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# Efficient Rare-Earth-Based Coordination Polymers as Green Photocatalysts for the Synthesis of Imines at Room Temperature

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**S** Supporting Information

ABSTRACT: Five new rare-earth coordination polymers (CPs) were designed in order to offer a remarkable platform that contains light-harvesting antennas and catalytic active centers to achieve solar-energy conversion as green alternatives in the synthesis of imines. These five new spirobifluorenecontaining Ln-CPs, named [Er<sub>3</sub>(Hsfdc)<sub>3</sub>(sfdc)<sub>3</sub>(H<sub>2</sub>O)]·xH<sub>2</sub>O (RPF-30-Er), [Ln(Hsfdc)(sfdc)(EtOH)]·S (RPF-31-Ln, where Ln = La, Nd, and Sm and  $S = H_2O$  or EtOH), and



 $[Ho(Hsfdc)(sfdc)(H_2O)]$  (RPF-32-Ho) (RPF = rare-earth polymeric framework and H<sub>2</sub>sfdc = 9,9'-spirobi[9H-fluorene]-2,2'dicarboxylic acid), have been solvothermally synthesized, and their structural features can be described as follows: (i) RPF-30-Er shows a 3D framework in which the inorganic trimers (secondary building units) are cross-linked by  $Hsfdc^{-}$  and  $sfdc^{2-}$  linkers displaying a pcu topology. (ii) The isostructural RPF-31-Ln series of materials, together with RPF-32-Ho, exhibit a 1D network of chains growing along the a axis with a ribbon-of-rings topology type. The photocatalytic activity of the RPF-n materials was tested in the oxidative coupling of amines using molecular oxygen and air as oxidizing agents under warm light. Among the materials investigated, RPF-31-Nd was chosen to further investigate the approach in the selectivity of different amine derivates.

# 1. INTRODUCTION

Rare-earth-based coordination polymers (CPs) have been extensively studied for their diversified structures and promising applications, such as gas storage/separation,<sup>1,2</sup> information storage,<sup>3–5</sup> chemical sensing,<sup>6–8</sup> and heterogeneous cataly-sis,<sup>9–13</sup> among others.<sup>14–16</sup> Our work always being focused on control of the material properties, from both the compositional and structural points of view, has proved that catalysis 17-20 and photoluminescence 10,21-24 are the fields where the route to improve the properties is more straightforward. In this context, we had previously designed and synthesized several rare-earthbased metal-organic frameworks (MOFs), with high catalytic activity in several organic transformations including multicomponent (one-pot or cascade) catalytic reactions. These materials were conceptually planned to contain catalytic active sites in both the organic linkers and metal centers.<sup>10,11,25,26</sup> The development of new and selective heterogeneous catalysts is crucial for the advancement in new catalytic processes, particularly in the oxidation of organic compounds. This type of reaction usually undergoes the generation of considerable amounts of byproducts and waste, which can be avoided with higher selectivity and recyclability of the catalyst, combined with the use of molecular oxygen or air as oxidizing agents instead of the traditional organic peroxides.

In the case of imines, which are well-known for being important intermediates in the synthesis of biologically active

heterocyclic compounds,  $\alpha$ -amino acids, and  $\alpha$ -amino alcohols,<sup>27,28</sup> great research efforts have been dedicated to finding different environmentally friendly alternatives to achieve the selective synthesis of imines.<sup>29–31</sup> Recently, several studies based on transition-metal-mediated catalytic routes have been developed.32-38

In the event of the selective oxidation of amines using light as a clean and renewable energy resource, some advances has been achieved using heterogeneous catalysts,  $^{39-42}$  but for the direct synthesis of imines from benzylamines, the use of CPs and MOFs as catalysts appears to have been rarely studied.<sup>43–49</sup>

However, it seems important to highlight the advantage of using CPs in photocatalytic processes because of their ability to integrate both light-harvesting and catalytic active sites in a single solid platform, allowing the conversion of solar energy to chemical energy.<sup>13</sup> In this respect, lanthanide CPs (Ln-CPs) are interesting candidates because of their stability in water, their strong Lewis acid properties, and their higher stability in front of their transition-metal-based analogues.

Herein, we present five new Ln-CP materials obtained by solvothermal synthesis using La, Nd, Sm, Ho, and Er as metal sources, together with the quite rigid dipodal ligand 9,9'spirobi[9H-fluorene]-2,2'-dicarboxylic acid (H<sub>2</sub>sfdc; Scheme

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1). The photocatalytic activities of all materials have been explored, and the true heterogeneous nature of the catalyst is demonstrated.

Scheme 1. Organic Ligand H<sub>2</sub>sfdc Reacting with Several Lanthanide Metals To Form a Series of New Ln-CPs



#### 2. EXPERIMENTAL SECTION

**2.1. Materials.** The following reagents were commercially available and were used as supplied without further purification:  $Ln(NO_3)_3$ .  $xH_2O$  (Ln = La, Nd, Sm, Ho, and Er; all 99% Strem Chemicals).

