Lanthanide-based Near-Infrared Emitting Metal-Organic Frameworks with Tunable Excitation Wavelengths and High Quantum Yields

Tu N. Nguyen,[a] Gloria Capano,[a] Andrzej Gładysiak,[a] Fatmah Mish Ebrahim,[a] Svetlana V. Eliseeva,[b] Arunraj Chidambaram,[a] Bardiya Valizadeh,[a] Stéphane Petoud,[b,c] Berend Smit,[a] Kyriakos C. Stylianou[*,a]

[a]*Laboratory of Molecular Simulation (LSMO), Institut des Sciences et Ingénierie Chimiques (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL Valais), Rue de l'Industrie 17, 1951 Sion Switzerland.*

[b]*Centre de Biophysique Moléculaire CNRS UPR 4301, F-45071 Orléans Cedex 2, France.*

[c]*Department of Inorganic, Applied and Analytical Chemistry, University of Geneva, 1211 Geneva 4, Switzerland.*

Supporting Information

Table of Contents

1. General information

All chemicals were purchased from commercial vendors and used without further purification. All reactions were carried out under aerobic conditions. Single crystal X-ray diffraction data and variable temperature powder X-ray diffraction (VT PXRD) data were collected using synchrotron radiation at BM01, ESRF. PXRD data were collected on a Bruker D8 Advance using Cu Kα radiation (λ = 1.5418 Å, 50 kW/40mA). Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 3.7. Topologies of the MOFs were calculated by the program ToposPro v.5.0.0.0. Elemental analyses were performed on a FLASH 2000 elemental analyzer (Thermo Scientific). Thermogravimetric analysis (TGA) was performed in air on a TGA 8000 instrument with a heating rate of 5 ^{o}C/min. Infrared spectra were collected on a Spectrum Two FTIR Spectrometer (PerkinElmer) from 400 to 4000 cm^{-1}. Sorption data were acquired using the BELSORP mini. UV/vis absorbance for solutions and diffuse reflectance spectra for solid state samples were obtained with a Lamda 950S PerkinElmer UV/vis Spectrometer. The reflectance values (R) were transformed into Kubelka-Munk function ($KM = (1-R)^2/(2R)$).

2. Synthesis

Synthesis of **SION-100**: 22.3 mg (0.050 mmol) of $Yb(NO_3)_3.5H_2O$, 21.9 mg (0.050 mmol) of H_3btb, and 18.0 mg (0.10 mmol) of phen were dissolved in 4.0 mL of DMF, to which 2.0 mL of H_2O was added. The solution mixture was kept in a 12 mL glass vial, sealed, and heated at 120 ^{o}C for 72 hours. Single crystals of **SION-100** were formed, filtered, washed with DMF and dried in air. Yield: ~ 20 mg.

Synthesis of **SION-100-NH_2**: 22.3 mg (0.050 mmol) of $Yb(NO_3)_3.5H_2O$, 21.9 mg (0.050 mmol) of H_3btb, and 30.0 mg (0.15 mmol) of aphen were dissolved in 4.0 mL of DMF, to which 2.0 mL of H_2O was added. The solution mixture was kept in a 12 mL glass vial, sealed, and heated at 120 ^{o}C for 72 hours. Single crystals of **SION-100-NH_2** were formed, filtered, washed with DMF and dried in air. Yield: ~ 20 mg.

3. Single-crystal X-ray diffraction

3.1 Crystal structures

High-quality single crystals of **SION-100** and **SION-100-NH_2** were isolated from the respective reaction mixtures. Each crystal was in turn mounted onto a KUMA KM6-CH diffractometer at the BM01 beamline (European Synchrotron Radiation Facility, Grenoble, France) and probed with X-rays (λ = 0.72179 Å). Intensities of Bragg reflections were recorded with the PILATUS2M detector, and the crystal was kept at 100(2) K during data collection. Raw data were processed with CrysAlisPro (2015) program suite, and the empirical absorption correction was performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Crystal structures of **SION-100** and **SION-100-NH_2** were solved with the XT structure solution program using Intrinsic Phasing[1] and refined with the XL refinement package using least-squares minimization,[2] implemented in the Olex2 program suite.[3] Atomic positions were found from the electron density maxima and refined anisotropically for all non-H atoms. Positions of aromatic H-atoms were refined using a riding model, while those of H-atoms in the

