We report the formation of novel open framework lanthanide (La, Ce, Pr and Dy) MOFs using the ligand 4,4′-bifenzoic acid-2,2′-sulfone. In the case of Ce and Pr, an unprecedented single-crystal-to-single-crystal transformation at room temperature was discovered.

Porous, metal-organic frameworks (MOFs) or coordination polymers (PCPs) represent an important class of crystalline open framework solids with diverse chemical composition and porosity characteristics and hold great promises for important industrial applications, especially in the field of gas storage and catalysis. These multifunctional materials result from molecular self-assembly reactions usually under hydro(solvo)thermal conditions between metal ions or clusters and bridging multidentate organic ligands.

The large number of available organic linkers, offers not only the potential for the construction of structurally and topologically diverse MOFs but also the opportunity to create functionalized porous frameworks with the functional species (atoms or groups) being exposed inside the pore space. This could lead to tailor-made materials for specific applications. However, while the currently extensive studies are focus on MOFs based on transition metals, lanthanide MOFs are also considered of equal importance.

Recently, we published two novel sulfone functionalized Zn-based MOFs (UoC-1 and UoC-2) with unprecedented inorganic and organic secondary building units (SBU’s) and overall structures, using for the first time the ligand 4,4'-bifenzoic acid-2,2'-sulfone (H2L, see Scheme 1). In an effort to explore further the potential to synthesize new MOFs with important properties, using this particular ligand, we have extended our work in the lanthanide family of metal cations.

We have discovered a significant structural diversity using different lanthanide cations (La, Ce, Pr and Dy) and more important, in the same Ln/H2L/DMF system, very different phases can be isolated, under different reaction conditions.

The reaction between La(NO3)3·6H2O (0.332 mmol) and H2L (0.164 mmol) in 10 ml of DMF at 95 °C for 12 h afforded a crystalline phase in high yield (>80%), denoted here as La-1. However, the quality of the crystals was not sufficient for single-crystal X-ray diffraction measurements. When the supernatant solution from this mixture was kept at room temperature for two weeks, rod-like single crystals of high quality were formed (see ESI),† denoted here as La-2.

The system is a new 3D non-interpenetrating MOF that crystallizes in the monoclinic system (space group P21/c) and features one-dimensional channels, as shown in Fig. 1. The inorganic part in La-2 is made of two crystallographically non-equivalent La2(μ2-CO2)2(CO2)4 dimers that bridged together and form one-dimensional chains running down the a axis (see Fig. 1 & 2). In one dimer, the La-La distance is 4.106(2) Å while in the other is 4.372(1) Å. The La1–La2 distance between two bridged dimers, is 5.841(1) Å. All La atoms in La-2 were found nine coordinated. The two out of the nine

**Scheme 1** The non-linear sulfone functionalized ligand L°°. The angle between the terminal carboxylate groups is 163°.
Coordination sites are occupied by DMF molecules. Four carboxylate groups serve as a bridge between the two La atoms within each dimer while the four other bridge two La atoms from adjacent dimers. The connectivity between adjacent chains is shown in Fig. 2, Overall, the neutral framework formula is La$_2$L$_3$(DMF)$_4$. It is important to note here that the calculated powder X-ray diffraction pattern (PXRD) of La-2 do not match with the experimental PXRD pattern of La-1 (see Fig. S8 in ESI).† Therefore, La-1 and La-2 are different crystalline phases.

In order to simplify the 3D structure of La-2 and identify the corresponding net topology, we considered the dimers as the central nodes of the net (the center of gravity of each unit is considered as the node) and the organic ligands as connectors. The topological analysis using the software package TOPOS,* revealed that La-2 is an 8-connected bcu type network (Schläfi symbol 426), as shown schematically in Fig. 2 at the bottom.

In the case of Ce, following an identical synthetic procedure, we first isolated the solid product, Ce-1, from the solvothermal reaction in DMF and the supernatant solution was kept at room temperature. From the later, we isolated the isostructural analogue of La-2, denote here as Ce-2. The Ce1–Ce1 and Ce2–Ce2 distance, of the two crystallographically independent dimers is 4.4643(9) Å and 4.2568(8) Å, respectively. The Ce1–Ce2 distance between two bridged dimers is 5.6772(13) Å (see ESI for single crystal data).†

