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Introduction

Lanthanide coordination polymers based on 5-(2'-carboxylphenyl) nicotinate: syntheses, structure diversity, dehydration/hydration, luminescence and magnetic properties†

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Twelve lanthanide coordination polymers associated with the organic ligand 5-(2'-carboxylphenyl) nicotinic acid (H₂cpna): {[Ln(Hcpna)(cpna)(phen)] \cdot H₂O}_n (Ln = Sm (1), Tb (2), Ho (3), phen = 1,10-phenanthroline), {[Sm(Hcpna)(cpna)(phen)] \cdot 2H₂O}_n (4), {[Ln₂(cpna)₃(H₂O)₃] \cdot 4H₂O}_n (Ln = Y (5), Tb(6), Dy (7), Ho (8)), $[Lu_2(cpna)_3(H_2O)_2]_n$ (9), $\{[Y_2(cpna)_3(phen)_2(H_2O)] \cdot H_2O\}_n$ (10), and $[Ln(cpna)(phen)(NO_3)]_n$ (Ln = Tm (11), Lu (12)) have been prepared by hydrothermal methods and structurally characterized. The structure analyses reveal that complexes 1-3 are isostructural and possess unique three-dimensional (3D) frameworks based on the dodecanuclear Sm/Tb/Ho macrocycles. Complex 4 exhibits a one-dimensional (1D) wheel-chain structure, which further builds three-dimensional (3D) supramolecular architecture via O-H...N hydrogen-bonding interactions. Complexes 5-8 are also isostructural and display threedimensional (3D) open frameworks, which possess two types of channels along the a- and b-axis, respectively. Complexes 9 and 10 feature three-dimensional (3D) frameworks and are created from tetranuclear and dinuclear units, respectively. Complexes 11 and 12 are isostructural and demonstrate one-dimensional (1D) double chain structures, which further build three-dimensional (3D) supramolecular architecture via C-H···O hydrogen-bonding. The results show that the pH value of the reaction system, anion, auxiliary ligand and lanthanide contraction play a significant role in determining the structures of the complexes. In addition, the results of luminescent measurements for compounds 2 and 6 in the solid state at room temperature indicate that the different types of structures have a dissimilar influence on their characteristic luminescence. The magnetic properties of compounds 1, 3, 4, 7 and 11 have been investigated. Furthermore, thermal stabilities for 1-12 and the dehydration/hydration properties of compound 6 have also been studied

Recently, the preparation of lanthanide coordination polymers has provoked considerable current interest owing to their enormous variety of intriguing structural topologies as well as great potential applications in the area of catalysis, gas storage, separation, magnetism and luminescence.¹ In comparison with

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transition metal ions, lanthanide ions have higher coordination numbers and more flexible coordination geometries, which make it even more difficult to control the structures. Thus, it is a great challenge to control structures with desired properties because many factors affect the result, such as the coordination geometry of the central metal ions, connection modes of organic ligands, reaction temperature, the ratio of reagents, solvents, pH value, anions, and so on.² Investigations on how these factors affect the final structures will help us understand which reaction conditions afford lanthanide coordination polymers with expected structures. Recently, we have been interested in the coordination chemistry of 5-(2'-carboxylphenyl) nicotinic acid (H_2 cpna), a semi-rigid ligand with multiple coordination sites. H₂cpna has been proven to be useful in the construction of coordination polymers, which can be attributed to the different protonated extend depending on the pH and free rotation of the C-C single bond between pyridyl and phenyl rings.³

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[†]Electronic supplementary information (ESI) available: Tables of selected bond distances and angles, hydrogen bonds in crystal packing of the complexes, 3D renderings of Fig. S1 and S2, results of the temperature-dependent powder XRD study of compound 6, luminescent data for complexes 2 and 6. CCDC 900086–900097 for 1–12. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32674d

In this contribution, by using ligand H₂cpna, changing the reaction pH value and the anion of the metal salt, and/or using an auxiliary ligand, a series of lanthanide coordination polymers { $[Ln(Hcpna)(cpna)(phen)] \cdot H_2O_{ln}$ (Ln = Sm (1), Tb (2), Ho (3), phen = 1,10-phenanthroline), {[Sm(Hcpna)(cpna) (phen)]·2H₂O₁ (4), {[Ln₂(cpna)₃(H₂O)₃]·4H₂O₁ (Ln = Y (5), Tb (6), Dy (7), Ho (8)), $[Lu_2(cpna)_3(H_2O)_2]_n$ (9), $\{[Y_2(cpna)_3 (phen)_2(H_2O)] \cdot H_2O_n$ (10), and $[Ln(cpna)(phen)(NO_3)]_n$ (Ln = Tm (11), Lu (12)) were prepared by a hydrothermal method. Their structural diversities show that the pH value of the reaction system, anion, auxiliary ligand and lanthanide contraction are key factors in the structural self-assembly process.

Experimental

Materials and methods

All chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) was performed under N2 atmosphere with a heating rate of 10 °C min⁻¹ on a LINSEIS STA PT1600 thermal analyzer. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu-Ka radiation $(\lambda = 1.54060 \text{ Å})$, in which the X-ray tube was operated at 40 kV and 40 mV. Excitation and emission spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer at room temperature for the solid samples. The quantum yields of the complexes were determined by an absolute method using an integrating sphere (150 mm diameter, BaSO₄ coating) from Edinburgh Instruments FLS920. The lifetime measurement was measured on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with Nd pumped OPOlette laser as the excitation source. Magnetic susceptibility data were collected in the 2-300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

