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Ni(II)-MOF: reversible guest adsorption and heterogeneous catalytic property for silylcyanation of aromatic aldehydes

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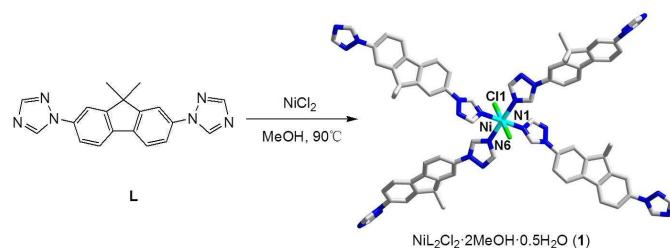
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A porous Ni(II)-MOF, which was constructed from a new bent fluorene-bridged ligand and NiCl₂ under solvothermal conditions, can reversibly uptake organic solvent molecules and iodine species in a single-crystal-to-single-crystal (SC-SC) fashion. Furthermore, the obtained I₂⊂Ni(II)-MOF can be a highly active heterogeneous catalyst to promote solvent-free silylcyanation of aromatic aldehydes under mild conditions.

Metal-organic frameworks (MOFs), as an emerging class of hybrid functional porous materials, provide a new tunable platform to fabricate heterogeneous catalysts.¹ As we know, MOFs themselves are inherent heterogeneous catalysts due to their inorganic-organic hybrid composition and polymeric nature. For example, heterogeneous catalytic MOFs which contain active catalytic metal-moieties can be prepared by direct assembly or postsynthetic approach. On the other hand, porous MOFs are still ideal supporters for the composite heterogeneous catalysts by incorporation of the catalytic active guest species into their pores.² The later approach provides a useful and practical way to construct new type of composite heterogeneous catalysts based on the host-guest concept.

In this contribution, we report a new porous Ni(II)-MOF (**1**) which is generated from fluorene-bridged ligand **L** (ESI[†]) and NiCl₂ under solvothermal conditions. It can reversibly uptake organic solvent guest molecules and iodine species in a SC-SC fashion. The resulted I₂⊂Ni(II)-MOF host-guest system which can be a highly active composite heterogeneous catalyst to promote silylcyanation³ of aromatic aldehydes under mild conditions.

Scheme 1. Synthesis of **1**.

As shown in Scheme 1, compound **1** (2MeOH·0.5H₂O⊂NiL₂Cl₂) was obtained as blue rod-like crystals by the combination of **L** and NiCl₂ in MeOH at 90°C for 72 h in a sealed glass tube. Single-crystal X-ray diffraction analysis (ESI[†]) revealed that each Ni²⁺ node in **1** adopts a distorted octahedral {NiN₄Cl₂} coordination sphere. The basal plane is composed of four N-triazole ($d_{\text{Ni-N}} = 2.097(3) \sim 2.128(3)$ Å) donors. The axial positions are occupied by the two coordinated Cl⁻ anions ($d_{\text{Ni-Cl}} = 2.4328(19)$ Å). Compound **1** is very stable in air as well as in common organic solvents.

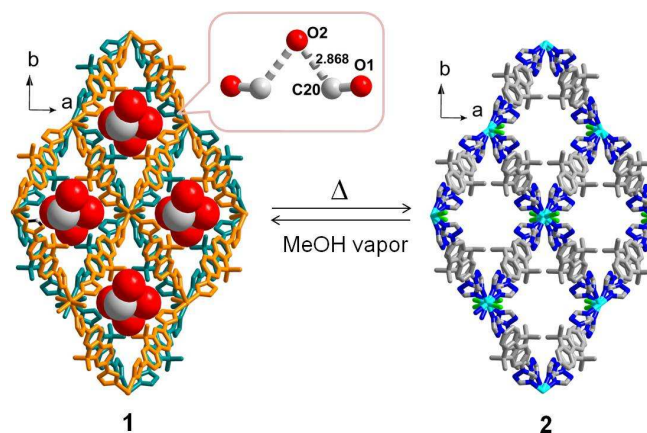


Fig. 1 Reversible adsorption of MeOH/H₂O guests in a SC-SC fashion based on **1** (guest species are shown as space filling model for clarity). The H-bonded guest trimer is inserted.

