

Supporting Information

**Synthesis of New ATN-Type Zeolitic Imidazolate
Framework Through Cooperative Effects of N,N-
dipropylformamide and n-Butylamine**

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Experimental materials and instruments

Chemicals

Zinc acetate dehydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 98.0 %) and imidazole (Im, $\text{C}_3\text{H}_4\text{N}_2$, 99.0 %) were purchased from Sigma Aldrich Trading Co., Ltd. n-Butylamine ($\text{C}_4\text{H}_{11}\text{N}$, 99.5 %) was purchased from Aladdin Reagent Co., Ltd. N,N-dipropylformamide ($\text{C}_7\text{H}_{15}\text{NO}$, 96.0 %) was purchased from Meryer Chemical Technology Co., Ltd. All chemical reagents were obtained from commercial suppliers and used without any further purification.

Synthesis and activation of ZIFs

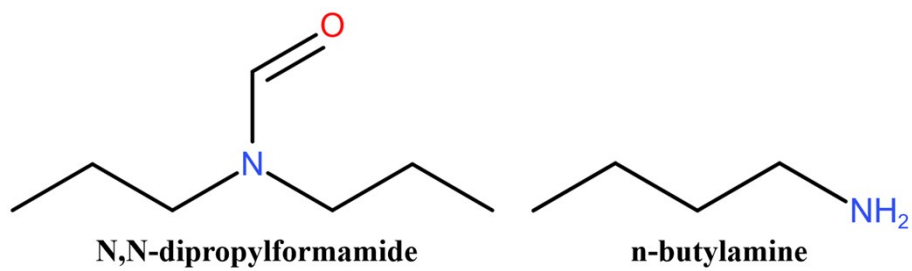
A mixture of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, 110 mg) and n-butylamine (2 mL) was added to a 20 mL glass bottle. Imidazole (1 mmol, 68 mg) was dissolved in N,N-dipropylformamide (3 mL). The imidazole solution was slowly added to the glass bottle containing $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and N,N-dipropylformamide. The glass bottle was sealed and heated at 40 °C for 3 d. The resulting stick-like crystals of $\text{ATN}[\text{Zn}(\text{Im})_2]$ were collected by filtration. $\text{nog}[\text{Zn}(\text{Im})_2]$ was prepared in the absence of N,N-dipropylformamide, using n-butylamine as solvent. $\text{AFI}[\text{Zn}(\text{Im})_2]$ was synthesized in the absence of n-butylamine, using N,N-dipropylformamide as the solvent.

Prior to the N_2 sorption measurement, the $\text{AFI}[\text{Zn}(\text{Im})_2]$ and $\text{nog}[\text{Zn}(\text{Im})_2]$ samples were immersed in dry acetone for 48 h and then activated under vacuum at 50 °C. The activated samples have the same structures as those of the as-synthesized samples (Fig. S13†). In contrast, by acetone exchanged, the flexible structure of $\text{ATN}[\text{Zn}(\text{Im})_2]$ (acetone exchanged) was formed (Fig. S14†).

Characterization

Powder X-ray diffraction (PXRD) data were collected using a Rigaku MiniFlex-II diffractometer with $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. Thermogravimetric analysis (TGA) was performed under an air atmosphere on a Labsystems EVO analyzer. IR spectroscopy was recorded using KBr pellets on a Shimadzu IRSpirit spectrometer. N_2 adsorption isotherms were recorded on a Micromeritics ASAP2020 surface area and porosity analyzer at 77 K. SEM images were obtained using a Hitachi TM3000 scanning electron microscope. $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization (CP) magic angle spinning (MAS) solid-state NMR spectroscopy was performed using a Bruker Avance III 600 WB spectrometer at 151 MHz and a magnetic field of 14.2 T using a 4 mm double-tuned MAS probe with a spinning speed of 10 kHz. Single crystal X-ray diffraction data

collection for ATN-[Zn(Im)₂] was performed on an Agilent Xcalibur Eos Gemini CCD plate diffractometer operating using graphite monochromatized CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at 293 K.



Scheme S1. The structural formula of N,N-dipropylformamide (DPF) and n-butylamine (BA).

