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# Coordination pillared-layer type compounds having pore surface functionalization by anionic sulfonate groups†

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**Pillared-layer type 3D porous coordination polymers with 2-sulfonylterephthalate, 4,4′-bipyridine and $Zn^{2+}$ have metal-free sulfonate groups on the pore walls, providing Lewis basic property for acid guest sorption.**

There is a growing interest in the study of porous coordination polymers (PCPs) with functionalized pore surfaces.[1] Porous frameworks with functional groups exhibit intriguing properties such as separation for gas molecules,[2] catalytic activity[3] and polymer synthesis.[4] By anchoring the functional groups onto the pore surface of PCPs *via* a self-assembly process, we could obtain nanospaces with regularly arranged and highly dense active sites. Recently, PCPs with Lewis acid structures, *i.e.* coordinatively unsaturated sites after solvent removal have been reported with focus on their functions.[5] Contrary to this, the rational synthesis of PCPs with Lewis base functional groups are scarcely observed because of difficulties in the formation of metal-free base groups in the channel walls by self-assembly. However, the sparse reports on basic micropore surfaces reveal significant sorption phenomena for selective binding or catalysis[6] and PCP frameworks with basic properties and their synthetic guidelines have been strongly required.

One of the most familiar examples of PCPs is constructed using transition metal cations with both an anionic multi-carboxylate ligand and a neutral bipyridyl linker,[7] whereas it has also been known that a ligand containing a sulfonate group can generate various extended networks with a combination of alkali or alkaline earth metal cations.[8] We reported the immobilization of acidic $Na^+$ cations on the pore surfaces of PCP by employing a bifunctional carboxylate–sulfonate ligand as anionic connector.[9] By utilization of the different coordination ability of each group, the soft base ($-CO_2^-$) acts as a connector to transition metals and the hard base ($-SO_3^-$) acts as a $Na^+$ trapping site. Inspired by the different coordination properties, a PCP framework containing coordinatively-free base groups inside the pores could be synthesized by controlling the affinity of building blocks and basicity of reaction. Herein we describe the construction of robust PCPs containing channels functionalized with $-SO_3^-$ Lewis base groups and their sorption properties.

The reaction of $Zn(NO_3)_2{\cdot}4H_2O$ with 2-sulfonylterephthalate (2-stp) and 4,4′-bipyridine (bpy) and NaOH in $H_2O$–EtOH medium at room temperature yields colorless microcrystals of composition $\{[Zn_3(\mu_3\text{-}OH)_3(2\text{-stp})(bpy)_{1.5}(H_2O)](EtOH)(2H_2O)\}_n$ ($\mathbf{1}\supset\mathbf{G}$). This structure was determined by single crystal X-ray diffraction at −50 °C.§ The asymmetric unit of $\mathbf{1}\supset\mathbf{G}$ contains three zinc atoms, one 2-stp, 1.5 bpy, three $\mu_3$-$OH^-$ groups, one coordinated $H_2O$, and two $H_2O$ and one EtOH as guests. As shown in Fig. 1a, Zn1 is coordinated to five O atoms from three different $\mu_3$-$OH^-$ groups, one water and one carboxylate group of 2-stp, and one N atom from bpy to complete its octahedral coordination environment. Zn2 is coordinated to one O atom of the carboxylate group of 2-stp and three $\mu_3$-$OH^-$ groups and one N atom from bpy to form a trigonal bipyramidal fashion. Zn3 is coordinated to two O atoms of the carboxylate group of 2-stp and three $\mu_3$-$OH^-$ groups and one N atom from bpy to form an octahedral fashion. The two ZnO zigzag single chains are

