Suppporting Information on

MOF Luminescence in the Yellow Gap by Co-doping of the Homoleptic Imidazolate $^{3}_{\infty}[BaIm_2]:Eu^{2+}$ with Divalent Europium

Jens-Christoph Rybak[¥], Michael Hailmann[¥], Philipp R. Matthes[¥], Alexander Zurawski[¥], Jörn Nitsch[¥], Andreas Steffen[¥], Joachim G. Heck[#], Claus Feldmann[#], Stefan Götzendörfer[|], Jürgen Meinhardt[|], Gerhard Sextl[|], Holger Kohlmann[&,#], Stefan J. Sedlmaier[§], Wolfgang Schnick[§] and Klaus Müller-Buschbaum*,[¥].

[¥] Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[#] Institut für Anorganische Chemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 15, 76131 Karlsruhe, Germany

[|] Fraunhofer Institut für Silicatforschung ISC, Neunerplatz 2, 97082 Würzburg, Germany

[&] Anorganische Festkörperchemie, Universität des Saarlandes, 66125 Saarbrücken, Germany

[#] Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany

[§] Department Chemie, Universität München LMU, Butenandtstraße 5-13, 81377 München, Germany

Crystallographic data:

Investigation by powder diffraction shows that **1** – **5** build structures isotypic to the non-doped compound **6** (see Fig. 1). The structure of **6** was solved from PXRD date exclusively. Crystallographic data is displayed in Table 1.

Further information was deposited at the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223336033 or e-mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposition number CCDC-856315, the names of the authors and the literature citation.

Fig. 2 shows the complete coordination spheres and linkage of the Ba centers in **6**. The octahedral coordination polyhedra for the two Ba atoms are depicted in Fig. 3. Selected interatomic distances and angles can be found in Table 2.

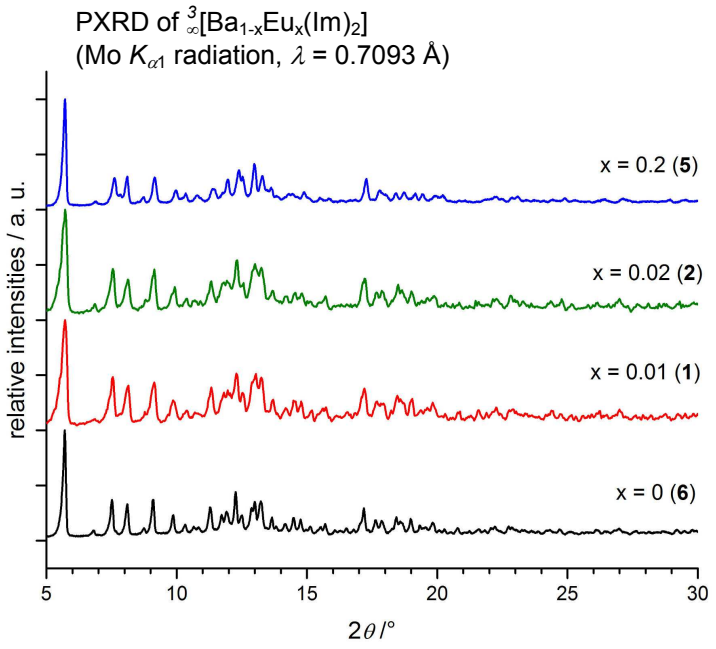

Fig. S1: Powder diffraction data of $^{3}_{\infty}[Ba_{1-x}Eu_x(Im)_2]$ (x = 0.01, 0.02, 0.2) (**1, 2, 5**) and $^{3}_{\infty}[Ba(Im)_2]$ (**6**).

Tab. S1: Crystallographic data for $^{3}_{\infty}[Ba(Im)_2]$ (**6**). Standard deviations are given in parentheses.

