# **RSC Advances**



View Article Online

View Journal | View Issue

# PAPER



Cite this: RSC Adv., 2016, 6, 63425

Received 22nd May 2016 Accepted 27th June 2016 DOI: 10.1039/c6ra13242a

www.rsc.org/advances

# Introduction

Over the past decades, lanthanide coordination polymers have emerged as promising multifunctional materials due to their diverse structures and potential applications such as gas storage and separation,<sup>1</sup> luminescence,<sup>2</sup> magnetism,<sup>3</sup> and heterogeneous catalysis.<sup>4</sup> So far a large number of Ln-based coordination polymers with interesting architectures and topologies have been synthesized by selecting appropriate ligands.<sup>5</sup> However, discovering the controlling factors for the construction of lanthanide coordination polymers with desired structures still remains a great challenge due to their variable coordination numbers and flexible coordination geometries.<sup>6</sup> In addition, the change of lanthanide ionic radius, referred to as

# From 1D to 3D lanthanide coordination polymers constructed with pyridine-3,5-dicarboxylic acid: synthesis, crystal structures, and catalytic properties<sup>†</sup>

Xiao-Ming Lin, \*<sup>ab</sup> Ji-Liang Niu,<sup>a</sup> Pei-Xian Wen,<sup>a</sup> Yan-Na Lu,<sup>a</sup> Lei Hu,<sup>a</sup> Da-Liang Zhang<sup>b</sup> and Yue-Peng Cai<sup>\*a</sup>

Three series of lanthanide coordination polymers with formula  $[Ln_2(PDC)_3(H_2O)_2(DMF)] \cdot 4H_2O$  (type I) (Ln = La **1**, Pr **2**, Sm **3**),  $[(CH_3)_2NH_2][Ln_2(PDC)_3(HCOO)(H_2O)_3] \cdot 2H_2O$  (type II) (Ln = Tb **4**, Ho **5**) and  $[Ln(HPDC)_3(H_2O)_2] \cdot H_2O$  (type III) (Ln = Er **6**, Lu **7**) (H\_2PDC = pyridine-3,5-dicarboxylic acid), have been successfully synthesized by the solvothermal reaction of pyridine-3,5-dicarboxylic acid (H\_2PDC) with the corresponding lanthanide nitrate. Compounds **1–3** are isomorphous and all crystallize in triclinic space group  $P\overline{I}$ , showing a 3D microporous framework of *pcu* topology with square channels along the *b*-axis. Isostructural compounds **4** and **5** show the same 2D layer network of (4,4)-grid in the monoclinic  $P2_1/c$  space group. Isomorphic **6** and **7** crystallize in the monoclinic *Cc* space group and present 1D zigzag chains which expand to a 3D supramolecular structure through  $\pi \cdots \pi$  stacking interactions. The structural diversity of these three classes of compounds may be attributed to the effect of lanthanide contraction. They were characterized by infrared spectra (IR), elemental analysis (EA), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), and X-ray single crystal diffraction. Furthermore, the catalytic properties of these compounds were investigated and experiments revealed that compounds **1–3** show size-selective catalytic performance for cyanosilylation reactions and could be reused without losing their catalytic activity.

the lanthanide contraction, may lead to different coordination numbers and diverse topological structures.<sup>7</sup>

On the other hand, Ln<sup>3+</sup> ions have higher coordination numbers than transition metal ions, and it is possible to incorporate more solvent molecules in the coordination networks. The solvent molecules can be easily removed and the framework remains intact with available coordinatively unsaturated sites, which makes them have great potential to be excellent heterogeneous catalysts.8 Up to now, plenty of aromatic multicarboxylate or pyridine-carboxylate ligands as connectors have been employed in the construction of Lncontaining coordination polymers.9 Recently, we have reported a range of new Ln-based structures through using aromatic multicarboxylate ligands and engaged in their applications in gas adsorption, fluorescence, and so on.10 As a continuation of our previous work, herein we utilized the pyridine-3,5-dicarboxylate ligands (H<sub>2</sub>PDC) as connectors to construct new lanthanide coordination polymers. As one of the simplest linker, H<sub>2</sub>PDC ligand can be partially or completely deprotonated to form HPDC<sup>-</sup> or PDC<sup>2-</sup> anions to bridge metal ions, yielding a variety of fascinating structures due to the flexible and versatile coordination modes. Furthermore, the  $\pi$ electric conjugated system of the pyridine group is beneficial for

<sup>&</sup>lt;sup>a</sup>School of Chemistry and Environment, South China Normal University, Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, 510006, P. R. China. E-mail: linxm@scnu.edu.cn; caiyp@scnu.edu.cn

<sup>&</sup>lt;sup>b</sup>State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

<sup>†</sup> Electronic supplementary information (ESI) available. CCDC 1472125-1472131 for 1-7. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ra13242a

the formation of stable supramolecular structures. In this contribution, we reported the synthesis and characterization of seven lanthanide coordination polymers,  $[Ln_2(PDC)_3(H_2O)_2(DMF)]\cdot 4H_2O$  (type I) (Ln = La 1, Pr 2, Sm 3),  $[(CH_3)_2NH_2]$   $[Ln_2(PDC)_3(HCOO)(H_2O)_3]\cdot 2H_2O$  (type II) (Ln = Tb 4, Ho 5) and  $[Ln(HPDC)_3(H_2O)_2]\cdot H_2O$  (type III) (Ln = Er 6, Lu 7), with three distinct types of structures. Their structures and topologies, as well as their catalytic properties were also studied.

## Experimental section

## Materials and general methods

All reagents and solvents employed were purchased from commercial sources and used without further purification. Infrared spectra were collected from KBr pellets in the range of  $4000-400 \text{ cm}^{-1}$  region on a Nicolet/Nexus-670 FT-IR spectrometer. The elemental analyses were obtained by a Perkin-Elmer 240 elemental analyzer. Thermogravimetric analyses (TGA) were performed on a Netzsch Thermo Microbalance TG 209 F3 Tarsus from room temperature to 700 °C with a heating rate of 10 °C min<sup>-1</sup> under flowing nitrogen. The X-ray powder diffraction patterns were measured on a Bruker D8 Advance diffractometer at 40 kV and 40 mA with a Cu target tube and a graphite monochromator. <sup>1</sup>H NMR spectra were recorded with a Varian Mercury Plus 300 MHz spectrometer. The sorption isotherms were measured with a Quantachrome Autosorb-iQ-MP gas sorption analyzer.