**2.2.** Preparation and Characterization of the Organic Linker ( $H_2$ sfdc) and RPF Materials. 2.2.1. Preparation and Characterization of 9,9'-Spirobi[9H-fluorene]-2,2'-dicarboxylic acid ( $H_2$ sfdc).  $H_2$ sfdc was easily prepared in two successive steps; selective 2,2'-diacetylation of 9,9-spirobi[9H-fluorene] by acetyl chloride in nitromethane (2,2'-diacetyl-9,9'-spirobi[9H-fluorene]), followed by a treatment with sodium hypobromite (NaOHBr<sub>2</sub>) and acidification. Characterization by NMR spectroscopy and mass spectrometry (MS) and a comparison with published data confirmed its chemical structure (see the Supporting Information).<sup>50–52</sup>

2.2.2. Preparation and Characterization of RPF Materials. RPF-**30-Er** with the formula  $[Er_3(Hsfdc)_3(sfdc)_3(H_2O)]$  was synthesized as follows: 0.019 g (0.047 mmol) of H<sub>2</sub>sfdc was added to a solution of  $Er(NO_3)_3$ ·5H<sub>2</sub>O (0.028 g, 0.063 mmol) in water (9 mL). The mixture was then magnetically stirred at room temperature for 15 min in a Teflon-lined stainless steel autoclave and heated at 200 °C for 72 h. After cooling to room temperature, the crystalline product was filtered and washed with water, ethanol, and acetone. Yield: 0.017 g (72%). Elem anal. Found (calcd for C<sub>162</sub>H<sub>97</sub>Er<sub>3</sub>O<sub>29</sub>): C, 64.95 (64.66); H, 3.47 (3.25). IR<sub>KB</sub> (cm<sup>-1</sup>): 3589, 3428, 3061–2922, 1924, 1682, 1608– 1590, 1539, 1490, 1425-1393, 1303, 1265, 1239, 1156, 1126-1109, 1077, 1006, 910, 876, 848, 799-794, 756, 730, 680, 655, 638, 552, 503, 497. TG (N2, 10 °C/min): the framework loses its solventencapsulated molecules (~0.5%) under 100 °C; between 200 and 350 °C, the structure loses 5% of the material content, which corresponds to the coordinated water molecule and the third part of a protonated linker. Then the framework is stable up to 420 °C, and between 430 and 490 °C, the loss of 94% of the material content is observed, which corresponds to the rest of the framework material.

Materials **RPF-31-Ln** with the formula [Ln(Hsfdc)(sfdc)(EtOH)]· xS [Ln = La, Nd, and Sm and S = solvent (H<sub>2</sub>O or EtOH)] weresynthesized under the same reaction conditions, as follows: Alanthanum compound (0.032 g, 0.079 mmol) of H<sub>2</sub>sfdc was addedto a solution of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.016 g, 0.037 mmol) in a mixtureof water and ethanol (1 and 8 mL, respectively). The mixture first wasstirred at room temperature for 15 min in a Teflon-lined stainless steelautoclave and then heated at 200 °C for 96 h. After cooling to roomtemperature, the crystalline product was filtered and washed with

water, ethanol, and acetone. Yield: 0.025 g (68% La), 0.064 g (83% Nd), and 0.020 g (83% Sm). RPF-31-La. Elem anal. Found (calcd for  $C_{56}H_{35}LaO_0 \cdot 0.5H_2O$ : C, 67.25 (67.21); H, 3.99 (3.63).  $IR_{KBr}$  (cm<sup>-1</sup>): 3589, 3428, 3061-2922, 1924, 1682, 1608-1590, 1539, 1490, 1425-1393, 1303, 1265, 1239, 1156, 1126-1109, 1077, 1006, 910, 876, 848, 799–794, 756, 730, 680, 655, 638, 552, 503, 497. TG (N<sub>2</sub>, 10 °C/ min): the framework loses its solvent-encapsulated molecules ( $\sim 0.5\%$ ) under 100 °C, and then the framework is stable up to 420 °C, and between 430 and 490 °C, the loss of 95% of the material content is observed, which corresponds to the rest of the framework material. RPF-31-Nd. Elem anal. Found (calcd for C56H35NdO9·EtOH): C, 66.51 (66.67); H, 3.86 (3.95). IR<sub>KBr</sub> (cm<sup>-1</sup>): 3616, 3419, 3065–2925, 2648-2609, 2499, 1953-1918, 1692, 1609-1588, 1535, 1491, 1464-1455, 1422-1395, 1344, 1303, 1265, 1238, 1155, 1124, 1109, 1077, 1046, 1028, 1006, 908, 876, 849, 820, 800-794, 756, 727, 680, 652-638, 553, 501–497. TG (N $_2$ , 10 °C/min): the framework loses its solvent-encapsulated molecules (~1%) under 100 °C, and then the framework is stable up to 400 °C, and between 440 and 490 °C, the loss of 98% of the material content is observed, which corresponds to the rest of the framework material. RPF-31-Sm. Elem anal. Found (calcd for C<sub>56</sub>H<sub>35</sub>SmO<sub>9</sub>·1.5H<sub>2</sub>O): C, 65.43 (65.41); H, 3.68 (3.72). IR<sub>KBr</sub> (cm<sup>-1</sup>): 3428, 3064–2923, 1685, 1609–1589, 1532, 1491, 1463-1454, 1422, 1395, 1344, 1301, 1265, 1233, 1156, 1125-1109, 1006, 908, 849, 800-794, 755, 729, 679, 653, 638, 554, 503. TG (N<sub>2</sub>, 10 °C/min): the framework loses its solvent-encapsulated molecules (~2%) at 100  $^{\circ}$ C, and then the framework is stable up to 400  $^{\circ}$ C, and between 430 and 500 °C, the loss of 98% of the material content is observed, which corresponds to the rest of the framework material.

