

## **Supplementary Materials**

### **Oxygen-consumption-induced phosphorescence enhancement: both charge- and energy-involved mechanisms**

Guowei Zhang,<sup>a,b</sup> Songchao Bai,<sup>c</sup> Fushun Liang,<sup>\*a,b</sup> and Xuesi Chen<sup>d</sup>

a. Faculty of Chemistry and Life Sciences, Changchun University of Technology, 3000 Yuanda Street, Changchun, Jilin, 130120, China.

b. College of Chemistry, Liaoning University, Shenyang 110036, China

c. College of Physics, Liaoning University, Shenyang 110036, China

d. State Key Laboratory of Polymer Science and Technology, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China

### **Experimental Section**

#### **Materials**

All chemical reagents used in this work were purchased from commercial source. Methyl indole-6-carboxylate (**MI6C**) was purchased from Energy Chemical, indole-6-carboxylic acid (**I6CA**) was purchased from Adamas-beta and polyvinyl alcohol (PVA-1788) with the alcoholysis degree of 87-89% was purchased from General-reagent. Both the guests **MI6C** and **I6CA** were used with recrystallization for three times using hexyl hydride and anhydrous ethanol, the PVA host was used directly without further purification.

#### **Characterization**

Powder X-ray diffraction (PXRD) was recorded with a Bruker AXS D8 advanced automated diffractometer at 40 kV and 40 mA with Cu-K $\alpha$  radiation (1.54056 Å) as the X-ray source in the  $2\theta$  range of 5-50°. Shimadzu ultraviolet visible spectrophotometer UV-2700 was used to test the light transmittance of the sample. The photoluminescence spectra, the phosphorescence spectra, the excitation spectra, the decay curves and the photoluminescence quantum efficiency were carried out using an Edinburgh fluorescence spectrometer (FLS980/FS5). The LEDs were driven by a Keithley 2400 source meter and the emission spectra and intensity were recorded by the Everfine ATA-500 photoelectric analysis system. All the photos were taken by

Apple 12 camera.

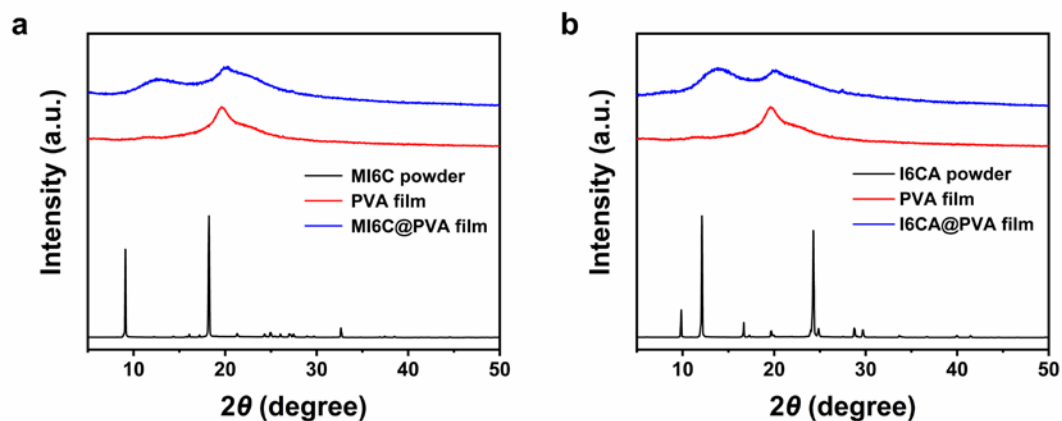
### **Theoretical calculations**

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the Gaussian 16 program (Revision A.03). Conduct geometry optimization of **MI6C** and **I6CA** in an isopropanol-containing solvent systems by using B3LYP functional and 6-311G (d, p) basis set to simulate the interaction between the guest molecules and PVA. The ORCA program was utilized for simulate spin-orbit coupling (SOC) matrix elements between the singlet excited states and the triplet excited states. The SOC calculations were based on geometries optimized at the B3LYP/6-311G (d, p) level. In addition, the excited state energy level, oscillator strength ( $f$ ) and spin-orbit coupling constant ( $\zeta$ ) were provided.

