Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

$Zn_{10}(Im)_{20}$•4DBF: An unprecedented 10-nodal zeolitic topology with 10-MR channel and 10 crystallographically independent Zn atoms

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Table of Contents

Section S1 Materials and Instrumentation

Materials: Imidazole (Im, 98.0 %), zinc acetate dihydrate ($Zn(OAC)_2 \cdot 2H_2O$, 98.0 %) were purchased from Sigma-Aldrich Chemical Co., and *N,N*-dibutylformamide (DBF, 98.0 %) were obtained from TCI (Shanghai) Development Co. Ltd.. All raw chemicals were used without further purification.

Instrumentation: PXRD patterns were recorded with a X-ray diffractometer (Rigaku, MiniFlex Ⅱ) using $Cu_{K\alpha}$ radiation (λ=1.5418 Å). TG-DSC measurements were performed under a static air atmosphere on a simultaneous thermal analyzer (Setaram, Labsys evo) at a heating rate of 5 °C min^{-1}. CHN analysis was carried out on an elemental analyzer (Elementar, Vario EL III). Nitrogen sorption isotherms were measured by using an automated volumetric adsorption apparatus (Micromeritics, ASAP2020). IR spectra were recorded on an FT-IR spectrometer (Shimadzu, Prestige-21).

Synthesis and activation procedure of $Zn_{10}(Im)_{20}$•4DBF

0.1 mol/L DBF solution (4ml) of $Zn(OAc)_2$•$2H_2O$ (grinding) and 2 mol/L DBF solution of Im (4ml) were added into 15ml Teflon-lined steel autoclave to give a precipitate. This heterogeneous mixture was standing at room temperature for 1 h and heated at 50 °C for 3 d. Then it was cooled to room temperature. As the autoclave was cooled down and opened, a pure phase of white needle crystals were separated by washed using ethanol three times and dried under ambient conditions for other measurements.

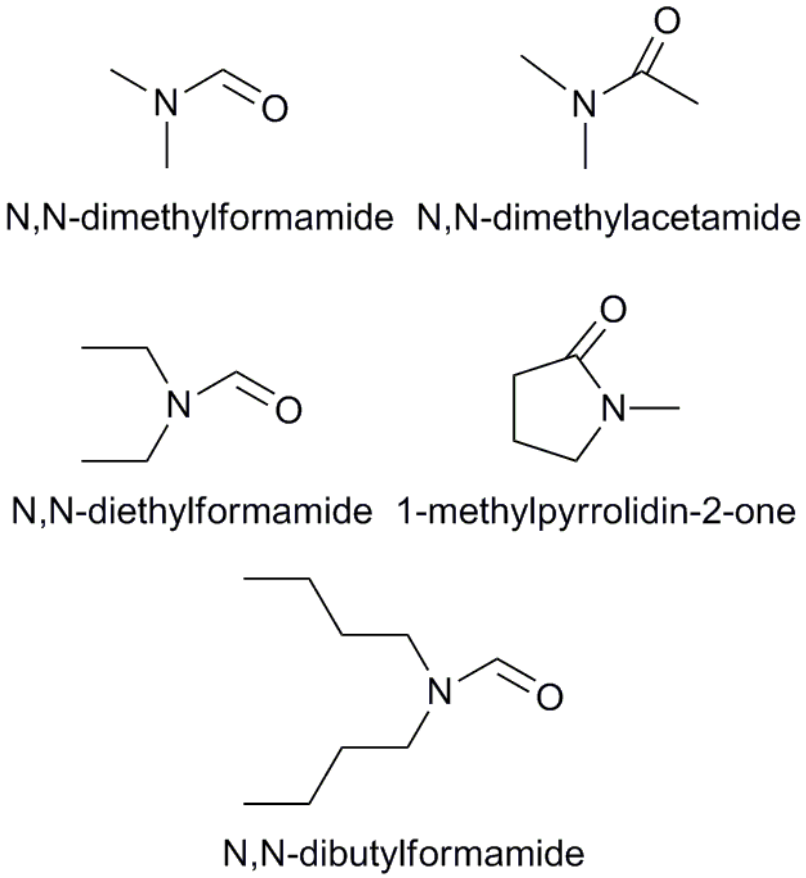
Elemental analysis (%) for $C_{96}H_{136}N_{44}O_4Zn_{10}$: calcd: C, 43.89 H, 5.18 N, 23.47 ; found: C, 44.8 H, 5.46 N, 22.33; FT-IR (KBr): 3131(w), 3107(w), 1669(w), 1497(vs), 1318(vs), 1172(vs), 1089(vs), 953(m), 835(vs), 757(m), 670(m).

