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Photoluminescent Metal–Organic Frameworks – Rapid Preparation, Catalytic Activity, and Framework Relationships

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An optimized microwave-assisted synthesis has been used to prepare an isotypical series of 3D Ln³⁺ metal-organic frameworks (MOFs) based on residues of 2,5-pyridinedicarboxylic (pydc), namely, $[Ln_2(pydc)_3(H_2O)_2]$ with $Ln^{3+} = Ce^{3+}$ (1), $(La_{0.95}Eu_{0.05})^{3+}$ (1-LaEu), $(La_{0.95}Tb_{0.05})^{3+}$ (1-LaTb), and $(La_{0.90}Eu_{0.05}Tb_{0.05})^{3+}$ (1-LaEuTb). The materials can be readily isolated as microcrystals after 1 min of reaction time at 120 °C. The compounds have been extensively studied in the solid state by vibrational spectroscopy (FTIR and FT-Raman), thermogravimetry, powder X-ray diffraction, elemental analysis, and electron microscopy (SEM, SEM mapping, and TEM). The structural relationships between the isolated materials and other solids reported in the literature have been investigated in detail from a structural and topological perspective with attention focused on the different connectivities of the employed organic ligand. The 3D densely packed

Introduction

Synthetic approaches towards the isolation of metal–organic frameworks (MOFs), also commonly designated as coordination polymers, have changed considerably since the seminal paper by Hoskins and Robson.^[1] Initially, the isolation of large single crystals was a strict requirement owing to the limitations of the single-crystal instruments. Approaches such as slow evaporation, diffusion in various media, and reflux reactions were preferred; however, these methods provided limited yields and were particularly time consuming.^[2] These approaches led to the discovery of amazing structural architectures and to the self-assembly of highly interpenetrated frameworks, which allowed structural chemists to find countless structures with topological features that mimic those typically found in minerals.^[3]

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 $[Ln_2(pydc)_3(H_2O)_2]$ compounds are very similar to the previously reported microporous 3D [Ce₂(pydc)₂(Hpydc)(H₂O)₂]-Cl·(9 + y)H₂O; layered [{Ce₂(pydc)₂(Hpydc)₂(H₂O)₄}·2H₂O]_n can be isolated at lower temperatures and transforms to [Ce2-(pydc)₃(H₂O)₂] under certain experimental conditions. Compound 1 is an effective solid catalyst for the ring opening of styrene with methanol under mild reaction conditions (55 °C) to give 2-methoxy-2-phenylethanol in 100% selectivity and ca. 80% conversion. The mixed-lanthanide materials are effective UV-to-visible light converters (red 1-LaEu, green 1-LaTb, and orange 1-LaEuTb). The compounds have very high absolute emission quantum yields (43 % for 1-LaEu and 75% for 1-LaTb) under indirect excitation of the UV ligand bands with lifetimes of 0.50 and 1.06 ms for 1-LaEu and 1-LaTb, respectively, and these properties result from effective intersystem crossing and ligand-to-metal transfer processes.

Later in the 1990s, coordination chemists transposed the hydro(solvo)thermal method from zeolite chemistry to the MOF field.^[4] This mimicking of zeolite chemistry allowed immediately a considerable reduction of reaction times (nowadays, a couple of days are typically employed) by increasing the temperature and (autogenously) the pressure, and also the isolation of other less stable thermodynamic phases. This method drove chemists worldwide to a rapid screen of possible structural architectures^[4a,5] and the production of enough material to allow the study of their various potential applications^[6] in the gas storage and (selective) adsorption fields,^[7] enantioselective separation of molecules,^[8] biomedicine,^[9] heterogeneous catalysis,^[10] magnetism,^[11] fabrication of membranes^[7g,12] or thin films,^[13] and photoluminescence.^[11j,11k,14]

At present, an outstanding question in the MOF field is how to produce functional materials by economically viable synthetic approaches. It is clear that even only the two or three days usually employed in the hydro(solvo)thermal method may not be viable. The most striking example concerns one of the few commercial MOFs: Basolite is produced by BASF by an electrochemical approach that completely replaces the traditional hydrothermal method re-

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ported by Williams.^[15] This alternative method is faster, more efficient, and also cleaner (with a minimum of waste disposal). If MOFs are to be employed in the near future in the fabrication of functional devices, more rapid, effective, and highly controllable synthetic approaches must be devised.

Microwave heating is a highly efficient method because it can heat simultaneously the whole reactants and ultimately remove convection and conduction effects inside the reactor. This approach has been successfully used in various branches of organic synthetic chemistry,^[16] as the smooth reaction conditions can improve and make some difficult chemical processes possible and, in addition, cleaner ("green") solvents can be used. Owing to the faster heating and higher homogeneous temperature distribution, microwave-assisted synthesis (MWAS) usually implies a considerable reduction in reaction times and increased overall yields. MWAS may allow morphology control and phase selectivity, which, in many cases, is accompanied by uniform particle-size distribution and a quicker and more efficient evaluation of the reaction parameters.^[17] The use of MWAS in MOF preparation is still in its infancy and remains far from industrial application. However, a number of interesting reports are now available.^[18]

In the last decade or so, we have been interested in all aspects of the synthesis and characterization of MOFs, and this has included specific studies towards the investigation of the best conditions to obtain a certain material.^[19] In particular, we have focused our attention on the use of lanthanides owing to their intrinsic photoluminescent properties.^[14b,14c,14g,20] While investigating MWAS for the lanthanide/2,5-pyridinedicarboxylic acid system (H₂pydc),^[14g,21] for which only a handful of structures is available in the literature,^[14g,22] we discovered a new MOF structure with large one-dimensional channels, [Ce2(pydc)2(Hpydc)(H2O)2]- $Cl(9 + y)H_2O$.^[18g] Although large single crystals of this compound were directly isolated from the reaction vial by filtration, a second phase was also systematically present. This latter material was identified as isotypical with the structures of [Pr₂(pydc)₃(H₂O)₂]^[22b] and [La₂(pydc)₃-(H₂O)₂]^[22a] reported by Shao and Hong. During our continuing studies on these systems, we have discovered that the substitution of small amounts of La³⁺ cations in the latter network by optically active lanthanide centers produces materials with remarkable photoluminescent properties, a feature that is highly unusual among related materials.^[14e] Indeed, even with one water molecule attached to the Ln³⁺ ions, the materials have very high absolute emission quantum yields (up to 43 and 75%), with lifetimes of ca. 0.50 and 1.06 ms for the isotypical La^{3+}/Eu^{3+} and $La^{3+}/$ Tb³⁺ materials, respectively. We have further explored the use of this framework as a heterogeneous catalyst in the conversion of styrene oxide into 2-methoxy-2-phenylethanol by epoxide ring opening with methanol under mild conditions. This reaction represents an important step in the preparation of β -alkoxy alcohols, which are often used as solvents or intermediates in several branches of organic and inorganic synthesis.^[23] In this paper, we summarize our results concerning the use of a new, faster, and cleaner synthetic methodology to obtain these functional materials and a detailed investigation of their catalytic and photoluminescent properties.

Results and Discussion

Microwave-Assisted Hydrothermal Synthesis

Shao and Hong have reported the structures of [Pr₂(pydc)₃(H₂O)₂] and [La₂(pydc)₃(H₂O)₂] based on singlecrystal data sets: the crystals were grown from hydrothermal synthesis over a period of three days.^[22a,22b] Based on our recent studies, this synthetic method is not only time consuming but also highly inefficient from the energetic standpoint.^[19] The change of the experimental conditions to MWAS^[18e] resulted in the isolation of microcrystalline powders, which were identified from powder X-ray diffraction (PXRD) as mixtures of phases. Therefore, the optimization of the MWAS conditions (hereafter, samples are denoted $T_m P_n t_p$, the subscripts indicate the specific experimental conditions employed for temperature T, power P, and reaction time t) for the $[Ln_2(pydc)_3(H_2O)_2]$ materials was pertinent to avoid the formation of secondary materials and take advantage of the short reaction times typical of this synthetic method.^[18e]

Rationale

In general, the test compounds have been prepared by using a different composition of the reactive gels used by Shao and Hong.^[22a,22b] We discovered that our experimental conditions produce better results for microwave irradiation:

(a) NaOH has been added to the reactive gel (in excess for the complete deprotonation of 2,5-H₂pydc). As MWAS is expected to induce a fast rate of nucleation, the addition of a strong base before the reaction ensures the immediate availability of carboxylate groups for coordination.

