Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic supplementary information for

Control of Catenation in CuTATB-n Metal-Organic Frameworks by Sonochemical Synthesis and its Effect on CO_2 Adsorption

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Simulated PXRD patterns for PCN-6 and -6′[1,2]

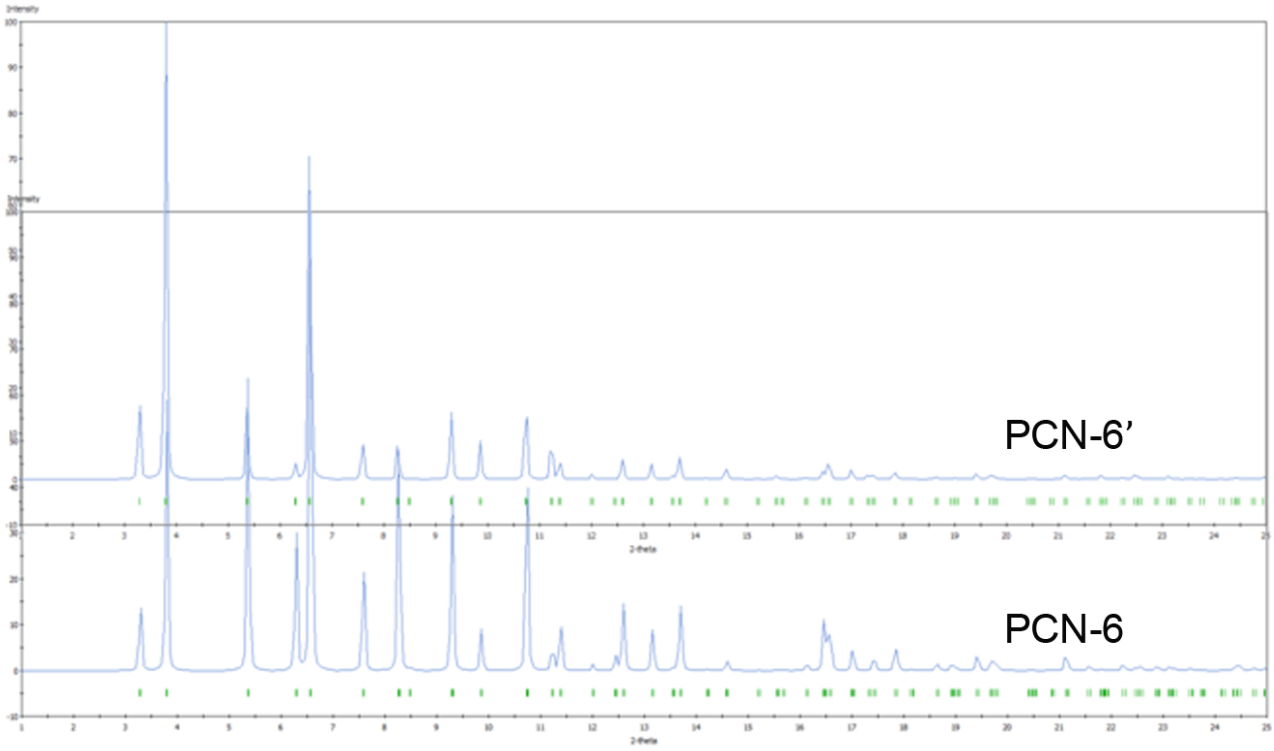

Fig. S1 Simulated PXRD patterns for PCN-6 and -6′.

Table S1. Elemental analyses of CuTATB as-prepared samples via a sonochemical synthesis route at 30 to 60% ultrasonic power levels

Samples	C (%)	H (%)	N (%)
Calcd. for $Cu_3(TATB)_2(DMF)_{0.6}(H_2O)_{6.1}$	**46.92**	**3.64**	**7.25**
CuTATB-30	47.02	3.65	7.24
CuTATB-40	46.99	3.68	7.27
CuTATB-50	46.03	4.12	7.63
CuTATB-60	45.08	4.70	8.36
Calcd. for $Cu_3(TATB)_2(DMF)_{3.1}(H_2O)_{9.9}$	**45.10**	**4.69**	**8.36**

cf. Elemental analyses data for PCN-6 and -6′.[1,2]

Samples	C (%)	H (%)	N (%)
Calcd. for PCN-6′, $Cu_3(TATB)_2(DMA)_{0.5}(H_2O)_9$	47.22	3.69	7.16
Calcd. for PCN-6, $Cu_3(TATB)_2(DMSO)_3(H_2O)_{11}$	41.74	4.54	5.41

Estimated compositions of CuTATB-40 and -50

The variation in the measured pore volumes can be used to estimate the portion of CuTATB-30 in CuTATB-40 and -50. For example, the pore volume of CuTATB-50, 1.30 (cm^3/g) can be represented simply by [1.07x + 1.55(1-x)] (cm^3/g) where x denotes the portion of CuTATB-30 in the mixed samples. A simple calculation suggests that CuTATB-50 is composed of CuTATB-30 and -60 in a ratio of 0.52 : 0.48. It was also estimated that CuTATB-40 consists of 85% CuTATB-30 and 15% CuTATB-60 (Table S2).

