

Vapor phase inclusion of ferrocene and its derivative in a microporous metal–organic porous material and its structural characterization by single crystal X-ray diffraction†

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The inclusion of ferrocene and its derivative in metal–organic porous material MOF-5 is achieved by vapor diffusion; single-crystal X-ray diffraction studies using synchrotron radiation of ferrocene-loaded MOF-5 reveal well-ordered guest molecules packed into the pores.

Metal–organic porous materials (MOPMs) are three-dimensional (3D) open frameworks with pores and channels self-assembled from metal ions and organic building units.¹ Since Hoskins and Robson first reported the designed synthesis of 3D frameworks from metal ions and molecular building blocks,² remarkable progress has been made in this field. With potential applications in such areas as ion exchange,² magnetism,³ catalysis,⁴ optoelectronics,⁵ separation,⁶ gas storage⁷ and sensors,⁸ these materials have been under intense investigation. In particular, the regular, highly-ordered pore and/or channel structures of MOPMs offer a unique opportunity to prepare ordered arrays of molecules and clusters, which may find useful applications, such as in the development of new magnetic or non-linear optical materials. As a part of our efforts to synthesize well-defined metal nanoclusters within the pores of MOPMs,^{9,10} we decided first to investigate the inclusion of organometallic compounds that may serve as precursors to metal nanoclusters in MOPMs. Although the inclusion of non-trivial guest molecules such as C₆₀,¹¹ dyes,¹¹ Keggin anions¹² and organometallic compounds¹⁰ in MOPMs have been reported, the presence of the guest molecules was usually confirmed by a color change, spectroscopic methods, powder X-ray diffraction and elemental analysis. The structural elucidation of non-trivial guests by single-crystal X-ray diffraction after their inclusion in MOPMs is seldom reported,¹³ even though such information may be useful for understanding the interactions between guests and host frameworks, and ultimately control the orientation of guests within the nanopores. Herein, we report the vapor phase inclusion of ferrocene and its derivative in MOF-5, a well-known MOPM made of Zn²⁺ and 1,4-benzenedicarboxylate (bdc) with large cavities (15.1 Å) and wide windows (7.5 Å),¹⁴ and

its structural characterization by the single-crystal X-ray diffraction method using synchrotron radiation.

As-synthesized single crystals^{14b} of MOF-5 were guest-exchanged with CHCl₃ and evacuated at room temperature for 3 h to remove the solvent. The guest-free, single-crystalline MOF-5 was then heated to 110 °C with ferrocene in a break-seal tube so that the organometallic compound could diffuse into the pores of the host framework without contaminating the surface of the crystals.¹⁵ Care was taken to protect the MOF-5 from airborne moisture, which deteriorates the structural integrity of MOF-5 when evacuated.

The successful inclusion of ferrocene into the MOF-5 crystals was evident, since the colorless crystals turned yellow while maintaining their transparency (see ESI†). Although the ferrocene-loaded single-crystals appeared to be suitable for structure determination, the diffraction data obtained using a conventional laboratory diffractometer was too weak to be solved. Therefore, a new set of the diffraction data was collected using high-flux synchrotron X-ray radiation. A successful solution and subsequent refinements of the structure revealed that there are, on average, seven ferrocene molecules per formula unit of MOF-5 ([Zn₄(O)(bdc)₃]). The composition of this ferrocene-containing framework (Fc@MOF-5) was independently confirmed by elemental analysis and ¹H-NMR (see below).

As reported in the original paper,^{14a} MOF-5 has two types of pore, with different internal diameters (11.0 and 15.1 Å), due to the tilted phenyl linkers connecting adjacent [Zn₄(O)(O₂CR)₃] nodes. The smaller and larger pores in the crystal structure of Fc@MOF-5 (Fig. 1)§ are found to contain six and eight ferrocene guests, respectively, with a slight distortion of the framework. The six ferrocene molecules in the smaller pores adopt an octahedral arrangement and those in the larger pores are positioned near the corners. As a consequence, the face-centered symmetry of the unit cell of the apo-host (space group *Fm-3m*) is lifted, and the unit cell of the ferrocene-loaded framework is best defined by the space group *Pa-3*. The change in the unit cell parameter (from 25.832 (1) to 25.507 (3) Å) is accompanied by a 3.7% decrease in the unit cell volume compared to the evacuated framework. A similar behavior of framework distortion and shrinkage upon guest inclusion has previously been noted in another MOPM.¹⁵ The observed packing of ferrocene guests into the pores seems to be quite efficient, leaving only 1.6% (258 Å per unit cell) of the crystal volume accessible to solvent molecules.¹⁶ In the smaller pores, six ferrocene molecules, which are symmetry related to one another, exist near the center of the pore windows, and no strong interaction with the host framework is apparent (Fig. 2). The two cyclopentadienyl

