

Electronic Supplementary Information (ESI) for *Dalton Trans*
**Phase transfer catalyst supported, room-temperature biphasic
synthesis: a new approach to the synthesis of coordination
polymers**

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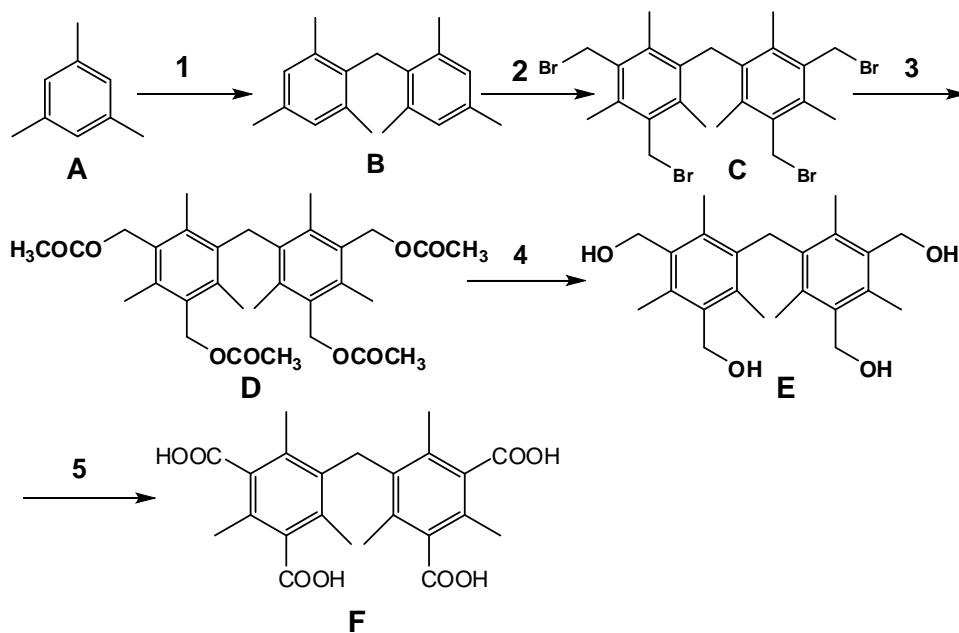
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General Information. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ¹H NMR spectra was measured on a Bruker AVANCE-400 NMR Spectrometer. Elemental analyses (C,H,N) were performed with a PerkinElmer 240 elemental analyzer. The thermogravimetric analysis (TGA) for **BPS-2** and **BPS-3** were carried out in a static N₂ with a heating rate of 10 °C/min.

Preparation of H₄BTMIPA, BPS-2 and BPS-3



Scheme 1. Synthesis of H₄BTMIPA

Preparation of H₄BTMIPA. Into a 250 ml round bottomed flask fitted with stirrer, thermometer, and reflux condenser were introduced 3.3 g of 91% paraformaldehyde and 25 g of 88% formic acid. The mixture was heated to 80 °C and stirred until the paraformaldehyde was dissolved. To the mixture was rapidly added 36 g of mesitylene, and the mixture was stirred under reflux for 6 hours. On cooling to room temperature, a large amount of colorless crystalline powder formed. The solid was collected by filtration and washed by stirring with 50ml benzene. This slurry of solid in benzene was filtered and sucked dry on a buchner funnel, to obtain the colorless crystals B 22.6 g (60%). ¹H NMR (CDCl₃): 6.8 (2H, CH), 4.0(1H, CH₂), 2.2 (3H, CH₃), 2.1(6H, CH₃).

To a mixture of B (18.9 g; 0.075 mol), paraformaldehyde (10.0 g; 0.33 mol), and 50 mL of glacial acetic acid was added 40 mL of a 45 wt% HBr/acetic acid solution rapidly. The

mixture was kept for 12 h at 95 °C and then poured into 100 mL of water. The product was filtered off and dried in vacuum, to obtain a white solid C (43 g, 92%). ¹H NMR (CDCl₃): 4.6 (4H, CH₂), 4.2 (1H, CH₂), 2.4 (3H, CH₃), 2.1 (6H, CH₃).