Prior to the N_2 sorption measurement, the as-synthesized $Zn_{10}(Im)_{20}$•4DBF sample was immersed in dried CH_2Cl_2:MeOH (v/v 1:1) mixture for 24 h. Then the sample was separated by centrifuging and dried at ambient temperature. Before the measurement, the samples was activated again by using the “degas” function of the surface area analyzer for 10 h at 30 °C.

Single-crystal X-ray crystallography

Single-crystal X-ray diffraction data for $Zn_{10}(Im)_{20}$•4DBF were collected at 150(2) K on a Bruker SMART CCD diffractometer with graphite-monochromatized Mo-Ka radiation (=0.71073 Å) controlled by the APEX2 software package[1] and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely by using the software interface Cryopad[2]. Data integration and reduction were processed with SAINT+[3] software. Absorption corrections were applied by the multiscan semiempirical method implemented in SADABS[4]. The structure was solved by direct method using SHELXS-97[5] and refined using SHELXL-97[5]. All non-hydrogen atoms were successfully refined with anisotropic displacement parameters. Hydrogen atoms bound to carbon were located at their idealized positions by employing AFIX 43, AFIX 23 and AFIX 137 instructions and included in subsequent refinement cycles in riding motion. The selected bond distances and angles have been given in Table S4. The detailed crystallographic data and structural refinement parameters have been summarized in Table S5. Complete crystallographic data for the structure reported in this paper have been deposited in the CIF format with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1022238. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

The references:
1 APEX2: Data Collection Software Version 2.1-RC13, Bruker AXS, Delft, The Netherlands, 2006.
2 Cryopad, Remote momitoring and control, Version 1.451: Oxford Cryosystems, Oxford, United Kingdom, 2006.
3 SAINT+: Data Integration Engine v. 7.23a. Bruker AXS, Madison, Wisconsin, USA, 1997-2005.
4 G.M. Sheldrick, SADABS v. 2.01: Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 1998.
5 G.M. Sheldrick, SHELXS-97: Program for Crystal Structure Solution, University of Göttingen, 1997.
6 G.M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Göttingen, 1997.



Scheme S1 The structural formula of N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N,N-diethylformamide (DEF), N-methylpyrrolidone/1-Methylpyrrolidin-2-one (NMP), and N,N-dibutylformamide (DBF).

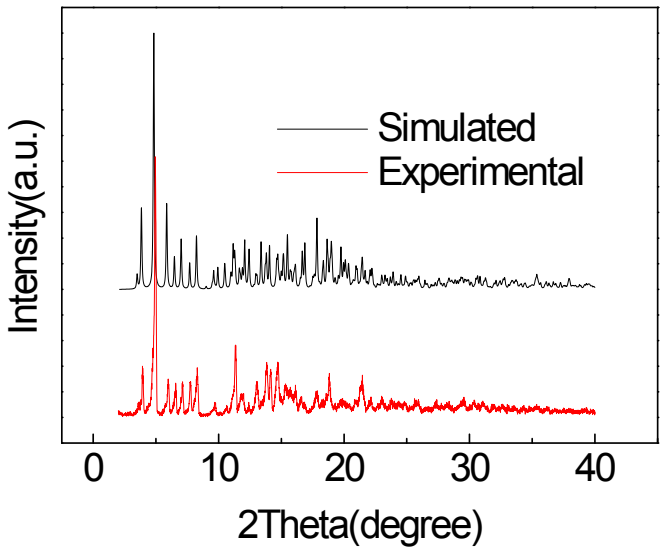


Figure S1 Experimental XRD pattern of sample $Zn_{10}(Im)_{20}$•4DBF and XRD pattern simulated from crystal structure data