Synthesis of complexes 1-12

{[Ln(Hcpna)(cpna)(phen)]·H₂O}_n (Ln = Sm (1), Tb (2), Ho (3)). A mixture of Ln(NO₃)₃·6H₂O (0.2 mmol), H₂cpna (72.9 mg, 0.3 mmol), phen (39.6 mg, 0.2 mmol) and H₂O (10 mL) was adjusted to pH = 4.0–5.0 with 0.5 M NaOH solution. The mixture was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C h⁻¹. Yellow block-shaped crystals were isolated manually, and washed with distilled water. Yield: 60% for 1; 55% for 2; 50% for 3 (based on H₂cpna). Calcd for C₃₈H₂₅N₄SmO₉ (1): C 54.86, H 3.03, N 6.73%. Found: C 55.17, H 3.41, N 6.35%. IR (KBr, cm⁻¹): 3424 w, 3056 w, 1687 m, 1613 s, 1580 w, 1533 w, 1417 w, 1392 s, 1257 m, 1158 w, 1132 w, 1099 w, 1055 w, 1026 w, 857 m, 792 m, 754 s, 732 w, 499 w, 429 w. Anal. calcd for $C_{38}H_{25}N_4TbO_9$ (2): C 54.30, H 3.00, N 6.66%. Found: C 53.95, H 3.37, N 6.97%. IR (KBr, cm⁻¹): 3424 w, 3054 w, 1687 m, 1614 s, 1584 s, 1535 w, 1517 w, 1421 m, 1393 s, 1258 m, 1158 w, 1131 m, 1099 w, 1054 w, 1025 w, 850 m, 791 w, 753 s, 731 m, 498 w, 430 m. Anal. calcd for $C_{38}H_{25}N_4HoO_9$ (3): C 53.91, H 2.98, N 6.62%. Found: C 54.32, H 3.26, N 6.38%. IR (KBr, cm⁻¹): 3423 w, 3052 w, 1687 m, 1616 s, 1583 s, 1537 w, 1517 w, 1423 m, 1392 s, 1258 m, 1158 w, 1131 m, 1099 w, 1056 w, 1024 w, 851 m, 791 w, 753 s, 730 m, 684 w, 499 w, 431 m.

{[Sm(Hcpna)(cpna)(phen)]·2H₂O}_{*n*} (4). The preparation of 4 was similar to that of 1 except using SmCl₃·6H₂O instead of Sm(NO₃)₃·6H₂O. After being cooled to room temperature, colorless block-shaped crystals of 4 were isolated manually, and washed with distilled water. Yield: 48% (based on H₂cpna). Calcd for $C_{38}H_{27}N_4$ SmO₁₀: C 53.69, H 3.20, N 6.59%. Found: C 53.31, H 3.46, N 6.25%. IR (KBr, cm⁻¹): 3494 w, 3059 w, 1695 m, 1611 s, 1581 w, 1543 w, 1491 w, 1443 w, 1385 s, 1296 m, 1166 w, 1135 w, 1100 w, 1051 w, 1029 w, 847 m, 810 m, 791 m, 766 m, 726 m, 528 w, 428 m.

 ${[Ln_2(cpna)_3(H_2O)_3] \cdot 4H_2O_n}$ (Ln = Y (5), Tb (6), Dy (7), Ho (8)). A mixture of $Ln(NO_3)_3 \cdot 6H_2O$ (0.2 mmol), H_2cpna (72.9 mg, 0.3 mmol), and H_2O (10 mL) was adjusted to pH = 5.5 with 0.5 M NaOH solution. The mixture was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C h⁻¹. Yellow block-shaped crystals were isolated manually, and washed with distilled water. Yield: 55% for 5, 6; 50% for 7, 8 (based on H_2 cpna). Anal. calcd for $C_{39}H_{35}N_3Y_2O_{19}$ (5): C 45.59, H 3.43, N 4.09%. Found: C 45.93, H 3.24, N 4.45%. IR (KBr, cm⁻¹): 3401w, 3060 w, 1645 w, 1605 s, 1574 w, 1548 m, 1492 w, 1435 m, 1396 s, 1295 w, 1134 w, 1100 w, 1029 w, 953 w, 863 w, 793 w, 762 s, 688 w, 570 w, 431 w. Anal. calcd for C₃₉H₃₅N₃Tb₂O₁₉ (6): C 40.12, H 3.02, N 3.60%. Found: C, 40.60; H, 3.36; N 3.90%. IR (KBr, cm⁻¹): 3358 w, 3066 w, 1646 m, 1605 s, 1573 m, 1544 s, 1518 w, 1430 m, 1389 s, 1272 m, 1161 w, 1134 m, 1100 w, 1055 w, 1028 w, 860 m, 794 w, 760 s, 686 m, 566 w, 421 m. Anal. calcd for C₃₉H₃₅N₃Dy₂O₁₉ (7): C 39.88, H 3.00, N 3.58%. Found: C 40.21, H 3.36, N 3.25%. IR (KBr, cm⁻¹): 3369 w, 3065 w, 1647 m, 1605 s, 1573 m, 1545 m, 1493 w, 1431 m, 1392 s, 1272 m, 1160 w, 1134 m, 1101 w, 1055 w, 1028 w, 954 w, 861 m, 793 w, 762 s, 687 m, 569 w, 426 m. Anal. calcd for $C_{39}H_{35}N_3Ho_2O_{19}$ (8): C 39.71, H 2.99, N 3.56%. Found: C 40.09, H 3.41, N 3.85%. IR (KBr, cm⁻¹): 3360 w, 3064 w, 1647 w, 1605 s, 1573 w, 1547 s, 1494 w, 1430 m, 1392 s, 1296 m, 1134 w, 1100 w, 1055 w, 1028 w, 862 m, 793 w, 761 s, 687 w, 594 w, 428 m.

 $[Lu_2(cpna)_3(H_2O)_2]_n$ (9). The preparation of 9 was similar to that of 5 except using Lu(NO₃)₃·6H₂O instead of Y(NO₃)₃·6H₂O. After being cooled to room temperature, yellow block-shaped crystals of 9 were isolated manually, and washed with distilled water. Yield: 50% (based on Lu). Calcd for C₃₉H₂₅N₃Lu₂O₁₄: C 42.22, H 2.27, N 3.79%. Found: C 42.61, H 2.59, N 3.35%.