A mixture of C (2.65 g, 4.16 mmol), anhydrous sodium acetate (2.6 g, 31 mmol), and glacial acetic acid (52 mL) was heated in a sealed tube at 130–140 °C overnight. The resulting heterogeneous mixture was cooled to room temperature, transferred to a flask, and the solvent was evaporated to dryness under reduced pressure. The resulting white solid was partitioned between water (100 mL) and CH₂Cl₂ (100 mL). The separated organic layer was successively washed with a saturated aqueous sodium bicarbonate (100 mL) and water (50 mL). The collected organic layer was dried with anhydrous sodium sulfate and the solvent was evaporated to dryness. The resulting white solid was recrystallized from methanol to give D (1.96 g, 87%) as long white needles. ¹H NMR (CDCl₃): 5.2 (4H, CH₂), 4.2 (1H, CH₂), 2.4 (3H, CH₂), 2.2 (3H, CH₃), 2.1 (6H, CH₃).

A mixture of D (1.96 g, 3.6 mmol), and lithium hydroxide hydrate (0.80 g, 19.2 mmol) in reagent grade ethanol (60 mL) was stirred under reflux overnight. The resulting heterogeneous reaction mixture was cooled to room temperature and evaporated to dryness. The resulting white solid was suspended in cold water (120 mL), filtered, and washed with water (48 mL), dried under heating to 150 °C in vacuo to provide E (1.2 g, 90%) as a white solid. ¹H NMR ([d₆]DMSO): 4.6 (2H, CH₂), 4.4 (4H, CH₂), 4.1 (1H, OH), 2.4 (3H, CH₃), 2.1 (6H, CH₃).

A suspension of E (1.2 g, 3.2 mmol) in reagent grade acetone (50 mL) was treated dropwise with Jones reagent (14 mL, 38.5 mmol CrO₃) at 4 °C. The mixture was stirred for 20 min at 4 °C, 20 min at room temperature, and 5 min at 30 °C. The resulting green

heterogeneous mixture was poured into cold water (150 mL) and extracted with diethyl ether (3×50 mL). The combined organic fractions were extracted with water (50 mL), separated, dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The resulting gray solid was recrystallized from acetonitrile to afford **F** as a white solid (0.56 g, 41%). ¹H NMR ([d₆]DMSO): 13.2 (2H, CO₂H), 4.1(1H, CH₂), 2.2 (3H, CH₃), 2.1(6H, CH₃).

Preparation of BPS-2. A solution of H₄BTMIPA (3 mg, 0.007 mmol) in 0.5 mL cyclohexanol and toluene (v:v 1:1) was layered on an aqueous solution (0.5 mL) of CuCl₂·2H₂O (3mg, 0.017mmol) and 18-crown-6 (1 mg, 0.0038 mmol) in a glass tube at room temperature. Blue block crystals of **BPS-2** were formed in water phase after one day. Yield: 85%. Elemental analysis calcd (%) for **BPS-2**: C 44.45, H 6.27, N 5.13; found: C 44.71, H 5.75, N 4.88 %.

Preparation of BPS-3: Similar procedure as synthesis of **BPS-2** was carried out, except 1,10-phenanthroline (1 mg, 0.005 mmol) was added in the organic phase. Blue block crystals of **BPS-3** were formed in water phase after one week. Yield: 10%.

Crystal structure determination for BPS-2 and BPS-3: Single crystals of the **BPS-2** and **BPS-3** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for them were collected on a Bruker Apex II CCD single-crystal diffractometer with graphite-monochromated Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each, each frame corresponds to a 0.5° scan in 10 s, followed by spot integration and least-squares refinement. Data were

measured using ω scans of 0.5° per frame for 50 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS. In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97 and refined on F^2 by full-matrix least-squares procedures with SHELXL-97. Atoms were located from iterative examination of difference F -maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. For **BPS-3**, The hydrogen atoms attached to water molecules were refined with O-H = 0.85 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. All structures were examined using the Addsym subroutine of PLATON to assure that no additional symmetry could be applied to the models.

