Targeted synthesis of electroactive porous organic frameworks containing triphenyl phosphine moieties

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A novel electroactive porous aromatic framework (JUC-Z4-Cl) was designed and synthesized via Yamamoto-type Ullmann cross-coupling reaction with the monomer tris(4-chlorophenyl)phosphine. By simple redox chemical reactions, stable, reductive, porous polytri(p-phenyl)phosphine (JUC-Z4) and polytri(p-phenyl)phosphine oxide (JUC-Z5) could be obtained as off-white powders. The structures of JUC-Z4 and JUC-Z5 were confirmed using magic-angle spinning nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, etc. The microporous architectures exhibit high stability (471°C for JUC-Z4 and 484°C for JUC-Z5) and large surface area (793 and 648 m² g⁻¹ for JUC-Z4 and JUC-Z5, respectively). JUC-Z4 also exhibits efficient recognition ability of greenhouse gases from dry air.

1. Introduction

Recently, ultra high surface area covalent-linked porous organic frameworks (POFs) such as porous aromatic
framework (PAF) [1–5], conjugated microporous polymer [6–10], covalent triazine-based framework [11], polymers of intrinsic microporosity [12,13], hyper-cross-linked polymer [14,15] and covalent organic framework [16–18] formed by organic polymerization method have emerged as an important platform in host–guest chemistry. The properties of POFs are crucially affected by their porosity when applied as a sorbent. In this respect, there have been many efforts aimed at developing methods of controlling the porosity, such as tailoring of the pore size, grafting of functional groups on the frameworks and inlaying of effective binding sites onto the organic frameworks [19–25]. Unfortunately, synthesized POFs have definite pore size and porous properties which are always fixed owing to the rigidity of frameworks. So far, few reports have focused on in situ control of porosity and on properties of POFs. It remains a great challenge to develop a method of preparing POFs with controllable pore structure and porous properties.

Recently, we have prepared an electroactive POF (JUC-Z2) that shows reversible pore structure through controlling redox state by electrochemistry [5]. But the oxidized and reduced states of JUC-Z2 were not stable and could not be isolated. This prompted us to find a suitable electroactive POF whose pore structure could be controlled by simple chemical redox reaction. Herein, we describe the synthesis of an electroactive porous organic framework (JUC-Z4-Cl) by polymerizing tris(4-chlorophenyl)phosphine via Yamamoto-type [26] Ullmann cross-coupling reaction [27]. It exhibits excellent physico-chemical stability, reversible redox state and controllable high surface area.

2. Experimental

(a) Material
Tris(4-chlorophenyl)phosphine, bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)2), 1,5-cyclooctadiene (cod), N,N-dimethylformamide (DMF) and 2,2′-bipyridyl were purchased from Sigma-Aldrich and used as received.

(b) Synthesis of JUC-Z4-Cl (scheme 1)
1,5-Cyclooctadiene (2.0 ml, 16.1 mmol, dried over CaH2) was added to a solution of Ni(cod)2 (4.4 g, 16.1 mmol) and 2,2′-bipyridyl (2.5 g, 16.1 mmol) in dehydrated DMF (400 ml), and the mixture was heated at 80°C for 1 h. Tris(4-chlorophenyl)phosphine (3.9 mmol) was added to the resulting purple solution, and the mixture was stirred at that temperature overnight to obtain a deep purple suspension. After cooling to room temperature, concentrated HCl was added to the mixture until it turned into a green suspension. After filtration, the residue was washed with H2O, C2H5OH and CHCl3, successively, and dried in vacuum to achieve JUC-Z4-Cl as an off-white powder (1.0 g, 98% yield).

