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# Lanthanide coordination compounds with 1*H*-benzimidazole-2-carboxylic acid: syntheses, structures and spectroscopic properties<sup>†</sup>

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A flexible multidentate ligand, 1H-benzimidazole-2-carboxylic acid, was synthesized to construct a series of lanthanide coordination polymers  $[Ln(HBIC)_3]_n$  (Ln = Eu (1), Tb (2), Gd (3), Pr (4), Nd (5);  $H_2BIC = 1H$ -benzimidazole-2-carboxylic acid) under hydrothermal conditions. All the compounds were fully characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, thermal analysis and various spectroscopic techniques. Structural analyses reveal that they are isostructural and feature a 2D wave-like layer structure with distorted grids, in which the adjacent  $Ln^{3+}$  centers are bridged by the HBIC<sup>-</sup> ligands with two kinds of new coordination modes and the adjacent HBIC<sup>-</sup> ligands are tightly bound by two types of distinct intra-layer hydrogen bonds. The adjacent 2D layers are further interconnected by strong inter-layer hydrogen bond ring motifs  $R_2^{2}(10)$ to generate a 3D supramolecular architecture. Optical studies indicate that the compounds 1, 2, 4 and 5 exhibit characteristic luminescence emission bands of the corresponding lanthanide ions in the visible or near-infrared regions at room temperature. In particular, compound 2 displays bright green luminescence in the solid state with a satisfactory  ${}^{5}D_{4}$  lifetime of 1.2 ms and a high overall quantum yield of 31%, due to an ideal energy gap between the lowest triplet state energy level of H<sub>2</sub>BIC ligand and the  ${}^{5}D_{4}$  state energy level of Tb<sup>3+</sup>. The energy transfer mechanisms in compounds 1 and 2 were also described and discussed.

## Introduction

Over the past decade, the rational design and synthesis of lanthanide-based metal-organic frameworks (Ln-MOFs) have provoked great interest for their fascinating architectures and potential technological application as functional materials.<sup>1</sup> Especially, owing to their unique photophysical properties (characteristic sharp emission and high color purity, long excited-state luminescence lifetimes up to milliseconds) as a result of transitions within the partially-filled 4f shells of the trivalent lanthanide ions, Ln-MOFs are excellent candidates for the development of optical devices.<sup>2</sup> However, the lanthanide ions usually give weak luminescence because of the low molar absorption coefficient (less than 10  $M^{-1}$  cm<sup>-1</sup>) of the Laporte forbidden f–f transitions.<sup>3</sup> An effective approach to circumvent this problem is to efficiently transfer the energy from the ligand-centered triplet excited states of an adjacent strongly absorbing chromophore to the lanthanide metal centers.<sup>4</sup> Therefore, searching for suitable organic antenna chromophores with high absorption in the UV/near-UV spectral region is an attractive task.

Given that lanthanide ions have high affinities for hard donor atoms such as the oxygen of carboxylic groups<sup>5</sup> and a delocalized  $\pi$ -electric system could provide a strongly absorbing chromophore.<sup>6</sup> Aromatic multidentate ligands with oxygen or hybrid oxygen-nitrogen atoms might be a good sensitizer to stimulate lanthanide ion luminescence. Recently, we have focused on a multidentate ligand, 1H-benzimidazole-2-carboxylic acid (H<sub>2</sub>BIC), in which the large  $\pi$ -conjugated system of the benzimidazole moiety is expected as an effective chromophore for lanthanide luminescence. The H<sub>2</sub>BIC ligand possesses four potential metal binding sites and shows flexible and various coordination modes (Scheme 1), wherein the oxygen atoms of the carboxylic group could coordinate with the lanthanide ions in terminal monodentate or diverse bridging motifs, or chelate Ln<sup>3+</sup> with the help of the N atoms from the benzimidazole group. Meanwhile, depending on the degree of deprotonation, the H<sub>2</sub>BIC ligand can act as a hydrogen bond acceptor and donor to

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Scheme 1 Diverse coordination modes of  $H_2BIC$  (M = metal).

benefit the formation of stable supramolecular structures. On the other hand, it was found that the presence of water molecules in the first coordination sphere of the lanthanide ion is prone to quench the emission due to the activation of nonradiative decay pathways.<sup>7</sup> So ancillary ligands with excellent chelating ability such as oxalate are widely used to prevent solvent and water molecules from entering the lanthanide coordination sphere.<sup>8</sup> For the deprotonated HBIC<sup>-</sup> or BIC<sup>2-</sup> ligands, the sufficiently strong chelate ability like  $C_2O_4^{2-}$  makes them excellent candidates to form stable Ln-MOFs without coordinated water or solvent molecules.<sup>9</sup>

It is worth noting that lanthanide coordination polymers based on 1*H*-benzimidazole-2-carboxylic acid ligands have not been explored.<sup>10</sup> In this contribution, five new two-dimensional Ln-MOFs based on H<sub>2</sub>BIC ligands,  $[Ln(HBIC)_3]_n$  (Ln = Eu (1), Tb(2), Gd(3), Pr(4) and Nd(5)), were hydrothermally synthesized and structurally characterized. The photophysical properties and thermal stability of them were also investigated. To the best of our knowledge, 1–5 are the first instances of Ln-MOFs constructed with H<sub>2</sub>BIC ligands.

## Experimental

#### Materials and analytical methods

The 1H-benzimidazole-2-carboxylic acid (H2BIC) ligand was prepared using o-phenylenediamine as the starting material by oxidizing 2-(hydroxymethyl)benzimidazole in alkaline conditions (Scheme 2). Other chemicals and reagents were obtained from commercial sources and used without further purification. Elemental analyses for C, H, and N were performed on an Elementar Vario EL III analyzer. IR spectra were recorded on a Tensor 27 spectrometer (Bruker Optics, Ettlingen, Germany) as KBr pellets in the range of 4000-400 cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum was recorded on an INOVA-400 Varian 400 MHz instrument in DMSO- $d_6$  solution at room temperature. Chemical shifts are reported in ppm relative to TMS. TG-DTG-DSC experiments were carried out in a simulated air atmosphere ( $N_2$ : 80 mL min<sup>-1</sup>, O<sub>2</sub>: 20 mL min<sup>-1</sup>) using a NETZSCH STA 449F3 equipment at a heating rate of 10 °C min<sup>-1</sup> from 30 to 1000 °C, an empty Al<sub>2</sub>O<sub>3</sub> crucible was used as a reference. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray



Scheme 2 Synthetic procedures for the ligand 1*H*-benzimidazole-2-carboxylic acid.

powder diffractometer (Cu K $\alpha$ , 1.5418 Å). Optical diffuse reflectance and UV absorption studies were carried out with a Shimadzu UV-2450 spectrophotometer. The solid-state photoluminescence analyses and lifetime measurements were performed on an Edinburgh FLSP920 fluorescence spectrometer.

#### Synthesis of H<sub>2</sub>BIC

**2-(Hydroxymethyl)benzimidazole.** A mixture of *o*-phenylenediamine (16.2 g, 0.15 mol), sodium glycolate (35.2 g, 0.6 mol) in 300 mL HCl (4 mol L<sup>-1</sup>) was stirred at 120 °C for 2 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was adjusted to pH  $\approx$  7 by saturated sodium hydroxide solution and finally filtered to give a large amount of white microcrystals of 2-(hydroxymethyl)benzimidazole. Yield: 19.0 g (85.7%). M.p.: 131–132 °C. Anal. Calc. For C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O ( $M_r$  = 148.16): C, 64.85 H, 5.44 N, 18.91. Found: C, 64.22 H, 5.88 N, 19.01%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm: 12.344 (s, 1 H), 7.484–7.491 (d, 2 H), 7.110–7.151 (m, 2 H), 5.744 (s, 1 H), 4.705 (s, 2H) (see Fig. S1, ESI†). IR (KBr, v/cm<sup>-1</sup>): 3270(m), 2918(s), 2850(s), 1623(w), 1580(w), 1490(m), 1452(s), 1439(s), 1380(m), 1351(m), 1274(m), 1207(m), 1106(w), 1055(s), 1034(s), 1002(s), 995(m), 958(w), 871(w), 828(w), 769(w), 750(s), 740(s), 639(w), 451(w).

