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## COMMUNICATION

## Benzene Absorption in a Protuberant-Grid-Type Zinc(II)–Organic Framework Triggered by the Migration of Guest Water Molecules

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The 2D protuberant-grid-type Zn(II)-organic framework consists of unusual racemic interdigitated bilayers and is comprised of a 3D intersecting channel system. The framework is thermally stable and the channels contain multiple water aggregates. Accompanying the migration of guest water molecules, only the specific channels in the bilayers along the *b* axis can easily and efficiently absorb guest benzene molecules in a regular manner.

A significant amount of efforts have been expended in exploring new crystalline materials with host–guest properties in the solid state over the past decade,<sup>1</sup> because these materials potentially exhibit intriguing properties and have promise for use in applications for selective gas sorption, separation<sup>2</sup> as well as sensing<sup>3</sup> and the removal of harmful organic molecules in the area of green industry.<sup>4</sup> In particular, the elimination or reduction in the levels of carcinogenic compounds that contaminate drinking water and environmental toxic substances continues to be one of the most alarming challenges for sustainable development in the future.<sup>5</sup> Despite the fact that zeolites and activated carbon compounds have porous characteristics and can absorb toxic molecules,<sup>6</sup> metal–organic frameworks (MOFs) with their designable, flexible, and adaptable structural characteristics would have great potential as more specific and/or more efficient absorbers of harmful chemicals.<sup>7</sup> To our surprise, significantly less efforts have been expended in developing such absorbing MOFs for removing benzene from the environment.<sup>8</sup>

As part of our ongoing efforts in the exploration of functional crystalline materials,<sup>8b,9</sup> we report herein on the production of an interesting Zn(II)–organic framework:  $\{[\text{Zn}(\text{pbc})_2] \cdot 2\text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}\}_n$  (**1**,  $\text{pbc}^- = 2\text{-(3'-pyridinyl)-benzimidazole-5-carboxylate}$ ) that can

effectively absorb benzene molecules to produce  $\{[\text{Zn}(\text{pbc})_2] \cdot \text{C}_6\text{H}_6 \cdot 0.5\text{CH}_3\text{OH} \cdot 7.5\text{H}_2\text{O}\}_n$  (**2**, see Figure 1). The unusual frameworks feature: 1) specific racemic 2D protuberant-grid-type networks that consist of four-connected tetrahedral Zn(II) centers and display a 4<sup>4</sup>-*sql* topology; 2) each of the pairs of the racemic networks is interdigitated and coupled to form a bilayer

Chart 1 The multifunctional Hpbc ligand and its conformational chirality

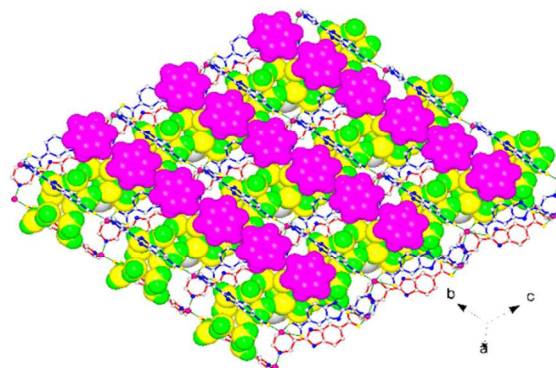
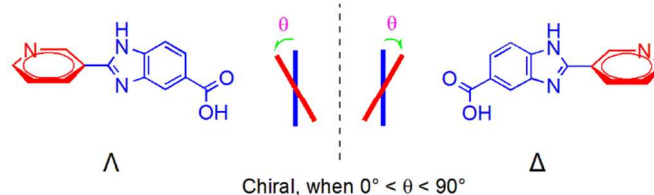


Fig. 1 A packing diagram of **2** showing the regular array of benzene molecules in pink with space-filling representation (along the *b* axis) and multiple water aggregates along the *c* axis (O in yellow and H in green).

