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Supporting Information

Pressure-Regulated Synthesis of Cu(TPA)·(DMF) in Microdroplets for Selective CO_2 Adsorption

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Contents

S1. Assumptions for the simulation of microdroplet evaporation

1) Chemicals reactions within the droplet during evaporation are ignored.
2) The initial diameter of the DMF droplets was assumed to be 2 μm.
3) The initial temperature of the microdroplets was 298 K. During the spray process, the temperature was assumed to be uniform within the microdroplets, as the thermal equilibrium characteristic time is much shorter than the evaporation time.
4) Compared with solvent evaporation and vapor diffusion, other dynamics (e.g., droplet coagulation, diffusion and thermophoresis) are not important.
5) The sizes of all particles are larger than 100 nm, making the Kelvin effect negligible.
6) Free convention is not decisive and was not considered in this simulation.

S2. Calculation of the supersaturation ratio

The supersaturation ratio (S) of the solute was calculated by using the following equation:

$$S = \frac{c_t}{c_s} \tag{S1}$$

where, c_t is the concentration of solute at reaction time t; c_s is the solubility of the solute. At the same reaction time t, c_s was considered to have the same value under various operation pressures by neglecting the temperature variations. Given the same initial precursor, the supersaturation ratio in this case is proportional to c_t. Therefore,

$$\frac{S_{P1}}{S_{P2}} = \frac{c_{tP1}}{c_{sP2}} = \frac{V_{P2}}{V_{P1}} = \frac{(D_{dP2})^3}{(D_{dP1})^3} \tag{S2}$$

where, V is the volume of droplet; D_d is the droplet diameter; the subscripted $P1$ and $P2$ represent the operation pressures.

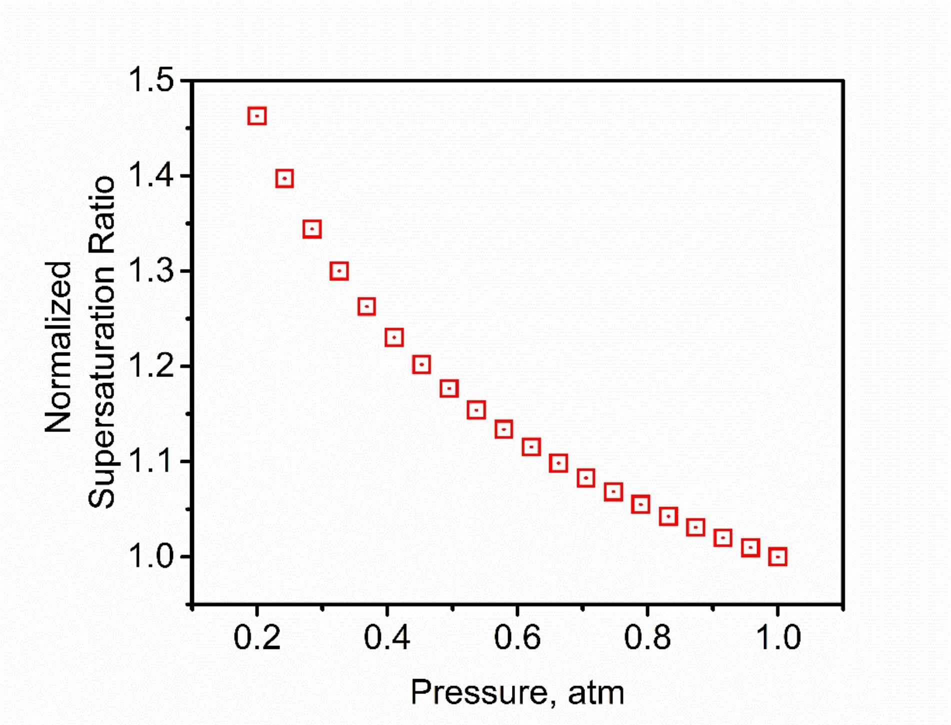

Figure S1. Normalized supersaturation ratios as a function of operation pressures at the evaporation time of 0.04 ms. Note: All the supersaturation ratios were normalized to the value calculated under 1 atm.

