Moisture-responsive Films Consisted of Luminescent Polyoxometalate and Agarose

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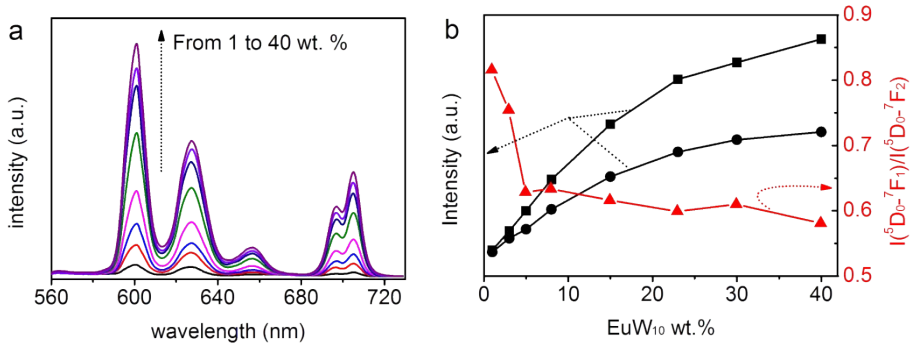

Fig. S1 (a) The luminescence spectra were measured as a function of EuW_{10} contents from 1 to 40 wt. %. (b) The plots of the intensity of $^5D_0 \rightarrow {}^7F_1$ (black square), $^5D_0 \rightarrow {}^7F_2$ (red circle), and the ratio of $I(^5D_0 \rightarrow {}^7F_1)/I(^5D_0 \rightarrow {}^7F_2)$ (black triangle) against EuW_{10} contents ranging from 1 to 40 wt. %.

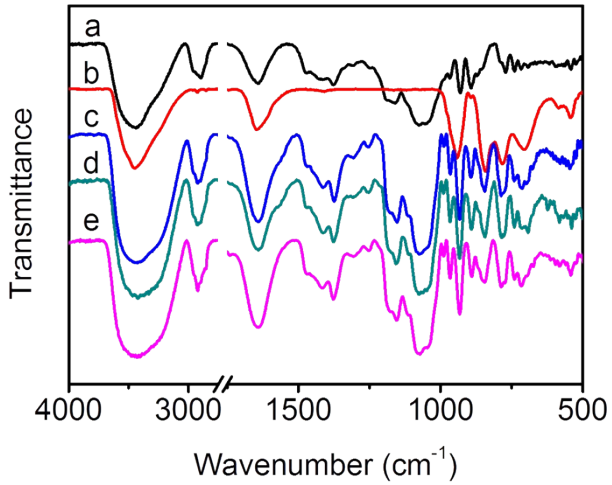

Fig. S2 FTIR spectra of (a) agarose, (b) EuW_{10} crystalline powders, (c) as-prepared EuW_{10}/agarose composite film (7 wt.%), (d) irradiated film by 2 Kw UV lamp for 10 min, and (e) recovered film after exposure to 78 RH%.

Table S1 The assignments of infrared spectra of EuW_{10} in its solid state, the as-prepared composite film, and the film irradiated by 2 Kw UV for 10 min. The unit of wavenumber is cm^{-1}.

Assignments	Solid state	As-prepared	Irradiated	Recovered
$W = O_d$	942	Overlapping	Overlapping	Overlapping
$W\text{-}O_b\text{-}W$	841	845	844	845
$W\text{-}O_c\text{-}W$	781	788	785	787
	705	697	692	696

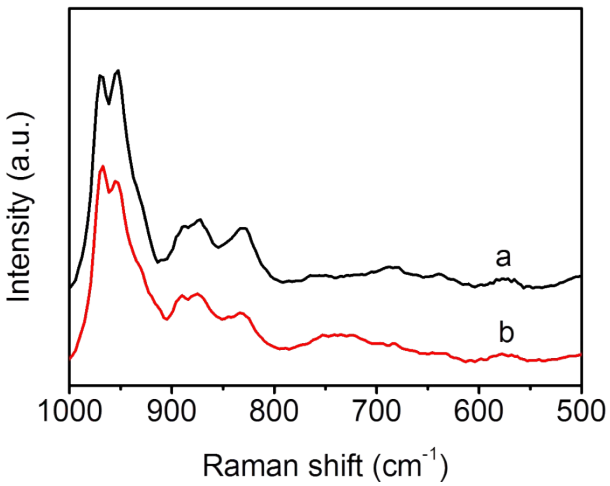

Fig. S3 (a) Raman spectra of EuW_{10} crystalline powders, and (b) as-prepared EuW_{10}/agarose composite film (7 wt.%).

