Hydrophilic microporous lanthanide-organic frameworks based on 4,4’-biphenyldiacetate: Synthesis, crystal structures and sorption properties

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Fifteen microporous coordination polymers of symmetrical and flexible 4,4’-biphenyldiacetate (bpda2–) with lanthanide(III) cations (Ln1+) of formula \([\text{[Ln}_2(\text{bpda})_3(\text{H}_2\text{O})_n}\text{2H}_2\text{O}]_n\) (Ln = La (1), Ce (2), Pr (3), Nd (4), Sm (5), Eu (6), Gd (7), Tb (8), Dy (9), Ho (10), Er (11), Tm (12), Yb (13), Lu (14), Y (15)), have been synthesized and characterized. Single crystal X-ray diffraction for (1, 3 and 4) in combination with powder X-ray diffraction showed isosstructural compounds with an infinite secondary building unit (SBU). In this SBU, two crystallographically independent lanthanide ions are connected by three carboxylate groups in chelating-bridging mode to zig-zag Ln-carboxylate chains. These chains are assembled by the biphenyl part of the ligand to a 3D network with water molecules in channels with rectangular cross-sections of \(\sim 1.6 \times 3 \text{ Å}^2\). Thermogravimetric analysis indicates complete removal of the water molecules at 150 °C and thermal stability up to 380 °C. Stability studies on compound 1 show no degeneration in crystallinity after refluxing in water or different organic solvents. The dehydrated compound 1 exhibited no N₂ or H₂ uptake at 77 K and no CH₄ or CO₂ uptake at 273 K up to 1 bar. High-pressure (17 bar, 273 K) CO₂ uptake of dehydrated \([\text{[Ln}_2(\text{bpda})_3(\text{H}_2\text{O})_n}\text{2H}_2\text{O}]_n\) corresponded to the formation of \([\text{[Ln}_2(\text{bpda})_3(\text{CO}_2)_n}\text{2H}_2\text{O}]_n\) with about 40% of the adsorbed CO₂ retained upon desorption. Water vapor sorption of activated and hygroscopic \([\text{[Ln}_2(\text{bpda})_3(\text{H}_2\text{O})_n}\text{2H}_2\text{O}]_n\) reformed \([\text{[Ln}_2(\text{bpda})_3(\text{H}_2\text{O})]\text{2H}_2\text{O}]_n\) 4,4’-Biphenyldiacetic acid (H₂bpda) shows blue emission, its europium 6 and terbium 8 compounds show red and weak green luminescence under UV light irradiation, with the bpda2– ligand acting as an antenna ligand for the europium(III) ions.

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1. Introduction

Metal-organic frameworks (MOFs) are porous organic–inorganic hybrid materials built from metal ions or clusters with bridging organic multidentate ligands. Different from amorphous silica gel and active carbons, MOFs feature ordered structures with open frameworks of high crystallinity [1]. This makes them attractive for potential applications such as gas storage [2] and separation [3], catalysis [4] and water adsorption for heat transformation [5]. A special group of MOFs are the so called LOFs (lanthanide-organic frameworks), which combine the luminescence properties of lanthanide(III) ions with organic linkers resulting in promising potential light-emitting materials or luminescent probes [6] and attract thereby growing attention over the last years [7,8]. Lanthanide materials often exhibit sharp and intense luminescence emission lines, as a metal-based luminescence from the mostly trivalent ions [7,9] due to transitions between 4f-states (e.g. red for Eu³⁺, green for Tb³⁺) [10]. In LOFs, the organic ligands not only act as joints between the metals but also as antenna (sensitizers) for the rare earth metals [11]. Compared to MOFs with transition metal ions the construction of novel LOFs is more challenging due to their high coordination numbers (up to 12) and more flexible coordination geometries. The prediction of topologies has made progress in recent years in the area of molecular crystal engineering [12] but it is still very demanding to predict network geometries [13]. LOFs often show high stability towards water [14] or thermal stress [15].

