

## Taking Lanthanides out of isolation: tuning the optical properties of metal-organic frameworks

Samantha L. Anderson,<sup>†,§</sup> Davide Tiana,<sup>†,‡,§</sup> Christopher P. Ireland,<sup>†,§</sup> Gloria Capano,<sup>†</sup> Maria Fumanal,<sup>†</sup> Andrzej Gładysiak,<sup>†</sup> Stavroula Kampouri,<sup>†</sup> Aiman Rahmanudin,<sup>¶</sup> Néstor Guijarro,<sup>¶</sup> Kevin Sivula,<sup>¶</sup> Kyriakos C. Stylianou,<sup>†</sup> and Berend Smit\*<sup>†</sup>

<sup>†</sup> Laboratory of molecular simulation (LSMO), Institut des Sciences et Ingénierie Chimiques, Valais Ecole Polytechnique Fédérale de Lausanne (EPFL), Rue de l'Industrie 17, CH-1951 Sion, Switzerland

<sup>‡</sup> School of Chemistry, University College Cork, College Rd, Cork, Ireland

<sup>¶</sup> Laboratory for Molecular Engineering of Optoelectronic Nanomaterials (LIMNO), Institut des Sciences et Ingénierie Chimiques (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

<sup>§</sup> Contributed equally to this work

E-mail: berend.smit@epfl.ch

## Table of Contents

1. Experimental.....	3
1.1: Materials and characterization methods.....	3
1.2: Synthesis of <b>Ln-SION-2</b> and <b>Ln-SION-1</b> .....	3
2. Single crystal X-ray diffraction.....	4
3. Characterization for <b>Ln-SION-2</b> and <b>Ln-SION-1</b> .....	4
3.1: Powder X-ray diffraction of <b>Ln-SION-2</b> and <b>Ln-SION-1</b> .....	4
3.2: UV/Vis of <b>Ln-SION-2</b> and <b>Ln-SION-1</b> .....	8
4. Computational details.....	10
5. Computed cell parameters.....	11
6. Optimized bond distances.....	12
7. Density of states of DHBDC and Ln-SION-2.....	14
8. Density of states of Ln-SION-1.....	16
9. Electronic transition.....	24
10. Current voltage (I-V) curves.....	26
11. H <sub>2</sub> generation.....	28
12. References.....	30

# 1 Experimental

## 1.1 Materials and Characterization Methods

All chemicals were purchased from Sigma Aldrich, Alfa Aesar, and Carl Roth and used without further purification. Elemental analyses were performed on a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Powder X-ray diffraction data were collected on a Bruker D8 Advanced using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , 50 kW/40mA). Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 3.0. The diffuse reflectance spectra were obtained with a PerkinElmer UV-Vis Spectrometer Lambda-950S on solid state samples using a quartz holder. The diffuse reflectance/Kubelka-Munk transformation ( $\alpha/S = (1-R)^2/2R$ ) was then plotted.

## 1.2 Synthesis of Ln-SION-1 and Ln-SION-2

**Synthesis of Ln-SION-2.** 2,5-dihydroxyterephthalic acid (20 mg), Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (20 mg) (where Ln: Ce, Nd, Eu, Gd, Tb, and Yb) were weighed into a 10 mL scintillation vial. 2 mL of DMF were added, and stirred until the entire solution was clear. Following this, 0.5 mL of H<sub>2</sub>O was added, and the vials were subsequently sealed. The vials were placed in an oven and heated at 120°C, for 24 hrs with a temperature ramp of 2.0°C, and cooling ramp of 0.2°C (67 % yield based on Tb(III)). The formula of **Tb-SION-2** was determined to be [Tb<sub>2</sub>(DHBDC)<sub>3</sub>(DMF)<sub>4</sub>] $\cdot$ 2DMF on the basis of the combined results of single-crystal X-ray diffraction (SCXRD) and elemental analysis (EA). Anal. Calcd for [Tb<sub>2</sub>(DHBDC)<sub>3</sub>(DMF)<sub>4</sub>] $\cdot$ 2DMF : C 37.51, H 3.05, N 6.25. Experimental: C 37.27, H 4.14, N 6.20.

**Ln-SION-1** (where Ln: Ce, Nd, Eu, Gd, Tb, Dy, Er, Yb and Lu) was synthesized using the same conventional heating parameters as **SION-2** with the exception of increasing the time to 72 hrs (76 % yield based on Tb). The formula of **Tb-SION-1** was determined to be [Tb<sub>2</sub>(DHBDC)(DOBDC)(DMF)<sub>2</sub>] (DOBDC = 2,5-dioxido-1,4-benzenedicarboxylate) on the basis of the combined results of SCXRD and EA. Anal. Calcd for [Tb<sub>2</sub>(DHBDC)(DOBDC)(DMF)<sub>2</sub>] : C 30.93, H 2.36, N 3.28. Experimental: C 28.34, H 2.44, N 3.34. Collection of all materials was done via filtration, in which all powders were washed with DMF (3 x 10 mL).

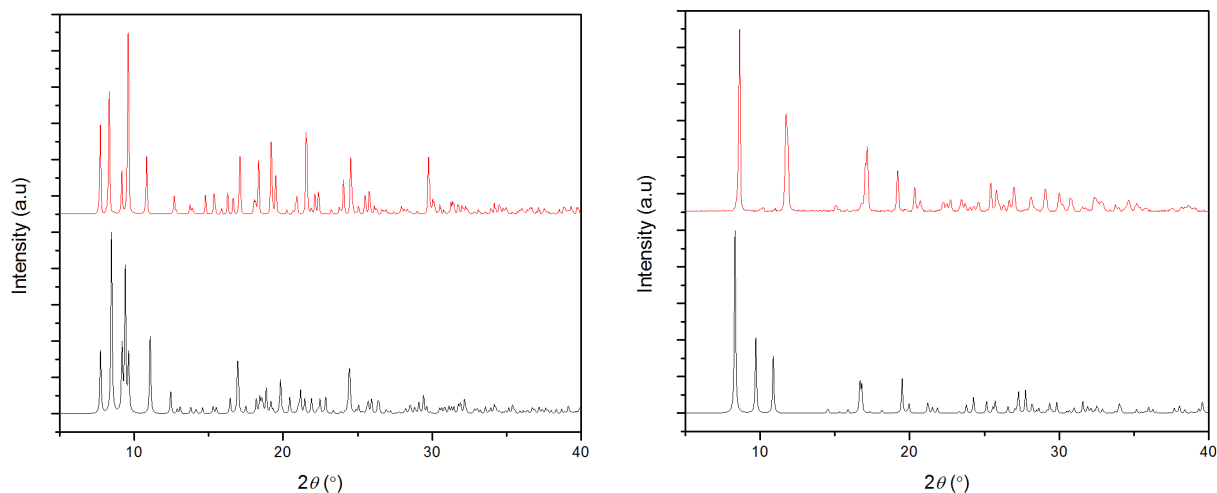
The phase purity of all **Ln-SION-1** and **Ln-SION-2** frameworks was confirmed by the comparison of the experimental PXRD pattern with the simulated generated from the single crystal structure (**Tb-SION-1/Tb-SION-2**).

