Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Syntheses of New Zeolitic Zeolitic Imidazolate Frameworks in Dimethyl Sulfoxide

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1. Materials and Characterization

All reagents were purchased commercially and used without further purification. All syntheses were carried out in a 20 ml vial under autogenous pressure. All Powder X-ray diffraction analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 5°. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. The gases adsorption isotherms were measured by using ASAP 2020 volumetric adsorption equipment.

2. Single crystal synthesis and characterization of compounds 1-6

2.1. Synthesis of Compounds 1-6

Synthesis of $Zn_8(Im)_{16}$·xDMSO (**1**, ACO topology): The $Zn(CH_3CO_2)_2·2H_2O$ (1 mmol, 0.219 g) was dissolved in 3 mL dimethyl sulfoxide (DMSO), Imidazole (2 mmol, 0.136 g) was added to the above solution and then reacted in an oven at 60 °C for 3 days. The colorless rhomboid block crystal was obtained, washed with DMSO, and dried at room temperature (Yield: ca. 81% Based on the mole ratio of zinc salts). The crystal can be synthesized with zinc acetate dihydrate and imidazole in a wide range of ratios from 1:1 to 1:8.

Synthesis of $Zn_3(Im)_6$·xDMSO (**2**, hlw topology): The $Zn(CH_3CO_2)_2·2H_2O$ (0.5 mmol, 0.109 g) was dissolved in 3 mL DMSO, Imidazole (2 mmol, 0.136 g) and 2-Ethylimidazole (0.5 mmol, 0.048 g) was added to the above solution and then reacted in an oven at 100 °C for 3 days. The colorless strip crystal was obtained, washed with DMSO, and dried at room temperature (Yield: ca. 56% Based on the mole ratio of zinc salts). Compound 1 is also easily obtained by this scheme, and pure phase Compound 3 can be obtained in some specific ratio.

Synthesis of $Zn_4(Im)_8$·xDMSO (**3**, coi topology): The $Zn(CH_3CO_2)_2·2H_2O$ (0.5 mmol, 0.109 g) was dissolved in 3 mL DMSO, Imidazole (2.5 mmol, 0.170 g) and 2-

Propylimidazole (0.5 mmol, 0.055 g) was added to the above solution and then reacted in an oven at 100 °C for 3 days. The colorless rod-shaped crystal was obtained, washed with DMSO, and dried at room temperature (Yield: ca. 84% Based on the mole ratio of zinc salts).

Synthesis of $Zn_2(Im)_2(mim)_2 \cdot xDMSO$ (**4**, zni topology): The $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.5 mmol, 0.109g) was dissolved in 3 mL DMSO, Imidazole (1 mmol, 0.068 g) and 2-Methylimidazole (Hmim, 0.5 mmol, 0.041 g) was added to the above solution and then reacted in an oven at 100 °C for 3 days. The colorless spindle crystal was obtained, washed with DMSO, and dried at room temperature (Yield: ca. 55% Based on the mole ratio of zinc salts).

Synthesis of Zn(Im)(dmbim)·xDMSO (**5**, GIS topology): The $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.5 mmol, 0.109 g) was dissolved in 3 mL DMSO, Imidazole (1 mmol, 0.068 g) and 5,6-Dimethylbenzimidazole (Hdmbim, 0.5 mmol, 0.073 g) was added to the above solution and then reacted in an oven at 100 °C for 3 days. The colorless crystal was obtained, washed with DMSO, and dried at room temperature (Yield: ca. 76% Based on the mole ratio of zinc salts).

Synthesis of $Zn(eim)_2 \cdot xDMSO$ (**6**, ANA topology): The $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.5 mmol, 0.109 g) was dissolved in 3 mL DMSO, 2-Ethylimidazole (2 mmol, 0.192 g) was added to the above solution and then reacted in an oven at 100 °C for 3 days. The colorless polyhedral crystal was obtained, washed with DMSO, and dried at room temperature (Yield: ca. 49% Based on the mole ratio of zinc salts).

2.2. Characterization of Compounds 1-6

2.2.1. Summary of Im-based ZIFs with different topological networks

Table *S1*. Summary of Im-based ZIFs with different topological networks.

Topology	Name or CCDC code	Formula	Solvent/SDAs	Density Mg/m^3	Pore volume cm^3/g	BET m^2/g	Ref.
AFI	AFI-$[Zn(Im)_2]$	$Zn(Im)_2$	DPF	--	0.64	1386	[1]
BCT/crb	ZIF-1	$Zn_2(Im)_4$	DMF	1.471	-	-	[2]
BCT/crb	ZIF-2	$Zn_2(Im)_4$	DMF	1.390	-	-	[2]

