

Supplementary information for

Inter-conversion between zeolitic imidazolate frameworks: a dissolution- recrystallization process

Min Tu,^{a} Suttipong Wannapaiboon,^b and Roland A. Fischer^{c*}*

^aCentre for Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions (cMACS), KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

^bSynchrotron Light Research Institute, 111 University Avenue, Nakhon Ratchasima 30000, Thailand

^cChair of Inorganic and Metal-Organic Chemistry, Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85787, Garching, Germany

Contents

1	Crystal structures of studied MOFs.....	3
2	Inter-conversion of ZIF powders	3
2.1	Materials.....	3
2.2	Synthesis of ZIF powders	4
2.3	Conversion of ZIF-7 powder.....	4
2.4	Conversion of ZIF-8 powder.....	8
2.5	Conversion of ZIF-71 powder.....	12
2.6	Conversion of ZIF-76 powder.....	17
2.7	Summary of inter-conversion of ZIF powders.....	19
2.8	SEM imaging of inter-conversion of ZIF powders	19
3	Conversion of ZIF thin films.....	20
3.1	Fabrication of ZIF thin films	20
3.2	Inter-conversion of MOF films.....	21
4	Encapsulation of guest molecules via an inter-conversion process.....	24
4.1	Encapsulation of ZnTPP in ZIF-76 via the conversion of ZIF-8.....	24
4.2	Encapsulation of CACD in ZIF-8 via the conversion of ZIF-7.....	27
5	Reference.....	29

1 Crystal structures of studied MOFs

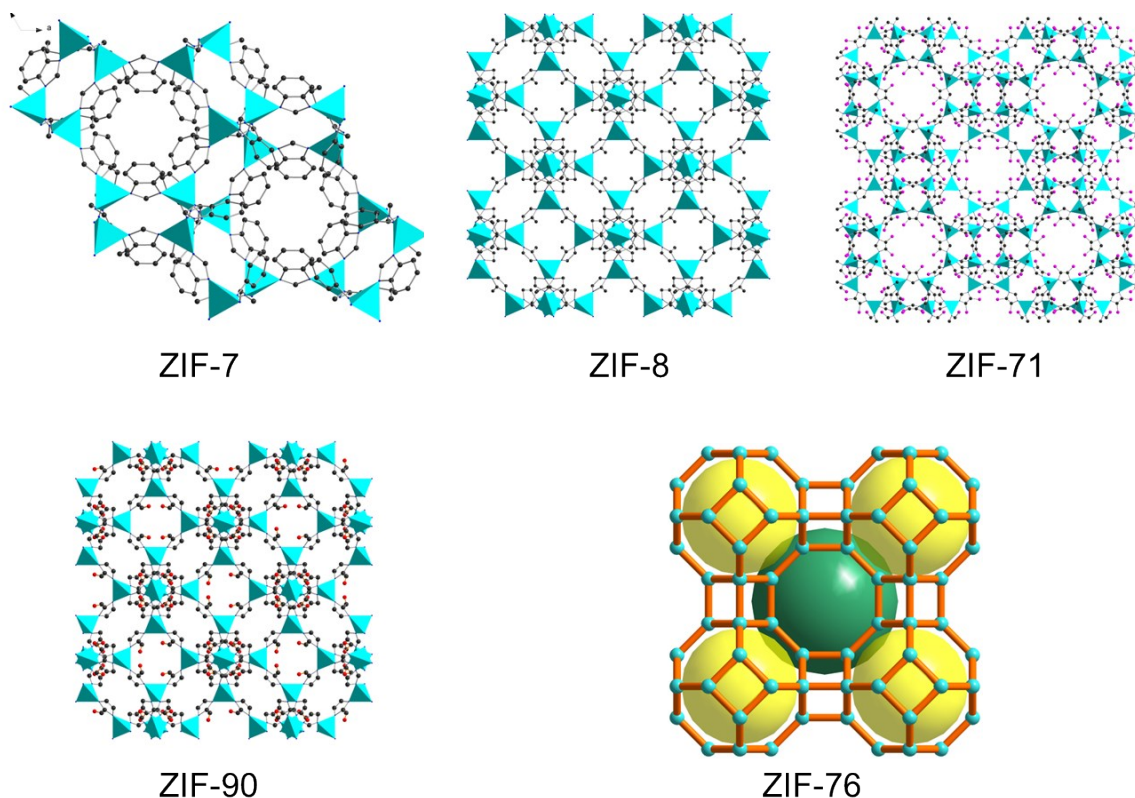


Fig. S1 Crystal structures of studied ZIFs in this work. Color code: Zn, light green; C, black; N, blue; Cl, pink; O, red. Hydrogen is omitted for clarity. Due to the random distribution of Im and cbIm in the framework of ZIF-76, only LTA topology is given. ZIF-76 contains two types of cages (α cage (light blue) and β or SOD cage (yellow)): The large α cage is surrounded by 12 eight-membered rings, eight 12-membered rings and six 16-membered rings.

2 Inter-conversion of ZIF powders

2.1 Materials

All the chemicals were purchased from commercial chemical companies, and used without further purification. The abbreviations and purity of the chemicals are given below. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ($\text{Zn}(\text{Ac})_2$, 98%), benzimidazole (blm, 98%), 2-methylimidazole (mlm, 99%), 4,5-dichloroimidazole (dclm, 98%), imidazole carboxyaldehyde (lca, 97%), imidazole (Im, 99%), 5-chlorobenzimidazole (cbIm, 96%), N,N-Dimethylformamide (DMF, 99%), methanol (MeOH, anhydrous, 99.9%), dichloromethane (DCM, 99.9%), Zinc tetraphenylporphyrin (ZnTPP, 99%), 9-

chloroanthracene-10-carbaldehyde (97%, CACD).

2.2 Synthesis of ZIF powders

All the ZIF powders (ZIF-7 ($\text{Zn}(\text{blm})_2$), ZIF-8 ($\text{Zn}(\text{mlm})_2$), ZIF-71($\text{Zn}(\text{dclm})_2$) and ZIF-90 ($\text{Zn}(\text{lca})_2$)) were synthesized by simply mixing the metal and linker solutions, and following keep them at room temperature for 3 hours. Afterwards, the as-synthesized bulk ZIF powders were collected by centrifugation and washed with methanol by 3 repetitions of sonication-centrifuge cycles to remove unreacted chemicals. After washing, the ZIF powders were immersed into DCM for 1 day and then were activated at 120 °C at reduced pressure. The activated powders were introduced into a glovebox for further inter-conversion experiments. The parameters of metal sources, concentrations and solvents are given below.

ZIF-7:¹ 270 mg $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was dissolved in 20 ml DMF, and 480 mg blm (4 mmol) was dissolved in 20 ml MeOH. After complete dissolved, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ DMF solution was poured into blm MeOH solution quickly.

ZIF-8:² 1.18 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4 mmol) was dissolved in 50 ml MeOH, and 660mg mlm (8 mmol) was dissolved in 50 ml MeOH. After complete dissolved, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ MeOH solution was poured into mlm MeOH solution quickly.

ZIF-71:¹ 440 mg $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) was dissolved in 20 ml DMF, and 640 mg dclm (4mmol) was dissolved in 20 ml MeOH. After complete dissolved, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ DMF solution was poured into dclm MeOH solution quickly.

ZIF-90:³ 440 mg $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) was dissolved in 20 ml DMF. 390 mg lca (4 mmol) was dissolved in 20 ml MeOH and heated to 60 °C for several hours until completely dissolved. After cooling to room temperature, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ DMF solution was poured into lca MeOH solution quickly.

2.3 Conversion of ZIF-7 powder

Dried ZIF-7 powders (ca. 45mg, 0.2 mmol equiv. of mlm for ZIF-7) was immersed into 5mL DMF solution of 1 mmol other daughter linkers (mlm: 82mg; lm: 67mg; lca: 96 mg; mixture of cblm and lm, 75mg and 34 mg, respectively). The mixture was ultrasonicated for 1h to get a uniform suspension of ZIF-7 in the solution. Afterwards, the suspension was kept in an oven at 60 °C. After every 24 hours

reaction, the solution was replaced with a fresh solution of the same concentration of imidazolate linkers as the original until ~100% conversion was achieved. The obtained powder was washed with DMF by 3 repetitions of sonication-centrifuge cycles and subsequently exchanged with MeOH for 1day.

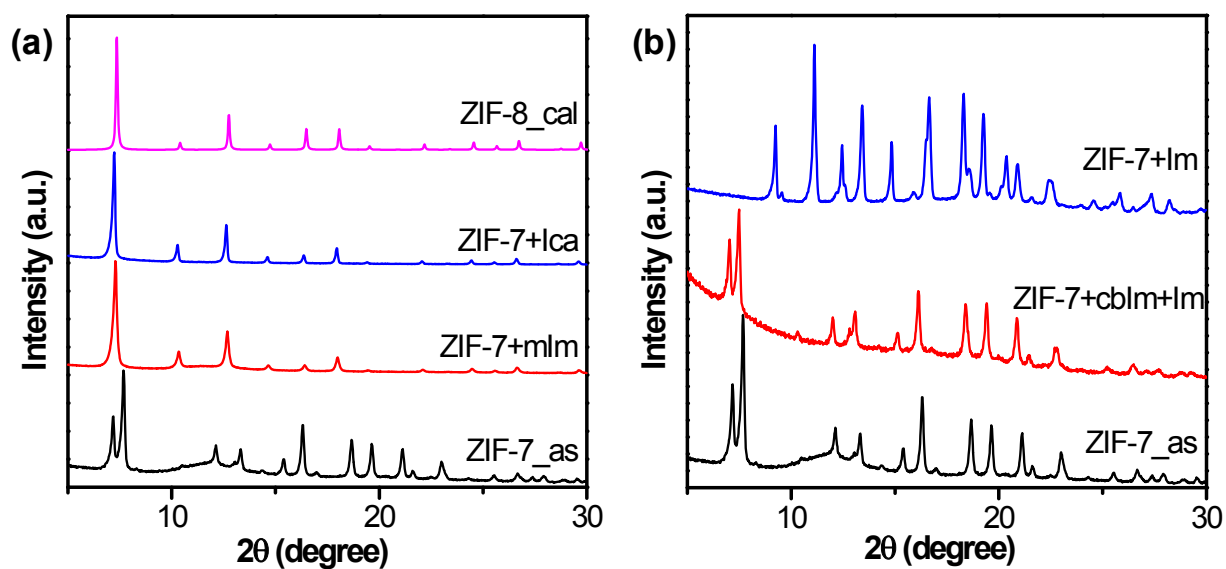


Fig. S2 (a) PXRD patterns of calculated ZIF-8, as-synthesized ZIF-7, and the ZIFs converted by mIm and lca for 3 and 5 days, respectively. (b) PXRD patterns of as-synthesized ZIF-7 and the ZIF converted by lm and the mixture of cbIm and lm for 5 days. As shown, after reacting ZIF-7 with mIm and lca solutions, the structure turned to ZIF-8 and ZIF-90, respectively. However, the structure keeps unchanged after soaking in the mixture solution of cbIm and lm even for 5 days.

