

Supporting Information

Water stimulus-responsive room temperature afterglow materials with color tunability from inorganic/organic H–G hybrid system

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Experimental Procedures and Characterization

Materials

All chemicals used in the experiments without further purification. Boric acid and Phthalic acid (PA) were purchased from Aladdin. Isophthalic acid (IPA) was purchased from RHAWN reagent. Terephthalic acid (TPA) was purchased from TCI.

Synthesis of IPA_x@HBA

Separately add IPA (1 g, 100 mg, 50 mg, 10 mg), BA (1 g) and appropriate amount of agate beads were added into a 30 mL ball mill pot and ground at 1500 rpm/min for 30 min. The well mixed powders were spread on a surface dish and then heated it in an oven at 150 °C for 15 min. They are defined as IPA₁@HBA, IPA_{0.1}@HBA (IPA@HBA), IPA_{0.02}@HBA, and IPA_{0.01}@HBA, respectively.

Synthesis of IPA@HBA-x wt % L

Weigh 100 mg IPA@HBA into 2 mL centrifuge tube and add 10 uL, 20 uL, 30 uL, 40 uL, 60 uL, 80 uL, 100 uL deionized water, respectively. They are defined as IPA@HBA-10 wt % L, IPA@HBA-20 wt % L, IPA@HBA-30 wt % L, IPA@HBA-40 wt % L, IPA@HBA-60 wt % L, IPA@HBA-80 wt % L, IPA@HBA-100 wt % L.

Synthesis of TPA@HBA

TPA (100 mg), BA (1 g) and appropriate amount of agate beads were added into a 30 mL ball mill pot and ground at 1500 rpm/min for 30 min. The well mixed powders were spread on a surface dish and then heated it in an oven at 150 °C for 15 min.

Synthesis of TPA@HBA-water

Weigh 100 mg TPA@HBA into 2 mL centrifuge tube and add 80 uL deionized water, defined as TPA@HBA-water.

Synthesis of PA@HBA

PA (100 mg), BA (1 g) and appropriate amount of agate beads were added into a 30 mL ball mill pot and ground at 1500 rpm/min for 30 min. The well mixed powders were spread on a surface dish and then heated it in an oven at 150 °C for 15 min.

Synthesis of PA@HBA-water

Weigh 100 mg PA@HBA into 2 mL centrifuge tube and add 80 μ L deionized water, defined as PA@HBA-water.

Characterizations

Delay and prompt emission spectra, fluorescence and phosphorescence decay curves and quantum efficiency were measured on a fluorescence spectrometer (FLSP920, Edinburgh Instruments) equipped with a xenon arc lamp (Xe 900), microsecond flash (μ F 900) and nanosecond flash (nF900). The phosphorescence spectrum in the main text is delayed spectrum, which is obtained by time-gated technology with a delay time (td) of 0.1 ms. And phosphorescence lifetime was also obtained with a delay time (td) of 0.1 ms on Edinburgh FLSP920 spectrometer. The X-ray diffraction (XRD) patterns were collected using an X-ray diffractometer from Bruker AXS D8 Discover in Germany with Cu K α radiation. Fourier transform infrared spectroscopy (FTIR) were measured on a BRUKER TENSOR 27 spectrometer by using KBr pellets. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific K-Alpha X-ray photoelectron spectrometer. ^{13}C NMR spectra was measured by a Bruker Biospin AG AVANCE400. DSC was performed on the DSC250 of TA in the United States using cooling and heating rates of 5 K/min. The TGA curves were tested by synchronous thermal analyzer using SDT/Q600. The samples were heated at 5 K \cdot min $^{-1}$ rate under air atmosphere. Energy dispersive X-ray (EDX) mapping observations were performed on a Talos F200S microscope.

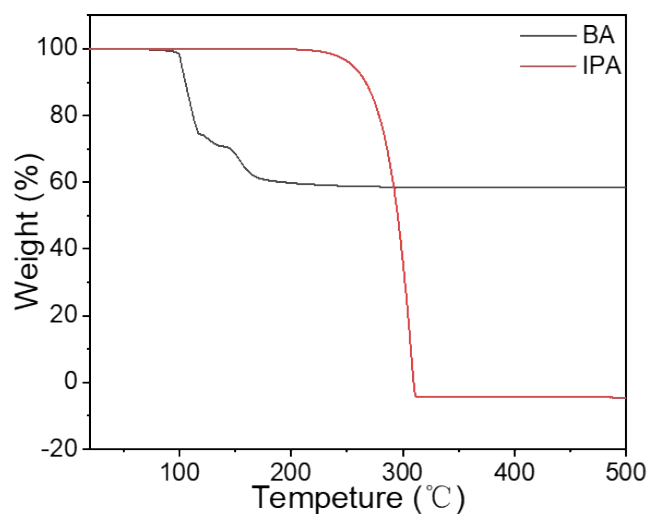


Fig. S1. TGA curve of IPA and BA. The thermogravimetric analysis (TGA) shows that the weight of IPA remains almost constant in the temperature range of 20 °C to 197 °C, indicating that there is basically no water in the IPA sample and its good thermal stability.¹ Subsequently, the quality decreased sharply as it was decomposed when the temperature is higher than 197 °C.² The weight of BA decreases sharply in the temperature range of 100 °C to 150 °C, reaching an equilibrium with 29.83 % of weight burned. This is due to the dehydration of boric acid to form metaborate acid (HBA). As the heating temperature increases, BA is further dehydrated and gradually converted to boron oxide. When the temperature is higher than 400 °C, BA is all converted to boron oxide.³