Recently MOFs are investigated in connection with sorption-based environmentally friendly heating and cooling technologies [16–22]. In this technology, a working fluid, typically water, is driven to evaporation by an activated porous material. The heat of evaporation of the working fluid then generates useful cold in a cooling case and heat of adsorption, which is released to the environment, or used when the device is operated as a heat pump. For regeneration of the porous adsorbent, heat from an external source such as a solar collector or waste heat is applied to desorb the...
working fluid. The vapor of the working fluid is adsorbed reversibly. The sorption material should be hydrophilic and water stable. For less water vapor stable porous materials a working fluid like methanol may be used [17,23,24]. The hydrophilicity of lanthanide salts and the potentially sizeable amount of labile water molecules in the coordination sphere of large lanthanide cations prompted us to check on the water vapor sorption of lanthanide-organic frameworks.

In this work, we present structural, stability and luminescence studies of lanthanide(III) coordination polymers based on the easy to synthesize organic linker 4,4′-biphenyldiacetic acid (H2bpda) [25] (Scheme 1a), which has been reported only once for transition metal coordination polymers [26]. Thereby we identify a novel infinite lanthanide-carboxylate chain topology. Although the coordination properties in the dinuclear lanthanum-carboxylate repeating unit are known [27], the infinite elongation, with solely three carboxylate groups in chelating-bridging mode (Scheme 1b) is a novel variant of carboxylate bridging motifs between Ln atoms.

2. Experimental

2.1. Materials and methods

The chemicals used were obtained from commercial sources. No further purification has been carried out. Doubly de-ionized water was used. The H2bpda ligand has been synthesized from 4,4′-bis (chloromethyl)-1,1′-biphenyl according to a previously reported [28] but modified procedure (details in Supp. Info.). Elemental (CHN) analyses were performed on a Perkin Elmer CHN 2400 Analyzer. Electron impact (EI) mass spectra were obtained on a Finnigan MAT TSQ 7000. 1H-NMR spectra were recorded with a Bruker Avance DRX-200 at 290 K. FT-IR spectra were measured in ATR-mode (Platinum ATR-QL, Diamond) on a Bruker TENSOR 37 IR spectrometer in the range of 4000–600 cm⁻¹. The intensity of absorption has been described with the terms strong (s), medium (m) and weak (w). Solid-state fluorescence spectra (2D) were obtained with a FluoroMax spectrometer from Horiba at 293 K. The samples were ground to a powder and pressed to fit in the sample holder. The reflection angle was set to be 60°. Thermogravimetric analyses (TGA) were done with a Netzsch TG 209 F3 Tarsus in the range 25–600 °C, equipped with Al-crucible and applying a heating rate of 1 K min⁻¹. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D2 Phaser powder diffractometer equipped with a flat silicon, low background sample holder using Cu-Kα radiation (λ = 1.5418 Å) with scan speed of 0.2°/step and a step size of 0.02° (20) at 290 K in the range of 2θ = 5–70°. The samples were ground in an agate mortar in air till fine granularity. Simulated PXRD patterns were calculated with CCDC Mercury 3.6 program using the single-crystal data of compound 1. The isostructural character of 1–15 and the phase purity of the bulk products were confirmed by comparing the experimental powder patterns with the simulated powder pattern from the single-crystal dataset of compound 1. Experimental and simulated powder patterns were always found in good agreement with each other (see Figs. S5–S20 for compounds 1–15 in Supp. Info.). A HITACHI S–4800 FE SEM instrument was used for acquiring scanning electron microscopy (SEM) images of gold-coated samples under vacuum. Nitrogen physisorption isotherms (0–1 bar) for BET surface determination were measured with a Quantachrome Nova 4200e at 77 K after activation by degassing at 473 K and 10⁻³ mbar for three hours. Adsorption isotherms for H2 (77 K) and for CO2 and CH4 (273 K) up to 1 bar were measured on a Micromeritics ASAP 2020 gas sorption analyzer. High-pressure adsorption properties for carbon dioxide were recorded with a RUBOTHERM IsoSORB STATIC up to 17 bar and for H2 high-pressure adsorption a Quantachrome iSorbHP1 was used up to 80 bar. All gases were of ultra-pure grades (99.999%). Solvent vapor adsorption properties were measured with a Quantachrome Autosorb iQ MP automated gas sorption analyzer at 293 K using vapor from solvents for analytical purposes grades (min. 99.5% purity).

2.2. Syntheses

For the syntheses, IR and CHN analytical details of compounds 2 and 5–15 see Supp. Info.

