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COMMUNICATION

A 2D azine-linked covalent organic framework for gas storage applications

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5 **A new azine-linked covalent organic framework, ACOF-1 was synthesized by condensation of hydrazine hydrate and 1,3,5-triformylbenzene under solvothermal conditions. ACOF-1 has high surface area and small pore size, and it can store up to 177 mg g^{-1} of CO$_2$, 9.9 mg g^{-1} of H$_2$, and 11.5 mg g^{-1}**
10 **of CH$_4$, at 273 K and 1 bar, with high selectivity towards CO$_2$ over N$_2$ and CH$_4$.**

Covalent organic frameworks (COFs) are a new class of porous crystalline materials that have received great attention as a result of their potential in areas including gas storage, catalysis, and
15 optoelectronics.[1] Compared with inorganic zeolites and metal-organic frameworks (MOFs), COFs are constructed from lightweight elements linked by strong covalent bonds, which makes them extremely low density and robust. In addition, the most intriguing character is their atomically precise integration of
20 building units into periodic two- or three-dimensional structures, endowing COFs with excellent flexibility in the design of frameworks with distinct structures and properties. To date, COFs containing boronate ester,[2-4] boroxine,[5] borosilicate,[6] triazine,[7] imine,[8] hydrazone,[9] squaraine,[10] borazine[11] and azine[12] linkages
25 have been constructed. Although COFs based on B–O bands formation have been well developed, their weakly chemical stability leads to rapid decomposition upon exposure to water vapour or moisture and limits their effective usage in gas uptake under practical conditions. The recently developed COFs
30 constructed through the formation of C–N bonds have overcame this drawback and found to have enhanced chemical robustness.[8,9] However, the reported C–N linked COFs typically possess moderate specific surface areas and mesoporous pores that hinder their application in gas uptake.[8b,d,g,10,16] Therefore, the
35 construction of new COFs that combines the requirement in high crystallinity, robust stability, excellent porosity with high specific surface area and small pore size for gas storage is also strongly desired.

Very recently, a highly crystalline polymer, Py-Azine COF,[12]
40 has been synthesized by condensation of hydrazine with 1,3,5,8-tetrakis(4-formylphenyl)pyrene. We are interested in azine-linked COFs because they not only possess exceptional chemical and thermal stability, but also can be easily to take predetermined to make smaller pore sizes originated from the short structural
45 length of the azine unit. With these considerations in mind, we report herein on the targeted synthesis of a new azine linkage covalent organic framework (ACOF-1), which has been synthesized via condensation reaction between 1,3,5-triformylbenzene and hydrazine. Pleasingly, this crystalline
50 framework has a relatively small pore size compared with most of previously reported 2D-COFs.[1,2,8] We further highlight that the synergistic functions of high surface area, appropriate pore size,

and accessible nitrogen active sites endow the COF with excellent performances for small gas storage (CO$_2$, H$_2$, and CH$_4$).
55 The ACOF-1 was synthesized under solvothermal conditions by co-condensation of hydrazine hydrate with 1,3,5-triformylbenzene in a sealed glass ampoule at 120 $^{\circ}$C for 72 h (Scheme 1). Different from the previously reported COFs that require harsh reaction conditions, ACOF-1 with high crystallinity
60 and large surface area is easy to be synthesized in mild condition. We have screened a number of solvent systems such as mesitylene/dioxane (1/1 by vol), ethanol, mesitylene, and dioxane in the presence of acetic acid catalyst (6 M), and thus obtained framework materials always give high BET specific surface areas
65 of more than 1000 m^2 g^{-1} with high crystallinities (Table S1 and Fig. S1). We speculated that the formation of high porous crystalline framework material is not only attributed to the good solubility of monomers, but also the strong force between the layers of ACOF-1 still plays an important role.

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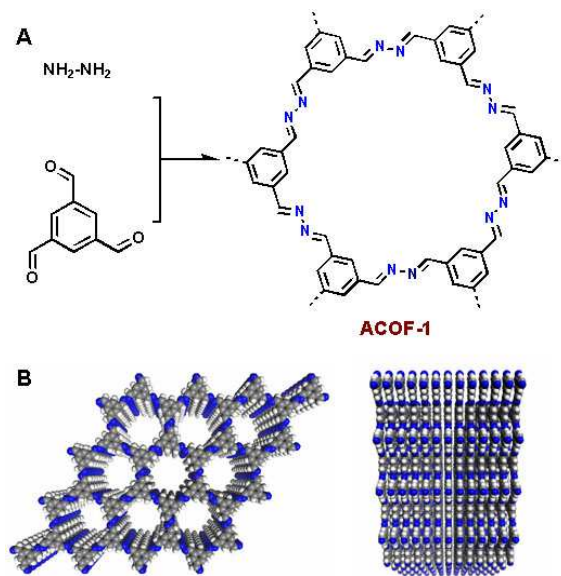
Scheme 1. (**A**) Schematic representation of the synthesis of ACOF-1. (**B**) Top and side views of the AA stacking structure of ACOF-1.

