Electronic Supplementary Information (ESI)

Fast luminescence from rare–earth–codoped $BaSiF_6$ nanowires with high aspect ratios

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Results

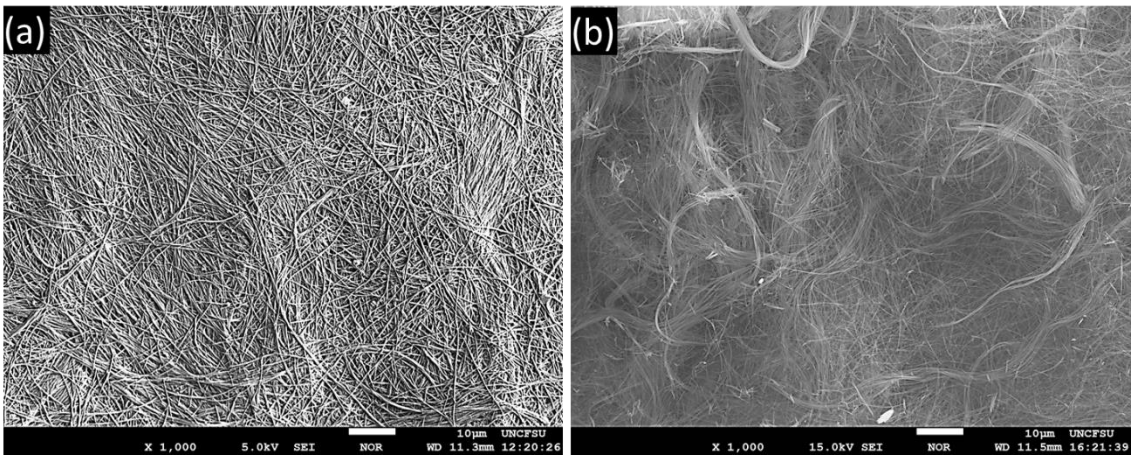

Fig. S1 Low magnification SEM image of (a) $BaSiF_6$ nanowires and (b) BaF_2, depicting the length of the nanowires.

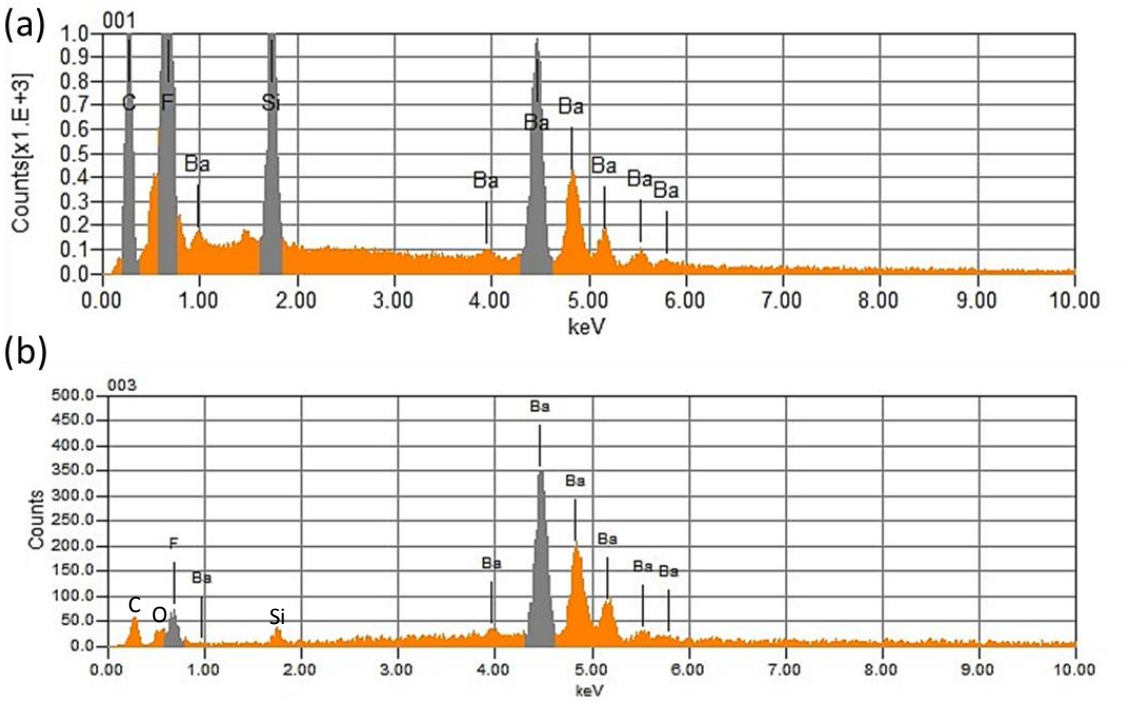

Fig. S2 EDS results of (a) $BaSiF_6$ and (b) BaF_2 nanowires. C is from surface coating, and a low content of Si, possibly from SiO_2, is retained in BaF_2 samples.