IR (KBr, cm⁻¹): 3360 w, 3052 w, 1603 s, 1578 w, 1552 s, 1491 w, 1441 m, 1400 s, 1294 w, 1267 w, 1158 w, 1100 w, 1026 w, 902 w, 865 m, 814 m, 761 m, 706 m, 685 m, 661 w, 577 w, 424 m.

 $\{ [Y_2(cpna)_3(phen)_2(H_2O)] \cdot H_2O \}_n$ (10). A mixture of Y(NO₃)₃·6H₂O (76.6 mg, 0.2 mmol), H₂cpna (72.9 mg, 0.3 mmol), phen (39.6 mg, 0.2 mmol), and H₂O (10 mL) was adjusted to pH = 5.5 with 0.5 M NaOH solution. The mixture was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C h⁻¹. Yellow block-shaped crystals were isolated manually, and washed with distilled water. Yield: 60% (based on H₂cpna). Calcd for C₆₃H₄₁N₇Y₂O₁₄ (10): C 58.30, H 3.18, N 7.55%. Found: C 58.66, H 3.01, N 7.27%. IR (KBr, cm⁻¹): 3422 w, 3051 w, 1617 s, 1585 s, 1538 m, 1517 w, 1424 m, 1394 s, 1258 m, 1158 w, 1100 m, 1025 w, 851 m, 792 w, 752 m, 732 w, 708 m, 684 w, 605 w, 434 w.

[Ln(cpna)(phen)(NO₃)]_n (Ln = Tm (11), Lu (12)). The preparation of **11** and **12** was similar to that of **10** except using Tm-(NO₃)₃·6H₂O and Lu(NO₃)₃·6H₂O instead of Y(NO₃)₃·6H₂O. Yield: 50% for **10**; 55% for **11** (based on H₂cpna). Calcd for C₂₅H₁₅N₄TmO₇ (**11**): C 46.03, H 2.32, N 8.59%. Found: C 45.71, H 2.67, N 8.21%. IR (KBr, cm⁻¹): 3384 w, 1615 s, 1576 w, 1519 s, 1392 s, 1286 s, 1144 w, 1101 w, 1027 w, 858 m, 811 m, 765 m, 727 m, 690 w, 661 w, 591 w, 424 w. Calcd for C₂₅H₁₅N₄LuO₇ (**12**): C 45.61, H 2.30, N 8.51%. Found: C 45.29, H 2.57, N 8.78%. IR (KBr, cm⁻¹): 3366 m, 1617 s, 1578 w, 1520 s, 1420 m, 1394 s, 1348 w, 1288 s, 1144 w, 1101 w, 1028 w, 859 m, 766 w, 727 m, 690 w, 661 w, 592 w, 423 w.

X-Ray crystallography

The X-ray single-crystal data collection for complexes was performed on a Bruker Smart CCD diffractometer, using

graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs.⁴ All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 . All the hydrogen atoms (except the those bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of water molecules were located by difference maps and constrained to ride on their parent O atoms. Crystallographic data as well as details of data collection and refinement for these complexes are summarized in Table 1 and Table S1 (ESI⁺). Important bond lengths bond angles are listed in Table S2 (ESI⁺). Hydrogen bonds in crystal packing for the compounds 1–10 are listed in Table S3 (ESI⁺).

Results and discussion

Description of the structures

Structures of 1–3. Single-crystal X-ray diffraction analysis reveals that complexes **1–3** are isostructural 3D frameworks based on the dodecanuclear Sm/Tb/Ho macrocycles, and the structure of **1** is selected and described in detail. Complex **1** crystallizes in the trigonal space group $R\bar{3}$. The asymmetrical unit of compound **1** contains one crystallographically unique Sm(m) ion, one Hcpna[–] ligand, one cpna^{2–} ligand, one phen ligand, and one lattice water molecule. As shown in Fig. 1a, Sm(m) ion is nine-coordinated by five carboxylate O atoms of four individual cpna^{2–} ligands, two carboxylate O atoms from one Hcpna[–] ligand, and two N atoms of one phen ligand,

Table 1 Crystal data and structure refinement parameters for complexes 1, 4, 6, 9–11

Compound	1	4	6	9	10	11
Formula	C ₃₈ H ₂₅ SmN ₄ O ₉	C38H27SmN4O10	C ₃₉ H ₃₅ Tb ₂ N ₃ O ₁₉	C39H25Lu2N3O14	C ₆₃ H ₄₁ Y ₂ N ₇ O ₁₄	C ₂₅ H ₁₅ TmN ₄ O ₇
Formula mass	831.97	849.99	1167.54	1109.56	1297.85	652.34
Crystal system	Trigonal	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	RĪ	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	31.18(3)	9.128(3)	12.788(2)	11.476(2)	8.371(7)	12.366(8)
b/Å	31.18(3)	13.654(4)	13.670(2)	12.667(2)	13.459(11)	10.426(7)
c/Å	18.229(19)	14.128(4)	14.211(2)	13.512(3)	24.53(2)	17.438(12)
$\alpha/^{\circ}$	90	97.222(3)	66.1690(10)	103.635(2)	75.911(8)	90
$\beta/^{\circ}$	120	96.653(3)	66.9470(10)	99.747(2)	86.628(8)	93.717(7)
γ/°	90	105.169(3)	77.0190(10)	108.5040(10)	79.871(8)	90
$V/Å^3$	15353(27)	1665.5(9)	2084.5(6))	1745.5(6)	2638(4)	2244(3)
<i>T</i> /K	296(2)	293(2)	296(2)	296(2)	296(2)	293(2)
Ζ	18	2	2	2	2	4
$D_c/\mathrm{g~cm}^{-3}$	1.620	1.695	1.860	2.111	1.634	1.931
F(000)	7470	850	1144	1068	1316	1272
Data collected	17 322	12 312	15 080	12 924	18 661	15 657
Unique data	5935	6119	7643	6418	9358	4183
R _{int}	0.0837	0.0493	0.0324	0.0243	0.0729	0.0827
GOF on F^2	1.006	1.037	1.051	1.050	1.002	1.029
$R_1 (I \ge 2\sigma(I))$	0.0568	0.0412	0.0305	0.0252	0.0549	0.0486
$wR(F^2)$ values $(I > 2\sigma(I))$	0.1292	0.0859	0.0766	0.0467	0.0966	0.0996
R_1 values (all data)	0.1054	0.0534	0.0372	0.0334	0.1291	0.0776
$wR(F^2)$ values (all data)	0.1514	0.0919	0.0790	0.0489	0.1178	0.1114