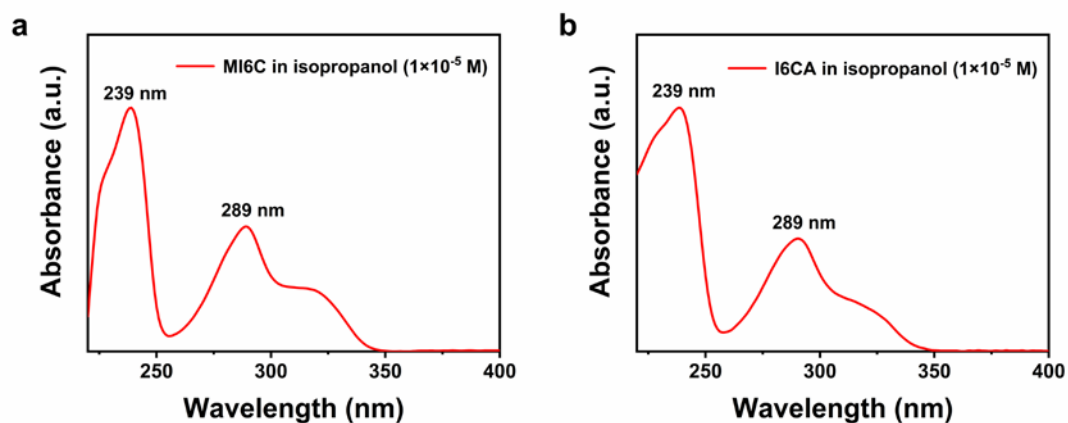
### **Preparation of polymer-based afterglow materials**

First a stock solution of **PVA** was prepared by heating 0.3 g of the polymer in 10 ml of deionized water at 80°C for 3 hours under stirring conditions. **MI6C-PVA** hybrids were prepared by adding appropriate amount of **MI6C** to 1 ml of **PVA** stock solutions (for example, for 0.33 wt. % **MI6C-PVA**, 0.1 mg of **MI6C** is used and dissolved in 1 mL anhydrous Ethanol). Ultrasonicated the mixed solution for 1 hour and dropping about 0.3 mL onto a 2×2 cm quartz sheet. Drying in the oven at 80 °C for 2 hours, uniform **MI6C@PVA** doped films were obtained. The preparation of **I6CA@PVA** doped films followed the same procedure. All PVA doped films with different concentrations (0.33, 1.0, 1.6, 3.3, 6.6 wt.%) followed the same procedure.