amino group of **SION-100-NH$_2$** were determined from the diffraction intensities. *Uiso* for H-atoms were set to 1.2 times *Ueq* of neighboring atoms, and 1.5 times *Ueq* of atoms in terminating groups. In **SION-100**, positions of two DMF molecules were found from the difference–Fourier maps; the N1A molecule was refined freely, while the N1B one was refined as a rigid body, with carbonyl O atom disordered over two positions of unequal occupancy (respectively 0.383, 0.617). In **SION-100-NH$_2$**, one DMF molecule and one H_2O molecule were also found from the difference–Fourier maps, and refined freely. All atoms of the second DMF molecule were found to be disordered over three positions of unequal occupancy (respectively 0.248, 0.453, 0.299), and refined as elements of a rigid body.

Table S1. Crystal data and structure refinement for **SION-100 (**CCDC: 1823643).

Identification code	**SION-100**
Empirical formula	$C_{45}H_{37}N_4O_8Yb$
Formula weight	934.82
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4314(2)
b/Å	17.63950(10)
c/Å	21.5389(2)
α/°	90
β/°	95.1330(10)
γ/°	90
Volume/Å^3	3947.36(9)
Z	4
ρ_{calc}g/cm^3	1.573
μ/mm^{-1}	2.516
F(000)	1876.0
Crystal size/mm^3	0.18 × 0.06 × 0.03
Radiation	synchrotron (λ = 0.72179)
2Θ range for data collection/°	3.036 to 51.446
Index ranges	$-8 \le h \le 8$, $-20 \le k \le 20$, $-25 \le l \le 25$
Reflections collected	14461
Independent reflections	4266 [R_{int} = 0.0285, R_{sigma} = 0.0235]
Data/restraints/parameters	4266/114/522
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0288, wR_2 = 0.0789
Final R indexes [all data]	R_1 = 0.0295, wR_2 = 0.0795
Largest diff. peak/hole / e Å^{-3}	1.40/-0.92

Table S2. Crystal data and structure refinement for **SION-100-NH_2**.(CCDC: 1823644)

Identification code	**SION-100-NH_2**
Empirical formula	$C_{45}H_{40}N_5O_9Yb$
Formula weight	967.86
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.16010(10)
b/Å	17.58130(10)
c/Å	22.5318(3)
α/°	90
β/°	96.2130(10)
γ/°	90
Volume/$Å^3$	4001.17(7)
Z	4
$\rho_{calc}g/cm^3$	1.607
μ/mm^{-1}	2.487
F(000)	1948.0
Crystal size/mm^3	0.09 × 0.07 × 0.03
Radiation	synchrotron (λ = 0.72179)
2Θ range for data collection/°	2.99 to 51.286
Index ranges	$-11 \le h \le 11$, $-20 \le k \le 20$, $-26 \le l \le 26$
Reflections collected	14648
Independent reflections	5477 [R_{int} = 0.0172, R_{sigma} = 0.0183]
Data/restraints/parameters	5477/4/510
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0375, wR_2 = 0.1008
Final R indexes [all data]	R_1 = 0.0383, wR_2 = 0.1017
Largest diff. peak/hole / e $Å^{-3}$	1.62/-1.89