**RPF-32-Ho.**  $[Ho(Hsfdc)(sfdc)(H_2O)]$  was synthesized as follows: 0.019 g (0.047 mmol) of H2sfdc was added to a solution of  $H_0(NO_3)_3$ ·5H<sub>2</sub>O (0.025 g, 0.057 mmol) in water (9 mL); the mixture was then magnetically stirred at room temperature for 15 min in a Teflon-lined stainless steel autoclave and heated at 200 °C for 96 h. After cooling to room temperature, the crystalline product was filtered and washed with water, ethanol, and acetone. Yield: 0.010 g (43%). Elem anal. Found (calcd for  $C_{56}H_{35}HoO_9 \cdot 1.5H_2O$ ): C, 64.12 (64.37); H, 3.60 (3.67). IR<sub>KBr</sub> (cm<sup>-1</sup>): 3428, 3064–2923, 1685, 1609–1589, 1532, 1491, 1463-1454, 1422, 1395, 1344, 1301, 1265, 1233, 1156, 1125-1109, 1006, 908, 849, 800-794, 755, 729, 679, 653, 638, 554, 503. TG (N<sub>2</sub>, 10 °C/min): the framework loses its solventencapsulated molecules (~8%) at 150 °C, and then between 200 and 300 °C, the framework loses the coordinated water molecule. The framework remains stable up to 400 °C, and between 430 and 500 °C, the loss of 92% of the material content is observed, which corresponds to the rest of the framework material.

**2.3. Visible-Light-Induced Oxidation of Amine Catalysis.** In a 3 mL Pyrex reactor was placed 5 mg (~0.005 mmol) of **RPF**-*n* material and benzylamine (5  $\mu$ L, 0.048 mmol) in acetonitrile (ACN; 1 mL). The mixture was stirred and irradiated with a 100 W warming lamp for 18 h. The temperature of the reaction system was precisely controlled at 25 °C. The reaction product was analyzed by mass-coupled gas chromatography (GC–MS).

# 3. CHARACTERIZATION TECHNIQUES

The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range 4000–250 cm<sup>-1</sup> on a Bruker IFS 66 V/S spectrometer. Thermogravimetric (TG) and differential thermal (DTA) analyses were performed using a Seiko TG/ DTA 320U equipment in a temperature range between 25 and 1000 °C in air and N<sub>2</sub> (100 mL/min flow) with a heating rate of 10 °C/min. A PerkinElmer CNHS Analyzer 2400 was employed for elemental analysis. Powder X-ray diffraction analysis was performed using a Bruker D8 diffractometer, with step size = 0.02° and exposure time = 0.5 s/step. Powder X-ray diffraction measurements were used to check the purity of the obtained microcrystalline products by a comparison of the experimental results with the simulated patterns obtained from single-crystal X-ray diffraction data. UV–visible studies were

Table 1. Main Crystallographic and Refi	ement Data for the Compounds	H <sub>2</sub> sfdc, RPF-30	, RPF-31, and RPF-32
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	H <sub>2</sub> sfdc	RPF-30-Er	RPF-31-Nd	RPF-31-Sm	RPF-32-Ho
formula	$C_{27}H_{16}O_4$	C162H87Er3O25	C56H35NdO9	C56H35SmO9	$C_{54}H_{31}HoO_9$
mol wt/(g/mol)	404.40	2935.09	996.08	1002.19	988.72
temperature/K	200	296	200	200	296
wavelength/Å	1.54178	1.54184	1.54178	1.54178	1.54178
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	C2/c	P1	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	36.035(5)	14.3779(6)	11.6558(4)	11.7296(5)	11.6105(4)
b/Å	14.3544(19)	14.6340(6)	14.3929(5)	14.4538(7)	14.6839(5)
c/Å	8.3818(10)	14.7237(7)	15.0469(5)	15.1994(7)	14.8117(5)
$\alpha/\deg$	90	91.940(3)	111.891(2)	112.026(2)	65.450(2)
$\beta/\text{deg}$	102.630(9)	94.008(3)	109.916(2)	109.758(3)	89.574(2)
γ/deg	90	91.914(3)	96.232(2)	96.449(3)	68.298(2)
$V/\text{\AA}^3$	4230.6(9)	3086.6(2)	2120.38(13)	2162.08(18)	2101.94(13)
Ζ	8	1	2	2	2
$D_x/(g/cm^3)$	1.270	1.579	1.557	1.539	1.562
$\mu/\text{mm}^{-1}$	0.691	4.287	9.865	10.711	4.026
F(000)	1680	1463	1002	1010	988
GOF of $F^2$	0.962	1.010	1.090	1.108	1.157
final <i>R</i> indexes $[I > 2\sigma(I)]$	R1 = 0.0801, wR2 = 0.1808	R1 = 0.0611, wR2 = 0.1598	R1 = 0.0533, wR2 = 0.1521	R1 = 0.0450, wR2 = 0.1295	R1 = 0.0591, wR2 = 0.1759
R indices (all data)	R1 = 0.1666, wR2 = 0.2265	R1 = 0.0908, wR2 = 0.2004	R1 = 0.0667, wR2 = 0.1819	R1 = 0.0501, wR2 = 0.1411	R1 = 0.0851, wR2 = 0.2442

carried out on a PerkinElmer Lambda XLS+ spectrometer. Fluorescence spectra were recorded on an Aminco SLM 8000 spectrophotometer.

