Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Fluorescence to multi-colored phosphorescence interconversion of a novel, asterisk-shaped luminogen via multiple external stimuli

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Table of Contents

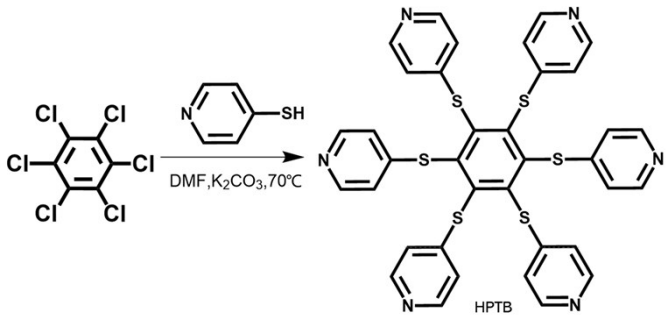
1. General Experimental Details

General. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 400L spectrometer. High-resolution mass spectrometry (HRMS) data was measured by Matrix Assisted Laser Desorption Ionization-Time of Flight/Time of Flight Mass Spectrometer (5800). The UV-vis absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. The emission spectra were recorded on Shimadzu RF-5301, and the lifetime spectra were recorded on FLS 920 (Edinburgh Instruments). The PL lifetime was measured under degassed condition. It was degassed by three cycles of freeze-pump-thaw. After the final thaw cycle, the flask was backfilled with N_2. The photoirradiation was carried out using a hand-held UV lamp (with the irradiation wavelength of 365 nm in a sealed 10 mm quartz cell. Scanning electron microscopy (SEM) was performed on a JEOL JEM 2100 with an accelerating voltage of 200 kV. Dynamic Light Scattering (DLS) were experiments were carried out with Nano-Zeta Potential Analyzer ZS-90. Isothermal titration calorimetry (ITC) measurements were carried out in triplicate using a Microcal PeaQ- ITC. X-ray diffraction measurements (XRD) were made by a PANalytical X'Pert PRO with Cu Kα radiation (λ = 0.1542 nm; operating energy, 40kV; cathode current, 40 mA; scan rate, 20 min-1).

Materials. PDMS**,** 4-Mercaptopyridine, 1,2,3,4,5,6-hexachlorobenzene, K_2CO_3, $AgNO_3$ were commercially available from Sigma-Aldrich. NaOH, N,N-Dimethylformamide (DMF), Ethyl acetate, Petroleum ether, Methanol, Tetrahydrofuran, Hydrochloric acid (36%-38%) were commercially available from Adamas. All reagents were of analytical or reagent grades and used without further purification. Deionized water (18.2 MΩ cm) was obtained from an F'DEER water purification system.

Synthetic Details

Synthesis of compound HPTB: Hexachlorobenzene (0.284 g, 1 mmol, 1.00 eq.), dry K_2CO_3 (2.48 g, 18 mmol, 18 eq.) and 4-Mercaptopyridine (1.332 g, 12 mmol, 12 eq.) were added into a round bottom flask capped with a septum under nitrogen atmosphere. Dry DMF (30 mL) was injected via a syringe and the mixture was stirred at 70 °C for 48 h. Deionized water (200 mL) was poured into the flask while stirring, and brown precipitate appeared. After collecting the solid by filtration, it was rinsed with ethanol (10 mL), diethyl ether (20 mL), and then dried under high vacuum. The crude product was purified by silica gel chromatography (petroleum ether/ ethyl acetate = 4:1) to afford brown compound HPTB (0.312 g, 42.6%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ = 7.06 (m, 12H), 8.28 (m, 12H).^{13}C NMR (100 MHz, DMSO, 298 K): δ = 124.21, 130.38, 141.62, 150.63. HRMS m/z: $[M + H]^+$ 734.05.



