Electronic supplementary information

# Metal-free 2D layered organic ammonium halide framework realizing full-color persistent room-temperature phosphorescence

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## Experimental

### Materials

1,8-Naphthyl anhydride (98%) were purchased from Shanghai Macklin Biochemical Corp. Phenylethylammonium chloride (99.5%) and phenylethylammonium bromide (99.5%) were obtained from Xi'an p-OLED. 2,3-Naphthalic anhydride (95%), *N*-Boc-ethylenediamine (98%), 1-naphthalene methylamine (98%), HBr (48 wt%, aqueous solution) and 3,4-methylenedioxyphenylamine (97%) were purchased from J&K Scientific LTD. Concentrated hydrochloric acid (36 wt.%, aqueous solution) were purchased from Sinopharm Chemistry Reagent Co. 1-Pyrene methylamine hydrochloride were purchased from Shanghai Tansoole. All reagents and solvents were used without further purification unless otherwise stated. BPAB, BPAC, NTAB, NTAC, NIAB, NIAC and NAAC were synthesized by the reported method.[1, 2]

### General Methods

NMR spectra were measured in DMSO on a Bruker Ascend 400 FT-NMR spectrometer. $^{1}$H NMR spectra were quoted relative to the internal standard tetramethylsilane. Absorption was obtained on a Shimadzu UV-2600 spectrophotometer. The crystalline structure of samples was confirmed by Powder Xray diffraction (PXRD) using a Rigaku Dmax 2500 diffractometer with Cu-Kα radiation (λ= 1.54056 Å) with a step size of 5°/min. Steady-state photoluminescence spectra and quantum yield of the samples were obtained at the room temperature using a Edinburgh FS5 spectrofluorometer with an integrating sphere for absolute photoluminescence quantum yield determination. Delay photoluminescent spectra and time-resolved photoluminescence decay curves were obtained using a FLS920 Fluorescence Spectrometer equipped with a xenon arc lamp (Xe900), a microsecond flash-lamp (μF900), and a nanosecond hydrogen flash-lamp (nF920). Thermal analyses were performed with a Mettler 851e analysis system. Single crystal structure was analysed by using an Agilent Technologies SuperNova single crystal diffractometer equipped with graphite monochromated Mo-Kα radiation.

**Synthesis of HLB (or HLC)**

Homopiperonylamine (0.7 mmol, 0.1 ml) was dissolved in 10 ml of ethyl acetate at room temperature, following by slowly adding 0.5 ml of HBr (or HCl) under stirring conditions. Then white precipitate was formed and separated to obtain HLB (or HLC) in a yield larger than 95%. $^{1}$H NMR (400 MHz, DMSO) δ 8.07 (s, 3H), 6.87 (d, J = 1.8 Hz, 1H), 6.84 (s, 1H), 6.71 (d, J = 9.4 Hz, 1H), 5.98 (s, 2H), 3.05 – 2.91 (m, 2H), 2.89 – 2.68 (m, 2H).

**Synthesis of doped HLB bromides**

HLB (25 mg) and a certain amount of guest ammonium salt were dissolved in 1 ml of ethanol, heated at 70 ℃ for half an hour, and cooled to obtain crystals. Then, the crystals were filtered and vacuum dried at 60 ℃ overnight.

**Synthesis of doped HLC chlorides**

HLC (20 mg) and a certain amount of guest ammonium salt were dissolved in 1 ml of ethanol, heated at 70 ℃ for half an hour, and cooled to obtain crystals. Filter and vacuum dry at 60 ℃ overnight.

**Synthesis of PEAB-BPAB**

PEAB (25 mg) and BPAB (1 mg) were dissolved in 1 ml of ethanol, heated at 70 ℃ for half an hour. Then the solution was placed under ether steam for 12 h to give crystal precipitate. The crystals were filtered and vacuum dried at 60 ℃ overnight.

**Synthesis of PEAC-BPAC**

PEAC (20 mg) and BPAC (1 mg) were dissolved in 1 ml of ethanol, heated at 70 ℃ for half an hour. Then the solution was placed under ether steam for 12 h to give crystal precipitate. The crystals were filtered and vacuum dried at 60 ℃ overnight.

**Production of anti-counterfeiting Ink**

25 mg of PEAB-BPAB, or 20 mg of HLC-NAAC, HLC-NIAC, HLC-PYAC were dissolved in 1 ml of ethanol, heated at 60 ℃ and stirred for 30 min for standby.

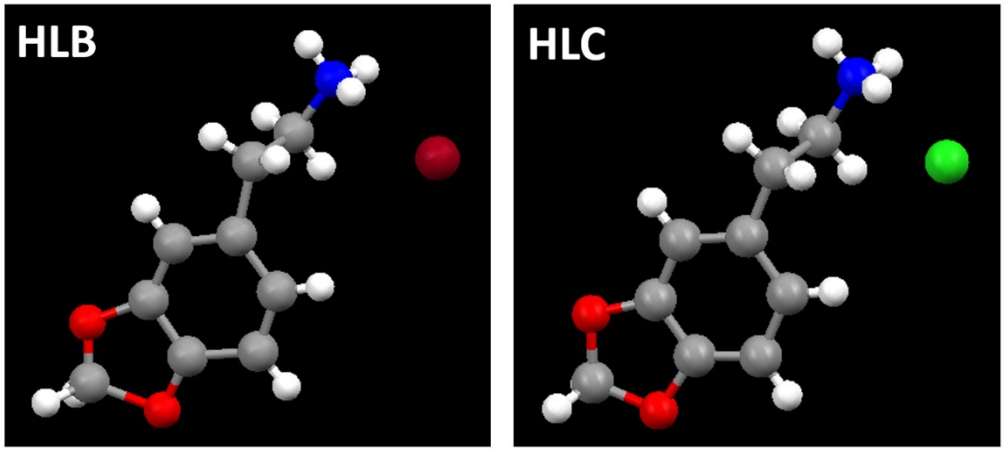


**Fig. S1** Molecular structure of HLB and HLC obtained by SC XRD.

**Table S1** Crystal data and structure refinement for TIM and TAD.

| Crystal | HLB | HLC |
|---|---|---|
| Formula | $C_9H_{13}BrNO_2$ | $C_{18}H_{24}Cl_2N_2O_4$ |
| Formula weight | 247.11 | 403.29 |
| Shape | needle | needle |
| Crystal system | orthorhombic | orthorhombic |
| Space group | P 2c -2n | P 2c -2b |
| a (Å) | 35.8606(14) | 5.97246(16) |
| b (Å) | 4.54960(10) | 9.0205(2) |
| c (Å) | 6.1929(3) | 36.0997(9) |
| α(deg) | 90.00 | 90.00 |
| β(deg) | 90.00 | 90.00 |
| γ(deg) | 90.00 | 90.00 |
| V ($Å^3$) | 1010.38(7) | 1944.86(9) |
| Z | 4 | 4 |
| $D_{calcd.}(g/cm^3)$ | 1.625 | 1.353 |
| F(000) | 500 | 848 |
| R (int) | 0.0458 | 0.0345 |
| GOF on $F^2$ | 1.122 | 1.071 |
| R1[I > 2σ(I)] | 0.0512 | 0.0884 |
| wR2 [I>2σ(I)] | 0.1359 | 0.2492 |
| R1 (all data) | 0.0677 | 0.0910 |
| wR2 (all data) | 0.1516 | 0.2533 |

