

Storage of hydrogen, methane, carbon dioxide in electron-rich porous aromatic framework (JUC-Z2)

Cuiying Pei · Teng Ben · Yan Cui · Shilun Qiu

Received: 2 May 2012 / Accepted: 4 September 2012 / Published online: 24 October 2012
© Springer Science+Business Media, LLC 2012

Abstract A 2D microporous electron-rich porous aromatic framework JUC-Z2 with high physicochemical stability and large surface area was studied in detail for their low-pressure N₂, Ar, H₂, CO₂, CH₄ sorption. Its hydrogen, methane, and carbon dioxide storage capacities are 181 cm³ g⁻¹ (77 K/760 mmHg), 25 cm³ g⁻¹ (273 K/760 mmHg), and 71 cm³ g⁻¹ (273 K/760 mmHg), respectively. Gas molecule recognition at 273 K was performed and results show only greenhouse gases such as carbon dioxide and methane could be adsorbed onto JUC-Z2.

Keywords Porous aromatic framework · Gas storage · Microporous materials · Electron-rich frameworks · Polytriphenylamine

1 Introduction

Carbon dioxide emission deriving from the burning of fossil fuels brings a pressing global environment problem, such as global warming, sea level rise, and an irreversible increase of the acidity levels of the oceans. There are many efforts aimed at reducing greenhouse gas emissions and moving toward a cleaner energy future even though several technical challenges existed in each case. Employing highly porosity materials as storage media in carbon capture and storage (CCS) (IPCC 2005) and clean energy application is a promising strategy. In these decades, porous

organic frameworks (POFs) such as metal-organic frameworks (MOFs) (Yaghi et al. 2003; Mulfort et al. 2010; Salles et al. 2010; Sumida et al. 2012; Guo et al. 2011), covalent organic frameworks (COFs) (Côté et al. 2005; El-Kaderi et al. 2007; Wan et al. 2008, 2009; Mohanty et al. 2011), conjugated microporous polymers (CMPs) (Jiang et al. 2007; Chen et al. 2010; Dawson et al. 2011; Li et al. 2010), polymers of intrinsic microporosity (PIMs) (McKeown et al. 2005; McKeown and Budd 2006; Ghanem et al. 2010), hyper-crosslinked polymers (HCPs) (Wood et al. 2007; Tsyurupa and Davankov 2002; Germain et al. 2007), and porous aromatic frameworks (PAFs) (Ben et al. 2009, 2011a, 2011b; Peng et al. 2011; Ren et al. 2010; Yuan et al. 2011; Lu et al. 2011) have been synthesized and their application in gas storage, catalysis, molecular recognition were explored (Cao et al. 2009; Trewin et al. 2008; Alam and Mokaya 2010). The first gas sorption method to detect the pore structure of POFs was established by Yaghi et al. and Williams et al. in 1998 and 1999 by Langmuir and Brunauer-Emmett-Teller (BET) theory respectively, which was proved to be a standard of characterization of porosity of microporous organic frameworks (Eddaoudi et al. 1998; Chui et al. 1999). In 2009, Yaghi and coworkers studied the hydrogen, methane, and carbon dioxide in COFs for the first time, which showed a significant gas storage capacities at that time (Furukawa and Yaghi 2009).

In 2009, our group have developed a method to synthesize the first long range ordered PAFs, PAF-1 (Ben et al. 2009), with *dia* topology, ultrahigh surface area ($S_{\text{BET}} = 5640 \text{ m}^2 \text{ g}^{-1}$) and exceptional physicochemical stability via a nickel(0)-catalyzed Yamamoto-type (Yamamoto 1999) Ullmann cross-coupling (Zhou et al. 2007). Besides, PAF-1 also show very high uptakes of hydrogen (7.0 wt% excess at 77 K/48 bar) and carbon dioxide (1.3 g g⁻¹ at 40 bar, 298 K) to make it a good candidate for gas storage. To

C. Pei · S. Qiu (✉)
State Key Laboratory of Inorganic Synthesis & Preparative
Chemistry, Jilin University, Changchun, 130012, China
e-mail: sqiu@jlu.edu.cn

