

## *Supporting Information*

### **Ultralong Room-Temperature Phosphorescence from Polycyclic Aromatic Hydrocarbons by Accelerating Intersystem Crossing within Rigid Polymer Network**

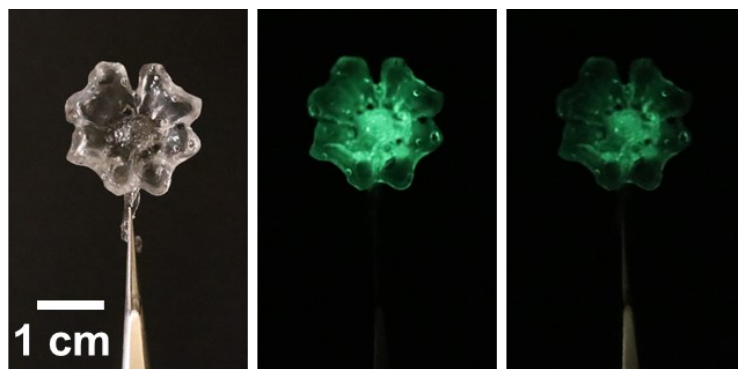
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School of Physical Science and Technology, Shanghai Tech University, Shanghai 201210, China

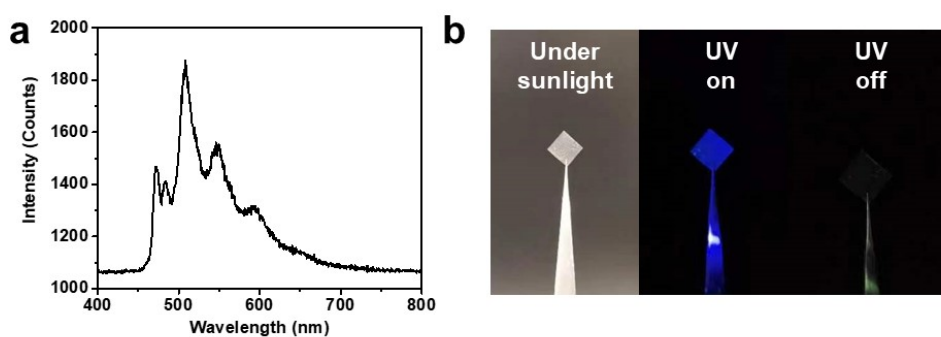
Email: [yechh@shanghaitech.edu.cn](mailto:yechh@shanghaitech.edu.cn), [zhuxj1@shanghaitech.edu.cn](mailto:zhuxj1@shanghaitech.edu.cn)

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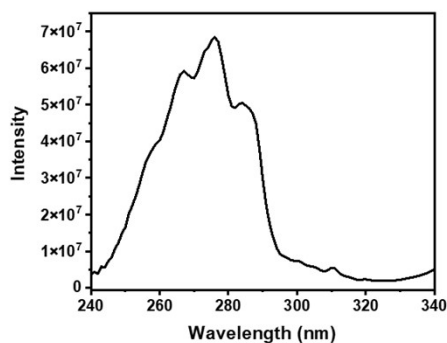
<sup>†</sup> Contributed equally



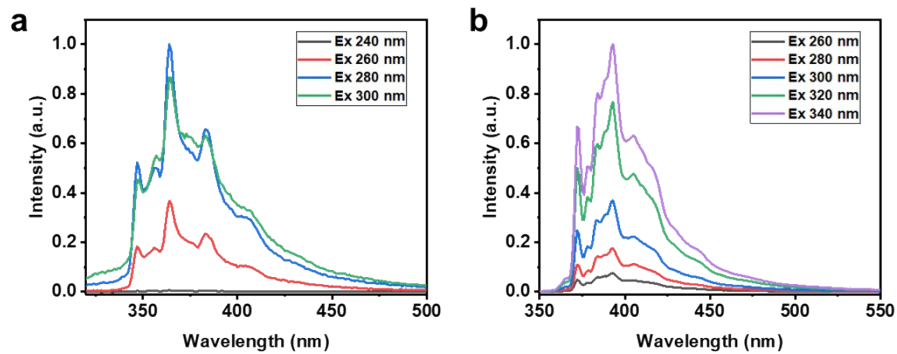
**Figure S1.** Transparent 3D flower of Nap@PMMA showing long-lived RTP under different duration time.



