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

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Abstract

Fifteen microporous coordination polymers of symmetrical and flexible 4,4'-biphenyldiacetate (bpda²⁻) with lanthanide(III) cations (Ln³⁺) of formula {[Ln₂(bpda)₃(H₂O)]·2H₂O}_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 isostructural 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 ~1.6 x 3 Å². 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 [Ln₂(bpda)₃]_n corresponded to the formation of {[Ln₂(bpda)₃]·CO₂}_n with about 40% of the adsorbed CO₂ retained upon desorption. Water vapor sorption of activated and hygroscopic [Ln₂(bpda)₃]_n reformed {[Ln₂(bpda)₃(H₂O)]·2H₂O}_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.

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 [16,17,18,19,20,21,22]. 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 ad/desorbed 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 a structural, stability and luminescence study of lanthanide(III) coordination polymers based on the easy to synthesize organic linker 4,4'-biphenyldiacetic acid (H_2 bpda) [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.



Scheme 1 Structure of (a) lanthanide (Ln)-4,4' biphenyldiacetate (bpda) showing the coordination mode (μ - κ O,O':O') and (b) dinuclear repeating unit as part of infinite zig-zag chain with the Ln

coordination numbers and coordination modes as well as carboxylate bridging mode observed in compounds **1-15**.

2. Experimental Section

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 to 600 °C, equipped with Alcrucible and applying a heating rate of 1 K min¹. 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-K_a radiation ($\lambda = 1.5418$ Å) with scan speed of 0.2 s/step and a step size of 0.02° (20) at 290 K in the range of $2\theta = 5-70^{\circ}$. The samples were ground in an agate mortar in air till fine granularity. Simulated P-RD patterns were calculated with CCDC Mecury 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 power patters were always found in good agreement with each other (see Figure 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}_n (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 eg) 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), 614 (w), 581 (w), 561 (w). Elemental analysis, calcd. (%) for C48H38O13La22H2O (1136.67 g/mol) C 50.72, H 3.72; for C48H38O13La21.5H2O (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 patterns of compound **1** (Figure 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 H_2 bpda (182 mg, 0.67 mmol).

2.2.2. {[$Pr_2(bpda)_3(H_2O)$]·2H₂O}_n (3)

Tiny colorless crystals were obtained from $Pr(NO_3)_3 \cdot 5H_2O$ (188 mg). Yield: 227 mg, 89 %. IR (ATR, cm⁻¹): 1980 (w), 1903 (w), 1664 (w), 1574 (m), 1525 (s), 1499 (m), 1416 (s), 1393 (s), 1286 (s), 1200 (w), 1154 (w), 1131 (w), 1023 (w), 1006 (w), 952 (m), 939 (w), 871 (w), 856 (w), 802 (m), 782 (w), 747 (m), 739 (m), 696 (m), 653 (m), 629 (w), 615 (w), 581 (w), 561 (w). Elemental analysis, calcd. (%) for $C_{48}H_{38}O_{13}Pr_2 \cdot 2H_2O$ (1140.67 g/mol) C 50.54, H 3.71; for $C_{48}H_{38}O_{13}Pr_2 \cdot 1H_2O$ (1122.66 g/mol) C 51.35, H 3.59; found: C 51.42, H 3.57.

2.2.3. {[Nd₂(bpda)₃(H₂O)] \cdot 2H₂O}_n (4)

Tiny colorless crystals were obtained from Nd(NO₃)₃·6H₂O (197 mg). Yield: 227 mg, 89 %. IR (ATR, cm⁻¹): 1982 (w), 1961 (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 (w), 857 (w), 802 (m), 782 (w), 747 (m), 697 (m), 653 (m), 629 (w), 616 (w), 582 (w), 562 (w). Elemental analysis, calcd. (%) for $C_{48}H_{38}O_{13}Nd_2 \cdot 2H_2O$ (1147.33 g/mol) C 50.25, H 3.69; for $C_{48}H_{38}O_{13}Nd_2 \cdot 1H_2O$ (1129.32 g/mol) C 51.05, H 3.57; found: C 51.19, H 3.59.

