

Supporting Information

Pillar height dependent formation of unprecedented Pd₈ molecular swing and Pd₆ molecular boat via multicomponent self-assembly

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Experimental Section

General: The tetratopic donor 1,2,4,5-Tetrakis(1-imidazolyl)benzene (tim)¹ and *cis*-(tmen)Pd(NO₃)₂ [tmen = N,N,N',N'-tetramethylethane-1,2-diamine]² were synthesized following the reported procedures. *Trans*-1,2-bis(4-pyridyl)ethylene (bpe) and 4,4'-bipyridine (bpy) were purchased from Sigma-Aldrich (USA) and used without further purification. The chemical shifts (δ) in the ¹H NMR spectra are reported in ppm relative to tetramethylsilane (Me₄Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the solvent D₂O at 4.6 ppm and spectra were recorded on Bruker 400 MHz instrument. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed in Bruker Daltonics (Esquire 300 Plus ESI model) using standard spectroscopic grade solvent H₂O. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Fluorescence study was carried out in HORIBA JOBIN YVON made Fluoromax-4 Spectrometer using the standard spectroscopic solvents. TGA analyses of **1** and **2** were carried out on a Mettler-Toledo TGA-851 thermo-balance under a

stream of nitrogen (flow rate = 50 mL min⁻¹) in the temperature range 30–600 °C (heating rate = 5°C min⁻¹) on alumina crucibles of 70 µL volume.

General procedure for synthesis of swing (1) and boat (2): A clear aqueous yellow solution of *cis*-(tmen)Pd(NO₃)₂ was added into a solid mixture of linear dipyridyl donor (bpy or bpe) and 1,2,4,5-Tetrakis(1-imidazolyl)benzene (tim). The suspensions then stirred at room temperature for 12 h to get clear colorless solution. After completion of reaction, the reaction mixture was filtered, concentrated under reduced pressure and pure form of complex **1** and **2**, were isolated after triturating with cold-acetone.

Synthesis of 1: The aqueous solution of *cis*-(tmen)Pd(NO₃)₂ (10 mg, 0.0288 mmol) was added into a solid mixture of 4,4'-bipyridine (2.2 mg, 0.0144 mmol) and 1,2,4,5-tetraimidazole benzene (2.5 mg, 0.0072 mmol) in H₂O to obtain molecular swing **1**. Isolated yield: 83 %. Anal. Calcd for (vacuum dried sample) C₁₂₄H₁₈₈N₅₆O₄₈Pd₈: C, 36.48; H, 4.64; N, 19.21. Found: C, 36.77; H, 5.01; N, 19.38. IR: ν (cm⁻¹) = 1320.09 (C-N), 1468.82 (C=C), 1536.81 (C=C), 1613.29 (C=N). ¹H NMR (400 MHz, D₂O): δ = 9.09 (d, 8H, H _{α} -bpy), 9.06 (d, 4H, H_{imidazole}-tim), 8.78 (d, 8H, H _{α'} -bpy), 8.64 (s, 2H, H_{phenyl}-tim), 8.43 (s, 2H, H_{phenyl}-tim), 7.96 (d, 4H, H_{imidazole}-tim), 7.70 (d, 8H, H _{β} -bpy), 7.64 (d, 8H, H _{β'} -bpy), 7.34 (s, 4H, H_{imidazole}-tim), 6.98 (s, 4H, H_{imidazole}-tim), 6.19 (s, 4H, H_{imidazole}-tim), 6.02 (s, 4H, H_{imidazole}-tim), 2.92 (m, 32H, H_{CH2}-tmen), 2.49 (m, 96H, H_{CH3}-tmen). ESI-MS (m/z) = 975.87 [**1**- 4NO₃⁻ + H₂O]⁴⁺, 957.07 [**1**- 4NO₃⁻]⁴⁺, 284.20 [**1**- 12NO₃⁻ + 4H₂O]¹²⁺.