3.1. Single-Crystal Structure Determination. Crystals were selected under a polarizing optical microscope for a singlecrystal X-ray diffraction experiment. Single-crystal X-ray data were obtained on a Bruker four-circle  $\kappa$  diffractometer equipped with a Cu INCOATED microsource, operated at 30 W power (45 kV, 0.60 mA) to generate Cu K $\alpha$  radiation ( $\lambda$  = 1.54178 Å), and a Bruker VANTEC 500 area detector (microgap technology). Diffraction data were collected by exploring over a hemisphere of the reciprocal space in a combination of  $\varphi$  and  $\omega$  scans to reach a resolution of 0.85 Å, using a Bruker APEX2 software suite (each exposure, depending on  $\omega$ , was of 56, 90, or 140 s covering 1° in  $\omega$  or  $\varphi$ ). Unit cell dimensions were determined for a least-squares fit of the reflections with  $I > 4\sigma$ . The structures were solved by intrinsic phase methods. The hydrogen atoms were fixed at their calculated positions using distances and angle constraints. All calculations were performed using APEX2 software for data collection and OLEX2-1.2 and SHELXTL for resolution and refinement of the structure.

# 4. RESULTS AND DISCUSSION

**4.1. Crystal Structures.** The crystal structure for each compound was determined using single crystal X-ray diffraction; crystals of suitable size were obtained through the solvothermal synthesis using conventional heating. Details of data collection, refinement, and crystallographic data for the compounds  $H_2$ sfdc, RPF-30, RPF-31, and RPF-32 are summarized in Table 1.

**4.2. Structural Description.** The dipodal ligand  $H_{2}$ sfdc presents several alternatives of the ligand coordination to metal centers. In the present work, three different coordination modes can be appreciated for the fully deprotonated sfdc<sup>-2</sup> linker and three for the protonated Hsfdc<sup>-1</sup> species (Scheme 2).

In the CCDC database,<sup>53</sup> we found that in 1983 the organic ligand  $H_2$ sfdc was reported as a solvate with *N*,*N*-

Scheme 2. Different Coordination Modes of the Half-Protonated (Hsfdc<sup>-</sup>) and Fully Deprotonated (sfdc<sup>2-</sup>) Organic Linkers in RPF-n



dimethylformamide.<sup>54</sup> In our work, we were able to obtain colorless plate-shaped single crystals (see Figure S1) of this organic ligand without any cosolvent from recrystallization of the freshly synthesized  $H_2$ sfdc using a microwave treatment (Table 1).

Only one work with  $sfdc^{2-}$  as the organic linker in a CP has been reported.<sup>52</sup> In such a case, calcium is the metal center selected and the corresponding CP (named SHU-1) consists of 2D layers built by square-planar Ca<sub>4</sub>O clusters connected by the  $sfdc^{2-}$  linker. The existence of rhombic windows is a common attribute observed in our materials and in the reported SHU-1, which is a consequence of the linker geometry.

**R P F - 3 0 - E r** material with the formula  $[Er_3(Hsfdc)_3(sfdc)_3(H_2O)]$  crystallizes in the triclinic P1 space group. Although reflection statistics (Wilson plot) indicate a centrosymmetric cell with Er2 in the inversion center, it is the asymmetric coordination of this atom in the  $ErO_6$  octahedron that makes it acentric. The asymmetric unit of **RPF-30** consists of three different crystallographic  $Er^{3+}$  ions, three molecules of the half-deprotonated linker Hsfdc<sup>-</sup>, three anions of the fully deprotonated sfdc<sup>2-</sup> linker, and a coordinated water molecule (Figure 1). The sfdc<sup>2-</sup> linker



Figure 1. (Top) Atomic and polyhedral representation of a RPF-30 3D structure, showing the asymmetric unit (left) and a (111) view of one of the 3D frameworks (right). (Bottom) SBU and view of the pcu topological representation (left) using the *ToposPro* program.<sup>55</sup>

(ii)  $L_2$  with  $\eta^2 \cdot \eta^2$ . Meanwhile, the Hsfdc<sup>-</sup> linker displays only a  $\eta^1 \cdot \eta^2 \mu$  coordination mode, named  $L_4$  from now on (Scheme 2). There are three crystallographically independent erbium metal centers, two of them in an ErO<sub>8</sub> coordination environment and one in an ErO<sub>6</sub> octahedral environment. As a result, the formation of two  $-[ErO_8]$ - primary building units (PBUs) of eight-coordinated erbium centers and one  $-[ErO_6]$ - PBU of an octahedral erbium center is observed.

The environment of the first erbium metallic center (Er1) is built by four Er–O bonds in a chelate way from the L<sub>1</sub> and L<sub>2</sub> modes of the fully deprotonated linker, one Er-O bond from the monodentate part of the  $L_4$  coordination mode of the Hsfdc<sup>-</sup>linker, and three Er–O bonds from the bridging part of the  $L_4$  coordination mode of the Hsfdc<sup>-</sup> linker. The environment of the second erbium metallic center (Er2) is formed by five Er–O bonds from the bridging O–C–O groups of the sfdc<sup>2-</sup> and Hsfdc<sup>-</sup> linkers ( $L_1$  and  $L_4$ , respectively) and one Er-O from a coordinated water molecule. It is precisely this coordinated water molecule that breaks the octahedron symmetry and thus avoids the  $P\overline{1}$  space group. The third erbium (Er3) environment consists of three Er-O bonds from the bridging part of the L1 linker type, one Er-O bond from the monodentate part of the L4 linker type, and four Er-O bonds from the chelating part of the  $L_1$  and  $L_2$  linker types.