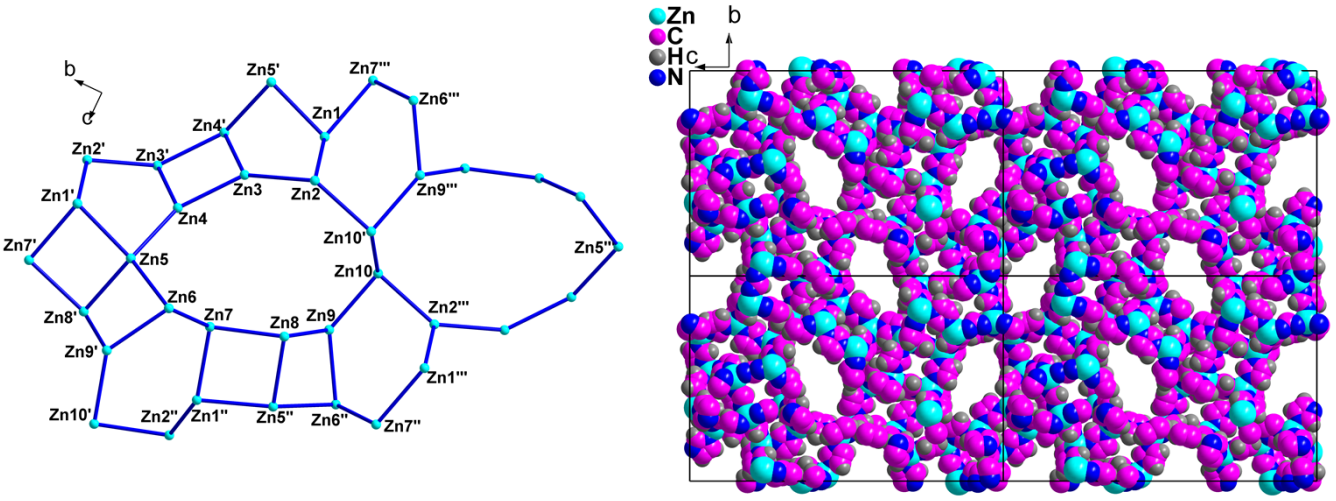


Figure S2 (left) Ball-and-stick diagram displays that one 10-ring is surounded with five 4-rings, two 5-rings, three 6-rings and one 10-ring in $Zn_{10}(Im)_{20}$•4DBF, respectively. (Im molecules and guests were omitted for clarity); (right) A space filling representation of the supercell (2X2X2) framework of $Zn_{10}(Im)_{20}$•4DBF shows the 10-membered ring size is about 9.8635(2)X12.1150(2) Å (DBF guest molecules were omitted to see the channels)

