

Postsynthetic Metalation of a Robust Hydrogen-Bonded Organic Framework for Heterogeneous Catalysis

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Supporting Information

ABSTRACT: Hydrogen-bonded organic framework (HOF)-based catalysts still remain unreported thus far due to their relatively weak stability. In the present work, a robust porous HOF (HOF-19) with a Brunauer–Emmett–Teller surface area of 685 m² g⁻¹ was reticulated from a cage-like building block, amino-substituted bis-(tetraoxacalix[2]arene[2]triazine), depending on the hydrogen bonding with the help of π – π interactions. The postsynthetic metalation of HOF-19 with palladium acetate afforded a palladium(II)-containing heterogeneous catalyst with porous hydrogen-bonded structure retained, which exhibits excellent catalytic performance for the Suzuki–Miyaura coupling reaction with the high isolation yields (96–98%), prominent stability, and good selectivity. More importantly, by simple recrystallization, the catalytic activity of deactivated species can be recovered from the isolation yield 46% to 92% for 4-bromobenzonitrile conversion at the same conditions, revealing the great application potentials of HOF-based catalysts.

Heterogeneous catalysis plays a dominant role in the chemical and pharmaceutical industry.¹ As a result, continuous efforts have been paid toward developing effective methods for synthesizing heterogeneous catalysts with high efficiency and in particular with an easy recovery and recycling nature. In the past several years, by immobilizing homogeneous catalysts inside the porous supports such as zeolites,² metal–organic frameworks (MOFs),³ and covalent organic frameworks (COFs),⁴ diverse heterogeneous catalysts with boosted activity and stability have been fabricated. However, the regeneration of these heterogeneous catalysts is still challenging due to their nonrenewable porous supports.

In the same way as MOFs and COFs, porous hydrogen-bonded organic frameworks (HOFs) are self-assembled from discrete molecular modules as well.⁵ Despite the outstanding properties of HOFs revealed in the fields of gas storage,⁶ small-molecule separation,⁷ sensing,⁸ and proton conduction,⁹ reports over HOF-based catalysts still remain unknown, to the best of our knowledge, due to the relatively poor stability associated with the weak hydrogen bonding connection between discrete building blocks in HOFs.^{5–9} Fortunately, the introduction of

additional π – π interactions would significantly enhance the stability when aromatic building blocks are employed for constructing HOFs,^{5g,6f} rendering it possible to fabricate heterogeneous catalysts with robust frameworks as the porous support of homogeneous species. In particular, the excellent recyclability of HOFs through simple recrystallization enables them to be regenerated easily, thus endowing the sustainable advantage to HOF-based catalysts.

Herein, a novel organic cage of amino-substituted bis-(tetraoxacalix[2]arene[2]triazine) (L) composed of five six-membered aromatic rings has been designed and prepared as a building block for assembling HOFs (Figure 1a and Scheme S1, Supporting Information). Depending on the hydrogen bonding between neighboring building blocks with the help of rich π – π interactions between intercage aromatic moieties, the first cage-

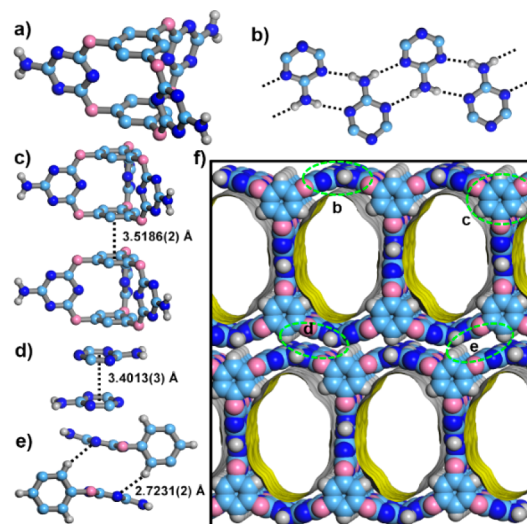


Figure 1. Crystal structure of HOF-19 showing (a) molecular organic cage L; (b) hydrogen bonding ribbon comprising neighboring AT groups; (c, d) two kinds of intercage cofacial π – π interactions; (e) the C–H... π interaction; and (f) a packing diagram of HOF-19 showing the 1D channel surfaces highlighted as yellow/gray (inner/outer) curved planes (C, slight cyan; O, pink; N, blue; H, white).