2.2.1. [La2(bpda)3(H2O)]2H2O Scheme 1

A colorless solution of La(NO3)3·6H2O (195 mg, 0.45 mmol, 2 eq) in water (5.5 mL) was added to a yellow-orange solution of H2bpda (182 mg, 0.67 mmol, 3 eq) in dimethylacetamide (5.5 mL). The mixture became turbid and was transferred to a Pyrex® tube and sealed with a silicon cap. The tube was placed in a preheated oven at 90 °C for 3 d. After cooling to room temperature the solvent was decanted off, the solid washed three times with dimethylacetamide (5 mL) and three times with water (5 mL). Tiny colorless crystals of compound 1 were obtained after drying at 50 °C overnight in vacuum at 50 mbar. Yield: 215 mg, 85%. IR (ATR, cm⁻¹): 1981 (w), 1902 (w), 1659 (w), 1541 (s), 1527 (s), 1499 (m), 1415 (s), 1392 (s), 1284 (m), 1200 (w), 1153 (w), 1130 (w), 1024 (w), 1006 (w), 951 (w), 937 (w), 871 (m), 856 (w), 802 (m), 782 (w), 746 (m), 739 (m), 696 (m), 652 (m), 629 (m), 561 (w), 514 (w), 508 (w), 501 (w). Elemental analysis, calcd. (%) for C36H18O11La2·2H2O (1136.67 g/mol) C 50.72, H 3.72; for C48H36O12La2·1.5H2O (1127.66 g/mol) C 51.13, H 3.66; found C 51.19, H 3.68. Thus, the observed values on the dried sample correspond to compound 1 containing only about one and a half lattice water molecules per formula unit instead of two as found from single crystal X-ray structure refinement. The phase purity of the bulk product was confirmed by positively matching the experimental powder pattern and the simulated powder pattern of compound 1 (Fig. S5, Supp. Info.).

Compounds 3 and 4 were prepared following the synthetic procedure for 1 using two equivalents of the Ln salt (0.45 mmol) and three equivalents of H2bpda (182 mg, 0.67 mmol).
2.2.2. \([\text{Pr}(_2\text{bpda})_3(_2\text{H}_2\text{O})_n]2\text{H}_2\text{O}]_{n}(3)\)

Tiny colorless crystals were obtained from Pr(NO\(_3\))\(_3\)-5H\(_2\)O (188 mg), Yield: 227 mg, 89%. IR (ATR, cm\(^{-1}\)): 3020 (w), 1646 (w), 1474 (m), 1376 (s), 1152 (m), 1023 (s), 952 (m), 871 (m), 856 (w), 820 (m), 782 (m), 747 (m), 739 (m), 696 (m), 653 (m), 629 (w), 615 (w), 581 (w), 561 (w). Elemental analysis, calcd. (%) for C\(_{60}\)H\(_{48}\)O\(_{34}\)Pr\(_2\)·2H\(_2\)O (1140.67 g/mol) C 50.54, H 3.71; for C\(_{48}\)H\(_{38}\)O\(_{13}\)Pr\(_2\)·1H\(_2\)O (1122.66 g/mol) C 51.35, H 3.59; found: C 51.42, H 3.59.

2.2.3. \([\text{Nd}(_2\text{bpda})_3(_2\text{H}_2\text{O})]2\text{H}_2\text{O}]_{n}(4)\)

Tiny colorless crystals were obtained from Nd(NO\(_3\))\(_3\)-6H\(_2\)O (197 mg), Yield: 227 mg, 89%. IR (ATR, cm\(^{-1}\)): 3020 (w), 1646 (w), 1901 (w), 1701 (w), 1657 (w), 1578 (m), 1526 (s), 1499 (m), 1415 (s), 1394 (s), 1334 (w), 1286 (s), 1200 (w), 1154 (w), 1131 (w), 1109 (w), 1024 (w), 1006 (w), 952 (w), 939 (w), 871 (m), 857 (w), 802 (m), 782 (w), 747 (m), 697 (m), 653 (m), 629 (w), 616 (w), 582 (w), 562 (w). Elemental analysis, calcd. (%) for C\(_{60}\)H\(_{48}\)O\(_{34}\)Nd\(_2\)·2H\(_2\)O (1147.33 g/mol) C 50.25, H 3.69; for C\(_{48}\)H\(_{38}\)O\(_{13}\)Nd\(_2\)·1H\(_2\)O (1129.32 g/mol) C 51.05, H 3.57; found: C 51.19, H 3.59.