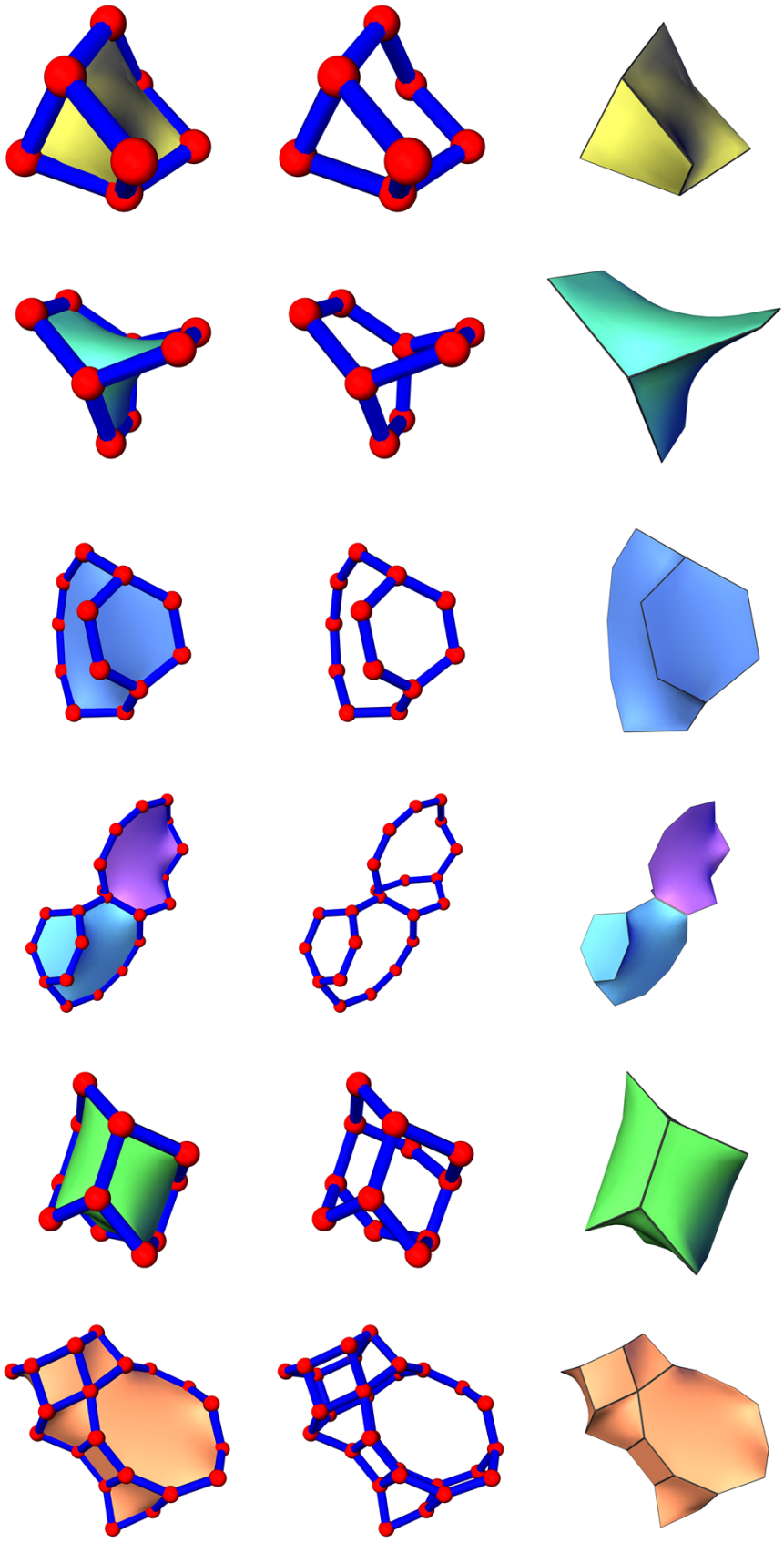


Figure S3 Six kinds of tiles in a primitive proper tiling (Fig. 3b) corresponding to $[4.6^2]$, $[6^3]$, $[6.10^2]$ (=6g.10a.10c), $[6.10^2]$ (=6h.10b.10c), $[6^5]$ and $[4^5.5^4.6^4.10^2]$ (represented in 6 different colours)

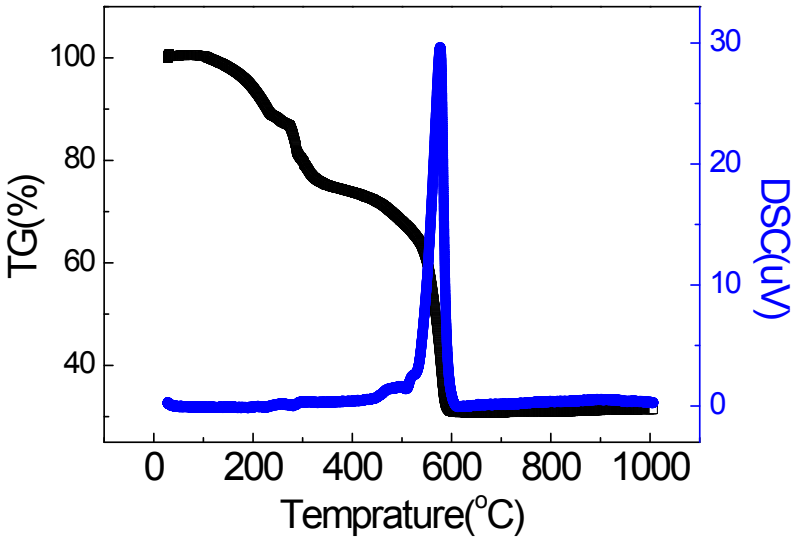


Figure S4 TG-DSC curves for $Zn_{10}(Im)_{20}$·4DBF

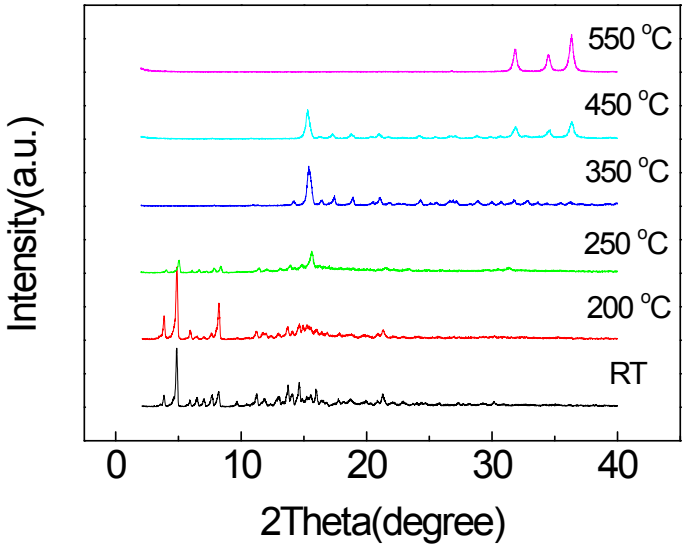


Figure S5 PXRD patterns for the $Zn_{10}(Im)_{20}$·4DBF heated in air at 5 °C/ min

