Supporting information

Stepwise, Multicomponent Assembly of a Molecular Trapezoid Possessing Three Different Metals

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Experimental Section.

**General Procedures.** Reagents and solvents were purchased from Sigma-Aldrich and used without purification. Thin layer chromatography (TLC) was performed on flexible sheets (Baker-flex) precoated with Al₂O₃ (IB-F) or SiO₂ (IB2-F) and 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, ¹³C, 2D COSY, and NOESY NMR spectra were recorded on a Varian NMR 500 (MHz).

ESI mass spectrometry (MS) experiments were performed on a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer, which contains a triwave device between the Q and ToF analyzers, consisting of three collision cells in the order trap cell, ion mobility cell, and transfer cell. Trap and transfer cells are pressurized with Ar and the ion mobility cell is pressurized with N₂ flowing in a direction opposite to that of the entering ions. D-Ala²-Leucine Enkephalin was used to calibrate all ESI mass spectra. In the TWIM-MS experiments, a pulsed field is applied to the ion mobility cell ("traveling wave" field) to separate the ions drifting inside by their charge state and collision cross-section. The proteins, used to calibrate the drift time scale in the TWIM-MS experiments in order to obtain the collision cross-section data, were acquired from Sigma-Aldrich. The ESI-TWIM-MS experiments were performed using the following parameters: ESI capillary voltage: 3.2 kV; sample cone voltage: 15 V; extraction cone voltage: 0.5 V; desolvation gas flow: 500 L/h (N₂); trap collision energy (CE): 6 eV; transfer CE: 4 eV; trap gas flow: 1.5 mL/min (Ar); ion-mobility cell gas flow: 22.7 mL/min (N₂); sample flow rate: 5µL/min; source temperature: 70 °C; desolvation temperature: 150 °C; TWIM traveling-wave height: 7.5 V; and TWIM traveling-wave velocity: 350 ms⁻¹. The sprayed solution was prepared by dissolving the sample in MeCN. Data analyses were conducted using the MassLynx 4.1 and DriftScope 2.1 programs provided by Waters. Theoretical collision cross sections were calculated from energy minimized structures using the trajectory method available in the MOBCAL software.

For the TEM investigation, the sample was dissolved in MeCN at a concentration within the range 10⁻⁶ to 10⁻⁷ M. The solution was drop cast onto a carbon-coated copper grid and extra solution was absorbed by filter paper to avoid aggregation. The TEM images of the drop cast samples were taken with a Jeol JEM-1230 transmission electron microscope.

**Collision Cross-section Calibration.** The drift time scale of the TWIM-MS experiments was converted to a collision cross-section scale, following the calibration procedure of Scrivens *et al.*[¹] Briefly, the corrected collision cross sections of the molecular ions of ubiquitin (bovine red blood cells) obtained from published work,[²] were plotted against the corrected drift times (arrival times) of the corresponding molecular ions measured in TWIM-MS experiments at the same traveling-wave velocity, traveling-wave height, and ion-mobility gas flow settings, viz. 350 ms⁻¹, 7.5 V, and 22.7 mL/min. Charge states observed for the calibrant from 6+ to 10+ were used in the construction of the curve.
**Molecular Modeling.** Energy minimization of these structures was conducted with the Materials Studio version 6.0 program using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. An initially energy-minimized structure was subjected to 20 annealing cycles with initial and mid-cycle temperatures of 300 and 1500 K, respectively, five heating ramps per cycle, one hundred dynamics steps per ramp, and one dynamics step per femtosecond. A constant volume/constant energy (NVE) ensemble was used; the geometry was optimized after each cycle. All geometry optimizations used a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters. 50 Candidate structures were generated for the calculation of collision cross sections.

2,5-Dibromobenzene-1,4-diol (S1) was prepared by a known procedure: \(^{[3]} \) m.p. 161-164 °C.

\[
\begin{align*}
\text{OH} & \quad \text{+} \quad \text{Br}_2 \quad \text{CH}_2\text{Cl}_2 \\
\text{OH} & \quad \text{Br} \\
\text{OH} & \quad \text{Br}
\end{align*}
\]

Synthetic route for 2,5-dibromobenzene-1,4-diol.

1,4-Dibromo-2,5-*bis*(hexadecyloxy)benzene (S2), was prepared by a known procedure: \(^{[4]} \) m.p. 70 °C.

\[
\begin{align*}
\text{Br} & \quad \text{+} \quad \text{C}_{16}\text{H}_{33}\text{Br} \quad \text{K}_2\text{CO}_3 \\
\text{Br} & \quad \text{Br} \\
\text{OH} & \quad \text{OC}_{16}\text{H}_{33} \\
\text{OH} & \quad \text{Br} \\
\text{OH} & \quad \text{OC}_{16}\text{H}_{33}
\end{align*}
\]

Synthetic route for 1,4-dibromo-2,5-*bis*(hexadecyloxy)benzene.