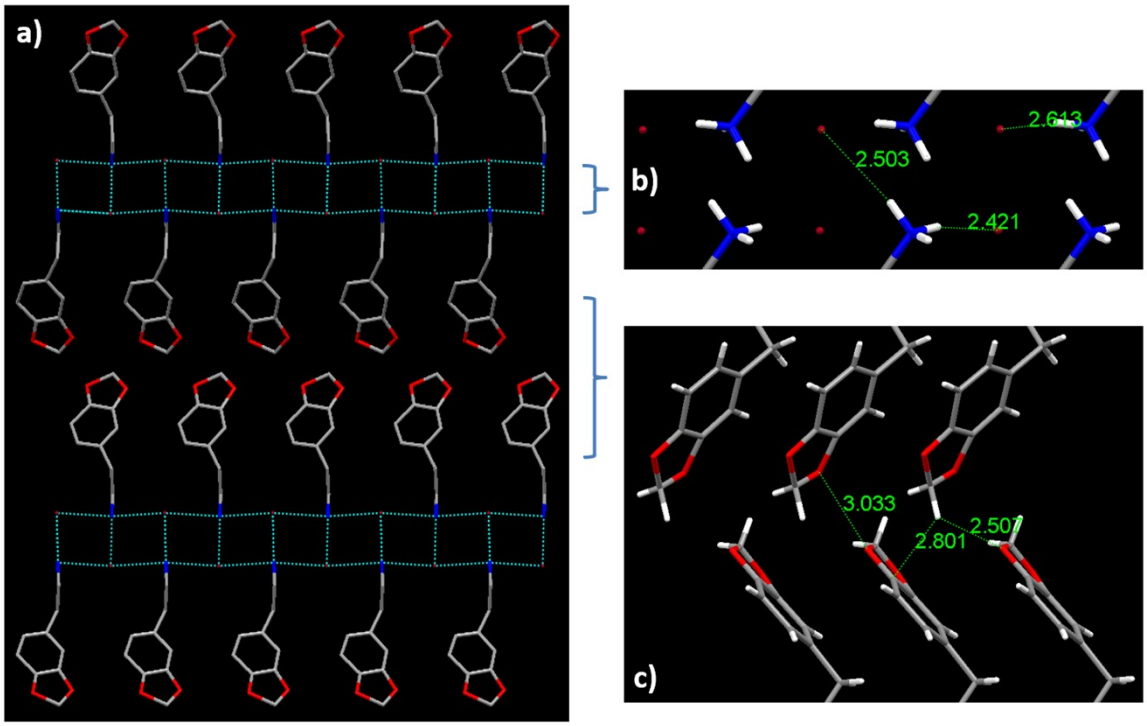


**Fig. S2** (a) 2D layered structure of HLB viewing from b axis. (b) H-bonding interactions in ammonium salt layers. (c) Intermolecular weak interactions between organic layers.

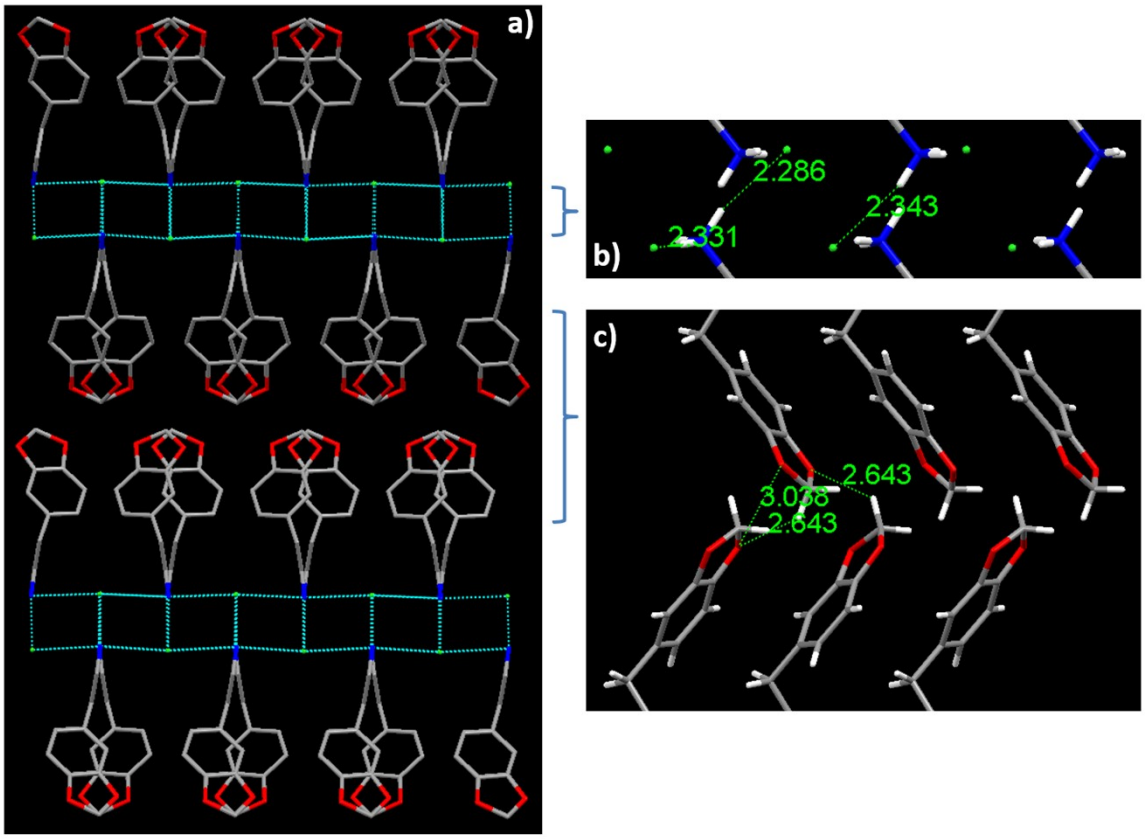


**Fig. S3** (a) 2D layered structure of HLC viewing from b axis. (b) H-bonding interactions in ammonium salt layers. (c) Intermolecular weak interactions between organic layers.

