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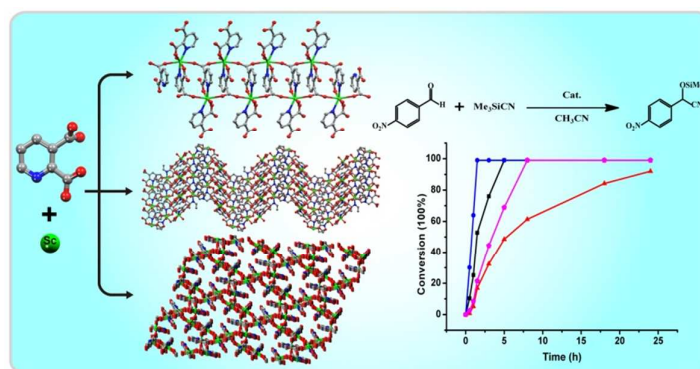You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

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$Sc_2(pydc)_2$ Unit Based 1D, 2D and 3D Metal-Organic Frameworks as Heterogeneous Lewis Acid Catalysts for Cyanosilylation

Yu Cao,[a] Ziqian Zhu,[a] Jianing Xu,[a] Li Wang,[a] Jiayin Sun*,[b] Xiaobo Chen,[c] and Yong Fan*[a]

ABSTRACT FOR WEB PUBLICATION

Three new Sc-MOFs have been synthesized by using the organic H_2pydc linker and Sc (III) ions. **1** features a ladder-shaped chain, **2** displays a waved layer and **3** exhibits a (3, 3)-connected **nbo-a** network containing left and right helixes structure features. All the three compounds show good heterogeneous Lewis acid catalytic abilities for the cyanosilylation of aldehyde.

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ARTICLE

Sc₂(pydc)₂ Unit Based 1D, 2D and 3D Metal-Organic Frameworks as Heterogeneous Lewis Acid Catalysts for Cyanosilylation

Yu Cao,[a] Ziqian Zhu,[a] Jianing Xu,[a] Li Wang,[a] Jiayin Sun*,[b] Xiaobo Chen,[c] and Yong Fan*,[a]

Three scandium metal-organic frameworks (Sc-MOFs), [Sc(pydc)(Hpydc)(H$_2$O)]·H$_2$O (**1**), [Sc$_2$(pydc)$_3$(H$_2$O)$_4$]·5H$_2$O (**2**) and [Sc(pydc)(H$_2$O)(NO$_3$)] (**3**) with similar Sc$_2$(pydc)$_2$ building unit, were prepared by using 2,3-pyridinedicarboxylic acid (H$_2$pydc) ligand under hydrothermal conditions. Compound **1** exhibits a ladder-shaped chain with Sc$_2$(pydc)$_2$ units which further construct a supramolecular characteristic with water molecules via hydrogen bond. Compound **2** features a waved layer made up of pydc^{2-} ligands and two kinds of crystallographically different Sc(III) ions, among which Sc2 and pydc^{2-} ligands constructed the Sc$_2$(pydc)$_2$ units. In compound **3**, left and right helixes were alternate linked by the Sc$_2$(pydc)$_2$ units forming a hexagonal network with **nbo-a** topology. All the prepared compounds present effective heterogeneous Lewis acid catalytic functionality for the cyanosilylation of aldehyde.

Introduction

Over the past few years, intensive efforts have been devoted to the development of trivalent metal derivatives heterogeneous Lewis acid catalysts.[1] Compared to traditional Lewis acid catalysts, these trivalent metal compound catalysts express outstanding catalytic activities in terms of carbon-carbon bond forming reactions and Friedel-Crafts reactions due to their low toxicity and high selectivity. A variety of organic reactions can be effectively promoted by such novel lewis acid catalysts under mild conditions, which reveals a promising application prospect. The design and synthesis of novel trivalent metal compound catalysts with high chemical selectivity and high stereoselectivity, however, remains a challenge. As an emerging functional material, metal-organic frameworks (MOFs) or coordination polymers (CPs) have attracted much attention due to their distinguishing applications and fascinating structural diversities.[2, 3] In particular, MOFs have great potential applications as catalyst owing to their unusual pore shapes and tunable pore size.[4] The first coordination polymeric catalyst, [Cd(4,4'-bpy)$_2$(NO$_3$)$_2$]$_n$, was reported by M. Fujita and co-workers. They found that the square network material is highly shape-selective.[5] J. S. Chang et al. reported that trimeric chromium(III) octahedral clusters of MIL-101 possess terminal water molecules, it could provide the coordinatively unsaturated metal sites (CUS) as Lewis acid sites after vacuum treatment at 150 °C for 12 hours.[6] B. Gomez-Lor et al. prepared In$_2$(OH)$_3$[O$_4$C$_8$H$_4$]$_{1.5}$ and studied the catalytic effect of selective oxidation organic sulfide reactions.[7]