### Preparation of the compounds

A mixture of  $Ln(NO_3)_3 \cdot 6H_2O$  (0.1 mmol),  $H_2PDC$  (0.05 mmol), HNO<sub>3</sub> (0.2 mL), DMF (6 mL) and  $H_2O$  (3 mL) was placed in a 15 mL Teflon-lined stainless steel autoclave and heated at 120 °C for three days. After cooling to room temperature at a rate of 5 °C h<sup>-1</sup>, block crystals of 1–7 were obtained, washed with water and air-dried, respectively.

 $[La_2(PDC)_3(H_2O)_2(DMF)] \cdot 4H_2O$  (1). Yield: 51% based on La. Anal. calcd for  $C_{24}H_{28}N_4O_{19}La_2$  (954.32): C, 30.21; H, 2.96; N, 5.87. Found: C, 30.25; H, 2.97; N, 5.85. IR (KBr, cm<sup>-1</sup>): 3212(vs), 1607(m), 1574(s), 1442(s), 1416(s), 1298(m), 1243(m), 1152(m), 945(w), 841(m), 739(m), 694(m), 591(w).

 $[Pr_2(PDC)_3(H_2O)_2(DMF)] \cdot 4H_2O$  (2). Yield: 58% based on Pr. Anal. calcd for  $C_{24}H_{28}N_4O_{19}Pr_2$  (958.32): C, 30.08; H, 2.95; N, 5.85. Found: C, 30.12; H, 2.90; N, 5.89. IR (KBr, cm<sup>-1</sup>): 3209(vs), 1607(s), 1572(s), 1443(s), 1417(s), 1299(m), 1244(m), 1152(m), 946(w), 841(m), 740(m), 695(m), 589(w).

 $[Sm_2(PDC)_3(H_2O)_2(DMF)] \cdot 4H_2O$  (3). Yield: 56% based on Sm. Anal. calcd for  $C_{24}H_{28}N_4O_{19}Sm_2$  (977.20): C, 29.50; H, 2.89; N, 5.73. Found: C, 29.52; H, 2.85; N, 35.76. IR (KBr, cm<sup>-1</sup>): 3211(vs), 1608(m), 1573(s), 1443(s), 1415(s), 1297(m), 1245(m), 1152(m), 944(w), 840(m), 741(m), 693(m), 590(w).

 $[(CH_3)_2NH_2][Tb_2(PDC)_3(HCOO)(H_2O)_3] \cdot 2H_2O$  (4). Yield: 62% based on Tb. Anal. calcd for  $C_{24}H_{28}N_4O_{19}Tb_2$  (994.34): C, 28.99; H, 2.84; N, 5.63. Found: C, 28.95; H, 2.85; N, 5.61. IR (KBr, cm<sup>-1</sup>): 3269(w), 1614(w), 1575(w), 1506(m), 1466(m), 1377(m), 1317(m), 1264(m), 1185(w), 1108(s), 981(m), 740(w), 621(m).

 $\label{eq:constraint} \begin{array}{l} [(CH_3)_2NH_2][Ho_2(PDC)_3(HCOO)(H_2O)_3] \cdot 2H_2O \quad (5). \quad \mbox{Yield:} \\ 65\% \mbox{ based on Ho. Anal. calcd for $C_{24}H_{28}N_4O_{19}Ho_2$ (1006.36): C, $28.64; H, 2.80; N, 5.57. Found: C, 28.63; H, 2.82; N, 5.55. IR (KBr, $cm^{-1}$): $3270(w), 1616(w), 1574(w), 1505(m), 1465(m), 1379(m), $1315(m), 1266(m), 1185(w), 1107(s), 980(m), 740(w), 620(m). \end{array}$ 

 $[\text{Er}(\text{HPDC})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (6). Yield: 50% based on Er. Anal. calcd for  $C_{21}H_{18}N_3O_{15}\text{Er}$  (719.64): C, 35.05; H, 2.52; N, 5.84. Found: C, 35.08; H, 2.52; N, 5.89. IR (KBr, cm<sup>-1</sup>): 3210(vs), 1708(m), 1616(s), 1442(s), 1385(m), 1235(m), 1151(m), 940(w), 847(m), 751(m), 663(m).

 $[Lu(HPDC)_3(H_2O)_2] \cdot H_2O$  (7). Yield: 50% based on Lu. Anal. calcd for  $C_{21}H_{18}N_3O_{15}Lu$  (727.35): C, 34.68; H, 2.49; N, 5.78. Found: C, 34.66; H, 2.45; N, 5.77. IR (KBr, cm<sup>-1</sup>): 3211(vs), 1709(m), 1613(s), 1440(s), 1384(m), 1234(m), 1150(m), 943(w), 846(m), 753(m), 663(m).

## X-ray crystallographic studies

Suitable single crystals of these compounds were carefully selected under an optical microscope and glued to thin glass fibers. Structural measurements were collected on a Bruker APEX II diffractometer at 296 K using graphite monochromatic Mo-Ka radiation ( $\lambda = 0.71073$  Å). Absorption corrections were applied by using the multi-scan program SADABS.<sup>11</sup> Structural solutions and full-matrix least squares refinements based on  $F^2$ were performed with the SHELXS-97,12 and SHELXL-97 (ref. 13) program packages, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. The largest residual density peaks in 1-3 appear adjacent to the Ln atom, typical of strong absorption of heavy metal atom. Due to the typical large thermal displacements of coordinated DMF molecules in 1-3, constrained refinements were applied by using ISOR/SIMU to approximate to isotropic behaviours. Because free solvent molecules (for 1-3) and guest molecules  $[(CH_3)_2NH_2]^+$  in the channels (for 4 and 5) were highly disordered and could not be modeled properly, the SQUEEZE routine of PLATON was applied to remove their contributions to the scattering.14 The reported refinements of the guest-free structures are obtained by the SQUEEZE routine, and the results were attached to the CIF file. A summary of the crystal structure refinement data is provided in Table 1, and selected bond angles and distances are listed in Table S1.<sup>†</sup> Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with CCDC reference numbers 1472125-1472131.†