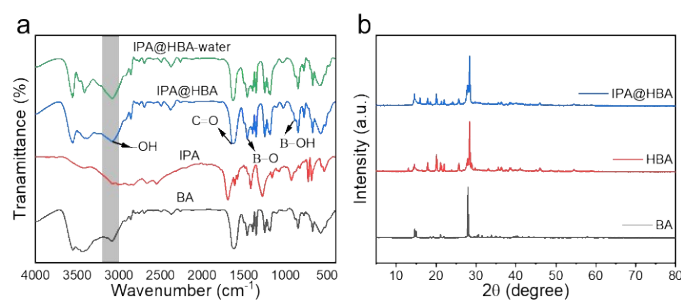


Fig. S2. (a) FTIR spectra of BA, IPA, IPA@HBA, IPA@HBA-water. (b) XRD patterns of inorganic BA, HBA, IPA@HBA.

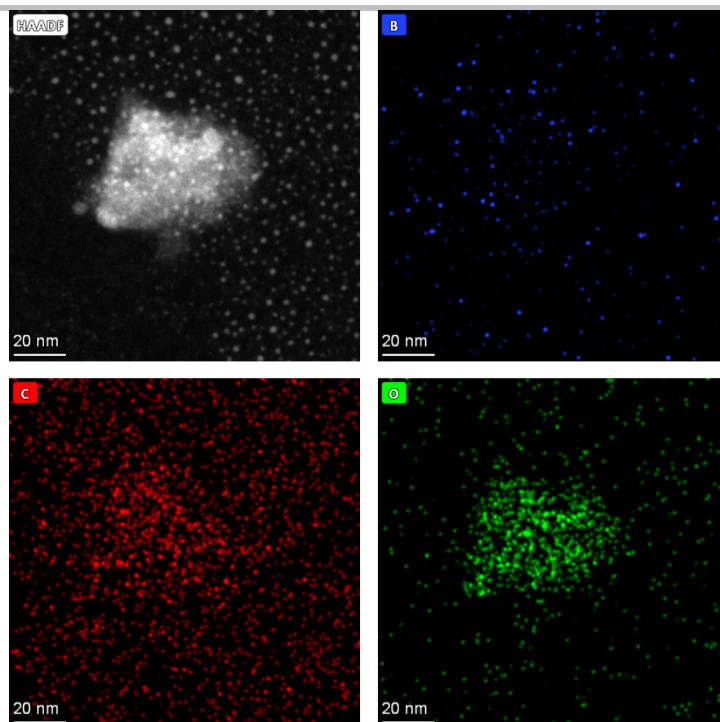


Fig. S3. EDX mapping of IPA@HBA particles.

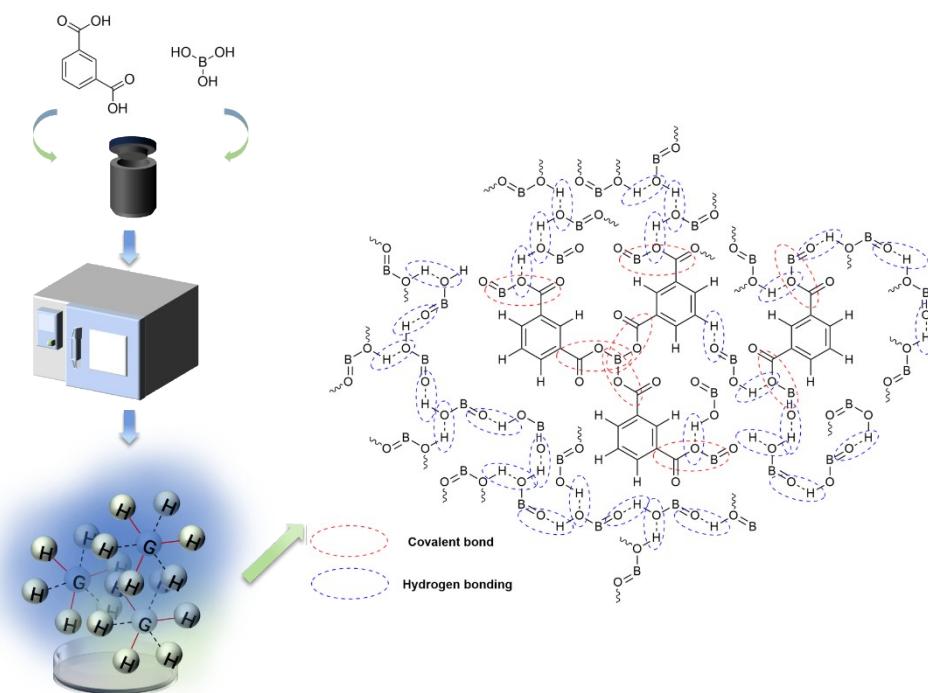


Fig. S4. Schematic diagram of synthesis and structure of host-guest composites.

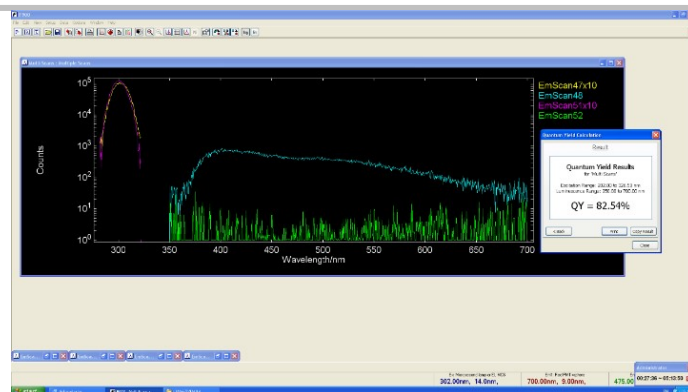


Fig. S5. The phosphorescence quantum yield of IPA@HBA excited by 302 nm.