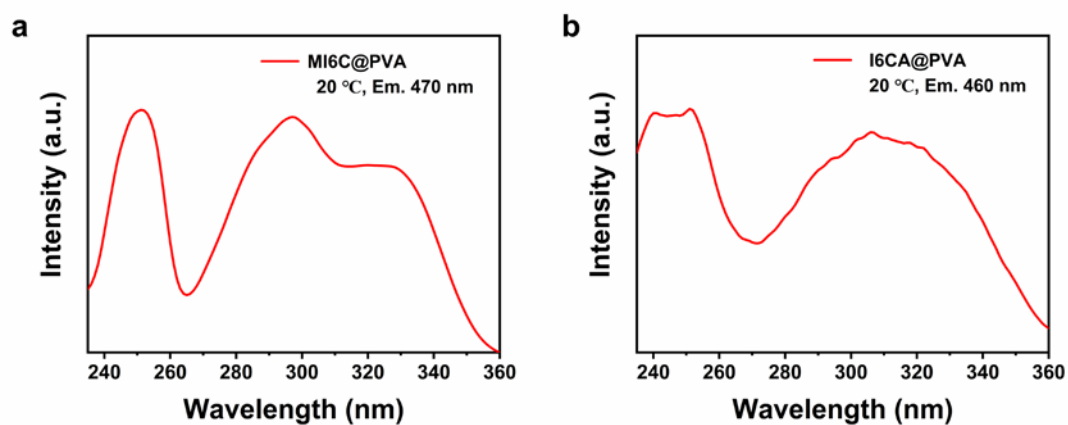
## Supplementary figures and tables



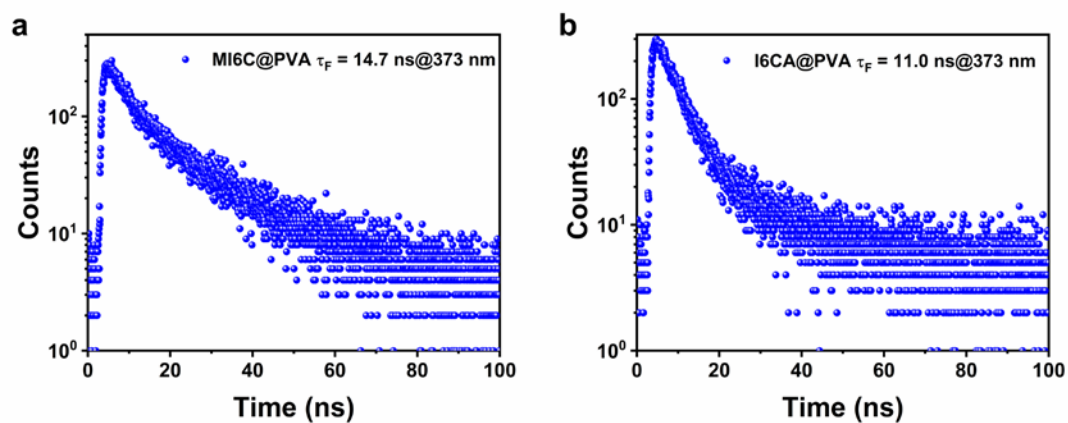
**Figure S1.** PXRD patterns of (a) **MI6C@PVA** film, PVA film and **MI6C** powder; (b) **I6CA@PVA** film, PVA film and **I6CA** powder.



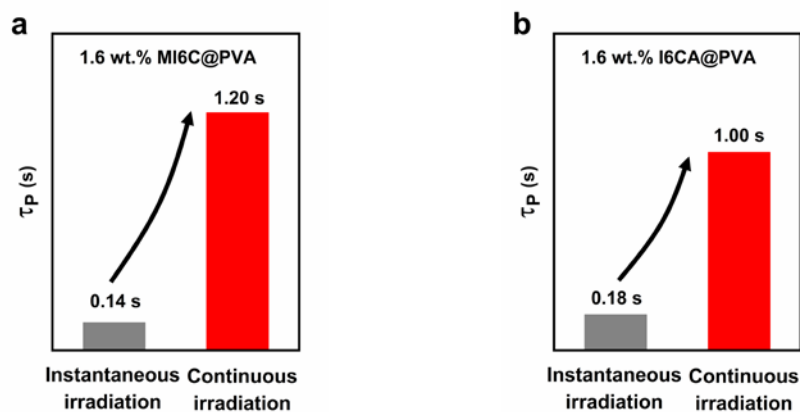
**Figure S2.** UV-vis absorption spectra of (a) **MI6C** and (b) **I6CA** in dilute isopropanol solution ( $1 \times 10^{-5}$  M) under ambient conditions.



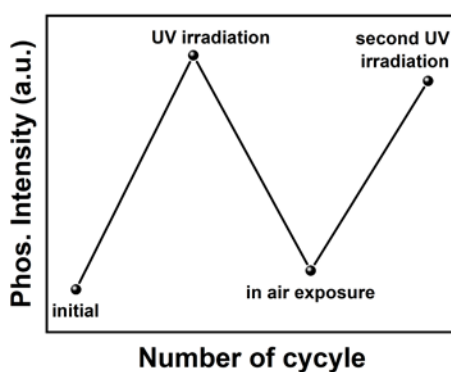
**Figure S3.** Excitation spectra of (a) **MI6C@PVA** and (b) **I6CA@PVA** doped films (1.6 wt.%) under ambient conditions.