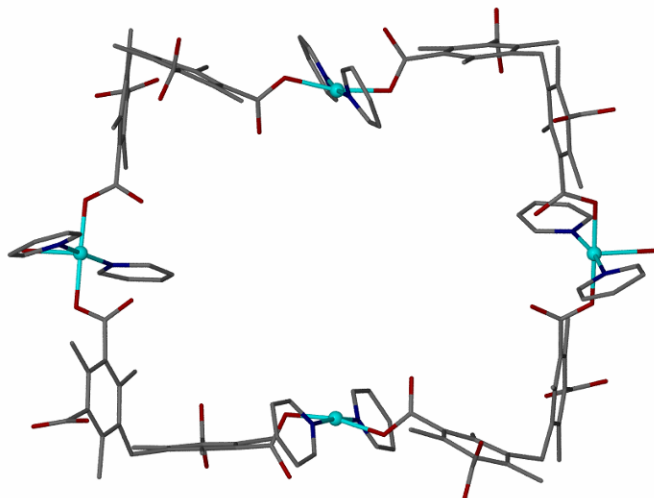


Figure S1. The rectangular subunit formed by four BTMIPA ligands linking four copper ions.

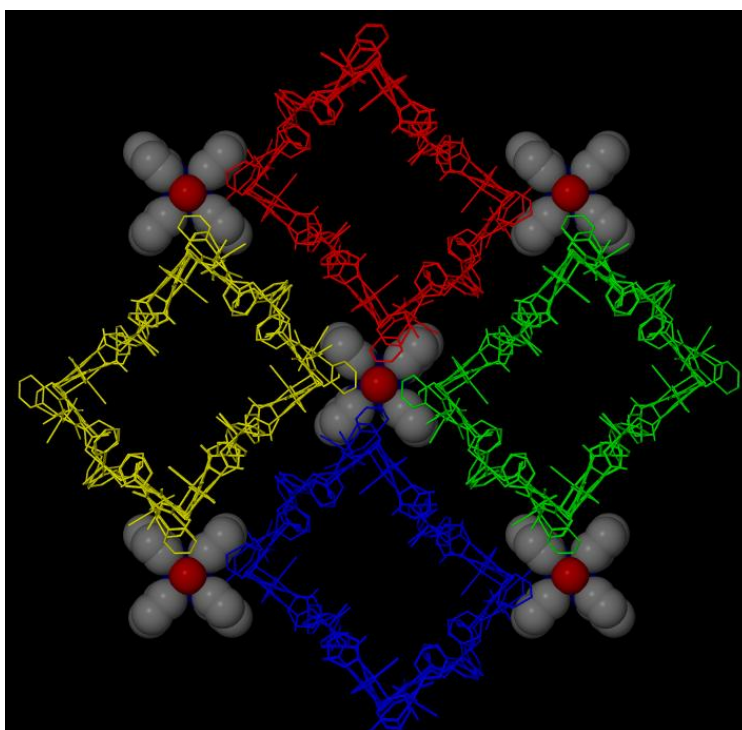


Figure S2. The 3D packing of **BPS-2**. Different independent MONTs are shown in different colors and the $[\text{Cu}(\text{py})_4\text{Cl}-\text{Cl}]$ was shown in a space-filling mode.

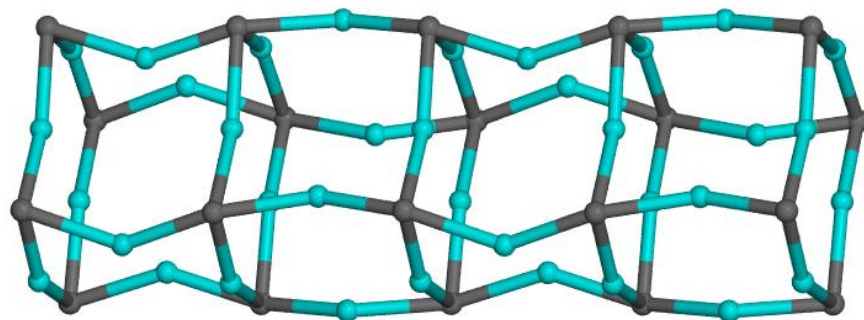


Figure S3. Schematic representation of the anionic metal-organic nanotube after predigesting the BTMIPA ligand as 4-connected linker and copper ion as a linear node.

