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In situ spectroscopy studies of CO_2 adsorption in a dually functionalized microporous metal-organic framework

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Supporting Information

1. Synthesis

Synthesis of 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine (H_6TDPAT):

5-aminoisophthalic acid (7.6 g, 0.042 mol), NaOH (2.68 g, 0.067 mol), and $NaHCO_3$ (4.37 g, 0.052mol) were mixed in 70 mL H_2O. The mixture was stirred at 0 ^oC, during which cyanuric chloride (1.84 g, 0.01 mol) in 1,4-dioxane (35 mL) was added dropwise. The mixture was then stirred at 100 ^oC for 24 hours before cooling down to room temperature. The solution was adjusted to pH =2 with HCl solution and the resulting solid was collected by filtration, rinsed several times with distilled water and then hot methanol and dried to give pure H_6TDPAT (5.0 g, yield: 90%). ^1H NMR ([D6] DMSO, 300 MHz): δ=8.12 (3H), 8.47 (6H), 9.67 (3H) ppm.

Synthesis of Cu-TDPAT (1)

$Cu(NO_3)_2 \cdot 3H_2O$ (492 mg, 2.04 mmol), H_6TDPAT (90 mg, 0.147 mmol) were dissolved in 6 mL DMA, 6 mL DMSO, 0.3 mL H_2O and 2.7 mL HBF_4. The mixture was sonicated until homogeneous solution was achieved and then sealed in a vial and heated at 85 ^oC for 5days. Upon cooling to room temperature, blue crystals were collected after filtration and washing with DMA for several times. The as-made Cu-TDPAT sample was immersed in methanol for 3 days to exchange the nonvolatile solvents, during which the extract was decanted and replaced with fresh methanol every 3 hours.

2. Powder X-ray diffraction experiment

Powder X-ray diffraction patterns of **1** were recorded on a 2D detector at X18A of NSLS in Brookhaven National Lab. All the measurements were operated at room temperature using 10keV X-ray right after the corresponding XAFS scans.

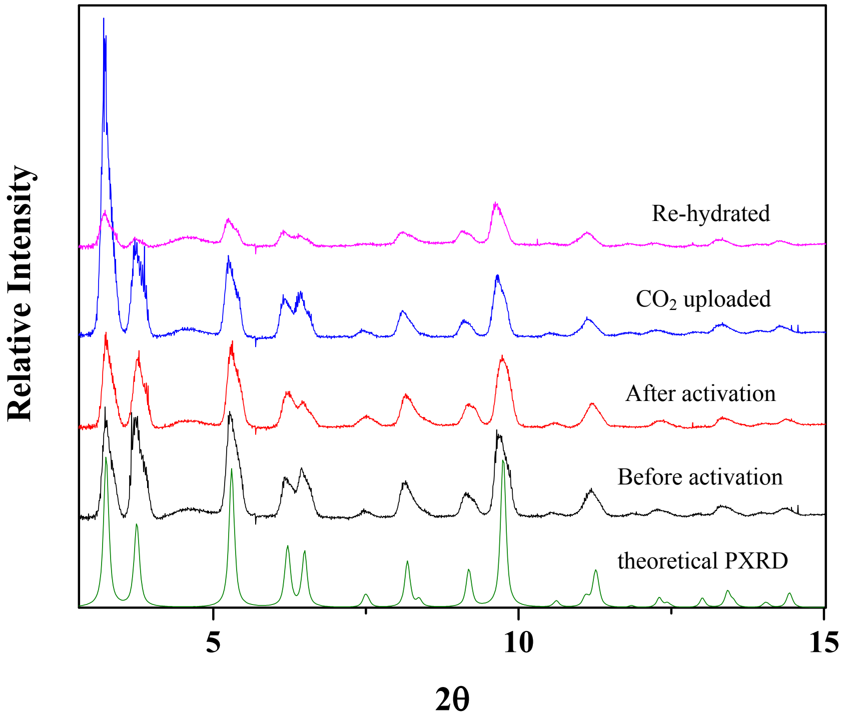

Figure S1. PXRD patterns of **1**before and after activation, upon CO_2 loading and rehydration. Bottom trace: theoretical PXRD pattern

3. DFT computational methods.

The geometry optimization and vibrational modes of TDPAT was calculated using the Gaussian 03 program package[1] at the density functional theory (DFT) level with Beck's three parameter functional and Lee-Yang-Parr functional (B3LYP) method. 6-31G basis set was used. A summary of the calculated frequencies for the most Raman active vibrational modes is provided in Table S1. The vibrational mode anharmonicities were compensated using of a scaling factor of 0.96 in reporting their frequencies.