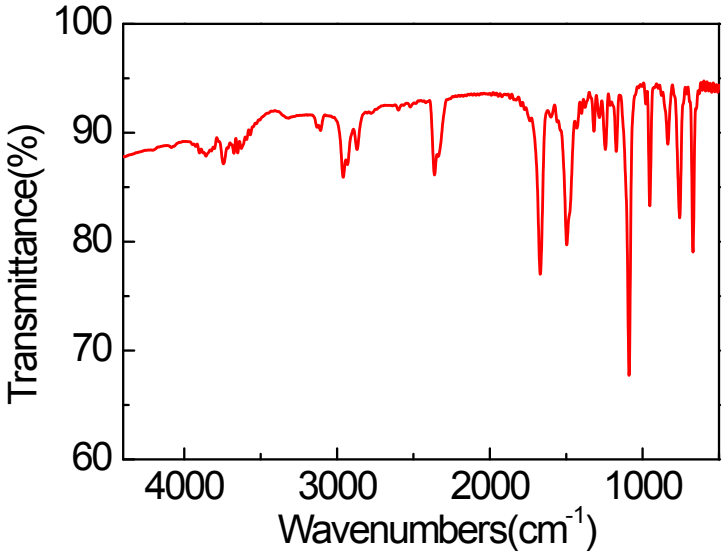


Figure S6 FT-IR spectra of $Zn_{10}(Im)_{20}\cdot 4DBF$

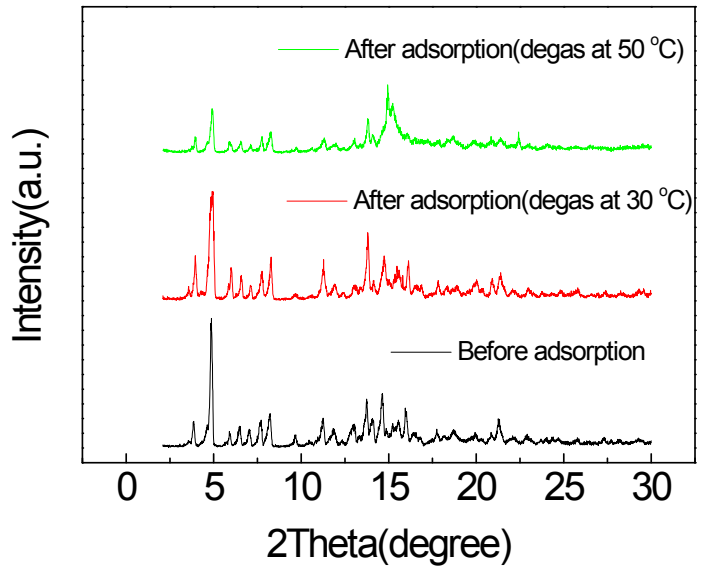


Figure S7 PXRD patterns of $Zn_{10}(Im)_{20}$•4DBF before adsorption and after adsorption.

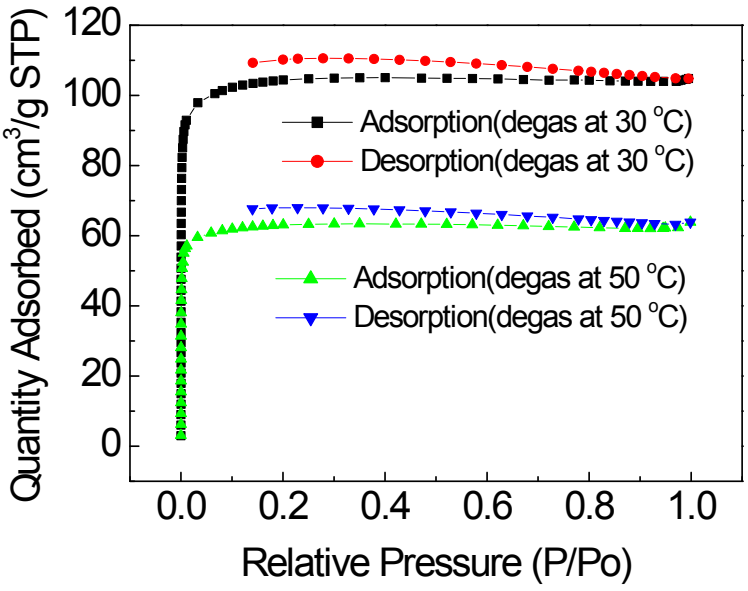


Figure S8 Nitrogen gas adsorption isotherm at 77 K for $Zn_{10}(Im)_{20}$•4DBF.

TableS1. Calculated pore volume based on the crystallographic data of $Zn_{10}(Im)_{20}$•4DBF.

compound	$Zn_{10}(Im)_{20}$•3.5DBF	$Zn_{10}(Im)_{20}$•3DBF	$Zn_{10}(Im)_{20}$•2DBF	$Zn_{10}(Im)_{20}$•DBF	$Zn_{10}(Im)_{20}$
Location of removed DBF	center of 10-MR (half)	center of 10-MR (half) center of 10-MR (half)	center of 10-MR connection of 10-MR and 4-MR	center of 10-MR connection of 10-MR and 4-MR 6-MR	center of 10-MR connection of 10-MR and 4-MR 6-MR 4-MR
Pore volume / $cm^3\ g^{-1}$	0.09	0.16	0.25	0.37	0.49

Method: The calculation was carried out using Calcsolv command within Platon [1]. The relevant guest molecule-removal cif files were used for this calculation.