## 2 Single-Crystal X-ray Diffraction

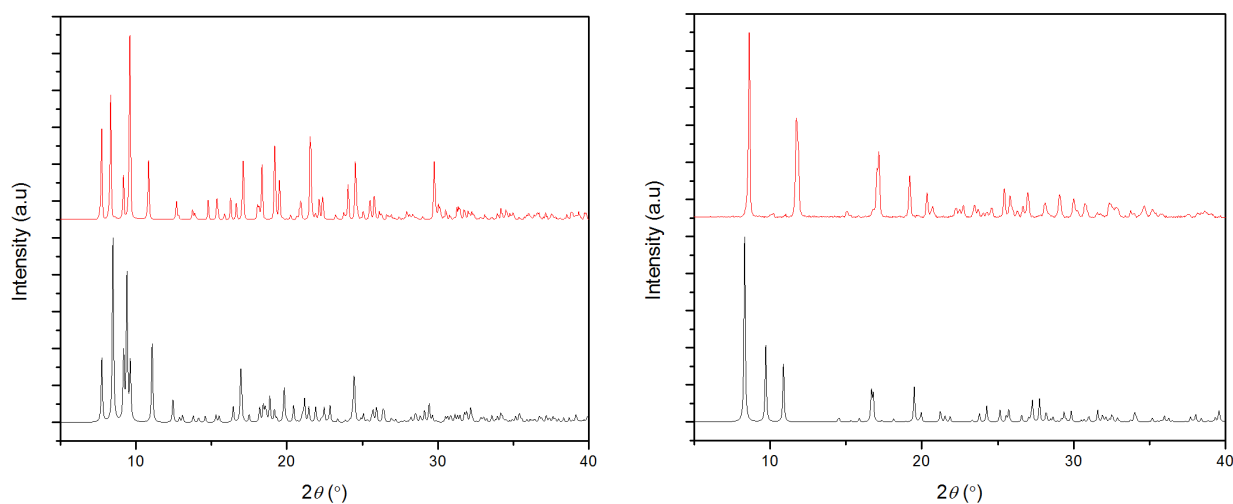
Structures for **Tb-SION-1** and **Tb-SION-2** can be found in the Cambridge Crystallographic Data Center (CCDC) under reference codes CAQHEK (CCDC number: 1503702) and CAQVOI (CCDC number: 1503701).

### 3 Characterization of Ln-SION-2 and Ln-SION-1

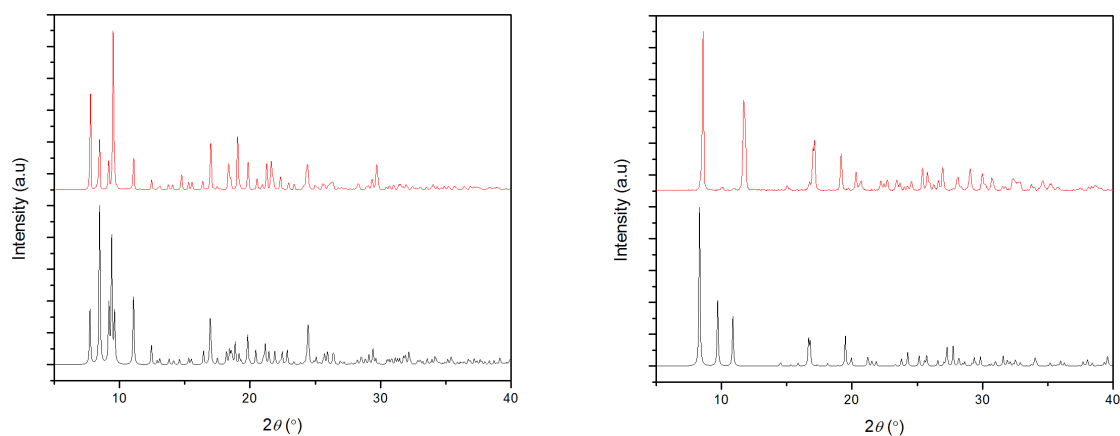
#### 3.1 PXRD of Ln-SION-2 and Ln-SION-1



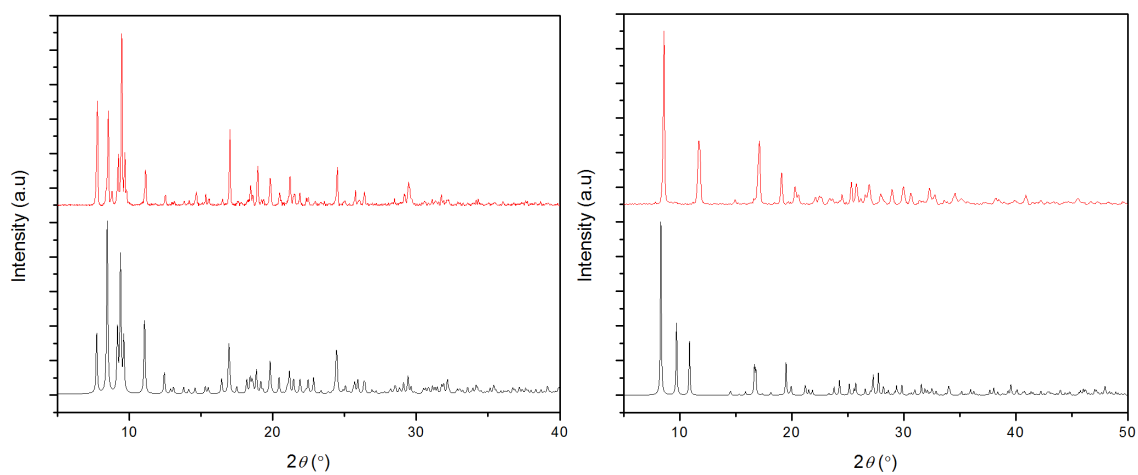
**Figure S1:** Left, PXRD of **Ce-SION-2**. Right, **Ce-SION-1**. Color scheme for both spectrum: black, theory; red, experimental.



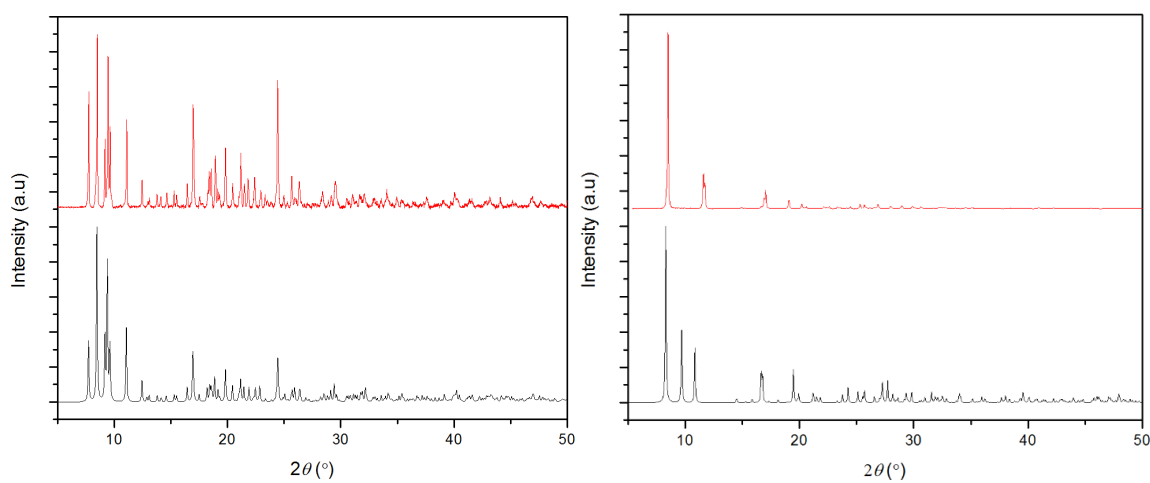
**Figure S2:** Left, PXRD of **Nd-SION-2**. Right, **Nd-SION-1**. Color scheme for both spectrum: black, theory; red, experimental.



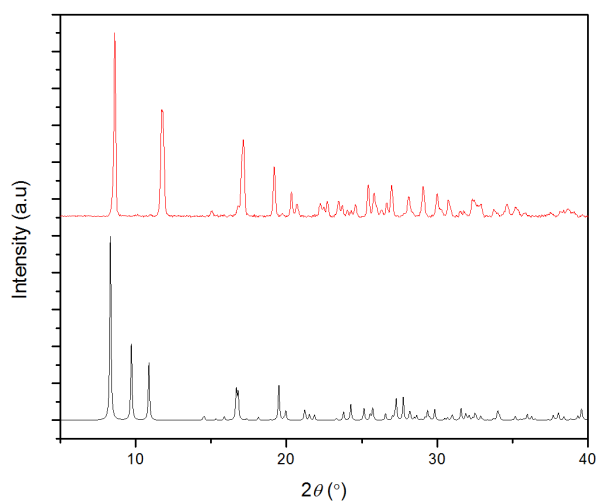
**Figure S3:** Left, PXRD of **Eu-SION-2**. Right, **Eu-SION-1**. Color scheme for both spectrum: black, theory; red, experimental.



