

Electronic Supplementary Information

Solar ultraviolet sensor based on fluorescent polyoxometalate and viologen

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Synthesis of EuW₁₀

EuW₁₀ was synthesized according to literature method.^[1] Na₂WO₄·2H₂O (8.3 g, 25.2 mmol) was dissolved in 20 ml of water and the solution pH was adjusted to 7.3 with CH₃COOH. An aqueous solution (2 ml) containing EuCl₃·6H₂O (0.91 g, 2.47 mmol) was added dropwise to the above-mentioned solution with stirring at 85 °C. Cooling the solution at room temperature yielded colorless crystals which were filtered off and dried in air.

Synthesis of AV²⁺

AV²⁺ was synthesized according to literature method.^[2] A mixture of 4,4'-dipyridine (0.20 g, 1.3 mmol), 3-bromopropylamine hydrobromide (0.84 g, 3.8 mmol) and MeCN (7 ml) was heated under stirring vigorously at 80 °C for 12 hours. After cooling to room temperature, pale yellow powder was obtained and washed twice with acetonitrile (20 ml), and then dried under vacuum.

[1] M. Sugeta and T. Yamase, Bull. Chem. Soc. Jpn., 1993, **66**, 444-449.

[2] M. S. Simon and P. T. Moore, J. Polym. Sci., Part A: Polym. Chem., 1975, **13**, 1-16.

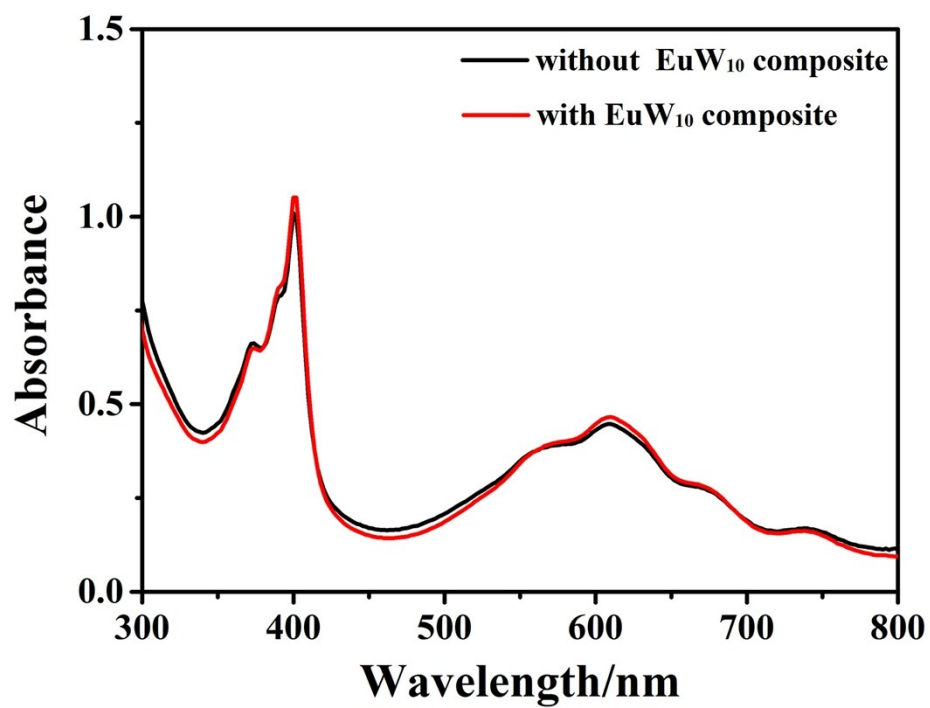


Fig. S1 UV-vis spectra of colored composite films (red line, containing EuW₁₀; black line, without EuW₁₀).

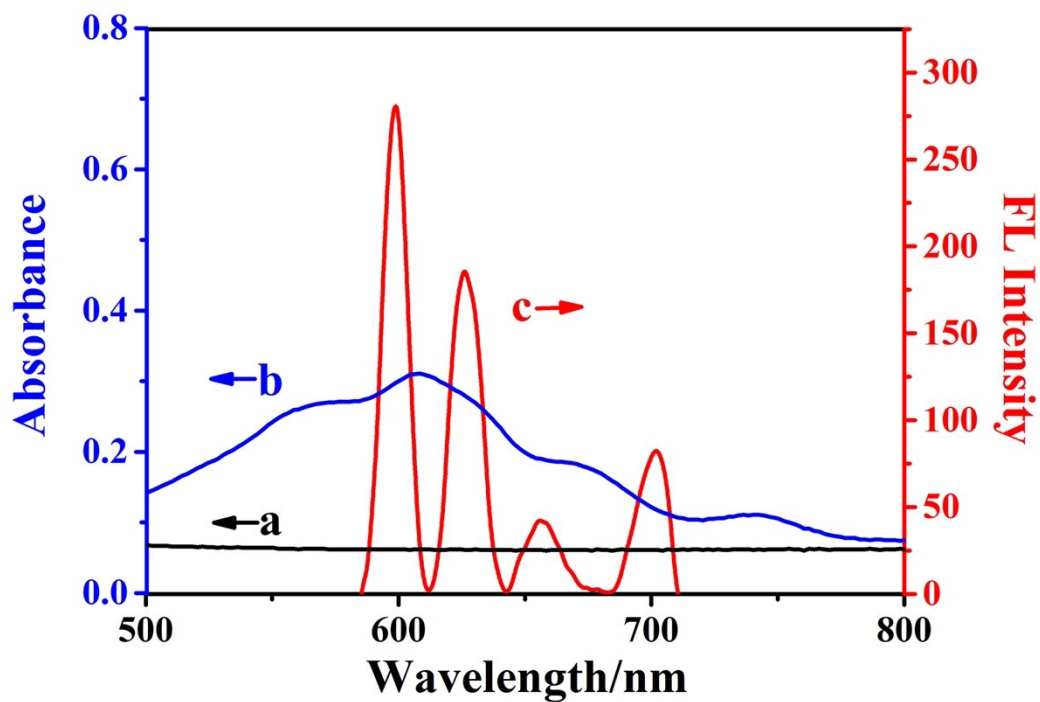


Fig. S2 UV-vis spectra of the composite film before (a) and after (b) UV irradiation for 4 min. The emission spectrum of the composite film was detected upon 254 nm excitation (c).