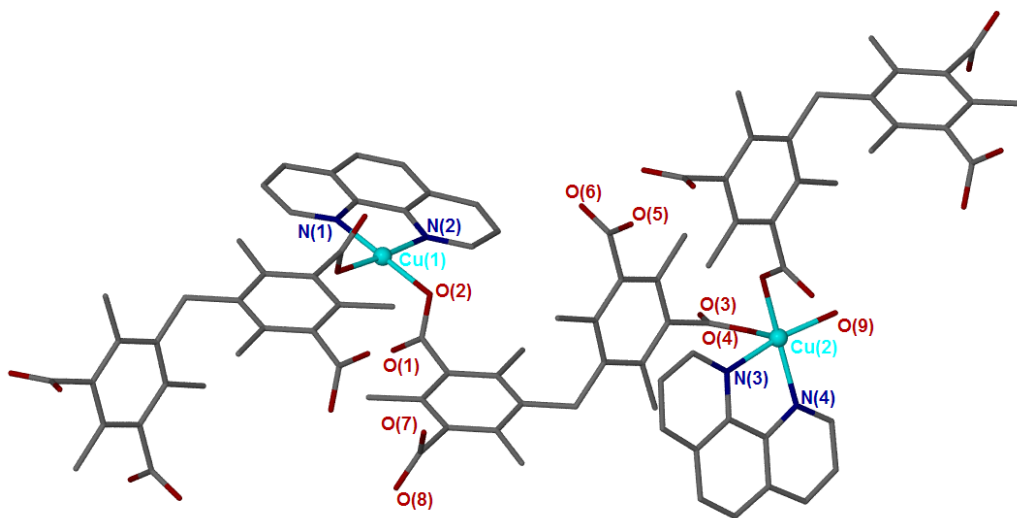


Figure S4. The coordination environment of copper ions in **BPS-3**.

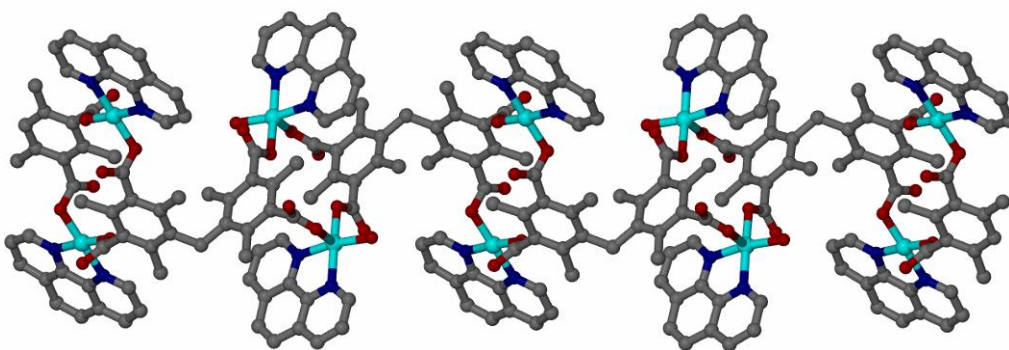


Figure S5. The 1D coordination polymer of **BPS-3**.

