# Two unprecedented strontium(ii) and cadmium(ii) coordination polymers constructed from 2-naphthyl imidazole dicarboxylate ligand

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## **Supplementary Information**

#### Materials and general procedures

All chemicals were commercially available and used as purchased. The organic ligand, 2-Naphthyl-1H-imidazole-4,5-dicarboxylic acid (H<sub>3</sub>NIDC) was prepared according to the literature.<sup>1</sup> IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the region of 400–4000 cm<sup>-1</sup>. Elemental analyses (C, H and N) were carried out on a Flash EA 1112 elemental analyzer. Themogravimetric analyses were carried out with a Netzsch STA 409PC unit at a heating rate of 10°C·min<sup>-1</sup> under a nitrogen atmosphere. X-ray powder diffraction measurements were recorded on a PANalytical X'pert PRO X-ray diffractometer using graphite monochromatized CuK $\alpha$  radiation ( $\lambda = 1.541874$  Å). Single-crystal X-ray diffraction was performed using a Bruker Smart 1000 diffractometer with a graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The solid-state photoluminescence measurements were carried out on Edinburgh Analytical Instruments FLSP920 (Spectrofluorimeter).

#### Preparation of [Sr(µ<sub>5</sub>-HNIDC)(H<sub>2</sub>O)] (1)

A mixture of  $Sr(NO_3)_2 \cdot 2H_2O$  (0.0105 g, 0.05 mmol),  $H_3NIDC$  (0.0142 g, 0.05 mmol), and  $CH_3OH/H_2O$  (3/4, 7 mL),  $Et_3N$  (0.014 mL, 0.1 mmol) were sealed in a 25 mL Teflon-lined stainless steel reactor. The reactor was heated at 160°C for 72 h and then cooled to room temperature at the rate of 5°C /h. The pH values of the solution before and after reaction were ca.8 and 6, respectively. Pale yellow cuboid crystals of **1** were obtained (yield: 69%, based on Sr). Anal. Calcd. for  $C_{15}H_{10}N_2O_5Sr$ : C, 46.69; H, 2.61; N, 7.26%. Found: C, 46.39; H, 2.33; N, 7.05%. IR (cm<sup>-1</sup>, KBr): 3624 (m), 3256 (m), 3026 (m), 1604 (s), 1567 (s), 1463 (s), 1389 (s), 1265 (m), 1112 (m), 1018 (w), 898 (w), 808 (s), 753 (s), 721 (w), 643 (w), 620 (w).

#### Preparation of [Cd(µ<sub>3</sub>-HNIDC)(CH<sub>3</sub>CH<sub>2</sub>OH)] (2)

A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.0156 g, 0.05 mmol), H<sub>3</sub>NIDC (0.0142 g, 0.05 mmol), and CH<sub>3</sub>CH<sub>2</sub>OH/H<sub>2</sub>O (3/4, 7 mL), Et<sub>3</sub>N (0.014 mL, 0.1 mmol) were sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 160 °C for 72 h, and then cooled to room temperature at the rate of 5 °C /h. The pH values of the solution before and after reaction were ca. 8 and 6, respectively. The needlelike colorless crystals of **2** were isolated, washed with distilled water, and dried in air (45% yield, based on Cd). Anal. Calcd. for  $C_{17}H_{13}CdN_2O_5$ : C, 46.65; H, 2.99; N, 6.40%. Found: C, 46.46; H, 2.68; N, 6.11%. IR (cm<sup>-1</sup>, KBr): 3349 (m), 3056 (w), 1672 (s), 1559 (s), 1268 (s), 1122 (m), 1038 (m), 943 (w), 898 (w), 753 (m), 640 (w), 557 (w).