In **1**, the octahedral Ni(II) nodes and **L** linkages build up a 2D net consisting of rhombus-like grids. The nets extend in the crystallographic *ab* plane and stack along the crystallographic *c* axis to generate open rhombic channels (dimensions $\sim 14 \times 10$ Å). As shown in Fig. 1, the channels contain MeOH and H₂O solvent guest molecules, which was further confirmed from the ¹H NMR and via thermogravimetric analysis (TGA, ESI[†]). Single-crystal analysis indicated that one H₂O and two MeOH molecules formed an H-bonded trimer (Fig. 1) and no obvious interactions between the H-bonded trimer and framework are found.

The trapped guest molecules can be completely removed *via* heating. For example, when the crystals of **1** were heated at 100°C for 4 h, single-crystal analysis and TGA measurement (ESI†) indicated that the encapsulated solvent molecules in **1** were removed to result in the desolvated compound NiL₂Cl₂ (**2**). Interestingly, this guest uploaded process based on Ni(II)-MOF is reversible. When **1** was suspended in the MeOH vapour in air for 24 h at ambient temperature, the MeOH and H₂O were taken inside again to regenerate compound **1** (**1'**), which is further supported by ¹H NMR spectroscopy and TGA results (ESI†). Notably, the single crystal nature of **1** was retained during this reversible guest loaded process. The single-crystal analysis (ESI†) indicated that compounds **1**, **2** and **1'** are identical, and only some structural parameters are slight different caused by guest species change. For example, the cell volumes of **1**, **2** and **1'** are 3956(5), 3926(5) and 3969(5) Å³, respectively (ESI†).

Besides MeOH and H₂O, desolvated Ni(II)-MOF (**2**) can also reversibly uptakes molecular I₂ in vapour phase with retention of X-ray diffracting property.

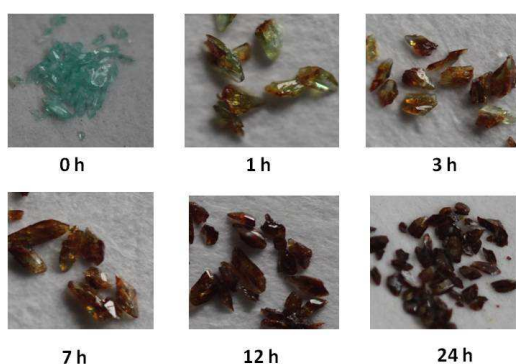


Fig. 2 Photographs showing the color change of the bulk crystal samples of **2** in I₂ vapour at 0, 1, 3, 7, 12 and 24 h. The single crystal nature was kept during the I₂-uploaded process.

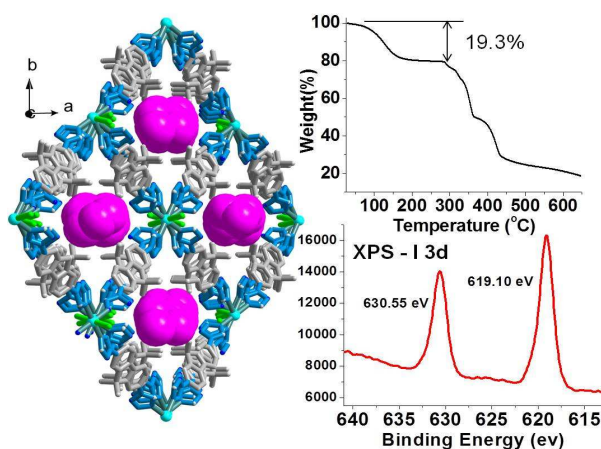


Fig. 3 left: Single-crystal structural packing of **3** (I₂ species is shown as space filling model for clarity); right: TGA trace (observed 19.3%, calculated 19.5%) and XPS spectrum of **3**.

