

Homoleptic imidazolate frameworks ${}^3\infty[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ —hybrid materials with efficient and tuneable luminescence†‡

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Homoleptic frameworks of the formula ${}^3\infty[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ (**1**) ($x = 0.01\text{--}1.0$; $\text{Im}^- = \text{imidazolate anion, C}_3\text{H}_3\text{N}_2^-$) are hybrid materials that exhibit an intensive green luminescence. Tuning of both emission wavelength and quantum yield is achieved by europium/strontium substitution so that a QE of 80% is reached at a Eu content of 5%. Even 100% pure europium imidazolate still shows 60% absolute quantum efficiency. Substitution of Sr/Eu shows that doping with metal cations can also be utilized for coordination compounds to optimize materials properties. The emission is finely tuneable in the region 495–508 nm *via* variation of the europium content. The series of frameworks ${}^3\infty[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ presents dense MOFs with the highest quantum yields reported for MOFs so far.

Framework and MOF chemistry¹ have attracted attention, as interesting properties were reported like conductivity,² catalytic effects,³ luminescence⁴ and porosity.⁵ They are mainly known for oxygen coordinating ligands, mostly metal carboxylates⁶ which include the alkaline earth and 4f elements.⁷ Because of the oxophilicity of lanthanides oxygen-free multi-dimensional coordination networks are rarely found except for a few rare earth imidazolates and triazolates.⁸ Among transition metals the imidazole ring system is of exceptional interest together with several 3d metals as they adopt zeolite structures (ZIFs)⁹ that can be used for sorption and gas separation. Different from many solid state phosphors, coordination compounds can exhibit luminescence by metal ions although they contain 100% luminescence centres.¹⁰ An expected quenching by concentration is suppressed by ligand shielding. They are furthermore interesting luminescent hybrid materials, as emission can be achieved either *via* a fluorescence of the ligand system¹¹ or the metal centres, mainly by the use of lanthanides.⁴ The excitation can benefit from antenna effects, *viz.* the ligand system is excited primarily followed by a transfer of the energy to the luminescence centres.¹² However

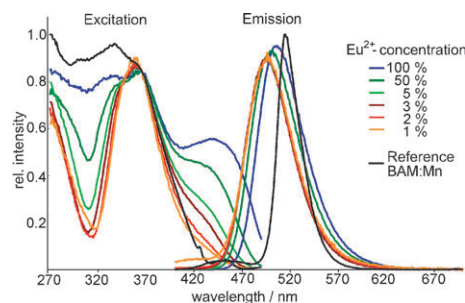


Fig. 1 Selected and normalized excitation and emission spectra of ${}^3\infty[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ (**1**) ($x = 0.05\text{--}1.0$) in comparison to $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu, Mn}$ as reference phosphor.

there are only little coordination compounds for which effective emission characterized by high quantum efficiencies has been reported.^{4,11,13} Mostly, no quantum yields were determined, although luminescence becomes important for MOFs concerning sensing and lighting from UV to near IR.^{14,15}

We now report a series of homoleptic imidazolate frameworks containing divalent strontium and europium that shows an exceptional combination of properties: an effective luminescence with the highest quantum yield reported for coordination polymers today, together with multiple excitation options including excitation maxima at the applicationally important wavelengths 370 and 460 nm (for Hg and blue LED excitation). The emission can be finely tuned in the region 495–508 nm (blue-green to green) *via* variation of the Eu content (Fig. 1). Furthermore a low quenching by concentration is observed, combined to a high thermal stability of the frameworks up to 530 °C.