Scheme S1 Synthetic route for compound **HPTB**

2. Additional Data

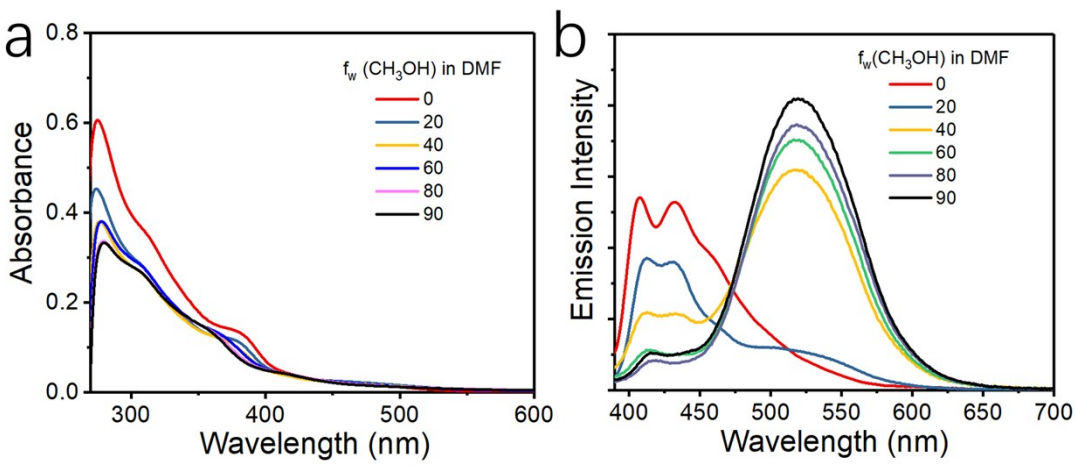


Figure S1 (a) UV-vis absorption spectra and (b) emission spectra of **HPTB** in DMF/CH_3OH with a series of CH_3OH fractions. These measurements were performed at room temperature with the concentration of **HPTB** 1.0×10^{-5} M under 365 nm excitation wavelength.

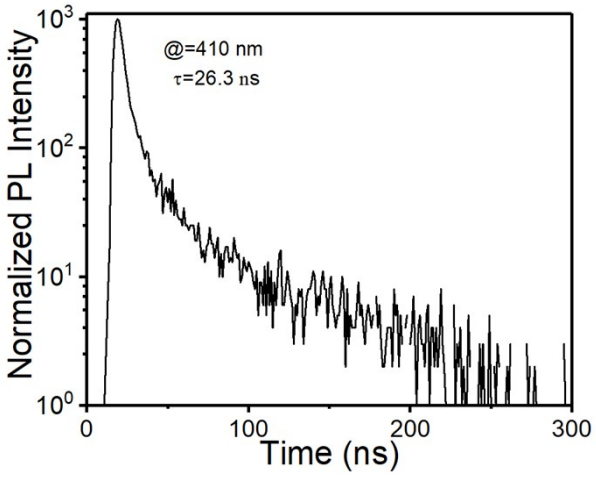


Figure S2 Photo-luminescent (PL) lifetime of **HPTB** in DMF solution

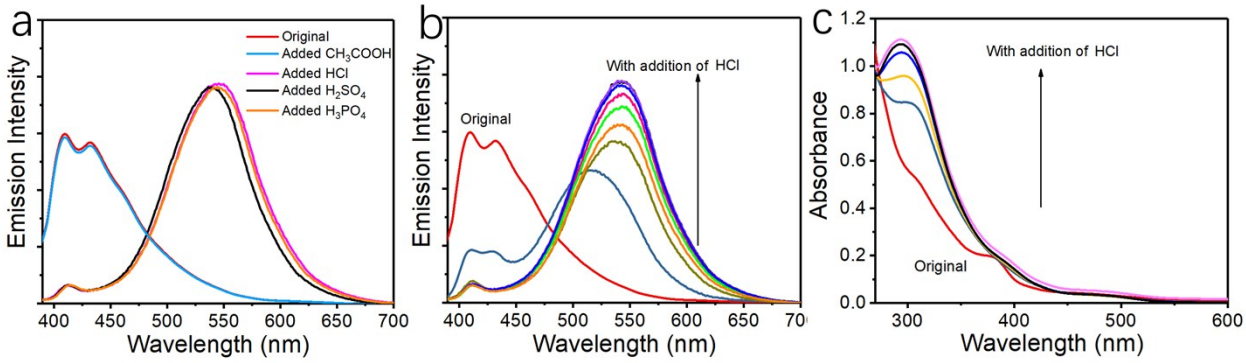


Figure S3 (a) Emission spectra of **HPTB** with the addition of different acids, (b) emission spectra and (c) UV-vis absorption spectra of **HPTB** in DMF solution upon a stepwise addition of HCl. These measurements were performed at room temperature with the concentration of **HPTB** at 1.0×10^{-5} M under 365 nm excitation wavelength.