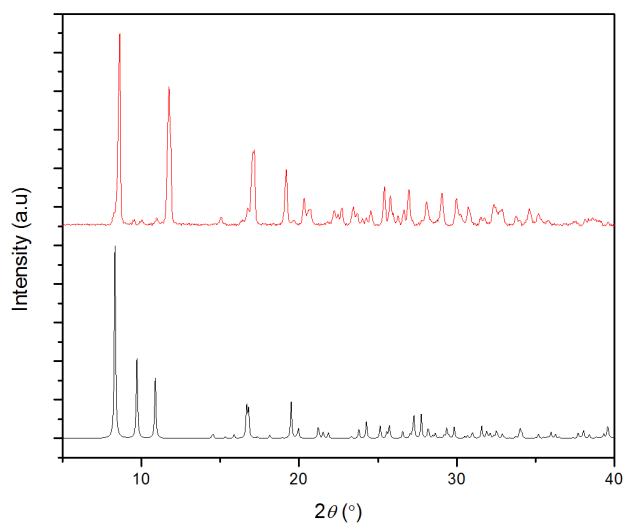
**Figure S4:** Left, PXRD of **Gd-SION-2**. Right, **Gd-SION-1**. Color scheme for both spectrum: black, theory; red, experimental.



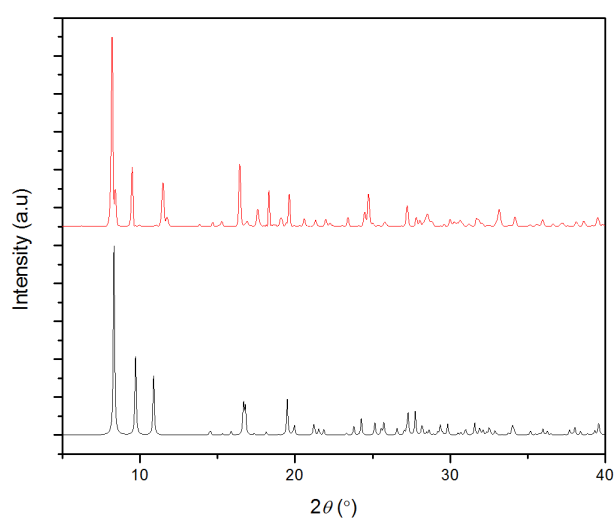
**Figure S5:** Left, PXRD of **Tb-SION-2**. Right, **Tb-SION-1**. Color scheme for both spectrum: black, theory; red, experimental.



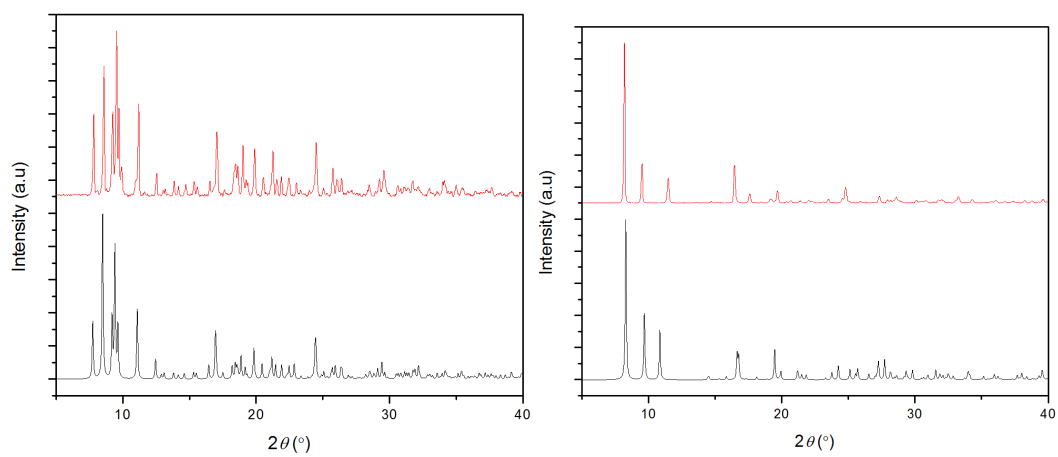
**Figure S6:** PXRD of **Dy-SION-1**. Color scheme: black, theory; red, experimental.



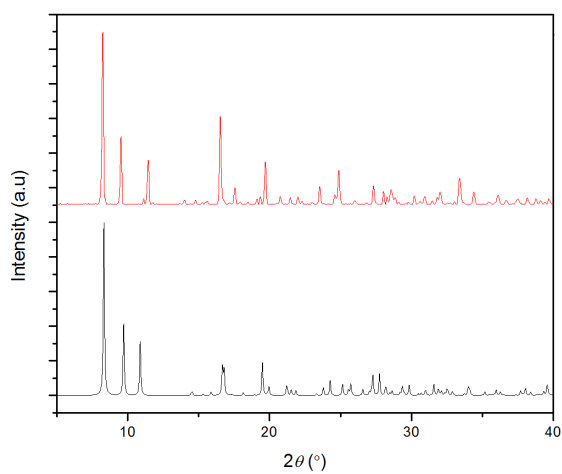
**Figure S7:** PXRD of **Ho-SION-1**. Color scheme: black, theory; red, experimental.



**Figure S8:** PXRD of **Er-SION-1**. Color scheme: black, theory; red, experimental.

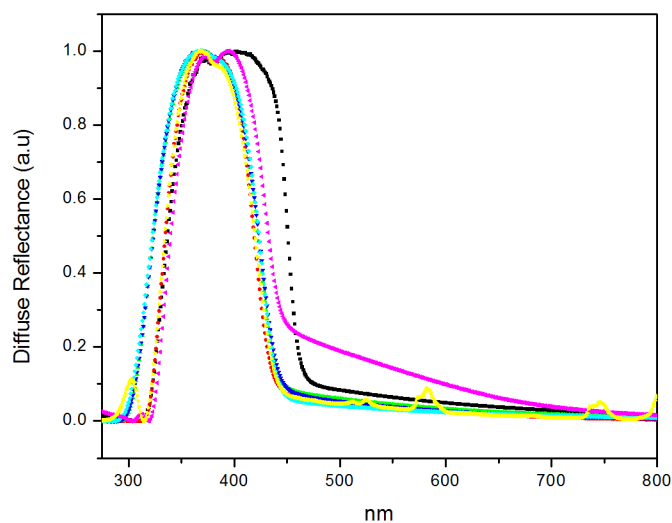


**Figure S9:** Left, PXRD of **Yb-SION-2**. Right, **Yb-SION-1**. Color scheme for both spectrum: black, theory; red, experimental.

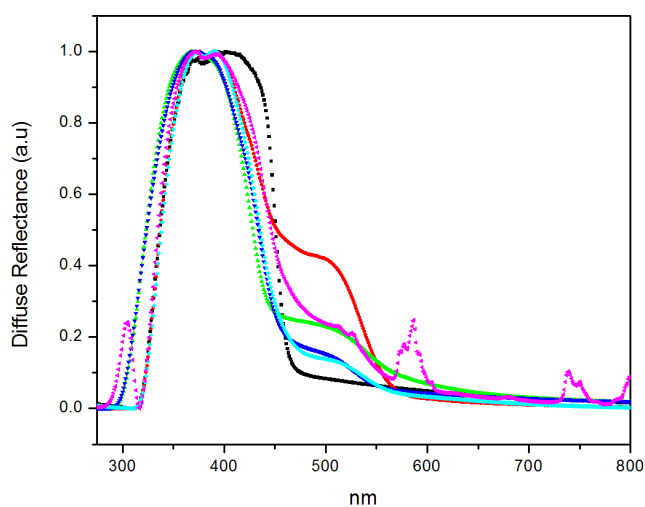


**Figure S10:** PXRD of **Lu-SION-1**. Color scheme: black, theory; red, experimental.

### 3.2 UV/Vis of Ln-SION-2 and Ln-SION-1

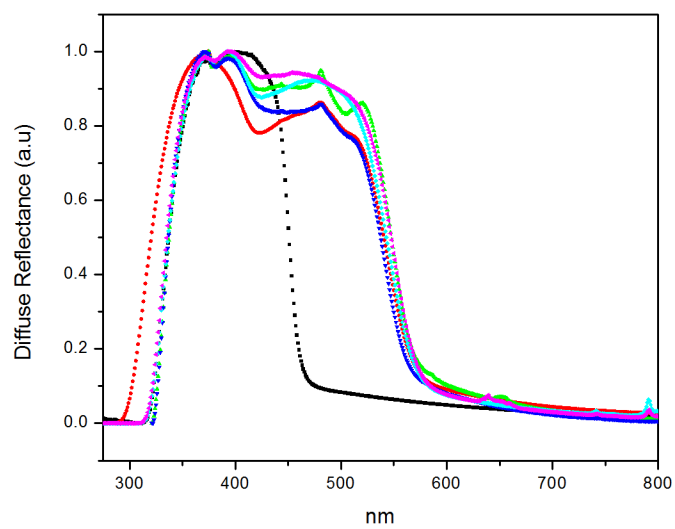


**Figure S11:** Diffuse reflectance spectra of Ce-to-Yb-SION-2. Colour scheme: black, ligand; light blue, Ce; yellow, Nd; dark blue, Eu; magenta, Gd; red, Tb; neon green, Yb.



