10886 *Inorg. Chem.* **2009**, *48*, 10886–10888
DOI: 10.1021/ic901804a

Inorganic Chemistry
Communication

Guest-Induced Irreversible Sliding in a Flexible 2D Rectangular Grid with Selective Sorption Characteristics

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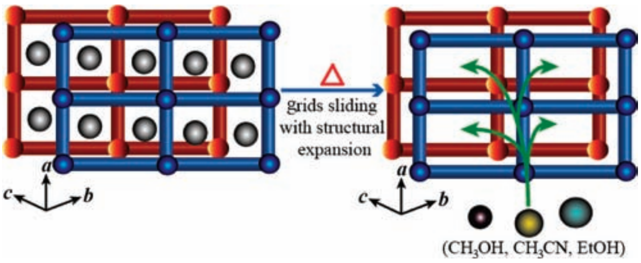
Received September 10, 2009

A 2D noninterpenetrated flexible metal-organic porous solid, $\{[Cu_2(\textit{cis}\text{-chdc})_2(\text{bpee})]\cdot H_2O\}_n$ (**1**) based on a paddle-wheel building unit has been constructed using a mixed-ligand system. Guest-induced irreversible internetwork displacements of the 2D grids result in permanent porosity in the framework, as realized by the selective CO_2 sorption over N_2. The different affinity and selectivity of the solvent molecules was correlated with the internal polarity of the pore surfaces.

The flexible and dynamic porous frameworks have attracted current attention because of their advantages in selective sorption, separation, molecular recognition, and sensing properties.[1] Guest-induced structural transformation, such as expansion and contraction in the frameworks, is ultimately realized by the pore deformation.[2] This can be raised by several dynamic behaviors, like sliding motion between the networks, rotation or distortion of the organic linkers, or change in geometry around the metals ions.[3] Internetwork displacement in the 2D sheets may lead to the permanent porosity and can allow the diffusion of oversized guest species.[4] Moreover, porous solid with high thermal stability and different polarity of the pore surfaces will be useful for the separation of molecules based on their polarity.[5] For this purpose, it is of significance to build a well-associated network using the mixed ligand system which facilitate the incorporation of functionality based on the chemical modification in the linkers.[6] With the aim of studying the influence of organic linkers on the polarity of the pore surfaces, we decided to pursue the grafting of the 1,4-cyclohexanedicarboxylic acid ($chdcH_2$) and bpee

Scheme 1. Guest induced sliding of the 2D rectangular grids toward structural expansion



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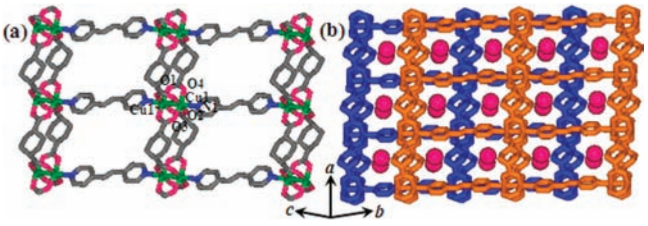

Figure 1. (a) 2D rectangular grid of **1** composed of paddle-wheel $Cu_2(CO_2)_4$ core connected by the *cis*-chdc^{2-} and bpee; (b) 2D grid stacks parallel to *a*-axis forming 1D water filled channel.

(1,2-bis(4-pyridyl)ethylene) in the Cu(II) system. The linker chdc have a constitutional flexibility with a hydrophobic backbone and hydrophilic dicarboxylate parts,[7] whereas bpee can provide the environment of high π-electron density. The flexibility of the $chdcH_2$ is associated with three possible conformations of two carboxylate groups, a,a-*trans*-, e,e-*trans*-, and a,e-*cis*-$chdcH_2$.[7,8] The e,e-trans form is thermodynamically more stable than the e,a-cis form and the a,a-trans form is least stable because of the 1,3-diaxial interaction. Here in this communication, we present synthesis, structural characterization and guest induced dynamic behavior of a 2D metal-organic network, $\{[Cu_2(\textit{cis}\text{-chdc})_2(\text{bpee})]\cdot H_2O)\}_n$ (**1**) constructed using a mixed-ligand system (see Scheme 1). The sorption studies of different gases and solvent molecules exhibit the selectivity of CO_2 over N_2, and the diffusion of solvent H_2O, MeOH, CH_3CN, and EtOH molecules into the pore surfaces, but not C_6H_6 molecules. Sorption selectivity and different affinities of the adsorbates were correlated by the size and polarity of the pore surfaces.

