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Robust anionic pillared-layer framework with triphenylamine-based linkers: ion exchange and counterion-dependent sorption properties[†]

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A new anionic pillared-layer cobalt(II) metal-organic framework combining the 4,4',4"nitrilotribenzoic acid (H₃ntb) as linker and terephthalic acid (H₂bdc) as pillar-ligand with the formula { $((CH_3)_2NH_2)_2[Co_3(ntb)_2(bdc)]$ }, (JUMP-1, JUMP = Jena University Magnetic Polymer) has been solvothermally synthesized and characterized. The crystal structure of JUMP-1 was determined to belong to the orthorhombic space group Cmca. It displays a three-dimensional (3D) framework for which the topological analysis revealed a 3,8-connected net with tfz-d topology. The 3-connected organic node is linked to an 8-connected secondary building unit composed of a linear trinuclear cobalt(II) cluster with a mixed arrangement of coordination geometries (T_{d-} $O_{\rm h}-T_{\rm d}$) leading to two-dimensional layers which are further linked by terephthalic acid to give the pillared-layer arrangement. The magnetic properties are characterized by an antiferromagnetic coupling between the central octahedrally coordinated cobalt(II) ion and the two outer tetrahedral cobalt(II) centers, whereas only a very weak inter-cluster coupling is observed. Moreover, a moderate zero-field splitting is detected for the tetrahedral cobalt(II) ions. The organic counterions could successfully be exchanged by lithium ions under retention of the anionic 3D network leading to JUMP-1(Li). For both compounds JUMP-1 and JUMP-1(Li) N2 and CO2 adsorption isotherms were measured. The pore distribution analyses revealed improved microporosity for the lithium exchanged MOF.

Introduction

The field of coordination polymers and in particular that of metalorganic frameworks (MOFs) has become an ever more popular area of interest in recent years. This is, no doubt, due to the many applications of this class of compounds some of which include catalysis, gas storage, separation and sequestration, ion exchange, magnetism and sensing.¹ The most common strategy in obtaining them, so far, has been the simple combination of metals and polytopic ligands mostly under solvothermal conditions in a process of self-assembly with emphasis on slim organic linkers to provide access to high porosity.² As the functional groups are concerned polycarboxylate linkers, particularly aromatic based, have been subjected to frequent use since they confer rigidity and stability on the obtained frameworks.³ This approach has even been extended by use of spacer groups to expand the existing ligands thus increasing the potential for better surface properties such as in the case of the isoreticular series.⁴ While this method has worked quite well till date, it has also had its drawbacks such as in the case of interpenetrated or even fragile structures due to the frameworks being poorly reinforced.⁵

Even so total control over the synthesis of MOFs still remains an elusive goal in particular the ability to tune properties such as the pore sizes which is most desirable. One of the attempts to achieve this level of controllability has been the construction of pillared-layer structures.⁶ A major advantage of this strategy is that it offers new levels of functionality in addition to avoiding the stress of searching for new linkers while at the same time making the most of existing ones. This approach has subsequently led to the discovery of MOFs with some of the highest reported surface areas currently known such as the UMCM-1^{5,7} and MOF-210² of which the latter was only surpassed by the discovery of the NU-110 with over 7000 m² g⁻¹.⁸

These pillared-layer systems have been found to be effective routes in obtaining three dimensional frameworks in addition to offering the possibility of chemically functionalizing the channels for selective adsorption behavior via modification of the pillar ligands.⁹ Selecting appropriate pillared ligands can be used to generate flexible MOFs which have the ability to undergo structural

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[†] Structural figures, XRPD patterns, TGA curves, topological data and sorption data are included in the ESI. See DOI: 10.1039/b000000x/

changes during adsorption and desorption of guests and are interesting for applications in selective gas adsorption/separation or chemical sensing.¹⁰ This approach has also been used to facilitate the interconnection of layered structures with interesting magnetic properties¹¹ and, moreover, to introduce redox-active organic linkers in relevant frameworks.¹²

A common approach in synthesizing such mixed-ligand frameworks has been the coordination copolymerization route usually involving mixing two different linkers.^{7,13} When combined, the organic linkers tend to cooperate thus avoiding formation of two separate single ligand MOFs.¹⁴ Subtle changes in reaction conditions such as reactant ratios, temperature or even solvent often lead to slight variations in the final structure obtained.¹⁵ Common ligands acting as pillars include the dicarboxylates like terephthalate or its derivatives and nitrogen based ligands such as imidazoles or bipyridines.¹⁶

We herein report the construction of a new anionic pillaredlayer MOF, named JUMP-1 (JUMP = Jena University Magnetic Polymer), which is based on the redox-active ligand 4,4',4''nitrilotribenzoic acid (H₃ntb) with the inclusion of terephthalic acid as pillar ligand containing a linear trinuclear cobalt(II) cluster as secondary building unit (SBU). The anionic nature of the resulting framework will be used for post-synthetic modification via cation exchange and the resulting sorption properties before and after exchange will be reported.

