

Supporting information

Rhenium-based molecular rectangular boxes with large inner cavity and high shape selectivity towards benzene molecule

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Experimental Section

All starting materials and products were found to be stable toward moisture and air. Commercial grade reagents, $\text{Re}_2(\text{CO})_{10}$, chloranilic acid ($\text{H}_2\text{-CA}$), 5,8-dihydroxy-1,4-naphthoquinone ($\text{H}_2\text{-dhnq}$), 4,4'-bipyridine (bpy), 1,2-bis(4-pyridyl)ethylene (bpe) and solvents were used as received. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer PARAGON 1000. ^1H NMR spectra were recorded on a Bruker AVA-300, and AMX-400 FT-NMR spectrometer. FAB-MS data were obtained using a JEOL JMS-700 double focusing mass spectrometer. The electronic absorption spectra were recorded on a Hewlett Packard 8453 spectrophotometer. The solvents used in this study were of spectroscopic grade.

All titrations were conducted at 300 K in THF on a Hewlett Packard 8453 spectrophotometer. A general procedure for UV-vis titration was as follows. Before the investigation of the binding properties of **1**, we removed the included guest molecules by washing with diethyl ether several times. The complete removal of solvent molecules from the cavities was counterchecked by ^1H NMR spectroscopy. In general, electronic spectra of guest molecules were measured by changing concentration of the host molecules. A 1.0×10^{-4} M solution of host and 0.1 to 1.0×10^{-4} M solution of guests in THF were prepared separately. Aliquots of the host solution (2.0×10^{-6} – 2.2×10^{-5} M) were added to the guest solution (2.0×10^{-6} – 2.0×10^{-3} M) and the spectrum was recorded after each addition. Experiments were duplicated and found to be in excellent agreement within the experimental error (90% confidence).

Syntheses of **1a**·2*p*-xylene and **1a**·mesitylene

A suspension containing a mixture of $\text{Re}_2(\text{CO})_{10}$ (125.3 mg, 0.192 mmol) and chloranilic acid (50.0 mg, 0.239 mmol) and 4,4'-bipyridine (30.0 mg, 0.192 mmol) in 6 mL *p*-xylene in a 23 mL Teflon vessel was placed in a steel autoclave. The autoclave was placed in an oven maintained at 140 °C for 48 h and then cooled to 25 °C. Good quality black single crystals of $[\{(\text{CO})_3\text{Re}(\mu\text{-CA})\text{Re}(\text{CO})_3\}_2(\mu\text{-bpy})_2]\cdot p\text{-xylene}$ (**1a**·2*p*-xylene, 163.3 mg, 0.809 mmol, 84% based on $\text{Re}_2(\text{CO})_{10}$) was obtained. The crystals were separated by filtration and washed with *p*-xylene. IR (THF): $\nu_{\text{co}} = 2023$ (s), 1923 (m), 1899 (m) cm^{-1} ; ^1H NMR (300 MHz, d_6 -DMSO): $\delta = 8.72$ (d, $^3J = 5.8$ Hz, 8 H, $\text{H}_\alpha\text{-Py}$), 8.07 (d, $^3J = 5.7$ Hz, 8 H, $\text{H}_\beta\text{-Py}$), 7.04 (m, 8 H, $\text{C}_4\text{H}_4\text{-}p\text{-xylene}$, CH-CA), 2.23 (s, 6 H, $\text{CH}_3\text{-}p\text{-xylene}$); Anal. Calc for $(\text{Re}_4\text{C}_{44}\text{H}_{16}\text{Cl}_4\text{N}_4\text{O}_{20})\cdot(\text{C}_8\text{H}_{10})_2$: C 35.69, H 1.80, N 2.77. Found: C 35.96, H 1.71, N 2.31; MS (FAB, ^{187}Re): $m/z = 1809.3$ (M^+). The similar reaction in the presence of mesitylene instead of *p*-xylene as solvent yields **1a**·mesitylene. One single crystal of

1a·mesitylene was selected for X-ray diffraction analysis.

Synthesis of **1b**·2toluene

Compound **1b** was obtained by adopting a similar procedure as **1a**·*p*-xylene, using $\text{Re}_2(\text{CO})_{10}$, H_2CA and bpe in toluene. Yield: 81%. IR (THF): $\nu_{\text{co}} = 2023(\text{s}), 1909(\text{m}), 1889(\text{m}) \text{ cm}^{-1}$; ^1H NMR (300 MHz, d_6 -DMSO): $\delta = 8.38(\text{d}, 8 \text{ H}, \text{H}_\alpha\text{-Py}), 7.70(\text{d}, 8 \text{ H}, \text{H}_\beta\text{-Py}), 7.54(\text{s}, 4 \text{ H}, \text{vinyl}), 7.18(\text{m}, 18 \text{ H}, \text{C}_5\text{H}_5\text{-toluene}, \text{CH-CA}), 2.29(\text{s}, 6 \text{ H}, \text{toluene})$; Anal. Calc for $(\text{Re}_4\text{C}_{48}\text{H}_{20}\text{Cl}_4\text{N}_4\text{O}_{20}) \cdot (\text{C}_7\text{H}_8)_2$: C 36.44, H 1.78, N 2.74. Found: C 36.83, H 1.81, N 2.65; MS (FAB, ^{187}Re): $m/z = 1859.3 (\text{M}^+)$.