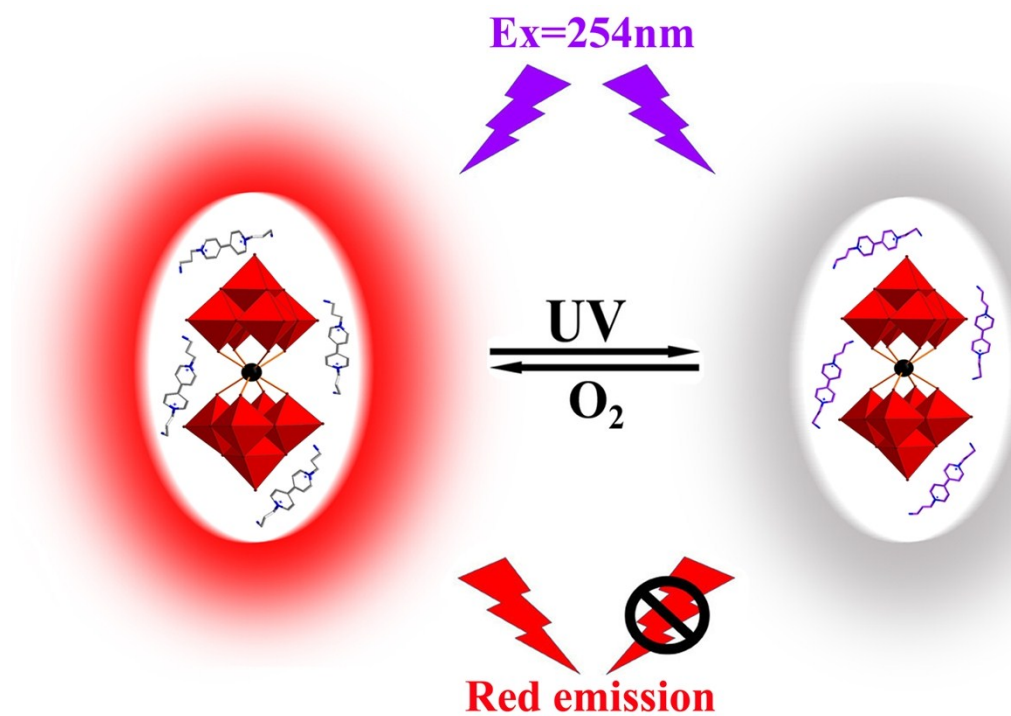


Fig. S3 Illustration of the composite film containing EuW_{10} with AV^{2+} before (left) and after (right) UV irradiation and the reverse transformation under ambient conditions.

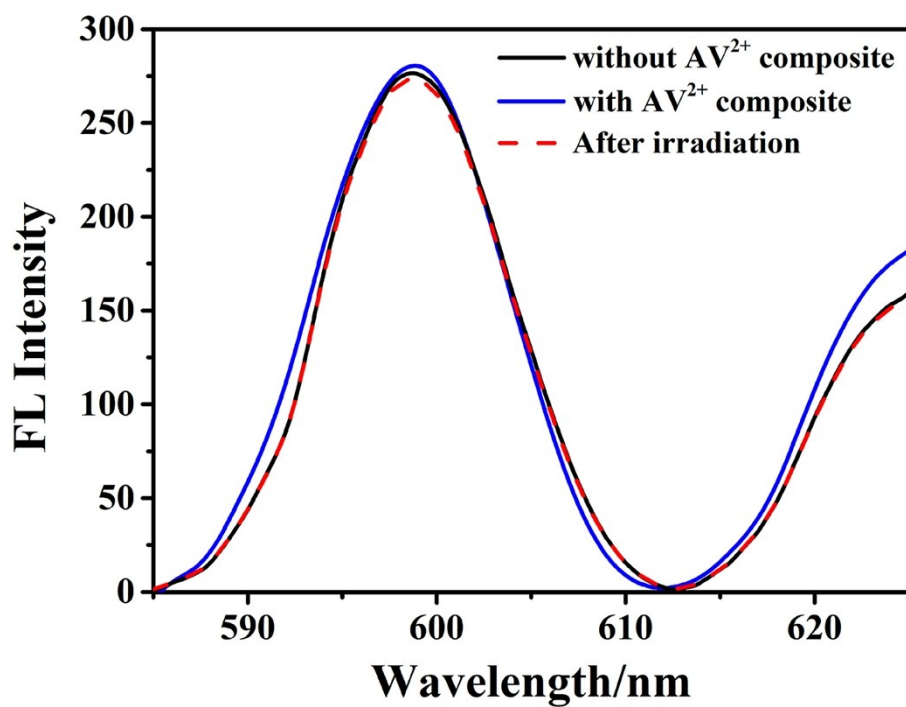


Fig. S4 Emission spectra of the composite film with AV²⁺ (blue line) and without AV²⁺ (black line) before UV irradiation and without AV²⁺ but upon UV irradiation for 4 min (dashed red line).