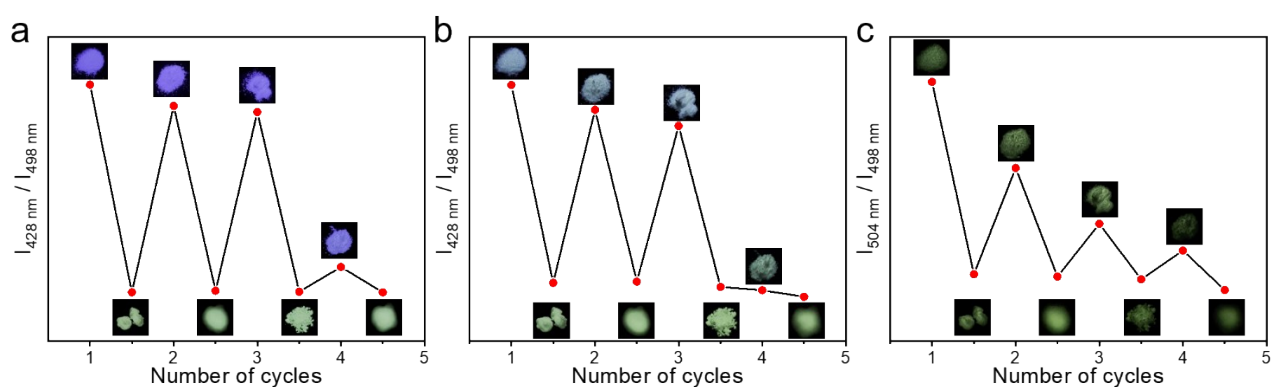


Fig. S6. IPA@HBA afterglow emission intensity ratio at 428 nm and 498 nm after adding water and heating excited at (a) 254, (b) 302 and (c) 365 nm.

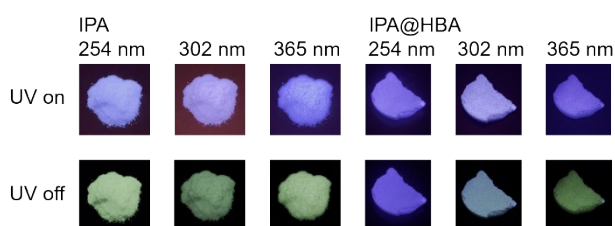


Fig. S7. Photo of IPA and IPA@HBA under UV on/off.

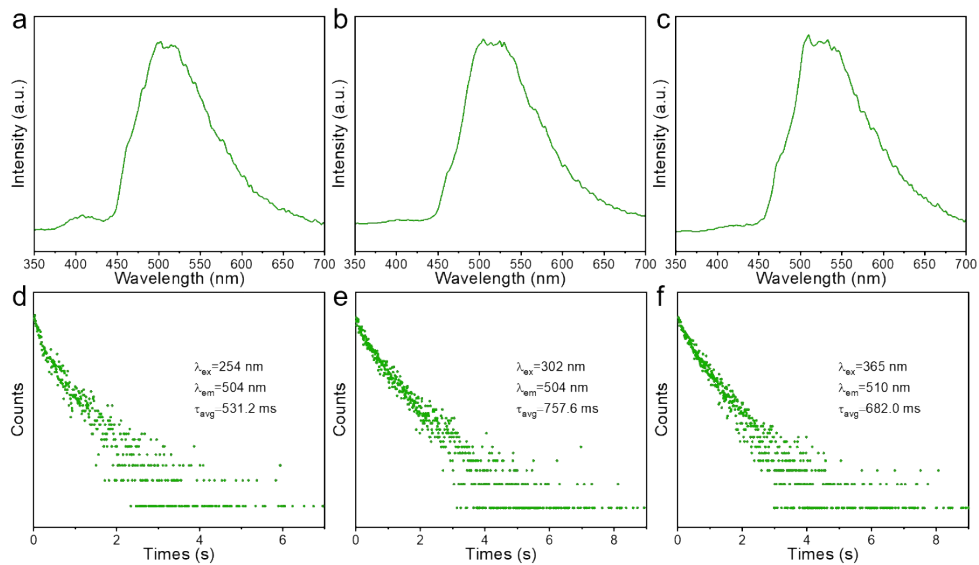


Fig. S8. Decay emission spectra of IPA excited at (a) 254, (b) 302 and (c) 365 nm, respectively. (d-f) Phosphorescence decay curves of IPA.

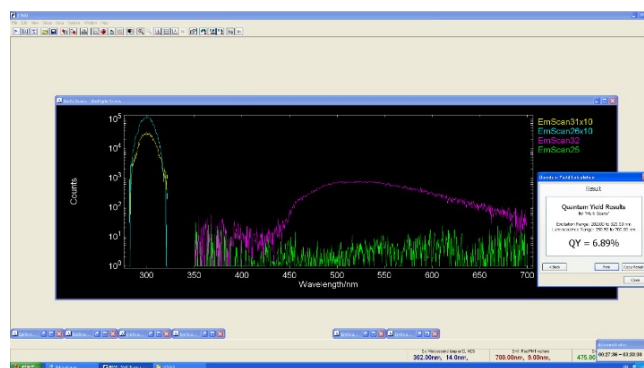


Fig. S9. The phosphorescence quantum yield of IPA excited by 302 nm.