2.3. X-ray crystallography

Suitable single crystals placed in viscous oil were carefully selected under a polarizing microscope and mounted in air onto a nylon loop. Accurate unit cell parameters were determined by a least-squares fit of 2\(\theta\) values and intensity data were measured on a Bruker APEX DUO with APEX II CCD area detector equipped with microfocus sealed tube, Mo-K\(_\alpha\) radiation. Suitable single crystals placed in viscous oil were carefully selected under a polarizing microscope and mounted in air onto a nylon loop. Accurate unit cell parameters were determined by a least-squares fit of 2\(\theta\) values and intensity data were measured on a Bruker APEX DUO with APEX II CCD area detector equipped with microfocus sealed tube, Mo-K\(_\alpha\) radiation.

2.3.1. \([\text{La}(_2\text{bpda})_3(_2\text{H}_2\text{O})]2\text{H}_2\text{O}]_{n}(5)\)

The asymmetric unit consists of two half-occupied crystallographically independent lanthanum(III) cations, one and a half symmetry independent bpda-ligands, a half-occupied aqua ligand (with O7 Fig. 2a) and one crystal water molecule. Atom La1 sits on a 2-fold rotation axis and La2 on an inversion center. The “half”-ligand with donor atoms O5 and O6 sits on the special position of an inversion center between the C\(_6\) rings of the biphenyl system. This gives a formula unit of two lanthanum(III) cations with three bpda anions plus an aqua ligand and two crystal water molecules. The adjacent lanthanum(III) ions are connected by three bridging oxygen atoms from three carbonyl groups with a La-La distance of 4.013 Å. Each of these three carbonyl groups is chelating or \(\eta^2\)-bound to one of the La atoms and bridging or \(\eta^1\)-bound towards the other La atom through one of the carbonyl oxygen atoms.

The two lanthanum(III) cations differ in their coordination numbers and coordination spheres (cf. Scheme 1). La1 shows coordination number nine by the coordination of eight oxygen donors from six carbonyl groups and one oxygen atom from a water molecule (Fig. 2b). Two of the six carbonyl groups on La1 are chelating (\(\eta^1\)) and four are coordinated through a bridging oxygen atom (\(\eta^1\)). The coordination polyhedron of La1 is unsymmetrical and cannot be classified topologically (Fig. 2c). La2 shows elongated square-bipyrimal coordination (Fig. 2d) by the coordination of ten oxygen donors from six carbonyl groups (Fig. 3b). Four of the six carbonyl groups on La2 are chelating (\(\eta^1\)) and two are coordinated through a bridging oxygen atom (\(\eta^1\)) (see also Scheme 1b). The La-O (carboxylate) bond distances range from 2.475(4) to 2.763(6) Å and the La-OH\(_2\) (aqua ligand) bond is 2.413(1) Å. These values are in good agreement with previously reported nine- or ten-coordinated lanthanum(III) complexes with oxygen donor ligands [33]. Selected bond distances are presented in Table 2.