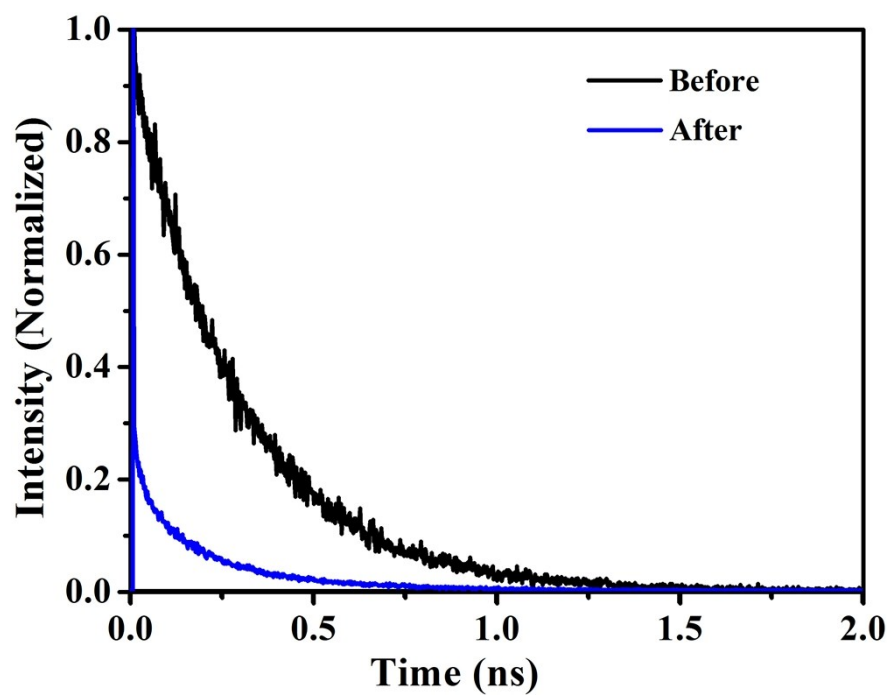


Fig. S5 Fluorescence decay curves of the composite films before and after exposure to solar UV (at 2:30 pm) for 10 min.

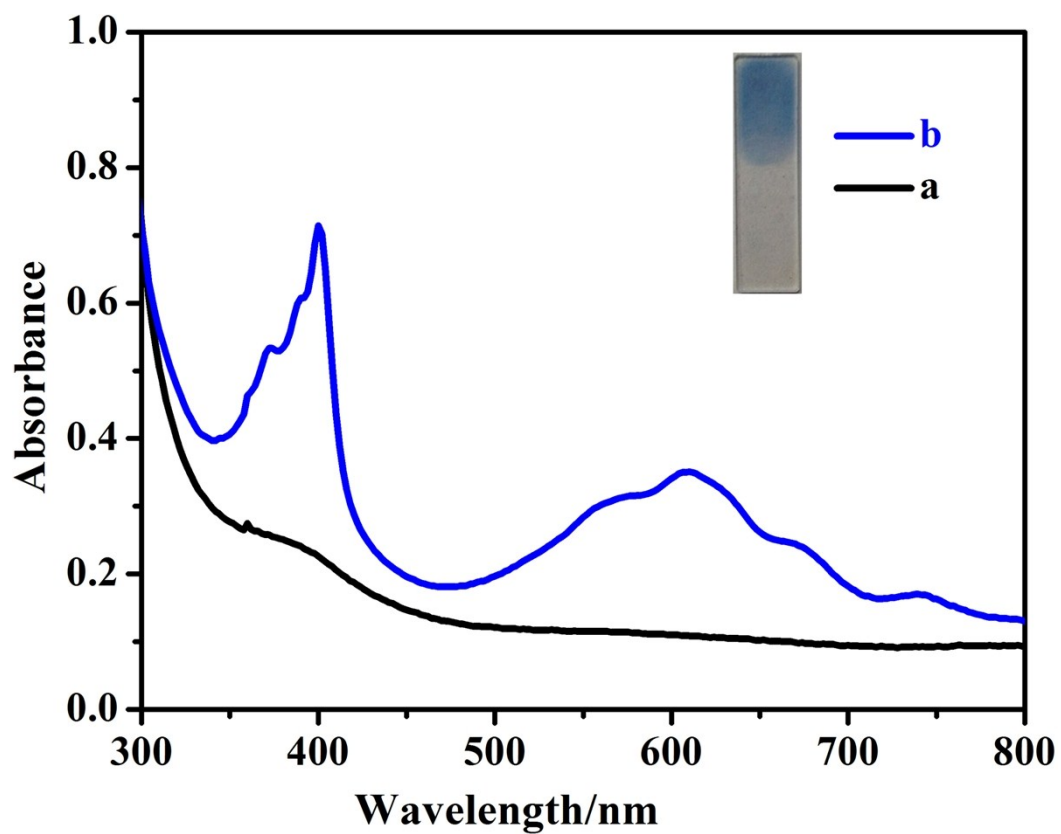


Fig. S6 UV-vis spectra of the composite film after exposure to the sunlight (at 1:00 pm) for 10 min with (a) and without (b) UV filter. The inset shows the color change of the composite film in the sunlight, of which the bottom part is covered by UV filter.