Formula	$C_6H_6BaN_4$
Formula weight [g/mol]	271.48
Crystal system, space group	monoclinic, $P2_1/c$
	a = 934.21(5)
Lattice parameters [pm]	b = 2209.82(9)
	c = 764.54(3)
Monoclinic angle [°]	β = 95.597(3)
Cell volume [nm^3]	1570.84(12)
Z	8
Density [g/cm^3]	2.2957(2)
μ [cm^{-1}]	38.941
X-ray radiation	Cu-$K_{\alpha 1}$, λ = 154.059 pm
Diffractometer	STOE STADI P
d range	1.80643– 9.29765
Data Points	4000
Reflections	276
Refined parameters	70 (18 for background)
R_P	0.038
wR_P	0.047
R_{bragg}	0.009
χ^2	1.120
Wght. Durbin-Watson	1.288

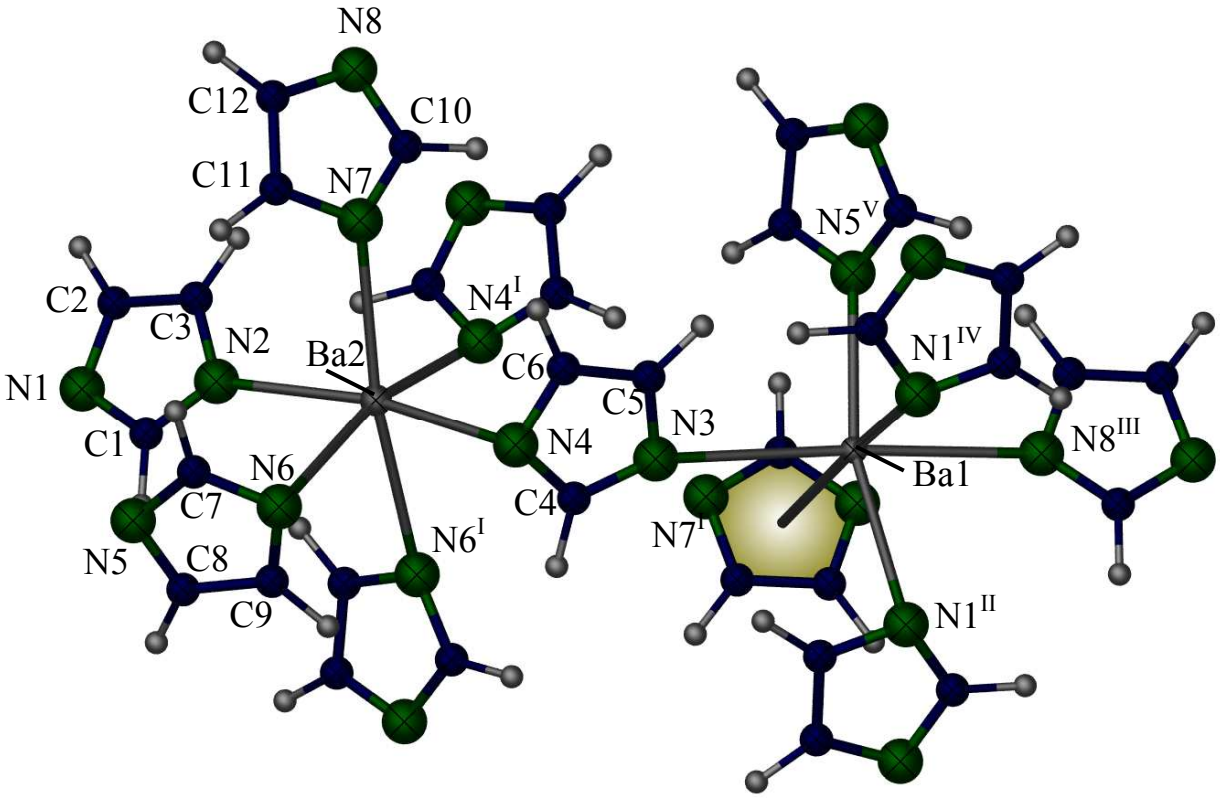

Fig. S2: The coordination spheres and linkage of Ba1 and Ba2 in $^{3}_{\infty}[Ba(Im)_2]$. Symmetry operations: I: x, 3/2-y, z-1/2; II: 1-x, y-1/2, ½-z; III: 2-x, y-1/2, ½-z; IV: 1+x, 3/2-y, ½+z; V: 1+x, 3/2-y, z-1/2;