In **RPF-30-Er**, the secondary building unit (SBU) is formed by three different PBUs joined through the binding of O-C-Ogroups, giving rise to a trimer that grows in the [111] direction. These trimers are connected through the Hsfdc<sup>-</sup> and sfdc<sup>2-</sup> linkers in all directions. The result is a 3D structure with pcu topology of a 6-connected uninodal net (Figure 1).

**RPF-31-Ln** material with the formula  $[Ln(Hsfdc)(sfdc)-(EtOH)] \cdot nS$  (Ln = La, Sm and Nd and S = H<sub>2</sub>O or EtOH)

crystallizes in the triclinic  $P\overline{1}$  space group. The asymmetric unit consists of one  $Ln^{3+}$  ion, half-deprotonated linker molecules Hsfdc<sup>-</sup>, one molecule of the fully deprotonated sfdc<sup>2-</sup> linker, and one coordinated ethanol molecule (Figure 2). The sfdc<sup>2-</sup> linker shows the coordination mode  $L_3$  with  $\eta^2 \mu - \eta^3 \mu$ , and in the case of the Hsfdc<sup>-</sup> linker, a  $\eta^1 - \eta^2$  coordination mode ( $L_5$ ) is observed (Scheme 2).

The lanthanide cation is nine-coordinated to one ethanol molecule and eight oxygen atoms from the linker, forming  $-[\text{LnO}_9]-$  PBUs. The carboxylate groups of the linker exhibited different coordination behaviors in both Hsfdc<sup>-</sup> and sfdc<sup>2-</sup> species. In **RPF-31-Ln**, the SBU is formed by two face-sharing  $-[\text{LnO}_9]-$  polyhedra (Ln1 and Ln1') related by symmetry, forming a dimer in the [010] direction, which are connected through Hsfdc<sup>-</sup> and sfdc<sup>2-</sup> linkers, giving rise to a 1D framework that grows along the *a* axis and presents a chainlike topology with the RoR type (Figure 2).

The supramolecular network is built up through two types of weak interactions, which increase the dimensionality of the framework, connecting the 1D covalent chains: (i) Ar–H···Ar interaction from two neighboring chains (C11–H11··· $\pi$ , D = 3.576 Å, d = 2.688 Å, and  $\theta = 155.85^{\circ}$ ) displaying a T geometry; (ii) several Ar–H···C<sub>Ar</sub> weak interactions (C36–H36···C11, D = 3.624 Å, d = 2.684 Å, and  $\theta = 172.01^{\circ}$ ; C3–H3···C45, D = 3.490 Å, d = 2.699 Å, and  $\theta = 141.22^{\circ}$ ; C5–H5···C47, D = 3.526 Å, d = 2.786 Å, and  $\theta = 140.72^{\circ}$ ); (iii) C55–H5SA<sub>EtOH</sub>···C23<sub>Ar</sub>, D = 3.670 Å, d = 2.891 Å, and  $\theta = 136.26^{\circ}$ ; all of these interactions allow the RoR chains to be aligned along the [001] direction as a hexagonal rod packing (Figure 2).



Figure 2. (Top) Atomic and polyhedral representation of a RPF-31 1D structure, showing the dimer SBU (left) and the (001) view of the 1D framework (right). (Middle) View of different supramolecular weak interactions between neighboring chains in RPF-31-Nd. (Bottom) Parallel alignment in the [100] direction of chains showing the supramolecular hexagonal rod packing.

**RPF-32-Ho** material with the formula  $[Ho(Hsfdc)(sfdc)-(H_2O)]$  crystallizes in the triclinic  $P\overline{1}$  space group. The asymmetric unit consists of one  $Ho^{3+}$  ion, one half-deprotonated linker molecule  $Hsfdc^-$ , one molecule of the fully deprotonated  $sfdc^{2-}$  linker, and one coordinated water molecule (Figure 3).

The structural difference between **RPF-31** and **RPF-32** relies in the coordination mode of the organic linker. Whereas for **RPF-32-Ho**, it is L<sub>3</sub> and L<sub>6</sub>, in **RPF-31**, it is L<sub>3</sub> and L<sub>5</sub> for sfdc<sup>2-</sup> and Hsfdc<sup>-</sup>, respectively. Therefore, nine- and eight-coordinated holmium centers are formed for **RPF-31** and **RPF-32** correspondingly.

The  $-[HoO_8]$  – PBU is formed with one Ho–O bond from the coordinated water molecule and seven Ho–O bonds from the linker (Hsfdc<sup>-</sup> and sfdc<sup>2-</sup> species). In **RPF-32-Ho**, the SBU is formed by two face-sharing  $-[HoO_8]$  – polyhedra (Ho and Ho') related by symmetry. These dimeric units (that run along the [001] direction), which are connected through the Hsfdc<sup>-</sup> and  $\text{sfdc}^{2-}$  linkers, give rise to a 1D framework that grows along the *a* axis and presents a chainlike topology with the RoR type (Figure 3).