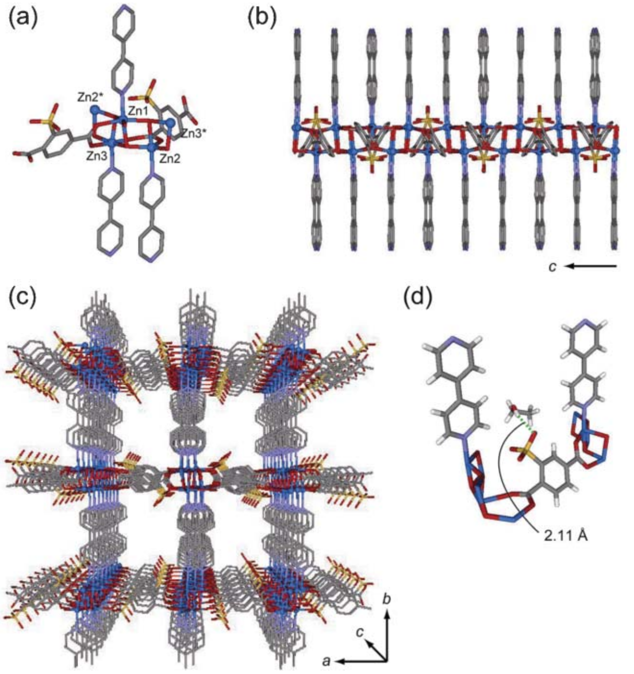

**Fig. 1** Crystal structure of **1** for (a) the coordination environment around $Zn^{2+}$ ions, (b) view along the *a* axis, (c) 3D assembled system along the *c* axis. Guests and H atoms are omitted. (d) Partial structure of H-bonding between EtOH and framework. Framework Zn, C, N, O and S atoms are shown as sky blue, gray, purple, red, and yellow.

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connected through Zn–O bonds to form an extended 1D ribbon-like structure along the *c* axis (Fig. 1b),[10] and the carboxylate groups of 2-stp bridge the ribbon-like 1D chains to construct 2D sheets lying in the *a*c plane with the remaining uncoordinated sulfonate group of 2-stp. The 2D sheets are neutral because of the charge balance with deprotonated sulfonate groups.[11] The linear bpy ligands along the *b* axis act as a pillar and serve to link adjacent layers to form an extended 3D porous coordination network (Fig. 1c). The three independent bpy moieties lie across mirror planes and it is the combination of these with glide-plane and inversion operations which generates the three-dimensional structure. As a consequence of the assembly process, 1D channels with undulated surfaces are formed with the smallest cross section of $4.6 \times 4.6$ Å$^2$ and the 1D channels are occupied with guest water and EtOH molecules. Notably, the uncoordinated sulfonate groups of 2-stp are directed into the rectangular pores and form hydrogen bonds with guest EtOH (O(–$SO_3^-$)···H(EtOH) = 2.11 Å) (Fig. 1d). Therefore the porous framework of **1** has a basic property and good binding ability for acidic guests such as alcohol. The density of the –$SO_3^-$ group in the framework is 1.35 mmol g$^{-1}$.

The powder sample of this compound is stable in air and insoluble in common organic solvents, and the bulk synthesis of **1** depends heavily on the concentration of each ion and can be successful only under basic conditions with the molar ratio of $Zn^{2+}$ : 2-stp :bpy : $OH^-$ = 3 : 1 : 1.5 : 5. When the concentration of $OH^-$ is halved or doubled, by-products are formed. The X-ray powder diffraction (XPD) pattern of as-prepared $\mathbf{1}\supset\mathbf{G}$ measured at 298 K is in good agreement with that of a simulated pattern obtained from the single-crystal structure (Fig. 2a and 2b). The EtOH molecules inside the pores of **1** are hardly removed by room temperature evacuation because of the hydrogen bonding with –$SO_3^-$ groups. The thermogravimetric analysis (TGA) of $\mathbf{1}\supset\mathbf{G}$ is consistent with the crystallographic observation.† The framework releases the two guest water and one coordinate water and one EtOH (calcd 12.1%, found 12.5%) between 25 and 105 °C. The guest-free **1** shows no clear weight loss until it reaches 220 °C and the anhydrous framework has enough structural strength as a solid adsorbent. The total potential solvent-accessible volume of the unit cell of **1** is 31.9%, calculated using the PLATON program.[12] The cross section of the 1D channel of **1** running parallel to the *c* axis is represented in Fig. 3. This representation is drawn showing the guest-accessible pore surface, which is defined by the possible surface of a rolling sphere with a diameter of 2.8 Å and the colors indicate the atom charges (red: negatively charged, blue: positively charged). The zig-zag 1D pores extend along the *c* axis and the negatively charged sulfonate groups line up with an interatomic distance of 10.55 Å.