BCT/crb	ZIF-64	$Zn_4(Im)_8$	DMF	1.449	-	-	[3]
BCT/crb	VEJYEP01	$Zn_2(Im)_4$	DMA	1.465	-	-	[4]
BCT/crb	VEJYIT01	$Zn_2(Im)_4$	DMF	1.428	-	-	[4]
CAN	CAN-[$Zn(Im)_2$]	$Zn_3(Im)_6$	DBF	1.181	0.54	1178	[1]
DFT	ZIF-3	$Zn(Im)_2$	DMF+NMP	1.092	0.348	2030	[2]
DFT	HIFVOI	$Zn(Im)_2$	NMP	0.931	-	-	[4]
GIS	ZIF-6	$Zn(Im)_2$	DMF	0.794	0.749	1076	[2]
GIS	HIFVUO	$Zn(Im)_2$	DEF	0.719	-	-	[4]
MER	ZIF-10	$Zn(Im)_2$	DMF	0.787	-	-	[2]
MER	mer-$MeMeCH_2$@-$Zn_{16}Im_{32}$	$Zn_{16}(Im)_{32}$	$MeMeCH_2$	1.561	0.74	1970	[5]
RHO	x$MeMeCH_2$@RHO-$Zn_{16}Im_{32}$	$Zn_{16}(Im)_{32}$	$MeMeCH_2$	1.183	0.70	1650	[6]
cag	ZIF-4	$Zn_2(Im)_4$	DMF	1.444	0.343	300	[2]
cag	VEJYUF01	$Zn_2(Im)_4$	DMF	1.434	-	-	[4]
coi	EQOCOC	$Zn_4(Im)_8$	H_2O	-	-	-	[7]
neb	KEVLEE	$Zn(Im)_2$	pyridine	1.543	-	-	[8]
nog	HIFWAV	$Zn_5(Im)_{10}$	DEF	1.258	-	-	[4]
unknown	GOQSIQ	$Zn_{10}(Im)_{20}$	DBF	1.401	0.49	319	[9]
zec	HICGEG	$Zn_5(Im)_{10}$	DEF	1.081	-	-	[4]
zni	IMIDZB	$Zn_2(Im)_4$	H_2O	1.57	-	-	[10]
ATN	ATN-[$Zn(Im)_2$]	$Zn_2(Im)_4$	DPF+BA	0.938	0.48	48	[11]
nog	nog-[$Zn(Im)_2$]	$Zn_2(Im)_4$	BA	-	0.41	1032	[11]
ACO	Compound 1	$Zn_8(Im)_{16}$	DMSO	0.920			This work
hlw	Compound 2	$Zn_3(Im)_6$	DMSO	1.187	0.23	524	This work
coi	Compound 3	$Zn_4(Im)_8$	DMSO	1.575			This work

DMF = N,N-dimethylformamide; DMA = N,N-dimethylacetamide; DPF = N,N-dipropylformamide; DBF = N,N-dibutylformamide; BA = n-butylamine; NMP = N-methyl pyrrolidone; DMSO = Dimethyl Sulfoxide; DEF = N,N-Dimethylacetamide; $MeMeCH_2$ = 1, 7, 11, 15, 21, 23, 25, 28-octamethyl-2,20:3,19-dimetheno-1H, 21H, 23H, 25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin. SDAs = Structure directing-agent.

2.2.2. Single crystal structure determination

Table *S2*. Crystal data and structure refinement for Compounds 1-6.

Compounds	1	2	3	4	5	6
Formula	$C_{48}H_{48}N_{32}Zn_8$	$C_{18}H_{18}N_{12}Zn_3$	$C_{24}H_{24}N_{16}Zn_4$	$C_{14}H_{16}N_8Zn_2$	$C_{12}H_{12}N_4Zn$	$C_{10}H_{14}N_4Zn$
Weight	1596.12	598.55	798.07	426.06	277.63	255.61
Crystal system	trigonal	monoclinic	tetragonal	tetragonal	tetragonal	cubic
Space group	*R*-3*c*	*C*2/*m*	$I4_1$	$I4_1/acd$	$I41/a$	*Ia*-3*d*
a/Å	24.6591(3)	14.10730(10)	22.8159(8)	23.5113(7)	16.5658(2)	26.5050(3)

b/Å	24.6591(3)	24.1246(2)	22.8159(8)	23.5113(7)	16.5658(2)	26.5050(3)
c/Å	32.7669(5)	19.8844(2)	12.9339(7)	12.6103(14)	21.3167(3)	26.5050(3)
α/°	90	90	90	90	90	90
β/°	90	98.2080(10)	90	90	90	90
γ/°	120	90	90	90	90	90
Volume/Å^3	17255.2(5)	6697.99(10)	6732.9(6)	6970.7(9)	5849.85(16)	18620.2(6)
Z	6	8	8	16	16	48
ρ_{calc}g/cm^3	0.920	1.187	1.575	1.616	1.261	1.086
GOOF	1.052	1.071	1.048	1.142	1.063	1.129
Final R indexes [I>=2σ (I)]	R_1 = 0.0557, wR_2 = 0.1856	R_1 = 0.0404, wR_2 = 0.1174	R_1 = 0.0469, wR_2 = 0.1218	R_1 = 0.1015, wR_2 = 0.2590	R_1 = 0.0723, wR_2 = 0.1921	R_1 = 0.0374, wR_2 = 0.1114
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.1891	R_1 = 0.0455, wR_2 = 0.1201	R_1 = 0.0529, wR_2 = 0.1260	R_1 = 0.1095, wR_2 = 0.2658	R_1 = 0.0856, wR_2 = 0.2011	R_1 = 0.0418, wR_2 = 0.1157
CCDC No.	2115206	2115210	2115208	2115211	2115209	2115207

Table *S3*. The summary of experimental results from imidazole ligands in DMSO.