[1] Spek, A. L. J. Appl. Crystallogr. 2003, 36, 7.

From the N_2 sorption isotherms (Figure S8), a micropore volume of 0.14 cm^3/g (total pore volume: 0.16 cm^3/g) are estimated for the activated samples (degas at 30 °C). The value is considerably lower than the calculated pore volume of $Zn_{10}(Im)_{20}$(0.49 cm^3/g, removed all four DBF guests), and is in agreement with the calculated pore volume of $Zn_{10}(Im)_{20}$•3DBF(0.16 cm^3/g, removed only one DBF molecule). Furthermore, we attempted to improve the porosity using higher activation temperatures, up to 50 °C; however, the surface areas and pore volume did not improve because a reduction in crystallinity and collapse of the framework were observed (Figure S7 and S8). These results indicate that the activated samples still contains a large amount of residual DBF that could not be desorbed from the cavities of $Zn_{10}(Im)_{20}$•4DBF.

Thus, the two DBF molecules (each occupies half crystallographic sites) in the near center of a 10-MR channel could be fully removed owing to the unimpeded channel. The other three DBF guest molecules can not be released due to the space hindrance and causing the collapse of framework under the experimental conditions. TG analysis (Figure S4) under the air atmosphere showed a gradual weight loss of 11.8 wt. % between 30 and 250 °C, probably due to the loss of the two DBF molecules. Thermal stability was also investigated by PXRD analysis (Figure S5), which shows that the framework is only stable up to temperatures of 200 °C (5.9 wt. % in TG, removed one DBF). All results are in a good agreement and indicate that the other three DBF molecules could not be released before the framework collapsed (Figure S7 in degas conditions). In addition, the DBF molecules trapped in the 6-membered ring and 4-membered ring could not be released because of smaller pore aperture.

So in summary, the DBF molecule (in the near center of a 10-MR channel) is much easier to be released due to the unobstructed 10-membered ring channel than other DBF molecule guests which have varying degrees of obstruction on their paths for removal before the framework collapsed.

Table S2. Topology, structure-directing agent, channel, and crystallographically Independent Zn, tiling (vertices, edges, Faces, and Tiles) parameters of all $Zn(im)_2$ polymorphs reported thus far[1](two examples of $Zn_4(Im)_8(HIm)$ and $Zn(im)_{1.7}(mim)_{0.3}$ were also added).

RCSR topoIogy or zeolite code	Name (CCDC code)	Framework formula	solvent or structure-directing agent	n-MR channel opening	Crystallographically Independent Zn	**Vertices[d]**	Edges	Faces	Tiles	Ref.
zni	IMIDZB	$Zn_2(Im)_4$	H_2O	nonporous[a]	2	**1**	3	4	2	2
coi	EQOCOC	$Zn_4(Im)_8$	H_2O	nonporous[a]	4	**4**	8	-	-	3
moc	KUMXEW	$Zn_4(Im)_8$ (HIm)	ionic liquid[b]	nonporous[a]	4	**2**	3	3	2	4
SOD	SALEM-2	$Zn(im)_{1.7}$ $(mim)_{0.3}$	SALE[c]	6	1	**1**	1	2	1	5
cag	ZIF-4	$Zn_2(Im)_4$	DMF	6	2	**1**	4	3	1	6
cag	VEJYUF01	$Zn_2(Im)_4$	DMF	6	2	**1**	4	3	1	7
BCT	ZIF-1	$Zn_2(Im)_4$	DMF	8	2	**1**	2	3	2	6
BCT	VEJYEP01	$Zn_2(Im)_4$	DMA	8	2	**1**	2	3	2	7
BCT	ZIF-2	$Zn_2(Im)_4$	DMF	8	2	**1**	2	3	2	6
BCT	VEJYIT01	$Zn_2(Im)_4$	DMF	8	2	**1**	2	3	2	7
BCT	ZIF-64	$Zn_4(Im)_8$	DMF	8	4	**1**	2	3	2	8
MER	ZIF-10	$Zn(Im)_2$	DMF	8	1	**1**	4	6	3	6
DFT	ZIF-3	$Zn(Im)_2$	DMF+NMP	8	1	**1**	3	5	3	6
DFT	HIFVOI	$Zn(Im)_2$	NMP	8	1	**1**	3	5	3	7
GIS	ZIF-6	$Zn(Im)_2$	DMF	8	1	**1**	2	3	1	6
GIS	HIFVUO	$Zn(Im)_2$	DEF	8	1	**1**	2	3	1	7
nog	HIFWAV	$Zn_5(Im)_{10}$	DEF	8	5	**5**	10	8	3	7
zec	HICGEG	$Zn_5(Im)_{10}$	DEF	10	6	**2**	4	7	4	7
New	**1022238**	**$Zn_{10}(Im)_{20}$**	**DBF**	**10**	**10**	**10**	**20**	**16**	**6**	**Our**

a、nonporous (primarily 4-membered ring)

b、ionic liquid: 1-ethyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide

c、SALE: obtained by solvent-assisted linker exchange

d、one topological kind of vertex: uninodal; 10 topological kind of vertex: 10-nodal

(1) A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, Michael O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58.

