Electronic Supplementary Information (ESI)

Single Crystal Coordinating Solvent Exchange as a General Method for the Insertion of Functional Groups into Lanthanide MOFs and Enhancement of Their Photoluminescence Properties

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EXPERIMENTAL SECTION

Materials. Reagent grade chemicals were obtained from Aldrich and used without further purification. **UCY-8** and **EuN-BDC** and their Gd^{3+} analogues were prepared as described elsewhere (reference 23, 24 in main text).

Syntheses.

UCY-8 or **EuN-BDC**/X (X= py, merpdH_2, 2mpy): Single crystals of **UCY-8** or **EuN-BDC** (0.04 mmol) and the solvent or organic liquid compound (5 mL) were mixed in a 23 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an oven operated at 50 ˚C, remained undisturbed at this temperature for 2 days and then was allowed to cool at room temperature. The crystals of the exchanged compound were isolated by filtration and dried in the air.

UCY-8 or **EuN-BDC**/Y (Y= 2hmp, m2hmp): These materials were isolated in similar manner to **UCY-8** or **EuN-BDC**/X with the difference that the single crystals of the MOFs were reacted with a mixture of 2hmp (5.18 mmol) and $CHCl_3$ (5 mL) instead of using pure liquid 2hmp (because reaction of the crystals with pure 2hmp results in their deterioration**)**.

UCY-8 or **EuN-BDC**/Z (Z = Im, 2mIm, 4(5)mIm, etmIm, Ima, mIma, bzIm, atzH, 2hpH_2, hmIm): Single crystals of **UCY-8** or **EuN-BDC** (0.03-0.04 mmol) and a solution of Z (0.32-0.59 mmol) in $CHCl_3$ or CH_3NO_2 (5 mL) were mixed in a 23 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an oven operated at 50 ˚C, remained undisturbed at this temperature for 2 days and then was allowed to cool at room temperature. The crystals of **UCY-8** or **EuN-BDC**/Z were isolated by filtration and dried in the air.

UCY-8 or **EuN-BDC** /Im-atzH: Single crystals of **UCY-8** or **EuN-BDC** (0.04 mmol) and a solution of atzH (0.050 g, 0.59 mmol) and Im (0.040 g, 0.59 mmol) in $CHCl_3$ (5 mL) were mixed in a 23 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an oven operated at 50 ˚C, remained undisturbed at this temperature for 2 days and then was allowed to cool at room temperature. The crystals of **UCY-8** or **EuN-BDC**/Im-atzH were isolated by filtration and dried in the air.

Single crystal X-ray crystallography. Single Crystal X-ray diffraction data were collected on an Agilent Supernova A diffractometer, equipped with a CCD area detector utilizing Mo-Kα (λ = 0.71073 Å) or Cu-Kα (λ = (1.5418 Å) radiation.

Suitable crystals were attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.[1] The structures were solved by direct methods using SIR2004[2] and refined on F^2 using full-matrix least squares using SHELXL97.[3] Software packages used: CrysAlis CCD for data collection,[1] CrysAlis RED for cell refinement and data reduction,[1] WINGX for geometric calculations,[4] and DIAMOND[5] for molecular graphics. The non-H atoms were treated anisotropically, whereas the aromatic, hydroxy- and alkyl-hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. The H atoms of water and the formyl-group of DMF terminal ligands could not be located. Electron density contributions from disordered guest molecules were handled using the SQUEEZE procedure from the PLATON software suit (ref. 25 in main text). CCDC 941883-941909 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.

Physical measurements. Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Cyprus, Chemistry Department. IR spectra were recorded on KBr pellets in the 4000-400 cm^{-1} range using a Shimadzu Prestige – 21 spectrometer.

PL measurements. Steady state emission and excitation spectra were measured on a Perkin Elmer LS55 fluorimeter equipped with a phosphorescence accessory. The light source was a Xe arc lamp and the detector a red sensitive Hamamatsu R928 photomultiplier tube (PMT). A PMT voltage of 775 was used for all measurements. The emission and excitation slit widths were 3 nm for the **EuN-BDC** series and 7 nm for the **UCY-8** series. A long pass cutoff filter at 435 nm was used to remove the higher harmonics of the emission monochromator in the emission spectra. The excitation spectra were recorded using a long pass cutoff filter at 515 nm. All emission spectra were corrected for detector response using the correction function provided by the instrument.

The time resolved emission spectra have been recorded at the Central Laser Facility of University of Ioannina, Greece. The excitation wavelengths at 382 and 267nm, chosen according to the sample UV- Vis absorption, are produced via spectral

compression of the fundamental (800nm) of a Ti:Sapphire femtosecond laser system in a 25mm thick KDP nonlinear crystal [6] and a typical frequency-mixing scheme of the second harmonic and the fundamental on a type-II BBO crystal, respectively. In both cases, the excitation beams are of sub-picosecond duration while the pulse energy is reduced to a sub- micro joule level and focused loosely on the samples to avoid thermal damaging or multi photon absorption. The femtosecond laser system (Coherent Duo USX) provides output pulses centered at 800nm (67nm FWHM bandwidth), with a duration of 20fs and energy of 6mJ/per pulse. Time resolved emission spectra are recorded at different delay times with respect to initial photo-excitation using the Andor iStar-CCD camera coupled to an imaging spectrograph (Andor _ Shamrock 303i). In most cases, a 1800 l/mm grating was used offering a 0.1nm spectral resolution and the ability to record in a single shot a region of 26nm visible spectrum. Time "slices" of the emission spectra, using gated amplification, in the order of 20 to 50μsec have been recorded for different time delays (0 – 2 milliseconds). The delay time was controlled with sub-nanosecond accuracy via a time-delay-generator (Stanford Research Instruments), "clocked" to the output of the femtosecond laser system. The laser is operated at a relatively low repetition rate (30Hz) in order to exclude further excitation of photo-products between subsequent laser pulses.

References

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ELEMENTAL ANALYSIS

Compound **UCY-8**/Im was analyzed as **UCY-8**/Im·5H_2O. Anal. Calcd(%) for $C_{44}H_{42}Eu_2N_{10}O_{17}$: C, 41.07; H, 3,29; N, 10.89. Found: C, 41.12; H, 3,33; N, 10.79.

Compound **UCY-8**/2hpH_2 was analyzed as **UCY-8**/2hpH_2·4.5H_2O. Anal. Calcd(%) for $C_{52}H_{55}Eu_2N_4O_{22.5}$: C, 44.61; H, 3.96; N, 4.00. Found: C, 44.56; H, 4.00; N, 4.06.

Compound **UCY-8**/2mIm was analyzed as **UCY-8**/2mIm·3H_2O. Anal. Calcd(%) for $C_{46}H_{48}Eu_2N_8O_{17}$: C, 42.87; H, 3.75; N, 8.69. Found: C, 42.79; H, 3.85; N, 8.72.

Compound **UCY-8**/Ima was analyzed as **UCY-8**/Ima·4H_2O. Anal. Calcd(%) for $C_{40}H_{32}Eu_2N_6O_{18}$: C, 40.42; H, 2.71; N, 7.07. Found: C, 40.37; H, 2.82; N, 7.03.

Compound **UCY-8**/mIma was analyzed as **UCY-8**/mIma·8H_2O. Anal. Calcd(%) for $C_{42}H_{44}Eu_2N_6O_{22}$: C, 39.14; H, 3.44; N, 6.52. Found: C, 39.41; H, 3.65; N, 6.78.

