Supporting information

Thermally controlling the intra- and intermolecular proton transfer reaction: a distinct gateway to luminescent switching

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1、Experimental Section

Materials. 2-(2-hydroxyphenyl)benzothiazole (HBT) was prepared according the literature reported before.[1] Stearyl alcohol, imidazole (IM), 4-dimethylaminopyridine (DMAP), 2-aminopyridine (NH_2-PY) and piperazine (PPZ) were purchased from Energy Chemical (Shanghai, China). Unless otherwise noted, all the other materials were purchased from Beijing Chemical (Beijing, China) without further purification.

Instruments. Absorption spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer. Steady state fluorescence spectra were measured using a Shimadzu RF-5301 PC spectrophotometer. Fluorescence images were recorded under UV irradiation at an excitation wavelength of 365 nm. Dierential scanning calorimetry was measured using NETZSCH DSC 204 under pure nitrogen gas with the heating and cooling rates both set to 10 °C min^{-1}. Variable temperature fluorescence emission spectra were measured on Edinburgh FLS 980 steady state spectrometer. The fluorescence quantum yields (Φ_f) and fluorescence lifetimes were measured on Edinburgh FLS 920 steady state spectrometer.

Preparation of binary systems of HBT-NH_2-PY, HBT-DMAP, HBT-PPZ and HBT-IM. The blend systems were prepared by dissolving the HBT in molten imidazole (IM), 4-dimethylaminopyridine (DMAP), 2-aminopyridine (NH_2-PY) and piperazine (PPZ).

The fluorescence measurement for solid samples. Unless otherwise noted, the blend samples were loaded in 1 mm thick cuvettes for the fluorescence measurement at room temperature and high temperature.