**Figure S12:** Diffuse reflectance spectra of Ce-to-Tb-SION-1. Colour scheme: black, ligand; dark blue, Ce; magenta, Nd; lime green, Eu; neon blue, Gd; red, Tb.





**Figure S13:** Diffuse reflectance spectra of **Dy-to-Lu-SION-1**. Colour scheme: black, ligand; neon blue, Dy; magenta, Ho; lime green, Er; red, Yb; dark blue, Lu.

## 4 Computational details

All the calculations were done using the solid-state quantum chemical code Quantum Espresso (version 6.0). All the geometry optimisations were performed at the gamma point using the semi-local PBEsol exchange correlation functional, using norm-conserving pseudopotentials with a cut-off of 170 Ry. Dispersion force corrections were also employed. The force and energy thresholds were set to 1E-05 Ry and 1E-04 Ry, respectively, while the pressure convergence was set to 1E-01 Kbar. The spin state of single atoms were allowed to relax during the optimization with an SCF convergence threshold of 1E-09. The Density of States were calculated by performing single point calculations at the PBEsol optimized geometries using the non-local hybrid GAUPBE functional. The Brillouin zone for these calculations were sampled using a Monkhorst-Pack grid of 2x3x2 and 2x2x2 k-points for **SION-1** and **SION-2** respectively. Here, the calculations have been performed after solvent removal.

It should be noted that for spin-orbit coupling (and correction) (SO), while it is relevant for the description of the 4f energy level in Ln-based materials, the **SION-1** and **SION-2** electronic structures (top VB and bottom CB) and their related properties (optical transitions) are characterized by  $\pi$  and  $\pi^*$  organic orbitals and 5d metal state, for whose SO coupling (and correction) is negligible. More information on the different spin configurations can be found in in the following sections.

## 5 Computed cell parameters

**Table S1:** Computed cell parameter of the Ln-SION-1, -2 families. The experimental data are from single crystal data (Cambridge Crystallographic Data Center (CCDC) under reference codes CAQHEK (CCDC number: 1503702) and CAQVOI (CCDC number: 1503701).

Ln-SION-1	a	b	c	$\alpha$	$\beta$	$\gamma$
La	14.123	6.303	13.691	90.00	93.04	90.01
Ce	14.028	6.274	13.762	90.01	93.66	89.98
Nd	13.485	6.261	13.683	90.01	92.10	89.98
Sm	12.723	6.317	13.800	90.01	92.29	89.99
Eu	12.714	6.290	13.842	90.02	90.76	89.97
Gd	13.971	6.347	14.161	90.05	96.63	89.94
Tb	14.003	6.386	14.333	90.02	97.42	90.01
Tb (exp)	13.399(3)	6.6366(12)	15.567(2)	90.00	98.599(14)	90.00
Dy	14.028	6.337	13.941	90.06	96.91	89.97
Ho	14.081	6.406	14.506	90.11	97.80	87.97
Er	13.610	6.289	13.960	89.99	96.16	89.99
Tm	12.634	6.542	16.991	90.02	97.83	89.10
Yb	14.040	6.378	14.488	90.11	97.71	89.98
Lu	12.234	6.284	14.032	90.03	92.14	90.00
Y	13.945	6.430	14.365	89.99	97.63	90.02
Ln-SION-2	a	b	c	$\alpha$	$\beta$	$\gamma$
Tb	10.251	10.876	12.614	103.76	110.19	96.30
Tb (exp)	10.4608(8)	10.9006(10)	12.52939(10)	104.610(5)	107.840(4)	97.204(4)

## 6 Optimized bond distances

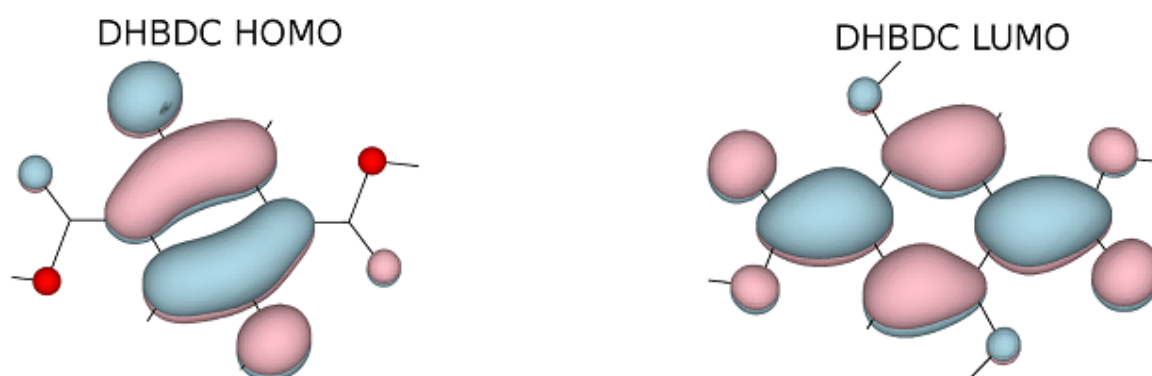
**Table S2:** DFT PBEsol distances in Angstrom for **Ln-SION-1**. O<sub>ac</sub> = Carboxylate Oxygen, O<sub>oxido</sub> = Oxido Oxygen, O<sub>avg</sub> = average distance.

Distance	Ce	Nd	Eu	Gd	Tb	Er	Yb	Lu
Ln-O <sub>ac1</sub>	2.635	2.685	2.726	2.432	2.398	2.432	2.359	2.515
Ln-O <sub>ac2</sub>	2.579	2.525	2.543	2.472	2.450	2.412	2.379	2.405
Ln-O <sub>ac3</sub>	2.520	2.530	2.511	2.415	2.409	2.378	2.361	2.370
Ln-O <sub>ac4</sub>	2.650	2.645	2.637	2.714	2.675	2.681	2.690	2.642
Ln-O <sub>ac5</sub>	2.500	2.498	2.497	2.396	2.376	2.330	2.332	2.299
Ln-O <sub>ac6</sub>	2.760	2.675	2.660	2.382	2.365	2.326	2.326	2.345
Ln-O <sub>oxido</sub>	2.495	2.473	2.491	2.340	2.308	2.287	2.308	2.275
Ln-O <sub>dmf</sub>	2.550	2.551	2.546	2.431	2.409	2.396	2.387	2.350
Ln-O <sub>avg</sub>	2.589	2.573	2.576	2.448	2.424	2.406	2.393	2.366