Syntheses of **2a**·2toluene and **2a**·2benzene

Compound **2a**·toluene was obtained by adopting a similar procedure as **1a**·*p*-xylene, using $\text{Re}_2(\text{CO})_{10}$, H_2dhnq and bpy in toluene. Yield: 76%. IR (CH_2Cl_2): $\nu_{\text{co}} = 2018(\text{s}), 1917(\text{s}), 1896(\text{s}) \text{ cm}^{-1}$; ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 8.57(\text{d}, {}^3J = 5.2 \text{ Hz}, 8 \text{ H}, \text{H}_\alpha\text{-Py}), 7.95(\text{d}, 8 \text{ H}, \text{H}_\beta\text{-Py}), 7.22(\text{s}, 8 \text{ H}, \text{CH-dhnq}), 7.25\text{--}7.11(\text{m}, \text{C}_5\text{H}_5\text{-toluene}), 2.28(\text{s}, \text{CH}_3\text{-toluene})$; ^{13}C NMR (125 MHz, d_6 -DMSO): $\delta = 200.4, 197.8(1:2, \text{CO}), 171.0(\text{C}^1, \text{C}^4), 151.6(\text{C}^2, \text{bpy}), 150.4(\text{C}^4, \text{bpy}), 145.0(\text{C}^5, \text{C}^8), 138.0(\text{C}^2, \text{C}^3), 137.3(\text{C}^1, \text{toluene}), 128.9(\text{C}^2, \text{toluene}), 128.2(\text{C}^3, \text{toluene}), 125.3(\text{C}^4, \text{toluene}), 123.9(\text{C}^3, \text{bpy}), 121.4(\text{C}^7, \text{C}^6), 114.5(\text{C}^9, \text{C}^{10}), 21.0(\text{C}^\alpha, \text{toluene})$; Anal. Calc for $(\text{Re}_4\text{C}_{52}\text{H}_{24}\text{N}_4\text{O}_{20}) \cdot (\text{C}_7\text{H}_8)_{1.8}$: C 40.10, H 2.00, N 2.89. Found: C 40.09, H 1.95, N 3.09; MS (FAB, ^{187}Re): $m/z = 1772 (\text{M}^+)$. The similar reaction in the presence of benzene instead of toluene as solvent yields **2a**·2benzene. One single crystal of **2a**·2benzene was selected for X-ray diffraction analysis.

Synthesis of **2b**·2toluene

Compound **2b** was obtained by adopting a similar procedure as **1a**·*p*-xylene, using $\text{Re}_2(\text{CO})_{10}$, H_2dhnq and bpe in toluene. Yield: 63%. For **2b**: IR (THF): $\nu_{\text{co}} = 2015(\text{s}), 1916(\text{s}), 1896(\text{s}) \text{ cm}^{-1}$; ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 8.45(\text{d}, {}^3J = 6.6 \text{ Hz}, 8 \text{ H}, \text{H}_\alpha\text{-Py}), 7.66(\text{d}, 8 \text{ H}, \text{H}_\beta\text{-Py}), 7.48(\text{s}, 4 \text{ H}, \text{vinyl}), 7.19(\text{s}, 8 \text{ H}, \text{CH-dhnq}), 7.26\text{--}7.11(\text{m}, \text{C}_5\text{H}_5\text{-toluene}), 2.29(\text{s}, \text{CH}_3\text{-toluene})$; ^{13}C NMR (125 MHz, d_6 -DMSO): $\delta = 200.5, 197.8(1:2, \text{CO}), 171.0(\text{C}^1, \text{C}^4), 151.3(\text{C}^2, \text{bpe}), 148.5(\text{C}^4, \text{bpe}), 146.0(\text{C}^5, \text{C}^8), 137.9(\text{C}^2, \text{C}^3), 137.3(\text{C}^1, \text{toluene}), 131.7(\text{vinyl}), 128.9(\text{C}^2, \text{toluene}), 128.2(\text{C}^3, \text{toluene}), 125.3(\text{C}^4, \text{toluene}), 123.8(\text{C}^3, \text{bpe}), 121.9(\text{C}^7, \text{C}^6), 114.5(\text{C}^9, \text{C}^{10}), 21.0(\text{C}^\alpha, \text{toluene})$; Anal. Calc for $(\text{Re}_4\text{C}_{56}\text{H}_{28}\text{N}_4\text{O}_{20}) \cdot (\text{C}_7\text{H}_8)_2$: C 41.91, H 2.21, N 2.79. Found: C 41.96, H 2.14, N 2.94; MS (FAB, ^{187}Re): $m/z = 1824 (\text{M}^+)$.