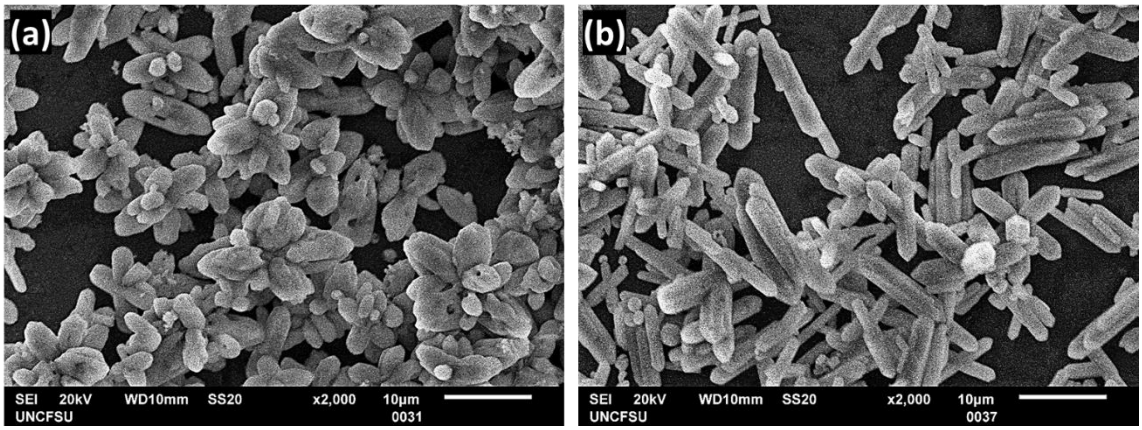

Fig. S3 SEM images of (a) BaSiF6 and (b) BaF_2 microparticles.

Mechanism of formation of $BaSiF_6$ nanowires

The formation of the nanowires comprises two steps, nucleation in the first step and growth in the second stage. The growth of the nanowires takes place in the individual reaction chambers created by the microemulsion (Fig. S4). During the growth process, it is presumed that the wormlike reverse micelle formed around the water droplets by CTAB and 1–pentanol control the growth of the rods. The presence of silicon initiates the nucleation and subsequently, the growth of the nucleus continues to form nanowires in the micelles. The ability of silicon as the substrate for the preferential growth of nanomaterials is well known, and it is true in the case of $BaSiF_6$ nanorod formation also. As a matter of fact, an experiment conducted following the same reaction condition in the absence of silicon did not yield any nanowires. Ultimately, the growth of nanowires is a result of the synergic action of Si–ions and the microemulsions. In the case of doped nanowires, the trivalent dopant ions replace the divalent Ba ions. Equations S1 and S2 correspond to the overall chemical reaction involved in the formation of nanowires.