The successful preparation of ACOF-1 was confirmed by Fourier transform infrared (FT-IR) spectroscopy and solid state
75 ^{13}C cross polarization magic angle spinning (CP-MAS) NMR technology. The FT-IR spectrum of an activated sample of ACOF-1 showed a stretching vibration band at 1623 cm^{-1}, assignable to the C=N bond (Fig. S2). A small molecular model compound was synthesized, and it also displayed the C=N
80 vibration band at 1623 cm^{-1}. The ^{13}C CP-MAS NMR spectrum

displayed a characteristic signal for the C=N band at 161 ppm, whereas additional signals in the aromatic range arise from the aromatic carbons of benzene cores (Fig. S3). Elemental analysis of the ACOF-1 reveled that the C, H, and N contents were 64.62, 5.40, and 23.67%, respectively, which were close to the calculated values of 69.22, 3.87, and 26.91% expected for an infinite 2D sheet. Thermogravimetric analysis (TGA) was done on the ACOF-1 under nitrogen atmosphere, which revealed that it was stable up to 300 °C (Fig. S4). The high temperature test results indicated that ACOF-1 had sufficient thermal stability (Fig. S5) Scanning electron microscopy (SEM) revealed only one morphologically unique crystalline phase (Fig. S6).
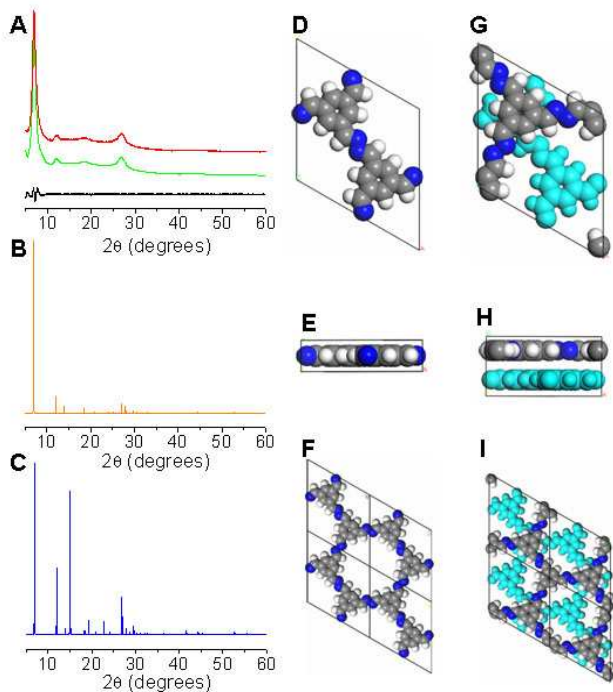

Fig. 1 (**A**) PXRD patterns of the ACOF-1. The red curve is experimentally observed pattern, green curve is Pawley refinement and black curve is their difference. (**B**) The orange curve is the calculated XRD pattern based on eclipsed model. (**C**) The blue curve is from staggered model. The unit-cell structure of ACOF-1 derived using the AA stacking model (**D**) along z axis, and (**E**) along y axis. (**F**) A single pore structure. The unit-cell structure derived using the AB stacking model (**G**) along z axis, and (**H**) along y axis. (**I**) A staggered pore structure.