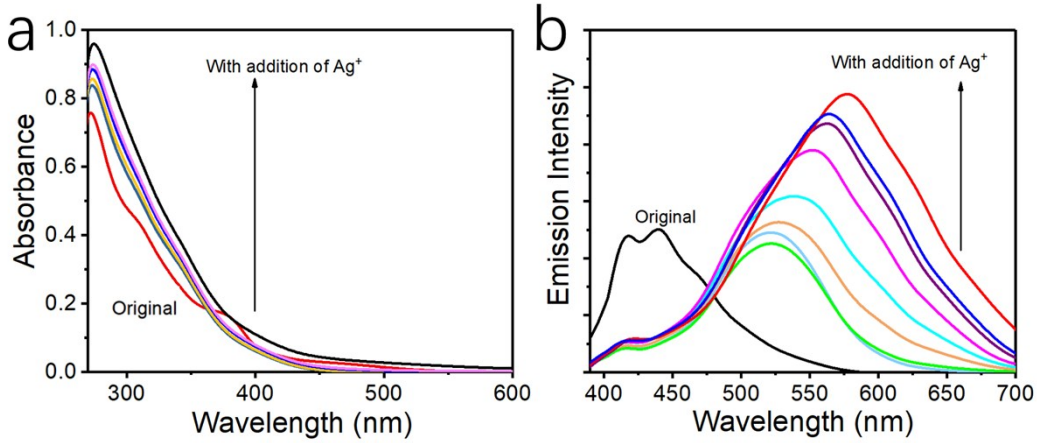


Figure S4 (a) UV-vis absorption spectra and (b) emission spectra of **HPTB** in DMF solution upon stepwise addition of $AgNO_3$. These measurements were performed at room temperature with the concentration of **HPTB** 1.0×10^{-5} M under 365 nm excitation wavelength.

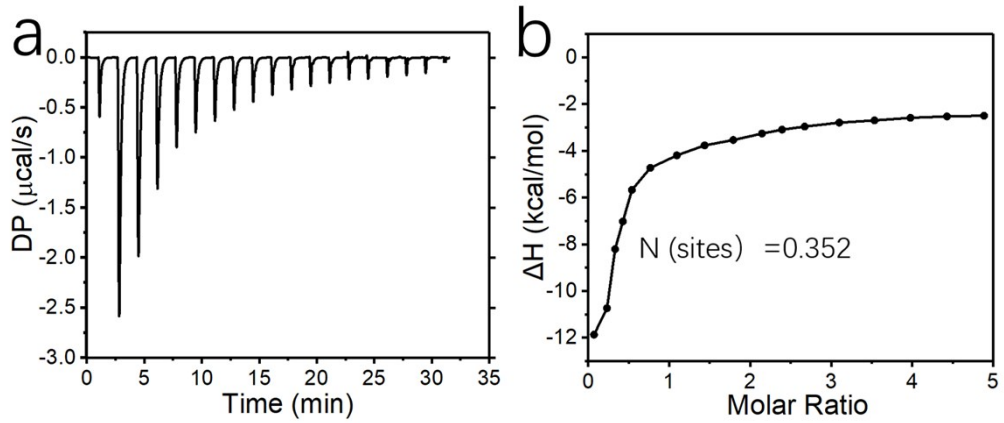


Figure S5 ITC binding isotherms of $AgNO_3$ to HPTB. The binding experiment was carried out at 25 °C.

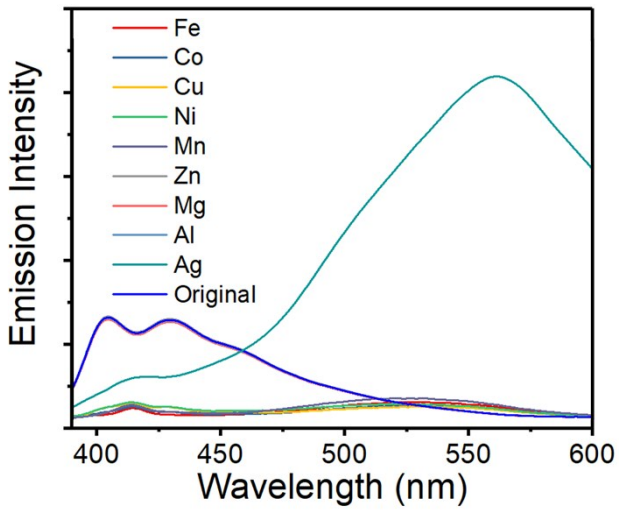


Figure S6 The emission spectra of **HPTB** in DMF solution upon stepwise addition of different metal ions. These measurements were performed at room temperature with the concentration of **HPTB** 1.0×10^{-5} M under 365 nm excitation wavelength.