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O \quad \text{(S1)}$$

$$H_2SiF_6 + BaCl_2 \longrightarrow BaSiF_6 + 2HCl + 2H_2O \quad \text{(S2)}$$

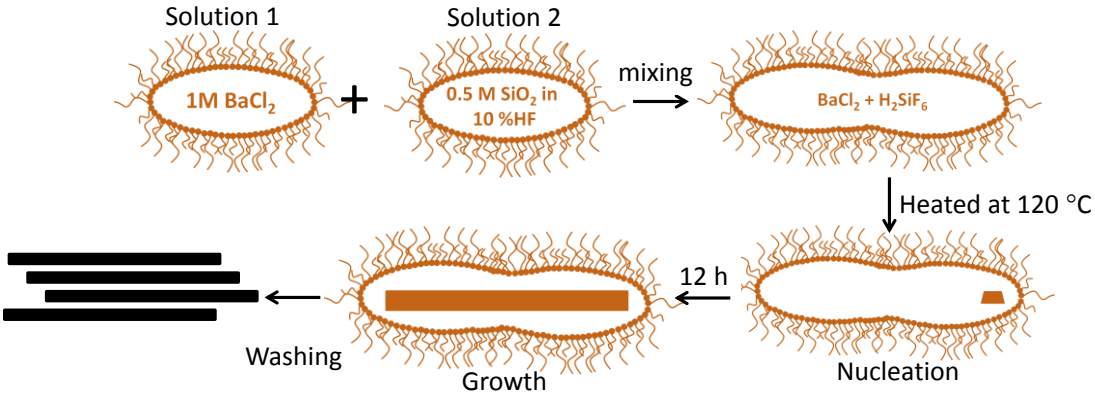

Fig. S4 Mechanism of formation of $BaSiF_6$ nanowires from microemulsion.

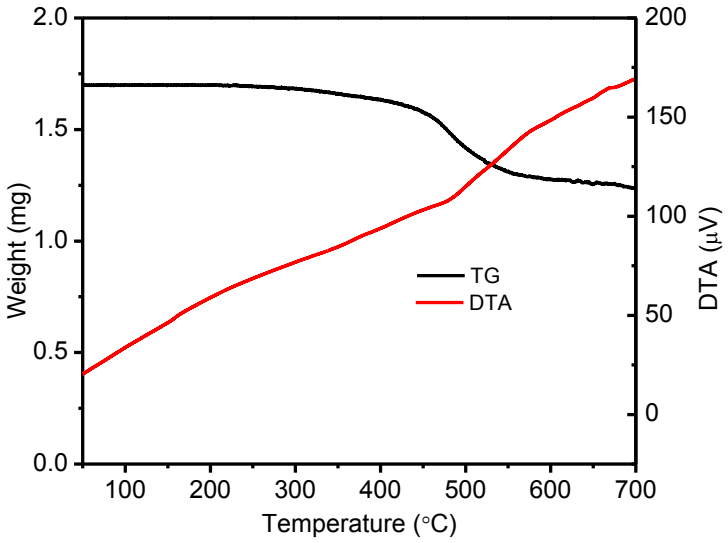

Fig. S5 TG Analysis of $BaSiF_6$ nanowires.

Table S1 ICP-OES results

Sample	Mol.% of Ba	Mol.% of Ce	Mol.% of Eu	Mol.% of Tb
BSF	100	-	-	-
BSF 1Ce-5Tb	96.39	0.57		3.04
BSF 1Ce-30Tb	96.31	0.14		3.54
BSF 1Ce-10Tb -1Eu	96.45	0.38	0.24	3.17
BSF 1Ce-20Tb -1Eu	94.39	0.30	0.19	5.31
BSF 2Ce-20Tb -0.5Eu	95.43	0.44	0.07	4.13
BF	100	-	-	-
BF 1Ce-5Tb	96.69	0.33	0	2.98
BF 1Ce-30Tb	96.82	0.12	0	3.06
BF 1Ce-10Tb -1Eu	96.45	0.36	0.24	3.19
BF 1Ce-20Tb -1Eu	94.92	0.28	0.17	4.81
BF 2Ce-20Tb -0.5Eu	92.65	0.67	0.02	6.68