## Typical procedure for carbonyl cyanosilylation

Prior to the catalytic test, the samples are activated *via* the following procedure: the as-prepared samples are activated in vacuum at 150 °C for 8 h to generate unsaturated metal centres. Then a mixture of benzaldehyde (26.5 mg, 0.25 mmol) and trimethylsilyl cyanide (TMSCN, 49.6 mg, 0.5 mmol) was placed into a Pyrex-glass screw-cap vial (10 mL), and catalyst Ln-PDC (4 mol%) was added and the resulting reaction mixture was stirring with a Teflon-coated magnetic stir bar at room temperature. The conversions of the products were determined by <sup>1</sup>H NMR analysis.

Table 1 Crystallographic data and structure refinement summary for 1 to 7

View Article Online

Compound	1	2	3	4	5	6	/
Empirical formula	$C_{24}H_{28}La_2N_4O_{19}\\$	$C_{24}H_{28}N_4O_{19}Pr_2\\$	$C_{24}H_{28}N_4O_{19}Sm_2\\$	$C_{24}H_{28}N_4O_{19}Tb_2^{\ c}$	$C_{24}H_{28}N_4O_{19}Ho_2{}^c$	$C_{21}H_{18}N_3O_{15}Er$	$\mathrm{C}_{21}\mathrm{H}_{18}\mathrm{N}_{3}\mathrm{O}_{15}\mathrm{Lu}$
Formula weight	954.32	958.32	977.20	994.34	1006.36	719.64	727.35
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	Сс	Сс
a (Å)	8.9602(13)	8.8723(12)	8.8475(18)	10.0739(19)	10.0690(9)	21.091(5)	20.994(14)
b (Å)	10.7764(16)	10.7152(15)	10.716(2)	20.130(4)	20.0854(19)	11.959(2)	11.889(8)
c (Å)	19.041(3)90	18.920(3)	18.895(4)	17.349(3)	17.3482(13)	9.6220(19)	9.577(6)
α (°)	75.382(2)	75.496(2)	75.521(2)	90	90	90	90
$\beta$ (°)	83.782(2)	83.797(2)	83.777(2)	113.934	113.898	100.456(4)	100.552(7)
$\gamma$ (°)	69.363(2)2	69.336(2)	69.306(2)	90	90	90	90
$V(\text{\AA}^3)$	1664.5(4)	1629.0(4)	1622.2(6)	3215.6(10)	3207.7(5)	2386.6(9)	2350(3)
Ζ	2	2	2	4	4	4	4
ho (cald) (mg m <sup>-3</sup> )	1.904	1.954	2.001	2.110	2.084	2.003	2.056
$T(\mathbf{K})$	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
$\mu (\mathrm{mm}^{-1})$	2.618	3.044	3.673	4.452	4.987	3.603	4.289
F(000)	932	940	952	1928	1944	1412	1424
R <sub>int</sub>	0.0433	0.0355	0.0622	0.0266	0.0345	0.0308	0.0452
GOF	1.038	1.017	1.026	1.028	1.068	1.076	1.033
$R_1[I > 2\sigma (I)]^a$	0.0395	0.0299	0.0564	0.0248	0.0251	0.0302	0.0412
$wR_2$ (all data) <sup>b</sup>	0.0980	0.0757	0.1547	0.0580	0.0645	0.0790	0.0907

 ${}^{a} R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b} wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum (F_{o}^{2})^{2} \}^{1/2}, \text{ where } w = 1 / (\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP), P = (F_{o}^{2} + 2F_{c}^{2}) / 3. {}^{c} \text{ Distorted } [(CH_{3})_{2}NH_{2}]^{+} \text{ were calculated by PLATON/SQUEEZE program and confirmed by EA, which is not shown in final formula in CIF files.}$ 

## Results and discussion

# Crystal structure of $[Ln_2(PDC)_3(H_2O)_2(DMF)] \cdot 4H_2O$ (Ln = La 1, Pr 2, Sm 3)

X-ray single-crystal diffraction analyses reveal that compounds 1-3 are isostructural and crystallize in the triclinic  $P\bar{1}$  space group. As a representative example, the crystal structure of 3 is described in detail. The asymmetric unit of 3 contains one unique Sm<sup>3+</sup> ion, three PDC<sup>2-</sup> ligands, two coordinated aqua ligands, one coordinated DMF molecule, and four guest water molecules. As shown in Fig. 1a, the Sm(1) ion is ninecoordinated and has a distorted tricapped trigonal prismatic geometry surrounding by an [O<sub>9</sub>] donor set, generated by seven carboxylate oxygen atoms of six different PDC<sup>2-</sup> ligands and two oxygen atoms from two coordinated water molecules. The Sm(2) is also nine-coordinated by eight carboxylate oxygen atoms of six PDC ligands, together with an oxygen atom from a DMF molecule, displaying a distorted monocapped square antiprism coordination geometry (Fig. 1b). The Sm-O bond lengths vary from 2.3334(2) to 2.752(3) Å, and the O-Sm-O bond angles are in the range of 48.10(2) to 154.1(2)° (Table S1<sup>+</sup>). Due to the effect of lanthanide contraction, the average La-O bond length (2.5732 Å) in 1, the Pr–O bond length (2.5315 Å) in 2 are slightly longer than the corresponding Sm-O bond (2.5194 Å) in 3. As for the PDC<sup>2-</sup> ligand, one carboxylic group adopts the bidentate chelating/bridging coordination mode, while the other employs tridentate bridging coordination mode (Scheme 1a). The neighboring Sm(m) ions are connected through the carboxylate groups of PDC<sup>2–</sup> ligand to generate a infinite 2D layer structure (Fig. 1c), which could be simplified to a (4,4)-connected grid net through defining the binuclear units as nodes and PDC<sup>2-</sup> ligands as connectors (Fig. 1d). These 2D networks are further extended to the 3D cubic framework, which contains 1D square channels with the diameter of  $9.7 \times 9.7$  Å along the *bc* plane. By using PLATON/SOLV, the accessible total volumes in the desolvated structures are estimated to 36%.