Compound **UCY-8**/atzH was analyzed as **UCY-8**/atzH·3H_2O. Anal. Calcd(%) for $C_{42}H_{44}Eu_2N_{12}O_{17}$: C, 39.02; H, 3.43; N, 13.00. Found: C, 39.12; H, 3.48; N, 12.95.

Compound **UCY-8**/etmIm was analyzed as **UCY-8**/etmIm·2H_2O. Anal. Calcd(%) for $C_{48}H_{52}Eu_2N_6O_{16}$: C, 45.29; H, 4.12; N, 6.60. Found: C, 45.18; H, 4.18; N, 6.65.

Compound **UCY-8**/merpdH_2 was analyzed as **UCY-8**/merpdH_2·2H_2O. Anal. Calcd(%) for $C_{44}H_{50}Eu_2N_4O_{20}S_2$: C, 39.95; H, 3.81; N, 4.24; S, 4.85. Found: C, 40.10; H, 3.70; N, 4.32; S, 4.75.

Compound **UCY-8**/py was analyzed as **UCY-8**/py·3H_2O·3py. Anal. Calcd(%) for $C_{57}H_{51}Eu_2N_7O_{17}$: C, 48.55; H, 3.65; N, 6.95. Found: C, 48.67; H, 3.78; N, 6.87.

Compound **UCY-8**/bzIm was analyzed as **UCY-8**/bzIm·5H_2O·2bzIm. Anal. Calcd(%) for $C_{46}H_{46}Eu_2N_6O_{21}$: C, 41.77; H, 3.51; N, 6.35. Found: C, 41.82; H, 3.45; N, 6.43.

Compound **UCY-8**/4(5)mIm was analyzed as **UCY-8**/4(5)mIm·H_2O·2(4(5)mIm). Anal. Calcd(%) for $C_{48}H_{46}Eu_2N_{10}O_{15}$: C, 44.11; H, 3.55; N, 10.72. Found: C, 44.05; H, 3.68; N, 10.85.

Compound **UCY-8**/2mpy was analyzed as **UCY-8**/2mpy·3H_2O·2(2mpy). Anal. Calcd(%) for $C_{50}H_{54}Eu_2N_6O_{19}$: C, 44.59; H, 4.04; N, 6.24. Found: C, 44.51; H, 4.22; N, 6.15.

Compound **UCY-8**/Im-atzH was analyzed as **UCY-8**/Im-atzH·4H_2O·2atzH. Anal. Calcd(%) for $C_{42}H_{44}Eu_2N_{14}O_{18}$: C, 37.74; H, 3.32; N, 14.67. Found: C, 37.80; H, 3.29; N, 14.95.

Compound **UCY-8**/2hmp was analyzed as **UCY-8**/2hmp·7H_2O. Anal. Calcd(%) for $C_{44}H_{44}Eu_2N_4O_{21}$: C, 41.65; H, 3.50; N, 4.42. Found: C, 41.80; H, 3.55; N, 4.48.

Compound **EuN-BDC**/Im was analyzed as **EuN-BDC**/Im·3.5H_2O. Anal. Calcd(%) for $C_{36}H_{38}Eu_2N_{11}O_{15.5}$: C, 36.75; H, 3.26; N, 13.09. Found: C, 36.85; H, 3.19; N, 13.21.

Compound **EuN-BDC**/2mIm was analyzed as **EuN-BDC**/2mIm·5.5H_2O. Anal. Calcd(%) for $C_{38}H_{52}Eu_2N_9O_{19.5}$: C, 36.49; H, 4.19; N, 10.08. Found: C, 36.42; H, 4.22; N, 10.02.

Compound **EuN-BDC**/4(5)mIm was analyzed as **EuN-BDC**/4(5)mIm·3H_2O. Anal. Calcd(%) for $C_{38}H_{47}Eu_2N_9O_{17}$: C, 37.85; H, 3.93; N, 10.46. Found: C, 37.70; H, 3.98; N, 10.40.

Compound **EuN-BDC**/Ima was analyzed as **EuN-BDC**/Ima·6H_2O. Anal. Calcd(%) for $C_{32}H_{35}Eu_2N_7O_{20}$: C, 33.67; H, 3.09; N, 8.59. Found: C, 33.48; H, 3.25; N, 8.67.

Compound **EuN-BDC**/mIma was analyzed as **EuN-BDC**/mIma·9H_2O. Anal. Calcd(%) for $C_{34}H_{45}Eu_2N_7O_{23}$: C, 33.37; H, 3.71; N, 8.01. Found: C, 33.41; H, 3.67; N, 8.13.

Compound **EuN-BDC**/bzIm was analyzed as **EuN-BDC**/bzIm·3H_2O. Anal. Calcd(%) for $C_{44}H_{47}Eu_2N_9O_{17}$: C, 41.36; H, 3.71; N, 9.87. Found: C, 41.41; H, 3.65; N, 9.93.

Compound **EuN-BDC**/atzH was analyzed as **EuN-BDC**/atzH·5.5H_2O. Anal. Calcd(%) for $C_{34}H_{48}Eu_2N_{13}O_{19.5}$: C, 32.55; H, 3.86; N, 14.51. Found: C, 32.47; H, 3.75; N, 14.48.

Compound **EuN-BDC**/2hpH_2 was analyzed as **EuN-BDC**/2hp$H_2 \cdot 4H_2O$. Anal. Calcd(%) for $C_{44}H_{53}Eu_2N_5O_{22}$: C, 40.41; H, 4.09; N, 5.36. Found: C, 40.21; H, 3.99; N, 5.53.

Compound **EuN-BDC**/py was analyzed as **EuN-BDC**/py$\cdot 4H_2O$. Anal. Calcd(%) for $C_{38.2}H_{44}Eu_2N_{6.4}O_{18}$: C, 38.73; H, 3.74; N, 7.57. Found: C, 38.52; H, 3.90; N, 7.61.

Compound **EuN-BDC**/m2hmp was analyzed as **EuN-BDC**/m2hmp$\cdot 3H_2O \cdot$2hmp. Anal. Calcd(%) for $C_{44}H_{46}Eu_2N_6O_{18}$: C, 42.25; H, 3.71; N, 6.72. Found: C, 42.23; H, 3.78; N, 6.62.

Compound **EuN-BDC**/Im-atzH was analyzed as **EuN-BDC**/Im-atzH$\cdot 4.5H_2O$. Anal. Calcd(%) for $C_{34}H_{40}Eu_2N_{15}O_{16.5}$: C, 33.29; H, 3.29; N, 17.13. Found: C, 33.35; H, 3.35; N, 17.08.

Compound **EuN-BDC**/hmIm was analyzed as **EuN-BDC**/hmIm$\cdot 3H_2O$. Anal. Calcd(%) for $C_{38}H_{47}Eu_2N_9O_{19}$: C, 36.87; H, 3.83; N, 10.19. Found: C, 36.72; H, 3.88; N, 10.25.

Compound **EuN-BDC**/2mpy was analyzed as **EuN-BDC**/2mpy$\cdot 11H_2O$. Anal. Calcd(%) for $C_{30}H_{50}Eu_2N_4O_{26}$: C, 30.36; H, 4.25; N, 4.72. Found: C, 30.30; H, 4.37; N, 4.62.

Table S1. Selected crystal data for some of the exchanged analogues of **UCY-8**.