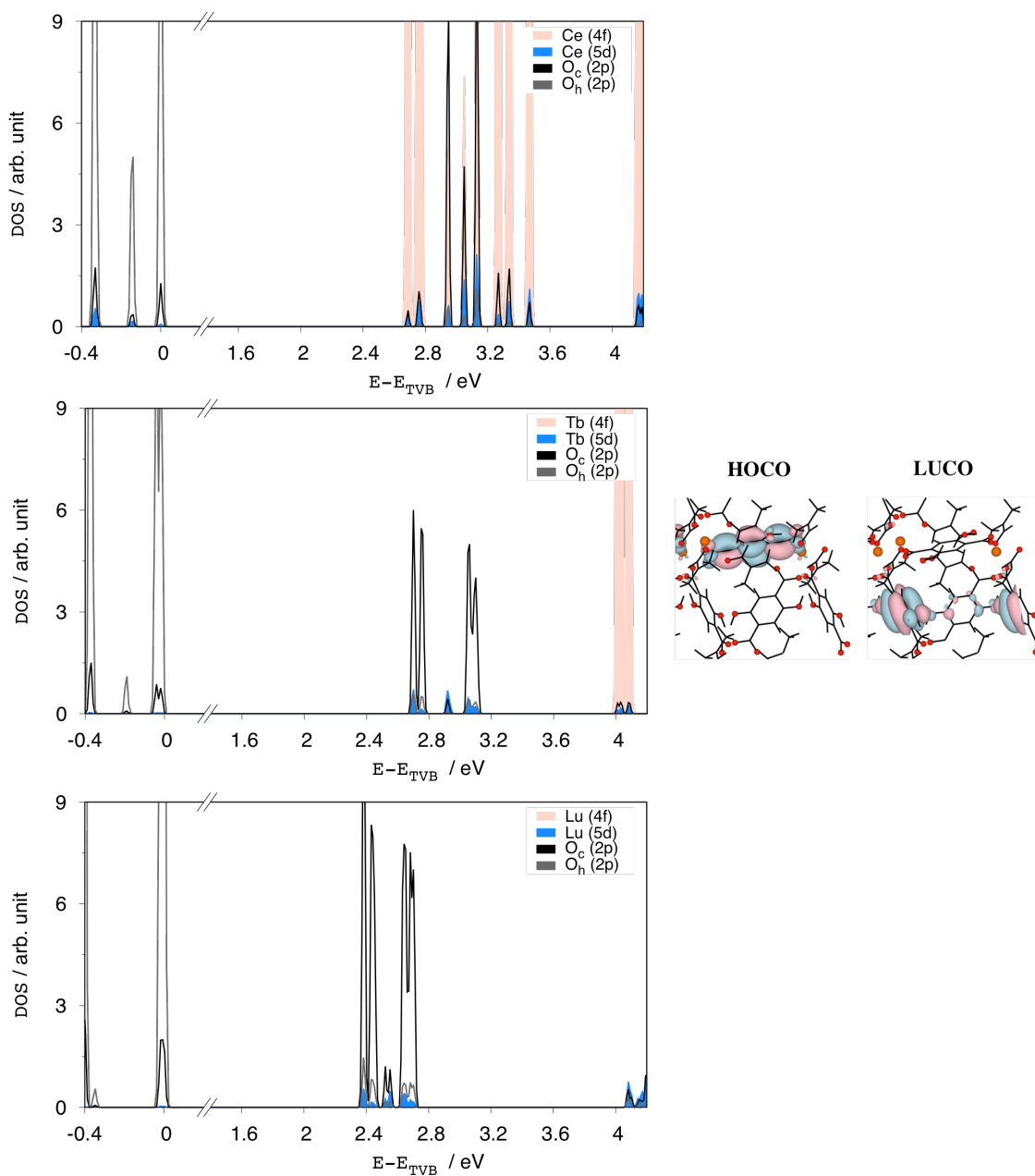
**Table S3:** DFT PBEsol distances in Angstrom for CO of the oxido group in **Ln-SION-1**. O<sub>oxido</sub> = Oxido Oxygen. A comparison with the CO<sub>oxido</sub> bond distance of the ligand (DHBDC = 1.354), its anionic form (DOBDC = 1.270), its semiquinone (1,4-Cyclohexanedione-2,5-dicarboxylic radical = 1.252), and its quinone form (1,4-Cyclohexanedione-2,5-dicarboxylic acid = 1.229) reveal that the ligand it is always in its anionic state and that an interaction with the metal is present producing an of bond elongation.

M	C-O <sub>oxido</sub>
Ce	1.302
Nd	1.282
Eu	1.274
Gd	1.313
Tb	1.321
Er	1.306
Yb	1.300
Lu	1.285

## 7 Frontier orbitals of DHBDC and density of states of Ln-SION-2



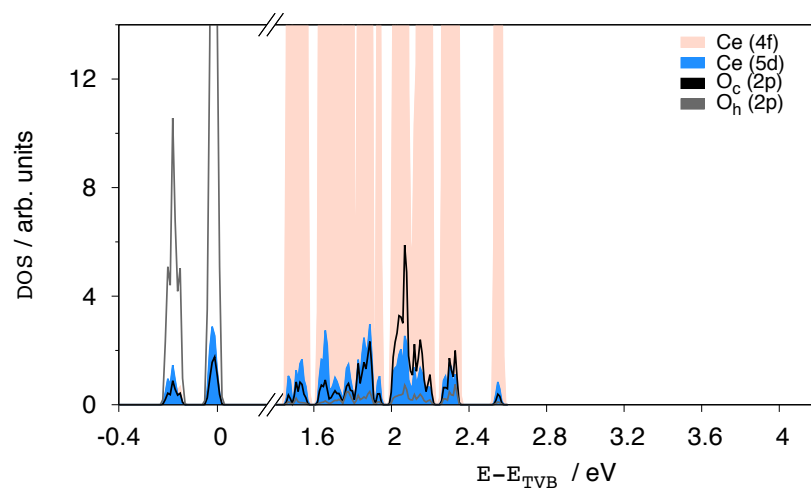
**Figure S14:** Frontier orbitals for the isolated in vacuum DHBDC. Atoms scheme colour: red, O; dark grey, C. The electronic transition is  $\pi \rightarrow \pi^*$  with a band gap of 3.40 eV.



**Figure S15:** The GAUPBE partial Density of State (left) and the corresponding frontier orbitals (right) for the isolated in vacuum **Ce-**, **Tb-** and **Lu-SION-2**. For the DOS the Fermi level was aligned to the HOCOs. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals. Atoms color scheme: red, O; orange, Tb, dark grey, C.

## 8 Density of state of Ln-SION-1

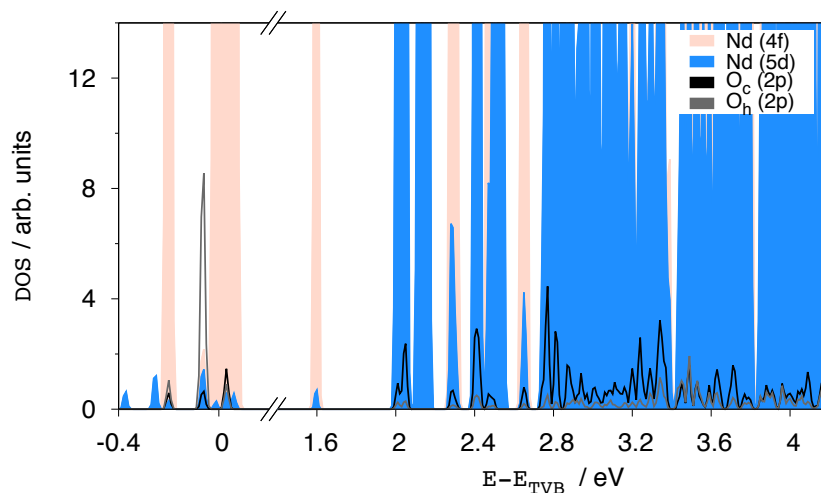
### Ce-SION-1



**Figure S16:** pDOS of Ce-SION-1. The valence of Ce(III) is  $[\text{Xe}]4f^15d^0$ . The HOCOs are mainly composed of the ligand  $\pi$ -orbitals whilst the LUCOs are made by the empty f-orbitals. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

