Supplementary Material (ESI) for Chemical Communications
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Supplementary material on

Homoleptic Imidazolate Frameworks $^3_\infty[Sr_{1-x}Eu_x(Im)_2]$ – Hybrid Materials with Efficient and Tuneable Luminescence

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¥ ***Syntheses*:**

The reaction of the 4*f* metal europium, and the alkaline earth metal strontium with amine melts are redox reactions that give hydrogen gas in addition to the amide products. All reactions were carried out under inert conditions using dry box as well as standard Schlenk and ampoule techniques due to air- and moisture-sensitivity.

Syntheses: $^3_\infty[Sr_{1-x}Eu_x(Im)_2]$ (**1**) and (**2**): Europium/strontium metal ($1*10^{-3}$ mol; Smart Elements 99.99 % / Aldrich 99.99%; ratios: Sr/Eu: x = 1.0: m(Eu) = 152.0 mg; x = 0.5: m(Sr) = 43.8 mg, m(Eu) = 76.0 mg; x = 0.05: m(Sr) = 83.2 mg, m(Eu) = 7.6 mg; x = 0.03: m(Sr) = 85.0 mg, m(Eu) = 4.6 mg; x = 0.02: m(Sr) = 85.9 mg, m(Eu) = 3.0 mg; x = 0.01: m(Sr) = 86.7 mg, m(Eu) = 1.5 mg; $^3_\infty[Sr(Im)_2]$: m(Sr) = 87.6 mg), were filled in a DURAN glas ampoule, and 4.0 ml NH_3 (Linde, 99.999%) were condensed on top by the use of liquid nitrogen. After warming to > -78 °C the metals dissolved under formation of a dark blue solution. NH_3 was evaporated after 1h by warming up to RT. The homogenous powder mixture of the metals was sealed in the ampoule together with 1H-imidazole (BtzH, $C_6H_5N_3$; 204 mg = $3*10^{-3}$ mol) under vacuum. The reaction mixture was heated in 80 h to 160 ^oC. The temperature was held for 336 h. The melt was cooled to 75 ^oC in 760 h and to room temperature in 10 h. The reaction gave reflective yellow crystals of **1** next to an excess of imidazole and was purified by evaporation of imidazole at 110 °C under vacuum.

Analysis and yield: $^3_\infty[Sr_{1-x}Eu_x(Im)_2]$: x = 1.0: Yield (Eu): 269 mg (94 %); CHN-Analyssis for $C_6H_6N_4Eu$ (%): C 25.25, H 2.41, N 19.54; calc.: C 25.19, H 2.11, N 19.58; MIR (KBr): (3122 w, 3076 w, 1666 w, 1606 m, 1528 m, 1480 m, 1454 vs, 1423 ssh, 1323 m, 1302 m, 1253 w, 1246 m, 1218 s, 1212 ssh, 1152 w, 1133 s, 1101 s, 1093 s, 1074 vs, 1066 vs, 947 m, 923 vs, 914 ssh, 852 m, 828 s, 784 s, 769 vs, 756 vs, 682 vs, 658 s, 607 s) cm^{-1}; FIR (PE) (348 w, 179 m, 133 m, 120 m) cm^{-1}. x = 0.5: Yield (Sr/Eu): 237 mg (93 %); CHN-Analysis for $C_6H_6N_4Sr_{0.5}Eu_{0.5}$ (%): C 28.65, H 2.52, N 20.95; calc.: C 28.38, H 2.38, N 22.06. x = 0.05: Yield (Sr/Eu): 205 mg (91 %); CHN-Analysis for $C_6H_6N_4Sr_{0.95}Eu_{0.05}$ (%): C 32.10, H 3.03, N 24.93; calc.: C 32.03, H 2.69, N 24.90. x = 0.03: Yield (Sr/Eu): 207 mg (93 %); CHN-Analysis for $C_6H_6N_4Sr_{0.97}Eu_{0.03}$ (%): C 32.18, H 3.07, N 25.14; calc.: C 32.22, H 2.70, N 25.05. x = 0.02: Yield (Sr/Eu): 201 mg (90 %); CHN-Analysis for $C_6H_6N_4Sr_{0.98}Eu_{0.02}$ (%): C 32.57, H 2.78, N 25.13; calc.: C 32.31, H 2.60, N 25.12. x = 0.01: Yield (Sr/Eu): 198 mg (89 %); CHN-Analysis for $C_6H_6N_4Sr_{0.99}Eu_{0.01}$ (%): C 32.48, H 2.49, N 24.94; calc.: C 32.40, H 2.72, N 25.19.

Analysis and yield: ${}^{3}_{\infty}[Sr(Im)_2]$: Yield (Sr): 203 mg (92 %); CHN-Analysis for $C_6H_6N_4Sr$ (%): C 32.45, H 2.86, N 25.35; calc.: C 32.50, H 2.73, N 25.26; MIR (KBr): (3103 w, 3086 w, 1671 m, 1611 m, 1531 w, 1482 s, 1458 vs, 1450 vs, 1324 w, 1304 s, 1246 s, 1217 vs 1213 vs, 1135 vs, 1103 s, 1071 vs, 948 s, 924 vs, 854 s, 831 s, 786 ssh, 775 vs, 682 vs, 663 ssh, 648 ssh, 612 m) cm^{-1}; FIR (PE) (192 m, 135 w, 129 w, 118 m) cm^{-1}.

${}^{2}_{\infty}[Eu(Im)_2(ImH)_2]$ (**3**): Eu (1 mmol, 152.0 mg, Smart Elements 99.99 %) and 1*H*-imidazole (3 mmol, 204.2 mg, Acros Organics 99 %) were sealed in an evacuated DURAN glass. The reaction mixture was heated in a glass oven (Büchi) in 1 h to 90 ^{o}C. The temperature was held for 336 h. The melt was cooled to room temperature in 0.5 h. The reaction gave yellow single crystals of **3** next to a slight amount of the reagents. Analysis and Yield: Yield (Eu): 247 mg (58 %); CHN-Analysis for $C_6H_6N_4Eu$ (%): C 33.28, H 4.04, N 26.68; calc.: C 34.13, H 3.34, N 26.54; MIR (KBr): (3311 s, 3122 w, 3076 w, 2964 w, 1666 w, 1613 w, 1528 m, 1483 w, 1453 vs, 1423 w, 1324 m, 1302 m, 1262 s, 1240 ssh, 1220 s, 1212 ssh, 1152 w, 1137 m, 1101 s, 1093 ssh, 1075 vs, 1066 vs, 949 w, 927 vs, 914 m, 827 s, 802 s, 769 vs, 756 vs, 682 vs, 658 s, 607 s, 506 w) cm^{-1}; FIR (PE) (180 w, 129 w, 121 w) cm^{-1}.