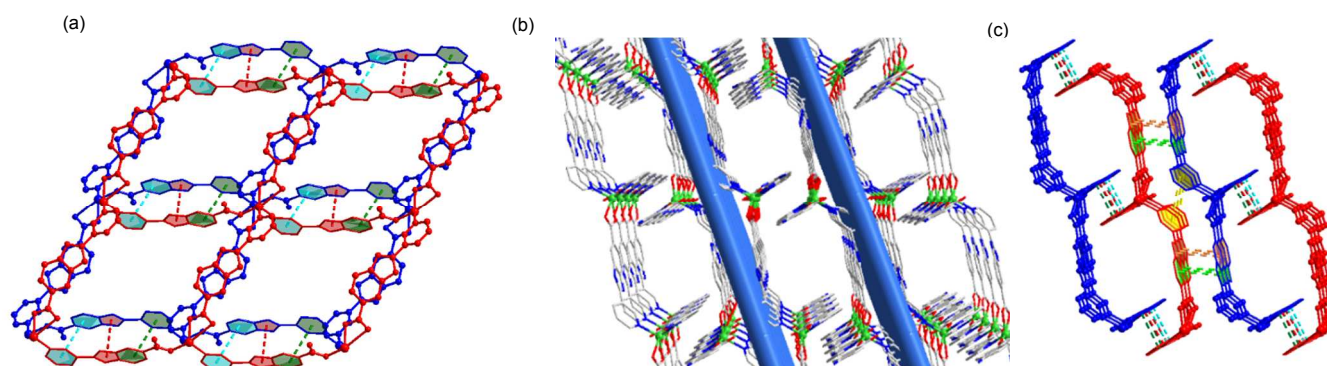
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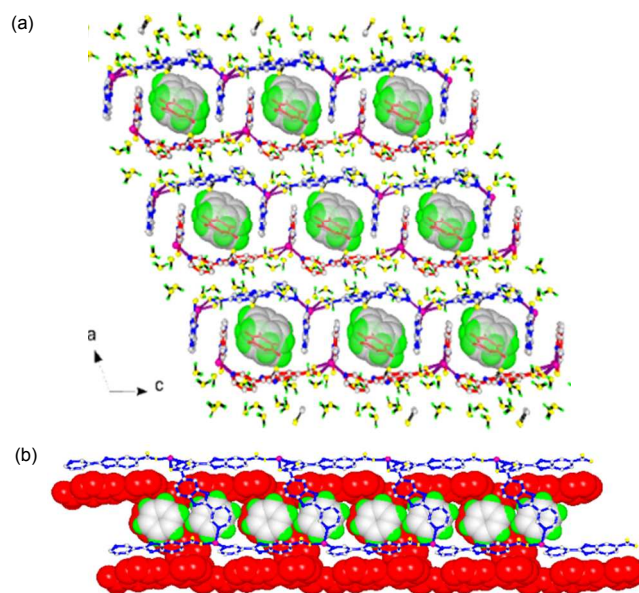


**Fig. 2** The structures of **1**: (a) showing two 2D racemic protuberant networks were coupled and interdigitated via  $\pi\cdots\pi$  interactions between the coplanar  $\text{pbc}^-$  ligands viewed along the  $a$  axis; (b) a perspective view of the hydrophilic channels (highlighted in blue) and hydrophobic channels; (c) showing the  $\pi\cdots\pi$  interactions in the 3D framework viewed along the  $b$  axis.

containing special channels with an interior channel size of  $8.5 \times 8.1 \text{ \AA}^2$  that can accommodate guest molecules; 3) the overall framework is a 3D intersecting channel system and is thermally stable at temperatures of up to  $295 \text{ }^\circ\text{C}$ ; 4) the complex can be used as an efficient absorber for benzene molecules, which is accompanied by the migration of guest water molecules. This interdigitated bilayer containing channels exhibits a special host-guest encapsulating effect, which is mediated by the migration of multiple water molecules. To the best of our knowledge, such a regular packing array of absorbed benzene molecules in a MOF with a 3D intersecting channel system is currently unprecedented.<sup>10</sup>

The reaction of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the Hpbc ligand in a solution of MeOH,  $\text{H}_2\text{O}$ , and THF at ambient temperature afforded crystalline **1** as yellow plates. The multifunctional benzimidazole ligand, Hpbc was deliberately designed and contains pyridyl and carboxylate groups that provide effective coordination sites and permit suitable intermolecular interactions. As a result of the free rotation of the pyridyl and benzimidazole rings of the Hpbc ligand, two chiral conformations in  $\Lambda$  and  $\Delta$  forms are present (Chart 1).<sup>9a</sup> This plays a critical role, permitting the formation of the bilayer framework, rather than the typical dense sheet structure. Compared with other elongated multifunctional ligands bearing the pyridyl-benzimidazole moiety,<sup>11</sup> the incorporation of a  $\text{pbc}^-$  ligand into MOFs has not yet been explored.