Synthesis of 2: The aqueous solution of *cis*-(tmen)Pd(NO₃)₂ (10 mg, 0.0288 mmol) was added into a solid mixture of 1,2-bis(4-pyridyl)ethylene (2.6 mg, 0.0144 mmol) and 1,2,4,5-tetraimidazole benzene (2.5 mg, 0.0072 mmol) in H₂O to obtain molecular boat **2**. Isolated yield: 92 %. Anal. Calcd for (vacuum dried sample) C₉₆H₁₄₄N₄₄O₃₆Pd₆: C, 36.85; H, 4.64; N, 19.70.

Found: C, 36.92; H, 4.70; N, 19.76. IR: ν (cm^{-1}) = 1322.93 (C-N), 1471.65 (C=C), 1531.14 (C=C), 1611.88 (C=N). ^1H NMR (400 MHz, D_2O): δ = 8.97 (d, 4H, $\text{H}_{\text{imidazole-tim}}$), 8.95 (d, 4H, $\text{H}_{\text{imidazole-tim}}$), 8.56 (s, 2H, $\text{H}_{\text{phenyl-tim}}$), 8.45 (s, 2H, $\text{H}_{\text{phenyl-tim}}$), 7.93 (d, 4H, $\text{H}_{\alpha\text{-bpe}}$), 7.65 (d, 4H, $\text{H}_{\beta\text{-bpe}}$), 7.52 (s, 4H, $\text{H}_{\text{imidazole-tim}}$), 7.41 (s, 4H, $\text{H}_{\text{ethylene-bpe}}$), 7.31 (s, 4H, $\text{H}_{\text{imidazole-tim}}$), 6.78 (s, 4H, $\text{H}_{\text{imidazole-tim}}$), 6.66 (s, 4H, $\text{H}_{\text{imidazole-tim}}$), 2.93 (m, 24H, $\text{H}_{\text{CH}_2\text{-tmen}}$), 2.5 (m, 72H, $\text{H}_{\text{CH}_3\text{-tmen}}$). ESI-MS (m/z) = 286.27 [$\mathbf{2}$ - 9NO_3] $^{9+}$, 222.32 [$\mathbf{2}$ - 11NO_3] $^{11+}$.

X-ray Data Collection and Structure Refinements. The diffraction data of **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software.³ Intensity data were collected using graphite-monochromatic Mo-K α radiation (0.7107 Å) at 100 K on a crystal as obtained after several attempts. The structures were solved by direct methods using the SHELX-97⁴ incorporated in WinGX.⁵⁻⁷ Empirical absorption corrections were applied with SADABS.⁸ All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, $U(\text{H}) = 1.2U(\text{C})$ or $1.5U(\text{C-methyl})$, and their coordinates were allowed to ride on their respective carbons. The crystal structures of both the compounds have disordered counter ions and water molecules. Some residual peaks nearly $1.98\text{e}/\text{\AA}^3$ could not be accounted for and these may be the artifact of the disordered water electron densities. The crystal structures shows considerable void space which reflects the poor quality data obtained for them.

Fluorescence Quenching Titration Study. A 2 mL stock solution [1:1, MeOH + MeCN] (1×10^{-5} M) of **1** or **2** was placed in a quartz cell of 1 cm width, and Fullerene C_{60} stock solution (1×10^{-3} M) in toluene were added into it in an incremental fashion. The titration experiments were carried out at 298 K and each titration was repeated minimum three times to get concordant result. For all the measurements **1** and **2** was excited at 250 nm and 300 nm, respectively and

their corresponding emission intensity was monitored above 270 nm and 320 nm, respectively. Both the excitation and emission slit width was kept 5 nm for all measurements. No change in the shape of the emission spectra was observed except significant gradual quenching of the initial intensities. Analysis of the normalized fluorescence emission intensity (I_0/I) as a function of increasing concentration of fullerene C_{60} ($[Q]$) was well described by the Stern-Volmer equation: $I_0/I = 1 + K_{SV}[G]$. The Stern-Volmer binding constant was calculated from the slope of their corresponding Stern-Volmer plot.