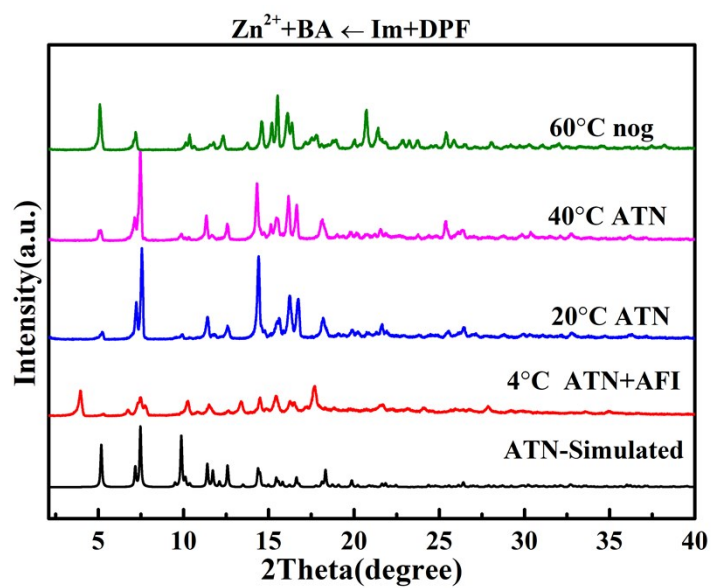


Fig. S1 The PXRD patterns of the samples by using N,N-dipropylformamide (DPF) and n-butylamine (BA) as the reaction solvents.

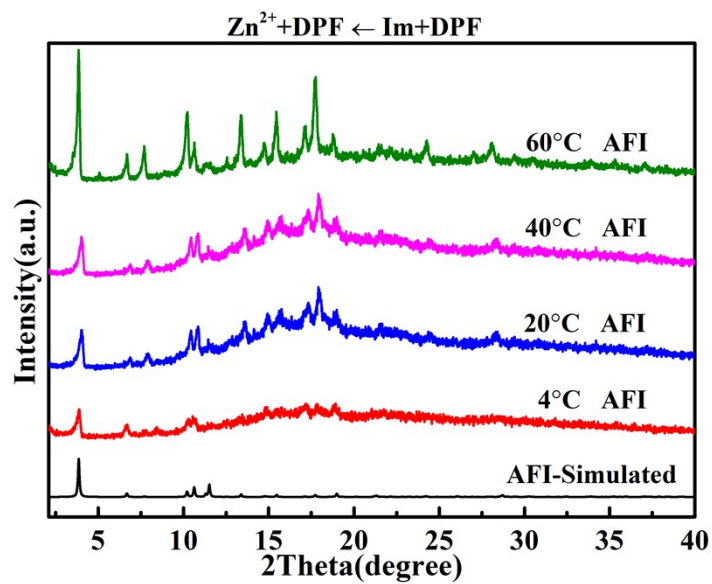


Fig. S2 The PXRD patterns of the samples by using N,N-dipropylformamide (DPF) as the reaction solvents.

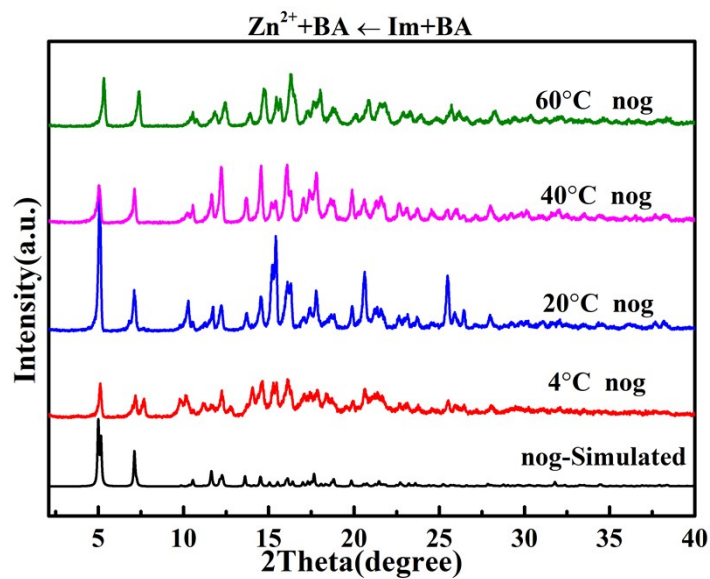


Fig. S3 The PXR D patterns of the samples by using n-butylamine (BA) as the reaction solvents.