Sc(III) readily forms MOFs with variable pore size and high thermal stability, which leads to a high stereoselectivity of catalytic effect. In 2003, the first highly thermally stable organic-inorganic 3D polymer, [Sc$_2$(OOCC$_2$H$_4$COO)$_{2.5}$(OH)], was prepared by Caridad et al,[8] which can be used as effective Lewis acid catalyst for Friedel-Crafts acylation and benzaldehyde acetylization, and can be easily recycled without any appreciable expense on activity. J. Perles et al. successfully synthesized [Sc$_2$(C$_4$H$_4$O$_4$)$_{2.5}$(OH)] and [Sc$_2$(C$_8$H$_4$O$_4$)$_3$] and evaluated their performance as heterogeneous Lewis acids catalysts in acetalization of aldehydes.[9] Inspired by their work, we aimed to develop new heterogeneous Lewis acid catalysts of Sc-MOFs hydrothermally by utilizing Sc (III) ions' small radius, high electronic charge and affinity to coordination with oxygen atoms. 2,3-pyridinedicarboxylic acid (H$_2$pydc) was selected as organic ligand, since O- and N-donors of H$_2$pydc can lead to a variety of promising spatial structures. We have, therefore, exploited H$_2$pydc as chelating ligand, which has limited steric hindrance combined with weak stacking interactions. As such, it facilities the formation of CPs with concomitant scopes for bridging metal ions through carboxylate groups to propagate the coordination chain. Three Sc-MOFs, [Sc(pydc)(Hpydc)(H$_2$O)]·H$_2$O (**1**), [Sc$_2$(pydc)$_3$(H$_2$O)$_4$]·5H$_2$O (**2**) and [Sc(pydc)(H$_2$O)(NO$_3$)] (**3**) were obtained and their structures and catalytic performances were characterized.

Compound **1** is a 1D ladder-shaped chain, compound **2** features a 2D waved layer, while compound **3** demonstrates a 3D network with **nbo-a** topology. It's worthwhile noting that all the three compounds have similar $Sc_2(pydc)_2$ unit, which may be attributed to their analogic preparation conditions. In addition, considering the high water and thermal stabilities and the unique nature of Sc(III), these compounds display good catalytic activities for the cyanosilylation of aldehyde.

Experimental

Materials and methods

All the reagents of analytical grade were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max-2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The infrared (IR) spectra were recorded within the 400-4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The thermal gravimetric analyses (TGA) were performed on a TGA Q500 thermogravimetric analyzer used in air with a heating rate of 10 °C min^{-1}. ^1H NMR spectra were measured on a Bruker Avance 300 console at a frequency of 300 MHz.

Synthesis of compound 1

A mixture of $ScCl_3 \cdot 6H_2O$ (0.3 mmol, 78 mg), H_2pydc (0.6 mmol, 43 mg), KOH (0.1 mL, 1 M) and H_2O (3 mL) was stirred at room temperature until a homogeneous mixture was obtained. The mixture was transferred into a Teflon-lined autoclave (23 mL) and heated at 100 °C for 24 hours and then cooled to room temperature under ambient conditions. Colorless acicular crystals of 1 were recovered by filtration, washed with distilled water, and dried in air (80.8% yield based on $ScCl_3 \cdot 6H_2O$). Anal. Calc. for 1: C, 39.32; H, 2.86; N, 6.67. Found: C, 40.79; H, 2.69; N, 6.79%. Selected IR data (KBr, cm^{-1}): 3387 (m), 3100 (m), 1658 (m), 1538 (s), 1424 (m), 1372 (m), 1115 (w), 849 (w).