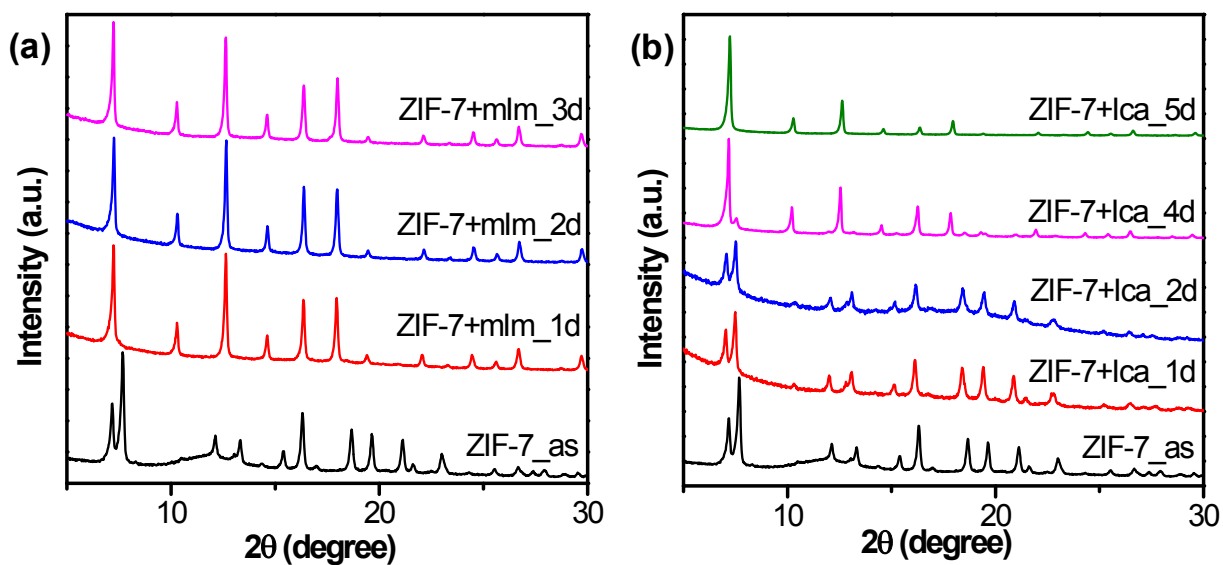


Fig. S3 PXRD patterns of as-synthesized ZIF-7 and the ZIFs converted by mIm (a) and lca (b) for different times.

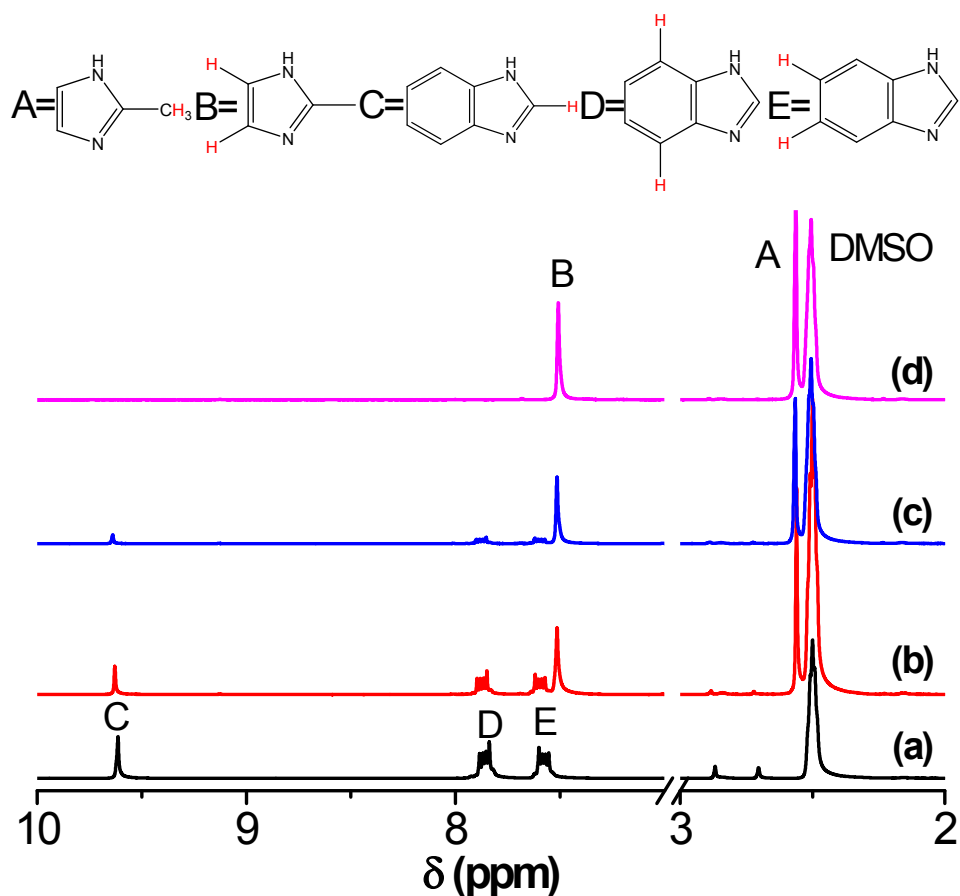


Fig. S4 Liquid-phase ^1H NMR spectra of digested samples of ZIF-7 (a) and the ZIFs converted by mIm for 1 day (b), 2 days (c) and 3 days (d). According to the ^1H NMR spectra, the ratios between blm and mIm linkers are calculated to be (a) blm_1 ; (b) $\text{blm}_{0.2}\text{mlm}_{0.8}$; (c) $\text{blm}_{0.08}\text{mlm}_{0.92}$ and (d) mlm_1 .

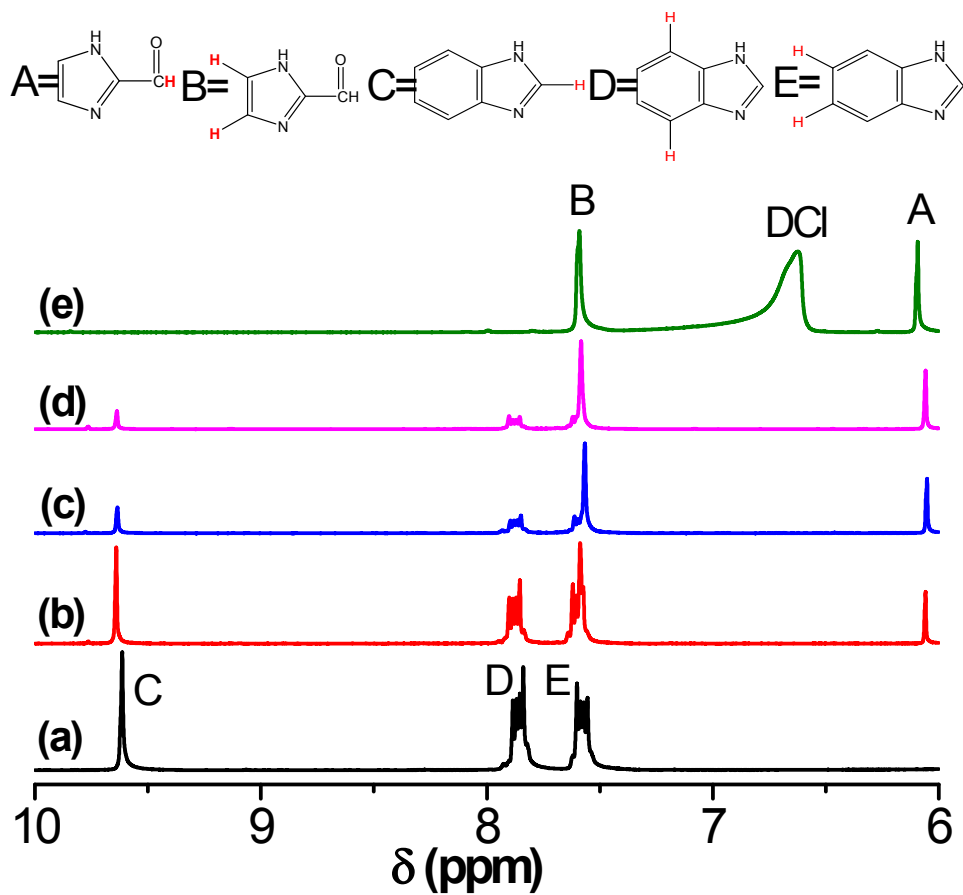


Fig. S5 Liquid-phase ^1H NMR spectra of ZIF-7 (a) and the ZIFs converted by Ica for 1 day (b), 2 days (c), 4 days (d) and 5 days (e). Accordingly, the ratios between blm and Ica linkers are calculated to be (a) blm_1 ; (b) $\text{blm}_{0.34}\text{Ica}_{0.66}$; (c) $\text{blm}_{0.65}\text{Ica}_{0.35}$; (d) $\text{blm}_{0.78}\text{Ica}_{0.22}$ and (e) Ica_1 .

2.4 Conversion of ZIF-8 powder

In the case of the conversion of ZIF-8 to other ZIFs, 30 mg activated ZIF-8 (ca. 0.2 mmol equiv. of mlm for ZIF-8) was immersed into 5 mL DMF solution of 1 mmol other imidazolate (blm:120mg; dclm: 140mg; lca: 96 mg; mixture of cblm and lm, 75mg and 34 mg, respectively). The mixture was ultrasonicated for 1h to get a uniform suspension of ZIF-8 in the solution. Afterwards, the suspension was kept in an oven at 60 °C. After each 24 hours reaction, the solution was replaced with a fresh solution of the same concentration of imidazolate linkers as the original until ~100% conversion was achieved. The obtained powder was washed with DMF by 3 repetitions of sonication-centrifuge cycles and subsequently exchanged with MeOH for 1day.