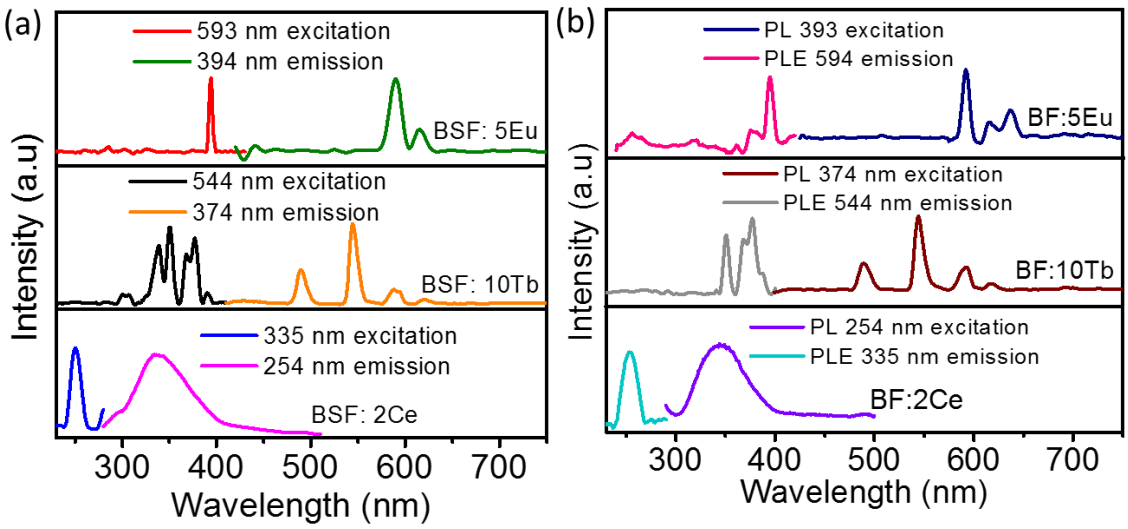

Fig. S6 PL and PLE spectra of representative Ce^{3+}–doped, Tb^{3+}–doped, and Eu^{3+}–doped (a) $BaSiF_6$ and (b) BaF_2 nanowires.

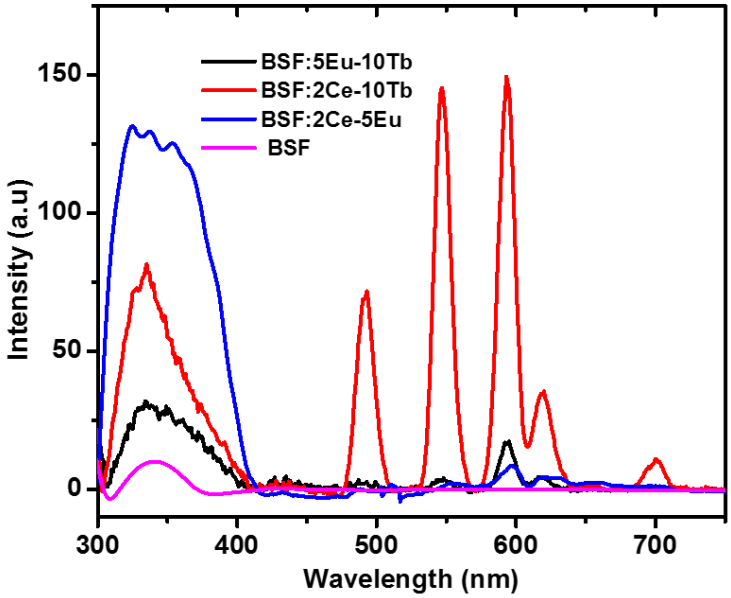

Fig. S7 PL spectra of pure and binary doped $BaSiF_6$ nanowires.

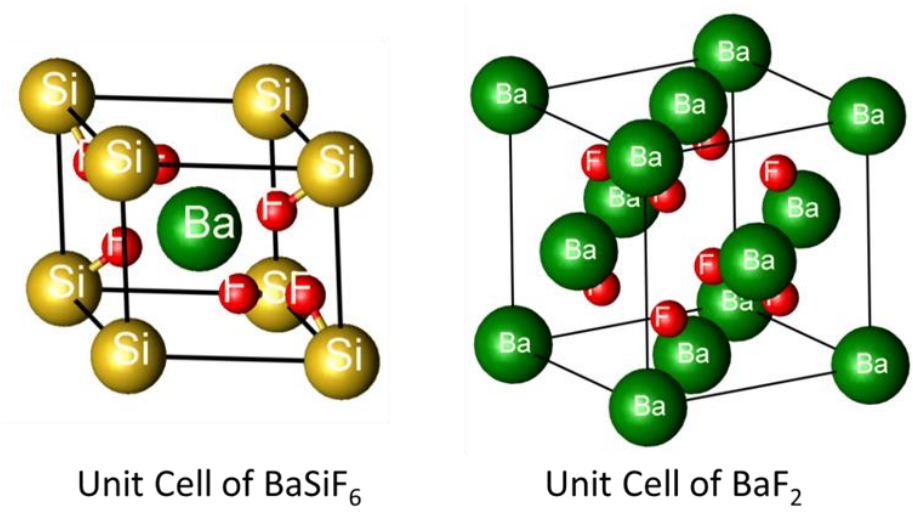

Fig. S8 Structure of $BaSiF_6$ and BaF_2.