Table S2. Density values of CuTATB-n samples and estimated composition of CuTATB-40 and -50.

	CuTATB-30	CuTATB-40	CuTATB-50	CuTATB-60
V_{pore}(DR) (cm^3/g)	1.07	1.14	1.30	1.55
d_{bulk} (g/cm^3)	0.66	0.63	0.57	0.50
d_{sk} (g/cm^3)	2.30	-	-	2.17
d_x (g/cm^3)	0.28	-	-	0.56
CuTATB-30 fraction	1	0.85	0.52	0

Bulk density estimation

After removing the coordinated water molecules in the crystal structure of PCN-6′, the void space was calculated by the PLATON SOLV program.[3] Using a probe radius of 1.3 Å (one-half of the kinetic diameter of He), the framework skeletal volume (V_{sk}, 12318.8 $Å^3$) was obtained by subtracting the void volume (V_v, 89110.6 $Å^3$) from the unit cell volume (V_{cell}, 101429.4 $Å^3$). By dividing the framework mass per unit cell (M_{sk}, 17077.92 g/mol) by V_{sk}, the skeletal density d_{sk} of PCN-6′ was obtained as 2.30 g/cm^3 (Table S2). The calculated crystal density d_x was 0.28 g/cm^3, and was obtained by dividing M_{sk} with V_{cell}. Similarly, the densities of PCN-6 were obtained as 2.17 and 0.559 g/cm^3 for d_{sk} and d_x, respectively. The calculated skeletal densities of CuTATB-30 and -60 are within the range observed for other porous solids: MOF-5, 1.92 g/cm^3; HKUST-1, 1.90 g/cm^3; activated carbon, 2.00 g/cm^3; MCM-41, 2.11 g/cm^3; NaA, 2.23 g/cm^3; POM, 3.60 g/cm^3.[4] Using a relationship between pore volume and densities, $V_{pore} = (1/d_{bulk}) - (1/d_{sk})$, the bulk density d_{bulk} of PCN-6′ was calculated as 0.66 g/cm^3. Likewise, the bulk density of PCN-6 was obtained as 0.50 g/cm^3.