 # *Crystallographic data*:

${}^{3}_{\infty}[Eu(Im)_2]$ (**1**): $C_6H_6N_4Eu$, M = 286.1 gmol^{-1}, single crystal X-ray determination; monoclinic, space group *C*2/c (No. 15), a = 943.6(3) pm, b = 1040.8(3), c = 717.7(2) pm, β = 90.05(2)°, T = 140 K, Z = 4, V = 704.9(4)·10^6 pm^3, $\rho_{\text{ber.}}$ = 2.696 g·cm^{-3}, $2\theta_{\text{max.}}$ = 60.50°, diffractometer STOE IPDS I, *φ*-scan with $\Delta\varphi$ = 1.7°, radiation $Mo_{K\alpha}$, λ = 0.71073*10^2 pm, 3648 overall reflections, 1030 independent reflections, 905 with I > 2σ(I) for 52 parameters, structure solution was achieved using direct methods (SHELXS-97),[1] structure refinement was achieved by a twin refinement using the matrix [100 0-10 00-1] (BASF 0.50192) and the least square deviation method (SHELXL-97)[1] for all independent reflections vs. $|F^2|$, R_1 = 0.0191 for 905 reflections with I > $2\sigma(I)$, wR_2 = 0.0404 for 1030 independent reflections, residual electron density +1.41/-0.75 e/(10^6 pm^3).

${}^{3}_{\infty}[Sr(Im)_2]$ (**2**): $C_6H_6N_4Sr$, M = 221.8 g·mol^{-1}, Rietveld refinement of X-ray powder data; refinement of the atom positions of the C,N ring atoms was achieved by rigid body constraints regarding the geometry of the planar five membered rings of the imidazolate anions starting with the positional, C-N distance and angle data gathered from **1**. This limits the No. of parameters to 3 translational and 3 rotational parameters for the complete ring system and prevents misrefinements of the light atom positions; monoclinic, space group *C*2/c (Nr. 15), a = 943.717(83), b = 1045.651(89), c = 723.539(63) pm, β = 89.958(13)°, T = 297 K, Z = 4, V = 713.99(11)·10^6 pm^3, $\rho_{\text{ber.}}$ = 2.06302 g·cm^{-3}, $2\theta_{\text{max.}}$ = 44.98°, powder diffractometer Stadi P (Fa. Stoe & Cie), Debye-Scherrer geometry with $\Delta\theta$ = 0.01°, radiation $Mo_{K\alpha_1}$, λ = 0.70930*10^2 pm, 4199 data points, 482 reflections determined, No. of parameters = 76, structure solution was achieved using the program TOPAS Academic V4.1,[1] R_p = 0.01935, wR_p = 0.02449, $R(F2)$ = 0.01040, χ^2 = 1.190.

${}^{2}_{\infty}[Eu(Im)_2(ImH)_2]$ (**3**): $C_{12}H_{14}N_8Eu$, M = 422.3 g·mol^{-1}, single crystal X-ray determination; monoclinic, space group $P2_1/n$ (No. 14), a = 1055.0(3), b = 1055.9(3), c = 1378.2(5) pm, β = 95.16(2)°, T = 140 K, Z = 4, V = 1529.2(8)·10^6 pm^3, $\rho_{\text{ber.}}$ = 1.834 g·cm^{-3}, $2\theta_{\text{max.}}$ = 51.00°, diffractometer STOE IPDS I, *φ*-scan with $\Delta\varphi$ = 1.4°, radiation $Mo_{K\alpha}$, Wellenlänge λ = 0.71073 Å, 9977 overall reflections, 2786 independent reflections, 1150 with I > 2σ(I) for 170 parameters, structure solution was achieved using direct methods (SHELXS-97),[1] structure refinement was achieved by the least square deviation method (SHELXL-97)[1] for all independent reflections vs. $|F^2|$, $R_1 = 0.0555$ for 2103 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1263$ for all 3357 independent reflections, residual electron density +1.00/-1.46 e/(10^6 pm^3). All non hydrogen atoms were refined anisotropically. The H atoms for **1** and **3** were geometrically positioned. Integrity of symmetry and crystal systems were separately checked (PLATON).[29]

Selected interatomic distances [pm] and angles [°] for $C_6H_6N_4Eu$ (**1**): Eu1-N1 268.4(4), Eu1-N2^{I} 259.3(4), Eu1-N2^{II} 259.3(4), Eu1-N1^{III} 268.4(4), Eu1-N1^{IV} 268.8(5), Eu1-N1^{V} 268.8(5); N2^{I}-Eu1-N2^{II} 86.9(2), N2^{I}-Eu1-N1 124.8(2), N2^{II}-Eu1-N1 58.2(2), N2^{I}-Eu1-N1^{III} 58.2(2), N2^{II}-Eu1-N1^{III} 124.8(2), N2^{II}-Eu1-N1^{IV} 109.4(2), N1-Eu1-N1^{IV} 97.7(2), N1^{III}-Eu1-N1^{IV} 79.8(2), N2^{I}-Eu1-N1^{V} 109.4(2), N1-Eu1-N1^{V} 79.8(2), N1^{III}-Eu1-N1^{V} 97.7(2), N1^{IV}-Eu1-N1^{V} 87.2(2). Symmetry operations: I: 1/2+x, 1/2-y, 1/2+z; II: 1/2-x, 1/2-y, -z; III: 1-x, y, 1/2-z; IV: x, -y, 1/2+z; V: 1-x, -y, -z.