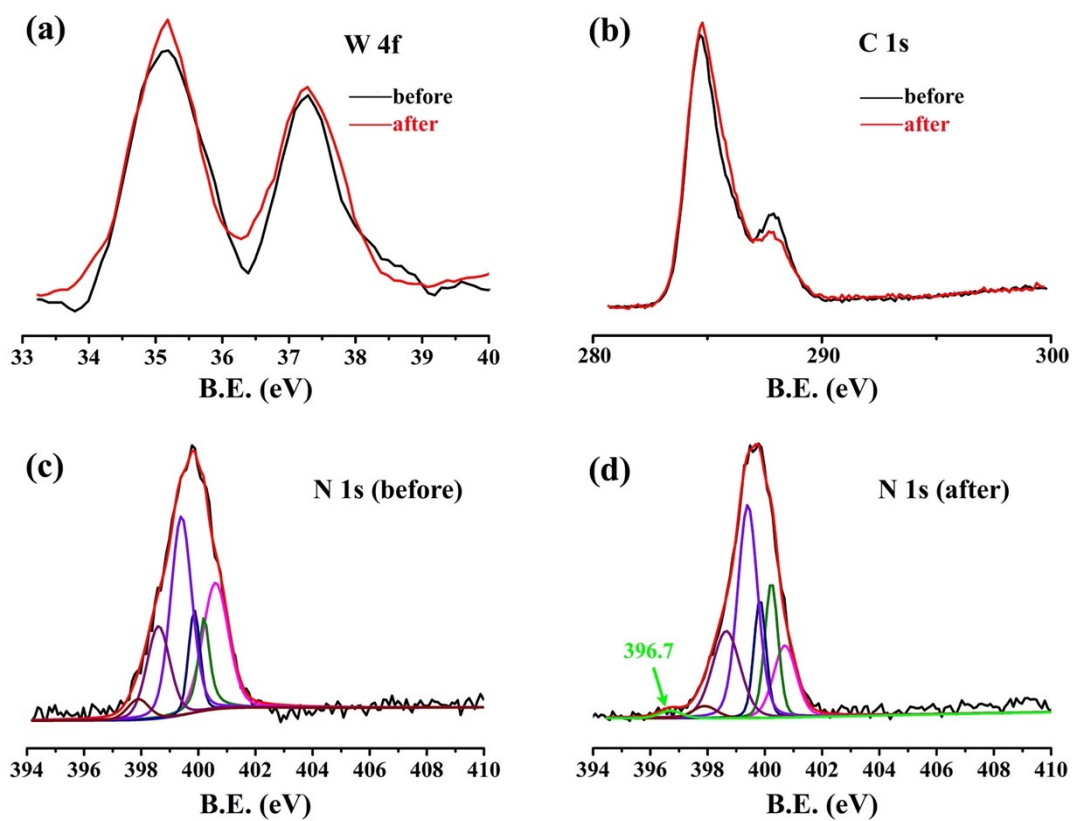


Fig. S7 XPS core-level spectra of W 4f (a), C 1s (b) and N 1s (c, d) in the composite film before and after UV irradiation.

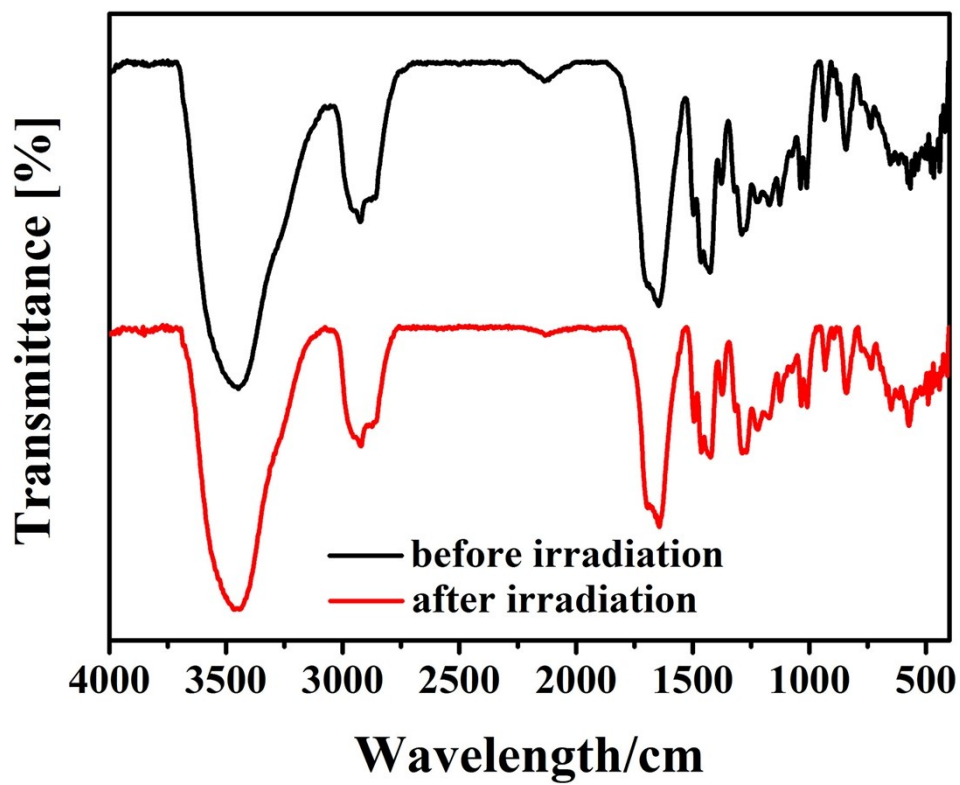


Fig. S8 FTIR spectra of the composite film before (black) and after (red) UV irradiation at room temperature in air for 4 min.