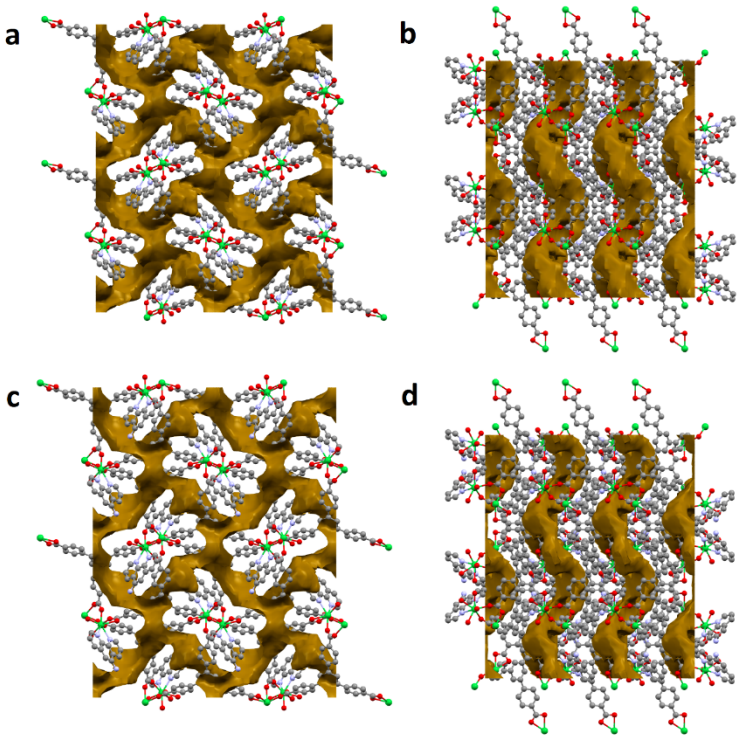

Figure S1. Crystal structures of **SION-100** (a, b) and **SION-100-NH$_2$** (c, d) with solvent accessible surfaces calculated with the program MERCURY[4] shown as golden surfaces. View along [100] (a, c), and along [001] (b, d).

3.2 Structural topology

Network topology for **SION-100** (for **SION-100-NH$_2$** the same result was obtained):

3-connected node (btb^{3-} ligand): "Sc1", point symbol: $\{4^3\}$, extended point symbol: [4.4.4]

6-connected node (Yb_2 cluster): "Ti1", point symbol: $\{4^6.6^6.8^3\}$, extended point symbol: [4.4.4.4.4.4.6(2).6(2).6(2).6(2).6(2).6(2).8(8).8(8).8(8)]

Structure consists of layers (1 0 –2) with "$TiSc_2$"; point (Schläfli) symbol for net: $\{4^3\}_2\{4^6.6^6.8^3\}$; 3,6-c net with stoichiometry $(3\text{-c})_2(6\text{-c})$; 2-nodal net

Topological type: ***kgd***; Shubnikov plane net (3.6.3.6)/dual (topos&RCSR.ttd)

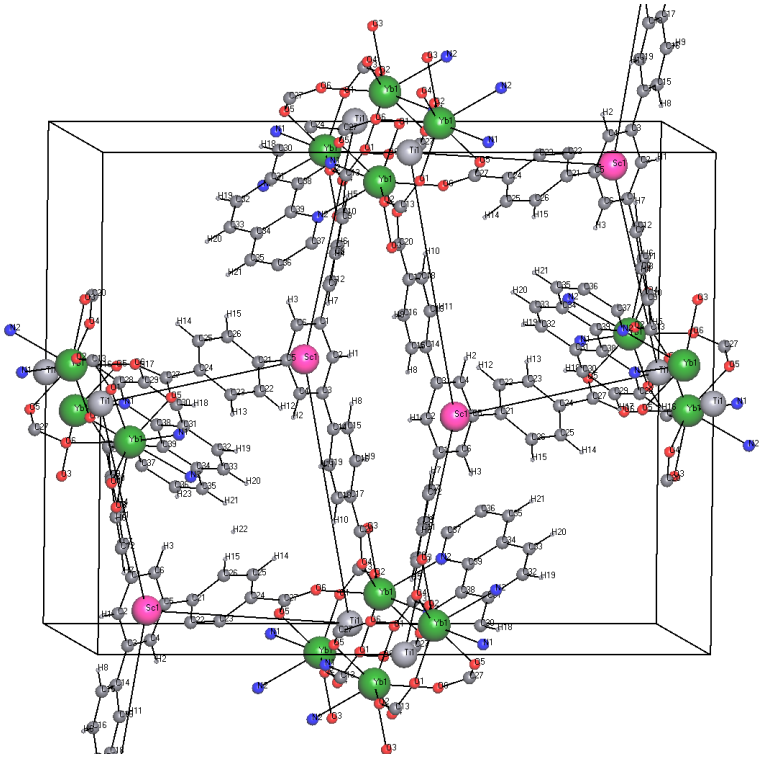

Figure S2. Content of the unit cell of **SION-100** (color code: C – dark gray, H – yellow, N – blue, Yb – green) overlaid with the nodes of the ***kgd*** net ("Sc1" – pink, "Ti1" – light gray). View approximately along the *a*-axis.