Selected interatomic distances [pm] and angles [°] for $C_6H_6N_4Sr$ (**2**): Sr1-N1 273.0(67), Sr1-N1^{III} 273.0(67), Sr1-N1^{V} 255.8(67), Sr1-N1^{IV} 255.8(67), Sr1-N2^{II} 268.9(61), Sr1-N2^{I} 268.9(61); N1-Sr1-N1^{V} 77.6(20), N1-Sr1-N1^{IV} 98.6(14), N1-Sr1-N2^{II} 58.6(25), N1-Sr1-N2^{I} 125.7(19), N1^{III}-Sr1-N1^{V} 98.6(14), N1^{III}-Sr1-N1^{IV} 77.6(20), N1^{III}-Sr1-N2^{II} 125.7(19), N1^{III}-Sr1-N2^{I} 58.6(25), N1^{V}-Sr1-N1^{IV} 87.1(25), N1^{V}-Sr1-N2^{I} 107.9(10), N1^{IV}-Sr1-N2^{II} 107.9(10), N2^{II}-Sr1-N2^{I} 91.2(22). Symmetry operations: I: 1/2+x, 1/2-y, 1/2+z; II: 1/2-x, 1/2-y, -z; III: -x, y, 1/2-z; IV: x, -y, 1/2+z; V: -x, -y, -z.

Selected interatomic distances [pm] and angles [°] for $C_{12}H_{14}N_8Eu$ (**3**): Eu1-N4^{I} 258(2), Eu1-N3 260(2), Eu1-N1 264(3), Eu1-N7 265(2), Eu1-N5 264(2), Eu1-N2^{II} 268(2); N4^{I}-Eu1-N3 92.4(6), N3-Eu1-N1 91.9(6), N4^{I}-Eu1-N7 82.2(6), N3-Eu1-N7 97.4(7), N1-Eu1-N7 86.6(7), N4^{I}-Eu1-N5 95.9(6), N3-Eu1-N5 84.6(7), N1-Eu1-N5 95.3(7), N4^{I}-Eu1-N2^{II} 88.4(6), N1-Eu1-N2^{II} 88.5(6), N7-Eu1-N2^{II} 88.7(6), N5-Eu1-N2^{II} 89.3(7). Symmetry operations: I: 1/2-x, 1/2+y, 3/2-z; II: 3/2-x, 1/2+y, 3/2-z

‡ Luminescence Spectroscopy

Excitation of Eu^{2+} leads to population of the $4f^{6}5d^{1}$-level followed by relaxation without emission to the t_{2g} $4f^{6}5d^{1}$-level. From this energy level emission occurs to the $^{8}S_{7/2}$ $4f^{7}$ ground state. Because of coordination of the N atoms of the imidazolate anions, lowering in energy of the $5d$ levels below the ^{6}P $4f^{7}$-level occurs. Parity forbidden *f-f* transitions are therefore neglectable.

Excitation and emission spectra were recorded using a photoluminescence spectrometer Horiba Jobin Yvon Spex Fluorolog 3 with a 450 W xenon lighting, double monochromator, an Ulbricht sphere and a photomultiplier as detector. Determination of the quantum yields was achieved without prerequisites by the method of *Friend*.[2] First, the diffuse reflection of the sample was determined under excitation conditions ($\lambda_{exc.}$= 366 und 450 nm). Second, the emission was measured for each excitation wavelength. Integration over the reflected and emitted photons by use of the Ulbricht sphere gives the absolute quantum yields.[3] Corrections were used regarding spectral power of the excitation source, reflection behaviour of the Ulbrecht sphere and sensitivity of the detector. In addition, the quantum yields were also determined comparatively to a reference phosphor material with a certified quantum yield. The phosphor $BaMgAl_{10}O_{17}$:Eu,Mn (BAM:Mn) was used as reference and has a quantum yield of 85 % at $\lambda_{exc.}$= 366 nm.[3]

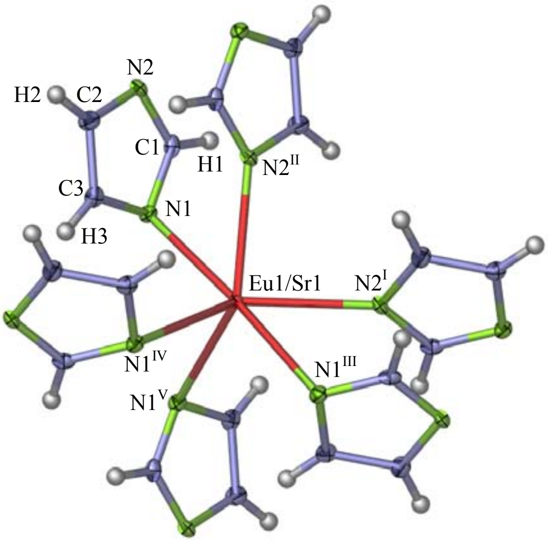

Figure S1: Fragment of the framework structure of $^{3}_{\infty}[Sr_{1-x}Eu_{x}(Im)_{2}]$ (**1**). The thermal ellipsoids depict 50 % of the probability level of the atoms. Symmetry operations: I: 1/2+x, 1/2-y, 1/2+z; II: 1/2-x, 1/2-y, -z; III: 1-x, y, 1/2-z; IV: x, -y, 1/2+z; V: 1-x, -y, -z.

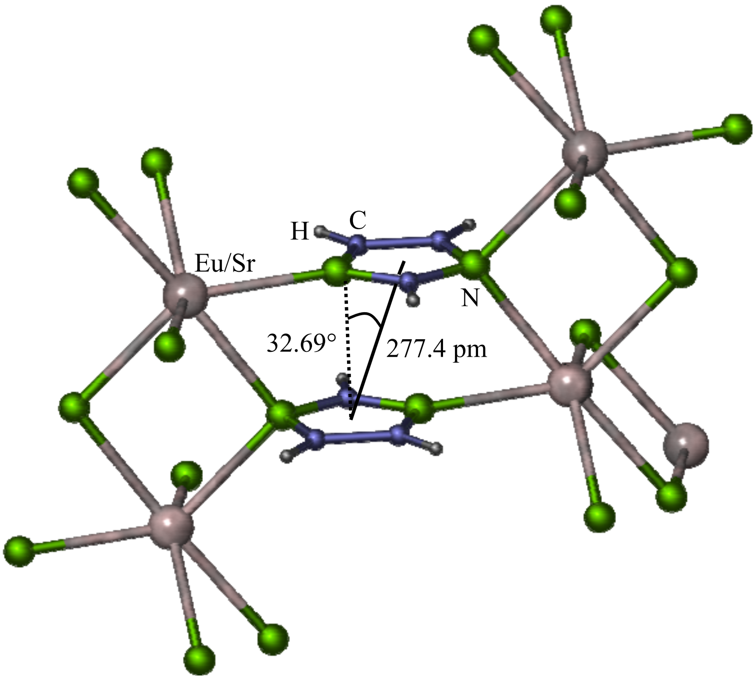

Figure S2: Fragment of the framework structure of $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$ (**1**) to visualise the offset π-stacking of two adjacent imidazolate ligands. The distance between the centres of the heterocyclic rings is only 277.4 pm and the angle to the ring normal 32.69°.