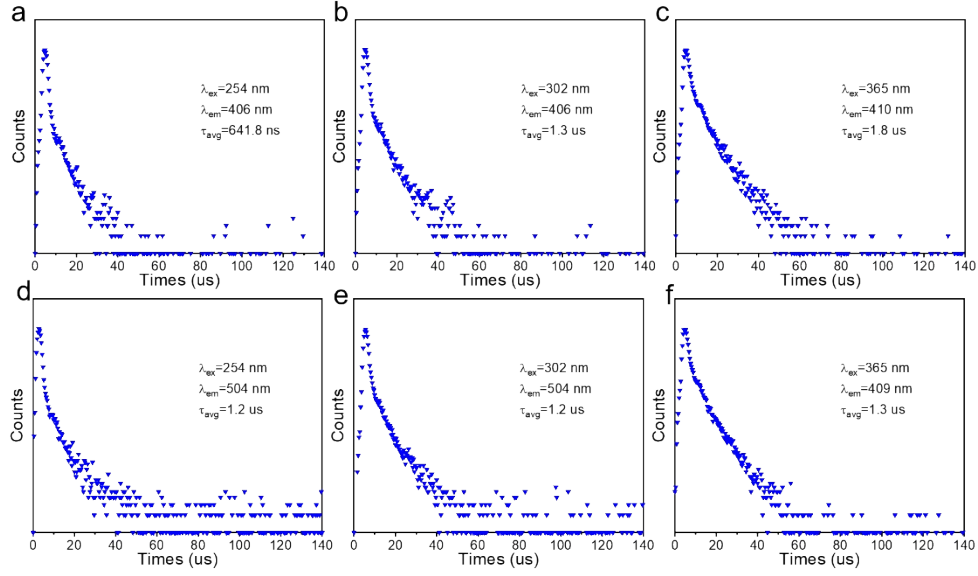


Fig. S10. Fluorescent decay curves of IPA and IPA@HBA excited at 254 (a, d), 302 (b, e) and 365 nm (c, f), respectively.

Table S1. Dynamic photophysical parameters of IPA and IPA@HBA.

	λ_{ex} (nm)	λ_{em} (nm)	Φ_{Phos} (%)	τ_{Phos} (ms)	τ_{Fluo} (us)	k_{nr}^{Phos} (s ⁻¹)[a]	k_{isc} (s ⁻¹)[b]	k_r^{Phos} (s ⁻¹)[c]
IPA	254	406	-	-	0.6	-	6.25×10^4	-
		504	3.75	531.2	-	1.81	-	7.06×10^{-2}
	302	406	-	-	1.3	-	5.3×10^4	-
		504	6.89	757.6	-	1.23	-	9.09×10^{-2}
IPA@HBA	254	412	-	-	1.2	-	2.95×10^5	-
		418	35.42	1071.9	-	0.60	-	0.330
	302	406	-	-	1.2	-	6.88×10^5	-
		428	82.54	1217.2	-	0.14	-	0.678

[a] $k_{nr}^{Phos} = (1 - \Phi_{Phos}) / \tau_{Phos}$. [b] $k_{isc} = \Phi_{Phos} / \tau_{Fluo}$. [c] $k_r^{Phos} = \Phi_{Phos} / \tau_{Phos}$

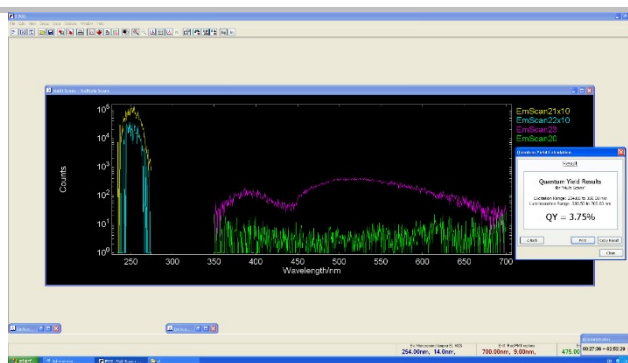


Fig. S11. The phosphorescence quantum yield of IPA excited by 254 nm.

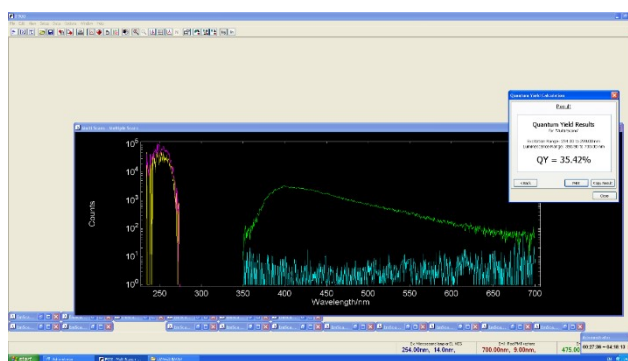


Fig. S12. The phosphorescence quantum yield of IPA@HBA excited by 254 nm.

