Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Lanthanide-centered luminescence evolution, and potential anti-counterfeiting application of Tb^{3+}/Eu^{3+} grafted melamine cyanurate hydrogen-bonded triazine framework

Chaoqing Yang, [a] Anna M. Kaczmarek, *[a] Karel Folens, [b] Gijs Du Laing, [b] Henk Vrielinck, [c] Samira Khelifi, [c] Kai Li, *[a] and Rik Van Deun *[a]

a L^3 – Luminescent Lanthanide Lab, Department of Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Ghent, Belgium.
b Department of Green Chemistry and Technology, Ghent University, Coupure Links 653, 9000 Ghent, Belgium.
c Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1, 9000 Ghent, Belgium.

Supplementary Information

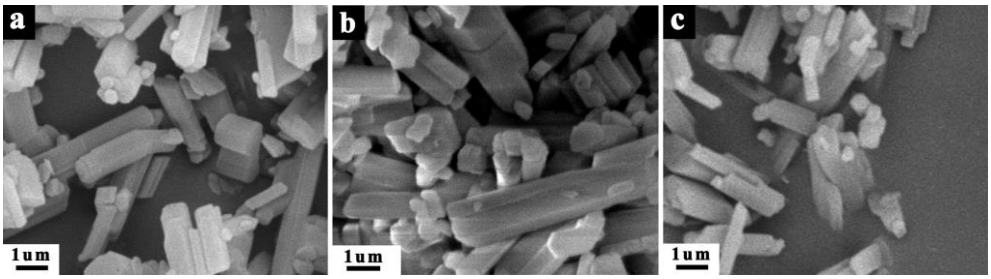
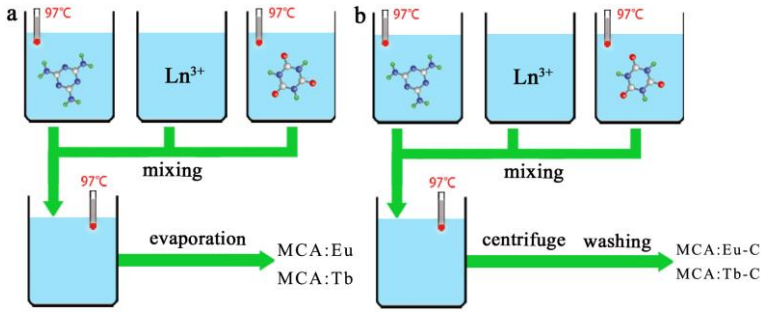


Figure S1. SEM images of (a) MCA, (b) MCA:Tb, and (c) MCA:Eu.



Scheme S1. illustration of the synthesis of MCA:Ln phosphors: (a) centrifugal route, (b) evaportion route.

Table S1: Actual Ln^{3+} contents for the MCA:Ln samples determined by ICP-MS analysis.

Sample	Eu^{3+} ions	Tb^{3+} ions
MCA:Eu	0.729%	
MCA:Eu-C	0.111%	
MCA:Tb		0.518%
MCA:Tb-C		0.121%

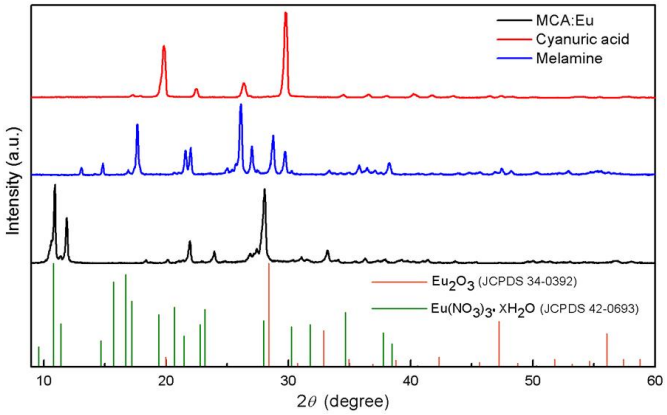


Figure S2. Normalized PXRD patterns of MCA:Eu, melamine, and cyanuric acid [Vertical bars at the bottom are the positions of standard Eu_2O_3 (JCPDS 34-0392), standard $Eu(NO_3)_3 \cdot xH_2O$(JCPDS 42-0693)].

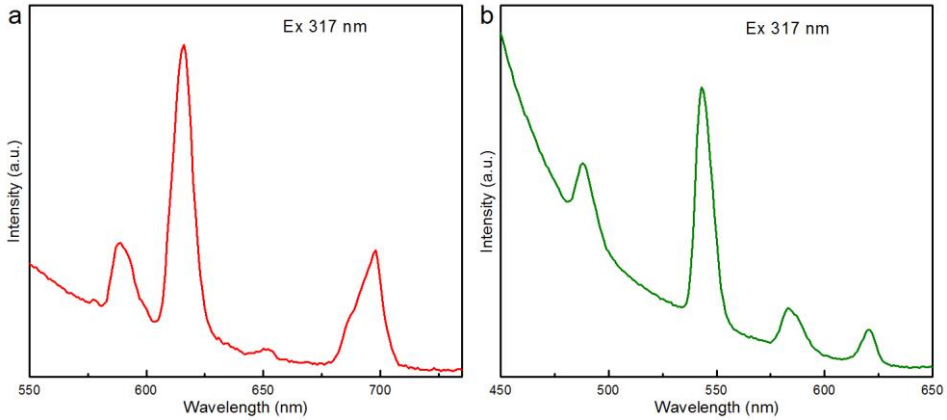


Figure S3. PL emission spectra of (a) MCA:Eu-C and (b) MCA:Tb-C.