Synthesis of Compound 2

A mixture of $ScCl_3 \cdot 6H_2O$ (0.3 mmol, 78 mg), H_2pydc (0.6 mmol, 43 mg), KOH (0.2 mL, 1 M) and H_2O (3 mL) was stirred at room temperature until a homogeneous mixture was obtained. The mixture was transferred into a Teflon-lined autoclave (23 mL) and heated at 100 °C for 2 days and then cooled to room temperature under ambient conditions. Colorless club-shaped crystals of 2 were recovered by filtration, washed with distilled water, and dried in air (75.2% yield based on $ScCl_3 \cdot 6H_2O$). Anal. Calc. for 2: C, 45.02; H, 2.81; N, 9.66. Found: C, 44.91; H, 2.74; N, 9.52%. Selected IR data (KBr, cm^{-1}): 3406 (m), 3097 (w), 1651 (s), 1583 (m), 1401 (s), 1108 (m), 864 (w).

Synthesis of Compound 3

A mixture of $Sc(NO_3)_3 \cdot 6H_2O$ (0.3 mmol, 102 mg), H_2pydc (0.6 mmol, 43 mg), and H_2O (3 mL) was stirred at room temperature until a homogeneous mixture was obtained. The mixture was transferred into a Teflon-lined autoclave (23 mL) and heated at 120 °C for 3 days and then cooled to room temperature under ambient conditions. Colorless block crystals of 3 were recovered by filtration, washed with distilled water, and dried in air (68.3% yield based on $Sc(NO_3)_3 \cdot 6H_2O$). Anal. Calc. for 3: C, 28.89; H, 1.86; N, 9.78. Found: C, 28.98; H, 1.72; N, 9.66%. Selected IR data (KBr, cm^{-1}): 3179 (m), 1635 (m), 1583 (s), 1416 (s), 1113 (m), 831 (m).

The phase purity of as-synthesized samples was confirmed by the evident similarities between the simulated and experimental X-ray powder diffraction patterns (Fig. S1~S3†). The IR spectra for **1~3** were shown in Supporting Information Fig. S4†.

X-ray Structure Determinations

Suitable single crystals of **1~3** were selected for single-crystal X-ray diffraction analyses. Crystal data for **1~3** were collected on a Rigaku RAXIS-RAPID diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL Version 5.1.[10] All the metal atoms were located first, and then the oxygen, nitrogen, and carbon atoms of the compounds were subsequently found in difference Fourier maps. The hydrogen atoms of the ligands were placed geometrically, and the hydrogen atoms of the water molecules could not be located but were included in the formula. All non-hydrogen atoms were refined anisotropically. The final formula was derived from crystallographic data combined with elemental and thermogravimetric analysis data. Crystallographic data for **1~3** (CCDC 976321-976323) have been deposited with Cambridge Crystallographic Data Centre. Data can be obtained free of charge upon request at www.ccdc.cam.ac.uk/data_request/cif. The detailed crystallographic data and structure refinement parameters for **1~3** are summarized in Table **1**. Topology information for **2** and **3** were obtained using TOPOS 4.0 program.[1]

Results and discussion

Crystal Structure of compound 1

Single-crystal X-ray diffraction analysis reveals that compound 1 crystallizes in monoclinic space group $P2_1/c$. The selected bond distances and bond angles are summarized in Table S1†. The asymmetric unit of compound 1 contains a crystallographically independent Sc(III) atom, two pydc^{2-} ligands, one coordinated water molecule and one lattice water molecule. As depicted in Fig. S5†, Sc1 center is seven-coordinated with five oxygen atoms and two nitrogen atoms, in which four coordinated oxygen atoms are from the carboxylic group of four different pydc^{2-} ligands, the remaining oxygen atom is from terminal water molecule, two nitrogen atoms are provided by the pyridyl group of two pydc^{2-} ligands. The Sc-O

bond lengths vary from 2.297(2) to 2.526(3) Å, and the Sc-N bond length is 2.291(3) Å, which are all in the normal ranges.[12]

Table 1 Crystal data and structure refinement for compounds **1~3**.

