Electronic supplementary information for:

Eliminating the need for independent counterions in the construction of metal organic rotaxane frameworks (MORFs)

Lisa K. Knight, V. Nicholas Vukotic, Elizabeth Viljoen, Christopher B. Caputo and Stephen J. Loeb*

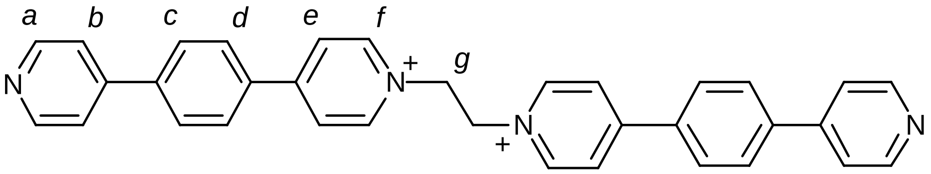
Synthesis of 1,4'-bis(4-pyridyl)benzene):

This compound was prepared by a slight modification of the literature method (Y.-F. Han, Y.-J. Lin, W.-G. Jia and G.-X. Jin, *Organometallics*, 2008, **27**, 4088.) Into a 100 mL Schlenk flask were charged 1,4-dibromobenzene (1.014 g, 4.30 x 10^{-3} mol) and 4-pyridylbenzeneboronic acid (1.322 g, 1.08 x 10^{-2} mol). The Schlenk flask was evacuated and flushed with nitrogen and dry, degassed DMF (40 mL) was added to the reagents. Into a separate 50 mL Schlenk flask, Na_2CO_3 (2.277 g, 2.15 x 10^{-2} mol) was added and it was also evacuated and flushed with nitrogen. The Na_2CO_3 was dissolved in degassed water (20 mL) and transferred by syringe to the first flask containing the organic compounds. The catalyst, $Pd(PPh_3)_4$ (0.247 g, 2.14 x 10^{-4} mol) was added to the Schlenk flask and the reaction mixture was refluxed for 24 h. Yield: 0.309 g, 31 %, ^{1}H NMR ($CDCl_3$): δ = 8.67 (d, 4H, *o*-C_5H_4, *J* = 6.0 Hz), 7.97 (s, 4H, C_6H_4), and 7.79 (d, 4H, *m*- NC_5H_4, *J* = 6.1 Hz).

Synthesis of [2][Br]$_2$:

A three-neck round bottom flask was charged with 1,4-bis(4'-pyridyl)benzene (0.136 g, 5.85 x 10^{-4} mol) and acetonitrile (10 mL). The reaction mixture was refluxed and the 1,4-bis(4'-pyridyl)benzene dissolved generating a clear, yellow solution. 1,2-Dibromoethane

(0.055 g, 2.90 x 10^{-4} mol) was weighed into a separate 10 mL beaker and dissolved in acetonitrile (10 mL). The 1,2-dibromoethane solution was then slowly added dropwise over the course of 1 h to the refluxing 1,4-bis(4'-pyridyl)benzene. The reaction mixture was refluxed for 72 h. A significant amount of beige powder precipitated from the solution. The product was isolated via filtration and washed with dichloromethane to remove any unreacted 1,4-bis(4'-pyridyl)benzene or 1,2-dibromoethane. The residue was heated in toluene/water mixture and the layers separated while warm. Pure product was obtained after removal of the water on a rotary-evaporator. Yield: 0.033 g, 17 %. ^{1}H NMR (DMSO-d^6): δ = 9.07 (*f* - d, 4H, *J* = 6.7 Hz), 8.73 (*a* - d, 4H, J = 6.0 Hz), 8.71 (*e* - d, 4H, J = 6.7 Hz), 8.28 (*d* - d, 4H, *J* = 8.4 Hz), 8.13 (*c* - d, 4H, *J* = 8.4 Hz), 7.87 (*b* - d, 4H, *J* = 6.0 Hz), and 5.25 (*g* - s, 4H, CH_2).



Synthesis of {[$Cu_2(OBn)_4(1\subset DSDB24C8)$]}$_x$:

The metal complex, $Cu_2(OBn_2)_4$ (0.006 g, 9.81 x 10^{-6} mol), [**1**][BF_4]$_2$ (0.005 g, 9.73 x 10^{-6} mol) and [NMe_4]$_2$[**DSDB24C8**] (0.008 g, 1.06 x 10^{-5} mol) were each weighed into separate vials. The axle and metal salts were each dissolved in DMF (1.5 mL). The crown ether [NMe_4]$_2$[**DSDB24C8**] was dissolved in MeOH (3.0 mL). The crown ether solution of was then added to the copper complex and the solution became blue in colour. This crown ether plus copper solution was layered carefully on top of the solution of [**1**][BF_4]$_2$ to allowing for a very small degree of mixing. (If the reaction mixture is mixed too thoroughly, a precipitate begins to form immediately.) After sitting several days at room temperature, and in conjunction with yellow crystals of [2]pseudorotaxane, small, deep green block crystals formed that were isolated by manual selection. These crystals were used for single crystal X-ray diffraction experiments of both the copper complex $\{[Cu_2(OBn)_4(\mathbf{1}\subset\mathbf{DSDB24C8})]\}_x$ and the pseudorotaxane $[(\mathbf{1}\subset\mathbf{DSDB24C8})]$.

Synthesis of $\{[CuBr(2\subset DSDB24C8)]\}_x$:

The axle $\mathbf{2}[BF_4]_2$ (0.019 g, 2.92×10^{-5} mol) and CuBr (0.004 g, 2.92×10^{-5} mol) were dissolved in water and this solution layered onto a solution of $[Me_4N]_2[\mathbf{DSDB24C8}]$ (0.024 g, 3.18×10^{-5} mol) in MeOH. After slow evaporation for a week at room temperature, yellow crystals of $\{[CuBr(\mathbf{2}\subset\mathbf{DSDB24C8})]\}_x$ suitable for X-ray diffraction were isolated.