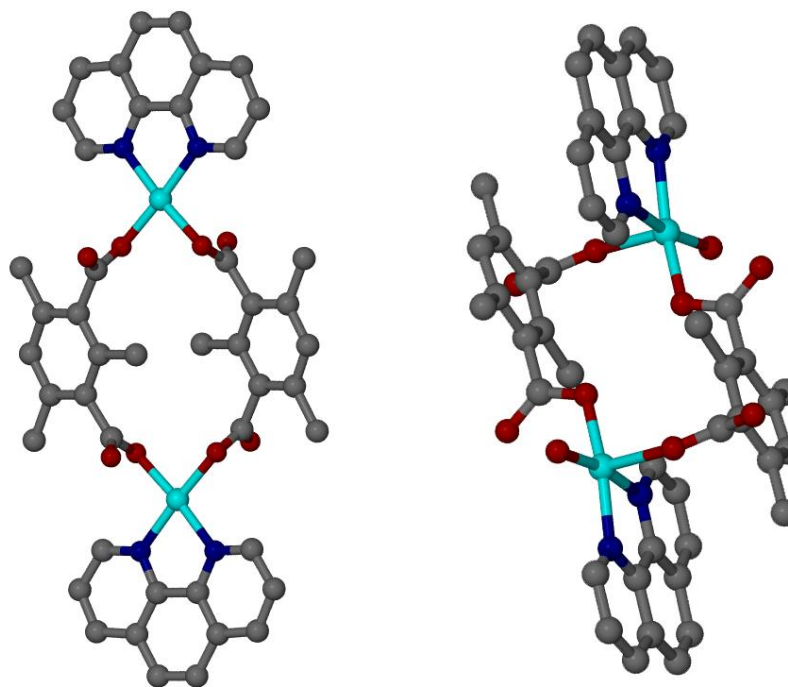


Figure S6. The two types of metallocycles in the 1D coordination polymer.

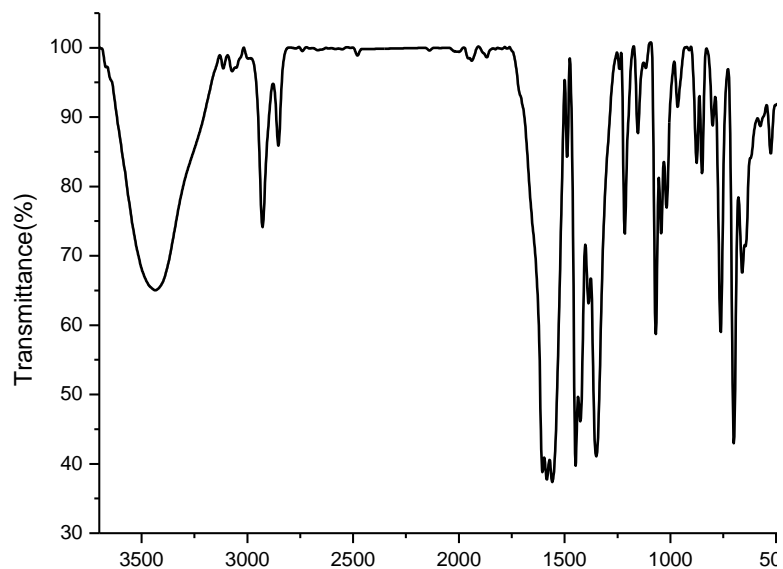


Figure S7. IR for **BPS-2**.

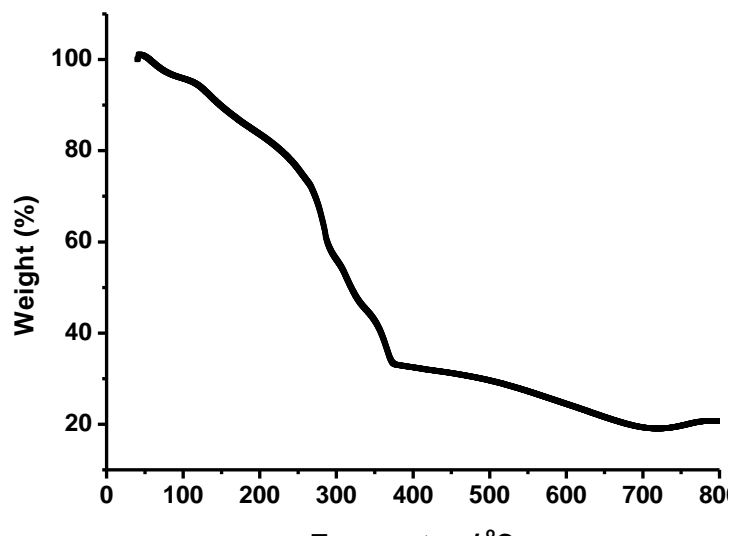


Figure S8. TGA for **BPS-2**. TGA measurement for **BPS-2** revealed that the gradual weight loss of 22.3% from 50 to 240 °C corresponds to the loss of 56 uncoordinated water molecules and 8 coordinated water molecules (calcd: 23.4%).

