Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for

Connection of zinc paddle-wheels in a pto-type metal-organic framework with 2-methylimidazolate and subsequent incorporation of charged organic guests

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Section S1 General Procedures

2-methylimidazole (mIm), zinc(II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), and anhydrous methanol were purchased from Sigma-Aldrich. *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) werepurchased from Daejung Chemicals & Metals Co., Ltd. All starting materials were used without further purifications.1,3,5-Tris(4′-carboxyphenyl)benzene (H_3BTB) was prepared according to published procedures.[S1]Elemental analyses were carried out on an EA 1110, CE instrument. IR spectra were recorded on a JASCO FT/IR-4000 spectrophotometer with samples prepared as KBr pellets. ^{1}H-NMR spectra of digested MOF crystals in DCl/DMSO were obtained on a Bruker 400 MHz NMR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a RigakuMiniFlexdiffractometer with Cu Kαradiation (λ= 1.5418 Å). Adsorption isotherms of N_2 and CO_2 at pressures up to 1 bar were measured by standard volumetric procedures on BELSORP-mini (BEL-Japan, INC.) equipment. Each sample was dried and fully outgassed at 80 ºC for 10hrunder vacuum ($< 1.0 \times 10^{-3}$torr)immediately before measurement. The dead volume of the sample cell was automatically measured using helium gas. Pressure equilibrium points were also collected automatically by the equipment. Each sample’s weight was measured without exposing it to air. Using nitrogen isotherm points below $P/P_0 = 0.20$, BET surface areas were determined by the equation provided by the manufacturer. For CO_2 adsorption measurements, sample cells were maintained at 253 K in an ice/acetone bath, at 273 K in an ice/water bath, or at 298 K in a water bath. The isosteric heats of adsorption were calculated using a virial equation; zero-coverage values were regarded as each MOF’s heat of adsorption.

Section S2 Syntheses of Materials

Synthesis of mIm-MOF-14. To the solution of H_3BTB (192 mg, 0.44mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (510 mg, 1.71mmol) in DMF(30 mL), 2-methylimidazole (H-mIm; 160 mg, 1.95mmol) was added. The resulting solution was transferred in a vial (31 mL), which was tightly capped and heated in an isothermal oven at 95 °C for 48 h to give light-yellowblock crystals. After the reaction mixture was allowed to cool naturally to room temperature, the crystals were filtered, washed with DMF, and dried in air.Yield: 197 mg, 72% based on 1 mol of H_3BTB.Elemental analysis for the framework of mIm-MOF-14, $[(H_2\text{-mIm}^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}] \equiv C_{63}H_{43.5}N_{4.5}O_{12}Zn_3$,calcd(%): C 60.45, H 3.50, N 5.04. Elemental analysis for $[(H_2\text{-mIm}^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}]{\bullet}(H_2O)_{2.2} \equiv C_{63}H_{47.9}O_{14.2}N_{4.5}Zn_3$,calcd. (%): C 58.59, H 3.74, N 4.88;found (%): C 58.48, H 3.90, N 5.05. FT-IR (KBr, 4,000-400 cm^{-1}): 3200 (br, m), 1588 (vs), 1543 (s), 1388 (vs), 1182 (w), 1137 (w), 1108 (w), 1015 (m), 855 (m), 811 (w), 780 (s), 705 (m), 673 (m), and 479 cm^{-1}(w).

Preparation of TMA@mIm-MOF-14.A solution of tetramethyl ammonium chloride (TMA^+Cl^-)inMeOH(0.1 M) was prepared. Cation exchange was performed as follows: (a) the as-synthesized mIm-MOF-14was rinsed with fresh MeOH (30 mL x 5); (b) the material was then soaked in the TMA^+Cl^- solution (100 mL), which was heated at 100°C for24 h undera reflux; c) the material was again rinsed with fresh MeOH (100 mL x 3) followed by step (b) once again. The reaction mixture was allowed to cool naturally to room temperature and the crystals were washed with fresh MeOH. Elemental analysis for the framework of TMA@mIm-MOF-14, $[(TMA^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}] \equiv C_{66}H_{51.8}N_{5.3}O_{12}Zn_3$,calcd. (%): C 60.67, H 3.99, N 5.04. Elemental analysis for $[(TMA^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}]{\bullet}(H_2O)_{5.6} \equiv C_{66}H_{63}O_{17.6}N_{5.3}Zn_3$,calcd. (%): C 56.32, H 4.51, N5.23;found (%): C 55.97, H4.01, N 5.03. FT-IR (KBr, 4,000-400 cm^{-1}): 3193 (br, m), 1589 (vs), 1544 (s), 1385 (vs), 1181 (w), 1136 (w), 1108 (w), 1015 (m), 949 (w), 855 (m), 810 (w), 780 (s), 705 (m), 673 (m), 562(w), and 479 cm^{-1} (w).

