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Honeycomb-shaped coordination polymers based on the self-assembly of long flexible ligands and alkaline-earth ions

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ABSTRACT

Two novel coordination polymers, namely, $[Ca(NCP)_2]_\infty$ (**I**) and $[Sr(NCP)_2]_\infty$ (**II**) were synthesized under hydrothermal conditions based on 2-(4-carboxyphenyl)imidazo(4,5-f)-(1,10)phenanthroline (HNCP) and characterized by elemental analysis, infrared spectrometry, X-ray powder diffraction and single crystal X-ray diffraction. Findings indicate that **I** and **II** are isomorphous and isostructural, containing the unit of $M(NCP^-)_4$ (M=Ca(II) and Sr(II)), based on which to assemble into three-dimensional (3D) porous 4-fold interpenetration honeycomb-shaped neutral coordination polymers (CPs). Between the adjacent lamellar structures in **I** and **II**, there exist π–π interactions between the pyridine rings belonging to phenanthroline of NCP^- which stabilize the frameworks. Both **I** and **II** display stronger fluorescence emissions as well as high thermal stability.

1. Introduction

Coordination polymers (CPs) consisting of inorganic metal ions or clusters and organic ligands, which may generate a huge number of novel interpenetration networks, have become one of the fastest growing fields in chemistry and attract immense interest. [1–5]. CPs may allow rational design strategies for assembling porous materials to target some diverse functionalities and potentially industrial applications, such as gas storage and separation, catalysis, guest-exchange, molecular recognition, magnetic properties and selective luminescent probes [6–19]. Obviously, the topological features the geometry of metal centers and the coordination mode of bridging ligands. Selection of suitable ligands with fixed geometry and variable bonding modes is very important for the design and synthesis of coordination polymers with interesting geometric configurations [20–24]. The long flexible conjugated HNCP ligand acting as conjugation-bridge linker with carboxylato oxygen and phenanthroline nitrogen donor atoms in either end may construct non-centeric coordination polymers with topological and thermallystable frameworks. What's more, HNCP exhibits specific spatial structure of benzene, imidazole and phenanthroline, which is benefit to construct the C–H⋯π and π⋯π interactions and form hydrogen bonds [25–27].

However, coordination assemblies constructed by highly symmetrical multitopic ligands and suitable metals has been systematically investigated, the major of which focused on the assembly of the lanthanide ions and the transition metal ions in combination with organic linkers. The coordination polymers of the alkaline-earth metal ions still remain much less developed [21–24]. Up to now, only several metal coordination polymers based on 2-(4-carboxyphenyl)imidazo(4,5-f) -(1,10)phenanthroline have been reported [26–35]. Following our ongoing efforts towards the synthesis and isolation of novel coordination polymers [36–40], in this work, we describe the synthesis, structures, and luminescent properties of two 3D coordination polymers obtained from the self-assembly of bridging 2-(4-carboxyphenyl) imidazo(4,5-f)-(1,10)phenanthroline and alkaline-earth metal ions, which are formulated as$[Ca(NCP)_2]_\infty$ (**I**) and $[Sr(NCP)_2]_\infty$ (**II**).

2. Experimental section

2.1. Materials and physical measurements

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed with a Perkin-Elmer 240 CHN Elemental Analyzer. IR spectra in the range of 400–4000 cm^{-1} were recorded with an AVATAR 360 FT-IR spectrometer (KBr pellets were used). The crystal structure was determined with a Bruker Smart CCD X-ray single-crystal diffractometer. TG analysis was conducted with a Perkin-Elmer TGA7 instrument in flowing N_2 at a heating rate of

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10 °C min^{-1}. Excitation and emission spectra were obtained with an F-7000 FL spectrofluorometer at room temperature. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were conducted with a Perkin-Elmer TGA7 system under flowing N_2 stream (flow rate 40 mL/min) from room temperature to 1000 °C at a heating rate of 10 K/min. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance instrument with Cu-Kα radiation (λ=1.54056 Å) in the range 2θ=5–42.5° at room temperature.