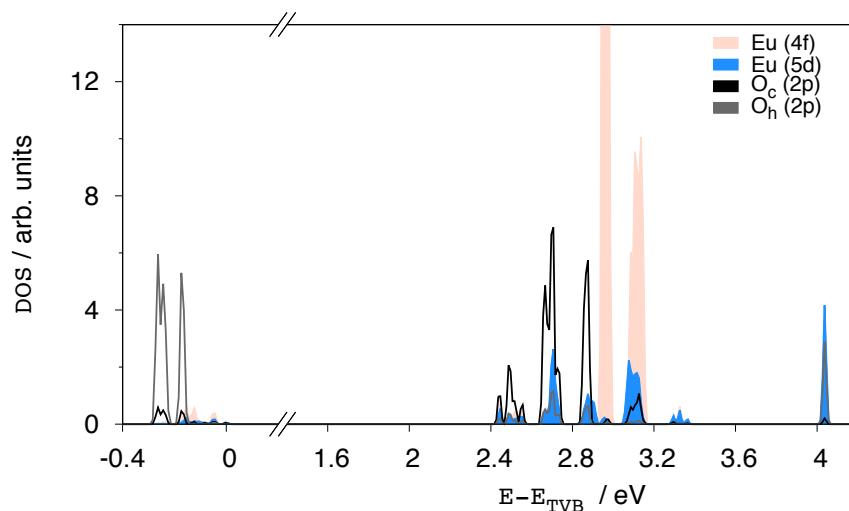


## Nd-SION-1



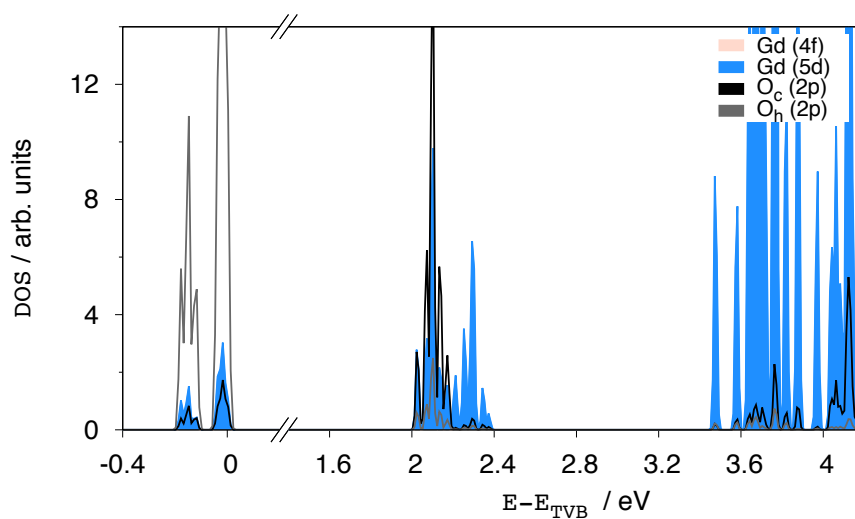
**Figure S17:** pDOS of **Nd-SION-1**. The valence of Nd(III) is  $[\text{Xe}]4f^35d^0$ . The HOCOs are mainly composed of the ligand  $\pi$  orbitals whilst the LUCOs are made by the empty f-orbitals. After the conduction band several mixed metal states are present – many absorption bands are observed in the UV/vis spectrum. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

## Eu-SION-1



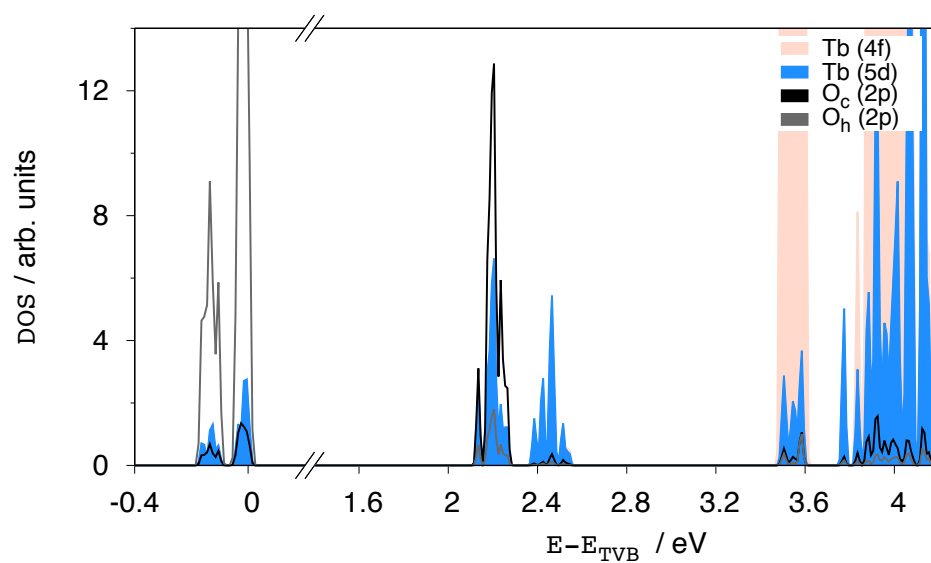
**Figure S18:** pDOS of **Eu-SION-1**. The valence of Eu(III) is  $[\text{Xe}]4f^65d^0$ . The HOCOs are mainly composed of the ligand  $\pi$ -orbitals whilst the LUCOs are made by the ligand's  $\pi^*$  orbitals with only a small amount of state arising from the Eu(5d) orbitals. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

## Gd-SION-1



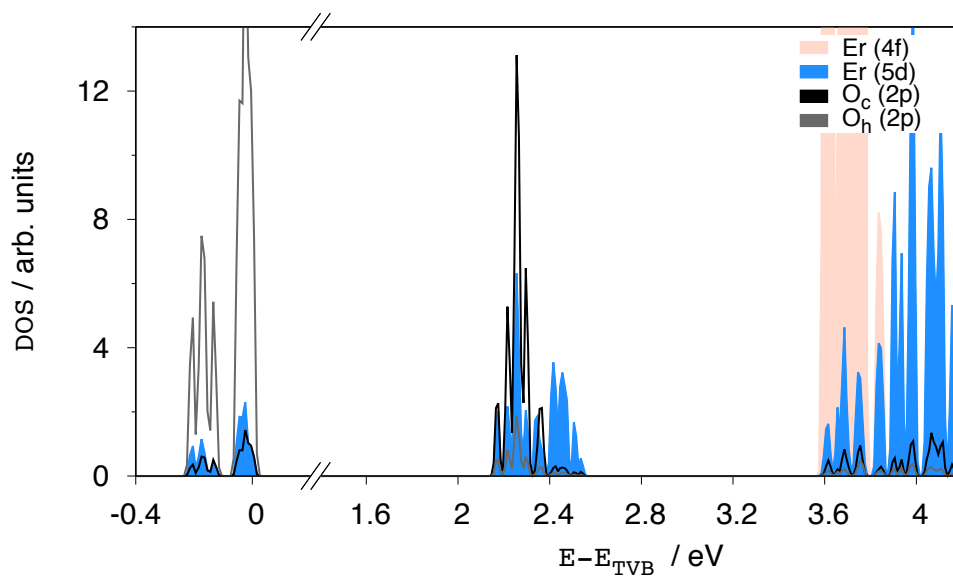
**Figure S19:** pDOS of **Gd-SION-1**. The valence of Gd(III) is  $[\text{Xe}]4f^75d^0$ . The HOCOs are mainly composed of the ligand  $\pi$ -orbitals while the LUCOs are made by a mixture of Ln(5d)/ligand( $\pi^*$ ) orbitals. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

## Tb-SION-1



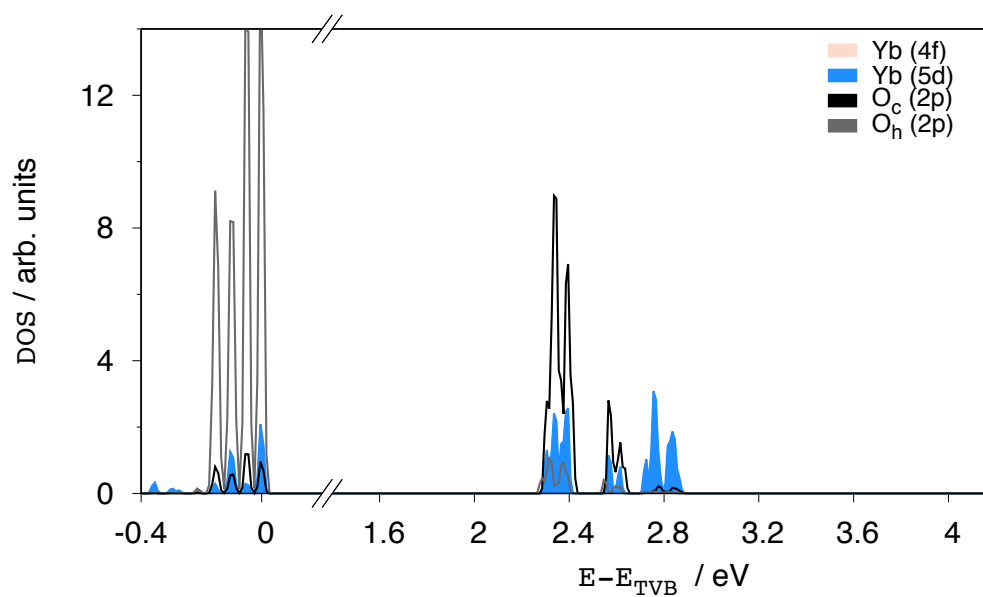
**Figure S20:** pDOS of **Tb-SION-1**. The valence of Tb(III) is  $[\text{Xe}]4f^85d^0$ . The HOCOs are mainly composed of the ligand  $\pi$ -orbitals whilst the LUCOs are made by a mixture of Ln(5d)/ligand( $\pi^*$ ) orbitals. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