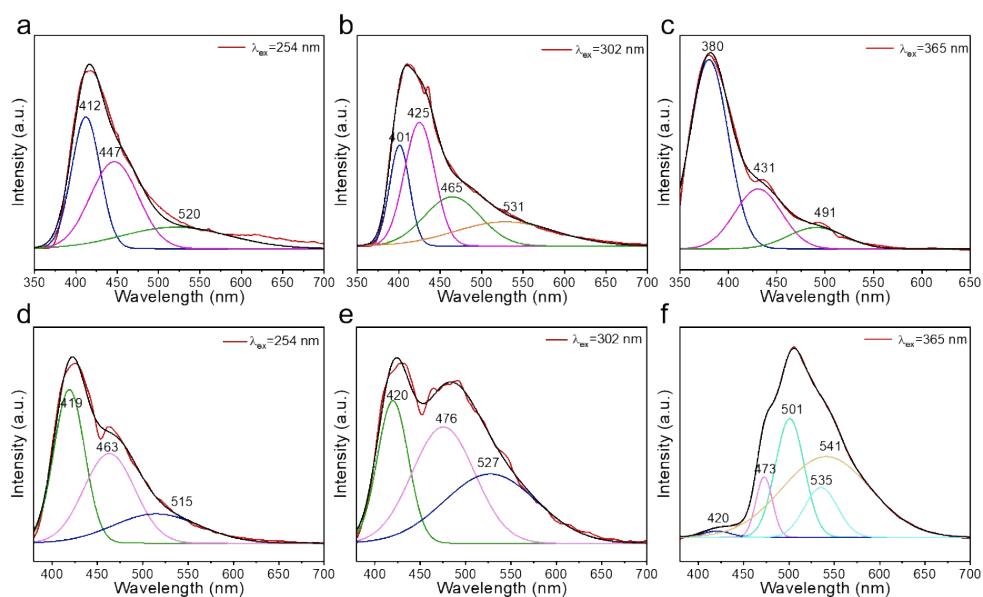


Fig. S13. The steady-state fluorescence spectrum (a, b, c) and afterglow spectrum (d, e, f) of IPA@HBA under excitation at 254 nm, 302 nm and 365 nm fitted by Gaussian function.

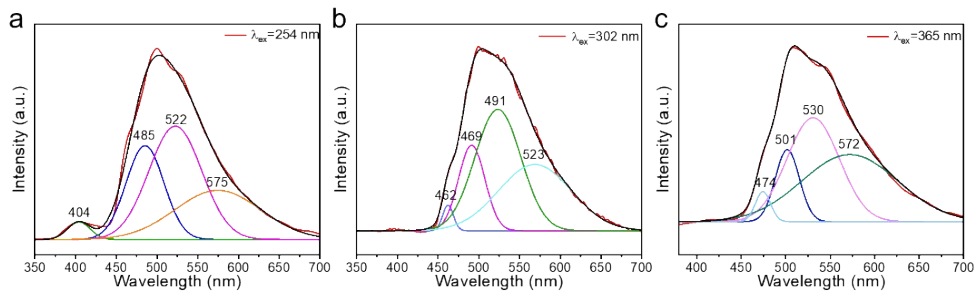


Fig. S14. The afterglow spectrum of IPA@HBA-water under excitation at a) 254 nm, b) 302 nm and c) 365 nm fitted by Gaussian function

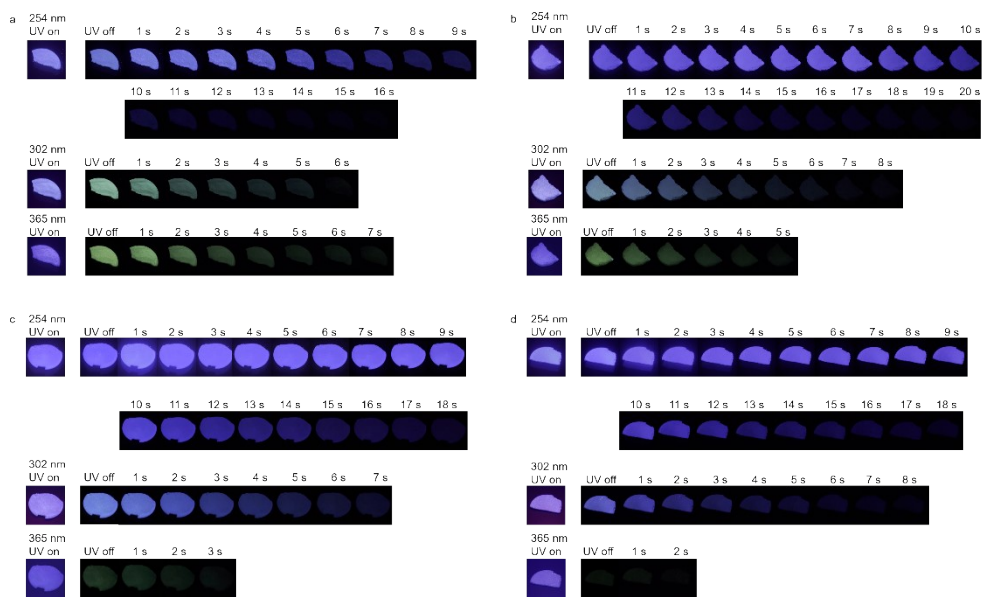


Fig. S15. Photo of IPA₁@HBA (a), IPA_{0.1}@HBA (b), IPA_{0.02}@HBA (c) and IPA_{0.01}@HBA (d) under UV on/off.