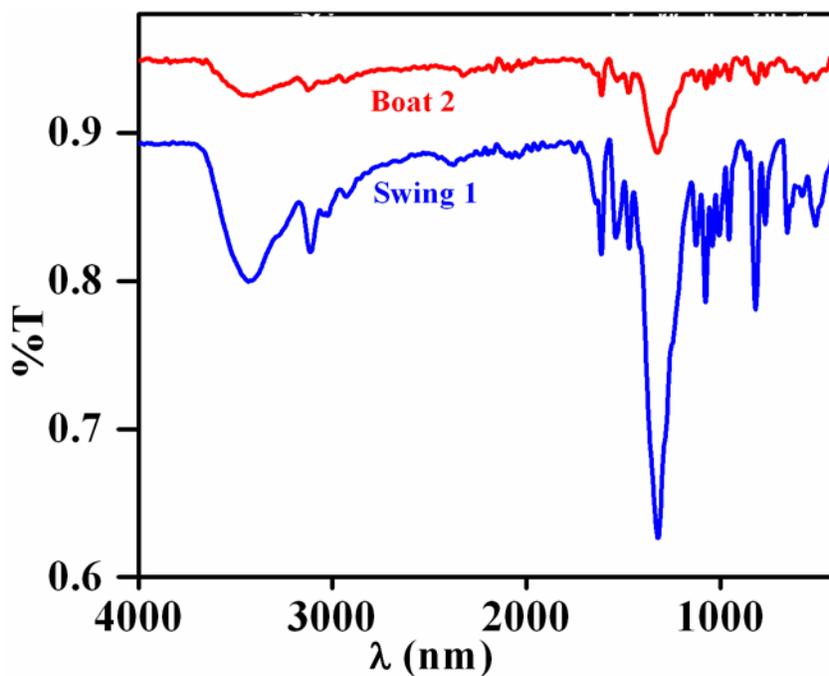


Fig.1. IR spectra of **1** and boat **2**.