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† Electronic supplementary information (ESI) available: The picture of a single-crystal of Fc@MOF-5 and various ¹H-NMR spectra. See DOI: 10.1039/b604925g

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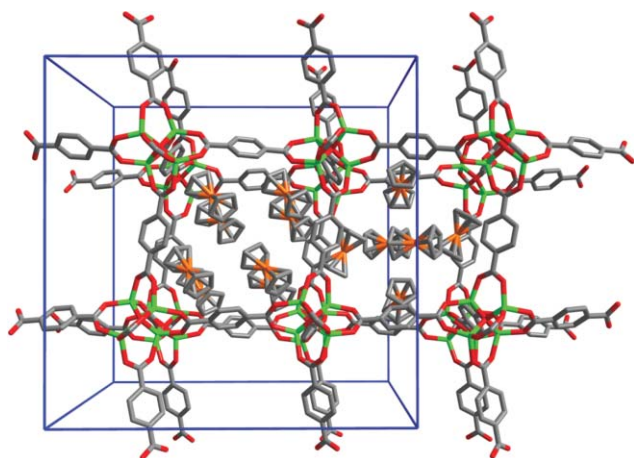


Fig. 1 X-Ray crystal structure of ferrocene-loaded MOF-5. Eight and six ferrocene guests are found in the larger and smaller pores, respectively. Hydrogen atoms are omitted for clarity.

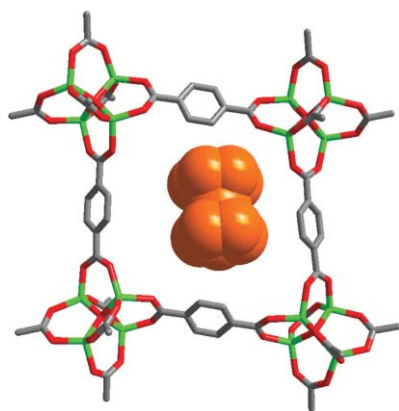


Fig. 2 A view of a ferrocene molecule placed near the center of a window of the smaller pore.

(Cp) rings of the guest molecules are almost eclipsed by each other, and other geometrical parameters conform to known values.¹⁷ In the larger pore, there are two crystallographically-independent ferrocene guests, one of which is ordered, while the other is conformationally-disordered, since the molecule lies on a crystallographic three-fold axis.¹⁸ A total of eight ferrocene molecules exist, and they are located near the corners of the pore. Extensive π - π interactions exist among the guests, as well as between the guest and the framework, as judged by the orientation of the aromatic rings and the short intermolecular distances (Fig. 3).

X-Ray powder diffraction profiles of the as-synthesized MOF-5 and Fc@MOF-5 were compared with the simulated diffraction pattern of guest-free MOF-5 (Fig. 4). After the inclusion, a number of new peaks are observed due to the ferrocene guests, while the peaks corresponding to the porous host remain unchanged. These results confirm that metal-organic porous materials can act as a new type of host (or container) for small molecular species.

The inclusion of ferrocene was attempted in the solution phase by immersing evacuated MOF-5 crystals into a ferrocene solution in DMF. However, the inclusion of ferrocene molecules was not evident by UV/vis spectroscopy, even though the color of the

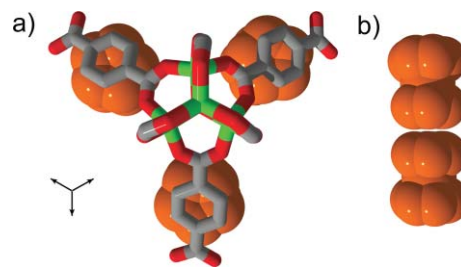


Fig. 3 (a) The orientation of ferrocene guests (orange) in the larger pore of MOF-5. (b) The π -stacked ferrocene molecules in the pore are 3.53 Å apart.