T. Ben · Y. Cui
Department of Chemistry, Jilin University, Changchun, 130012,
China

our best knowledge, a very recent reported PPN-4 (Yuan et al. 2011) have the highest surface area of $6461 \text{ m}^2 \text{ g}^{-1}$ among all microporous solids, which was synthesized by optimized Yamamoto-type Ullmann cross-coupling reaction. This polymer was firstly reported by Cooper et al. ($S_{\text{BET}} = 1102 \text{ m}^2 \text{ g}^{-1}$) (Holst et al. 2010) and our group (known as PAF-3, $S_{\text{BET}} = 2932 \text{ m}^2 \text{ g}^{-1}$) (Ben et al. 2011a). Combined with such an impressive surface area, PPN-4 can adsorb 2121 mg g^{-1} carbon dioxide (212 wt%) at 50 bar/295 K and hydrogen 158 mg g^{-1} at 77 K/90 bar and methane 389 mg g^{-1} at 295 K/55 bar. Compared with MOFs, covalently linked POFs such as CMPs, PIMs, HCPs and PAFs share excellent physicochemical stability and high surface area. According to these studies, the key features of such ideal material are high porosity, large surface areas, high physicochemical stability and suitable heats of sorption.

Previously we had reported a 2D microporous aromatic framework JUC-Z2 with *hcb* topology (Ben et al. 2011b). It was prepared *via* Yamamoto-type Ullmann cross-coupling reaction combining the thermodynamic strength of covalent bond with the triphenylamine (TPA) unit. TPA possesses a central nitrogen atom and three electron-rich phenyl groups, which intrigued us to design and synthesize JUC-Z2 with *hcb* topology by self-polymerization of C3 TPA derivatives. Since JUC-Z2 entirely constructed from electron-rich secondary building unit (SBU) and strong covalent bond, it has high thermal stabilities (430°C), combined with high surface area ($S_{\text{BET}} = 2034 \text{ m}^2 \text{ g}^{-1}$). According to our previously study, PAFs show high uptakes and high selectivity of greenhouse gases such as CO_2 and CH_4 . Herein, we report the application of JUC-Z2 in clean energy storage and greenhouse gases capture.

2 Experimental section

2.1 TGA experiment

The thermogravimetric analysis (TGA) was performed using a SHIMADZU DTG-60 thermal analyzer with a ramp rate of $10^\circ\text{C min}^{-1}$ in dry air atmosphere.

2.2 CO_2 cyclic adsorption and regeneration measurement

CO_2 cyclic adsorption (25°C) and regeneration (85°C) was measured on SHIMADZU DTG-60 thermal analyzer in ultra-high-purity grade carbon dioxide atmosphere. In this case, 2.26 mg sample was heated from 25°C to 85°C at the heating rate of $10^\circ\text{C min}^{-1}$, and then cooled to 25°C in ultra-high-purity grade carbon dioxide.

2.3 Low-pressure gas adsorption measurements

Samples of a known weight (50 mg) were loaded into a pre-weighed sample tube. The sample was immersed in water, ethanol and chloroform respectively to remove solvent residue and starting materials in the pore. All the volatile entities were removed by heating at 200°C under vacuum for 10 h. Low-pressure Ar, H_2 , CH_4 and CO_2 adsorption measurements (up to 760 mmHg) were performed on Micromeritics ASAP 3020 surface area and porosimetry analyzer. After evacuation, the tube containing degassed samples were precisely weighted again to obtain the mass of evacuated samples. Ultra-high-purity grade Ar, H_2 , CO_2 (99.999 % purity) and CH_4 gases (99.99 % purity) were used for all adsorption measurements. Free space was measured using helium (99.999 % purity), assuming that the helium is not adsorbed at any of the studied temperatures. H_2 isotherms at 77 K were measured in a liquid nitrogen bath, H_2 isotherms at 87 K were measured in liquid argon bath, H_2 , Ar, N_2 , CO_2 and CH_4 isotherms at 273 K were measured in an ice-water bath.

3 Results and discussion

3.1 Material synthesis and characterization

The as-synthesized sample JUC-Z2 were obtained according the published literatures (Ben et al. 2011b). Yamamoto-type (Yamamoto 1999) Ullmann reaction (Zhou et al. 2007) route was used to synthesize JUC-Z2, in which $\text{Ni}(\text{COD})_2$ catalyst would restrict the cross-coupling of paratribromotribenzylaniline (TBTA) monomer at the 4-position. To verify the identity, Fourier transform infrared (FTIR), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and N_2 adsorption measurement were performed on the sample. The results demonstrated that the as-synthesized sample with *hcb* topology exhibited well-defined uniform micropore distribution (1.2 nm), high surface area ($S_{\text{BET}} = 2034 \text{ m}^2 \text{ g}^{-1}$), high physical stability (stable up to 430°C). These confirmed the success of synthesis.