In a typical synthesis, the reaction of $Cu(ClO_4)_2$, Na_2chdc (mixture of cis and trans isomer), and bpee in H_2O-EtOH medium at room temperature results in green single crystals (see the Supporting Information). IR spectrum (Figure S1) reveals the broad and intense band at ~1608 cm^{-1} [ν_a(COO)] and 1419 cm^{-1} [ν_s(COO)], corroborating that all the oxygen atoms of the carboxylate group are involved in coordination with Cu(II). The peak around ~3400 cm^{-1} indicates the presence of water molecules.

Compound **1** crystallizes in triclinic $P\bar{1}$ space group[9a] and structural determination reveals that a 2D rectangular grid of Cu(II) built up by the *cis*-chdc^{2-} and bpee linkers (Figure 1a & S2). In **1**, the paddle-wheel binuclear $Cu_2(CO_2)_4$ units are linked by two chdc^{2-} to form 1D chains that are further connected by bpee linkers resulting in a 2D rectangular grid like structure lying in the (022) plane. Each Cu(II) displays a slightly distorted octahedral geometry with equatorial Cu−O bond distances in the range of 1.965(4)−1.980(4) Å, which are comparable to similar-type of Cu_2-dicarboxylate building unit.[6c,d,7a] The axial positions are occupied by the bpee nitrogen (Cu1−N1 = 2.164(5) Å) and other symmetry related Cu(II) at 2.634 Å. The degrees of distortion from an ideal geometry are reflected in cisoid angles [88.62(17)−100.48(17)°] and transoid angles [167.32(18)−172.81(18)°] (see Table S1 in the Supporting Information). The Cu···Cu separations in the 2D sheet along the Cu···bpee···Cu and Cu···chdc···Cu are 13.687 and 8.553 Å, respectively, and the effective grid dimension considering the van der Waals radii is about 11.0 × 5.5 Å^2.[10a] It is worth mentioning that the adjacent sheets stack in a staggered ABAB manner in parallel to *a*-axis, forming 1D channels occupied by the water molecules (Figure 1b and S3). The 2D sheets are stabilized by $\pi\cdots\pi$ interactions between the pyridine rings of bpee linkers [the cg···cg (center of gravity of py) distance is 4.964(4) Å]. The staggered arrangements of the 2D grids drastically reduces the effective pore size to 5.50 × 2.75 Å^2 and the rectangular pore surfaces is decorated by the hydrophobic chdc backbone and hydrophilic carboxylate and pyridine unit (see Figure S4 in the Supporting Information). The effective solvent accessible void space was calculated using the PLATON[10b] and it shows 15.5% void space to the total crystal volume. Recently, Chen et al.[7a] have reported interpenetrated α-Po-type network, composed of Cu_2(*trans*-chdc)$_2$ paddle-wheel building blocks, which are pillared by bipy and bpee, respectively and interpenetration drastically reduces the void space. The cis conformation of the chdc in **1** results 1D chain of $Cu_2(chdc)_2$ instead of 2D square grid of $Cu_2(chdc)_2$ with trans conformation, which ultimately leads to the noninterpenetrated 2D porous structure.