1,2-Dibromo-4,5-*bis*(hexadecyloxy)benzene (S3) was prepared according to literature procedure: \(^{[5]} \) m.p. 72 °C.

\[
\begin{align*}
\text{Br} & \quad \text{+} \quad \text{C}_{16}\text{H}_{33}\text{Br} \quad \text{K}_2\text{CO}_3 \\
\text{Br} & \quad \text{Br} \\
\text{OH} & \quad \text{OC}_{16}\text{H}_{33} \\
\text{OH} & \quad \text{Br} \\
\text{OH} & \quad \text{OC}_{16}\text{H}_{33}
\end{align*}
\]

Synthetic route for 1,2-dibromo-4,5-*bis*(hexadecyloxy)benzene.
Synthesis of Ligand 1.

In a three neck round bottom flask, a mixture of 1,4-dibromo-2,5-bis(hexadecyloxy)benzene (2.15 g, 3 mmol), 4′-(4-boronaophenyl)[2,2′:6′,2″]-terpyridine (3.05 g, 9 mmol), Na₂CO₃ (1.28 g, 12 mmol), and PdCl₂(PPh₃)₂ (485 mg, 600 μmol) were dissolved in a mixture of water (120 mL), t-butyl alcohol (80 mL), and toluene (200 mL) under an nitrogen atmosphere. After refluxing at 100 °C for 24 h, a white precipitate was obtained, then filtered in vacuo, and washed with MeOH. The crude white precipitate was column chromatographed (Al₂O₃) eluting with a mixture of n-hexane:CHCl₃:EtOAc (12:1:1) first and then with CHCl₃ to afford 1, as a white solid: 1.73 g, 49%; m.p. 114-116 °C; 1H NMR (CDCl₃, 500 MHz, ppm) (see Figure S1): δ 8.86 (s, 4H, 3′,5′-tpy H), 8.78 (d, 4H, J = 6 Hz, 6,6′′-tpy H), 8.71 (d, 4H, J = 9 Hz, 3,3′′-tpy H), 8.0 (d, 4H, J = 9 Hz, Ph Hₐ), 7.87-7.93 (m, 4H, 4,4″-tpy H), 7.78 (d, 4H, J = 9 Hz, Ph Hₖ), 7.35-7.39 (m, 4H, 5,5″-tpy H), 7.09 (s, 2H, Ph Hₐ), 3.98 (t, 4H, OC H₂), 1.67-1.76 (m, 4H, alkyl protons), 1.11-1.44 (m, 52H, alkyl protons), 0.86 (t, 6H, -CH₃); 13C NMR (CDCl₃, 125 MHz, ppm) (see Figure S2): δ 156.37, 155.97, 150.54, 149.98, 149.13, 136.79, 133.04, 132.22, 132.12, 132.04, 132.03, 131.89, 131.87, 131.85, 130.07, 128.51, 128.41, 126.86, 123.75, 121.34, 118.73, 31.89, 29.68, 29.66, 29.64, 29.61, 29.41, 29.32, 26.12, 22.66, 14.08; MALDI-MS (m/z) (see Figure S3): 1173.1 [M]+.

Synthesis of bisRuIII adduct 2.

To a 250 mL round bottom flask, (1; 127 mg, 108 μmol), RuCl₃ (45 mg, 216 μmol), and EtOH (50 mL) were added then refluxed for 36 h at 80 °C. The reaction mixture was filtered in vacuo and washed with EtOH (100 mL) to give a red powder: 321 mg, 93%. MALDI-MS (m/z) (see Figure S4): 1588.34 [2]+, 1553.37 [2-Cl]+, 1517.40 [2-2Cl]+, 1482.43 [2-3Cl]+.
Ligand 3 was prepared according to known procedure:[5] m.p. > 300 °C.

Synthetic route for ligand 3

Synthesis of bisRuII dimer 4.

