

Electronic Supporting information (ESI) for

Quantum cryo-sieving for H₂ isotope separation in microporous frameworks: An experimental study on the correlation between effective quantum sieving and pore size

Hyunchul Oh^a, Kyosung Park^b, Suresh Babu Kalidindi^c, Roland A. Fischer^c, Michael Hirscher^{*a}

^a Max Planck Institute for Intelligent Systems, Heisenbergstrasse 3, Stuttgart, Germany. E-mail: hirscher@is.mpg.de

^b Department of Chemistry, University of Liverpool, Liverpool, UK

^c Inorganic Chemistry II-Organometallics & Materials Faculty of Chemistry and Biochemistry, Ruhr University Bochum 44780 Bochum, Germany

Experimental methods

Materials synthesis

ZIF-7: ZIF-7 was synthesized by modifying the reference given in ref.¹. Benzimidazole (BzIm) (500mg, 4.23mmol) and zinc nitrate tetrahydrate (1500mg, 5.75 mmol) were dissolved in 150ml of dimethylformamide(DMF). The solution was transferred in 200ml glass jar and tightly capped. The jar was heated at a rate of 5 °C/min to 130 °C in a programmable oven, held at this temperature for 48 hrs, then cooled at rate of 0.4°C/min to room temperature. White crystalline solid was collected by filtration and washed with DMF (20ml X 3) and dried in air. (680mg of solid was obtained.) **ZIF-8:** Commercially available sample of ZIF-8 (Basolite Z1200) is kindly provided by BASF SE

COFs: 1,4-benzene diboronic acid (BDDBA) was purchased from sigma Aldrich and Tetra(4-(dihydroxy)borylphenyl)methane was prepared from tetraphenylmethane according to literature procedure. COF-1 and COF-102 was prepared following the procedure reported by Yaghi et al.^{2,3} **COF-1:** The synthesis was carried out in a glass tube equipped with a Teflon stop-cock, measuring o.d. × i.d. = 80 × 64 mm² and length around 18 cm. The glass tube was loaded with 1,4-benzene diboronic acid (BDDBA) (300 mg) and 12 mL of a 1:1 v:v solution of mesitylene:dioxane. The tube was degassed at liquid N₂ temperature and Teflon stop-cock was closed under vacuum. The self-condensation reaction was carried out by aging the reaction tube for 3-4 days at 85 °C. The obtained product was filtered from the reaction mixture using a G2 crucible inside a glove box. The isolated white product was washed with 50 mL of THF and stored overnight in a fresh THF solvent. The solvent was removed under vacuum and later the framework was heated at 150 °C under vacuum (10⁻³ mbar) for 12-14 h to remove the solvent molecule from the pores. acetone (30 mL). The final product was established as COF-1 using IR spectroscopy, Powder XRD, and NMR(MAS) techniques. Yield: ~210 mg. **COF-102:** The synthesis of COF-102 is carried out using a procedure similar to COF-1. The reaction tube was charged with around 300 mg (0.60 mmol) of tetra(4-(dihydroxy)borylphenyl)methane and about 6.0 mL of a 1:1(v:v) mixture of mesitylene:dioxane solvent under argon. The rest of reaction was carried out similar to COF-1. The final product was established as COF-102 using IR spectroscopy, Powder XRD, N₂ BET and NMR(MAS)techniques. Yield: ~170 mg.

High-resolution low-pressure cryogenic H₂ BET measurement

The hydrogen adsorption/desorption isotherms of ZIF-7, -8, COF-1, -102 at various temperature (from 19.5 K to 70K) were measured with laboratory-designed volumetric adsorption equipment with temperature controlled cryostat and are described in details elsewhere⁴. Around 20 mg of ZIF-7, -8, COF-1 and -102 were activated under ultra-high vacuum at 400 K for overnight prior to each measurement. For the laboratory-designed cryostat, the temperature control was calibrated by measuring the liquefaction pressure for hydrogen, deuterium and nitrogen in the empty sample chamber at various temperatures.

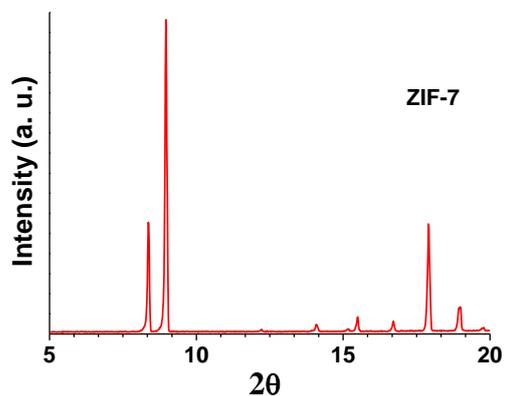


Figure S1. Powder XRD patterns of ZIF-7 (Mo source)