2.3. X-ray crystallography

CCF

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 leastsquares fit of 20 values and intensity data were measured on a Bruker APEX DUO with APEX II CCD area detector equipped with microfocus sealed tube, Mo-Ka radiation ($\lambda = 0.71073$ Å) and multilayer mirror monochromator at 100 K. The intensities were corrected for empirical absorption based on multi-scan technique using the SADABS program [29]. The structures were solved by direct methods and refined by full-matrix least-squares fitting on F2 by SHELX 97 [30]. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters. Aromatic hydrogen atoms (CH = 0.95 Å) and CH₂ (CH = 0.99 Å) were refined using a riding model (AFIX 43, AFIX 23, respectively) with $U_{iso}(H) = 1.2U_{eq}(C)$. The unique hydrogen atom on the solvent water molecule (oxygen atom on the two-fold axis) which is coordinated to La1 was found and refined using DFIX O-H bond length restraints with $U_{iso}(H) = 1.2U_{eq}(O)$. The hydrogen atoms of the crystal water molecules could not be found. Crystallographic data are summarized in Table 1. For the X-ray structure analyses we picked the largest crystals we could locate in the compounds. Even these were of very small size (cf. Table 1). It is known that very small crystals diffract weaker than larger crystals, resulting in lower data quality and subsequent problems during refinement [31]. Some of the checkcif alerts are due to the small crystal size, e.g., poor data/parameter ratio.

Compound	1	3	4
Data set	bpda-La	bpda-Pr	bpda-Nd
CCDC no.	1485624	1485625	1485626
Empirical formula	C ₄₈ H ₃₈ O ₁₅ La ₂	C ₄₈ H ₃₈ O ₁₅ Pr ₂	C ₄₈ H ₃₈ O ₁₅ Nd ₂
M/g mol ⁻¹	1132.60	1136.60	1142.25
Crystal size/mm ³	0.08 x 0.01 x	0.05 x 0.002 x	0.01 x 0.002 x
	0.01	0.002	0.002
Exposure time (s)	30	120	120
Temperature/K	150(2)	100(2)	100(2)
θ range/° (completeness)	2.22-21.18	2.17-20.31	2.55-18.37
	(99.5%)	(98.3%)	(98.6%)
h; k; l range	±31; ±10; ±14	±35; ±11; ±16	-33,32; ±11; -
			15,14
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C 2/c (no. 15)	C 2/c (no. 15)	C 2/c (no. 15)
a/Å	30.346(3)	30.231(5)	30.174(4)
b/Å	10.0323(10)	9.875(2)	9.9839(15)
c/Å	14.3326(14)	14.191(2)	14.099(2)
β/°	97.694(6)	97.128(10)	97.353(6)
V/Å ³	4324.1(7)	4203.7(14)	4212.5(11)
Z	4	4	4
D _{calc} /g cm ^{−3}	1.740	1.796	1.801
μ (Mo Kα)/mm ⁻¹	2.022	2.366	2.513
F(000)	2240	2256	2260
Max./min. transmission	0.7447/0.6872	0.7451/0.6512	0.7449/0.6848
Reflections collected	31453	16838	18788
Independent reflect. (R _{int})	2539 (0.1036)	3521 (0.1257)	3092 (0.1249)
Data/restraints/parameters	2539/2/300	3521/2/299	3092/2/298
Max./min. Δρ/e Å ^{-3a}	0.623/-0.538	0.845/-0.829	0.641/-0.620
$R_1/wR_2 [I>2\sigma(I)]^{b}$	0.0343/0.0726	0.534/0.0876	0.0492/0.0832
R ₁ /wR ₂ (all data) ^b	0.0545/0.0818	0.1083/0.1357	0.1007/0.1102
Goodness-of-fit on F ^{2c}	1.034	1.049	0.998

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

^a Largest difference peak and hole.