${}^3\infty[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ ($x = 0.01\text{--}1.0$; $\text{Im}^- = \text{imidazolate anion, C}_3\text{H}_3\text{N}_2^-$) (**1**) are obtained by reactions of the metals europium and strontium together with a melt of the ligand *1H*-imidazole in excellent yields up to 90%.§ Solvent free reaction conditions avoid co-ordination of solvent molecules and drive the system towards homoleptic products.¹⁶ Strontium and europium form isotopic compounds that allow complete mixing throughout all molar ratios as the two ions Sr^{2+} and Eu^{2+} have almost identical ionic radii.¹⁷ Also the monometallic frameworks ${}^3\infty[\text{Sr}(\text{Im})_2]$ (**2**) and ${}^3\infty[\text{Eu}(\text{Im})_2]$ (**1**) were prepared, corroborated by single crystal X-ray and powder diffraction. Although an oxidation to Eu^{3+} could be expected, the reaction finishes at a metal to ligand ratio of 1 : 2. Even upon excess of imidazole no reaction to Eu^{3+} is observed until decomposition.¶ For combination of Eu and Sr the ratio of the two metals can be setup and controlled by the use of liquid ammonia. Both metals dissolve under formation of ammonia complexes and electride solutions, so that perfect mixing on the atomic level is

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achieved.¹⁸ ${}^3_{}[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ form at 160 °C. Excess imidazole can be evaporated with the MOFs being stable up to 530 °C.†

In addition to **1** and **2** further Eu/Sr imidazoles were obtained. Imidazole containing networks of the formula ${}^2_{}[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2(\text{ImH})_2]$ can be obtained at lower temperatures. Evidence is given again by X-ray single crystal diffraction of ${}^2_{}[\text{Eu}(\text{Im})_2(\text{ImH})_2]$ (**3**) and powder diffraction for Sr/Eu combinations. Alike HO– groups, HN– groups are known to function as quenchers. Accordingly, **3** is not a luminescent material and no emission is observed.

Luminescence of the series ${}^3_{}[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ (**1**) is based on a broad band excitation that ranges from $\lambda = 250$ nm to 460 nm. Independent from the europium content excitation *via* the imidazolate ligands is possible with excitation maxima at 270 and 366 nm. With an increasing europium content additional excitation maxima emerge at 345 and 450 nm. Thus both Eu and the ligand as an antenna effect can be used for excitation. For ligand excitation the energy is then transferred to the Eu ions. Emission is observed from europium centres only. Both ${}^3_{}[\text{Sr}(\text{Im})_2]$ (**2**) and 1*H*-imidazole were also investigated and neither displays a referring emission.** The broad emission band in **1** is typical for divalent europium as observed for $\text{SrSi}_2\text{O}_2\text{N}_2 : \text{Eu}^{2+}$ and $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$.¹⁹ Emission derives from transitions between the 5d energy levels and the $4f^8\text{S}_{7/2}$ levels. Different from 4f–4f transitions of Eu^{3+} these transitions are parity allowed, therefore strong in intensity, and influenced by the chemical surrounding by inclusion of the Eu 5d levels into the process.²⁰ For imidazolate this results in an emission of **1** in the green region. Participation of Eu^{3+} in the emission can be excluded as the typical line emission ${}^5\text{D}_4$ to the ${}^7\text{F}_J$ states is not observed.²⁰

The emission maximum can be finely tuned by the content of europium over 14 nm and range from 495 nm for 1% Eu to 508 nm for 100% Eu and results in a pronounced shift of the colour points and thereby of the emission colour from blue green to bright green according to CIE (Commission Internationale de l'Eclairage).²¹ Most efficient emission is observed for Sr : Eu = 95 : 5 with a quantum yield of about 80% ($\lambda_{\text{exc}} = 366$ nm, see Table 1).** This is in the region of commercial phosphors like $\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}$: QE = 80–85%, $\text{Zn}_2\text{SiO}_4 : \text{Mn}$: 75–80%, $\text{YVO}_4 : \text{Eu}$: 65–70%, $\lambda_{\text{exc}} = 254$ nm,¹⁹ higher than the peak of the known Eu coordination compounds $[\text{Eu}(\text{nta})_3(\text{dmsO})_2]$ ²² and twice as high as GWMOF-6,^{15,22} the MOF with the so far highest quantum yield (QE = 39%). Even for 100% Eu and no Sr content the quantum yield still is 60% for an excitation at 450 nm (blue LED). It is also remarkable that these quantum yields were determined for room temperature and not for low