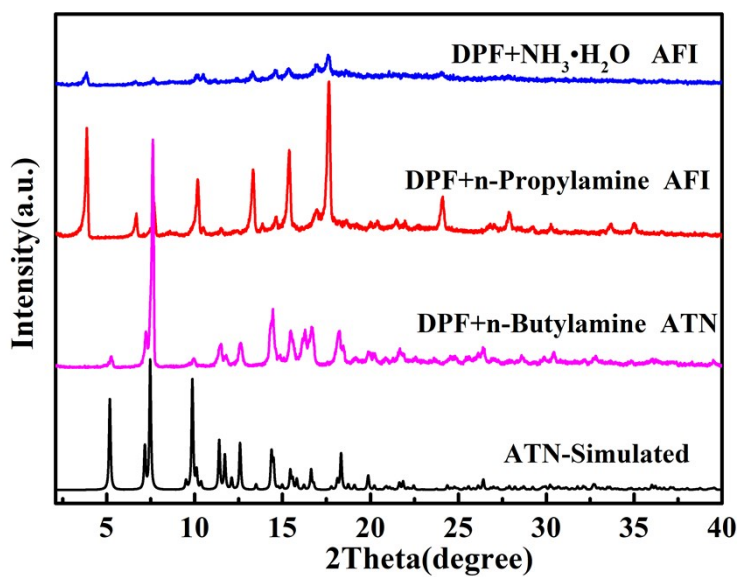


Fig. S4 The PXR D pattern of samples by using N,N-dipropylformamide (DPF) and n-butylamine (BA)/ $NH_3 \cdot H_2O$ /n-propylamine as the reaction solvents.

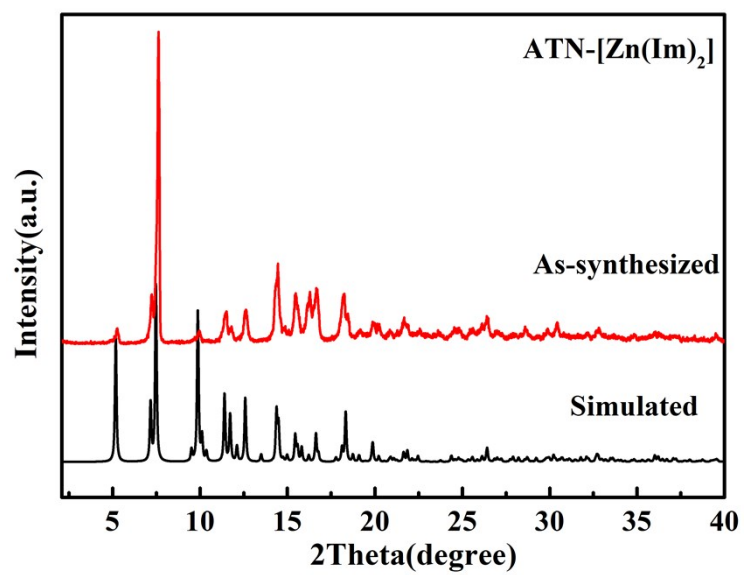


Fig. S5 Experimental PXRD pattern of as-synthesized ATN-[Zn(Im)₂] sample.

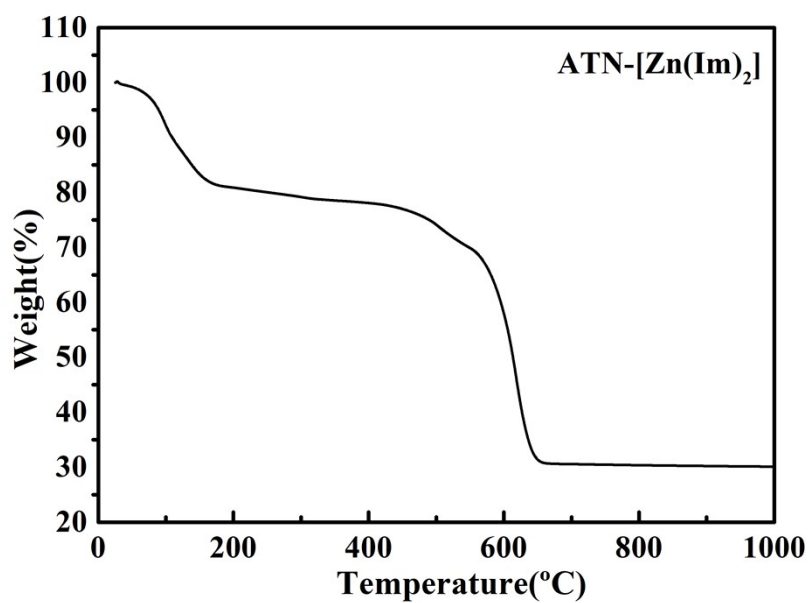


Fig. S6 The TG plots of as-synthesized ATN-[Zn(Im)₂] sample.