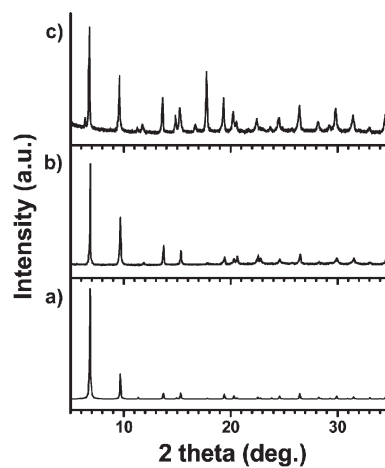


Fig. 4 X-Ray powder diffraction patterns: (a) guest-free MOF-5 (simulated), (b) as-synthesized MOF-5 and (c) Fc@MOF-5.

crystals turned yellow, that may be due to competition with DMF. Considering the competition with solvent molecules, sublimation seems to be a better choice for the inclusion of organometallic compounds with a reasonable vapor pressure.

We have also studied the inclusion of ferrocene aldehyde (FcCHO) in MOF-5 because it carries a reactive functional group, useful for organic transformations. Despite exhaustive attempts, we failed to locate ferrocene aldehyde in the MOF-5 crystals by single crystal X-ray diffraction, which turned dark red upon guest inclusion.¹⁹ However, the presence of ferrocene aldehyde in the pores of MOF-5 has been confirmed and quantified by elemental analysis and ¹H-NMR spectroscopy after digesting the guest-loaded crystals in DCI/DMSO-*d*₆ (see ESI[†]). We are currently investigating organic reactions of the guest confined within the nanopores of the MOPM.

In conclusion, we have successfully demonstrated the vapor phase inclusion of ferrocene and its derivative into metal-organic porous material MOF-5. Single-crystal X-ray diffraction studies using synchrotron radiation revealed a well-ordered array of ferrocene molecules in the pores of the host framework, which appears to be stabilized by π - π interactions. This method is applicable to the inclusion of other organometallic species in MOPMs, as also recently demonstrated by others.¹⁰ Furthermore, this result suggests that a highly-ordered array of guest molecules can be prepared within MOPMs, which may show interesting magnetic or non-linear optical properties. Considering the

potential use of metallocenes as precursors for carbon-based materials,²⁰ it would be also interesting to see how these molecular species behave inside the nanopores of metal-organic porous materials under various conditions.

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Notes and references

§ MOF-5 was synthesized according to the literature.^{14b} The chloroform-exchanged crystals were placed under a vacuum at room temperature for 1 d to give guest-free MOF-5. A powdery form of ferrocene (25 mg) and single-crystals of MOF-5 (14 mg) were loaded in two separate chambers of a break-seal tube, and after breaking the seal, the tube was heated to 110 °C for 1 d. Anal. calc. for C₉₄H₈₂O₁₃Fe₇Zn₄ (MOF-5-7Fc): C, 54.49; H, 3.99. Found: C, 54.22; H, 3.98; N, 0.00. Ferrocene aldehyde-loaded MOF-5 was prepared similarly. Anal. calc. for C₇₄H₆₂O₁₃Fe₅Zn₄ (MOF-5-5FcCHO): C, 52.28; H, 3.68. Found: C, 52.64; H, 3.68; N, 0.03. The diffraction data from a yellow cubic crystal of Fc@MOF-5, measuring 0.25 × 0.20 × 0.14 mm, mounted on a loop, were collected at 100 K on an ADSC Quantum 210 CCD diffractometer with synchrotron radiation ($\lambda = 0.80000 \text{ \AA}$) at the Macromolecular Crystallography Wiggler Beamline 4A, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The crystal was rotated through a total of 180°. The raw data were processed and scaled using the program HKL2000. The structure was solved by direct methods and the refinements were carried out with full-matrix least-squares on F^2 using appropriate software implemented within the SHELXTL program package. X-Ray data for Fc@MOF-5: C₉₄H₈₂O₁₃Fe₇Zn₄, $M = 2072.03$, cubic, $Pa-3$ (no. 205), $a = 25.507(3)$, $V = 16594(3) \text{ \AA}^3$, $Z = 8$, $T = 100 \text{ K}$, $\mu(\text{synchrotron}) = 3.279 \text{ mm}^{-1}$, $d_{\text{calc}} = 1.659 \text{ g cm}^{-3}$, 56088 reflections measured, 5689 unique ($R_{\text{int}} = 0.1020$), $R_1 = 0.0628$, $wR_1 = 0.1409$ for 5582 reflections ($I < 2\sigma(I)$), $R_1 = 0.0653$, $wR_2 = 0.1416$ (all data), $\text{GOF} = 1.241$, 348 parameters and no restraints. All the non-hydrogen atoms were refined anisotropically, except for a ferrocene molecule located on a three-fold axis. Hydrogen atoms were added in their geometrically-ideal positions. CCDC 603946. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604925g

