Structural Evolution in a Melt-Quenched Zeolitic Imidazolate Framework Glass during Heat-treatment

Supporting Information

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1. Experimental Section

1.1 ZIF-4 Synthesis

The method for synthesizing the crystalline ZIF-4 phase was modified from previous literature.[1] Specifically, $Zn(NO_3)_2\cdot6H_2O$ (0.73 g) and imidazole (0.5 g) were each dissolved in N, N-dimethylformamide (DMF) (25 ml). The resulting solutions were then mixed and stirred for approximately 10 min before the mixture was placed in a 90 ml Teflon-lined stainless-steel autoclave. The autoclave was tightly sealed and heated to 403 K for 72 hrs in an oven. After cooling to room temperature overnight, the obtained products were separated from the mother liquor and washed with DMF (approx. 50 ml) three times. The final product was then dried in a vacuum oven at 383 K for 12 hrs.

1.2 ZIF-4 glass preparation

ZIF-4 glass was prepared via melt-quenching of the ZIF-4 crystal. Specifically, the synthesized ZIF-4 crystal was heated to 853 K (melting point) at 10 K/min and quenched to 473 K at 20 K/min under argon gas (50 mL min^{-1}), then cooling down to room temperature by using a differential scanning calorimetry (DSC) instrument (STA 449 F1, Netzsch).

1.3 Heat-treatment ZIF-4 glass preparation

Heat treatments were performed in the DSC, also under argon. The heating and cooling rate of heat-treatments are 10 and 20 K/min, respectively.

2. Characterization

2.1 DSC measurements

DSC experiments were carried out using a Netzsch STA 449 F1 instrument in argon atmosphere (50 mL min^{-1}). The samples were placed in a platinum crucible situated on a sample holder of the

DSC. The C_p curve for each measurement was calculated relative to the C_p curve of a sapphire reference material of comparable mass.

2.2 Powder X-ray diffraction

Room-temperature powder X-ray diffraction (XRD) data (2θ=5−40°) were collected with a Rigaku-RU 200B diffractometer using Cu K_α (λ=1.540598 Å) radiation.

2.3 Liquid-state Nuclear Magnetic Resonance (LS-NMR)

LS-NMR spectroscopy was performed using a Bruker Avance Ⅲ 600 MHz spectrometer. A mixture of DCl (35%)/D_2O (0.1 ml) and DMSO-d_6 (0.5 ml) was used as the solvent. The spectra were processed with the MestreNova Suite.

2.4 X-ray Total Scattering

X-ray data were collected at the I15-1 beamline at the Diamond Light Source, UK (λ = 0.161669 Å, 76.7 keV). Samples were loaded into borosilicate glass capillaries of 1.17 mm (inner) diameter. Data on the sample, empty instrument and capillary were collected in the region of $\sim$0.4 $< Q < \sim$ 26 $Å^{-1}$. Background, multiple scattering, container scattering, Compton scattering and absorption corrections were performed using the GudrunX program.[2,3] Peaks were fitted with a Pseudo-Voigt function, using the Fityk software.[4]

Analysis was also performed using data from variable temperature measurements collected at the Advanced Photon Source, USA on the 11-ID-B beamline (λ=0.143 Å, 86.7 keV), in the range 0.6< Q ~24 $Å^{-1}$. The full experimental procedures were reported in.[5] Finely ground samples of a_gZIF-were loaded into a 1-mm-diameter silica capillary, along with glass wool to hold it in place during the melting process. Data were collected under flowing argon gas at room temperature, and then upon heating from 298 K in about 100 K steps to 778 K. Subsequent measurements were performed every 6 K. Data were corrected in the same manner as the room-temperature X-ray measurements.