Name	Compound 1	Compound 2	Compound 3
formula	$C_{14}H_{11}N_2O_{10}Sc$	$C_{33}H_{24}N_6O_{18}Sc_2$	$C_7H_5N_2O_8Sc$
fw	412.21	882.50	290.09
Temp (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	trigonal
Space group	$P2_1/c$	$P2_1/c$	R-3
a (Å)	6.3313(6)	9.817(2)	23.2465(2)
b (Å)	33.114(4)	10.987(2)	23.2465(4)
c (Å)	7.5538(6)	11.461(2)	10.2390(3)
β (deg)	93.400(6)	71.08(3)	90
Volume (Å^3)	1580.9(3)	1058.5(3)	4791.8(3)
Z	4	1	18
Dc (mg/m^3)	1.732	1.384	1.809
μ(mm^{-1})	0.529	0.398	0.730
$F(000)$	840	450	2628
Reflections collected	11404/3952	8452/3719	13232/2453
Unique (Rint)	[R_{int}=0.0888]	[R_{int}=0.0486]	[R_{int}=0.0767]
Goodness on fit	1.117	1.342	1.206
R_1, wR_2 [$I>2\sigma(I)$]	0.0774, 0.1814	0.0992, 0.3209	0.0769, 0.1886
R_1, wR_2 (all data)	0.1154, 0.2025	0.1293, 0.3498	0.0846, 0.1924

$R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

In compound 1, two pydc^{2-} ligands coordinate to two scandium centers with mode I (Fig. S10†) to form a Sc$_2$(pydc)$_2$ building unit (Fig. 5a) and the adjacent Sc$_2$(pydc)$_2$ units are linked with each other to generate a ladder-shaped chain (Fig. 1a), then the pydc^{2-} ligands with mode II (Fig. S10†) decorate beside the ladder-shaped chain along a-axis. These ladder-shaped chains interact with lattice water molecules via hydrogen bonds to construct a 3D supramolecular structure (Fig. 1b).
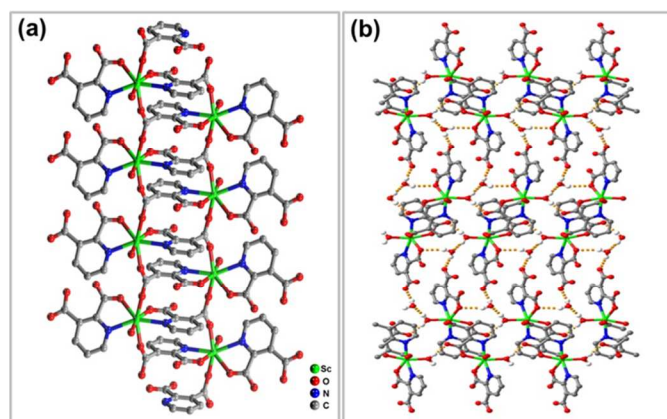

Fig. 1 (a) Presentation of the ladder-like chain in compound **1**; b) View of the hydrogen-bonding interaction between water chains and the ladder-like chains along [100] direction.

The coordinated water molecule acts as H-donors and offers two hydrogen atoms of H9A and H9B atoms to H-acceptors O10 of guest water molecule and O6 of pydc^{2-} ligand. Thus, these hydrogen bonding interactions result in the formation of a 2D supramolecular network. Additionally, the guest water acts as hydrogen-bonding donors and offers two hydrogen atoms to O4 and O1 atoms of two pydc^{2-} to form the final 3D

supramolecular structure (Fig. 1b and hydrogen bonding see Table S2).

Crystal Structure of compound 2

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent Sc(III) ions, three pydc^{2-} ligands, four terminal coordinated water molecules and five guest water molecules in the asymmetric unit. As shown in Fig. S6†, Sc1 is seven-coordinated and resides in a distorted pentagonal bipyramidal geometry, the pentagonal plane contains two nitrogen atoms and two oxygen atoms supplied by two pydc^{2-} ligands, one oxygen atom from water molecule, with the axial sites occupied by two oxygen atoms from one pydc^{2-} ligand and one water molecule (O-Sc-O bond angle is 172.52°). Sc2 is also lie on the center of a distorted pentagonal bipyramidal geometry, coordinated by four oxygen atoms and one nitrogen atoms from two chelating pydc^{2-} ligands, and one terminal water molecule occupying the corners of a pentagonal plane and two oxygen atoms from one pydc^{2-} ligand and one water molecule with the O-Sc-O bond angle of 174.92° locating at the axial positions.