The crystalline structure of the ACOF-1 was determined by powder X-ray diffraction (PXRD) measurements. The experimental PXRD pattern displayed a strong peak at 6.97° and relatively weak signals at 11.99, 13.83 and 18.35°, which were assigned to (100), (110), (200), and (120) facets, respectively. The slight broad peak at higher 2θ (~26.9°) is mainly due to π-π stacking between the COF layers and corresponds to the (001) plane (Fig. 1A, red curve). The d spacing for ACOF-1 was found to be 3.31 Å and it was smaller than that of previously reported 2D-COF,[1-10] which implied an existence of a stronger interaction the adjacent layers. The Pawley refined pattern (Fig. 1A, green curve) confirmed the diffraction peak assignments of the observed diffraction peaks (Fig. 1A, black curve). Simulations using the P1 space group with a = b = 14.724 Å, c = 3.310 Å and $\alpha = \beta = 90°$, $\gamma = 120°$ gave a PXRD pattern that was in good agreement with the experimentally observed pattern (Fig. 1B). The derived unit-cell structures in an eclipsed stacking fashion are shown in Fig. 3D-F. In contrast, the AB staggered stacking mode shows a PXRD pattern (Fig. 3C) that largely deviated from

the experimentally observed profile. Fig. 3G and H give the unit cell in a staggered stacking arrangement, where the benzene cores overlap on the pores of the neighboring plane (Fig. 3I).

The crystalline structure indicates that ACOF-1 possesses inherent one-dimensional (1D) channels. We thus investigated its porosity parameters through the nitrogen sorption isotherm measurements. Before the measurement, the fresh sample was degassed at 120 °C for 10 h. As shown in Fig. 2A, ACOF-1 exhibits a combination of type-I and II nitrogen sorption isotherm features according to the IUPAC classification and shows a steep nitrogen gas uptake at low relative pressure, thus reflecting the microporous nature of the network. The nitrogen sorption increases with increasing pressure, which indicates a large external surface area owing to the presence of small particles. In addition, a hysteresis can be observed at high relative pressures for ACOF-1 in the isotherms, which is associated with the irreversible uptake of gas molecules in the pores. The calculated Brunauer-Emmett-Teller (BET) surface area (SA_{BET}) evaluated form the $0.02 < P/P_0 < 0.11$ region of the adsorption curve is calculated to be 1176 m^2 g^{-1}, while the Langmuir model gives a surface area of 1318 m^2 g^{-1}. The SA_{BET} of ACOF-1 is higher than those reported for analogous 2D COFs such as COF-1 (711 m^2 g^{-1}),[13] CTF-1 (791 m^2 g^{-1}),[7] and PPy-COF (923 m^2 g^{-1}).[5b] Pore size distribution was evaluated using nonlocal density functional theory (NLDFT) and found to be centered at about 0.94 nm (Fig. 2B) and somewhat smaller than the theoretically predicted value. This difference may arise from imperfect solid-state stacking of the eclipsed 2D sheets that cannot be identified by PXRD studies as reported for many 2D COFs and predicated by theoretical studies.[11] The total volume calculated with from the nitrogen gas adsorbed at P/P$_0$ = 0.99 is 0.91 cm^3 g^{-1}.
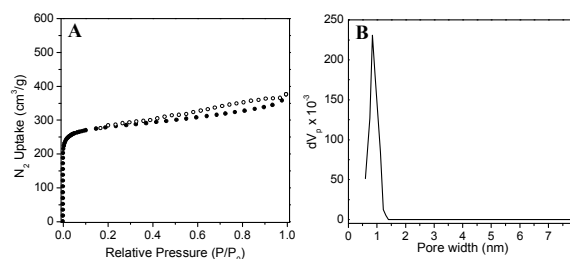

Fig. 2 Nitrogen adsorption/desorption isotherms (filled circles: adsorption, open circles: desorption) (**A**) and Pore size distribution (**B**) of ACOF-1.

Recently, carbon dioxide capture has attracted escalating attention due to global warming, which is mainly triggered by the emission of carbon dioxide from the combustion of fossil fuels. ACOF-1 has excellent microporous characteristics, good stability and abundant nitrogen atoms in the skeleton. These features prompted us to examine its adsorption properties for carbon dioxide. The CO_2 isotherms of ACOF-1 were measured at 298 and 273 K (Fig. **3A**), which showed 17.7 wt% CO_2 uptake at 273 K and 1 bar. This value is higher than previously reported COFs at the same condition like COF-5 (5.9 wt%, SA_{BET} = 1670 m^2 g^{-1}),[13] COF-103 (7.6 wt%, SA_{BET} = 3530 m^2 g^{-1}),[13] TDCOF-5 (9.2 wt%, SA_{BET} = 2497 m^2 g^{-1}),[14] and ILCOF-1 (6.0 wt%, SA_{BET} = 2723 m^2 g^{-1})[8e] even though they have larger surface area. The isosteric heats of adsorption (Q_{st}) for CO_2 were estimated from adsorption data collected under different temprature.[15] At zero coverage, the Q_{st} is 27.6 kJ mol^{-1}, which is higher than the values reported for COFs,[8e,13,14,16] imine-linked organic cages,[17] and diimide polymer.[18] The relatively high CO_2 uptake capacity and binding by ACOF-1 are attributed to the excellent porosity such as high specific surface areas, large pore volume, small pore size