1H-Benzimidazole-2-carboxylic acid (H<sub>2</sub>BIC). A mixture of 2-(hydroxymethyl)benzimidazole (7.40 g, 0.05 mol) and sodium hydroxide (4.00 g, 0.1 mol) in H<sub>2</sub>O (180 mL) was allowed to be stirred at 100 °C for 2 h, to which potassium permanganate (11.9 g, 0.075 mol) was added while kept stirring at 100 °C for 10 h. Then the reaction mixture was cooled to room temperature and filtered, and the filtrate was acidified with dilute hydrochloric acid to pH = 5. Upon being filtered off, washed with water, and air-dried, a large quantity of yellow solid was obtained. Yield: 7.15 g (64.9%, based on o-phenylenediamine). M.p.: 166-167 °C. Anal. Calc. For  $C_8H_6N_2O_2$  ( $M_r = 162.15$ ): C, 59.26 H, 3.73 N, 17.28. Found: C, 60.01 H, 3.81 N, 17.03%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$ , ppm: 7.66–7.62 (m, 2 H), 7.37–7.34 (m, 2 H) (see Fig. S2, ESI<sup> $\dagger$ </sup>). IR (KBr,  $v/cm^{-1}$ ): 2923(m), 2842(m), 1653(s), 1530(m), 1495(s), 1388(s), 1352(s), 1279(w), 1151(w), 1020(w), 905(m), 847(m), 802(w), 766(m), 731(m), 635(m), 585(m). After several days, colorless crystals of dihydrated 1H-benzimidazol-2carboxylate were obtained by slow evaporation of an ethanol solution of H<sub>2</sub>BIC, which was determined by single X-ray diffraction analysis (Fig. 1 and Table 1).<sup>10d</sup>

## Synthesis of $[Eu(HBIC)_3]_n$ (1)

A mixture of  $EuCl_3 \cdot 6H_2O$  (0.0366 g, 0.1 mmol),  $H_2BIC$  (0.0162 g, 0.1 mmol), NaOH (0.0040 g, 0.1 mmol) and NaN<sub>3</sub> (0.0065 g,



Fig. 1 (a) Perspective view of H<sub>2</sub>BIC·2H<sub>2</sub>O. (b) The intermolecular H-bonding interactions in H<sub>2</sub>BIC·2H<sub>2</sub>O.

0.1 mmol) was dissolved in 6 mL distilled water. The resulting solution was stirred for about 30 min at room temperature, sealed in a 10 mL Teflon-lined stainless steel autoclave, and heated at 110 °C for 3 days under autogenous pressure. The reaction system was then cooled to room temperature at a rate of 5 °C h<sup>-1</sup>. Colorless flaky crystals of **1** were collected in 48% yield (based on Eu). Anal. Calcd. for C<sub>24</sub>H<sub>15</sub>EuN<sub>6</sub>O<sub>6</sub> ( $M_r$  = 635.38): C, 45.37 H, 2.38 N, 13.23. Found: C, 45.81 H, 2.64 N, 12.99%. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3141(br, m), 1652(s), 1616(s), 1521(m), 1497(m), 1466(s), 1398(s), 1331(s), 1299(m), 1228(w), 1027(w), 988(w), 849(m), 821(m), 779(w), 739(s), 631(m), 580(m).

## Synthesis of $[Tb(HBIC)_3]_n$ (2)

An identical procedure with **1** was followed to prepare **2** except EuCl<sub>3</sub>·6H<sub>2</sub>O was replaced by TbCl<sub>3</sub>·6H<sub>2</sub>O (0.0374 g, 0.1 mmol) or Tb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.0357 g, 0.05 mmol). Colorless flaky crystals of **2** were collected in 54% yield (based on Tb). Anal. Calcd. for C<sub>24</sub>H<sub>15</sub>TbN<sub>6</sub>O<sub>6</sub> ( $M_r$  = 642.35): C, 44.88 H, 2.35 N, 13.08. Found: C, 44.61 H, 2.58 N, 13.01%. IR (KBr, *v*/cm<sup>-1</sup>): 3128(br, m), 1650(s), 1611(s), 1528(m), 1499(m), 1467(s), 1399(s), 1335(s), 1308(m), 1235(w), 1025(w), 987(w), 860(m), 825(m), 777(w), 748(s), 638(m), 584(m).

 Table 1
 Crystal data and structure refinement summary for H2BIC·2H2O and compounds 1–5

	$H_2BIC \cdot 2H_2O$	1	2	3	4	5
Empirical formula	$C_8H_{10}N_2O_4$	C24H15N6O6Eu	C <sub>24</sub> H <sub>15</sub> N <sub>6</sub> O <sub>6</sub> Tb	C24H15N6O6Gd	C24H15N6O6Pr	C <sub>24</sub> H <sub>15</sub> N <sub>6</sub> O <sub>6</sub> Nd
Formula weight	198.18	635.38	642.34	640.67	624.33	627.66
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	6.860(2)	9.7575(10)	9.7089(14)	9.7434(11)	9.8425(7)	9.853(2)
b (Å)	7.368(2)	8.9776(9)	8.9276(13)	8.9656(10)	9.0698(7)	9.073(2
c (Å)	18.967(5)	26.005(3)	25.930(4)	26.000(3)	26.084(2)	26.152(6)
α (°)	90	90	90	90	90	90
βΘ	109.738(9)	91.113(1)	91.090(2)	91.179(2)	91.216(1)	91.153(4)
γ (°)	90	90	90	90	90	90
$V(Å^3)$	902.4(4)	2277.5(4)	2247.1(6)	2270.8(4)	2327.9(3)	2337.3(10)
Z	4	4	4	4	4	4
$D_{\rm c} ({\rm g} {\rm cm}^{-3})$	1.459	1.853	1.899	1.874	1.781	1.784
$T(\mathbf{K})$	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
$\mu (\mathrm{mm}^{-1})$	0.119	2.810	3.204	2.977	2.147	2.276
F(000)	416	1248	1256	1252	1232	1236
Reflections collected/unique	4373/1596	11 759/4461	10 687/3983	11 088/4012	11 382/4131	11 228/4141
R(int)	0.0750	0.0316	0.0452	0.0535	0.0329	0.0716
Data/restraints/parameters	1596/0/127	4461/0/334	3983/0/334	4012/0/334	4131/0/338	4141/0/334
GOF on $F^2$	1.015	1.097	1.066	1.033	1.037	1.009
$R_1^{a} [I > 2\sigma(I)]$	0.0696	0.0250	0.0410	0.0373	0.0290	0.0549
$wR_2^{b}$ (all data)	0.2105	0.0785	0.1021	0.0774	0.0661	0.1249
$^{a} R_{1} = \sum   F_{o}  -  F_{c}   / \sum  F_{o} .^{b} w$	$R_2 = \left[\sum w(F_0^2 - H_0^2)\right]$	$(F_{\rm c}^2)^2 / \sum w[(F_{\rm o}^2)^2]^{1/2}.$				

## Synthesis of [Gd(HBIC)<sub>3</sub>]<sub>n</sub> (3)

An identical procedure with **1** was followed to prepare **3** except EuCl<sub>3</sub>·6H<sub>2</sub>O was replaced by GdCl<sub>3</sub>·6H<sub>2</sub>O (0.0372 g, 0.1 mmol). Colorless flaky crystals of **3** were collected in 61% yield (based on Gd). Anal. Calcd. for C<sub>24</sub>H<sub>15</sub>GdN<sub>6</sub>O<sub>6</sub> ( $M_r$  = 640.67): C, 44.99 H, 2.36 N, 13.12. Found: C, 45.21 H, 2.88 N, 12.92%. IR (KBr,  $\nu/$  cm<sup>-1</sup>): 3137(br, m), 1653(s), 1606(s), 1525(m), 1491(m), 1461(s), 1398(s), 1329(s), 1300(m), 1231(w), 1020(w), 986(w), 858(m), 820(m), 776(w), 743(s), 633(m), 585(m).