Fig. 1 (a) The coordination environment of the Sm(III) ion in **1**. The hydrogen atoms are omitted for clarity except those bonds to carboxylate oxygen atoms. Symmetry codes: i = -x + 4/3, -y + 5/3, -z + 2/3; ii = x - y + 1, x, -z + 1; iii = -x + y + 1/3, -x + 5/3, z - 1/3. (b) A dodecanuclear Sm(III) macrocycle. The green balls represent the dinuclear units. The hydrogen atoms are omitted for clarity. (c) The 2D layer consisting of the hexagonal rings. (d) The representation of the connection mode among the hexagonal rings. The green balls represent the dinuclear units.



Scheme 1 The various coordination modes for Hcpna^{-/}cpna²⁻ in compounds **1–12**. I: trans-1 $\kappa^2 O_i O_i'$; II: trans- μ_4 -1 $\kappa^2 O_i O_i'$: $2 \kappa O:3 \kappa O'':4 \kappa O'''$; III: cis-1 $\kappa^2 O_i O_i'$; IV: cis- μ_4 -1 $\kappa^2 O_i O_i'$: $2 \kappa O:3 \kappa O'':4 \kappa O'''$; V: cis- μ_4 -1 $\kappa O:2 \kappa O':3 \kappa O'':4 \kappa O'''$; VII: trans- μ_3 -1 $\kappa^2 O_i O_i'$: $2 \kappa O'':3 \kappa O'''$; VII: cis- μ_3 -1 $\kappa O:2 \kappa O':3 \kappa O''$; VIII: trans- μ_4 -1 $\kappa O:2 \kappa O':3 \kappa O''$; VIII: trans- μ_4 -1 $\kappa O:2 \kappa O'$: $3 \kappa O'''$; IX: trans- μ_4 -1 $\kappa O:2 \kappa O'$.

which resembles a distorted tricapped trigonal geometry. The Sm–O bond lengths range from 2.391(5) to 2.612(6) Å, the Sm–N distances vary from 2.616(7) to 2.636(7) Å. The Hcpna⁻ ligand adopts coordination mode I (Scheme 1), in which the deprotonated carboxylate group shows $\mu_1-\eta^1:\eta^1$ bidentate mode. The cpna²⁻ ligand takes coordination mode II, in which two carboxylate groups adopt $\mu_2-\eta^1:\eta^1$ bidentate mode and $\mu_2-\eta^1:\eta^2$ tridentate mode, respectively (Scheme 1). It should be mentioned that in 1–3, the N atoms of both Hcpna⁻ and cpna²⁻ ligands remain uncoordinated and involved in the intermolecular hydrogen bonding (O3–H3…N2ⁱ, i = –y + 4/3,

x - y + 2/3, z - 1/3). Two crystallographically equal Sm(III) centers are bridged by two O atoms of carboxylate groups from two different cpna²⁻ ligands and two carboxyl groups from two individual cpna²⁻ ligands in bidentate mode into a binuclear unit (Fig. S1, ESI⁺) with a Sm-Sm distance of 4.031(3) Å and Sm-Ocarboxylate-Sm angle of 107.26(19)°. The binuclear units are linked by $cpna^{2-}$ ligands forming a dodecanuclear Sm(m)macrocycle (Fig. 1b). The ring adopts a chair conformation resembling cyclohexane with the side length of 15.1229(15) Å (Fig. S2, ESI[†]). The ring is connected with six adjacent rings by co-corner forming a regular layer structure in the ab plane (Fig. 1c and 1d). The layers are further linked by the coordination interaction of cpna²⁻ ligands and Sm(III) ions to generate a 3D framework (Fig. S3, ESI⁺). The dihedral angles of the pyridyl and the phenyl rings in one Hcpna⁻ ligand are 66.74° for 1, 66.85° for 2, 67.60 for 3. Those in one $cpna^{2-}$ ligand are 56.29° for 1, 56.81° for 2, 56.94 for 3, respectively.

Structure of 4. Complex 4 crystallizes in the triclinic space group P1 and features a 1D wheel-chain structure based on a binuclear unit, which is isotypic with its Pr, Nd, Eu, and Gd analogues reported by our group.^{3b} The asymmetrical unit of compound 4 consists of one crystallographically independent Sm(m) ion, one Hcpna⁻ ligand, one cpna²⁻ ligand, and two lattice water molecules. Sm(III) ion is nine-coordinated by seven O atoms and two N atoms, which resembles a distorted tricapped trigonal geometry (Fig. 2a). The Sm-O bond lengths range from 2.375(3) to 2.756(4) Å, the Sm-N distances vary from 2.592(4) to 2.601(4) Å. The Hcpna⁻ ligand adopts coordination mode III, in which deprotonated carboxylate group shows $\mu_1 - \eta^1 : \eta^1$ bidentate mode. The cpna²⁻ ligand takes coordination mode IV, in which two carboxylate groups take $\mu_2 - \eta^1: \eta^1$ bidentate mode and $\mu_2 - \eta^1: \eta^2$ tridentate mode, respectively. It is noted that in 1-4, the related carboxylate groups in Hcpna⁻ and cpna²⁻ ligands take the same coordination modes, however, the Hcpna⁻ and cpna²⁻ ligands adopt different conformations (trans for 1-3 and cis for 4). In 4, the N atoms of both Hcpna⁻ and cpna²⁻ ligands remain uncoordinated and involved in the interchain hydrogen bonding. Two crystallographically equal Sm(m) centers are bridged by two O atoms of carboxylate groups from two different cpna^{2–} ligands