3 Supplementary Figures

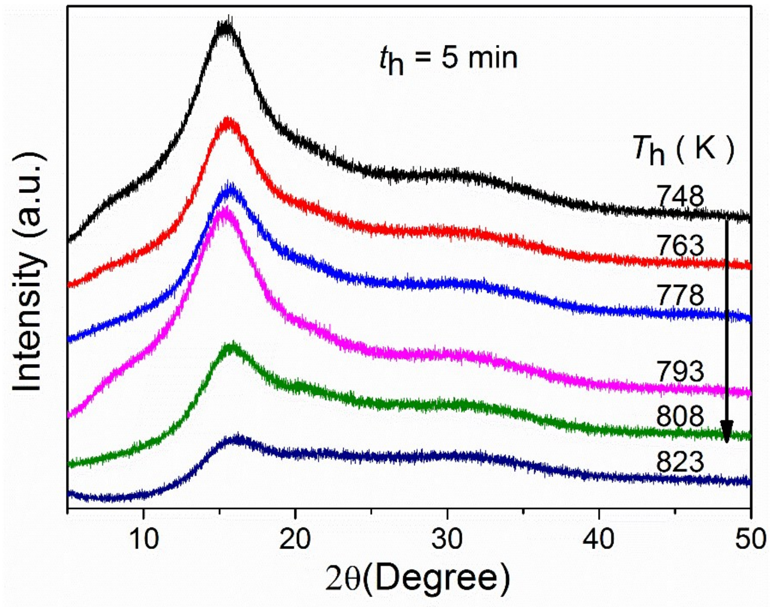

Figure S1. PXRD patterns of the fq-a_gZIF-4 heat-treated at various values of T_h for 5 min.

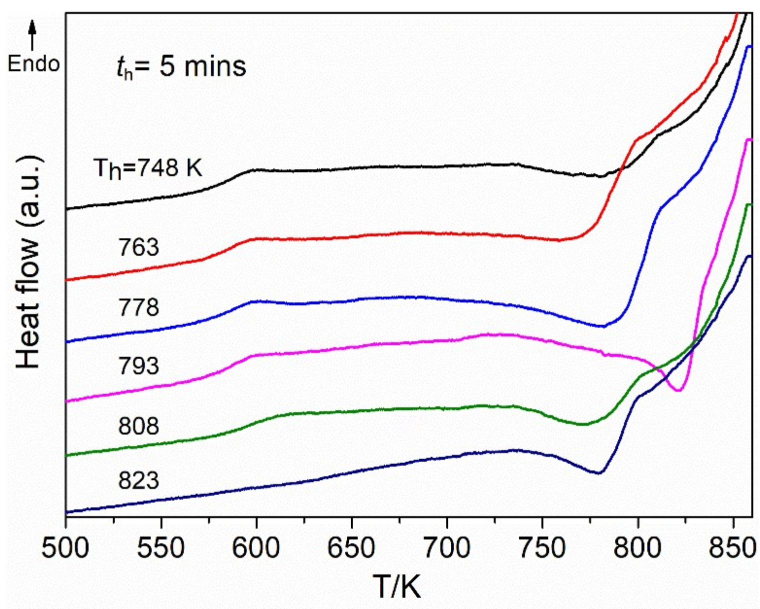

Figure S2. DSC experiments on the fq-a_gZIF-4 heat-treated at various values of T_h for 5 min.