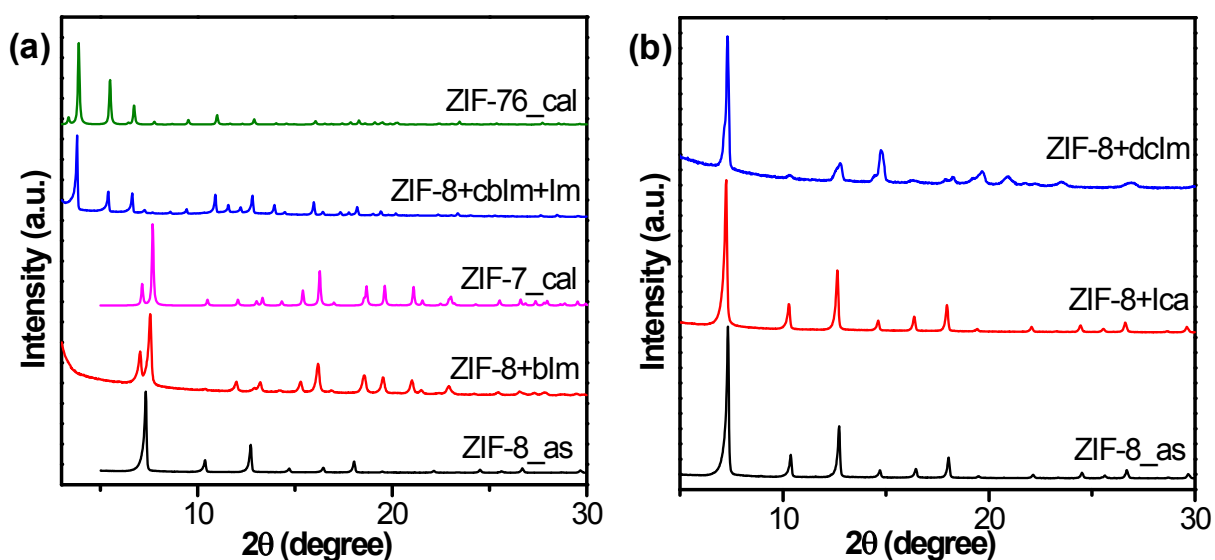


Fig. S6 (a) PXRD patterns of calculated ZIF-7 and ZIF-76, as-synthesized ZIF-8 and the ZIFs converted by blm, and the mixture of cblm and lm for 3 and 5 days, respectively. (b) PXRD patterns of as-synthesized ZIF-8 and converted by lca and dclm for 5 and 2 days, respectively. After reacting ZIF-8 with blm solution and the solution of cblm and lm mixture for 3 days and 5 days, respectively, the structure transformed to ZIF-7 and ZIF-76, respectively. The structure keeps unchanged after soaking in the lca and dclm solutions for 5 and 2 days.

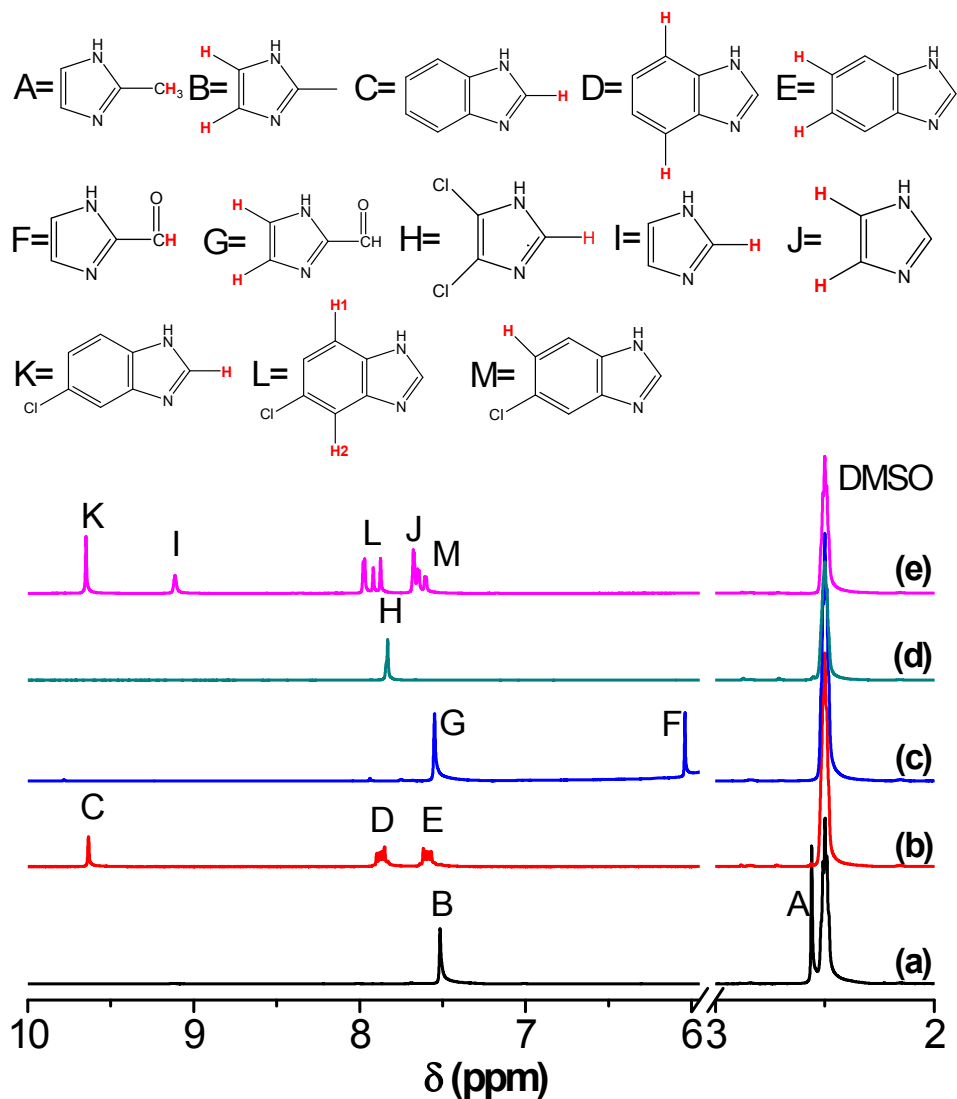


Fig. S7 Liquid-phase ^1H NMR spectra of ZIF-8 (a) and the ZIFs converted by blm, lca, dclm, and the mixture of cblm and lm for 3, 5, 2 and 5 days, respectively. Together with the XRD data shown in Figure S6, ZIF-8 can be converted to ZIF-7, ZIF-90, ZIF-8_dclm, and ZIF-76 without any residual mlm linker in the frameworks.

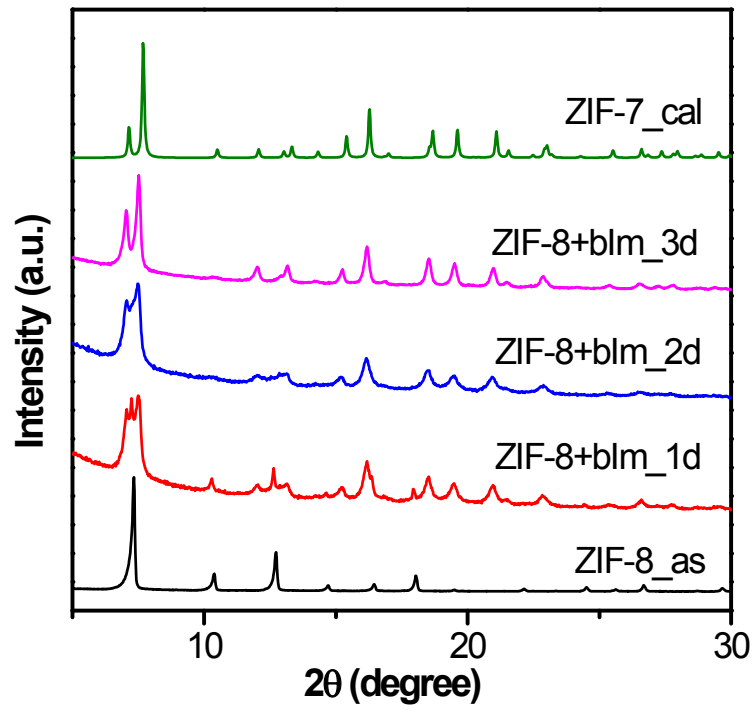


Fig. S8 PXRD patterns of as-synthesized ZIF-8 and converted by blm for different days.

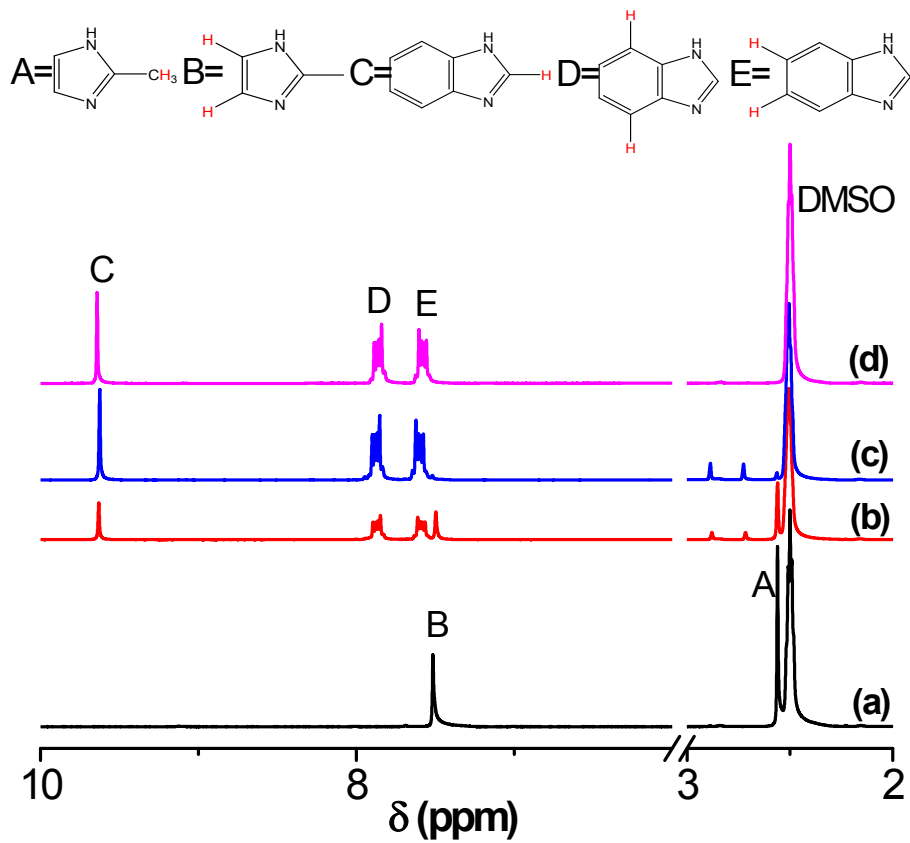


Fig. S9 Liquid-phase ^1H NMR spectra of digested samples of ZIF-8 (a) and converted by blm for 1 day (b), 2 days (c) and 3 days (d). Accordingly, the ratios between mIm and blm linkers are calculated to be (a) mIm_1 ; (b) $\text{mIm}_{0.33}\text{blm}_{0.67}$; (c) $\text{mIm}_{0.05}\text{blm}_{0.95}$ and (d) blm_1 .