Experimental section

Materials

Triphenylamine (Alfa Aesar) and cobalt(II) chloride hexahydrate (Aldrich) were obtained commercially and used without further purification. All other chemicals were of AR grade. The tribromotriphenylamine used was prepared from triphenylamine by a reported procedure.¹⁷ The final ligand 4,4',4"-nitrilotribenzoic acid (H₃ntb) was obtained in good yield following procedures already described in literature.^{18,19}

Analytical Data for H₃ntb. ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, δ in ppm): 7.13 (d, ³*J*_{H,H} = 8.7 Hz, 6H), 7.89 (d, ³*J*_{H,H} = 8.7 Hz, 6H), 12.76 (s, 3H). ¹³C NMR (100 MHz, [D₆]DMSO, 25 °C, δ in ppm): 123.7, 125.9, 131.2, 149.8, 166.7. Selected IR data (ATR, cm⁻¹): 1672s, 1591s, 1509m, 1417s, 1314s, 1275vs, 1173s, 1129m, 932m. EI-MS: *m*/*z* 377 (M⁺, 100%).

Physical measurements

Simultaneous TG/DTA analyses were performed under static air atmosphere using a Netzsch STA Luxx PC analyzer up to 1000 °C. The FT-IR spectra were measured on a VERTEX 70 IR spectrometer by Bruker Optics using the Specac Diamond ATR optional accessory. Mass spectrometry was performed on a MAT SSQ710 mass spectrometer made by Bruker. NMR spectra were recorded with a Bruker AVANCE400 spectrometer. The elemental analyses were done on a VARIO EL III analyzer. The magnetic susceptibilities were measured on the bulk vacuum dried materials in the 2–300 K temperature range with a Quantum Design MPMS-5 superconducting SQUID magnetometer. The data were corrected for diamagnetic contributions. The N₂ and CO₂ physisorption isotherms were measured on an Autosorb-IQ instrument from Quantachrome Instruments Corporation. Solvothermal reactions were carried out in a 23 mL Teflon-lined acid digestion vessel from Parr Instruments, utilizing a programmable oven by Binder. X-ray powder diffraction (XRPD) measurements were performed on a Stoe Powder Diffractometer with a Mythen 1K detector at room temperature. Measurements were done using capillary tubes while the Debye Scherrer Scan Mode was applied with a 2 θ scan type. The X-ray tube was a Cu-long fine focus tube. The powdered samples were suspended in DMF and transferred in a 0.5 mm glass capillary for measurement, which was carried out between 2 and 50° with steps of 2.1° per 20 seconds.

Synthesis

$\{((CH_3)_2NH_2)_2[Co_3(ntb)_2(bdc)]\}_n \cdot 4DMF \cdot 2H_2O$

(JUMP-1 \cdot 4DMF \cdot 2H₂O). Terephthalic acid (H₂bdc, 33 mg, 0.199 mmol) and H₃ntb (50 mg, 0.13 mmol) were dissolved and stirred in DMF (5 mL) for 15 min. Cobalt(II) chloride hexahydrate (126 mg, 0.52 mmol) was then added and stirred for a further 15 min after which all solid was dissolved. The solution was then placed in a Parr acid digestion vessel and heated at 140 °C for 72 h under autogenous pressure. It was then allowed to cool at a rate of $5 \,{}^{\circ}Ch^{-1}$. Deep blue-violet crystals could be seen in the room temperature sample which were washed repeatedly with DMF (3×5 mL) and subsequently dried in vacuo for 1h, leading the further denoted as-synthesized material JUMP-1 · 4DMF · 2H2O. Employing extended periods for the drying process lead to lower solvent content of the resulting material, as evidenced by CHN elemental analysis and TG measurements. Yield for JUMP-1 · 4DMF · 2H₂O: 71.0 mg, 0.047 mmol, 72 % based on ligand. CHN elemental analysis calcd for JUMP-1 · 4DMF · 2H₂O C₆₆H₇₆Co₃N₈O₂₂ (M = 1510.34): C, 52.5; H, 5.1; N, 7.4%. Found: C, 52.35; H, 5.0; N, 7.7%. Selected IR data (\tilde{v}_{max} /cm⁻¹): 1657s, 1592s, 1504w, 1385vs, 1312s, 1275s, 1171m, 1130m, 1092w, 834w, 779s, 675m.

