Electronic Supplementary Material (ESI) for CrystEngComm. This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information for MS:

Influence of amine group on highly efficient reversible adsorption of iodine in two isoreticular interpenetrated pillaredlayer microporous metal-organic frameworks

Vahid Safarifard and Ali Morsali*

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Islamic Republic of Iran

Email; morsali_a@modares.ac.ir

S1. Materials and measurements

Starting reagents for the synthesis were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Merck and others). Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Heraeus CHN-O- Rapid analyzer. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500-4000 cm⁻¹ using the KBr disk technique. The UV/vis absorption spectra were examined on a 4802 UV/Vis spectrophotometer Unico in the wavelength range of 190-800 nm. Thermogravimetric analysis (TGA) of the compounds were performed on a computer-controlled PL-STA 1500 apparatus. Single-phased powder samples of **TMU-16**, **TMU-16-NH2**, **I**₂@TMU-16 and **I**₂@TMU-16-NH2 were loaded into alumina pans and heated with a ramp rate of 10 °C/min from room temperature to 600 °C under argon atmosphere. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromated Cu-k_a radiation (λ =1.54056Å). The simulated XRD powder pattern based on single crystal data were prepared using Mercury software [1].

S2. Synthesis of TMU-16

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol), 4-bpdh (0.119 g, 0.5 mmol), H₂BDC (0.166 g, 1 mmol) were dissolved in 15 ml DMF. The mixture was placed in a Teflon reactor and heated at 115 °C for 3 days, and then it was gradually cooled to room temperature. The crystals were obtained in a 43% yield. Elemental microanalysis for $[Zn_2(BDC)_2(4-bpdh)]$.3DMF, calculated (%): C, 51.33; H, 4.75; N, 10.74. Found (%): C, 50.75; H, 4.19; N, 10.20. IR (cm⁻¹): 3444.16 (w), 1660.11 (vs), 1612.66 (vs), 1336.93 (vs), 1096.69 (m), 1096.96 (m), 826.63 (s), 749.10 (s), 547.64 (s).

S3. Synthesis of TMU-16-NH₂

 $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol), 4-bpdh (0.119 g, 0.5 mmol), H₂BDC-NH₂ (0.181 g, 1 mmol) were dissolved in 15 ml DMF. The mixture was placed in a Teflon reactor and heated at 80 °C for 3 days, and then it was gradually cooled to room temperature. The crystals were obtained in a 41% yield. Elemental microanalysis for $[Zn_2(NH_2-BDC)_2(4-bpdh)]$.3DMF, calculated (%): C, 49.48; H, 4.79; N, 13.31. Found (%): C, 50.02; H, 4.25; N, 12.88. IR (cm⁻¹): 3460.13 (s), 3348.32 (s), 1666.74 (vs), 1628.27 (vs), 1428.57 (vs), 1377.88 (vs), 1257.27 (s), 831.09 (s), 767.46 (s), 574.08 (s).

S4. Crystallographic Data Collection and Refinement.

Crystallographic measurements of compounds **TMU-16** and **TMU-16-NH**₂ were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo– K_{α} radiation (λ =0.71073Å) at 180 K. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections [2]. Data reduction was performed with the SAINT software. Absorption corrections were applied with the program SADABS [2]. The structure was solved by direct methods with SHELXS-97 [3]. The refinement and all further calculations were carried out with SHELXL-97 [3]. The N- and C-bound H-atoms were included in calculated positions and treated as riding atoms. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F². The SQUEEZE program implemented in PLATON [4] was used to remove these electron densities for **TMU-16** and **TMU-16-NH**₂. Thus, all of electron densities from free solvent molecules have been "squeezed" out. Crystallographic data and details of data collections and structure refinements of compounds **TMU-16** and **TMU-16-NH**₂ are listed in Table S1.

[1] Mercury 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK, 2001-2005.

[2] Bruker (2007). SMART, SAINT & SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.

[3] G. M. Sheldrick. Acta Crystallogr. A64 (2008) 112-122.

[4] P. v.d. Sluis, A.L. Spek. Acta Cryst. (1990), A46, 194.