Section S3 Powder X-ray Diffraction Patterns

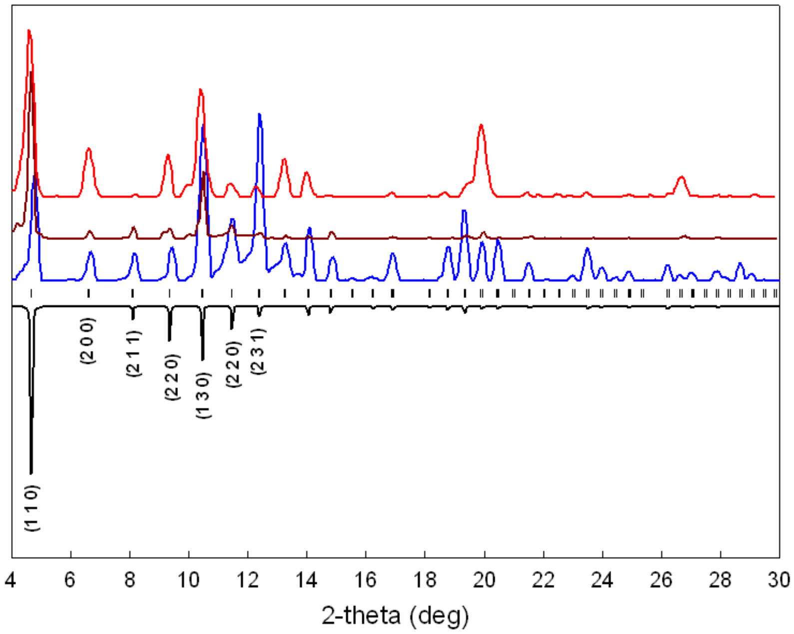

Fig. S1 Comparison of the PXRD patterns of mIm-MOF-14; as-prepared (blue), activated (brown) , TMA activated(red), and simulated (black) derived from single-crystal X-ray data.

Section S4 Single Crystal X-ray Diffraction Analyses

The diffraction data from a light-yellow block crystal measuring 0.30 × 0.32 × 0.33 mm^3 mounted on a glass fiber were collected at 147 K on a Bruker APEX CCD diffractometer with MoKα radiation (λ = 0.71073 Å). Data integration was processed using SAINT.[S2] Absorption correction was applied by SADABS.[S3] Crystal structure was solved using SHELX-TL software package with a cubic space group, $Im\bar{3}$ (No. 204).[S4] An initial model was obtained by direct methods using XS, and improved by subsequent refinements using XL. BTB sit on a Wyckoff position *f* and has site symmetry of 3. Two independent Zn1 and Zn2 were located in Wyckoff positions, *e* with different *x* positions. Therefore, one-eighth mIm was defined in an asymmetric unit. One of the carboxylate oxygen atoms was disordered over two sites (O2 and O2') in general positions. The bridging 2-methlyimidazolate (mIm) sits on a special position (0. 0.5, 0) which is a Wyckoff position*b* and has site symmetry of *mmm*. Therefore, one-eighth mIm was defined in an asymmetric unit, and N3I, C4I, C5I, and C6I atoms were assigned to the corresponding atoms. A dangling 2-methylimidazole (mIm) was also disordered over two sites. The N1I donor atom of mIms its on a Wyckoff position *e* with site symmetry of *mm*2. Due to the symmetry requirement, one-fourth mIm was unique in the asymmetric unit, and both C3I and N3I should have had the same location. Non-hydrogen atoms were refined anisotropically and most hydrogen atoms were placed in calculated positions and refined by applying a riding model. However, the hydrogen atoms bonded to the disordered C4I were fixed at ideal positions. As usually observed in highly porous and symmetric MOF structures, it was very difficult to find occluded solvent molecules from diffuse electron densities. Without including unidentified species in the pore, the refinement converged to R_1 = 0.0846, and wR_2 = 0.2743 for 2265 reflections of $I>2\sigma(I)$. Total potential solvent accessiblevolume calculated by PALTON SQUEEZE[4]was9516.7Å^3 which corresponds to 49.7 % of the unit cell volume, andtotal electron count in Voids/Cell was 3008. Using modified reflection data, the final refinement process converged to R_1 = 0.0536, wR_2 = 0.1600 ($I > 2\sigma(I)$). A part of the extended structure is in Figure S1, and crystal and refinement data are given in Table S1.CCDC-987525 contains the supplementarycrystallographic data for this paper. These data can be obtained free ofcharge from The Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for mIm-MOF-14.

Empirical formula	C63 H43.50 N4.50 O12 Zn3	
Formula weight	1251.63	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	*Im*-3 (No. 204)	
Unit cell dimensions	*a* = 26.7517(3) Å	α= 90°.
	b = 26.7517(3) Å	β= 90°.
	c = 26.7517(3) Å	γ = 90°.
Volume	19144.9(4) Å^3	
Z	8	
Density (calculated)	0.868 Mg/m^3	
Absorption coefficient	0.786 mm^{-1}	
F(000)	5112	
Crystal size	0.33 x 0.32 x 0.30 mm^3	
Theta range for data collection	1.08 to 29.14°.	
Index ranges	-36<=h<=35, -34<=k<=36, -36<=l<=33	
Reflections collected	80284	
Independent reflections	4235 [*R*(int) = 0.0908]	
Completeness to theta = 29.14°	92.7 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4235 / 65 / 172	
Goodness-of-fit on F^2	0.915	
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0536, wR_2 = 0.1515	
R indices (all data)	R_1 = 0.0927, wR_2 = 0.1600	
Largest diff. peak and hole	0.669 and -0.300 e.Å^{-3}	