Cation exchange

{Li₂[Co₃(ntb)₂(bdc)]}_n·4EtOH·8H₂O (JUMP-1(Li)·4EtOH ·8H₂O). The as-synthesized JUMP-1·4DMF·2H₂O was immersed in a saturated ethanolic LiNO₃ solution for 10 d. During this period the soaking solution was replaced every 24 h. After the 10 d period the lithium ion exchanged material was subsequently soaked for one week in ethanol to remove any residual free LiNO₃ molecules. According to the elemental analysis of the final product the organoammonium cations present in the as-synthesized JUMP-1·4DMF·2H₂O were fully replaced by the lithium cations. The obtained lithium ion exchanged framework is further denoted as JUMP-1(Li). CHN elemental analysis calcd for C₅₈H₆₈Co₃Li₂N₂O₂₈ (M = 1431.84): C, 48.65; H, 4.8; N, 2.0%. Found: C, 48.3; H, 4.95; N, 1.8%. Selected IR data (\tilde{v}_{max} /cm⁻¹): 3326br, 1589s, 1506w, 1378vs, 1313s, 1273s, 1174m, 1147m, 1087w, 1045m, 833w, 780s, 675m. Published on 23 March 2017. Downloaded by Fudan University on 24/03/2017 04:19:05.

X-ray structure determination

The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.²⁰ The structure was solved by direct methods (SHELXS)²¹ and refined by full-matrix least squares techniques against F_0^2 (SHELXL).²¹ The crystal structure of JUMP-1 contains large voids, filled with disordered dimethylammonium cations and solvent molecules. The total size of the voids is 13846 Å³/unit cell. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON²² resulting in 2787 electrons/unit cell. All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.²¹ Diamond 4.2.2 was used for structure representations.²³

Crystallographic and refinement parameters for JUMP-1. Formula $C_{50}H_{28}Co_3N_2O_{16}$, M = 1089.53, orthorhombic *Cmca*, a = 33.6004(6), b = 26.9604(5), c = 23.2138(5) Å, V = 21028.9(7) Å³, T = 133 K, Z = 8, $\rho_{calc} = 0.688$ g cm⁻³, $\mu = 0.501$ mm⁻¹, 69315 measured reflections, $\theta_{max} = 27.34^{\circ}$, 11978 unique reflections ($R_{int} = 0.0856$) and 7595 observed reflections ($I > 2\sigma(I)$), 321 parameters, goodness of fit on $F^2 S = 1.020$, $R_1 = 0.0649$ (observed reflections), $wR_2 = 0.1984$ (all unique reflections). More details can be found in the deposited cif file CCDC 1508581 which contains additional crystallographic data.

Sample pretreatment and sorption measurements

Dichloromethane activation. The as-synthesized JUMP-1 was activated by carrying out solvent exchange with dichloromethane. This was done by soaking the sample (50-70 mg) in dichloromethane (10 mL) for 7 d during which the solvent was replaced by decanting every 24 h. Finally the supernatant liquid was removed and the sample dried in air. The final resulting product is further denoted as JUMP-1^{dcm}.

Supercritical carbon dioxide activation. In an alternative pretreatment procedure the as-synthesized JUMP-1 (50-70 mg) was soaked in ethanol (10 mL) for one week during which the solvent was replaced every 24 h by decanting the supernatant. Subsequently this was followed by a drying process using supercritical CO₂. For this drying procedure the ethanol-immersed samples were decanted and the resulting slurry transferred into an autoclave (100 mL volume) and sealed. Liquid CO_2 was then introduced into the autoclave at a final pressure of 60 bar and allowed to stand 30 min. To ensure removal of any possible nonoccluded ethanol, the liquid CO2 was slowly removed over a period of 20 min. A second batch of liquid CO₂ was then introduced into the reactor (60 bar), but this time allowed to stand for 24 h. The temperature of the reactor was subsequently raised to 40 $^{\circ}\mathrm{C}$ to bring the CO_2 to supercritical conditions and maintained at this temperature for one hour. The CO₂ was then slowly released over 30 min with the temperature continuously maintained at 40 °C in order to prevent any cooling that might result from expansion of the gas during evaporation. This supercritical drying (scd) procedure was applied to the as-synthesized JUMP-1

and the lithium ion exchanged JUMP-1(Li) samples resulting in the products JUMP-1^{scd} and JUMP-1(Li)^{scd}, respectively.