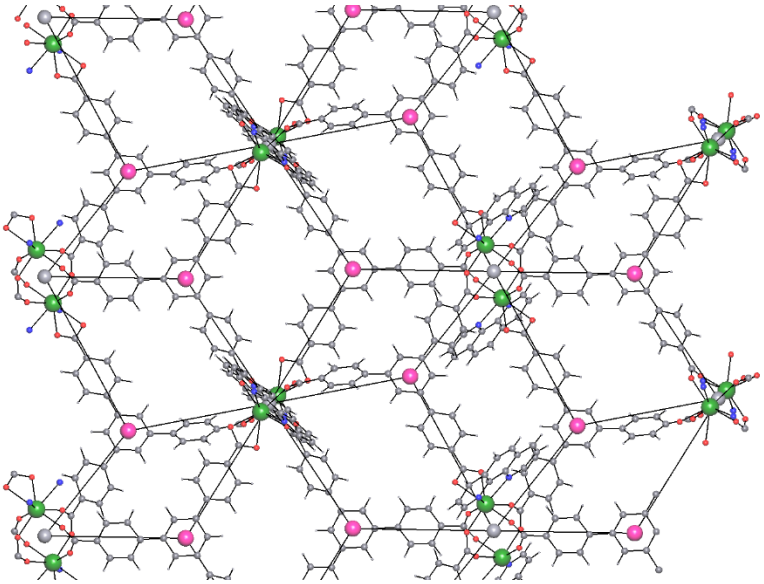

Figure S3. Overlay of the structure of **SION-100** (color code: C – dark gray, H – yellow, N – blue, Yb – green) with the nodes of the ***kgd*** net ("Sc1" – pink, "Ti1" – light gray), highlighting the presence of nearly-isohedral Kagome dual lattice. View along the [6 –2 –3] direction.

4. Characterization

4.1 Powder X-ray diffraction

4.1.1. Powder X-ray diffraction studies

The samples after activation (200 ^{o}C, under vacuum) were subjected to PXRD measurement. To investigate the water stability of **SION-100** and **SION-100-NH$_2$**, powder samples were submerged in deionized water for 24 hours, filtered, and dried in air before measuring the PXRD patterns.

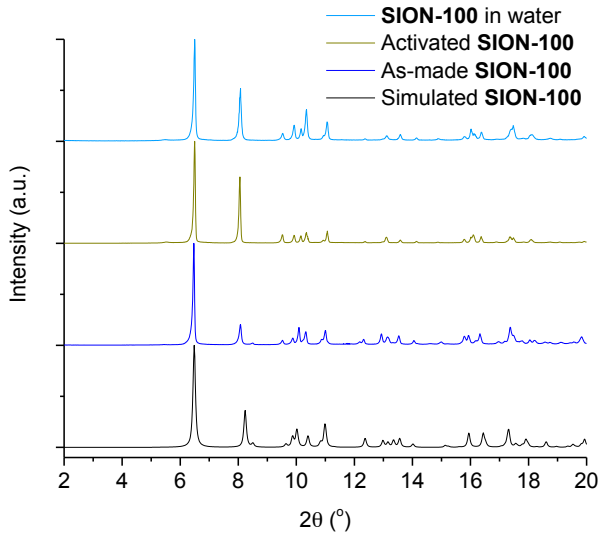

Figure S4. PXRD patterns of **SION-100** samples together with the simulated pattern.

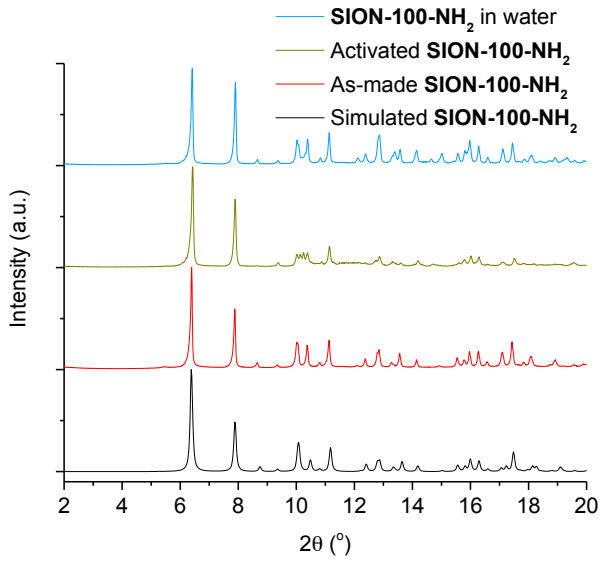

Figure S5. PXRD patterns of **SION-100-NH$_2$** samples together with the simulated pattern.