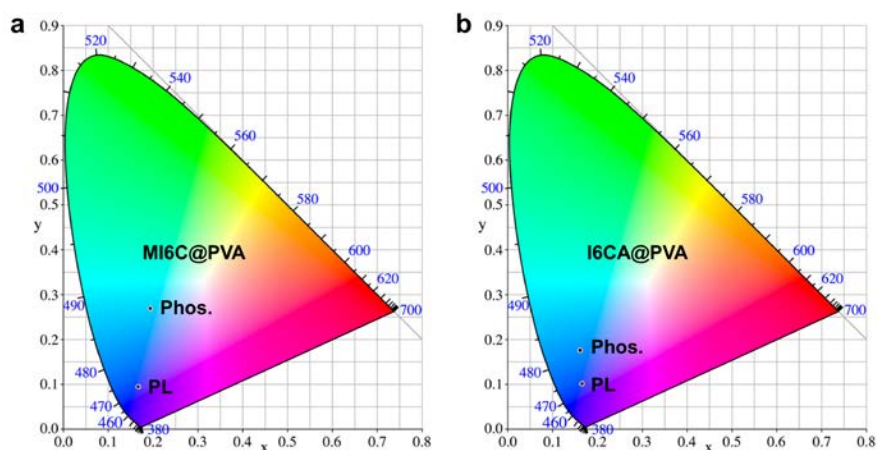
**Figure S4.** The photoluminescence decay curves of (a) **MI6C@PVA** and (b) **I6CA@PVA** doped films (1.6 wt.%).



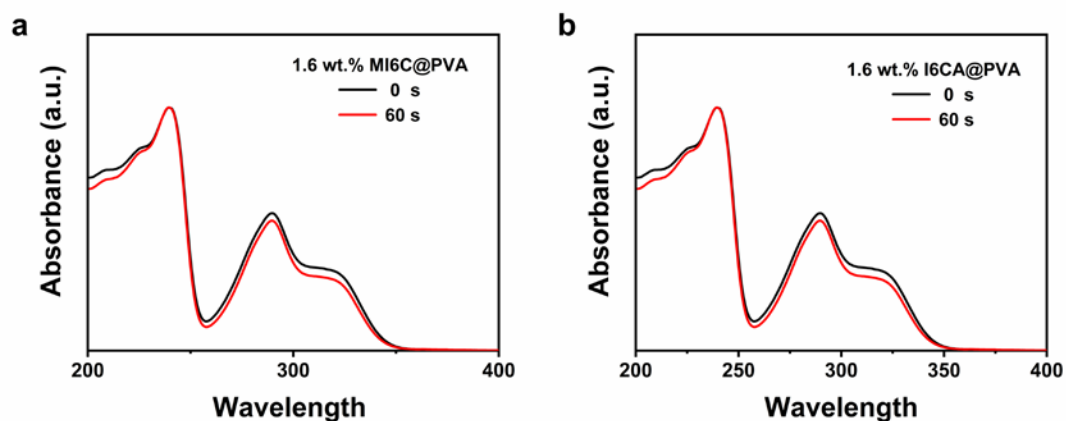
**Figure S5.** Comparison of phosphorescence lifetimes of (a) **MI6C@PVA** and (b) **I6CA@PVA** doped films (1.6 wt.%) at instantaneous irradiation and continuous irradiation.