Overall the bpda ligand bridges between four La atoms with bis-tridentate chelating-bridging (\(\eta^1\)-\(\eta^1\)) coordination behavior in trans-configuration (of the carbonylate groups) towards the four coordinated La atoms (cf. Scheme 1b). In the only previous struc-
Crystallographic data and structural refinements for compounds 1, 3 and 4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Data set</th>
<th>CCDC No.</th>
<th>Empirical formula</th>
<th>Mg mol⁻¹</th>
<th>Crystal size (mm³)</th>
<th>T (K)</th>
<th>d (°) (completeness)</th>
<th>h; k; l range</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>μ (μ)</th>
<th>V (Å³)</th>
<th>Z</th>
<th>Dcalc (g cm⁻³)</th>
<th>F(000)</th>
<th>Max./min. transmission</th>
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<tbody>
<tr>
<td>1</td>
<td>bpda-La</td>
<td>1485624</td>
<td>C₈H₁₂O₆La₂</td>
<td>1132.60</td>
<td>0.08 x 0.01 x 0.01</td>
<td>30</td>
<td>22.2–21.18 (99.5%)</td>
<td>±31; ±10; ±14</td>
<td>30.346(3)</td>
<td>10.0323(10)</td>
<td>14.3326(14)</td>
<td>97.694(6)</td>
<td>4324.1(7)</td>
<td>4</td>
<td>1.740</td>
<td>2240</td>
<td>0.7447/0.6872</td>
</tr>
<tr>
<td>3</td>
<td>bpda-Pr</td>
<td>1485625</td>
<td>C₈H₁₂O₆Pr₂</td>
<td>1136.60</td>
<td>0.05 x 0.002 x 0.002</td>
<td>120</td>
<td>21.7–20.31 (98.3%)</td>
<td>±35; ±11; ±16</td>
<td>30.231(5)</td>
<td>9.875(2)</td>
<td>14.191(2)</td>
<td>97.128(10)</td>
<td>4203.7(14)</td>
<td>4</td>
<td>1.796</td>
<td>2256</td>
<td>0.7451/0.6512</td>
</tr>
<tr>
<td>4</td>
<td>bpda-Nd</td>
<td>1485626</td>
<td>C₈H₁₂O₆Nd₂</td>
<td>1142.25</td>
<td>0.01 x 0.002 x 0.002</td>
<td>120</td>
<td>25.5–18.37 (98.6%)</td>
<td>±33.2; ±11; −15.14</td>
<td>30.174(4)</td>
<td>9.9839(15)</td>
<td>14.099(2)</td>
<td>97.353(6)</td>
<td>4212.5(11)</td>
<td>4</td>
<td>1.801</td>
<td>2260</td>
<td>0.7449/0.6848</td>
</tr>
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</table>

Table 1

Crystallographic data and structural refinements for compounds 1, 3 and 4.

In this compound each zig-zag chain can be seen as an infinite one-dimensional SBU. The sole chelating-bridging (η²:η¹) coordination of the carboxylate groups to lanthanide atoms in this chain shows a novel variant of known Ln-carboxylate bridging motifs. The (η²:η¹) coordination was known in the infinite one-dimensional SBU of La with the o-toluic acetate ligand [27,34] which, however, additionally include an (η¹:η¹) bridging-mode for the carboxylates, depicted between La1 and La3 in Fig. S3 (Supp. Info.) [34b].

The unit cell packing of 1 can be seen as a typical separation [35] of the hydrophilic lanthanum-carboxylate zig-zag chains with the aqua ligand on La1 and the crystal water molecules and the hydrophobic biphenyl rings (sandwiched between the hydrophilic layers) (Fig. 3). The lanthanum–carboxylate zig-zag chains with the aqua ligand on La1 and the crystal water molecules are arranged in layers parallel to the bc plane. So is the biphenyl moiety of the bpda linker. Hydrophilic and hydrophobic bc layer then alternate along a (Fig. 3).

The crystal water molecules and aqua ligands reside in channels along the c direction (Fig. S2b, Supp. Info., Fig. 3b). Removal of the water molecules and aqua ligands should give rise to channels with rectangular cross-sections of approximately 1.6 x 3 Å² (taking into account the van der Waals radii of surrounding atoms) depicted in Fig. S4 (Supp. Info.). Elemental (CH) analyses indicated that 1.5–2 crystal water molecules (out of 2) were already removed after drying at 50 °C overnight in vacuum at 50 mbar. The coordinated and crystal water molecules can be fully removed through heating the sample at 150 °C and ambient pressure (Fig. 4 for TGA) with retention of crystallinity and network structure (Fig. 5).

3.3. Stability and analysis

Prior to thermogravimetric analysis (TGA), the samples were dried at 50 °C overnight in vacuum at 50 mbar, followed by storing...
at ambient conditions under air. The TGA profiles of all compounds, 1–15, exhibited a weight loss of 3.6–5.3% in the first step (25–150 °C), which corresponds to the loss of one to three water molecules per formula unit (Fig. 4, Figs. S38–S52, Supp. Info.). This is in good agreement with the crystal structure, which indicates the presence of one terminal coordinated water molecule and two lattice water molecules. Complete dehydration could be achieved by drying sample of 1 at 200 °C and 10–3 mbar for three hours. Such an activated sample (activ. in Fig. 4) was then immediately subjected to TG analysis and showed essentially no weight loss up to 380 °C. When the fully dehydrated sample was stored under ambient air with 60–70% humidity, the water uptake could be followed by the mass gain with time. After 10 min already 1 mol water/mol MOF was adsorbed again. The subsequent water uptake occurs slowly (Fig. S54, Supp. Info.).