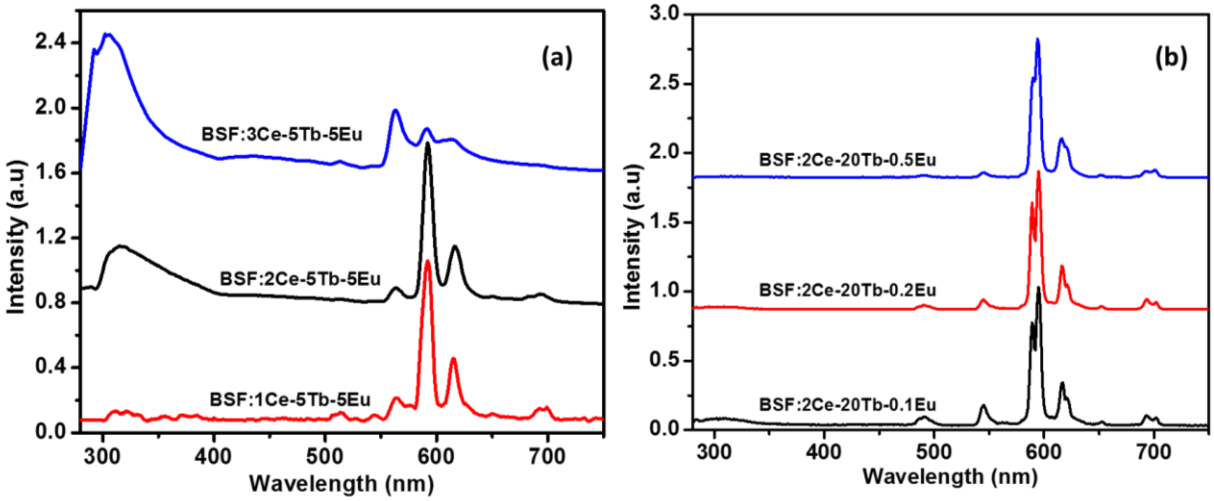

Fig. S9 Effect of (a) Ce^{3+} and (b) Eu^{3+} doping on the PL emission of BSF:*x*Ce–*y*Tb–*z*Eu nanowires.

The energy transfer between $Ce^{3+}\rightarrow Tb^{3+}\rightarrow Eu^{3+}$ ions in the doped nanowires begins with the 5*d* excited state of Ce^{3+} ions. The non-radiative energy release by these ions is absorbed by the $^5D_3$ level of Tb^{3+} ions as their excitation energy is close to that energy. The electrons in $^5D_3$ are non-radiatively relaxed to the $^5D_4$ level. This energy is then transferred to $^5D_1$ levels of Eu^{3+} and finally, the Eu^{3+} ions release energy radiatively [1]. The low lattice phonon energy of fluorides might result in the efficient energy transfer from Tb^{3+} to Eu^{3+} ions, as a result, the nanowires do not exhibit a strong green emission corresponding to the Tb^{3+} ions.

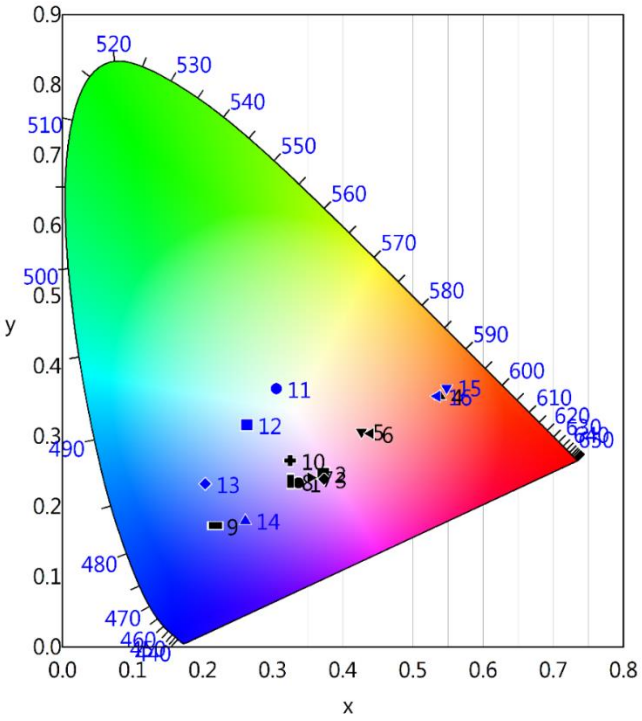

Fig. S10 CIE coordinates of BSF codoped nanowires.

The CIE coordinates of BSF:xCE–yTb and BSF:xCE–yTb–zEu codoped nanowires excited by 376 nm sources were calculated using Colorcalculator 7.21 [2] from the respective PL emission spectra and the chromaticity coordinates and CIE chromaticity diagram are shown in Table S1 and Fig. S10, respectively.