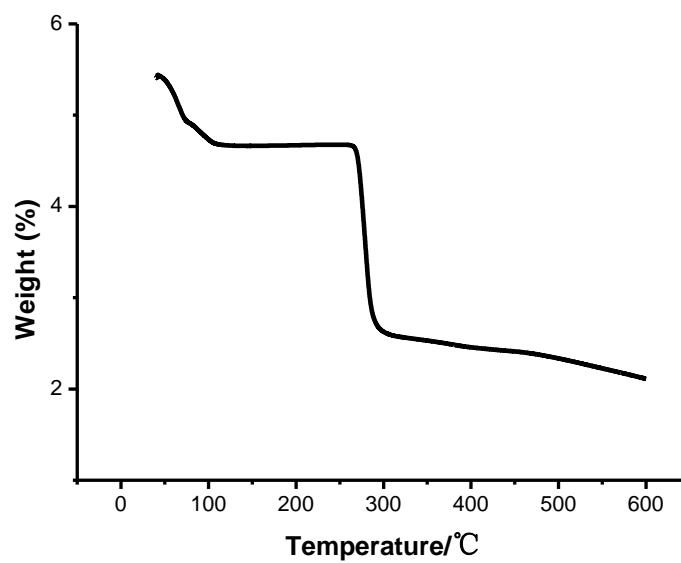


Figure S8. TGA for BPS-3.

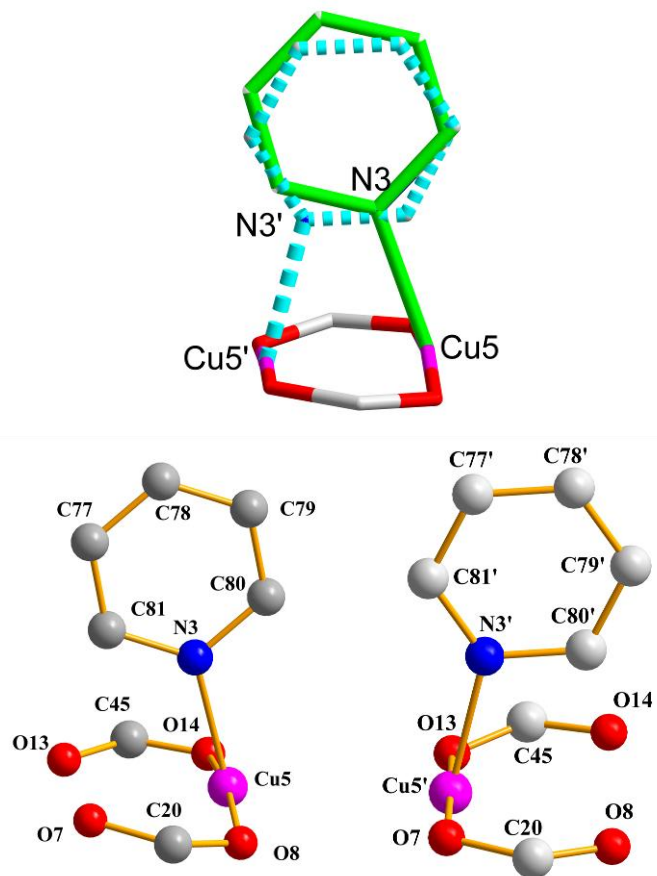


Figure S9. The illustration for disordered parts in BPS-2. Two disordered parts (N3, C77 > C81 and N3', C77' > C81') of pyridine ligand were modeled with the occupancy of 45% and 55%, respectively.