Electronic supplementary information (ESI)

Unprecedented Crystal Dynamics: Reversible Cascades of Single-Crystal-to-Single-Crystal Transformations

Gao-Chao Lv, Peng Wang, Qing Liu, Jian Fan, Kai Chen and Wei-Yin Sun*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

Experiment Section

Materials and Methods. All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The ligand H_3T_4 was synthesized according to the reported procedure.[1] Solid state ^{13}C NMR spectra were measured on a Bruker AVANCE III 400MHz NMR spectrometer at 295 K. N_2 and CO_2 sorption isotherms were measured on a volumetric adsorption apparatus (Bel-max).

Crystal Structure Determination. The crystallographic data collections for **1-3** and **3a** were carried out on a Bruker Apex DUO CCD with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K using the ω-scan technique. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the *SHELXL* crystallographic software package.[2] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms from ligands were generated geometrically and the hydrogen atoms from coordinated solvent molecules are hard to be located in the flourier map, so all the hydrogen atoms from coordinated solvent are absent in the frameworks. The free solvent molecules in all the complexes are highly disordered and cannot be modeled, thus the SQUEEZE routine[3] was applied to remove the contributions to the scattering from the solvent molecules.

Computational Details. To determine the total energy of each compound, the crystallographic data of **1-3** were used for the first principle density functional theory calculations with the CASTEP module1 inside the Materials Studio package. The exchange-correlation functional was calculated by using Perdew-Burke-Ernzerhof (PBE)[4] within the GGA approximation. Valence electrons were described by the Vanderbilt-type nonlocal ultrasoft pseudopotentials,[5] that is H $1s^1$, C $2s^2 2p^2$, N $2s^2 2p^3$, O $2s^2 2p^4$, S $3s^3 3p^4$, Cu

$3d^{10}4s^1$. The parameters used in the calculations and convergence criteria were set by the default values. The Monkhorst-Pack scheme of k-point sampling was used for integration over the first Brillouin zone.[6] A kinetic energy cut-off of 300 eV was used for all the calculations. In order to reduce the cost of the calculation for isolated molecules such as H_2O, MeOH and DMSO, we also built a cubic box with the lattice length of 10 Å. A 4×4×4 Monkhorst-Pack mesh of k-points and the energy cutoff of 380 eV were employed.

REFERENCES

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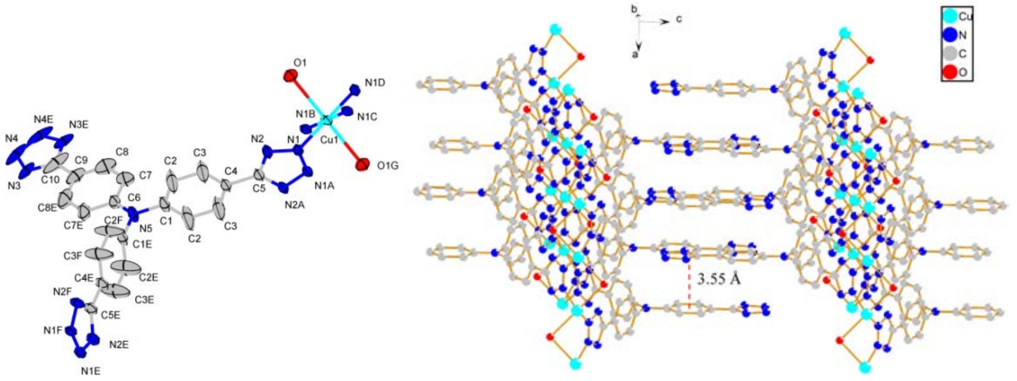

(a) (b)

Fig. S1 (a) Coordination environment of the Cu^{II} in **1** with the ellipsoids drawn at the 30% probability level. Hydrogen atoms and free water molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A 0.5-x, y, z; B 1-x, y, -z; C x, -y, z; D 1-x, -y, -z; E 0.5-x, 1-y, z; F x, 1-y, z; G -0.5+x, -y, -z. (b) Stacking interactions between the tert-C_6H_4 arms of **1**.