Compound	**UCY-8**/2hmp	**UCY-8**/2hp	**UCY-8**/2mIm	**UCY-8**/2mpy	**UCY-8**/4(5)mIm
Chemical formula	$C_{22}H_{14}EuN_2O_7$	$C_{49}H_{36}Eu_2N_3O_{18}$	$C_{23}H_{19}EuN_4O_7$	$C_{19}H_{14}EuN_2O_8 \bullet C_6H_7N$	$C_{20}H_{14}EuN_3O_7 \bullet C_4H_5N_2$
Formula Mass	570.31	1258.73	615.38	643.42	641.41
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	29.103(3)	28.257(2)	29.974(3)	28.735(2)	29.705(2)
b/Å	13.950(2)	14.6878(9)	12.421(2)	14.2112(9)	12.9699(6)
c/Å	14.231(2)	13.6390(8)	14.3039(9)	14.3322(8)	13.8285(6)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	94.20(2)	99.327(7)	93.371(7)	95.126(5)	95.247(5)
γ/°	90.00	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	5762.0(2)	5585.9(6)	5316.4(8)	5829.2(6)	5305.4(5)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
No. of formula units per unit cell, *Z*	8	4	8	8	8
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
No. of reflections measured	11915	13447	13921	34801	21125
No. of independent reflections	5065	4918	5507	5113	4679
R_{int}	0.0613	0.0487	0.0542	0.0711	0.0429
Final R_1[a] values ($I > 2\sigma(I)$)	0.0756	0.0536	0.0538	0.0647	0.0304
Final $wR(F^2)$[b] values ($I > 2\sigma(I)$)	0.2056	0.1518	0.1312	0.1825	0.0778
Final R_1 values (all data)	0.1013	0.0752	0.0770	0.0765	0.0354
Final $wR(F^2)$ values (all data)	0.2230	0.1677	0.1422	0.1900	0.0800
Goodness of fit on F^2	1.126	1.067	1.044	1.113	1.067

[a] $R1 = \Sigma \mid Fo \mid - \mid Fc \mid / \Sigma \mid Fo \mid$. [b] $wR(F^2) = [\Sigma [w(Fo^2 - Fc^2)2] / \Sigma [wFo^2)2]]^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (m \cdot p)^2 + n \cdot p]$, $p = [\max(Fo^2, 0) + 2Fc^2]/3$, and m and n are constants

Table S2. Selected crystal data for some of the exchanged analogues of **UCY-8**.

Compound	**UCY-8**/atzH	**UCY-8**/bzIm	**UCY-8**/etmIm	**UCY-8**/Im	**UCY-8**/Ima
Chemical formula	$C_{21}H_{15}EuN_6O_7$	$C_{16}H_8EuNO_8 \cdot C_7H_5N_2 \cdot O$	$C_{24}H_{22}EuN_3O_7$	$C_{22}H_{14}EuN_5O_6$	$C_{20}H_{12}EuN_3O_7$
Formula Mass	615.35	627.32	616.42	596.35	558.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	29.602(2)	29.547(2)	29.463(2)	28.663(2)	29.081(2)
b/Å	13.4780(7)	12.9685(7)	14.619(2)	14.0581(4)	13.394(2)
c/Å	13.3524(6)	14.2361(7)	12.281(2)	13.1543(5)	13.538(2)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	96.594(4)	94.610(4)	98.518(8)	102.307(4)	98.053(8)
γ/°	90.00	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	5292.1(4)	5437.3(5)	5231.3(9)	5178.6(3)	5221.4(8)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
No. of formula units per unit cell, *Z*	8	8	8	8	8
Radiation type	MoKα	MoKα	MoKα	CuKα	MoKα
No. of reflections measured	11772	27654	11119	9538	13020
No. of independent reflections	4652	4780	4591	4601	4603
R_{int}	0.0293	0.0606	0.0547	0.0368	0.0458
Final R_1[a] values ($I > 2\sigma(I)$)	0.0388	0.0430	0.0626	0.0602	0.0571
Final $wR(F^2)$[b] values ($I > 2\sigma(I)$)	0.1102	0.1201	0.1609	0.1761	0.1643
Final R_1 values (all data)	0.0462	0.0531	0.0779	0.0645	0.0637
Final $wR(F^2)$ values (all data)	0.1151	0.1256	0.1719	0.1820	0.1700
Goodness of fit on F^2	1.137	1.082	1.062	1.084	1.070

[a] $R1 = \Sigma \mid Fo \mid - \mid Fc \mid / \Sigma \mid Fo \mid$. [b] $wR(F^2) = [\Sigma [w(Fo^2 - Fc^2)2] / \Sigma [wFo^2)2]]^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (m \cdot p)^2 + n \cdot p]$, $p = [\max(Fo^2,0) + 2Fc^2]/3$, and m and n are constants

Table S3. Selected crystal data for some of the exchanged analogues of **UCY-8**.

Compound	**UCY-8**/Im-atzH	**UCY-8**/merpdH$_2$	**UCY-8**/mIma	**UCY-8**/py
Chemical formula	$C_{19}H_{11}EuN_3O_7$•C_2HN_4•O	$C_{22}H_{19}EuN_2O_9S$	$C_{21}H_{12}EuN_3O_7$	$C_{42}H_{26}Eu_2N_4O_{14}$•3($C_5H_5N$)
Formula Mass	642.35	639.43	570.30	1351.89
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
a/Å	29.793(2)	29.055(2)	28.6032(8)	13.6903(4)
b/Å	12.793(2)	14.1152(7)	14.3668(7)	14.7432(5)
c/Å	13.7893(7)	13.4991(7)	12.8150(5)	15.6518(7)
α/°	90.00	90.00	90.00	95.222(3)
β/°	95.185(4)	97.912(5)	103.057(3)	112.945(4)
γ/°	90.00	90.00	90.00	90.244(3)
Unit cell volume/Å^3	5234.2(5)	5483.6(5)	5130.0(4)	2894.4(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	$P\bar{1}$
No. of formula units per unit cell, *Z*	8	8	8	2
Radiation type	CuKα	MoKα	CuKα	MoKα
No. of reflections measured	9312	11221	9363	20194
No. of independent reflections	4673	4823	4562	10176
R_{int}	0.0439	0.0442	0.0261	0.0410
Final R_1[a] values ($I > 2\sigma(I)$)	0.0813	0.0687	0.0474	0.0529
Final $wR(F^2)$[b] values ($I > 2\sigma(I)$)	0.2331	0.2150	0.1445	0.1315
Final R_1 values (all data)	0.0881	0.0801	0.0504	0.0654
Final $wR(F^2)$ values (all data)	0.2420	0.2263	0.1482	0.1404
Goodness of fit on F^2	1.117	1.104	1.121	1.026

[a]R1= Σ ｜F o ｜ - ｜ Fc ｜/ Σ ｜F o ｜. [b] wR(F^2)=[Σ [w(Fo^2 - Fc^2)2]/ Σ [wFo^2)2]]$^{1/2}$, w=1/[σ ^{2}(Fo^2) + (m · p)^2 + n · p], p=[max(Fo^2,0) +2Fc^2]/3, and m and n are constants

Table S4. Selected crystal data for some of the exchanged analogues of **EuN-BDC**.