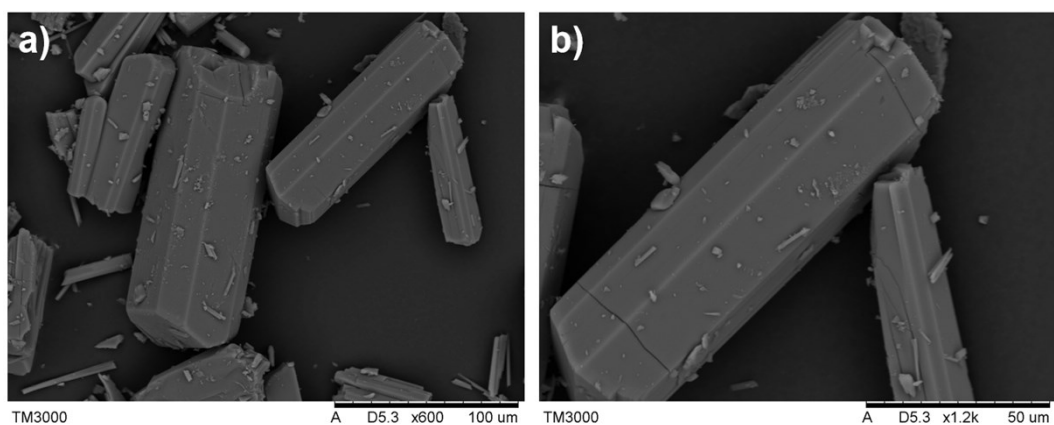


Fig. S7 Different magnification SEM images of as-synthesized ATN-[Zn(Im)₂] sample.

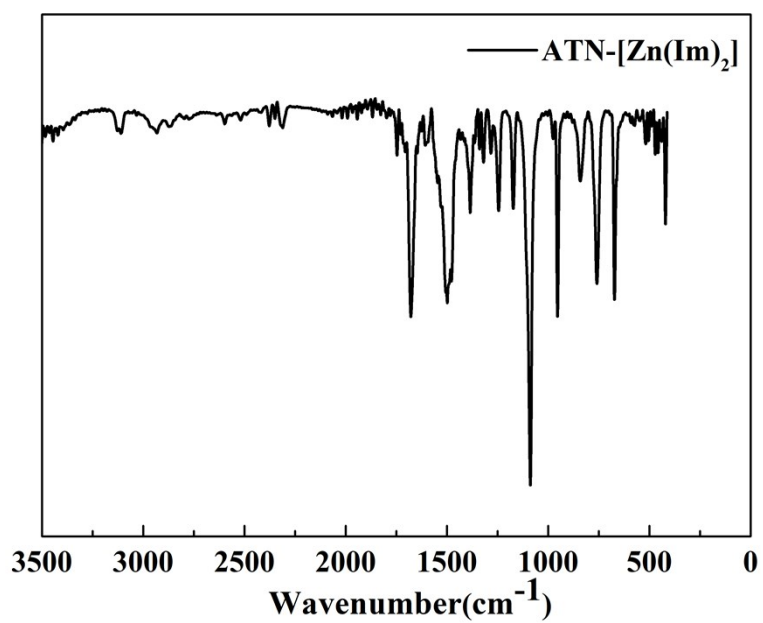


Fig. S8 The FT-IR curve for ATN-[Zn(Im)₂] sample.

Table S1. RCSR topology or zeolite codes, Name or CCDC codes, Framework formulas, Solvent or structure directing-agents of selected $[\text{Zn}(\text{Im})_2]$.

RCSR topology or zeolite code	Name or CCDC code	framework formulas	solvent or structure directing-agent ^a	Ref.
AFI	AFI- $[\text{Zn}(\text{Im})_2]$	$\text{Zn}(\text{Im})_2$	DPF	1
BCT/crb	ZIF1	$\text{Zn}_2(\text{Im})_4$	DMF	2
BCT/crb	ZIF2	$\text{Zn}_2(\text{Im})_4$	DMF	2
BCT/crb	ZIF64	$\text{Zn}_4(\text{Im})_8$	DMF	3
BCT/crb	VEJYEP01	$\text{Zn}_2(\text{Im})_4$	DMA	4
BCT/crb	VEJYIT01	$\text{Zn}_2(\text{Im})_4$	DMF	4
CAN	CAN- $[\text{Zn}(\text{Im})_2]$	$\text{Zn}_3(\text{Im})_6$	DBF	1
DFT	ZIF-3	$\text{Zn}(\text{Im})_2$	DMF+NMP	2
DFT	HIFVOI	$\text{Zn}(\text{Im})_2$	NMP	4
GIS	ZIF-6	$\text{Zn}(\text{Im})_2$	DMF	2
GIS	HIFVUO	$\text{Zn}(\text{Im})_2$	DEF	4
MER	ZIF-10	$\text{Zn}(\text{Im})_2$	DMF	2
MER	mer-MeMeCH ₂ @ RHO- $\text{Zn}_{16}\text{Im}_{32}$	$\text{Zn}_{16}(\text{Im})_{32}$	MeMeCH ₂	5
RHO	xMeMeCH ₂ @RHO - $\text{Zn}_{16}\text{Im}_{32}$	$\text{Zn}_{16}(\text{Im})_{32}$	MeMeCH ₂	6
cag	ZIF-4	$\text{Zn}_2(\text{Im})_4$	DMF	2
cag	VEJYUF01	$\text{Zn}_2(\text{Im})_4$	DMF	4
coi	EQOCOC	$\text{Zn}_4(\text{Im})_8$	H ₂ O	7
neb	KEVLEE	$\text{Zn}(\text{Im})_2$	pyridine	8
nog	HIFWAV	$\text{Zn}_5(\text{Im})_{10}$	DEF	4
unknown	GOQSIQ	$\text{Zn}_{10}(\text{Im})_{20}$	DBF	9
zec	HICGEG	$\text{Zn}_5(\text{Im})_{10}$	DEF	4
zni	IMIDZB	$\text{Zn}_2(\text{Im})_4$	H ₂ O	10
ATN	ATN-$[\text{Zn}(\text{Im})_2]$	$\text{Zn}_2(\text{Im})_4$	DPF+BA	This work
nog	nog-$[\text{Zn}(\text{Im})_2]$	$\text{Zn}_2(\text{Im})_4$	BA	This work