In compound **2**, the pydc^{2-} ligands, which express two types of coordination modes (III and IV) (Fig. S10†), coordinate to scandium atoms to generate a 2D waved layer along b axis. As shown in Fig. 2a, Sc1 or Sc2 bridged pydc^{2-}
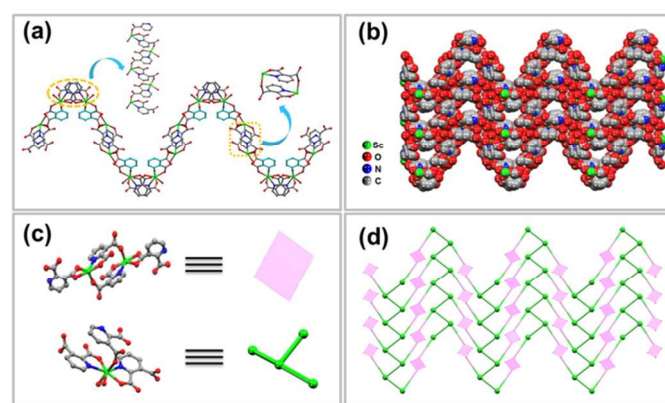

Fig. 2 (a) View of the waved layer in compound **2** along [100] direction; (b) CPK model; (c) the Sc$_2$(pydc)$_2$ unit of compound **2** which can be simplified as a 2-connected node; (d) a schematic representation of the **2-nodal** net.

ligand generate two parts in the 2D waved layer: one is a 1D S-shaped chain formed Sc1 via pydc^{2-} ligand with mode III (Fig. S10†), and the other is a Sc$_2$(pydc)$_2$ unit (Fig. 5b) constructed with Sc2 and pydc^{2-} ligand with mode IV (Fig. S10†). After that, the S-shaped chains connect to the intermediate Sc$_2$(pydc)$_2$ units through the pydc^{2-} ligands with coordination mode IV (Fig. S10†) forming 2D waved layer. Moreover, the 2D waved networks are lying in the ab plane stacking in parallel without interpenetration (Fig. 2b) and further extended into 3D supramolecular architecture through the interactions of the hydrogen bonds (Fig. S7†). From the topological view, another prominent feature of **2** is the presence of 2-nodal net (Fig. 2d),

if each $Sc_2(pydc)_2$ unit can be seen as a square-planar 2-connected node linked two $pydc^{2-}$ ligands, each Sc1 can be simplified as a 3-connected node (Fig. 2c).

Crystal Structure of compound 3

Crystal structure determination reveals that compound **3** crystallizes in trigonal space group *R*-3. In the asymmetric unit of **3**, there is one crystallographically independent Sc(III) center, one $pydc^{2-}$ ligand, one coordinated water molecule and one coordinated nitrate anion. Sc1 is seven-coordinated, in which three oxygen atoms and one nitrogen atoms are provided by three different $pydc^{2-}$ ligands, two oxygen atoms from nitrate anion and one oxygen atom from a terminal water molecule, to form a distorted pentagonal bipyramidal geometry, $[ScO_6N]$ (Fig. S8†). The Sc-O bond lengths vary from 2.025 to 2.238 Å, the Sc-N bond length is 2.326 Å, which are all in the normal ranges[12]. In turn, each $pydc^{2-}$ ligand coordinates to Sc(III) atom with coordination mode V (Fig. S10†) to generate the $Sc_2(pydc)_2$ unit (Fig. 5c). More interestingly, as shown in Fig. 3,
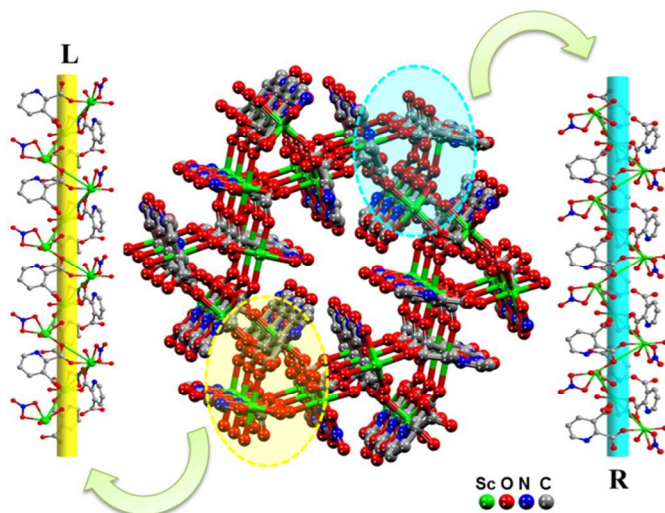