3.2 Hydrogen storage

Hydrogen storage is of great interest as a possible substitute for fossil fuels for zero-emission energy technology. We first investigated the hydrogen storage properties of JUC-Z2 because it has suitable micropore, large surface area, microporous volume, and stability against moisture which makes it proper for clean energy storage.

The low-pressure H_2 isotherms of JUC-Z2 were shown in Fig. 1. In the case of JUC-Z2, an initial steep increase in H_2 uptake at low pressure is observed, which is common in

Fig. 1 (a) Low pressure H_2 adsorption (solid symbols) and desorption (open symbols) isotherms of JUC-Z2 at 77 K (black circle) and 87 K (red triangle), insert shows the structure of JUC-Z2 in stick style (carbon in white, nitrogen in blue); (b) Q_{stH_2} of JUC-Z2 as a function of the amount of H_2 adsorbed

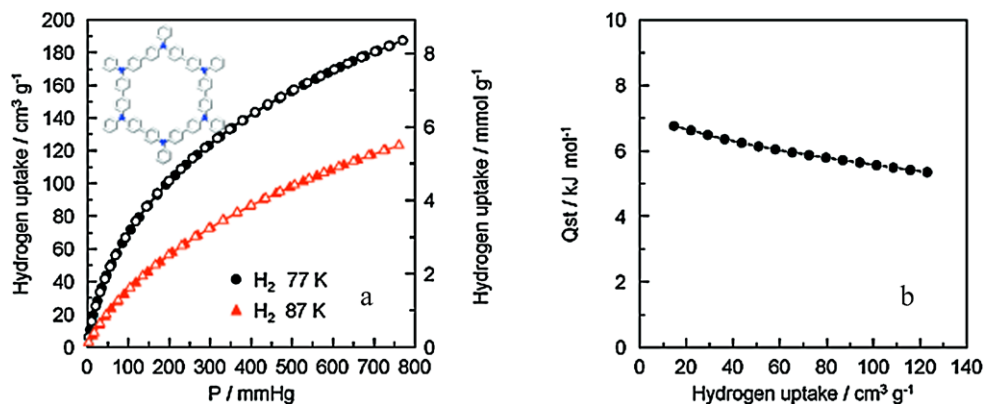
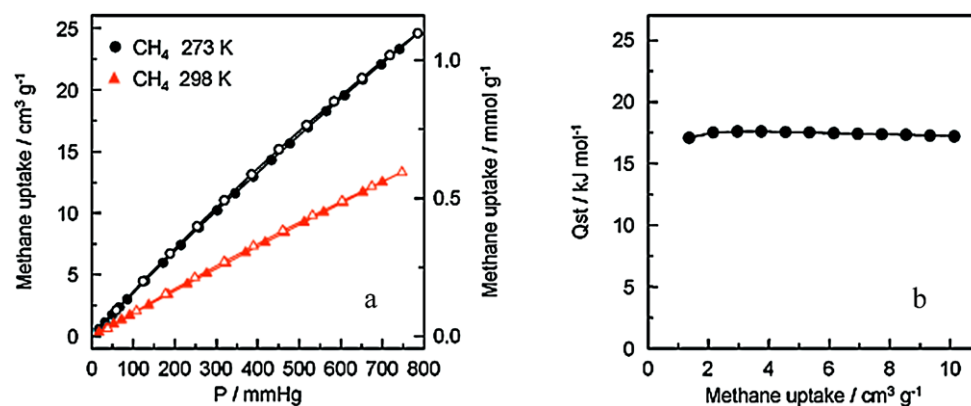


Fig. 2 (a) Low pressure CH_4 adsorption (solid symbols) and desorption (open symbols) isotherms of JUC-Z2 at 273 K (black circle) and 298 K (red triangle); (b) Q_{stCH_4} of JUC-Z2 as a function of the amount of CH_4 adsorbed