a: DMF=N,N-dimethylformamide; DMA=N,N-dimethylacetamide; DPF=N,N-dipropylformamide; DBF=N,N-dibutylformamide; BA=n-butylamine; NMP=N-methylpyrrolidone; MeMeCH₂=1,7,11,15,21,23,25,28-octamethyl-2,20:3,19-dimetheno-1H,21H,23H,25Hbis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin.

References:

- [1] Q. Shi, W. J. Xu, R. K. Huang, W. X. Zhang, Y. Li, P. Wang, F. N. Shi, L. Li, J. Li and J. Dong. *J. Am. Chem. Soc.* 2016, **138**, 16232-16235.
- [2] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi. *PNAS*. 2006, **103**, 10186-10191.
- [3] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi. *Science* 2008, **319**, 939-943.

- [4] Y. Q. Tian, Y. M. Zhao, Z. X. Chen, G. N. Zhang, L. H. Weng and D. Y. Zhao. *Chem. Eur. J.* 2007, **13**, 4146-4154.
- [5] J. R. Ramirez, H. Y. Yang, C. M. Kane, A. N. Ley and K. T. Holman. *J. Am. Chem. Soc.* 2016, **138**, 12017-12020.
- [6] I. Brekalo, C. M. Kane, A. N. Ley, J. R. Ramirez, T. Feiscic and K. T. Holman. *J. Am. Chem. Soc.* 2018, **140**, 10104-10108.
- [7] Y. Q. Tian, C. X. Cai, X. M. Ren, C. Y. Duan, Y. Xu, S. Gao and X. Z. You. *Chem. Eur. J.* 2003, **9**, 5673-5685.
- [8] C. A. Schroder, I. A. Baburin, L. V. Wullen, M. Wiebcke and S. Leoni. *CrystEngComm* 2013, **15**, 4036-4040.
- [9] Q. Shi, X. Z. Kang, F. N. Shi and J. X. Dong. *Chem. Commun.* 2015, **51**, 1131-1134.
- [10] R. Lehnert and F. Z. Seel. *Anorg. Allg. Chem.* 1980, **464**, 187-194.

X-ray crystallography. The reflection data was consequently corrected for empirical absorption corrections and Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELXL-97 package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically with fixed isotropic thermal parameters, and included in the structure factor calculations. The block of SQUEEZE in PLATON was employed to eliminate the highly disordered solvent molecular.

Table S2. Crystallographic data and refinement parameters of ATN-[Zn(Im)₂]

Complex	ATN-[Zn(Im) ₂]
Formula	C ₁₂ H ₁₂ N ₈ Zn ₂
Mr	399.04
Crystal system	monoclinic
Space group	C2/m
a (Å)	25.7398(1)
b (Å)	23.6271(1)
c (Å)	9.7094(5)
α (°)	90
β (°)	106.926(3)
γ (°)	90
V(Å ³)	5649.0(5)
Z	8
Dcalcd(g·cm ⁻³)	0.938
μ(mm ⁻¹)	2.131
GOF	1.092
R ₁ [I > 2σ(I)] ^a	0.0753
wR ₂ [I > 2σ(I)] ^b	0.1984
R ₁ ^a (all data)	0.0934
wR ₂ ^b (all data)	0.2184
R _{int}	0.0740

$$^a R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|} \quad ^b wR_2 = \frac{\sum w(|F_o|^2 - |F_c|^2)}{\sum w(F_o^2)^2}^{1/2}$$