**Fig. 1** Crystal structure of **3**. (a) Coordination environment of the Sm(m) ion; (b) tricapped trigonal prism and monocapped square antiprism coordination geometry of the Sm ion; (c) 2D layer network extending along the *ac* plane; (d) (4,4)-grid network; (e) polyhedral view of 3D porous framework showing 1D square channels along the *bc* plane; (f) 3D cubic framework. H atoms are omitted for clarity.



## Crystal structure of $[(CH_3)_2NH_2][Ln_2(PDC)_3(HCOO)(H_2O)_3]$ 2H<sub>2</sub>O (Ln = Tb 4, Ho 5)

Compounds 4 and 5 are isostructural and crystallize in the monoclinic  $P2_1/c$  space group, therefore, only the structure of 4 is selected herein as an example. As shown in Fig. 2a, Tb(1) atom is eight-coordinated with distorted bicapped trigonal prism geometry: six oxygen atoms from five PDC<sup>2-</sup> ligands and two O atoms from coordinated water molecules. While Tb(2) is nine-coordinated with a distorted monocapped square antiprism coordination environment: seven O atoms from five PDC<sup>2-</sup> ligands, one coordinated water molecules, together with the formic acid ligand from the decomposition of DMF molecule. Owing to the effect of lanthanide contraction, the average Tb–O bond length (2.4481 Å) in 4 is slightly longer than the corresponding Ho–O bond (2.4372 Å) in 5. As seen in



**Fig. 2** Crystal structure of **4**. (a) Coordination environment of the Tb(|||) ion; (b) bicapped trigonal prism and monocapped square antiprism coordination geometry of the Tb ions; (c) 1D zigzag chain extending along the *b*-axis; (d) polyhedral view of 2D layer along the *ac* plane; (e) (4,4)-grid network; (f) a space-filling view of the porous network between the adjacent layers with ABAB order, showing 1D rectangular channels along the crystallographic *c*-axis. H atoms are omitted for clarity.

Fig. 2c, the neighboring Tb(III) ions are connected together through the carboxylate groups of  $PDC^{2-}$  ligands to form a 1D infinite zigzag chain with the Tb…Tb distance of 4.0679(6) Å, in which the carboxylate group adopts the bidentate chelating, bidentate bridging, and tridentate bridging coordination modes (Scheme 1b). These zigzag chains are further linked by PDC<sup>2-</sup> ligands using the two carboxylate groups with bidentate bridging coordination mode to give rise to a 2D layer network, which can be ascribed as (4,4)-connected grid net (Fig. 2d and e). Although the adjacent layers are packed in an ABAB arrangement, 1D rectangular channels are still formed along the *c*-axis with an effective pore size of  $5.1 \times 6.2 \text{ Å}^2$  (after considering the van der Waals radii), in which the void space is filled with DMF and H<sub>2</sub>O molecules (Fig. 2f). PLATON calculation suggested a solvent accessible volume of 860.7  $Å^3$ (approximately 26.8% of unit cell) by excluding the guest solvent molecules.

## Crystal structure of $[Ln(HPDC)_3(H_2O)_2] \cdot H_2O$ (Ln = Er 6, Lu 7)

Compounds 6 and 7 are isomorphic and crystallize in the monoclinic Cc space group. Thus only the structure of 7 is described in detail. The asymmetric unit of 7 contains one unique Lu<sup>3+</sup> ion, three HPDC<sup>-</sup> ligands, two coordinated aqua ligands and one guest water molecules. As shown in Fig. 3a, the Lu<sup>3+</sup> ion shows a distorted bicapped trigonal prism geometry surrounding by six carboxylate oxygen atoms of five different HPDC<sup>-</sup> ligands and two O atoms from coordinated water molecules. Because of the effect of lanthanide contraction, the average Lu–O bond length (2.343 Å) in 7 is slightly shorter than the corresponding Er–O bond (2.365 Å) in 6. As for the partially deprotonated HPDC<sup>-</sup> ligand, one carboxylic group takes the bidentate chelating coordination mode, while the other one adopts bidentate bridging coordination mode (Scheme 1c). Thus, Lu<sup>3+</sup> are linked *via* HPDC<sup>-</sup> anions to give a 1D zigzag chain with the Lu…Lu separation of 4.7969(4) Å (Fig. 3b). The strong  $\pi \cdots \pi$  interactions (centroid-to-centroid distance of 3.866) Å) between pyridine rings of HPDC<sup>-</sup> ligands help to stabilize the 3D supramolecular network of 7. To analyze the network topology, the PDC ligands and Lu<sup>3+</sup> centre can be simplified as zigzag chain.

#### Structural effect of lanthanide contraction

Based on the above description of the syntheses and crystal structures, we found lanthanide contraction has a great influence on the features and overall structures in the formation of compounds 1–7. The ionic radius of the lanthanide ion decreases with increasing atomic number, which may lead to



**Fig. 3** Crystal structure of 7. (a) Coordination environment of the Lu(III) ion (all hydrogen atoms are omitted for clarity except the highlighted protonated carboxylate group); (b) bicapped trigonal prism coordination geometry of the Lu atom; (c) 1D zigzag chain extending along the *b*-axis; (d) 1D zigzag chain along the *c*-axis; (e) 3D supramolecular structure through  $\pi \cdots \pi$  stacking interactions between two adjacent 1D chains in *ab* plane.