PAFs (Ben et al. 2009, 2011a, 2011b; Peng et al. 2011; Ren et al. 2010; Yuan et al. 2011). The hydrogen isotherms with unsaturated loaded and no hysteresis loops confirmed the physisorption reversibility. In this low-pressure range, JUC-Z2 exhibits the maximum hydrogen uptake ($181 \text{ cm}^3 \text{ g}^{-1}$) corresponding to 1.62 wt% at 77 K and it appears to be $123 \text{ cm}^3 \text{ g}^{-1}$ at 87 K. This H_2 uptake is almost the same as PAF-1 ($186 \text{ cm}^3 \text{ g}^{-1}$ at 77 K/1 bar) reported by us previously (Ben et al. 2011a). Microporous volume and surface area of JUC-Z2 were not only the factor impacting the capacity of hydrogen uptake; H_2 heat of adsorption (Q_{stH_2}) related to the H_2 -adsorbent interaction was 6.8 kJ mol^{-1} , which was calculated with Clausius-Clapeyron equation from the sorption data collected at 77 K and 87 K.

3.3 Methane storage

Concerning over the carbon dioxide emission resulting from the burning of high-carbon fossil fuels, such as coal and petroleum, alternative fuel methane which is featured by higher hydrogen-carbon ratio, low cost, huge reserves around the world, becomes a good candidate. However, methane can't be liquefied at room temperature which will cost much on transporting and storage. Previously reports revealed that methane could be adsorbed in microporous materials and reversibly released at mild condition. During

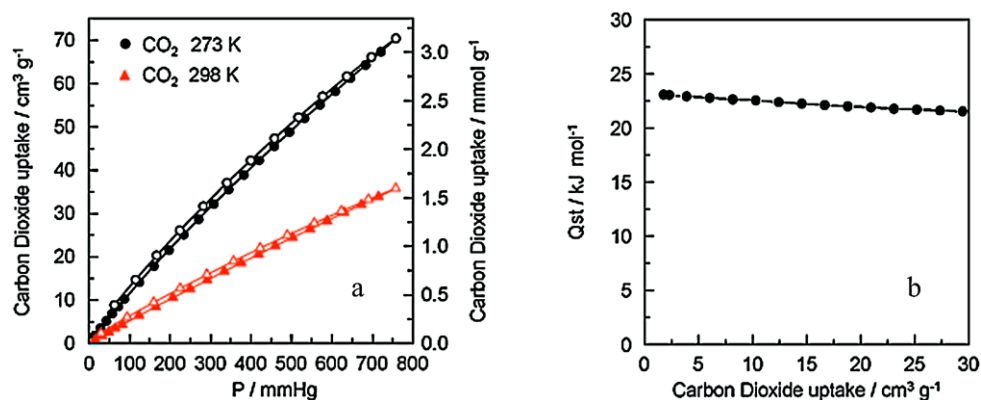
the sorption process, host framework holds guest methane via H- π interaction, it is anticipated that JUC-Z2 with aromatic building blocks and lone pairs at the nitrogen atoms will possess optimal methane uptake.

The adsorption isotherms of CH_4 were measured at 273 K and 298 K with activated JUC-Z2; it shows a nearly linear isotherm in a pressure change within 760 mmHg (Fig. 2). The uptake value of CH_4 was $25 \text{ cm}^3 \text{ g}^{-1}$ at 273 K and 760 mmHg, corresponding to 1.76 wt%. When the temperature increased to 298 K, the CH_4 uptake decreased to $13 \text{ cm}^3 \text{ g}^{-1}$ at 760 mmHg. The CH_4 heat of adsorption (Q_{stCH_4} for short) is 17.1 kJ mol^{-1} . Which is higher than PAF-1 (Ben et al. 2011a) ($Q_{stCH_4} = 14.0 \text{ kJ mol}^{-1}$) suggests that the electro-rich framework has special strong interactions with CH_4 .

3.4 Carbon dioxide storage

Figure 3 shows the low-pressure adsorption and desorption properties for CO_2 determined through the volumetric measurements at 273 K and 298 K. No hysteresis on adsorption and desorption isotherms demonstrate the reversible process of CO_2 storage in JUC-Z2. The electron-rich JUC-Z2 has an exceptionally high density of binding sites with a strong affinity for CO_2 , it is expected that 0.76 CO_2 occupied one SBU of JUC-Z2 at 273 K and 760 mmHg, resulting in

Fig. 3 (a) Low pressure CO₂ adsorption (solid symbols) and desorption (open symbols) isotherms of JUC-Z2 at 273 K (black circle) and 298 K (red triangle); (b) Q_{stCO_2} of JUC-Z2 as a function of the amount of CO₂ adsorbed



71 cm³ g⁻¹ CO₂ uptake in that condition. Additionally, the quantity of CO₂ adsorbed in JUC-Z2 is higher than that in PAF-1 as a result of the Lewis acid-base interactions which existed between the electron rich aromatic constituents and the electron poorer carbon dioxide molecules, and also between lone pairs at the nitrogen atoms and carbon dioxide.