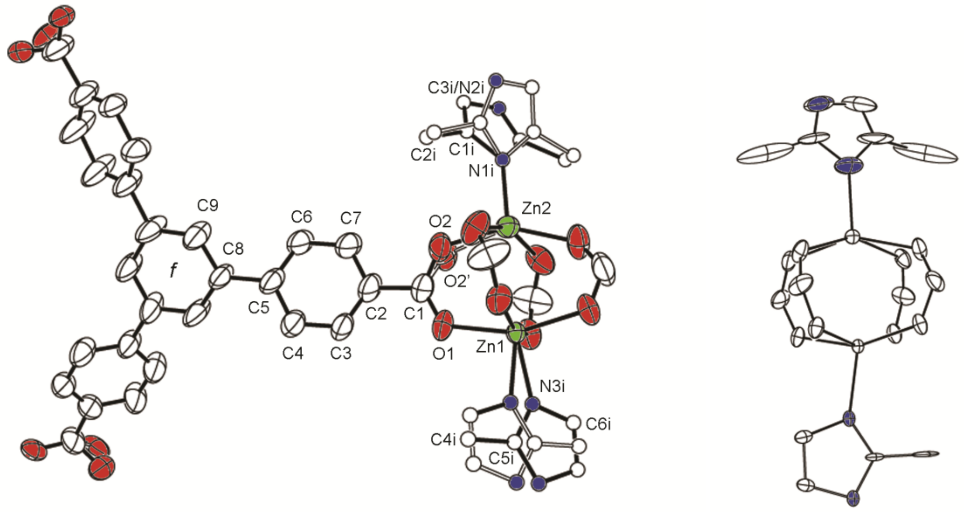

Fig. S2(left) ORTEP drawing (50% probability) of a fragment in mIm-MOF-14 is displayed with selected atomic labels. The labeled atoms constitute an asymmetric unit. A tripodal ligand, BTB sits on a special position having site symmetry of 3 (Wyckoff position, *f* which is marked in the central benzene ring of BTB). **(right)** Disordered 2-methlyimidazole and 2-methylimidazoalte are drawn by ORTEP with a 20% probability level.

Section S5 ^{1}H-NMR Spectrums of Digested MOFs

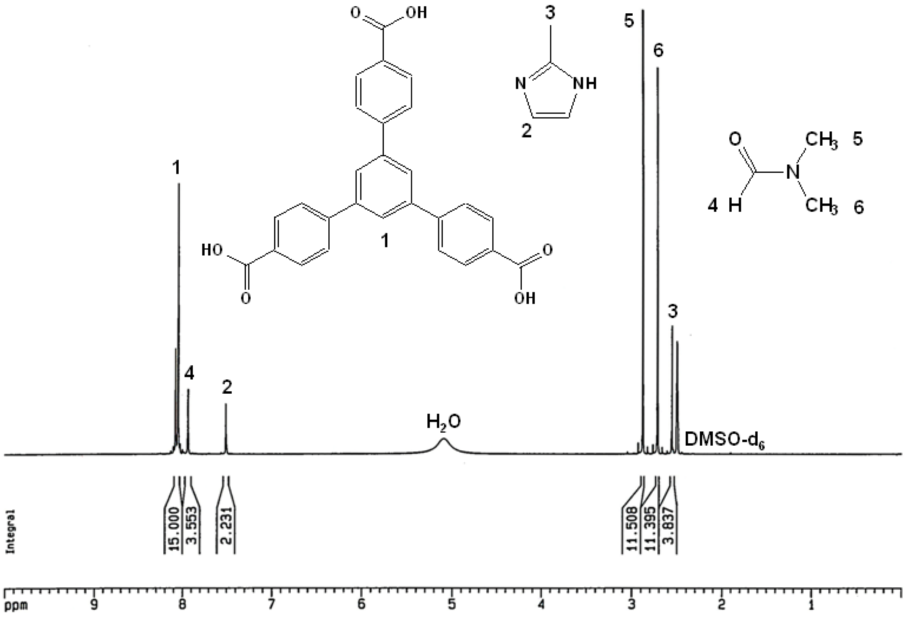

Fig. S3 ^{1}H-NMR spectrum measured for the as-synthesized mIm-MOF-14dissolved ina DCl/DMSO solution, resulting in a proposed formula as $[(H_2\text{-mIm}^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}]\bullet(DMF)_{7.3}$ based on the integration ratios of the proton signals as follows.

In the acidic solution, it is assumed that the mIm-MOF-14 framework is dissociated into 3 Zn(II), 2 H_3BTB, and 2.25 H-mIm (or $H_2\text{-mIm}^+$), which is approximately represented as $Zn_3(BTB)_2(H\text{-mIm})_{2.25}$.A possible formula has been determined as follows based on the integration of the signals in the spectrum.

Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	$-CH_3$	3	3.84	1.28	2.56	2.25
DMF	$-CH_3$	6	22.90	3.82	7.64	6.71
Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	$-CH_3$ and -CH	5	5.07	1.01	2.02	2.25
DMF	$-CH_3$ and -CH	7	25.46	3.64	7.28	8.11
Compd.				**# of compd. (avg.)**		**formula**
H_3BTB					2	2
H-mIm					2.29	2.25
DMF					7.46	7.33