Table S3. Selected bond lengths and angles for ATN-[Zn(Im)₂]

Selected bond lengths/Å			
Zn(1)-N(1)	1.969(5)	Zn(1)-N(2)	1.988(5)
Zn(1)-N(5)	1.959(5)	Zn(1)-N(7)	1.980(5)
Zn(2)-N(2)	1.985(5)	Zn(2)-N(4)#1	1.976(5)
Zn(2)-N(6)#2	1.964(5)	Zn(2)-N(8)	1.972(5)
N(4)-Zn(2)#3	1.976(5)	N(6)-Zn(2)#2	1.964(5)
Selected angles/°			
N(1)-Zn(1)-N(3)	106.9(2)	N(1)-Zn(1)-N(7)	110.7(2)
N(5)-Zn(1)-N(1)	110.9(2)	N(5)-Zn(1)-N(3)	108.6(2)
N(5)-Zn(1)-N(7)	109.5(2)	N(7)-Zn(1)-N(3)	110.1(2)
N(4)#1-Zn(2)-N(2)	108.5(2)	N(6)#2-Zn(2)-N(2)	107.9(2)
N(6)#2-Zn(2)-N(4)#1	113.1(2)	N(6)#2-Zn(2)-N(8)	107.9(2)
N(8)-Zn(2)-N(2)	108.26(19)	N(8)-Zn(2)-N(4)#1	111.0(2)
Symmetry transformations used to generate equivalent atoms: #1 +x,+y,1+z; #2 1/2-x,1/2-y,1-z; #3 +x,+y,-1+z; #4 -x,+y,-z; #5 +x,-y,+z.			

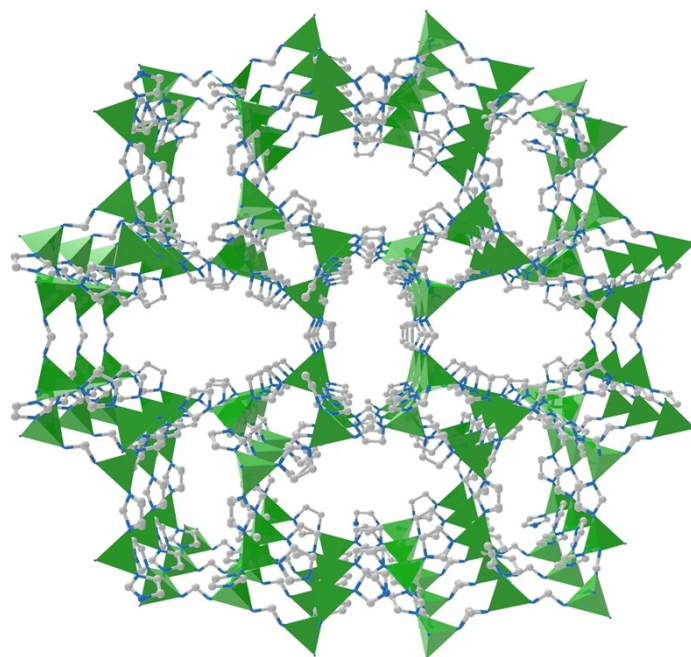


Fig. S9 The 3D framework of ATN-[Zn(Im)₂].

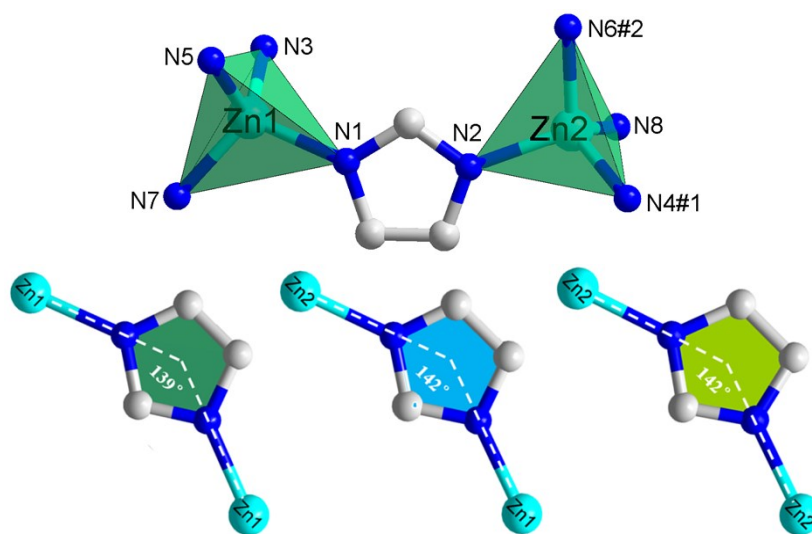


Fig. S10 The Zn-Im-Zn angles in ATN-[Zn(Im)₂].