In the TG analyses, after the water removal a slight weight loss was observed up to ∼380 °C. Then an abrupt weight loss above 380 °C corresponds to the decomposition of the compounds, as exemplarily depicted in Fig. 4 for compounds 1, 3 and 4. No attempt was made to identify the decomposition products. The remaining mass percent at 600 °C indicates the existence of miscellaneous decomposition products. It is known that the final decomposition of lanthanide organic compounds to Ln2O3 occur at higher temperatures up to 1200 °C [36].

The lanthanum compound 1 was used as an example for the stability studies against water and other solvents and degassing of the [Ln2(bpda)3]n compounds (Fig. 5). The powder X-ray diffraction (PXRD) pattern for the sample heated (activated) at 200 °C for three hours under high vacuum (10−3 mbar) is identical to that of the as-synthesized sample, which indicates that the loss of the lat-
tice water and coordinated water molecules does not lead to an observable phase transformation (Fig. 5, details in Fig. S20, Supp. Info.). The crystalline compounds \(1 \text{–} 15\) are insoluble in water or common organic solvents such as dimethylacetamide, ethanol or dimethylformamide. Refluxing a sample of \(1\) for two hours in different organic solvents and neutral water did not show any variations or just slightly broader reflections in the powder pattern (Fig. 5, Figs. S21 and S22, Supp. Info.). Also after water sorption of the activated sample the PXRD matches the simulation for \([\text{La}_2(-\text{bpda})_3(\text{H}_2\text{O})]\)\(_2\text{H}_2\text{O}\).n\((1)\).

### 3.4. Gas and vapor adsorption

The gas sorption properties were explored exemplarily for the lanthanum-compound \(1\). The crystal structure indicates that the cross sections of the water-depleted channels (~1.6 × 3 Å²) may be too small for most gases and solvent molecules. Yet, through the flexible ligand there might be the possibility of increasing pore size akin to the ‘breathing’ effect of MIL-53 which exists in a large-pore and water-filled small pore structure [37]. Also, the [Ni\(_6(4,4′-\text{bipy})_3(\text{NO}_3)_3\)]\(_n\) - 2EtOH network has only very small channels with dimension of ca. 1.1 Å × 1.1 Å [38,39]. The two ethanol guest molecules per formula unit are rather located in cavities ("zero-dimen-

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**Table 2**

Selected bond distances for [La\(_2(-\text{bpda})_3(\text{H}_2\text{O})]\)\(_2\text{H}_2\text{O}\).a

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
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<tr>
<td>La1–O1</td>
<td>2.575(4)</td>
</tr>
<tr>
<td>La1–O2</td>
<td>2.602(5)</td>
</tr>
<tr>
<td>La1–O4(^{\text{iii}})</td>
<td>2.499(6)</td>
</tr>
<tr>
<td>La1–O5</td>
<td>2.477(5)</td>
</tr>
<tr>
<td>La1–O7</td>
<td>2.413(11)</td>
</tr>
<tr>
<td>La2–O1</td>
<td>2.475(4)</td>
</tr>
<tr>
<td>La2–O2</td>
<td>2.554(6)</td>
</tr>
<tr>
<td>La2–O3(^{\text{iii}})</td>
<td>2.641(5)</td>
</tr>
<tr>
<td>La2–O4(^{\text{iii}})</td>
<td>2.763(6)</td>
</tr>
</tbody>
</table>

*Selected bond angles are given in Table S4 in Supp. Info. Symmetry transformations: (ii) = –x + 1/2, y + 1/2, –z + 1.5; (iii) = x + 1/2, y + 1/2, z.*

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**Scheme 2.** Known coordination modes of bpda with different metal atoms [26].

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**Fig. 3.** (a) and (b) chain connectivity along the a and b axis in the 3D coordination network of \(1\) (crystal water molecules are not shown in the 3D network).

**Fig. 4.** Thermogravimetric analysis (TGA) curves of compound \(1, 3, 4\) and an activated sample of \(1\) (activ.). (For detailed mass difference assignments see Figs. S38–S52, Supp. Info.)