2、Supplementary Figures

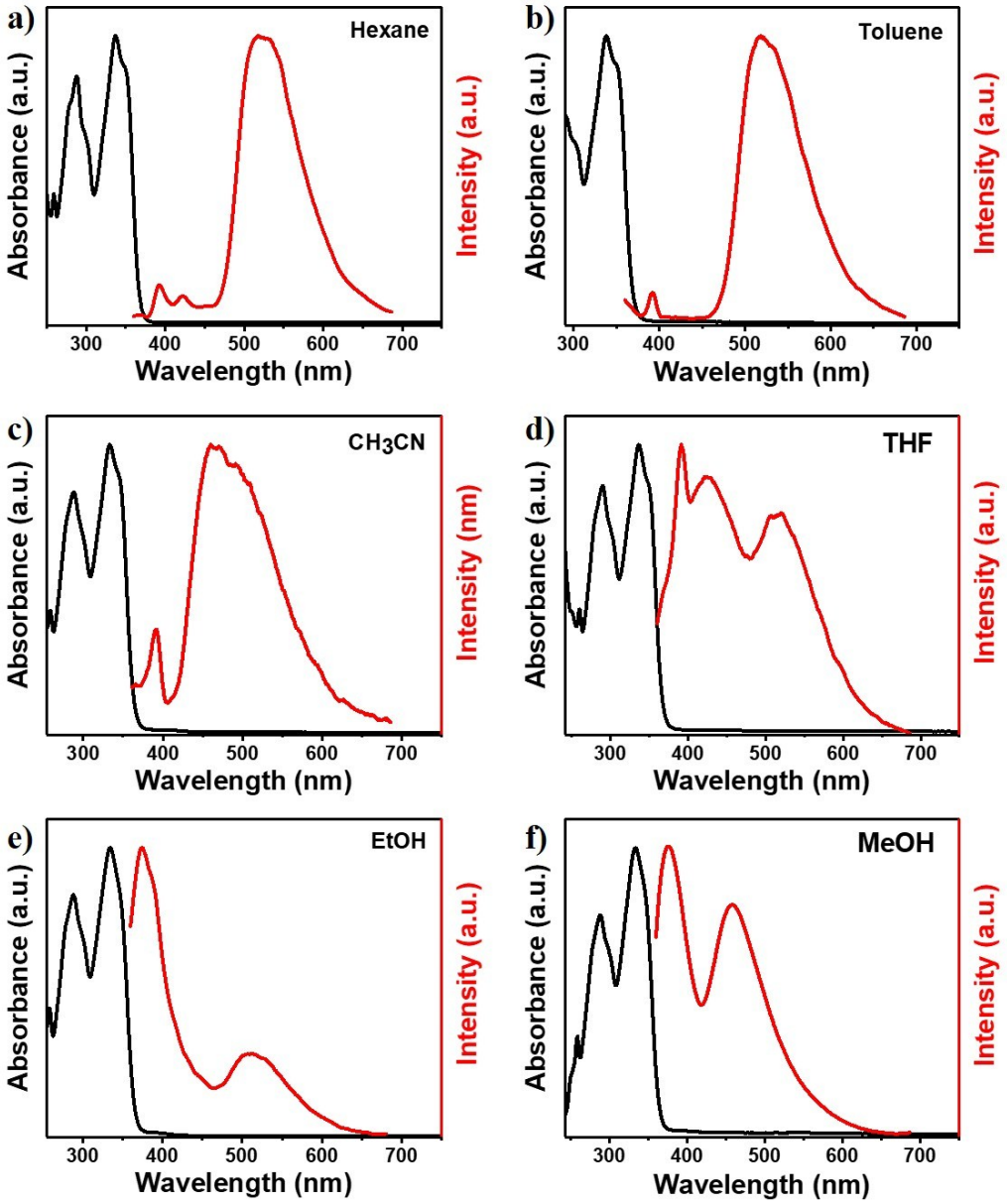

Fig. S1 UV-vis absorption (black line) and Fluorescence emission (red line) spectra of HBT in (a) hexane, (b) toluene, (c) CH_3CN, (d) THF, (e) EtOH and (f) MeOH. λex = 350 nm; slit width (5 nm, 5 nm); C (HBT) = 1.0×10^{-5} M.

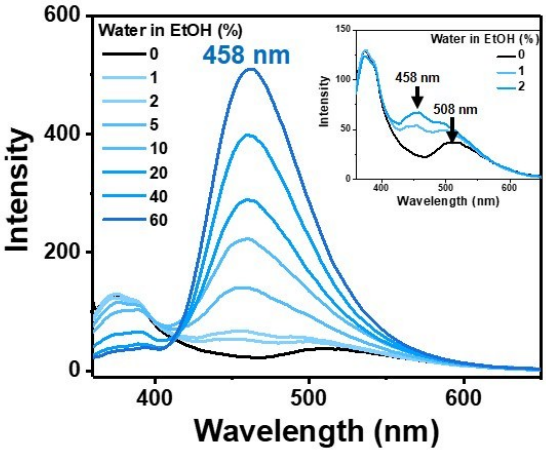

Fig.S2 Fluorescence emission spectra of HBT in ethanol with different content of water (0 to 60 %). Insert: Fluorescence emission spectra of HBT in ethanol with different content of water (0 to 2 %). λex = 350 nm; slit width (5 nm, 5 nm); C = 1.0×10^{-5} M.

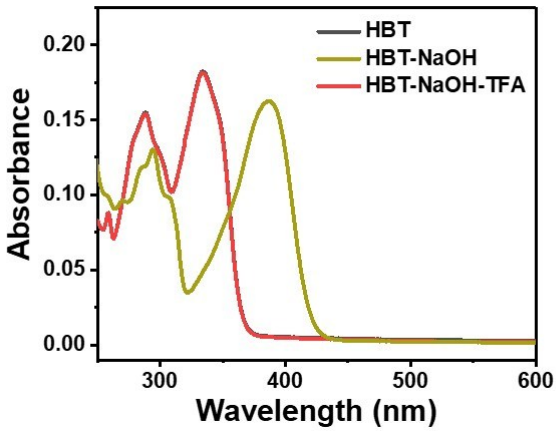

Fig. S3 UV-vis absorption spectra of HBT in ethanol upon addition of NaOH, and then neutralized with trifluoroacetic acid (TFA). C = 1.0×10^{-5} M.