Remarkably, and in contrast to the La-1 phase, we found that the initially isolated solid, Ce-1, consisting of low quality plate-like single crystals, when putted in fresh DMF and kept at room temperature for one month, was quantitatively transformed into high quality large, cubic-like single crystals (see Fig. 3, left). This new phase, denoted here as Ce-3, crystallized in the trigonal system (space group R3) and is a novel non-interpenetrating 3D MOF with 3D intersecting channels (see Fig. 3, right). As shown in Fig. 4, the inorganic SBU is a novel, linear anionic trimuclear cluster, with formula [Ce$_3$(CO$_2$)$_{12}$]$.\textsuperscript{3-}$. Bond valence calculations are in full agreement with Ce$^{3+}$. In this SBU, there are two crystallographically non-equivalent Ce$^{3+}$ atoms and the distance between Ce1–Ce2 is 3.981(4) Å. In terms of the coordination environment of Ce$^{3+}$ atoms in Ce-3 as compared to Ce-2, there are distinct differences; in Ce-3 there are no coordinated DMF molecules and also, while Ce1 is nine coordinated, Ce2 is twelve. The Ce1–O and Ce2–O bond lengths are found in the range 2.482(4)–2.556(4) Å and 2.624(4)–2.699(4), respectively. Notably, as in the case of UoC-1 and UoC-2,7 each SBU is linked to six other by twelve L$_2$$_2$$_2$ ligands, following a pseudo-octahedral connectivity, as shown in Fig. 4. Accordingly, in each direction, two ligands stack in parallel one on the top of the other and serve as linkers between two adjacent SBUs. The distance between these two ligands is approximately 3.6 Å, which is typical of aromatic, face-to-face π–π stacking. Each pair of ligands is in fact an organic SBU, stabilized by weak π–π interactions, which link together the six-connected inorganic SBUs (see Fig. 4, right), resulting in the non-interpenetrating 3D open structure of Ce-3. Considering the trimeric units as nodes and the organic SBUs (pairs of L$_2$$_2$$_2$ ligands) as single connectors, the network topology of Ce-3 is identical to that of 6-connected single pcu net (Schläfi symbol 426$\textsuperscript{3}$), as shown schematically in Fig. 4 at the bottom.

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* TOPOS
† Experimental PXRD patterns of Ce-2 match with the calculated PXRD pattern.
this phase is denoted here as Pr-3. Despite this notable similarity with
the Ce system, the supernatant solution from the Pr reaction did not
yield the isostructural Ce-2 and La-2. In contrast, the isolated phase
denoted here as Pr-2, is a 2-fold interpenetrating 3D MOF made of
simple Pr dimers linked together through a single L\textsuperscript{2}\textsuperscript{-} ligand,
following a pseudo-octahedral connectivity (Fig. S6 and S7 in ESI). \dagger
The Pr1–Pr2 distance is 4.2803(2) Å. This material is isostructural
with the very recently reported Nd, Eu and Gd phases obtained with
using the non-functionalized parent ligand 4,4-biphenyl dicarboxylic
acid. \dagger The origin of this structural diversity is attributed in part
to both the non-linear bridging mode of the ligand H2L (the angle
between the two carboxylate end-groups is 163°) and its increased
acidity caused by the electronegative sulfone group attached to the
phenyl rings.

An unprecedented discovery in this work is the room temperature
single-crystal-to-single-crystal quantitative transformation of yet
unknown Ce-1 and Pr-1 to the remarkable 3D open-framework,
isostructural Ce-3 and Pr-3, respectively. It is important to note here
that the above crystalline phases based on
the H2L ligand are different that those reported in some lanthanides
using the non-functionalized parent ligand 4,4-biphenyl dicarboxylic
acid. \dagger The novel anionic trinuclear [Ce3(CO2)\textsubscript{12}]\textsuperscript{-3} SBU (top left) in Ce-3
and its pseudo-octahedral connectivity to six adjacent SBUs, through six
pairs of L\textsuperscript{2}\textsuperscript{-} ligands (top right). The 6-connected pcu type network
topology of Ce-3 (bottom). Each node of the net (blue circles) represents
a cerium trimer.

The single-crystal X-ray diffraction analysis of Ce-3 did not reveal
an exact location of charge balancing cations for the anionic framework [Ce3L\textsubscript{6}]\textsuperscript{+}. Given the fact that it is generally difficult to
completely formulate the exact composition of all guest molecules in
highly porous MOFs and also that dimethylammonium cations,
(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}+, are formed in situ upon heating of DMF, \textsuperscript{8}it is natural
to consider these as charge balancing cations. In combination with
thermogravimetric analysis (TGA) results (see Fig. S3 in ESI), \dagger the
overall chemical formula of Ce-3 is [(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}][Ce3L\textsubscript{6}](DMF)\textsubscript{6}.