mmol ratio(Zn : Im) / Temature	100 °C	80 °C	60 °C
0.5 : 0.5	Compound 1	solution	solution
0.5 : 1	Compound 1+ Compound 3	Compound 1	Compound 1
0.5 : 1.5	Compound 1+ Compound 3	Compound 1+ Compound 3	Compound 1
0.5 : 2	Compound 1+ Compound 3	Compound 1+ Compound 3	Compound 1
0.5 : 2.5	Compound 1+ Compound 3	Compound 1+ Compound 3	Compound 1
0.5 : 3	Compound 1+ Compound 3	Compound 1+ Compound 3	Compound 1
0.5 : 3.5	Compound 1+ Compound 3	Compound 1+ Compound 3	Compound 1
0.5 : 4	Compound 1+ Compound 3	Compound 1	Compound 1
0.5 : 4.5	Compound 1+ Compound 3	Compound 1	Compound 1+ Compound 3
0.5 : 5	Compound 1+ Compound 3	Compound 1	Compound 1+ Compound 3
0.5 : 5.5	Compound 1+ Compound 3	Compound 1	Compound 1
0.5 : 6	Compound 1+ Compound 3	Compound 1+ Compound 3	Compound 1

The mixture of Zinc acetate +DMSO+ Imidazole was heated at different temperatures for three days. The amount of DMSO was 3mL.

Table *S4*. The summary of experimental results from imidazole and 2-Propylimidazole mixed ligands in DMSO.

mmol ratio(Zn : Im) / Temature	100 °C	80 °C	60 °C
0.5 : 0.5	Compound 3	solution	solution
0.5 : 1	Compound 3	Compound 3	Compound 1
0.5 : 1.5	Compound 3	Compound 3	Compound 1
0.5 : 2	Compound 3	Compound 3	Compound 1
0.5 : 2.5	Compound 3	Compound 3	Compound 1
0.5 : 3	Compound 3	Compound 3	Compound 1

0.5 : 3.5	Compound 3	Compound 3	Compound 1
0.5 : 4	Compound 3	Compound 3	Compound 1
0.5 : 4.5	Compound 3	Compound 3	Compound 3
0.5 : 5	Compound 3	Compound 3	Compound 3
0.5 : 5.5	Compound 3	Compound 3	Compound 3
0.5 : 6	Compound 3	Compound 3	Compound 3
1 : 0.5	-	-	solution
1 : 1	Compound 3	Compound 3	solution
1 : 1.5	Compound 3	Compound 1	Compound 1
1 :2	Compound 1	Compound 1	Compound 1
1 : 2.5	Compound 1	Compound 3	Compound 1
1.5 : 0.5	Compound 3	-	solution
1.5 : 1	-	Compound 1	Compound 1
1.5 : 1.5	-	Compound 1	Compound 1
1.5 : 2	Compound 3	-	Compound 3
1.5 : 2.5	Compound 3	Compound 3	Compound 1
1 : 3	Compound 1	Compound 1	Compound 1

The mixture of Zinc acetate +DMSO+ Imidazole + 2-Propylimidazole was heated at different temperatures for three days. The amount of 2-Propylimidazole was fixed at 0.5 mmol and DMSO was 3mL.

Table *S5*. The summary of experimental results from 2-ethylimidazole and imidazole mixed ligands in DMSO.

mmol ratio(Zn : Im) / Temature	100 °C	80 °C	60 °C
0.5 ： 0.5	solution	solution	solution
0.5 ： 1	Compound 1	Compound 1	Compound 1
0.5 ： 1.5	Compound 2	Compound 1	Compound 1
0.5 ： 2	Compound 2	Compound 2	Compound 2
0.5 ： 2.5	Compound 2	Compound 2	Compound 2
1：0.5	solution	solution	solution
1：1	solution	solution	solution
1：1.5	Compound 1	Compound 1	Compound 1
1：2	Compound 2	Compound 2	Compound 2
1：2.5	Compound 2	Compound 2	Compound 2

The mixture of Zinc acetate +DMSO+ Imidazole + 2-Ethylimidazole was heated at different temperatures for three days. The amount of 2-ethylimidazole was fixed at 0.5 mmol and DMSO was 3mL.

Table *S6.* The comparison of the solvents for the syntheses of compounds 3-6 and earlier reported isostructural compounds.

	Solvent	Name or CCDC code	Earlier reported	Ref
Compound 3	DMSO	EQOCOC	Pyridine+ Ethanol	[7]
Compound 4	DMSO	ZIF-61	DMF+DEF	[12]
Compound 5	DMSO	TIF-5Zn	2-amino-1-butanol+ *p*-xylene	[13]
Compound 6	DMSO	MAF-5	Methanol+ benzene	[14]