## Synthesis of $[Pr(HBIC)_3]_n$ (4)

An identical procedure with **1** was followed to prepare **4** except EuCl<sub>3</sub>·6H<sub>2</sub>O was replaced by Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.0435 g, 0.1 mmol) or PrCl<sub>3</sub>·6H<sub>2</sub>O (0.0355 g, 0.1 mmol). Light-green flaky crystals of **4** were collected in 33% yield (based on Pr). Anal. Calcd. for C<sub>24</sub>H<sub>15</sub>PrN<sub>6</sub>O<sub>6</sub> ( $M_r$  = 624.33): C, 46.17 H, 2.42 N, 13.46. Found: C, 46.67 H, 2.50 N, 13.98%. IR (KBr,  $\nu/cm^{-1}$ ): 3133(br, m), 1657(s), 1609(s), 1531(m), 1500(m), 1463(s), 1401(s), 1325(s), 1302(m), 1238(w), 1027(w), 990(w), 854(m), 822(m), 779(w), 741(s), 635(m), 581(m).

## Synthesis of [Nd(HBIC)<sub>3</sub>]<sub>n</sub> (5)

An identical procedure with **1** was followed to prepare **5** except EuCl<sub>3</sub>·6H<sub>2</sub>O was replaced by Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.0438 g, 0.1 mmol). Light-purple flaky crystals of **5** were collected in 39% yield (based on Nd). Anal. Calcd. for C<sub>24</sub>H<sub>15</sub>NdN<sub>6</sub>O<sub>6</sub> ( $M_r$  = 627.66): C, 45.93 H, 2.41 N, 13.39. Found: C, 45.51 H, 2.44 N, 13.11%. IR (KBr,  $v/cm^{-1}$ ): 3132(br, m), 1652(s), 1604(s), 1528(m), 1489(m), 1466(s), 1402(s), 1330(s), 1303(m), 1238(w), 1029(w), 988(w), 851(m), 823(m), 779(w), 741(s), 634(m), 580(m).

## X-ray crystallography

Single-crystal X-ray diffraction data for H<sub>2</sub>BIC·2H<sub>2</sub>O and compounds 1–5 were collected on a Bruker SMART APEXII CCD diffractometer, equipped with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using  $\omega$  and  $\varphi$  scan mode. All the structures were solved by direct methods and refined with full-matrix least-squares refinements based on  $F^2$  using SHELXS-97 and SHELXL-97.<sup>11</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The detailed crystallographic data and the structure refinement parameters of H<sub>2</sub>BIC·2H<sub>2</sub>O and1–5 are listed in Table 1. Selected bond distances, angles and hydrogen bonds are given in Tables S1 and S2 (see ESI<sup>†</sup>).

## **Results and discussion**

## Synthesis

As well known, the hydro/solvothermal method used to be a non-ignorable "hero" in the preparation of metal–organic coordination frameworks with fascinating architectures and function. It gives a more convenient and effective route to synthesize high-quality single crystals of MOFs over other methods.<sup>12</sup> However, because of the limitation of unintuitive reaction phenomenon and hard-to-monitor reaction process, the research on the complex mechanism of reaction phase at present,

and many possible mechanisms could only be deduced by the intuitive results. Therefore, according to the reaction conditions and results of isolating 1–5, it is not difficult to find that the different anions of lanthanide salts (Cl<sup>-</sup>,  $SO_4^{2-}$  or  $NO_3^{-}$ ) have no effects on the formation of 1–5. Moreover, it should be noted that the presence of a molar equivalent of NaN<sub>3</sub> as the structure-directing agent was a prerequisite for the preparation of 1–5.

#### Structural description

Fig. 1a depicts that the ligand 1H-benzimidazole-2-carboxylic acid crystallizes as the dihydrate, and the organic molecule exists in a zwitterionic form with the carboxyl group deprotonated and the benzimidazole group protonated,<sup>10d</sup> which has a significant advantage for the formation of abundant hydrogen bonds. As shown in Fig. 1b, both the benzimidazole N atoms are involved in forming hydrogen bonds as donors: one gives N2-H2...O1 hydrogen bonds to connect two parallel adjacent 1H-benzimidazole-2-carboxylate molecules, yielding a centrosymmetric hydrogen-bond motif  $R_2^2(10)$ ; and the other N atom (N1) is attracted by O3 from a lattice water molecule to give a intermolecular N1-H1...O3 hydrogen bond. Notably, the carboxyl O atom (O2) exhibits a three-connected hydrogenbond motif, in which O2 is employed as accepter to form three kinds of different hydrogen bonds with lattice water molecules (Table S2, ESI<sup>†</sup>). In the crystal, molecules are packed into a three-dimensional network (Fig. 2a) via these hydrogen bonds and two distinct  $\pi - \pi$  stacking interactions between the benzimidazole groups of adjacent molecules [centroid-centroid distances = 3.7602(10) and 3.6135(10) Å] (Fig. 2b). It is of interest to note that a helical chain generated by the hydrogen-bond interactions between carboxyl oxygen atoms (O2) and lattice water molecules is observed (Fig. 2c).

X-ray analyses performed on single crystals of compounds 1-5 reveal an isostructural mode possessing one 2D wave-like layer structure with distorted grids. Hence, only the structure of 1 is described in detail. Compound 1 crystallizes in the monoclinic space group  $P2_1/n$ , and the asymmetric unit consists of one crystallographically independent Eu<sup>3+</sup> ion and three HBIC<sup>-</sup> ligands. As illustrated in Fig. 3a, the central Eu<sup>3+</sup> cation is eightcoordinated by five carboxyl oxygen atoms (O1, O3-O6) and three nitrogen atoms (N1, N3 and N5) from five HBIC<sup>-</sup> ligands, resulting in a distorted bicapped triangle prism coordination geometry (Fig. 3b). The Eu-O bond distances range from 2.338(3) to 2.487(3) Å with the mean of 2.415(3) Å, which is slightly shorter than the average Eu-N distance, 2.549(3) Å. The average O-Eu-O bond angle is 105.56(10)°, similar to that of N-Eu-N [105.43(10)°], but much lager than the mean O-Eu-N bond angle value,  $94.87(11)^{\circ}$ . All of the bond lengths and angles in 1 are within normal ranges and comparable with those observed in other reported Eu<sup>3+</sup>-carboxylates (Table S1, ESI<sup>†</sup>).<sup>13</sup>

Due to the effect of lanthanide contraction, the  $Ln^{3+}$  ions radii are very close [Shannon's ionic radii of  $Ln^{3+}$  in 1–5: 1.126 Å (Pr<sup>3+</sup>), 1.109 Å (Nd<sup>3+</sup>), 1.066 Å (Eu<sup>3+</sup>), 1.053 Å (Gd<sup>3+</sup>), and 1.04 Å (Tb<sup>3+</sup>)]. Comparing the geometries of isomorphic 1–5 (Table 2), it is evident to find out that the differences on the Ln– O/N bond lengths and correlative bond angles are very subtle, and the variation of some geometry in 1–5 shows dependency on the respective Shannon's effective ionic radii. For example, the



**Fig. 2** (a) 3D supramolecular network of  $H_2BIC \cdot 2H_2O$  formed by intermolecular hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions. (b) The two distinct  $\pi$ - $\pi$  stacking interactions in  $H_2BIC \cdot 2H_2O$ . (c) Helical chain structure generated by the hydrogen-bond interactions between carboxyl oxygen atoms and lattice water molecules.