4.1.2 Variable temperature powder X-ray diffraction

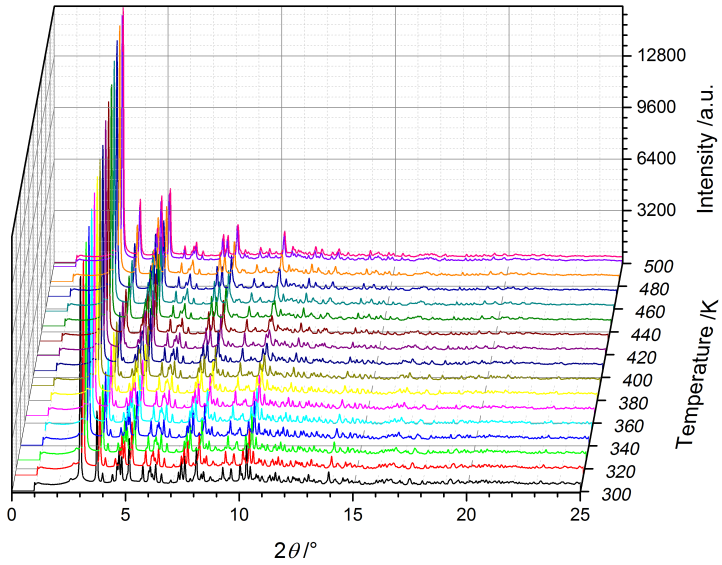

Figure S6. Variable-temperature powder diffractograms of **SION-100** recorded at BM01 of the ESRF with the wavelength λ = 0.72179 Å.

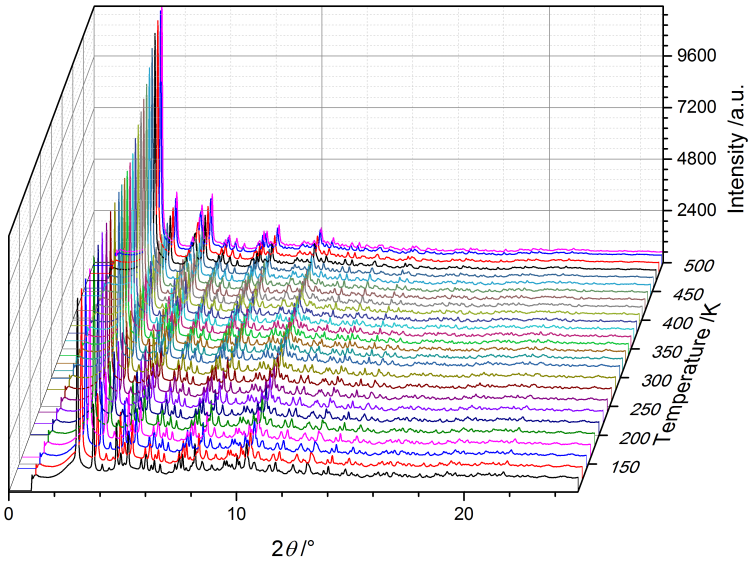

Figure S7. Variable-temperature powder diffractograms of **SION-100-NH_2** recorded at BM01 of the ESRF with the wavelength λ = 0.72179 Å.

4.2 Elemental analysis

As-made **SION-100**

Calculated for [Yb(phen)(btb)]·2DMF ($C_{45}H_{37}N_4O_8Yb$)

C 57.82 H 3.99 N 5.99

Found

C 58.13 H 4.20 N 5.57

As-made **SION-100-NH$_2$**

Calculated for [Yb(aphen)(btb)]·2DMF ($C_{45}H_{38}N_5O_8Yb$)

C 56.90 H 4.03 N 7.37

Found

C 57.27 H 4.39 N 7.32

Note: The H_2O molecule observed in the crystal structure is probably removed after washing with DMF and dried in air.

