Cyclic pyridyltriazole-Cu(II) dimers as supramolecular hosts

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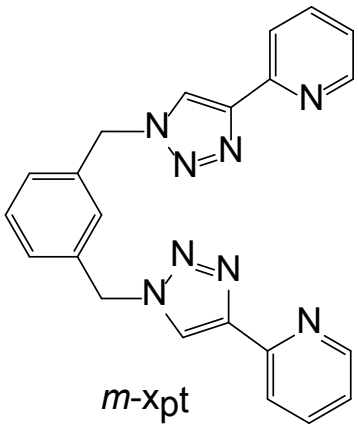
Electronic Supplementary Information (ESI)

Experimental.

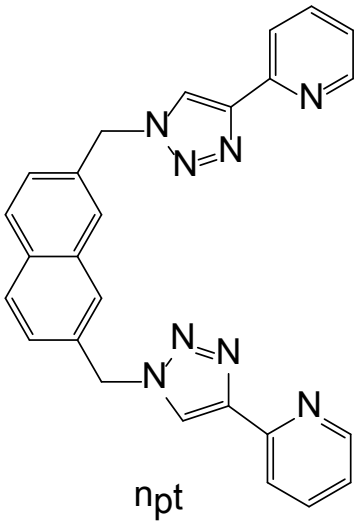
***m*-Xylylenebis(pyridyltriazole), *m*-xpt.** The compound was prepared by following the reported procedure[1] with a slight modification in the final work-up. To a stirred solution of α,α'-dibromo-*m*-xylene (792 mg, 3.0 mmol) in DMF/H_2O (15 mL, 4:1 v/v) was added NaN_3 (410 mg, 6.30 mmol), Na_2CO_3 (312 mg, 3.0 mmol), $CuSO_4 \cdot 5H_2O$ (300 mg, 1.2 mmol), and ascorbic acid (420 mg, 2.4 mmol), followed by 2-ethynylpyridine (640 mg, 6.0 mmol). The reaction mixture was stirred for 20 h at room temperature, and then poured into NH_3/EDTA solution (2.00 g of $Na_2H_2EDTA \cdot 2H_2O$ in 5 mL of 28% aqueous NH_3, diluted to 100 mL with H_2O) and the mixture extracted with chloroform (2 x 100 mL). The organic layer was collected, dried over $MgSO_4$, and evaporated to dryness. The crude product was purified by trituration with cold diethyl ether to give *m*-xpt (910 mg, 77%) as a light-brown solid. All physical and spectroscopic characterization data were consistent with the product reported by Crowley et al.[1]



m-xpt

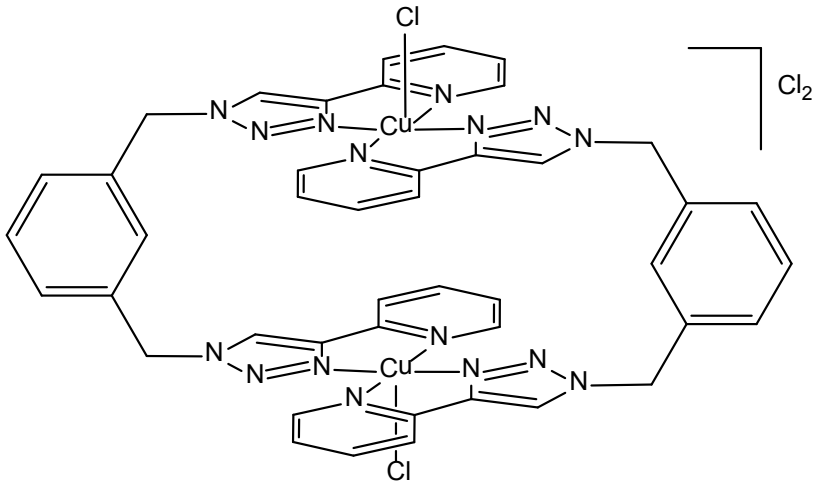
(2,7-Naphthalenediylbis(methylene))bis(pyridyltriazole), npt. To a stirred solution of 2,7-bis(bromomethyl)naphthalene (prepared by the method of Katz and Ślusarek[2]) (500 mg, 1.59 mmol) in DMF/H_2O/THF (14 mL, 3:2:2 v/v) was added NaN_3 (228 mg, 3.50