(c) Oxidation of JUC-Z4-Cl (scheme 1)
H2O2 (200 ml, 30%) was added to a suspension of JUC-Z4-Cl (1.0 g, 3.9 mmol) in 100 ml EtOH, and the mixture was stirred for 12 h at room temperature. After that, H2O2 (50 ml, 30%) was added to the system again. Then the mixture was stirred at that temperature overnight. After filtration with 0.2 µm poly(vinylidene difluoride) membrane, the residue was washed with C2H5OH and CHCl3 several times and dried in vacuum to obtain JUC-Z5 as an off-white powder (1.1 g, 96% yield).

(d) Reduction of JUC-Z4-Cl (scheme 1, method 1)
JUC-Z4-Cl (1.0 g), 1,1,3,3-tetramethyldisiloxane (TMDS, 4.8 mmol), titanium(IV) isopropoxide (Ti(Oi-Pr)4, 0.4 mmol) and methylcyclohexane (50 ml) were mixed in a three-neck round-bottomed
flask under N$_2$. After stirring at 100°C for 24 h, the mixture was cooled to 0°C, and then 3 N KOH/EtOH was added. Then the ice bath was removed, and the mixture was stirred for 2 h at 50°C. The resulting mixture was washed with H$_2$O, HF and EtOH and dried under vacuum, yielding JUC-Z4 as an off-white powder (1.0 g).

**(e) Reduction of JUC-Z4-Cl (scheme 1, method 2)**

JUC-Z4-Cl (1.0 g, 3.63 mmol), CeCl$_3$·7H$_2$O (2.7 g, 6.26 mmol) and NaBH$_4$ (0.2 g, 5.45 mmol) were mixed in a three-neck flask under Ar atmosphere. MeOH (300 ml) was added at −84°C. The mixture was stirred for 90 min at that temperature, and then quenched by adding EtOAc (20 ml). Then, it was warmed to room temperature and washed with water under N$_2$ atmosphere several times. The residue was dried under vacuum and an off-white powder was obtained (0.90 g).
(f) Material characterization

The identities of JUC-Z4-Cl, JUC-Z4 and JUC-Z5 were confirmed by N₂ adsorption measurements, magic-angle spinning nuclear magnetic resonance (MAS NMR), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy.

(g) Low-pressure N₂ adsorption measurements

N₂ sorption isotherm measurements were performed with a Micromeritics Tristar II 3020 surface area and pore size analyser. Before the measurement, the sample was subjected to a degas vacuum system under ultra high vacuum (90 mtorr) at 200°C for 12 h. The sample was backfilled with nitrogen and transferred to the analysis system. A sample of 50 mg and ultra high purity-grade nitrogen (99.999%) gas source were used in the nitrogen sorption measurements at 77 K, maintained with liquid nitrogen throughout the measurement. Helium was used for the free space determination after sorption analysis, both at ambient temperature and at 77 K. Apparent surface areas were calculated from nitrogen adsorption data by multi-point Brunauer–Emmett–Teller (BET) analysis. Apparent micropore distributions were calculated from carbon dioxide adsorption data by the density functional theory (DFT) method.

(h) Magic-angle spinning nuclear magnetic resonance experiments

All solid-state NMR spectroscopy experiments were carried out at 9.4 T with a Varian Infinityplus-400 spectrometer, equipped with a Chemagnetic triple-resonance 7.5 mm probe, with resonance frequencies of 100.6 and 161.9 MHz for ¹³C and ³¹P, respectively. The MAS rate was set to 3–5 kHz. For the ¹H–¹³C cross-polarization (CP)/MAS NMR experiments, the Hartmann–Hahn condition was achieved using hexamethylbenzene (HMB), with a contact time of 2.0 ms and a repetition time of 2.0 s. ³¹P single-pulse experiments were performed with a 3.8 µs pulse width (π/2) and a 20 s recycle delay. The chemical shifts of ¹³C and ³¹P were referenced to HMB and an aqueous solution of H₃PO₄ (1 M).