2.2.3. Optical photographs of compounds 1-6

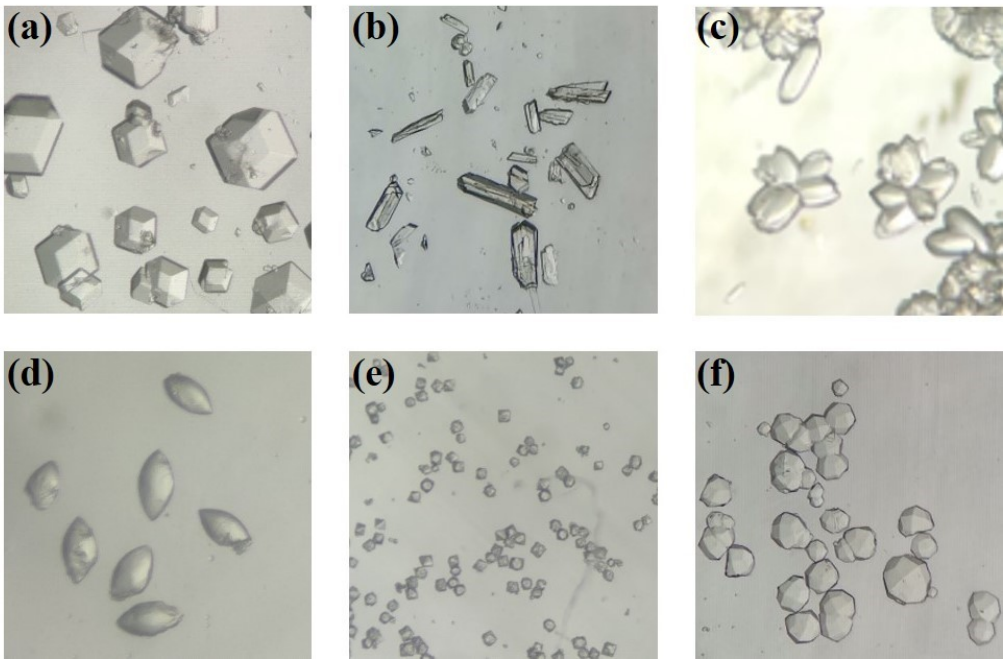

Figure S1. Crystal photographs of Compounds 1-6 corresponding to (a)-(f) respectively.

2.2.4. Crystal structure diagrams of compounds 2-6

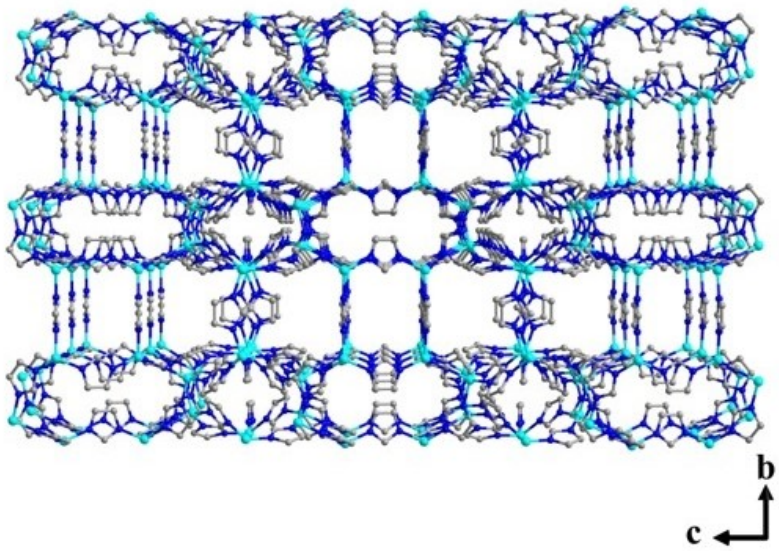

Figure S2. View of the 3D framework of compound 2 along a-axis.

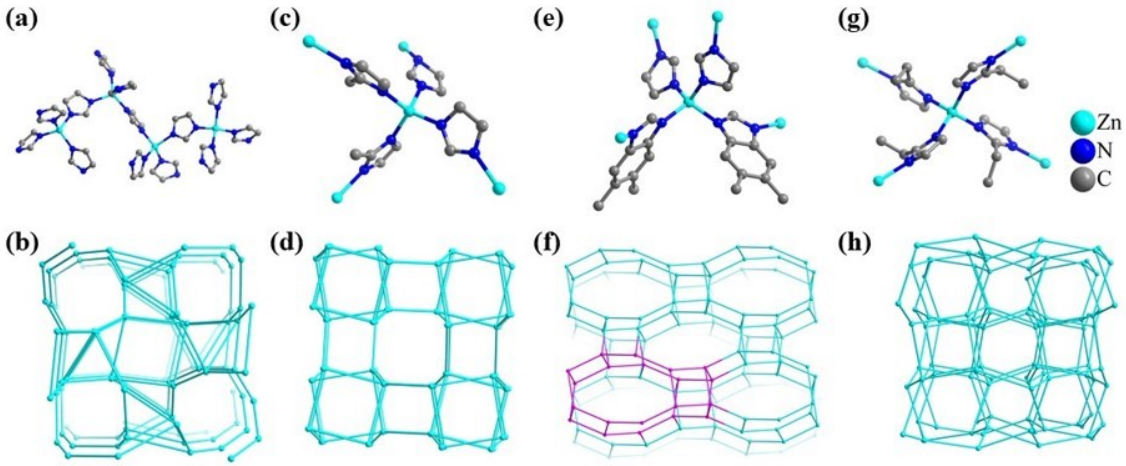

Figure S3. (a) the coordination environment of Zn atoms in compound 3; (b) the coi topology of compound 3; (c) the coordination environment of Zn atoms in compound 4; (d) the zni topology of compound 4; (a) the coordination environment of Zn atoms in compound 5; (b) the GIS topology of compound 5, one gis cage was highlighted in pink; (a) the coordination environment of Zn atoms in compound 6; (b) the ANA topology of compound 6.