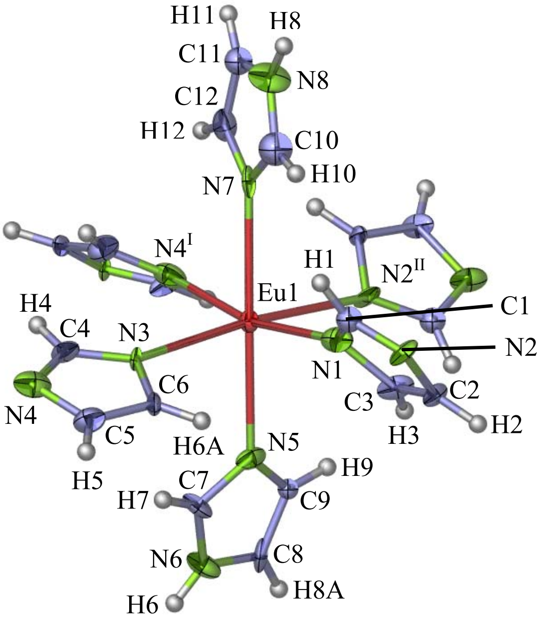

Figure S3: Fragment of the framework structure of $^{2}_{\infty}[Eu(Im)_2(ImH)_2]$ (**3**). The thermal ellipsoids depict 50 % of the probability level of the atoms. Symmetry operations: **I**: 1/2-x, 1/2+y, 3/2-z; **II**: 3/2-x, 1/2+y, 3/2-z.

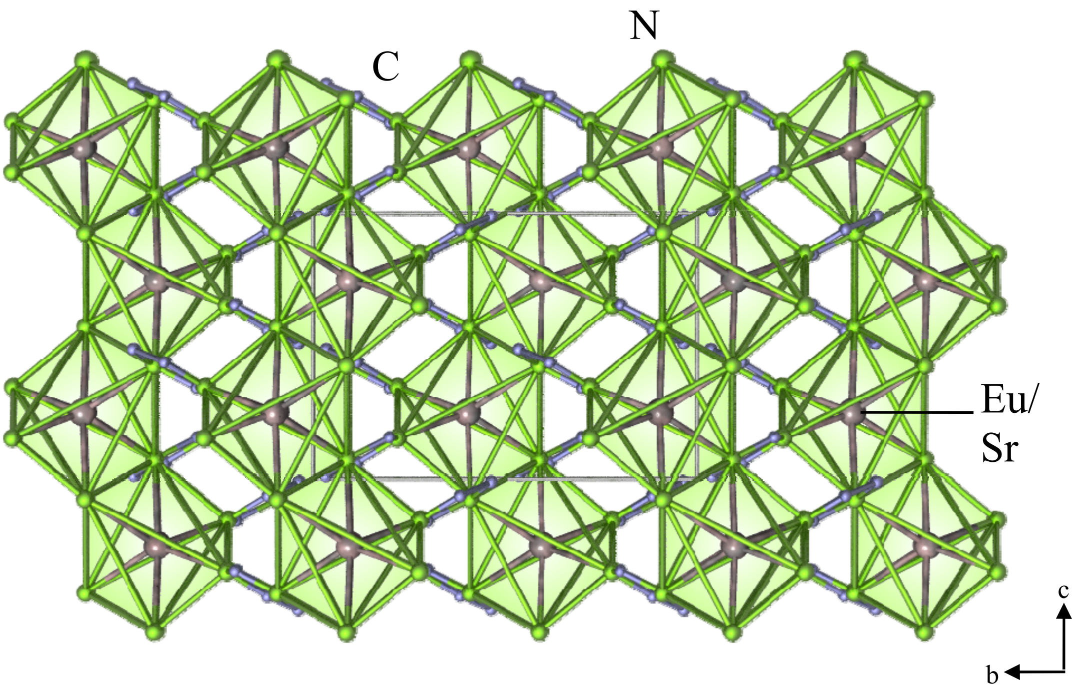

Fig.S4 The crystal structure of the dense 3D-MOF 1 along [100].

