Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

SUPPORTING INFORMATIONS

Ratiometric multiplexed barcodes based on luminescent metal-organic framework films

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The calculation method of the dye contents in MOF films

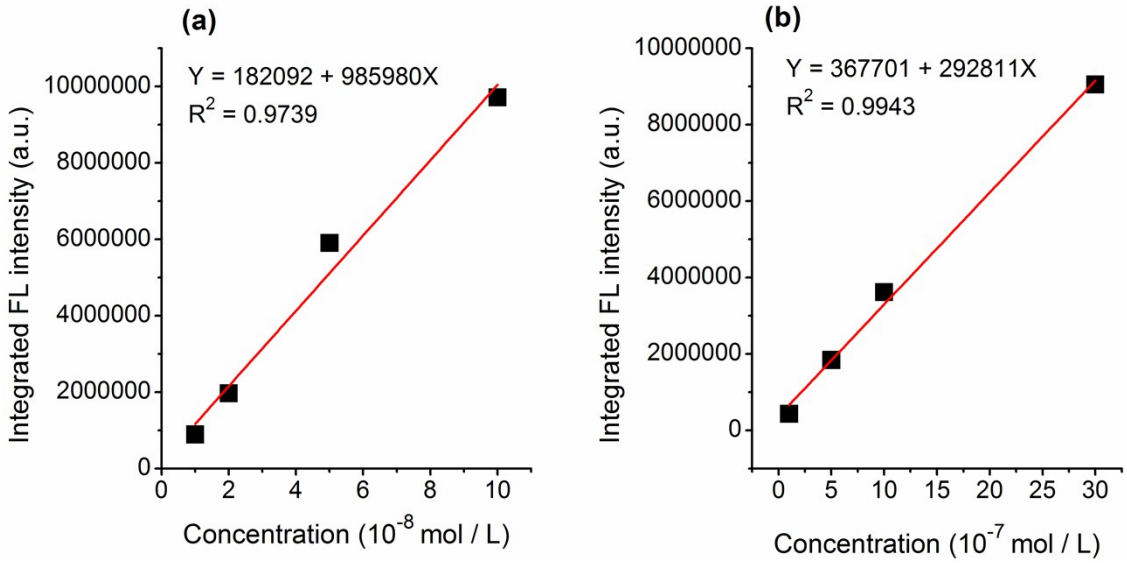

Figure S1. The integrated photoluminescence (PL) intensity-concentration diagrams for the fluorescein isothiocyanate (a) and methylene blue (b) solutions in ethanol. The red solid lines plotted in (a) and (b) are the linear fitted curves.

In order to determine to the amount of loaded dyes at the MOF films, we measured the luminescence spectra of ethanol solutions of fluorescein isothiocyanate (FL) and methylene blue (MB) with various concentrations. Figure R1a and Figure R1b show the relationships for the intensity-concentration of the FL and MB in ethanol solutions, respectively. The luminescence intensities in Figure R1a and Figure R1b were the average values calculated from three repeated luminescence measurements. The relationships for the intensity of FL and MB in ethanol solution can be fitted as respective functions of

$$y = 182092 + 985980\ x \quad (1)$$

$$y = 367701 + 292811\ x \quad (2)$$

where x is the concentration of dyes, and y is the luminescent intensity. Therefore, the dye contents in ethanol solution can be determined from their

luminescence intensity through Equation 1 and 2.