The light blue crystals of **2** and some crystals of iodine were brought together in a closed system at ambient temperature (*p*(I₂) is ~0.3 mm Hg). As the time went on, the color of the crystals gradually changed from light blue to dark brown (Fig. 2), and the saturated adsorption of I₂ was reached in 24 h (monitored by TGA). The crystal analysis (ESI†) revealed that large peaks of electron

density within the framework void are evenly assigned to disordered iodine centers. The NiL₂Cl₂ framework was unchanged, and resulted in a new host-guest system 0.75I₂·NiL₂Cl₂ (**3**). The unit cell expanded from 3926(5) (**2**) to 3986(5) Å³ (**3**) after iodine loaded (ESI†).

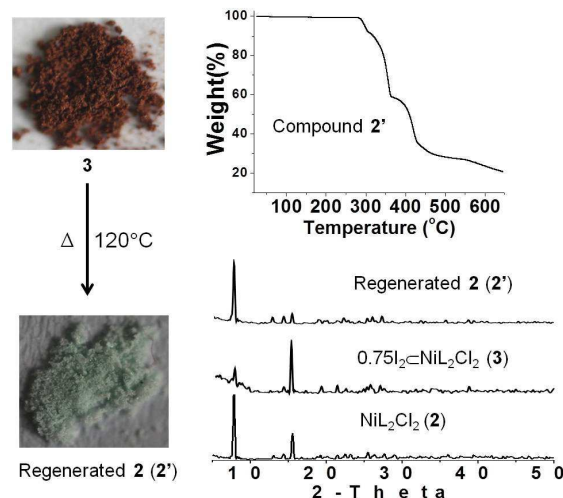


Fig. 4 Left: Photographs showing **3** to **2** (**2'**) by heating; right: TGA trace of the regenerated **2** (**2'**), and XRPD patterns of **2**, **3** and **2'**.

The sum of the site occupancies indicates that there are approximately 0.75 I₂ molecules per unit cell, which is consistent with the TGA measurement (ESI†). So 1 g of **2** can upload around 0.217 g I₂ (an iodine content of up to 19.50%). X-ray photoelectron spectroscopy (XPS) indicated that the valence of the encapsulated iodine species is zero, which further confirmed that the included iodine species exists as I₂ (Fig. 3).⁴ The I₂ molecules are stabilized in the channels through the N···I₂ interactions (ESI†).⁵ Notably, the iodine adsorption is also reversible, and the uploaded iodine can also be removed by heating. When **3** was heated at 120°C for 10 h, the iodine species was completely removed and compound **2** (**2'**) was regenerated (Fig. 4). The XRPD patterns clearly demonstrated that the framework of Ni(II)-MOF is stable (Fig. 4), although the single-crystal nature could not be maintained during this iodine desorption process.

Table 1. Silylcyanation of benzaldehyde catalyzed by **3**.

Entry	Time	%Yield ^[a]	TOF [h ⁻¹] ^[b]
1	0.5 h	97	58.99
2	1.0 h	98	29.8
3	1.0 h	95	28.74
4	1.5 h	93	18.88

^[a]Yields are determined by GC-MS. ^[b]TOF = %yield (mol of substrate/mol of cat. h)

It is well known that molecular iodine is a useful catalyst,⁶ and it is widely used in organic synthesis such as silylcyanation of aldehydes and ketones.^{3c} As a natural resource, however, iodine is

very scarce.⁷ In most of the cases, iodine is used as a homogeneous catalyst which makes its cyclic utilization almost impossible. Therefore, the cyclic utilization of iodine is very significant. Within this in mind, $0.75\text{I}_2\text{-NiL}_2\text{Cl}_2$ (**3**) was used as the heterogeneous catalyst to catalyze the silylcyanation reaction of aromatic aldehydes.