4.3 Thermogravimetric analysis

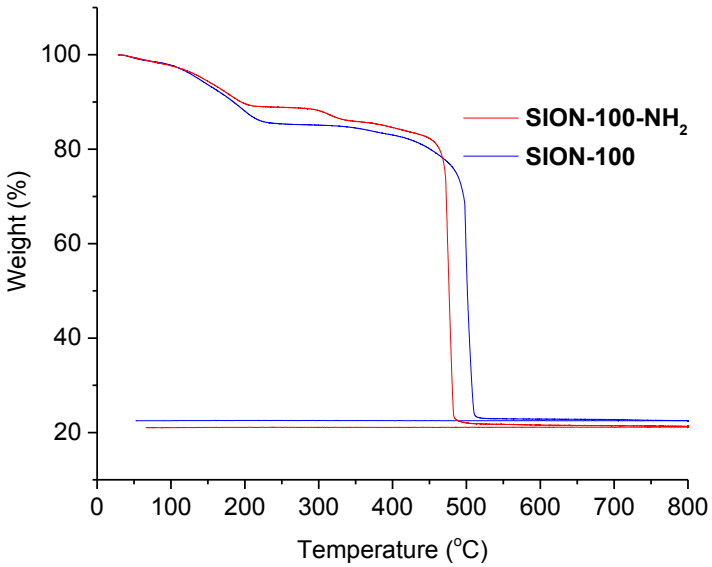

Figure S8. TGA profiles of **SION-100** and **SION-100-NH$_2$**

4.4 Infrared spectroscopy

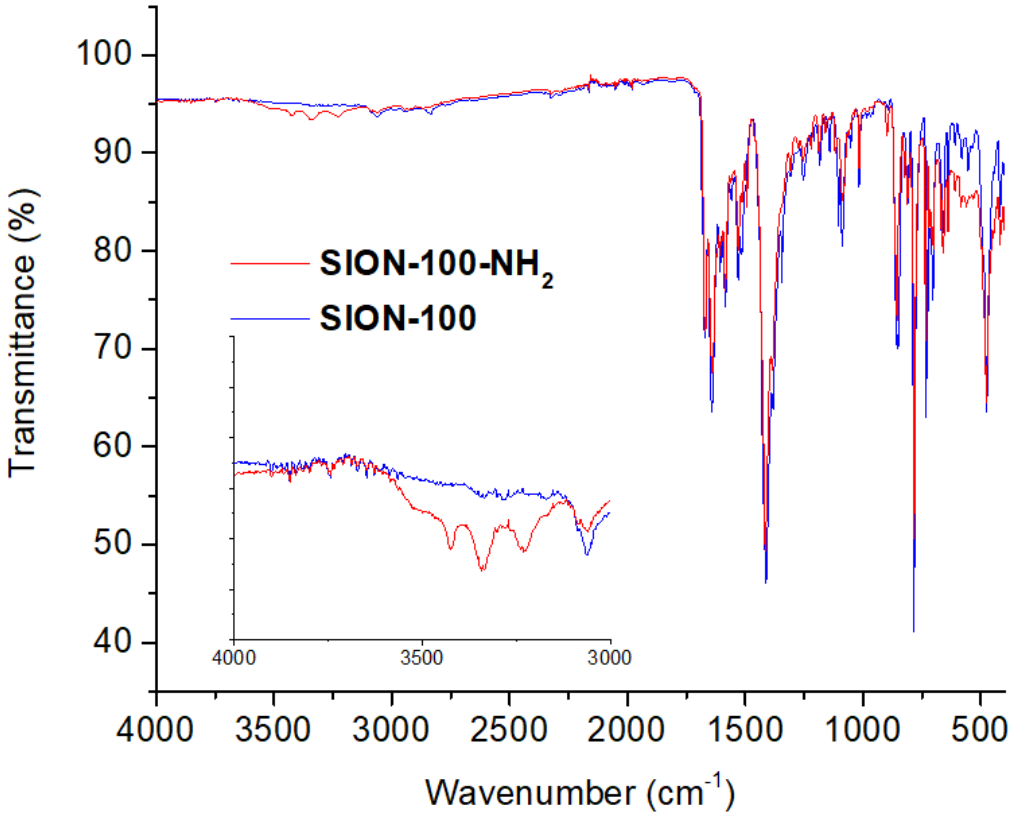

Figure S9. FTIR spectra of **SION-100** and **SION-100-NH$_2$** showing nearly identical features except for the N-H stretching vibrations in the energy range of 3500-3200 cm^{-1} of the -NH$_2$ group in the latter (inset).