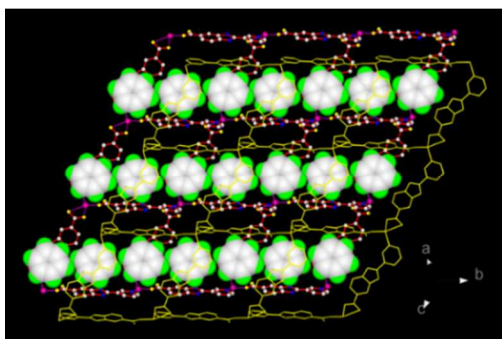
Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the triclinic space group  $P\bar{1}$  and consists of one  $\text{Zn}^{\text{II}}$  ion, two  $\text{pbc}^-$  ligands, and two methanol and six guest water molecules in the asymmetric unit. Each  $\text{Zn}^{\text{II}}$  center is bound to two pyridyl nitrogen atoms, three carboxylate oxygen atoms from four distinct  $\text{pbc}^-$  ligands in a distorted square-pyramidal manner (Fig. S1†). One  $\text{pbc}^-$  ligand adopts a coplanar structure manner and uses the  $\eta^1$ -carboxylate and the 3-pyridyl motifs to coordinate to two  $\text{Zn}(\text{II})$  centers. The other  $\text{pbc}^-$  ligand is in a twisted form, and adopts its  $\eta^2$ -anti-syn-carboxylate and pyridyl motifs to bridge two  $\text{Zn}(\text{II})$  centers. In particular, the  $\text{Zn}^{\text{II}}$  atom is connected to four  $\mu_2$ - $\text{pbc}^-$  ligands in a tetrahedral fashion. Thus, the structure has an unusual 2D protuberant grid-layer network with a **sql**-type topology (Fig. S2†). Each of the two grid networks containing the twisted  $\text{pbc}^-$  ligand in  $\Delta$  and  $\Lambda$  conformations, respectively, are mutually coupled to form a bilayer assembly. As shown in Fig. 2a, this bilayer structure is comprised of two 2D racemic protuberant networks,



**Fig. 3** Structures of **2**: (a) the interlayers are filled with methanol and guest water aggregates; benzene molecules are encapsulated in channels along the  $b$  axis in a space-filling model, (b) the included benzene molecules are aligned in a 1D array, resembling a pea pod.

which are coupled and interdigitated via  $\pi\cdots\pi$  interactions between the coplanar  $\text{pbc}^-$  ligands. It is interesting that there are two kinds of channels in the framework and the overall structure resembles two hands holding something together (Figs. 2b,c). Such a special MOF containing tetrahedral nodes and 2-connected linkers is very interesting.<sup>12</sup> In the case of the adjacent nonplanar  $\text{pbc}^-$  ligands, the bilayers are further stacked via  $\pi\cdots\pi$  interactions, resulting in the formation of a 3D supramolecular framework (Fig. 2c).

The other very intriguing and significant feature of **1** is that the overall framework contains a 3D intersecting channel system, which contains many water and methanol molecules, as observed along the  $b$ ,  $c$ , and  $a$  axes, respectively (Fig. S5). When the crystals of **1** were filtrated from mother liquid, their transparency was quickly reduced. This phenomenon showed that the guest molecules were easily escaped from the 3D intersecting channel system. A thermogravimetric analysis (TGA) of **1** showed that the water and



**Fig. 4** The perspective view of 1D arrays of guest benzene molecules encapsulated within the channels in the 2D bilayer.

methanol molecules are eliminated from the channels of the framework (calcd 24.2%; found 18.5%) sooner or later at a temperature of about 100 °C, after which it was thermally stable at temperatures of up to 295 °C (Fig. S12†). Powder X-ray diffraction (PXRD) patterns showed that the crystallinity of **1** does not change appreciably upon the removal of the guest molecules at temperatures of up to 200 °C. In spite of the 3D interesting channel system, this framework remains robust and is relatively thermally stable.<sup>9a</sup> This phenomenon is very rare and shows interesting host–guest properties that could have numerous applications.<sup>13</sup> Therefore, compound **1** would be expected to be available for further investigations of the exchanging behaviors of the included guests and may serve as a suitable candidate for adsorbing certain types of small organic molecules.