Scheme 2 Construction of compounds  $1{-}7$  with different dimensional topologies.

diversity in crystal structure. As shown in Scheme 2, all the compounds are synthesized from the similar starting materials at 120 °C under solvothermal conditions. However, three different kinds of structures (type I for 1–3, type II for 4 and 5, type II for 6 and 7) were obtained. Type I crystallizes in triclinic space group  $P\bar{1}$ , showing 3D cubic framework with 1D square channels. Type II represents a 2D layer network of (4,4)-grid in

the monoclinic  $P2_1/c$  space group. While type III has a 1D zigzag chain structure with monoclinic Cc space group. Generally, as the radii of Ln<sup>3+</sup> ion decrease, the repulsions of the coordination atoms around the centre metal ion increase, until a new structure was formed. As a result, the coordination numbers (9 in type I, 8 and 9 in type II, and 8 in type III) decrease by the trend of the gradual reduction of the radius of lanthanide ions, presumedly to minimize the repulsions among the coordination atoms. The coordination geometries of centre metal ions in these compounds are tricapped trigonal prism and monocapped square antiprism in type I, bicapped trigonal prism and monocapped square antiprism in type II, bicapped trigonal prism geometry in type III, respectively. Meanwhile, the numbers of the PDC<sup>2-</sup> ligands around the Ln<sup>3+</sup> ion also decreases from six (for type I) to five (for type II and type III). The average bond lengths of Ln-O for 1-7 continuously decrease from 2.5732 (for 1), 2.5315 (for 2), 2.5194 (for 3), 2.4481 (for 4), 2.4372 (for 5), 2.3652 (for 6) to 2.3435 Å (for 7). Based on the theory of HSAB (Hard and Soft Acids and Bases), the Ln ions have high affinity and prefer O to N atom. Therefore, the nitrogen atom didn't participate into the coordination among these compounds. The H<sub>2</sub>PDC ligand also affects the architectures of their final products. As shown in Scheme 1, the PDC ligand exhibits six distinct coordination modes. The variable coordination modes of the PDC ligand in compounds 1-3 (a), 4-5 (b), and 6-7 (c) lead to the different topologies and structural diversity of 1-7.

## Characterization

To confirm the phase purity of compounds **1** to **7**, the XRPD patterns for the bulk samples were measured at room temperature (Fig. S1<sup>†</sup>). The well-matched patterns between the simulated and experimental results indicate the phase purity of the products. The intensity differences may be due to the preferred orientation of the crystalline powder samples.

To examine the thermal stability, the thermogravimetric analyses (TGA) for crystal samples were also performed under a nitrogen atmosphere. Since the compounds 1–3, 4–5, and 6–7 have similar structures. Herein, the TGA results of 3, 5, and 7 were selected as examples to be discussed in detail. As shown in Fig. S2,† the TG curves in the range of 25–350 °C show a total loss of 18.44 (for 3), 9.26 (for 5) and 7.15% (for 7), respectively, which corresponds to the loss of all solvent molecules (calcd 18.54, 8.95, and 7.42%, respectively). Above 350 °C, an abrupt weight loss appears, indicative of the collapse of the whole frameworks.

Infrared spectrum (IR) analysis showed that the characteristic adsorption peaks around 3250 cm<sup>-1</sup> for all the compounds corresponded to the  $\nu$ (OH) vibrations of the water molecules. The absence of the characteristic bands at around 1700 cm<sup>-1</sup> for **1–5** indicated the complete deprotonation of the PDC<sup>2–</sup> ligand, while the presence of the absorption around 1703 cm<sup>-1</sup> for **6–7** confirmed the incomplete deprotonation of the carboxylic groups. Strong peaks at 1610 and 1379 cm<sup>-1</sup> were assigned to asymmetric and symmetric stretching vibrations for the carboxylate groups.

### Catalytic performances

To activate the sample, Sm-PDC (3) was desolvated by immersing the samples in CH<sub>3</sub>OH for 2 days and evacuating under high vacuum at 150 °C for 8 h. No obvious weight loss of the dehydrated phase was observed at the stating temperature (Fig. S2<sup>†</sup>), suggesting the removal of all the uncoordinated and coordinated solvent molecules. PRXD patterns further confirmed the preservation of its crystallinity (Fig. S6<sup>†</sup>). Based on the nitrogen adsorption/desorption isotherms in Fig. S3,† the porous Sm-PDC presented typical type-I curve with a Brunauer-Emmett-Teller surface area of 850 m<sup>2</sup> g<sup>-1</sup> and a total pore volume of 0.58 cm<sup>3</sup> g<sup>-1</sup>. As for Ho-PDC (5), the microporous behavior was also observed and had the surface area of 546  $m^2 g^{-1}$  and pore volume of 0.39 cm<sup>3</sup> g<sup>-1</sup>. The porous property will provide a platform for catalyzing the substrates. For a typical procedure, benzaldehyde was reacted with (TMSCN) in the presence of the catalyst Sm-PDC (4 mol% with respect to the amount of benzaldehyde). As shown in Table 2, the Sm-PDC catalyst gives a 87% conversion of benzaldehyde after 5 h, which exhibited higher catalytic efficiency in comparison to most of the other reported MOFs.15 Mn<sub>3</sub>[(Mn<sub>4</sub>Cl)<sub>3</sub>(BTT)<sub>8</sub>]<sub>2</sub> reported by Long afforded a 98% conversion of benzaldehyde after 9 h with a loading of 11 mol%.<sup>15c</sup> HKUST-1, Cu<sub>3</sub>(BTC)<sub>2</sub> gave a yield of 57% at 313 K.15d Recently, Sun reported a lanthanideorganic framework, Tm(BDC)1.5, which showed moderate activity of 57.4% conversion in 5 h.15e The yield in our work is slightly less than the powerful Lewis acid catalyst Nd(btc) with a 99% conversion in 2 h with 9.0% catalyst.16

To make a comparison, a black experiment without any catalyst was performed under the similar conditions, where no product was detected. When  $Eu(NO_3)_3 \cdot 6H_2O$  was used as homogeneous catalyst instead of Sm-PDC, which is less efficient to prompt the catalytic transformation (yield: 4%). These results

R	о Н + М	Ae <sub>3</sub> SiCN —	$\frac{1-\text{PDC (4 mol\%)}}{n-\text{hexane, } rt} R^{1}$	OSiMe <sub>3</sub> CN H
Entry	1	2	3	4
Substrate	о Н	H_O	©-©- <sup>°</sup>	
Size <sup>d</sup> (Å) Yield <sup>e</sup> (%) TON <sup>f</sup>	$8.9 \times 6.7$ 87, $0^{b}$ , $4^{c}$ 22	9.6 imes 8.6 48 12	13.1  imes 6.9 10 3	$egin{array}{c} 12.5 imes10.6\ 0\ 0\ 0 \end{array}$