Sorption measurements. The isotherms of all pretreated and dried products were measured immediately after degassing the samples for 30 min at room temperature. Pore size distribution curves were calculated by fitting the experimental data using a quenched solid density functional theory (QSDFT) kernel based on adsorption models for N₂ on carbon at 77 K with cylindrical/slit pores, which was provided by QUANTACHROME Instruments.²⁴ The Brunauer-Emmett-Teller (BET) surface areas for both materials were determined from the adsorption data over different relative pressure ranges all between 0.005–0.28 while ensuring compliance with the consistency criteria.²⁵

Results and discussion

Synthesis

The title compound JUMP-1 was prepared utilizing the copolymerization technique. It was shown earlier that this reaction technique requires a subtle balance between geometry and statistics.⁵ To evaluate these conditions it was found that the geometric ratio between the length of the ditopic (L_d) and tritopic (L_t) linkers is an important parameter (see Scheme 1). It was reported that the ratio L_d/L_t should not be too high with the ideal value of just around one, as using a higher ratio might lead to the formation of two distinct coordination polymers based on the individual linkers rather than the expected copolymer. Moreover, when using a mixture of ditopic and tritopic linkers, reported results show that an excess of the ditopic linker is beneficial for the generation of the desired copolymerization product.⁵



Scheme 1 Linkers used for the synthesis of JUMP-1. L_d and L_t define the characteristic lengths for the ditopic and tritopic linkers, respectively $(L_d/L_t = 1.01)$.

The tritopic linker 4,4',4"-nitrilotribenzoic acid being utilized in our synthesis leads to an almost ideal L_d/L_t ratio when combined with terephthalic acid (see Scheme 1). The ditopic linker was used in slight excess of approximately 6:4 (M_d/M_t). The linkers were predissolved in DMF solution followed by the addition of four equivalents of cobalt(II) chloride hexahydrate, all under continuous stirring. The solvent DMF was deliberately chosen, as to provide a source for the in situ generation of organic cations to stabilize the desired anionic framework. Solvothermal treatment of the resulting solution at 140 °C for 3 days followed by slow cooling (5 °C h⁻¹) leads to the formation of a violet crystalline material in rather high yields. Based on elemental and thermal analysis performed on samples dried in vacuo the composition of the final material corresponds to the dimethylammonium salt

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Fig. 1 Cut-out view of the trinuclear SBU showing the coordination environments around the cobalt(II) ions. Only carboxylate groups are depicted for clarity. Symmetry codes: $A = -\frac{1}{2} - x$, +y, $\frac{3}{2} - z$; $B = -\frac{1}{2} - x$, $\frac{3}{2} - y$, 1 - z; C = + x, $\frac{3}{2} - y$, $\frac{1}{2} + z$; $D = \frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$; E = + x, $\frac{1}{2} + y$, $\frac{3}{2} - z$.

 $\{((CH_3)_2NH_2)_2[Co_3(ntb)_2(bdc)]\}_n$ (JUMP-1) which contains additional four molecules of DMF and two molecules of water per formula unit.

X-ray crystal structure

Crystals suitable for structural analysis were obtained directly from the solvothermal synthesis and are found to crystallize in the orthorhombic space group *Cmca*. The data reveals the presence of a 3D network with a pillared-layer structural arrangement. The crystallographic asymmetric unit contains two independent cobalt atoms, one ntb^{3–} linker and the half of a terephthalic acid moiety (see Fig. S1). One of the cobalt(II) ions (Co1) is located on a crystallographic inversion center leading to the overall formula $\{[Co_3(ntb)_2(bdc)]\}_n^{2n-}$ for the anionic 3D framework.

The two crystallographically independent cobalt(II) ions show distinct differences in their coordination geometry. The atom Co1 is situated on an inversion center and shows an octahedral coordination provided by six carboxylate oxygen atoms each from a different ntb³⁻ linkers. Whereas the Co2 center possesses a distorted tetrahedral coordination geometry and is surrounded by three oxygen atoms from three different ntb³⁻ ligands with the fourth position being taken up by an oxygen atom (O7) from the terephthalic acid. The central Co1 ion together with the two crystallographically equivalent Co2 and Co2A ions at the terminal positions are giving rise to a linear trinuclear cluster which can be regarded as an SBU (see Fig. 1). Although linear trinuclear arrangements have been reported as SBUs in coordination frameworks,^{26,27} the observed mixed coordination geometries at the cobalt(II) ions $(T_d - O_h - T_d)$ in JUMP-1 are unusual with respect to the carboxylate ligand environment.²⁸⁻³⁰ The trinuclear cluster SBUs are linked together via the ntb³⁻ ligands leading to the formation of neutral 2D networks with the formula $\{[Co_3(ntb)_2]\}_n$. These layers are then in turn connected with each other via the terephthalic acid linkers which serve as pillars holding up the structure. A representation of the resulting anionic 3D framework structure is depicted in Fig. 2 (see also Figs. S2 and S3).