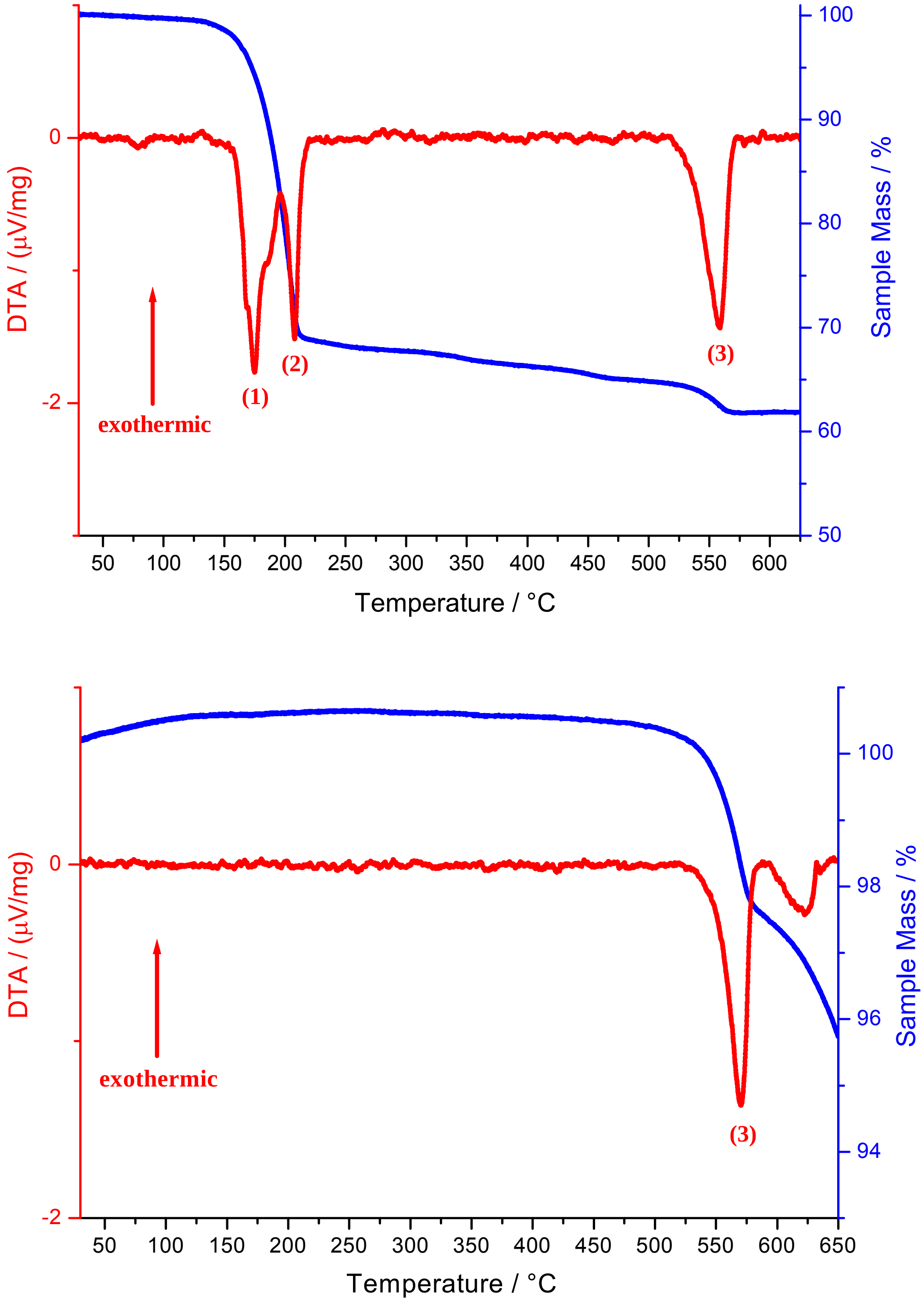

Figure S5: Simultaneous DTA / TG analysis of the bulk sample of $^{2}_{\infty}[Eu(Im)_2(ImH)_2]$ (**3**) between 30 and 625 °C with a heating rate of 10 °C/min (He) (top). The condensation reaction of (**3**) to $^{3}_{\infty}[Eu(Im)_2]$ (**1**) starts at 160 °C under the release of two equivalents of imidazole (signal 1). The amine itself is volatile prior to its boiling point (255 °C) and evaporated from the sample from 200 °C on (signal 2). The network of (**1**) is thermally highly stable and starts to decompose at 530 °C (signal 3) (bottom).

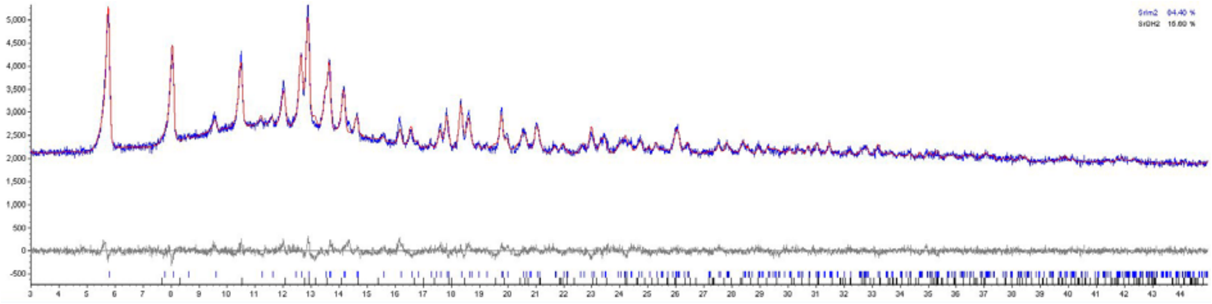

Figure S6: X-ray powder pattern and Rietveld fit of $^{3}_{\infty}[\mathrm{Sr(Im)_2}]$ (**2**).

Analytical and Crystallographic Data of $^{3}_{\infty}[\mathrm{Sr_{1-x}Eu_x(Im)_2}]$ (1) (x = 0.02-0.5)

$^{3}_{\infty}[\mathrm{Sr_{0.5}Eu_{0.5}(Im)_2}]$

Rietveld refinement ($C_6H_6N_4Sr_{0.5}Eu_{0.5}$, M = 223.0 g·mol^{-1}): space group $C2/c$ (No. 15), a = 943.73(13), b = 1045.74(14), c = 724.15(9) pm, β = 89.97(2)°, T = 297 K, Z = 4, V = 714.66(16)·10^6 pm^3, $\rho_{\text{calc.}}$ = 2.36008 g·cm^{-3}, 2$\theta_{\text{max.}}$ = 44.99°, Stadi P Powder Diffractometer (Co. Stoe & Cie), measurement type Debye-Scherrer-geometry with$\Delta\theta$ = 0.01°, radiation Mo$_{K\alpha_1}$, wave length λ = 0.70930 Å, 4200 data points, 482 measured reflections, number of refined parameters 76, the structure refinement was carried out by the program TOPAS-Academic V4.1,[1] Rietveld refinement of X-ray powder data; refinement of the atom positions of the C,N ring atoms was achieved by rigid body constraints regarding the geometry of the planar five membered rings of the imidazolate anions starting with the positional, C-N distance and angle data gathered from **1**. This limits the No. of parameters to 3 translational and 3 rotational parameters for the complete ring system and prevents misrefinements of the light atom positions; R_p = 0.07499, wR_p = 0.09483, $R(F2)$ = 0.02408, χ^2 = 0.954.