Fig. 2 (a) The coordination environment of the Sm(III) ion in 4. The hydrogen atoms are omitted for clarity except those bonds to oxygen atoms of the carboxy-late groups. Symmetry codes: i = -x + 2, -y + 1, -z; ii = -x + 1, -y + 1, -z; iii = x - 1, *y*, *z*. (b) Views of the 1D wheel chain along the *ab* plane. The hydrogen atoms are omitted for clarity except those bonds to oxygen atoms of the carboxy-late groups.

and two carboxyl groups from two individual cpna^{2–} ligands in bidentate mode into a dimeric unit with a Sm–Sm distance of 4.001(2) Å and Sm–O_{carboxylate}–Sm angle of 102.21(12)°, which is further joined by cpna^{2–} ligands to form a 1D wheel-chain structure (Fig. 2b). The 1D chains are further extended into a 3D metal–organic supramolecular framework by O–H…N hydrogen-bonding interactions (Table S3, Fig. S4, ESI†). The dihedral angles of the pyridyl and the phenyl rings in one Hcpna[–] ligand and one cpna^{2–} ligand are 73.32° and 69.74°, respectively.

Structures of 5-8. Compounds 5-8 are isostructural and feature a three-dimensional open framework structure. Hence, only the structure of 6 is selected and described in detail. Complex 6 crystallizes in the triclinic space group $P\bar{1}$. In the asymmetrical unit, there are two crystallographically unique Tb(III) atoms, three cpna²⁻ ligands, three coordinated water and four lattice water molecules. As depicted in Fig. 3a, Tb1 atom is eight-coordinated by seven carboxylate O atoms of six different cpna²⁻ ligands, and one O atom of one coordinated water molecule, constructing a distorted bicapped trigonal prism. Tb2 atom is also eight-coordinated by six carboxylate O atoms of five independent cpna²⁻ ligands, and two O atoms of two coordinated water molecules, forming a distorted bicapped trigonal prism (Fig. 3b). The lengths of Tb-O bonds are in the range of 2.248(3)-2.528(3) Å. The cpna²⁻ ligands adopt three different coordination modes (Scheme 1,

modes II, V and VI), in which carboxylate groups show $\mu_1 - \eta^1 : \eta^1$ bidentate mode, $\mu_2 - \eta^1: \eta^1$ bidentate mode, and $\mu_2 - \eta^1: \eta^2$ tridentate mode, respectively. The dihedral angles of the pyridyl and the phenyl rings in the cpna²⁻ ligands are 35.46°, 56.96° and 50.51°, respectively. Adjacent Tb atoms are bridged by O atoms of carboxylate groups and carboxyl groups into a [Tb1₂Tb2₂] tetranuclear unit (Fig. S5, ESI⁺). The tetranuclear units are further linked by the coordination interaction of cpna²⁻ ligands and Tb(III) ions to generate a open 3D framework (Fig. 3c). The dimension of each channel is 5.63 Å \times 11.0 Å measured by atom-to-atom distances (N3…N3ⁱ = 5.63, Tb2...Tb2ⁱ = 11.0 Å, i = x + 2, y + 2, z). The N atoms of cpna²⁻ ligands point toward the open channel. The channels are filled with guest water molecules. Viewed down the *b*-axis (Fig. S6, ESI[†]), the framework of compound 6 also displays long narrow shaped channels with size about 15.2 Å \times 10.6 Å measured by atom-to-atom distances (Tb2...Tb2ⁱⁱ = 15.2 Å, C30...C30ⁱⁱ = 5.63, ii = x + 1, y + 2, z). When removing guest water molecules, we computed its effective free volume as being 18.2% by PLATON analysis of the crystal volume.⁵ If removing both coordinated waters and guest water molecules, the effective free volume of compound 6 is calculated by PLATON analysis as being 21.1% of the crystal volume.

Structure of 9. Complex **9** crystallizes in the triclinic space group $P\overline{1}$. The asymmetrical unit of compound **9** contains two crystallographically unique Lu(III) atoms, three cpna²⁻ ligands, and two coordinated water molecules. As shown in Fig. 4a, Lu1 atom is eight-coordinated by seven carboxylate O atoms of six





Fig. 3 (a) The coordination environment of the Tb1 ion in **6**. The hydrogen atoms are omitted for clarity except those bound to oxygen atoms of the coordinated water molecules. Symmetry codes: i = -x, -y + 2, -z + 2; ii = x, y, z + 1; iii = -x + 1, -y + 2, -z + 1; iv = -x + 1, -y + 2, -z + 2. (b) The coordination environment of the Tb2 ion in **6**. The hydrogen atoms are omitted for clarity except those bound to oxygen atoms of the coordinated water molecules. Symmetry codes: i = -x, -y + 2, -z + 2; iii = -x + 1, -y + 2, -z + 1; v = -x + 1, -y + 2, -z + 2. (c) A perspective of 3D framework along the *bc* plane. The hydrogen atoms and water molecules are omitted for clarity.