(i) Thermogravimetric analysis, Fourier transform infrared spectroscopy and UV-visible experiments

The TGA was performed using a Shimadzu DTG-60 thermal analyser system at a heating rate of 10°C min⁻¹ to 800°C in a dried air atmosphere and the air flow rate was 30 ml min⁻¹. The sample was loaded in an alumina pan. The FTIR spectra (KBr, Aldrich) were measured using a Shimadzu IRAFFINITY-1 FTIR spectrometer. Samples were packed firmly to get transparent films. UV-visible spectra were recorded using a quartz cell of 1 cm path length with a Shimadzu UV-2450 spectrophotometer by dispersing samples in poly(ethylene glycol) (PEG) (Mₜₜ = 400, Aldrich).

(j) Low-pressure gas adsorption measurements

Low-pressure H₂, CH₄ and CO₂ adsorption measurements (up to 1 bar) were performed with a Micromeritics Tristar II 3020 surface area and pore size analyser. Ultra high-purity grade H₂, CO₂ (99.999%) and CH₄ gases (99.99%) were used for all adsorption measurements. Free space was measured using helium (99.999%), assuming that helium is not adsorbed at any of the studied temperatures. H₂ isotherms at 77 K were measured in a liquid nitrogen bath, H₂ isotherms at 87 K were measured in liquid argon bath, and CO₂ and CH₄ isotherms at 273 K were measured in an ice-water bath.

(k) Electrochemical experiments

Electrochemical experiments were performed with a CHI660C electrochemical workstation (CH Instruments, Inc.). The electrochemical behaviour of samples was investigated by using
Table 1. Parameters of dual-site Langmuir–Freundlich equation by fitting adsorption of pure CO₂, CH₄, H₂ and N₂.

<table>
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<th>k₁</th>
<th>n₁</th>
<th>N₂</th>
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<td>8.4664</td>
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A conventional three-electrode cell consisting of a platinum (Pt, 0.5 mm diameter) working microelectrode, a Pt foil auxiliary electrode and a non-aqueous Ag/Ag⁺ reference electrode. A JUC-Z4/Pt powder microelectrode was prepared according to the method reported in the literature [28]. All experiments were carried out at room temperature (25 ± 2°C).

(I) The ideal adsorption solution theory calculations

The excess adsorption data for pure CO₂, N₂, H₂ and CH₄ measured at 273 K were first converted to absolute loadings, along with Peng–Robinson equation of state. In order to perform the ideal adsorption solution theory (IAST) calculations, the single-component isotherms should be fitted by a proper model. The absolute component loadings were fitted using the dual-site Langmuir model:

\[ N^o(f) = \frac{N_1 k_1 f^{n_1}}{1 + k_1 f^{n_1}} + \frac{N_2 k_2 f^{n_2}}{1 + k_2 f^{n_2}}, \]

where \( f \) is the fugacity of bulk gas at equilibrium with adsorbed phase, \( N_i, k_i \) and \( n_i \) are model parameters of maximum adsorption amount at site \( i \) (\( i = 1 \) or 2), the affinity constant and the deviation from the simple Langmuir equation, respectively. The fitted constants are listed in table 1.

To investigate the separation of binary mixtures, the adsorption selectivity is defined by

\[ S_{ij} = \frac{x_i / y_i}{x_j / y_j}, \]

and calculated using the IAST of Myers & Prausnitz [29], where the selectivity refers to the first component over the second one, and \( x_i, x_j \) and \( y_i, y_j \) denote the molar fractions of species \( i, j \) in the adsorbed and bulk phases, respectively.