Compound	**EuN-BDC**/2hp	**EuN-BDC**/2mIm	**EuN-BDC**/2mpy	**EuN-BDC**/4(5)mIm	**EuN-BDC**/atzH	**EuN-BDC**/bzIm
Chemical formula	$C_{44}H_{28}Eu_2N_5O_{18}$	$C_{38}H_{28}Eu_2N_9O_{14}$	$C_{30}H_{13}Eu_2N_4O_{15}$	$C_{38}H_{28}Eu_2N_9O_{14}$	$C_{34}H_{18}Eu_2N_{13}O_{14}$	$C_{44}H_{28}Eu_2N_9O_{14}$
Formula Mass	1218.63	1138.61	973.38	1138.61	1136.53	1210.67
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	10.4369(9)	10.3371(5)	10.538(2)	10.416(2)	10.3923(6)	10.336(2)
b/Å	11.2951(7)	11.1671(6)	11.3009(8)	11.218(2)	11.2942(8)	11.240(2)
c/Å	12.7861(2)	11.8689(9)	12.944(2)	11.806(2)	12.3282(8)	11.773(2)
α/°	101.639(7)	94.257(5)	107.074(7)	93.30(2)	98.464(6)	91.931(9)
β/°	111.064(8)	107.004(5)	107.41(2)	109.64(2)	109.478(6)	108.44(2)
γ/°	98.473(6)	108.419(5)	92.773(8)	106.95(2)	102.788(6)	109.73(2)
Unit cell volume/Å^3	1337.2(2)	1221.9(2)	1390.3(3)	1224.1(3)	1291.3(2)	1206.1(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
No. of formula units per unit cell, *Z*	1	1	1	1	1	1
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα
No. of reflections measured	8569	8080	8890	7780	9151	7428
No. of independent reflections	4710	4289	4891	4283	4550	4228
R_{int}	0.0412	0.0299	0.0345	0.0676	0.0356	0.0328
Final R_1 values ($I > 2\sigma(I)$)	0.0537	0.0665	0.0659	0.0742	0.0561	0.0507
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1471	0.1829	0.1636	0.1855	0.1596	0.1416
Final R_1 values (all data)	0.0645	0.0733	0.0766	0.1077	0.0634	0.0567
Final $wR(F^2)$ values (all data)	0.1562	0.1894	0.1705	0.2116	0.1678	0.1466
Goodness of fit on F^2	0.931	1.051	0.990	0.985	1.047	1.084

*$R1 = \Sigma |Fo| - |Fc| / \Sigma |Fo|$. [b] $wR(F^2) = [\Sigma [w(Fo^2 - Fc^2)2] / \Sigma [wFo^2)2]]^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (m \cdot p)^2 + n \cdot p]$, $p = [\max(Fo^2, 0) + 2Fc^2]/3$, and m and n are constants

Table S5. Selected crystal data for some of the exchanged analogues of **EuN-BDC**.

Compound	**EuN-BDC**/hmIm	**EuN-BDC**/Im	**EuN-BDC**/Ima	**EuN-BDC**/Im-atzH	**EuN-BDC**/m2hmp
Chemical formula	$C_{38}H_{28}Eu_2N_9O_{16}$	$C_{36}H_{16}Eu_2N_{11}O_{12}$	$C_{32}H_{10}Eu_2N_7O_{14}$	$C_{34}H_{14}Eu_2N_{15}O_{12}$	$C_{38}H_{22}Eu_2N_5O_{14}$•2($C_3H_{3.50}N_{0.50}O_{0.50}$)
Formula Mass	1170.61	1098.54	1020.39	1128.52	1185.65
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	10.436(2)	10.3405(5)	10.3980(9)	10.4200(8)	10.391(2)
b/Å	11.200(2)	11.1627(6)	11.2742(8)	11.1657(8)	11.337(2)
c/Å	11.736(2)	11.7693(6)	11.468(2)	11.9254(8)	12.817(2)
α/°	93.47(2)	89.563(4)	95.510(7)	90.062(6)	106.322(8)
β/°	110.05(2)	69.495(5)	109.490(9)	110.667(7)	98.730(8)
γ/°	106.44(2)	69.743(5)	104.801(7)	109.830(7)	103.042(9)
Unit cell volume/Å^3	1216.8(3)	1183.7(2)	1200.8(2)	1209.7(2)	1373.8(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
No. of formula units per unit cell, *Z*	1	1	1	1	1
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
No. of reflections measured	8005	6854	7742	7650	9445
No. of independent reflections	4280	4152	4219	4254	4816
R_{int}	0.0370	0.0288	0.0376	0.0399	0.0310
Final R_1[a]values ($I > 2\sigma(I)$)	0.0581	0.0481	0.0525	0.0618	0.0575
Final $wR(F^2)$[b] values ($I > 2\sigma(I)$)	0.1622	0.1324	0.1423	0.1701	0.1669
Final R_1 values (all data)	0.0658	0.0554	0.0592	0.0729	0.0666
Final $wR(F^2)$ values (all data)	0.1713	0.1379	0.1481	0.1797	0.1742
Goodness of fit on F^2	1.091	1.153	1.051	1.112	1.175

[a]R1= Σ |F o | - | Fc| / Σ | F o | . [b] wR(F^2)=[Σ [w(Fo^2 - Fc^2)2]/ Σ [wFo^2)2]]$^{1/2}$, w=1/[σ^2(Fo^2) + (m · p)^2 + n · p], p=[max(Fo^2,0) +2Fc^2]/3, and m and n are constants

Table S6. Selected crystal data for some of the exchanged analogues of **EuN-BDC**.

Compound	**EuN-BDC**/mIma	**EuN-BDC**/py
Chemical formula	$C_{34}H_{14}Eu_2N_7O_{14}$	$C_{19\cdot10}H_{12\cdot20}EuN_{3\cdot20}O_{6\cdot70}$•0.3(O)
Formula Mass	1048.44	550.48
Crystal system	Triclinic	Triclinic
a/Å	10.4457(7)	10.3929(2)
b/Å	11.3042(9)	11.2670(2)
c/Å	13.964(2)	12.4706(2)
α/°	110.218(7)	96.847(9)
β/°	107.559(7)	110.856(2)
γ/°	91.119(6)	103.830(9)
Unit cell volume/Å^3	1461.0(2)	1291.00(9)
Temperature/K	100(2)	100(2)
Space group	$P\bar{1}$	$P\bar{1}$
No. of formula units per unit cell, *Z*	1	2
Radiation type	MoKα	MoKα
No. of reflections measured	9876	8918
No. of independent reflections	5156	4535
R_{int}	0.0317	0.0336
Final R_1[a]values ($I > 2\sigma(I)$)	0.0697	0.0535
Final $wR(F^2)$[b] values ($I > 2\sigma(I)$)	0.1965	0.1410
Final R_1 values (all data)	0.0822	0.0646
Final $wR(F^2)$ values (all data)	0.2095	0.1496
Goodness of fit on F^2	1.074	1.002

[a]$R1 = \Sigma \mid Fo \mid - \mid Fc \mid / \Sigma \mid Fo \mid$. [b] $wR(F^2) = [\Sigma [w(Fo^2 - Fc^2)2] / \Sigma [wFo^2)2]]^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (m \cdot p)^2 + n \cdot p]$, $p = [\max(Fo^2,0) + 2Fc^2]/3$, and m and n are constants