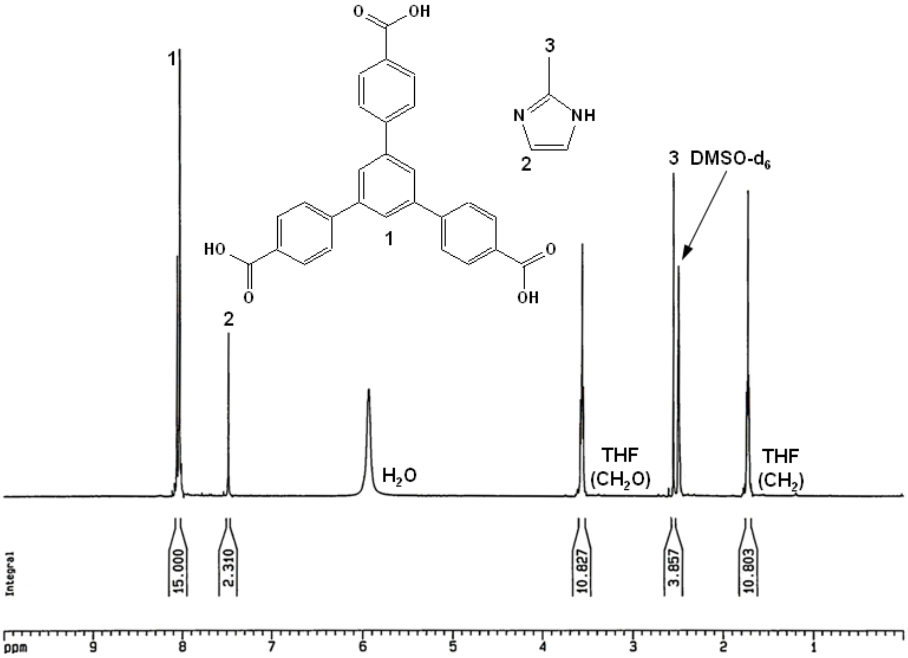

Fig. S4 ^{1}H-NMR spectrum for the THF-exchangedmIm-MOF-14 dissolved in a DCl/DMSO solution, resulting in a proposed formula as $[(H_2\text{-mIm}^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}]\bullet(THF)_{2.5}$ based on the integration ratios of the proton signals as follows.

In the acidic solution, it is assumed that the mIm-MOF-14 framework is dissociated into 3 Zn(II), 2 H_3BTB, and 2.25 H-mIm (or $H_2\text{-mIm}^+$), which is approximately represented as $Zn_3(BTB)_2(H\text{-mIm})_{2.25}$. A possible formula has been determined as follows based on the integration of the signals in the spectrum.

Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	$-CH_3$	3	3.86	1.29	2.58	2.25
THF	$-CH_2$	8	10.83	1.35	2.70	2.35
Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	$-CH_3$ and -CH	5	6.16	1.23	2.26	2.25
THF	$-CH_2$	8	10.83	1.35	2.70	2.69
Compd.				**# of compd. (avg.)**		**formula**
H_3BTB					2	2
H-mIm					2.42	2.25
THF					2.70	2.51

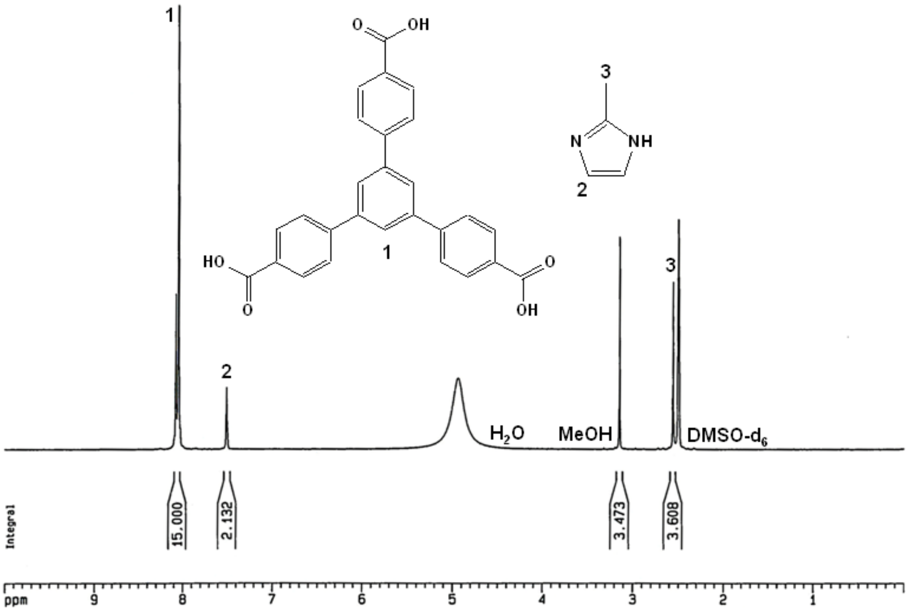

Fig. S5 ^{1}H-NMR spectrum forthe MeOH-exchangedmIm-MOF-14 dissolved ina DCl/DMSO solution, resulting in a proposed formula as $[(H_2\text{-mIm}^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}]\cdot(MeOH)_{2.2}$based on the integration ratios of the proton signals as follows.

In the acidic solution, it is assumed that the mIm-MOF-14 framework is dissociated into 3 Zn(II), 2 H_3BTB, and 2.25 H-mIm (or $H_2\text{-mIm}^+$), which is approximately represented as $Zn_3(BTB)_2(H\text{-mIm})_{2.25}$. A possible formula has been determined as follows based on the integration of the signals in the spectrum.

Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	$-CH_3$	3	3.61	1.20	2.40	2.25
MeOH	$-CH_3$	3	3.47	1.16	2.32	2.16
Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	$-CH_3$ and -CH	5	5.74	1.15	2.30	2.25
MeOH	$-CH_3$	3	3.47	1.16	2.32	2.27
Compd.				**# of compd. (avg.)**		**formula**
H_3BTB					2	2
H-mIm					2.35	2.25
MeOH					2.32	2.22

