI-MS ($m/z$): Calcd. for [M-3PF$_6$]$^{-3}$+: 1114.9, Found: 1114.9; Calcd. for [M-4PF$_6$]$^{-4}$+: 799.7, Found: 799.7; Calcd. for [M-5PF$_6$]$^{-5}$+: 610.8, Found: 610.7; Calcd. for [M-6PF$_6$]$^{-6}$+: 484.8, Found: 484.8.

**Cd Triangle 4b.** To a solution of Cd(NO$_3$)$_2$·4H$_2$O (1.54 mg, 5.0 μmol) in MeOH (5 mL), a solution of ligand 1 (4.53 mg, 5.0 μmol) in CHCl$_3$ (1 mL) was added; the mixture was then stirred at 25 °C for 30 min. Excess NH$_4$PF$_6$ was added to the reaction mixture to afford a light-yellow precipitate, which was thoroughly washed by water to give the desired triangle 4b with PF$_6^-$ as counterion: 6.1 mg (93%); $^1$H NMR (500 MHz, CD$_3$CN, ppm): 8.91 (s, 12H, B$_{tpy-H^{3,5}}$), 8.73 (d, $J = 8.0$ Hz, 12H, B$_{tpy-H^{3,3''}}$), 8.12 (t, $J_1 = J_2 = 8.0$ Hz, 12H, B$_{tpy-H^{4,4''}}$), 8.08-8.05 (m, 24H, B$_{tpy-H^{6,6''}}$, A$_{Ph-H}$), 7.57-7.54 (m, 24H, A$_{Ph-H}$, C$_{Ph-H}$), 7.48-7.40 (m, 30H, C$_{Ph-H}$, B$_{tpy-H^{5,5''}}$), 7.31 (s, 6H, B$_{Ph-H}$), 5.34 (s, 12H, OCH$_2$Ph); $^{13}$C NMR (125 MHz, CD$_3$CN, ppm): 155.69, 153.09, 151.27, 150.65, 149.80, 145.02, 142.24, 138.31, 135.32, 133.40, 132.22, 129.67, 129.19, 128.90, 128.88, 128.69, 128.32, 124.72, 122.64, 72.09;
ESI-MS (m/z): Calcd. for [M-3PF$_6$]$^{3+}$: 1161.9, Found: 1161.9; Calcd. for [M-4PF$_6$]$^{4+}$: 835.2, Found: 835.2; Calcd. for [M-5PF$_6$]$^{5+}$: 639.0, Found: 639.0

**Zn Rhomboid 5a.** To a solution of Zn(NO$_3$)$_2$·6H$_2$O (2.97 mg, 10.0 μmol) in MeOH (5 mL), a solution of ligands 1 (4.53 mg, 5.0 μmol) and 2 (3.91 mg, 5.0 μmol) in CHCl$_3$ (2 mL) was added; the mixture was then stirred at 25 °C for 30 min. Excess NH$_4$PF$_6$ was added to afford light-yellow precipitate, which was thoroughly washed by water to give the crude 5a with PF$_6$$^-\text{ as counterion, along with 4a. The } ^1\text{H NMR and ESI-mass spectra are shown in Fig. S3 and Fig. 1C, respectively, confirming the presence of rhomboid 5a in the presence of the known triangle 4a.**

**Cd Rhomboid 5b.** To a solution of Cd(NO$_3$)$_2$·4H$_2$O (3.08 mg, 10.0 μmol) in MeOH (5 mL), a solution of ligands 1 (4.53 mg, 5.0 μmol) and 2 (3.91 mg, 5.0 μmol) in CHCl$_3$ (2 mL) was added; then the mixture was stirred at 25 °C for 30 min. Excess NH$_4$PF$_6$ was added to the reaction mixture to afford light-yellow precipitate, which was thoroughly washed by water to give the crude 5b with PF$_6$$^-\text{ as counterion, along with 4a. The } ^1\text{H NMR and ESI-mass spectra are shown in Fig. S4 and Fig. 1C, respectively, confirming the presence of rhomboid 5b in the presence of the known triangle 4a.**
counterion, along with triangle 4b. \(^1\)H NMR and ESI-mass spectra are shown in Fig. S4 and Fig. S2-C, respectively, again confirming the presence of rhomboid 5b in the presence of the known triangle 4b.