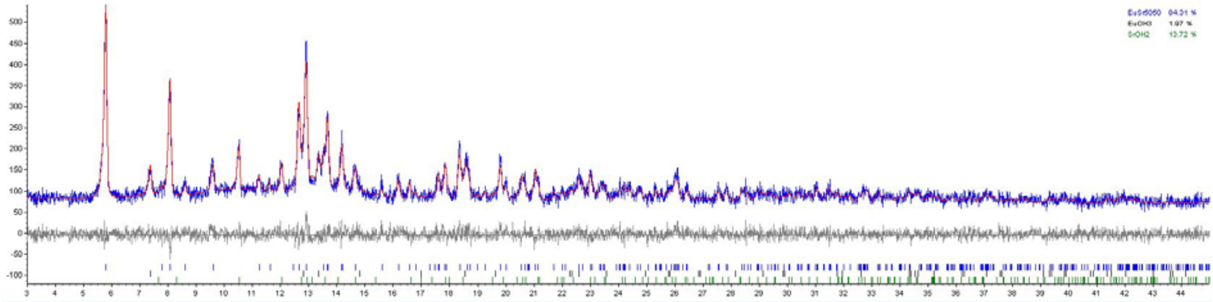

Figure S7: X-ray powder pattern and Rietveld fit of $^{3}_{\infty}[\mathrm{Sr_{0.5}Eu_{0.5}(Im)_2}]$ (**1**).

Vibrational spectroscopy ($C_6H_6N_4Sr_{0.5}Eu_{0.5}$): MIR (KBr): (3104 w, 3085 w, 1680 m, 1611 m, 1481 m, 1457 s, 1448 s, 1303 m, 1246 s, 1218 s, 1212 s, 1134 s, 1102 m, 1070 vs, 947 m, 924 vs, 853 s, 830 m, 786 ssh, 776 vs, 683 vs, 648 m) cm^{-1}; FIR (PE) (191 m, 135 m, 130 w, 122 w, 117 m) cm^{-1}.

$^3_\infty[Sr_{0.95}Eu_{0.05}(Im)_2]$

Rietveld refinement ($C_6H_6N_4Sr_{0.95}Eu_{0.05}$, M = 225.0 g·mol^{-1}): space group $C2/c$ (No. 15), a = 944.04(7), b = 1046.39(7), c = 723.95(4) pm, β = 89.99(1)°, T = 297 K, Z = 4, V = 715.134(8)·10^6 pm^3, $\rho_{calc.}$ = 2.08958 g·cm^{-3}, $2\theta_{max.}$ = 44.99°, Stadi P Powder Diffractometer (Co. Stoe & Cie), measurement type Debye-Scherrer-geometry with $\Delta\theta$ = 0.01°, radiation $Mo_{K\alpha_1}$, wave length λ = 0.70930 Å, 4200 data points, 482 measured reflections, number of refined parameters 75, the structure refinement was carried out by the program TOPAS-Academic V4.1,[1] Rietveld refinement of X-ray powder data; refinement of the atom positions of the C,N ring atoms was achieved by rigid body constraints regarding the geometry of the planar five membered rings of the imidazolate anions starting with the positional, C-N distance and angle data gathered from **1**. This limits the No. of parameters to 3 translational and 3 rotational parameters for the complete ring system and prevents misrefinements of the light atom positions; R_p = 0.02250, wR_p = 0.02956, $R(F2)$ = 0.01881, χ^2 = 1.460.

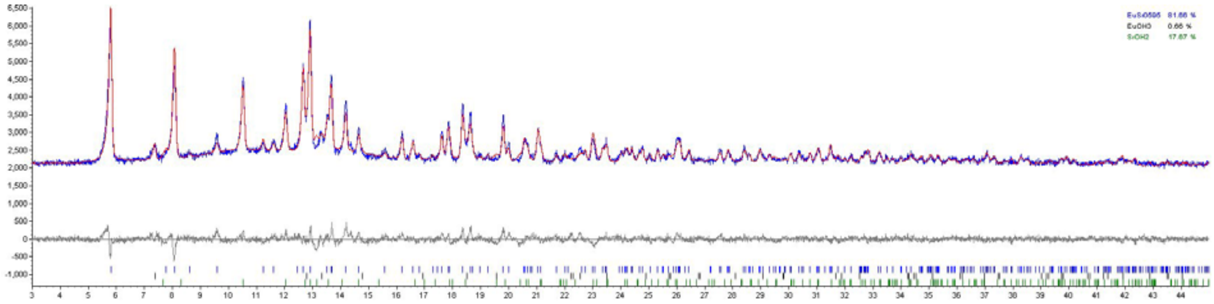

Figure S8: X-ray powder pattern and Rietveld fit of $^3_\infty[Sr_{0.95}Eu_{0.05}(Im)_2]$ (**1**).

Vibrational spectroscopy ($C_6H_6N_4Sr_{0.95}Eu_{0.05}$): MIR (KBr): (3272 w, 3103 w, 3086 w, 1671 m, 1611 m, 1482 m, 1458 s, 1450 s, 1304 m, 1246 s, 1218 s, 1212 s, 1134 s, 1103 m, 1070 vs, 948 m, 924 vs, 854 s, 831 m, 786 ssh, 776 vs, 683 vs, 648 w) cm^{-1}; FIR (PE) (192 m, 136 m, 130 w, 122 w, 118 m) cm^{-1}.

$^{3}_{\infty}[\mathbf{Sr_{0.97}Eu_{0.03}(Im)_2}]$

Rietveld refinement ($C_6H_6N_4Sr_{0.97}Eu_{0.03}$, M = 223.7 g·mol^{-1}): space group $C2/c$ (No. 15), a = 944.43(11), b = 1046.78(12), c = 724.52(7) pm, β = 90.00(2)°, T = 297 K, Z = 4, V = 716.27(14)·10^6 pm^3, $\rho_{\text{calc.}}$ = 2.07436 g·cm^{-3}, $2\theta_{\text{max.}}$ = 44.99°, Stadi P Powder Diffractometer (Co. Stoe & Cie), measurement type Debye-Scherrer-geometry with $\Delta\theta$ = 0.01°, radiation Mo$_{K\alpha_1}$, wave length λ = 0.70930 Å, 4200 data points, 482 measured reflections, number of refined parameters 67, the structure refinement was carried out by the program TOPAS-Academic V4.1,[1] Rietveld refinement of X-ray powder data; refinement of the atom positions of the C,N ring atoms was achieved by rigid body constraints regarding the geometry of the planar five membered rings of the imidazolate anions starting with the positional, C-N distance and angle data gathered from **1**. This limits the No. of parameters to 3 translational and 3 rotational parameters for the complete ring system and prevents misrefinements of the light atom positions; R_p = 0.02981, wR_p = 0.03756, $R(F2)$ = 0.01619, χ^2 = 1.058.