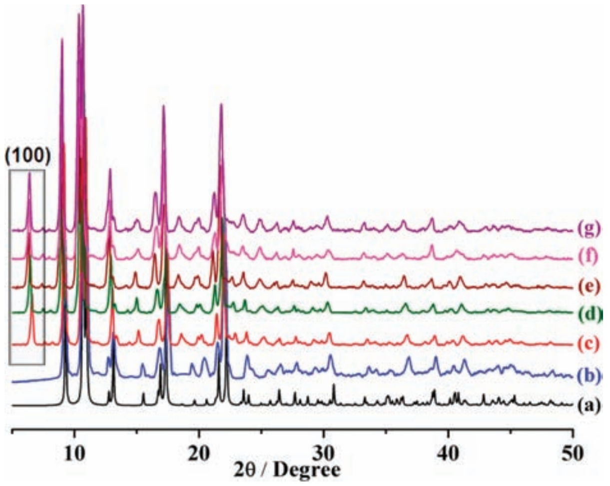

Figure 2. PXRD pattern of **1** in different state. (a) simulated, (b) as-synthesized, (c) dehydrated at 130 °C, (d) H_2O, (e) MeOH, (f) EtOH, (g) CH_3CN vapor exposed for three days.

Thermogravimetric analysis of **1** shows a weight loss in the range of 30−95 °C, corresponding to the water guest molecules and the dehydrated framework (**1′**) is stable up to 260 °C (see Figure S5 in the Supporting Information). The PXRD pattern of the dehydrated solid (**1′**) exhibits an intense peak at low angle around 2θ = 6.722° and other peaks remain almost the same, suggesting a structural transformation after dehydration (Figure 2c). The powder pattern was indexed and the cell parameters[9b] suggest that the *a*-axis expands (55.6%), keeping *b*- and *c*-axis almost the same (see the Supporting Information) and showing a significant

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(9) (a) Crystal data for **1**: Formula $C_{28}H_{32}Cu_2N_2O_9$, fw = 667.66, triclinic, $P\bar{1}$ (No. 2), a = 8.5387(2) Å, b = 9.2448(3) Å, c = 10.4427(3) Å; α = 111.759(2)°; β = 96.228(2)°; γ = 100.746(2)°; V = 737.79(4) Å^3, Z = 1; ρ_{calcd} = 1.503 g cm^{-3}, μ ($Mo_{K\alpha}$) = 1.496 mm^{-1}, F(000) = 344, T = 298 K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{max} = 27.9°, total data = 14 922, unique data = 3466, R_{int} = 0.091, observed data [$I > 2\sigma(I)$] = 2162, R = 0.0605, R_w = 0.1673, GOF = 1.01. (b) Cell parameters for **1′**: a = 13.292(13) Å, b = 9.245(10), Å c = 10.345(13) Å, α = 111.57(12)°, β = 96.67(10)°, γ = 91.85(11)°; V = 1170.32 Å^3.

(10) (a) The size is measured by considering van der Waals radii for the constituting atoms: (b) Spek, A. L. *PLATON*; The University of Utrecht: Utrecht, The Netherlands, 1999.

increase in cell volume (43.7%). During heating, the 2D sheet in the (022) plane at high temperature is expected to undergo a random shift in different directions. However, among different possible displacements, the most stable configuration must have the least degree of freedom. By analyzing the ambient temperature configuration of the sheets, we noticed that the puckered and flexible chdc ligand lies parallel to *a*-axis and rigid bpee ligand lies in the *bc*-plane and almost perpendicular to *a*-axis. The puckered conformation of chdc is not in the lowest energy. Thus, we concluded that *b*- or *c*-axis became rigid but the heating supplies energy to the chdc ligand to overcome the puckering force. Therefore, the least degree of freedom might be provided by the expansion of chdc along [100] direction to achieve lowest energy conformation. The (100) reflection in the low-angle area shows the conformation change of the chdc ligand which shifts the 2D sheets apart from one another resulting in an expansion of the overall framework.

The porosity of **1′** was examined by the gas sorption measurements. Upon heating the sample at 473 K, a CO_2 (kinetic diameter, 3.4 Å)[11] sorption isotherm run at 195 K, and observed rapid onset of CO_2 sorption at very low pressure attributed to the microporosity of the compound (see Figure S6 in the Supporting Information). A small hysteresis correlates a strong interaction of CO_2 with the pore surface and Langmuir analysis gave a surface area of 168 m^2/g. A N_2 (kinetic diameter, 3.4 Å) sorption isotherm at 77 K shows no occlusion with type-II sorption behavior and results in a strikingly smaller surface area. This kind of selectivity results from the combination of stronger affinity of the CO_2 for the host solid and also because of the critical difference in kinetic diameters relative to the pore size in **1′**.[5e]