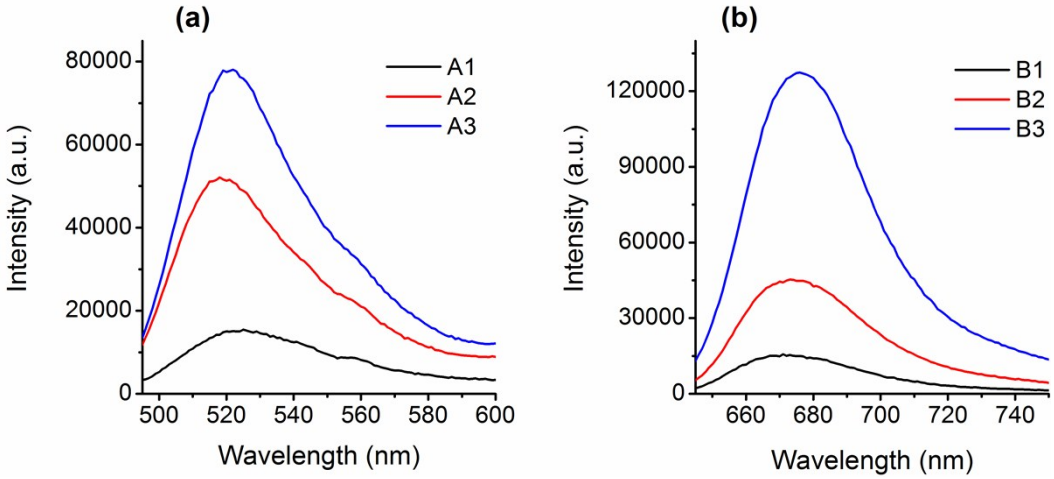

Figure S2. The luminescence spectra of the ethanol solutions containing the dissolved isothiocyanate loaded Tb^{3+}@MIL-100 films (a) and methylene blue loaded Tb^{3+}@MIL-100 films (b).

The dye loaded MOF films were dissolved in 5 mL ethanol solution containing 20 μL HCl (12 mol/L). The luminescence intensity of the resulted solutions was measured (Figure S2a, b), and then the dye concentration was calculated through Equation 1 and 2. The amount of the MOF of the film was estimated from the In^{3+} content of the as-obtained ethanol solutions, which was determined by ICP measurements. Based on the above discussions, the dye contents of the MOF films were estimated and provide in Table S1.

Table S1. The dye contents in the Ln^{3+}@MOF films.

Materials	Dye contents (wt%)	
	FL	MB
A_1	0.24	—
A_2	0.87	—
A_3	1.29	—
B_1	—	0.43
B_2	—	2.06
B_3	—	6.43

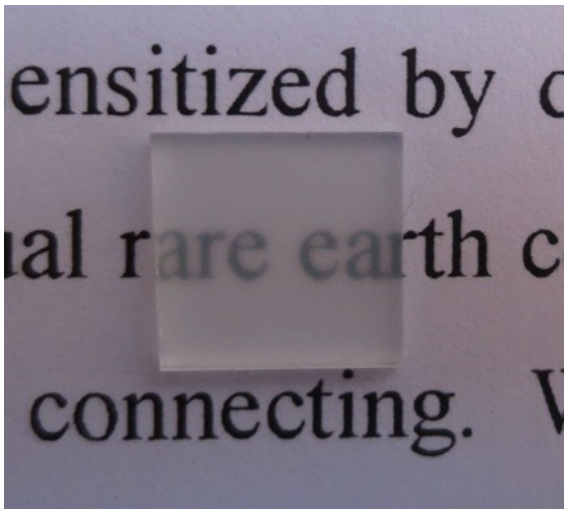

Figure S3. The photograph of the obtained MIL-100 (In) film. The ITO substrate is ~1 × 1 cm.

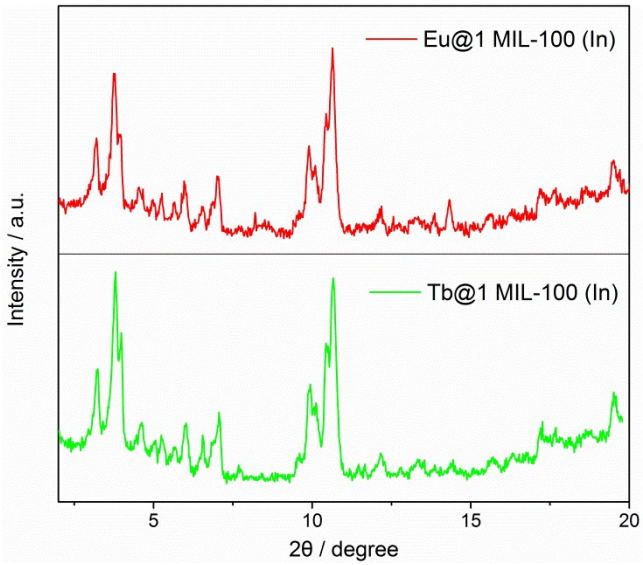

Figure S4. PXRD patterns of Eu@MIL-100 (In) and Tb@ MIL-100 (In) films.

