# A series of luminescent lanthanide–cadmium–organic frameworks with helical channels and tubes†

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**Lanthanide (Ln) oxides and cadmium (Cd) salts as sources of metals provided the first series of luminescent Ln–Cd–organic frameworks, [LnCd(imdc)(SO$_4$)(H$_2$O)$_3$]·0.5H$_2$O (Ln = Tb, Eu, Dy, Gd, Er, Yb, Y, Nd, Pr; H$_3$imdc = 4,5-imidazoledicarboxylic acid), in which the Ln atoms are linked by imdc ligands with skew coordination orientation, resulting in novel hetero-metallic–organic frameworks with left–/right–handed helical tubes (L1/R1) and channels (L2/R2) along the *b* axis.**

The current increasing interest in designing and making hetero-metallic complexes has been significantly provoked not only by their impressive structural diversity in architectures but also by their versatile applications in optoelectronic, magnetic, and porous materials.[1–5] However, most of the work has so far focused on the assembly of the 3d–4f(5f) metal systems[3–5] and the investigation of the interaction between 3d and 4f metal centers, especially copper–lanthanide (Cu–Ln) interactions,[4,5] while the construction of 4d–4f(5f) hetero-metallic complexes and their physical properties remains less developed.[6] To date, the systematic investigation of 4d–4f hetero-metallic coordination polymers with luminescent properties is rare.[7] Therefore, the introduction of group 12 metals of Zn/Cd/Hg into the Ln–organic frameworks not only should be a rational synthetic strategy but also could open the way to new luminescent materials.

Generally, the Ln ions prefer O- to N-donors, while d-block metal ions have a strong tendency to coordinate to both N- and O-donors. Thus, the ligands with N- and O-donors can elaborately be selected and employed to make hetero-metallic–organic frameworks. Recently, we reported a series of porous Ln–organic frameworks constructed from 4,5-imidazoledicarboxylic acid (H$_3$imdc).[8a] So far, H$_3$imdc has been used to make metal–organic frameworks with single transition metal (TM) or Ln ions,[8] but the assembly in Ln–TM–organic frameworks remains unexplored. We select H$_3$imdc as a candidate for assembling heterometallic complexes, based on the following consideration: (a) it is a flexible ligand with O- and N-donors, enabling the imdc to serve as a bridge between Ln and TM ions, (b) the skew coordination orientation of the carboxyl groups is favorable for the formation of the helical structure, and (c) it is suitable for the sensitization of luminescence of Ln$^{3+}$ and group 12 metal ions.[8a,8d]

On the basis of the aforementioned points, our aim is to make novel Ln–Cd–organic frameworks with luminescent properties by using the H$_3$imdc ligand. In this communication, we first report the systematic syntheses, structures and luminescence of a series of Ln–Cd–organic frameworks, [LnCd(imdc)(SO$_4$)(H$_2$O)$_3$]·0.5H$_2$O (Ln = Tb **1**, Eu **2**, Dy **3**, Gd **4**, Er **5**, Yb **6**, Y **7**, Nd **8** and Pr **9**). The frameworks not only display 1D helical channels occupied by water molecules and SO$_4^{2-}$ anions but also contain helical tubes constructed from three distinct helical chains.

Single crystals of nine complexes were obtained by the hydrothermal reaction of Ln$_2$O$_3$, CdSO$_4$·8H$_2$O and H$_3$imdc in water at pH 4 and 170 °C. X-ray crystal structure analyses reveal that the complexes are isomorphous and crystallize in the monoclinic space group $P2_1/c$.‡ Therefore, only the structure of **1** is described in details. The coordination geometry for the nine-coordinate Tb$^{3+}$ ion is close to that of a tricapped trigonal prism and the Cd$^{2+}$ ion displays a distorted octahedral configuration (Fig. 1).

The most striking structural feature of **1** is the linkages between Tb$^{3+}$ and Cd$^{2+}$ ions *via* imdc with one unique coordinate mode (Scheme 1) to form an unprecedented 3D framework made of 2D layers, arranged alternately left-/right-handed helical tubes (L1/R1), and 1D left-/right-handed 12-membered ring (MR) helical channels (L2/R2) (Fig. 2a, S1). The helical tubes consist of three distinct helices: two ones are served as the helical tubular walls, the third one as the fillers. The Tb$^{3+}$ and Cd$^{2+}$ ions linked by four carboxyls of imdc units form the first kind helical chains of