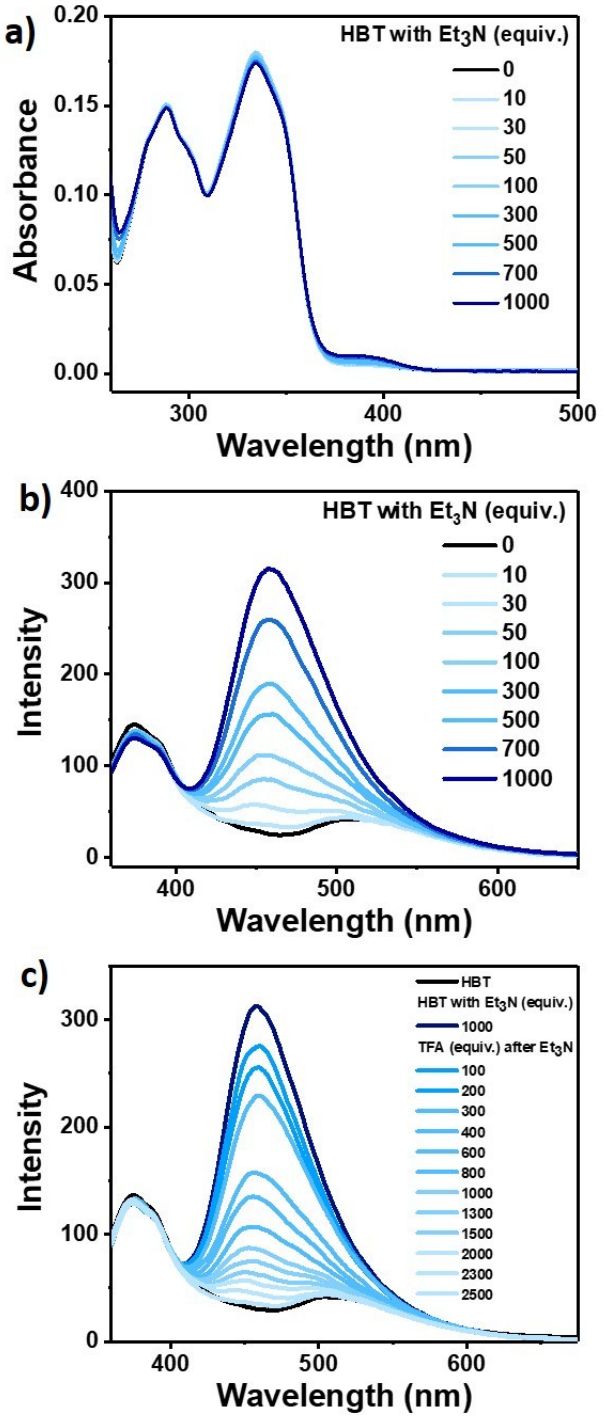

Fig. S4 (a) UV-vis absorption and (b) Fluorescence emission pectra of HBT upon gradually addition of Et_3N in ethanol. (c) Fluorescence emission spectra for HBT after adding Et_3N and then adding TFA after Et_3N treatment. λex = 350 nm; slit width (5 nm, 5 nm); C = 1.0×10^{-5} M in ethanol.

Table S1. The melting points and pKa of NH_2-PY, IM, DMAP and PPZ.