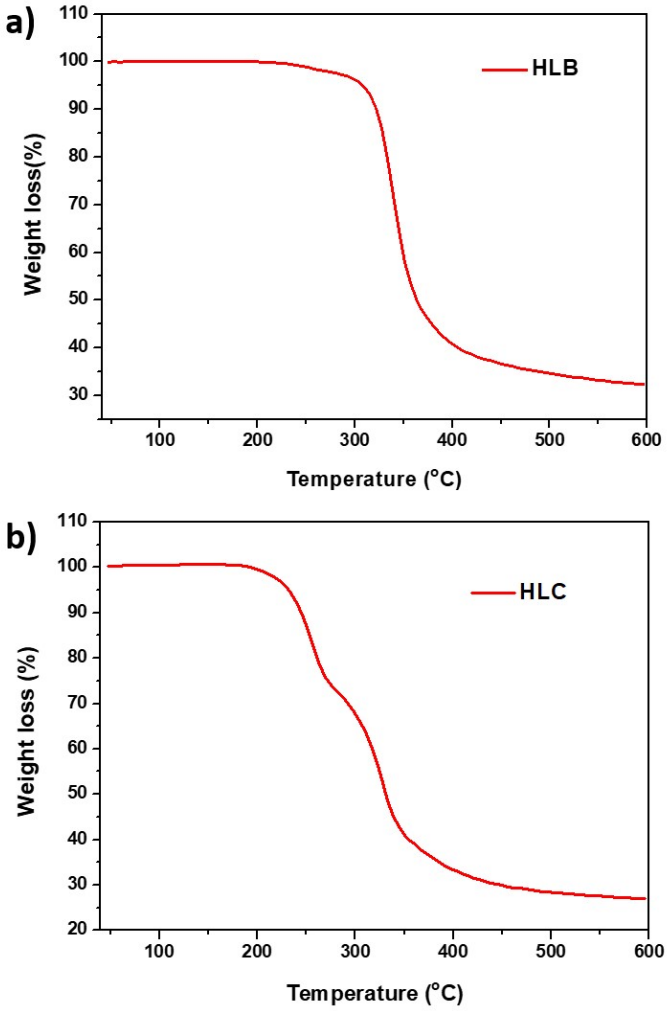


**Fig. S4** Thermogravimetric curves of HLB and HLC.

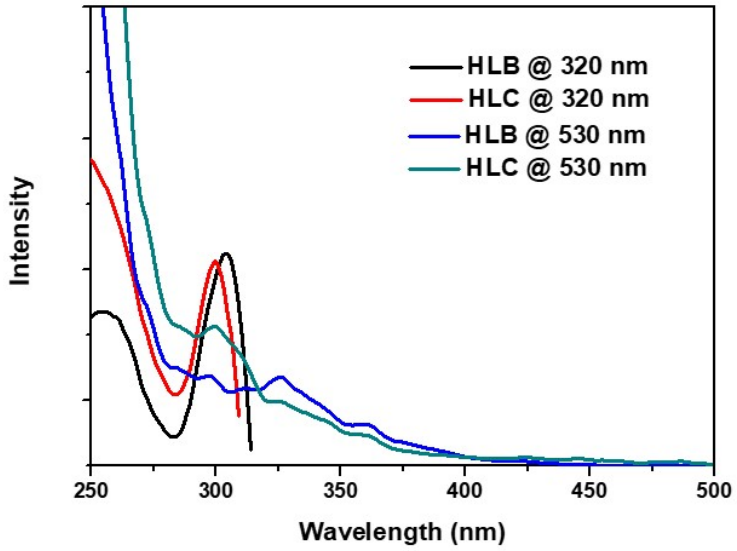


**Fig. S5** Excitation spectra of HLB and HLC crystals monitored at 320 nm and 530 nm.

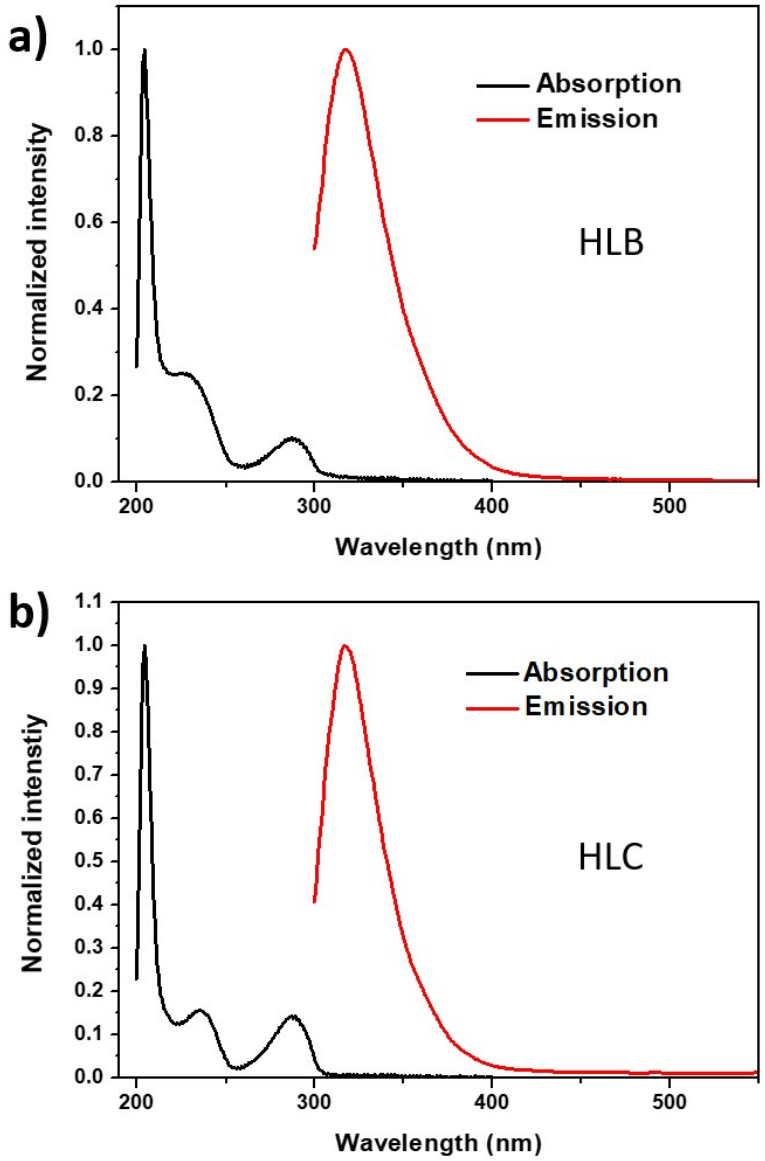


**Fig. S6** Absorption and emission of HLB (a) and HLC (b) in ethanol solution ($1\times10^{-5}$ M).

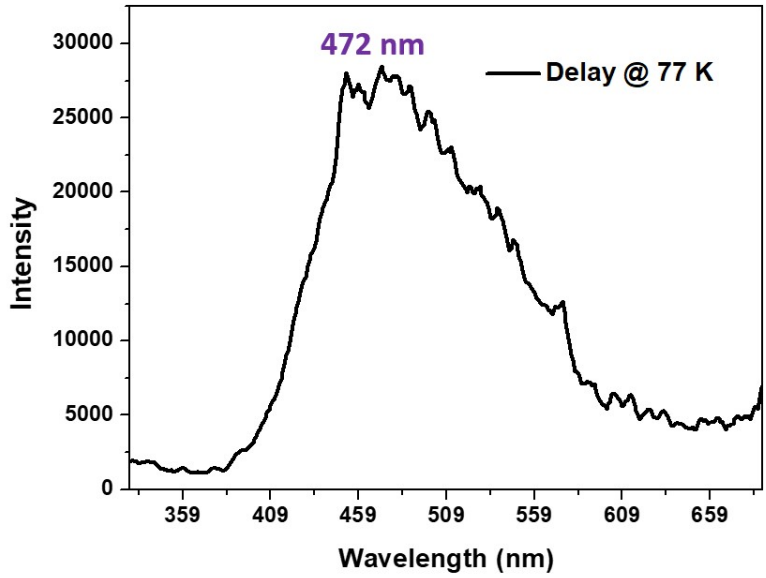