We have also studied the adsorption properties with the different solvent vapors (H_2O, CH_3CN, EtOH, and C_6H_6 at 298 K and MeOH at 295 K) having different polarity to understand sorption selectivity and their affinity to the pore surfaces of **1′** (Figure 3). The sorption profiles of H_2O (kinetic diameter, 2.65 Å),[11] MeOH (3.8 Å), CH_3CN (4.0 Å), and EtOH (4.3 Å) reveal a type I curve with small hysteresis and sorption amount increases with increasing pressure. The calculations using the final sorption amount suggest an uptake of 1.5, 1.75. 1.3, and 1.0 molecule H_2O, MeOH, CH_3CN, and EtOH, respectively, per formula unit of **1′**, which is consistent with the structural expansion. All the profiles were analyzed by the DR equation and the values of βE_0, which reflect adsorbate−adsorbent affinity, are 3.03 kJ/mol for H_2O, 6.14 kJ/mol for MeOH, 2.15 kJ/mol for CH_3CN and 9.40 kJ/mol for EtOH indicating that the affinity of **1** is much more to MeOH and EtOH compared to H_2O and CH_3CN. MeOH, CH_3CN, and EtOH unveil steep uptake at low-pressure region compared to H_2O. The careful observation of the channels environment in **1′** suggests that the hydrophobic $-CH_2$ moieties of the chdc and $-CH{=}CH-$ of bpee would be exposed to the central region of the pore, whereas hydrophilic carboxylate part would be oriented to the corners of the rectangular pore. MeOH/CH_3CN/EtOH molecule consisting of hydrophobic $-CH_3$/$-CH_2CH_3$ part and hydrophilic −OH/CN part, feels ideal space for accommodation. The weak affinity of CH_3CN compared to MeOH or EtOH was realized by the stronger polar character and hence can not interact effectively with chdc backbone. Moreover, this also explains the low uptake of smaller size H_2O compared to MeOH. Consistent with the smaller pore size, **1′** completely excludes C_6H_6 (5.8 Å) molecules at 298 K (Figure 3e). The PXRD patterns of the vapor exposed state of **1′** reveal that (100) peak is shifted more toward low angles with increase in guest size (Figures 2 and S7). This reflects the accommodation of the larger guest as the intersheet separation also increases.

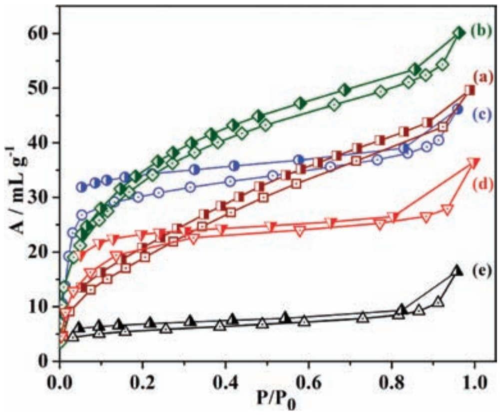

Figure 3. Vapor sorption isotherm for **1′**. (a) H_2O (298 K); (b) MeOH (295 K); (c) CH_3CN (298 K); (d) EtOH (298 K) and (e) benzene (298 K). P_0 is the saturated vapor pressure of the adsorbates at respective temperature (open symbol; adsorption and half filled symbol; desorption).

In summary, we have synthesized a 2D network of Cu(II) using the mixed ligand system. The 2D network shows unprecedented guest induced irreversible sliding, resulting in a 1D channel structure with permanent porosity, realized by the selective sorption of CO_2 over N_2. The guest-accessibility of solvent vapors with different polarity has been demonstrated, which suggests a more hydrophobic nature of the pore surfaces. Structural flexibility results in regularity and selectivity in the framework with well-defined pore surfaces, which may find application in separation on the basis of polarity.

Acknowledgment. T.K.M. is grateful to DST for the financial support (fast track proposal). The authors are thankful to Dr. G. Mostafa for helpful discussion.

Supporting Information Available: Detailed experimental procedure and Figures S1−S7 (PDF); X-ray crystallographic files in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org

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