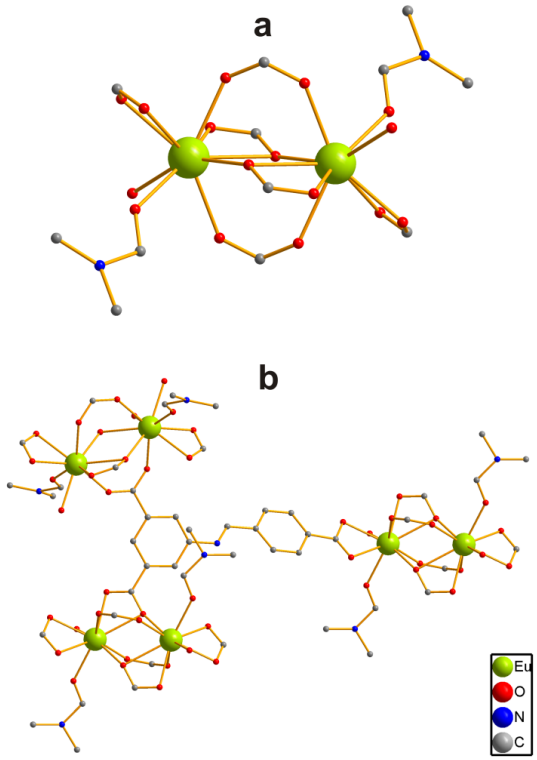

Fig. S1. Representations of the a) dinuclear SBU and b) connectivity of three SBUs via one CIP^{3-} ligand of **UCY-8**. The H atoms have been omitted for clarity.

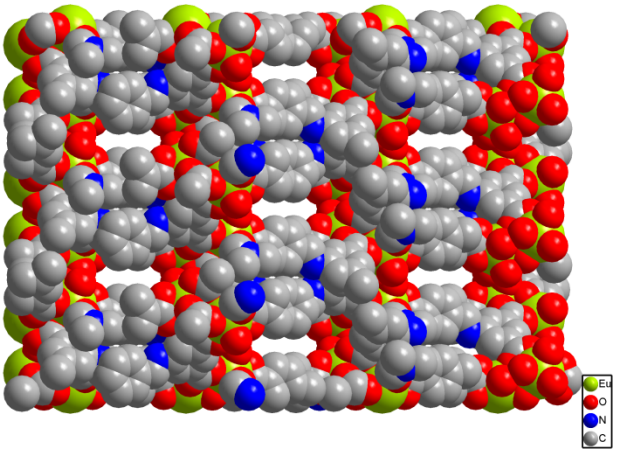

Fig. S2. Representation of the 3-D porous structure of **UCY-8**. The H atoms have been omitted for clarity.

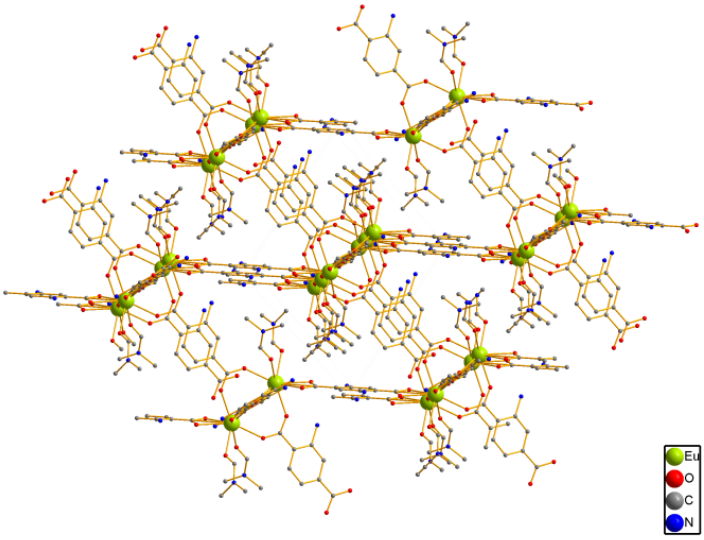

Fig. S3. Representation of the 3-D structure of **EuN-BDC**. The H atoms and guest DMF molecules have been omitted for clarity.

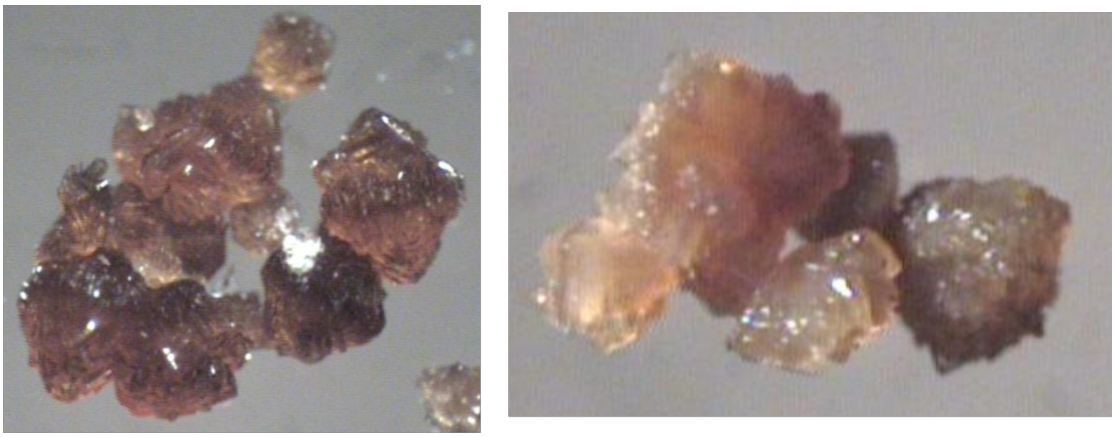

Fig.S4. Photos of single crystals of **UCY-8** (left) and **UCY-8**/etmIm (right).

Fig. S5. Photos of single crystals of **EuN-BDC** (left) and **EuN-BDC**/4(5)mIm (right).