#### **Crystal Structure Determinations**

Suitable single crystals of polymers **1** and **2** were selected for single-crystal X-ray diffraction analyses. The intensity data were measured on a Bruker Smart 1000 diffractometer with a graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Single crystals of **1** and **2** were selected and mounted on a glass fiber. All data were collected at room temperature using the  $\omega$ - $2\theta$  scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The two structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The disorder atoms can be found in both two polymers: C8, C9 and C10 in compound **1**; C9-10, C17-18 and C21-22 in compound **2**. We have tried to model them, but no better model for them. Thus, we have fixed the ADPs

for them, and refined the crystal data. All calculations were performed using the SHELX-97 crystallographic software package.<sup>2</sup> The crystallographic data of the two complexes are given in Table S1. Selected bond lengths and angles of the two polymers are listed in Tables S2 and S3, respectively.

#### **Quantum-chemical Calculation**

The optimized geometries, natural bond orbital (NBO) charge distributions and the energies of the frontier molecular orbital of the free ligands were given by the GAUSSIAN 03 suite of programs.<sup>3</sup> And all calculations were carried out at the B3LYP/6-311++G(d, p) level of theory.

#### **Computational studies**

In order to further predict the influence of the naphthyl on the H<sub>3</sub>NIDC ligand, the optimized geometries and natural bond orbital (NBO) charge distributions of the free ligand H<sub>3</sub>NIDC have been calculated by the B3LYP/6-311++G(d,p) level of theory. The computed results (Scheme S1 and Table S4) reveal that the negative NBO charges mainly distribute on the oxygen and nitrogen atoms in the free ligand H<sub>3</sub>NIDC. The NBO charges are -0.635 for O1, -0.663 for O2, -0.647 for O6, -0.598 for O13, -0.500 for N4, and -0.459 for N7 in the free ligand H<sub>3</sub>NIDC (Table S4). The naphthyl group plays the role of electron donor and the oxygen has a wealth of electrons. Compared with the case of the free ligand H<sub>3</sub>IDC, the introduction of naphthyl group into H<sub>3</sub>NIDC has a slight effect on the NBO charge distributions of oxygen and nitrogen atoms. These values indicate that the oxygen and nitrogen atoms of the H<sub>3</sub>NIDC ligand can have potential coordination ability, and may show various coordination modes under appropriate reaction conditions. This can be confirmed by our present experimental results. In polymer 1, the organic ligand shows an unusual coordination mode of  $\mu_5$ -HNIDC<sup>2-</sup>. And in polymer 2, HNIDC<sup>2-</sup> cation linkages to the alternate left- and right-handed helical chains to form an interesting 3D structure. What's more the strong coordination ability of the N and O atoms in the ligand overrides the steric effect of the bulky naphthyl unit.

#### References

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Scheme S1. The optimized geometries of the free ligand  $H_3NIDC$  (the blue ball represents N atom, the red ball represents O atom and the gray ball represents C atom).



**Scheme S2.** Coordination modes of HNIDC<sup>2-</sup> anions.

	1	2
formula	$C_{15}H_{10}N_2O_5Sr$	$C_{17}H_{13}CdN_2O_5$
fw	385.87	438.70
crystal system	Monoclinic	Tetragonal
crystal size, mm	$0.22 \times 0.20 \times 0.19$	$0.22 \times 0.21 \times 0.19$
space group	$P2_{1}/c$	I4 <sub>1</sub> /a
<i>a</i> , Å	17.236(2)	22.658(3)
<i>B</i> , Å	6.6721(8)	22.658(3)
<i>C</i> , Å	12.6429(15)	14.766(4)
α, °	90	90
$\beta$ , °	104.020(2)	90
γ, °	90	90
$V, Å^3$	1410.7(3)	7580(3)
Dc, Mg m <sup>-3</sup>	1.817	1.538
Ζ	4	16
$\mu$ , mm <sup>-1</sup>	3.851	1.179
reflns collected/unique	10473/ 2527	27516 / 3329
	R(int) = 0.0856	R(int) = 0.0774
data/restraints/parameters	2527/0/208	3329 / 117 / 213
Final <i>R</i> indices [ <i>I</i> > 2sigma( <i>I</i> )]	$R_1 = 0.0437$	$R_1 = 0.0694$
	$wR_2 = 0.0827$	$wR_2 = 0.2166$
<i>R</i> indices (all data)	$R_1 = 0.0765$	$R_1 = 0.0974$
	$wR_2 = 0.0896$	$wR_2 = 0.2419$
GOF on $F^2$	1.070	1.013
$\Delta  ho_{\rm min}$ and $\Delta  ho_{\rm max}$ , e Å <sup>-3</sup>	-0.575 and 0.880	-1.021 and 0.996