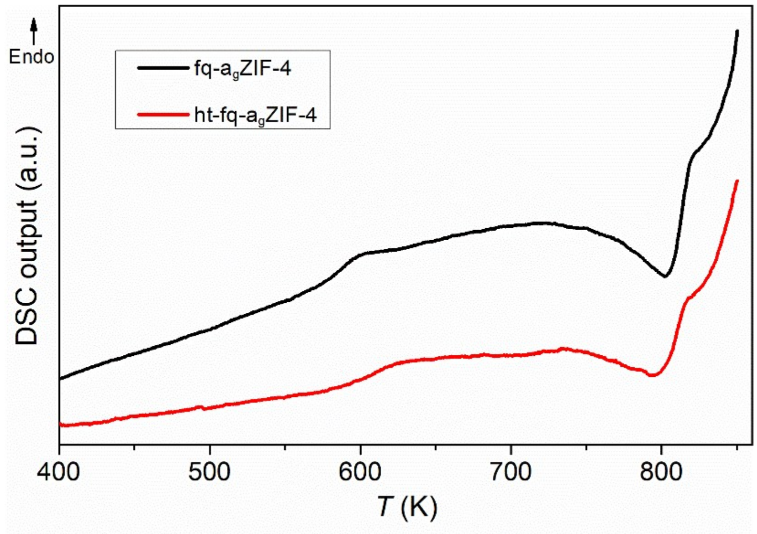

Figure S3. DSC experiments on fq-a$_g$ZIF-4 and ht-fq-a$_g$ZIF-4.

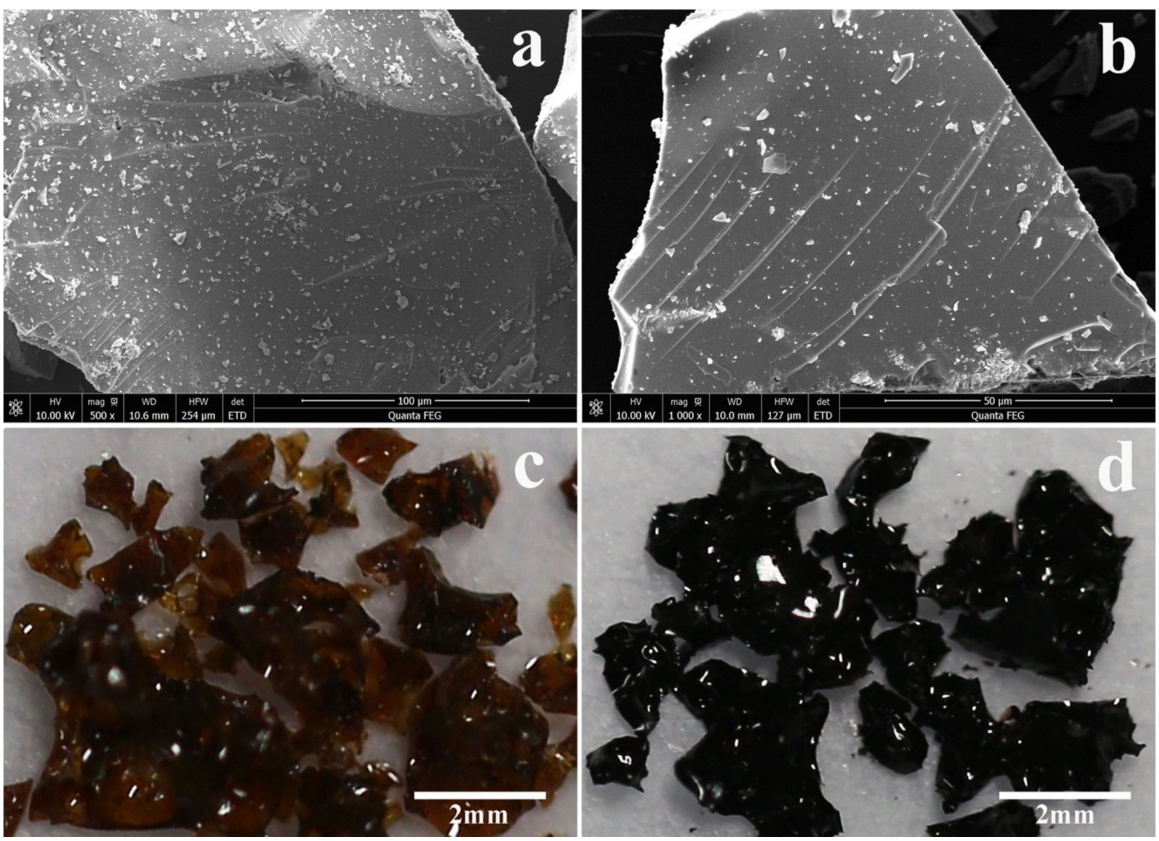

Figure S4. SEM images of (a) fq-a$_g$ZIF-4 and (b) ht-fq-a$_g$ZIF-4. Optical images of (c) fq-agZIF-4 and (d) ht-fq-a$_g$ZIF-4.

