Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2022, **51**, 7420

Four series of lanthanide coordination polymers based on the tetrabromobenzene-1,4-dicarboxylate ligand: structural diversity and multifunctional properties†

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Four series of lanthanide-based coordination polymers (LnCPs), namely $[Ln(Br_4bdc)_{1.5}(MeOH)_3]$ (**1**$_{Ln}$; Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy), $[Ln_2(Br_4bdc)_2(NO_3)_2(MeOH)_4]$ (**2**$_{Ln}$; Ln = Ce, Pr, Nd, Sm), $[Ln(Br_4bdc)(NO_3)(MeOH)]$ (**3**$_{Ln}$; Ln = Gd, Tb, Dy), and $[Ln_2(Br_4bdc)_3(H_2O)_{2.3}(MeOH)_{2.7}]$ (**4**$_{Ln}$; Ln = Gd, Tb, Dy) have been synthesized by reacting hydrated lanthanide(III) salts with tetrabromobenzene-1,4-dicarboxylic acid (H_2Br_4bdc) in different solvents under solvothermal conditions. The structural diversity found in the system mainly resulted from the effects of anions, solvents, and the variation in the ionic radii of the lanthanide(III) ions. Compounds in series **1**$_{Ln}$ feature a two-dimensional (2D) layered structure with **sql** topology based on $\{(Ln(COO)_2)_2(\mu\text{-}COO)_2\}$ secondary building units (SBUs). Compounds in series **2**$_{Ln}$ and **3**$_{Ln}$ comprise, respectively, infinite uniform and alternate chains of $\{Ln(COO)_2\}_n$ SBUs that are assembled into a similar network topology to **1**$_{Ln}$. Meanwhile, compounds in series **4**$_{Ln}$ feature 3D coordination networks of a **pcu** α-Po topological net consisting of binuclear $\{Ln_2(COO)_3\}$ SBUs. The formation of polymeric networks in series **1**$_{Ln}$–**4**$_{Ln}$ is facilitated by the numerous coordination sites of the ligand Br_4bdc^{2-} and the fact that its bromine atoms can participate in the formation of various types of intermolecular interactions. The solid-state photoluminescence studies on Eu- (**1**$_{Eu}$) and Tb- (**1**$_{Tb}$, **3**$_{Tb}$, **4**$_{Tb}$) containing compounds indicate that the Br_4bdc^{2-} ligands can efficiently sensitize Eu^{3+} and Tb^{3+} emission. Notably, such compounds exhibit highly sensitive fluorescence sensing for acetone, water, and Fe^{3+} ions *via* the fluorescence quenching effect. As the representatives of the series, activated **1**$_{Eu}$, **2**$_{Pr}$, **3**$_{Tb}$, and **4**$_{Tb}$ show the maximum CO_2 uptake capacities of 170.4, 273.7, 255.3, and 303.5 $cm^3\ g^{-1}$, respectively, at 50 bar and 298 K with good repeatability of the adsorption–desorption properties. Magnetic studies indicate that the Gd- and Dy-based compounds **1**$_{Gd}$, **1**$_{Dy}$, **3**$_{Gd}$, **3**$_{Dy}$, and **4**$_{Gd}$ show simple paramagnetic behaviours, whereas compound **4**$_{Dy}$ exhibits weak ferromagnetic interactions.

Received 2nd January 2022,
Accepted 13th April 2022

DOI: 10.1039/d2dt00007e

rsc.li/dalton

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†Electronic supplementary information (ESI) available: Additional PL spectra, CO_2 adsorption isotherms, FT-IR spectra, PXRD patterns, UV-vis spectra, and selected bond lengths and angles. CCDC 1940034, 1940036–1940041, 1940047, 1940048, 1940050, 1940051, 1940054–1940057, 1940063, 1940091, 2130091, 2130102 and 2130103. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2dt00007e