The treatment of benzaldehyde (1.0 mmol) with trimethylsilyl cyanide (TMSCN, 1.2 mmol) in the presence of 3.3 mol% of **3** (equivalent to 5.0 mol% of iodine) at room temperature afforded the corresponding trimethylsilylated cyanohydrins in excellent yields within half an hour (Table 1). It is worth pointing out that the cyanation reaction herein needed no additional organic solvent except the reaction substrates. Thus the reaction is ease of manipulation and avoids toxic and volatile solvents, which could be considered as a clean catalytic organic synthesis.

It is different from the previous classical I_2 -catalyzed organic reactions,^{6,3c} **3** herein exhibits a heterogeneous catalyst nature (**3** is insoluble in aromatic aldehydes) and can be reused. After each catalytic cycle, **3** could be easily recovered by centrifugation and filtration, and then directly reused in the next run under the same reaction conditions. Table 1 shows that **3** is highly active for this cyanation reaction. Moreover, **3** can be recycled and reused four times to generate the products in very high yields, but the reaction times are slighter longer during the second, third and fourth cycles. As indicated in Fig. 5, even after four consecutive catalytic runs, **3** was demonstrated to be highly crystalline by XRPD patterns, which confirmed the reusability of **3** as a heterogeneous catalyst. Furthermore, the encapsulated iodine species cannot be exchanged by the reaction substrates such as benzaldehyde and TMSCN based on ^1H NMR measurement, so the porous Ni(II)-MOF herein is an ideal carrier to load catalytic active iodine species for the heterogeneous catalytic reactions.

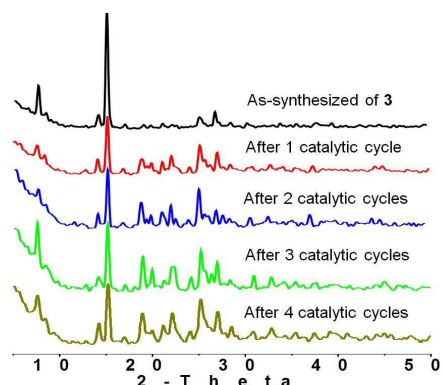


Fig. 5 XRPD pattern of **3** and its XRPD patterns after each catalytic cycle.

In addition, the catalytic ability of the I_2 -free Ni(II)-MOF (**2**) was also explored under the same reaction conditions. The results demonstrated that **2** is also able to catalyze the silylcyanation reaction of benzaldehyde, but in much lower yields. The yields (based on GC-MS) obtained from two catalytic cycles are only 76 and 44 %, respectively. The catalytic activity of **2** is comparable to that of $[\text{Cd}(4,4'\text{-bipy})_2](\text{NO}_3)_2$ which is previously reported by Fujita.⁸ So the high catalytic activity exhibited by **3** might be a synergistic effect of the predominant iodine species and the catalytic Ni(II)-MOF supporter. On the other hand, **3** is an iodine fully loaded host-guest system, so the catalysis based on **3** might occur on the external surface. In order to prove it, larger sized aromatic aldehydes 2-naphthaldehyde and 1-formylpyrene were subjected to conditions of above reaction (ESI†). The corresponding cyanation products were obtained in quantitative yields (based on ^1H NMR spectra), which supported that the catalytic reactions herein are a surface catalytic process. Furthermore, the XPS measurements performed on

3 before and after the catalytic reactions further confirm that it is a surface catalytic behavior (ESI†).

In conclusion, a porous Ni(II)-MOF was successfully synthesized based on NiCl_2 and a new bent fluorene-bridged ligand. It is able to reversibly adsorb guest solvent molecules and iodine species in a SC-SC fashion. More importantly, the obtained $\text{I}_2\text{-Ni(II)-MOF}$ supramolecular system can be a highly active heterogeneous catalyst to promote the silylcyanation of aromatic aldehydes without additional organic solvents under mild conditions. The guest-loaded strategy developed herein provides an alternative approach to access the heterogeneous catalysts for clean organic reactions. More heterogeneous catalysts of this type are currently under investigation in our lab.