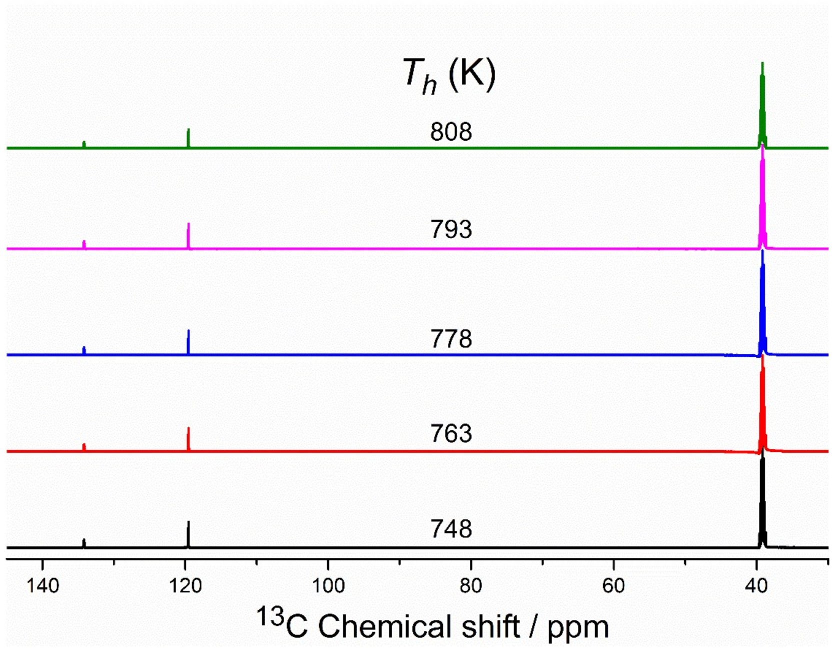

Figure S5. ^{13}C LS-NMR (600 MHz, DMSO-d6) spectra of fq-agZIF-4 heat-treated at 748, 763, 778, 793 and 808 K for 5 mins. δ (ppm) 39.20 (DMSO), 119.56 (**C**H**C**HN), 134.17 (N**C**HN).

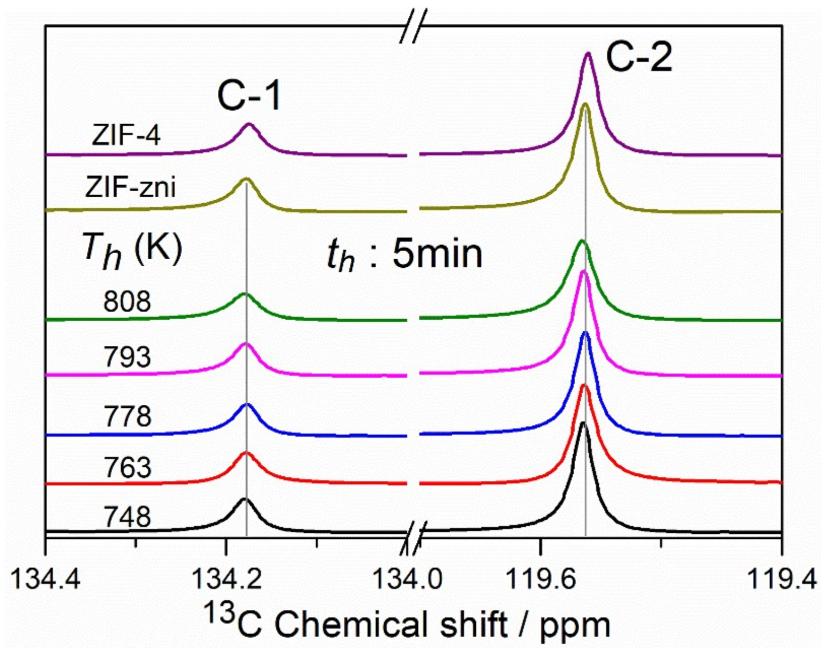

Figure S6. An enlarged area of ^{13}C LS-NMR spectra of ZIF-4, ZIF-zni and fq-a_gZIF-4 heat-treated at 748, 763, 778, 793 and 808 K for 5 mins.