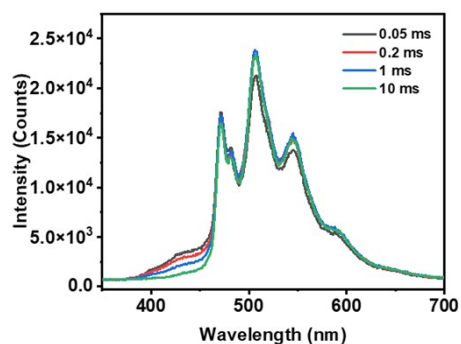
**Figure S2.** Phosphorescence spectra and photographs of PMMA with naphthalene by simple blending.



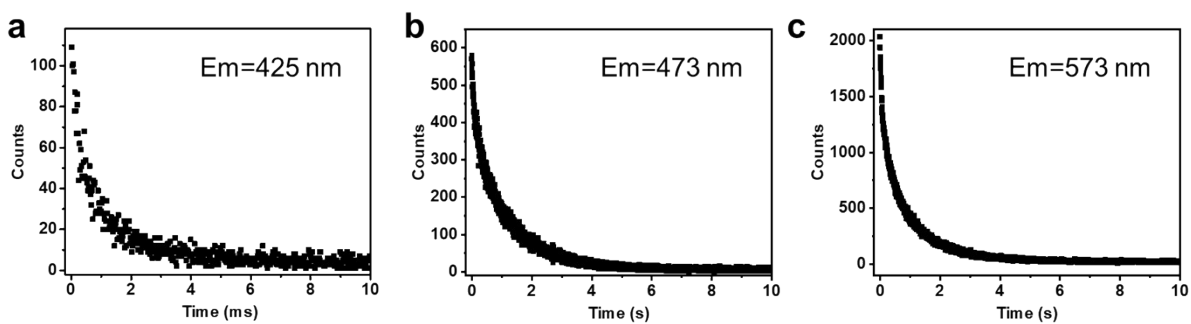
**Figure S3.** Fluorescence-excitation spectrum of Nap@PMMA ( $\lambda_{em}=320$  nm).



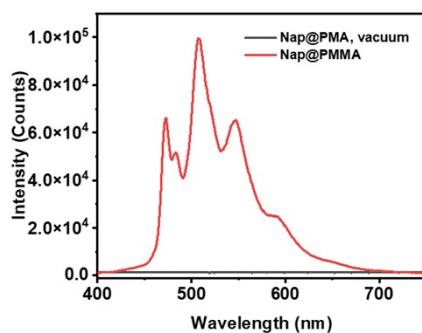
**Figure S4.** Fluorescence spectra with different wavelength excitation of (a) Phe@PMMA; (b) Pyr@PMMA.



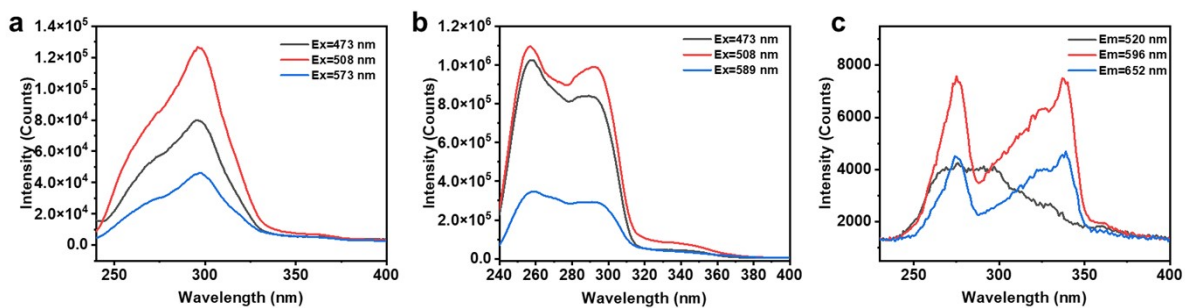
**Figure S5.** Phosphorescence spectra of Nap@PMMA with different delayed time.



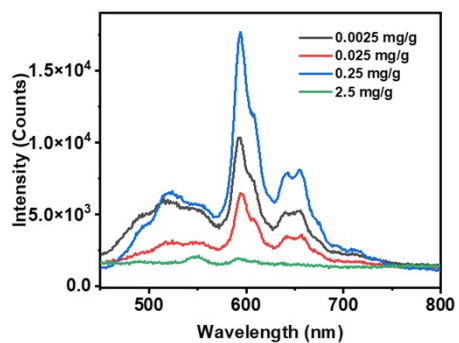
**Figure S6.** Time-resolved RTP decay curves of Nap@PMMA at 425, 473 and 573 nm.