3. Results and discussion

(a) Synthesis

The as-synthesized JUC-Z4-Cl was obtained via optimized Yamamoto-type Ullmann cross-coupling reaction developed by our group in 2009 [1]. The reaction procedure was monitored by FTIR. The disappearance of C–Cl vibration at 507 cm⁻¹ indicated both the elimination of halogen and the success of phenyl–phenyl coupling (figure 1). The peak at 1180 cm⁻¹ was attributed to P=O stretching vibration [30], which clearly indicates that JUC-Z4-Cl is a partially oxidized or an intermediate oxidation state. After the reduction of JUC-Z4-Cl, the intensity of (P=O) of JUC-Z4 decreased accordingly, which demonstrated the partial cleavage of P=O bonds. We had tried different reduction methods (scheme 1, methods 1 and 2) to reduce the JUC-Z2-Cl, and the results indicated that it is difficult to obtain the pure reductive JUC-Z4 (figure 1). On the other hand, JUC-Z5, formed by oxidation of JUC-Z4, exhibits strong P=O infrared vibration signal.

The local structure of the purified JUC-Z4 and JUC-Z5 was revealed by \(^{13}\)C and \(^{31}\)P MAS NMR. As shown in the \(^{13}\)C CP/MAS NMR spectrum of JUC-Z4 (figure 2b), three pronounced
Figure 1. FTIR spectra of TCPP (tris(4-chlorophenyl)phosphine, the monomer), JUC-Z4-Cl, JUC-Z4 obtained from method 1, JUC-Z4 obtained from method 2 and JUC-Z5 from (a) 400 to 4000 cm\(^{-1}\) and (b) 400 to 2000 cm\(^{-1}\). (Online version in colour.)

signals are resolved at \(\delta = 144.0, 132.7\) and 128.5 ppm, respectively, which are associated with the bridging benzene units. Two intense signals at 132.7 and 128.5 ppm can be assigned to C2 and C3, respectively, in the benzene ring, while the relatively weaker signal at 144.0 ppm is attributed to C1 and C4 atoms that cannot be distinguished. As C2 and C3 are directly connected to protons, the two signals at 132.7 and 128.5 ppm exhibit a much stronger CP enhancement with respect to the signal at 144.0 ppm. Similarly, for JUC-Z5 (figure 2a), the signal at 143.5 ppm was owing to C1 and C4 of the benzene ring and the two intense signals at 132.7 and 127.8 ppm were assigned to C2 and C3, respectively. These results indicated that the targeted cross-coupling of JUC-Z4 and JUC-Z5 really occurred under the present conditions. \(^{31}\)P MAS NMR experiments were used to detect the local environment of P atoms. The only one signal at 26.0 ppm shown in the \(^{31}\)P MAS NMR spectrum of JUC-Z5 can be attributed to the pentavalent P atom in the framework unit (figure 2c). After reduction, in addition to the 26 ppm signal, a high-field signal at \(-8.4\) ppm appeared in figure 2d, owing to the formation of trivalent P [31]. Analysis of the signal intensity shows that \(\sim 33\%\) of original P was reduced.

(b) Electrochemical property of JUC-Z4

The nature of JUC-Z4 is electroactive, in which the radical redox centre of P is stabilized by aromatic organic framework. In addition, only JUC-Z2 and JUC-Z4 exhibit electroactive properties among the porous polymers containing group 15 elements [32]. Figure 3 shows
the cyclic voltammogram of the JUC-Z4 powder film in dry and degassed 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆)/acetonitrile solution in which the JUC-Z4 film is insoluble. JUC-Z4 undergoes an oxidation process from the onset potential (E\text{onset}) of +0.55 V. Subsequently, an oxidation peak is observed at +0.95 V, while a corresponding

Figure 2. (a) $^{13}$C CP/MAS NMR spectrum of JUC-Z5; (b) $^{13}$C CP/MAS NMR spectrum of JUC-Z4; (c) $^{31}$P MAS NMR spectrum of JUC-Z5; and (d) $^{31}$P MAS NMR spectrum of JUC-Z4. (Online version in colour.)

Figure 3. Cyclic voltammograms of JUC-Z4 powder film on Pt microelectrode in degassed acetonitrile solution containing 0.1 M Bu4NPF6. Solid line, first cycle; dashed line, fourth cycle. (Online version in colour.)