Two intramolecular hydrogen bonds are observed for **RPF**-**32-Ho**: (i) O8–H8A<sub>w</sub>···O1<sub>L</sub> (1.757 Å, 2.649 Å, and 150.66°); (ii) O9–H9<sub>L</sub>···O3<sub>L</sub> (1.919 Å, 2.718 Å, and 164.32°). The supramolecular network is built up through two types of weak interactions, which increase the dimensionality of the framework, connecting the 1D covalent chains along the *b* and *c* axes: (i) Ar–H···Ar from two neighboring chains with distances of 2.683 and 3.612 Å displaying a T geometry (82.97°) with an angle of 175.49°; (ii) several C–H···O weak interactions  $[d_{D-A}(C-H···O1) = 3.219$  Å and 175.61°;  $d_{D-A}(C-H···O5) = 3.569$  Å and 163.79°]. Like **RPF-31**, these weak interactions connect the RoR chains along the [100] direction as a hexagonal rod packing.

**4.3. Photocatalytic Activity of RPF**-*n* **Materials.** In order to evaluate the stability and capacity of these novel **RPF** 



**Figure 3.** (Top) View in the (001) direction of the atomic and polyhedral representation of a **RPF-32** 1D structure. (Bottom) Augmentation of the small cages of **RPF-32** (left) and a close-up in the SBU dimer showing the coordination linker types and an intramolecular O–H…O hydrogen bond (right).

Scheme 3. (Top) Oxidative Condensation of Benzylamine Catalyzed by RPF-*n* Materials and (Bottom) Cross-Condensation of Benzylamine with Aniline



materials as heterogeneous photocatalysts, the oxidative coupling of amines to imines was chosen as a model organic transformation. Furthermore, cross-condensation between different amines was studied to analyze the selectivity scope of the best catalyst (Scheme 3).

For the initial trials, the self-coupling of benzylamine (~5  $\mu$ L, 0.05 mmol) was selected as a model reaction at room temperature (25 °C) using a commercial 100 W warm light lamp under an oxygen atmosphere purged with balloon using ACN (1 mL) as the solvent (Table 2, entries 1–5). Given that the H<sub>2</sub>sfdc linker has an extinction coefficient several orders of magnitude higher than the corresponding the metal, the samples had to be diluted (5  $\mu$ g/mL) to observe the absorption band in the visible region (Figure S12).

The progress of the reaction was monitored by GC–MS. Blanks run in the absence of catalyst and without light gave nonrepresentative reactivity under the same conditions (Table 2, entries 17 and 18, respectively). The use of **RPF** materials as catalysts (10%mol) provided good conversion in the 60–76% range of the **1a** product with high selectivity (Table 2, entries 1–5). Although several MOFs have been used as catalysts in the oxidation of amines (entries 6–16), in some cases higher temperatures were used in order to afford good conversions with high selectivity (Table 2, entries 7–13). Only a few of the MOFs explored so far in this reaction used light as an energy source (Table 2, entries 14–16). However, in the case of Zn-PDI and NH<sub>2</sub>-MIL-125(Ti) catalysts, the use of high-power light sources was necessary to achieve high conversions without

<b>Fab</b>	le 2. S	Screening	of RPF-n	Materials	s as l	Photocatal	lysts i	n the	Oxidation	of Benz	ylamine"
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entry	catalyst	metal CN, dimensionality	time (h)	conversion (%)	selectivity to 1a (%)	ref
1	RPF-30-Er	6 and 8, 3D	18	76	>99	this work
2	RPF-31-La	9, 1D	18	71	>99	this work
3	RPF-31-Nd	9, 1D	18	60	>99	this work
4	RPF-31-Sm	9, 1D	18	65	>99	this work
5	RPF-32-Ho	8, 1D	18	74	>99	this work
6	MOF-253 (Al) <sup>b</sup>	6, 3D	6	>99	>99	46
7	ZrMOF-BIPY <sup>b</sup>	6, 3D	6	38	38	46
8	DUT-5 <sup>b</sup>	6, 3D	6			46
9	NHPI/Fe(BTC) <sup>c</sup>	6, 3D	24	98	90	43
10	MIL-100(Fe) <sup><i>c</i></sup>	6, 3D	24	67	97	43
11	$Cu_3(BTC)_2^c$	4, 3D	24	17	98	43
12	$Al_2(BDC)_3^c$	6, 3D	24	61	97	43
13	Mn/Co-MOF <sup>d</sup>	6, 3D	4	92	92	45
14	Zn-PDI <sup>e</sup>	4, 2D	4	74	unspecified	47
15	NH <sub>2</sub> -MIL-125(Ti) <sup>f</sup>	6, 3D	12	73	86	48
16	UNLPF-12 <sup>g</sup>	8, 3D	2	>99	>99	49
17	without catalyst		18	7	95	this work
18	without light		18	22	96	this work
19	$H_2L$		18	15	74	this work