Table S2 Calculated CIE Coordinates of BSF:xCe–yTb–zEu codoped nanowires excited by 376 nm source.

Sample No	Sample composition	CIE (X)	CIE (Y)
1	1Ce–5Tb	0.2182	0.1725
2	1Ce–10Tb	0.3248	0.2651
3	1Ce–15Tb	0.3051	0.3677
4	1Ce–20Tb	0.2631	0.3162
5	1Ce–30Tb	0.2036	0.2322
6	1Ce–5Tb–1Eu	0.3434	0.2191
7	1Ce–10Tb–1Eu	0.3803	0.2391
8	1Ce–15Tb –0.5Eu	0.5342	0.357
9	1Ce–20Tb –0.5Eu	0.5478	0.3702
10	1Ce–20Tb –1Eu	0.3758	0.2366
11	1Ce–30Tb –1Eu	0.5459	0.359
12	2Ce–10Tb –3Eu	0.3595	0.2332
13	2Ce–10Tb –5Eu	0.3329	0.2186
14	2Ce–20Tb –0.1Eu	0.2607	0.1804
15	2Ce–20Tb –0.2Eu	0.4666	0.3245
16	2Ce–20Tb –0.5Eu	0.4508	0.3033

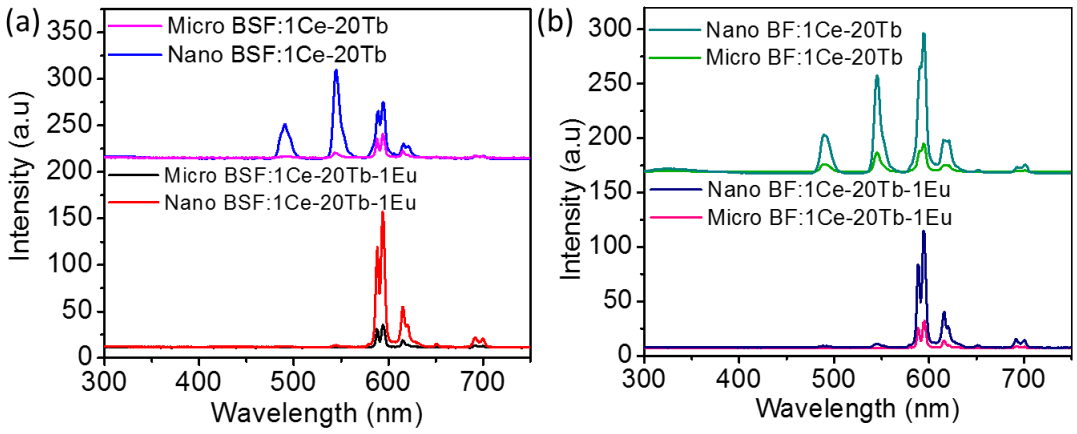

Fig. S11 Comparison of PL emission from codoped microparticle material and nanowires (a) $BaSiF_6$ and (b) BaF_2.

The lifetime curves of all the samples can be fitted to double exponential function consisting of fast and slow lifetime components (Equation S3) and the constants in the fitting parameters is presented in Table 1.

$$I(t) = \alpha_1 . e^{(-t/\tau_1)} + \alpha_2 . e^{(-t/\tau_2)} \quad \text{(S3)}$$

Where (t) is the light intensity at any time, t, after switching off the excitation illumination, α_i is a time-invariant constant and τ_i is a decay constant (or lifetime) for the exponential components. The average lifetime is calculated as per Equations S4 and S5 [3];

$$\tau_{\text{average}} = \sum_{i=1}^{n} f_{\text{i}} . \tau_{\text{i}} \quad \text{(S4)}$$

Where f_i is the fractional contribution,

$$f_{\text{i}} = \alpha_{\text{i}}\tau_{\text{i}} / (\sum_{i=1}^{n} \alpha_{\text{i}}\tau_{\text{i}}) \quad \text{(S5)}$$

References

1 X. Zhang, M. Gong, *Ind. Eng. Chem. Res.*, 2015, **54**, 7632–7639.

2 LED ColorCalculator | OSRAM SYLVANIA https://www.osram.us/cb/tools-and-resources/applications/led-colorcalculator/index.jsp (accessed Jan 26, 2018).

3 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer US, 2006.