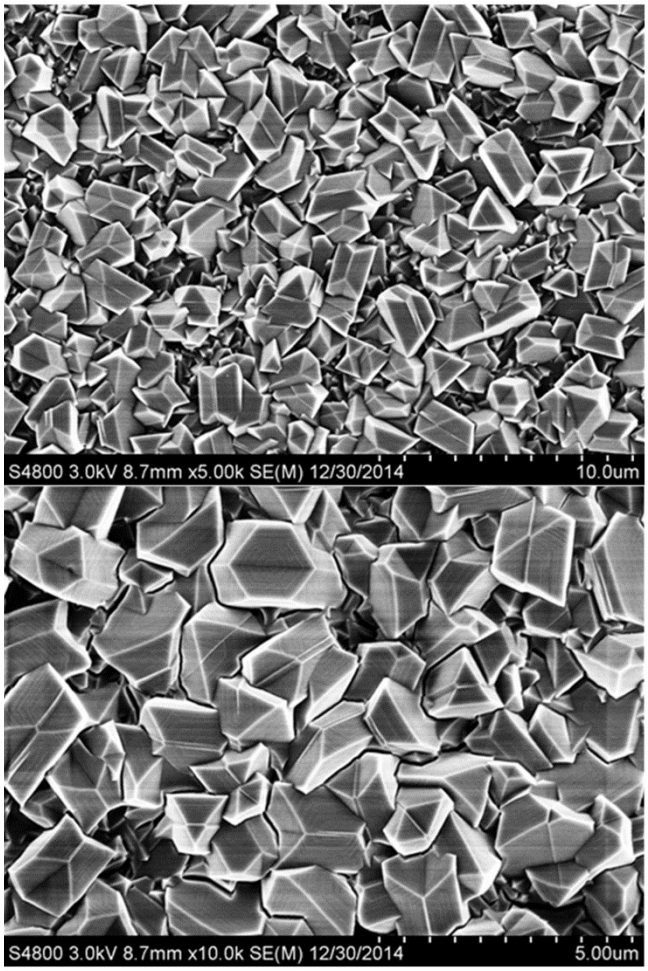

Figure S5. SEM images of Tb@ MIL-100 (In) film with different magnifications.

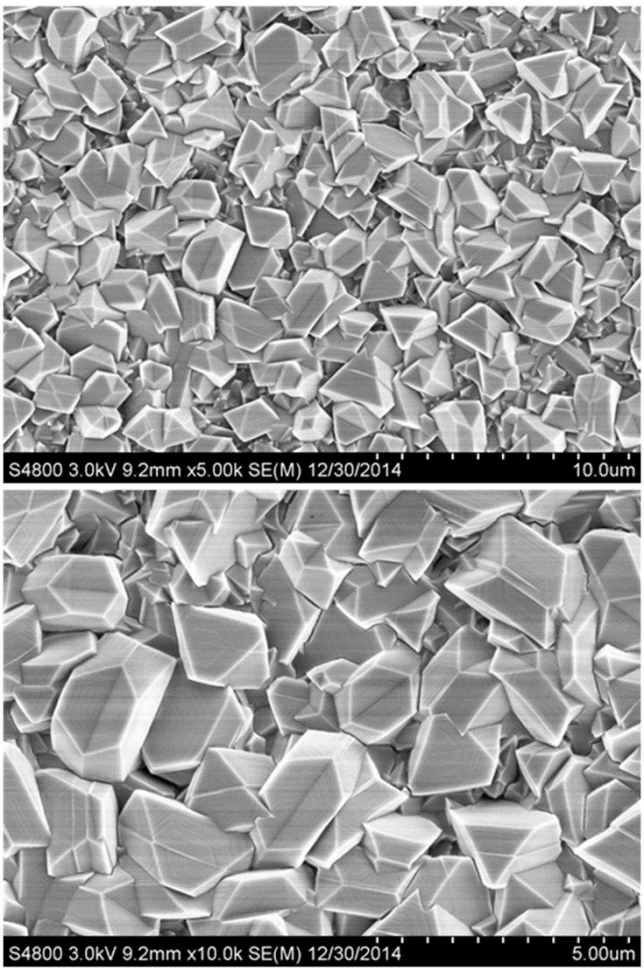

Figure S6. SEM images of Eu@ MIL-100 (In) film with different magnifications.