Table 2Cyanosilylation of aromatic aldehydes catalyzed by MOF Sm- $PDC^a$ 

<sup>*a*</sup> 0.25 mmol of benzaldehyde; 0.5 mmol of TMSCN; catalyst (4 mol%), 2 mL of *n*-hexane, room temperature. <sup>*b*</sup> Without any catalyst. <sup>*c*</sup> Catalyzed by Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (8 mol%). <sup>*d*</sup> These molecular sizes are calculated based on the MM2 energy minimization mode *via* Chem 3D program followed by measuring the longest atom-to-atom separations in two dimensions. <sup>*e*</sup> Yield determined by <sup>1</sup>H NMR analysis. <sup>*f*</sup> TON = (yield)/ (mol% cat.).

evidently demonstrated that Sm-PDC could be acted as an effective catalyst. Unlike the lamellar lanthanide bisphosphonates or the 2D [Ln(3,5-DSB)(phen)], (3,5-DSB = 3,5-disulfobenzoate; phen = 1,10-phenathroline), both of which can swell to accommodate a variety of substrates,<sup>17</sup> a significant size-selective effect was found in our case. As evident from Table 2, substrates of increasing dimensions are also tested. In the case of 1-naphthaldehyde (9.6  $\times$  8.6 Å<sup>2</sup>), the conversion was 48% in 5 h (Table 2, entry 2). As for the even larger 4-phenylbenzaldehyde (13.1  $\times$  6.9 Å<sup>2</sup>), the yield decreased obviously to 10% under the same conditions (Table 2, entry 3). With the substrates further increases, for example, 4-(N,N-diphenylamino)benzaldehyde (12.5  $\times$  10.6 Å<sup>2</sup>), the reaction did not proceed (Table 2, entry 4). Since the pore size of Sm-PDC is 9.7  $\times$  9.7 Å<sup>2</sup>, larger substrates were excluded by Sm-PDC, demonstrating that the reactions occur inside the pores. Similar sizeselective behaviors can also be observed in the previously reported MOF-based heterogeneous catalysts.18

As is well-known, the Lewis acid strength of lanthanide metals is closely related with the ionic radii. Therefore, the cyanosilylation of benzaldehyde was also carried out with catalysts 1 (La-PDC) and 2 (Pr-PDC). As shown in Table 3, the reactivity activity decreases in an order of La < Pr < Sm, and the obtained yields are 100% and 93% after 5 h, respectively. This trend is opposite to some cases, where the reactivity increases with a decrease of the ionic radius.<sup>19</sup> In our case, the decrease reactivity of the Ln-PDC catalysts may be ruled by the increasing steric interactions between the substrates and the coordinatively unsaturated Ln ions in the whole framework.<sup>20</sup> These can be also verified by a comparison of the catalysts 4 (Tb-PDC) and 5 (Ho-PDC). They showed much lower activity with 49% and 42%, respectively, even extending the reaction time from 5 h to 10 h. This can be ascribed to the smaller porous size of the frameworks and the substrates cannot be easily accessed to the coordinatively unsaturated Ln centres. For 6 and 7, they showed negligible conversions due to the lacking of structural porosities and activity sites.

With the above observations, the possible catalytic reaction mechanism in this case has been reasonably shown in Scheme 3. When using the Ln-PDC (Ln = La, Pr, Sm) as catalysts, the coordinatively unsaturated active sites can be obtained after removal of the coordinated  $H_2O$  and DMF molecules. The suitable substrates could enter the framework more easily and have more chances to access the vacant position of the Ln<sup>3+</sup> ions.

Entry	Catalyst	Time (h)	Yield (%)	TON	
1	1 (La-PDC)	5	100	25	
2	2 (Pr-PDC)	5	93	23	
3	3 (Sm-PDC)	5	87	22	
4	4 (Tb-PDC)	10	49	12	
5	5 (Ho-PDC)	10	42	10	
6	6 (Er-PDC)	10	3	0.8	
7	7 (Lu-PDC)	10	2	0.5	



Scheme 3 Possible mechanism for cyanosilylation reaction in the case of Ln(PDC) (Ln = La, Pr and Sm) after activation.

The heterogeneous catalysis test was carried out for the Sm-PDC catalyst. The Sm-PDC catalyst was isolated after two 2 hours and the filtrate was allowed to stir for another 3 hours. Only 4% additional conversion was found during the same time, demonstrating the reaction was basically heterogeneous (Fig. S4†). The recovered catalyst can be reused at least five cycles without loss of the activity (Fig. S5†). The PXRD pattern of the Sm-PDC solid after the fifth recycling reaction is similar to that before the catalytic reaction, confirming that the maintenance of the crystalline structure during the reaction processes (Fig. S6†).

# Conclusions

In summary, we have developed three different types of lanthanide-based coordination polymers based on pyridine-3,5dicarboxylate under solvothermal conditions. Compounds 1-3 show a 3D open network with *cbu* topology. Compounds 4 and 5 exhibit a (4,4)-grid layered structure with ABAB arrangement. While compound 6 and 7 have a 1D zigzag chain. The structural diversity of crystal structures may be ascribed to the effect of lanthanide contraction. Moreover, the size-selective catalytic activity towards cyanosilylation reaction was also discussed and the catalysts can be readily recovered and repeatedly used.

# Acknowledgements

This work was supported by the National Natural Science Foundation of P. R. China (Grant No. 21401059 and 21471061), Applied Science and Technology Planning Project of Guangdong Province (2015B010135009), Science and Technology Program of Guangzhou (Grant No. 2014J4100051), Open Project of State Key Laboratory of Inorganic Synthesis and Preparative Chemistry (2015–24).