The Co1 and Co2 ions within the trinuclear cluster are solely bridged by the carboxylate groups of the ntb³⁻ linkers. Overall there are three carboxylate bridges, one in a monodentate $\mu_{1,1}$



Fig. 2 3D framework of JUMP-1 viewed along [010] direction. 2D networks composed of linear trinuclear cobalt(II) SBUs and ntb^{3-} ligands are arranged along the (100) plane and interconnected by the bdc^{2-} pillars. Red polyhedra represent cobalt(II) centers.

mode (O3) and two in a bidentate *syn–syn* $\mu_{1,3}$ mode (O1/O2 and O5/O6), leading to a Co1–Co2 distance of 327 pm. The bridging angle Co1–O3–Co2 at the monodentate carboxylate is found to be 103°. This leads to only slight distortions from the octahedral coordination at the central Co1 ion with bond lengths and angles within the expected range (see Tables S1 and S2). On the other hand a significant distortion from the tetrahedral coordination is observed for the Co2 ions which is evident from the bond angles. In fact, the largest O–Co2–O bond angle is found to be about 133°, whereas the smallest is only about 96°. This is caused by steric effects of the non-coordinated oxygen atoms of the monodentate carboxylate ligands.

The linear trinuclear SBUs within the 2D networks are well separated with distances of about 1350 pm between their central Co1 centers. For the SBUs also a large interlayer separation is observed with a distance of about 1076 pm between the terminal Co2 centers of corresponding SBUs bridged by a terephthalate ligand. The charge of the resulting anionic 3D framework (see Scheme 2) needs to be balanced. This is attributed to the presence of two dimethylammonium cations in the void formed by the well-known thermal decomposition of DMF under the given reaction conditions.³¹ Although these counterions could not be located in the crystal structure, due to the presence of large amounts of diffuse solvent molecules in the void of the framework structure, their formation is evidenced by elemental and thermogravimetric analysis.

The overall anionic 3D framework can be described as a stack of 2D sheets separated by terephthalic acid ligands to give the 3D cage-structure as shown in Fig. 2 (see also Figs. S2 and S3). The topological analysis of the crystal structure of JUMP-1 utiPublished on 23 March 2017. Downloaded by Fudan University on 24/03/2017 04:19:05.

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Scheme 2 Schematic representation showing the build up of the anionic 3D framework of JUMP-1.

lizing TOPOS 5.0³² revealed a binodal net (Tables S3 and S4). The simplification of the network results in two different types of nodes which are eight- and three-connected. The corresponding topological net is depicted in Fig. 3 (cf. Figs. S4 and S5). The eight-connected node represents the linear trinuclear cobalt cluster, i.e. the SBU with eight attached carboxylate groups. Six of these connecting carboxylate groups originate from the ntb^{3-} ligands. The central nitrogen atom of the latter can be regarded as the three-connected node (see also Fig. S5). The other two carboxylate groups belong to the terephthalic acid pillars solely linking the eight-connected nodes. The analysis of the topology thus reveals a 3,8-connected net with tfz-d topology and the point symbol $(4^3)_2(4^6.6^{18}.8^4)$.



Fig. 3 Representation of the tfz-d topology of the network of JUMP-1 viewed approximately along the crystallographic [010] direction. The red and blue spheres represent the trinuclear cobalt clusters (8-connected nodes) and the nitrogen atoms of the ntb^{3-} ligands (3-connected nodes), respectively.

Powder diffraction and thermal analysis

The phase purity of the bulk material of JUMP-1 was confirmed by X-ray powder diffraction (XRPD) measurements. Their is close agreement of the experimental data with the simulations based on the single crystal structure, except for intensity differences that might be attributed to the presence of extra framework species within the pores (see Fig. S6).³³

The thermal analysis of JUMP-1 showed a gradual weight loss up to about 380 °C before the compound starts to thermally decompose (see Fig. S7). The first step consists of two individual partially overlapping events as indicated by the differential thermal gravimetric analysis, which can be attributed to the loss of solvent molecules. The lower mass loss at the first event (about 3.7%) suggest the water molecules to be more loosely bonded than the DMF molecules. The overall mass loss of 21.9% for the temperature range up to about 200 °C nicely compares to the calculated value for two water and four DMF molecules (21.7%). The following temperature range up to the onset of the decomposition of the organic ligand framework at about 380 °C corresponds to a weight loss of about 7% and can be attributed the loss of the two dimethylammonium counterions (calcd 6.1%). The further decomposition of the organic ligand framework consists of several steps which finally led to a rest mass of 15.0% at 600 °C which is in good agreement with the theoretical value of 14.9% expected for CoO.