In the case of Pr, based on the PXRD pattern of the solid isolated
after the solvothermal reaction in DMF, Pr-1 (again, poor quality
crystals, see Fig. S4 in ESI), \dagger we may conclude that this phase is
isostructural to Ce-1 (see Fig. S9 in ESI). \dagger When this solid was
transferred in a fresh DMF solution and kept at room temperature
for a period of one month, it was quantitatively transformed into the
isostructural Ce-3 phase, again through a remarkable single-crystal-
to-single-crystal transformation (see Fig. S4 in ESI). \dagger Accordingly,
this phase is denoted here as Pr-3. Despite this notable similarity with
the Ce system, the supernatant solution from the Pr reaction did not
yield the isostructural Ce-2 and La-2. In contrast, the isolated phase
denoted here as Pr-2, is a 2-fold interpenetrating 3D MOF made of
simple Pr dimers linked together through a single L\textsuperscript{2}\textsuperscript{-} ligand,
following a pseudo-octahedral connectivity (Fig. S6 and S7 in ESI). \dagger
The Pr1–Pr2 distance is 4.2803(2) Å. This material is isostructural
with the very recently reported Nd, Eu and Gd phases obtained with
the ligand H2L. \textsuperscript{8} The topological analysis\textsuperscript{9} revealed that these 3D
MOFs are examples of 2-fold interpenetration related by a center of
symmetry (Class IIA)\textsuperscript{10} with an sxb network topology (Schaffli symbol
4\textsuperscript{2}5\textsuperscript{6}6). \textsuperscript{10}

In the case of Dy, the solvothermal reaction afforded good quality
single crystals, suitable for X-ray structural determination. No other
phases were obtained in this system. This material is a new 3D non-
interpenetrating MOF crystallized in the triclinic system (space
group P1) and features 3D intersecting channels (see Fig. 5). The
framework is made of isolated Dy2(μ-1,2 CO\textsubscript{2})\textsubscript{3}(CO\textsubscript{2})\textsubscript{2} dimers, each of
which is linked to six other by six L\textsuperscript{2}\textsuperscript{-} ligands; four of them adopt a
bis(bidentate) coordination mode while the other two adopt a
bis(chelating) mode (see Fig. 5 right). Interestingly, there are two
crystallographically non-equivalent dimers; the Dy1–Dy1 and Dy2–
Dy2 distance is 4.1027(10) Å and 4.2444(13) Å, respectively. All Dy
atoms are found eight coordinated, having two of the coordination
sites being occupied by DMF molecules. The overall neutral frame-
work formula is Dy2L\textsubscript{6}(DMF)\textsubscript{6}. Considering the dimers as nodes and
and the L\textsuperscript{2}\textsuperscript{-} ligands as connectors, the network topology of Dy is 6-
connected single pcu (Schaffli symbol 4\textsuperscript{2}5\textsuperscript{6}6), similar to that shown in
Fig. 4 at the bottom.

The structural diversity discovered in the lanthanide series La, Ce,
Pr and Dy could be explained in part by the well known lanthanide
contraction phenomenon. Accordingly, in the isostructural neutral
framework phases La-2 and Ce-2, the large size of the nine coordi-
nated lanthanide atoms results in bridged dimers while in the case of
Pr-2, the smaller size of the nine coordinated Pr atoms results in
isolated dimers and two-fold interpenetration. The situation does not
change in moving to Nd, Eu and Gd as the corresponding phases are
isostructural with Pr-2. However, in going to Dy, interpenetration is
not any more allowed due the smaller eight coordinated Dy atoms. It
is important to note here that the above crystalline phases based on
the H2L ligand are different that those reported in some lanthanides
using the non-functionalized parent ligand 4,4-biphenyl dicarboxylic
acid. \dagger The topological analysis
revealed that these 3D
isostructural Ce-3 and Pr-3, respectively. It is important to note here
that no product was formed when the corresponding lanthanide salts
were combined with H2L ligand in DMF solution and kept at room
temperature for months. These results suggest that the initial sol-
volthermal reaction is very crucial, promoting not only the necessary
deprotonation of H2L molecules and presumably the formation of lanthanide building blocks, but also the decarbonylation of DMF

Fig. 4 The novel anionic trinuclear [Ce3(CO2)\textsubscript{12}]\textsuperscript{-3} SBU (top left) in Ce-3
and its pseudo-octahedral connectivity to six adjacent SBUs, through six
pairs of L\textsuperscript{2}\textsuperscript{-} ligands (top right). The 6-connected pcu type network
topology of Ce-3 (bottom). Each node of the net (blue circles) represents
a cerium trimer.

Fig. 5 A 2 × 2 × 1 representation of Dy looking down the a axis (left) and the corresponding six-connected dimeric SBUs (right).
and the release of dimethylamine. The later can easily protonated and act as a counterion for the construction of Ce-3 and Pr-3. After this important step, the interplay between thermodynamic and kinetic parameters presumably controls the formation of the final structure, in each particular system. We are currently exploring different reaction conditions in the above systems in order to understand and elucidate the formation mechanism of the different phases.

Finally, we currently investigate the properties of these materials and in particular, the possibility to remove the guest molecules from the open-framework solids La-2, Ce-2, Ce-3, Pr-3 and Dy and access the available pore space.

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