In order to examine the adsorption properties of **1**, the isotherms were measured for sorption of $CO_2$ and MeOH (Fig. 4, filled circles and squares). Before the measurements, we dried the microcrystals at 110 °C under reduced pressure for 12 h to remove guests. Although the amount of $CO_2$ adsorption at 195 K is not high (36 mL g$^{-1}$ at $P/P_0 = 0.95$), the isotherm exhibits Type I behaviour, confirming the presence of uniform micropores and the saturated amount of $CO_2$ is consistent with 1.6 molecules per –$SO_3^-$ group. From this sorption profile and the molecular cross section area of $CO_2$ (0.216 nm$^2$), the surface area has been determined using the BET equation, which gives 99 m$^2$ g$^{-1}$. In the case of MeOH, the isotherm also exhibits an initial uptake indicating a strong sorbate–sorbent interaction at low pressure, and shows a linear increase in the pressure range $P/P_0 > 0.1$. The amount of MeOH at $P/P_0 = 0.93$ is 4.2 molecules per –$SO_3^-$ group and the void spaces would be filled with guest molecules and the desorption curve does not trace the adsorption curve, showing large hysteresis below $P/P_0 = 0.05$.† From this wide range of hysteresis, we can assume that the sorption is promoted in the micropores with considerable acid–base interaction. We also measured MeCN whose size is comparable to MeOH, and the adsorption–desorption isotherm gave a small hysteresis, though the total amount is similar to MeOH.† This result also supports the specific sorption property of **1** for acidic guests.

The structural motif of compound **1** is a pillared-layer type structure which consists of a 2D sheet of $Zn^{2+}$ and 2-stp and a bipyridyl pillar ligand, and the pore dimensions are apparently controllable depending on the length of pillar ligands used.[13] To construct this kind of PCP with larger pores, we chose 1,2-di(4-pyridyl)ethylene (dpe) as a pillar instead of bpy. The powder sample of $\{[Zn_3(\mu_3\text{-}OH)_3(2\text{-stp})(dpe)_{1.5}](EtOH)(2H_2O)\}_n$ ($\mathbf{2}\supset\mathbf{G}$) was successfully synthesized by using similar procedures to the preparation of $\mathbf{1}\supset\mathbf{G}$ and the XPD pattern of $\mathbf{2}\supset\mathbf{G}$ is shown in Fig. 2c. The shifts of the (0*n*0) reflections demonstrate the elongated *b* axis from 12.64 Å ($\mathbf{1}\supset\mathbf{G}$) to 15.92 Å ($\mathbf{2}\supset\mathbf{G}$), which is

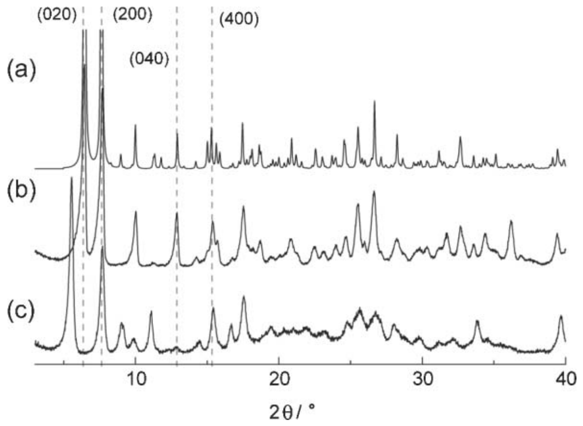

**Fig. 2** XPD patterns of (a) simulated **1** from single-crystal X-ray analysis, (b) as-synthesized $\mathbf{1}\supset\mathbf{G}$, (c) as-synthesized $\mathbf{2}\supset\mathbf{G}$.