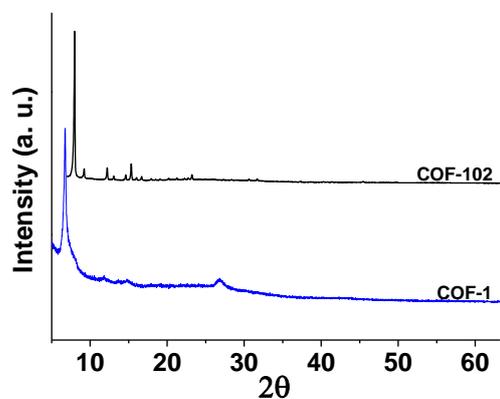


Figure S2. Powder XRD patterns of COF-1 and COF-102 (Cu source)

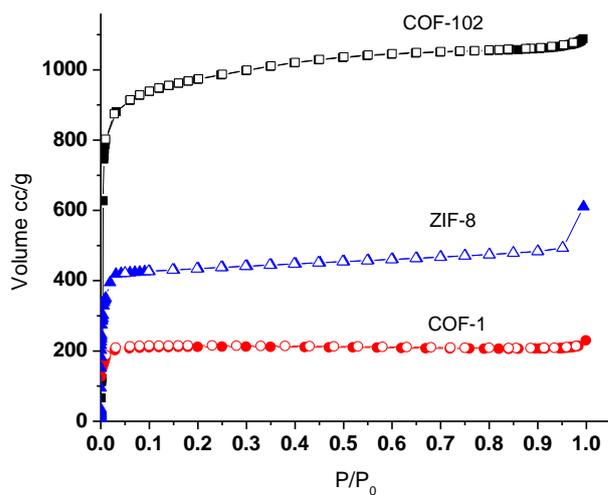


Figure S3. Nitrogen adsorption/desorption isotherm of ZIF-8, COF-1 and COF-102. Closed symbol indicates adsorption and open symbol indicates desorption isotherm.

Hydrogen and deuterium adsorption and desorption isotherm: closed symbol is adsorption and open symbol is desorption at various temperature (19.5 K to 70 K).