N-containing compounds	Melting point (°C)	pKa (25 °C)
NH_2-PY	58-59	6.71 [S2]
IM	90-91	6.95 [S3]
DMAP	112-113	9.20 [S3]
PPZ	110-111	9.83 [S4]

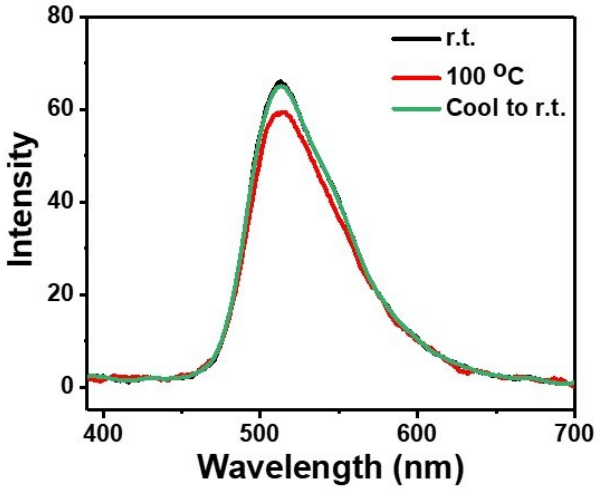

Fig. S5 Fluorescence spectra of pure HBT at room temperature and 100 °C. λex = 365 nm. The powder of HBT placed between two quartz chips was used for tests.

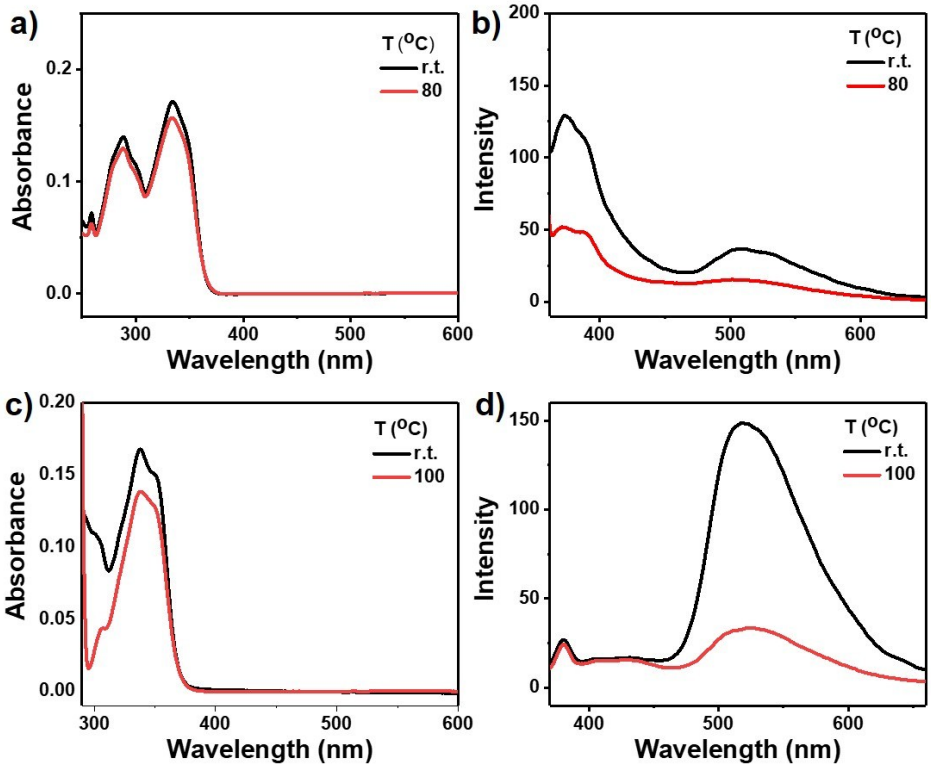

Fig. S6 (a) UV-vis absorption and (b) Fluorescence emission spectra of HBT in ethanol at room temperature and 80 °C. λex = 350 nm; slit width (5 nm, 5 nm); C (HBT) = 1.0×10^{-5} M. (c) UV-vis absorption and (d) Fluorescence emission spectra of HBT in toluene at room temperature and 100 °C. λex = 340 nm; slit width (5 nm, 5 nm); C (HBT) = 1.0×10^{-5} M.