Fig. 3 (a) Coordination environment of Eu<sup>3+</sup> in 1, H atoms are omitted for clarity. Symmetry code: #1, 1/2 - x, -1/2 + y, 1/2 - z; #2, 3/2 - x, -1/2 + y, 1/2 - z; (b) Coordination polyhedron geometry of Ln<sup>3+</sup> in 1–5.

	1 (Eu <sup>3+</sup> )	<b>2</b> (Tb <sup>3+</sup> )	<b>3</b> (Gd <sup>3+</sup> )	<b>4</b> (Pr <sup>3+</sup> )	<b>5</b> (Nd <sup>3+</sup> )		
$Ln-O^{a}$ (Å)	2.338(3)-2.487(3)	2.318(4)-2.467(4)	2.326(4)-2.480(4)	2.376(3)-2.524(3)	2.370(5)-2.522(5)		
$Ln-O^{b}(A)$	2.415(3)	2.394(4)	2.405(4)	2.455(2)	2.451(5)		
$Ln-N^{a}(A)$	2.519(3)-2.567(3)	2.493(6)-2.546(5)	2.514(5)-2.557(5)	2.593(3)-2.631(3)	2.586(7)-2.656(7)		
$Ln-N^{b}$ (Å)	2.549(3)	2.526(5)	2.541(5)	2.612(3)	2.618(7)		
$O-Ln-O^{a}(^{\circ})$	70.63(9)-157.00(10)	70.36(15)-157.36(16)	70.70(12)-156.80(14)	70.64(8)-157.05(9)	70.48(19)-157.2(2)		
$O-Ln-O^b$ (°)	105.56(10)	105.57(15)	105.51(12)	105.65(8)	105.66(5)		
$O-Ln-N^{a}$ (°)	63.63(9)-152.20(11)	63.99(16)-152.26(16)	64.09(13)-152.23(13)	63.14(9)-152.29(9)	62.97(19)-152.5(2)		
$O-Ln-N^{b}$ (°)	94.87(11)	94.87(16)	94.90(13)	94.78(9)	94.79(6)		
N–Ln–N <sup><math>a</math></sup> (°)	70.80(11)-152.32(11)	71.00(18)-152.56(18)	70.67(16)-152.53(15)	70.02(10)-151.46(10)	70.2(2)-151.7(2)		
N–Ln–N <sup><math>b</math></sup> (°)	105.43(10)	105.67(17)	105.60(15)	104.53(10)	104.76(6)		
Grid size $(\text{\AA} \times \text{\AA})$	$6.9561(5) \times 6.7012(5)$	$6.9219(8) \times 6.6662(8)$	$6.9443(7) \times 6.6949(6)$	$7.0167(4) \times 6.7600(4)$	$7.0234(12) \times 6.7663(11)$		
<sup>a</sup> Range of bond length or bond angle. <sup>b</sup> Average bond length or bond angle.							

 Table 2
 The geometry comparison for compounds 1–5

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average length of Ln-O decreases along with reducing of the  $Ln^{3+}$  radii (Ln–O:  $Pr^{3+} > Nd^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+}$ ), and the average bond angle of N-Ln-N increases accordantly with the  $Ln^{3+}$  radii increasing ( $\angle_{N-L,n-N}$ :  $Pr^{3+} < Nd^{3+} < Eu^{3+} <$  $Gd^{3+}$  <  $Tb^{3+}$ ). However, because the final formation of lanthanide compounds may be influenced by many complicated factors, not all the geometry variations in 1-5 are in line with the consistent tendency, there are also some exceptions. The average lengths of Ln-N in these compounds are 2.618(7), 2.549(3), 2.541(5) and 2.526(5) Å for compounds 5, 1, 3 and 2, steadily decreasing from Nd<sup>3+</sup> to Tb<sup>3+</sup>, respectively. Yet the average Pr-N distance [2.612(3) Å] is shorter than the average Nd–N length, which is not in good agreement with the radii of the two  $Ln^{3+}$ ions. Meanwhile, the situation of average O-Ln-N bond angle is similar:  $\angle_{O-Pr-N}$  [94.78(9)°] <  $\angle_{O-Nd-N}$  [94.79(6)°] <  $\angle_{O-Eu-N}$  $[94.87(11)^{\circ}] < \angle_{O-Tb-N} [94.87(16)^{\circ}], \text{ just } \angle_{O-Gd-N} [94.90(13)^{\circ}] >$  $\angle_{O-Tb-N}$  [94.87(16)°], while the average O-Ln-O bond angles in 1-5 seemingly look random in the changing tendency:  $\angle_{O-Nd-O}$  $[105.66(5)^{\circ}] > \angle_{O-Pr-O} [105.65(8)^{\circ}] > \angle_{O-Tb-O} [105.57(15)^{\circ}] >$  $\angle_{O-Eu-O} [105.56(10)^{\circ}] > \angle_{O-Gd-O} [105.51(12)^{\circ}].$ 

In compound 1, all H<sub>2</sub>BIC ligands are present in the monodeprotonated form, HBIC<sup>-</sup>. Two kinds of new coordination modes of HBIC<sup>-</sup> (Modes I and II in Scheme 1) are first observed. One is the HBIC<sup>-</sup> ligand chelating one Eu<sup>3+</sup> center with one carboxyl oxygen atom and one imidazole nitrogen atom first, and the other carboxyl oxygen atom further bridges another  $Eu^{3+}$  ion, leading to a chelating-bridging  $\mu_2$ - $\kappa N$ , O: κO coordination fashion (Mode I); the other is the HBIC ligand chelating the  $Eu^{3+}$  center with a simple  $\mu_1$ - $\kappa N$ , O coordination fashion (Mode II). The adjacent Eu<sup>3+</sup> centers are bridged by the HBIC<sup>-</sup> ligands in Mode I into 1D infinite chains (Fig. 4), and these chains are further interweaved each other, generating a 2D wave-like layered structure in the ab plane (Fig. 5a). In this 2D network, each Eu<sup>3+</sup> center is coordinated by four HBIC<sup>-</sup> ligands in Mode I, and the remaining two sites are occupied by another HBIC<sup>-</sup> ligand in Mode II. From the viewpoint of network topology, the structure of 1 can be



Fig. 4 1D infinite chain structure in compound 1.

simplified as a four-connected 2D (4,4) network with the Eu<sup>3+</sup> ions as nodes (Fig. 5b), in which each distorted grid has a size of 6.7012(5) Å × 6.9561(5) Å, slight larger than those in compounds **2** [6.9219(8) × 6.6662(8)] and **3** [6.9443(7) × 6.6949(6)], and smaller than those in compounds **4** [7.0167(4) × 6.7600(4)] and **5** [7.0234(12) × 6.7663(11)] (Table 2).