4. Reference Raman Spectra

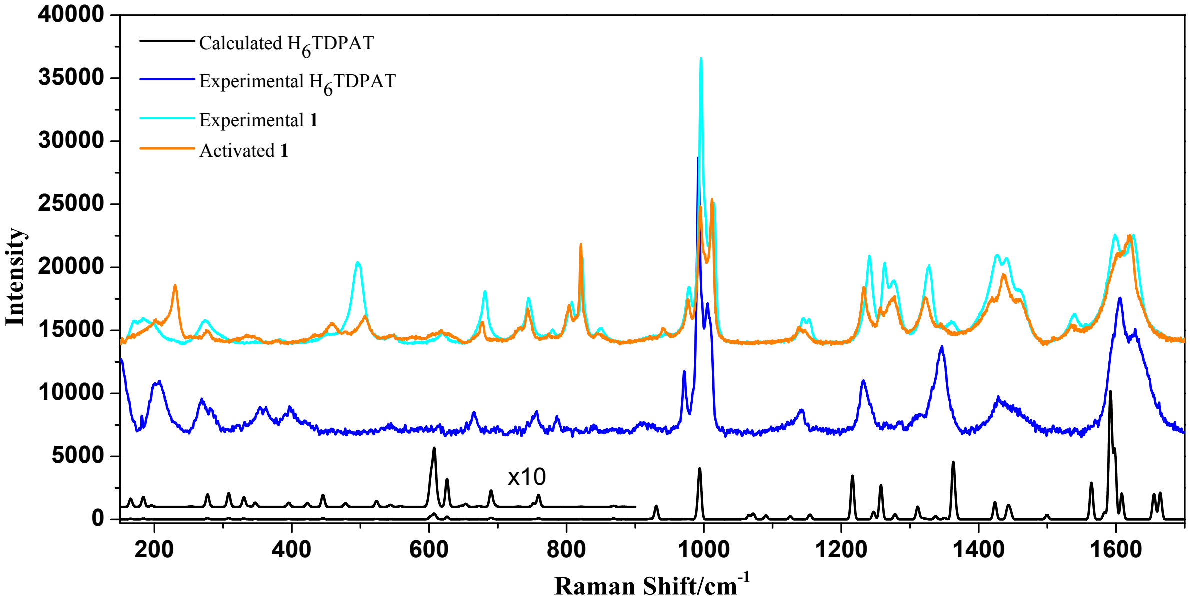

Figure S2. Experimental (orange) and calculated (black) Raman spectra of H_6TDPAT ligand. The calculated low frequency peaks were scaled up for better view.

Table S1. Experimental and calculated Raman active vibrational mode frequencies with descriptions of dominant components of the corresponding vibrational mode assignments for the H_6TDPAT ligand

Exp. Frequency of H_6TDPAT	Calc. Frequency	Raman assignment
199.5	165	In plane Phenyl Ring tilt
207.1	184	Out plane Phenyl Ring tilt
269.1	277	δ Phenyl Ring
354.2	308	β(COOH)
396.5	330	ν(COOH)
665.7	607	δ Phenyl Ring
756.9	690	In plane δ benzene ring
786.0	759	δ Phenl Ring + γ(N-H)$_{amine}$
971.5	931	Triazine ring breath
992.1	994	Phenyl ring breath
1232.0	1216	ν(C-N)$_{tirazine}$
-	1258	ν(C-C)$_{phenyl}$+ν(C-N)+β(C-H)+β(N-H)+β(O-H)
1346.8	1363	ν(C-C)$_{phenyl}$+ν(C-N)+β(C-H)+β(N-H)+β(O-H)
1428.5	1424	ν(C-C)$_{phenyl}$+ν(C-N)+β(C-H)+β(N-H)
-	1443	ν(C-C)$_{phenyl}$+ν(C-N)+β(C-H)+β(N-H)
-	1499	ν(C-C)$_{phenyl}$+ν(C-N)+β(C-H)+β(N-H)
1605.3	1592	ν(C-C)$_{phenyl}$

1626.2	1608	ν(C-OH)

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