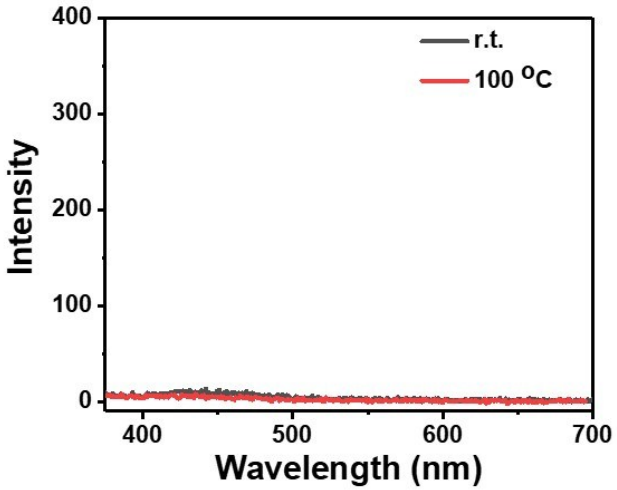

Fig. S7 Fluorescence spectra of IM at room temperature and 100 °C. λex = 365 nm; slit width (1.5 nm, 1.5 nm).

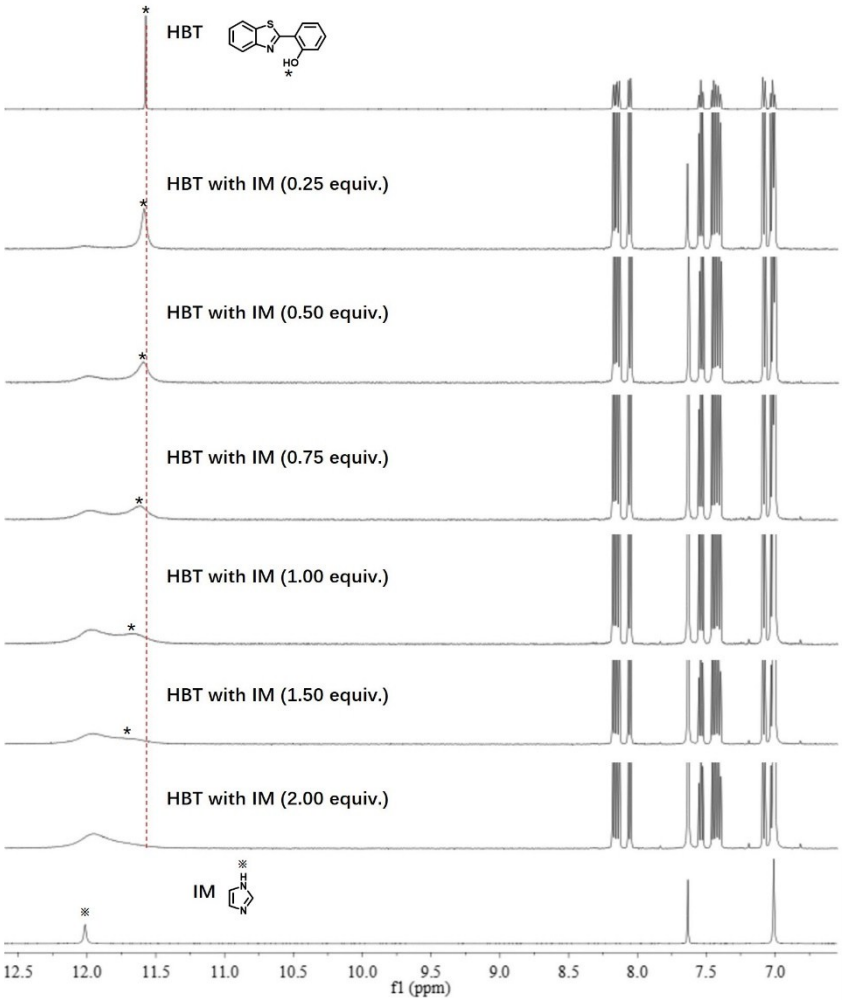

Fig. S8 Partial ^{1}H NMR spectra of HBT, HBT with gradual addition of IM, and IM in DMSO.