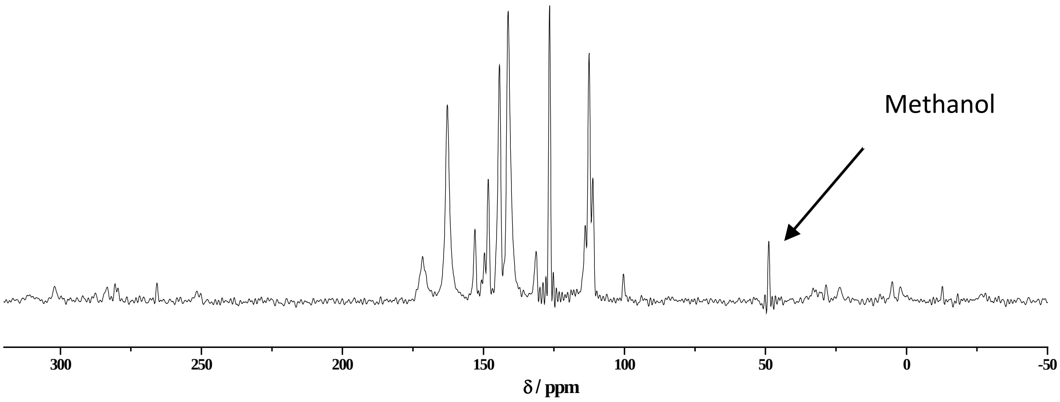

Fig. S2. Solid state ^{13}C NMR spectrum for **1**.

Fig. S3. The energies of the three single-crystal to single-crystal substitution reactions.

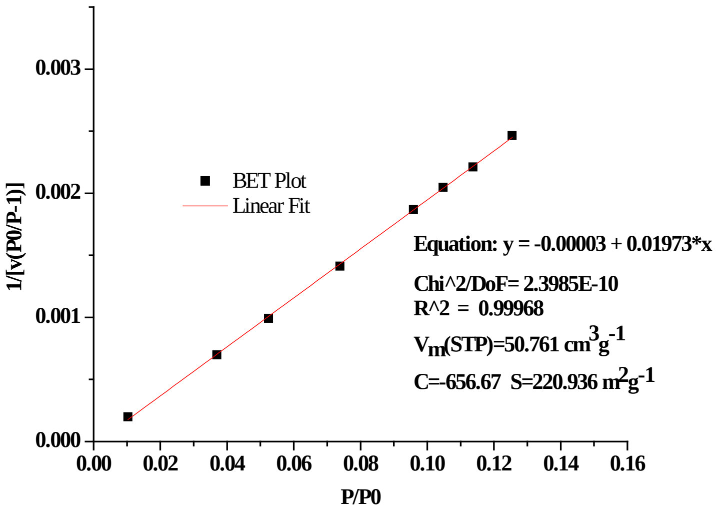

Fig. S4. Langmuir plot of **1** (black squares, selected range of P/Po from 0.01 to 0.13); and its linear fit (red line).

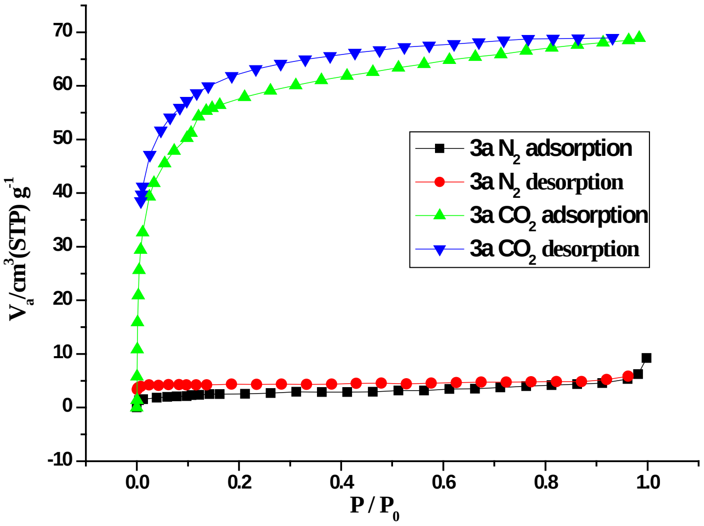

Fig. S5 N_2 (77 K) and CO_2 (195 K) adsorption isotherms of desolvated **3a**.

Table S1 Ground State Energies without the Phonon Contribution

Compound	E (eV)
1	-8778.14
2	-9411.70
3	-8950.48
H_2O	-468.55
DMSO	-1118.21
CH_3OH	-655.23