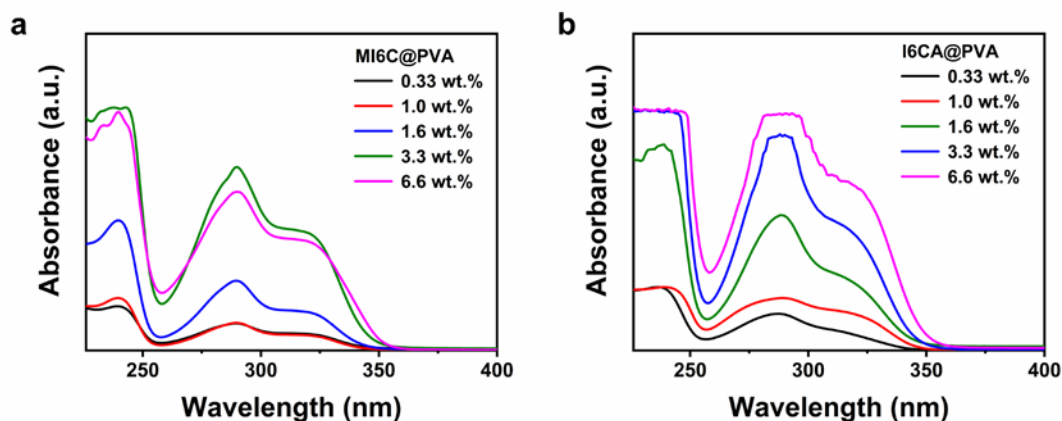
**Figure S6.** Comparison of phosphorescence intensity of **MI6C@PVA** (1.6 wt.%) decreased after standing in air exposure (5 h) and recovered by UV irradiation.



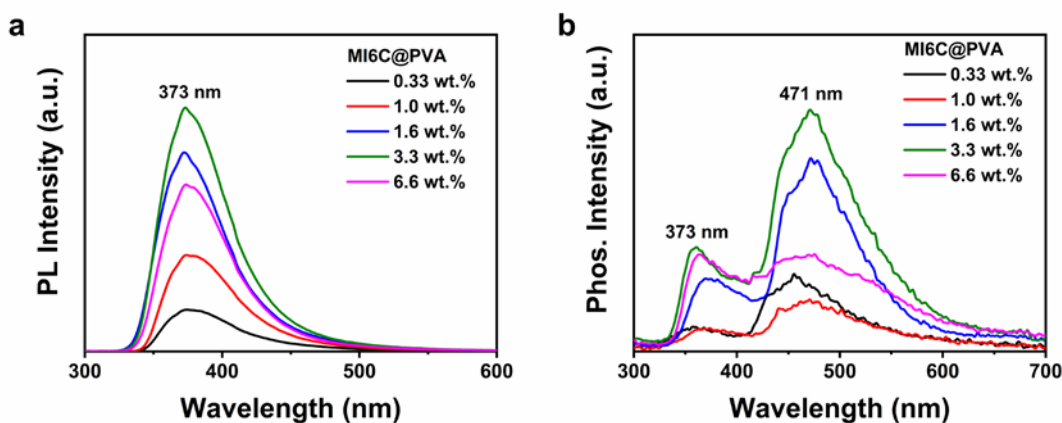
**Figure S7.** The CIE coordinates based on the photoluminescence and phosphorescence spectra of (a) **MI6C@PVA** and (b) **I6CA@PVA** doped films (1.6 wt.%) at 254 nm continuous UV irradiation.



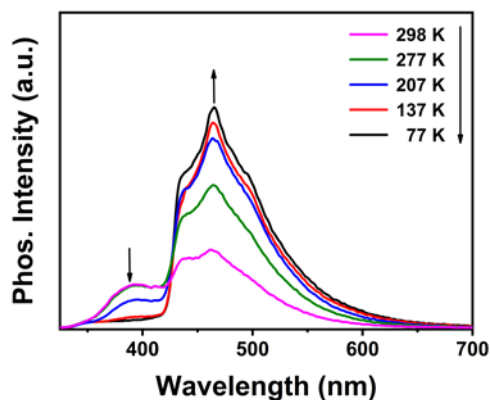
**Figure S8.** UV-vis absorption spectra of (a) **MI6C@PVA** and (b) **I6CA@PVA** doped films (1.6 wt.%) with different UV irradiation times.