 ${}^{a}R = \Sigma[|Fo|-|Fc|]/\Sigma|Fo|$   ${}^{b}R_{w} = [\Sigma(|Fo|-|Fc|)^{2} / \Sigma|Fo|^{2}]^{1/2}$ 

O(1)-Sr(1)#2	2.546(3)	O(1)-Sr(1)	2.715(3)
O(2)-Sr(1)#3	2.494(3)	O(2)-Sr(1)	2.712(3)
O(3)-Sr(1)#3	2.525(3)	O(3)-Sr(1)#1	2.803(3)
O(4)-Sr(1)#4	2.647(3)	O(4)-Sr(1)#1	2.700(3)
O(1W)-Sr(1)	2.785(4)	Sr(1)-O(2)#2	2.494(3)
Sr(1)-O(3)#2	2.525(3)	Sr(1)-O(1)#3	2.546(3)
Sr(1)-O(4)#4	2.647(3)	Sr(1)-O(4)#5	2.700(3)
Sr(1)-O(3)#5	2.803(3)		
Sr(1)#3-O(2)-Sr(1)	99.65(9)	Sr(1)#4-O(4)-Sr(1)#1	96.22(11)
Sr(1)#3-O(3)-Sr(1)#1	113.46(12)	Sr(1)#2- O(1)- Sr(1)	98.27(10)
O(2)#2-Sr(1)-O(1)#3	157.34(10)	O(3)#2-Sr(1)-O(1)#3	97.05(10)
O(2)#2-Sr(1)-O(4)#4	64.69(10)	O(3)#2-Sr(1)-O(4)#4	115.53(10)
O(1)#3-Sr(1)-O(4)#4	106.39(10)	O(2)#2-Sr(1)-O(4)#5	133.06(10)
O(3)#2-Sr(1)-O(4)#5	113.11(10)	O(1)#3-Sr(1)-O(4)#5	69.00(10)
O(4)#4-Sr(1)-O(4)#5	131.32(5)	O(2)#2-Sr(1)-O(2)	118.07(9)
O(3)#2-Sr(1)-O(2)	170.96(9)	O(1)#3-Sr(1)-O(2)	74.53(9)
O(4)#4-Sr(1)-O(2)	70.80(9)	O(4)#5-Sr(1)-O(2)	61.16(9)
O(2)#2-Sr(1)-O(1)	75.30(9)	O(3)#2-Sr(1)-O(1)	139.12(10)
O(1)#3-Sr(1)-O(1)	122.06(8)	O(4)#4-Sr(1)-O(1)	67.36(10)
O(4)#5-Sr(1)-O(1)	75.01(9)	O(2)-Sr(1)-O(1)	48.33(9)
O(2)#2-Sr(1)-O(1W)	88.33(10)	O(3)#2-Sr(1)-O(1W)	70.10(11)
O(1)#3-Sr(1)-O(1W)	69.29(10)	O(4)#4-Sr(1)-O(1W)	64.43 (10)
O(4)#5-Sr(1)-O(1W)	138.24 (10)	O(2)-Sr(1)-O(1W)	109.02(10)
O(1)-Sr(1)-O(1W)	131.57 (10)	O(2)#2-Sr(1)-O(3)#5	109.73(9)
O(3)#2-Sr(1)-O(3)#5	66.54(12)	O(1)#3-Sr(1)-O(3)#5	81.17(10)
O(4)#4-Sr(1)-O(3)#5	171.44(10)	O(4)#5-Sr(1)-O(3)#5	47.07(9)
O(2)-Sr(1)-O(3)#5	108.23(9)	O(1)-Sr(1)-O(3)#5	105.40(10)
O(1W)-Sr(1)-O(3)#5	123.03(10)	O(2)#2-Sr(1)-O(3)#2	70.96(9)