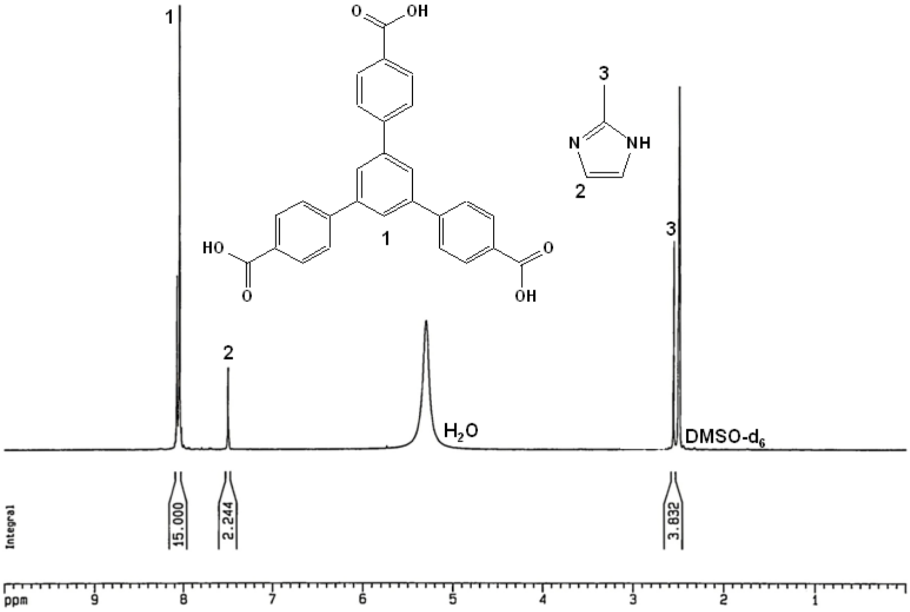

Fig. S6 ^{1}H-NMR spectrum for the activated mIm-MOF-14 dissolved ina DCl/DMSO solution, resulting in a proposed formula as $[(H_2\text{-mIm}^+)_{3/4}][Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/4}]$ based on the integration ratios of the proton signals as follows.

In the acidic solution, it is assumed that the mIm-MOF-14 framework is dissociated into 3 Zn(II), 2 H_3BTB, and 2.25 H-mIm (or $H_2\text{-mIm}^+$), which is approximately represented as $Zn_3(BTB)_2(H\text{-mIm})_{2.25}$. We assumed that when $(TMA^+)_{3/4}[Zn_3(BTB)_2(mIm)_{3/4}(H\text{-mIm})_{3/2}]$ was disintegrated and dissolved in the DCl/DMSO, all the imidazoles became fully protonated and indistinguishable. Therefore, the ratio of H_3BTB and H-mIm was suggested to be 2 :(9/4), where 9/4 was obtained by the addition of (3/4) and (3/2). This table shows that the integration value of the H_3BTB (Ar-H) signals is smaller than that predicted by the X-ray formula.

Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	-CH_3	3	3.85	1.28	2.56	2.25
Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	-CH_3 and -CH	5	6.08	1.22	2.44	2.25
Compd.				**# of compd. (avg.)**		**formula**
H_3BTB					2	2
H-mIm					2.50	2.25

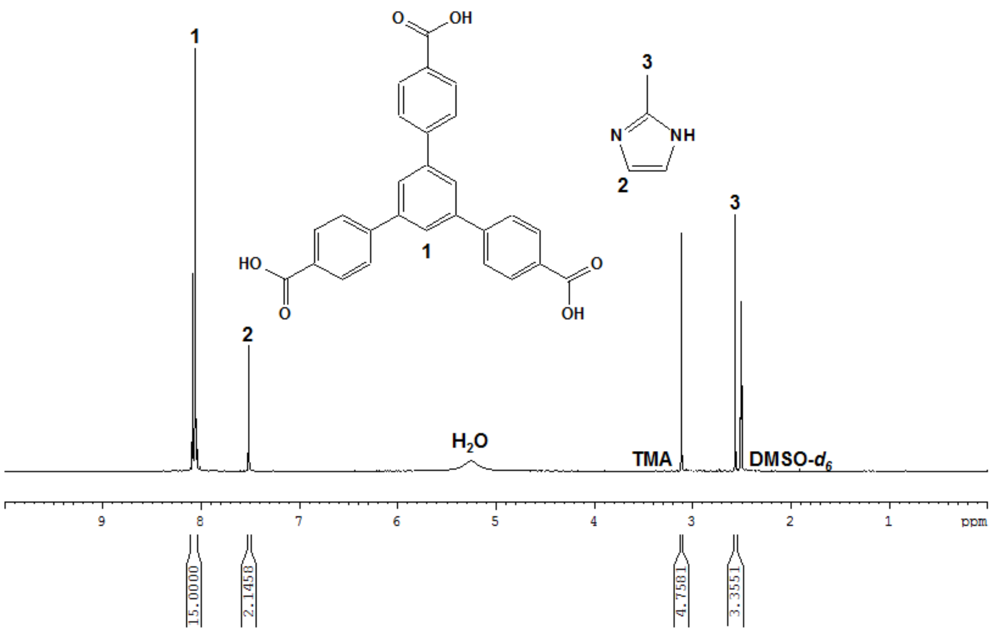

Fig. S7 ^{1}H-NMR spectrumfor TMA@mIm-MOF-14(48 h) dissolved ina DCl/DMSO solution, resulting in a proposed formula as $(TMA^+)_{0.75}[Zn_3(BTB)_2(mIm)_{3/4}(H\text{-}mIm)_{3/2}]$ based on the integration ratios of the proton signals as follows.

In the acidic solution, it is assumed that the mIm-MOF-14 framework is dissociated into 3 Zn(II), 2 H_3BTB, and 2.25 H-mIm (or H_2-mIm$^+$), which is approximately represented as $Zn_3(BTB)_2(H\text{-}mIm)_{2.25}$. A possible formula has been determined as follows based on the integration of the signals in the spectrum.

Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	-CH_3	3	3.36	1.12	2.24	2.25
TMA	-CH_3	12	4.76	0.40	0.79	0.79
Compd.	**Ref. Hs**	**# of Hs**	**integration**	**# of compd.**		**formula**
H_3BTB	Ar-H	15	15	1	2	2
H-mIm	-CH_3 and -CH	5	5.50	1.10	2.20	2.25
TMA	-CH_3	12	4.76	0.40	0.79	0.79
Compd.				**# of compd. (avg.)**		**formula**
H_3BTB					2	2
H-mIm					2.34	2.25
TMA					0.79	0.76

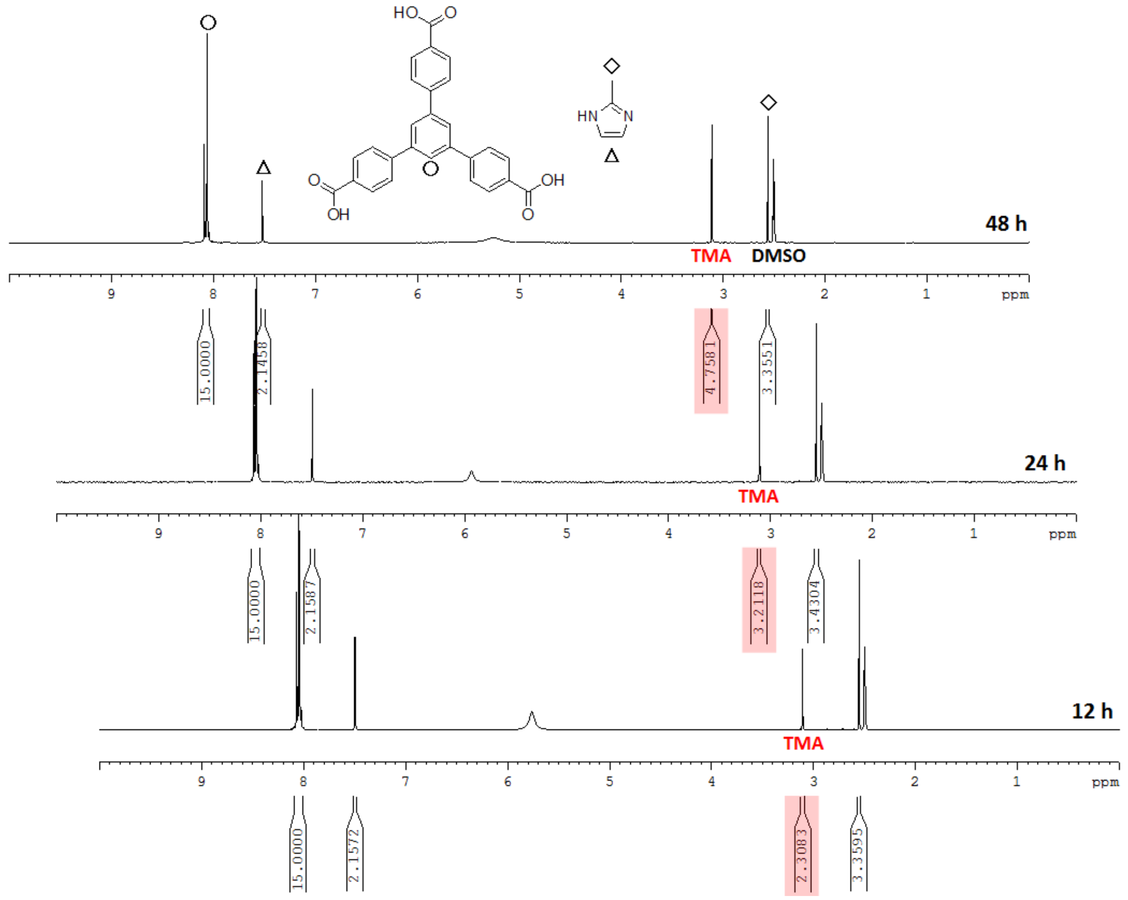

Fig. S8 ^{1}H-NMR spectrum for the TMA@mIm-MOF-14 samples collected after 12, 24, and 48 h reflux in the (TMA)Cl/MeOH solution. Each collected sample was dissolved in a DCl/DMSO-d_6 solution for the NMR measurements. The changes in the integration values corresponding to the –CH_3 protons of the TMA cation are converted to 53, 72, and 100% replacement of the protons in the H_2-mIm$^+$.

Section S6 Thermogravimetric Analyses

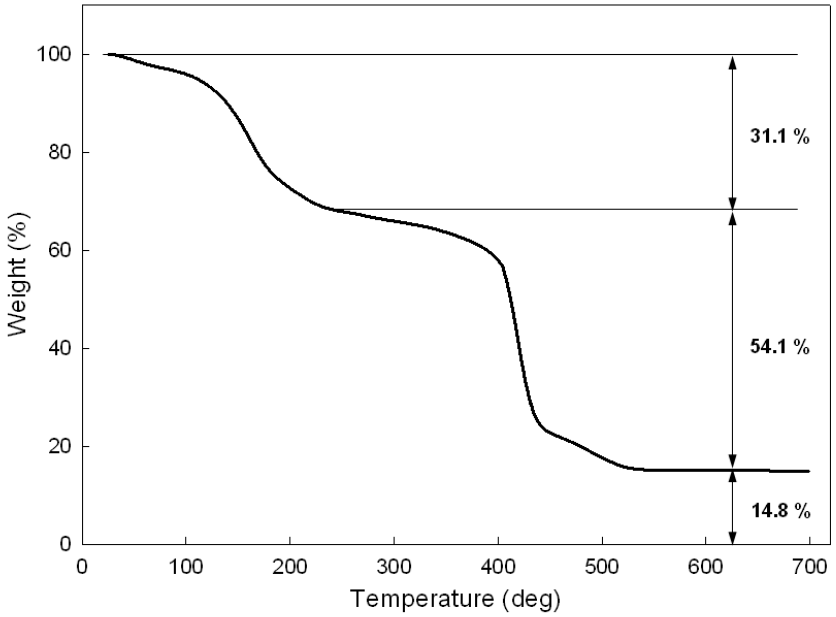

Fig.S9 TGA thermogram for the as-prepared mIm-MOF-14. The first weight loss is due to the liberation of 7.3 DMF molecules (29.9%).