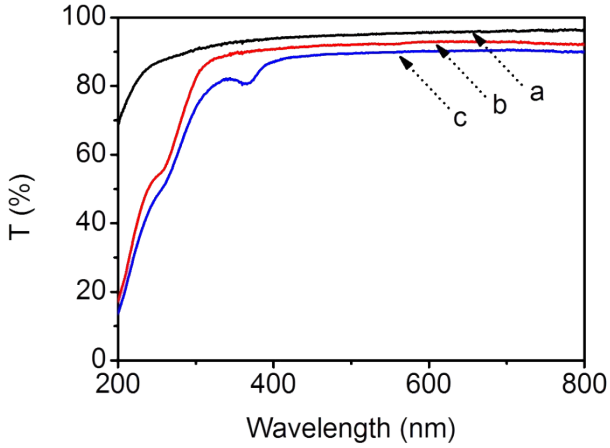

Fig. S4 Transmittance spectra of the Agarose (a) and EuW_{10}/Agarose composite films before (b) and after (c) irradiation by 2 Kw UV lamp for 10 min.

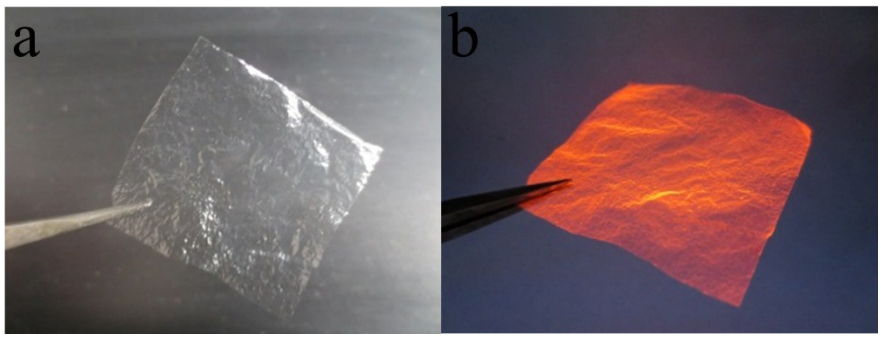

Fig. S5 Optical images of composite film under day light (a) and UV lamp (b). The composite film can peel off from ITO substrate to form free-standing film. The red luminescence originated from EuW_{10} is clear to see under UV light.

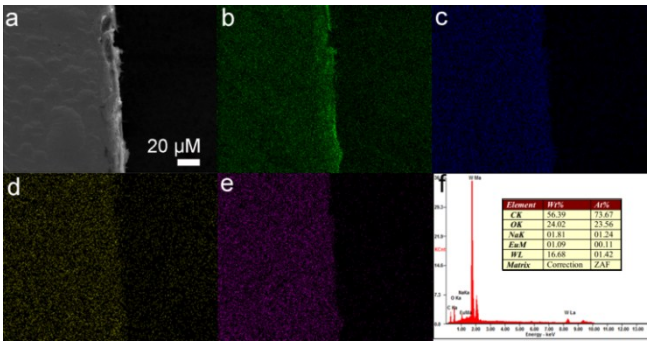

Fig. S6 Elemental mapping of the composite film. SEM image on Si substrate (a), elements distributions of C (b), Na (c), Eu (d), and W (e). (f) EDX of corresponding region. Inset is the atomic percentage of all elements. Na, Eu, W, and O come from EuW_{10}, and C and partial O are from agarose, respectively.

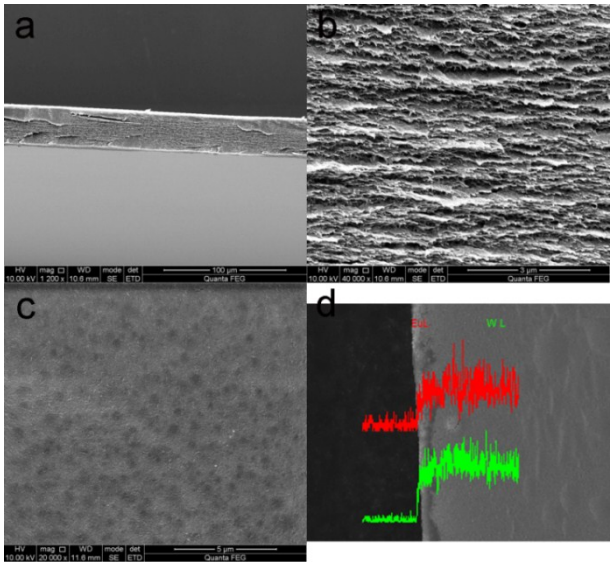

Fig. S7 SEM cross-sectional images of composite film at (a) low magnification and (b) high magnification. The thickness is ca. 40 μM in this batch, which can be tuned by adjusting the dropping volume or concentration of stock solution. The surface morphology of EuW_{10}/Agarose is shown in (c), in which the black dots are caused by the electron beam damage. The surface is smooth without any obvious aggregation. (d) EDS result of line spectra of Eu and W elements in composite film. The increase of elemental signals is a direct proof for the incorporation of EuW_{10} in composite film comparing to the Si substrate (Dark gray region).