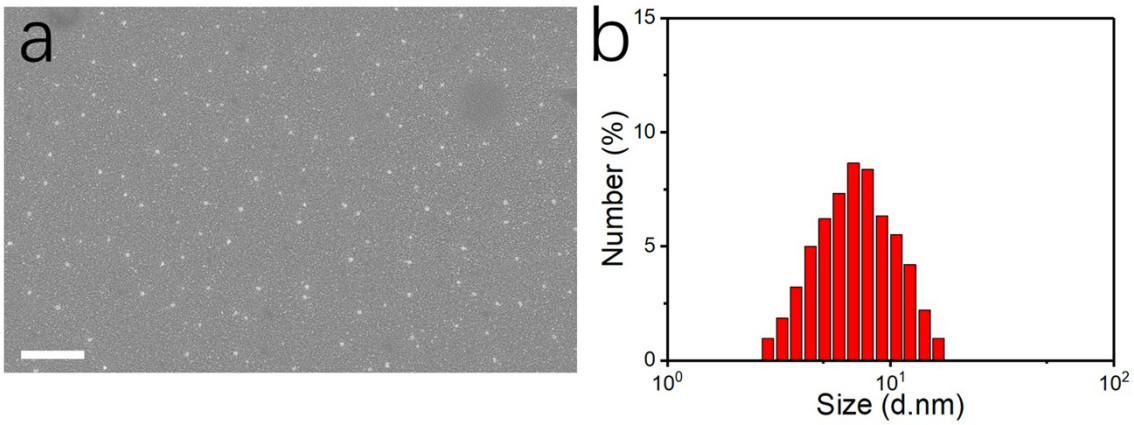


Figure S7 (a) SEM image and (b) DLS data of HPTB in DMF solution. Scale bar =1 μm

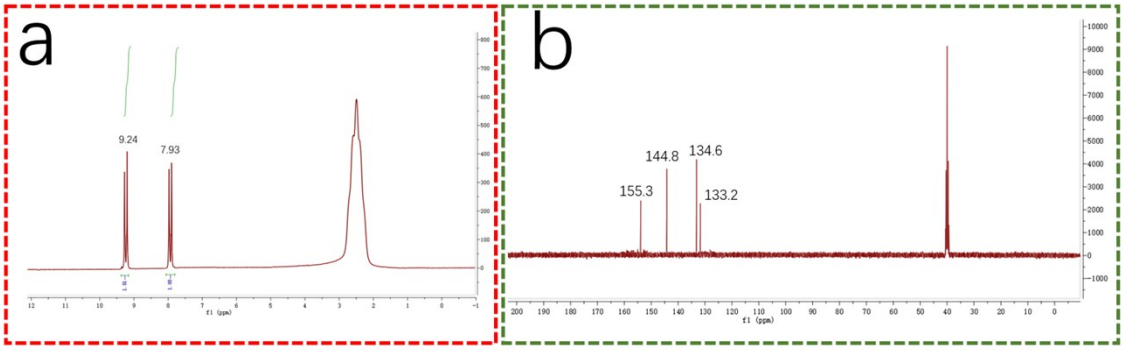


Figure S8 (a) The ^{1}HNMR spectrum and (b) ^{13}CNMR spectrum of **HPTB** after combined with HCl in DMSO-d_6