^b $R_1 = [\sum(||F_o| - |F_c||)/\sum|F_o|]; wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}.$

^c Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

3. Results and Discussion

3.1. Synthesis

The tris(4,4'-biphenyldiacetato)dilanthanum(III) compounds have been obtained in high yields as microcrystalline powders through solvothermal syntheses from two equivalents of lanthanide(III) nitrates or chlorides with three equivalents of 4,4'-biphenyldiacetic acid in a 1:1 (v:v) mixture of water and dimethylacetamide. All compounds are visually identical tiny needle-shaped crystals, which appear yellowish in bulk material, except for the holmium and erbium compounds which are orange and pink, respectively. The reproducibility of the syntheses was tested by repeated preparations also with different stoichiometric ratios. Scanning electron microscopy (SEM) images of the bulk material show about 20 µm large hedge-hog-like spheres, consisting of radially-grown needle shaped crystals (Figure S1, Supp. Info.). The IR spectra of the compounds are similar (Figure S23-S37, Supp. Info.). The absence of characteristic carboxyl bands at 907, 1247, 1422 and 1720 cm⁻¹ for H₂bpda indicates the complete deprotonation and metal coordination of bpda²⁻. The strong absorption bands between 1280 and 1550 cm⁻¹ indicate coordinated carboxylate groups [32]. The compounds contain water as aqua ligands and crystal water as was evident from elemental analysis and X-ray structure determination. Drying at 50 °C overnight in vacuum at 50 mbar removes part of the crystal water as evidenced from the difference of the X-ray crystallographically found water and the CH analysis.

3.2. Crystal structure

The lanthanum, praseodymium and neodymium compounds **1**, **3** and **4**, respectively, were structurally characterized using single-crystal X-ray analyses. For the remaining compounds, the single crystals were too small and the isostructural nature of all compounds was established by powder X-ray diffraction analyses (Figure 1). From single-crystal X-ray analysis the isostructural compounds are formulated empirically as 3D coordination polymers of formula $\{[Ln_2(bpda)_3(H_2O)]\cdot 2H_2O\}_n$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y; bpda = 4,4'-biphenyldiacetate dianion). The structure of compound **1** is described here in detail (compounds **3** and **4** are isostructural).





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 Figure 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 C₆ 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 carboxyl groups with a La-La distance of 4.013 Å. Each of these three carboxyl groups is chelating or η^2 -bound to one of the La atoms and bridging or η^1 -bound towards the other La atom through one of the carboxyl 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 carboxylate groups and one oxygen atom from a water molecule (Figure 2b). Two of the six carboxylate groups on La1 are chelating (η^2) and four are coordinated through a bridging oxygen atom (η^1). The coordination polyhedron of La1 is unsymmetrical and cannot be classified topologically (Figure 2c). La2 shows elongated square-bipyramidal coordination (Figure 2d) by the coordination of ten oxygen donors from six carboxylate groups (Figure 3b). Four of the six carboxylate groups on La2 are chelating (η^2) and two are coordinated through a bridging oxygen atom (η^1) (see also Scheme 1b). The La-O (carboxylate) bond distances range from 2.475(4) to 2.763(6) Å and the La-OH₂ (aqua ligand) bond is 2.413(11) 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.



Figure 2 (a) Extended asymmetric unit in **1** with (b-d) coordination environment around the crystallographically independent lanthanum(III) atoms (50% thermal ellipsoids, except for O7 with 20%). Water of crystallization is not shown for clarity. Symmetry codes: i = -x+1, y, -z+3/2; ii = -x+1/2, y+1/2, -z+1.5; iii = x+1/2, y+1/2, z; iv = -x+1, -y+1, -z+1; v = -x+1/2, -y+1/2, -z+1; vi = x-1/2, y-1/2, z; vii = -x+3/2, -y+1/2, -z+1; viii = x+1/2, y-1/2, z. Selected bond distances and angles are given in Table S4 in Supp. Info. For bond lengths, see Table 2 (for bond angles see Table S4 in Supp. Info.).

La1—01	2.575(4)	La2—O1	2.475(4)
La1—02	2.602(5)	La2—O3"	2.554(6)
La1—O4"	2.499(6)	La2—O4 ⁱⁱⁱ	2.641(5)
La1—05	2.477(5)	La2—O5	2.763(6)
La1—07	2.413(11)	La2—O6	2.514(5)

Table 2 Selected bond distances for [La₂(bpda)₃(H₂O)]·2H₂O ^a

^a 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.