2.5 Conversion of ZIF-71 powder

In the case of the conversion of ZIF-71 to other ZIFs, 48 mg activated ZIF-71 (ca. 0.2 mmol equiv. of mIm for ZIF-71) was immersed into 5 mL DMF solution of 1 mmol other imidazolate (blm:120mg; mIm: 82mg; lca: 96 mg; mixture of cblm and lIm, 75mg and 34 mg, respectively). The mixture was ultrasonicated for 1h to get a uniform suspension of ZIF-71 in the solution. Afterwards, the suspension was kept in an oven at 60 °C. After each 24 hours reaction, the solution was replaced with a fresh solution of the same concentration of imidazolate linkers as the original until ~100% conversion was achieved. The obtained powder was washed with DMF by 3 repetitions of sonication-centrifuge cycles, and subsequently exchanged with MeOH for 1day.

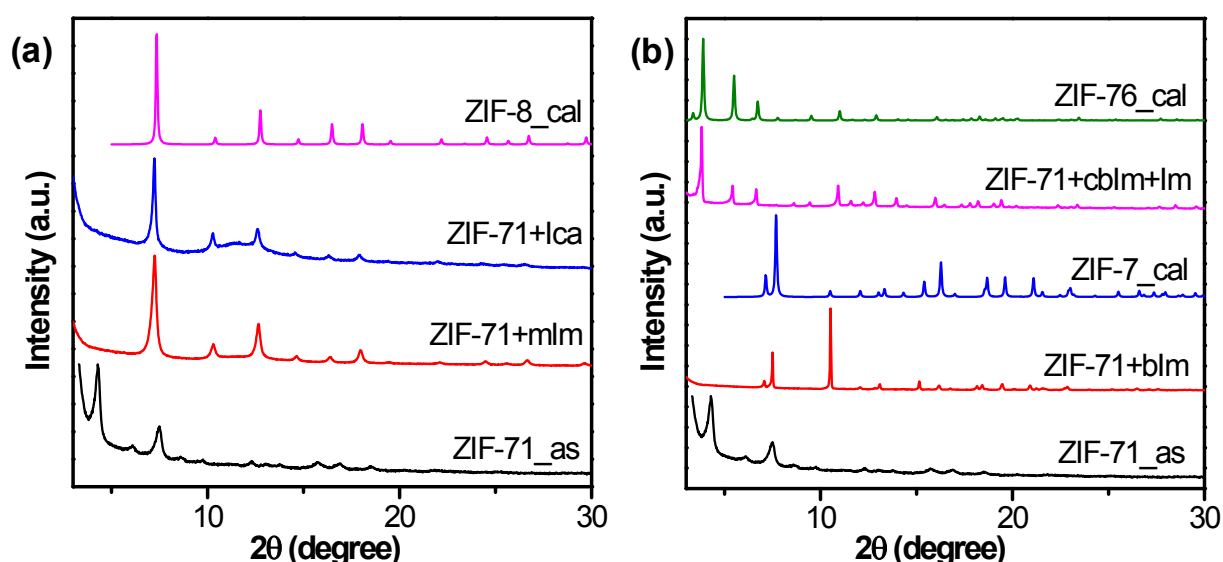


Fig. S10 (a) PXRD patterns of calculated ZIF-8, as-synthesized ZIF-71 and the ZIFs converted by mIm and lca for 3 and 5 days, respectively. (b) PXRD patterns of calculated ZIF-7 and ZIF-76, as-synthesized ZIF-71 and converted by blm and the mixture of cblm and lIm for 3 and 5 days, respectively. As shown, after reacting ZIF-71 with the solutions of mIm, lca, blm, and the mixture of cblm and lIm for 3, 5, 3, and 5 days, respectively, ZIF-71 can be converted to ZIF-8, ZIF-90, ZIF-7, and ZIF-76, respectively.

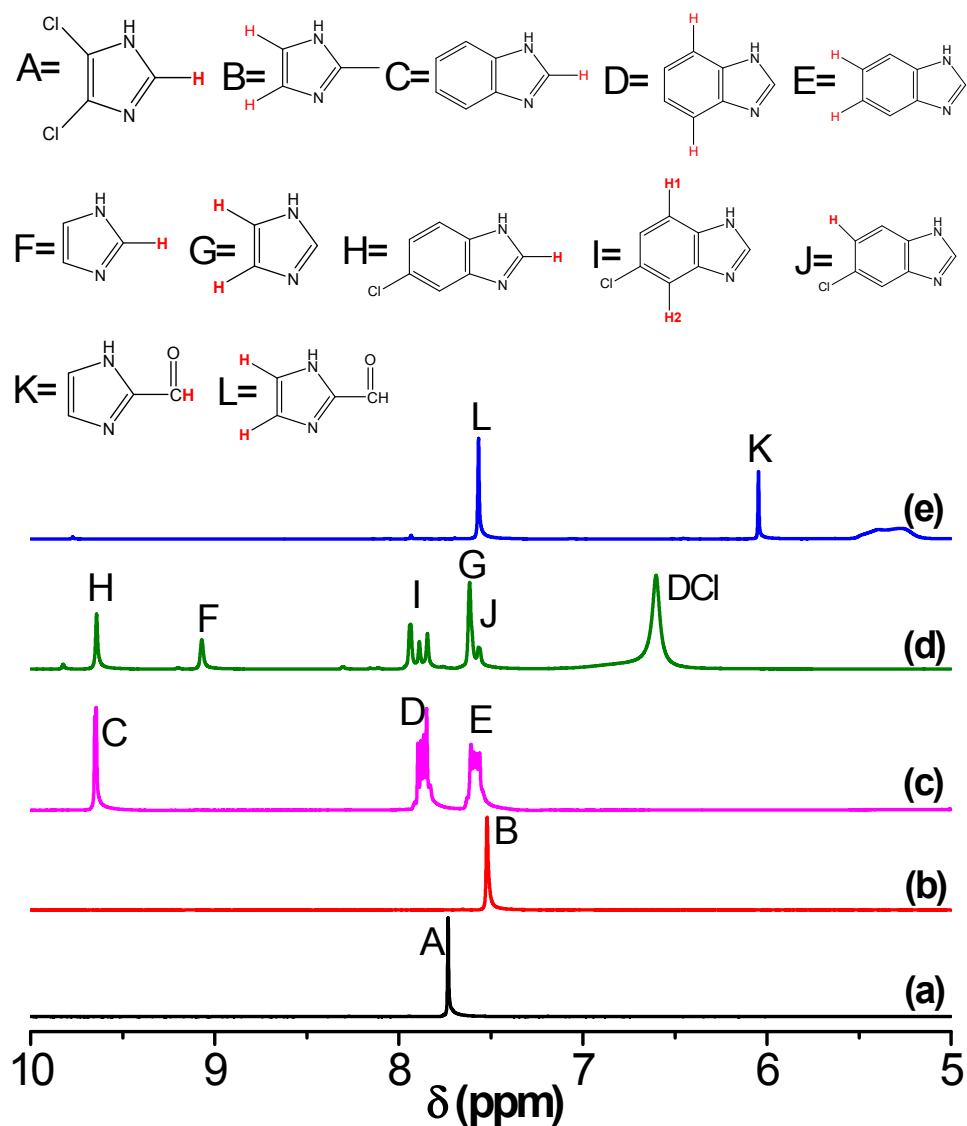


Fig. S11 Liquid-phase ^1H NMR spectra of ZIF-71 (a) and converted by mlm, lca, blm and mixture of cblm and lm for 3, 5, 3 and 5 days, respectively. Together with the XRD data in Figure S10, ZIF-71 can be completely converted to ZIF-8, ZIF-90, ZIF-7 and ZIF-76 without any residual dclm linker in the frameworks.

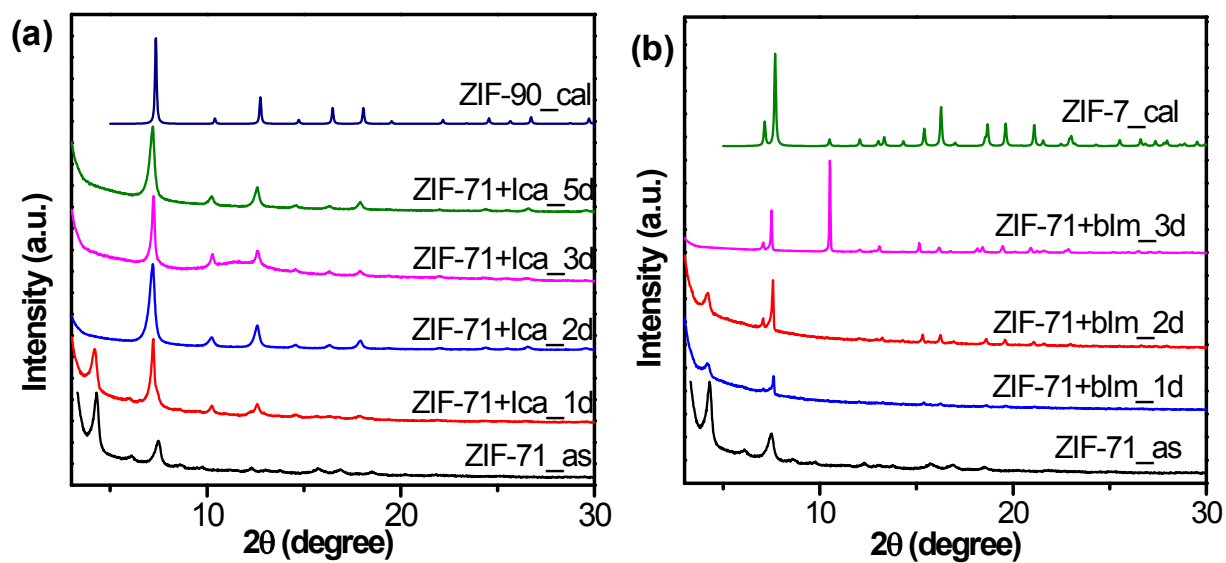


Fig. S12 PXRD patterns of as-synthesized ZIF-71 and the ZIFs converted by lca (a) and blm (b) for different days.