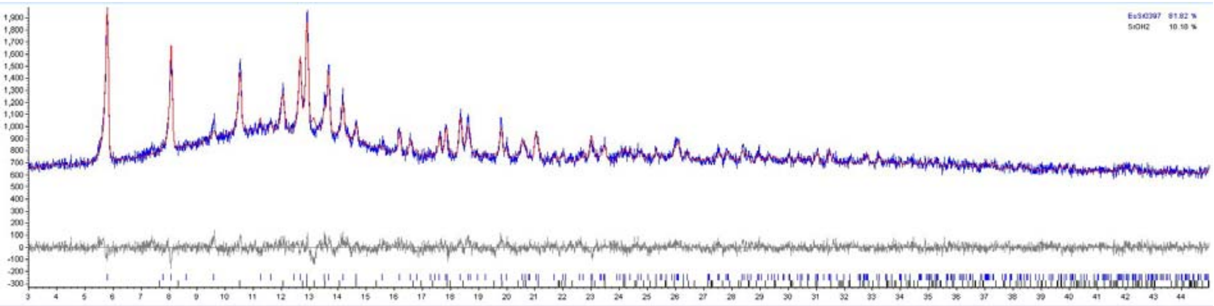

Figure S9: X-ray powder pattern and Rietveld fit of $^{3}_{\infty}[Sr_{0.97}Eu_{0.03}(Im)_2]$ (**1**).

Vibrational spectroscopy ($C_6H_6N_4Sr_{0.97}Eu_{0.03}$): MIR (KBr): (3272 w, 3103 w, 3086 w, 1671 m, 1611 m, 1482 m, 1458 s, 1450 s, 1304 m, 1247 s, 1218 s, 1212 s, 1135 s, 1103 m, 1071 vs, 948 m, 924 vs, 854 s, 831 m, 786 ssh, 775 vs, 683 vs, 648 w) cm^{-1}; FIR (PE) (191 m, 135 m, 129 w, 122 w, 117 m) cm^{-1}.

$^{3}_{\infty}[\mathbf{Sr_{0.98}Eu_{0.02}(Im)_2}]$

Rietveld refinement ($C_6H_6N_4Sr_{0.98}Eu_{0.02}$, M = 223.0 g·mol^{-1}): space group $C2/c$ (No. 15), a = 943.67(9), b = 1046.32(9), c = 724.11(6) pm, β = 89.99(1)°, T = 297 K, Z = 4, V = 714.97(11)·10^6 pm^3, $\rho_{\text{calc.}}$ = 2.07214 g·cm^{-3}, $2\theta_{\text{max.}}$ = 43.70°, Stadi P Powder Diffractometer (Co. Stoe & Cie), measurement type Debye-Scherrer-geometry with

$\Delta\theta$ = 0.01°, radiation $\mathrm{Mo}_{\mathrm{K}\alpha_1}$, wave length λ = 0.70930 Å, 4071 data points, 450 measured reflections, number of refined parameters 76, the structure refinement was carried out by the program TOPAS-Academic V4.1,[1] Rietveld refinement of X-ray powder data; refinement of the atom positions of the C,N ring atoms was achieved by rigid body constraints regarding the geometry of the planar five membered rings of the imidazolate anions starting with the positional, C-N distance and angle data gathered from **1**. This limits the No. of parameters to 3 translational and 3 rotational parameters for the complete ring system and prevents misrefinements of the light atom positions; R_p = 0.02372, wR_p = 0.03005, $R(F2)$ = 0.01176, χ^2 = 1.055.

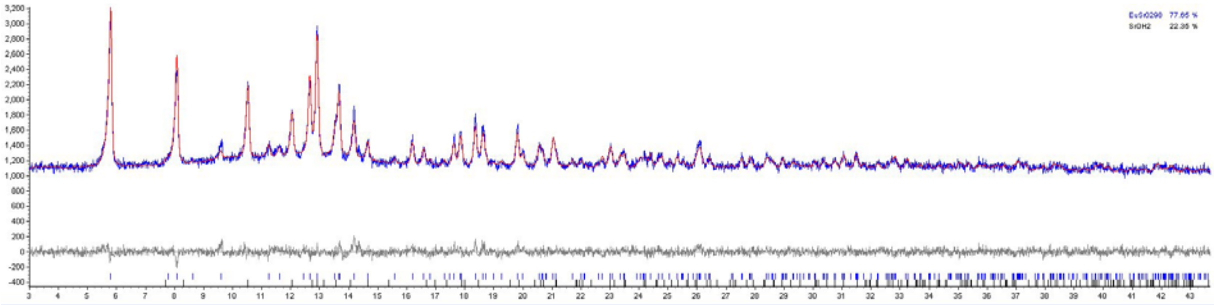

Figure S10: X-ray powder pattern and Rietveld fit of $^3_\infty[\mathrm{Sr}_{0.98}\mathrm{Eu}_{0.02}(\mathrm{Im})_2]$ (**1**).

Vibrational spectroscopy ($C_6H_6N_4Sr_{0.98}Eu_{0.02}$): MIR (KBr): (3104 w, 3086 w, 1671 w, 1597 m, 1482 m, 1458 s, 1450 s, 1304 m, 1247 s, 1218 s, 1213 s, 1135 s, 1111 wsh, 1103 m, 1071 vs, 948 m, 924 vs, 854 s, 831 m, 786 ssh, 776 vs, 684 vs, 648 w) cm^{-1}; FIR (PE) (192 m, 135 m, 130 w, 119 m) cm^{-1}.