2.2. *Synthesis of the coordination polymers I and II*

2.2.1. *Synthesis of $[Ca(NCP)_2]_\infty$(**I**)*

A mixture of 2-(4-carboxyphenyl)imidazo(4,5-f)(1,10)phenanthroline) (17.0 mg, 0.05 mmol), calcium chloride (3.3 mg, 0.03 mmol)and water (10 mL) was homogenized by stirring for 30 min, then transferred into 25 mL Teflon-lined stainless steel autoclave under autogenous pressure at 180 °C for 3 days. After cooling the reaction system to room temperature at a rate of 5 °C/h, clear block orange crystals were isolated (with the yield of 65%, based on the HNCP reagent). Calc. for $C_{40}H_{22}N_8O_4Ca$ (%): C, 66.84; H, 3.09.; N, 15.59. Found: C, 66.81; H, 3.01; N, 15.53. IR data (KBr pellet, cm^{-1}): 3227(br), 3043(w), 1933(w), 1665(m), 1612(m), 1593 (s), 1573(s), 1557(s), 1522(s), 1483(m), 1451(m), 1433(m), 1402(s), 1386(s), 1321(m), 1290(m), 1273(m), 1232(m), 1183(m), 1125(w), 1103(w), 1072(m), 1033 (m), 973(w), 867(m), 843(m), 807(s), 785 (s), 737(s), 723(m), 705(s), 643(w), 631(w), 545(w), 529(w), 439 (w), 415(m).

2.2.2. *Synthesis of $[Sr(NCP)_2]_\infty$(**II**)*

A mixture of 2-(4-carboxyphenyl)imidazo(4,5-f)(1,10)phenanthroline) (34.0 mg, 0.1 mmol), strontium nitrate (12.7 mg, 0.6 mmol)and water (10 mL) was homogenized by stirring for 30 min, then transferred into 25 mL Teflon-lined stainless steel autoclave under autogenous pressure at 180 °C for 3 days. After cooling the reaction system to room temperature at a rate of 5 °C/h, clear block orange crystals were isolated (with the yield of 61%, based on the HNCP reagent). Calc. for $C_{40}H_{22}N_8O_4Sr$ (%): C, 70.58; H, 3.55.; N, 16.46. Found: C, 70.51; H, 3.51; N, 16.42. IR data (KBr pellet, cm^{-1}): 3228(br), 3045(w), 1931(w), 1668(m), 1615(m), 1596 (s), 1571(s), 1554(s), 1521(s), 1480(m), 1452(m), 1430(m), 1400(s), 1385(s), 1320(m), 1291(m), 1275(m), 1234(m), 1185(m), 1127(w), 1105(w), 1070(m), 1031(m), 971(w), 869(m), 845(m), 809(s), 789 (s), 739(s), 724(m), 704(s), 645(w), 631(w), 547(w), 528(w), 438 (w), 411(m).

2.3. *Crystallographic data collection and refinement*

Single-crystal diffraction data **I** and **II** were collected suitable single crystals of the coordination polymers on a Bruker Smart CCD X-ray single-crystal diffractometer with graphite monochromated MoKα-radiation (λ=0.71073 Å) at 296(2) K. All independent reflections were collected in a range of 1.75–25.00° for coordination polymer **I** and 2.19–25.00° for coordination polymer **II** (determined in the subsequent refinement). Multi-scan empirical absorption corrections were applied to the data using the SADABS. The crystal structure was solved by direct methods and Fourier synthesis. Positional and thermal parameters were refined by the full-matrix least-squares method on F^2 using the SHELXTL software package. The final least-square cycle of refinement gave R_1=0.0405, wR_2=0.1215 for coordination polymer **I** and R_1=0.0423, wR_2=0.1301 for coordination polymer **II**, the weighting scheme $w=1/[\sigma^2(F_0^2)+(0.0992P)^2+0.000P]$ for coordination polymer **I** and $w=1/[\sigma^2(F_0^2)+(0.0785P)^2+1.175P]$ for coordination polymer **II**, where $P=(F_0^2+2F_c^2)/3$. The crystallographic data, selected bond lengths and bond angles for coordination polymers **I** and **II** are listed in Table 1 and Table 2, respectively.