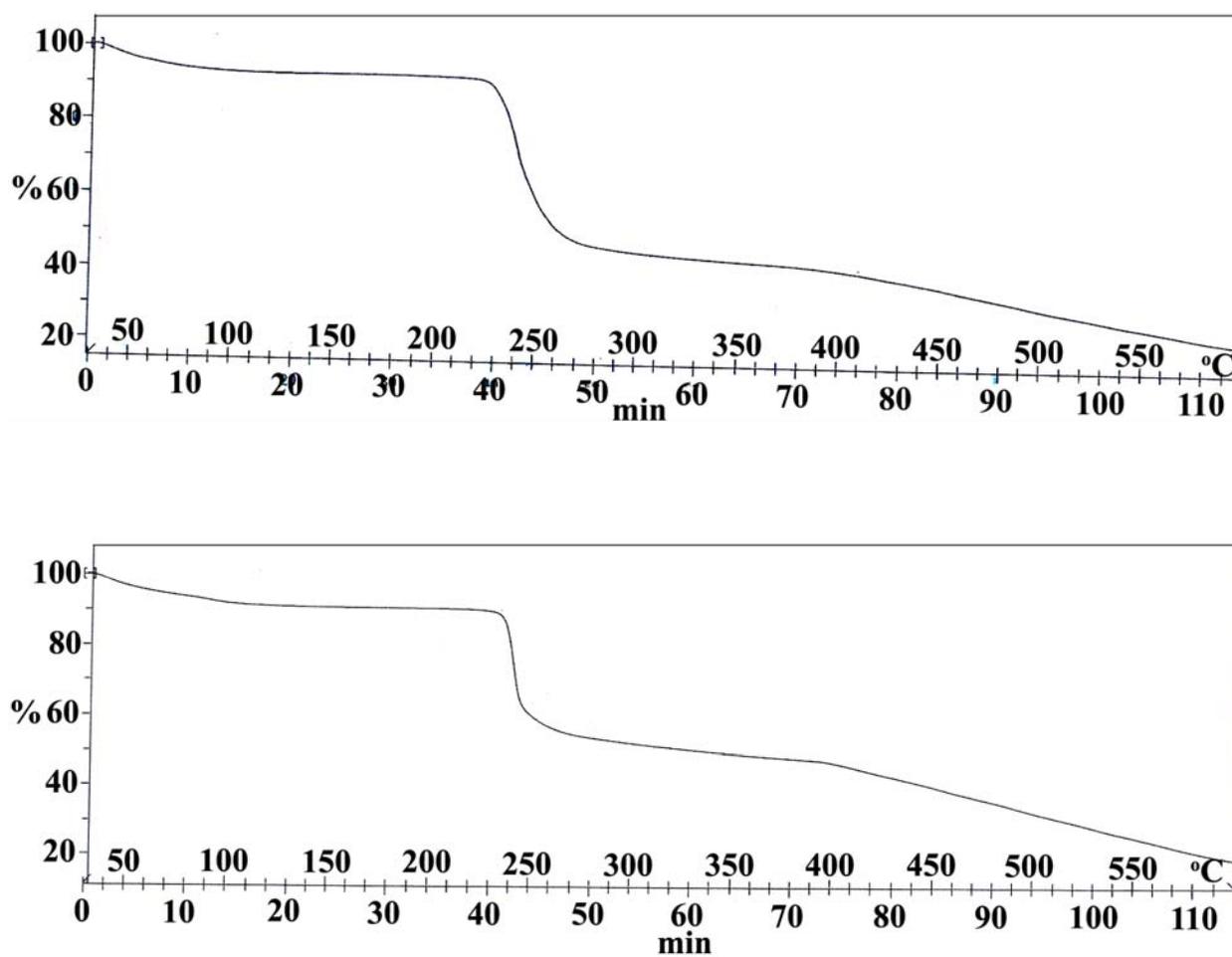


Fig.2. TGA plots of **1** (top) and **2** (bottom). Weight loss upto 130 °C correspond to 17 H₂O and 18 H₂O molecules for **1** and **2**, respectively.

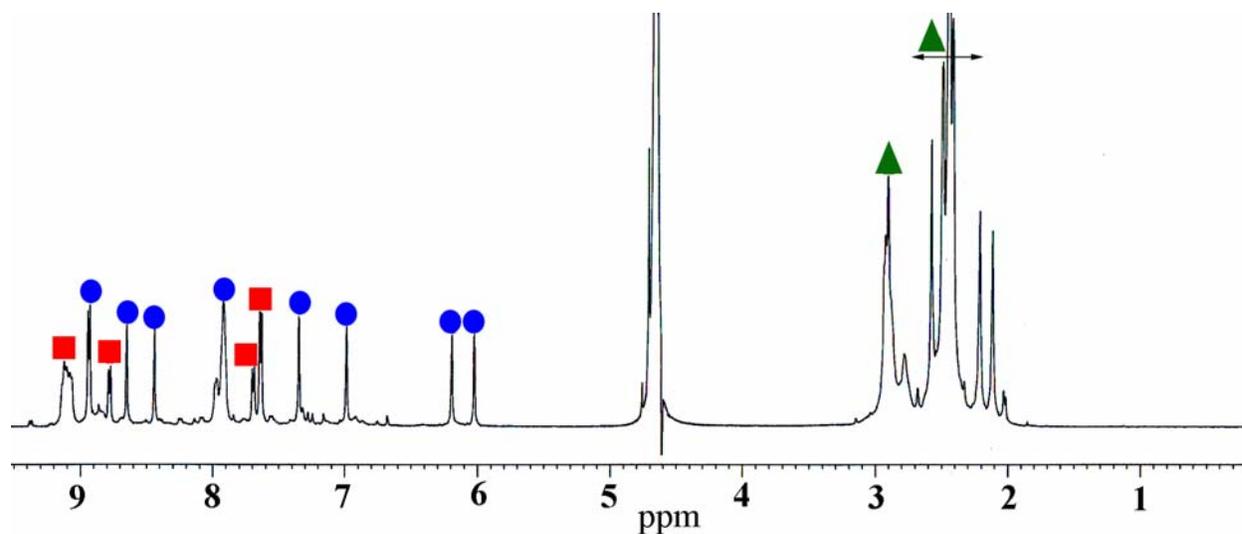


Fig.3. ^1H NMR spectra of the swing **1** recorded in D_2O (colour code: blue circle = tim, red square = bpe, green triangle = tmen).