# Notes and references

1 (a) J. Luo, H. Xu, Y. Liu, Y. Zhao, L. L. Daemen, C. Brown, T. V. Timofeeva, S. Ma and H.-C. Zhou, J. Am. Chem. Soc., 2008, **130**, 9626–9297; (*b*) Y.-P. He, Y.-X. Tan and J. Zhang, *Inorg. Chem.*, 2013, **52**, 12758–12762; (*c*) X. Liu, H. Lin, Z. Xiao, W. Fan, A. Huang, R. Wang, L. Zhang and D. Sun, *Dalton Trans.*, 2016, **45**, 3743–3749; (*d*) P. P. Bag, X.-S. Wang and R. Cao, *Dalton Trans.*, 2015, **44**, 11954– 11962; (*e*) Y. Chen and S. Ma, *Rev. Inorg. Chem.*, 2012, **32**, 81–100; (*f*) C. Wang, L. Li, J. G. Bell, X. Lv, S. Tang, X. Zhao and K. M. Thomas, *Chem. Mater.*, 2015, **27**, 1502–1516.

- 2 (a) Y. Li, S. Zhang and D. Song, Angew. Chem., Int. Ed., 2013,
  52, 710-713; (b) J. Rocha, L. D. Carlos, F. A. A. Paz and D. Ananias, Chem. Soc. Rev., 2011, 40, 926-940; (c) H. Xu,
  H.-C. Hu, C.-S. Cao and B. Zhao, Inorg. Chem., 2015, 54, 4585-4587; (d) J. Zhang, B. Zheng, T. Zhao, G. Li, Q. Huo and Y. Liu, Cryst. Growth Des., 2014, 14, 2394-2400.
- 3 (a) F. Zhang, X. Zou, P. Yan, J. Sun, G. Hou and G. Li, Cryst. Growth Des., 2015, 15, 1249–1258; (b) S. Biswas, A. K. Mondal and S. Konar, Inorg. Chem., 2016, 55, 2085–2090; (c) K. Liu, J.-M. Zhou, H.-M. Li, N. Xu and P. Cheng, Cryst. Growth Des., 2014, 14, 6409–6420; (d) X.-H. Wei, L.-Y. Yang, S.-Y. Liao, M. Zhang, J.-L. Tian, P.-Y. Du, W. Gu and X. Liu, Dalton Trans., 2014, 43, 5793–5800; (e) X.-F. Huang, J.-X. Ma and W.-S. Liu, Inorg. Chem., 2014, 53, 5922–5930.
- 4 (a) A. Karmakar, S. Hazra, M. F. C. Guedes da Silva, A. Paul and A. J. L. Pombeiro, *CrystEngComm*, 2016, **18**, 1337–1349;
  (b) Y. Liu, K. Mo and Y. Cui, *Inorg. Chem.*, 2013, **52**, 10286– 10291; (c) D. Dang, Y. Bai, C. He, J. Wang, C. Duan and J. Niu, *Inorg. Chem.*, 2010, **49**, 1280–1282; (d) P. Wu, C. He, J. Wang, X. Peng, X. Li, Y. An and C. Duan, *J. Am. Chem. Soc.*, 2012, **134**, 14991–14999; (e) R. F. D'Vries, N. Snejko, M. Iglesias, E. Gutierrez-Puebla and M. A. Monge, *Cryst. Growth Des.*, 2014, **14**, 2516–2521.
- 5 (a) X. Shen and B. Yan, RSC Adv., 2016, 6, 28165–28170; (b)
  S.-R. Zhang, D.-Y. Du, J.-S. Qin, S.-L. Li, W.-W. He,
  Y.-Q. Lan and Z.-M. Su, Inorg. Chem., 2014, 53, 8105–8113;
  (c) P.-P. Cui, X.-D. Zhang, Y. Zhao, A.-Y. Fu and W.-Y. Sun,
  Dalton Trans., 2016, 45, 2591–2597; (d) X.-D. Zhu, Z.-J. Lin,
  T.-F. Liu, B. Xu and R. Cao, Cryst. Growth Des., 2012, 12,
  4708–4711; (e) S.-Y. Zhang, W. Shi, P. Cheng and
  M. J. Zaworotko, J. Am. Chem. Soc., 2015, 137, 12203–12206;
  (f) G. E. Gomez, M. C. Bernini, E. V. Brusau, G. E. Narda,
  W. A. Massad and A. Labrador, Cryst. Growth Des., 2013,
  13, 4735–4745.
- 6 (a) M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, Chem. Rev., 2014, 114, 1343-1370; (b) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, Chem. Soc. Rev., 2014, 43, 5561-5593; (c) X. Luo, L. Sun, J. Zhao, D.-S. Li, D. Wang, G. Li, Q. Huo and Y. Liu, Cryst. Growth Des., 2015, 15, 4901-4907; (d) D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, Chem. Soc. Rev., 2009, 38, 1257-1283.
- 7 (a) J. Xu, J. Cheng, W. Su and M. Hong, Cryst. Growth Des.,
  2011, 11, 2294–2301; (b) X. Zhou, Y. Guo, Z. Shi, X. Song,
  X. Tang, X. Hu, Z. Zhu, P. Lia and W. Liu, Dalton Trans.,
  2012, 41, 1765–1775; (c) X.-L. Sun, B.-X. Shen, S.-Q. Zang
  and C.-X. Du, CrystEngComm, 2013, 15, 5910–5918; (d)
  L.-N. Jia, L. Hou, L. Wei, X.-J. Jing, B. Liu, Y.-Y. Wang and

Q.-Z. Shi, Cryst. Growth Des., 2013, **13**, 1570–1576; (e) H.-N. Li, H.-Y. Li, L.-K. Li, L. Xu, K. Hou and S.-Q. Zang, Cryst. Growth Des., 2015, **15**, 4331–4340; (f) G.-L. Zhuang, X.-J. Kong, L.-S. Long, R.-B. Huang and L.-S. Zheng, CrystEngComm, 2010, **12**, 2691–2694.