Table 1
Summary of crystallographic data for coordination polymers **I** and **II**.

Data	I	II
Empirical formula	$C_{40}H_{22}N_8O_4Ca$	$C_{40}H_{22}N_8O_4Sr$
Formula weight	716.72	766.28
Temperature/ K	296(2)	296(2)
Wavelength / Å	0.71073	0.71073
Crystal system	*Orthorhombic*	*Orthorhombic*
space group	*Pnna*	*Pnna*
a/Å	18.045 (5)	18.0519(11)
b/Å	11.490(4)	11.7574(7)
c/Å	15.228(5)	15.2235(9)
$\alpha=\beta=\gamma$ / (°)	90	90
Z	4	4
Density(calculated)	1.508 Mg/m^3	1.575 Mg/m^3
F(000)	1472	1552
Crystal size/mm^3	0.24 × 0.18 × 0.17	0.49 × 0.34 × 0.25
Range for data collection/(°)	1.75 to 25.00	2.19 to 25.00
Limiting indices	$-21\le h\le 14$, $-13\le k\le 13$, $-18\le l\le 18$	$-21\le h\le 21$, $-13\le k\le 13$, $-18\le l\le 12$
Reflections collected/ unique	27928/3544 [$R_{(\text{int})}$ =0.0294]	28376/3249 [$R_{(\text{int})}$ =0.0344]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	3544/0/240	3249/0/240
Goodness-of-fit on F^2	1.078	1.062
Volume/Å^3	3157.4(17)	3231.1(3)
Final *R* indices [$I>2\text{sigma}(I)$]	R_1=0.0405, wR_2 =0.1215	R_1=0.0423, wR_2=0.1301
R indices (all data)	R_1=0.0490, wR_2 =0.1269	R_1=0.0566, wR_2=0.1364
Largest diff. peak and hole/ (e Å^{-3})	0.688 and −0.449	0.440 and −0.984

3. Results and discussion

3.1. *FT-IR spectroscopy and X-ray powder diffraction*

Coordination polymers **I** and **II** are insoluble in common solvents such as CH_3COCH_3, CH_3CH_2OH, CH_3OH, and $CH_3CH_2OCH_2CH_3$, but they are slight soluble in DMSO and DMF. The coordination polymers are characterized by satisfactory elemental analysis as well as FT-IR and X-ray powder diffraction. The FT-IR spectra of the two as-synthesized coordination polymers are similar. The strong and broad absorption bands the region of 1668–1615 cm^{-1} and 1480–1400 cm^{-1} may be ascribed to the asymmetric (COO^-) and symmetric (COO^-) stretching of carboxyl groups of NCP^- ligands in **I** and **II**. The values of $\Delta[\nu_{as}-\nu_s]$ are about 268–215 cm^{-1}, which indicate that the carboxyl groups are coordinated with the metal ions *via* both bidentate-chelating modes [41–43]. The absence of the characteristic bands around 1700 cm^{-1} shows that the HNCP ligands are completely deprotonated in the form of NCP^- anions upon reaction with the metal ions [44]. The same conclusions are also supported by the results obtained from X-ray diffraction measurements.

The powder XRD of coordination polymer **II** has been investigated. As shown in Fig. 1, the experimental powder XRD pattern is consistent with the simulated one on the basis of the single-crystal structure, which indicated that the sample is pure.

3.2. *Structural description of the coordination polymers*

Single crystal X-ray diffraction analysis reveals that the three-