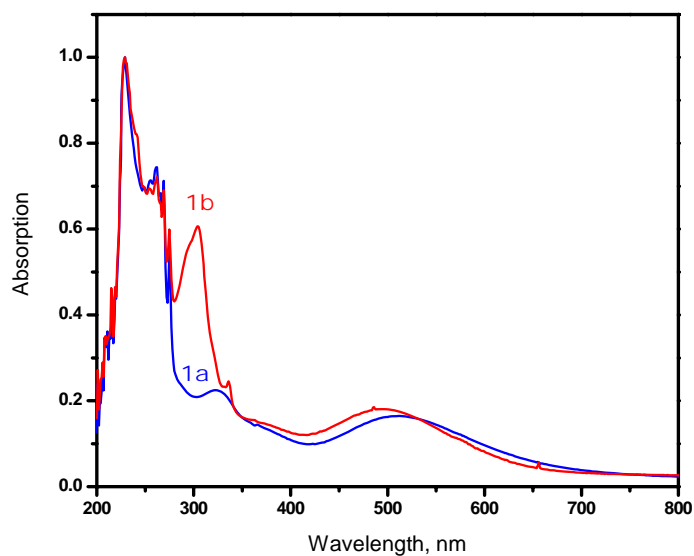


Figure S1. Electronic absorption spectra of **1a** and **1b** in THF.

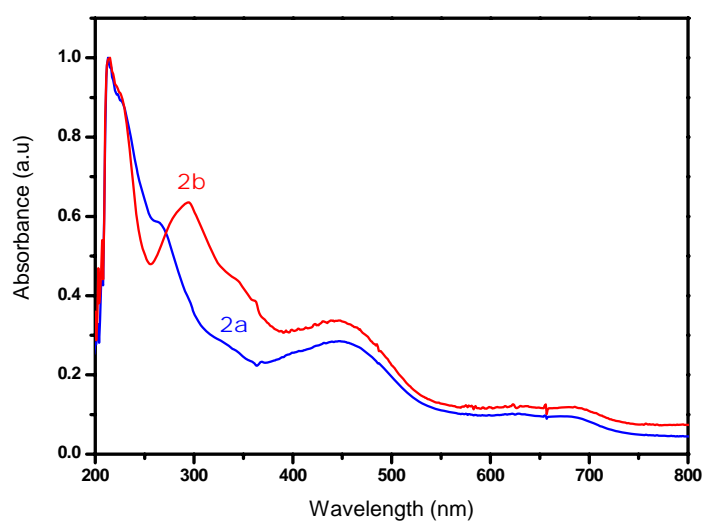


Figure S2. Electronic absorption spectra of **2a** and **2b** in THF.

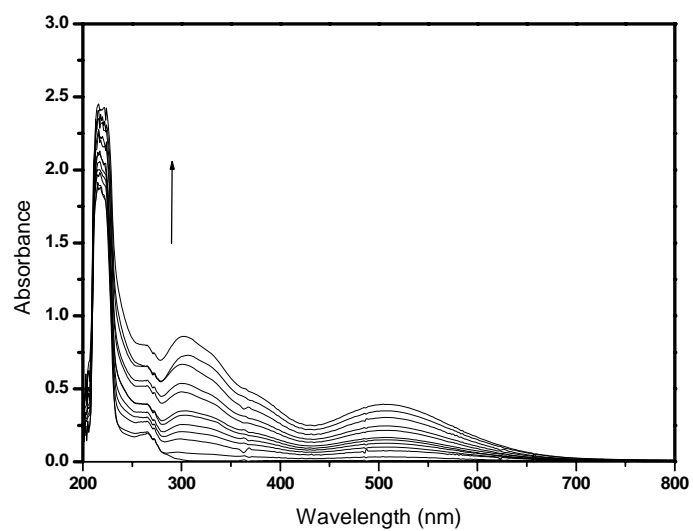


Figure S3. Changes in absorbance of mesitylene with the gradual addition of **1b** in THF.

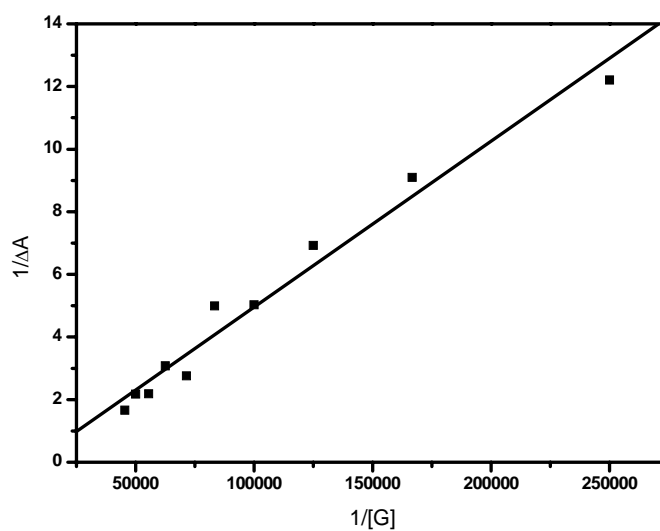


Figure S4. Benesi-Hildebrand plot for **1b** with mesitylene in THF.