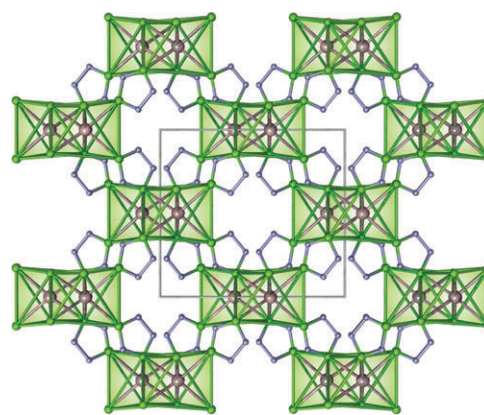


Fig. 2 The crystal structure of the dense 3D-MOF **1** along [001] with coordination polyhedra. H atoms omitted for clarity.

temperatures. Altogether **1** could be interesting even for solid lighting as a green phosphor component for a pLED.

The complete series ${}^3_{}[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ (**1**) and ${}^3_{}[\text{Sr}(\text{Im})_2]$ (**2**) crystallize isotypic in the monoclinic space group $C2/c$.†† This is responsible for an isopointal exchange of Eu *vs.* Sr and the excellent doping possibilities. The metal ions are coordinated by six nitrogen atoms of six imidazolate anions. The imidazolate anions are committed in a $\mu^3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ coordination mode and coordinated by three metal ions. Each Sr/EuN₆ polyhedron is edge connected to two other polyhedra. This results in zig-zag chains of polyhedra that are interlinked *via* nitrogen atoms of the imidazolate ligands in the (a, b) plane to give 3D-framework structures (see Fig. 2). The overall structure is a dense framework.

Distances M(Sr,Eu)–N of **1** range from 259.3(4) to 268.8(5) pm and are in the expected region for Eu^{II} .¹⁷ Additionally, an offset π -stacking is observed for each imidazolate ligand to a neighbouring aromatic ring. The distance between the centroids of neighbouring rings is only 277.4 pm, shorter than in molecular coordination compounds with N-heterocycles.²³ According to Hunter and Sanders and the shift between both rings it can be classified as an electrostatic interaction,²⁴ which is in good accordance to the Lewis acidic ionic character of Eu/Sr. The short ring distance is a result of a decrease in the electron density of the π -systems and of the electrostatic ring distraction. We believe π -stacking also influences the luminescence, but this effect and the low quenching by concentration cannot be fully interpreted by the literature.²⁵

Prior to formation of **1** and **2**, another Eu containing imidazolate was isolated at lower temperatures.§ Different from **1** and **2** this compound exhibits a 2D network structure of the formula ${}^2_{}[\text{M}(\text{Im})_2(\text{ImH})_2]$, M = Sr/Eu (**3**) and contains imidazole ligands as interplanar end-on ligands. The Eu/Sr atoms are octahedrally coordinated by N atoms, with the square plane of the octahedron containing four $\mu^2\text{-}\eta^1\text{:}\eta^1$ -bridging imidazolate anions and the caps being N atoms of end-on imidazole molecules to form one layer of the structure. The next layer shows a parallel offset so that the SnF_4 structure type is adopted (see Fig. 3). The Eu–N distances range from 258(2) to 265(2) pm being in the expected region for Eu^{II} .

3 is a low temperature phase in the system Sr/Eu/imidazole. Upon thermal treatment it is converted into the homoleptic dense MOF structure of **1**. Conversion is combined to a stepwise release of imidazole and can be observed with thermal analysis and powder

Table 1 Luminescence properties of ${}^3_{}[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ (**1**)‡