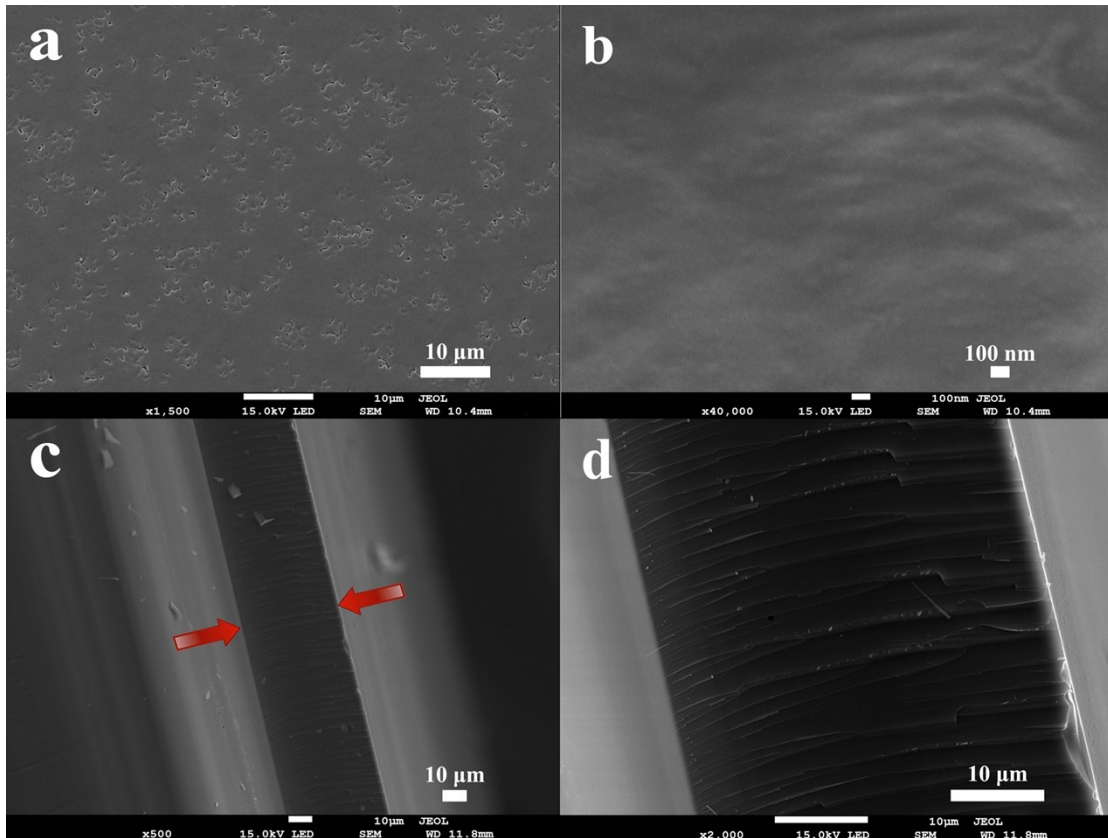


Fig. S9 SEM images of the composite films at low (a and c) and high (b and d) magnification. The surface morphology is shown in (a) and (b), in which the black dots are caused by the electron beam damage. The surface is smooth without any obvious aggregation. SEM cross-sectional images of composite film are shown in (c) and (d), the thickness is ca. 42.67 μm in this batch, which can be tuned by adjusting the dropping volume or concentration of stock solution.

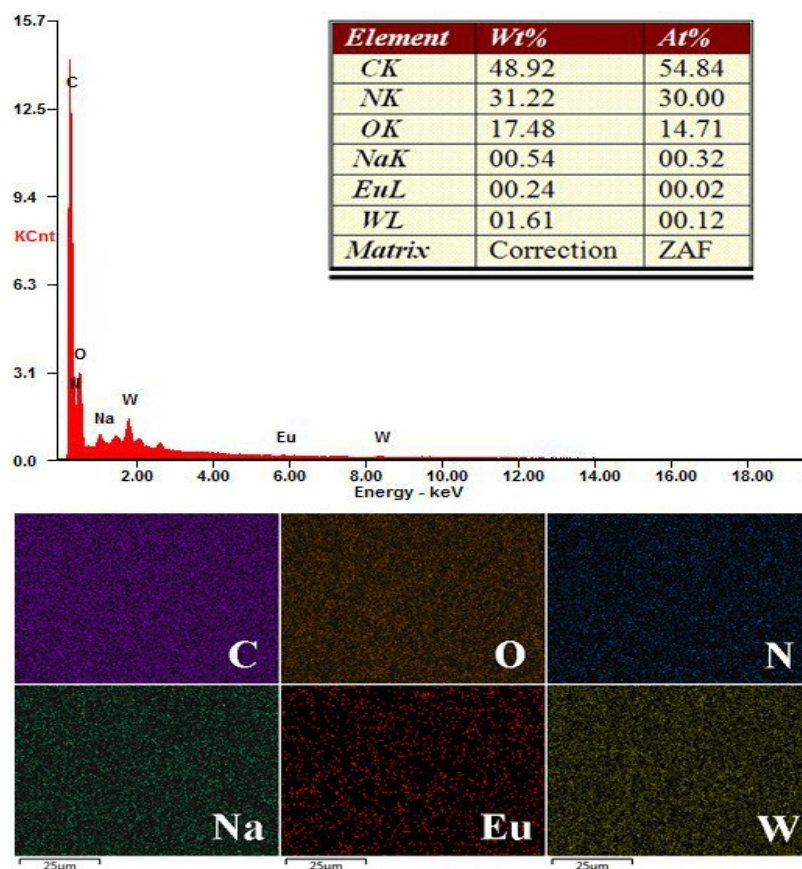


Fig. S10 Energy dispersive X-ray spectra (EDS) analysis and mapping of each element of the composite film. Na, Eu, W, and partial O originate from EuW_{10} ; C, N, and partial O originate from polyvinylpyrrolidone, polyethyleneimine and AV^{2+} .