<sup>*a*</sup>Reaction conditions: benzylamine (0.05 mmol); catalyst (10 mol %); ACN as the solvent (1 mL); an oxygen atmosphere purged with balloon at 25 °C; 3000K LED 14 W (100 W) of warm light (distance  $\approx$  8 cm). Yields by GC–MS. <sup>*b*</sup>Reaction conditions: benzylamine (10 mmol); catalyst (1.5 mol %); 1 bar of oxygen; *T* = 100 °C; without light. Yields by GC–MS. <sup>*c*</sup>Reaction conditions: benzylamine (0.5 mL); an oxygen atmosphere purged with balloon, *T* = 100 °C, without light. Yields by GC–MS. <sup>*c*</sup>Reaction conditions: benzylamine (0.5 mL); an oxygen atmosphere purged with balloon, *T* = 100 °C, without light. Yields by GC–MS. <sup>*c*</sup>Reaction conditions: benzylamine (1 mmol); *tert*-butyl hydroperoxide (2 mmol); Mn/Co-MOF (10 mg) in ACN (2 mL) at room temperature; without light. <sup>*c*</sup>Reaction conditions: benzylamine (1 mmol); catalyst (1 mol %); ACN (5 mL); in air; 500 W xenon lamp with a cut filter below 420 nm. <sup>*f*</sup>Reaction conditions: benzylamine (0.1 mmol); NH<sub>2</sub>-MIL-125(Ti) (5 mg); ACN (2.0 mL); an oxygen atmosphere; irradiated for 12 h with a 300 W xenon lamp with a UV-cut filter to remove all wavelengths of less than 420 nm; an IR-cut filter to remove all wavelengths larger than 800 nm. <sup>*g*</sup>Reaction conditions: catalyst (1.0  $\mu$ mol; 0.4 mol % based on porphyrin moiety); benzylamine (0.27 mmol); 1 mL of dry ACN; 14 W white compact fluorescent lamp (distance  $\approx$  8 cm).

complete selectivity to the desired product (1a). The UNLPF-12 material, although it seems to have incredible conversion and selectivity at shorter time, owes its activity to the doping of porphyrin present in the MOF with tin(IV), and the activity does not proceed from the indium-based MOF itself.

The **RPF-30**, **RPF-31**, and **RPF-32** materials show good activity (around 70%) and excellent selectivity (>99%) in the oxidation of the benzylamine reaction. From the small differences among their activities, we can infer the following: (i) The nature of the metal source itself does not seem to have much influence on the reactivity and/or selectivity of the catalyst. (ii) The amount and accessibility of the active catalytic sites  $(Ln^{3+})$  in the structure, together with the  $Ln^{3+}$  coordination number (CN), and the presence of easily displaced labile ligands, make the reactivity order displayed by these **RPF-n** materials perfectly understandable. For example, the small upper conversion displayed by **RPF-30** is related to its higher number of metal centers, or the lower CN (8) in **RPF-32** favors better conversions in front of **RPF-31** with a CN of 9.

After these tests, additional trials were performed using **RPF-31-Nd** (Figure 4) as the catalyst (Table 3, entries 1–4). This material was chosen because of its high yield in its synthesis preparation, which allowed the performance of several experiments. On the other hand, we assumed that the above-described characteristics make the results obtained for **RPF-31** scalable to the other catalysts **RPF-n**. The reactions were performed under both molecular oxygen and air.

The results show that when using air instead of molecular oxygen (Table 3, entry 2), the selectivity remains at >99% but the conversion drops considerably from 60% to only 30% after 48 h. When the catalyst amount decreases to 5% and 1%, longer



Figure 4. SEM images of the synthesized RPF-31-Nd material before  $(600 \times \text{magnification}, \text{ left})$  and after  $(75 \times \text{magnification}, \text{ right})$  photocatalysis.

reaction times are needed to obtain the same conversion, although the selectivity is kept at >99% (Table 3, entries 3 and 4). Thus, the chosen conditions to perform the oxidative coupling of amines were 10 mol % (based on metal), ACN as the solvent, and an oxygen atmosphere purged with balloon at 25  $^{\circ}$ C.

The oxidation of several amines was examined, and when 1phenylethan-1-amine was used (Table 3, entry 5), the rate of reaction was lower and was attributed to the large size of this reactant, reaching only 22% conversion with 96% of the selectivity. In the case of anilines (without a hydrogen atom at the  $\alpha$  carbon atom), a small rate of conversion to the diphenylamine product was observed to be <10%, still with high selectivity (Table 3, entries 6 and 7). A primary aliphatic amine such as butan-1-amine was also transformed toward the corresponding imine (Table 3, entry 8).

Having determined the relative ability of amines to undergo catalytic aerobic oxidation in the presence of **RPF-31-Nd**, we Table 3. Screening of RPF-31-Nd as the Photocatalyst in the Oxidation of Several Amines with Molecular Oxygen<sup>a</sup>

					CH3
	1a 2a	3a		4a	5a
entry	amine	<i>t</i> (h)	product	conversion (%)	selectivity (%)
1	1	18	1a	60	>99
2	$1^b$	18	1a	30	>99
3	$1^c$	36	1a	58	>99
4	$1^d$	18	1a	28	>99
5	1-phenylethan-1-amine	24	2a	22	96
6	aniline	24	3a	6	>99
7	<i>p</i> -chloroaniline	24	4a	2	>99
8	butan-1-amine <sup>e</sup>	18	5a	99	>99