Overall the bpda ligand bridges between four La atoms with bis-tridentate chelating-bridging (η^2 : η^1) coordination behavior in trans-configuration (of the carboxylate groups) towards the four coordinated La atoms (cf. Scheme 1b). In the only previous structural investigation of metal-bpda compounds [26] the ligand shows trans-configuration, but coordination of the individual carboxyl groups differ from solvent hydrogen bonding up to penta-dentate behavior towards transition metals in different coordination environments (cf. Scheme 2).



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

The lanthanum atoms and the chelating-bridging carboxyl groups of bpda form infinite zigzag chains along the crystallographic c direction, with La1 atoms occupying the vertex positions (Figure S2a, Supp. Info.). The aqua ligand and the crystal water molecules connect adjacent chains along the b direction by hydrogen bonding (Figure S2b, Supp. Info.).

Along the *a* direction, the bpda linkers connect each chain to four surrounding chains giving a 3D coordination network (Figure 3). In this compound each zig-zag chain can be seen as an infinite one-dimensional SBU. The sole chelating-bridging (η^2 : η^1) coordination of the carboxylate groups to lanthanide atoms in this chain shows a novel variant of known Ln-carboxylate bridging motifs. The (η^2 , η^1) coordination was known in the infinite one-dimensional SBU of La with the o-toluic acetate ligand [27,34] which, however, additionally include an (η^1 : η^1) bridging-mode for the carboxylates, depicted between La1 and La3 in Figure S3 (Supp. Info.) [34b].



Figure 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)

The unit cell packing of **1** can be seen as a typical separation [35] of the hydrophilic lanthanumcarboxylate zig-zag chains with the aqua ligand on La1 and the crystal water molecules and the hydrophobic biphenyl rings (sandwiched between the hydrophilic layers) (Figure 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* (Figure 3).

The crystal water molecules and aqua ligands reside in channels along the *c* direction (Figure S2b, Supp. Info., Fig. 3b). Removal of the water molecules and aqua ligands should give rise to channels with rectangular cross-sections of approximately $1.6 \times 3 \text{ Å}^2$ (taking into account the van der Waals radii of surrounding atoms) depicted in Figure S4 (Supp. Info.). Elemental (CH) analyses indicated that 1.5 to 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 (Figure 4 for TGA) with retention of crystallinity and network structure (Figure 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 (Figure 4, Figure 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 (Figure S54, Supp. Info.).



Figure 4 Thermogravimetric analysis (TGA) curves of compound **1**, **3**, **4** and an activated sample of **1** (activ.). (For detailed mass difference assignments see Figure S38-S52, 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 Figure 4 for compound **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 Ln_2O_3 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 { $[Ln_2(bpda)_3]_n$ compounds (Figure 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 lattice water and coordinated water molecules does not lead to an observable phase transformation (Figure 5, details in Figure S20, Supp. Info.). The crystalline compounds **1-15** 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 (Figure 5, Figure S21 and S22, Supp. Info.). Also after water sorption of the activated sample the PXRD matches the simulation for { $[La_2(bpda)_3(H_2O)] \cdot 2H_2O_n$ (**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 x 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 $[Ni_2(4,4'-bipy)_3(NO_3)_4]_n \cdot 2EtOH$ network has only very small channels with dimension of ca. 1.1 Å x 1.1 Å [38,39]. The two ethanol guest molecules per formula unit are rather located in cavities ("zero-dimensional closed space") [38]. These ethanol molecules are hydrogen-bonded to the nitrate ligands and are removed upon heating to 100 °C and reversibly re-adsorbed again by exposure of the activated network to ethanol vapor. It is suggested that the passage of ethanol molecules through the small 1.1 Å x 1.1 Å channel windows proceeds by a temporary expansion of the window size. N₂ adsorption measurement on $[Ni_2(4,4'-bipy)_3(NO_3)_4]$ at 77 K showed that under these conditions N₂ is not adsorbed [40].

Removal of the coordinated and crystal water molecules from $\{[Ln_2(bpda)_3(H_2O)] \cdot 2H_2O\}_n$ could give a porous framework with coordinatively unsaturated and Lewis-acidic lanthanide ions. The absence of changes in the powder XRD pattern after removing the coordinated and lattice water molecules (Figure 5) indicates 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 $^{\circ}$ under vacuum for three hours, causing complete dehydration (cf. TG analysis of **1** that indicated complete dehydration at 150 $^{\circ}$ C and ambient pressure, "activ." in Figure 4).