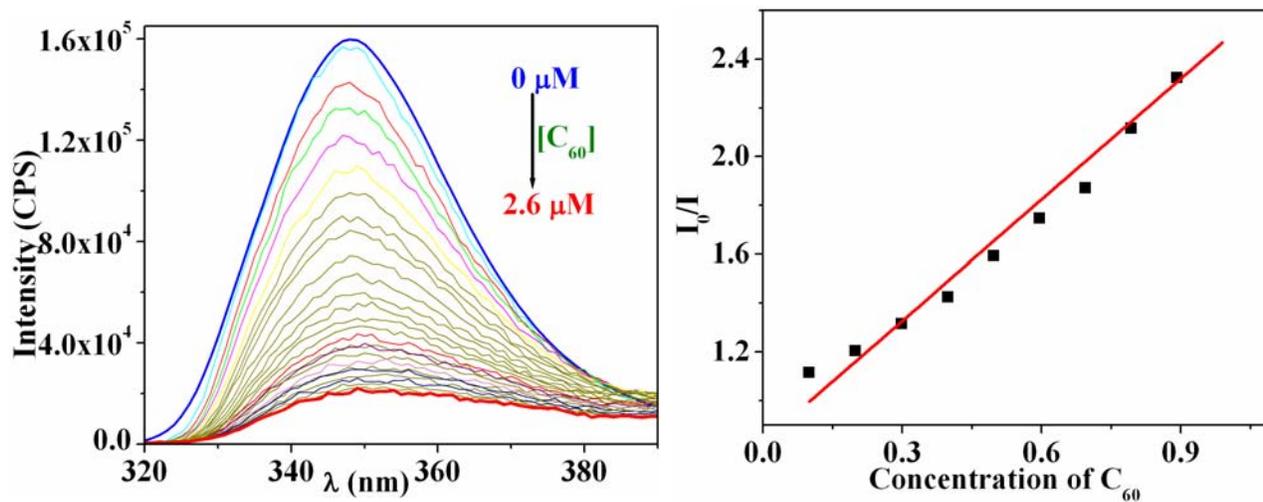


Fig.4. Reduction in the emission intensity of molecular swing **1** (left) upon gradual addition of C_{60} and its Stern–Volmer plots (right).

Crystallographic data for 1: C₁₂₄H₂₃₈N₅₆O₇₃Pd₈, *M* = 4532.90, pale yellow block (0.15 × 0.08 × 0.05 mm), triclinic, space group *P*-1, *a* = 17.324(2) Å, *b* = 24.071(3) Å, *c* = 24.118(3) Å, α = 83.797(5)°, β = 88.998(5)°, γ = 71.065(4)°, *V* = 9456(2) Å³, *T* = 100(2) K, *Z* = 2, ρ_{calcd} = 1.605 mg/m³, μ = 0.846 mm⁻¹, GOF = 0.984, Mo-K α radiation (graphite-monochromatic, λ = 0.71073 Å), Final R indices [*I*>2 σ (*I*)]: *R*₁ = 0.1104, *wR*₂ = 0.2535. CCDC = 848487.

Crystallographic data for 2: C₉₆H₁₈₄N₄₄O₅₆Pd₆, *M* = 3489.27, pale yellow block (0.20 × 0.15 × 0.08 mm), triclinic, space group *P*-1, *a* = 17.8552(18) Å, *b* = 82.207(4) Å, *c* = 21.522(2) Å, α = 69.828(4)°, β = 82.207(4)°, γ = 82.086(4)°, *V* = 7522.1(13) Å³, *T* = 100(2) K, *Z* = 2, ρ_{calcd} = 1.572 mg/m³, μ = 0.803 mm⁻¹, GOF = 1.114, Mo-K α radiation (graphite-monochromatic, λ = 0.71073 Å), Final R indices [*I*>2 σ (*I*)]: *R*₁ = 0.1177, *wR*₂ = 0.3669. CCDC = 848488.

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