**Fig. S7** Delay emission spectrum of HLB dilution ($1\times10^{-5}$ M) in ethanol at 77 K.

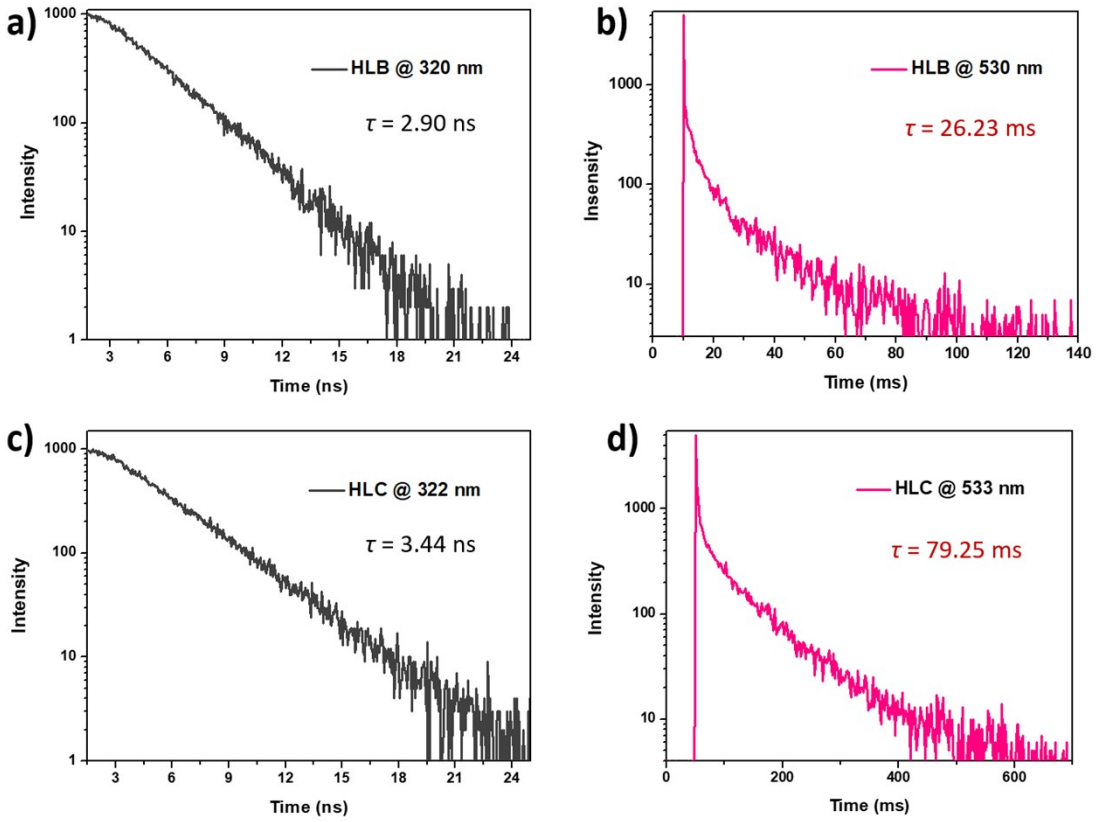


**Fig. S8** Transient luminescent decay plots of HLB (a, b) and HLC (c, d) crystals.

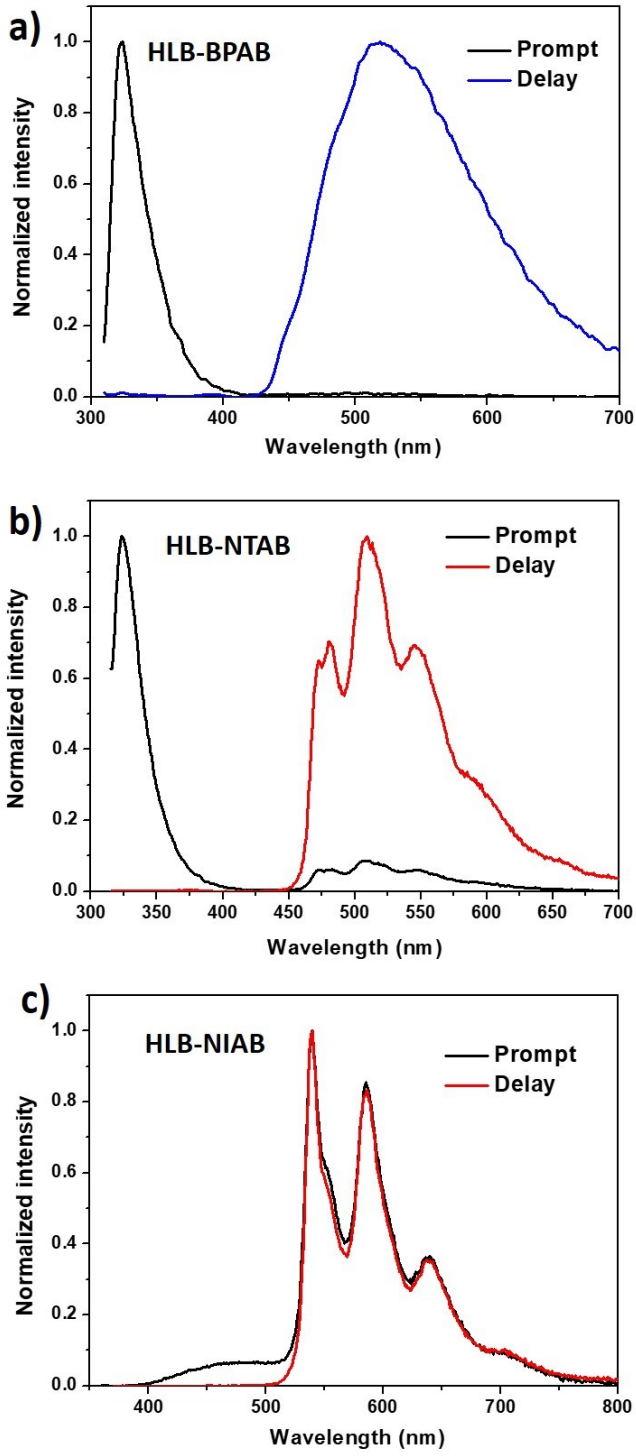


**Fig. S9** Prompt and delay emission spectra of HLB-BPAB (a), HLB-NTAB (b), and HLB-NIAB (c).

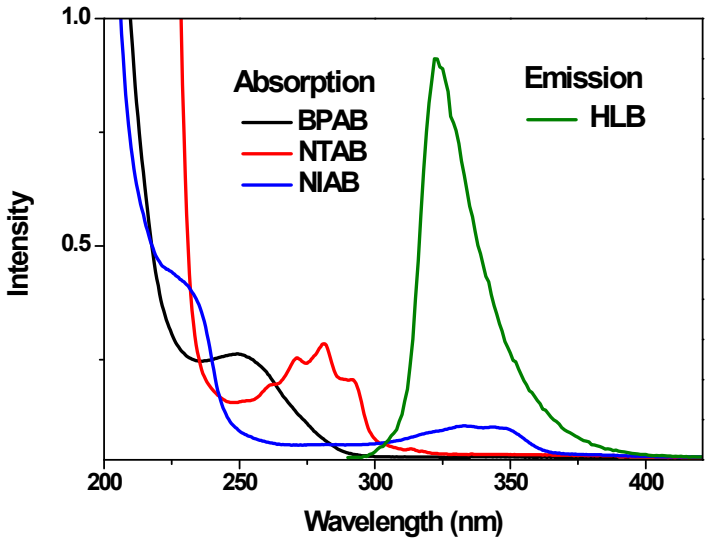