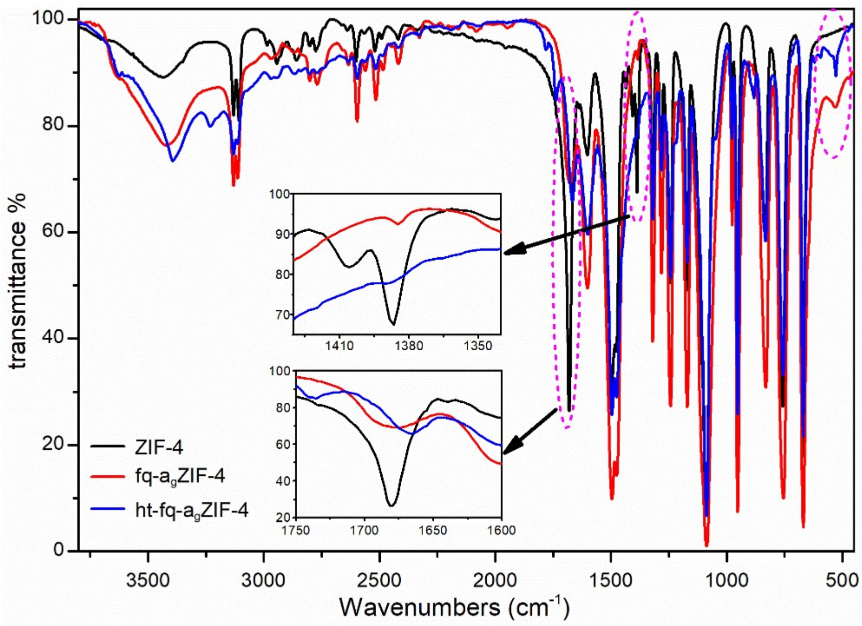

Figure S7. FT-IR absorption curves in KBr of ZIF-4, fq-a_gZIF-4 and ht-fq-a_gZIF-4. The magenta circles marked the main changed areas. Inset: enlarged images of the chosen areas.