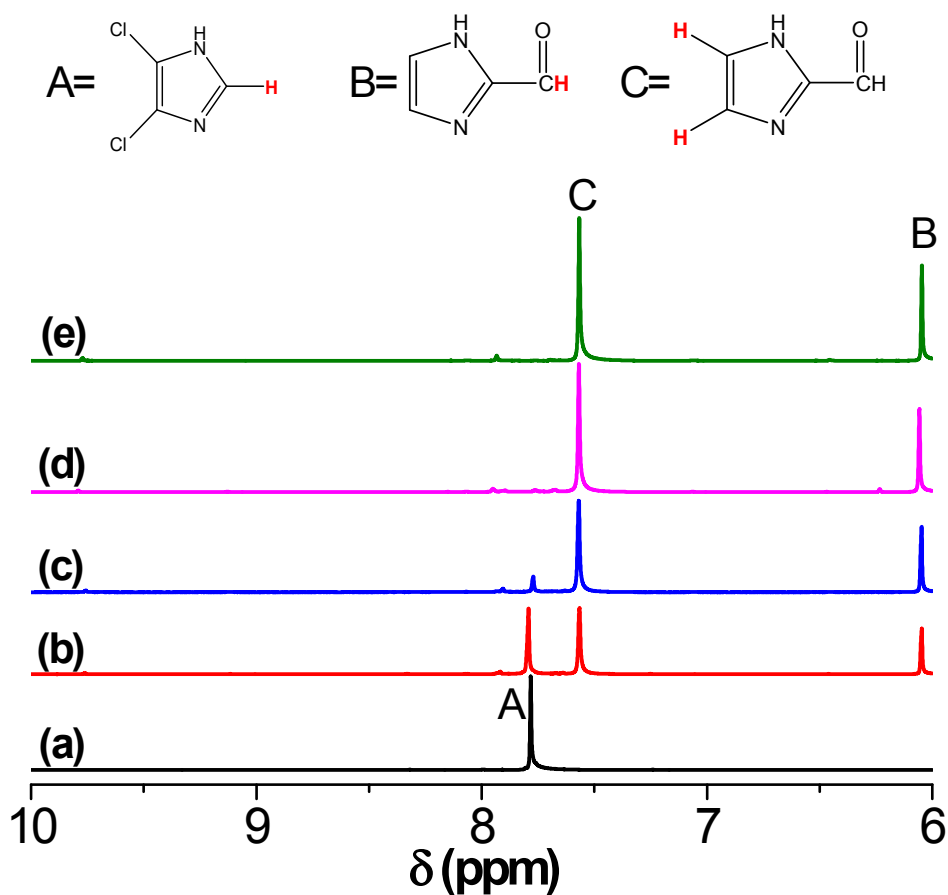


Fig. S13 Liquid-phase ^1H NMR spectra of digested samples of ZIF-71 (a) and converted by Ica for 1 day (b), 2 days (c), 3 days (d) and 5 days (e). Accordingly, the ratios between dclm and Ica linkers are calculated to be (a) dclm₁; (b) Ica_{0.38}dclm_{0.62}; (c) Ica_{0.76}dclm_{0.24}; (d) Ica_{0.92}dclm_{0.08} and (e) Ica₁.

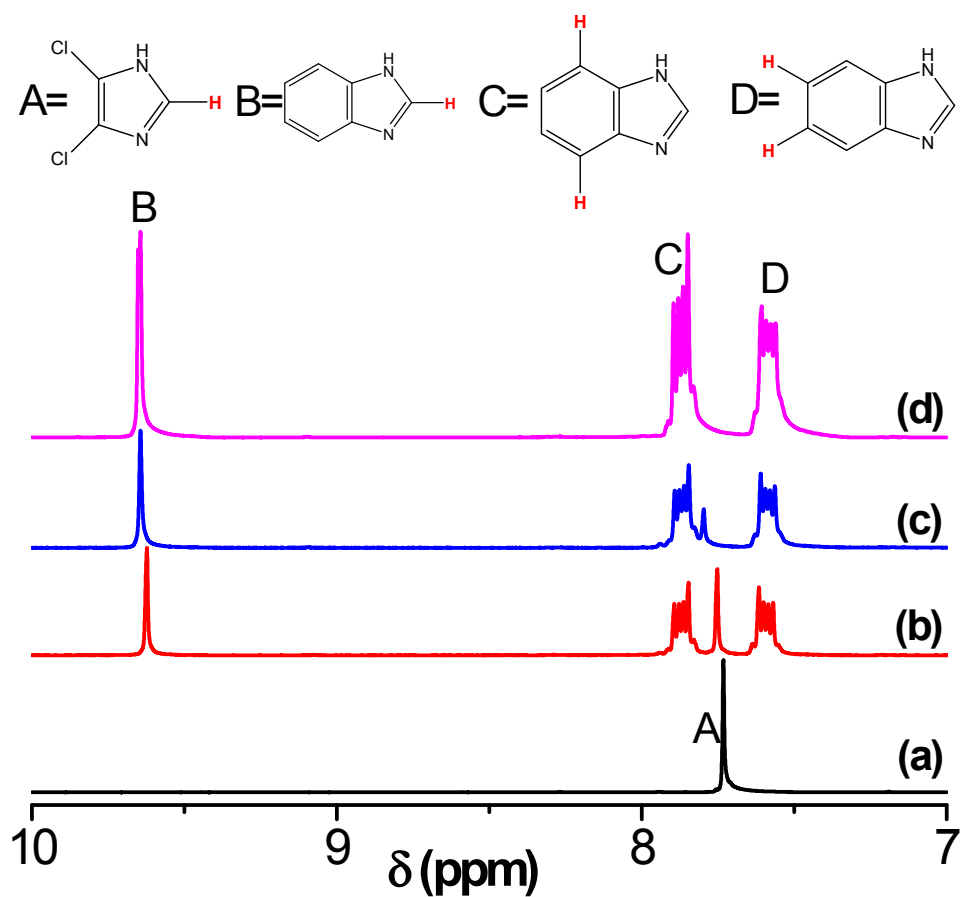


Fig. S14 Liquid-phase ^1H NMR spectra of digested samples of ZIF-71 (a) and converted by blm for 1 day (b), 2 days (c) and 3 days (d). Accordingly, the ratios between dclm and blm linkers are calculated to be (a) dclm₁; (b) blm_{0.45}dclm_{0.55}; (c) lca_{0.72}dclm_{0.28} and (d) blm₁.

2.6 Conversion of ZIF-76 powder

In the case of the conversion of ZIF-76 to other ZIFs, 40 mg activated ZIF-76 (ca. 0.2 mmol equiv. of mIm for ZIF-76) was immersed into 5mL DMF solution of 1 mmol other imidazolate (blm:120mg; mIm: 82mg; dIm: 140 mg). The mixture was ultrasonicated for 1h to get a uniform suspension of ZIF-76 in the solution. Afterwards, the suspension was kept in an oven at 60 °C. After each 24 hours reaction, the solution was replaced with a fresh solution of the same concentration of imidazolate linkers as the original until ~100% conversion was achieved. The obtained powder was washed with DMF by 3 repetitions of sonication-centrifuge cycles, and subsequently exchanged with MeOH for 1day.

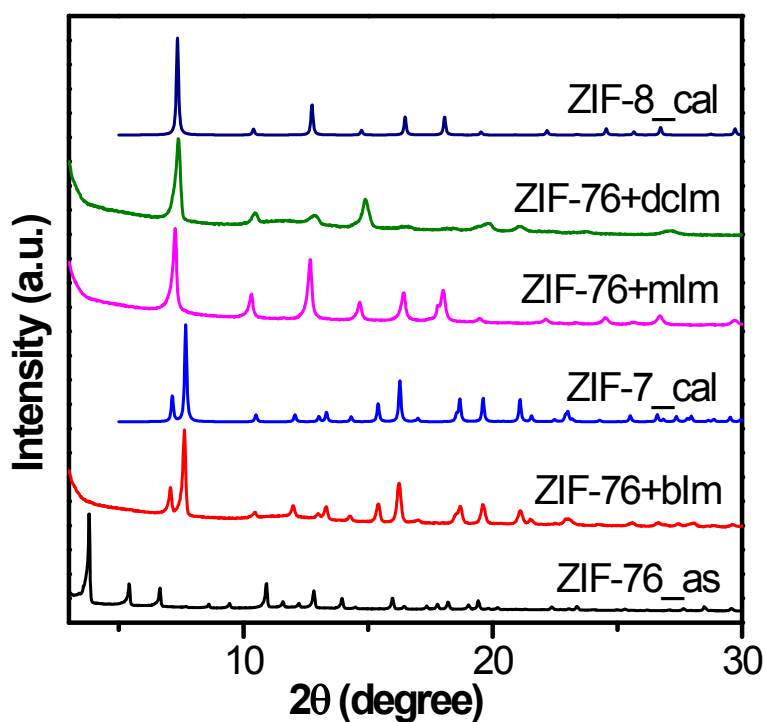


Fig. S15 PXR D patterns of calculated ZIF-7 and ZIF-8, as-synthesized ZIF-76 (obtained by the conversion of ZIF-8) and converted by blm, mIm, and dclm 5 days, respectively. After reacting ZIF-76 with solutions of blm, mIm, and dclm solutions for 5 days, ZIF-76 can be converted to ZIF-7, ZIF-8, and ZIF-8_dclm, respectively.