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based HOF (HOF-19) is constructed, and its hydrogen-bonded structure is clearly revealed by single-crystal X-ray diffraction analysis. The N_2 sorption measurement at 77 K discloses a Brunauer–Emmett–Teller (BET) surface area of $685 \text{ m}^2 \text{ g}^{-1}$ for activated HOF-19. Postfunctionalization of this HOF with palladium acetate gives a palladium(II)-containing HOF-19 \supset Pd(II) with parent hydrogen-bonded structure maintained according to the powder X-ray diffraction (PXRD) analysis, indicating the robustness of HOF-19. Further evidence on the robustness of HOF-19 comes from the excellent stability and recyclability of HOF-19 \supset Pd(II) in *p*-xylene in the presence of potassium carbonate at 150 °C. Under such experimental conditions, the Suzuki–Miyaura coupling reaction is able to be selectively promoted in high isolation yields (96–98%), revealing the predominant catalytic activity of HOF-based materials for the first time. Nevertheless, the catalytic activity of deactivated species, with the 46% isolation yield for the conversion of 4-bromobenzonitrile, is recovered to 92% by simple recrystallization regeneration, revealing the great application potentials of HOF-based catalysts.

A facile reaction between chloride-substituted bis-(tetraoxacalix[2]arene[2]triazine)¹⁰ and ammonium hydroxide afforded **L** (Scheme S1 and Figures S1 and S2, Supporting Information). The slow evaporation of the formic acid solution of **L** gave single crystals of HOF-19 with poor solubility in common organic solvents (except only DMSO). Single-crystal X-ray diffraction data confirms the three-dimensional (3D) porous structure of HOF-19 (Figure 1; Tables S1 and S2, Supporting Information). As exhibited in Figure 1, depending on the multiple N–H \cdots N hydrogen bonding between intercage 2-aminotriazinyl (AT) groups with the help of π – π interactions from intercage benzene moieties, two-dimensional porous hydrogen-bonded supramolecular structures containing one-dimensional (1D) channels with the size of $8.0 \times 13.6 \text{ \AA}$ along the [010] direction are formed, which are further packed into the 3D architecture of HOF-19 depending on the intercage cofacial π – π interaction between AT groups and C–H \cdots π interaction (actually a kind of π – π interaction). The PLATON calculation discloses 47% void space for HOF-19,¹¹ which should be favorable for the molecular substrate diffusion.

The bulk material of HOF-19 with good thermal stability was obtained by diffusing acetone into the formic acid solution of **L** (Figure S3, Supporting Information). Acetone-exchanged HOF-19 was degassed at 25 °C to give an activated sample (HOF-19a). The PXRD pattern of HOF-19a is well consistent with the simulated profile of HOF-19 (Figures S4 and S5, Supporting Information), indicating its robust nature. The N_2 sorption measurement at 77 K reveals its type I adsorption curve with a N_2 uptake of $287 \text{ cm}^3 \text{ g}^{-1}$ at 1.0 bar (Figure 2). The experimental pore volume of $0.45 \text{ cm}^3 \text{ g}^{-1}$ is well consistent with the theoretical value ($0.48 \text{ cm}^3 \text{ g}^{-1}$; Table S1).¹¹ The BET surface area of HOF-19a was calculated to be $685 \text{ m}^2 \text{ g}^{-1}$.