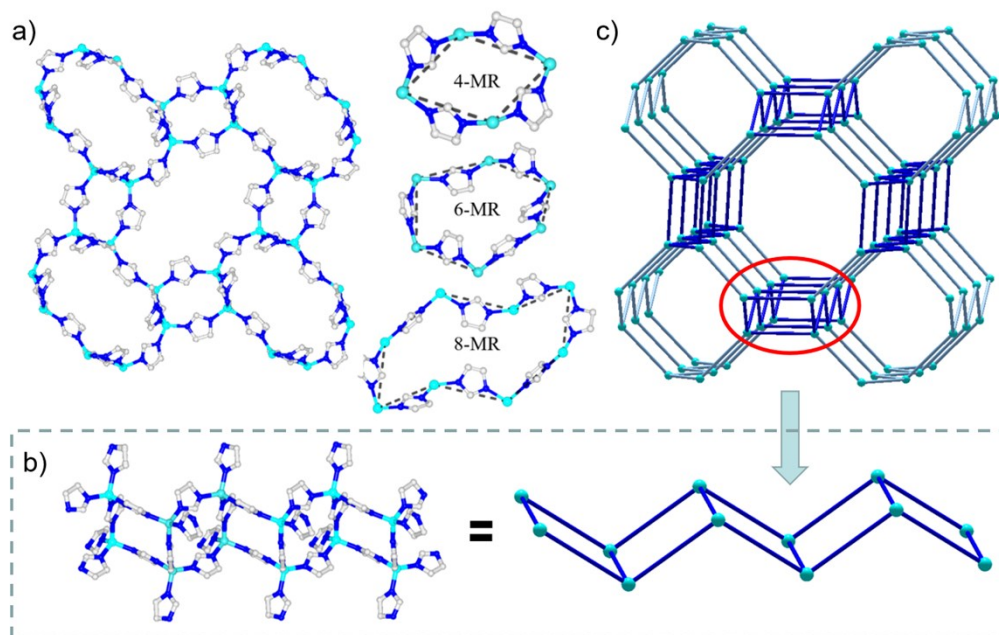


Fig. S11 a) The 4-, 6- and 8-membered rings (MRs) constructed by Im ligands with Zn(II) in ATN-[Zn(Im)₂]; b) The 4-MRs **dzc** chains; c) The simplified topology of ATN-[Zn(Im)₂].

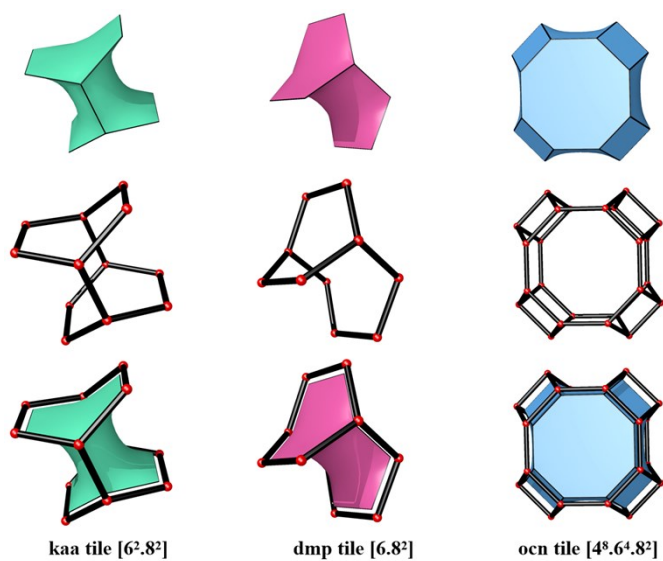


Fig. S12 The composition part of tiling in the framework ATN-[Zn(Im)₂]: t-kaa+t-dmp+t-ocn tiles.