It is worth mentioning that the deprotonated carboxylate and protonated benzimidazole N atom of the HBIC<sup>-</sup> ligand make the amphoteric HBIC<sup>-</sup> ligand a good candidate to be involved in the construction of strong hydrogen bonds as a donor or acceptor. As can be seen from Fig. 6a, each grid in the 2D layer is formed by four HBIC<sup>-</sup> ligands bridging four Eu<sup>3+</sup> centers with Mode I, and the grid is further twisted by two types of distinct intra-layer hydrogen bonds  $[N2-H2\cdotsO5^{\#1} = 2.718(4) \text{ Å}$  and N6–H6···O1<sup>#2</sup> = 2.782(4) Å. Symmetry code: #1, -x + 3/2, y + 3/21/2, -z + 1/2; #2 - x + 1/2, y + 1/2, -z + 1/2], where the adjacent HBIC<sup>-</sup> ligands are tightly bound together like the bis(chelating)bridging oxalate, thus resulting in a wave-like 2D layer. Moreover, the HBIC<sup>-</sup> ligands with Mode II are arranged face to face between two adjacent layers, and the exposed carboxylic O atoms and H atoms participate in constructing the strong inter-layer hydrogen bond  $R_2^2(10)$  ring motifs [N4–H4···O2<sup>#3</sup> = 2.824(5) Å, #3: -x + 1, -y + 1, -z] (Fig. 6b), which finally bridges the adjacent layers into a 3D supramolecular architecture (Fig. 6c).

#### Thermal analysis

To examine the thermal stability of 1-5, the thermogravimetric analyses for crystal samples of 1-5 were performed under a simulated air atmosphere with a heating rate of 10 °C min<sup>-1</sup> from ambient temperature up to 1000 °C. As shown in Fig. S3, ESI,† TG analyses indicate that all these compounds have high thermal stability and exhibit similar thermal behavior due to their isostructural nature. Herein, only the thermal stability of 1 was taken as a representative example for discussion. The TG curve depicted in Fig. 7 reveals that 1 remains stable up to 354.7 °C, which could be ascribed to the abundant intra-layer and inter-layer hydrogen bonds occurring in framework 1. Then the compound experiences almost one-step weight loss of 71.85% from 354.7 to 528.3 °C, which is attributed to the thermal decomposition of the organic components. The final mass of the residue is 28.15% of the initial weight, which agrees well with that expected value for the formation of a stoichiometric quantity of Eu<sub>2</sub>O<sub>3</sub> (calcd. 27.69%). The end product was



Fig. 5 (a) A wave-like 2D network in compound 1, H atoms are omitted for clarity. (b) A schematic view of the topology framework of 1.



**Fig. 6** (a) Intra-layer hydrogen-bonding interactions in 1, the benzene rings of the benzimidazole groups are omitted for clarity. (b) Inter-layer hydrogen-bonding interactions in 1. (c) 3D supramolecular architecture assembled *via* intra-layer and inter-layer hydrogen bonds in 1, where pink and green dashed lines denote intra-layer and inter-layer hydrogen-bonding interactions, respectively.



Fig. 7 TG-DTG-DSC curves of compound 1 with a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>.

identified as the body-centered cubic  $Eu_2O_3$  by PXRD (Fig. S4, ESI;† JCPDS NO. 34-0392).

The DTG curve for **1** shows that the whole process of weight loss consists of two sequential thermal decomposition processes, and the sharp peaks located at 391.1 °C and 462.7 °C, respectively, represent the fastest decomposition of the two processes, which may caused by the two distinct binding fashions between  $\text{Eu}^{3+}$  ions with ligands in **1**. In addition, the broad exothermic peak of the DSC curve shows that the compound decomposes with a large heat of 7002 J g<sup>-1</sup>.

The DSC experiments were also carried out from room temperature to 1000 °C under a simulated air atmosphere to investigate the heat variation of the lanthanide compound system. As illustrated in Fig. 8, the DSC curves of 1–5 are similar, and each of them shows a broad downward band with two consecutive exothermic peaks, corresponding to the two sequential thermal decomposition processes. There are also some significant differences on the heat release and the decomposition



**Fig. 8** DSC plots of compounds 1–5 with a heating rate of  $10 \,^{\circ}\text{C min}^{-1}$ .

peak temperature. As can be seen from Fig. 8, all the five compounds display high heats, the maximum 2 (7697 J g<sup>-1</sup>) outputs about 1330 J g<sup>-1</sup> more than the minimum 5 (6361 J g<sup>-1</sup>). Correspondingly, the greatest decomposition peak temperature occurred in 2 (480.6 °C) is approximately 25 °C higher than that in 5 (454.4 °C). It should be noted that the variation tendency of both heat release and decomposition peak temperature are consistent with that of the average Ln–N/O lengths, that is, the decomposition heat and peak temperature decrease with the increase of average Ln–N/O lengths. This finding confirms that the shorter distance between Ln<sup>3+</sup> ion and O/N atom, the greater the heat yielded by thermo-decomposition.

#### UV-vis spectra

The UV-vis absorption spectra of the free ligand H<sub>2</sub>BIC and its corresponding  $\text{Ln}^{3+}$  compounds 1–5 were recorded in DMSO solution ( $c = 2 \times 10^{-5}$  M), as shown in Fig. 9. The identical trends in absorption spectra of compounds 1–5 and the free ligand, demonstrate that the coordination of the Ln<sup>3+</sup> ion does



Fig. 9 UV-vis absorption spectra of H<sub>2</sub>BIC and compounds 1–5 in DMSO solution (2  $\times$  10<sup>-5</sup> M).

not have a significant influence on the singlet excited state of the free ligand. Nevertheless, compared with the H<sub>2</sub>BIC ligand, a slight blue shift is discernible in the absorption maximum of the five compounds, which could be attributable to the perturbation induced by the metal ion coordination. The H<sub>2</sub>BIC ligand displays three absorption bands at 269, 275, and 281 nm, which are assigned to singlet–singlet  ${}^{1}\pi$ – $\pi$ \* absorptions of the aromatic rings. The molar absorption coefficient values for compounds 1–5 at about 273 nm of  $3.35 \times 10^4$ ,  $3.55 \times 10^4$ ,  $3.02 \times 10^4$ ,  $3.49 \times 10^4$  and  $3.44 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>, respectively, are approximately three times as high as that of the ligand (1.11 × 10<sup>4</sup> at 275 nm), indicating the presence of three ligands in each compound, this is also in good agreement with the crystallographic analysis. The aforementioned features suggest that the H<sub>2</sub>BIC ligand has a strong ability to absorb light.

## Energy transfer between the $H_2BIC$ ligand and $Ln^{3+}$ (Ln = Eu, Tb)

For lanthanide coordination compounds, the trivalent lanthanide ion luminescence generally needs to be stimulated by a strong chromophore ligand via the "antenna effect", and the details can be described as the following steps: the chromophore ligand is first excited from ground state into the first excited singlet state due to the UV absorption, immediately nonradiative intersystem crossing of the ligand from the singlet to the triplet state occurs; and the intramolecular energy is further transferred from the ligand-centered triplet state to the excited 4f states of lanthanide ion, followed by internal conversion to the lower emitting states simultaneously; finally, the characteristic lanthanide emission is generated by the radiative transition from the lanthanide ion emissive states to the lower different energy states.<sup>14</sup> So it can be seen that the intramolecular energy migration efficiency from the organic ligand to the central Ln<sup>3+</sup> ions plays a key role in the luminescence property of the lanthanide coordination compound.