**Fig. 5.** Powder X-ray diffractograms (PXRDs) for compound \(1\) as-synthesized (a.s.), after refluxing in water for two hours (reflux), after degassing at 200 °C in high vacuum for three hours (activated) and after water adsorption experiment (sorption) in comparison with the simulated diffractogram (sim) which based on the X-ray data refinement of compound \(1\) (for details see Figs. S20–S22, Supp. Info.).
adsorbed carbon dioxide was retained (16 mg) in to 0.4 mol CO₂ per formula unit of [La₂(bpda)₃] (Fig. 6). We sug-
preparative-scale sample of compound 1 range up to 1 bar. For testing of pore dilatation, we also examined
hydrogen and carbon dioxide adsorption properties in the pressure
framework stability. So, we examined the nitrogen, methane,
hydrogen and carbon dioxide adsorption properties in the pressure
range up to 1 bar. For testing of pore dilatation, we also examined
the high-pressure adsorption properties of hydrogen (100 bar) and
carbon dioxide (17 bar). Before the sorption measurements a
preparative-scale sample of compound 1 was heated at 200 °C
under vacuum for three hours, causing complete dehydration (cf.
TG analysis of 1 that indicated complete dehydration at 150 °C
and ambient pressure, “activ.” in Fig. 4).

The adsorption measurements of nitrogen (at 77 K), methane
and carbon dioxide (at 273 K) up to 1 bar did not show any appreciable gas uptake. Hence, no BET surface area could be derived from very low N₂ adsorption. Also in subsequent low- and high-pressure H₂ adsorption measurements (at 77 K) we did not observe a gas uptake.

At the cryogenic temperature of 77 K, diffusion of N₂ and similar sized molecules into small micropores is very slow. In other words, with slow thermal motion at 77 K the N₂ molecules will statistically only seldom approach the small pore aperture with the correct orientation for penetration, that is, in line with its molecule axis. Diffusion limitations at this temperature influence adsorption in micropores (particularly in pores smaller than 7 Å diameter). Such materials would require time-consuming N₂ adsorption measurements and may still have under-equilibration of measured adsorption isotherms, which will give lower than real surface areas. Such errors can usually be avoided by using CO₂ adsorption analysis at 273 K. The saturation pressure of CO₂ at 0 °C is very high (~26141 Torr), so that low relative pressure measurements for the micropore analysis are achieved in the range of moderate absolute pressures (1–760 Torr). At 273 K, CO₂ molecules can more easily access small micropores than N₂ at 77 K [41]. The kinetic diameters of the used gases were 3.64 Å for N₂, 3.3 Å for CO₂, 2.9 Å for H₂ and 3.8 Å for CH₄. For activated 1 it still required higher CO₂ pressure to enforce a significant CO₂ uptake. The carbon dioxide high pressure adsorption measurement up to 17 bar gave a gas uptake of 39 mg CO₂ per gram compound 1 (corresponding to 1 mol CO₂ per formula unit of [La₂(bpda)₃], that is, [[La₂(bpda)₃]·CO₂]n) (Fig. 6). In the degassing process to 0 bar over 40% of the adsorbed carbon dioxide was retained (16 mg) in 1, corresponding to 0.4 mol CO₂ per formula unit of [La₂(bpda)₃] (Fig. 6). We suggest that the high affinity of the coordinatively unsaturated open metal site on La₁ (to which a water molecule was coordinated) to oxygen atoms leads to chemisorption, that is, coordination of carbon dioxide molecules to every second La₁ atom. Thereby, we also explain the low carbon dioxide uptake up to 1 bar (at 273 K). The CO₂ molecules can block the pore mouths by chemisorption to La₁ and thereby prevent a further access of carbon dioxide molecules at low pressure.

The same retention effect could be observed in solvent vapor ad- and desorption measurements. For methanol and water vapor, activated 1 shows an uptake of 20 cm³/g MeOH (28.5 mg/g at p/p₀ = 0.9) and 63 cm³/g H₂O (51 mg/g at p/p₀ = 0.9), corresponding to ~1 mol MeOH and 3 mol H₂O per formula unit of [La₂(bpda)₃] (M = 1100 g/mol), respectively (Fig. 7). Desorption at 10⁻² mbar and 293 K retains over 80% of the adsorbed methanol molecules and 50% of the adsorbed water molecules remain in [La₂(bpda)₃]. Thus, high vacuum and heating is required to remove the coordinated molecules, analogous to the activation step at 200 °C.