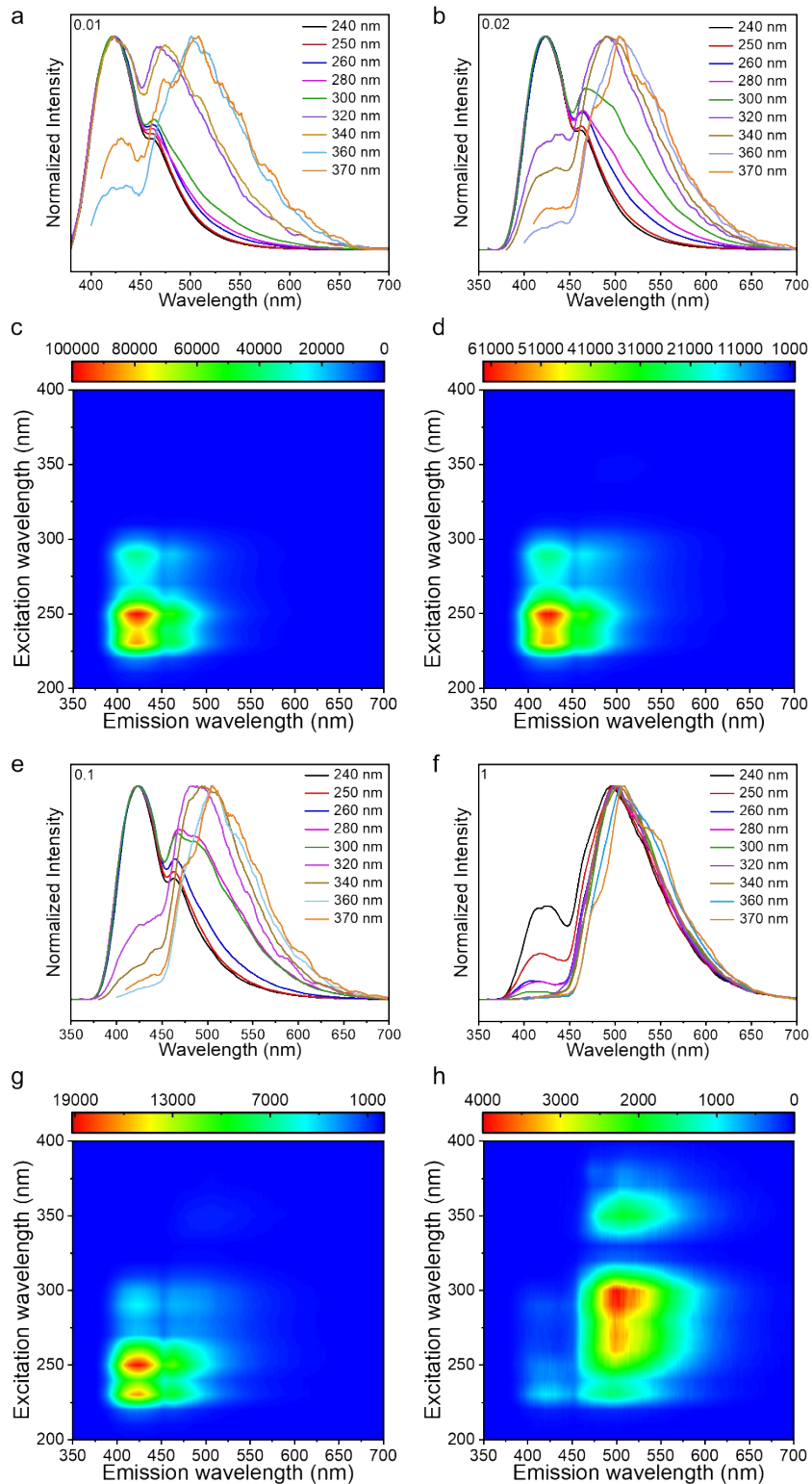


Fig. S16. (a, b, e, f) The delay emission spectra of $\text{IPA}_x\text{@HBA}$ ($x=0.01, 0.02, 0.1, 1$) upon different excitation wavelengths. (c, d, g, h) Excitation-phosphorescence emission mapping of $\text{IPA}_x\text{@HBA}$ ($x=0.01, 0.02, 0.1, 1$), respectively.