$^3_\infty[\mathrm{Sr}_{0.99}\mathrm{Eu}_{0.01}(\mathrm{Im})_2]$

Rietveld refinement ($C_6H_6N_4Sr_{0.99}Eu_{0.01}$, M = 223.0 g·mol^{-1}): space group $C2/c$ (No. 15), a = 943.85(18), b = 1046.61(18), c = 724.46(11) pm, β = 90.00 (2)°, T = 297 K, Z = 4, V = 715.65(22)·10^6 pm^3, $\rho_{\mathrm{calc.}}$ = 2.06420 g·cm^{-3}, $2\theta_{\mathrm{max.}}$ = 44.99°, Stadi P Powder Diffractometer (Co. Stoe & Cie), measurement type Debye-Scherrer-geometry with $\Delta\theta$ = 0.01°, radiation $\mathrm{Mo}_{\mathrm{K}\alpha_1}$, wave length λ = 0.70930 Å, 4200 data points, 482 measured reflections, number of refined parameters 74, the structure refinement was carried out by the program TOPAS-Academic V4.1,[1] Rietveld refinement of X-ray powder data; refinement of the atom positions of the C,N ring atoms was achieved by rigid body constraints regarding the geometry of the planar five membered rings of the imidazolate anions starting with the positional, C-N distance and angle data gathered from **1**. This limits the No. of parameters to 3 translational and 3 rotational parameters for the complete ring system and prevents misrefinements of the light atom positions; R_p = 0.02360, wR_p = 0.02977, $R(F2)$ = 0.00673, χ^2 = 0.968.

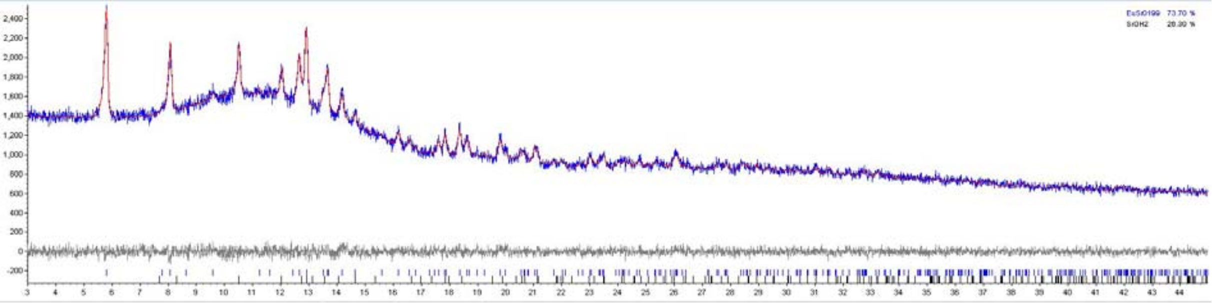

Figure S11: X-ray powder pattern and Rietveld fit of $^{3}_{\infty}[Sr_{0.99}Eu_{0.01}(Im)_2]$ (**1**).

Vibrational spectroscopy ($C_6H_6N_4Sr_{0.99}Eu_{0.01}$): MIR (KBr): (3104 w, 3086 w, 1671 w, 1598 m, 1482 m, 1458 s, 1450 s, 1304 m, 1247 s, 1218 s, 1212 s, 1135 s, 1111 wsh, 1103 m, 1071 vs, 948 m, 924 vs, 854 s, 831 m, 786 ssh, 775 vs, 683 vs, 648 w) cm^{-1}; FIR (PE) (192 m, 136 m, 130 w, 118 m) cm^{-1}.

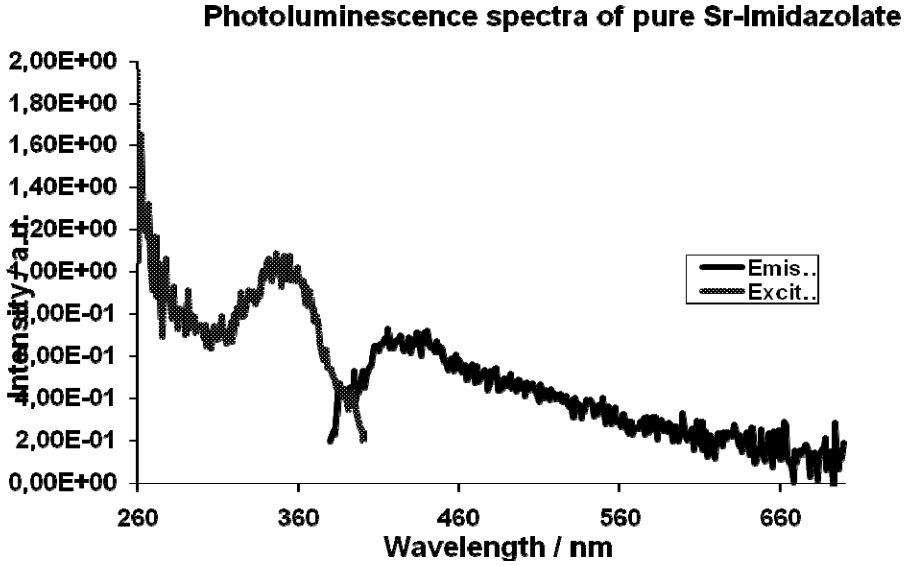

Figure S12: Excitation (dark grey) and emission spectra (black) of $^{3}_{\infty}[Sr(Im)_2]$ (**2**). The characteristic emission of europium containing **1** is not observed proving that emission neither derives from Sr nor from the imidazolae anions.

1 J. V. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.,* 1997, **9**, 230; M. Mai, C. Feldmann, in preparation.

2 K. Y. Jung, H. W. Lee, Y. C. Kang, S. B. Park, Y. S. Yang, *Chem. Mater.,* 2005, **17**, 2729.

3 G. M. Sheldrick, *SHELXS-97, Program for the resolution of Crystal Structures,* Göttingen, 1997; G. M. Sheldrick, *SHELXL-97, Program for the refinement of Crystal Structures,* Göttingen, 1997; A. A. Coelho, TOPAS-Academic V4.1, *Program for indexing*, *structure resolution and Rietveld refinement on powder data*, 2007; STOE WINXPOW v.1.04, *Program package for the operation of powder diffractometers and analysis of powder diffractograms,* Darmstadt, 1999;

4 A. A. Coelho, TOPAS-Academic V4.1, *Program for indexing, structure resolution and Rietveld refinement on powder data*, **2007**.