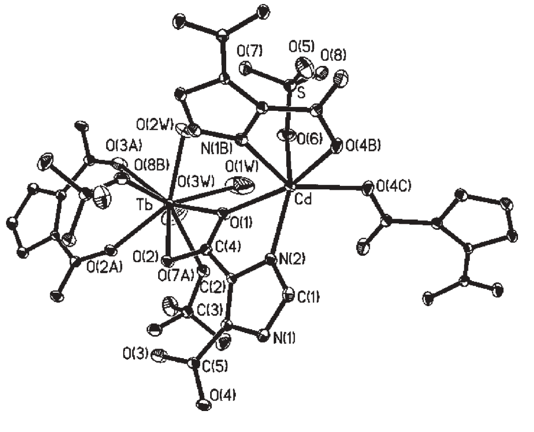

**Fig. 1** The coordination environments of Tb$^{3+}$ and Cd$^{2+}$ in **1**. Thermal ellipsoids are at 50% probability. Atoms having "A", "B", "C", "D" and "E" in their labels are symmetry-generated (A: $-x + 2$, $-y + 2$, $-z$; B: $x$, $-y + 3/2$, $z - 1/2$; C: $-x + 2$, $y + 1/2$, $-z + 1/2$; D: $-x + 3$, $y - 1/2$, $-z + 1/2$; E: $x$, $-y + 5/2$, $z + 1/2$).

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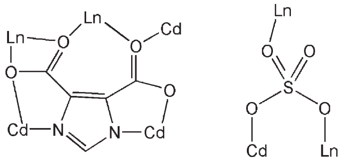

**Scheme 1** Coordination mode of the imdc ligand and $SO_4^{2-}$ ion in **1**.

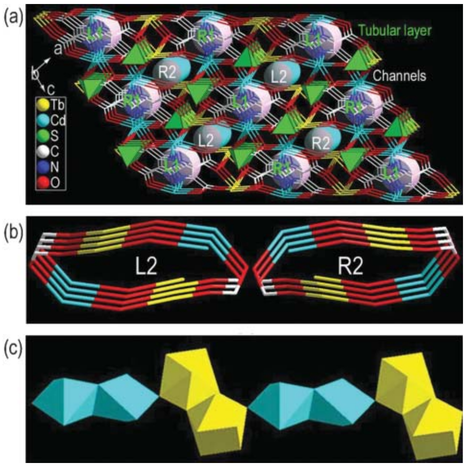

**Fig. 2** (a) The framework of **1** viewed down the approximate [010] direction, showing two types of helical tubes (L1/R1) and helical channels (L2/R2), respectively. L/R: left-/right-handed helices. (b) Two types of helical channels containing –O1–Cd–O4–C5–O3–Tb– helices in **1** down the approximate [010] (L2) and [0–10] (R2) directions. (c) Polyhedral view of the inorganic heterometallic chain made of $\{Cd_2\}$ and $\{Tb_2\}$ dimeric cluster units running along the [101] direction. Polyhedral color: yellow, $TbO_9$; cyan, $CdN_2O_4$.

opposite chirality; the second kind helical chains of opposite chirality are made of $H_2O$ and $SO_4^{2-}$ anions linked by the hydrogen bonds; the above two kinds of helical chains having the same orientation and pitch of 10.46 Å are further connected by $SO_4^{2-}$ ions to make the tubular walls of opposite chirality with the dimensions of 4.2 × 6.2 Å (L1/R1, Fig. 3a, S2). In the tubes, adjacent $Cd^{2+}$ ions are bridged by the imidazole (im) ring of an imdc ligand to form a chiral helical chain displaying the similar helical orientation to the helical tubes. In fact, the –Cd–im– helices as the fillers are trapped in the inner of the helical tubes (Fig. 3b,c, S2). The left-/right-helical tubes are alternately arranged by sharing $Tb^{3+}$ ions to generate a 2D tubular layer in the *ab*-plane (Fig. 3d,e S3). Furthermore, adjacent tubular layers are linked together by $\mu_2$-O4 atoms from carboxyls and $SO_4^{2-}$ anions to form a 3D framework with 1D 12-MR helical channels with the dimensions of 3.9 × 6.7 Å (Fig. 2b). The coordinated water molecules and $SO_4^{2-}$ anions protrude into the 12-MR helical channels. There are strong H-bonds between the water molecules, as well as between the water molecules and the oxygen atoms from $SO_4^{2-}$ ions (O···O 2.712(5)–2.994(5) Å).

Remarkably, there are two types of dimeric cluster units, $Tb_2O_2$ and $Cd_2O_2$, in **1**, which are alternately connected through bridging $\mu_2$-O1 to form an interesting 1D zigzag heterometallic chain, which is first observed in Ln–TM–organic frameworks (Fig. 2c, S4).