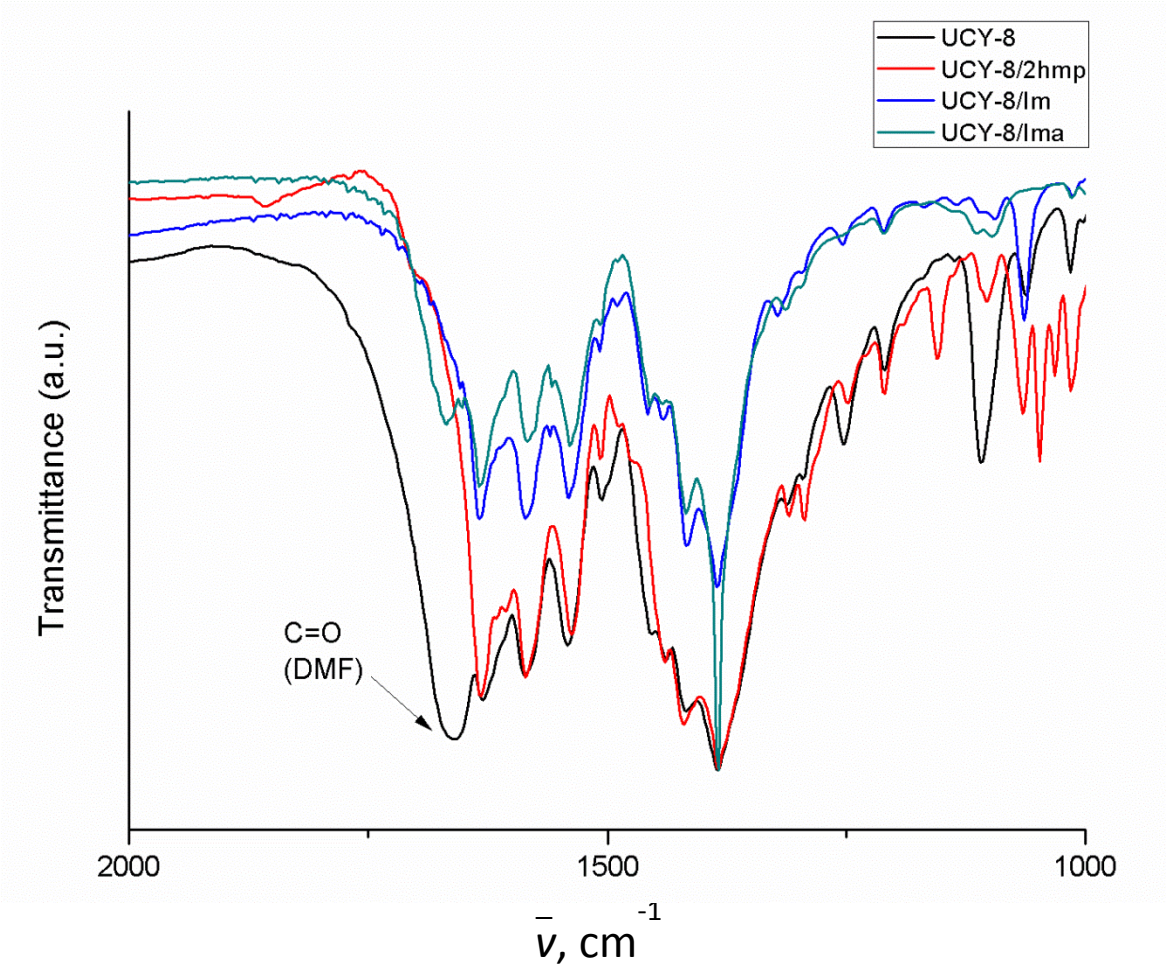

Fig. S6. IR spectra of **UCY-8, UCY-8**/2hmp, **UCY-8**/Im and **UCY-8**/Ima. The spectra of the exchanged compounds do not contain the characteristic band of the aldehyde group of DMF at 1660 cm^{-1} existing in the spectrum of **UCY-8**.

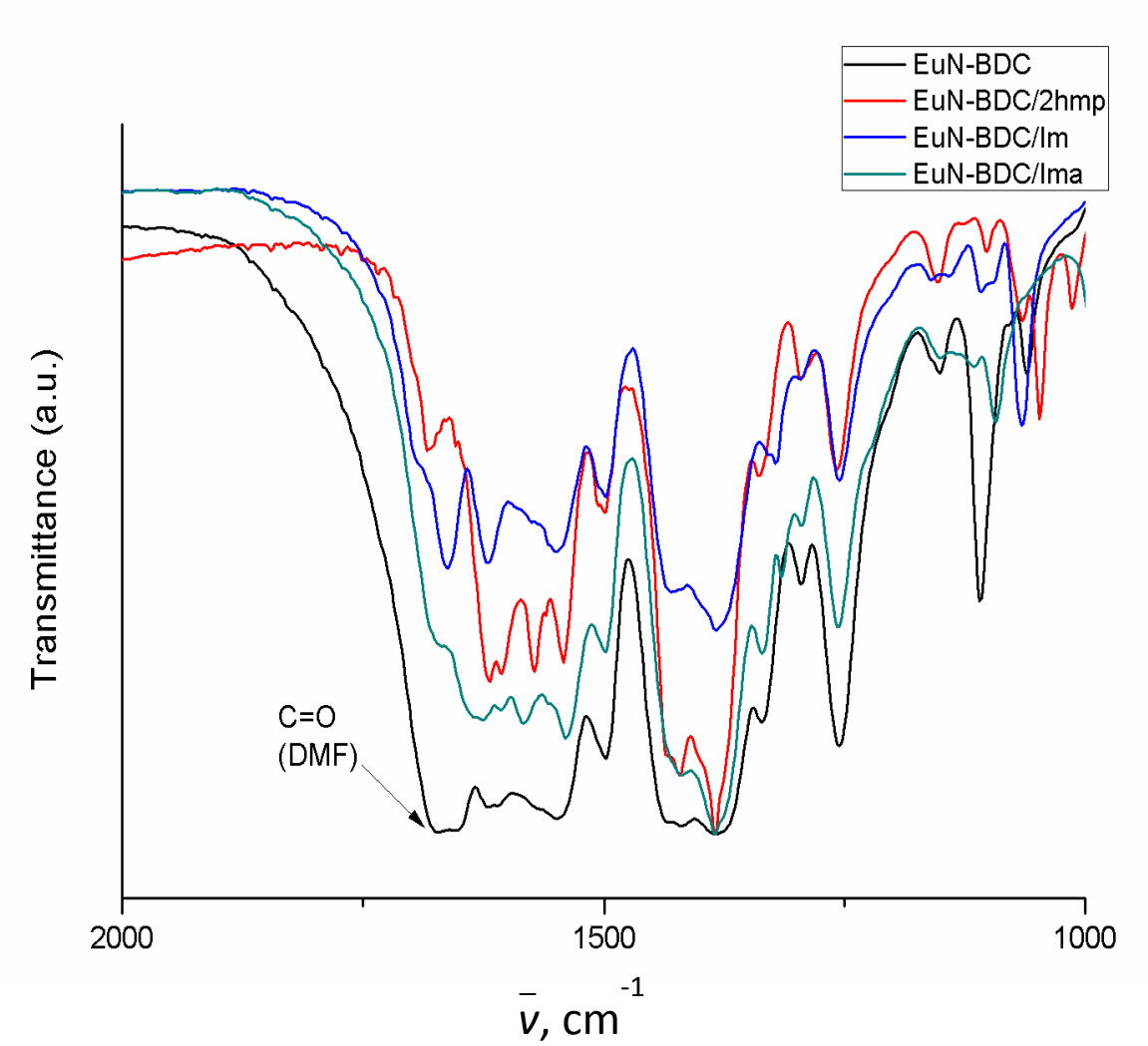

Fig. S7. IR spectra of **EuN-BDC**, **EuN-BDC**/2hmp, **EuN-BDC**/Im and **EuN-BDC**/Ima. The spectra of the exchanged compounds do not contain the characteristic band of DMF (C=O bond) at 1660 cm^{-1} existing in the spectrum of **EuN-BDC**.