2.2.5. Basic characterization of compounds 1-6

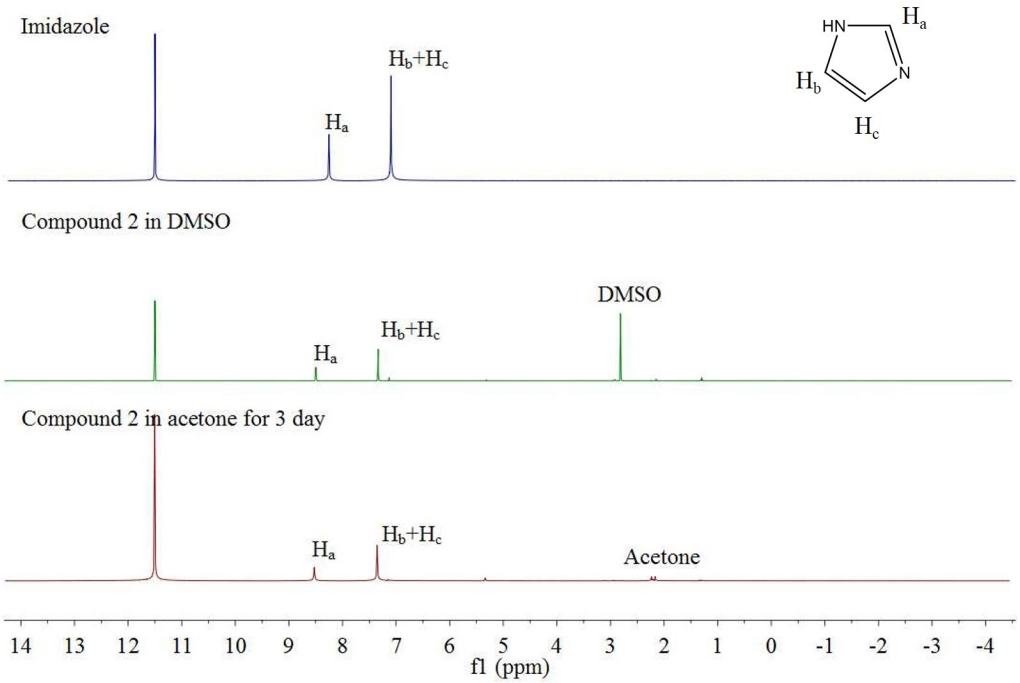

Figure S4. the ^{1}H NMR spectra of Imidazole, compound 2 in DMSO and acetone for 3 day. Sample was washed with DMSO and dissolved with Trifluoroacetic Acid-d(Isotopic) (δ = 11.50).

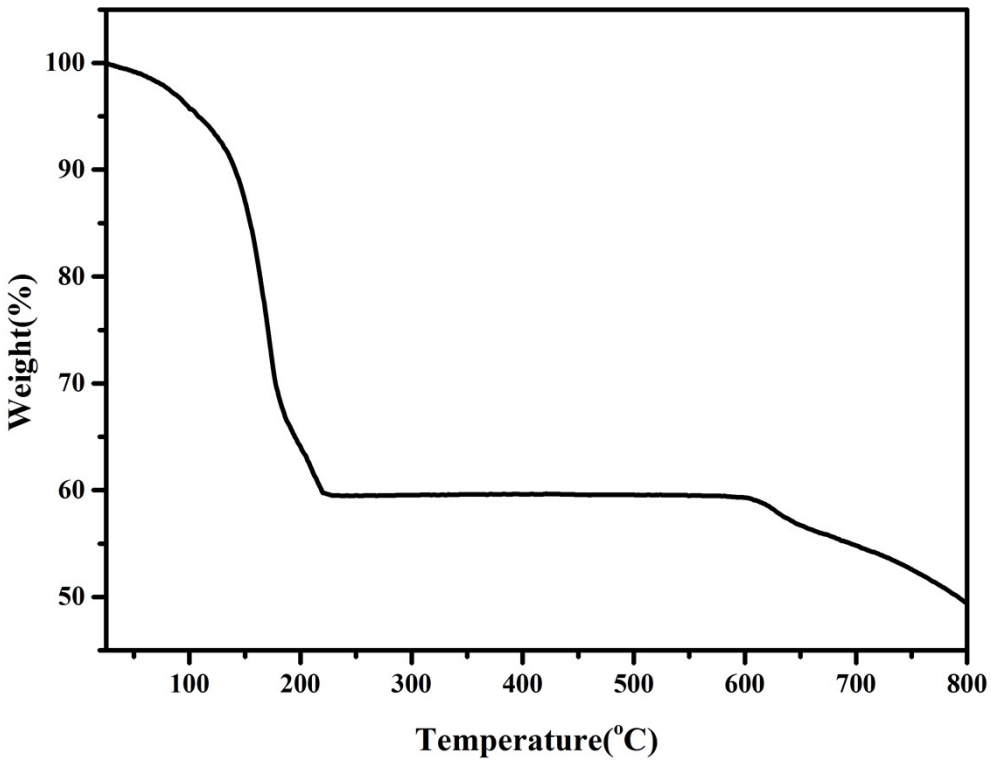

Figure S5. The TG plots of as synthesized samples compound 1.