(2) R. Lehnert, F. Z. Seel, *Anorg. Allg. Chem.*,1980, **464**, 187; X. C. Huang, D. Li, Y. X. Tong, X. M. Chen, *Acta Scientiarum Naturalium Universitatis Sunyatseni*, 1998, **37**, 55.

(3) Y. Q. Tian, C. X. Cai, X. M. Ren, C. Y. Duan, Y. Xu, S. Gao, X. Z. You, *Chem. Eur. J.,* 2003, **9**, 5673.

(4) G. A. V. Martins, P. J. Byrne, P. Allan, S. J. Teat, A. M. Z. Slawin, Y. Li, R. E. Morris, *Dalton Trans.* **2010**, *39*, 1758.

(5) O. Karagiaridi, M. B. Lalonde, W. Bury, A. A. Sarjeant, O. K., Farha, J. T. Hupp, *J. Am. Chem. Soc.,* 2012, **134**, 18790.

(6) 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, *Proc. Natl. Acad. Sci. USA*, 2006, **103**, 10186.

(7) Y. Q. Tian, S.Y. Yao, D. Gu, K. H. Cui, D.W. Guo, G. Zhang, Z. X. Chen and D. Y. Zhao, *Chem. Eur. J.*, 2010, **16**, 1137.

(8) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939.

Table S3 Coordination sequences and vertex symbols of $Zn_{10}(Im)_{20}$•4DBF.

Nodes	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Vertex Symbol:** ***Point symbol /Extended point symbol /Vertex symbol***
Zn1	4	11	22	36	65	92	125	161	213	275	$4.5^2.6^3$ /$4.6_2.5.6_2.5.6_2$ /$4.6.5.6_2.5.6_2$
Zn2	4	12	22	40	65	95	122	160	215	277	$5^2.6^3.8$ /$5.6_2.5.6_2.6.8_2$ /$5.6_2.5.6_2.6.10_3$
Zn3	4	10	20	36	59	86	123	168	200	255	$4^2.5^2.6.7$ /$4.5.4.5.6.7_2$ /$4.5.4.5.8_3.10_3$
Zn4	4	10	20	36	57	87	129	164	204	247	$4^2.5^2.6.7$ /$4.5.4.5.7_2.6_2$ /$4.5.4.5.10_3$.*
Zn5	4	10	21	37	59	97	127	166	211	257	$4^2.5.6.7.8$ /$4.5_2.4.8_3.7_2.6$ /$4.5_2.4.8_3.8_3.8_4$
Zn6	4	11	23	37	63	92	134	166	208	258	$4.6^4.8$ /$4.6_2.6.6_3.6_2.8_5$ /$4.6_2.6.6_3.6_2.8_2$
Zn7	4	11	22	39	55	93	127	170	211	260	4.6^5 /$4.6_2.6.6_2.6.6_2$ /$4.6_2.6.6_2.6.6_2$
Zn8	4	10	23	38	65	87	128	170	217	257	$4^2.6^4$ /$4.6.4.6_2.6.6_2$ /$4.6.4.6_2.6.6$
Zn9	4	11	22	44	64	91	122	171	209	266	4.6^5 /$4.6.6.6_2.6.6_2$ /$4.6.6.6_2.6.6_2$
Zn10	4	12	27	45	69	96	125	162	218	282	6^6 /$6.6.6.6.6_2.6_2$ /$4.6.6.6_2.6.6_2$

Table S4 Crystallographic data and structure refinement summary for $Zn_{10}(Im)_{20}$•4DBF

Compound	$Zn_{10}(Im)_{20}$·4DBF
Formula	$C_{96}H_{136}N_{44}O_4Zn_{10}$
Formula weight	2624.19
Crystal system	Orthorhombic
Space group	*P2(1)2(1)2(1)*
Cell parameters(Å)	*a*= 9.5161 (2) *b*= 30.1575(5) *c*= 45.9367(8)
Cell volume (Å^3)	13183.0(4)
Z	4
Calculated density (g/cm^3)	1.401
Temperature	150(2) K
Reflections collected/unique	71094
GOF	1.055
Final R indices [I > 2sigma (I)]	R_1 = 0.0560, wR_2 = 0.1271

Table S5 Selected Bond Lengths [Å] and Selected Bond Angles [deg] for $Zn_{10}(Im)_{20}$·4DBF