mmol), Na_2CO_3 (168 mg, 1.59 mmol), $CuSO_4 \cdot 5H_2O$ (158 mg, 0.64 mmol) and ascorbic acid (223 mg, 1.27 mmol). 2-Ethynylpyridine (328 mg, 3.18 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The mixture was worked up as described above, giving npt (452 mg, 64%) as a colorless solid, mp: 212-214 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 5.74 (s, 4H, CH_2), 7.18-7.20 (m, 2H, Ar), 7.44 (dd, 2H, ^3J = 8.5 Hz, ^4J = 1.5 Hz, Ar), 7.74-7.77 (m, 4H, Ar), 7.84 (d, 2H, ^3J = 8.5 Hz, Ar), 8.06 (s, 2H, triazole), 8.17 (d, 2H, ^3J = 8 Hz), 8.51 (d, 2H, ^3J = 4.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 54.6, 112.75, 120.4, 122.2, 123.1, 126.5, 127.8, 129.3, 133.0, 133.2, 133.4, 137.1, 149.1, 149.6, 150.3. ESI-MS: m/z 445.19 $[M + H]^+$.



npt

$[Cu_2(m\text{-xpt})_2Cl_2]Cl_2$, 1: To a stirred solution of $CuCl_2 \cdot 2H_2O$ (86 mg, 0.51 mmol) in acetonitrile (25 mL), *m*-xpt (200 mg, 0.51 mmol) dissolved in chloroform (25 mL) was added dropwise. The reaction mixture was allowed to stir at room temperature for 3 h. The green precipitate was separated by filtration, washed with acetonitrile followed by chloroform, and dried to give **1** (242 mg, 90.2%) as a green powder. ESI-MS: m/z 1019.11 $[M - Cl]^+$, 984.14 $[M - Cl_2]^+$, 886.23 $[M - CuCl_3]^+$, 425.63 $[M - CuCl_4]^{2+}$. Anal. Calc. for $[Cu_2(m\text{-xpt})_2Cl_2]Cl_2 \cdot 3H_2O$: C 47.53, H 3.81, N 20.16 Cl 12.76. Found: C 47.52, H 3.78, N 20.46, Cl 12.58. Slow evaporation of solution in a mixture of water and DMF over several weeks gave blue crystals $[Cu_2(m\text{-xpt})_2Cl_2]Cl_2 \cdot 4DMF$ which were suitable for X-ray analysis.



$[Cu_2(m\text{-xpt})_2Cl_2]Cl_2$, **1**

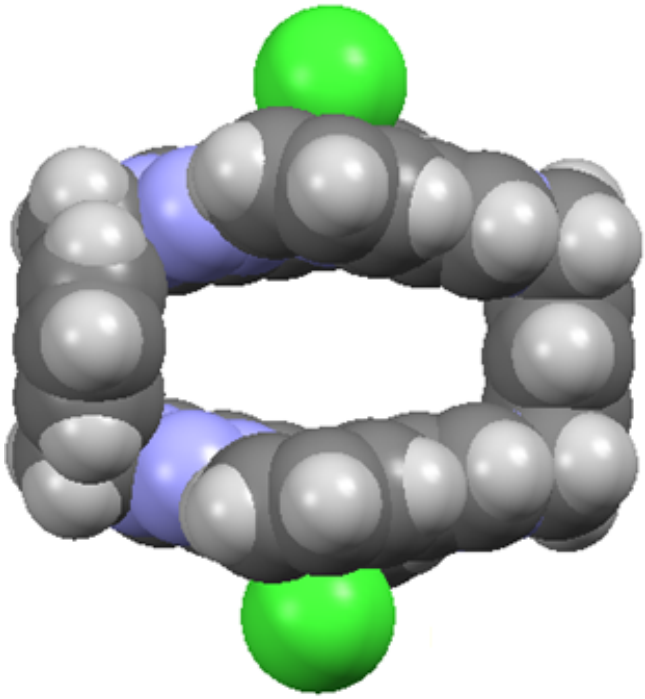
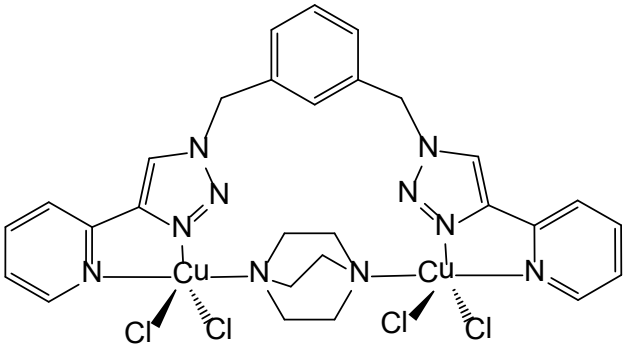


Figure S1. Space-filling model of macrocycle $[Cu_2(m\text{-xpt})_2Cl_2]^{2+}$, **1**, showing its internal cavity.