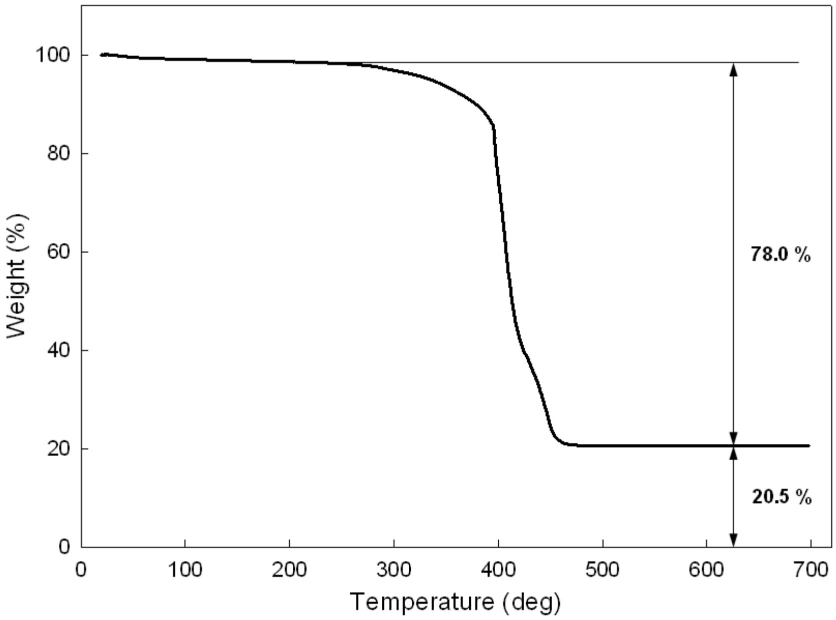

Fig. S10 TGA thermogram for the activated mIm-MOF-14.

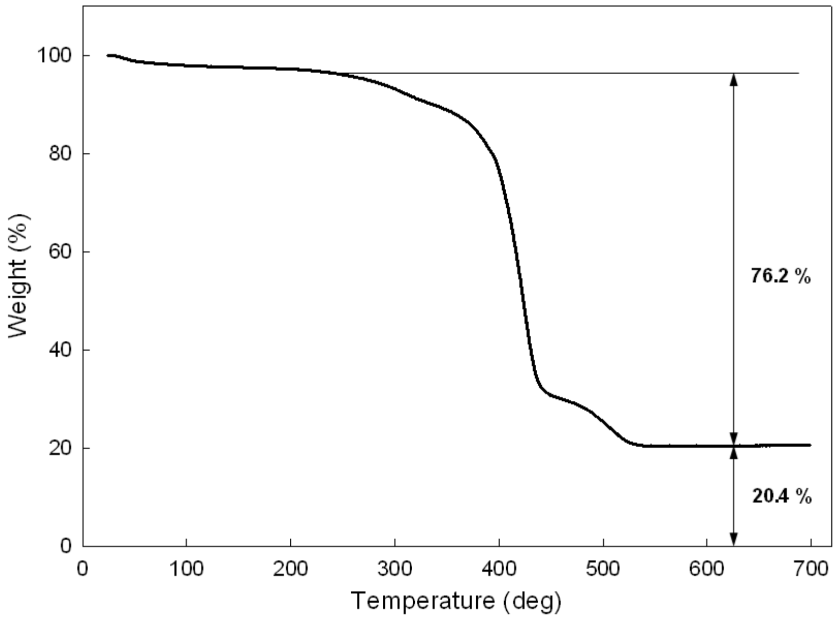

Fig.S11 TGA thermogram for the activated TMA@mIm-MOF-14 (48 h).

Section S7 Gas Adsorption Analyses

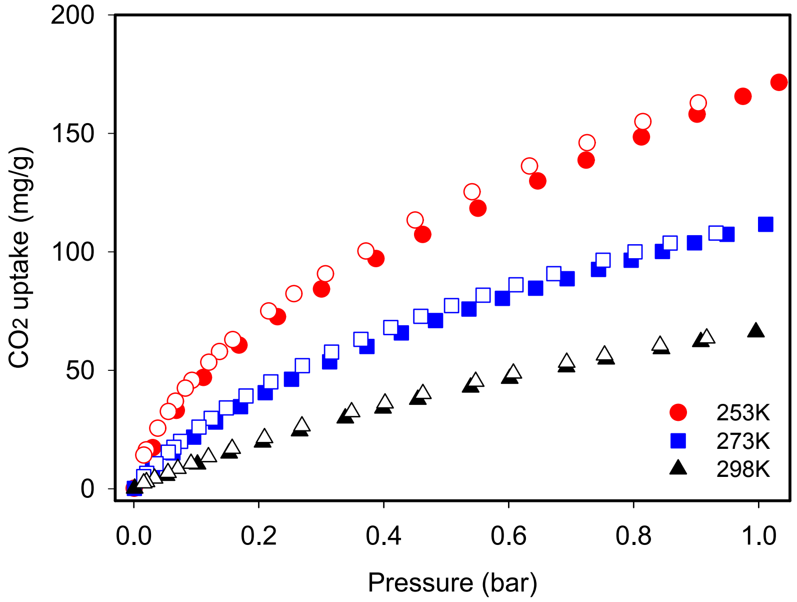

Fig. S12 CO_2 gas isotherms for mIm-MOF-14 measured at 253(red circle), 273(blue square), and 298K(black triangle).