After gradual addition of IM into solution of HBT, the signal of the active hydrogen of HBT gradually was shifted to lowfield region, and merged to a braod signal with the the active hydrogen signal of IM (Fig. S8). During this process, and the other singals were almost no change compared to HBT and IM, respectively. (Fig. S8). These results indicate that it really tend to form hydrogen bond (-OH…N) between HBT and IM in solution.

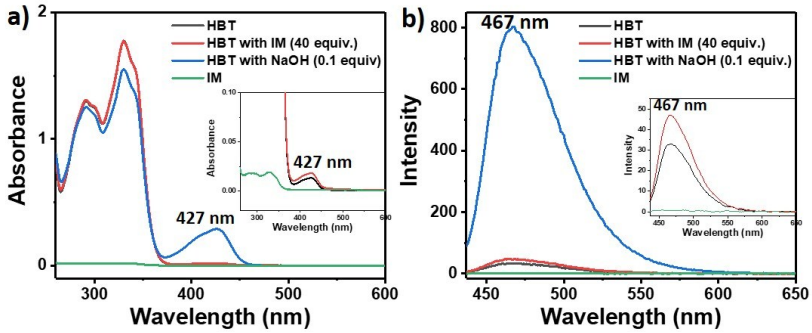

Fig. S9 (a) UV-vis absorption and (b) Fluorescence emission spectra of HBT, IM and HBT with NaOH or IM in DMSO, respectively. λex = 427 nm; slit width (3 nm, 1.5 nm); C (HBT) = 1.0 × 10^{-4} M, C (IM) = 4.0 × 10^{-3} M. Inserts of panel a and b are the local enlarged spectra.

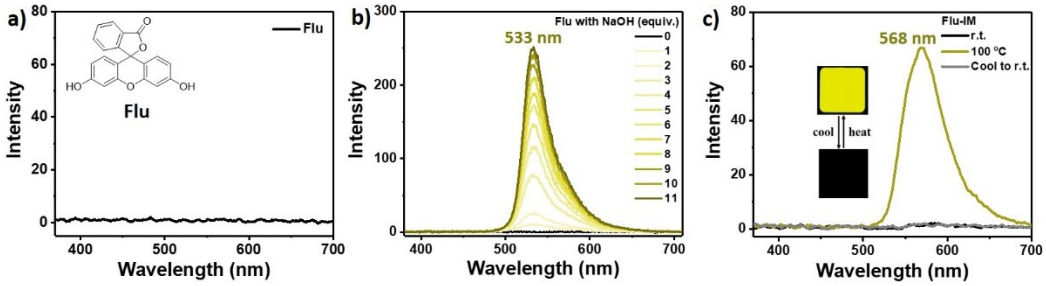

Fig. S10 (a) Fluorescence emission spectrum of Flu powder. λex = 365 nm; slit width (1.5 nm, 1.5 nm). (b) Fluorescence emission spectra of Flu with gradual addition of NaOH in CH_3CN. λex = 365 nm; slit width (1.5 nm, 1.5 nm); C (Flu) = 1.0 × 10^{-5} M. (c) Fluorescence spectra of Flu in IM at room temperature and in molten state. The content of Flu in IM was 0.5 wt%; λex = 365 nm; slit width (1.5 nm, 1.5 nm).

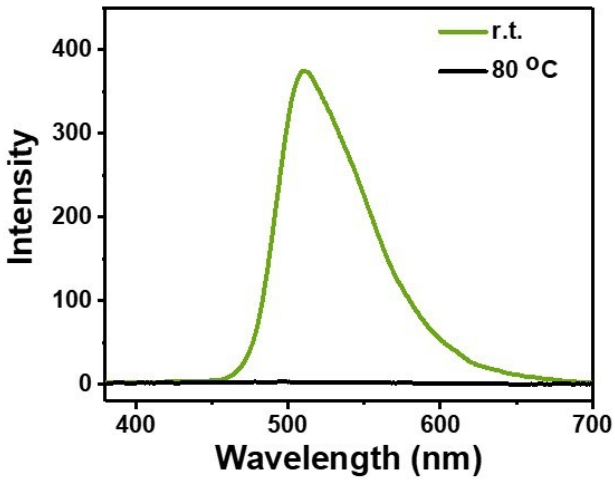

Fig. S11 Fluorescence spectra of HBT in stearyl alcohol (HBT-SA) at room temperature and 80 °C. The content of HBT was 1 wt%; λex = 365 nm; slit width (1.5 nm, 1.5 nm). The melting point of stearyl alcohol is ~60 °C.