**Fig. S10** Emission spectrum of HLB, and absorption spectra of BPAB, NTAB, and NIAB.

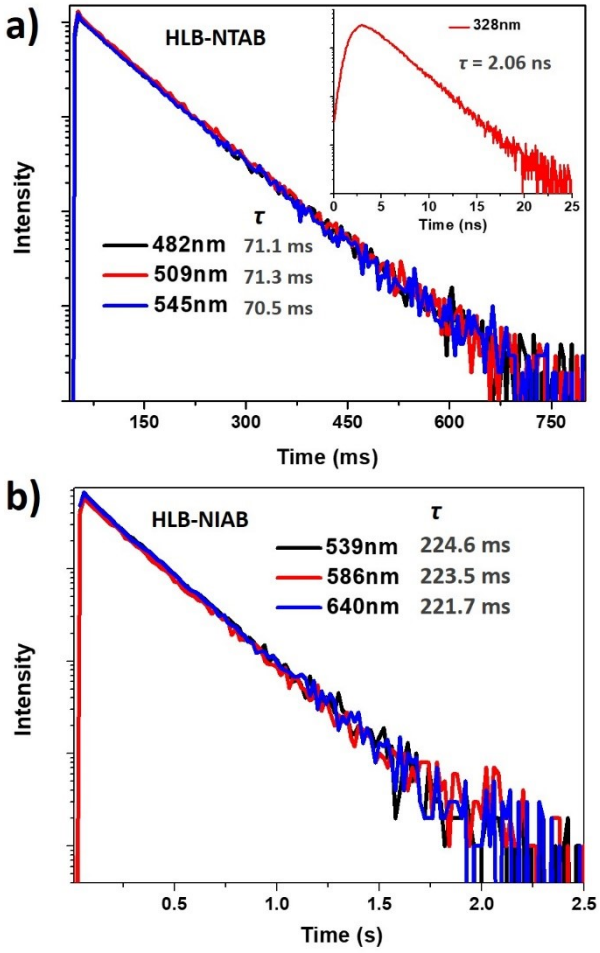


**Fig. S11** Transient luminescent decay plots of HLB-NTAB (a) and HLB-NIAB (b).

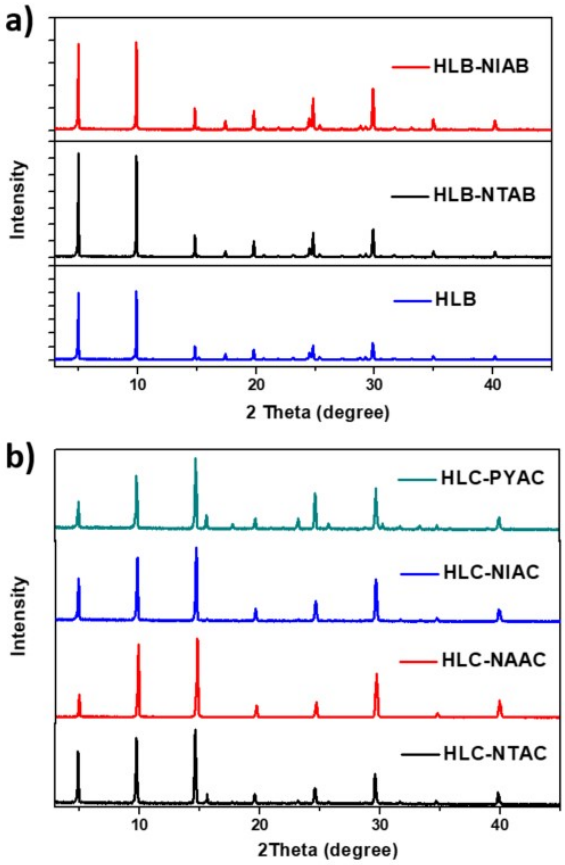


**Fig. S12** a) Experimental PXRD pattern of HLB-NTAB and HLB-NIAB. b) Experimental PXRD pattern of HLC-NTAC, HLC-NAAC, HLC-NIAC and HLC-PYAC.