Fig. 4 (a) The coordination environment of the Lu1 ion in **9**. The hydrogen atoms are omitted for clarity except those bonds to oxygen atoms of the coordinated water molecules. Symmetry codes: i = -x + 1, -y + 1, -z + 2; ii = -x + 1, -y, -z + 1; iii = -x + 1, -y + 1, -z + 2; ii = -x + 1, -y, -z + 1; iii = -x + 1, -y + 1, -z + 2; ii = -x + 1, -y + 1, -z + 2; ii = -x + 1, -y + 1, -z + 2; ii = -x + 1, -y + 1, -z + 2; ii = -x + 1, -y + 1, -z + 2; ii = -x + 1, -y, -z + 1; vi = -x + 2, -y + 1, -z + 2. (c) Tetranuclear unit. The hydrogen atoms are omitted for clarity. The hydrogen atoms are omitted for clarity except those bound to oxygen atoms of the coordinated water molecules. Symmetry code: i = -x + 1, -y + 1, -z + 2; ii = -x + 2, -y + 1, -z + 2, -y + 1, -z + 2.

individual cpna²⁻ ligands, and one O atom of one coordinated water molecule, forming a distorted bicapped trigonal prism. Lu2 atom is six-coordinated by five carboxylate O atoms of five independent cpna²⁻ ligands, and one O atom of one coordinated water molecule, constructing a distorted octahedral geometry (Fig. 4b). The distances of Lu-O span the range of 2.127 (4)–2.503(3) Å. The cpna^{2–} ligands adopt three different coordination modes coordination (Scheme 1, modes II, VII and VIII), in which carboxylate groups show $\mu_2 - \eta^1: \eta^1$ bidentate mode, $\mu_2 - \eta^1: \eta^2$ tridentate mode, and $\mu_1 - \eta^1: \eta^0$ monodentate mode, respectively. The dihedral angles of the pyridyl and the phenyl rings in the cpna²⁻ ligands are 39.33°, 77.24° and 70.82°, respectively. Adjacent Lu atoms are bridged by O atoms of carboxylate groups and carboxyl groups into a [Lu1₂Lu2₂] tetranuclear unit (Fig. 4c). The tetranuclear units are further linked by the coordination interaction of $cpna^{2-}$ ligands and Lu(III) ions to generate a 3D framework (Fig. S7, ESI⁺).

Structure of 10. Complex **10** crystallizes in the triclinic space group $P\bar{1}$. The asymmetrical unit of compound **10** consists of two crystallographically unique Y(III) atoms, three cpna^{2–} ligands, two phen ligands, one coordinated water and one lattice water molecule. As shown in Fig. 5a and 5b, both Y1 and Y2 ions are eight-coordinated in a distorted bicapped trigonal prism geometry. Y1 ion is coordinated by five carboxy-late O atoms of five individual cpna^{2–} ligands, two N atoms from one phen ligand, and one O atom of one coordinated water molecule, while Y2 ion is bonded to six carboxylate O atoms of five independent cpna^{2–} ligands, and two N atom of one phen ligand. The distances of Y–O and Y–N bonds span the range of 2.175(4)–2.551(4) Å and 2.529(5)–2.557(5) Å. The cpna^{2–} ligands adopt three different coordination modes (Scheme 1, modes IV, V and IX), in which carboxylate groups



Fig. 5 (a) The coordination environment of the Y1 ion in **10**. The hydrogen atoms are omitted for clarity. Symmetry codes: i = -x, -y + 2, -z + 1; ii = -x - 1, -y + 2, -z + 1; iii = x + 1, y, z. (b) The coordination environment of the Y2 ion in **10**. The hydrogen atoms are omitted for clarity. Symmetry codes: iv = -x + 1, -y + 1, -z; v = x - 1, y, z; vi = -x, -y + 1, -z. (c) A perspective of 3D framework along the *bc* plane. The hydrogen atoms are omitted for clarity.

show $\mu_2 - \eta^1 : \eta^1$ bidentate mode, and $\mu_2 - \eta^1 : \eta^2$ tridentate mode, and $\mu_1 - \eta^1 : \eta^0$ monodentate mode, respectively. The dihedral angles of the pyridyl and the phenyl rings in the cpna²⁻ ligands are 59.75°, 57.17° and 44.99°, respectively. Two crystallographically equal Y1 centers are bridged by four carboxyl groups from four individual cpna^{2–} ligands in bidentate mode into a binuclear unit (Fig. S8, ESI⁺) with a Y1-Y1 distance of 4.301(3) Å. Meanwhile, two crystallographically equal Y2 atoms are bridged by two O atoms of carboxylate groups from two different cpna²⁻ ligands and two carboxyl groups from two individual cpna²⁻ ligands in bidentate mode into a dimeric unit (Fig. S9, ESI⁺) with a Y2-Y2 distance of 3.876(2) Å. These dimeric units are joined by cpna²⁻ ligands to form 1D chains, which further connected by the cpna^{2–} ligands to construct 2D sheet (Fig. S10, ESI[†]). The sheets are extended into a 3D metal-organic framework by the coordination interaction of $cpna^{2-}$ ligands and Y(III) ions (Fig. 5c).

Structures of 11 and 12. X-Ray single crystal diffraction analyses reveal that complexes 11 and 12 are also isostructural and feature a 1D chain structure, hence, only the structure of 11 is described in detail here. Complex 11 crystallizes in the monoclinic space group $P2_1/n$. In the asymmetrical unit, there is one crystallographically unique Tm(III) atom, one cpna²⁻ ligand, one phen ligand, one nitrate ligand. As shown in Fig. 6a, Tm(III) ion has an eight-coordinate environment, six of which are occupied by four O atoms of carboxyl groups from three individual $cpna^{2-}$ ligands and two O atoms from one nitrate ligand, and the remaining two sites are occupied by two N atoms of one phen ligand, forming a distorted bicapped trigonal prism. The Tm-O distances range from 2.208(6) to 2.412(7) Å, the Tm–N distances vary from 2.475(7) to 2.498(6) Å. All the Ln–O and Ln–N distances in compounds 1-12 are comparable to those reported for other Ln-O and Ln-N donor complexes.^{1e,f,h,j,l,q,6} The cpna^{2–} ligand takes coordination mode VI, in which two carboxylate groups take $\mu_1 - \eta^1: \eta^1$ and $\mu_2 - \eta^1: \eta^1$ bidentate modes, respectively. In this way, cpna²⁻ ligands linked neighboring Tm(m) ions to yield an 1D double chain along the c axis (Fig. 6b). The dihedral angle of the pyridyl and the phenyl rings in the cpna²⁻ ligand is 62.16°. The chains are further extended into a 3D metal-organic