"Reaction conditions: amine (0.05 mmol); catalyst (10 mol %, based on metal); ACN as the solvent; an oxygen atmosphere purged with balloon at 25 °C. <sup>b</sup>Reaction conditions: benzylamine (0.05 mmol); catalyst (10 mol %); ACN as the solvent; in air; at 25 °C. <sup>c</sup>Reaction conditions: benzylamine (0.52 mmol); catalyst (5 mol %); ACN as the solvent; an oxygen atmosphere at 25 °C. <sup>d</sup>Reaction conditions: benzylamine (5.2 mmol); catalyst (1 mol %); ACN as the solvent; an oxygen atmosphere at 25 °C. <sup>d</sup>Reaction conditions: benzylamine (5.2 mmol); catalyst (1 mol %); ACN as the solvent; an oxygen atmosphere purged with balloon; T = 25 °C. Conversion by GC–MS. <sup>e</sup>Reaction conditions: biphenyl as the internal standard.

tested the reaction of a mixture of benzylamine and aniline (Table 4).

 Table 4. Cross-Condensation of Benzylamine with Aniline

 Using RPF-31-Nd as the Photocatalyst<sup>a</sup>

$\bigcirc$		$\square$		$\bigcirc$	сн3
	1a	6	a		7a
				selec	tivity (%)
entry	ratio of 1:3	time (h)	conversion (%)	1a	6a
1	1:1	36	55	85	15
2					_
2	1:3	36	60	92	8

<sup>*a*</sup>Reaction conditions: benzylamine (0.05–0.10 mmol); aniline (0.05–0.15 mmol); catalyst (10 mol %); ACN as the solvent; an oxygen atmosphere purged with balloon; at 25 °C. <sup>*b*</sup>Reaction conditions: benzylamine (0.05 mmol); butylamine (0.01 mmol); catalyst (10 mol %); ACN as the solvent, an oxygen atmosphere purged with balloon; at 25 °C. Conversion by GC–MS. The values inside parentheses are the corresponding yields for each product.

When the reaction was carried out with equal stoichiometry of amines, we obtain a mixture of products in 85/15 yield (1a/6a)because of the lack of aniline oxidation (Table 4, entry 1). We tried to increase the selectivity toward *N*-benzylideneaniline by performing the reaction with 3 equiv of aniline, although the selectivity toward *N*-benzylideneaniline does not augment. When the reaction was performed between benzylamine and butan-1-amine, we obtained a mixture 36/41 for 1a and the cross-condensation product *N*-butyl-1-phenylmethanimine (Table 4, entry 3).

**4.4. Recyclability and Leaching Test.** To meet the practical applicability and to improve the process economy, the photocatalytic activity of **RPF**-*n* materials must be enhanced; therefore, we next investigated the recyclability of the **RPF**-**31**-**Nd** catalyst using the standard reaction. To verify this, the catalytic activity of the material (10 mol % loading) was analyzed after stirring with benzylamine (5  $\mu$ L in 1 mL of ACN) for 18 h using 100 W of warm light. The product reaction was then analyzed by GC–MS, and the catalyst was

filtered and then washed with water and ethanol. This process of reuse was then repeated five times. The efficiency of **RPF-31-Nd** was reached even after five cycles of repetition. Moreover, the powder X-ray diffraction analysis of **RPF-31-Nd** after the recycling events showed that the material crystalline structure remained unchanged (Figure S19). To verify that no leaching from the catalyst occurs during the photocatalytic reaction, the reaction was carried out under optimized conditions and the solid was removed by hot filtration after 3 h; after removal, the mixture is again exposed to light and oxygen for the next 16 h. As expected, no significant conversion to the product **1a** was observed.

# 5. CONCLUSIONS

Herein we report five new rare-earth CPs that contain lightharvesting antennas and catalytic active centers and represent green alternatives in the synthesis of imines. **RPF-30-Er** shows a 3D framework in which the inorganic trimers (SBUs) are cross-linked by the Hsfdc<sup>-</sup> and sfdc<sup>2-</sup> linkers, displaying a pcu topology. The isostructural **RPF-31-Ln** series and **RPF-32-Ho** compound exhibit 1D networks of chains with a RoR topology type. The photocatalytic activity of the **RPF-n** materials was tested in the oxidative coupling of amines using molecular oxygen and air as oxidizing agents under warm light.

The first example of 1D rare-earth-based CPs **RPF** $\cdot$ *n* as efficient photocatalysts for the oxidation of amines is reported. Reactions have been performed under both oxygen and air atmospheres, using mild conditions without any cosolvent. The catalysts can be reused without loss in selectivity toward the desired product.

From this study, it can be inferred that the nature of the metal source itself does not seem to have much influence in the reactivity and/or selectivity of the catalyst. The experimental data (Table 2 and Figure S12) show that the metals act as connectors among the organic antennas through what seems to be a ligand-to-metal charge-transfer mechanism in the visible range. However, the results obtained for the lanthanum (f<sup>0</sup>) compound and the multiple  $CH_3-\pi$  interactions all over the structures do not allow one to rule out a cooperative ligand-to-ligand charge-transfer mechanism. To further investigate this point, more research with this ligand and no rare-earth metal is being carried out.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00465.

Structural determination of 9,9'-spirobi[9H-fluorene]-2,2'-dicarboxylic acid, experimental data for all **RPF**-*n* materials, and heterogeneous photocatalytic activities for **RPF**-*n* materials (PDF)

#### **Accession Codes**

CCDC 1810728–1810730 and 1811714–1811716 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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