The small methanol uptake relative to water is due to the larger molecule size. The methanol molecules will coordinate to the unsaturated La₁ site with its methyl group occupying the in-between space (the space previously taken by the crystal water molecule).

3.5. Luminescence properties

The solid-state luminescence spectra of the free ligand, H₂bpda and visible-light emitting europium- and terbium-compounds, 6 and 8, were recorded at room temperature and are depicted in Fig. 8a. H₂bpda exhibited a broad emission band with the peak maximum at around 434 nm, when excited at 365 nm, which imparts a blue color (Fig. 8b). The molar absorptivity values of Ln³⁺ absorption transitions are very low (<100 L mol⁻¹ cm⁻¹). The europium compound 6 exhibited the emission band of the ligand and the characteristic emission peaks of europium(III) ion (at 579, 592, 616, 651 and 698 nm) when excited at the ligand excitation band (λex = 370 nm). This indicates that the sensitization of the Eu³⁺ ions via the excited states of the ligand are efficient and that the bpda²⁻ ligand acts as an antenna ligand for europium(III) ions. The most intense transition is observed at 616 nm, corresponding to the hypersensitive ⁵D₀ → ⁷F₂ transition, which is responsible for the red color of compound 6, under UV irradiation (Fig. 8b). The peaks at 579, 592, 651 and 698 nm result from the deactivation of the excited ⁵D₀ state to the ground ⁷F₀, ⁷F₁, ⁷F₃ and ⁷F₄ levels, respectively (see Fig. 5 in Supp. Info. for assignment).

A close match between the energy of the ligand triplet state and the energy of the receiving 4f level of the lanthanide ion is not desirable, because energy back transfer from the lanthanide ion to the triplet state of the ligand can occur. The main resonance level, ⁵D₀ of Eu³⁺ ion is situated at 17250 cm⁻¹ (579 nm), which may be energetically compatible for energy transfer from blue or green emitting ligands like H₂bpda. Whereas, the resonance level of Tb³⁺ ion is situated at 20430 cm⁻¹ (489 nm), so the back energy transfer from the metal to ligand may be present in this case [42].

When excited at the ligand excitation band (λex = 370 nm), the emission peaks of terbium(III) ions in compound 8 are found to overlap with the strong ligand emission band, implying that the ligand bpda²⁻ is a poor sensitizer for terbium(III) ions. The peaks...
We have presented fifteen novel isostructural 3D lanthanide metal–organic frameworks \([\text{Ln}_2(\text{bpda})_3(\text{H}_2\text{O})_2\text{H}_2\text{O}]\) with 4,4’-biphenyldiacetate (bpda\(^{2-}\)) linker. Despite its flexibility, the linker shows only one coordination motif towards Ln\(^{3+}\). The triply chelating-bridging (\(\eta^1:\eta^1::\eta^1\)) coordination of three carboxylate groups between two lanthanide atoms gives a zig-zag chain as an infinite one-dimensional SBU. The triply-bridging (\(\eta^1::\eta^1::\eta^1\)) coordination of three carboxylate groups is a variant of previous infinite one-dimensional Ln-carboxylate SBUs which also featured simple bridging (\(\eta^1::\eta^1\)) carbonate groups. The 3D metal–ligand arrangement gives a channel structure with coordinated aqua ligands and lattice water molecules in these channels. The water molecules in these channels can be reversibly removed in vacuum without observing a phase transition by powder X-ray diffraction. The dehydrated material \([\text{Ln}_2(\text{bpda})_3]\) (activated 1) is hygroscopic and shows a water uptake of about 2.5 mol/mol MOF under ambient air (about 60–70% humidity). Complete water uptake to 3.0 mol/mol MOF as found in the crystal structures could be achieved at 100% humidity during water sorption experiments. The small channel cross-section of \(\sim 1.6 \times 3\) \(\text{Å}^2\) prevents gas adsorption at low pressures up to 1 bar. CO\(_2\) adsorption was enforced in activated 1 at pressures up to 17 bar to a composition of \([\text{Ln}_2(\text{bpda})_3] \cdot \text{CO}_2\) and about 40% of the adsorbed CO\(_2\) was retained upon desorption. Furthermore the framework is robust against different solvents and thermal stress.

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Appendix A. Supplementary data

CCDC 1485624–1485626 contains the supplementary crystallographic data for 1, 3 and 4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2017.01.038.

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