Table S2. Selected Bond Distances (Å) and Angles (deg) for polymer  $\mathbf{1}$ 

Symmetry transformations used to generate equivalent atoms: #1: x, -y+3/2, z+1/2; #2: -x+1, y-1/2, -z-1/2; #3: -x+1, y+1/2, -z-1/2; #4: -x+1, -y+1, -z ; #5 x, -y+3/2, z-1/2.

Cd(1)-N(1)	2.183(6)	Cd(1)-N(2)#1	2.251(6)
Cd(1)-O(3)#2	2.294(6)	Cd(1)-O(5)	2.327(8)
Cd(1)-O(3)#1	2.396(6)	Cd(1)-O(1)	2.529(7)
N(2)-Cd(1)#3	2.251(6)	O(3)-Cd(1)#4	2.294(6)
O(3)-Cd(1)#3	2.396(6)		
N(1)-Cd(1)-N(2)#1	112.1(3)	N(1)-Cd(1)-O(3)#2	100.2(2)
N(2)#1-Cd(1)-O(3)#2	145.1(2)	N(1)-Cd(1)-O(5)	122.2 (3)
N(2)#1-Cd(1)-O(5)	94.0(3)	O(3)#2-Cd(1)-O(5)	79.2(3)
N(1)-Cd(1)-O(3)#1	145.8 (3)	N(2)#1-Cd(1)-O(3)#1	72.3 (2)
O(3)#2-Cd(1)-O(3)#1	73.5(2)	O(5)-Cd(1)-O(3)#1	90.2 (2)
N(1)-Cd(1)-O(1)	71.9(2)	N(2)#1-Cd(1)-O(1)	96.2(3)
O(3)#2-Cd(1)-O(1)	81.0(3)	O(5)-Cd(1)-O(1)	157.5(3)
O(3)#1-Cd(1)-O(1)	74.0(2)		

Table S3. Selected Bond Distances (Å) and Angles (deg) for polymer 2

Symmetry transformations used to generate equivalent atoms: #1: y+1/4, -x+5/4, z+1/4; #2: -y+7/4, x-1/4, -z+7/4; #3: -y+5/4, x-1/4, z-1/4; #4: y+1/4, -x+7/4, -z+7/4.

NBO Charge
-0.635
-0.665
-0.647
-0.598
-0.500
-0.459
0.026
0.060
0.790
0.410
0.761
-0.122
-0.153
-0.137
-0.171
-0.151
-0.182
-0.175
-0.178
-0.201
0.504
0.438
0.487
0.208
0.206
0.207
0.232
0.193
0.204
0.208

### Table S4. NBO Charge Distributions of the Free Ligand H<sub>3</sub>NIDC



Fig. S1 The distorted capped square antiprism geometry of Sr1 atom in polymer 1.



Fig. S2 1-D chain of 1 along the *b*-axis.



Fig. S3 Coordination environment of Cd(II) atom in polymer 2 (Partial H atoms omitted for clarity).



Fig. S4 The distorted octahedron of Cd atom in polymer 2.



**Fig. S5**. The subunit of the sheet (Partial atoms of  $HNIDC^{2-}$  omitted for clarity).



Fig. S6. XRPD patterns of compounds 1 and 2 at room temperature; simulated pattern is generated from single-crystal diffraction data.