Fig. 3 Left and right helical chains of compound **3**.

there are two kinds of helical chains along the *c* axis in compound **3**. These two helical chains can be viewed as Sc atoms linked by two ligands arranged in clockwise/anticlockwise direction with a pitch of 10.239 Å. Each left helical chain links with three adjacent right helical chains through $Sc_2(pydc)_2$ unit, and so does the right one (Fig. 3 and Fig. S9†). The left and right helical chains interconnect with each other through $Sc_2(pydc)_2$ unit and finally form a 3D framework (Fig. 4c). Accordingly, the Sc(III) atom can be regarded as a 3-connected node, each $pydc^{2-}$ unit coordinated to three Sc(III) atoms can be viewed as a triangular 3-connected node (Fig. 4a). Consequently, compound **3** can be described as a (3, 3)-connected network with mineral-like **nbo-a** topology (Fig. S9†).[13]

Comparing the structures, we found that these three compounds possess an increasing dimensionality from 1D chain to 2D layer

and to 3D network, all of them contain alike $Sc_2(pydc)_2$ building units. The result can be attributed to that the $pydc^{2-}$ ligand exhibits different coordination modes and constructs various architectures by bridging Sc(III) ions under similar synthesis conditions.
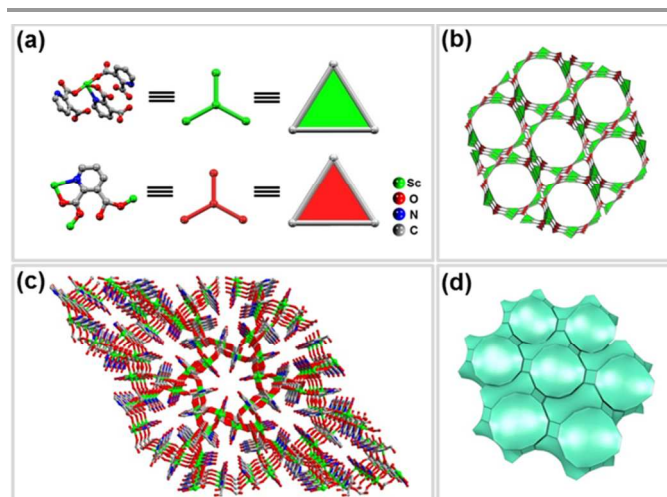

Fig. 4 (a) The coordination environment of Sc(III) which can be viewed as a 3-connected node (green) and the ligand H₂pydc coordinates three scandium atoms which can be simplified as a 3-connected node (red) in compound **3**; (b) a schematic representation of the **nbo-a** net; (c) Ball and Stick representation of the 3D framework along [110] direction. (d) topological features of compound **3** displayed by tiling style.
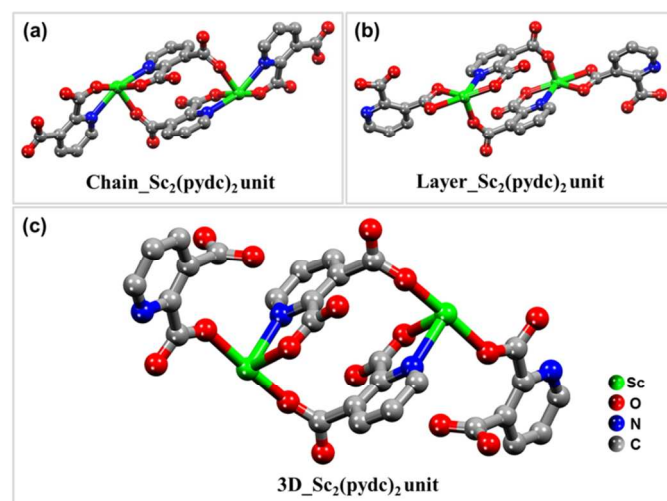
Fig. 5 $Sc_2(pydc)_2$ unit of compound **1~3**.