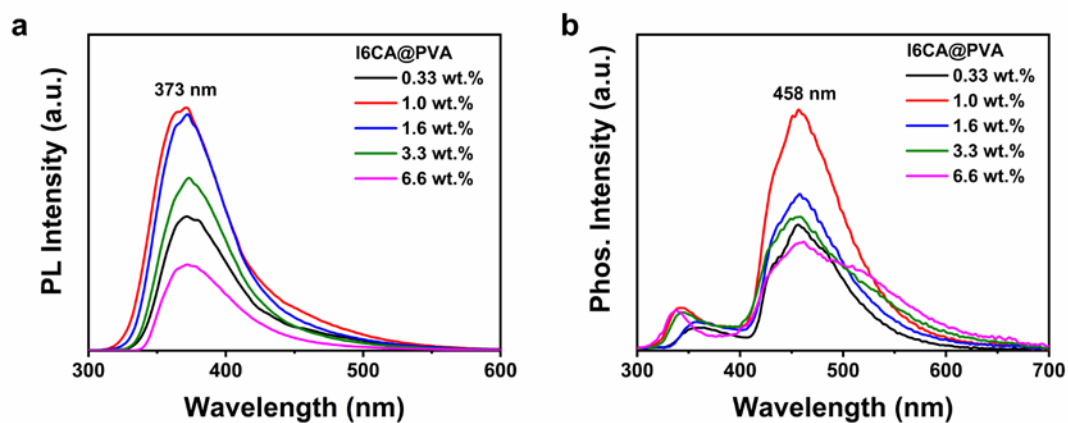
**Figure S9.** UV-vis absorption spectra of MI6C@PVA and I6CA@PVA doped films at different doping concentrations under ambient conditions.



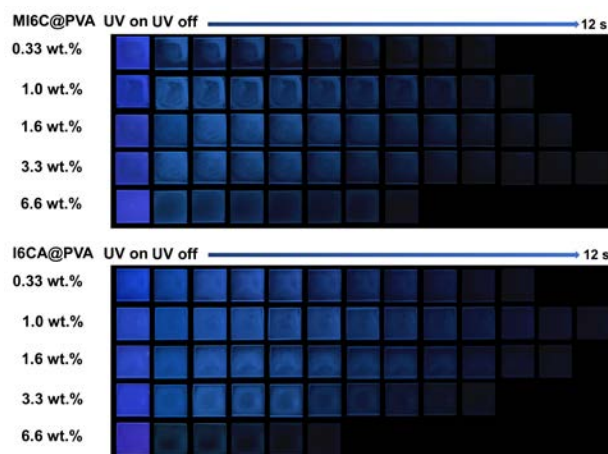
**Figure S10.** The MI6C@PVA doped films at different concentrations under ambient conditions instantaneous irradiation ( $\lambda_{\text{ex}} = 245 \text{ nm}$ ): (a) the normalized photoluminescence spectra; (b) the normalized phosphorescence spectra (delayed time = 0.1 s).