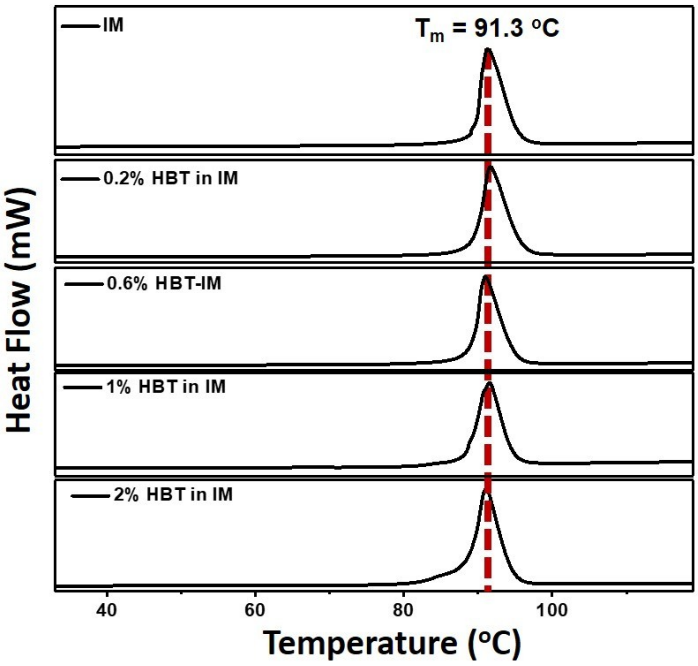

Fig. S12 Differential scanning calorimetry (DSC) thermograms of IM and the blend of HBT-IM with different content of HBT in IM (0.2%, 0.6%, 1% and 2%).

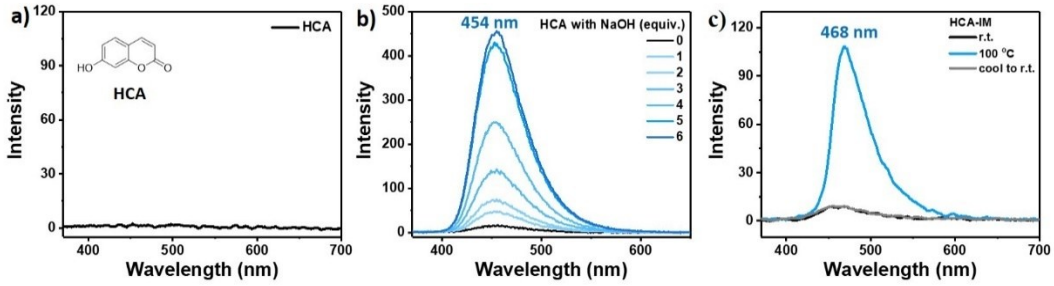

Fig. 13 (a) Fluorescence emission spectrum of HCA powder. λex = 365 nm; slit width (1.5 nm, 1.5 nm). (b) Fluorescence emission spectra of HCA with gradual addition of NaOH in EtOH. λex = 365 nm; slit width (1.5 nm, 1.5 nm); C (HCA) = 1.0×10^{-5} M. (c) Fluorescence spectra of HCA in IM at room temperature and in molten state. The content of HCA in IM was 1 wt%; λex = 365 nm; slit width (1.5 nm, 1.5 nm).

3、Reference

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S4. Sanjay Bishnoi, Gary T. Rochelle, Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem. Eng. Sci.* **2000**, 55, 5531-5543.