	TMU-16	TMU-16-NH ₂	
Chemical formula	$C_{30}H_{22}N_4O_8Zn_2$	$C_{39.38}H_{45.88}N_{9.13}O_{11.13}Zn_2$	
formula mass	697.26	955.72	
<i>T</i> (K)	298(2)	180(2)	
Crystal syst	Monoclinic	Monoclinic	
Space group	C_2/c	C_2/c	
<i>a</i> (Å)	16.2326(19)	17.1558(6)	
<i>b</i> (Å)	14.5987(19)	13.4604(4)	
<i>c</i> (Å)	36.175(4)	36.1586(11)	
α (deg)	90.00	90.00	
β (deg)	94.930(9)	97.233(2)	
γ (deg)	90.00	90.00	
V (Å ³)	8540.9(18)	8283.4(5)	
Z	8	8	
μ calcd.(g/m ³)	1.163	1.231	
F(000)	2832	3960	
Reflections collected	5295 / 3430	8015 / 5035	
R(int)	0.1976	0.0802	
Goodness-of-fit on F^2	1.126	1.150	
$R_1^a [I \ge 2\sigma(I)]$	0.0973	0.0722	
wR_2^{b}	0.2692	0.2239	

Table S1 Crystal data and structure refinements for components	ounds TMU-16 and TMU-16-NH ₂ .
--	---

 ${}^{a}R_{1} = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|. \ {}^{b}wR_{2} = |\Sigma w(|Fo|^{2} - |Fc|^{2})| / \Sigma |w(Fo^{2})^{2}|^{1/2}.$



Fig. S1 (a) Representation of the Zn_2 paddlewheel unit within TMU-16. (b) Asymmetrical paddle wheel $Zn_2(BDC)_2(4$ -bpdh) unit and its coordination geometry in TMU-16. (c) Square layers of Zn(II)-BDC pillared by 4-bpdh in TMU-16, viewed along *b* axis. (d), (e) and (f) 3D two-fold interpenetrated TMU-16, viewed along *a*, *b* and *c* axes, respectively. All hydrogen atoms and the disordered guest molecules in TMU-16 are omitted for clarity.



Fig. S2 (a) Asymmetrical paddle wheel $Zn_2(NH_2-BDC)_2(4-bpdh)$ unit and its coordination geometry in TMU-16-NH₂. (b) an elongated primitive cubic net of TMU-16-NH₂ viewed along *c* axis which contains 1D channels of 14.4×12.1 Å. (c), (d) and (e) 3D two-fold interpenetrated TMU-16-NH₂, viewed along *a*, *b* and *c* axes, respectively. All hydrogen atoms and the disordered guest molecules in TMU-16-NH₂ are omitted for clarity.



Fig. S3 TGA curves of TMU-16 (red) and TMU-16-NH $_2$ (blue).



Fig. S4 I_2 enrichment progress when 100 mg of TMU-16-NH₂ were soaked in 3 mL of a cyclohexane solution of I_2 (0.005 mol L⁻¹).



Fig. S5 I_2 enrichment progress when 100 mg of TMU-16 were soaked in 3 mL of a cyclohexane solution of I_2 (0.005 mol L⁻¹).



Fig. S6 TGA curves of $I_2@TMU-16$ (red) and $I_2@TMU-16-NH_2$ (blue). Solvent was removed after immersing MOFs in a hexane solution of I_2 (0.005 mol L⁻¹).



Fig. S7 Comparison of adsorption rates of TMU-16 (red) and TMU-16-NH₂ (blue).



Fig. S8 Photographs showing progress of the iodine release from $I_2@TMU-16-NH_2$ when the containing iodine crystals were immersed in ethanol.

0 min	1 min	2 min	3 min	4 min	5 min	6 min
7 min	9 min	10 min	13 min	16 min	20 min	3 0 min

Fig. S9 Photographs showing progress of the iodine release from $I_2@TMU-16$ when the containing iodine crystals were immersed in ethanol.



Fig. S10 Comparison of desorption rates of TMU-16 (red) and TMU-16-NH $_2$ (blue).



Fig. S11 X-Ray powder diffraction patterns of **TMU-16** after releasing I_2 (brown), **TMU-16** soaked in a cyclohexane solution (0.005 mol L⁻¹) of I_2 at room temperature for 30 minutes (blue), as-synthesized **TMU-16** (red) and simulated **TMU-16** (black).



Fig. S12 PXRD patterns of **TMU-16** exposed in the air for a week (green), immersed in ethanol (brown), immersed in cyclohexane (blue), as-synthesized **TMU-16** (red) and simulated **TMU-16** (black).



Fig. S13 X-Ray powder diffraction patterns of **TMU-16-NH**₂ after releasing I_2 (green), **TMU-16-NH**₂ soaked in a cyclohexane solution (0.005 mol L⁻¹) of I_2 at room temperature for 30 minutes (brown), as-synthesized **TMU-16-NH**₂ (blue) and simulated **TMU-16-NH**₂ (red).



Fig. S14 PXRD patterns of $TMU-16-NH_2$ exposed in the air for a week (black), immersed in ethanol (green), immersed in cyclohexane (brown), as-synthesized $TMU-16-NH_2$ (blue) and simulated $TMU-16-NH_2$ (red).



Fig. S15 FT-IR spectra of fresh TMU-16 and I₂ adsorption at room temperature.



Fig. S16 FT-IR spectra of fresh TMU-16-NH₂ and I_2 adsorption at room temperature.