**Rhomboidal Zn Bistriple 6a.** To a solution of Zn(NO\(_3\))\(_2\)-6H\(_2\)O (3.72 mg, 12.5 \(\mu\)mol) in MeOH (5 mL), a solution of ligands 1 (4.53 mg, 5.0 \(\mu\)mol) and 3 (5.45 mg, 5.0 \(\mu\)mol) in CHCl\(_3\) (2 mL) was added; the mixture was then stirred at 25 °C for 30 min. Excess NH\(_4\)PF\(_6\) was added to afford a light-yellow precipitate, which was thoroughly washed by water to give the desired 6a with PF\(_6^-\) as counterion: 13.6 mg (94%); \(^1\)H NMR (500 MHz, CD\(_3\)CN, ppm): 8.95 (s, 8H, \(\text{CpymH}^{3',5'}\)), 8.94 (s, 8H, \(\text{BpymH}^{3',5'}\)), 8.72 (s, 4H, \(\text{DpymH}^{3',3''}\)), 8.70-8.67 (m, 16H, \(\text{BpymH}^{3',3'',}\text{CpymH}^{3',3''}\)), 8.56 (d, \(J = 8.0\) Hz, 4H, \(\text{DpymH}^{3',3''}\)), 8.12-8.03 (m, 32H, \(\text{BpymH}^{6',6'',}\text{CpymH}^{6',6''}\), \(\text{GPhH}\)), 7.83-7.80 (m, 20H, \(\text{BpymH}^{6',6''}\), \(\text{CpymH}^{6',6''}\), \(\text{GPhH}\)), 7.67 (d, \(J = 5.02\) Hz, 4H, \(\text{DpymH}^{6',6''}\)), 7.61-7.55 (m, 24H, \(\text{APhH}\), \(\text{FPhH}\), \(\text{CPhH}\)), 7.49-7.46 (t, \(J_1 = J_2 = 7.5\) Hz, 8H, \(\text{CPhH}\)), 7.43-7.41 (m, 8H, \(\text{CPhH}\), \(\text{GPhH}\)), 7.36-7.33 (m, 12H, \(\text{BpymH}^{5',5''}\), \(\text{BPhH}\)), 7.30 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 5.0\) Hz, 8H, \(\text{CpymH}^{5',5''}\)), 7.17 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 5.0\) Hz, 4H, \(\text{DpymH}^{5',5''}\)), 5.36 (s, 8H, OCH\(_2\)Ph), 4.15 (s, 6H, OMe), 3.85 (s, 12H, OMe); \(^{13}\)C NMR (125 MHz, CD\(_3\)CN, ppm): 156.93, 156.74, 156.64, 152.48, 152.44, 150.82, 150.80, 150.71, 150.62, 149.85, 148.98, 148.90, 148.87, 148.69, 147.55, 147.27, 145.12, 142.19, 142.00, 141.27, 139.98, 139.53, 138.34, 135.34, 135.28, 133.80, 133.46, 133.30, 132.29, 132.07, 129.68, 129.20, 128.93, 128.79, 128.75, 128.55, 128.49, 128.41, 128.19, 128.16, 127.77, 124.24, 122.40, 122.33, 118.30, 72.12, 61.87, 61.75; ESI-MS (m/z): Calcd. for [M-4PF\(_6^-\)]\(^{1+}\): 1296.2, Found: 1296.2; Calcd. for [M-
Rhomboidal Cd Bistriangle 6b. To a solution of Cd(NO$_3$)$_2$·4H$_2$O (3.86 mg, 12.5 μmol) in MeOH (5 mL), a solution of 1 (4.53 mg, 5.0 μmol) and 3 (5.45 mg, 5.0 μmol) in CHCl$_3$ (2 mL) was added; then the mixture was stirred at 25 °C for 30 min. Excess NH$_4$PF$_6$ was added to the reaction mixture to afford a light-yellow precipitate, which was thoroughly washed by water to give the desired 6b with PF$_6^-$ as counterion: 14.0 mg (93%); $^1$H NMR (500 MHz, CD$_3$CN, ppm): 8.90 (s, 8H, $^{Ct}$py-$H^{3,5}$), 8.89 (s, 8H, $^{Bt}$py-$H^{3,5}$), 8.72 (d, $J = 8.0$ Hz, 16H, $^{Bt}$py-$H^{3,3'}$, $^{Ct}$py-$H^{3,3'}$), 8.69 (s, 4H, $^{Dt}$py-$H^{3,5}$), 8.59 (d, $J = 8.0$ Hz, 4H, $^{Dt}$py-$H^{3,3'}$), 8.15-8.04 (m, 48H, $^{Bt}$py-$H^{4,4'}$, $^{Ct}$py-$H^{4,4'}$, $^{Aph}$-H, $^{Fph}$-H, $^{Bt}$py-$H^{6,6'}$, $^{Ct}$py-$H^{6,6'}$), 7.95-7.90 (m, 8H, $^{Dt}$py-$H^{4,4'}$, $^{Dt}$py-$H^{6,6'}$), 7.79 (d, $J = 8.0$ Hz, 4H, $^{Gph}$-H), 7.58-7.53 (m, 24H, $^{Aph}$-H, $^{Cph}$-H, $^{Fph}$-H), 7.48-7.38 (m, 32H, $^{Cph}$-H, $^{Bt}$py-$H^{5,5'}$, $^{Ct}$py-$H^{5,5'}$), 7.31 (s, 4H, $^{Bph}$-H), 7.25 (dd, $J_1 = 8.0$ Hz, $J_2 = 5.0$ Hz, 4H, $^{Dt}$py-$H^{5,5'}$), 5.34 (s, 8H, OCH$_2$Ph), 4.14 (s, 6H, OMe), 3.84 (s, 12H, OMe); $^{13}$C NMR (125 MHz, CD$_3$CN, ppm): 155.19, 154.97, 154.95, 154.91, 151.71, 150.54, 150.45, 150.43, 150.36, 149.90, 149.75, 149.07, 149.05, 148.88, 146.53, 144.26, 142.39, 141.50, 141.33, 140.43, 137.60, 135.88, 134.67, 134.58, 134.37, 133.02, 132.99, 132.75, 132.70, 132.52, 131.50, 131.33, 128.93, 128.45, 128.18, 127.93, 127.54, 127.45, 127.33, 126.88, 123.84, 121.97, 121.86, 117.56, 71.37, 61.13, 60.98; ESI-MS ($m/z$): Calcd. for [M-4PF$_6$]$^{4+}$: 1355.2, Found: 1355.1; Calcd. for [M-5PF$_6$]$^{5+}$: 1055.0, Found:

### 3. ESI-MS and ESI-TWIM-MS of Cd Complexes.

**Fig. S1.** (A) ESI-MS of 6b (B) ESI-MS of 4b (C) ESI-MS of the mixture of 5b and 4b (D) 2D ESI-TWIM-MS plot (m/z vs drift time) for 6b. The charge states of intact assemblies are marked.
4. $^1$H NMR of the Complex

Fig. S2. $^1$H NMR spectra of ligands 3 and 1 in CDCl$_3$ and complexes 6b and 4b in CD$_3$CN.

Fig. S3. $^1$H NMR spectra of isolated 4a and the mixture of 4a and 5a in CD$_3$CN.
Fig. S4. $^1$H NMR spectra of isolated 4b and the mixture of 4b and 5b in CD$_3$CN.

5. MALDI-ToF-MS

Fig. S5. MALDI-ToF-MS of 6a (Linear Mode)

Fig. S6. MALDI-ToF-MS of Ligand 1
6. Photophysical Properties of the Complexes

**Fig. S7.** Absorption and emission spectra of complexes 4 & 6 in MeCN (10^{-6} M) at 25 °C; the emission spectra were recorded at the excitation wavelength of 285 nm

**Table. S1.** Photophysical properties of complexes 4 & 6 in dilute solutions (10^{-6} M) at 25 °C

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_{max} Absorption (ε×10^{-6})</th>
<th>λ_{max} Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>284 nm (0.17), 326 nm (0.10)</td>
<td>456 nm</td>
</tr>
<tr>
<td>4b</td>
<td>284 nm (0.21), 326 nm (0.13)</td>
<td>450 nm</td>
</tr>
<tr>
<td>6a</td>
<td>284 nm (0.26), 326 nm (0.18)</td>
<td>461 nm</td>
</tr>
<tr>
<td>6b</td>
<td>283 nm (0.31), 324 nm (0.22)</td>
<td>443 nm</td>
</tr>
</tbody>
</table>

7. NMR Data (^{13}C, COSY & NOESY)

**Fig. S8.** ^{13}C NMR spectrum of ligand 1 in CDCl₃
Fig. S9. COSY NMR spectrum of 6a in CD$_3$CN

Fig. S10. NOESY NMR spectrum of 6a in CD$_3$CN
Fig. S11. $^{13}$C NMR spectrum of 6a in CD$_3$CN

Fig. S12. COSY NMR spectrum of 6b in CD$_3$CN
**Fig. S13.** NOESY NMR spectrum of 6b in CD$_3$CN

**Fig. S14.** $^{13}$C NMR spectrum of 6b in CD$_3$CN
**Fig. S15.** COSY NMR spectrum of 4a in CD$_3$CN

**Fig. S16.** $^{13}$C NMR spectrum of 4a in CD$_3$CN
Fig. S17. COSY NMR spectrum of 4b in CD$_3$CN

Fig. S18. $^{13}$C NMR spectrum of 4b in CD$_3$CN
8. Isotope Patterns (ESI-MS)

**Fig. S19.** Isotope patterns for the different charge states (4+ to 9+) observed from 6a (PF₆⁻ as counterion).
**Fig. S20.** Isotope patterns for the different charge states (4+ to 10+) observed from 6b (PF$_6^-$ as counterion).
**Fig. S21.** Isotope patterns for the different charge states (3+ to 6+) observed from 4a (PF₆⁻ as counterion).

**Fig. S22.** Isotope patterns for the different charge states (3+ to 5+) observed from 4b (PF₆⁻ as counterion).
**Fig. S23.** Isotope patterns for the different charge states (4+ to 8+) observed from 5a (PF$_6^-$ as counterion).
Fig. S24. Isotope patterns for the different charge states (5+ to 8+) observed from 5b (PF\textsubscript{6}^- as counterion).

9. References