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Notes and references

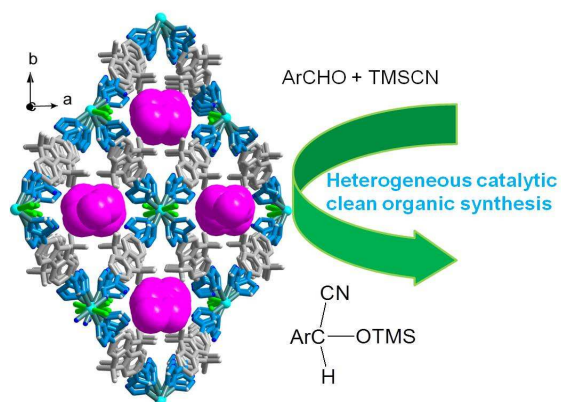
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† Electronic Supplementary Information (ESI) available: Synthesis and characterization data for the ligand and **1-3**, and catalytic experimental details, including tables and figures for ORTEP, TGA, XPS, XRPD patterns, CIF file, crystal data. See DOI: 10.1039/c000000x/

- a) C. Wang, D. Liu, W. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 13222. b) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.*, 2012, **112**, 1196. c) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011.
- a) B. Li, Y. Zhang, D. Ma, T. Ma, Z. Shi, S. Ma, *J. Am. Chem. Soc.*, 2014, **136**, 1202. b) S. Pullen, H. Fei, A. Orthaber, S. M. Cohen, S. Ott, *J. Am. Chem. Soc.*, 2013, **135**, 16997. c) D. T. Genna, A. G. Wong-Foy, A. J. Matzger, M. S. Sanford, *J. Am. Chem. Soc.*, 2013, **135**, 10586. d) L. B. Vilhelmen, K. S. Walton, D. S. Sholl, *J. Am. Chem. Soc.*, 2012, **134**, 12807. e) C. Wang, K. E. deKrafft, W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 7211. f) J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle, C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839.
- Silylcyanation reaction of aldehydes can be promoted by Lewis acids: a) D. A. Evans, L. K. Truesdale, G. L. Carroll, *J. Chem. Soc., Chem. Commun.*, 1973, 55. b) M. Hayashi, Y. Miyamoto, T. Inoue, N. Oguni, *J. Chem. Soc., Chem. Commun.*, 1992, 1752. c) J. S. Yadav, B. V. S. Reddy, M. S. Reddy, A. R. Prasad, *Tetrahedron Lett.*, 2002, **43**, 9703. d) K. Mo, Y. Yang, Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 1746. e) D. Dang, P. Wu, C. He, Z. Xie, C. Duan, *J. Am. Chem. Soc.*, 2012, **132**, 14321.
- Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *Chem. Commun.*, 2011, **47**, 7185.
- S. Reiling, M. Besnard, P. A. Bopp, *J. Phys. Chem. A* 1997, **101**, 4409.
- a) B. Das, P. Balasubramanyam, M. Krishnaiah, B. Veeranjanyulu, G. C. Reddy, *J. Org. Chem.*, 2009, **74**, 4393. b) K. Žmitek, M. Zupan, S. Stavber, J. Iskra, *J. Org. Chem.*, 2007, **72**, 6534. c) N. Deka, D. J. Kalita, R. Borah, J. C. Sarma, *J. Org. Chem.*, 1997, **62**, 1563.
- a) T.-H. Cheng, *Economic Botany*, 1969, **23**, 215. b) M. F. Wahab, *J. Chem. Ed.*, 2009, **86**, 206.
- M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.

For Table Content



$I_2C-Ni(II)$ -MOF can be a highly active heterogeneous catalyst to promote solvent-free silylcyanation of aromatic aldehydes under mild conditions.