4.5 Photophysical studies

Luminescence data were collected on samples in the solid state placed in 2.4 mm i.d. quartz capillaries. Emission and excitation spectra were measured on a custom-designed Horiba Scientific Fluorolog 3 spectrofluorimeter equipped with either a visible photomultiplier tube (PMT) (220-850 nm, R928P; Hamamatsu) and a NIR PMT (950-1650 nm, H10330-75; Hamamatsu). Excitation and emission spectra were corrected for the instrumental functions.

Luminescence lifetimes were determined under excitation at 355 nm provided by a Nd:YAG laser (YG 980; Quantel). Signals were detected in the NIR range (980 nm) with the help of a H10330-75 PMT. The output signals from the detectors were fed into a 500 MHz bandpass digital oscilloscope (TDS 754C; Tektronix), transferred to a PC for data processing with the program Origin 8®. Luminescence lifetimes are averages of at least three independent measurements. Quantum yields were determined with the Fluorolog 3 spectrofluorimeter based on an absolute method with the use of an integration sphere (Model G8, GMP SA, Renens, Switzerland). Each sample was measured several times under comparable experimental conditions, varying the position of samples. Estimated experimental error for quantum yield determination is ~10 %.

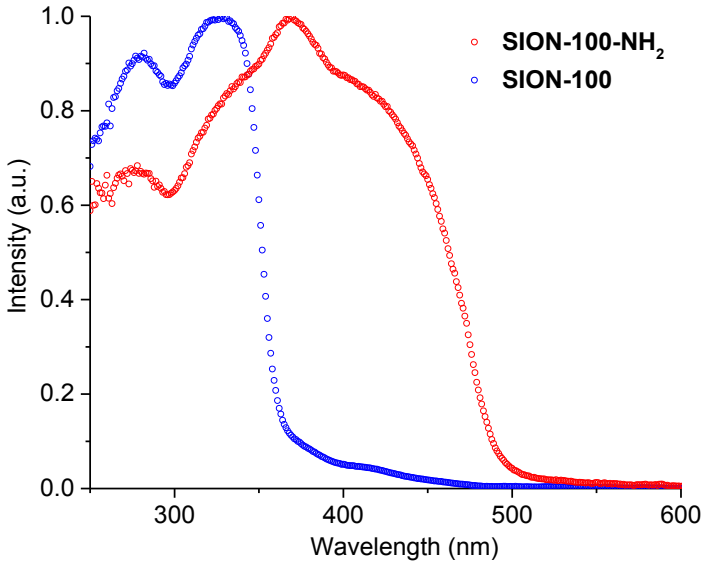

Figure S10. Corrected and normalized excitation spectra of **SION-100** and **SION-100-NH$_2$** obtained in the solid state by monitoring the emission of the Yb ion (λ_{em} = 980 nm) at room temperature.