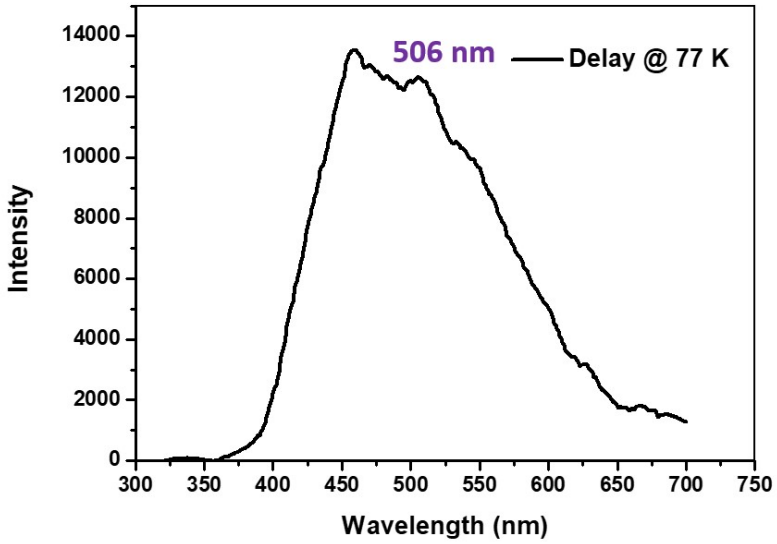


**Fig. S13** Delay emission spectrum of NTAB dilution ($1\times10^{-5}$ M) in ethanol at 77 K.

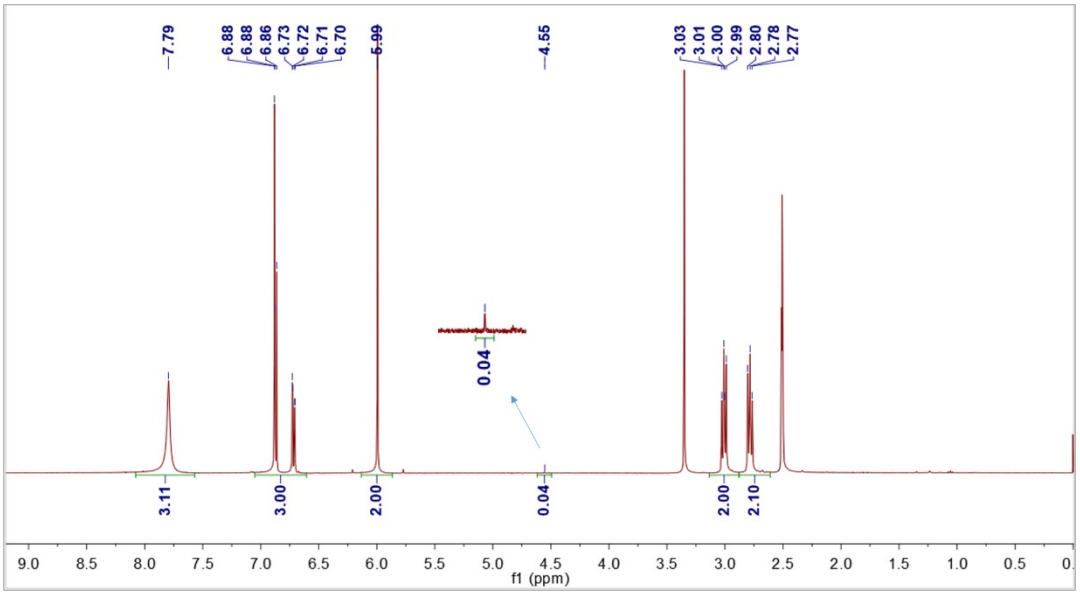


**Fig. S14** $^{1}$H NMR of HLB-NTAB with the theory doping ratio of 37.5% in *d*-DMSO.

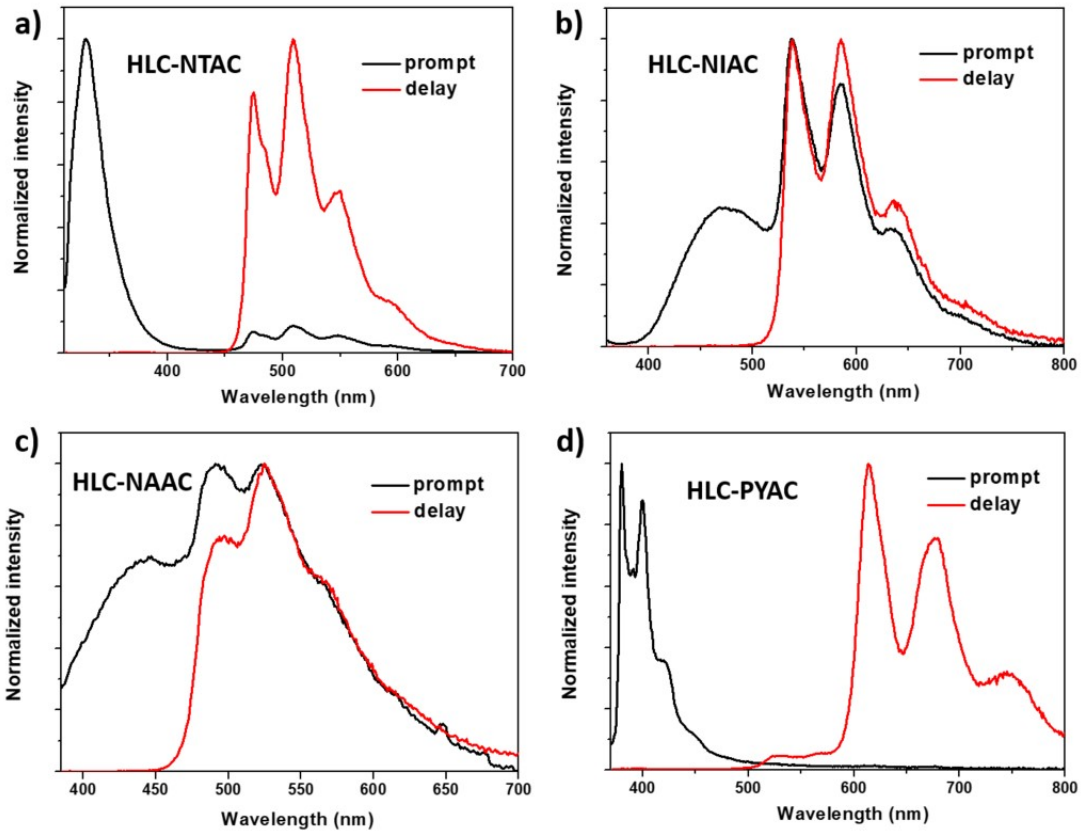


**Fig. S15** Prompt and delay emission spectra of HLC-NTAC (a), HLC-NIAC (b), HLC-NAAC (c) and HLC-PYAC (d).

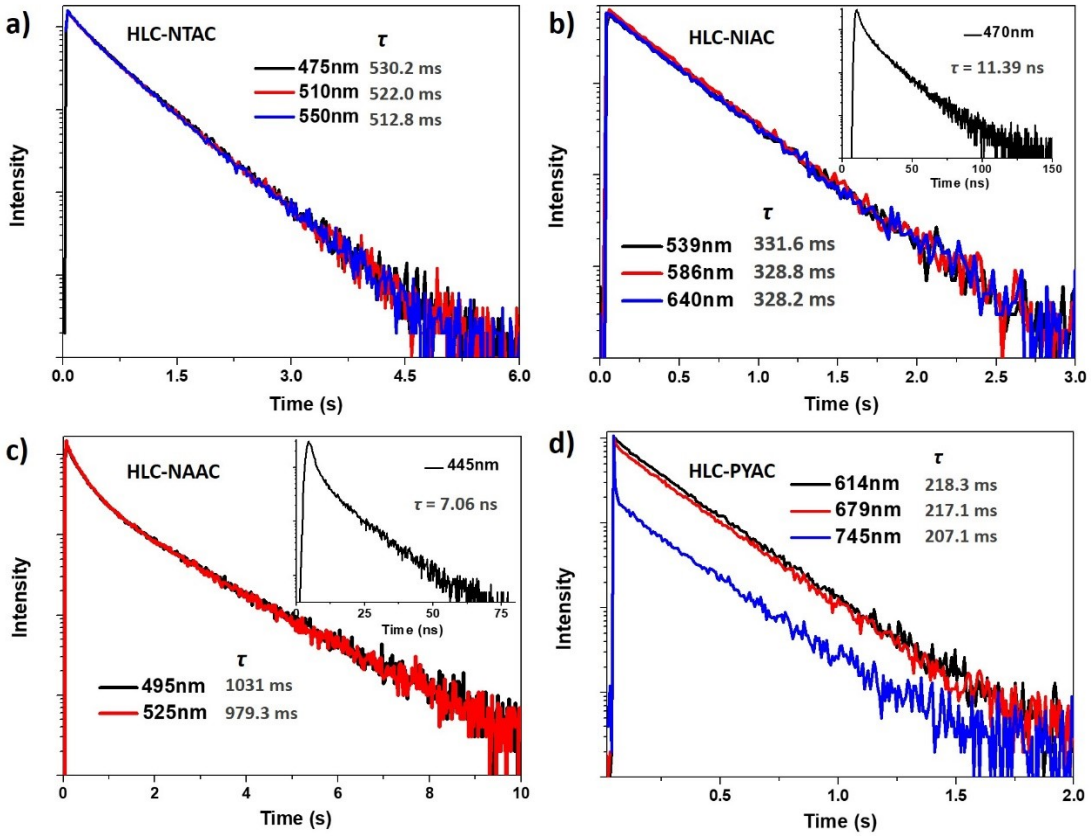