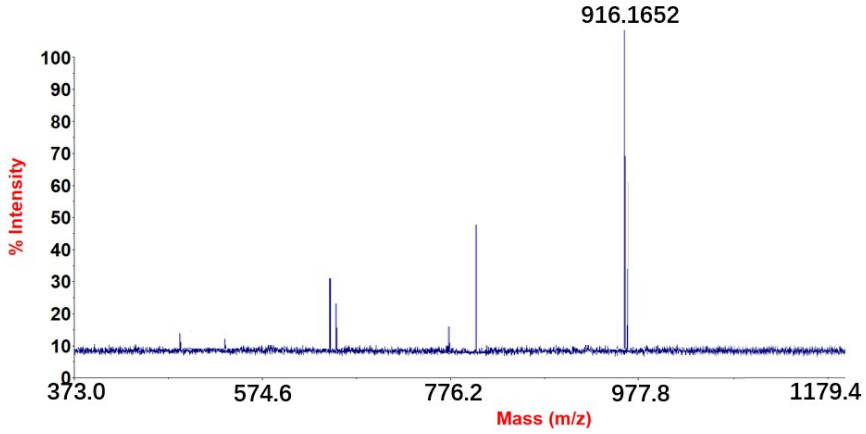


Figure S9 The HRMS spectrum of HPTB after the combination with HCl**.**

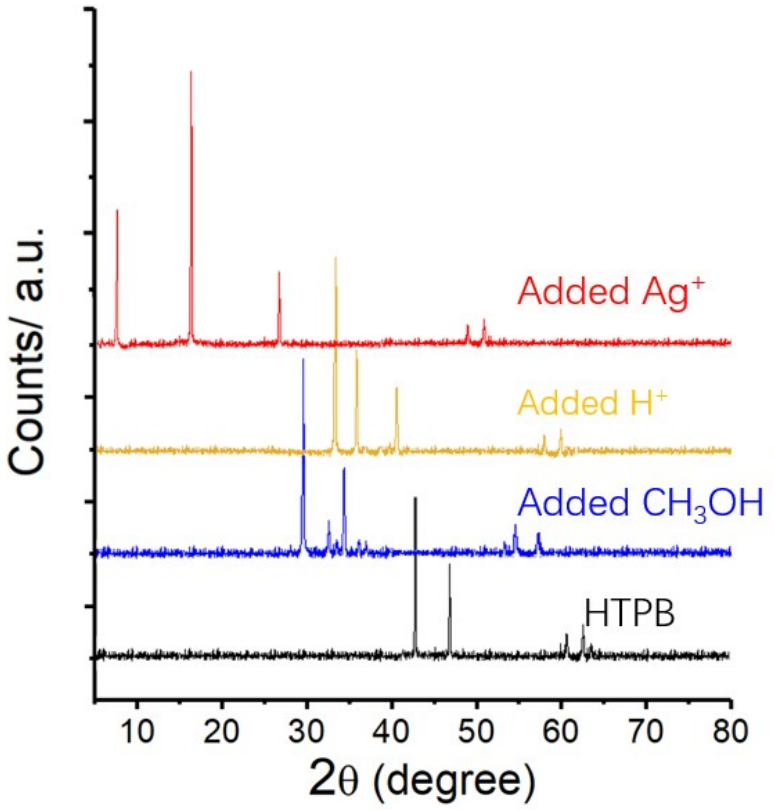


Figure S10 X-ray diffraction traces of the solid samples after different stimuli.

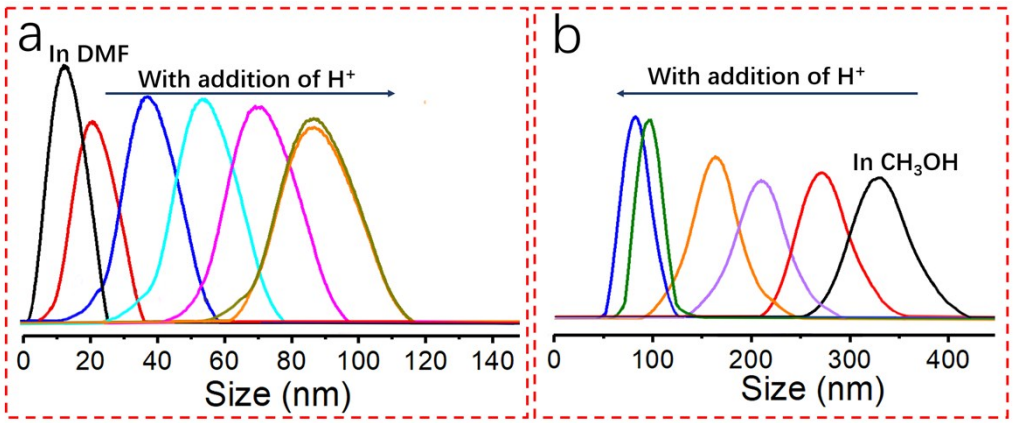


Figure S11 Changes of particle size distribution with H^+ addition. (a) Add H^+ to the DMF solution of HPTB, (b) Add H^+ to the CH_3OH solution of HPTB. HPTB can be well dispersed in DMF solvent and the particle size is less than 10 nm. With addition of H^+, six pyridine groups combine with H^+ and the cationic HPTB molecules formed. The cationic HPTB molecules cannot disperse well in DMF and start to aggregate. Because of coulomb repulsion, the particle size of aggregates can reach about 90 nm (see Fig. S12). HPTB cannot be well dispersed in CH_3OH solution and thus will form aggregates, with particle size about 350 nm. With addition of H^+, the cationic HPTB molecules formed. Because of coulomb repulsion, in order to maintain the balance of static electricity, the big aggregates will become small aggregates under the effect of coulomb repulsion.