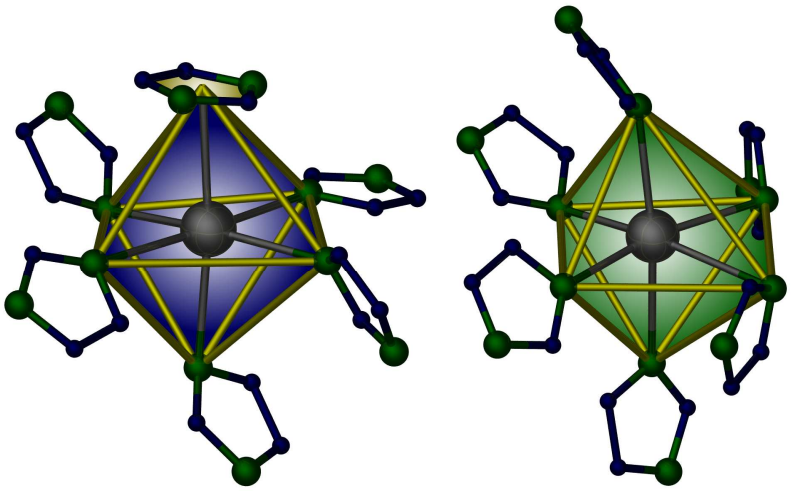

Fig. S3: Coordination polyhedra of the atoms Ba1 (left) and Ba2 (right) in $^{3}_{\infty}[Ba(Im)_2]$ (**6**). Ba atoms are displayed in grey, N in green and C in blue. H atoms have been omitted for clarity. Edges of the polyhedra do not represent bonds.

Tab. S2: Selected interatomic distances and angles in $^{3}_{\infty}[Ba(Im)_2]$, deviations given in brackets

Atom sites	Distance /pm	Atom sites	Angle /°
Ba1 – N5^{V}	279(2)	N3 – Ba1 – Cent1$^{I*)}$	86.1
Ba1 – Cent1$^{I*)}$	286	N3 – Ba1 – N1^{II}	93.8(5)
Ba1 – N1^{IV}	287(2)	N1^{II} – Ba1 – Cent1$^{I*)}$	96.9
Ba1 – N8^{III}	290(1)	N1^{II} – Ba1 – N5^{V}	164.6(5)
Ba1 – N1^{II}	293(3)	N1^{IV} – Ba1 – Cent1$^{I*)}$	173.8
Ba1 – N3	309(2)	N3 – Ba1 – N8^{III}	176.4(4)
Ba2 – N4^{I}	269(2)	N2 – Ba2 – N7	90.6(6)
Ba2 – N2	270(2)	N2 – Ba2 – N6	91.3(8)
Ba2 – N4	277(1)	N6 – Ba2 – N7	99.7(4)
Ba2 – N7	282(1)	N2 – Ba2 – N4	166.8(8)
Ba2 – N6^{I}	300(1)	N6 – Ba2 – N4^{I}	167.6(4)
Ba2 – N6	310(2)	N7 – Ba2 – N6^{I}	169.6(6)

Sym. op. I: x, 3/2-y, z-1/2; II: 1-x, y-1/2, ½-z; III: 2-x, y-1/2, ½-z; IV: 1+x, 3/2-y, ½+z; V: 1+x, 3/2-y, z-1/2.

*) Cent1: centroid created from the atoms N7-C10-N8-C12-C11

Photoluminescence and determination of quantum yield:

Excitation and emission spectra were recorded using a photoluminescence spectrometer Horiba Jobin Yvon Spex Fluorolog 3, equipped with a 450 W Xenon lamp, double monochromators, Ulbricht sphere and photomultiplier as detector. Determination of the absolute quantum yield was performed as suggested by *Friend*.[1] In addition, the quantum yield was determined in comparison to a reference phosphor material with known quantum yield. To this concern, BaMgAl$_{10}$O$_{17}$:Eu (BAM) was used, having a quantum yield of 80% at $\lambda_{exc.}$= 365 nm.