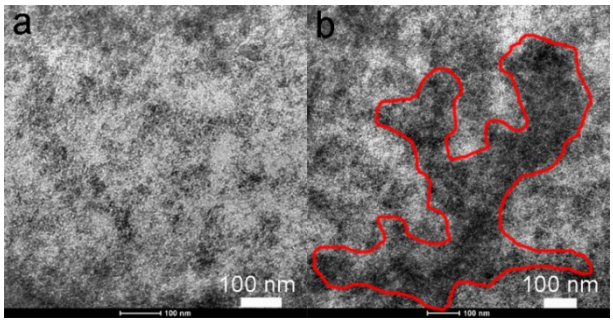

Fig. S8 TEM images of the composite films with 7 wt.% (a) and 30 wt.% EuW_{10} contents.

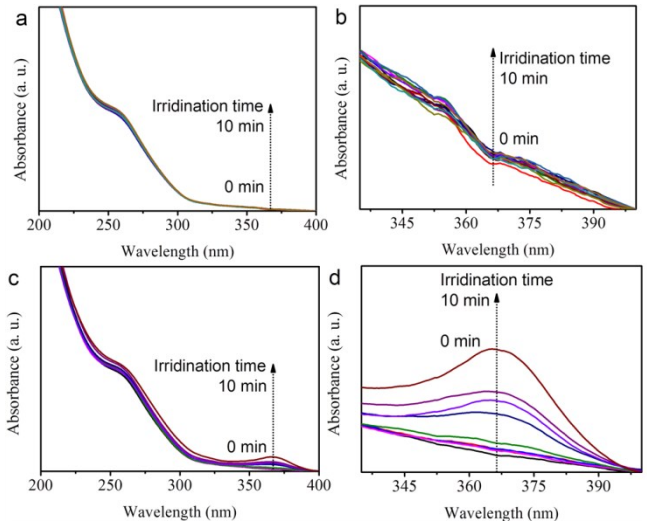

Fig. S9 UV-vis spetra of EuW_{10}/agarose composite film on quartz substrate as a function of illumination time by 125 w (a and b) and 2 Kw UV (c and d) lamps. All curves are almost overlapping in the case of illumination by 125 w UV lamp, however, a new peak at 365 nm was increased gradually under illumination by 2 Kw UV lamp.

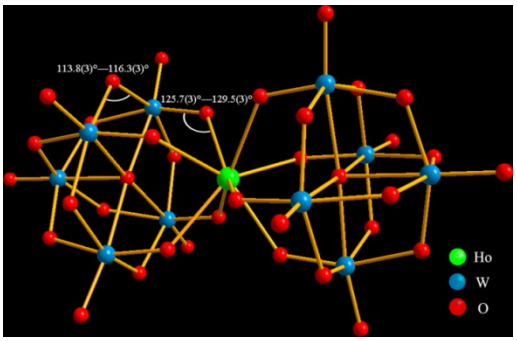

Fig. S10 Crystal structure of HoW_{10}, which is the isostructure of EuW_{10}. The W–O–W bond angle is between 113.8(3) to 116.3(3)°; the Eu–O–W bond angles is between 125.7(3) to 129.5(3)°. It should be noted that the crystal structure of HoW_{10} is drawn according to the CIF information in previous work. [1]

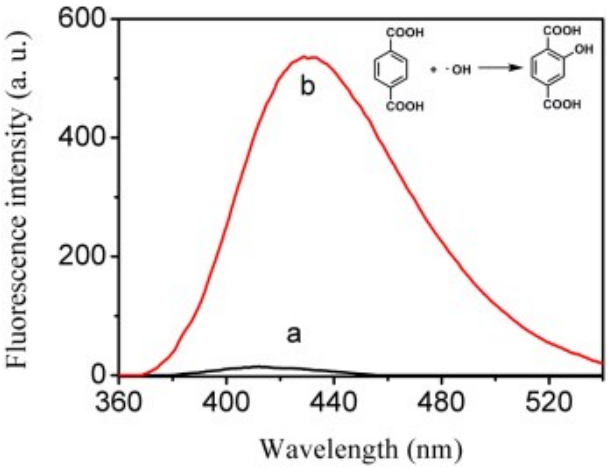

Fig. S11 Luminescence spectra changes of TA solution (2×10^{-3} M) in the presence of different amount of 7 wt% EuW_{10}/agarose composite. (a) 0 mg and (b) 20 mg at room temperature initially and after irradiation by 2 Kw UV lamp for 10 min, respectively.

1. Y.-Y. Li, F. Gao, J. E. Beves, Y.-Z. Li and J.-L. Zuo, *Chem. Commun.*, 2013, **49**, 3658-3660.