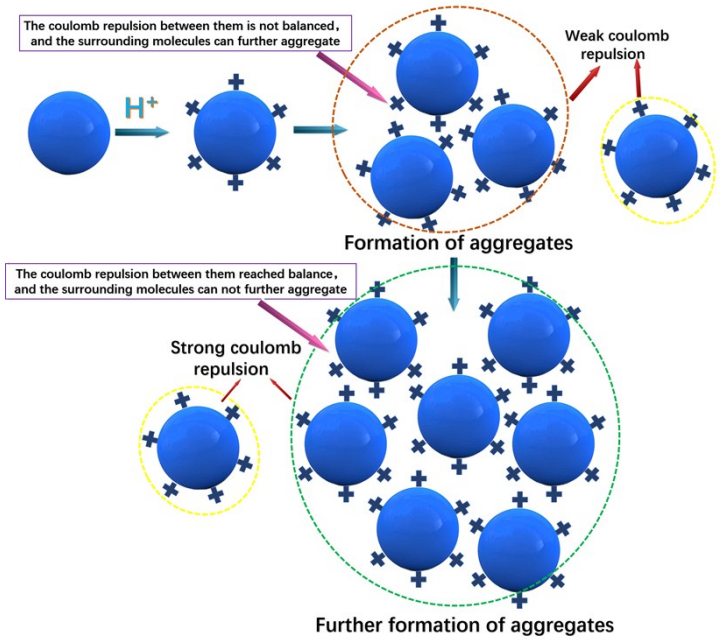


Figure S12 Schematic illustration of aggregation process after H^+ added. There are the following steps : (1) When the six pyridine groups combine with H^+, the cationic **HPTB** molecules start to aggregate. In the early stages, a few molecules aggregate together. The coulomb repulsion among the aggregates and the surrounding molecules is weak. Thus the surrounding molecules can be close to the aggregates and further aggregate to form larger aggregates. (2) This process can continue until the coulomb repulsion reaches equilibrium. In this moment, aggregates are made up of many cationic HPTB molecules. Coulomb repulsion between these molecules is in equilibrium. In addition, these molecules act as a whole, it will form strong Coulomb repulsion between it and the surrounding molecules. Thus the surrounding molecules cannot get close to it. And aggregation process will stop, causing particle size to stay at 90 nm.

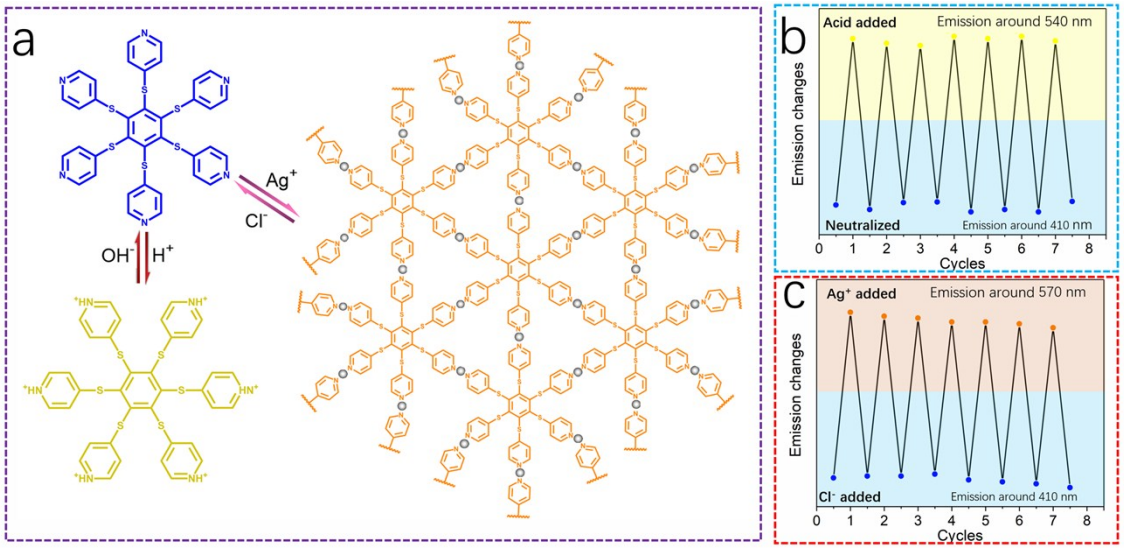


Figure S13 Phosphorescence–fluorescence switching controlled by pH and ion. (a) Schematic illustration of phosphorescence–fluorescence switching controlled by pH and ion, (b) Emission intensity changes between 540 nm and 410 nm under the pH between 6 (acid added) and 7 (Neutralized) by alternatively added the HCl and NaOH solution, (c) Emission intensity changes between 410 nm and 570 nm by alternatively added the $AgNO_3$ and NaCl solution.

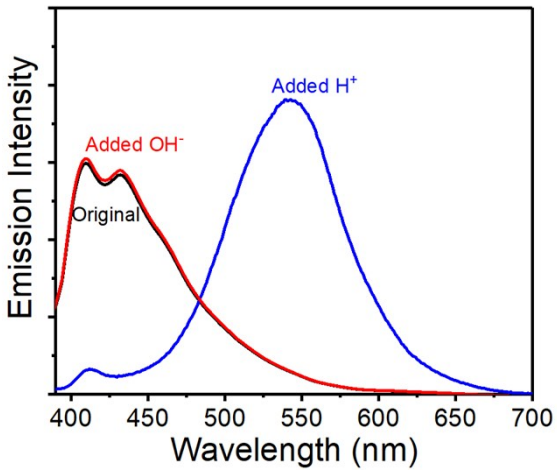


Figure S14 The emission spectra of **HPTB** in DMF solution before and after addition of H^+ and OH^-. These measurements were performed at room temperature with the concentration of **HPTB** at 1.0×10^{-5} M under 365 nm excitation wavelength.