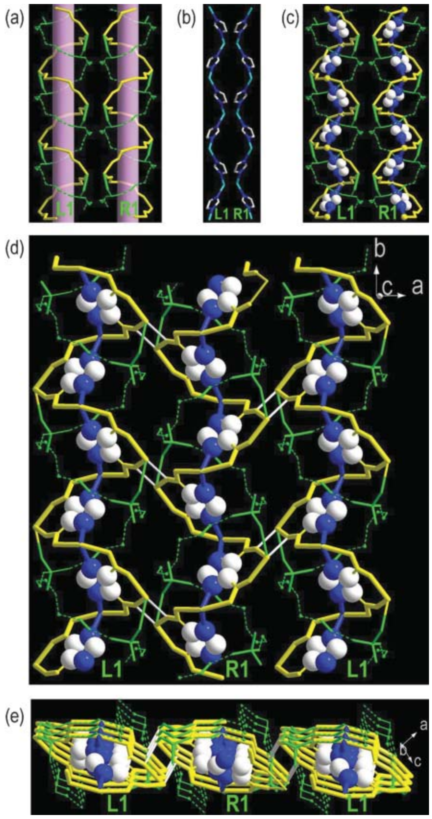

**Fig. 3** (a) The walls of the helical tubes made of two distinct helical chains with similar chirality along the [010] (L1) and [0–10] (R1) directions, in which the helical chains, –Cd–O1–C4–O2–Tb–O3–C5–O4– and –S–O5···O3W···O1W···O7···O2W···O8–, are marked yellow and green for identification, similarly hereinafter. (b) View of the left-/right-handed –Cd–Im– helices trapped in the inner of the helical tubes along the [010] (L1) and [0–10] (R1) directions. (c) View of two types of helical tubes in combination with the helical walls and the helical fillers with similar chirality. (d) 2D tubular layer viewed down the *c* axis. (e) 2D tubular layer viewed down the approximate [010] direction. Color code: Tb, yellow; C, white; N, blue; Cd, green.

The emission spectra of compounds **1–7** are depicted in Fig. 4. Complex **1** emits green light when excited at 309 nm and exhibits the characteristic transition of $^5D_4 \rightarrow {}^7F_J$ ($J$ = 4–6) of the $Tb^{3+}$ ion. The lifetime for $^5D_4 \rightarrow {}^7F_5$ is 0.72 ms. Two intense emission bands at 490 and 544 nm correspond to $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ while the weaker emission bands at 584 nm originate from $^5D_4 \rightarrow {}^7F_4$. The typical emission band at 620 nm corresponding to $^5D_4 \rightarrow {}^7F_3$ disappears due to a double-frequency effect.[9] **2** yields intense red luminescence and exhibits the characteristic transition of $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–4) of the $Eu^{3+}$ ion. The lifetime for $^5D_0 \rightarrow {}^7F_2$ is 178 µs. The $^5D_0 \rightarrow {}^7F_2$ transition is clearly stronger than the $^5D_0 \rightarrow {}^7F_1$ transition, which indicates the absence of inversion symmetry at the $Eu^{3+}$ site. This is in agreement with the result of the single-crystal X-ray analysis. When the Dy complex **3** was excited at 312 nm, it gave a typical $Dy^{3+}$ emission spectrum. The emission at 478, 573 and 657 nm is attributed to the characteristic emission of $^4F_{9/2} \rightarrow {}^6H_J$ ($J$ = 15/2, 13/2 and 11/2) transitions of the $Dy^{3+}$ ion with the lifetime of 1.13 ms. The relative intensity ratio for the emission lines at 478 and 573 nm is indicative of the larger probability for the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. **4** exhibits three broad bands when excited at 310 nm. The emission ranging from 400 to 465 nm originates from the coordination of $imdc^{3-}$ to the Cd ion. The other two emission bands originate from the imdc ligand. The broad band with a maximum around 335 nm may be attributed to