Framework Stability

The thermal and water stabilities of the compounds **1~3** were expected to play a critical role in their performance as a heterogeneous Lewis catalysts for the cyanosilylation of aldehyde. All compounds display good framework stabilities, here only the data of compound **3** was presented as an example. The PXRD patterns of compound **3**, which immersed in water for 5 days at room temperature, is in good agreement with the simulated pattern (Fig. S3†), showing good water stability. Variable-temperature PXRD patterns further indicate that the

structure of the framework for compound **3** are retained up to 350 °C, exhibits high thermal stability (Fig. S13†). Thermogravimetric analysis (TGA) experiment was carried out to investigate the thermal stability of **3** in the temperature range of 25-800 °C (Fig. S12†). For **3**, the weight loss of 74.55% in the temperature range 345~505 °C (calcd 74.8%) corresponds to pydc^{2-} ligands and nitrates, after which there is no apparent loss until about 505 °C. As far as we know, there are few examples of porous MOFs with such high thermal and water stability.[14]

Catalytic Studies

The catalytic properties of compounds **1~3** were investigated as heterogeneous Lewis catalysts for the cyanosilylation of *p*-nitrobenzaldehyde (Table 2).[15] Typically, the catalyst powders were suspended in acetonitrile (CH$_3$CN). Aldehydic substrate and trimethylsilyl cyanide (1:2 molar ratio) were subsequently added at room temperature and the reaction was running for 24 h. Yields of the reactions were determined by ^{1}H NMR spectroscopy (Fig. S14†).[16]

Table 2. Results for the heterogeneous cyanosilylation of carbonyl substrates in the presence of **1**, **2**, **3** and **4**.


Cat.	Types	Time (h)	Conversion (%)
1	1D	8	99
2	2D	1.5	99
3	3D	24	85.2
4	3D (after activation)	5.5	99

Reaction conditions: room temperature; Me$_3$SiCN, 1.2 mmol; *p*-nitrobenzaldehyde, 0.5 mmol; catalysts, 0.05 mmol (10 mol %); cat.1 represents for compound **1**, cat.2 represents for compound **2**, cat.3 represents for compound **3** and cat.4 represents for compound **3** after activation (150℃ for 1hour). The yields were determined by ^{1}H NMR.

Blank reaction was performed by carrying the cyanosilylation of *p*-nitrobenzaldehyde without catalyst at room temperature. The test reaction shows that it can hardly catalyze the reaction after a reaction time of 24 h. Also, Sc(NO$_3$)$_3$ and ScCl$_3$ were added to test the catalytic effect, a conversion of 43.9% and 24.1% was reached after 24 h, respectively. When 30 mg of compound **3** was used as catalyst, a conversion of 85.2% of *p*-nitrobenzaldehyde was obtained after 24 h in CH$_3$CN (Table 2 and Fig. 6). The conversion suggests that compound **3** acts as an efficient catalyst for this reaction.