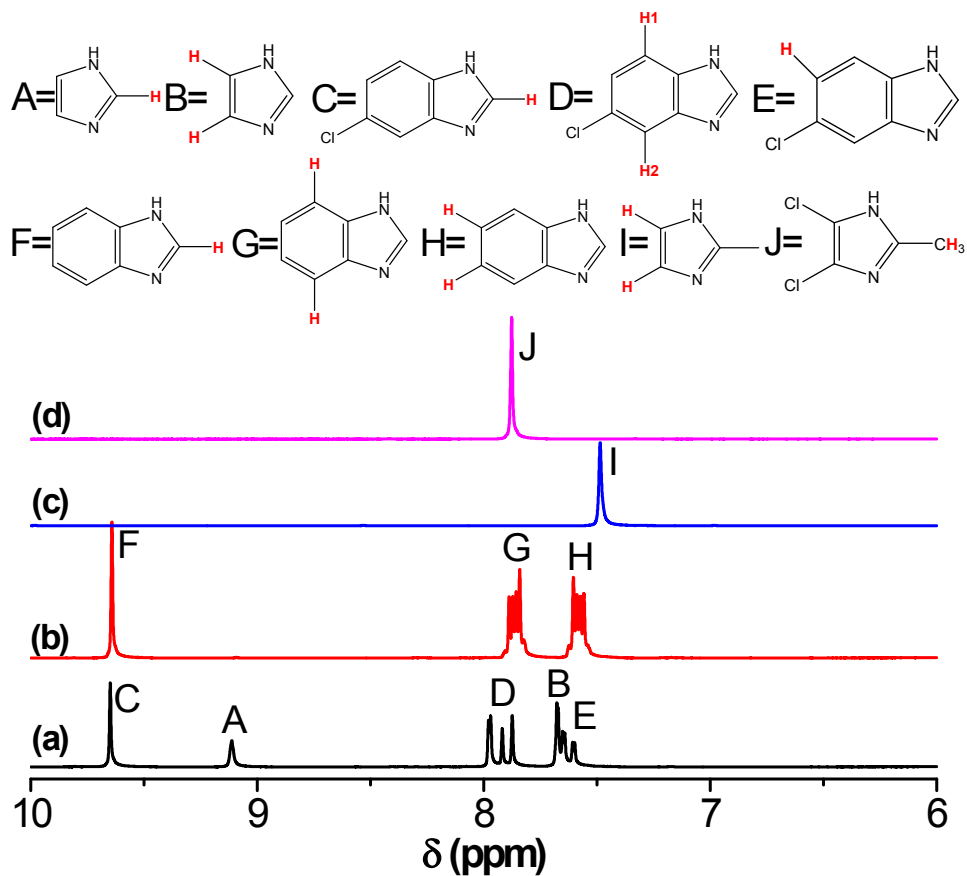


Fig. S16 Liquid-phase ^1H NMR spectra of digested samples of ZIF-76 (a) and the ZIFs converted by blm, mlm and dclm for 5 days. Together with the XRD data in Figure S15, ZIF-76 can be completely converted to ZIF-7, ZIF-8, and ZIF-8_dclm without any residual cbIm and Im linker in the frameworks.

2.7 Summary of inter-conversion of ZIF powders

Table S1 Summary of the conversions of ZIF powders following PSE procedure

Parent ZIF	Daughter ZIF					
	ZIF-7	ZIF-8	ZIF-8_dclm	ZIF-71	ZIF-76	ZIF-90
ZIF-7		Y	ND	ND	N	Y
ZIF-8	Y		Y	N	Y	Y
ZIF-71	Y	Y	ND		Y	Y
ZIF-76	Y	Y	Y	N		Y

Y: possible conversion; N: impossible conversion; ND: not determined

2.8 SEM imaging of inter-conversion of ZIF powders

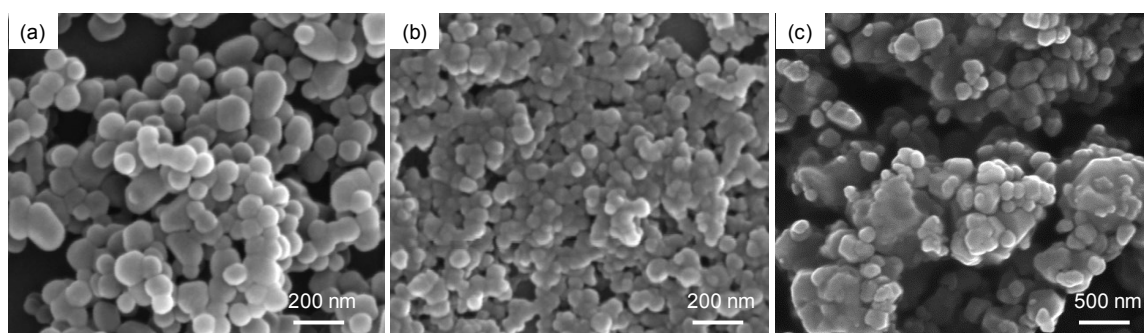


Fig. S17 SEM images of the powder samples of as-synthesized ZIF-71 (a), ZIF-8 (b) and ZIF-76 (c). ZIF-8 and ZIF-76 are obtained by the tandem conversion of ZIF-71 (ZIF-71 → ZIF-8 → ZIF-76). The ZIF-71 sample consists of individual crystallites of ca. 100 nm in diameter. After the conversion to ZIF-8, no significant changes in the particle size can be observed, but with some extent of intergrowth. Further transformation to ZIF-76 leads to heavy intergrowth, consisting of polycrystalline aggregates and individual particles.

3 Conversion of ZIF thin films

3.1 Fabrication of ZIF thin films

ZIF thin films were fabricated on commercial SiO₂ coated QCM substrates (AT-cut, 5MHz, q-sense) following our previously reported method.³ The substrates were pretreated by subsequently immersing in acetone and ethanol under sonication for 30 min and then dried under Ar. Prior to the deposition of ZIF films, the substrates were activated in the UV Ozone chamber for 1h to remove the organic contaminants and increase -OH groups on the surfaces. The MOF thin films were deposited by automatic pump controlled process as shown in Figure S16. The pretreated substrate was fixed on a home-made Teflon sample holder and placed into the deposition cell in a face-down-to-bottom fashion. Subsequently, the metal and linker solutions were simultaneously dosed to the sample cell to grow the MOF film on the QCM substrate. After a certain time (30 or 60 min), the mixed solution was removed from the growth cell. Before start the next deposition cycle, the substrate was washed with methanol (10 min) and dried under the atmosphere (10 min). After 10 cycles' repetition of this procedure, MOF thin films can be obtained. The optimized metal source, solvent, precursor concentration as well as deposition time are different in each case and given below. **ZIF-8 film**: metal solution: 20 mM Zn(NO₃)₂·6H₂O in methanol; linker solution: 40 mM mlm in methanol; deposition time: 30 min. **ZIF-71 film**: metal solution: 1 mM Zn(Ac)₂·2H₂O in methanol; linker solution: 4 mM dclm in methanol, deposition time: 1h.

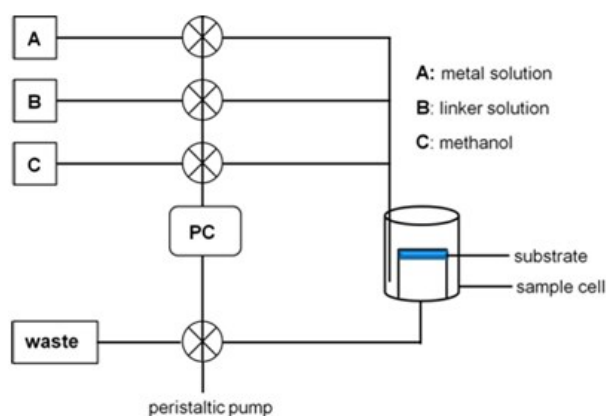


Fig. S18 Schematic illustration of automatic program-controlled repeated direct growth of MOF thin films on SiO₂ coated QCM substrates at room temperature.

3.2 Inter-conversion of MOF films

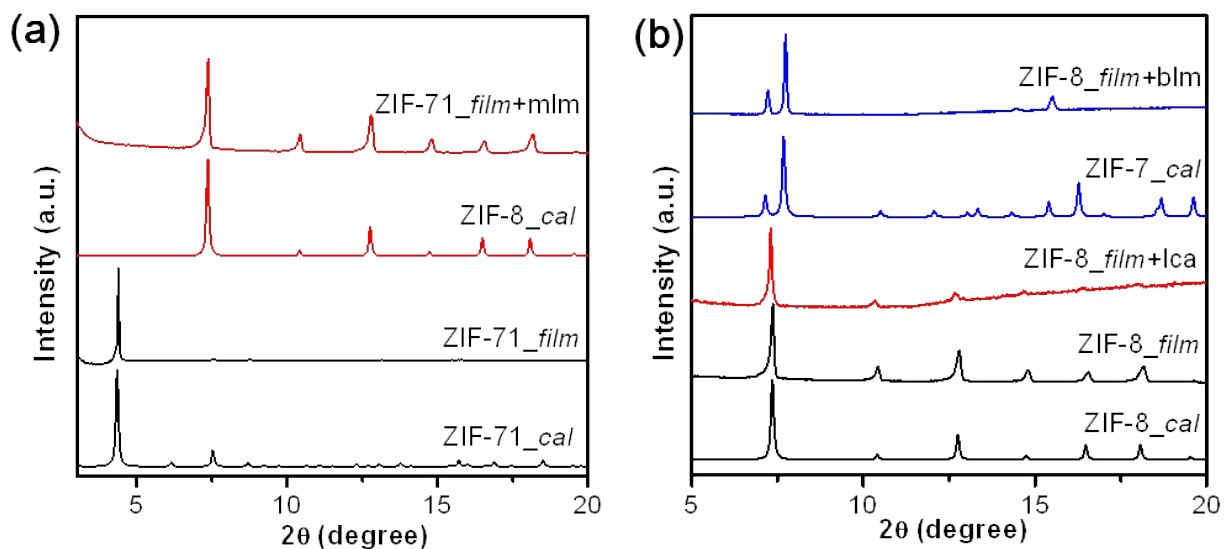


Fig. S19 (a) XRD patterns of fabricated ZIF-71 film and the films after the reaction in mlm solution at 60 °C for 1 day. (b) XRD patterns of fabricated ZIF-8 film and after reaction in lca and mlm solutions at 60 °C for 1 day. The XRD data can confirm that the MOF films (ZIF-71 and ZIF-8) can be converted to the target daughter ZIF films similar to their powder form. Due to the strong etching effect of dclm, we cannot obtain any XRD data for films converted by dclm solution.