Magnetic properties

The magnetic susceptibility data for JUMP-1 were measured in the temperature range from 2 to 300 K with an applied field of 2 kOe and is depicted in Fig. 4 as a temperature-dependent plot of $\chi_{\rm M}T$ and $\chi_{\rm M}^{-1}$. The room temperature $\chi_{\rm M}T$ value of 8.5 cm³ K mol⁻¹ is significantly higher than the corresponding spin-only value for three magnetically isolated cobalt(II) ions $(5.63 \text{ cm}^3 \text{ K} \text{ mol}^{-1})$ S = 3/2, g = 2) which clearly indicates strong spin-orbital coupling.³⁴ Upon decreasing the temperature the $\chi_M T$ value slowly decreases down to a temperature of 8K with a slightly increasing slope below 100 K and a further significant drop down to a value of $5.8 \text{ cm}^3 \text{ K} \text{mol}^{-1}$ at 2 K. The observed behavior can basically be attributed to spin-orbit coupling as well as the presence of antiferromagnetic exchange interactions between the cobalt(II) ions.^{27–29} As indicated by the $\chi_{\rm M}^{-1}$ vs. T data JUMP-1 displays paramagnetic behavior for temperatures above 50 K with a Curie constant of $8.86 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ and a Weiss constant of -12.3 K. The latter being consistent with the presence of antiferromagnetic coupling.

The field-dependent magnetization was measured in a temperature range from 2 to 5 K and up to fields of 5 T (see Fig. S8). The expected behavior for increasing field strength is observed with a value of about $6.3 N\beta$ at 2 K and 5 T. The data indicates that saturation has not been reached under the given conditions. Nevertheless, this value is consistent with the presence of an octahedral³⁵ and two distorted tetrahedral cobalt(II) ions^{36,37} as found in the crystal structure for the central and the two terminal cobalt centers, respectively.

The trinuclear cobalt(II) SBUs are found to be well-separated from each other within the framework structure, which suggests that the magnetic data of JUMP-1 can be analyzed based on the treatment of these isolated units. Nevertheless, additional exchange coupling between these SBUs through the bridging car-



Fig. 4 Temperature dependence of the magnetic susceptibility $\chi_M T$ (black squares) and χ_M^{-1} (black circles) for JUMP-1. The solid line represent the best fits (see text for parameters).

boxylate ligands cannot be fully excluded. However, a full treatment for the in turn resulting extended three-dimensional exchange coupled system is not feasible. Moreover, the occurrence of two geometries (O_h and T_d) within the trinuclear clusters requires a multi-parameter approach including spin-orbit coupling to allow a consistent description of the distinct magnetic properties of the corresponding cobalt(II) ions, ^{34,35,38} i.e. individual sets of zero-field splitting (ZFS) parameter D and g-factor for both the octahedral and the tetrahedral cobalt(II) centers. Corresponding attempts to fit the susceptibility data over the entire temperature range were unsuccessful due to an overparameterization and led to an inadequate description of the system.

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On the other hand, it is well-known that octahedral cobalt(II) ions can be treated as effective spin S' = 1/2 systems at low temperatures.³⁵ This in turn should allow to analyze the corresponding field-dependent magnetization data, which is measured at sufficiently low temperatures, by a simplified interaction model for the trinuclear cobalt(II) units. Since an effective spin of S' = 1/2is assumed for the central octahedral cobalt(II) ion, only the ZFS effects of the two terminal tetrahedral cobalt(II) centers are to be considered within this model by including an axial ZFS parameter *D* in the fit.²⁸ The resulting Hamiltonian utilized in fitting the field-dependent magnetization data are given in Eq. (1).

$$H = J(S_1S_2 + S_1S_{2A}) + 2D\left[S_2(z)^2 - \frac{1}{3}S_2(S_2 + 1)\right]$$
(1)

The fitting of the magnetization data were performed with the routine *MagProp* included in the software package *DAVE*.³⁹ An additional self-consistent mean-field approximation as implemented in *MagProp*⁴⁰ was introduced in the fitting to account for possible intercluster exchange within the framework. To avoid overparameterization only a single *g*-factor was used for both types of cobalt(II) ions. The experimental data are reproduced with the following fit parameters g = 2.75, D = -2.9 cm⁻¹, J = -6.5 cm⁻¹, and zJ' = -0.06 cm⁻¹ (see Fig. S8).