The choice of a suitable sensitizer is very important. According to Reinhoudt's empirical rule, the intersystem crossing process becomes effective when energy gap  $\Delta E$  [singlet energy level ( $^{1}\pi\pi^{*}$ ) - triplet energy level  $({}^{3}\pi\pi^{*})$ ] is at least 5000 cm<sup>-1</sup>.<sup>15</sup> Thus, the singlet and triplet energy levels of the H<sub>2</sub>BIC ligand should be firstly determined. The  ${}^{1}\pi\pi^{*}$  of H<sub>2</sub>BIC is estimated by reference to the wavelength of the UV-vis higher absorption edge of Gd<sup>3+</sup> compound 3, and the pertinent value is  $286 \text{ nm} (34965 \text{ cm}^{-1})$  (see Fig. 9). Because the first excited state of Gd<sup>3+</sup> (about 32 000  $cm^{-1}$ ),  ${}^{6}P_{7/2}$ , is too high to accept any energy from the first excited triplet state of the ligand through intramolecular ligand-to-metal energy transfer, the phosphorescence spectrum of the corresponding Gd<sup>3+</sup> compound could actually reveal the triplet energy level of the ligand.<sup>16</sup> As shown in Fig. S5, ESI,<sup>†</sup> the triplet energy level  $(^{3}\pi\pi^{*} = 24\ 630\ \text{cm}^{-1})$  of H<sub>2</sub>BIC is determined by the lower wavelength emission edge (406 nm) from the low-temperature phosphorescence spectrum of the  $Gd^{3+}$  compound 3.

Fig. 10 shows the diverse energy-level states of H<sub>2</sub>BIC, Eu<sup>3+</sup> and Tb<sup>3+</sup> and possible energy transfer pathways among them. The energy gap for the H<sub>2</sub>BIC ligand  $\Delta E ({}^{1}\pi\pi^{*} - {}^{3}\pi\pi^{*} = 10\ 335\ cm^{-1})$  is significantly higher than 5000 cm<sup>-1</sup>, which suggests that the intersystem crossing process is effective for the H<sub>2</sub>BIC ligand.<sup>15,17</sup> Further, the triplet energy level of H<sub>2</sub>BIC is also obviously higher than the  ${}^{5}D_{0}$  level of Eu<sup>3+</sup> (17 300 cm<sup>-1</sup>) and



Fig. 10 Schematic energy level diagrams and energy transfer mechanisms for compounds 1 and 2.  $S_1$  represents the first excited singlet state and  $T_1$  represents the first excited triplet state.

 ${}^{5}D_{4}$  level of Tb<sup>3+</sup> (20 500 cm<sup>-1</sup>), giving rise to an advantageous energy-transfer condition in 1 or 2. Of course, this does not mean that the higher the better, and the energy gap between the lowest triplet state of the H<sub>2</sub>BIC ligand and the  ${}^{5}D_{0}$  state (Eu<sup>3+</sup>) or the  ${}^{5}D_{4}$  state (Tb<sup>3+</sup>) must be appropriate. The gap may be too large or too small to get satisfactory luminescence efficiency; a large gap always yields an inefficient energy transfer and a small gap is beneficial to a back-energy transfer.<sup>18</sup> Latva's empirical rule states that an optimal ligand-to-metal energy transfer process for  $Ln^{3+}$  requires  $\Delta E (^{3}\pi\pi^{*} - {}^{5}D_{J}) = 2500-4000 \text{ cm}^{-1}$  for  $Eu^{3+}$  and 2500–4500 cm<sup>-1</sup> for Tb<sup>3+.<sup>19</sup> Given that the energy gap between</sup> the triplet state and  ${}^{5}D_{0}$  state of Eu<sup>3+</sup> is 7330 cm<sup>-1</sup>, the H<sub>2</sub>BIC ligand is not in an ideal situation for the sensitization of Eu<sup>3+</sup> luminescence. Whereas the energy gap between the triplet state and  ${}^{5}D_{4}$  state of Tb<sup>3+</sup> is 4130 cm<sup>-1</sup>, suggesting that the H<sub>2</sub>BIC ligand could strongly sensitize  $Tb^{3+}$  emission in 2.

## Photophysical property

#### Photoluminescence properties of 1 and 2

Considering that the H<sub>2</sub>BIC ligand is an adequate light-harvesting chromophore, and expected to be used for sensitizing lanthanide ion luminescence. The solid-state luminescence properties of **1–2** were studied at room temperature. The solidstate excitation and emission spectra of the Eu<sup>3+</sup> compound **1** recorded at room temperature are displayed in Fig. 11. The excitation spectrum (Fig. 11a) monitored around the intense <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> transition of the Eu<sup>3+</sup> exhibits a broad and relatively weak band between 250 and 350 nm ( $\lambda_{max} = 331$  nm), which can be assigned to the  $\pi$ - $\pi$ \* electronic transition of the H<sub>2</sub>BIC ligand. A series of sharp characteristic f-f transitions of the Eu<sup>3+</sup> at 361 (<sup>7</sup>F<sub>0</sub>  $\rightarrow$  <sup>5</sup>G<sub>6</sub>), 380 (<sup>7</sup>F<sub>0</sub>  $\rightarrow$  <sup>5</sup>H<sub>4</sub>) and 394 nm (<sup>7</sup>F<sub>0,1</sub>  $\rightarrow$  <sup>5</sup>L<sub>6</sub>) are also evident, which can be reasonably assigned to the transitions between the <sup>7</sup>F<sub>0,1</sub> and the <sup>5</sup>L<sub>6</sub> and <sup>5</sup>D<sub>2,1</sub> levels.<sup>20</sup> The more intense 4f absorption of Eu<sup>3+</sup> suggests that the luminescence sensitization *via* excitation of the H<sub>2</sub>BIC ligand is not very promising in **1**.

Under excitation at 394 nm, the ambient temperature emission spectrum of 1 displays characteristic sharp emission bands of Eu<sup>3+</sup> in the spectral range of 570–750 nm. As shown in Fig. 11b, the five anticipated transitions from the excited  ${}^{5}D_{0}$  state to the  ${}^{7}F_{J}$  ground-state multiplet are well resolved, that is,  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  at 579 nm,  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  at 593 nm,  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  at 613 nm,  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ at 654 nm, and  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  at 700 nm. ${}^{20a,20b,21}$  Compared with others, the maximum intensities at 579 and 654 nm are much weaker, because their corresponding  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transitions are both strictly forbidden in magnetic and electric dipole schemes.<sup>14c,21c</sup> The  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition is relatively stronger, which is a magnetic dipole. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  and  ${}^{5}D_{0} \rightarrow$  ${}^{7}F_{1}$  transitions consist of only one peak at 579 nm and three split peaks at 593 nm, respectively, which suggests the existence of a single chemical environment around the  $Eu^{3+}$  ion in 1.<sup>16a,22</sup> It is clear that the hypersensitive  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition (electric dipole) shows the highest intensity at 613 nm, pointing to a highly polarizable chemical environment around the Eu<sup>3+</sup> ion. The luminescent intensity ratio of the  $({}^{5}D_{0} \rightarrow {}^{7}F_{2})/({}^{5}D_{0} \rightarrow {}^{7}F_{1})$  is 11.53, which indicates that compound 1 exhibits bright red light emission and the Eu<sup>3+</sup> ion in it is not located in a site with inversion center symmetry.<sup>23</sup>

Fig. 12 summarizes the room-temperature excitation and emission spectra of  $Tb^{3+}$  compound **2** in the solid state. The



Fig. 11 Room-temperature excitation (a) and emission (b) spectra for 1 ( $\lambda_{ex}$  = 394 nm) with emissions monitored at approximately 613 nm.

excitation spectrum of **2** (Fig. 12a) monitored around the hypersensitive  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition (545 nm) of Tb<sup>3+</sup> reveals a broad band between 280 and 350 nm with a maximum at approximately 333 nm, which can be attributable to the  $\pi$ - $\pi$ \* electronic transition of the H<sub>2</sub>BIC ligand. Because this broad band overlaps the absorption spectrum of the H<sub>2</sub>BIC ligand in the region of 280–350 nm, the energy transfer from the ligand to Tb<sup>3+</sup> is operative. In addition, a series of faint f-f transitions  ${}^{7}F_{5} \rightarrow {}^{5}L_{9}$  (359 nm),  ${}^{7}F_{5} \rightarrow {}^{5}L_{10}$  (369 nm) and  ${}^{7}F_{5} \rightarrow {}^{5}G_{6}$  (378 nm) are also observed in the excitation spectrum of **2**,  ${}^{24}$  which are much weaker than the absorptions owing to the organic ligands. Apparently, luminescence sensitization *via* ligand excitation is significantly more efficient than the direct excitation of the Tb<sup>3+</sup> absorption level.