(b) We have selected Ce³⁺ as the metallic node because (i) $[Ce_2(pydc)_3(H_2O)_2]^{[22b]}$ is a secondary phase that appears in the preparation of microporous $[Ce_2(pydc)_2(Hpydc)-(H_2O)_2]Cl\cdot(9 + y)H_2O^{[18g]}$ and, more importantly, (ii) Ce³⁺ compounds find countless technological applications in photoluminescent materials, fuel cells, glass, the ceramic and metallurgic industries, catalytic materials, and several others.^[24]

For the engineering of photoluminescent materials, the presence of dilute amounts of Eu^{3+} and Tb^{3+} ions dispersed in a matrix of nonemitting ions, such as La^{3+} ions, is usually desirable. As $[Pr_2(pydc)_3(H_2O)_2]$ and $[La_2(pydc)_3(H_2O)_2]$ are isotypical, ^[22a,22b] we have employed La^{3+} as the main metallic node for the functional materials.

Optimization of MWAS for the Isolation of $[Ce_2(pydc)_3-(H_2O)_2]$ (1)

To identify the best experimental MWAS conditions (temperature, microwave irradiation power, and time of reaction) that lead to the desired material as a highly crystal-

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line phase-pure compound with uniform crystal morphology, a series of test compounds from distinct experimental conditions have been prepared (Scheme 1). The compounds were analyzed by using a combination of powder X-ray diffraction, SEM imaging, and CHN elemental analyses.



Scheme 1. $T_m P_n t_p$ diagram for the MWAS optimization of the synthesis of $[Ce_2(pydc)_3(H_2O)_2]$ (1). Red, absence of the desired material or amorphous phase; mixture, a mixture of the desired material with other phases; green, $[Ce_2(pydc)_3(H_2O)_2]$ (1) as a phase-pure material.

The study of the influence of the reaction parameters revealed the following:

(i) $[Ce_2(pydc)_3(H_2O)_2]$ (1) can be obtained over a wide range of experimental conditions as a pure material with high crystallinity.

(ii) Small modifications to the experimental conditions have considerable effects on the crystal size and overall crystallinity of the products; the crystallinity is significantly improved with increasing irradiation power.

(iii) At 90 °C, the recovered products were composed of 1 (for 1 min reaction periods) and another compound, which was, a posteriori, identified from PXRD as isotypical with the layered material $[{Ce_2(pydc)_2(Hpydc)_2(H_2O)_4} \cdot 2H_2O]_n$, which is isotypical with the Nd³⁺-based compound reported by Zhang et al.^[22i] For 5 min of reaction, the physical mixture was essentially composed of 1. Longer reaction periods ensured the presence of phase-pure, highly crystal-line compounds (Scheme 1 and Figure S1).

(iii) At 120 °C, highly crystalline 1 is isolated for most tested conditions. We further note that for this temperature, after the initial formation of the crystals, increased irradiation times lead to crystal degradation (Figure S2). This behavior is not unprecedented under MWAS and it was reported by Choi for the iconic MOF-5 structure.^[18d]

(iv) For most experimental conditions, crystals of 1 were obtained as large aggregates of microsized platelike crystals (Figure 1): we found that for this system under MWAS, there is a tendency for crystallites to aggregate, which leads to spherical clusters with dimensions ranging from a few micrometers to dozens of micrometers.

In summary, the optimal experimental conditions to obtain 1 as a pure phase are 120 °C, 50–80 W, and 1–10 min. Lower irradiation power and shorter reaction times ensure a significantly more efficient synthetic procedure than those reported for the analogous materials.^[22a,22b]



Figure 1. Electron microscopy images of 1 (a) isolated from hydrothermal synthesis (170 °C for 72 h) and (b) synthesized by using optimal MWAS conditions.

Crystal Structure

Description

All isotypical materials prepared and studied in the present manuscript have been systematically isolated as microcrystalline powders directly from the MWAS reaction vial: $[Ce_2(pydc)_3(H_2O)_2]$ (1), $[(La_{0.95}Eu_{0.05})_2(pydc)_3(H_2O)_2]$ (1-LaEu), $[(La_{0.95}Tb_{0.05})_2(pydc)_3(H_2O)_2]$ (1-LaTb), $[La_2-(pydc)_3(H_2O)_2]$ (1-La), and $[(La_{0.90}Eu_{0.05}Tb_{0.05})_2(pydc)_3-(H_2O)_2]$ (1-LaEuTb). Powder X-ray diffraction unequivocally identified the materials as having identical frameworks to those reported for $[Pr_2(pydc)_3(H_2O)_2]$ and $[La_2(pydc)_3-(H_2O)_2]$ by Shao and Hong.^[22a,22b] Rietveld and Le Bail whole-powder-profile fittings have been performed for all prepared materials, and the data for 1 is provided in the present manuscript (Figure 2 and Table 1; the data for the remaining four samples not shown).

Table 1. X-ray data collection, crystal data, and structure refinement details for 1.

Formula	C ₂₁ H ₁₃ Ce ₂ N ₃ O ₁₄
Formula weight	811.58
Crystal system	monoclinic
Space group	$P2_1/c$
<i>a</i> [Å]	6.5503(4)
b [Å]	17.9777(10)
c [Å]	9.4217(5)
β[°]	95.419(4)
Volume [Å ³]	1104.54(11)
Z	2
$D_{\rm c} \left[\rm g cm^{-3} \right]$	2.440
Profile function	pseudo-Voigt
η	0.489(9)
Caglioti law parameters	U = -0.10(1)
	V = 0.101(6)
	W = 0.0168(7)
Asymmetry parameters (up to $25^{\circ} 2\theta$)	0.069(3) and 0.0451(7)
Zero shift $[2\theta^{\circ}]$	-0.010(2)
Independent reflections	989
Global refined parameters	1
Profile refined parameters	11
Intensity-dependent refined parameters	64
$R_{\rm p}^{[\rm a]}$	3.99
$R_{ m wp}^{[a]}$	5.39
$R_{\rm exp}^{[a]}$	1.08
$\chi^{2[a]}$	25.0
R _{Bragg}	13.0
RE	19.0

[a] Reliability factors for all nonexcluded data points with Bragg contribution conventional – not corrected for background).





Figure 2. Final Rietveld plot for 1. Observed data points are indicated as red circles, and the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. The refinement details are given in Table 1. Inset: Crystal packing of 1 viewed in perspective along the [001] direction of the unit cell.

Compound 1 is formed by a single crystallographically independent Ce³⁺ metallic center, which is coordinated to one water molecule plus six organic ligands (Figure 3). However, the asymmetric unit of the material is only composed of a whole N,O-chelated pydc²⁻ organic ligand plus another half of such a moiety with its center of gravity located at a crystallographic inversion center. This latter crystallographic feature has a strong influence on the crystal features, as described below in more detail. Thus, the Ce³⁺ center is nine-coordinate with an overall {CeNO₈} coordination sphere, which strongly resembles a distorted square antiprism with one of the basal planes capped by the nitrogen atom of the N,O-chelated pydc^{2–} ligand (Figure 3, a and Table 2). Notably, although the O1/O6/O3/O5 base of the antiprism is almost planar, the O1/O2/O4/O7 base is significantly more distorted with distances from the atoms to the average plane of ca. 0.075–0.093 Å. In addition, the two average planes are not parallel and subtend a small angle of ca. 4.4° towards the coordinated water molecule (owing to the presence of hydrogen bonds with nearby carboxylate groups). As also depicted in Figure 3 (a), the central Ce³⁺ cation is also closer to the former basal plane (ca. 0.93 Å) than to the latter (ca. 1.82 Å), most likely because of the attractive effect of the coordinated nitrogen atom of the N,O-chelated pydc^{2–} organic ligand.