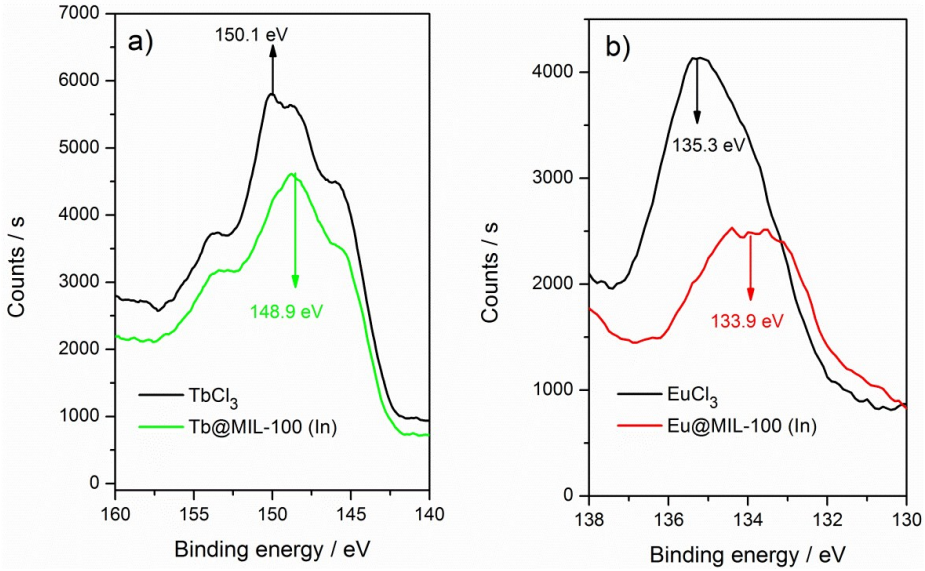

Figure S7. Tb (a) and Eu (b) 4d XPS spectra of $LnCl_3$ and Ln^{3+}@MIL-100 (In).

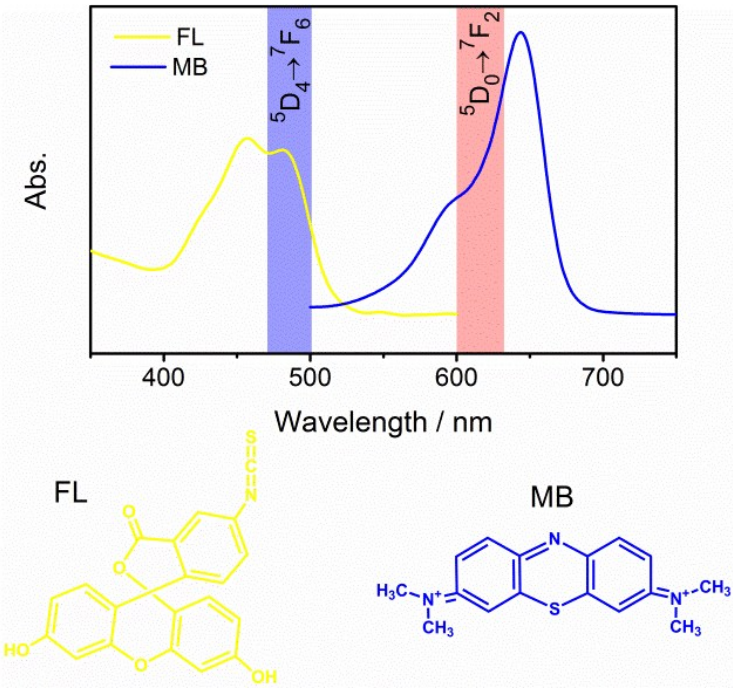

Figure S8. UV–vis absorption spectra and molecular structures of fluorescein isothiocyanate (FL, yellow) and methylene blue (MB, blue). The range of the filtered emission bands of Tb (blue) and Eu (red) is also shown with different color.

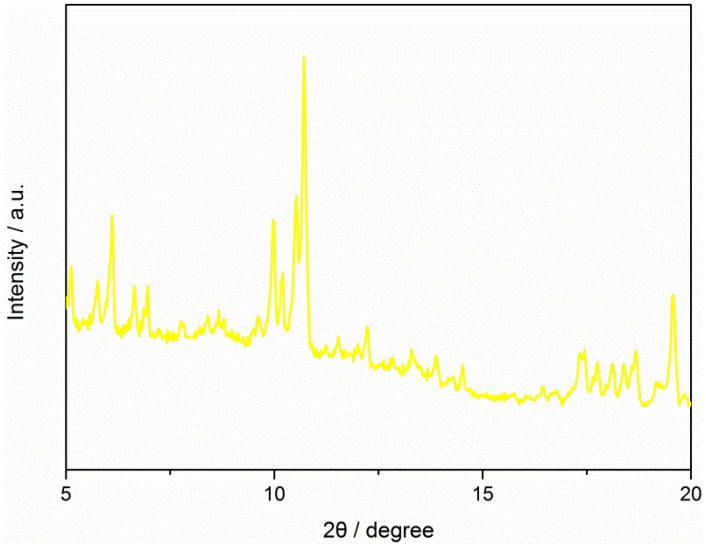

Figure S9. PXRD pattern of Eu/Tb@MIL-100 (In) film.