Based on the two CO₂ sorption isotherms at 273 K and 298 K, JUC-Z2 has a heat of adsorption of 23.1 kJ mol⁻¹ which is stronger than physical sorption interactions (about 5–20 kJ mol⁻¹) for storage considerable greenhouse gases, but weaker than strong chemisorptive interactions (>50 kJ mol⁻¹) for regeneration sorbent. Additionally, the heat of sorption curve does not change significantly with the increase of CO₂ loaded. These impressive uptake and adsorption enthalpies of JUC-Z2 exhibit potential application in CCS.

3.5 CO₂ cyclic adsorption and regeneration

The above mentioned experiments indicated that JUC-Z2 shows great promising to be a CO₂ adsorber with high CO₂ storage capacity, chemical stability towards H₂O, O₂ as well as good thermal stability. However, concerns were raised over the penalty of energy to regenerate the materials after CO₂ adsorption. Figure 4 shows the CO₂ cyclic adsorption (25 °C) and regeneration (85 °C) of JUC-Z2 at ambient pressure. It undergoes a regeneration process at 85 °C from the adsorption condition at 25 °C with the weight change of 3.78 %, subsequently, the weight change of 3.72 % was observed in the second CO₂ adsorption and regeneration cycle, while the weight change was found to be 3.73 % in the third cycle, which implies excellent repeatability when applying JUC-Z2 as a CO₂ adsorber. The reversible and stable adsorption and regeneration process at ambient temperature and pressure is a key factor in the capture of greenhouse gas carbon dioxide.

3.6 Gas recognition

There are two main carbon capture technologies to reduce CO₂ emissions to the atmosphere, namely precom-

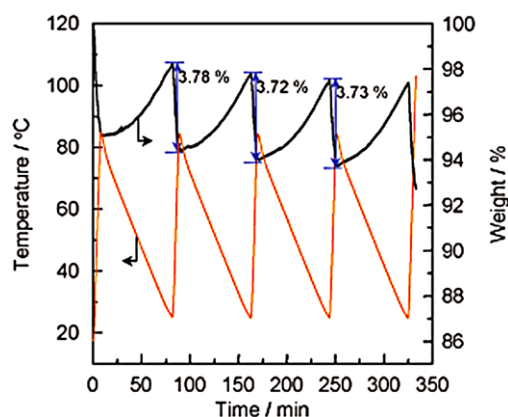


Fig. 4 CO₂ cyclic adsorption (25 °C) and regeneration (85 °C) of JUC-Z2 (black), temperature in red

bustion (predominantly CO₂/H₂ separation) and postcombustion (predominantly CO₂/N₂ separation after flue gas is dried) (Trachtenberg et al. 2007). Postcombustion flue gas emitted from coal-fired power plants at a total pressure of 1 bar consists of 15–16 % CO₂, 6–7 % H₂O, 3–4 % O₂ and about 70 % N₂, therefore the partial pressure of CO₂ is 0.13–0.16 bar (Granite and Pennline 2002; Jassim and Rochelle 2006; Lee and Sircar 2008; White et al. 2003). For the separation of CO₂ and CH₄ from N₂ in flue gas and natural gas respectively, sorbents with high and reversible gas uptake, high gas selectivity, good physicochemical stability and low cost are desired. Figure 5 compares the amounts of CO₂, CH₄, N₂, H₂ and Ar adsorbed in low-pressure range at 273 K on JUC-Z2, respectively. Almost no adsorption of N₂, H₂, Ar is observed, while CH₄ and CO₂ adsorption show much stronger at 760 mmHg. It demonstrated that JUC-Z2 could efficiently separate CO₂ and CH₄ from H₂, Ar and N₂. The observed results are consistent with the hypothesis that CO₂ and CH₄ could be concentrated primarily at typical atmospheric condition.