Figure 4. UV-visible curve of JUC-Z4 in PEG 400.

reduction peak with equivalent height is found at +0.60 V on the cathodic scan. After four repeat cycles, the voltammetric response changed only slightly. These observations demonstrate that JUC-Z4 exhibits an almost reversible and stable redox process within the potential range investigated. The energy level of the highest occupied molecular orbital (HOMO) of JUC-Z4 was calculated to be $-5.35$ eV, according to empirical formula: $E_{\text{HOMO}} = -e(E_{\text{onset}} + 4.80)$ (eV) [33]. As another reduction peak was not found until the potentials down to the lowest limitation (approx. $-2.20$ V) of the working window, the lowest unoccupied molecular orbital (LUMO) was thus estimated from the onset adsorption wavelength ($\lambda_{\text{abs, onset}} = 285.7$ nm) of the UV-visible absorption (figure 4). By subtracting the energy gap value ($1240/\lambda_{\text{abs, onset}} = 4.34$ eV) between the HOMO and the LUMO, the LUMO energy level of JUC-Z4 was obtained to be $-9.69$ eV.

The thermal stability of JUC-Z4-Cl, JUC-Z4 and JUC-Z5 samples was investigated by TGA. The samples were immersed in water, ethanol and chloroform, respectively, to remove volatile residue and starting materials in the pores. All the volatile entities were fully removed by heating...
at 200°C under vacuum for 10 h. As shown in figure 5a, the 5% decomposition temperature in dry air of JUC-Z4-Cl was 480°C. Both JUC-Z4 and JUC-Z5 were found to be stable up to 471°C and 484°C in dry air corresponding to 5% weight loss (figure 5b,c, respectively). The stability of JUC-Z4 obtained by both reduction methods was almost the same. For method 1, the 5% decomposition temperature of JUC-Z4 was 471°C, whereas for method 2, the value was 472°C. Moreover, the materials were also stable towards common organic solvents such as alkanes, alcohols, acetone and DMF, which suggested that the samples exhibit high chemical stability.

(c) Porosity of JUC-Z4-Cl, JUC-Z4 and JUC-Z5

N2 sorption isotherm measurements were performed on the degassed samples to investigate the porosity of JUC-Z4 and JUC-Z5 (figure 6). The resulting type I isotherms of JUC-Z4 and JUC-Z5 were similar and exhibited a sharp uptake in the low-pressure region (10^{-5} to 10^{-2} atm), which is a signature feature of microporous materials. The hysteresis loops observed for JUC-Z4 and JUC-Z5 were attributed to the swelling effects of soft porous organic materials and defects, which were also observed in other PAFs [1,2,5]. The BET surface area was evaluated as 793 m^2 g^{-1} for JUC-Z4. The Langmuir model value for relative pressure between 5 \times 10^{-2} and 2 \times 10^{-1} of JUC-Z4 was 979 m^2 g^{-1}. As expected, after the oxidation process, the BET surface area of JUC-Z5 was decreased to 648 m^2 g^{-1}. The apparent surface area calculated from Langmuir model of the reduction product of JUC-Z5 was 843 m^2 g^{-1} (figure 6b).

The pore size distribution calculated from the nitrogen sorption isotherms by DFT using the carbon model with a 0.08% and 0.05% fitting error, respectively, indicated that JUC-Z4 and JUC-Z5 share similar pore size distribution of around 0.8 nm. More accurate CO2 sorption isotherms were used to probe the pores smaller than 0.8 nm. Figure 6e indicates that two clear narrow-distributed peaks at 0.57 and 0.82 nm were observed for both JUC-Z4 and JUC-Z5. The peak intensity at 0.82 nm of JUC-Z5 was obviously weakened, which could be attributed to the oxidation of trivalent phosphorus. This result coincides with the results from FTIR, MAS NMR and N2 sorption.