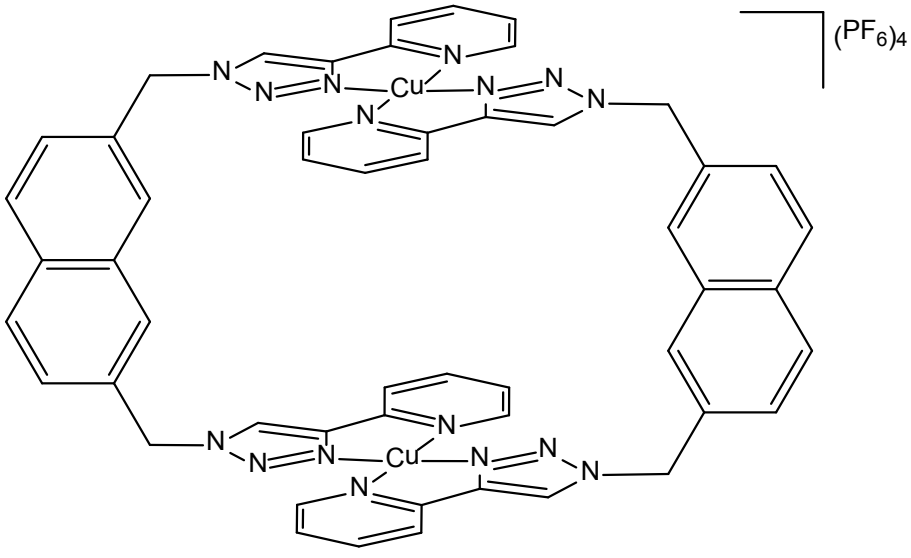
$[Cu_2(m\text{-xpt})(\mu\text{-dabco})Cl_4]$, 2: To a stirred solution of $CuCl_2{\cdot}2H_2O$ (43 mg, 0.25 mmol) in DMF (2 mL), a mixture of *m*-xpt (100 mg, 0.25 mmol) and dabco (14 mg, 0.13 mmol) dissolved in DMF (3 mL) was added. The mixture was brown at first but turned greenish yellow upon stirring. The reaction mixture was cooled overnight at −5 °C to give

microcrystalline solid **2** (78 mg, 80%). Anal. Calc. for $[Cu_2(m\text{-xpt})(\mu\text{-dabco})]Cl_4$: C 43.37, H 3.90, N 18.06, Cl 18.29. Found: C 43.32, H 3.95, N 18.22, Cl 18.32.



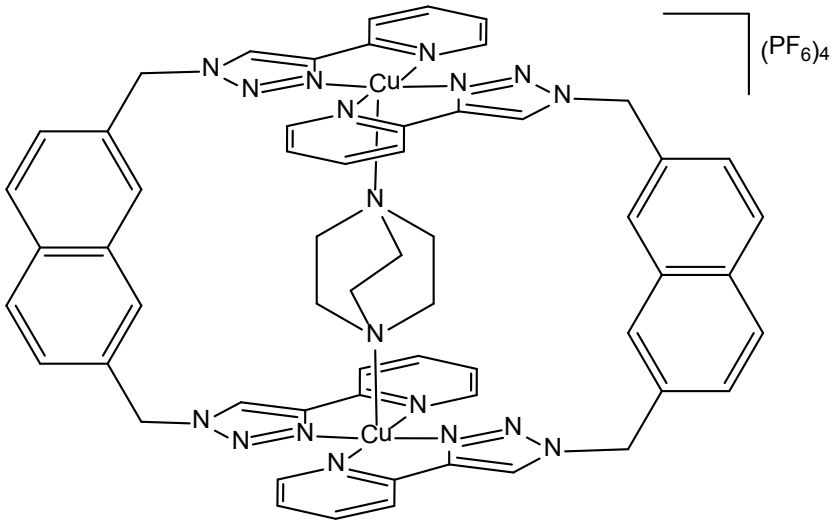
$Cu_2(m\text{-xpt})(\mu\text{-dabco})Cl_4$, **2**