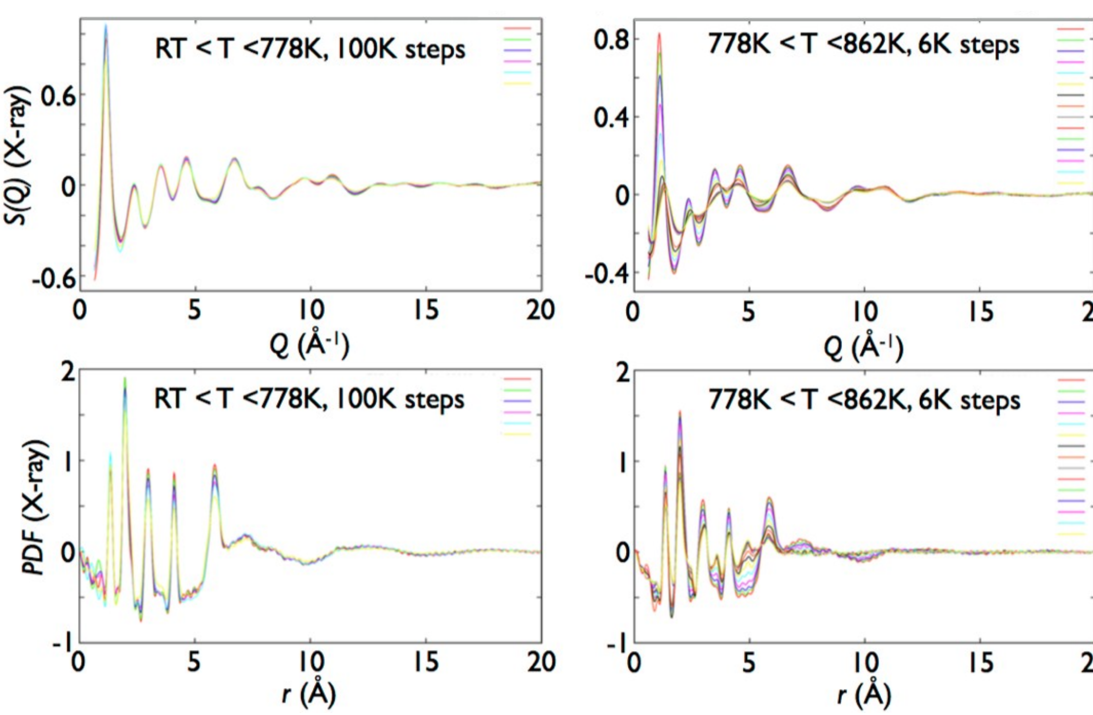

Figure S8. (Left) Synchrotron total scattering data S(Q) and (right) corresponding X-ray pair distribution functions D(r), collected on agZIF-4, during heating. Temperature increases on descending the legend from top to bottom.

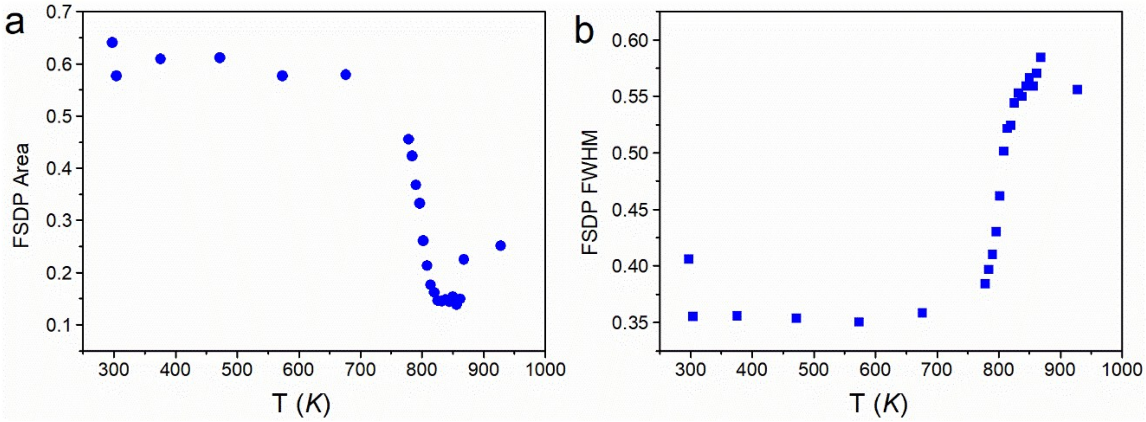

Figure S9. Variable temperature synchrotron X-ray total scattering data S(Q). Variance in the (a) area and (b) FWHM of the first sharp diffraction peak (FSDP) with temperature.

1. T. D. Bennett, J. C. Tan, Y. Yue, E. Baxter, C. Ducati, N. J. Terrill, H. H. Yeung, Z. Zhou, W. Chen, S. Henke, A. K. Cheetham and G. N. Greaves, Hybrid glasses from strong and fragile metal-organic framework liquids. *Nat Commun*, 2015, **6**, 8079.

2. Soper, A. K. GudrunN and GudrunX: Programs for Correcting Raw Neutron and X-ray Diffraction Data to Differential Scattering Cross Section. *Tech. Rep. RAL-TR-2011-013* (2011).

3. Soper, A. K. & Barney, E. R. Extracting the pair distribution function from white-beam X-ray total scattering data. *Journal of Applied Crystallography* 2011, **44**, 714-726.

4. Marcin Wojdyr, Fityk: a general-purpose peak fitting program. *Journal of Applied Crystallography* 2010, 43, 1126 -1128.

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