S3. Crystal structure of Cu(TPA)·(DMF) synthesized under 1 atm

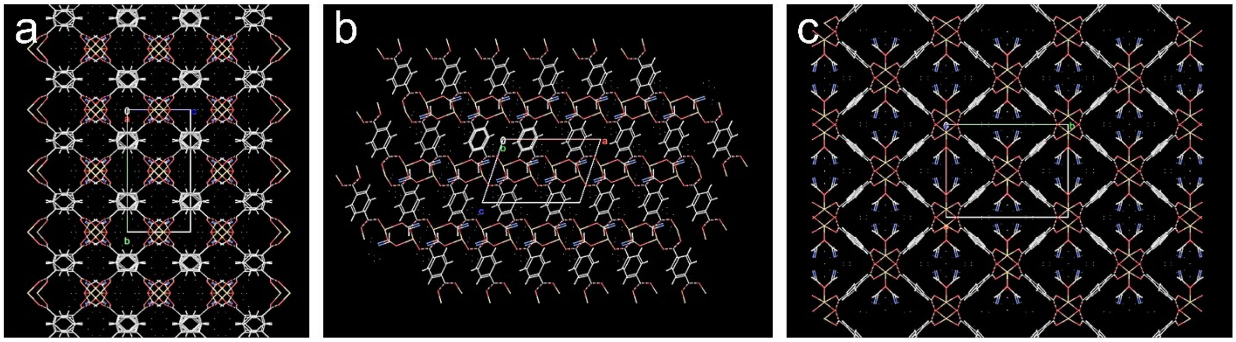

Figure S2. Crystal structure of Cu(TPA)·(DMF) synthesized under 1 atm (CCDC-687690). (a) view along a axis; (b) view along b axis; (c) view along c axis.

S4. FTIR and Raman spectra of Cu(TPA)·(DMF) synthesized under various pressures

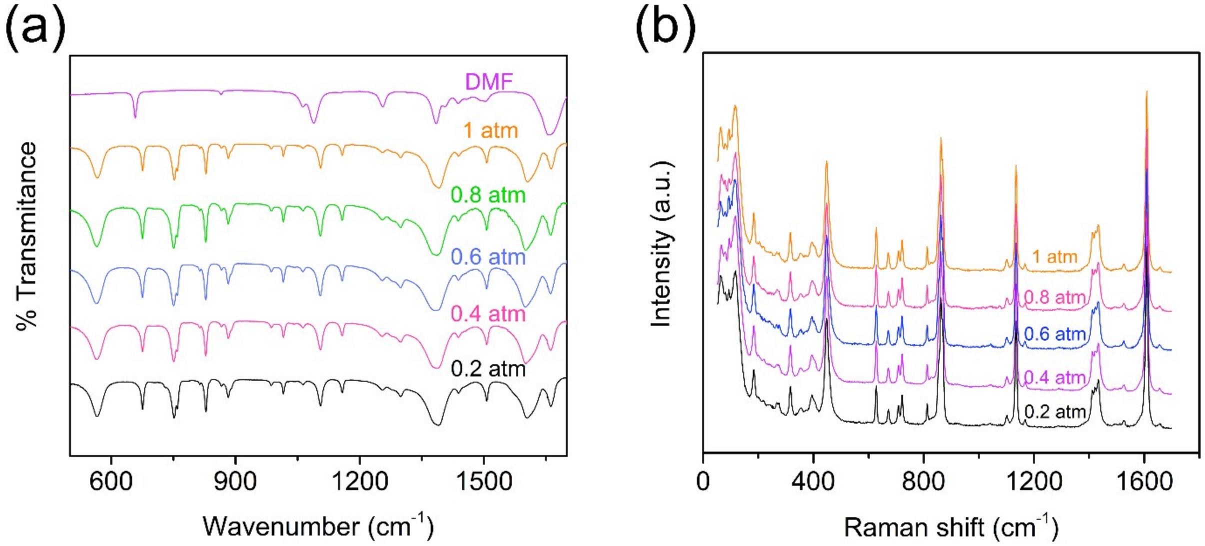

Figure S3. (a) FTIR spectra and (b) Raman spectra of Cu(TPA)·(DMF) synthesized under various pressures.