Eu ²⁺ content, x	0.01	0.02	0.03	0.05	0.50	1.00
max. Emission/nm ($\lambda_{\text{exc}}=366\text{nm}$)	495	495	495	495	502	508
CIE colour point x	0.137	0.130	0.127	0.128	0.149	0.169
y ²¹	0.415	0.425	0.415	0.415	0.502	0.584
absolute QY / %	11(1)	22(1)	68(2)	78(2)	47(2)	50(2)
relative QY / % ($\lambda_{\text{exc}}=366$ nm)	14(1)	24(1)	74(2)	83(3)	51(2)	52(2)
absolute QY / %	1(1)	3(1)	40(2)	66(2)	48(2)	60(2)
relative QY / % ($\lambda_{\text{exc}}=450$ nm)	1(1)	3(1)	42(2)	71(2)	50(2)	61(2)

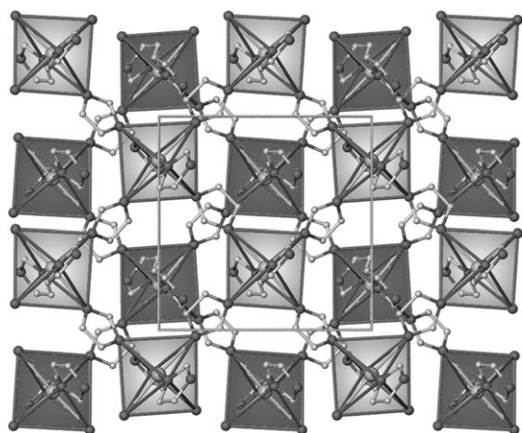


Fig. 3 The crystal structure of **3**. Coordination polyhedra of two different layers are marked in light grey and dark grey.

diffraction. ¶ With the NH groups of the imidazole molecules being known quenchers, **3** does not show any luminescence. Accordingly a suitable reaction temperature is vital to obtain the highly luminescent hybrid materials ${}^{\infty}[\text{Sr}_{1-x}\text{Eu}_x(\text{Im})_2]$ (**1**).

Notes and references

§ Reactions of the 4f metal europium, and the alkaline earth metal strontium with amine melts are redox reactions that give hydrogen gas in addition to the amide products.¹⁶ Detailed description on the *Experimental* of **1–3** is found in the ESI† including the results of IR and CHN-analysis.

¶ The trivalent oxidation state is stable for Eu ($E^{\circ}_{\text{Ln(III)}/\text{Ln(II)}} = 0.35$ V). But reactions with 1*H*-imidazole stop at Eu^{2+} , as proven by the luminescence being characteristic for Eu^{2+} . No further oxidation is observed until decomposition at 530 °C. **1–3** are stable vs. dry air and vs. normal air over six hours, after which hydrolysis is observed. Thermal properties were determined by simultaneous DTA/TG and powder diffraction. For detailed information please check the ESI.‡

|| Mixing of the metals Sr and Eu is essential for the luminescence properties of **1** but limited upon grinding. The problem is overcome by activation of the metals by electride formation in liquid NH_3 .^{16,18} The metals equally dissolve under formation of ammine complexes $[\text{M}(\text{NH}_3)_6]^{2+18}$ and solvated electrons identified by a dark blue solution. Upon removal of ammonia the metals are reformed as very small metal particles that fairly improve the mixing for the subsequent reaction with imidazole.

** Excitation of Eu^{2+} leads to population of the $4f^65d^1$ -level followed by relaxation without emission to the t_{2g} $4f^65d^1$ -level. Here emission occurs to the ${}^8\text{S}_{7/2}$ $4f^7$ ground state. Because of coordination of the imidazolate anions, lowering of the 5d levels in energy below the ${}^6\text{P}$ $4f^7$ -level occurs. Parity forbidden f–f transitions are therefore neglectable. In addition to the series of compounds **1**, excitation and emission spectra were also recorded for ${}^{\infty}[\text{Sr}(\text{Im})_2]$ (**2**) and the ligand 1*H*-imidazole. The characteristic emission of **1** can neither be detected for **2** nor for the free ligand. For further information, please see the ESI.‡

†† Crystallographic data: for detailed crystallographic data on **1–3**, please refer to the ESI‡ including interatomic distances and angles.

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