After submersing crystals of **1** in benzene at room temperature, the yellow colored crystals changed to a light-yellow color (as noted for compound **2**). Compound **2** continued to show crystalline characteristics. A single-crystal X-ray diffraction analysis revealed that compound **2** had a quite astonishing framework, which was similar to that of **1**, except that the absorbed guest benzene molecules were now located and regularly arrayed in the specific channels along the *b* axis.

Thus, the formula of **2** was determined to be  $\{[\text{Zn}(\text{pbc})_2] \cdot \text{C}_6\text{H}_6 \cdot 0.5\text{CH}_3\text{OH} \cdot 7.5\text{H}_2\text{O}\}_n$ . The water and methanol molecule aggregates in **1** migrated and were now located in the channels along the *a* and *c* axes. The retrapped guest benzene molecules in **2** were regularly packed and effectively aligned with a translation distance of 6.5 Å per benzene unit, analogous to a pea pod. To further illustrate the unique structure of **2**, as shown in Fig. 3a, the benzene molecules were only included in the channels along the *b* axis, and the other water and methanol molecules migrated to the channels along the *a* and *c* axes. As shown in Figure 4, the racemic bilayer trapped the benzene molecules in such a regular array. The intriguing migration of the guest water is responsible for its interior channel window sizes with  $8.5 \times 8.1 \text{ Å}^2$  within the adaptable MOF, which could provide the suitable channel size and  $\pi \cdots \pi$  interactions between benzene and the framework. Furthermore, the interdigitated bilayer, containing hydrophobic channels, could exhibit a special host–guest effect, therefore, it would be the ideal candidate for use in capturing toxic pollutants. To the best of our knowledge, a 2D MOF with a 3D intersecting channel system that

can efficiently reabsorb benzene molecules and also contains numerous migrating water aggregates is currently unprecedented.

After submersing crystals of **1** in toluene, the final crystallinity remained intact (noted as compound **3**). As revealed in the single-crystal X-ray diffraction analysis, compound **3** contains the regular arrays of toluene molecules that are arranged in the channels only along the *b* axis (Figure S11, in the Supporting Information) and has the formula  $\{[\text{Zn}(\text{pbc})_2] \cdot 0.5\text{C}_7\text{H}_8 \cdot 0.5\text{CH}_3\text{OH} \cdot 6.5\text{H}_2\text{O}\}_n$ . It is interesting that, in both compounds **2** and **3** the guest water and methanol molecules underwent an unusual migration upon the guest exchange. Furthermore, this bilayer not only provided potential channels for absorbing simple aromatic solvents, but also was able to accommodate hydrophilic guests in their inter-bilayer cavities.

Because of the intrinsic nature that upon the exchanges of the guest molecules, the window sizes of the channels along the *b* axis for **1**, **2**, and **3** undergo slight changes ( $8.53 \times 8.13$ ,  $8.75 \times 7.82$ , and  $8.76 \times 7.62 \text{ Å}$ , respectively), the PXRD patterns and EA data would show larger uncertainties. In addition, the amount of adsorbed toluene molecules in **3** is half that of benzene in **2**. This is attributed to the hindrance arising from the methyl group of toluene. These results indicate that this unique framework readily accommodates the notorious benzene.

In conclusion, we report on the preparation of a thermally stable Zn(II)–organic framework that consists of 2D protuberant-grid-type bilayers. The overall framework contains a 3D intersecting channel system, which offers unique 1D channels that can absorb benzene. This interdigitated bilayer containing channels exhibits a special host–guest effect that is mediated by the migration of multiple water molecules. We believe that this intriguing 2D network has great potential for applications related to environmental aromatic pollutants in the future. Further research is currently underway.