The multiple hydrogen bonding and π – π interactions between neighboring cages enhance the robustness of HOF-19. The poor solubility of HOF-19 in common organic solvents could effectively stabilize the framework in solution. In addition, abundant triazinyl nitrogen atoms and amino groups inside the pores of HOF-19 provide enough binding sites to incorporate catalytically active metal ions. All these characteristics inspire us to fabricate a heterogeneous catalyst with HOF-19 as the porous support. The immersion of activated HOF in an acetone solution of palladium acetate (0.100 mM) afforded palladium(II)-containing HOF-19 \supset Pd(II). Its PXRD pattern matches

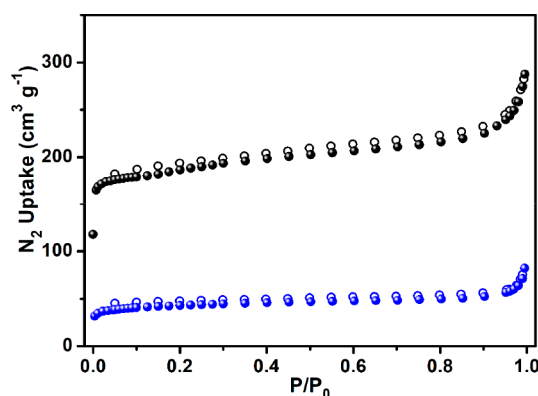
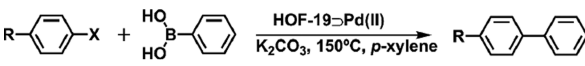


Figure 2. N_2 sorption isotherms of HOF-19a (black) and HOF-19 \supset Pd(II) (blue) at 77 K (solid symbols, adsorption; open symbols, desorption).

well with the simulated one for HOF-19 in Figure S6 (Supporting Information), indicating the hydrogen-bonded structure retained by the post-treated species and illustrating the HOF robustness again. Inductively coupled plasma (ICP) analysis gives a Pd content of 3.8 wt % included in HOF-19 \supset Pd(II). In the X-ray photoelectron spectrum shown in Figure S7 (Supporting Information), the observation of two peaks with the binding energy of 338.1 and 343.4 eV corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively, confirms divalent palladium ions bound by HOF-19. The slight downshift of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energy for HOF-19 \supset Pd(II) relative to that (338.3 and 343.6 eV) of palladium acetate indicates the presence of an interaction between Pd²⁺ ions and HOF-19.¹² The slight upshift for the binding energy of the amino group of HOF-19 after including palladium acetate not only indicates HOF-19 interacting with Pd²⁺ ions but also suggests the amino groups, instead of the intracage cavity, as active sites to bind the metal ions (Figure S8, Supporting Information). The energy-dispersive spectroscopy (EDS) mapping of HOF-19 \supset Pd(II) clearly hints at the homogeneous distribution of the Pd element, excluding the presence of Pd nanoparticles (Figure S9, Supporting Information). After postmodification with Pd(OAc)₂ to give HOF-19 \supset Pd(II) with palladium ions decorated on the surface of HOF channels, the BET surface area was decreased to $159 \text{ m}^2 \text{ g}^{-1}$, indicating the partial structural collapse of HOF after Pd²⁺ inclusion.

To illustrate the proof-of-concept of the HOF-based catalyst, the Suzuki–Miyaura coupling reaction was selected as a model reaction to examine the catalytic activity of HOF-19 \supset Pd(II). As can be found in Table 1, in the presence of 0.260 mmol % HOF-19 \supset Pd(II), the halogenated benzene substrates (entries 1–6) were successfully transformed to corresponding coupling products in the high isolation yields of 96–98% within a short time of 1.5–2.5 h. In particular, for the conversion of 1-bromo-4-nitrobenzene, only about 0.260% Pd content in HOF-19 \supset Pd(II) was revealed to be leached into the filtrate according to the ICP measurement, indicating the strong interaction between Pd²⁺ and HOF-19. Under the same conditions, the catalytic activity of 0.260 mmol % HOF-19 \supset Pd(II) is even comparable to the excellent performance of 0.500 mmol % COF-LZU1 \supset Pd(II) catalyst toward the reaction of 1-bromo-4-methoxybenzene with phenylboronic acid,¹² indicating the excellent catalytic activity of HOF-19 \supset Pd(II) (Table 1). Nevertheless, HOF-19 \supset Pd(II) shows a much higher catalytic efficiency in comparison with palladium acetate, a mixture of HOF-19 and