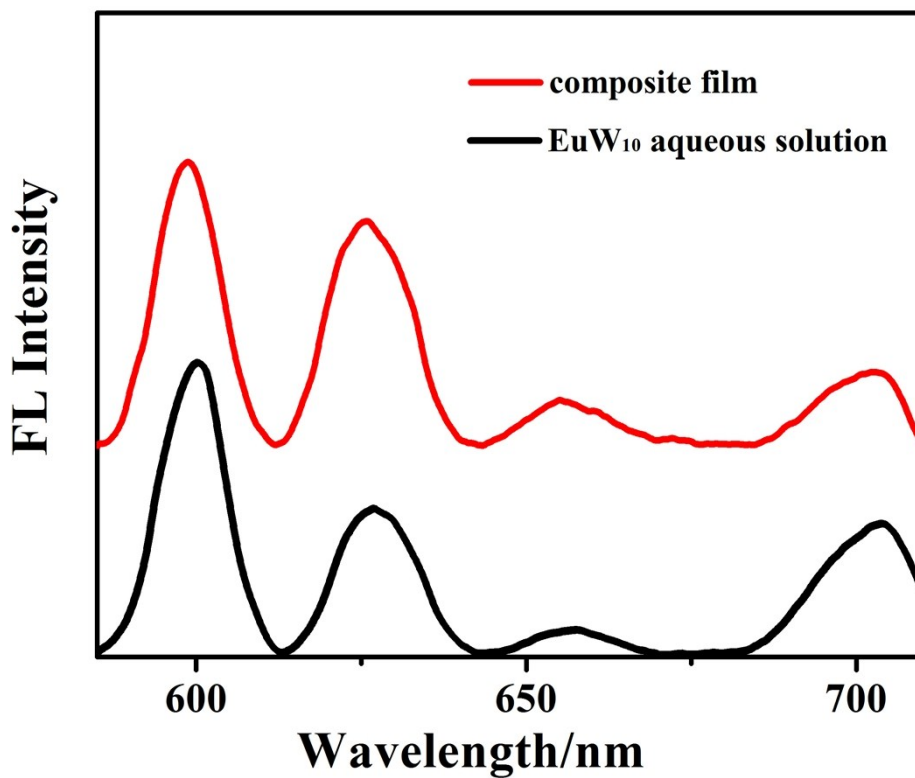


Fig. S11 Emission spectra of the composite film (before UV irradiation) and EuW₁₀ aqueous solution (8 wt%).

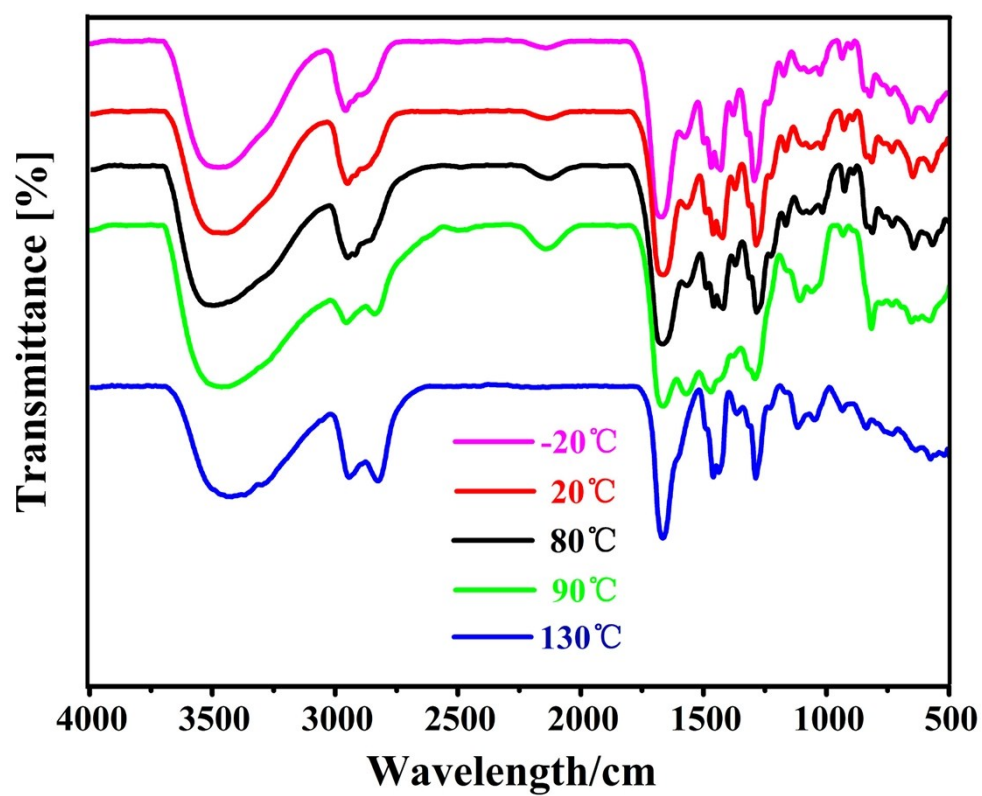


Fig. S12 FTIR spectra of the composite films at different temperatures (The temperature has little effect on the photochromism of the film from -20 to 80 °C. However, the film suffers structural change when the temperature exceeds 80 °C).