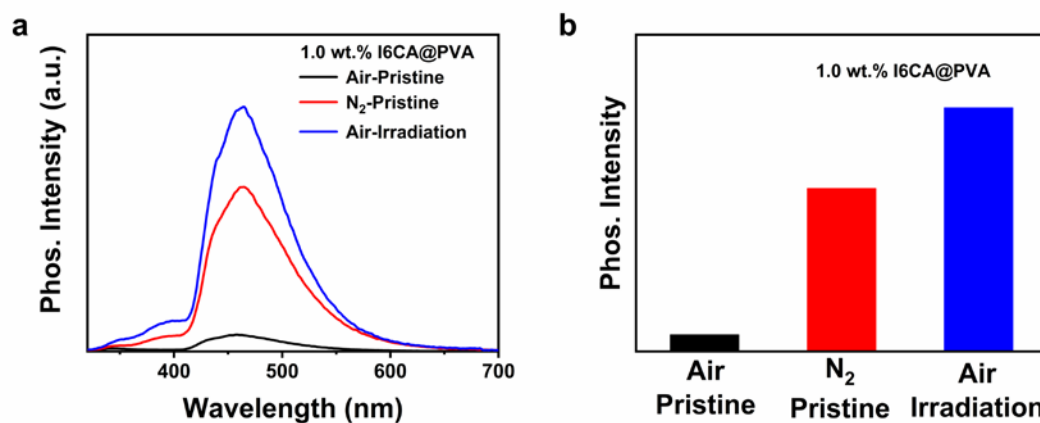
**Figure S11.** The phosphorescence spectra of 1.6 wt.% **MI6C@PVA** doped film under ambient conditions instantaneous irradiation at different temperatures ( $\lambda_{\text{ex}} = 245$  nm, delay time = 0.1 s).



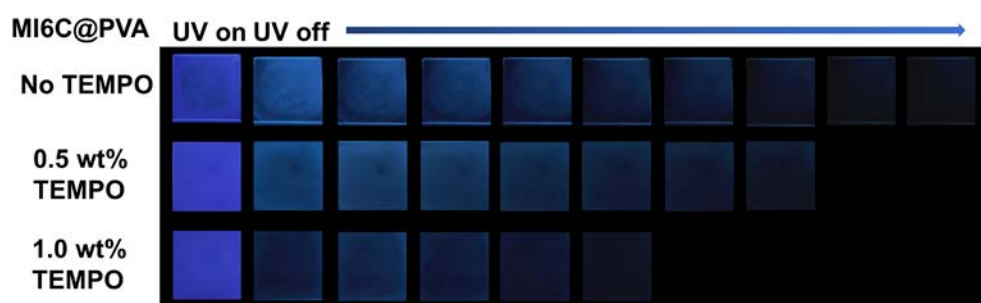
**Figure S12.** The **I6CA@PVA** doped films at different concentrations under ambient conditions instantaneous irradiation ( $\lambda_{\text{ex}} = 245$  nm): (a) the normalized photoluminescence spectra; (b) the normalized phosphorescence spectra (delayed time = 0.1 s).



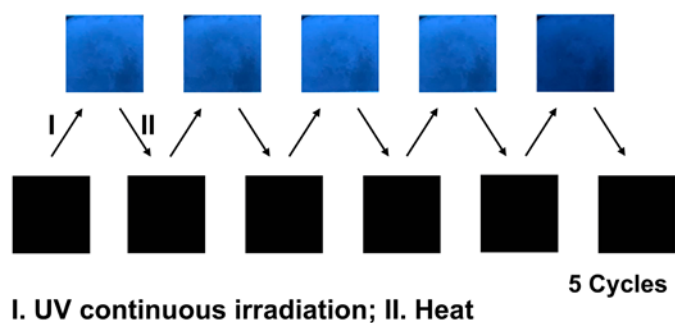
**Figure S13.** The luminescence photographs of **MI6C@PVA** and **I6CA@PVA** doped films at different doping concentrations under 254 nm continuous irradiation for 60 s.



**Figure S14.** (a) The phosphorescence spectra of 1.0 wt.% **I6CA@PVA** at instantaneous irradiation in air and nitrogen and continuous irradiation in air ( $\lambda_{\text{ex}} = 245 \text{ nm}$ , delayed time = 0.1 s). (b) Comparison of phosphorescence intensity of **I6CA@PVA** at instantaneous irradiation in air and nitrogen and continuous irradiation in air.



**Figure S15.** Photoluminescence images of **MI6C@PVA** doped film (3.3 wt.%) with different concentrations of TEMPO.



**Figure S16.** Afterglow pictures of **MI6C@PVA** doped film (3.3 wt.%). (I) Continuous UV irradiation for 60 s by 254 nm UV lamp and (II) heating at 80 °C for 30 min.