- 8 (a) S. Kitagawa, S. I. Noro and T. Nakamura, *Chem. Commun.*, 2006, 701–707; (b) Y. Zhu, Y. Wang, P. Liu, C. Xia, Y. Wu, X. Lu and J. Xie, *Dalton Trans.*, 2015, 44, 1955–1961; (c) A. Karmakar, S. Hazra, M. F. C. Guedes da Silva, A. Paul and A. J. L. Pombeiro, *CrystEngComm*, 2016, 18, 1337–1349; (d) Y. Liu, K. Mo and Y. Cui, *Inorg. Chem.*, 2013, 52, 10286–10291; (e) D. Dang, Y. Bai, C. He, J. Wang, C. Duan and J. Niu, *Inorg. Chem.*, 2010, 49, 1280–1282.
- 9 (a) S. Seth, G. Savitha, S. Jhulki and J. N. Moorthy, Cryst. Growth Des., 2016, 16, 2024–2032; (b) Q.-Y. Yang, M. Pan, S.-C. Wei, K. Li, B.-B. Du and C.-Y. Su, Inorg. Chem., 2015, 54, 5707–5716; (c) Q. Tang, S. Liu, Y. Liu, D. He, J. Miao, X. Wang, Y. Ji and Z. Zheng, Inorg. Chem., 2014, 53, 289– 293; (d) J. Zhang, B. Zheng, T. Zhao, G. Li, Q. Huo and Y. Liu, Cryst. Growth Des., 2014, 14, 2394–2400; (e) R. San and L. Xu, Chem. Commun., 2013, 49, 8344–8346.
- 10 (a) Y.-T. Liu, Y.-Q. Du, X. Wu, Z.-P. Zheng, X.-M. Lin, L.-C. Zhua and Y.-P. Cai, *CrystEngComm*, 2014, 16, 6797– 6802; (b) Y.-J. Ding, T. Li, X.-J. Hong, L.-C. Zhu, Y.-P. Cai, S.-M. Zhu and S.-J. Yu, *CrystEngComm*, 2015, 17, 3945– 3952; (c) J. Yang, G.-D. Xie, X.-F. Chen, D. Wu, X.-M. Lin, G. Zhang and Y.-P. Cai, *CrystEngComm*, 2015, 17, 1326– 1335; (d) Z.-G. Gu, H.-C. Fang, P.-Y. Yin, L. Tong, Y. Ying, S.-J. Hu, W.-S. Li and Y.-P. Cai, *Cryst. Growth Des.*, 2011, 11, 2220–2227; (e) M.-S. Liu, Q.-Y. Yu, Y.-P. Cai, C.-Y. Su, X.-M. Lin and X.-X. Zhou, *Cryst. Growth Des.*, 2008, 8, 4083–4091.
- 11 G. M. Sheldrick, *SADABS, Version 2.05*, University of Göttingen, Göttingen, Germany.
- 12 G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Göttingen, Germany, 1997.
- 13 G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

- 14 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7-13.
- 15 (a) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, J. Am. Chem. Soc., 1994, 116, 1151–1152; (b) X. Liu, H. Lin, Z. Xiao, W. Fan, A. Huang, R. Wang, L. Zhang and D. Sun, Dalton Trans., 2016, 45, 3743–3749; (c) S. Horike, M. Dincă, K. Tamaki and J. R. Long, J. Am. Chem. Soc., 2008, 130, 5854–5855; (d) K. Schlichte, T. Kratzke and S. Kaskel, Microporous Mesoporous Mater., 2004, 73, 81–88; (e) H. He, H. Ma, D. Sun, L. Zhang, R. Wang and D. Sun, Cryst. Growth Des., 2013, 13, 3154–3161.
- 16 M. Gustafsson, A. Bartoszewicz, B. Martin-Matute, J. L. Sun, J. J. Grins, T. Zhao, Z. Y. Li, G. S. Zhu and X. D. Zou, *Chem. Mater.*, 2010, 22, 3316–3322.
- 17 (a) O. R. Evans, H. L. Ngo and W. B. Lin, J. Am. Chem. Soc., 2001, 123, 10395–10396; (b) R. F. D'Vries, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla and M. A. Monge, Inorg. Chem., 2012, 51, 11349–11355.
- 18 (a) X.-S. Wang, J. Liang, L. Li, Z.-J. Lin, P. P. Bag, S.-Y. Gao, Y.-B. Huang and R. Cao, *Inorg. Chem.*, 2016, 55, 2641–2649;
  (b) J.-M. Gu, W.-S. Kim and S. Huh, *Dalton Trans.*, 2011, 40, 10826–10829; (c) Q.-R. Fang, D.-Q. Yuan, J. Sculley, J.-R. Li, Z.-B. Han and H.-C. Zhou, *Inorg. Chem.*, 2010, 49, 11637– 11642; (d) X.-M. Lin, T.-T. Li, L.-F. Chen, L. Zhang and C.-Y. Su, *Dalton Trans.*, 2012, 41, 10422–10429; (e) X.-M. Lin, T.-T. Li, Y.-W. Wang, L. Zhang and C.-Y. Su, *Chem.-Asian J.*, 2012, 7, 2792–2804.
- 19 (a) N. C. Jeong, J. S. Lee, E. L. Tae, Y. J. Lee and K. B. Yoon, Angew. Chem., Int. Ed., 2008, 47, 10128-10132; (b)
  R. F. D'Vries, N. Snejko, E. Gutiérrez-Puebla, M. Iglesias and M. Angeles Monge, Inorg. Chim. Acta, 2012, 382, 119-126; (c)
  R. F. D'Vries, M. Iglesias, N. Snejko, S. Alvarez-García, E. Gutierrez-Puebla and M. A. Monge, J. Mater. Chem., 2012, 22, 1191-1198; (d)
  H. Tsuruta, T. Imamoto and K. Yamaguchi, Chem. Commun., 1999, 1703-1704; (e)
  M. Yamanaka, A. Nishida and M. Nakagawa, Org. Lett., 2000, 2, 159-161; (f)
  S. Kobayashi, S. Nagayama and T. Busujima, J. Am. Chem. Soc., 1998, 120, 8287-8288.
- 20 M. Gustafsson, A. Bartoszewicz, B. Martín-Matute, J. Sun, J. Grins, T. Zhao, Z. Li, G. Zhu and X. Zou, *Chem. Mater.*, 2010, 22, 3317–3322.