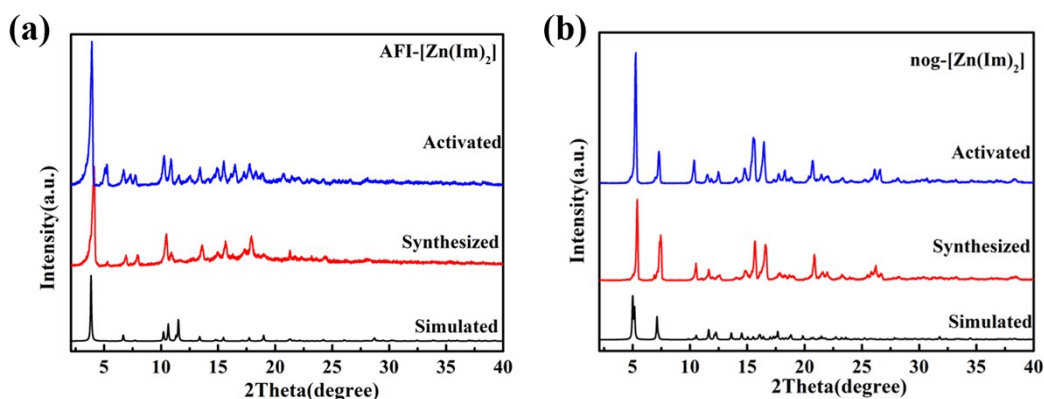


Fig. S13 PXRD patterns of synthesized and activated samples: (a) AFI-[Zn(Im)₂] and (b) nog-[Zn(Im)₂]

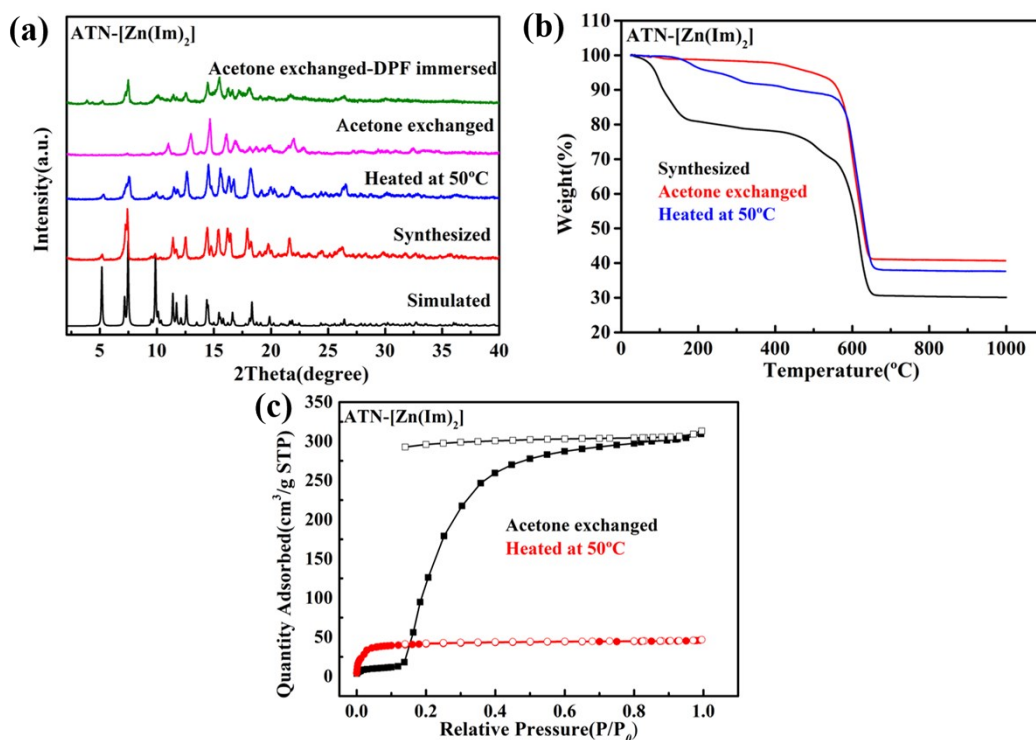


Fig. S14 ATN-[Zn(Im)₂] samples under different treated conditions: (a) PXRD patterns, (b) TG curves and (c) N₂ adsorption-desorption isotherms at 77 K.

The activated samples of AFI-[Zn(Im)₂] and nog-[Zn(Im)₂] were characterized by PXRD to confirm that they have the same structures as those of the as-synthesized samples (Fig S13[†]).

In contrast, by acetone exchanged, the guest DPF molecules were almost removed and the structure of ATN-[Zn(Im)₂] (acetone exchanged) was formed, as evidenced by the PXRD patterns and the long plateau in the TG traces (Fig S14[†]). Interestingly, when ATN-[Zn(Im)₂] (acetone exchanged) was soaked with DPF, the ATN-[Zn(Im)₂] structure could be reversed. Thus, PXPD

reveals the reversible nature of this transformation upon guest DPF adsorption-desorption. The occurrence of such a structural transformation was also hinted at by the observation of N₂ adsorption isotherm at 77 K. The hysteresis are observed in the relative pressure (P/P_0) range of 0.16–0.80.