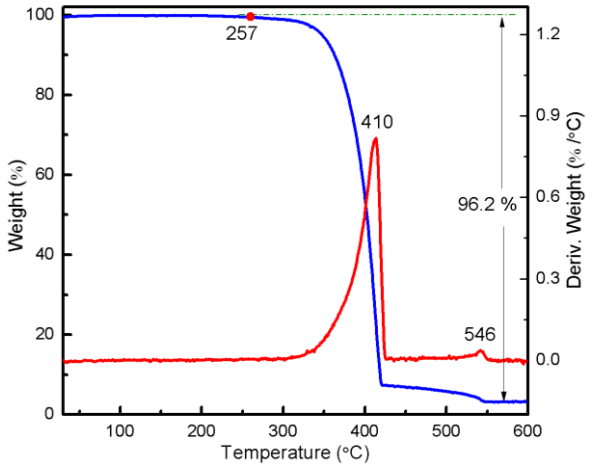


Figure S4. TG and DTG curves of MCA:Eu.

Table S2: Assignment of labelled peaks in the excitation and emission spectra of MCA:Eu. [1]

label	wavelength (nm)	wavenumber (cm^{-1})	transition
		excitation	
1	316	31646	$^5H_6 \leftarrow {}^7F_0$
2	359	27855	$^5D_4 \leftarrow {}^7F_0$
3	372	26882	$^5L_7, ^5G_5 \leftarrow {}^7F_1$ / $^5G_{2,4,6} \leftarrow {}^7F_0$
4	393	25445	$^5L_6 \leftarrow {}^7F_0$
5	414	24155	$^5D_3 \leftarrow {}^7F_1$
6	462	21645	$^5D_2 \leftarrow {}^7F_0$
		emission	
7	578	17301	$^5D_0 \rightarrow {}^7F_0$
8	591	16921	$^5D_0 \rightarrow {}^7F_1$
9	614	16287	$^5D_0 \rightarrow {}^7F_2$
10	652	15337	$^5D_0 \rightarrow {}^7F_3$
11	695	14389	$^5D_0 \rightarrow {}^7F_4$

Table S3: Assignment of labelled peaks in the excitation and emission spectra of MCA:Tb [1]

label	wavelength (nm)	wavenumber (cm^{-1})	transition
		excitation	
1	317	31546	$^5H_7 \leftarrow {}^7F_6$
2	323	30960	$^5D_{0,1} \leftarrow {}^7F_6$
3	338	29586	$^5L_{7,8}, {}^5G_3 \leftarrow {}^7F_6$
4	350	28571	$^5L_9 \leftarrow {}^7F_6$
5	359	27855	$^5G_5 \leftarrow {}^7F_6$
6	366	27322	$^5L_{10} \leftarrow {}^7F_6$
7	377	26525	$^5G_6 \leftarrow {}^7F_6$
		emission	
8	485	20619	$^5D_4 \rightarrow {}^7F_6$
9	543	18416	$^5D_4 \rightarrow {}^7F_5$
10	586	17065	$^5D_4 \rightarrow {}^7F_4$
11	618	16181	$^5D_4 \rightarrow {}^7F_3$

Table S4: CIE chromaticity coordinates for MCA:Tb and MCA:Eu after heating at different temperatures.

Sample	CIE coordinates (x, y)	Sample	CIE coordinates (x, y)
MCA:Tb	(0.187, 0.141)	MCA:Eu	(0.216, 0.129)
MCA:Tb-130	(0.215, 0.231)	MCA:Eu-130	(0.235, 0.128)
MCA:Tb-230	(0.298, 0.586)	MCA:Eu-230	(0.531, 0.314)
MCA:Tb-330	(0.321, 0.589)	MCA:Eu-330	(0.578, 0.303)
MCA:Tb-430	(0.198, 0.196)	MCA:Eu-430	(0.193, 0.133)

Table S5: Bi-exponential fitting of the decay curves of MCA:Tb heated at different temperatures.

T (°C)	No heat	130	230	330	430
τ_f (ms)	0.016	0.016	0.105	0.143	0.051
τ_s (ms)	0.542	0.626	0.689	0.856	0.739
τ_{ave} (ms)	0.506	0.593	0.656	0.787	0.717
R^2	0.998	0.999	0.999	0.999	0.995

Table S6: Bi-exponential fitting of the decay curves of MCA:Eu heated at different temperatures.

T (°C)	No heat	130	230	330	430
τ_f (ms)	0.013	0.017	0.108	0.132	0.033
τ_s (ms)	0.208	0.308	0.316	0.378	0.339
τ_{ave} (ms)	0.189	0.288	0.293	0.327	0.329
R^2	0.998	0.997	0.999	0.999	0.995

Supplementary References

1. W. Carnall, P. Fields and K. Rajnak, *The Journal of Chemical Physics*, 1968, **49**, 4424-4442.