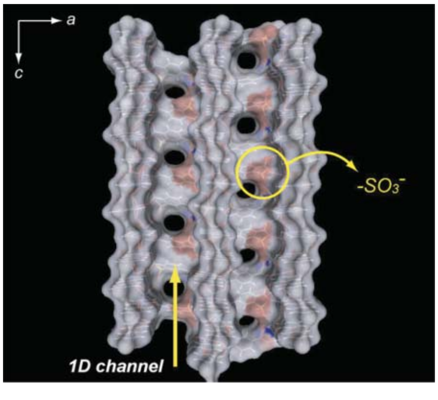

**Fig. 3** The cross section of guest-accessible pore surfaces of 1D channels of **1** (Radius of probe molecule is 1.4 Å).

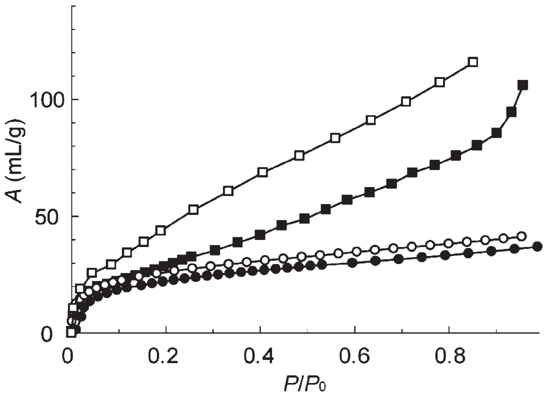

**Fig. 4** Adsorption isotherms for $CO_2$ (195 K) of (●) **1**, (○) **2**, and for MeOH (298 K) of (■) **1**, (□) **2**, respectively.

consistent with the difference in the length between bpy and dpe. Consequently, the smallest 1D channel dimension of **2⊃G** is estimated to be about 4.6 × 7.9 $Å^2$. The formula of this sample was also confirmed by elemental analysis and solid-state $^{13}C$ NMR.† The TGA curve of **2⊃G** also shows the stability after guest removal treatment and no clear weight loss was observed up to 280 °C. According to the expansion of the pore diameter, the adsorption isotherms for $CO_2$ and MeOH show larger amounts of sorption compared with **1** (Fig. 4, open circles and squares) and from the $CO_2$ sorption profile, the BET surface area can be calculated to be 117 $m^2\ g^{-1}$. A detailed mechanism for the gradual uptake of MeOH for **1** and **2** at $P/P_0 > 0.1$ has been not elucidated; however, the large hysteresis loop of the adsorption–desorption curves shows strong interaction between the MeOH and the sulfonate-containing pore surface and this would contribute to the slow diffusion of MeOH into the micropores of **1** and **2**.

In conclusion, pillared-layer type $Zn^{2+}$ PCPs functionalized by basic $–SO_3^-$ groups can be obtained by careful tuning of synthetic conditions and these compounds show sorption abilities for $CO_2$ and MeOH. Such an electrostatic undulating micropore surface has a polarized environment and is suitable for strong accommodation for acidic guests *via* acid–base interactions. This result can be regarded as a significant approach for creating a base functionalized open metal–organic framework for potential adsorptive applications.

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## Notes and references

§ Crystal data for **1⊃G**: $C_{25}H_{28}N_3O_{14}SZn_3$, FW = 822.64, Orthorhombic, space group *Pnma*, $a = 23.1451(14)$ Å, $b = 27.3976(16)$ Å, $c = 10.5482(6)$ Å, $V = 6688.8(7)$ $Å^3$, $Z = 8$, $T = 223$ K, $D_c = 1.626$ g $cm^{-3}$; $R_1 = 0.0870$, $wR_2 = 0.2361$, GOF = 1.169. CCDC 663301. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715481j

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