The obtained intercluster exchange is consistent with the previous assumption of only weakly interacting trinuclear units. The exchange coupling constants *J* within the trinuclear SBU is comparable to values reported for similar trinuclear systems.²⁹ Moreover, the antiferromagnetic coupling between the central and the terminal cobalt(II) ions is consistent with the observed *syn–syn* and $\mu_2 - \eta^2$ carboxylate bridging modes. This is based on the observation that *syn–syn* and *anti–anti* conformations generally favor antiferromagnetic coupling, while *syn–anti* promotes ferromagnetic coupling.⁴¹ On the other hand, for $\mu_2 - \eta^2$ carboxylate bridges a dependence on the Co–O–Co bridging angle is reported with values above 100° related to antiferromagnetic interactions between the adjacent cobalt(II) ions.⁴² This, in fact, is constituent with the corresponding angle of about 103° observed for JUMP-1 (see Table S2).

To further address the magnetic properties of JUMP-1 alternating-current susceptibility measurements as well as the a set of zero-field cooled and field cooled magnetization measurements have been performed. However, neither a signature for slow magnetization dynamics nor any kind of ordering could be detected.

Cation exchange studies

The possibility of replacing the organic cations present within the void of the framework was probed by immersing samples of JUMP-1 in solutions of the salt of a small monovalent cation such as lithium. This was done by soaking a sample of JUMP-1 in saturated ethanolic lithium nitrate solution for a period of 10 d followed by washing with ethanol. In order to remove any residual free lithium salt from the sample the resulting material was further soaked in ethanol for another 7 d. The corresponding lithium ion exchanged sample is further denoted as JUMP-1(Li). Post-exchange XRPD spectra obtained for JUMP-1(Li) are in good agreement with the patterns observed for the as-synthesized bulk material indicating that the framework was left intact even upon exchange of the organic counterions (see Fig. S9). The uptake of the lithium cation was further confirmed by CHN elemental analysis (see Experimental Section), which is consistent with the presence of two lithium ions per formula unit of the anionic framework. Additional evidence for a full exchange of the organic counterions comes from the thermal analysis of lithium ion exchanged sample JUMP-1(Li) which is lacking an corresponding mass loss (see Fig. S10). This nicely confirms the possibility of post-synthetic replacement of the counterions within the anionic framework of JUMP-1 without any detectable impact on the stability of the framework.

Gas-sorption properties

The porosity of the anionic framework JUMP-1 was studied by measuring the N_2 and CO_2 adsorption isotherms of the assynthesized and lithium ion exchanged materials. The activation of the as-synthesized sample was first attempted by a solventexchange process utilizing dichloromethane followed by gentle outgassing of the air-dried sample at room temperature to obtain JUMP-1^{dcm} (see Experimental Section for more details). However, this treatment led to the collapse of the accessible pores with a very low available surface area for gas sorption (see TaPublished on 23 March 2017. Downloaded by Fudan University on 24/03/2017 04:19:05.

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Fig. 5 N_2 isotherms of JUMP-1 $^{\rm scd}$ (red) and JUMP-1(Li) $^{\rm scd}$ (blue) at 77 K. Open shapes denote desorption.

Table 1 Characteristic adsorption parameters for the as-synthesized and lithium ion exchanged samples JUMP-1^{scd} and JUMP-1(Li)^{scd} after pretreatment by supercritical drying with CO₂

Parameter	JUMP-1 ^{scd}	JUMP-1(Li) ^{scd}
$a(BET) (m^2 g^{-1})$	113	355
Total Pore Volume ($cm^3 g^{-1}$)	0.13	0.22
Pore Width (Mean) (nm)	4.7	2.5
Pore Width (Mode) (nm)	1.0	0.6

ble S5), as indicated by the N_2 isotherm and the corresponding pore size distribution (Figs. S11 and S12). We therefore explored an alternative activation procedure which is based on the treatment of the samples with supercritical CO_2 to obtain JUMP-1^{scd} and JUMP-1(Li)^{scd} form the as-synthesized and the lithium ion exchanged samples, respectively (see Experimental Section for more details). This has been reported earlier to be a milder form of treating materials, which is attributed to a more gentle evacuation of the pores preventing mesopore collapse and thereby ensuring the accessibility of micropores.⁴³

The N₂ isotherms for the materials JUMP-1^{scd} and JUMP-1(Li)^{scd} are presented in Fig. 5 and the relevant data are summarized in Table 1. For JUMP-1^{scd} an appreciable BET surface area of about $113 \text{ m}^2 \text{ g}^{-1}$ together with a total pore volume of $0.13 \text{ cm}^3 \text{ g}^{-1}$ was obtained. Upon replacement of the organic cations by the lithium ions, a more than threefold increase in BET surface area to a value of $355 \text{ m}^2 \text{ g}^{-1}$ was observed. However, this is related with only a slight gain in the total pore volume to a value of $0.22 \text{ cm}^3 \text{ g}^{-1}$. With respect to the overall void given by the anionic framework ($0.96 \text{ cm}^3 \text{ g}^{-1}$ calculated from the crystal structure of JUMP-1), the total pore volume determined for JUMP-1^{scd} and JUMP-1(Li)^{scd} corresponds to about 14 and 23 %, respectively.