Figure 3. (a) Schematic representation of the capped nine-coordination {CeNO₈} coordination environment of the Ce³⁺ cation, which resembles a distorted square antiprism. The N,O-chelated $pydc^{2-}$ organic ligand is depicted to emphasize the capped polyhedral base. (b) Portion of the crystal structure of 1 showing the one-dimensional tape of {CeNO₈} polyhedra interconnected through the *syn,syn* bridges of the aforementioned N,O-chelated $pydc^{2-}$ ligand. For selected bond lengths and angles see Table 2. Symmetry transformations used to generate equivalent atoms: (i) -1 + x, *y*, *z*; (ii) 1 - x, -1/2 + y, 1.5 - z; (iii) 1 - x, 2 - y, 1 - z; (iv) *x*, 1.5 - y, -1/2 + z.



Table 2. Selected bond lengths [Å] and angles [°] for the crystallographically independent Ce³⁺ coordination environment in 1.^[a]

Ce1–O1	2.555(4)	Ce1–O5	2.644(14)
Ce1–O1 ^{iv}	2.682(7)	Ce1–O6 ⁱ	2.650(14)
Ce1-O2 ^{iv}	2.723(12)	Ce1–O7	2.618(15)
Ce1-O3 ⁱⁱⁱ	2.401(5)	Ce1-N1	2.745(6)
Ce1–O4 ⁱⁱ	2.432(10)		
O1–Ce1–O1 ^{IV}	142.4(4)	$O2^{iv}$ -Ce1-O6 ⁱ	143.2(4)
O1–Ce1–O2 ^{iv}	94.5(3)	O2 ^{iv} –Ce1–O5	71.6(4)
O1 ^{iv} -Ce1-O2 ^{iv}	48.3(2)	O2 ^{iv} -Ce1-N1	137.3(4)
O1-Ce1-O3 ⁱⁱⁱ	135.2(3)	O3 ⁱⁱⁱ –Ce1–O4 ⁱⁱ	140.6(7)
O1 ^{iv} -Ce1-O3 ⁱⁱⁱ	77.9(3)	O3 ⁱⁱⁱ –Ce1–O5	88.6(7)
O1 ^{iv} -Ce1-O4 ⁱⁱ	93.4(3)	O3 ⁱⁱⁱ –Ce1–O6 ⁱ	84.3(6)
O1-Ce1-O5	84.0(5)	O3 ⁱⁱⁱ –Ce1–O7	77.3(6)
O1 ^{iv} -Ce1-O5	79.1(5)	O3 ⁱⁱⁱ –Ce1–N1	76.9(2)
O1-Ce1-O4 ⁱⁱ	71.2(3)	O4 ⁱⁱ –Ce1–O5	127.8(5)
O1-Ce1-O6i	72.7(4)	O4 ⁱⁱ -Ce1-O6 ⁱ	77.4(5)
O1 ^{iv} -Ce1-O6 ⁱ	138.7(4)	O4 ⁱⁱ –Ce1–O7	64.8(5)
O1-Ce1-O7	130.8(4)	O4 ⁱⁱ -Ce1-N1	123.6(3)
O1 ^{iv} -Ce1-O7	62.9(4)	O5-Ce1-O6 ⁱ	137.8(5)
O1-Ce1-N1	58.7(3)	O5-Ce1-O7	141.3(5)
O1 ^{iv} -Ce1-N1	142.4(4)	O5-Ce1-N1	73.0(5)
O2iv-Ce1-O3iii	124.6(4)	O6 ⁱ -Ce1-O7	77.1(5)
O2iv-Ce1-O4ii	65.8(4)	O6 ⁱ -Ce1-N1	64.9(5)
O2 ^{iv} -Ce1-O7	87.0(4)	O7-Ce1-N1	135.6(5)

[a] Symmetry transformations used to generate equivalent atoms: (i) -1 + x, y, z; (ii) 1 - x, -1/2 + y, 1.5 - z; (iii) 1 - x, 2 - y, 1 - z; (iv) x, 1.5 - y, -1/2 + z.

The aforementioned N,O-chelated pydc²⁻ organic ligand is also the moiety responsible for the interconnection of individual {CeNO₈} polyhedra along the [001] direction of the unit cell by establishing a syn,syn bridge with an adjacent Ce^{3+} cation (Figure 3, b). This leads to the formation of a tape in which the shortest intermetallic Ce--Ce distance is 4.8875(4) Å. These moieties constitute the "core" of the densely packed Ce-pydc layers described in the following subsection. The centrosymmetric pydc²⁻ anionic ligand attaches itself to the remaining polyhedra coordination sites (depicted as orange circles in Figure 3, b), which leads to the densely packed crystal structure of 1 shown in the inset in Figure 2. As the nitrogen atom of this moiety is not attached to the metallic center and is located on a crystallographic center of inversion, the moiety appears highly disordered in the crystal structure.

Framework Relationships

For low reaction temperatures, compound 1 could be isolated alongside the layered compound [$\{Ce_2(pydc)_2(Hpydc)_2-(H_2O)_4\}\cdot 2H_2O]_n$, which is isotypical with that reported by Zhang et al.^[22i] By inspecting both crystal structures, one can find striking structural relationships that help explain the reason for this.

Both structures are formed by a core well-defined Ln– pydc layer in which the organic ligand is strongly N,O-chelated to the metallic center (Figure 4). For the Ce³⁺ framework that is isotypical with the Nd³⁺-based material, there is an extra ligand per formula unit and this same moiety is also N,O-chelated. As a consequence, the core Ce–pydc layers are very distant from each other and the external Hpydc⁻ ligand imposes steric hindrance in the structure (hence, the presence of small channels with solvent molecules). For **1** (and its isotypical members of the series), the Ce–pydc layers coalesce instead along the [100] direction of the unit cell, which leads to a densely packed material. This occurs mainly because the release of the extra organic ligand (see empirical formulae of the compounds) permits the remaining ones to accommodate and establish new connections. Under MWAS, this process seems to be clearly driven by increased reaction temperature (Scheme 1).

Topological Studies

The chemical possibility of the simultaneous formation of 1 and the porous $[Ce_2(pydc)_2(Hpydc)(H_2O)_2]Cl \cdot (9 + y)$ -H₂O material^[18g] previously reported by us can structurally be better understood by mathematically reducing both networks to nodes and connecting rods and, in this way, the materials can be topologically classified and mutual relationships can be found. By following the recommendations of Alexandrov et al.,^[25] who have suggested that any moiety (ligand or atoms) that connects more than two metallic centers (μ_n) should be considered as a network node, in 1 all crystallographically independent moieties (the Ce3+ cation and the two organic ligands) must then be considered as network nodes. Interestingly, [Ce2(pydc)2(Hpydc)(H2O)2]Cl· $(9 + y)H_2O$ has almost identical composition for the asymmetric unit: the inclusion of a chloride anion in the material promotes the protonation of the uncoordinated nitrogen atom and, hence, leads to a completely distinct network. By considering (1) the centers of gravity of each crystallographically independent pydc²⁻ anionic ligand and the Ce³⁺ metallic center as nodes and (2) the internodal connections through the organic ligands (only connections through the carboxylate ligands were considered) as bridges, the TOPOS^[26] software package reveals that although 1 is a 4,4,6-trinodal network with an overall Schäfli symbol of $\{4^{2}, 8^{4}\} \{4^{4}, 6^{2}\}_{2} \{4^{9}, 6^{6}\}_{2}$ (Figures 5 and S6), as described by Hong et al.,^[22a] [Ce₂(pydc)₂(Hpydc)(H₂O)₂]Cl·(9 + y)H₂O must only be considered as a 4,6-binodal network described by the $\{4^4.6^2\}_3\{4^9.6^6\}_2$ Schäfli symbol.