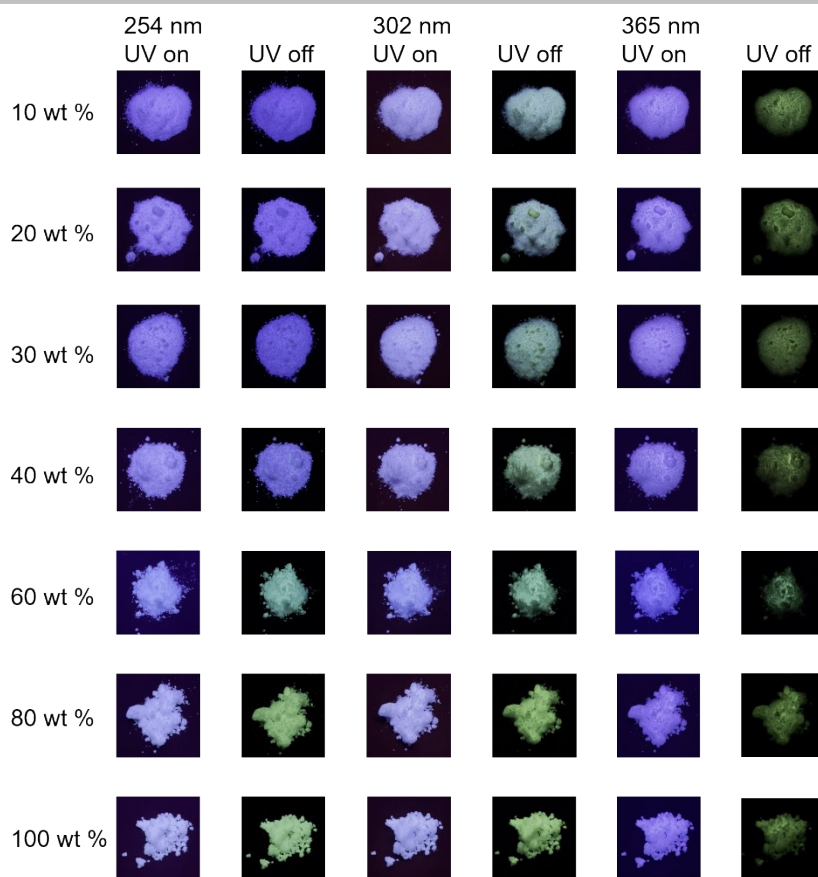


Fig. S17. Photo of IPA@HBA with different water content under UV on/off.

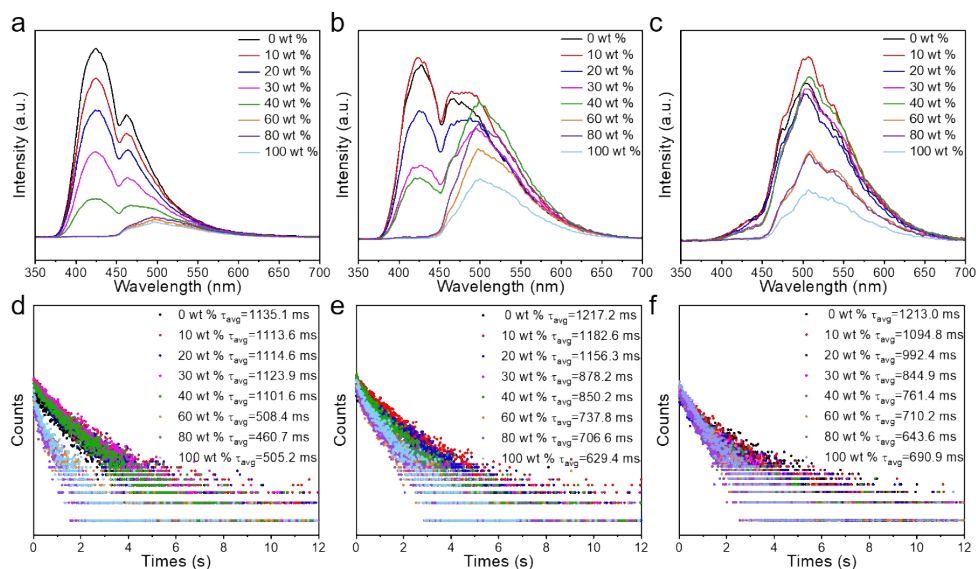


Fig. S18. Decay emission spectra (a, b, c) and phosphorescence decay curves (d, e, f) of IPA@HBA systems with different water contents at 254, 302 and 365 nm excitation, respectively.

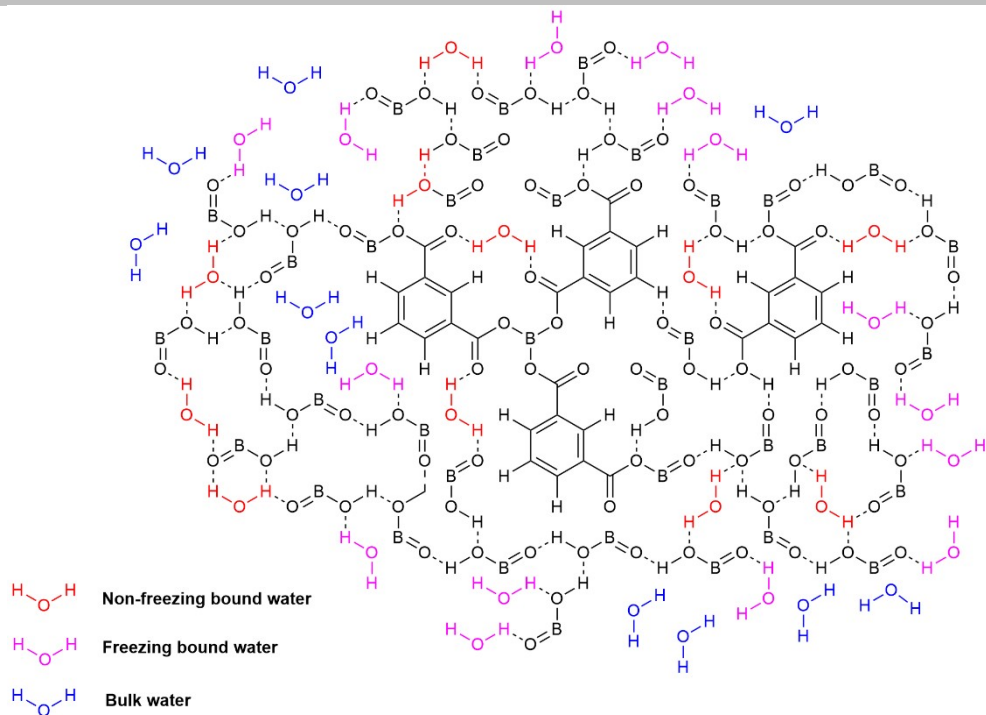


Fig. S19 Schematic illustration of the molecular interactions between IPA, HBA and water molecules.