To this end, we have proved that the polarity of frameworks, pore size and BET surface area could be controlled by simple redox reaction of these POFs by above-mentioned FTIR, MAS NMR and N2 and CO2 sorption experiments.

(d) Gas storage in JUC-Z4 and JUC-Z5

(i) Low-pressure hydrogen storage in JUC-Z4 and JUC-Z5

To evaluate the hydrogen storage performance of JUC-Z4 and JUC-Z5, low-pressure hydrogen sorption isotherms at 77 and 87 K were measured. As shown in figure 7a, the H2 isotherms showed unsaturation and no hysteresis loops confirmed the physisorption reversibility. The H2
uptake at 77 K/760 mmHg was 142 and 111 cm$^{3}$ g$^{-1}$ for JUC-Z4 and JUC-Z5, respectively, which corresponded to an uptake of 6.3 and 4.8 mmol g$^{-1}$. Compared with PAF-1 (186 cm$^{3}$ g$^{-1}$ at 77 K and 760 mmHg for hydrogen), the H$_2$ uptake of JUC-Z4 and JUC-Z5 was lower when the pressure increased up to 760 mmHg. But it exhibited sharp uptakes in the low-pressure region between 0 and 100 mmHg and the hydrogen storage of JUC-Z4 showed highest hydrogen uptake when pressure was lower than 370 mmHg, with a value of 120 cm$^{3}$ g$^{-1}$. These can be confirmed by the isosteric heats of adsorption ($Q_{st}$), and unexpectedly high hydrogen heats of adsorption of JUC-Z4 and JUC-Z5 were measured as 8.0 and 8.1 kJ mol$^{-1}$ (figure 7d). Compared with one of the highest surface area materials, PAF-1 [1], JUC-Z4 and JUC-Z5 show higher hydrogen uptakes and heat
of adsorption between frameworks and hydrogen atoms, which suggested that the P heteroatom could effectively improve the $Q_{stH_2}$ of microporous materials.

(ii) Low-pressure methane storage in JUC-Z4 and JUC-Z5

Because of the higher hydrogen-to-carbon ratio, CH$_4$ is considered to be an ideal clean energy source. This prompted us to explore an effective and safe CH$_4$ storage tank which can work at ambient conditions. Motivated by the above consideration, we explored the methane uptake properties of JUC-Z4 and JUC-Z5. Similarly, JUC-Z4 and JUC-Z5 showed reversible methane adsorption isotherms. As shown in figure 7b, the CH$_4$ uptake of JUC-Z4 was 20 cm$^3$ g$^{-1}$ while that of JUC-Z5 was 16 cm$^3$ g$^{-1}$ and that of PAF-1 was 18 cm$^3$ g$^{-1}$ at 273 K/760 mmHg. The heat of adsorption of CH$_4$ ($Q_{stCH_4}$ for short) is 20.4, 19.7 and 14.0 kJ mol$^{-1}$ for JUC-Z4, JUC-Z5 and PAF-1, respectively. In the case of JUC-Z4 and JUC-Z5, the surface area should be counted as a key factor of the total amount of CH$_4$ adsorption. However, special strong interactions between CH$_4$ and P moiety made CH$_4$ uptakes of JUC-Z4 and JUC-Z5 similar to PAF-1, although the specific surface area of JUC-Z4 and JUC-Z5 was much less than PAF-1 (figure 7e).

