Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Tailoring defect's structure and dopant's composition in Eu^{3+}&Tb^{3+} doped MgF_2 phosphors in order to generate a wide range of color characteristics

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Instrumentation:

X-Ray diffraction (XRD)

An X-ray diffractometer (Proto x-ray diffraction system) has been used to characterised all the powder samples using CuK_α (λ= 1.5406 and 1.5444 Å) monochromatic radiation as X-ray radiation source. All the XRD patterns were recorded within the 2θ range of 10-70 with a step width of 0.02 and scan rate of 5s. The samples were spread uniformly on the sample holder and then covered with scotch tape and sealing with plastic wrap in order to avoid exposure to the air during the XRD measurement.

Infrared study

We have used a Bruker Platinum ATR FTIR spectrometer to record the FTIR spectra of all the compounds in the spectral range 2000-500 cm^{-1} .

Photoluminescence study (PL)

An Edinburgh CD-920 unit with M 300 monochromator has been used to record the PL spectra of all the compounds. We have used F-900 software provided by Edinburgh Analytical Instruments, UK for the data acquisition and analysis. A Xenon flash with a frequency of 100 Hz has been used as excitation source to record the emission, excitation, and lifetime spectra. To minimize the peak intensity fluctuation and to maximize S/N ratio, we have taken at least five scans for each of the spectrum. The well-established Time-correlated single-photon counting (TCSPC) technique has been used to perform the lifetime study for the compounds.

Positron Annihilation Lifetime Spectroscopy (PALS) study

We have caried out the PALS measurements for all the powder compounds at room temperature using ^{22}Na as positron source (~ 10 μCi) and two BaF_2 scintillation detectors connected to a fast–fast coincidence system. At first the positron source was deposited in a thin Kapton foil and then this was kept inside the powder sample in an aluminum vial. The

vial was kept between two BaF_2 detectors. We measured a resolving time of 250 ps for the positron window settings with ^{60}Co source and the time calibration was 12.5 ps/channel. For each measurement, the spectrum with approximately 2 x 10^6 counts was acquired. We have used the PALSFIT analysis program to analyze all the data.