$[Cu_2(npt)_2](PF_6)_4$, 3: To a stirred solution of npt (100 mg, 0.23 mmol) in DMF (4 mL), $Cu(NO_3)_2{\cdot}3H_2O$ (54 mg, 0.23 mmol) was added. The blue-green solution was left to stand for 5 days, at which point a light blue precipitate had formed. The reaction mixture was filtered. The solid was washed with acetone, dissolved in hot water (50 mL), and excess NH_4PF_6 added. The resulting suspension was allowed to cool to room temperature and filtered. The solid was washed with water and dried to give light green **3** (147 mg, 82%). X-ray quality crystals of the product were obtained by vapor diffusion of diethyl ether into its solution in DMF. ESI-MS: m/z, 1449.11 $[M - PF_6]^+$, 1159.18 $[M - 3PF_6]^+$, 951.29 $[M - Cu - 4PF_6]^+$. Anal. Calc. for $Cu_2(npt)_2(PF_6)_4{\cdot}6DMF{\cdot}H_2O$: C 40.96, H 4.13, N 15.01. Found: C 40.85, H 4.07, N 14.92.



$[Cu_2(npt)_2](PF_6)_4$, **3**

$[Cu_2(npt)_2(\mu\text{-dabco})](PF_6)_4$, 4: To a stirred solution of **3** (50 mg, 0.03 mmol) in DMF (2 mL), dabco (17 mg, 0.15 mmol) was added. Vapor diffusion of diethyl ether into the resulting solution produced green block-shaped X-ray quality crystals after 4-5 days. The crystals were washed with diethyl ether and air-dried to give **4** (26 mg, 51%).