To better understand the catalyst, we also study the effect of other two MOFs. A conversion of 99% for compound **1** was achieved for the same reaction to compound **3**, while compound **2** reached a 99% conversion within 1.5 h (Table 2 and Fig. 6). Compared with these two cases, the lower conversion rate incurred by compound **3** may be attributed to its restricted small pore size. In compound **3**, the size of hexagonal channels is decreased by the coordinated water molecules and nitrate anions. It is much more difficult to get rid of coordinated nitrate anions than coordinated water molecules.[17] Hence, the same

catalysis reaction for compound **3** after activation (150℃ for 6 h) was performed, it was found that the conversion was increased to 99% after 5.5 h. This significantly improved
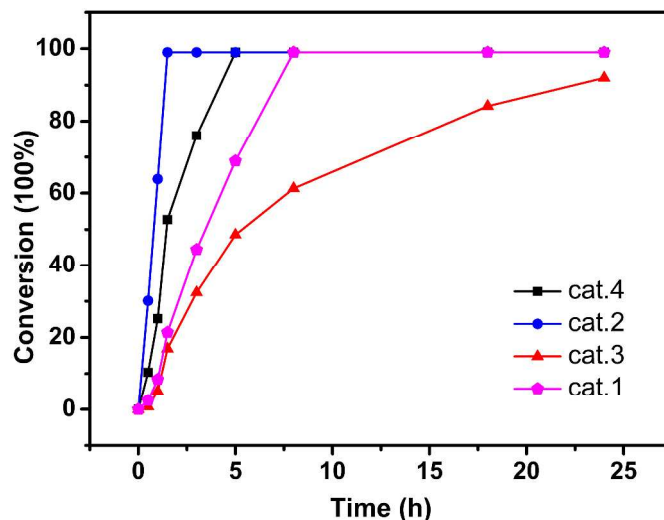
Fig. 6 Cyanosilylation of acetaldehyde with compound **1~3** as heterogeneous Lewis catalysts.

reactivity suggests that the unsaturated metal sites play important roles in this reaction. For its outstanding catalysis efficiency, compound **2** was selected as an example to study the recycling of these catalysts. The yield of the heterogeneous cyanosilylation was not reduced, after the fourth recycling, it decreased to 92% (Table 3).

Table 3. Study on Recycling of cat. 2 (compound **2**) for the heterogeneous cyanosilylation.

Entry	Recycling times	Time (h)	Conversion (%)
1	1	1.5	99
2	2	3.5	99
3	3	8	99
4	4	24	92

Reaction conditions: Me$_3$SiCN, 1.2 mmol; *p*-nitrobenzaldehyde, 0.5 mmol; cat.2 : 0.05mmol (10 mol %), room temperature under air.

To examine the heterogeneous nature of the catalyst in cyanosilylation reaction, we performed control experiments. Removal of the catalyst from the reaction mixtures by filtration did not result in any further conversion, even after a long time, which suggests that there was no dissolution of the catalyst during the reaction. Besides, the stability of the solid catalyst was checked by PXRD and the results show no change in the structure of the catalysts before and after reaction (Fig. S1~S3†).

It's worth noting that the above results overtake many reported MOFs materials for cyanosilylation of *p*-nitrobenzaldehyde (Table S5†). The good heterogeneous Lewis acid catalytic effect of the synthesized three Sc-MOFs may be attributed to their high thermal and water stabilities, and unsaturated Sc(III) metal sites, which providing the preconditions. The highlighted catalytic possessions show that these novel compounds are promising candidates of

heterogeneous Lewis acid catalytic for the cyanosilylation of aldehyde.

Conclusions

In summary, three Sc-MOFs were successfully constructed from the assembly of the simple H_2pydc ligand and Sc(III) ions. The different coordination geometry of scandium ion and H_2pydc ligand leads to the structural variety of three compounds from 1D to 3D. Compound **1** is a ladder-shaped chain, and constructed to a 3D supramolecular framework via hydrogen-bonding. Compound **2**, a waved layer, interacts with water molecules via hydrogen-bonding to construct a 3D supramolecular structure. Compound **3** is a 3D framework with **nbo-a** network topology. All the compounds based on the $Sc_2(pydc)_2$ building units exhibit high thermal and water stabilities, and can be used as effective heterogeneous Lewis acid catalysts for the cyanosilylation of aldehyde. These green Sc(III) catalysts can potentially be constructed by utilizing various ligands, and corresponding work is currently ongoing in our group.

Acknowledgements

Notes and references

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†Electronic Supplementary Information (ESI) available: Selected bond lengths and angles, hydrogen bonding, additional figures for crystal structures, PXRD, IR and TGA. CCDC 976321-976323. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

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