Figure 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 ℃ 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 Figure S20-S22, Supp. Info.).

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 N_2 adsorption. Also in subsequent low- and high-pressure H_2 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 CO_2 adsorption analysis at 273 K. The saturation pressure of CO_2 at 0 ℃ 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 CO_2 per formula unit of $[La_2(bpda)_3]$, that is, $\{[Ln_2(bpda)_3] \cdot CO_2\}_n\}$ (Figure 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 $[La_2(bpda)_3])$ (Figure 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.



Figure 6 High-pressure CO₂ sorption isotherms for [La₂(bpda)₃] (activated 1) at 20 °C.



Figure 7 Methanol and water sorption isotherm for $[La_2(bpda)_3]$ (activated 1) at 20 °C. For calculation of the uptake to gram/gram the value in cm³/g (STP) is divided by 22,414 cm³/mol (the molar gas volume at 0 °C and 1 atm = 1.013 bar) and multiplied by the molar mass of the adsorptive (32.04 g/mol for MeOH and 18.02 g/mol for water). This means division of the cm³/g value by 700 cm³/g for MeOH and 1243 cm³/g for water.

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 (Figure 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 inbetween 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 Figure 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 (Figure 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 (λ_{ex} = 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 \rightarrow ⁷F₂ transition, which is responsible for the red color of compound **6**, under UV irradiation (Figure 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. S55 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, ${}^{5}D_{0}$, of Eu³⁺ ion is situated at 579 nm (17 250 cm⁻¹), 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 489 nm (20 430 cm⁻¹), so the back energy transfer from the metal to ligand may be present in this case [42].

When excited at the ligand excitation band ($\lambda_{ex} = 370$ nm), the emission peaks of terbium(III) ion 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 at 488, 544, 584 and 621 nm arise due to the radiative deactivation of the excited ⁵D₄ state to the corresponding/different ground ⁷F_J (J = 6, 5, 4 and 3, respectively) levels of terbium(III) ions (see Fig. S56 in Supp. Info. for assignment). The peak at 544 nm (⁵D₄ \rightarrow ⁷F₅) gives the green color to compound **8** (Figure 8b).



Figure 8 (a) Solid-state room temperature emission spectra of compound **6** (red) and compound **8** (green) along with the spectrum of the free ligand H₂bpda (blue). Spectra with peak assignments for **6** and **8** are given in Figure S55 and Figure S56 in Supp. Info. (b) Images of the compounds under UV-irradiation red for **6**, green for **8** and blue for H₂bpda.

We have decided not to examine magnetic properties, because it is known that bridging carboxyl groups mediate only a very weak magnetic exchange interaction between lanthanide(III) ions and then the lanthanide(III) ions display essentially single-ion behavior [43].

4. Conclusion

We have presented fifteen novel isostructural 3D lanthanide metal-organic frameworks $[Ln_2(bpda)_3(H_2O) 2H_2O]$ with 4,4'-biphenyldiacetate (bpda²⁻)linker. Despite its flexibility, the linker shows only one coordination motif towards Ln³⁺. The triply chelating-bridging ($\eta^{2:}\eta^{1}$) coordination of three carboxylate groups between two lanthanide atoms gives a zig-zag chain as an infinite one-dimensional SBU. The triply-bridging ($\eta^{2:}\eta^{1}$) coordination of three carboxylate groups is a variant of previous infinite one-dimensional Ln-carboxylate SBUs which also featured simple bridging ($\eta^{1:}\eta^{1}$) carboxylate 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 $[La_2(bpda)_3]$ (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 ~1.6 x 3 Å²

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 $\{[La_2(bpda)_3] \cdot CO_2\}_n$ 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 material

CCDC 1485624-1485626 contain the supplementary crystallographic data for compounds **1**, **3** and **4**. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, 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 (Synthesis of 4,4'-biphenyldiacetic acid, additional images of crystal structure, powder X-ray patterns, IR-spectra, TGA curves, gas and vapor sorption isotherms, fluorescence spectra and crystallographic details of compounds **1**, **3** and **4**) can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.XXXXX.

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