To a 1 L round bottom flask, 2 (105 mg, 76 μmol), 3 (215 mg, 183 μmol), CHCl₃ (150 mL), MeOH (150 mL), and 4-ethylmorpholine (2 mL) were added. After refluxing for 24 h at 80 °C, the reaction mixture was concentrated in vacuo to give a red powder, which was purified by column chromatography (Al₂O₃) eluting with CHCl₃/MeOH (14:1), to afford the desired 4, as a red powder: 144 mg, 51%; m.p. > 300 °C; ¹H NMR (CD₃CN, 500 MHz, ppm) (see Figure S4): δ 9.10 (s, 4H, 3′,5′-tpyA), 9.04 (s, 4H, 3′,5′-tpyB), 8.80 (s, 4H, 3′,5′-tpyC), 8.70-8.73 (m, 8H, 3,3′′-tpyA and 3,3′′-tpyC), 8.67 (d, 4H, J = 8 Hz, 3,3′′-tpyB), 8.34 (d, 4H, J = 8 Hz, Ph^A), 8.17 (d, 4H, J = 8 Hz, Ph^B), 8.08 (d, 4H, J = 8 Hz, Ph^C), 7.89 (d, 4H, J = 8 Hz, Ph^D), 7.63 (d, 4H, J = 8 Hz, Ph^E), 7.50 (d, 4H, J = 8 Hz, Ph^F), 7.45-7.52 (m, 12H, 4,4″-tpyA and 6,6″-tpyC), 7.34 (s, 2H, Ph^G), 7.20-7.21 (m, 12H, 6,6″-tpyA and 5,5″-tpyB and 5,5″-tpyC), 7.19 (s, 4H, Ph^H and Ph^I), 4.18-4.23 (m, 12H, alkyl^A, alkyl^B, and alkyl^C), 1.48-1.51 (m, 12H, alkyl^I), 1.25-1.41 (m, 144H, alkyl^I), 0.88-0.91 (m, 12H, alkyl^I and alkyl^I), 0.82 (t, J = 7 Hz, 6H, alkyl^I); MALDI-MS (m/z) (see Figure S7): 3792.06 [4-2Cl]^+ (calcd m/z = 3792.02), 3757.06 [4-3Cl]^+ (calcd m/z = 3757.05).

Ligand 5 was prepared by a known procedure:[6] m.p. > 300 °C.
Synthesis of ligand 5

To a 1 L round bottom flask, (5; 3.1 g, 2.3 mmol), RuCl₂(DMSO)₄ (369 mg, 763 μmol), and CHCl₃:MeOH (1:1, 500 mL) were added, then the mixture was refluxed for 24 h at 70 °C. This reaction mixture was concentrated in vacuo to give a purple colored powder, which was purified by column chromatography (Al₂O₃) eluting with CHCl₃/MeOH (40:1). Upon removal of free 5, the desired 6 was isolated as a purple powder: 1.52 g, 50%; m.p. > 300 °C; ¹H NMR (CD₃CN, 500 MHz, ppm) (see Figure S8):  δ 9.26 (s, 4H, 3′,5′-tpyAH), 8.84 (s, 4H, 3′,5′-tpyBH), 8.75 (d, 4H, J = 6 Hz, 6,6″-tpyBH), 8.72 (d, 4H, J = 8.0 Hz, 3,3″-tpyAH), 8.67 (d, 4H, J = 8.0 Hz, 3,3″-tpyBH), 8.46 (d, 4H, J = 8 Hz, PhAHd), 8.19 (d, 4H, J = 8 Hz, PhAHc), 8.08 (d, 4H, J = 8 Hz, PhBHd), 8.03-7.89 (m, 12H, PhBHc, 4,4″-tpyAH and 4,4″-tpyBH), 7.76 (s, 2H, PhHc), 7.49-7.43 (m, 4H, 5,5″-tpyBH), 7.42 (s, 2H, PhAHc), 7.38 (s, 2H, PhBHc), 7.19 (d, 4H, J = 6 Hz, 6,6″-tpyAH), 7.16-7.09 (m, 4H, 5,5″-tpyAH), 4.04 (s, 6H, He). MALDI-MS (m/z) (see Figure S10): 1500.47 [M-2Cl]+ (calcd m/z = 1500.49).