4.6 UV/vis absorption and diffuse reflectance

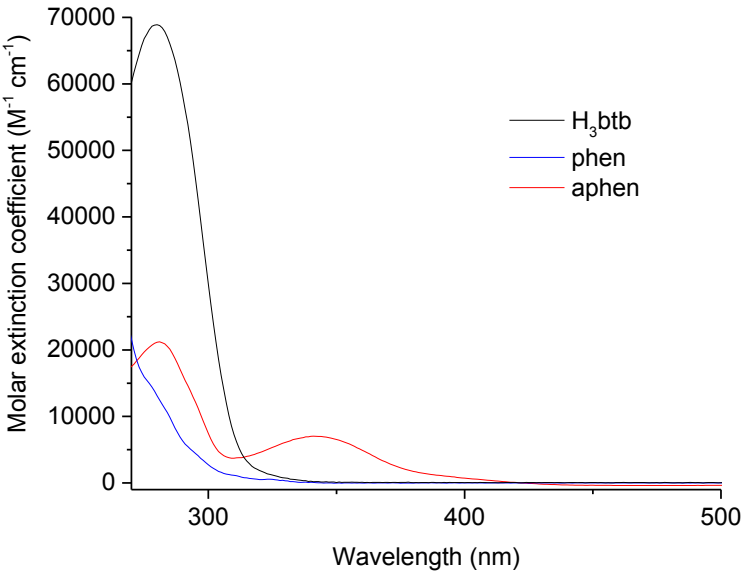

Figure S11. UV-vis absorption spectra of H_3btb (black, 14 µM), phenanthroline (blue, 22 µM) and 5-aminophenanthroline (red, 21 µM) in DMF at room temperature.

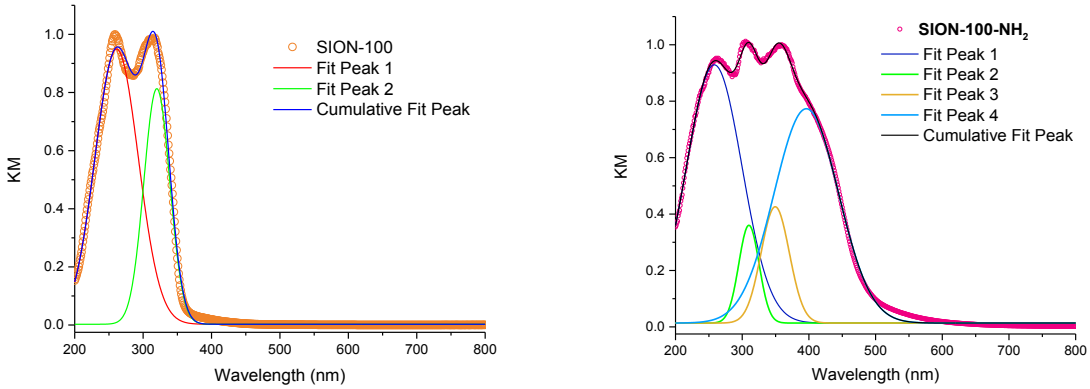

Figure S12. Gaussian deconvolution of the diffuse reflectance spectra of **SION-100** (left) and **SION-100-NH_2** (right).

5. Density Functional Theory Calculations

The calculations were performed using the Quantum Espresso suite. The wavefunction of the systems was described using ultrasoft pseudopotential and a cutoff of 170Ry. The geometrical structure of the two MOFs was calculated using a 2x2x1 Monkhorst-Pack grid and the PBEsol exchange and correlation functional. Electronic structure was determined at the Gamma point using the GauPBE exchange and correlation functional.
The electronic configuration of Yb(III) is $[Xe]4f^{13}$, meaning that each atom hosts an impaired electron. Each unit cell contains four Yb atoms and thus, different possible magnetic configurations are possible. We compared, for **SION-100**, four of them that we called ferromagnetic (FM), symmetric antiferromagnetic (AFMs), antisymmetric antiferromagnetic (AFMa), local ferromagnetic (LFM). For each configuration, we relaxed the structure (cell parameters and geometry) and we calculated the total energy. The results are summarized in Table S3. The most stable structure for **SION-100** is the AFM, and for **SION-100-NH_2** is the FM. The difference in energy between the AFM and FM configurations in the two MOF is on the order of 0.0002 a.u. (0.005 eV), much smaller than thermal energy at room temperature (298 K) (0.026 eV). We chose to calculate the electronic configuration at hybrid level for the FM configuration.

Table S3. Total PBEsol energy and energy gap of four different magnetic configurations in SION-100 and SION-100-NH_2.

	SION-100	**SION-100-NH_2**
	Energy (a.u.)	
FM	-3840.64183133	-3756.29590221
AFM	-3840.64184926	-3756.29571501
LFM	-3840.62459625	-3756.29590221

References

1. G. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.
2. G. Sheldrick, *Acta Crystallographica Section C*, 2015, **71**, 3-8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, **42**, 339-341.
4. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.