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## Notes and references

- (a) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012–1015; (b) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O’Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424–428.
- (a) S. Henke, R. Schmid, J. D. Grunwaldt and R. A. Fischer, *Chem. Eur. J.*, 2010, **16**, 14296–14306; (b) H. X. Deng, S. Grunler, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, **336**, 1018–1023; (c) C. Doherty, D. Buso, A. J. Hill, S. Furukawa, S. Kitagawa and P. Falcaro, *Acc. Chem. Res.*, 2014, **47**, 396–405; (d) X. L. Zhao, F. L. Liu, L. L. Zhang, D. Sun, R. M. Wang, Z. F. Ju, D. Q. Yuan and D. F. Sun, *Chem. Eur. J.*, 2014, **20**, 649–652.
- (a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125; (b) A. H. Khoshaman, B. Bahreyni, *Sensors and Actuators B*, 2012, **162**, 114–119; (c) Y. Q. Chen, G. R. Li, Z. Chang, Y. K. Qu, Y. H. Zhang and X. H. Bu, *Chem. Sci.*, 2013, **4**, 3678–3682; (d) H. Furukawa, K. E. Cordova, M. O’Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.
- (a) D. Britt, D. Tranchemontagne and O. M. Yaghi, *PANS*, 2008, **105**, 11623–11627; (b) P. Bansal, L. M. Bharadwaj, A. Deep and P. Kaushik, *Res. J. Recent Sci.*, 2013, **2**, 84–86; (c) L. Sarkisov, R. L. Martin, M. Hararanczyk and B. Smit, *J. Am. Chem. Soc.*, 2014, **136**, 2228–2231.
- S. Shimomura, S. Horike, R. Matsuda and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 10990–10991.
- (a) K. B. Payne and T. M. Abdel-Fattah, *J. Environ. Science & Health A*, 2004, **A39**, 2275–2291; (b) S. B. Wang and Y. L. Peng, *Chem. Engineer. J.*, 2010, **156**, 11–24; (c) S. Babel and T. A. Kurniawan, *J. Hazard.*