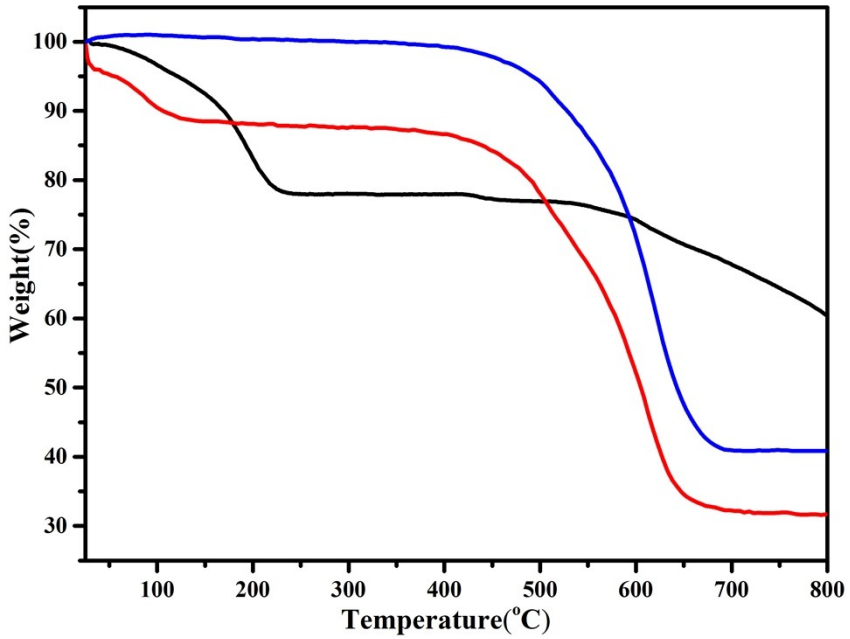

Figure S6. The TG plots of as synthesized samples compound 2 (black line), acetone exchanged samples (red line), activated samples at 100 °C (blue line).

The TGA descriptions of compounds 1 and 2:

For compound 1, the weight loss at 25℃~225℃ is close to 60%, and the reason is analysed that the compound gradually loses the DMSO guest molecules in the

periphery and pores; The stable platform can be shown that the structure can maintain good thermal stability before 600 °C. With the further increase of the temperature, the weight loss during the period of 600 °C to 800 °C indicates that the structure collapses. Similarly, for Compound 2, the weight loss of about 32% during the period from 25 °C to 227 °C is also the weight loss of DMSO guest molecules around the compound and in the pores. The plateau between 227°C and 500°C indicates that the structure remains stable during this period. As the temperature further increases, the compound begins to lose weight gradually, and the framework is destroyed.

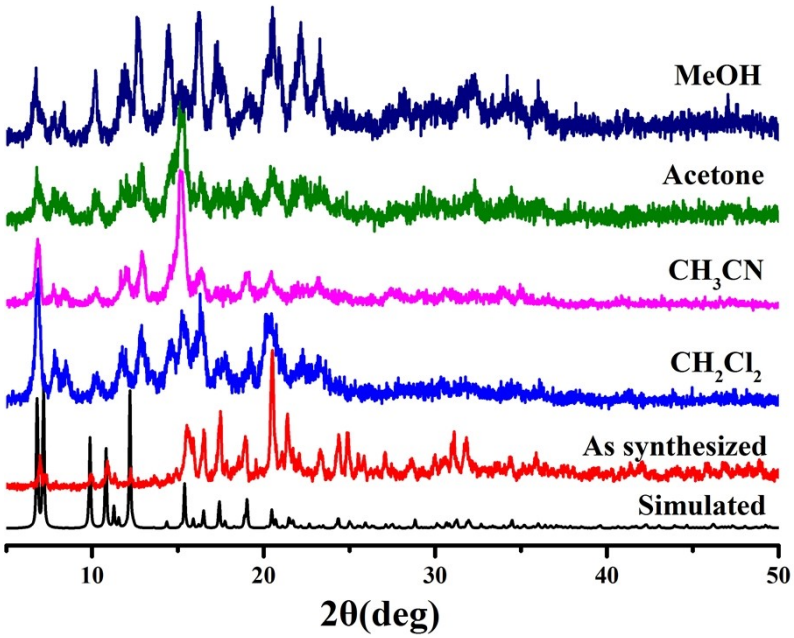

Figure S7. The PXRD patterns of compound 1 in different solutions.