In both compounds, the crystallographically independent Ce³⁺ cation appears as a six-connected node with identical point symbol ($\{4^9.6^6\}$). Nevertheless, the coordination sequences are distinct, and N_{10} is 252 for 1 and 227 for [Ce₂- $(pydc)_2(Hpydc)(H_2O)_2$ Cl·(9 + y)H₂O, which clearly demonstrates that the latter material is more open (i.e., it corresponds to a less dense network). Identical features are found for the N,O-chelated pydc²⁻ organic ligand: in both structures, these moieties are 4-connected nodes with $\{4^4 \cdot 6^2\}$ point symbol. Remarkably, the topological distinction between the two networks arises mainly from the disordered organic ligand: although the two ligands in [Ce2- $(pydc)_2(Hpydc)(H_2O)_2$ Cl·(9 + y)H₂O have identical coordination sequences up to the 10th shell, which makes the two ligands topologically equivalent (hence, the aforementioned binodal description), small differences occur in the fourth and eighth shells in 1 (even though N_{10} is the same for both ligands). Notably, the topological density (TD_{10}) of the structures clearly shows that 1 is significantly more dense



3D : $[Ce_2(pydc)_3(H_2O)_2]$



Figure 4. Framework deconstruction and comparison between the 3D [$Ce_2(pydc)_3(H_2O)_2$] (1) material herein reported and the 2D network [$Nd_2(pydc)_2(H_2O)_2$]·(1) material herein reported and the 2D network [$Nd_2(pydc)_2(H_2O)_4$]·2H₂O]_n described by Zhang et al.^[22i] The latter material has one extra organic ligand per metallic center, which occupies the interlayer spaces. This creates considerable steric hindrance and removes coordination sites at the Nd³⁺ center and ultimately prevents the connections along the [010] direction of the unit cell. In 1, this extra Hpydc ligand does not exist and this permits the formation of skew–skew bridging connections to form the 3D network.



Figure 5. Topological representation of the trinodal framework of 1 with overall Schäfli symbol of $\{4^2 \cdot 8^4\}\{4^4 \cdot 6^2\}_2\{4^9 \cdot 6^6\}_2$.

than $[Ce_2(pydc)_2(Hpydc)(H_2O)_2]Cl \cdot (9 + y)H_2O$ (TD₁₀ = 1226 and 1100, respectively).

Searches in the *Reticular Chemistry Structure Resource* (RCSR)^[27] and in EPINET^[28] reveal that both networks

have already been enumerated and found for MOF structures. Compound 1 belongs to the 4,4,6T19 topological type, whereas $[Ce_2(pydc)_2(Hpydc)(H_2O)_2]Cl\cdot(9 + y)H_2O$, as described previously, shares the topology with the stp framework. However, a literature search reveals that the 4,4,6T19 topology is also not very common and only appears for lanthanide-containing frameworks to date.^[22a,22b,29]

Thermal Stability - Influence of Crystal Size

Microcrystals of 1, obtained under MWAS, have a considerably higher external surface area, which can have a significant impact on the properties of the materials, for example, their thermal stability. In this context, the thermal stability of bulk (phase-pure) 1 was investigated between ambient temperature and ca. 800 °C for the materials prepared both under conventional hydrothermal conditions (see Experimental Section for details of the synthesis) and MWAS (Figure 6). We note that the thermal behavior described below only for the Ce³⁺-based compounds was also observed





Figure 6. Thermograms of 1 prepared by different synthetic procedures. Black line: phase-pure 1 obtained by MWAS; red line: phase-pure 1 obtained by conventional hydrothermal heating. Inset: SEM images of 1 isolated from (a) typical hydrothermal synthesis (170 °C, 72 h) and (b) optimal MWAS conditions (120 °C, 50–80 W, 1–10 min).

for the mixed-lanthanide materials in an independent experiment (data not shown).

 $[Ce_2(pydc)_3(H_2O)_2]$ prepared under static hydrothermal conditions is thermally stable to ca. 140 °C. Above this temperature, a gradual weight loss of ca. 4.8% is attributed to the release of two coordinated water molecules per formula unit (calculated 4.4%). Above ca. 340 °C, there is a second abrupt weight loss globally corresponding to ca. 50.9%, which is attributed to the decomposition of the organic component and the concomitant collapse of the framework. The materials prepared under MWAS do not show such remarkable distinct regions of thermal stability. As shown in Figure 6, decomposition starts immediately at low temperatures, and there are no well-defined stages of framework stability as described above for the large crystals. For example, the first and the second decomposition stages almost overlap. Clearly, these profile differences are a direct consequence of the expected larger surface area of the materials prepared by MWAS, which facilitates both the release of water molecules and the decomposition of the framework.

Another striking difference of the decomposition of the two materials prepared by the distinct synthetic approaches concerns the residue at ca. 500 °C. For 1 obtained by standard hydrothermal synthesis, the residue is ca. 44.2% of the initial mass, whereas for the small crystallites obtained by MWAS, the residue is only ca. 41.0%. For the formation of a stoichiometric amount of Ce₂O₃ with respect to the empirical formula of 1, a residue of ca. 40.4% would be expected. This value agrees much better with that observed for the calcination of the smaller crystallites of 1. The decomposition of the large crystals (obtained from hydrother-

mal synthesis) does not seem to be so uniform and most likely leads to the isolation of mixed-valence Ce^{3+}/Ce^{4+} oxides and/or to the presence of charcoal in the residue.

Catalytic Studies

Our recent investigations of new phosphonic-based MOFs introduced compounds with remarkable catalytic performances among other properties. Catalytic screening tests based on cis-cyclooctene epoxidation, acid-catalyzed isomerization of α -pinene oxide, ring opening of styrene oxide, and cyclodehydrogenation of xylose to furfural under different experimental conditions have been evaluated and reported.^[14b,20,30] As the ring-opening reaction of styrene oxide with methanol gave the best results, for comparative purposes, this reaction was chosen for the present set of catalytic tests for 1. Cerium-containing salts such as Ce-(OTf)₄ and (NH₄)₈[CeW₁₀O₃₆]·20H₂O are effective catalysts in the latter reaction.^[31] However, high regioselectivity and conversions have been also reported for the lanthanide precursor CeCl₃·7H₂O used herein.^[32] Nevertheless, the major limitation of these homogeneous catalysts is the difficult catalyst recyclability, which ultimately makes their potential application unattractive. Cu- and Fe-based MOFs have been tested in the same reaction. Despite their good catalytic performance, the 2-methoxy-2-phenylethanol yield was not quantitative because product selectivity was less than 100%.^[10m,33] We have reported lanthanide polyphosphonate MOFs as effective catalysts for this reaction, and, although they may have lower catalytic activities than other compounds (only up to 80% yield), they are truly hetero-



Figure 7. Kinetic curves of the ring-opening reaction of styrene oxide with methanol at 55 °C in the presence of a mixture of $[Ce_2(pydc)_2-(Hpydc)(H_2O)_2CI] \cdot (9 + y)H_2O$ and 1 (black square, ratio ca. 4:1) and phase-pure 1 (red circle, green triangle, blue upside down triangle). Black squares and red circles: similar catalyst amounts were used. Green triangles: half of the initial catalyst quantity was used. Blue upside down triangle: one fifth of the initial catalyst quantity was used. The dashed lines are guidelines and do not represent the tendency of the catalytic reaction. SEM images of 1 (top) and [Ce₂(pydc)₂(Hpydc)(H₂O)₂CI]·(9 + y)H₂O (needles) with ca. 20% of 1 (bottom) are shown on the right. The insets represent the structural drawings of 1 (top) and [Ce₂(pydc)₂(Hpydc)(H₂O)₂CI]·(9 + y)H₂O (bottom).

geneous in nature, highly selective, and typically present multifunctional behavior. $^{\left[20,30\right] }$