Being excited by UV light ( $\lambda_{ex} = 333$  nm), the solid-state emission spectrum of **2** recorded at room temperature (Fig. 12b) exhibits the characteristic narrow emission bands of Tb<sup>3+</sup>, which results from deactivation of the <sup>5</sup>D<sub>4</sub> excited state to the corresponding ground state <sup>7</sup>F<sub>J</sub> (J = 6, 5, 4, 3) of the Tb<sup>3+</sup> ion centered at 489, 545, 584, and 621 nm.<sup>20a-d</sup> The most intense emission centered at 545 nm represents the hypersensitive <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>5</sub> transition, which shows the strongest green emission of **2**.

Furthermore, the emission band from the  $H_2BIC$  ligand is not detected, implying efficient energy transfer from the ligand to the central  $Tb^{3+}$  ion in **2**, which is further confirmed by the very high emission intensity of  $Tb^{3+}$ .

For a deeper research on the photophysical behaviors of the compounds 1–2, the lifetime values for the  ${}^{5}D_{0}$  level of 1 and  ${}^{5}D_{4}$  level of 2 ( $\tau_{obs}$ ) were measured at ambient temperature based on the corresponding luminescent decay profiles by fitting with monoexponential functions (Fig. S6 and S7, ESI†), and the relevant values are summarized in Table 3. The typical decay profiles indicate that single chemical environments exist around the emitting Eu<sup>3+</sup>/Tb<sup>3+</sup> ions. The ideal luminescence lifetimes for 1 (0.952 ms) and 2 (1.207 ms) could be due to the strong chelating coordination ability and rational steric stabilization of the HBIC<sup>-</sup> ligand, which effectively prevented the solvent guest molecules from entering the coordination sphere of the lanthanide ion and greatly reduced the energy loss caused by the O–H vibrations.

In addition, to clearly explain the sensitization efficiency of the H<sub>2</sub>BIC ligand ( $\Phi_{sen}$ ), it should be necessary to determine the overall luminescence quantum yields ( $\Phi_{overall}$ ) of **1** and **2** first. In compliance with the method described by Bril *et al.*,<sup>18b,25</sup> the



Fig. 12 Room-temperature excitation (a) and emission (b) spectra for 2 ( $\lambda_{ex}$  = 333 nm) with emissions monitored at approximately 545 nm.

**Table 3** The radiative ( $A_{RAD}$ ) and nonradiative ( $A_{NR}$ ) decay rates,  ${}^{5}D_{0}/{}^{5}D_{4}$  lifetime ( $\tau_{obs}$ ), intrinsic quantum yield ( $\Phi_{Ln}$ ), radiative lifetimes ( $\tau_{RAD}$ ), energy transfer efficiency ( $\Phi_{sen}$ ), and overall quantum yield ( $\Phi_{overall}$ ) for compounds 1–2 in the solid state

Photophysical parameters	Compound 1 (Eu <sup>3+</sup> )	Compound <b>2</b> $(Tb^{3+})$	
$\overline{A_{\rm RAD}~(\rm s^{-1})}$	343		
$A_{\rm NR}$ (s <sup>-1</sup> )	706	_	
$\tau_{\rm obs}$ (µs)	$952 \pm 1$	$1207 \pm 1$	
$\tau_{RAD}$ (µs)	$2911 \pm 1$	$1380 \pm 1$	
$\Phi_{\rm Ln}$ (%)	33	87	
$\Phi_{\rm sen}$ (%)	8	36	
$\Phi_{\rm overall}$ (%)	$2 \pm 1$	$31 \pm 3$	

overall quantum yields of 1 and 2 were respectively estimated to be 2% and 31% through the following expression:

$$\Phi_{\text{overall}} = \left(\frac{1 - r_{\text{st}}}{1 - r_{x}}\right) \left(\frac{A_{x}}{A_{st}}\right) \Phi_{\text{st}}$$
(1)

where  $r_x$  and  $r_{\rm st}$  represent the diffuse reflectance of the compounds (with respect to a fixed wavelength) and the standard phosphor, respectively (Fig. S8, ESI†), and BaSO<sub>4</sub> was used as a reflecting standard to acquire absolute intensity values.  $A_x$  and  $A_{\rm st}$  are the areas under the compounds and the standard emission spectra, respectively.  $\Phi_{\rm st}$  is the quantum yield of the standard phosphor, peprylene (purchased from Aldrich), whose emission spectrum consists of an intense broad band with a maximum at around 580 nm and a constant  $\Phi$  value (98%) for excitation wavelength at 436 nm.<sup>26</sup> The final calculated  $\Phi_{\rm overall}$  value for each sample was taken from the average of three measurement values, and the corresponding test errors were estimated to be  $\pm 10\%$ .<sup>25b,c</sup>

As is well-known, when the internal process in the system (usually treated as a "black box") is not considered explicitly, the overall quantum yield ( $\Phi_{overall}$ ) for a lanthanide compound can be defined as the product of the intrinsic quantum yield of Ln<sup>3+</sup> ion ( $\Phi_{Ln}$ ) and the efficiency of energy transfer from the ligand to Ln<sup>3+</sup> ion ( $\Phi_{sen}$ ),<sup>18a,27</sup> which can be depicted as:

$$\Phi_{\rm overall} = \Phi_{\rm sen} \Phi_{\rm Ln} \tag{2}$$

Hence,  $\Phi_{Ln}$  can be used for calculating the sensitization efficiency of the ligand ( $\Phi_{sen}$ ). Eqn (3) shows the calculating formula of  $\Phi_{Ln}$ , in which  $A_{RAD}$ ,  $A_{NR}$ ,  $\tau_{obs}$  and  $\tau_{RAD}$  correspond to the radiative decay rate, nonradiative decay rate,  ${}^{5}D_{0}/{}^{5}D_{4}$  lifetimes and radiative lifetimes, respectively.

$$\Phi_{\rm Ln} = \left(\frac{A_{\rm RAD}}{A_{\rm RAD} + A_{\rm NR}}\right) = \frac{\tau_{\rm obs}}{\tau_{\rm RAD}}$$
(3)