The isotherms shown in Fig. 5 can be classified as Type II isotherms according to IUPAC rules.⁴⁴ The hysteresis loops observed can be described as Type H4 which are somewhat characteristic for the presence of slit-shaped pores. The lower surface area of the as-synthesized material can be attributed to the steric



Fig. 6 Pore size distribution data for JUMP-1 $^{\rm scd}$ (top) and JUMP-1(Li) $^{\rm scd}$ (bottom).

demand of the organic cations when present in the framework, as they should hamper the accessibility of the internal pores for incoming guest molecules. Interestingly, the lithium ion exchange led to a considerable increase in porosity, as it is indicated by both the significantly increase BET surface area and the larger total pore volume. This can be attributed to a reduced steric demand of the counterions upon replacement of the organic by the smaller lithium ions, thereby enabling greater access to the micropores.⁴⁵

To further elucidate this point a pore size analysis of the pretreated samples JUMP-1^{scd} and JUMP-1(Li)^{scd} was performed. The resulting pore size distribution plots are displayed in Fig. 6. The comparison clearly indicates a massive increase in the population of micropores for the lithium ion exchanged sample JUMP-1(Li)^{scd}, especially in the range below 1 nm. This is consistent with the above indicated stabilization of the mesopore structure by the gentle pretreatment with the supercritical CO_2 drying.⁴³ This clearly shows that the accessibility to micropores within an anionic framework can be adjusted via the variation of the size of cations residing in the pores.⁴⁶

A similar basic trend can be seen form the CO_2 adsorption isotherms of the pretreated samples JUMP-1^{scd} and JUMP-1(Li)^{scd} (see Fig. S13), as for the latter a slightly higher volume in total adsorbed CO_2 is observed. However, the ratio of adsorbed CO_2 does not follow that obtained in the case of the N₂ isotherms. This can be attributed to characteristics of the CO_2 adsorption process which does neither generally scale with the pore volume nor with the available BET surface area as obtained from N₂ adsorption. In fact, the CO₂ adsorption rather tends to prefer smaller pores, which is due to the possibility of increasing adsorbate—adsorbent interactions.⁴⁶ Furthermore, as indicated from the N₂ adsorption data there is only a moderate difference in the total pore volume between JUMP-1^{scd} and JUMP-1(Li)^{scd}. A combination of both factors is assumed to be responsible for the absence of appreciable variations in the amount of adsorbed CO₂ for the pretreated as-synthesized and lithium ion exchanged materials.

Conclusions

A pillared-layer cobalt(II) MOF JUMP-1 based on the redox-active triphenylamine linker H₃ntb was synthesized by a solvothermal reaction. The structure of JUMP-1 can be viewed as constructed from neutral 2D networks ${[Co_3(ntb)_2]}_n$, which in turn are linked by terephthalic acid as anionic pillar ligand. The charge of the resulting anionic 3D framework is compensated by in situ generated dimethylammonium cations. For the 3D framework this leads to a 3,8-coordinated net with tfz-d topology. The linear trinuclear SBUs observed in JUMP-1 exhibit mixed coordination geometries for the three cobalt(II) ions, i.e. octahedral for the central and tetrahedral for the two terminal ions. Such mixed geometries are uncommon for a solely carboxylate based coordination environment as observed in JUMP-1. The trinuclear SBUs were found to be magnetically well-separated and show an antiferromagnetic exchange coupling between the octahedral and the tetrahedral cobalt(II) ions. The porous material JUMP-1 is susceptible to exchange of the counterions present in the void of the 3D network indicating the robust nature of the anionic framework. Pretreatment prior to the gas-sorption experiments with supercritical CO₂ turned out to be very effective in making micropores accessible. The comparison of the as-syntheszied and the lithium ion exchanged sample clearly shows that the accessibility to micropores within the anionic framework can be adjusted by variation of cation size residing within the pores. In fact, this led to a massive increase in the population of micropores for the lithium ion exchanged material JUMP-1(Li)scd.

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Graphical Abstract

Tricarboxyltriphenylamine and terephthalic acid act as linkers in a pillared-layer anionic cobalt(II) framework. The counterions can be exchanged while keeping the framework intact, leading to improved sorption properties for the small lithium ions.