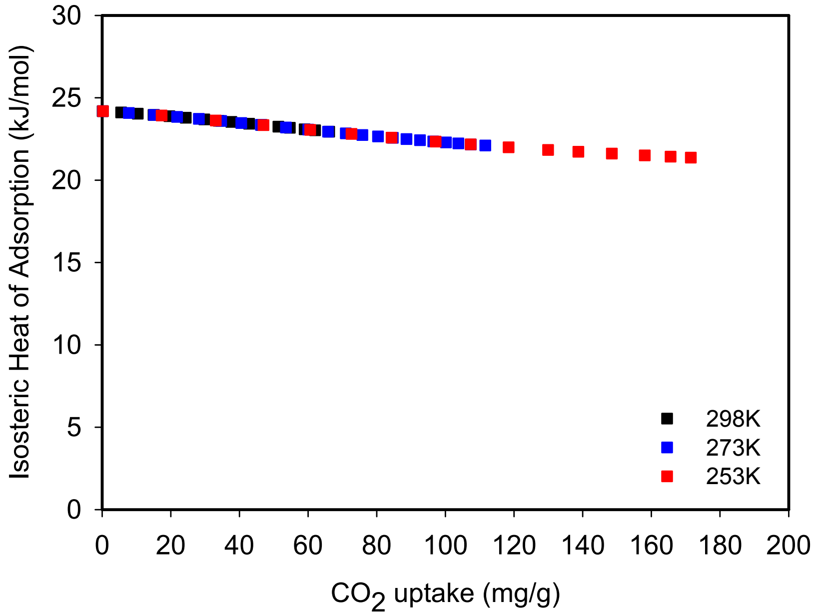

Fig. S13 Plot for isosteric heat of CO_2 adsorption of mIm-MOF-14.

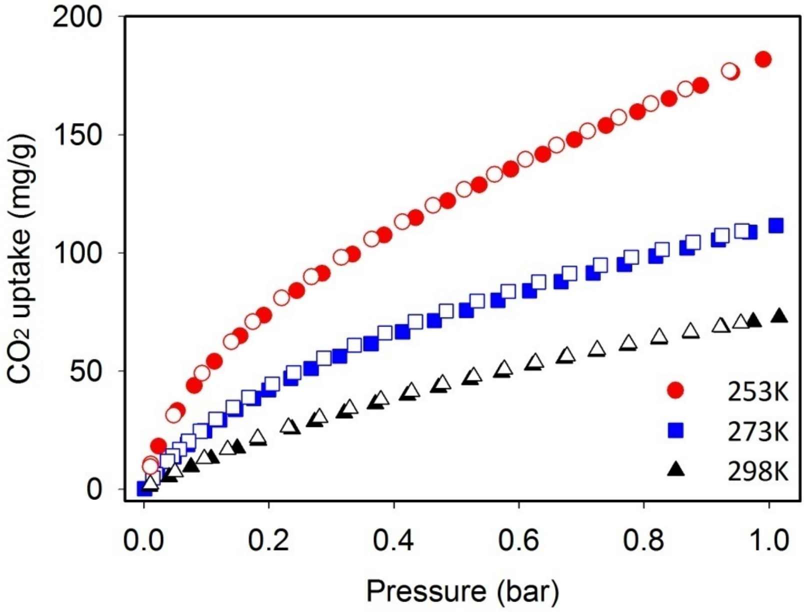

Fig. S14 CO_2 gas isotherms for TMA@mIm-MOF-14(48 h) measured at 253(red circle), 273(blue square), and 298K(black triangle).

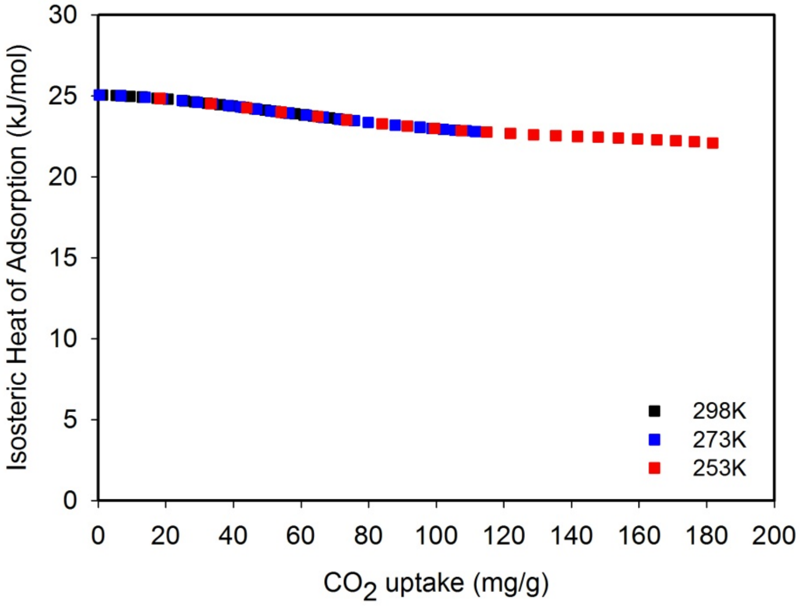

Fig. S15 Plot for isosteric heat of CO_2 adsorption of TMA@mIm-MOF-14 (48 h).

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