The microporous $[Ce_2(pydc)_2(Hpydc)(H_2O)_2]Cl \cdot (9 + y)$ -H₂O material can be obtained from the present reaction system under specific experimental conditions.^[18g] Its isolation as a pure phase could never be achieved; it always appeared as a mixture of phases with 1. The reported optimized synthetic conditions to obtain this material gave a maximum yield of 80 wt.-% with 1 as the other phase. This mixture was tested for the catalytic reaction of PhEtO with methanol under similar reaction conditions as those used for pure 1. MeOPhEtOH was the only product and formed in 18 and 32% yield after 24 and 48 h reaction (black squares in Figure 7). However, when the reaction of PhEtO was performed in the presence of phase-pure 1, a higher yield of MeOPhEtOH was obtained (73 and 77% after 24 and 48 h reaction; Figure 7, red circles). The use of half of the initial amount of 1 did not significantly affect the reaction rate (77% conversion after 24 h), whereas 1/5 of the initial amount of 1 led to slower reaction of PhEtO (50% conversion after 24 h, Figure 7). The catalytic experiment with 1/5 of the initial amount of 1 simulated the catalytic contribution of this phase (a similar mass of 1 was loaded). when the mixture of 1 and $[Ce_2(pydc)_2(Hpydc)]$ -

 $(H_2O)_2Cl]\cdot(9 + y)H_2O$ was used, and gave superior catalytic results in the former case. Hence, compound 1 possesses higher catalytic activity than $[Ce_2(pydc)_2(Hpydc)-(H_2O)_2]Cl\cdot(9 + y)H_2O$. Possibly, the concentration of accessible active sites is higher for 1 than for $[Ce_2(pydc)_2-(Hpydc)(H_2O)_2]Cl\cdot(9 + y)H_2O$ or the porosity of latter material may lead to strong internal diffusion limitations. On the other hand, we cannot rule out the possibility that defect sites possess intrinsic catalytic activity and these are different for the two materials.

Engineering Optically Active Materials

To design photoluminescent materials, we have included stoichiometric amounts of optically active lanthanide cations such as Eu^{3+} and Tb^{3+} into a La^{3+} -based isotypical matrix. We have prepared $[La_2(pydc)_3(H_2O)_2]$ (1-La), $[(La_{0.95}Eu_{0.05})_2(pydc)_3(H_2O)_2]$ (1-LaEu), $[(La_{0.95}Tb_{0.05})_2(pydc)_3(H_2O)_2]$ (1-LaTb), and $[(La_{0.90}Eu_{0.05}Tb_{0.05})_2(pydc)_3(H_2O)_2]$ (1-LaEuTb; see Experimental Section for ad-



ditional details). Powder X-ray diffraction (Figure 8) and electron microscopy studies (Figures S7–S9) of the prepared bulk mixed-lanthanide materials showed that all materials



Figure 8. Comparison between the experimental powder X-ray diffraction patterns for the isotypical **1**, **1**-LaEu, and **1**-LaTb materials. Vertical bars indicate the angular positions of the allowed Bragg reflections for each material as refined from a Le Bail^[46] whole-powder-pattern fitting of the powder patterns. Refined unitcell parameters for **1**-LaEu: a = 6.5656(4) Å, b = 18.0098(9) Å, c = 9.4416(5) Å, $\beta = 95.419(3)^\circ$, monoclinic $P2_1/c$. Refined unit-cell parameters for **1**-LaTb: a = 6.5676(3) Å, b = 18.0273(8) Å, c = 9.4432(5) Å, $\beta = 95.405(4)^\circ$, monoclinic $P2_1/c$.

share the same structural features and that the optically active lanthanide cations are uniformly distributed in the optically inert La^{3+} matrix.

The excitation spectra of 1-LaEu, 1-LaTb, and 1-LaEuTb were recorded and the strongest $Eu^{3+} {}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and $Tb^{3+} {}^{5}D_{4} \rightarrow {}^{7}F_{5}$ emission transitions were monitored (Figure 9). The spectra are dominated by two broad UV bands in the range 240–350 nm (peaking at ca. 276 and 310 nm for 1-LaEu at ambient temperature), which are attributable to the excited states of the organic ligands. The presence of two broad UV bands could arise from (1) the two crystallographically independent coordination modes of the organic ligand to the Ln³⁺ ions (see crystal structure description and Figure S3), (2) the distinct excited singlet states of the ligand, or (3) a combination of both. This attribution was further confirmed from the excitation spectrum of 1-La at 12 K (Figure 9) with the phosphorescence emission at 450 nm monitored (see discussion below).

The spectra of 1-LaEu, 1-LaTb, and 1-LaEuTb show a series of sharp lines assigned to the typical intra- $4f^6$ and $-4f^8$ transitions of Eu³⁺ and Tb³⁺, respectively. The fact that the Tb³⁺ intra- $4f^8$ transitions are only recognized after proper magnification indicates a more efficient sensitization through the ligand excited states for the Tb³⁺ emission than that of Eu³⁺. For 1-LaEuTb, there is no strong evidence for the occurrence of additional energy transfer from the Tb³⁺ to the Eu³⁺ cations as the intra- $4f^8$ Tb³⁺ excited lines are absent in the excitation spectrum of the Eu³⁺ emission mon-



Figure 9. Excitation spectra of 1-LaEu ($\lambda_{Em.} = 616$ nm, red), 1-LaTb ($\lambda_{Em.} = 543$ nm, green), 1-LaEuTb ($\lambda_{Em.} = 616$ nm, orange; $\lambda_{Em.} = 543$ nm, cyan), and 1-La ($\lambda_{Em.} = 450$ nm, black) with monitoring of the emission of the Eu³⁺ and Tb³⁺ ions and the ligand. The spectra were recorded at ambient temperature (solid lines) and 12 K (dotted lines).





Figure 10. Room-temperature emission spectra of 1-LaEu (red), 1-LaTb (green), and 1-LaEuTb (orange) with excitation at 310 nm. For 1-LaEu, the emission spectrum at 12 K (black line) and a magnification of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ spectral region are also provided. The inset images show the corresponding bright emissions of small pellet samples under a laboratory UV lamp ($\lambda = 254$ nm) and their corresponding CIE color coordinates.

itored at 616 nm. However, the presence of Eu^{3+} cations has a strong influence on the decrease of the Tb³⁺ sensitization by the ligand antenna effect. This is clearly demonstrated by the increase of the intra-4 f^8 Tb³⁺ transitions with respect to the excited broad bands of the ligand.

The emission spectra of 1-LaEu, 1-LaTb, and 1-LaEuTb recorded at ambient conditions (293 K) and excited at 310 nm are provided in Figure 10. The sharp Eu³⁺ and Tb³⁺ emission lines are mostly assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{0-4}$ and ${}^{5}D_{4} \rightarrow {}^{7}F_{6-0}$ transitions, respectively, which originate bright red, green, and orange emitted light (demonstrated by the inset pictures associated with each emission spectra of Figure 10). Although they have a negligible contribution to the total emission, for Eu³⁺ it is also possible to detect the ${}^{5}D_{1} \rightarrow {}^{7}F_{0-3}$ emission transitions, particularly at 12 K. The corresponding CIE (Commission International d'Eclairage) chromaticity (x,y) color coordinates are represented in Figure 11. For the Eu³⁺ and Tb³⁺ materials, the emission spectra are independent of the excited wavelength selected, namely, the ligand UV bands or intra-4f levels. For the mixed-lanthanide 1-LaEuTb material, the pure Eu3+ emission spectrum can be obtained by exciting at 393 nm (${}^{5}L_{6}$ excited Eu³⁺ level).

The Eu³⁺ emission is highly sensitive to small modifications to the first coordination sphere of the metal. In this way, this optical feature is widely used as a local probe for detailed structural features.^[34] For **1**-LaEu, the emission



Figure 11. CIE chromaticity diagram showing the location of the red, green, and orange room-temperature emission from 1-LaEu, 1-LaTb, and 1-LaEuTb under 310 nm excitation.

spectrum, both at ambient temperature and 12 K, shows a single ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition, a local-field splitting of the ${}^{7}F_{1,2}$ levels into three and five Stark components, respectively, and the predominance of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition relative to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, which agrees well with the presence of a single low-symmetry Eu³⁺ environment in the



structure. The small redshift of the ${}^5D_0 \rightarrow {}^7F_0$ transition observed at 12 K relative to that at ambient temperature is presumably caused by a slight contraction of the unit cell. Additionally, the Eu³⁺ 5D_0 and Tb³⁺ 5D_4 decay curves recorded at ambient temperature can be well-fitted by single exponential functions to yield lifetimes of 0.50 ± 0.01 and 1.06 ± 0.01 ms for 1-LaEu and 1-LaTb, respectively (Figure S10). These data agree well with the presence of a single Ln³⁺ crystallographic site for the mixed-lanthanide materials, in agreement with the crystallographic studies. For 1-LaEuTb, similar decay curves with exactly the same lifetime values were obtained by selecting the excitation and emission wavelengths for Eu³⁺ ($\lambda_{\rm Em.} = 616$ nm, $\lambda_{\rm Exc.} = 393$ nm) and Tb³⁺ ($\lambda_{\rm Em.} = 543$ nm, $\lambda_{\rm Exc.} = 376$ nm).