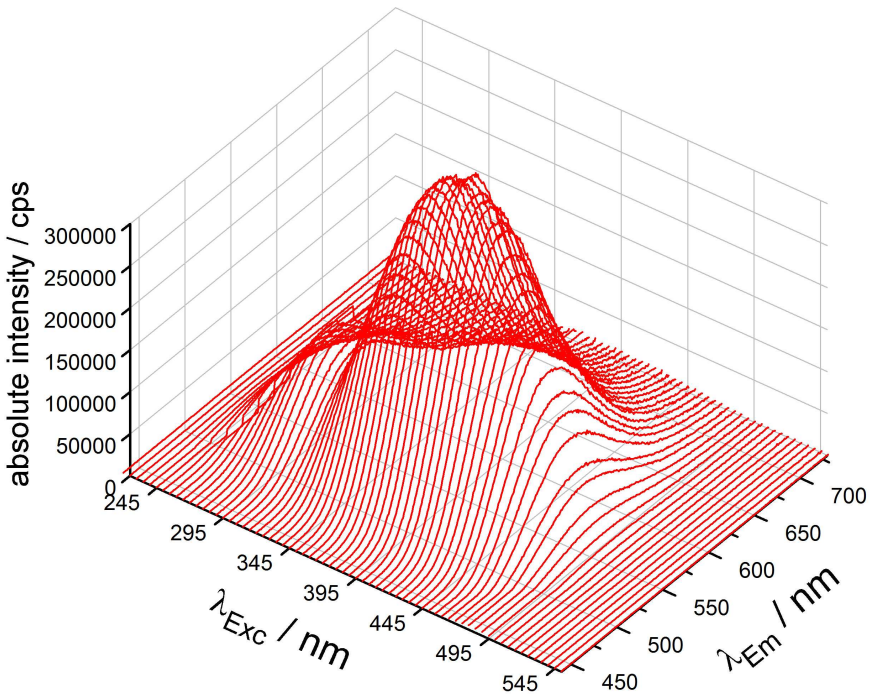

Fig. S4: Three-dimensional photoluminescence spectra of $^{3}_{\infty}$[Ba(Im)$_2$]:0.1Eu^{2+} (**4**), depicting the correlation of emission and excitation by an antenna triggered and metal triggered luminescence.

Lifetime/decay investigations:

Tab. S3: Observed decay times τ_{obs} of $^{3}_{\infty}$[Ba(Im)$_2$]:0.05 Eu (**3**), deviations are given in brackets.

T [K]	τ_1 [ns]	τ_2 [ns]	A_1 (f) [a]	A_2 (f) [a]
293	166(3)	444(3)	4016; 26 %	4085; 74 %
77	357(14)	947(4)	1667; 8 %	7566; 92 %

[a] $A_{1/2}$=Pre-exponential factor; $f_{1/2}$=contribution to steady state emission.

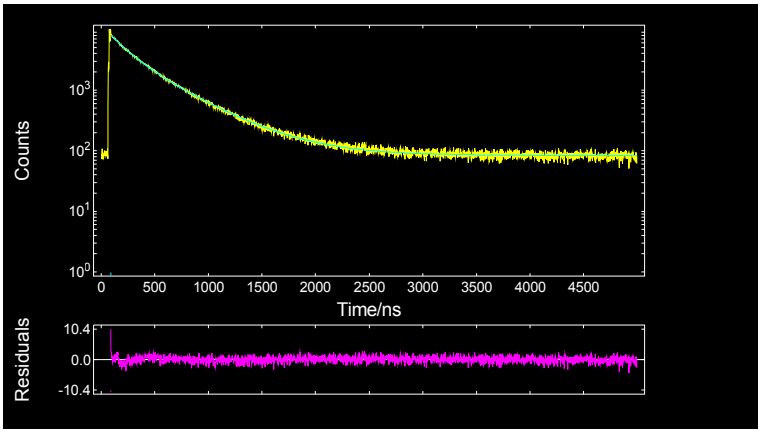

Fig. S5: Decay fitting by a bi-exponential fit (top) and residuals (bottom) of $^{3}_{\infty}$[Ba(Im)$_2$]:0.05Eu^{2+} (**3**) at 77K.

References:

(1) J. V. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230.