Zn1-N3	1.972(6)	Zn2-N40	1.963(6)
Zn1-N30	1.990(6)	Zn2-N2	1.978(7)
Zn1-N1	1.991(6)	Zn2-N5	1.993(6)
Zn1-N18	2.012(6)	Zn2-N4	2.008(6)
Zn3-N7	1.968(6)	Zn4-N8	1.968(5)
Zn3-N6	1.993(5)	Zn4-N11	1.992(6)
Zn3-N12	1.994(6)	Zn4-N13	1.996(6)
Zn3-N10	2.006(6)	Zn4-N9	2.007(5)
Zn5-N17	1.972(6)	Zn6-N21	1.979(5)
Zn5-N14	1.984(5)	Zn6-N25	1.980(5)
Zn5-N15	1.988(5)	Zn6-N20	1.985(6)
Zn5-N19	1.976(6)	Zn6-N23	1.990(6)
Zn7-N27	1.977(6)	Zn8-N28	1.975(5)
Zn7-N22	1.979(6)	Zn8-N33	1.979(6)
Zn7-N29	1.987(6)	Zn8-N31	1.994(6)
Zn7-N26	2.000(6)	Zn8-N16	1.984(6)
Zn9-N35	1.969(6)	Zn10-N37	1.945(8)
Zn9-N24	1.972(6)	Zn10-N39	1.959(6)

Zn9-N34	1.981(6)	Zn10-N36	1.967(6)
Zn9-N32	1.993(6)	Zn10-N38	1.988(8)
N3-Zn1-N30	119.2(2)	N40-Zn2-N2	110.3(3)
N3-Zn1-N1	110.6(2)	N40-Zn2-N5	108.1(3)
N30-Zn1-N1	107.6(2)	N2-Zn2-N5	112.6(2)
N3-Zn1-N18	105.0(2)	N40-Zn2-N4	109.7(3)
N30-Zn1-N18	109.2(2)	N2-Zn2-N4	111.0(2)
N1-Zn1-N18	104.4(2)	N5-Zn2-N4	104.9(2)
N7-Zn3-N6	108.3(2)	N8-Zn4-N11	114.6(2)
N7-Zn3-N12	113.5(2)	N8-Zn4-N13	112.3(2)
N6-Zn3-N12	107.6(2)	N11-Zn4-N13	108.7(2)
N7-Zn3-N10	113.3(2)	N8-Zn4-N9	111.4(2)
N6-Zn3-N10	108.8(2)	N11-Zn4-N9	102.2(2)
N12-Zn3-N10	105.2(2)	N13-Zn4-N9	106.8(2)
N17-Zn5-N14	108.0(2)	N21-Zn6-N25	103.4(2)
N17-Zn5-N15	112.0(2)	N21-Zn6-N20	112.7(2)
N14-Zn5-N15	105.7(2)	N25-Zn6-N20	112.3(2)
N17-Zn5-N19	108.8(2)	N21-Zn6-N23	114.9(2)
N14-Zn5-N19	110.9(2)	N25-Zn6-N23	109.2(2)
N15-Zn5-N19	111.4(2)	N20-Zn6-N23	104.6(2)
N27-Zn7-N22	112.1(2)	N28-Zn8-N33	113.7(2)
N27-Zn7-N29	114.6(2)	N28-Zn8-N31	112.0(2)
N22-Zn7-N29	111.9(2)	N33-Zn8-N31	104.6(2)
N27-Zn7-N26	105.3(2)	N28-Zn8-N16	106.0(2)
N22-Zn7-N26	105.4(2)	N33-Zn8-N16	109.0(2)
N29-Zn7-N26	106.7(2)	N31-Zn8-N16	111.6(2)
N35-Zn9-N24	113.7(2)	N37-Zn10-N39	105.6(3)
N35-Zn9-N34	107.0(2)	N37-Zn10-N36	110.4(3)
N24-Zn9-N34	110.3(2)	N39-Zn10-N36	111.9(3)
N35-Zn9-N32	108.5(2)	N37-Zn10-N38	110.5(3)
N24-Zn9-N32	112.0(2)	N39-Zn10-N38	110.4(3)
N34-Zn9-N32	104.8(2)	N36-Zn10-N38	107.9(3)

Symmetry transformations used to generate equivalent atoms：

(i) 1.5-x, -y, 0.5+z; (ii) 0.5+x, 0.5-y, 2-z; (iii) 0.5+x, -0.5-y, 2-z; (iv) -1+x, y, z;

(v) -0.5+x, 0.5-y, 2-z; (vi) 1-x, -0.5+y, 1.5-z; (vii) 1+x, y, z; (viii) 1-x, 0.5+y, 1.5-z;

(ix) 1.5-x, -y, -0.5+z; (x) -0.5+x, -0.5-y, 2-z.