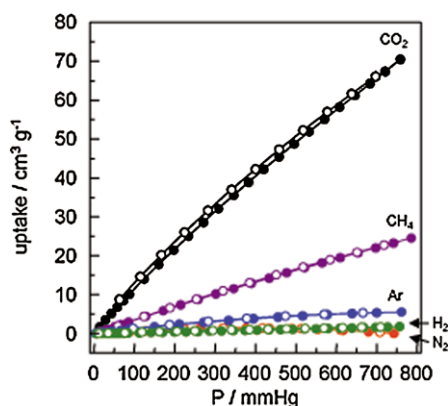


Fig. 5 Low pressure N₂ (red), Ar (blue), H₂ (olive), CO₂ (black) and CH₄ (purple) sorption of JUC-Z2 at 273 K

4 Conclusion

In conclusion, the results above demonstrate the importance of electron-rich JUC-Z2 for CO₂ capture and H₂, CH₄ storage. Electron-rich aromatic blocks and nitrogen atoms with lone pairs make JUC-Z2 a Lewis base, showing strong interaction with electron poor CO₂ molecular. In addition, high electron density structure leading to strong H– π interaction between CH₄ and JUC-Z2. These make JUC-Z2 show high CH₄ uptake and selectivity. The high amount of CO₂ adsorbed by JUC-Z2 at ambient condition and impressive selectivity for CO₂ over N₂ as well as low consumption regeneration process suggests JUC-Z2 to be an effective CO₂ catcher. The H₂, CO₂, CH₄ storage capability of electron-rich aromatic framework JUC-Z2 make it greatly promising for applications dealing with environmental greenhouse gases pollutant problems.

Acknowledgements This work was supported by the State Basic Research Project (2011CB808703), NSFC (Grant nos. 91022030, 20771041), “111” program of Ministry of Education, International Cooperation Project of Ministry of Science and Technology (2006DFA41190), Jilin Science and Technology Department Project (20106021).

References

Alam, N., Mokaya, R.: Evolution of optimal porosity for improved hydrogen storage in templated zeolite-like carbons. *Energy Environ. Sci.* **3**, 1773–1781 (2010)

Ben, T., Ren, H., Ma, S., Cao, D., Lan, J., Jing, X., Wang, W., Xu, J., Deng, F., Simmons, J.M., Qiu, S., Zhu, G.: Targeted synthesis of a porous aromatic framework with high stability and exceptionally high surface area. *Angew. Chem., Int. Ed. Engl.* **48**, 9457–9460 (2009)

Ben, T., Pei, C., Zhang, D., Xu, J., Deng, F., Jing, X., Qiu, S.: Gas storage in porous aromatic frameworks (PAFs). *Energy Environ. Sci.* **4**, 3991–3999 (2011a)

Ben, T., Shi, K., Cui, Y., Pei, C., Zuo, Y., Guo, H., Zhang, D., Xu, J., Deng, F., Tian, Z., Qiu, S.: Targeted synthesis of an electroactive organic framework. *J. Mater. Chem.* **21**, 18208–18214 (2011b)

Cao, D., Lan, J., Wang, W., Smit, B.: Lithium-doped 3D covalent organic frameworks: high-capacity hydrogen storage materials. *Angew. Chem., Int. Ed. Engl.* **48**, 4730–4733 (2009)

Chen, L., Honsho, Y., Seki, S., Jiang, D.: Light-harvesting conjugated microporous polymers: rapid and highly efficient flow of light energy with a porous polyphenylene framework as antenna. *J. Am. Chem. Soc.* **132**, 6472–6478 (2010)

Chui, S.S., Lo, S.M., Charmant, P., Orpen, H.A.G., Williams, I.D.: A chemically functionalizable nanoporous material [Cu₃(TMA)₂(H₂O)₃]_n. *Science* **283**, 1148–1150 (1999)

Côté, A.P., Benin, A.I., Ockwig, N.W., O’Keeffe, M., Matzger, A.J., Yaghi, O.M.: Porous, crystalline, covalent organic frameworks. *Science* **310**, 1166–1170 (2005)

Dawson, R., Stöckel, E., Holst, J.R., Adams, D.J., Cooper, A.I.: Microporous organic polymers for carbon dioxide capture. *Energy Environ. Sci.* **4**, 4239–4245 (2011)