$[Cu_2(^{n}pt)_2(\mu\text{-dabco})](PF_6)_4$, **4**

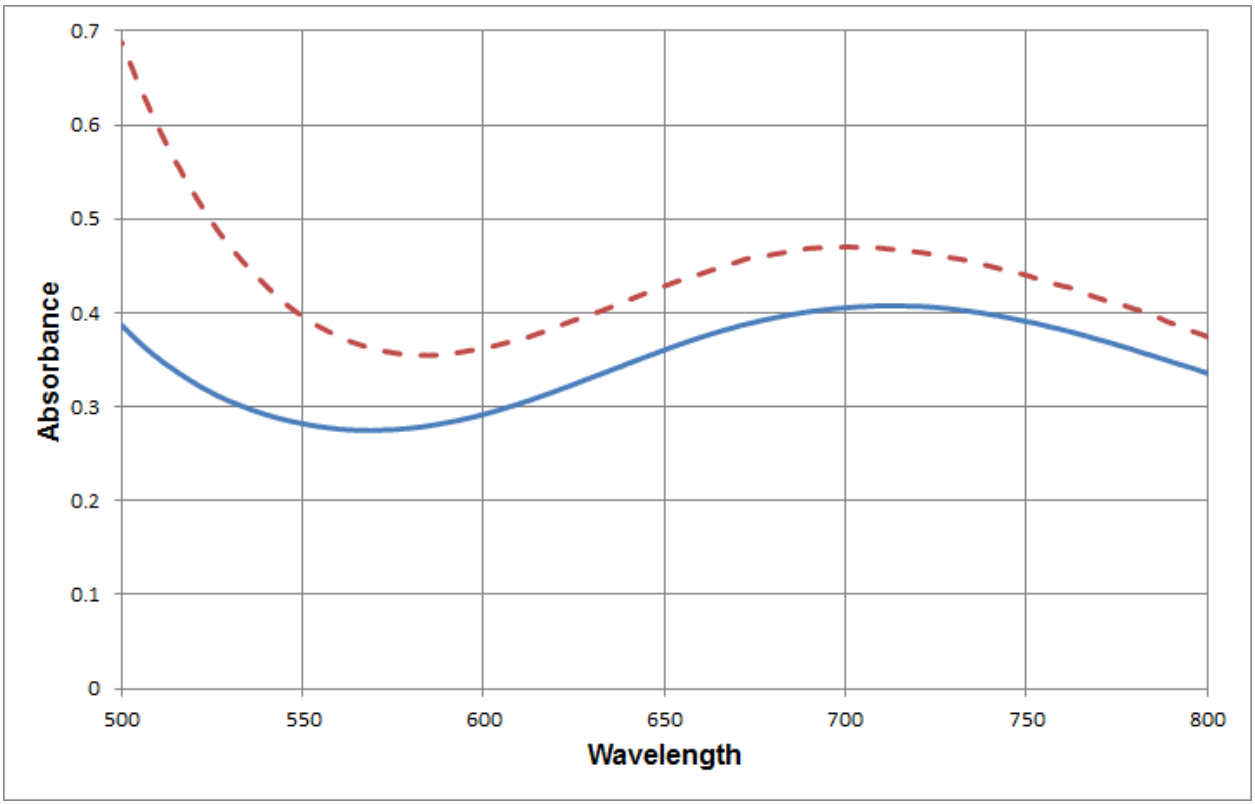


Figure S2. A portion of the electronic spectra of complex **3** (———) with λ_{max} = 714 nm, ε = 163 $M^{-1}cm^{-1}$ (2.5 mM in DMF); and complex **3** in the presence of dabco (5 mM in DMF) (— — —) with λ_{max} = 700 nm, ε = 188 $M^{-1}cm^{-1}$.

X-ray Experimental

The crystal structures of **1**, **2**, **3** and **4** were determined at low temperature using a Bruker Kappa Apex-II DUO diffractometer, with MoKα (for **1**) or CuKα (for **2**, **3**, and **4**) radiation. Crystal data: **1**, $[C_{44}H_{36}Cl_2Cu_2N_{16}]Cl_2 \cdot 4C_3H_7NO$, M = 1350.15, orthorhombic, a = 19.246(2), b = 14.0507(15), c = 22.037(3) Å, V = 5959.2(12) Å^3, T = 90 K, space group *Cmca*, Z = 4, 4699 unique reflections (R_{int} = 0.044), disordered solvent removed using SQUEEZE. Final R = 0.046 (3418 data with $I > 2\sigma(I)$), $wR(F^2)$ = 0.120 (all data), CCDC 931039. **2**, $C_{28}H_{30}Cl_4Cu_2N_{10} \cdot 1.085C_3H_7NO \cdot 1.085C_4H_{10}O$, M = 935.23, triclinic, a = 11.904(2), b = 12.344(2), c = 14.031(3) Å, α = 92.315(9), β = 91.163(9), γ = 105.201(8)°, V = 1987.0(6) Å^3, T = 100 K, space group $P\bar{1}$, Z = 2, 7076 unique reflections (R_{int} = 0.052), disordered solvent removed using SQUEEZE, two-component nonmerohedral twin. Final R = 0.043 (5569 data with $I > 2\sigma(I)$), $wR(F^2)$ = 0.121 (all data), CCDC 931040; **3**, $[C_{61}H_{63}Cu_2N_{19}O_4](PF_6)_4 \cdot 4C_3H_7NO$, M = 2125.65, triclinic, a = 12.8788(14), b = 13.7253(14), c = 25.452(3) Å, α = 83.482(7), β = 87.955(8), γ = 88.596(7)°, V = 4466.2(9) Å^3, T = 95 K, space group $P\bar{1}$, Z = 2, 12307 unique reflections (R_{int} = 0.071), two-component nonmerohedral twin. Final R = 0.077 (6796 data with $I > 2\sigma(I)$), $wR(F^2)$ = 0.215 (all data), CCDC 929880; **4**, $[C_{61}H_{61}Cu_2N_{19}O_2](PF_6)_4 \cdot 5.55C_3H_7NO$, M = 2204.93, triclinic, a = 13.0571(11), b = 14.5591(12), c = 24.932(2) Å, α = 88.774(3), β = 86.565(3), γ = 81.906(3)°, V = 4683.4(7) Å^3, T = 90 K, space group $P\bar{1}$, Z = 2, 16478 unique reflections (R_{int} = 0.037), disordered solvent removed using SQUEEZE. Final R = 0.076 (15083 data with $I > 2\sigma(I)$), w$R(F_2)$ = 0.214 (all data), CCDC 929881.

References:

1. J. D. Crowley and P. H. Bandeen, *Dalton Trans.*, 2010, **39**, 612-623.
2. T. J. Katz and W. Slusarek, *J. Am. Chem. Soc.*, 1979, **101**, 4259-4267.