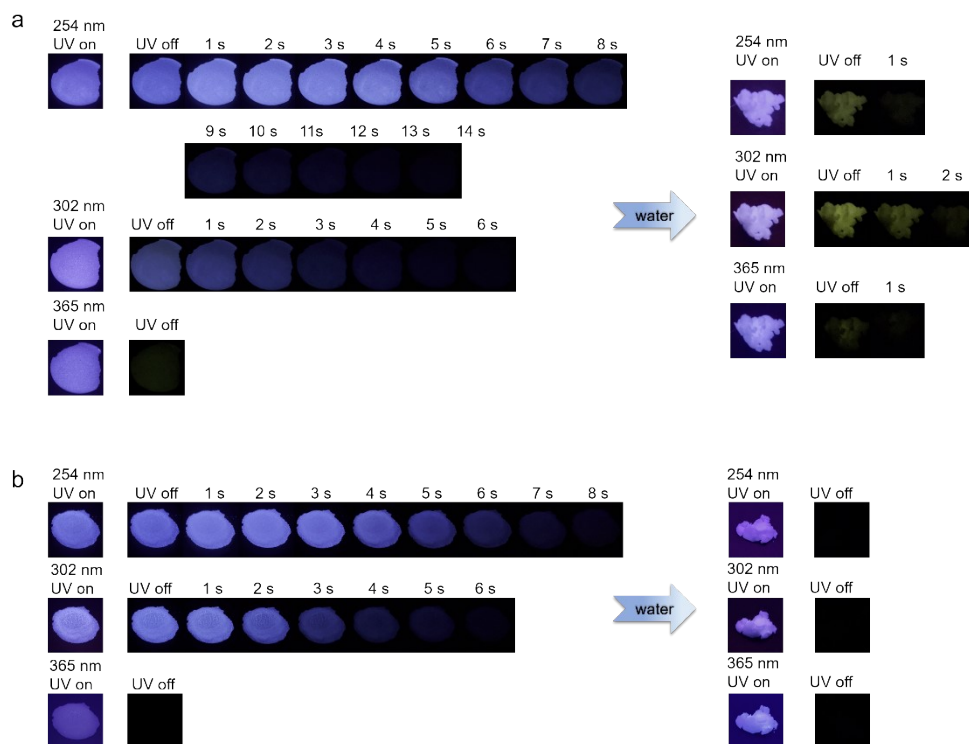


Fig. S20. Photo of TPA@HBA (a) and PA@HBA (b) under UV on/off before and after adding water

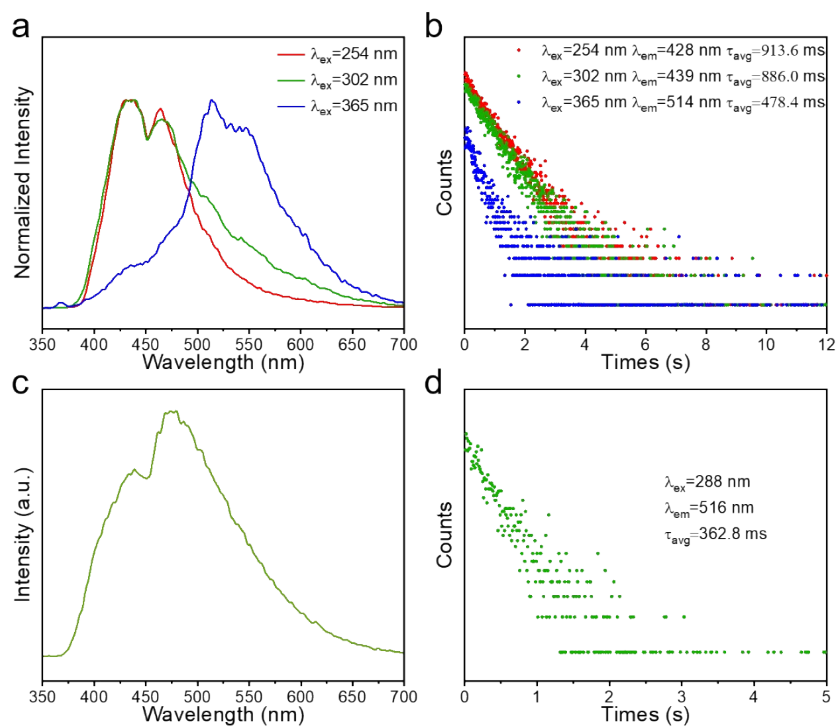


Fig. S21. Phosphorescence spectra (a, c) and lifetime decay curves (b, d) of TPA@HBA before and after water addition.

Rwference

1. Z. Z. Li, S. Cao, Y. Y. Zheng, L. Q. Song, H. C. Zhang, Y. L. Zhao, *Adv. Funct. Mater.* **2023**, DOI: 10.1002/adfm.202306956.
2. Y. Cheng, W. W. Fan, L. J. Wang, Y. X. Liu, S. X. Yang, Y. G. Shi, S. X. Liu, L. Y. Zheng, Q. E. Cao, *J. Mater. Chem. C* **2022**, 10, 8806-8814.
3. Z. Zhang, Y. E. Shi, Y. B. Liu, Y. F. Xing, D. Yi, Z. G. Wang, D. P. Yan, *Chem. Eng. J.* **2022**, 442, 136179.