of ACOF-1 and the abundant nitrogen sites on the pore wall as well as the molecular seieving effects of the ultramicropores and micropores.[19]
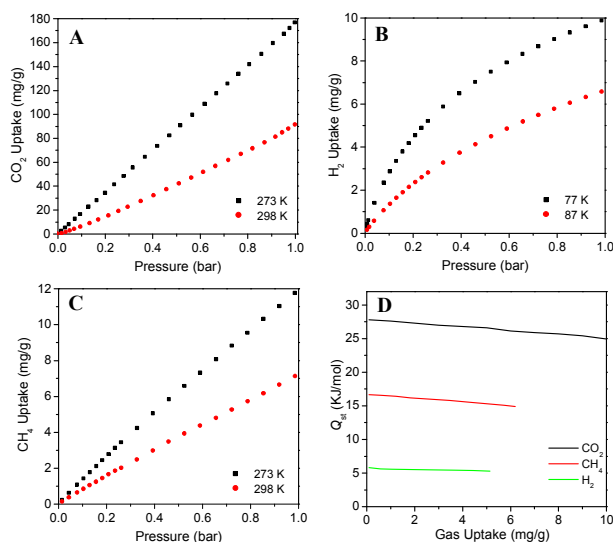

Fig. 2 Gas adsorption measurements for ACOF-1: (A) CO_2, (B) H_2, (C) CH_4, and (D) their respective isosteric heats of adsorption.

In addition to CO_2 storage and separation by porous materials, extensive research on hydrogen and methane has been contributed because of their potential in clean enegy applications. At 77 K and 1 bar, ACOF-1 exhibits 0.99 wt% hydrogen uptake (Fig. 3B) which is comparable to similar crystalline COFs such as COF-10 (0.82 wt%),[13] COF-5 (0.84 wt%)[13] and CoPc-PorDBA COF (0.8 wt%).[20] However, it is lower than that of COF-103 (1.29 wt%),[13] COF-18 Å (1.55 wt%),[2c] CTF-1 (1.55 wt%),[7] BLP-2(H) (1.5 wt%),[11] and TDCOF-5 (1.6 wt%).[14] The Q_{st} value for hydrogen at low pressure was found to be 6.02 kJ mol^{-1} which is within the range of 2D COF (6.0~7.0 kJ mol^{-1})[13] and other porous organic polymers.[19] We also measured methane storage properties with ACOF-1 at 273 and 298 K (Fig. 3C). The methane uptake of 1.15 wt% at 273 K and 1.0 bar is higher than those of ILCOF-1 (0.9 wt%),[8e] TDCOF-5 (1.07 wt%),[14] and almost 2-fold higher than COF-10 (0.58 wt%).[13] At zero coverage, Q_{st} for methane is 16.58 kJ mol^{-1} higher than for other reported imine linked polymers and COFs.[8e,13,14,20,21] A noticeable lower Q_{st} value of methane comprated to that of CO_2 is attributed to the nonpolar nature of methane. We also have investigated the selective uptake of small gases such as CO_2, CH_4 and N_2 to evaluate the potential application of ACOF-1 in gas separation field. On the basis of initial slope calculations in the pressure range of 0 to 0.1 bar, the ideal adsorption selectivity of CO_2/N_2 and CO_2/CH_4 is 40 and 37 at 273 K, respectively (Fig. S8). Interestingly, the selectivilty of CO_2/CH_4 surpasses imine-linked porous polymer frameworks[21] and electron-rich organonitridic frameworks.[22] The high selectivety of CO_2 over N_2 and CH_4 can be derived from that, the abundan nitrogens on the pore wall of ACOF-1 interact more favorably with polarizable CO_2 molecules through dipole-quadrupole interactions.

In summary, a 2D azine-linked covalent organic framework ACOF-1 was successfully designed and synthesized under mild condition. The new COF has an excellent porosity with a high BET surface area of over 1000 m^2 g^{-1}, large pore volume, relatively small pore size and displays the exceptional performances in small gas storage and separation at low pressure settings. Currently, the design and construction of new functional COFs for energy, environment and catalytic-related applications is underway in our laboratory.

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Notes and references

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