S5. XPS spectra of Cu(TPA)·(DMF) synthesized under various pressures

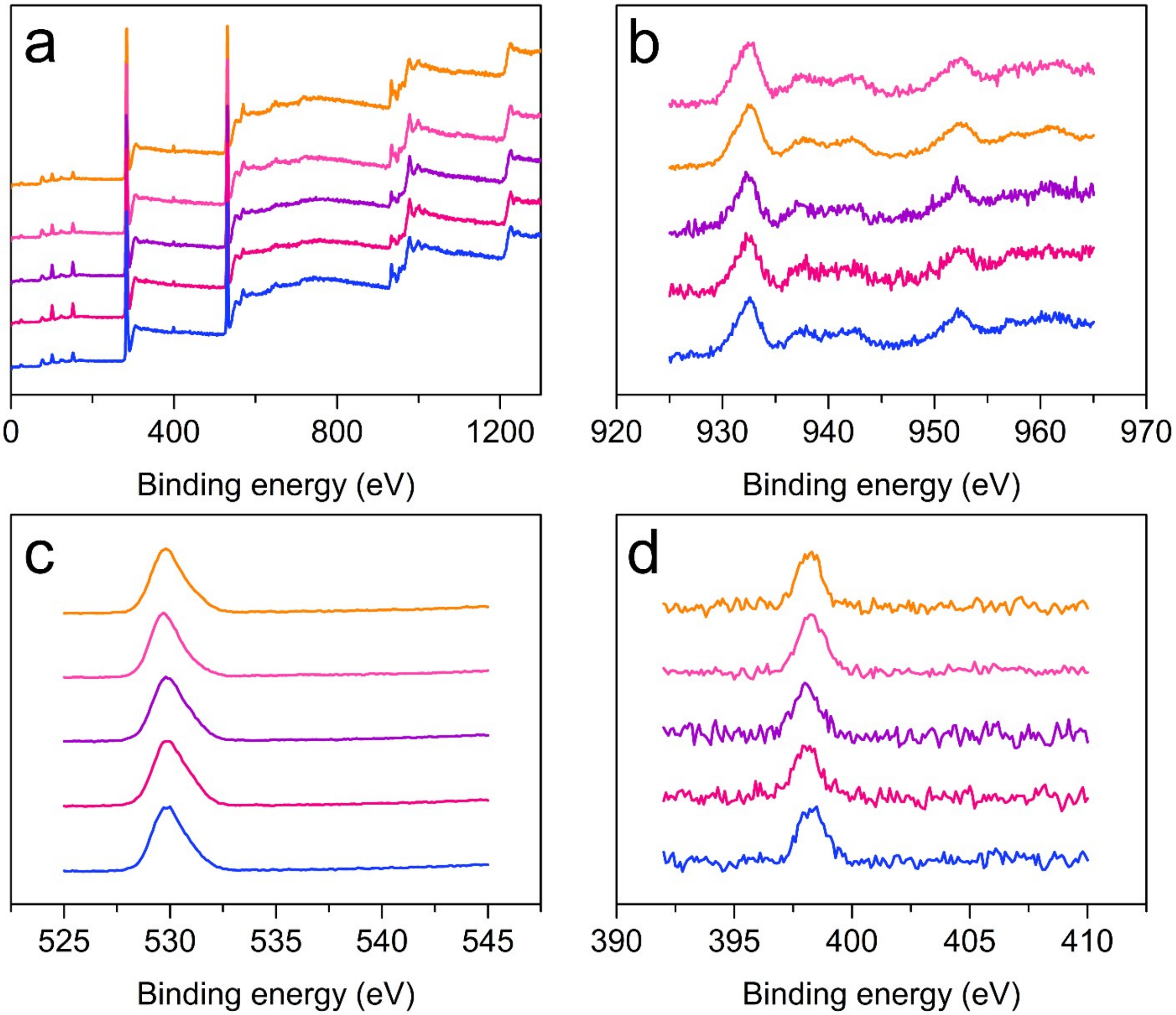

Figure S4. XPS spectra of Cu(TPA)·(DMF) synthesized under various pressures (from top to down: 1, 0.8, 0.6, 0.4, 0.2 atm). (a) survey scan; (b) Cu 2p; (c) O 1s; (d) N 1s.

S6. Determining surface areas of MOFs using BET method

It should be noted that the BET theory assumes multilayer adsorption, while adsorption in MOFs is mainly interpreted through a pore-filling mechanism. This inconsistency makes it questionable to use the BET theory to get the surface areas of MOFs. In 2007, a solid work was carried out by Snurr's group at Northwestern University to justify applicability of the BET theory for the adsorption in MOFs by carefully selecting the pressure range based on the established consistency criteria.[1] Firstly, they derived the BET surface areas from N_2 adsorption isotherms predicted from grand canonical Monte Carlo simulations. Then, they compared these BET values with the accessible surface areas calculated directly from the crystal structures. They found that these values matched well with each other, which indicates that the BET surface area is proper to characterize MOFs over the pressure ranges selected based on the established consistency criteria. Since then, the BET method has been widely accepted in MOFs-related studies.[2-5] In the current study, the surface areas of the samples were also derived using the BET theory based on the consistency criteria suggested in these prior literatures.

References:

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