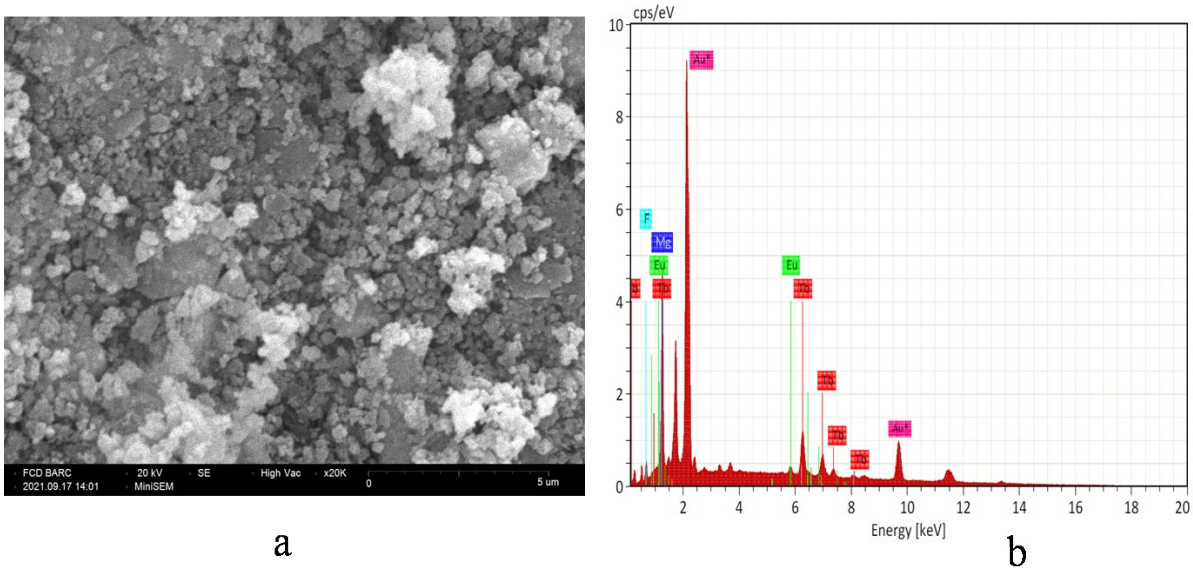

Figure S1. (a) SEM and (b) EDX spectra of $Tb_{0.5}Eu_{0.5}$:MF

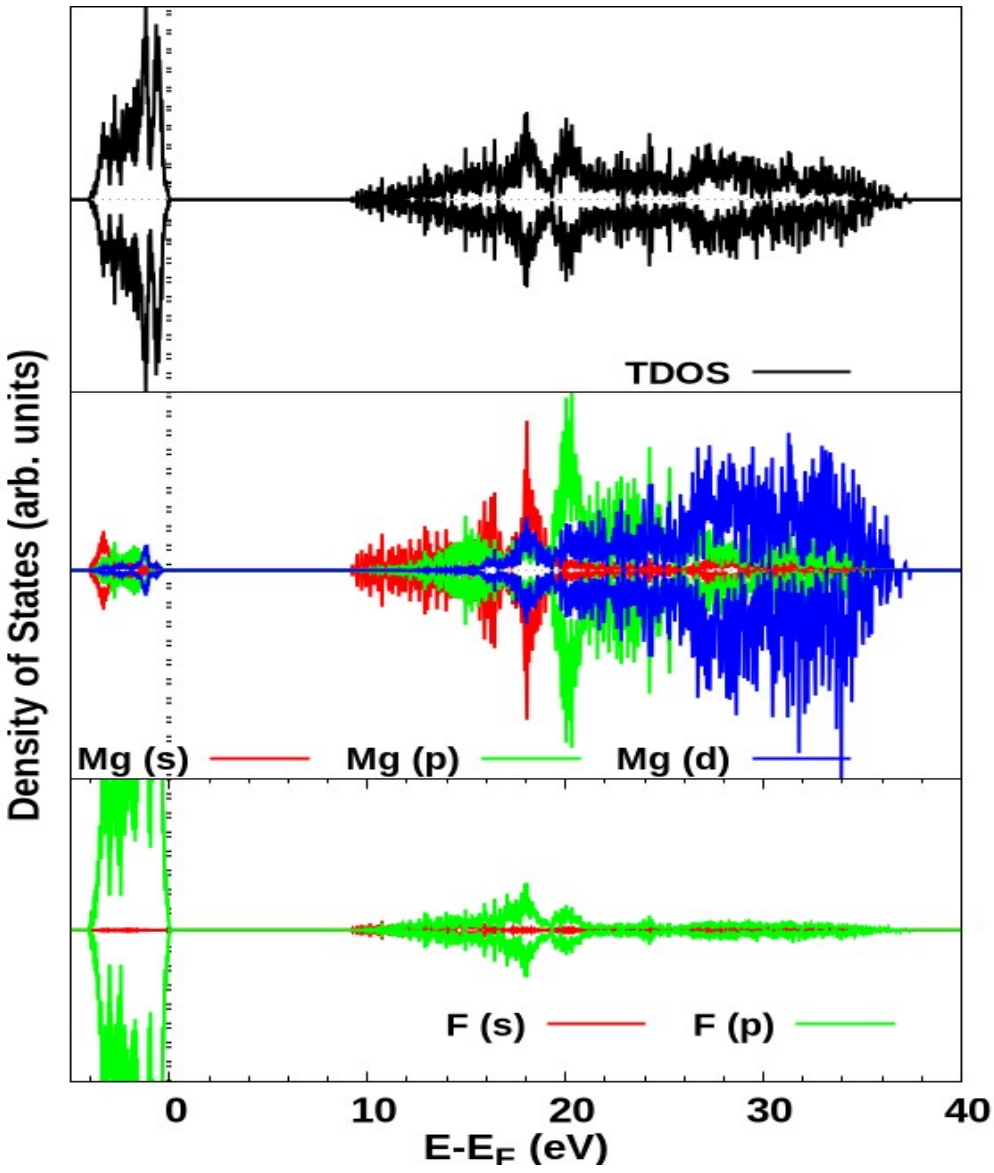

Figure S2. Total density of states (DOS) and l-projected partial DOS of pristine MgF_2