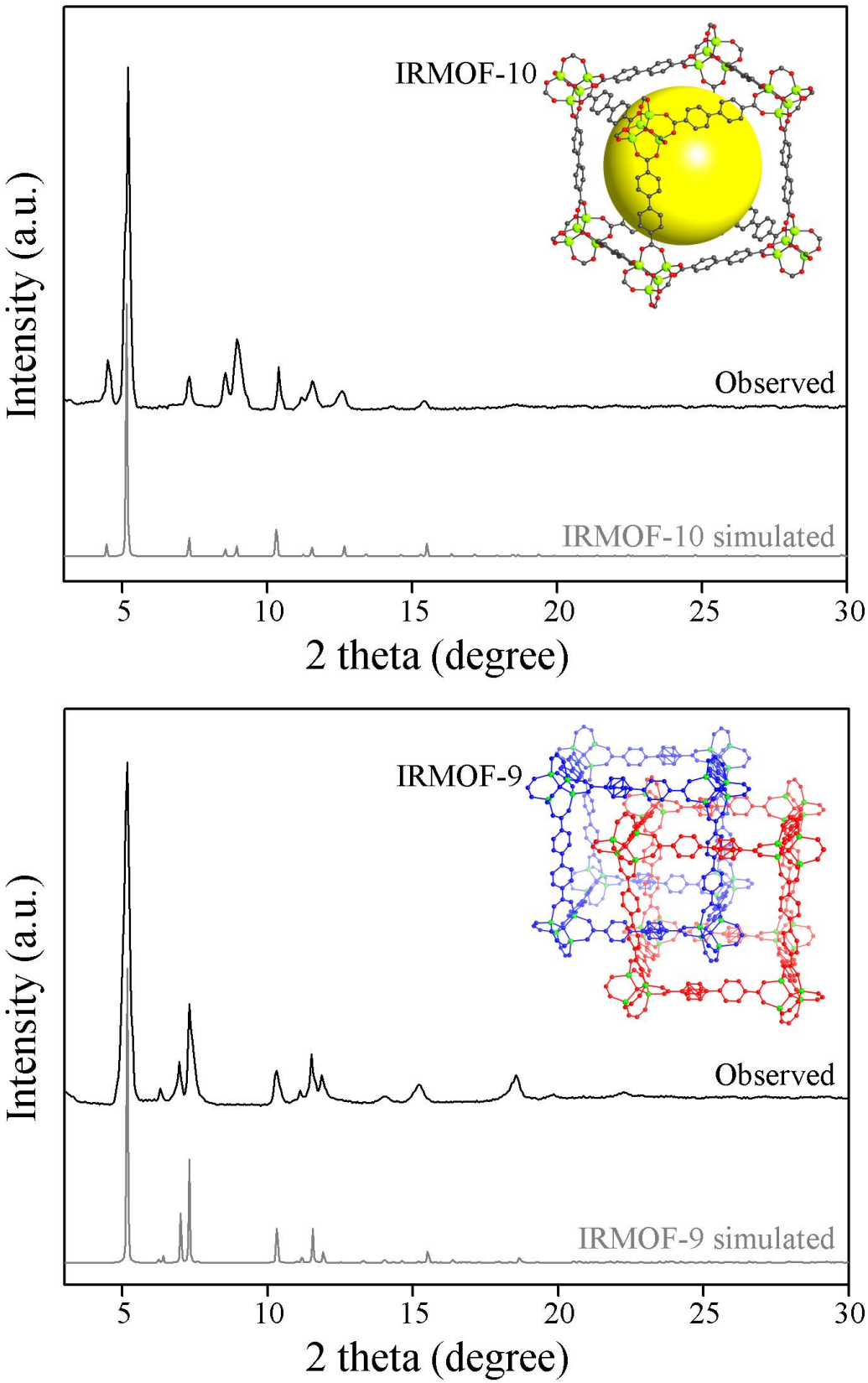

Fig. S2 PXRD patterns of IRMOF-9 and IRMOF-10 by sonochemical synthesis method. [5,6]

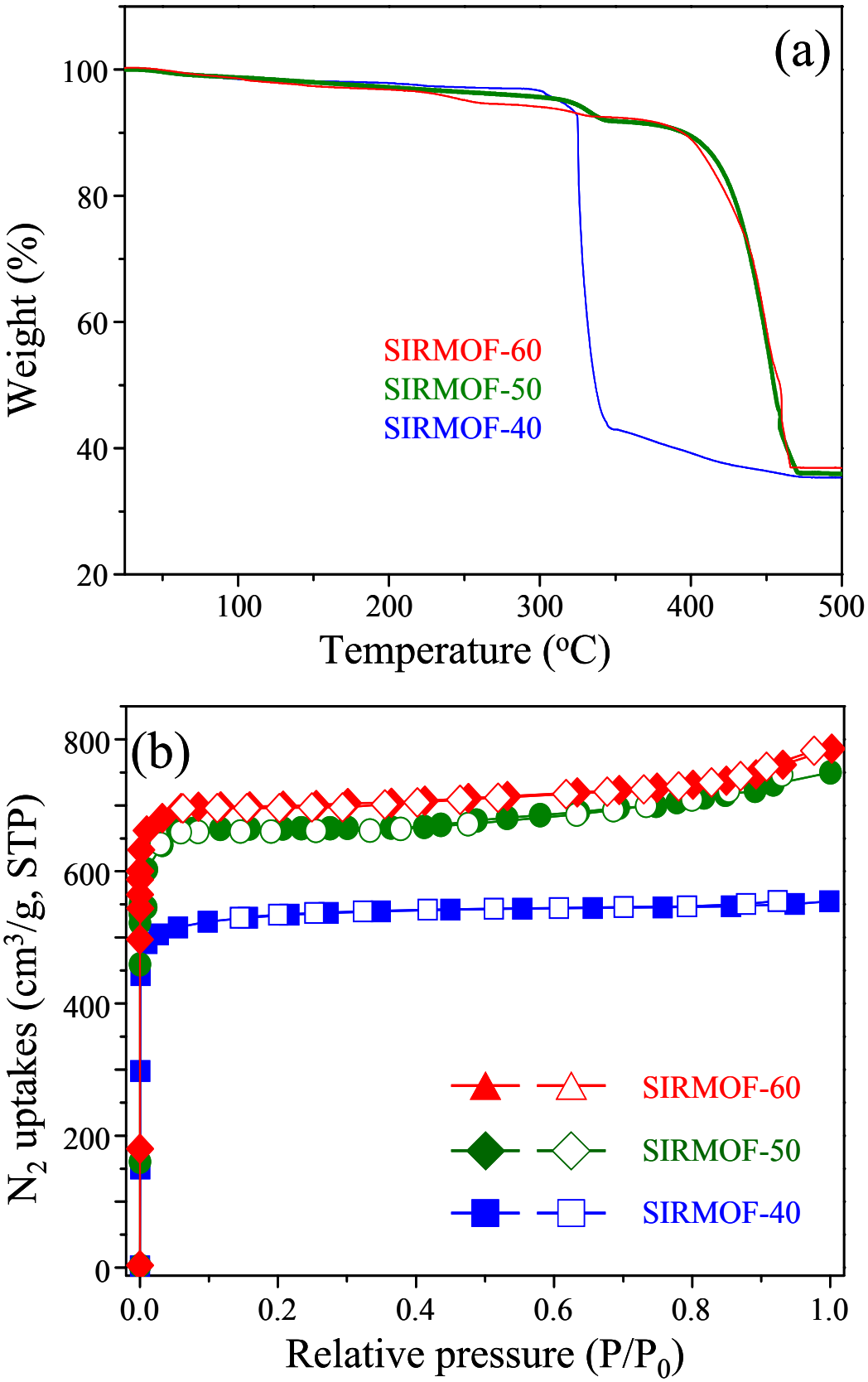

Fig. S3 (a) TGA measurement and (b) N_2 adsorption-desorption isotherms of SIRMOF-n samples.

References

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