## Er-SION-1



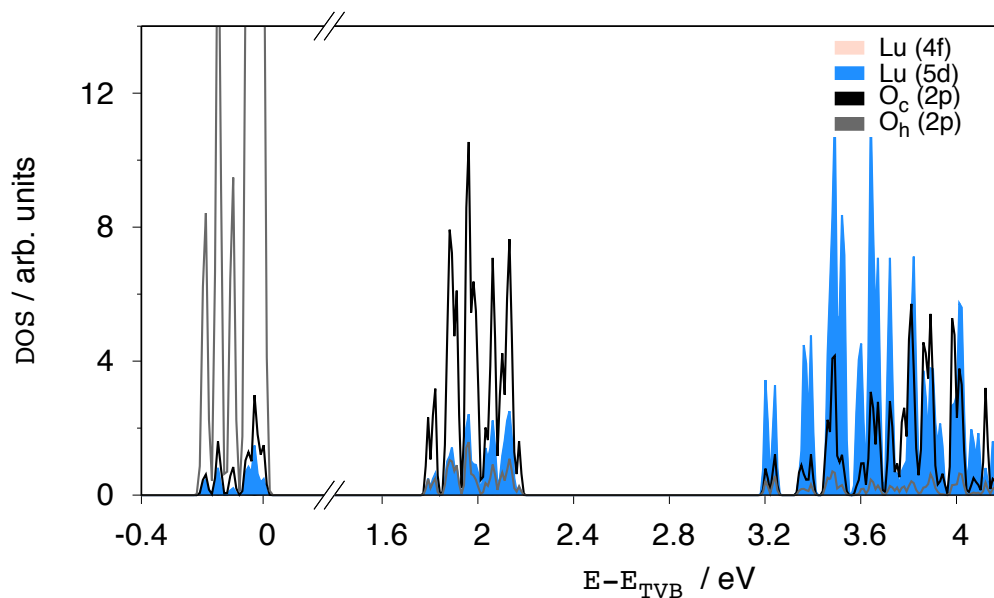
**Figure S21:** pDOS of Er-SION-1. The valence of Er(III) is  $[\text{Xe}]4f^{11}5d^0$ . The HOCOs are mainly composed of the ligand  $\pi$ -orbitals whilst the LUCOs are made by a mixture of Ln(5d)/ligand( $\pi^*$ ) orbitals. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

## Yb-SION-1



**Figure S22:** pDOS of Yb-SION-1. The valence of Yb(III) is  $[\text{Xe}]4f^{13}5d^0$ . The HOCOs are mainly composed of the ligand  $\pi$ -orbitals whilst the LUCOs are made by a mixture of Ln(5d)/ligand( $\pi^*$ ) orbitals. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

## Lu-SION-1



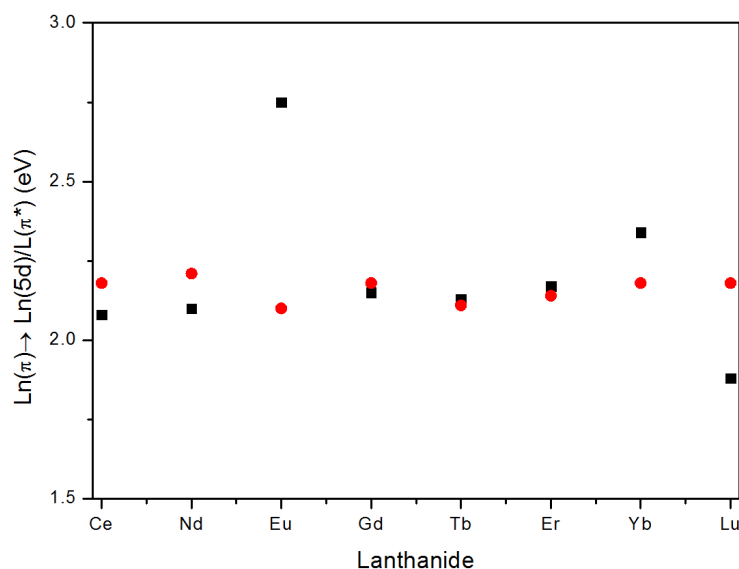
**Figure S23:** pDOS of **Lu-SION-1**. The valence of Lu(III) is  $[\text{Xe}]4f^{14}5d^0$ . The HOCOs are mainly composed of the ligand  $\pi$ -orbitals whilst the LUCOs is made by a mixture of Ln(5d)/ligand( $\pi^*$ ) orbitals. Color scheme for pDOS plots: grey, carboxylate O 2p; black, oxido O 2p orbitals; pale orange, Ln 4f orbitals; blue, Ln 5d orbitals.

## 9 Electronic transition

**Table S4:** DFT GAUPBE direct band gap, calculated Ln(5d)/ligand( $\pi^*$ ) and measured electronic transition for **Ln-SION-1**, and dispersion of the LUCOs through the b-axis. All data in eV.

M	Calculated Band Gap	Calculated L( $\pi$ ) $\rightarrow$ Ln(5d)/L( $\pi^*$ )	Measured L( $\pi$ ) $\rightarrow$ Ln(5d)/L( $\pi^*$ )	Calculated LUCO dispersion
Ce	1.63	2.08	2.18	0.04
Nd	0.43	2.10	2.21	0.04
Eu	2.75	2.75	2.10	0.04
Gd	2.15	2.15	2.18	0.05
Tb	2.13	2.13	2.11	0.05
Er	2.17	2.17	2.14	0.10
Yb	2.34	2.34	2.18	0.25
Lu	1.88	1.88	2.18	0.18





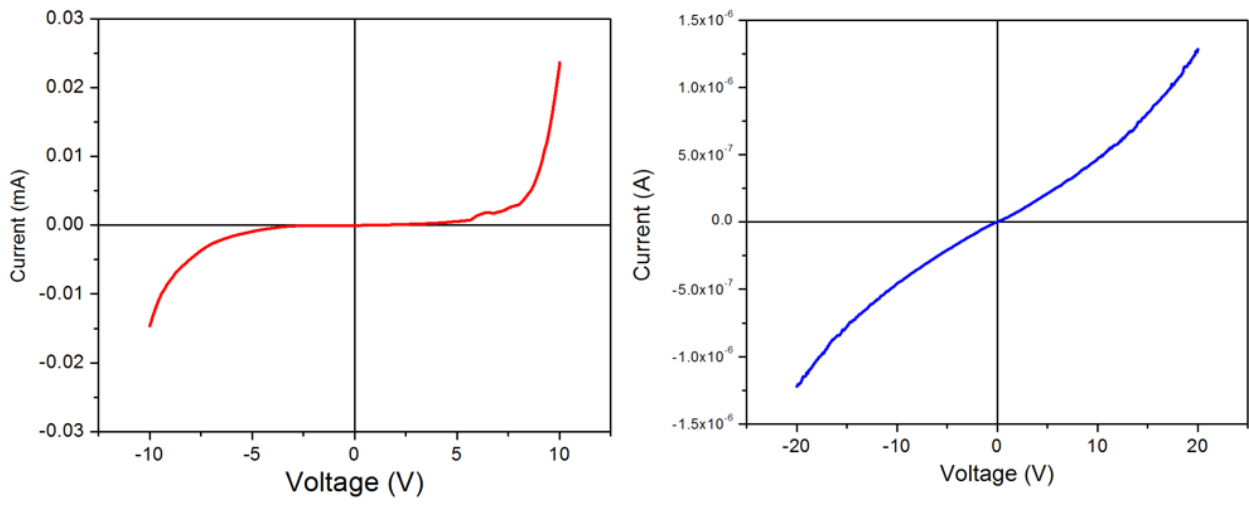
**Figure S24:** Plotted  $L(\pi) \rightarrow Ln(5d)/L(\pi^*)$  calculated (red dots) and measured (black squares).