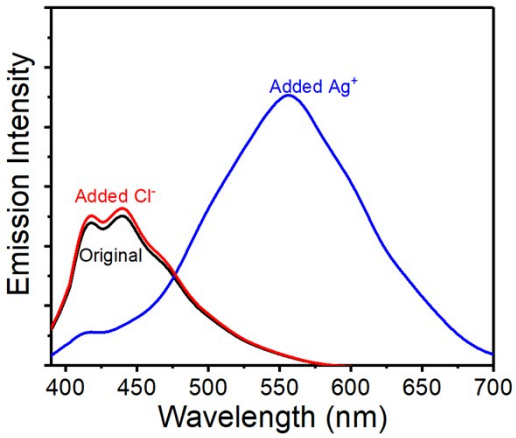


Figure S15 The emission spectra of **HPTB** in DMF solution before and after addition of Ag^+ and Cl^-. These measurements were performed at room temperature with the concentration of **HPTB** at 1.0×10^{-5} M under 365 nm excitation wavelength.

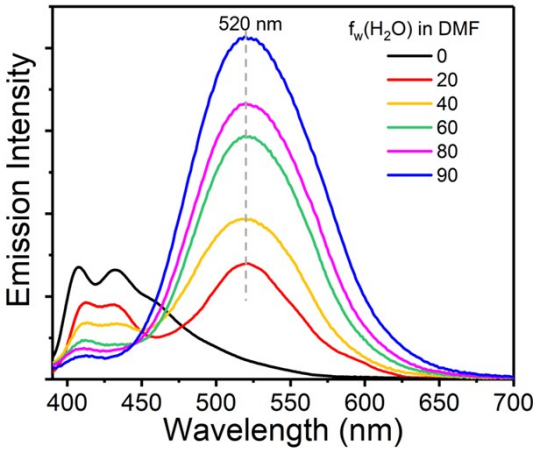


Figure S16 Emission spectra of **HPTB** in DMF solution with different H_2O fraction. These measurements were performed at room temperature with the concentration of **HPTB** at 1.0×10^{-5} M under 365 nm excitation wavelength.

Table S1 The fitting function for PL lifetime of 515 nm

Fitting function	$y = A_1 \exp(-x/t_1) + A_2 \exp(-x/t_2) + y_0$						
Parameter	A_1 (Cnts)	A_2(Cnts)	t_1(μs)	t_2(μs)	y_0	n_1%	n_2%
Value	132.34	1650.57	0.153	55.869	2.075	7.42	92.58

From above table we can know that the fitting function is " $y = A_1 \exp(-x/t_1) + A_2 \exp(-x/t_2) + 2.075$ " , where A_1 = 132.34, t_1 = 0.153, A_2 = 1650.57, t_2 = 55.869. Thus, the average lifetime $t = (A_1t_1^2 + A_2t_2^2)/(A_1t_1 + A_2t_2)$ = 55.857 μs, while t_1 and t_2 represent a short lifetime and long lifetime, respectively, and A_1 and A_2 represent their weighting coefficients. In this way, we can see that there is probably a little bit overlap of fluorescence and phosphorescence at the wavelength of 515 nm. The percentages for the occupation are $n_1 = A_1/(A_1 + A_2)$ = 7.42% and $n_2 = A_2/(A_1 + A_2)$ = 92.58%, respectively.

Table S2 A comparison of HPTB and other similar compounds

Compound	Solution luminescence	Stimuli-Response	Multi-color luminescence
1[1]	No fluorescence	Solvent;Mechanical	Blue; Yellow; White
2[2]	No fluorescence	Solvent	Green
3[3]	No fluorescence	UV light	Green
4[4]	Blue fluorescence	Solvent; pH	Blue; Green; Yellow
5[5]	No fluorescence	Metal ion	Green
6[6]	No fluorescence	Solvent; Mechanical	Blue; Green; Yellow
HPTB	Blue fluorescence	Solvent; pH; Metal ion	Blue; Green; Yellow; Orange