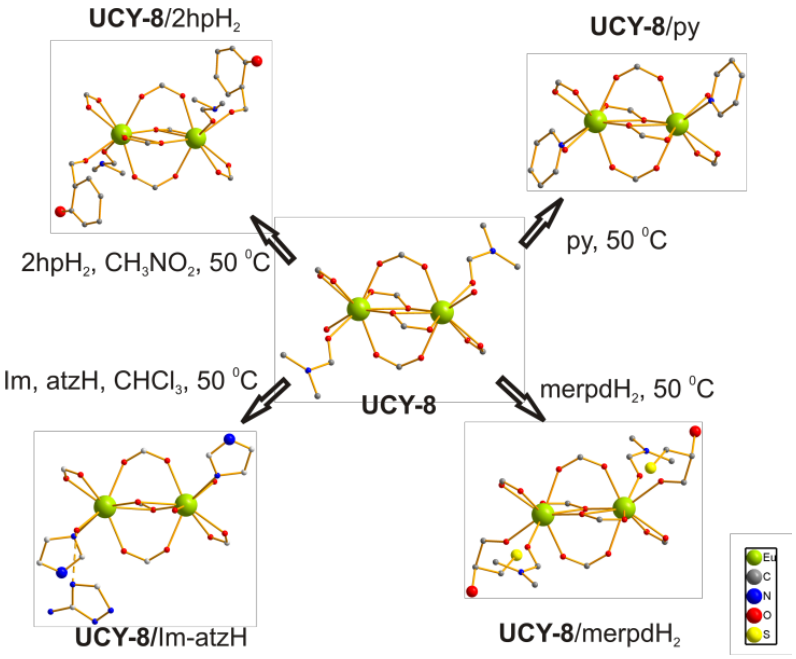

Fig. S8. SCSC transformations that resulted in the exchange of ligated solvent molecules of **UCY-8** by the ligands $2hpH_2$, py, Im-atzH and $merpdH_2$; only the SBUs of the pristine and the exchanged products (excluding H atoms) are shown for clarity. For emphasis, the free functional groups are depicted as large balls. The hydrogen bonding interactions between the guest atzH molecules and water terminal ligands in UCY-8/Im-atzH are indicated with a dashed line.

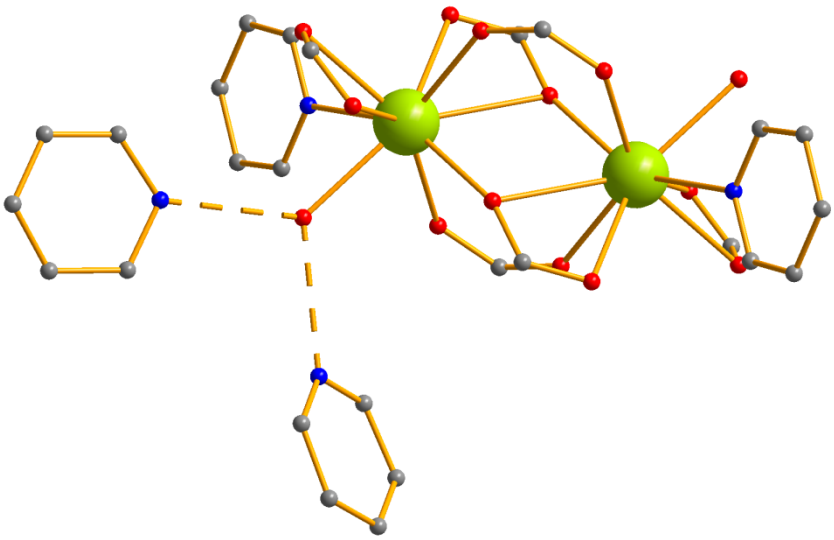

Fig. S9. The hydrogen-bonding interactions (indicated with dashed lines) between the N atoms of lattice py molecules and the O atom of one coordinated water ligand in **UCY-8**/py.

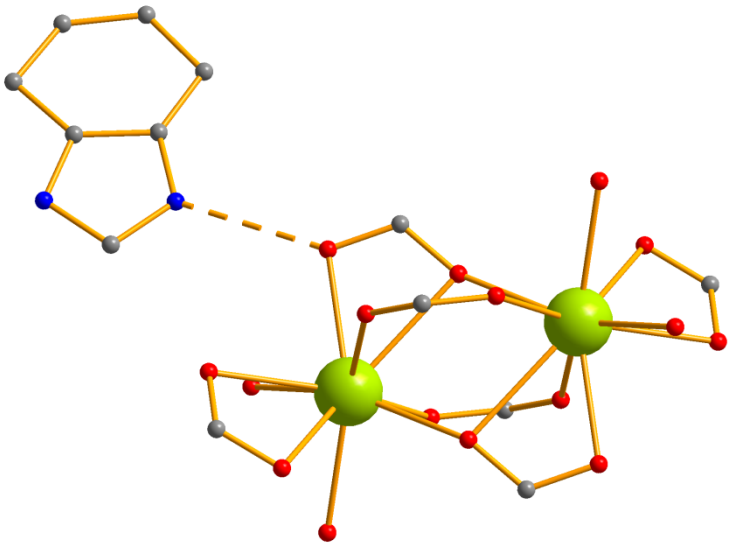

Fig. S10. Representation of the hydrogen-bond (indicated with a dashed line) between the N atom of a lattice bzIm molecule and O atom of a carboxylate ligand in **UCY-8**/bzIm.

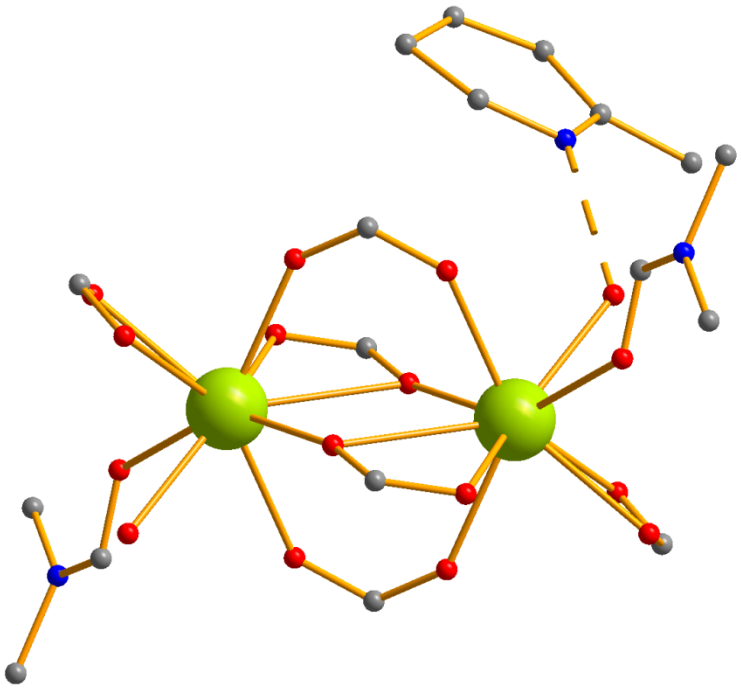

Fig. S11. Representation of the hydrogen-bond (indicated with a dashed line) between the N atom of a lattice 2mpy molecule and O atom of a water ligand in **UCY-8**/2mpy.