Based on the emission spectra, the 5D_0 lifetimes, empirical radiative and nonradiative transition rates, and assuming that only nonradiative and radiative processes are involved in the depopulation of the 5D_0 state, the 5D_0 quantum efficiency $\phi^{[27,35]}$ was determined for 1-LaEu. The theoretical basis of these calculations is provided in the Supporting Information. These data, including the absolute emission quantum yield, defined as the ratio between the number of emitted photons and the number of absorbed photons (measured experimentally), are collected in Table 3 for the three studied compounds.

Table 3. Experimental ${}^{5}D_{0}$ lifetime (τ), radiative (k_{r}) and nonradiative (k_{nr}) transition rates, and absolute emission quantum yield (ϕ) for 1-LaEu. The absolute emission quantum yield is also given for 1-LaTb and 1-LaEuTb. The data were collected at 293 K.

	τ [ms]	$k_{ m r} [m s^{-1}]$	$k_{ m nr}$ [s ⁻¹]	ϕ [%] ($\lambda_{\rm Exc.}$, nm)
1-LaEu 1-LaTb 1- LaEuTb	0.50 1.06 -	469 	1531 	32 (254), 43 (310), 4 (393) 63 (254), 75 (310), 3 (376) 37 (254), 49 (310), 3 (376), 4 (393)

Compound 1-LaEu has moderate quantum efficiency (23%) mostly because of the high nonradiative transition rate. This is most likely promoted by the presence of O-H oscillators associated with the coordinated water molecules, which lead to the concomitant decrease of the radiative transition rate. The measured absolute emission quantum yield under 4f direct excitation at 393 nm (4%) is far from the calculated quantum efficiency. Notably, the calculated ${}^{5}D_{0}$ quantum efficiency, determined under $4f^{6}$ excitation at 393 nm, by definition gives a limit for the corresponding absolute emission quantum yield if only nonradiative and radiative processes are involved in the depopulation of the ${}^{5}D_{0}$ state.^[36] In the present case, under excitation of the UV ligand bands, the maximum absolute emission quantum yield (43% at 310 nm excitation) almost doubles the calculated ${}^{5}D_{0}$ quantum efficiency, which invalidates the assumption that only nonradiative and radiative processes are involved in the depopulation of the ${}^{5}D_{0}$ state. Additional processes must then be present on population/depopulation of the ${}^{5}D_{0}$ state under UV excitation within the states of the ligands. Higher absolute emission quantum yields were obtained for the Tb³⁺-containing samples, and a maximum of 75% was reached for 1-LaTb excited at 310 nm. These high values, even with a water molecule coordinated to the Eu³⁺ and Tb³⁺ acceptor ions in the studied compounds, demonstrate a favorable balance between absorption and energy transfer emission process through the rates involved in the processes such as ligand-to-Ln³⁺ energy transfer (including intersystem-crossing relaxation), multiphonon relaxation, and back-transfer processes.^[37]

To get additional insight into the measured high absolute emission quantum yields under UV ligand excitation, we have recorded the photoluminescence of 1-La, which does not present detectable emission at ambient temperature. The stationary-state emission spectrum at 12 K is dominated by a structured broad band centered on the blue region (Figure 12; 390–550 nm) with a maximum intensity at ca. 450 nm. A similar spectrum was obtained in the timeresolved mode with an initial delay of 20 ms (Figure 12); this allows the emission to be unequivocally attributed to a phosphorescence emission, presumably from the ligand triplet states, and the corresponding zero-phonon energy level is estimated at ca. 390 nm (25640 cm⁻¹), which is much larger than those reported for a series of Eu³⁺ complexes.^[37,38] Furthermore, the emission decay curve monitored at ca. 450 nm with excitation at 300 nm (inset in Figure 12) reveals a biexponential behavior, which results in two distinct lifetime values of 82 ± 1 and 562 ± 5 ms. The nonexponential behavior can be attributed to the presence of the two distinct ligand modes, which can induce more complex ligand-to-ligand and ligand-to-metal energy transfer mechanisms.^[39] The higher absolute emission quantum yield of Tb³⁺ relative to Eu³⁺ can most probably be justified by a smaller energy difference between the ligand triplet zero-phonon energy level and the corresponding excited acceptor levels $({}^{5}D_{4}, 486 \text{ nm}/20576 \text{ cm}^{-1} \text{ for } \text{Tb}^{3+}; {}^{5}D_{1},$ 526 nm/19011 cm⁻¹ for Eu³⁺) as illustrated in Figure S11. As Ce^{3+} usually has the first possible emitting levels (⁵D₁, below 360 nm/27778 cm⁻¹) at higher energy than that of the zero-phonon triplet state, ligand-to-metal energy transfer does not occur for this lanthanide cation in the present material.

An inspection of the literature for photoluminescent coordination polymers based on lanthanide centers, in particular, the recent work by Daiguebonne and collaborators on benzene-polycarboxylate ligands,^[40] further supports that the properties of the compounds herein described are unusual among related materials. Studies on lanthanide coordination polymers based on terephthalate (bdc2-) or 4,4'oxybis(benzoic acid) (oba) ligands show interesting luminescent quantum yields and lifetimes of 72% and 0.85 ms for $[Tb_2(oba)_3(H_2O)_6 \cdot 3H_2O]^{[40d]}$ and 20% and 0.41 ms for $[Eu_6O(OH)_8(NO_3)_2(bdc)(Hbdc)_2 \cdot 2NO_3 \cdot H_2bdc].^{[40c]}$ The main breakthrough from the Daiguebonne group arises from heteronuclear lanthanide-based coordination polymers, in particular $[{Y_{6x}Tb_{6-6x}}_{6}O(OH)_8(NO_3)_2(bdc)-$ (Hbdc)₂·2NO₃·H₂bdc].^[40c] The dilution of Tb³⁺ ions by Y³⁺ ions resulted in quantum yields close to 100% and lifetimes





Figure 12. Time-resolved (dotted line; initial delay 20 ms and integration time of 20 ms) and stationary-state emission spectra (solid line) of 1-La recorded at 12 K under 300 nm excitation. The time-resolved emission spectrum was not corrected for the detection and optical spectral response of the spectrofluorimeter. The inset shows the decay curve and the best fit to a biexponential decay function of the phosphorescence emission detected at 450 nm.

of ca. 1.41 ms (ca. 59% and 1.40 ms for the solely Tb-based isotypical material). Mixtures of $\{Tb_{6x}Eu_{6-6x}\}$ also showed relevant values (53% and 1.12 ms).^[40c]

Conclusions

In this manuscript, we have described a rapid and efficient microwave-assisted synthesis of an isotypical series of 3D Ln³⁺-based MOFs based on residues of 2,5-pyridinedicarboxylic acid, namely, $[Ce_2(pydc)_3(H_2O)_2]$ (1), $[(La_{0.95}Eu_{0.05})_2(pydc)_3(H_2O)_2]$ (1-LaEu), $[(La_{0.95}Tb_{0.05})_2$ -(pydc)₃(H₂O)₂] (1-LaTb), and [(La_{0.90}Eu_{0.05}Tb_{0.05})₂(pydc)₃- $(H_2O)_2$] (1-LaEuTb). The reaction time was reduced from the typical 3 d (hydrothermal synthesis) to just 1 min under MWAS, and the reaction temperature was reduced from 170 to 120 °C (or 90 °C if the reaction time is increased to 10 min). So far, the method herein described represents the optimal experimental settings for a quick and economically viable isolation of these functional materials. In addition, this approach allows the simple preparation of optically active materials with intense photoluminescence in the visible region.