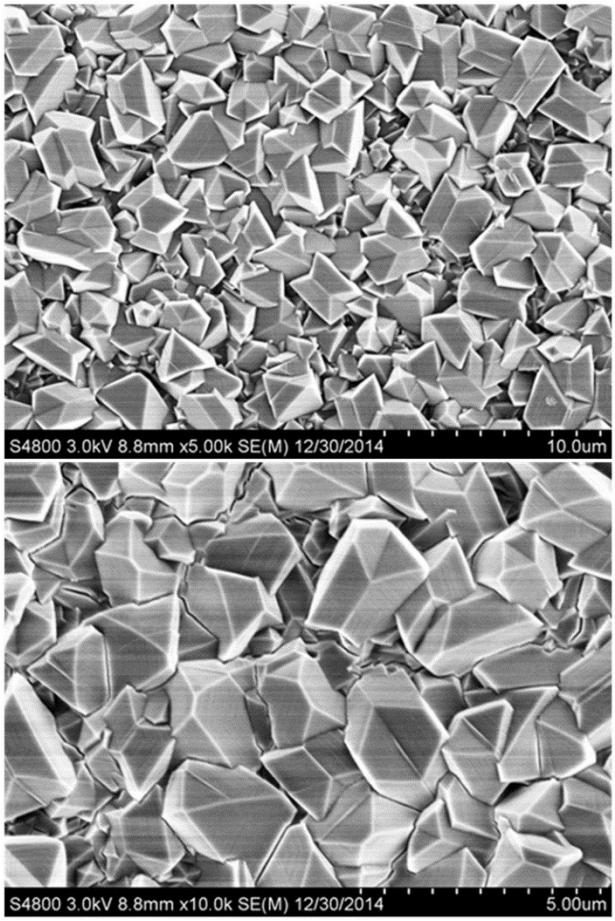

Figure S10. SEM images of Eu/Tb@ MIL-100 (In) film with different magnifications

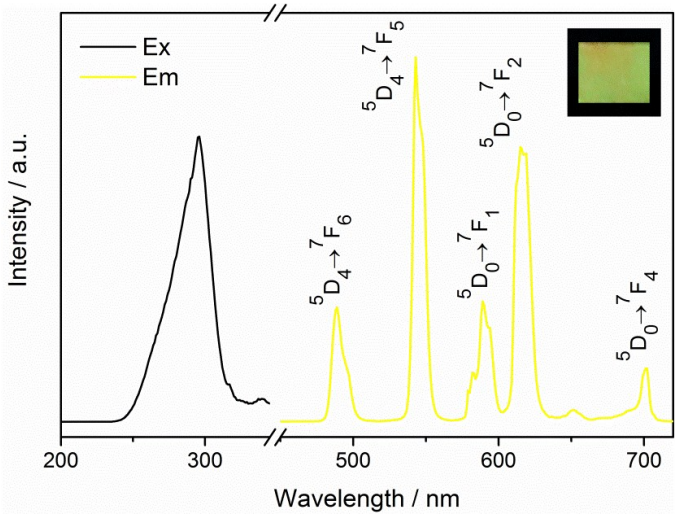

Figure S11. Excitation (λ_{em} = 544 nm) and excitation (λ_{em} = 297 nm) spectra of Eu/Tb@MIL-100 (In) film. The inset is the photograph of Eu/Tb@MIL-100 (In) film under UV irradiation

Table S2. Luminescent Lifetimes (τ) and Absolute Quantum Yields (ϕ) of Ln^{3+}@MIL-100 (In) (Ln = Eu, Tb, Eu/Tb).

Ln^{3+}	τ (ms)	ϕ (%)	λ_{ex} (nm)
Eu	0.596 [a]	10.3	297
Tb	1.401 [b]	26.4	297
Eu/Tb	1.081 [a]/0.815 [b]	22.7	297

[a] For the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}, λ_{em} = 615 nm. [b] The transition $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+}, λ_{em} = 544 nm.