Eddaoudi, H.L., Groy, T.L., Yaghi, O.M.: Establishing microporosity in open metal-organic frameworks: gas sorption isotherms for Zn(BDC) (BDC = 1,4-benzenedicarboxylate). *J. Am. Chem. Soc.* **120**, 8571–8572 (1998)

El-Kaderi, H.M., Hunt, J.R., Mendoza-Cortés, J.L., Côtés, A.P., Taylor, R.E., O’Keeffe, M., Yaghi, O.M.: Designed synthesis of 3D covalent organic frameworks. *Science* **316**, 268–272 (2007)

Furukawa, H., Yaghi, O.M.: Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy application. *J. Am. Chem. Soc.* **131**, 8875–8883 (2009)

Germain, J., Fréchet, M.J., Svec, F.: Hypercrosslinked polyanilines with nanoporous structure and high surface area: potential adsorbents for hydrogen storage. *J. Mater. Chem.* **17**, 4989–4997 (2007)

Ghanem, B.S., Hashem, M., Harris, K.D.M., Msayib, K.J., Xu, M., Budd, P.M., Chaukura, N., Book, D., Tedds, S., Walton, A., McKeown, N.B.: Triptycene-based polymers of intrinsic microporosity: organic materials that can be tailored for gas adsorption. *Macromolecules* **43**, 5287–5294 (2010)

Granite, E.J., Pennline, H.W.: Photochemical removal of mercury from flue gas. *Ind. Eng. Chem. Res.* **41**, 5470–5476 (2002)

Guo, Z., Wu, H., Srinivas, G., Zhou, Y., Xiang, S., Chen, Z., Yang, Y., Zhou, W., O’Keeffe, M., Chen, B.: A metal-organic framework with optimized open metal sites and pore spaces for high methane storage at room temperature. *Angew. Chem.* **123**, 3236–3239 (2011)

Holst, J.R., Stöckel, E., Adams, D.J., Cooper, A.I.: High surface area networks from tetrahedral monomers: metal-catalyzed coupling, thermal polymerization, and “click” chemistry. *Macromolecules* **43**, 8531–8538 (2010)

IPCC (Intergovernmental Panel on Climate Change): CO₂ Capture and Storage, a Special Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge (2005)

Jassim, M.S., Rochelle, G.T.: Innovative absorber/stripper configurations for CO₂ capture by aqueous monoethanolamine. *Ind. Eng. Chem. Res.* **45**, 2465–2472 (2006)

Jiang, J., Su, F., Trewin, A., Wood, C.D., Campbell, N.L., Niu, H., Dickinson, C., Ganin, A.Y., Rosseinsky, M.J., Khimyak, Y.Z., Cooper, A.I.: Conjugated microporous poly(aryleneethynylene) networks. *Angew. Chem., Int. Ed. Engl.* **46**, 8574–8578 (2007)

Lee, K.B., Sircar, S.: Removal and recovery of compressed CO₂ from flue gas by a novel thermal swing chemisorption process. *AIChE J.* **54**, 2293–2302 (2008)

Li, A., Lu, R., Wang, Y., Han, K., Deng, W.: Lithium-doped conjugated microporous polymers for reversible hydrogen storage. *Angew. Chem., Int. Ed. Engl.* **49**, 3330–3333 (2010)

Lu, W., Yuan, D., Sculley, J., Zhao, D., Krishna, R., Zhou, H.: Sulfonate-grafted porous polymer networks for preferential CO₂ adsorption at low pressure. *J. Am. Chem. Soc.* **133**, 18126–18129 (2011)