Reference

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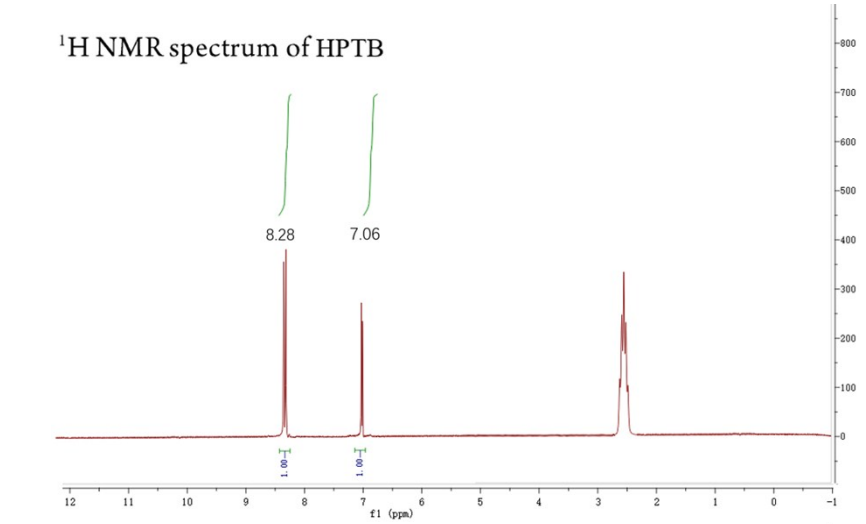
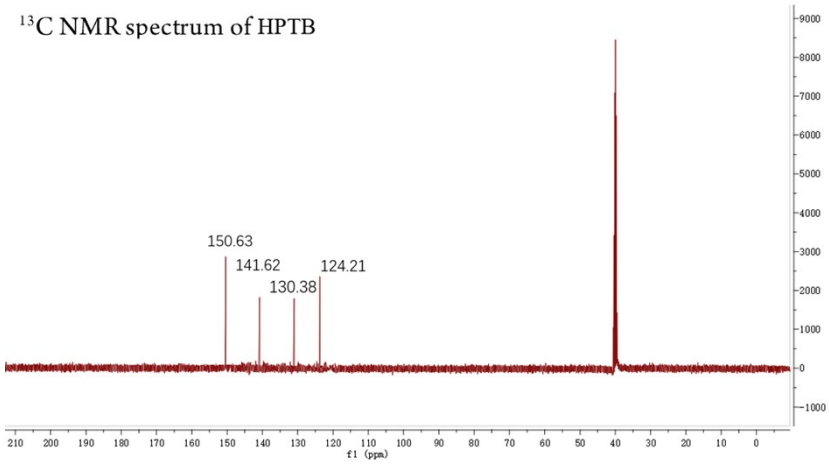
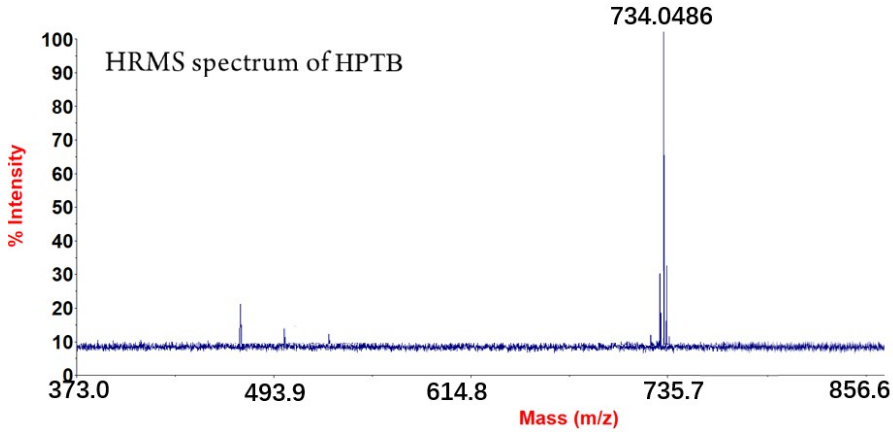
2 A. Fermi, G. Bergamini, R. Peresutti, E. Marchi, M. Roy, P. Ceroni and M. Gingras, *Dyes Pigm* 2014, ***110***, 113-122.
3 X. Jia, C. Shao, X. Bai, Q. Zhou, B. Wu, L. Wang, B. Yue, H. Zhu and L. Zhu, *Proc. Natl. Acad. Sci. U S A* 2019, ***116***, 4816-4821.
4 J. Xu, H. Feng, H. Teng, G. Chen, S. Pan, J. Chen and Z. Qian, *Chem. Eur.J.* 2018, ***24***, 12773-12778.
5 A. Fermi, G. Bergamini, M. Roy, M. Gingras and P. Ceroni, *J. Am. Chem. Soc.* 2014, ***136***, 6395-6400.
6 H. Wu, W. Chi, G. Baryshnikov, B. Wu, Y. Gong, D. Zheng, X. Li, Y. Zhao, X. Liu, H. Agren and L. Zhu, *Angew. Chem. Int. Ed.* 2019, ***58***, 4328-4333.

Appendix


^{1}H NMR spectrum of HPTB
8.28
7.06
f1 (ppm)


^{13}C NMR spectrum of HPTB
150.63
141.62
130.38
124.21
f1 (ppm)


HRMS spectrum of HPTB
734.0486
% Intensity
373.0
493.9
614.8
735.7
856.6
Mass (m/z)