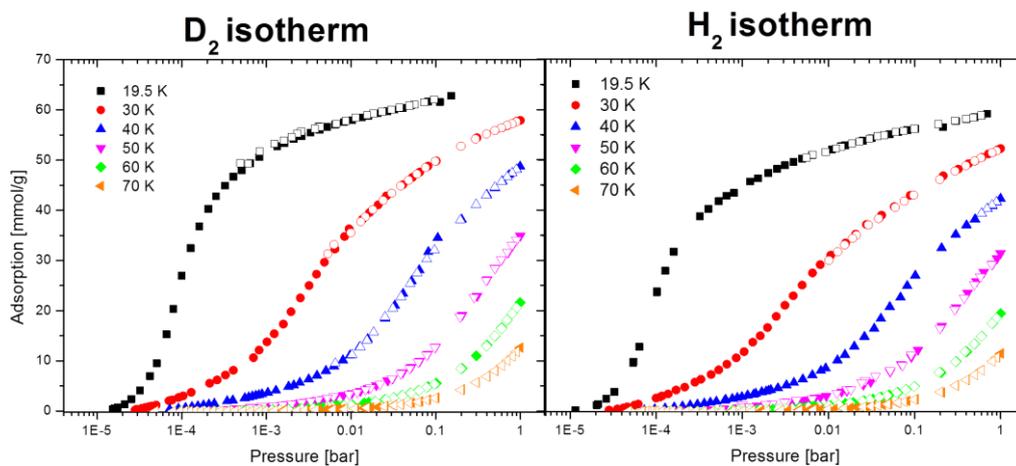


Figure S4. COF-102

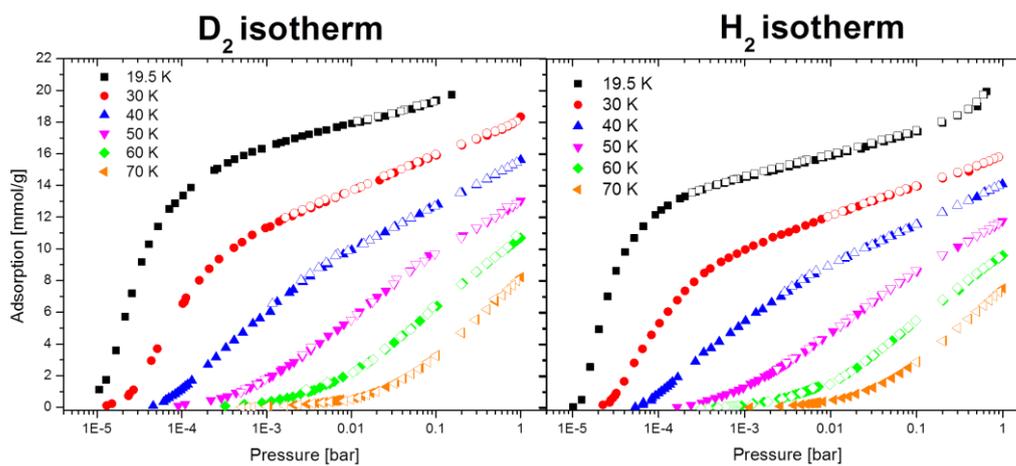


Figure S5. COF-1

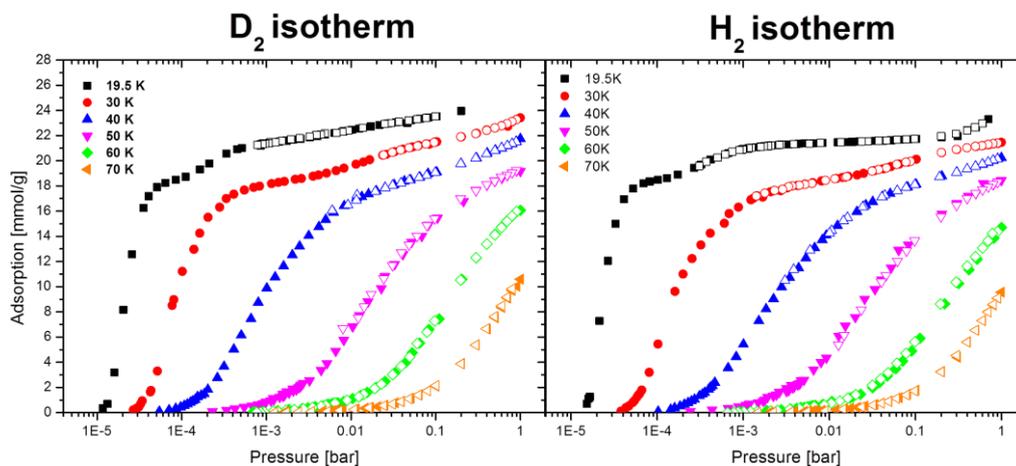


Figure S6. ZIF-8

Evaluation of the isosteric heat of adsorption

The isosteric heat of adsorption is typically calculated from hydrogen isotherm measurement, e.g. at liquid nitrogen (77 K) and liquid Ar (87 K) temperature. This simple calculation, however, results in a high uncertainty due to the small temperature range. Therefore, hydrogen adsorption isotherms are measured over a wider temperature range within 19.5 K to 70 K, allowing the determination of the heat of adsorption for a wide range of surface coverage in order to minimize the uncertainty. Although the uncertainty can be minimized by applying various temperatures, however, there also exist measurement errors as shown heat of adsorption step in figure 3. This is due to the variation of applied temperature from 19.5 K to 70 K (figure S7), and this heat of adsorption should be consecutive. The isosteric heat of adsorption is calculated from the measured absolute isotherms according to

$$\Delta H = R \cdot \left(\frac{\partial \ln(P)}{\partial \frac{1}{T}} \right)_{\theta}$$

where θ is the surface coverage, R is the gas constant, P the pressure and T the temperature. Therefore $\ln(P)$ is plotted versus the reciprocal temperature $1/T$ for different surface coverage θ . This is shown in figure S7 for ZIF-8, COF-1 and COF-102. The slope of the linear fit to this data for each surface coverage θ is proportional to the isosteric heat of adsorption.

$\ln(P)$ versus $1/T$

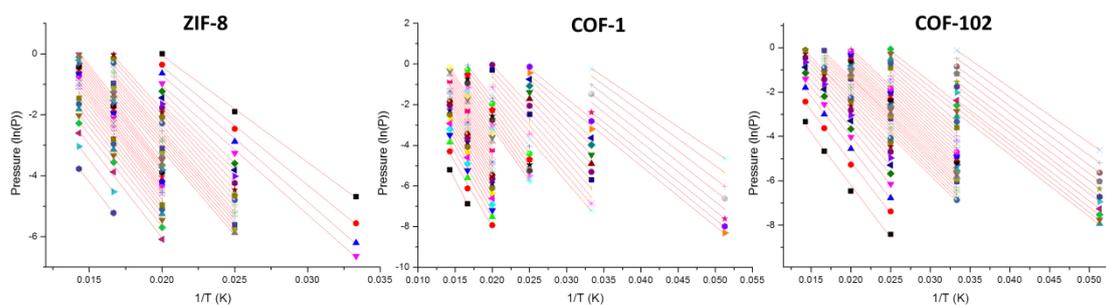


Figure S7 $\ln(P)$ versus $1/T$ of ZIF-8, COF-1 and COF-102 based on hydrogen adsorption isotherm

Reference

1. O. M. Yaghi, K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae and M. O'Keeffe, *P Natl Acad Sci USA*, 2006, **103**, 10186-10191.
2. A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166-1170.
3. O. M. Yaghi, H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Cote, R. E. Taylor and M. O'Keeffe, *Science*, 2007, **316**, 268-272.
4. B. Streppel and M. Hirscher, *Physical Chemistry Chemical Physics*, 2011, **13**, 3220-3222.