Fig. 6 (a) The coordination environment of the Tm ion in **11**. The hydrogen atoms are omitted for clarity. Symmetry codes: i = -x + 1, -y + 2, -z; ii = x, y - 1, z. (b) 1D double chain along the *c* axis. The hydrogen atoms are omitted for clarity.

supramolecular framework (Fig. S11, ESI[†]) by C–H···O hydrogen bond (C17ⁱ–H17ⁱ···O5, C17ⁱ···O5 = 3.636(10) Å, C3ⁱⁱ– H3ⁱⁱ···O6, C3ⁱⁱ···O6 = 3.336(11) Å, C6ⁱⁱⁱ–H6ⁱⁱⁱ···O7, C6ⁱⁱⁱ···O7 = 3.463(10) Å, i = -x + 0.5, y - 0.5, -z - 0.5, ii = -x + 0.5, y - 0.5, -z + 0.5, iii = x - 0.5, -y + 1.5, z - 0.5; Table S3, ESI[†]).

Structural diversity

Complexes 1-12 were successfully synthesized by reacting H₂cpna ligand (auxiliary ligand phen for 1-4 and 10-12) with the corresponding lanthanide salts at 160 °C for 3 days under hydrothermal conditions, as shown in Scheme 2. From the above description of crystal structures, it can be found that complexes 1-12 exhibit six different structures. On the basis of the structures, it was noted that the influence of the pH value on the structures is in fact based on the protonated extend of H_2 cpna ligand. For example, at pH = 4-5, partially deprotonated Hcpna⁻ and completely deprotonated cpna²⁻ forms coexist in 1–4. When pH value is adjusted to 5.5, only $cpna^{2-}$ form is observed in 5-12. Complexes 1 and 4 were synthesized under the same reaction conditions, except for the samarium salts (Sm(NO₃)₃·6H₂O for 1 and SmCl₃·6H₂O for 4). Their structural differences ambiguously indicate that the assembly process is anions-dependent. The different anions induce the Hcpna⁻ and cpna²⁻ ligands to adopt different conformations (trans for 1 and cis for 4), which result in different structures, that is, 1 shows 3D framework and 4 exhibits a 1D wheel-chain structure. The structural difference between 2 and 6 is ascribed to the different reaction pH (pH = 4-5 for 2 and 5.5 for 6) and adding auxiliary ligand phen in 2. The structural change between 5 and 10 (9 and 12) caused by adding auxiliary ligand phen in 10 (12) under the same reaction conditions. Complexes 10-12 were isolated under the same reaction conditions except using different lanthanide nitrates (Y(NO₃)₃·6H₂O for 10, $Tm(NO_3)_3 \cdot 6H_2O$ for 11, and $Lu(NO_3)_3 \cdot 6H_2O$ for 12), which result in different structures, that is, 10 show 3D framework and 11 and 12 possess a 1D double chain structure. It is the lanthanide contraction effect that results in forming the different crystal structures. In 10, the larger Y(m) ion can coordinate to five cpna²⁻ anions, one phen ligand, and/or one water molecule, while the smaller Tm(m) and Lu(m) ions in 11 and 12 can only coordinate to three cpna²⁻ anions and one phen ligand due to steric effects (Fig. 5a, 5b and 6a). Meanwhile, one Tm(III)/Lu(III) ion coordinated to one bidentate nitrate ligand for satisfaction with the coordination number and charge balance. These results imply that the reaction conditions including pH value, anions, auxiliary ligand and metal



Scheme 2 Synthetic strategy of compounds 1–12



Fig. 7 Thermogravimetric analyses (TGA) curves of compounds 1, 4, 6, and $9{-}11.$

ionic radii could well tune the structures of lanthanide coordination polymers.

Thermal analysis

To further determine the thermal stability of compounds 1–12, their thermal behaviors were investigated under nitrogen atmosphere by TGA. The results indicate that complexes 1–3 (5–8, 11 and 12) show similar thermal behavior owing to their isomorphous structures; thus only the thermal stabilities of complexes 1, 4, 6, and 9–11 are discussed in detail (Fig. 7). Compound 1 lost its one lattice water molecule (exptl, 2.46%; calcd, 2.16%) from 60 to 160 °C, and then decomposition occurs at 342 °C. For complex 4, there is one distinct weight loss procedure in the range of 70–165 °C, corresponding to the loss of two free water molecules per formula unit (exptl, 4.60%; calcd, 4.24%). The remaining structure was broken down at 330 °C.

Compound **6** lost its four lattice water and three coordinated water molecules (exptl, 10.7%; calcd, 10.8%) from 60 to 230 °C, and then decomposition occurs at 450 °C. For compound **9**, the weight loss corresponding to the release of two coordinated water molecule was observed from 120 to 220 °C (exptl, 3.65%; calcd, 3.24%), and the decomposition of the residue was observed at about 400 °C. The TGA curves of compounds **10** and **11** show their frameworks were stable up to 350 °C and 345 °C, respectively. Then, the frameworks began to decompose upon further heating.

Dehydration/hydration study

To study the dehydration/hydration properties of compounds **5–8**, compound **6** was heated to different temperatures (120 and 180 °C) for 3 h and then was treated with water (Fig. S12, ESI†). The XRD patterns indicate that the structure of compound **6** can be kept after heating at 180 °C, and the structure transformation occurs at 200 °C. Interestingly, when the calcined samples at 180 °C were suspended in water overnight, and then, the solid was filtered off and dried at room temperature, the same XRD patterns as those of the original crystal were regenerated. Thus, the dehydrated solids of these compounds may potentially be reversible adsorbent materials for water molecules.