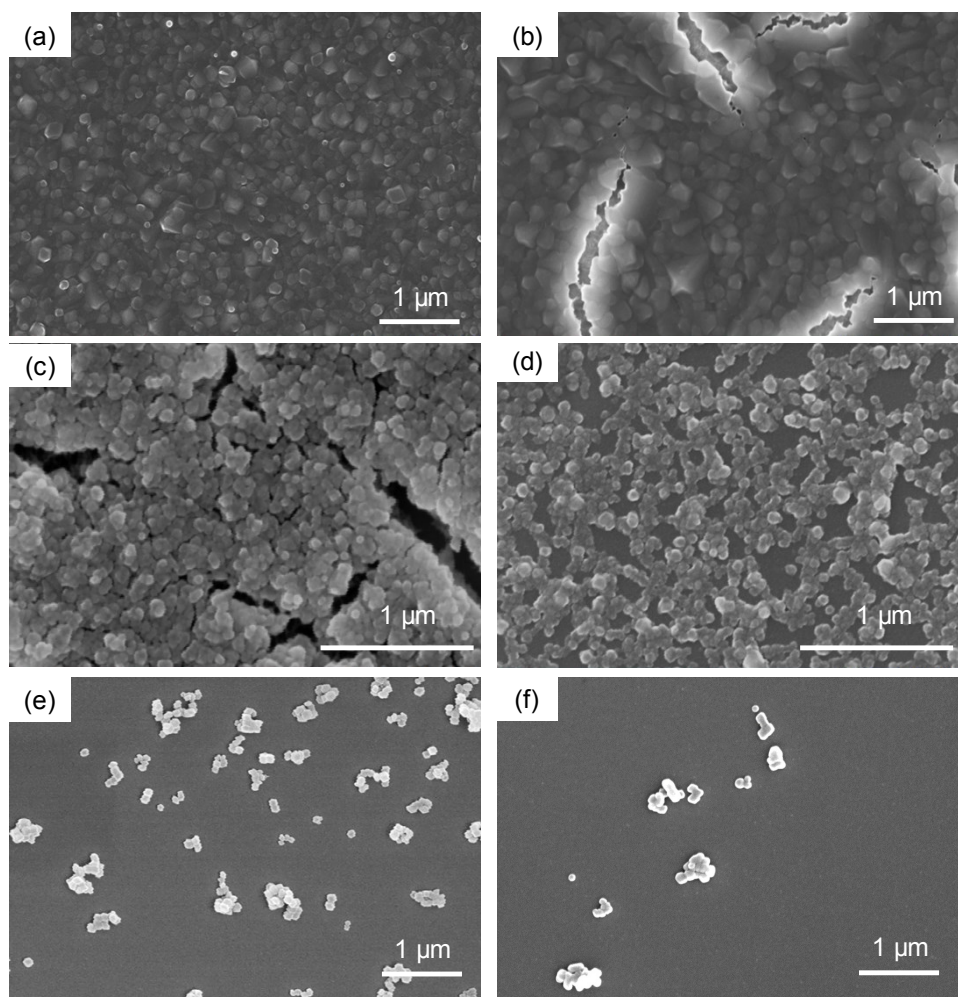


Fig. S20 Time-resolved SEM images of ZIF-8 film (a) incubated in dClm solution for 1 h (b), 3 h (c), 5 h (d), 16 h (e) and 24 h (f).

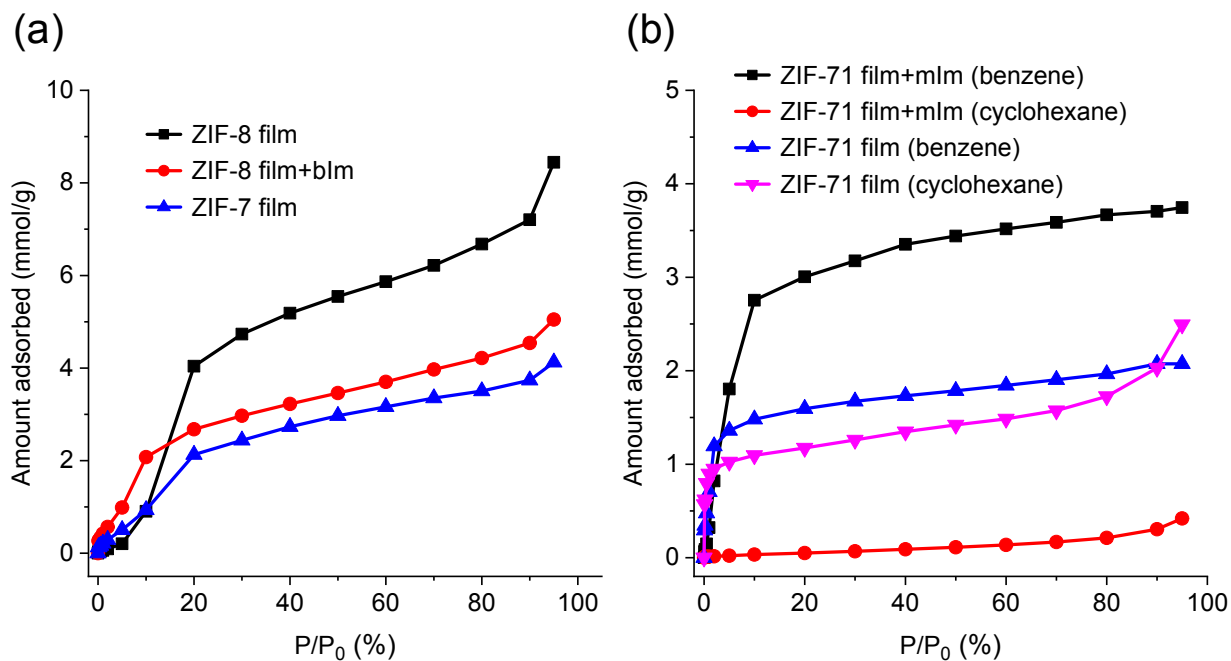


Fig. S21 (a) Adsorption isotherms of methanol vapor at 293 K on ZIF-8 film and the film converted by blm solution for 1 day. The adsorption isotherm of ZIF-7 film prepared by liquid-phase deposition (Fig. S18) is given for reference. (b) Adsorption isotherms of benzene and cyclohexane vapor at 293 K on ZIF-71 film and the film converted by mlm solution for 1 day. The transformed ZIF-7 film shows much lower uptake of methanol vapor compared to ZIF-8 film, due to its lower porosity. In addition, both the adsorption shape and uptake of methanol in the transformed ZIF-7 film are similar to the one obtained by liquid-phase deposition. Because of the larger pore opening of ZIF-71, it does not show preferred adsorption. However, after the conversion, the film exhibits selective adsorption of benzene over cyclohexane, because of the limited pore opening and structural flexibility

4 Encapsulation of guest molecules via an inter-conversion process

4.1 Encapsulation of ZnTPP in ZIF-76 via the conversion of ZIF-8

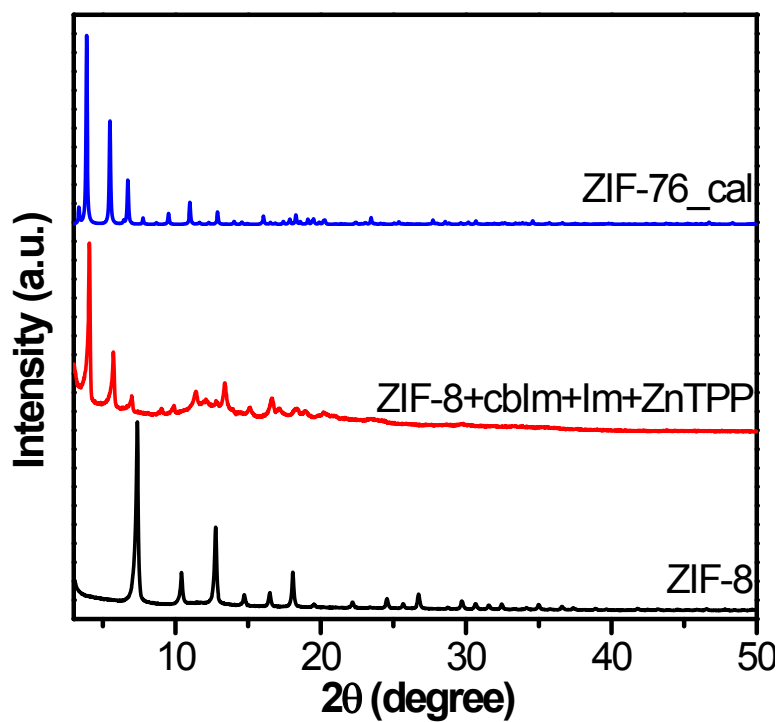


Fig. S22 PXR D patterns of ZIF-8, ZnTPP@ZIF-76 and calculated ZIF-76. The ZnTPP@ZIF-76 sample is obtained by the conversion of ZIF-8 in the presence of ZnTPP in the solution. The presence of ZnTPP does not interrupt the transformation process.

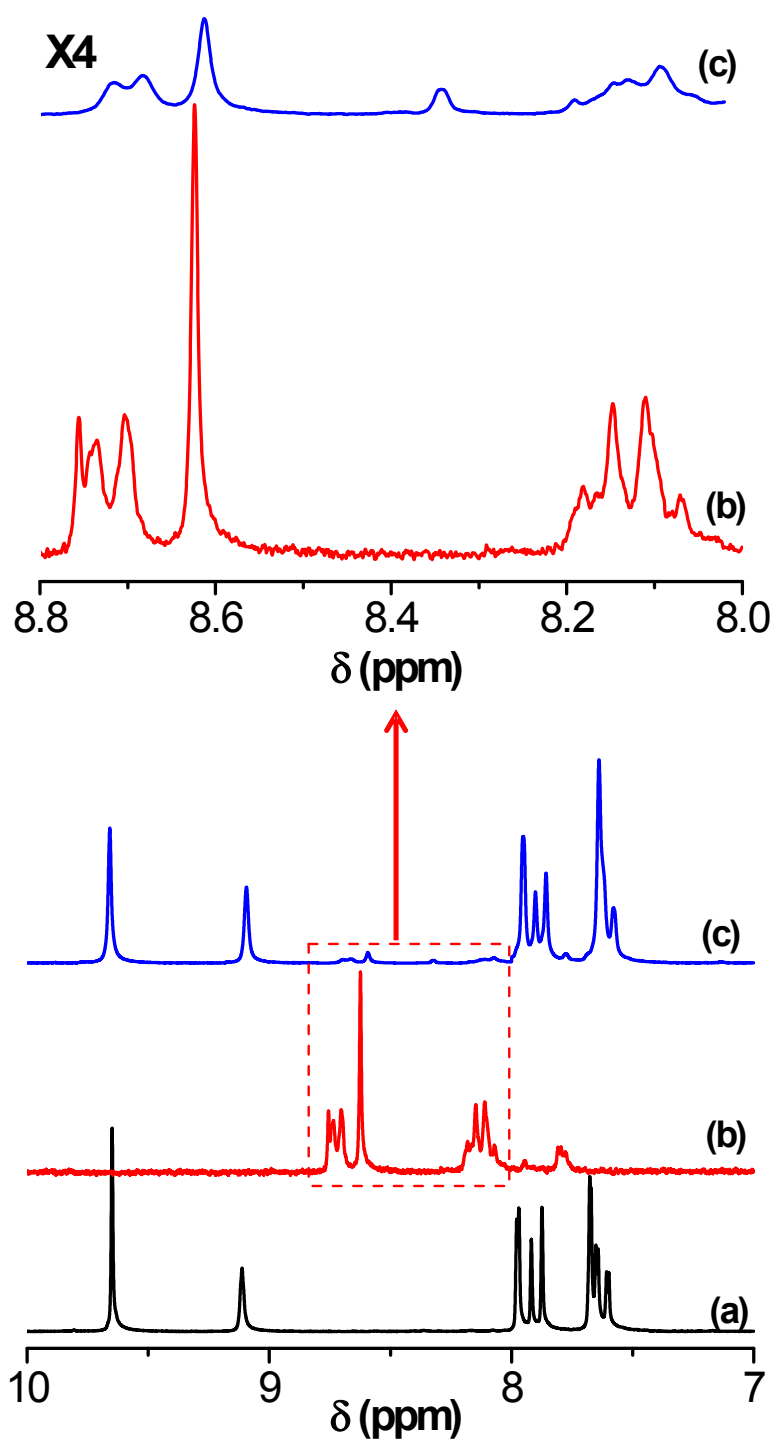


Fig. S23 Liquid-phase ^1H NMR spectra of digested samples of ZIF-76 (a), ZnTPP (b) and ZnTPP@ZIF-76 obtained by conversion of ZIF-8 in the presence of ZnTPP. Top, the enlarged spectra of ZnTPP and ZnTPP@ZIF-76 between the shift marked in the bottom spectra. ZnTPP can be incorporated into the framework of ZIF-76 via the conversion process. Based on the integral ratio of ZnTPP, Im and cblm, the composition is determined to be $\text{Zn}(\text{Im})_{0.86}(\text{cblm})_{1.14}\text{ZnTPP}_{0.01}$, corresponding to 2.2 wt% of ZnTPP in ZIF-76.