Table 1. Catalytic Performance of HOF-19 \supset Pd(II) Catalyst in the Suzuki–Miyaura Coupling Reaction^a


entry	R	X	time (h)	yield ^b (%)
1	–CHO	Br	2.5	97
2	–CN	Br	1.5	97
3	–H	Br	2.0	98
4	–NO ₂	Br	2.5	97
5	–OMe	Br	2.0	96
6	–OMe	I	1.5	97
7	–Ph	Br	4.0	19
8	–PhOMe	Br	4.0	13
9 ^c	–OMe	Br	4.0	96
10 ^d	–OMe	Br	4.0	71
11 ^e	–OMe	Br	4.0	70
12 ^f	–OMe	Br	4.0	~7
13 ^d	–Ph	Br	4.0	69
14 ^d	–PhOMe	Br	4.0	58

^aReaction conditions: aryl halide (1.00 mmol), phenylboronic acid (1.50 mmol), K₂CO₃ (2.00 mmol), HOF-19 \supset Pd(II) (7.5 mg, 0.260 mmol %), *p*-xylene (4 mL), 150 °C. ^bIsolation yield. ^c0.500 mmol % COF-LZU1 \supset Pd(II). ^d0.260 mmol % Pd(OAc)₂. ^e0.260 mmol % Pd(OAc)₂ and HOF-19 (7.5 mg). ^f0.260 mmol % Pd/C (10 wt %).

palladium acetate, and Pd/C catalyst, confirming the crucial role of palladium(II) ions deposited on the channel surfaces of HOF-19 on the present heterogeneous catalysis of the Suzuki–Miyaura coupling reaction. Interestingly, under the same reaction conditions, the substrates of 4'-bromo-1,1'-biphenyl and 4-methoxy-4'-bromo-1,1'-biphenyl with large molecular size of 7.5 × 13.9 and 7.5 × 16.0 Å, respectively, were converted into the corresponding product only with the isolation yield below 20% even after 4.0 h, which are even much lower than those with Pd(OAc)₂ as the catalyst (Table 1 and Table S3, Supporting Information), indicating the presence of pore size selectivity of the HOF-19 \supset Pd(II) catalyst.

The recyclability of HOF-19 \supset Pd(II) catalyst was evaluated in the conversion of 4-bromobenzonitrile. HOF-19 \supset Pd(II) kept an almost constant catalytic activity and good crystallinity for four cycles of reaction, indicating again the good stability of the HOF-based catalyst (Figures S6 and S10, Supporting Information). The isolated yield for the fifth reaction cycle was reduced to ca. 74%. After the continuous coupling reaction of 4-bromobenzonitrile for 20.0 h, HOF-19 \supset Pd(II) was deactivated with the low isolation yield of 46%. However, recrystallization of deactivated catalyst afforded a regenerated crystalline sample (Figure S11, Supporting Information). More importantly, this regenerated catalyst displayed a recovered catalytic activity toward 4-bromobenzonitrile with the 92% isolation yield (Figure S12, Supporting Information), revealing the sustainable advantage of this newly developed HOF-based catalyst.

In summary, a novel cage-based HOF with permanent porosity has been synthesized for the first time. Multiple hydrogen bonding interactions together with the π – π interactions enhance the stability of HOF. With this porous HOF as a robust support of palladium acetate, a highly efficient and selective HOF-based heterogeneous catalyst has been realized toward the Suzuki–Miyaura coupling reaction. In particular, by utilizing the recycling advantage of HOFs, this HOF-based catalyst could be easily regenerated through simple

recrystallization, exhibiting almost recovered activity. These results reveal the great application potentials of HOF-based catalysts. We hope the present result will ignite more research interest toward exploration of HOF-based catalysts and other applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b03766.

Experimental details, NMR spectra, TGA curve, SEM photos, PXRD patterns, XPS spectra, EDS mapping of HOF-19 and/or HOF-19 \supset Pd(II) (PDF)
Crystallographic data for HOF-19 (CIF)

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Notes

The authors declare no competing financial interest.

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