- Materials*, 2003, **B97**, 219–243; (d) B. Hatton, K. Landskron, W. Whitnall, D. Perovic and G. A. Ozin, *Acc. Chem. Res.*, 2005, **38**, 305–312.
7. (a) E. J. Cussen, J. B. Claridge, M. J. Rosseinsky and C. J. Kepert, *J. Am. Chem. Soc.*, 2002, **124**, 9574–9581; (b) K. Sujit, B. Sareeya, S. Kitagawa, *Angew. Chem., Int. Ed.*, 2008, **47**, 3403–3406; (c) P. Horcajada, F. Salles, S. Wuttke, T. Devic, D. Heurtaux, G. Maurin, A. Vimont, M. Daturi, O. David, E. Magnier, N. Stock, Y. Filinchuk, D. Popov, C. Riekel, Gérard Férey and C. Serre, *J. Am. Chem. Soc.*, 2011, **133**, 17839–17847; (d) S. Henke, A. Schneemann, A. Wütscher and R. A. Fischer, *J. Am. Chem. Soc.*, 2012, **134**, 9464–9474; (e) P. C. Guo, T. Y. Chen, X. M. Ren, C. Xiao and W. Jin, *Dalton Trans.*, 2014, **43**, 6720–6727; (f) Q. F. Zhang, A. J. Geng, H. N. Zhang, F. L. Hu, Z. H. Lu, D. H. Sun, X. L. Wei, C. L. Ma, *Chem. Eur. J.* **2014**, **20**, 4885–4890; (g) E. Barea, C. Montoro and J. A. R. Navarro, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C3CS60475F.
  8. (a) S. Y. Bhide and S. Yashonath, *J. Phys. Chem. B*, 2000, **104**, 11977–11986; (b) R. T. Liao, W. C. Yang, P. Thanasekaran, C. C. Tsai, M. Sathiyendiran, Y. H. Liu, T. Rajendran, H. M. Lin, T. W. Tseng and K. L. Lu, *Chem. Commun.*, 2008, 3175–3177; (c) Y. Peng, T. Ben, J. Xu, M. Xue, X. F. Jing, F. Deng, S. L. Qiu and G. S. Zhu, *Dalton Trans.*, 2011, **40**, 2720–2724; (d) A. Planchais, S. Devautour-Vinot, S. Giret, F. Salles, P. Trems, A. Fateeva, T. Devic, P. Yot, C. Serre, N. Ramsahye and G. Mau, *J. Phys. Chem. C*, **2013**, **117**, 19393–19401.
  9. (a) T. T. Luo, Y. H. Liu, C. C. Chan, S. M. Huang, B. C. Chang, Y. L. Lu, G. H. Lee, S. M. Peng, J. C. Wang and K. L. Lu, *Inorg. Chem.*, 2007, **46**, 10044–10046; (b) T. T. Luo, H. C. Wu, Y. C. Jao, S. M. Huang, T. W. Tseng, Y. S. Wen, G. H. Lee, S. M. Peng and K. L. Lu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9461–9464; (c) T. W. Tseng, T. T. Luo, S. Y. Chen, C. C. Su, K. M. Chi and K. L. Lu, *Cryst. Growth Des.*, 2013, **13**, 510–517; (d) T. W. Tseng, T. T. Luo, C. C. Su, H. H. Hsu, C. I. Yang and K. L. Lu, *CrystEngComm*, 2014, **16**, 2626–2633; (e) T. W. Tseng, T. T. Luo, K. H. Lu, *CrystEngComm*, 2014, **16**, 5516–5519.
  10. L. Ma, Y. C. Qiu, G. Peng, J. B. Cai and H. Deng, *Eur. J. Inorg. Chem.*, 2011, 3446–3453.
  11. (a) D. Choquesillo-Lazarte, B. Covelo, J. M. González-Pérez, A. Castiñeiras and J. Niclós-Gutiérrez, *Polyhedron*, 2002, **21**, 1485–1495; (b) C. K. Xia, C. Z. Lu, Q. Z. Zhang, X. He, J. J. Zhang and D. M. Wu, *Cryst. Growth Des.*, 2005, **5**, 1569–1574; (c) X. P. Li, M. Pan, S. R. Zheng, Y. R. Liu, Q. T. He, B. S. Kang and C. Y. Su, *Cryst. Growth Des.*, 2007, **7**, 2481–2490; (d) J. Li, C. C. Ji, L. F. Huang, Y. Z. Li and H. G. Zheng, *Inorg. Chim. Acta*, 2011, **371**, 27–35.
  12. D. S. Li, Y. P. Wu, J. Zhao, J. Zhang and J. Y. Lu, *Coord. Chem. Rev.*, 2014, **261**, 1–27.
  13. (a) P. D. Southon, L. Liu, E. A. Fellows, D. J. Price, G. J. Halder, K. W. Chapman, B. Moubaraki, K. S. Murray, J. F. Letard and C. J. Kepert, *J. Am. Chem. Soc.*, 2009, **131**, 10998–11009; (b) S. Shimomura, N. Yanai, R. Matsuda and S. Kitagawa, *Inorg. Chem.*, 2011, **50**, 172–177; (c) D. R. Xiao, H. Y. Chen, D. Z. Sun, J. H. He, S. W. Yan, J. Yang, X. Wang, R. Yuan and E. B. Wang, *CrystEngComm*, 2012, **14**, 2849–2858; (d) P. Díaz-Gallifa, O. Fabelo, L. Cañadillas-Delgado, J. Pasán, A. Labrador, F. Lloret, M. Julve and C. Ruiz-Pérez, *Cryst. Growth Des.*, 2013, **13**, 4735–4745.

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## Graphic Content

### Benzene Absorption in a Protuberant-Grid-Type Zinc(II)–Organic Framework Triggered by the Migration of Guest Water Molecules

Tien-Wen Tseng,<sup>\*a</sup> Tzuoo-Tsair Luo,<sup>b</sup> Chang-Hsiu Tsai,<sup>ab</sup> Chun-Chi Chen,<sup>b</sup> Gene-Hsiang Lee,<sup>c</sup> Chih-Chieh Wang,<sup>\*d</sup> and Kuang-Lieh Lu<sup>\*b</sup>

Benzene molecules have been reported to be easily and regularly absorbed into specific channels in a 2D protuberant-grid-type Zn(II)–organic framework, which consists of racemic interdigitated bilayers. In addition, the overall framework is comprised of a 3D intersecting channel system and could be used as a benzene absorber.