For Eu<sup>3+</sup> compound 1, the  $A_{RAD}$ ,  $A_{NR}$  and  $\tau_{RAD}$  are finally calculated to be 343 s<sup>-1</sup>, 706 s<sup>-1</sup> and 2911 µs *via* eqn (4), here, the energy of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition (MD) and its oscillator strength are assumed to be constant, and  $A_{MD,0}$  (14.65 s<sup>-1</sup>) represents the spontaneous emission probability of the  ${}^{5}D_{0} \rightarrow$  ${}^{7}F_{1}$  transition *in vacuo*,  ${}^{6c,28}$  *n* (1.5) is the average refractive index of the medium,  ${}^{14b}I_{TOT}/I_{MD}$  represents the ratio of the total area of the corrected Eu<sup>3+</sup> emission spectrum to the area of the  ${}^{5}D_{0} \rightarrow$  ${}^{7}F_{1}$  band. Combined with the measured  ${}^{5}D_{0}$  lifetime value (952 µs),  $\Phi_{Eu}$  of compound 1 is finally determined to be 33%. In comparison with the complicated measurement and calculation of  $\text{Eu}^{3+}$  compound **1**, the intrinsic quantum yield of  $\text{Tb}^{3+}$  ( $\Phi_{\text{Tb}}$ ) in **2** can be directly estimated by means of eqn (5) using the assumption that the decay process at 77 K in deuterated solvents is purely radiative (Fig. S9, ESI†).<sup>29</sup>

$$\Phi_{\rm Tb} = \frac{\tau_{\rm obs\,(298\,K)}}{\tau_{\rm RAD\,(77\,K)}}$$
(5)

The correlative photophysical parameters of compounds 1–2 are presented in Table 3, the lower sensitization efficiency of the ligand ( $\eta_{sen} = 8\%$ ) in 1 indicates that the energy transfer from the first excited triplet state of ligand to the excited  ${}^5D_0$  level of Eu<sup>3+</sup> is not an optimal process. It is also evident from Table 3 that the overall luminescence quantum yield of 2 is much higher than that of 1, though both of them have satisfactory luminescence lifetime. This could be due to the weak sensitization efficiency of the H<sub>2</sub>BIC ligand and smaller intrinsic quantum yield of the Eu<sup>3+</sup> ion in 1. On the other hand, because of the smaller energy gap between the ligand triplet and Tb<sup>3+</sup> ion excited states (4130 cm<sup>-1</sup>), the Tb<sup>3+</sup> compound 2 exhibits good luminescence efficiency with a overall quantum yield of 31% in the solid state, thus rendering it as a promising candidate for use in various photonic applications.

In summary, the coordinated solvent molecules, the conjugation effect of chromophores and/or co-ligands, and the energy gap between the ligand triplet state and the lowest-lying excited state of  $\text{Ln}^{3+}$  ion play cooperative roles in the photoluminescence properties of Ln-MOFs, as evidenced by some monomeric Ln-MOFs (Table S3, ESI<sup>†</sup>).

#### Photoluminescence properties of 4 and 5

Compared with the extensively studied europium and terbium compounds, less effort has been devoted to the investigation of Nd<sup>3+</sup>/Pr<sup>3+</sup>-containing compounds. Actually, they also exhibit good luminescent properties in both visible and near-infrared (800-1400 nm) regions, and especially the advantages of signal transmittance of near-infrared radiation enable widespread application in areas such as laser systems, medical diagnosis and telecommunications.<sup>2c,30</sup> Therefore, the photoluminescence properties of 4 and 5 were investigated in the solid state at room temperature. As shown in Fig. 13, compound 5 displays the characteristic emission bands of Nd<sup>3+</sup> ion in the near-infrared region upon 354 nm radiation excitation: two moderate-intensity emission bands at 869 and 893 nm ( ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ ), a very strong emission band at 1060 nm ( ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ ), and a series of weak bands around 1329 nm ( ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ ). The splitting of the  ${}^{4}F_{3/2}$  $\rightarrow$  <sup>4</sup>I<sub>9/2</sub> transition band is mainly due to the "crystal field effect" of the  $Nd^{3+}$  ion located at a  $C_1$  site.<sup>31</sup> The decay curves are well fitted with a monoexponential function. The lifetime of the excited  ${}^{4}F_{3/2}$  state of Nd<sup>3+</sup> ion at room temperature for 5 was measured to be 1.21  $\mu$ s (Fig. S11, ESI<sup>†</sup>). Because Pr<sup>3+</sup> can show emission lines originating from three different levels (<sup>3</sup>P<sub>0</sub>, <sup>1</sup>D<sub>2</sub> and  ${}^{1}G_{4}$ ) which span the visible and NIR regions, the



Fig. 13 Solid-state emission spectrum for 5 ( $\lambda_{ex} = 354$  nm) in the near-infrared region at room temperature.

luminescence spectrum of Pr<sup>3+</sup> compound is much more complex in comparison to that of other  $Ln^{3+}$  systems, leading to far fewer studies of  $Pr^{3+}$  emission spectra.<sup>32</sup> Fig. 14 depicts the room temperature emission spectrum of 4. Unlike 5, no characteristic emission bands of Pr<sup>3+</sup> in the NIR region were detected, whereas compound 4 exhibits a series of characteristic emission bands for  $Pr^{3+}$  ion in the visible region with a 399 nm excitation source. The emissions at 462 and 479 nm can be respectively assigned to  ${}^{1}I_{6} \rightarrow {}^{3}H_{4}$  and  ${}^{3}P_{1} \rightarrow {}^{3}H_{4}$  transitions. A series of emission bands centered at approximately 499, 545, and 614 nm correspond to the  ${}^{3}P_{0} \rightarrow {}^{3}H_{J}$  (J = 4, 5 and 6, respectively) transitions. The two peaks observed at 597 and 604 nm are attributed to the  ${}^{1}D_{2} \rightarrow$ <sup>3</sup>H<sub>4</sub> transition, and the weak signal with a maxima at 643 nm can be referred to the  ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$  transition.<sup>33</sup> All the observed transitions in Fig. 14 suggest that the triplet state of the H<sub>2</sub>BIC ligand is located in a suitable level and there is enough intramolecular energy transferred from the ligand-centered triplet state to the excited  ${}^{1}D_{2}$ ,  ${}^{3}P_{0}$ , even the higher  ${}^{3}P_{1}$  and  ${}^{1}I_{6}$ levels. Therefore, the energy transfer from the H<sub>2</sub>BIC ligands to the  $Pr^{3+}$  ions is effective.



Fig. 14 Solid-state emission spectrum for 4 ( $\lambda_{ex}$  = 399 nm) at room temperature.

## Conclusions

In this paper, a series of lanthanide frameworks involving 1H-benzimidazole-2-carboxylic acid ligands (1-5) have been hydrothermally synthesized and structurally characterized for the first time. The isostructural compounds 1-5 exhibit 2D (4,4) networks with distorted grids constructed by zwitterionic HBIC ligands with two kinds of unprecedented coordination modes. The thermal analyses indicate that their frameworks exhibit good thermal stability and release a large amount of heat during the decompositions. The detailed optical properties investigations reveal that: 1 and 2 exhibit remarkable lanthanide-centered luminescence emissions in the visible region showing luminescence lifetimes at millisecond order and intrinsic quantum yields of 33% and 87%, respectively; compound 5 emits strong characteristic luminescence in the near-infrared region. The results suggest that the strong chelating-bridging ligand HBIC<sup>-</sup>, which could efficiently occupy the first coordination sphere of the lanthanide ion, is an excellent chromophore for constructing luminescence materials. In addition, the more efficient energy migration  $\left[\Delta E \left({}^{3}\pi\pi^{*} - {}^{5}D_{4}\right) = 4130 \text{ cm}^{-1}\right]$  in **2** gives rise to a larger overall quantum yield of 31% over a poor value of 2% in 1, demonstrating that the suitable energy gap between the ligand triplet state and the lowest-lying excited state of Ln<sup>3+</sup> ion plays a crucial role in the efficient sensitization of Ln<sup>3+</sup> ion emission, and the HBIC<sup>-</sup> ligand is preferable for the sensitization of Tb<sup>3+</sup>centered luminescence.

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