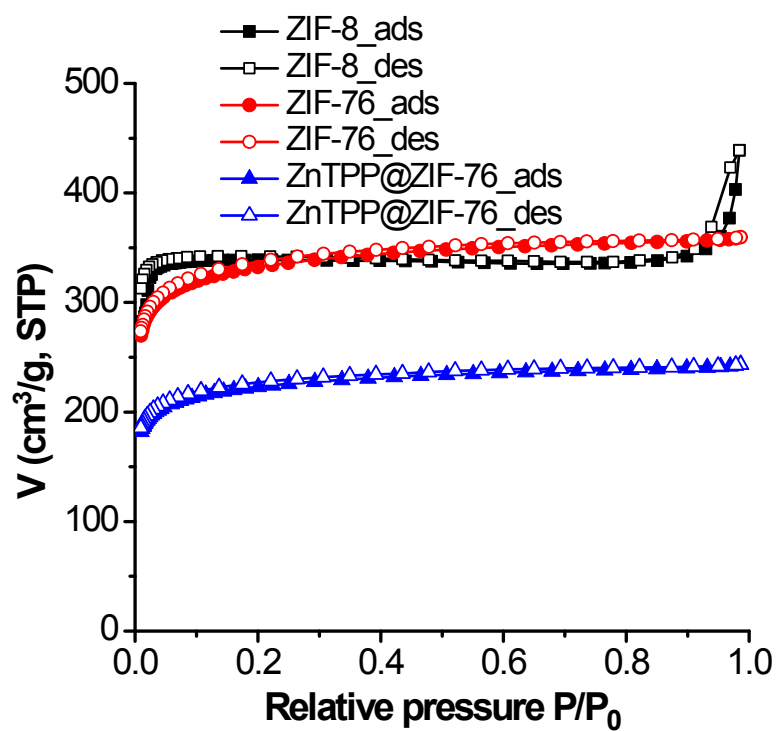


Fig. S24 N₂ sorption isotherm (at 77K) of ZIF-8, ZIF-76 (synthesized from the conversion of ZIF-8) and ZnTPP@ZIF-76 (synthesized from conversion of ZIF-8 with ZnTPP). The BET surface areas of ZIF-8, ZIF-76 and ZnTPP@ZIF-76 are calculated to be 1092, 1171 and 786 m²/g, respectively.

4.2 Encapsulation of CACD in ZIF-8 via the conversion of ZIF-7

48 mg ZIF-7 (ca. 0.2 mmol equiv. of blm for ZIF-7) was immersed into 5mL DMF solution of 9-chloroanthracene-10-carbaldehyde (CACD, 24mg, 0.1mmol) and mIm (82 mg, 1mmol). The mixture was then ultrasonicated for 1h to get a uniform suspension of ZIF-7 in the reaction solution. Subsequently, the suspension was kept in an oven at 60 °C for 3 days. After 3 days reaction, the obtained powder was washed with DMF by 8 repetitions of sonication-centrifuge cycles, and subsequently exchanged with MeOH for 1day. These exchanged samples were then dried at 120 °C.

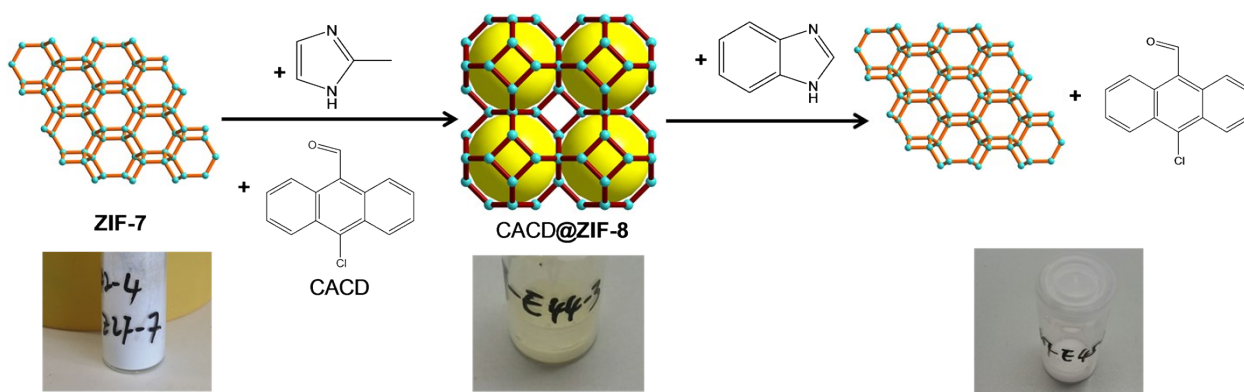


Fig. S25 Schematic presentation of the incorporation of CACD into ZIF-8 cavities (named as CACD@ZIF-8) via the conversion of ZIF-7 to ZIF-8 in the presence of CACD. After the conversion of CACD@ZIF-8 to ZIF-7, the CACD molecules are desorbed from the pores. At the first step, the color changes from white to yellow and subsequently changes back to white again. The color changes indicate that CACD can be incorporated into ZIF-8 cavities by conversion of ZIF-7 with CACD, while CACD cannot be encapsulated into ZIF-7 cavities.

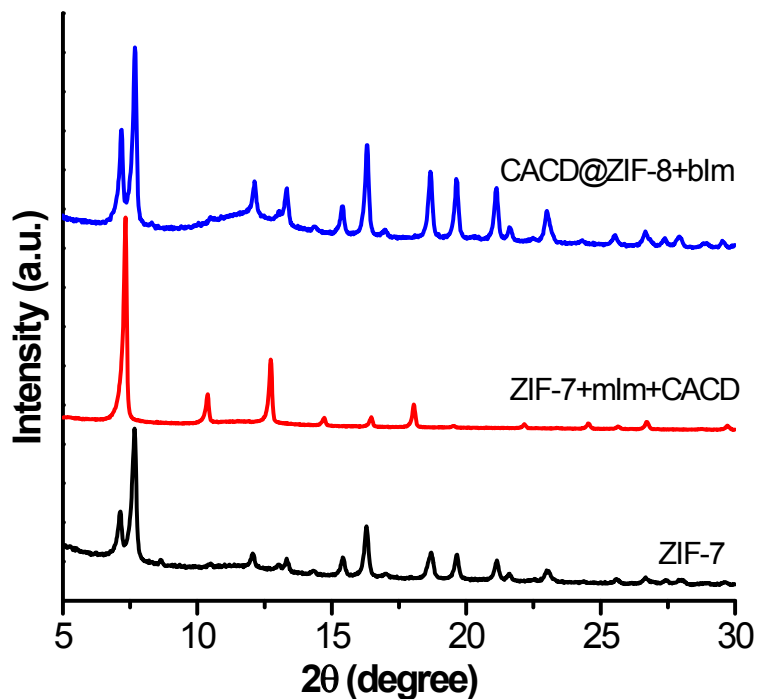


Fig. S26 PXR D patterns of ZIF-7, CACD@ZIF-8 (synthesized by the conversion of ZIF-7 with CACD) and ZIF-7 (synthesized by the conversion of CACD@ZIF-8 to ZIF-7).

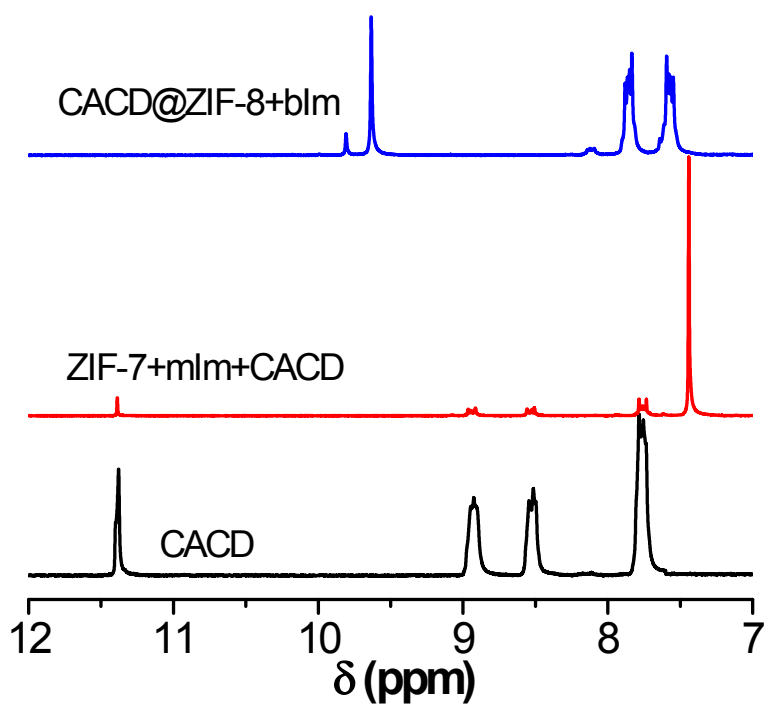


Fig. S27 Liquid-phase ¹H NMR Spectra of digested samples of CACD, CACD@ZIF-8 (synthesized by the conversion of ZIF-7 with CACD) and ZIF-7 (synthesized by the conversion of CACD@ZIF-8 to ZIF-7).

5 Reference

- 1 M. Tu, C. Wiktor, C. Rösler and R. A. Fischer, *Chem. Commun.*, 2014, **50**, 13258–13260.
- 2 J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.* 2009, **21**, 1410-1412
- 3 M. Tu, S. Wannapaiboon, K. Khaletskaya and R. A. Fischer, *Adv. Funct. Mater.*, 2015, **25**, 4470–4479.