Synthesis of metallotrapezoid 7.
To a solution of ligands 6 (2.6 mg, 1.7 μmol) and 5 (6.4 mg, 1.7 μmol) in CHCl₃/MeOH (5 mL), a methanolic solution (2 mL) of Zn(NO₃)₂·6H₂O (1 mg, 3.3 μmol) was added slowly. The solution was stirred for 2 hours at 25 °C, then treated with aqueous solution of NH₄PF₆ (excess) to obtain a red precipitate, which was filtered and washed repeatedly with MeOH and water to remove the excess NH₄PF₆, then dried in vacuo to give the complex 7, as dark red powder: 9.4 mg, 89%; m.p. > 300 °C; ¹H NMR (CD₃CN, 500 MHz) (see Figure S11): δ 9.31 (s, 4H, 3′,5′-tpyA_H), 9.10 (s, 4H, 3′,5′-tpyC_H), 9.09 (s, 4H, 3′,5′-tpyB_H), 9.05 (s, 4H, 3′,5′-tpyD_H), 9.02 (s, 4H, 3′,5′-tpyE_H), 8.79 (d, J = 8 Hz, 8H, 3,3″-tpyB_H), 8.76 (d, J = 8 Hz, 8H, 3,3″-tpyE_H), 8.68-8.72 (m, 12H, 3,3″-tpyC_H, 3,3″-tpyD_H, 3,3″-tpyA_H), 8.52 (d, J = 8 Hz, 4H, Ph⁴_H), 8.4 (d, J = 8 Hz, 4H, Ph⁵_H), 8.33 (d, J = 8 Hz, 4H, Ph⁶_H), 8.29 (d, J = 8 Hz, 4H, Ph⁷_H), 8.25 (d, J = 8 Hz, 4H, Ph⁸_H), 8.19-8.21 (m, 12H, Ph⁴_H, Ph⁵_H, 4,4″-tpyB_H), 8.15-8.17 (m, 4H, 4,4″-tpyE_H), 8.06 (d, J = 8 Hz, 4H, Ph⁶_H), 7.94-8.00 (m, 12H, 4,4″-tpyC_H, 4,4″-tpyD_H), 7.92 (s, 2H, H'm), 7.87-7.89 (m, 8H, 6,6″-tpyB_H, 6,6″-tpyE_H), 7.67-7.69 (m, 8H, Ph⁴_H, Ph⁵_H), 7.56 (s, 2H, Ph⁶_H), 7.54 (s, 2H, Ph⁷_H), 7.46-7.47 (m, 8H, 6,6″-tpy_A_H, 6,6″-tpyC_H), 7.40-7.45 (m, 8H, 5,5″-tpy_B_H, 5,5″-tpy_E_H), 7.32 (s, 2H, Ph⁶_H), 7.26-7.28 (m, 8H, 6,6″-tpyD_H, Ph⁵_H, Ph⁷_H), 7.19-7.24 (m, 8H, 5,5″-tpy_A_H, 5,5″-tpyC_H), 7.14-7.17 (m, 4H, 5,5″-tpyD_H), 4.23-4.25 (m, 8H, alkyl⁴-D,E_H), 4.17 (t, J = 6 Hz, 4H, alkyl⁴-C_H), 4.11 (s, 6H, H'n), 1.60-1.61 (m, 12H, alkyl H'e), 1.47-1.49 (m, 12H, alkyl H'f), 1.25-1.42 (m, 144H, alkyl H'g), 0.90-0.91 (m, 12H, alkyl⁵-D_H, alkyl⁶-E_H), 0.79 (t, J = 7 Hz, 6H, alkyl⁶-E_H); ESI-MS (m/z) (see Figure S15): 1555.9 [7-4PF₆]⁴⁺, 1215.7 [7-5PF₆]⁵⁺, 988.9 [7-6PF₆]⁶⁺, 826.9 [7-7PF₆]⁷⁺, 705.7 [7-8PF₆]⁸⁺, 610.9 [7-9PF₆]⁹⁺, 535.4 [7-10PF₆]¹⁰⁺.
NMR and ESI-MS Data

Figure S1. $^{1}$H NMR spectrum (500 MHz, 300 K) of 1 in CDCl$_3$.

Figure S2. $^{13}$C NMR spectrum (125 MHz, 300 K) of 1 in CDCl$_3$. 
Figure S3. MALDI mass spectrum for 1.

Figure S4. MALDI mass spectrum for 2.
Figure S5. $^1$H NMR spectrum (500 MHz, 300 K) of 4 in CD$_3$CN.

Figure S6. 2D $^1$H-$^1$H COSY NMR spectrum (300 K) of 4 in CD$_3$CN.
Figure S7. 2D $^1$H-$^1$H NOESY NMR spectrum (300 K) of 4 in CD$_3$CN.

Figure S8. MALDI mass spectrum for 4.
Figure S9. $^1$H-NMR spectrum (500 MHz, 300 K) of 6 in CD$_3$CN.

Figure S10. 2D $^1$H-$^1$H COSY NMR spectrum (300 K) of 6 in CD$_3$CN.
Figure S11. MALDI-MS spectrum for 6.

Figure S12. $^1$H-NMR spectrum (500 MHz, 300 K) of 7 in CDCl$_3$:CD$_3$CN (1:2).
Figure S13. 2D $^1$H-$^1$H COSY NMR spectrum (300 K) of $7$ in CDCl$_3$:CD$_3$CN (1:2).

Figure S14. 2D $^1$H-$^1$H NOESY NMR spectrum (300 K) of $7$ in CDCl$_3$:CD$_3$CN (1:2).
Figure S15. $^1$H-DOSY NMR of 7 in CDCl$_3$:CD$_3$CN (1:2).

Figure S16. a) ESI mass spectra for the three metal ions complex 7; b) 2D ESI-TWIM-MS plots (m/z versus drift time) for the three metal ions complex. The charge states of intact assemblies are marked.
Table S1. Drift times and collision cross sections for the complex 7.

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Figure S17. Calibration curve for the calibration of T-Wave drift time measurements.

Table S2. Ubiquitin drift times and corrected collision cross-section (Ω) values

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References