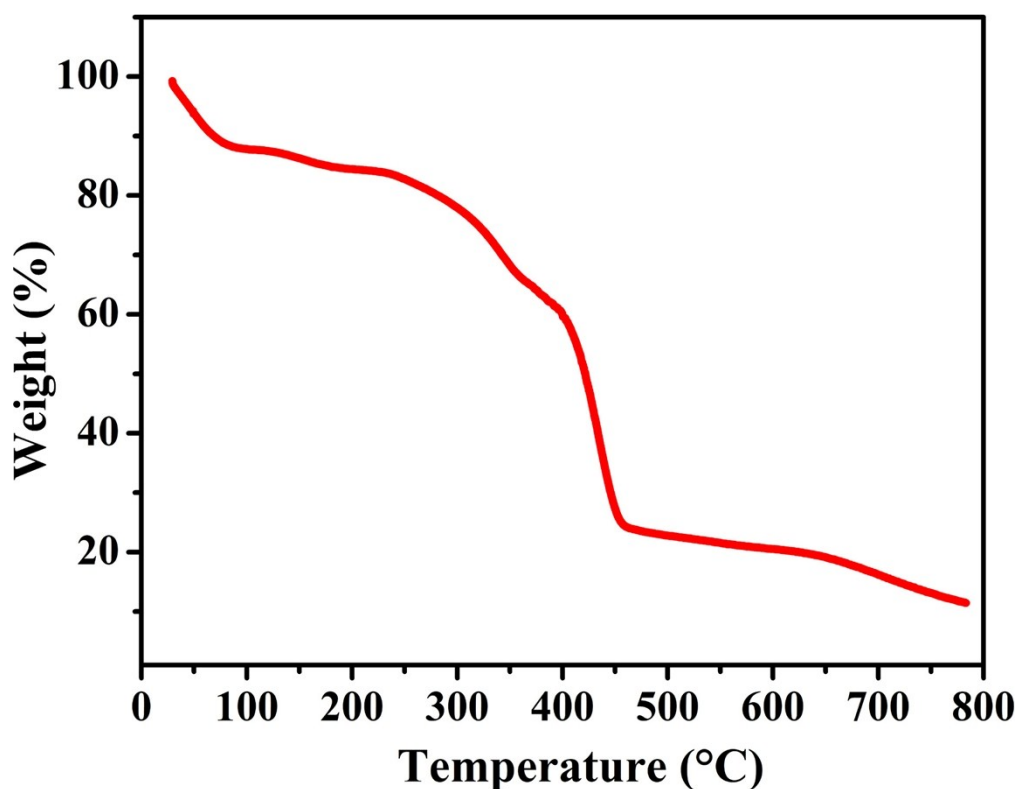


Fig. S13 TGA curves of the composite film ($10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $800\text{ }^{\circ}\text{C}$ under nitrogen atmosphere).

The weight losses are mainly divided into four parts. The temperature of $25\text{ }^{\circ}\text{C}$ to $86\text{ }^{\circ}\text{C}$, $86\text{ }^{\circ}\text{C}$ to $267\text{ }^{\circ}\text{C}$, $267\text{ }^{\circ}\text{C}$ to $450\text{ }^{\circ}\text{C}$, $450\text{ }^{\circ}\text{C}$ to $783\text{ }^{\circ}\text{C}$ correspond to the weight losses of 11%, 6%, 58% and 14%, respectively. An early weight loss from $25\text{ }^{\circ}\text{C}$ to $86\text{ }^{\circ}\text{C}$ may be due to the loss of free water molecules in the film. A consecutive steady weight loss from $86\text{ }^{\circ}\text{C}$ to $267\text{ }^{\circ}\text{C}$ may be due to the loss of small molecules or groups in PVP or PEI. A further weight loss from $267\text{ }^{\circ}\text{C}$ to $450\text{ }^{\circ}\text{C}$ is possibly caused by the loss of AV^{2+} and PVP. Then, the weight loss from $450\text{ }^{\circ}\text{C}$ to $783\text{ }^{\circ}\text{C}$ may be due to the loss of PEI and EuW_{10} .

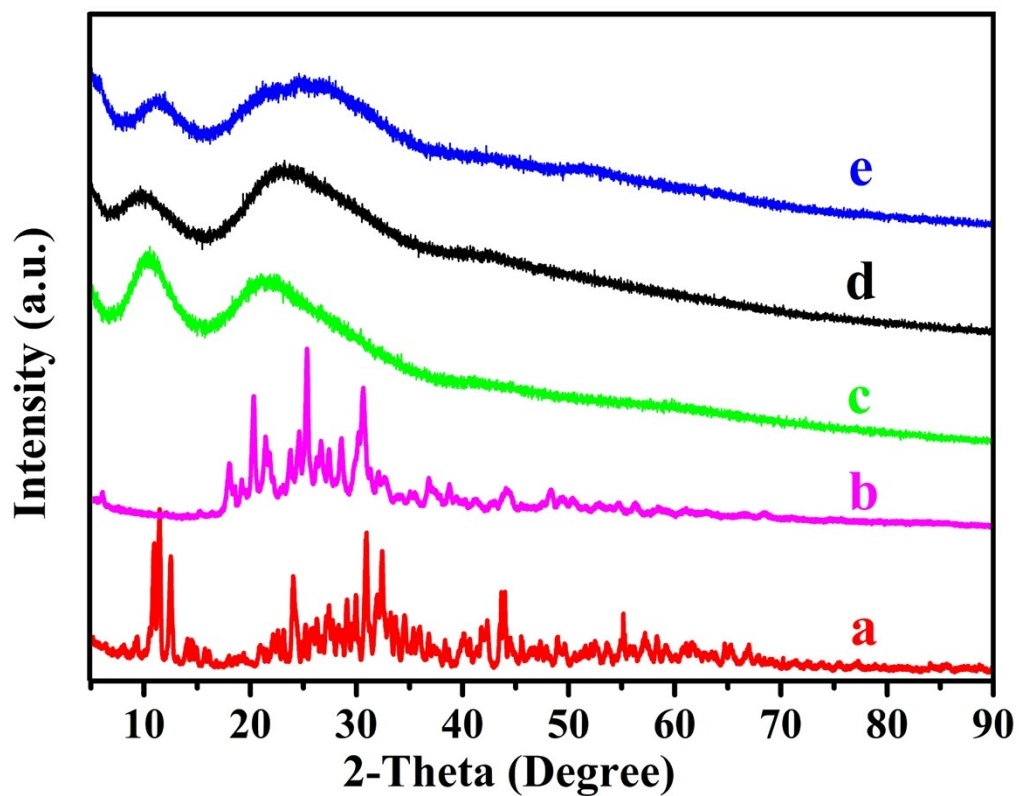


Fig. S14 XRD patterns for: (a) EuW₁₀; (b) AV²⁺; (c) the film containing PVP and PEI; the composite film before (d) and after (e) UV irradiation.