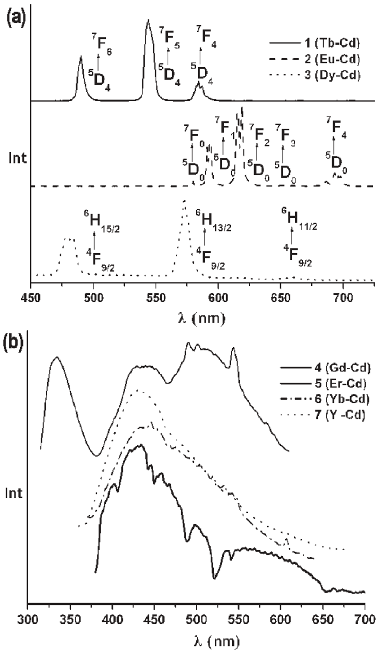

**Fig. 4** Emission spectra of (a) **1** ($\lambda_{ex}$ = 309 nm), **2** ($\lambda_{ex}$ = 394 nm), **3**($\lambda_{ex}$ = 312 nm), (b) **4** ($\lambda_{ex}$ = 310 nm), **5** ($\lambda_{ex}$ = 330 nm), **6** ($\lambda_{ex}$ = 350 nm) and **7** ($\lambda_{ex}$ =350 nm) in solid state at room temperature.

the ligand-centered $S_0 \rightarrow S_1$ (π,π*) transition of the imidazole moiety.[10] The emission peak at 544 nm may be related to the imdc phosphorescence due to the $T \rightarrow S_0$ transition.[10] The luminescence decay of this transition was recorded, the higher value of the emitting state lifetime ($\tau$ = 1.03 ms) provides evidence about the triplet state character of this state. The emission band observed for **5** shows a series of erbium self-absorptions. The presence of such self-absorption suggests that the radiative energy is probably converted into the typical erbium infrared emission. Both **6** and **7** show only strong fluorescent emission spectra. It can be observed that the intense emissions occurring at 433 nm ($\lambda_{ex}$ = 350 nm) for **6**, 430 nm ($\lambda_{ex}$ = 350 nm) for **7** are originated from the coordination of imdc$^{3-}$ to the $Cd^{2+}$ ion, respectively. It is noticeable that **6** and **7** exhibit quenching of the fluorescence with $\tau$ = 2.25 ns for **6** and $\tau$ = 2.60 ns for **7**. No near-infrared (NIR) fluorescence emission spectra were observed for **8** and **9**, though the sensitization of the NIR luminescence of $Nd^{3+}$ and $Pr^{3+}$ has been achieved by suitable ligands.[11] This indicates that the imdc$^{3-}$ cannot sensitize the NIR luminescence of $Pr^{3+}$ and $Nd^{3+}$ ions.

In summary, a series of Ln–Cd–organic frameworks have been successfully synthesized using the $H_3$imdc ligand with different donor atoms, and the systematic synthetic procedure has been well established. These compounds are the first structurally characterized 4d–4f MOFs containing 1D helical channels and tubes. The luminescence data suggested that the ligand fields at these centers are markedly different. For **1** (Tb-Cd), **2** (Eu-Cd), **3** (Dy-Cd), the efficient energy transfers from imdc to the Ln ions were observed, which result in intense characteristic green, red and yellow emission of Ln ions, respectively. In contrast, **4** (Gd-Cd), **5** (Er-Cd), **6** (Yb-Cd) and **7** (Y-Cd) all display broad bands, indicating an energy transfer between $Cd^{2+}$ and imdc$^{3-}$. No NIR luminescence was observed for **8** (Nd–Cd) and **9** (Pr–Cd), suggesting that imdc$^{3-}$ does not sensitize the NIR luminescence of $Pr^{3+}$ and $Nd^{3+}$ ions. The investigation of this series of Ln–Cd–organic frameworks provides a rational synthetic strategy for the construction of novel photoluminescent materials.

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## Notes and references

‡ Crystal data for **1**: $C_5H_8CdN_2O_{11.5}STb$, $M_r$ = 583.51, monoclinic, space group $P2_1/c$, $a$ = 8.6257(7), $b$ = 10.4624(7), $c$ = 13.8439(10) Å, $\beta$ = 101.284(3)°, $V$ = 1225.20(16) Å$^3$, $Z$ = 4, $\rho$ = 3.163 g cm$^{-3}$, $\mu$ = 7.701 mm$^{-1}$, $F(000)$ = 1092, GOF = 1.114. A total of 9101 reflections were collected and 2808 are unique ($R_{int}$ = 0.0206). $R1$ ($wR2$) = 0.0203 (0.0481) for 199 parameters and 2713 reflections [$I > 2\sigma(I)$]. The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda$ = 0.71073 Å) at room temperature. All absorption corrections were performed using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on $F^2$ using the SHELXTL-97 program package. CCDC 602025–602033 for **1–9**. For crystallographic data for **1–9** in CIF or other electronic format see DOI: 10.1039/b610892j

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