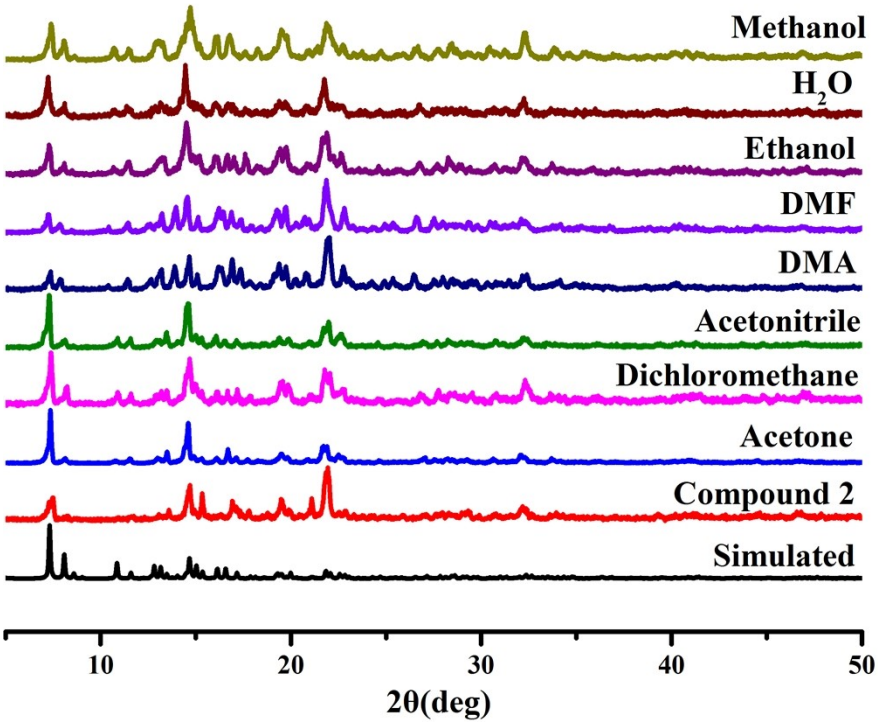

Figure S8. The PXRD patterns of compound 2 under different conditions.

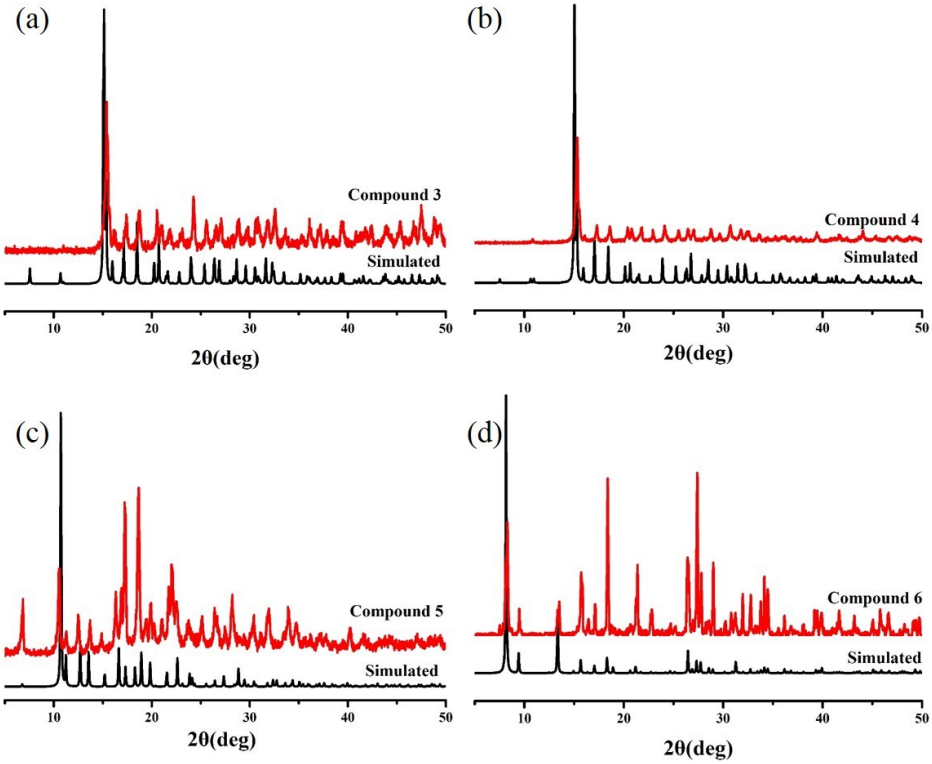

Figure S9. The PXRD patterns of Compounds 3-6 corresponding to (a)-(d) respectively.

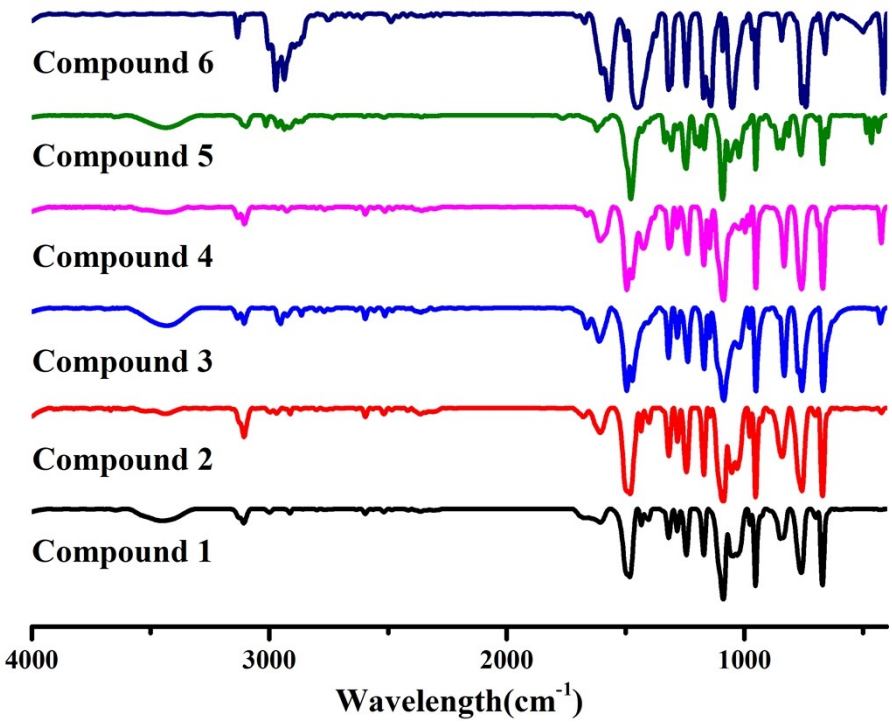

Figure *S10*. The IR of Compounds 1-6.