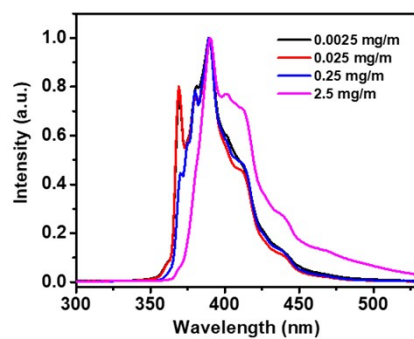
**Figure S7.** The comparison of phosphorescence spectra of Nap@PMA in vacuum and Nap@PMMA at room temperature.



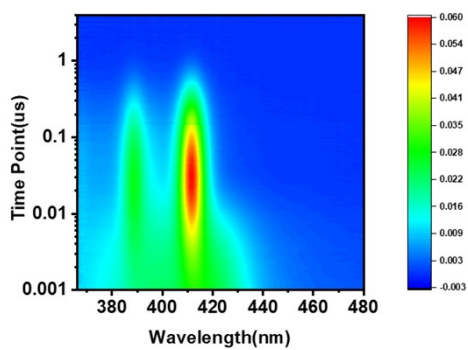
**Figure S8.** Excitation spectra of Nap, Phe and Pyr@PMMA at different wavelength.



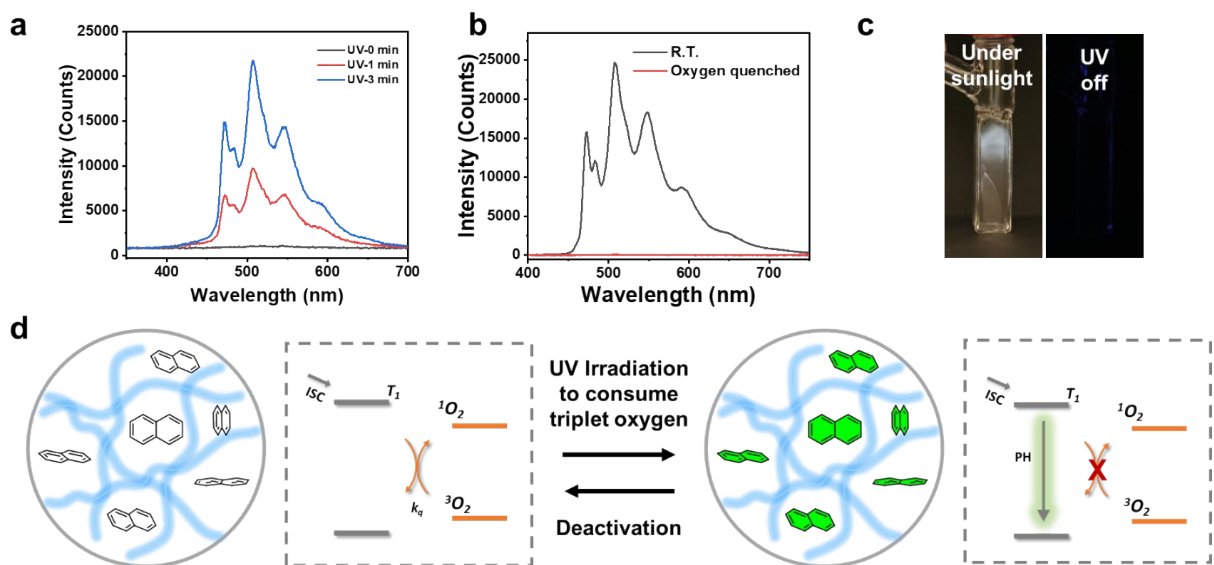
**Figure S9.** Phosphorescence spectra of Pyr@PMMA at different concentration (delay time=10 ms).



**Figure S10.** Fluorescence spectra of Pyr@PMMA at different concentrations.



**Figure S11.** Transient absorption two-dimensional temporal evolution spectra of naphthalene solution in hexane.



**Figure S12.** a. Delayed (10 ms) phosphorescence spectra of Nap@PMMA with different irradiation time; b. Afterglow spectra before and after oxygen quenched; c. the photographs of Nap@PMMA after oxygen quenched (no afterglow in sunlight and dark after UV turned off); d. Schematic illustration of oxygen effects.