By systematically varying the experimental conditions under MWAS (i.e., temperature, power of irradiation, and reaction time), at least three distinct phases could be isolated: 3D [Ln₂(pydc)₃(H₂O)₂], which is isotypical with the La³⁺- and Pr³⁺-based materials reported by the groups of Shao and Hong,^[22a,22b] the 3D microporous [Ce₂(pydc)₂-(Hpydc)(H₂O)₂]Cl·(9 + *y*)H₂O previously reported by us,^[18g] and layered [{Ce₂(pydc)₂(Hpydc)₂(H₂O)₄}·2H₂O]_n, which is isotypical with the Nd³⁺-based compound reported by Zhang et al.^[22i] Investigations into the fine structural details of these materials revealed that the latter layered materials are strongly related to the compounds herein reported and share almost identical structural building blocks. A transformation associated with the release of extra organic ligands can lead to the densely packed 3D $[Ln_2(pydc)_3(H_2O)_2]$ compounds, and this is achieved by preparing the materials at a higher temperature. On the other hand, the ability to either isolate dense, nonporous $[Ln_2(pydc)_3(H_2O)_2]$ MOFs or the cationic microporous $[Ce_2(pydc)_2(Hpydc)(H_2O)_2]Cl \cdot (9 + y)H_2O$ material was also studied from a topological perspective. As observed for the relationship between the 2D and 3D compounds, differences between the dense and microporous materials also arise with the variation of one type of connecting pydc²⁻ ligand. Whereas the two crystallographically independent ligands in the latter material have identical coordination sequences up to the 10th shell, in the former dense isotypical series, small differences occur in the fourth and eighth shells of the "gluing" ligands between the Ce-pydc layers. These subtle coordination differences are the main reason why, on the one hand, such distinct materials can ultimately be isolated from the same reaction batch and, on the other hand, why the microporous structure could not be isolated as a phase-pure material to date.

Compound 1 is an effective catalyst for the ring-opening reaction of styrene oxide with methanol to give 2-methoxy-2-phenylethanol as the sole product at 80% conversion. This result was superior to that for the microporous material $[Ce_2(pydc)_2(Hpydc)(H_2O)_2]Cl \cdot (9 + y)H_2O$, obtained as an 80 wt.-% mixture with 1, for which the maximum 2-

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methoxy-2-phenylethanol yield was 32% after 48 h reaction.

Optically active lanthanide cations have been stoichiometrically included and uniformly distributed among an isotypical La³⁺ matrix of 1 (as shown by electron microscopy studies) to promote the isolation of the effective UVto-visible light converters 1-LaEu (red), 1-LaTb (green), and 1-LaEuTb (orange). Detailed photoluminescent studies of 1-LaEu and 1-LaTb showed the presence of a single crystallographic lanthanide centre with lifetimes of ca. 0.50 and 1.06 ms, respectively. The materials have very high absolute emission quantum yields (43% for 1-LaEu and 75% for 1-LaTb) when the UV ligand bands are excited. Such values are much higher than the intrinsic calculated quantum efficiency and show that intersystem crossing and ligand-tometal transfer processes are both favorable for the presented compounds. These results, allied to the fact that the materials can be prepared as pure phases in high yields and in just under 1 min of microwave irradiation open up the possibility for future studies of their possible application in the fabrication of photoluminescent devices. In particular, we are exploring the preparation of thin photoluminescent films based on the deposition of nanocrystals directly isolated from the microwave-assisted synthesis procedure. Additionally, we are also designing and preparing new organic ligands with energy levels that can simultaneously sensitize effectively a wide range of optically active lanthanide cations, and the main objective is to produce efficient materials with a wide range of color pallets.

Experimental Section

General Instrumentation: Fourier-transform infrared (FTIR) spectra (in the spectral range $4000-400 \text{ cm}^{-1}$) were recorded in the attenuated total reflectance (ATR) mode with a Mattson 7000 galaxy series spectrometer equipped with a DTGS CsI detector and a Golden Gate ATR accessory by averaging 128 scans at a maximum resolution of 2 cm⁻¹.

FT-Raman spectra (spectral range 4000–50 cm⁻¹) were recorded with a Bruker RFS 100 spectrometer with a Nd:YAG coherent laser ($\lambda = 1064$ nm) by averaging 256 scans at resolution of 2 cm⁻¹ and using a power of 300 mW.

C, H, N elemental analyses were performed with an Exeter Analytical CE-440 Elemental Analyzer at the Department of Chemistry of the University of Cambridge. Samples were combusted under an oxygen atmosphere at 975 °C for 1 min with helium as the purge gas.

Thermogravimetric analyses (TGA) were performed with a Shimadzu TGA 50 instrument from ambient temperature to ca. 800 °C with a heating rate of 5 °C min⁻¹ under a continuous air stream with a flow rate of 20 cm³ min⁻¹.

SEM images were collected with either a Hitachi S4100 field emission gun tungsten filament instrument at 25 kV or a high-resolution Hitachi SU-70 instrument at 4 kV. The samples were prepared by deposition on aluminum sample holders followed by carbon coating by using an Emitech K950X carbon evaporator. EDS (energy-dispersive X-ray spectroscopy) data and SEM mapping images were recorded by using the latter microscope at 15 kV and with a Bruker Quantax 400 or a Sprit 1.9 EDS microanalysis system. TEM images were acquired with a Hitachi H9000na HR-TEM microscope. A suspension was sonicated for 180 s and one drop was placed on a carbon-coated copper grid and left to dry in air. TEM analysis revealed that the investigated materials are extremely sensitive to the electron beam, and under normal conditions the crystallites are destroyed after a few seconds of intense irradiation. To minimize damage, a minimum electron voltage was employed for TEM measurements (200 kV), and the magnification was kept as low as possible.

Conventional powder X-ray diffraction data suitable for structural refinements were collected at ambient temperature with a Philips X'Pert MPD diffractometer (Cu- $K_{\alpha 1,2}$ radiation, $\lambda_1 = 1.540598$ Å and $\lambda_2 = 1.544426$ Å) equipped with an X'Celerator detector and a flat-plate sample holder in a Bragg–Brentano para-focusing optics configuration (40 kV, 50 mA). The intensity data were collected by the step-counting method (step 0.01°; 700 s per step) in continuous mode in the ca. $5.0 \le 2\theta \le 90^{\circ}$ range.

Reagents: All chemicals were readily available from commercial sources and were used as received without further purification: 2,5-pyridinedicarboxylic acid (2,5-H₂pydc, $C_7H_5NO_4$, purum $\ge 98\%$, Fluka), lanthanide (III) chloride hydrates (LnCl₃·xH₂O, Ln³⁺ = Ce³⁺, Eu³⁺, Tb³⁺, La³⁺, and Pr³⁺; Sigma–Aldrich), sodium hydroxide (NaOH pellets, Panreac), styrene oxide (Fluka, $\ge 97\%$), and methanol (Sigma–Aldrich, 99%).

Hydrothermal Synthesis by Standard Convection Heating: A procedure based on that described by Shao and co-workers has been employed.^[22a,22b] A suspension containing 2,5-H₂pydc, LnCl₃•xH₂O, and NaOH in distilled water (molar ratio of ca. 1:1:2.5:800) was stirred thoroughly in air (ambient temperature) for 1 h. The resulting homogeneous suspension was transferred to a Teflon-lined Parr reaction vessel and placed inside a preheated MMM Venticell oven. The reaction occurred at 165 °C over 72 h, after which time the oven was turned off, and the samples were cooled slowly to ambient temperature (inside the oven). After that, the obtained compound was collected by vacuum filtration, washed with copious amounts of distilled water, and dried at room temperature. [Ce₂(pydc)₃(H₂O)₂] (817.62): calcd. C 30.85, H 2.34, N 5.14 (C/N = 6.00); found C 29.76, H 1.83, N 4.85 (C/N = 6.14).