The FTIR data for Compounds 1-6 have been shown in Figure S10. The Compounds 1-3 are all composed of imidazole, so the infrared images of compounds are basically consistent. The difference between Compound 4 and the former lies in the addition of 2-methylimidazole, while the characteristic peak of methyl is near 2900 cm^{-1}. Since imidazole also has a characteristic peak here, the difference is not obvious. For Compound 5, the characteristic peak of the ligand was weak at 2000-1660 cm^{-1}, and it was also easy to overlap with the peak of imidazole, but it was obviously different from the previous compounds on the whole. Compound 6, 2-ethylimidazole, showed a characteristic peak near 2900 cm^{-1} that was markedly different from the previous compounds.

3. Adsorption Characterization

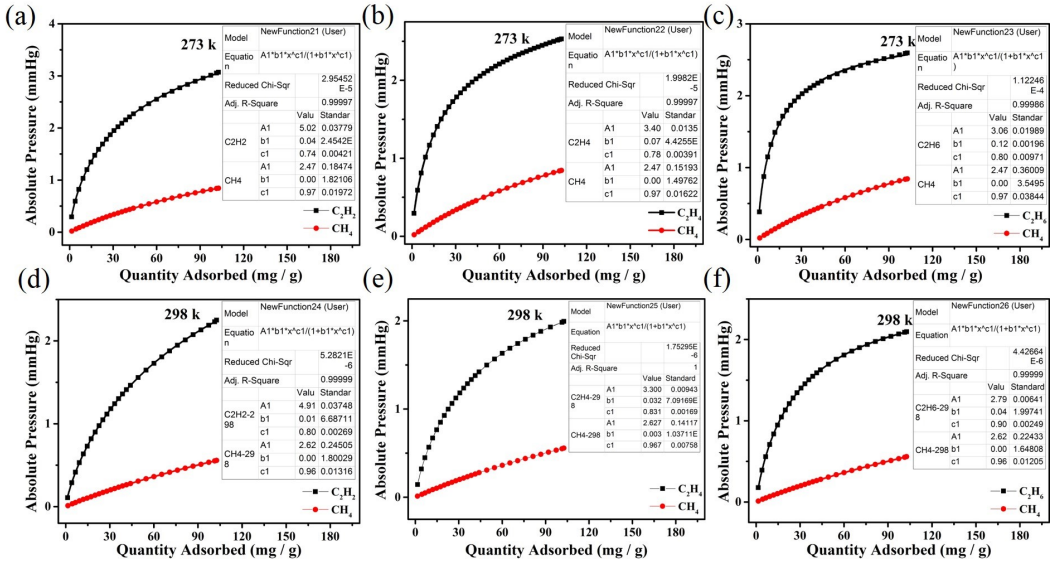

Figure S11. Gas adsorption L-F equation Fitting of Compound 2.

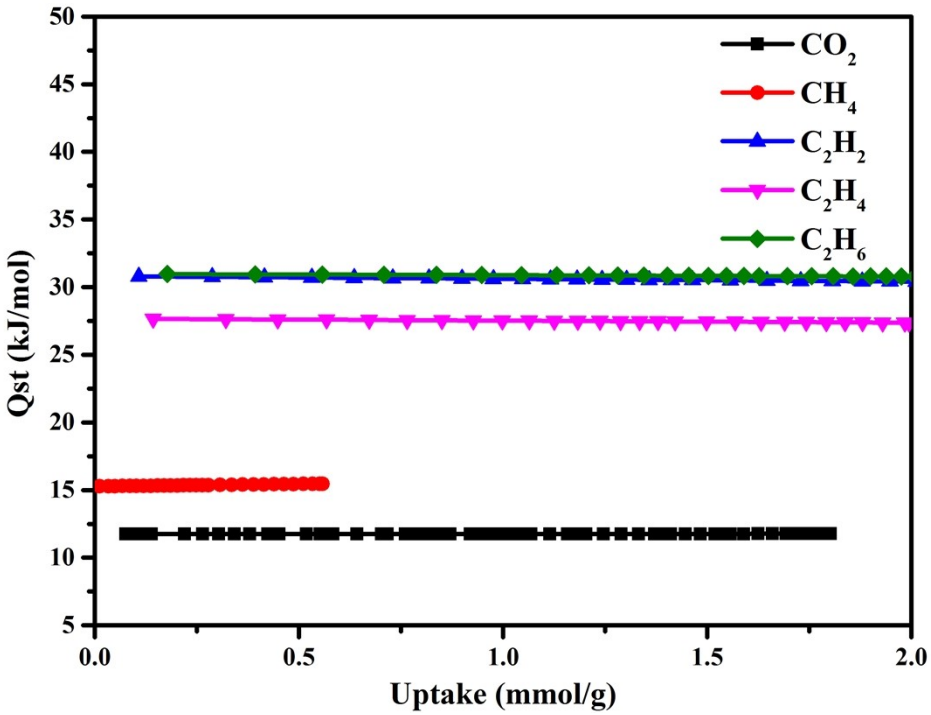

Figure S12. The isosteric heat of Compound 2 for light hydrocarbon and CO_2.

References

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