(iii) Low-pressure carbon dioxide storage in JUC-Z4 and JUC-Z5

Recently, reports revealed that a suitable pore size less than 1 nm was preferred to be sufficiently commensurate with the kinetic diameter of a CO$_2$ molecule in the case of CO$_2$ capture at ambient condition [34]. The excellent physico-chemical stability together with the well-defined micropore (pore size <1 nm) makes JUC-Z4 and JUC-Z5 very attractive candidates for carbon dioxide capture applications. Indeed, JUC-Z4 and JUC-Z5 exhibited enhanced CO$_2$ adsorption capacities, which showed complete reversibility at ambient conditions such as 273 K and 760 mmHg. Furthermore, no saturation was achieved in the 760 mmHg pressure range, which suggested
that a higher CO₂ capacity could be achieved by increasing the pressure above 760 mmHg. In
detail, the CO₂ storage capacities at 273 K and 760 mmHg were 59, 56 and 46 cm³ g⁻¹ for JUC-
Z4, JUC-Z5 and PAF-1, respectively. The CO₂ uptake of JUC-Z4, JUC-Z5 and PAF-1 is 38, 34
and 25 cm³ g⁻¹ at 298 K and 1 bar, which shows the enhancement of CO₂ sorption properties
at different temperatures (figure 7c). To further investigate the factors that affect the CO₂ uptakes,
heats of adsorption of CO₂ were measured depending on the degree of CO₂ loading at 273
and 298 K. An apparent tendency towards increased interaction between CO₂ and adsorbents
is shown in figure 7f and the Q_{stCO₂} value is up to 29.0 kJ mol⁻¹ for JUC-Z5. Apart from the
pore size effect (less than 1 nm for JUC-Z4 and JUC-Z5, 1.48 nm for PAF-1), we surmised that the
smaller pore size and strong interaction between pentavalent phosphorus moiety in JUC-Z5 and
CO₂ molecules are the key factors of the high Q_{stCO₂}.

Figure 8 shows the CO₂ reversible adsorption (25°C) and regeneration (85°C) of JUC-Z4 under
pure carbon dioxide at ambient pressure. It undergoes an average weight change of 2.08 wt% with
the sorption and regeneration cycles. The reversible and constant regeneration process at ambient
temperature and pressure is a key for more efficient CO₂ capture. It should be noted that for
PAF-1, the average weight change is 0.67 wt% during the cycles. JUC-Z4 is a much better sorbent
for carbon dioxide capture than PAF-1.

(e) Greenhouse gas recognition and adsorption

Figure 9a compares the uptakes of CO₂, CH₄, N₂, H₂ and Ar adsorbed in JUC-Z4 at 273 K. We
detected the selectivity of CO₂/N₂, CO₂/CH₄ and CO₂/H₂ of JUC-Z4 by the IAST [29]. The
selectivity of CO₂/N₂ was calculated under the post-combustion conditions (typically 15%
CO₂ and 85% N₂) at 273 K and 1 bar. As shown in figure 9b, JUC-Z4 exhibited high adsorption
selectivity of about 85 at about 0.3 bar while the selectivity decreased to 35 at 1 bar. In addition,
the selectivity of CO₂/CH₄ was estimated for a 15% CO₂ and 85% CH₄ mixture at 273 K. It ranged
from 6.0 to 8.5 and displays almost no pressure dependence in the low-pressure region (0–1
bar). This performance outperforms many reported metal–organic frameworks, such as MOF-5
(2.3) [35], UMCM-1 (1.8) [36] and ZIF-8 (1.4) [36]. We also explored the CO₂/H₂ separation of
JUC-Z4 and found that the selectivity is in the range of 165–265 under the 20% CO₂ and 80%
H₂ condition at 273 K. The exceptional separation performance makes JUC-Z4 a potential CO₂
capture sorbent.
4. Conclusion

In conclusion, an electroactive PAF, JUC-Z4-Cl, was effectively synthesized through a Yamamoto-type Ullmann cross-coupling reaction. By using simple redox reaction, JUC-Z4-Cl could be partially reduced to JUC-Z4 and fully oxidized to JUC-Z5. The structures of JUC-Z4 and JUC-Z5 were revealed by MAS NMR and FTIR. The pore size, BET surface area and the polarity of the frameworks could be controlled by simple redox reaction. Furthermore, the change in porosity leads to high CO$_2$ sorption capacity and results in high CO$_2$ selectivity over N$_2$, H$_2$ and CH$_4$.

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References