Microwave-Assisted Hydrothermal Synthesis

Optimization with Ce³⁺: A suspension similar to that described in the previous section was used (molar ratio 1:1:2.5:800). Typically, the reaction mixture was stirred thoroughly in air (ambient temperature) for five minutes, and the resulting homogeneous suspension was transferred to a 10 mL IntelliVent reactor, which was placed inside a CEM Focused MicrowaveTM Synthesis System Discover S-Class equipment. The reactions occurred with constant magnetic stirring (controlled by the microwave equipment), and the temperature and pressure inside the vessels were monitored. A constant flow of air (ca. 10 bar of pressure) ensured close control of the temperature inside the vessel. After completion of the reaction, a pale yellow suspension was obtained. The final product was recovered by vacuum filtration, washed with copious amounts of distilled water, and then air-dried overnight.

The following experimental conditions were systematically varied: (i) temperature (*T*), from 90 to 170 °C; (ii) power (*P*), from 50 and 150 W; (iii) reaction time (*t*), between 1 and 10 min of microwave irradiation. For simplicity, each sample is identified as $T_m P_n t_p$; the subscripts indicate the specific experimental conditions employed. [Ce₂(pydc)₃(H₂O)₂] (817.62): calcd. C 30.85, H 2.34, N 5.14 (C/N = 6.00); found C 28.28, H 1.67, N 4.68 (C/N = 6.05).

Optically Active Materials with Other Lanthanides: Mixed-lanthanide materials were prepared by using a similar experimental pro-



cedure to that described above. For simplicity, mixed-lanthanide samples will be mentioned on the basis of the lanthanides and the different percentages used in $[La_2(pydc)_3(H_2O)_2]$: $La_{0.95}Eu_{0.05}^{3+}$ (1-LaEu), $La_{0.95}Tb_{0.05}^{3+}$ (1-LaTb), and $La_{0.90}Eu_{0.05}Tb_{0.05}^{3+}$ (1-LaEuTb). The mixed-lanthanide materials were obtained by using microwave settings chosen to ensure the preparation of phase-pure compounds (see Scheme 1 for additional details).

The spatial distribution of the Eu³⁺ and Tb³⁺ ions in the La³⁺ matrices was further confirmed by electron microscopy EDX mapping studies on portions of 1-LaEu, 1-LaTb, and 1-LaEuTb. The EDX profiles (Figures S7–S9) indicate a homogeneous dispersion of the chemical elements in the $[Ln_2(pydc)_3(H_2O)_2]$ surface, and no compositional zoning was observed in any of the tested compounds.

Metal ion ratios estimated from EDX data. For 1-LaEu, La³⁺/Eu³⁺ ca. 9.7. For 1-LaTb, La³⁺/Tb³⁺ ca. 12.5. For 1-LaEuTb, La³⁺/Eu³⁺ ca. 8.5 and La³⁺/Tb³⁺ ca. 10.2.

Powder X-ray Diffraction Studies: The collected powder X-ray diffraction pattern for $[Ce_2(pydc)_3(H_2O)_2]$ (1, $pydc^{2-}$ is the diprotonated residue of 2,5-pyridinedicarboxylic acid) was indexed by means of the routines provided with DICVOL04^[41] and by employing the first 20 well-resolved reflections (located by using the derivative-based peak search algorithm provided with Full-prof.2k)^[42] and a fixed absolute error on each line of 0.03° 2 θ . The initial unit-cell metrics were obtained with reasonable figures-of-merit: M(20) = 33.3,^[43] F(20) = 65.0.^[44] An analysis of the systematic absences was performed by using CHECKCELL,^[45] which identified the monoclinic $P2_1/c$ space group as the most suitable, in good agreement with the crystal structure published by Shao and collaborators.^[22b] A Le Bail^[46] whole-powder-diffraction-pattern profile decomposition with fixed (and manually selected) background points produced a reasonable fit.

A Rietveld structural refinement^[47] of **1** was performed with FullProf.2k^[42] by using the reported atomic coordinates^[22b] for the isotypical Pr^{3+} compound as the starting premise. Fixed background points throughout the entire angular range and determined by the linear interpolation between consecutive (and manually selected) breakpoints in the powder pattern were employed. Typical pseudo-Voigt profile functions along with two asymmetry correction parameters were selected to generate the line shapes of the simulated diffraction peaks. The angular dependence of the individual reflections was also taken into account by employing a Caglioti function correction.^[48]

The overall structural refinement was performed in consecutive stages to avoid instability and divergence. Zero-shift, scale-factor parameters related to peak shape and unit-cell parameters were consecutively added as fully refineable variables upon previous full convergence of the remaining parameters to their optimal values. The fractional atomic coordinates for all non-hydrogen atoms were ultimately allowed to refine in conjunction with weighted soft distance constraints solely applied to the organic ligand (N–C, C–C, C–O, and O···O bond lengths and internuclear distances). This approach has the advantage of ensuring a final chemically feasible geometry for the organic moiety and allows the crystallographically independent Ce³⁺ center to refine freely. Each type of atom has been refined by using a common refineable isotropic parameter. No correction was made for absorption effects.

Table 1 collects the laboratory X-ray data collection, crystal data, and final Rietveld refinement details (profile and reliability factors) for **1**. The final Rietveld plot is supplied in Figure 2. Structural drawings have been created by using the Crystal Impact Diamond software package.^[49]

CCDC-930516 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Catalytic Studies: The batchwise reaction of the ring opening of styrene oxide in methanol was performed at 55 °C under air (autogenous pressure) and stirred magnetically in a closed borosilicate 10 mL reaction vessel immersed in a thermostatted oil bath. The reactor was loaded with $[Ce_2(pydc)_2(Hpydc)(H_2O)_2Cl]\cdot(9+y)-H_2O$ (35.9 mg) and $[Ce_2(pydc)_2(H_2O)_2]$ (1, 32.5 mg), styrene oxide (0.82 mmol), and methanol (2.0 mL). The progress of the reactions was monitored by using a Varian 3800 GC equipped with a BR-5 (Bruker) capillary column (30 m × 0.25 mm; 0.25 µm) and a flame ionization detector with H₂ as the carrier gas. The reaction products were identified by GC–MS with a GC 2000 Series (Thermo Quest CE Instruments) instrument and DSQ II (Thermo Scientific) spectrometer equipped with a fused silica capillary DB-5 column (30 m × 0.25 mm; 0.25 µm; 0.25 µm film thickness) and He as carrier gas.

Photoluminescence: The emission and excitation spectra were recorded at 12 and 300 K by using a Fluorolog-3® Horiba Scientific (Model FL3-2T) spectroscope with a modular double grating excitation spectrometer (fitted with a 1200 grooves/mm grating blazed at 330 nm) and a TRIAX 320 single emission monochromator (fitted with a 1200 grooves/mm grating blazed at 500 nm, reciprocal linear density of 2.6 nm/mm) coupled to a R928 Hamamatsu photomultiplier in the front-face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for the detection and optical spectral response of the spectrofluorimeter, and the excitation spectra were corrected for the spectral distribution of the lamp intensity by using a photodiode reference detector. Time-resolved measurements were performed with a 1934D3 phosphorimeter coupled to the Fluorolog-3® spectroscope, and a Xe-Hg flash lamp (6 µs/pulse half-width and 20-30 µs tail) was used as the excitation source. The variable-temperature measurements were performed by using a helium closed-cycle cryostat with a vacuum system measuring ca. 5×10^{-6} mbar and a Lakeshore 330 auto-tuning temperature controller with a resistance heater. The temperature can be adjusted from ca. 12 to 450 K.

The absolute emission quantum yields were measured at ambient temperature by using a Hamamatsu C9920-02 quantum yield measurement system with a 150 W Xenon lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as sample chamber, and a multichannel analyzer for signal detection. Three measurements were made for each sample, and the average value is reported. The method is accurate to within 10%.

Supporting Information (see footnote on the first page of this article): Additional experimental data on the microwave-assisted synthesis optimization, electron microscopy and vibrational spectroscopy, photoluminescence studies for the optically active materials.

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