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Fig. 8 Solid state emission spectra of compounds 2 and 6 at room temperature.

Luminescent properties

Lanthanide-containing compounds are interesting luminescence materials because they emit over the entire spectral range. Especially Tb(III) compounds show strong and characteristic luminescent emissions in the visible region upon excitation of ultraviolet radiation, making them good candidate materials for luminescent probes.7 The solid-state luminescence properties of compounds 2 and 6 were investigated at room temperature (Table S4, ESI⁺). As illustrated in Fig. 8, upon excitation at 331 and 312 nm, compounds 2 and 6 show the characteristic emission pattern of the Tb(III) ion. The strong emission lines at 489/488, 544/542, 584/582, and 622/621 nm are assigned to transitions between the first excited state, ${}^{5}D_{4}$, and the ground state multiplet ${}^{7}F_{I}$ (J = 6, 5, 5) 4, 3). It is noteworthy that compound 2 exhibits stronger emission intensities than compound 6, which can be attributed to their different structures. In compound 2, the phen ligands were introduced, which increased the efficiency of the energy transfer from the ligands to Tb(III) ions.^{8,9} Meanwhile, coordinated water and lattice water molecules in 6 play a part in the quenching effect of the luminescent state.^{7,10} Upon removal of the water molecules at 180 °C for 3 h, the intensity of the emission bands for the dehydrated sample are enhanced by a factor of approximately two. The luminescence of the re-hydrated sample returned to its original level. This process was reversible. Compound 6 shows promise as a luminescent probe to detect water.

Magnetic properties

Variable-temperature magnetic susceptibility measurements were performed on powder samples of **1**, **3**, **4**, **7** and **11** in the temperature range of 2–300 K (Fig. 9). For **1** and **4**, as shown in Fig. 9, the $\chi_{\rm M}T$ values at room temperature are 0.221 cm³ mol⁻¹ K for **1** and 0.258 cm³ mol⁻¹ K for **4**, which are larger than that (0.088 cm³ mol⁻¹ K) expected for one magnetically isolated Sm(m) ion (S = 5/2, L = 5/2, ${}^{6}H_{5/2}$, g = 2/7), because not only the ground state of the Sm(m) ion but also the first (${}^{6}H_{7/2}$) and even highly exited states can be populated at room temperature.¹¹ The monotonic decrease in $\chi_{\rm M}T$ with cooling temperature is not indicative of dominant antiferromagnetic interaction because of the strong spin–orbit coupling



Fig. 9 Temperature dependence of $\chi_M T$ (O) and $1/\chi_M$ (\Box) vs. *T* for compounds **1**, **3**, **4**, **7** and **11**. The black lines show the Curie–Weiss fitting.

of Sm^{3^+} coming from the strong unquenched orbital angular momentum.^{12,13}

For 3, at 300 K, the $\chi_{\rm M}T$ value of 14.6 cm³ mol⁻¹ K is close to the value expected (14.1 cm³ mol⁻¹ K) for one insulated Ho (m) ion ($S = 2, L = 6, {}^{5}I_{8}, g = 5/4$). $\chi_{\rm M}T$ value gradually decreases to reach 5.74 cm³ mol⁻¹ K at 2 K. Between 2 and 300 K, the magnetic susceptibilities can be fitted to the Curie–Weiss law, $\chi_{\rm M} = C_{\rm M}/(T - \theta)$, with $C_{\rm M} = 15.4$ cm³ K mol⁻¹, $\theta = -15.9$ K. On account of the larger spin–orbit coupling of Ho³⁺, these results can not be exactly ascribed to the antiferromagnetic interactions between the adjacent Ho(m) centers.

For 7, at 300 K, $\chi_{\rm M}T$ is equal to 28.5 cm³ mol⁻¹ K, which is close to the value expected (28.3 cm³ mol⁻¹ K) for two Dy(m) (S = 5/2, L = 5, ${}^{6}H_{15/2}$, g = 4/3). Upon lowering the temperature, the $\chi_{\rm M}T$ value decreases continuously to a value of 23.4 cm³ mol⁻¹ K at 2 K. Between 2 and 300 K, the magnetic susceptibilities can be fitted to the Curie–Weiss law with $C_{\rm M} = 29.0$ cm³ K mol⁻¹, $\theta = -6.53$ K. On account of the larger spin–orbit coupling of Dy³⁺, these results do not indicate a weak antiferromagnetic interaction between the neighboring Dy(m) ions.

For 11, at 300 K, the $\chi_M T$ value of 7.29 cm³ mol⁻¹ K is close to the value expected (7.14 cm³ mol⁻¹ K) for one magnetically isolated Tm(m) ion (S = 1, L = 5, ${}^{3}H_{6}$, g = 7/6). As the temperature is lowered, the $\chi_M T$ value gradually increases to reach a dispersed maximum of 7.83 cm³ K cm⁻¹ at $T \approx 78$ K and then abruptly decreases to the value of 3.78 cm³ K mol⁻¹ at 2 K. The maximum $\chi_{\rm M}T$ value may be related to a ferromagnetic exchange between the magnetic centers. Between 80 and 300 K, the magnetic susceptibilities can be fitted to the Curie–Weiss law with $C_{\rm M} = 7.06 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $\theta = 9.64 \text{ K}$.

Conclusions

In this work, by adjusting the reaction pH value and/or using auxiliary ligand, a series of lanthanide coordination compounds based on H_2 cpna ligand were synthesized by a hydrothermal method. These compounds possess 1D and 3D frameworks with different architectures. Their structural diversities demonstrate that the pH value of the reaction system, anion, auxiliary ligand and lanthanide contraction play a crucial role in determination of the structures of the coordination polymers. Luminescent measurements indicate the compound **6** is a potential luminescent sensor material.

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