- Recent reviews on metal-organic porous materials: (a) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658; (b) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. Reineke, M. O’Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330; (c) O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714; (d) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276–288; (e) C. Janiak, *Dalton Trans.*, 2003, 2781–2804; (f) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375; (g) C. N. R. Rao, S. Natarajan and R. Vaidyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466–1496; (h) I. Goldberg, *Chem. Commun.*, 2005, 1243–1254; (i) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670–4679; (j) R. J. Hill, D.-L. Long, N. R. Champness, P. Hubberstey and M. Schröder, *Acc. Chem. Res.*, 2005, **38**, 335–348; (k) N. W. Ockwig, O. Delgado-Friedrichs, M. O’Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176–182; (l) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273–282; (m) G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 217–225; (n) Special issue of *J. Solid State Chem.*, 2005, **178**, 2409–2573; (o) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109–109; (p) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Armdt and J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626–636.
- B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546–1554.
- (a) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Nature*, 2002, **298**, 1762–1765; (b) D. Maspoth, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190–195.

- (a) J. S. Seo, D. Wand, H. Lee, S. I. Jun, J. Oh, Y. Jeon and K. Kim, *Nature*, 2000, **404**, 982–986; (b) C. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940–8941; (c) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin and K. Kim, *Angew. Chem., Int. Ed.*, 2006, **45**, 916–920.
- O. R. Evans and W. Lin, *Chem. Mater.*, 2001, **13**, 2705–2712.
- (a) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295–296; (b) K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H.-C. Chang and T. Mizutani, *Chem.–Eur. J.*, 2002, **8**, 3586–3600; (c) D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2004, **126**, 6106–6114; (d) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 3269–3272; (e) M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 9376–9377.
- (a) S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2081–2084; (b) B. Chen, M. Eddaoudi, S. T. Hyde, M. O’Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021–1023; (c) R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H.-C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata and M. Takata, *Science*, 2002, **298**, 2358–2361; (d) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O’Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127–1129; (e) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 32–33; (f) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4745–4749; (g) J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Nature*, 2005, **309**, 1350–1354; (h) H. Chun, D. N. Dybtsev, H. Kim and K. Kim, *Chem.–Eur. J.*, 2005, **11**, 3521–3529; (i) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Science*, 2005, **436**, 238–241.
- K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392–3395.
- The formation of silver nanoparticles on the surface of metal-organic porous materials has been reported: H. R. Moon, J. H. Kim and M. Paik Suh, *Angew. Chem., Int. Ed.*, 2005, **44**, 1261–1265.
- S. Hermes, M.-K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, T. W. Fischer and R. A. Fischer, *Angew. Chem., Int. Ed.*, 2005, **44**, 6237–6241.
- H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O’Keeffe and O. M. Yaghi, *Nature*, 2004, **427**, 523–527.
- G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, **309**, 2040–2042.
- The structural elucidation of the crystal-to-crystal transformation, triggered by removal or exchange of guests, has been reported, see ref. 8 and (a) K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392–3395; (b) M. P. Suh, J. W. Ko and H. J. Choi, *J. Am. Chem. Soc.*, 2002, **124**, 10976–10977; (c) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 3269–3272. However, the focus of these studies, which usually involve trivial guests such as water, alcohols and benzene, are on the reversible transformation of framework structures.
- (a) H. Li, M. Eddaoudi, M. O’Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276–279; (b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469–472.
- D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033–5036.
- A. L. Spek, *PLATON*, a multi-purpose crystallographic tool, Utrecht University, Utrecht, The Netherlands, 2001.
- P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1982, **38**, 1741–1745.
- The Cp rings of the ferrocene molecule, lying on a crystallographic three-fold axis, are disordered over three sites. Five carbon atoms of the Cp rings were initially located from a difference electron density map and refined isotropically, with a constraint to have a regular pentagon ($d = 1.42 \text{ \AA}$). Recently, adsorbed hydrogen molecules have been found to occupy a similar site with three-fold symmetry (α site): E. C. Spencer, J. A. K. Howard, G. J. McIntyre, L. C. Rowsell, Jesse and O. M. Yaghi, *Chem. Commun.*, 2006, 278–280.
- The diffraction data clearly revealed the framework of MOF-5 with $a = 25.718(3) \text{ \AA}$; however, the guest molecules could not be located due to extensive disorder, which may be due to symmetry-mismatching for the 5 guest molecules residing in a single cube-like pore (having four- and three-fold symmetry).
- S.-H. Jeong, J.-H. Ko, J.-B. Park and W. Park, *J. Am. Chem. Soc.*, 2004, **126**, 15982–15983.