- McKeown, N.B., Budd, P.M.: Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage. *Chem. Soc. Rev.* **35**, 675–683 (2006)
- McKeown, N.B., Budd, P.M., Msayib, K.J., Ghanem, B.S., Kingston, H.J., Tattershall, C.E., Makhseed, S., Reynolds, K.J., Fritsch, D.: Polymers of intrinsic microporosity (PIMs): bridging the void between microporous and polymeric materials. *Eur. J. Chem.* **11**, 2610–2620 (2005)
- Mohanty, P., Kull, L.D., Landskron, K.: Porous covalent electron-rich organonitridic frameworks as highly selective sorbents for methane and carbon dioxide. *Nat. Commun.* (2011). doi:10.1038/ncomms1405
- Mulfort, K.L., Farha, O.K., Malliakas, C.D., Kanatzidis, M.G., Hupp, J.T.: An interpenetrated framework material with hysteretic CO₂ uptake. *Eur. J. Chem.* **16**, 276–281 (2010)
- Peng, Y., Ben, T., Xu, J., Xue, M., Jing, X., Deng, F., Qiu, S., Zhu, G.: A covalently-linked microporous organic-inorganic hybrid framework containing polyhedral oligomeric silsesquioxane moieties. *Dalton Trans.* **40**, 2720–2724 (2011)
- Ren, H., Ben, T., Wang, E., Jing, X., Xue, M., Liu, B., Cui, Y., Qiu, S., Zhu, G.: Targeted synthesis of a 3D porous aromatic framework for selective sorption of benzene. *Chem. Commun.* **46**, 291–293 (2010)
- Salles, F., Maurin, G., Serre, C., Llewellyn, P.L., Knöfel, C., Choi, H.J., Filinchuk, Y., Oliviero, L., Vimont, A., Long, J.R., Férey, G.: Multistep N₂ breathing in the metal-organic framework Co(1, 4-benzenedipyrazolate). *J. Am. Chem. Soc.* **132**, 13782–13788 (2010)
- Sumida, K., Rogow, D.L., Mason, J.A., McDonald, T.M., Bloch, E.D., Herm, Z.R., Bae, T., Long, J.R.: Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* **112**, 724–781 (2012)
- Trachtenberg, M.C., Cowan, R.M., Smith, D.A.: In: Proceedings of the Sixth Annual Conference on Carbon Capture & Sequestration, Pittsburgh (2007)
- Trewin, A., Darling, G.R., Cooper, A.I.: “Naked” fluoride binding sites for physisorptive hydrogen storage. *New J. Chem.* **32**, 7–20 (2008)
- Tsyurupa, M.P., Davankov, V.A.: Hypercrosslinked polymers: basic principle of preparing the new class of polymeric materials. *React. Funct. Polym.* **53**, 193–203 (2002)
- Wan, S., Guo, J., Kim, J., Ihee, H., Jiang, D.: A belt-shaped, blue luminescent and semiconducting covalent organic framework. *Angew. Chem., Int. Ed. Engl.* **47**, 8826–8829 (2008)
- Wan, S., Guo, J., Kim, J., Ihee, H., Jiang, D.: A photoconductive covalent organic framework: self-condensed arene cubes composed of eclipsed 2D polypyrene sheets for photocurrent generation. *Angew. Chem., Int. Ed. Engl.* **48**, 5439–5442 (2009)
- White, C.M., Strazisar, B.R., Granite, E.J., Hoffman, J.S., Pennline, H.W.: Separation and capture of CO₂ from large stationary sources and sequestration in geological formations-coalbeds and deep saline aquifers. *J. Air Waste Manage. Assoc.* **53**, 645–715 (2003)
- Wood, C.D., Tan, B., Trewin, A., Niu, H., Bradshaw, D., Rosseinsky, M.J., Khimyak, Y.Z., Campbell, N.L., Kirk, R., Stöckel, E., Cooper, A.I.: Hydrogen storage in microporous hypercrosslinked organic polymer networks. *Chem. Mater.* **19**, 2034–2048 (2007)
- Yaghi, O.M., O’Keeffe, M., Ockwig, N.W., Chae, H.K., Eddaoudi, M., Kim, J.: Reticular synthesis and the design of new materials. *Nature* **423**, 705–714 (2003)
- Yamamoto, T.: π -conjugated polymers bearing electronic and optical functionalities. Preparation by organometallic polycondensations, properties, and their applications. *Bull. Chem. Soc. Jpn.* **72**, 621–638 (1999)
- Yuan, D., Lu, W., Zhao, D., Zhou, H.: Highly stable porous polymer networks with exceptionally high gas-uptake capacities. *Adv. Mater.* **23**, 3723–3725 (2011)
- Yuan, Y., Sun, F., Ren, H., Jing, X., Wang, W., Ma, H., Zhao, H., Zhu, G.: Targeted synthesis of a porous aromatic framework with a high adsorption capacity for organic molecules. *J. Mater. Chem.* **21**, 13498–13502 (2011)
- Zhou, G., Baumgarten, M., Müllen, K.: Arylamine-substituted oligo(ladder-type pentaphenylene)s: electronic communication between bridged redox centers. *J. Am. Chem. Soc.* **129**, 12211–12221 (2007)