**Fig. S16** Transient luminescent decay plots of HLC-NTAC (a), HLC-NIAC (b), HLC-NAAC (c) and HLC-PYAC (d).

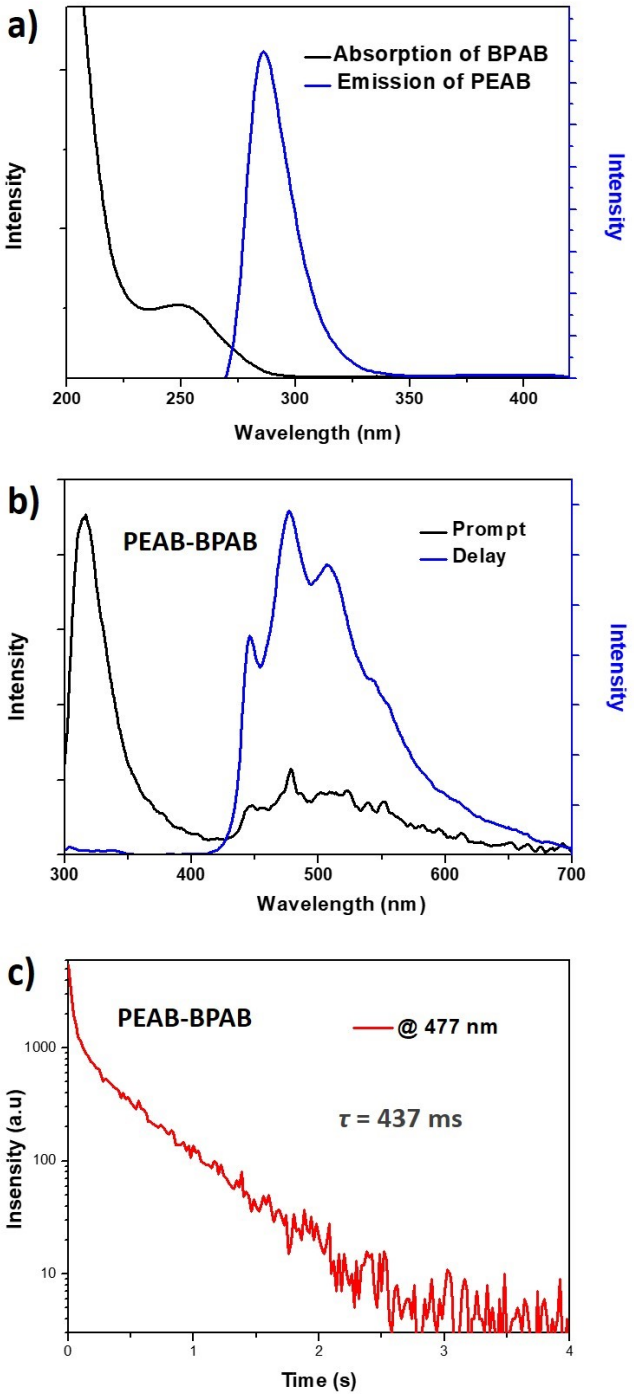


**Fig. S17** a) Absorption spectrum of BPAB, and emission spectrum of PEAB. b) Prompt and delay emission spectra of PEAB-BPAB. b) Transient luminescent decay plots of PEAB-BPAB monitored at 477 nm.

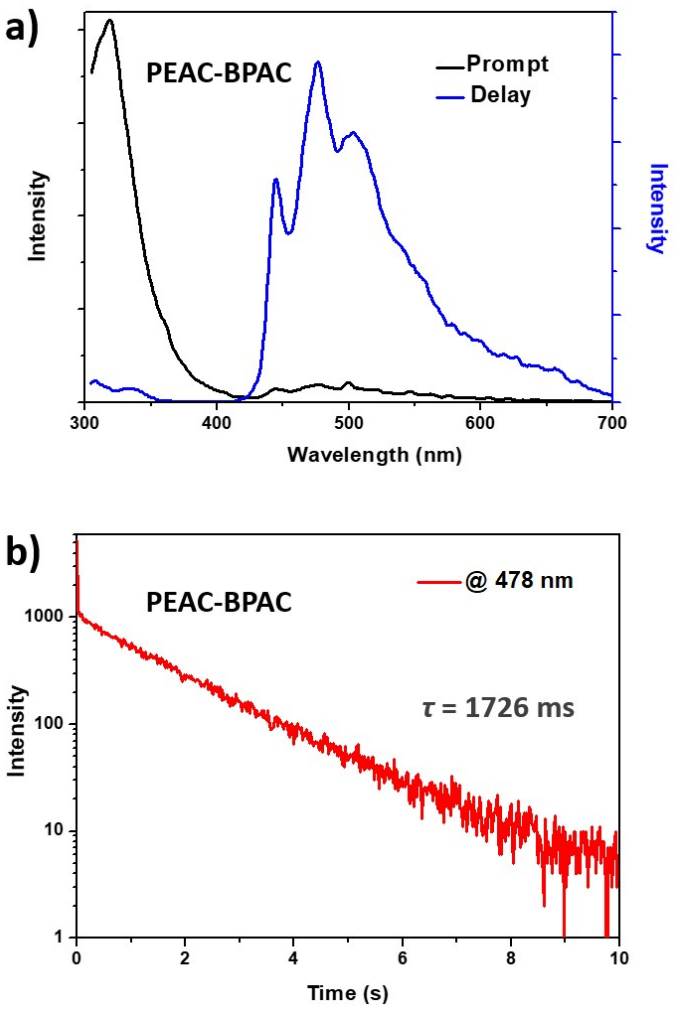


**Fig. S18** a) Prompt and delay emission spectra of PEAC-BPAC. b) Transient luminescent decay plots of PEAC-BPAC monitored at 478 nm.