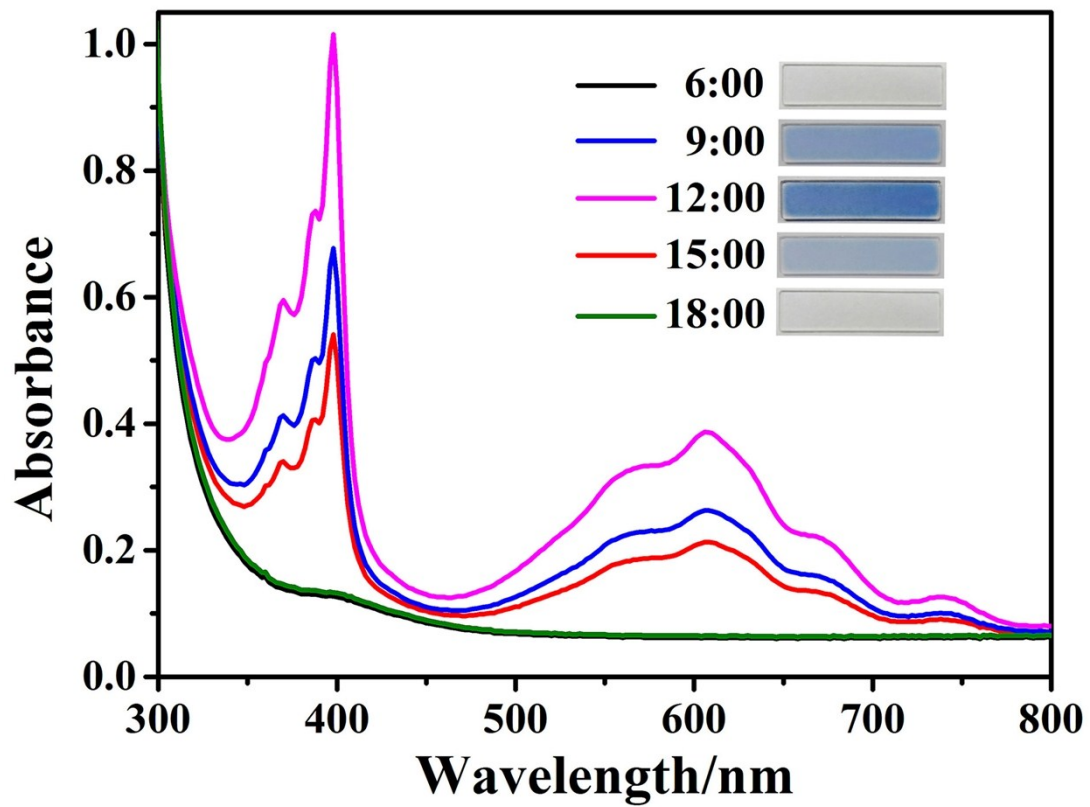


Fig. S15 UV-vis spectra of the composite film at different local time.

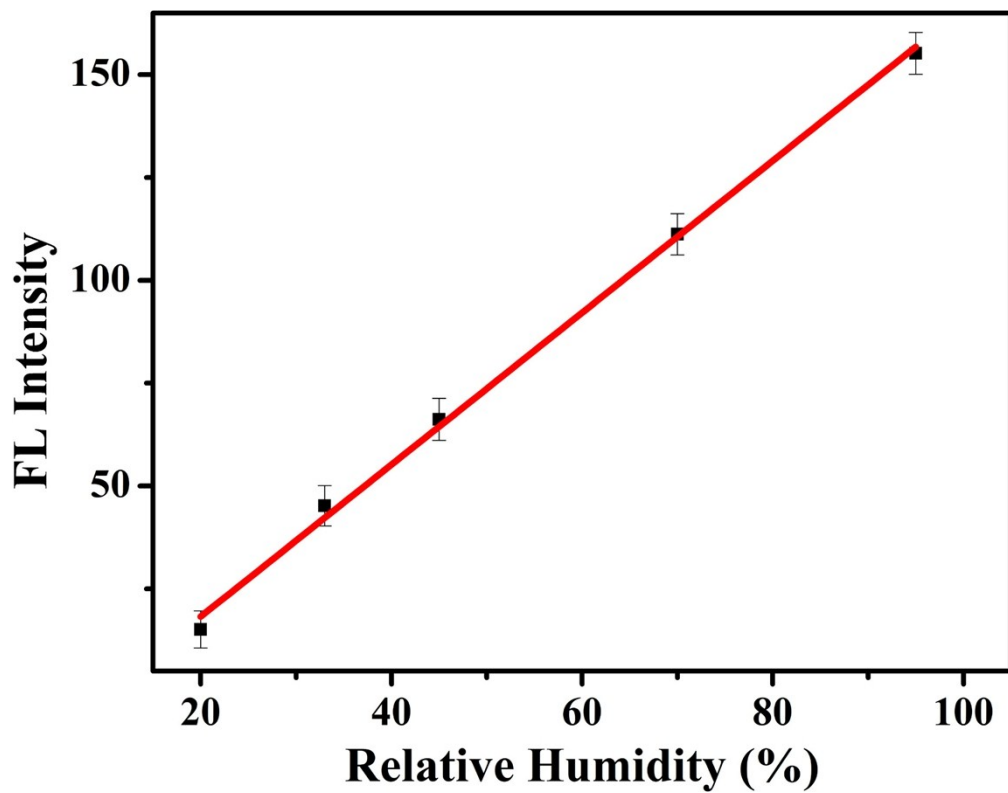


Fig. S16 Plots of the emission intensity at 600 nm of the composite film after exposure to different RH (20%, 33%, 45%, 70% and 95%) for 4 min.

Table S1 The fluorescence lifetimes of the composite films before and after exposure to solar UV (at 2:30 pm) for 10 min.

State	Excitation/nm	τ_1 (ns)	f_1 (%)	τ_2 (ns)	f_2 (%)	Average τ (ns)
Before	254	1.41	22.45	1.40	77.55	1.40
After	254	0.65	42.21	0.78	57.79	0.73

Table S2 Coloration and decoloration time of the composite film with different thickness.

Thickness of the film (μm)	Coloration time ^a (min)	Decoloration time ^b (min)
29.94	6.1	9.6
42.67	4.0	16.2
78.79	3.4	43.9
121.01	3.1	91.8
159.88	2.9	172.4

^a The composite films were irradiated upon 125 W high-pressure mercury lamp until the blue color can be observed.

^b The coloration films (125 W high-pressure mercury lamp for 10 min) are exposed to 95% RH until the blue color bleached.