The strong absorption band at about 400 nm, present in both **SION-1** and **SION-2** spectra, originates from ligand to ligand charge transfer transitions. This is confirmed by the pDOSs (SI Section 7 and Section 8) of the aforementioned materials, which show that the top of the valence band has a  $\pi$  character, localized on the organic moieties of the MOFs, while the conduction band has a strong  $\pi^*$  character. The additional peak at about 500 nm, observed only in the SION-1 series, can be explained by the mixed metal/organic nature of the lower energy lying conduction band present in these materials.

## 10 Current voltage (I-V) curves

We investigated the **Ln-SION-1** series through current-voltage (I-V) curves to determine if electron mobility in **Ce-SION-1** is present, however it is only isolated to the 1-dimension chains within the structure and cannot move freely within the MOF (**Yb-SION-1**). **Ln-SION-1** samples (10 mg) were first ground for 10 minutes in a Agate mortar, followed by dispersion in acetone via a sonicating bath (10 minutes). The samples were prepared by drop-casting the **Ln-SION-1** dispersion samples on F:SnO<sub>2</sub> (FTO) coated glass substrates, which had been coated with 20 nm of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEADOT:PSS). By varying the volume of acetone, we were able to control the thickness of the samples.

The current-voltage (I-V) profile for the FTO/**Ln-SION-1** samples were measured by using an In-Ga drop for the top-contact. Here, a Ga-In eutectic mixture was drop casted on the active layer and used as an electrode. A micromanipulator was used to form an electrical contact with the respective electrodes to measure the I-V characteristics of the device under a nitrogen atmosphere using a custom-built probe station and a Keithley 2612A dual-channel source measure unit. For each measurements, scans of voltage from -20V to 20V (**Yb-SION-1**) and -10V to 10V (**Ce-SION-1**) was swept while measuring the current to obtain the respective I-V curves. Various different locations on the active layer films were measure by moving the In-Ga bead with the micromanipulator. These I-V measurements demonstrate the qualitative semiconductor-like behavior of both the **Ce-SION-1** and **Yb-SION-1** MOFs.

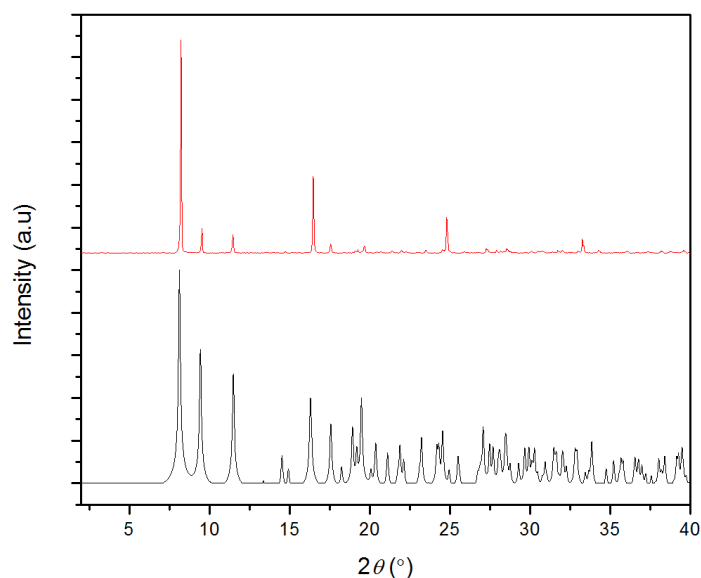


**Figure S25.** Current-Voltage (I-V) curves measured from of device using ITO/PEDOT.PSS/Active Layer/InGa in the dark: left, **Ce-SION-1**; right, **Yb-SION-1**.

## 11 H<sub>2</sub> generation

**Table S4: Electron mobility experiments of Yb-SION-1 and Ce-SION-1 via H<sub>2</sub> generation.** Here, optimized **Yb-SION-1** conditions are in bold, and were applied to the Ce-SION-1 below.

Sample	Conditions	Co-Cat	Irradiation time (hrs)	Area of Peak (GC)
Yb-SION-1	CH <sub>3</sub> CN: 81.96 v/v% H <sub>2</sub> O: 1.64 v/v% TEA: 16.39 v/v% MOF: 17 mg Volume of solution: 17 mL	Ni <sub>2</sub> P: 5.8 wt %	3	162.8
Yb-SION-1	CH <sub>3</sub> CN: 70 v/v% H <sub>2</sub> O: 15 v/v% TEA: 15 v/v% MOF: 50 mg Volume of solution: 20 mL	Ni <sub>2</sub> P: 9.4 wt %	24	549
Yb-SION-1	CH <sub>3</sub> CN: 70 v/v% H <sub>2</sub> O: 15 v/v% TEA: 15 v/v% MOF: 50 mg Volume of solution: 20 mL	Ni <sub>2</sub> P: 9.4 wt %	40	383
Yb-SION-1	CH <sub>3</sub> CN: 64.70 v/v% H <sub>2</sub> O: 17.64 v/v% TEA: 11.76 v/v% MOF: 20 mg Volume of solution: 17 mL	Pt: 0.8 wt %	40	240
<b>Yb-SION-1</b>	<b>CH<sub>3</sub>CN: 81.96 v/v%</b> <b>H<sub>2</sub>O: 1.64 v/v%</b> <b>TEA: 16.39 v/v%</b> <b>MOF: 17 mg</b> <b>Volume of solution: 17 mL</b>	<b>Ni<sub>2</sub>P: 5.8 wt %</b>	<b>20</b>	<b>612</b>
Ce-SION-1	CH <sub>3</sub> CN: 81.96 v/v% H <sub>2</sub> O: 1.64 v/v% TEA: 16.39 v/v% MOF: 17 mg Volume of solution: 17 mL	Ni <sub>2</sub> P: 5.8 wt %	24	0



**Figure S26:** PXRD of **Yb-SION-1** following photocatalytic experiments confirms that the material is stable and does not collapse. Color scheme: black, theory; red, experimental.

Based off of the calculated LUCO band dispersions of 0.04, 0.25 and 0.18 eV for **Ce-**, **Yb-**, and **Lu-SION-1**, electron mobility tests were performed. For this, photocatalytic  $H_2$  generation experiments were chosen to represent the potential for electron mobility because following light irradiation, electrons within the MOF have to move to the surface and interact with the co-catalyst and subsequently generate detectable amounts of  $H_2$  (See Table S4 for reaction conditions and results). From previous work published by our group, it is already known the co-catalysts under isolation do not generate  $H_2$ , and a blank sample with just the DHBDC ligand does not as well.<sup>1</sup> PXRD of **Yb-SION-1** performed after the reaction confirm the stability of the MOF under the reaction conditions.

Hydrogen generation was not seen for **Ce-SION-1**, which is attributed to the low band dispersion. Whereas with **Yb-SION-1** (largest band dispersion) electrons have sufficient mobility to reach the surface, and through the process previously described generate detectable amounts of  $H_2$ . It was further confirmed by PXRD that **Yb-SION-1** is stable (Figure S24), and does not undergo degradation.

## 9 References

1. Kampouri, S.; Nguyen, T. N.; Ireland, C. P.; Valizadeh, B.; Ebrahim, F. M.; Capano, G.; Ongari, D.; Mace, A.; Guijarro, N.; Sivula, K.; Sienkiewicz, A.; Forro, L.; Smit, B.; Stylianou, K. C. Photocatalytic hydrogen generation from a visible-light responsive metal-organic framework system: the impact of nickel phosphide nanoparticles. *J. Mater. Chem. A*. **2018**, *6*, 2476-2481.