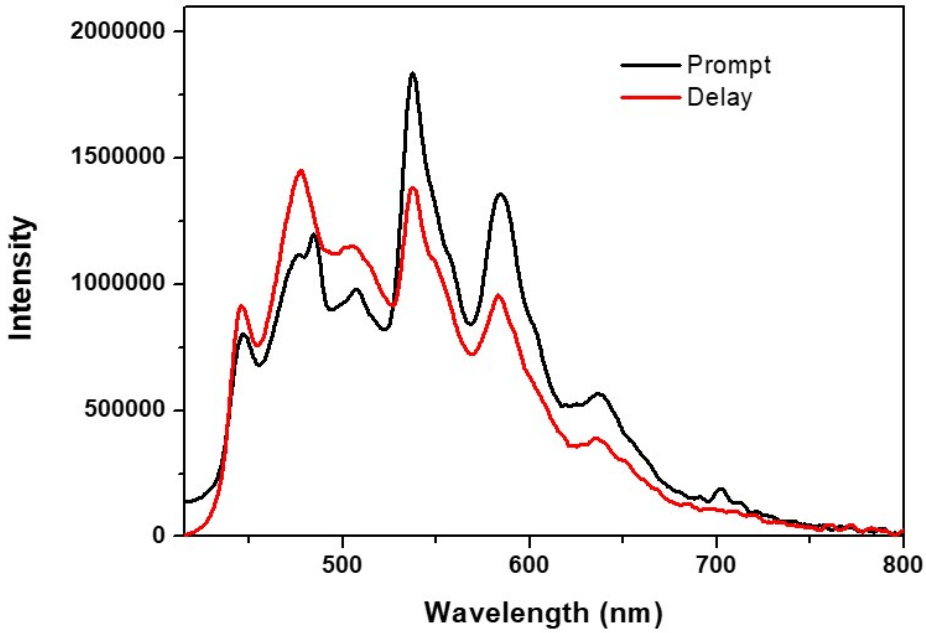


**Fig. S19** Prompt and delay emission spectra of PEAB-BPAB-NIAC.

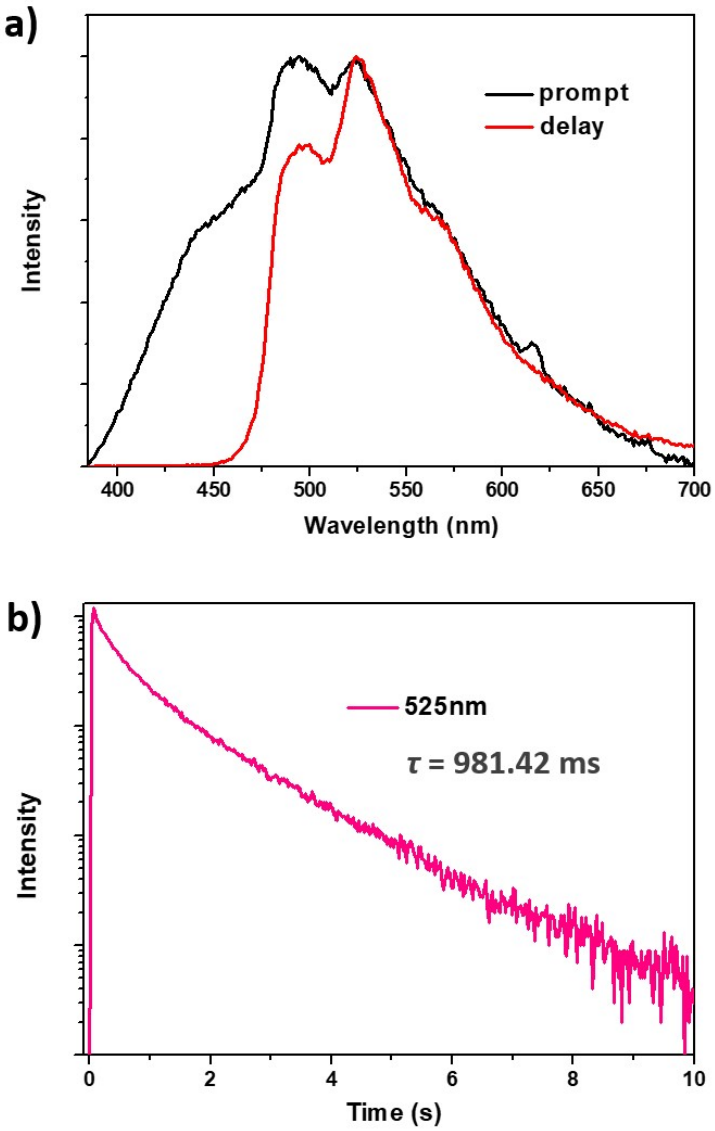


**Fig. S20** a) Prompt and delay emission spectra of large-scale (11g) HLC-NAAC. b) Transient luminescent decay plots of large-scale (11g) HLC-NAAC monitored at 525 nm.

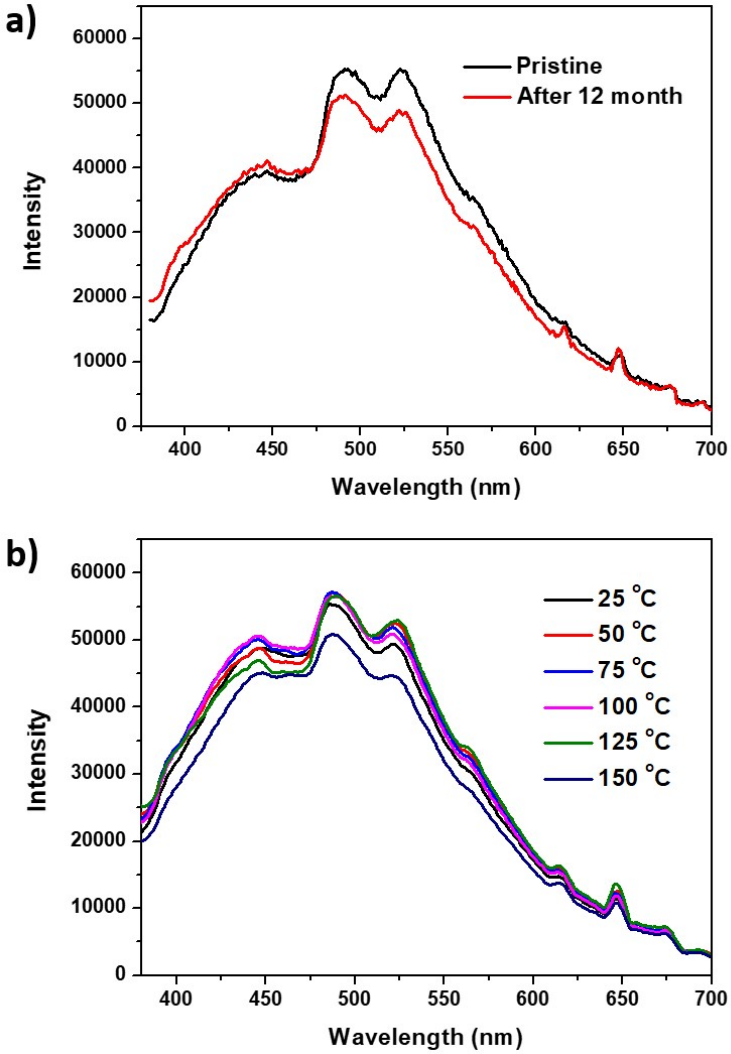


**Fig. S21** (a) Emission spectra changes of HLC-NAAC sample before and after preserved for 12 months at air. (b) Emission spectra of HLC-NAAC under different temperature.

## References


1 S. Yang, D. Wu, W. Gong, Q. Huang, H. Zhen, Q. Ling and Z. Lin, *Chemical Science*, 2018, **9**, 8975-8981.

2 H. Hu, D. Zhao, Y. Gao, X. Qiao, T. Salim, B. Chen, E. E. M. Chia, A. C. Grimsdale and Y. M. Lam, *Chemistry of Materials*, 2019, **31**, 2597-2602.