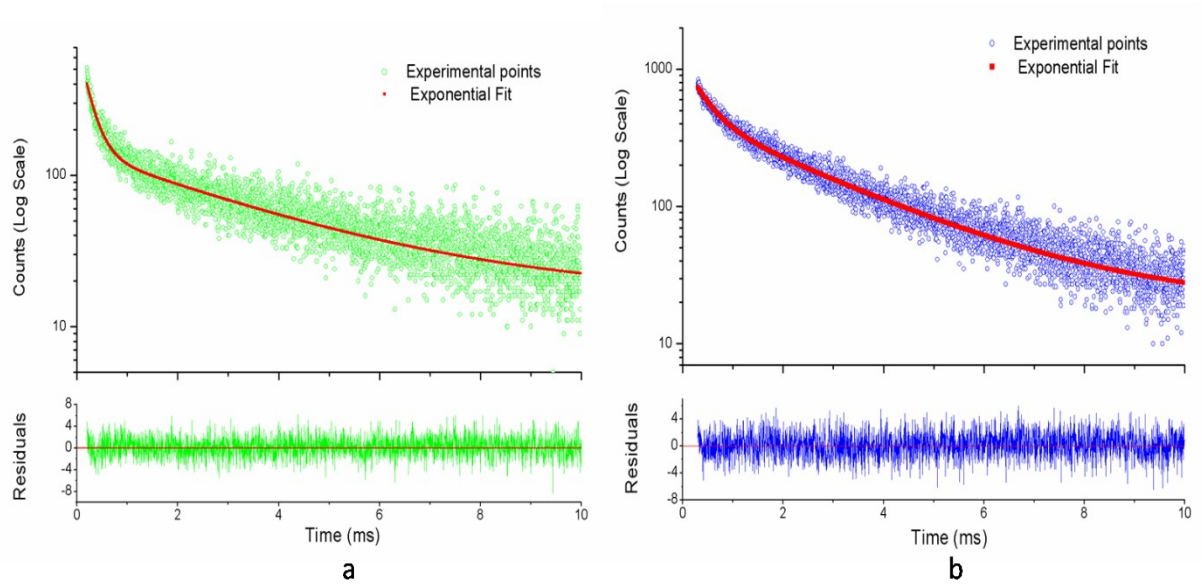

Figure S3: Photoluminescence decay profile of $Eu_{0.5}Tb_{0.5}$:MgF_2 λ_{ex} =233 nm excitation and (a) 545 nm (b) 615 nm emission wavelengths.

Table S1: Crystallographic parameters of MgF_2

Space Group	**Wyckoff position**					
	Atom	Site	x	y	z	occupancy
P42/mnm (136) (Tetragonal)	Mg	2a	0.0	0.0	0.0	1.0
	F	4f	0.304	0.304	0.0	1.0

Table S2: Lattice parameters and volume of the pristine and Eu and Eu and Tb co-doped MgF_2.

Phase	Lattice parameters (Å)	Volume (Å^3)
MgF_2	a=4.680 (4.6912)**[43]** , 4.625**[44]** 4.621**[45]** c=3.083 (3.096) **[43]** 3.052**[44]** 3.052**[45]**	67.542
Eu:MgF_2	a=4.720, c=3.106	69.178
Tb:MgF_2	a=4.726, c=3.110	69.457
Eu,Tb:MgF_2	a=4.744, c=3.131	70.474

Table S3: Theoretically calculated positron lifetime in MgF_2:

System	Calculated Lifetime (ps)
UndopedMgF_2[33]	
Bulk	204.8
Mg monovacancy $V_{Mg}^{''}$	227.1
Mg divacancy $2V_{Mg}^{''}$	234.3
A vacancy cluster created by removing four neighboring Mg atoms and associated eight F atoms (**VC1**)	397.8
A vacancy cluster created by removing five neighboring Mg atoms and associated ten F atoms (**VC2**)	440.9
Tb^{3+} doped MgF_2 system	
$Tb_{Mg}^{\cdot}$ (charge not balanced)	204.2
$Tb_{Mg}^{\cdot} + V_{Mg}^{''} + V_{F}^{\cdot}$ (charge balanced)	279.9
Li^{+} and Tb^{3+} doped MgF_2 system	
Bulk $Tb_{Mg}^{\cdot} + Li_{Mg}^{'}$	205.1
$Tb_{Mg}^{\cdot} + Li_{Mg}^{'} + VC1$ (Here the VC1 cluster remains intact)	398.2
$Tb_{Mg}^{\cdot} + Li_{Mg}^{'} + VC2$ (Here the VC2 cluster remains intact)	442.1
Tb^{3+} and Li^{+}replace two Mg atoms within the **VC1** cluster and the cluster contains only four $V_{F}^{\cdot}$ *to maintain the* required charge balanced condition	284.5
Tb^{3+} and Li^{+}replace two Mg atoms within the **VC2** cluster and the cluster contains only six $V_{F}^{\cdot}$ *to maintain the* required charge balanced condition	266.5
Eu^{3+} and Tb^{3+} doped MgF_2 system	
$Eu_{Mg}^{\cdot} + Tb_{Mg}^{\cdot} + V_{Mg}^{''}$	227.8
$Eu_{Mg}^{\cdot} + Tb_{Mg}^{\cdot} + 2V_{Mg}^{''}$	234.7
$Eu_{Mg}^{\cdot} + Tb_{Mg}^{\cdot} + V_{Mg}^{''} + VC1$ (Here the VC1 cluster remains intact)	428.6
$Eu_{Mg}^{\cdot} + Tb_{Mg}^{\cdot} + V_{Mg}^{''} + VC2$ (Here the VC2 cluster remains intact)	538.3
Eu^{3+} and Tb^{3+}replace two Mg atoms within the **VC1** cluster and the cluster contains only two	269.2

$V_{\dot{F}}$ $to\ maintain\ the$ required charge balanced condition	
Eu^{3+} and Tb^{3+}replace two Mg atoms within the **VC2** cluster and the cluster contains only four $V_{\dot{F}}$ $to\ maintain\ the$ required charge balanced condition	270.5