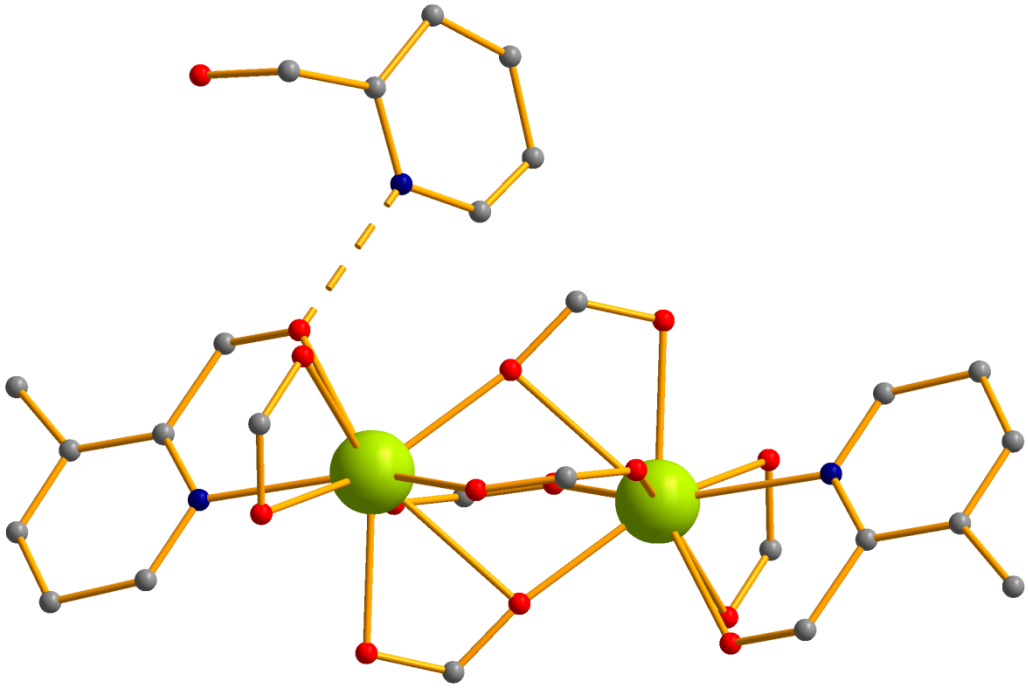

Fig. S12. Representation of the hydrogen-bond (indicated with a dashed line) between the N atom of a lattice 2hmp molecule and OH group of m2hmp ligand in **EuN-BDC**/m2hmp.

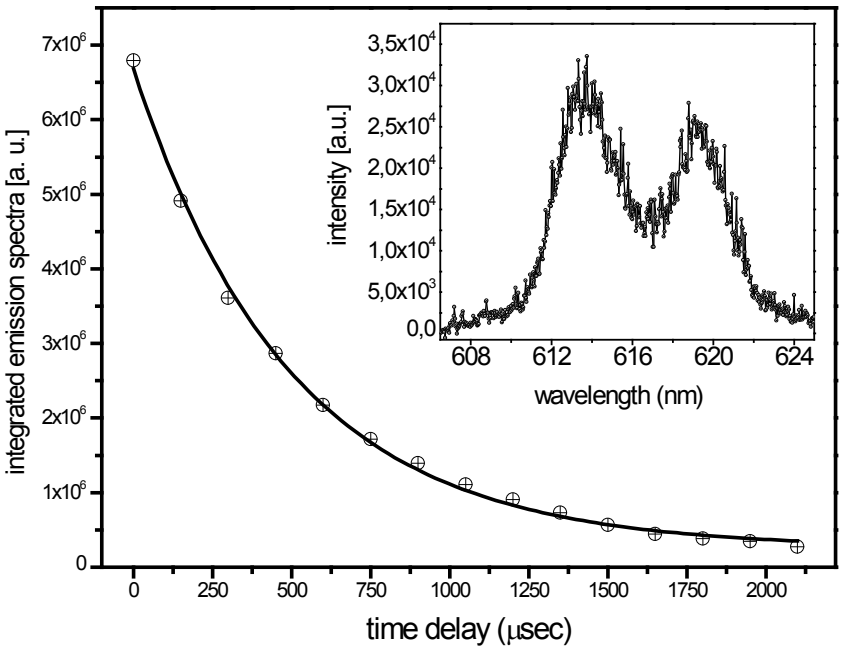

Fig. S13. Luminescence decay trace of **EuN-BDC**/4(5)mIm. The data points are experimental and the solid line represents the best fitting of the data. Inset: The $^5D_0 \rightarrow {}^7F_2$ emission peak of **EuN-BDC**/4(5)mIm as it was recorded using a CCD camera –see above for description of the experimental setup.

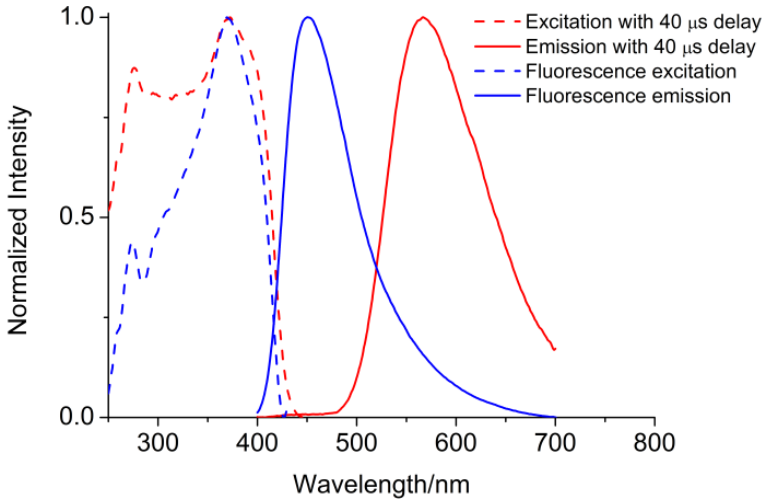

Figure S14. Solid state emission (solid lines, λexc = 370 nm) and excitation spectra (dotted lines) of **GdN-BDC** taken in fluorescence mode and in phosphorescence mode after a time delay of 40 μs. The fluorescence excitation spectrum was monitored at 450 nm and the phosphorescence excitation spectrum at 565 nm.

The solid state emission spectrum of **GdN-BDC**, upon excitation at 370 nm, is dominated by a broad peak centered at 451 nm due to ligand based fluorescence from the first $^{1}\pi$-π^* (S_1) excited state as confirmed by the excitation spectrum. When a time delay of 40 μs was applied to remove short – lived fluorescence, we observed a broad emission band centered at ca. 567 nm. This band is attributed to ligand based phosphorescence from the first $^{3}\pi$-π^* (T_1) excited state.

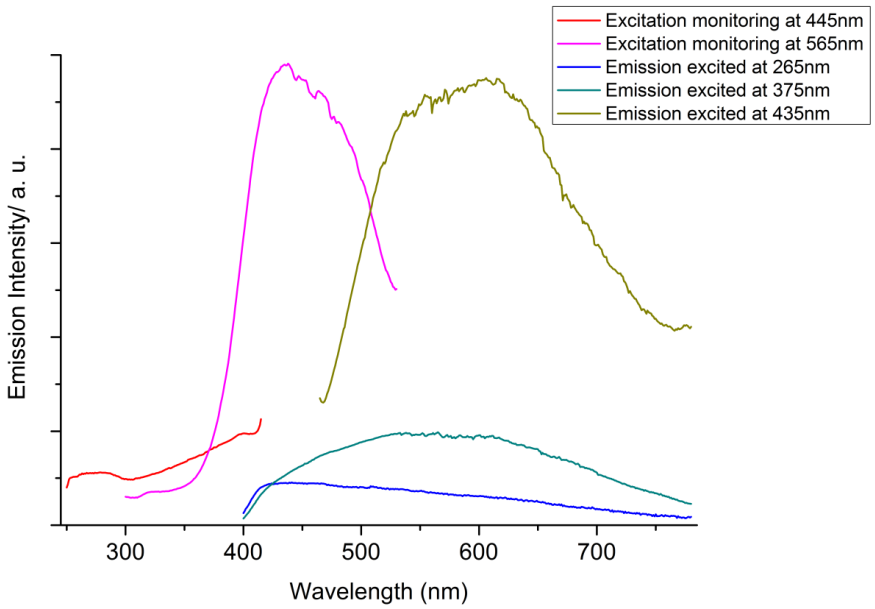

Fig. S15. Excitation and emission spectra for **UCY-9**.