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Electronic Supplementary Information

Dynamic tuning of metal-ligand coordination through water molecules to induce multicolor fluorescence variations for humidity monitoring and anti-counterfeiting applications

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Experimental

Materials and Measurements

All starting materials and reagents were acquired commercially and used without further purification. ^{1}H NMR (400 MHz) spectrum was recorded on a Bruker ACF400 spectrometer at 298 K using deuterated solvents. Mass spectra were recorded on a Bruker autoflex MALDI-TOF MS. Fluorescence spectral changes of polymer films upon changing RHs were meas-ured with an Edin-burgh Instrument FLS980 combined flu-orescence lifetime and steady state spectrophotometer that was equipped with a red-sensitive single-photon counting photomultiplier in Peltier Cooled Housing.

Synthesis of BPPA

In nitrogen atmosphere, $Pd(PPh_3)_4$ (80.7 mg, 0.07 mmol) was added into the mixture of (4-(diphenylamino) phenyl) boronic acid (1 g, 3.5 mmol) and 4,4'-dibromo-2,2'-bipyridine (434 mg, 1.4 mmol) and 2.7 mg K_2CO_3.and THF (50 mL). The reaction was at 65℃ for 40 h. The product was purified through column chroma-tography, yield 64%. ^{1}H NMR (400 MHz, CD_3Cl) δ (ppm): 9.16 (s, 2H), 8.80 (d, J = 4.0 Hz, 2H), 7.9 (d, J = 8.0 Hz, 4H), 7.81 (d, J = 4.0 Hz, 2H), 7.7 (m, 2H), 7.58 (m, 2H), 7.49 (m, 2H), 7.35 (t, J = 16.0 Hz, 6H), 7.21 (m, 12H). [m/z]: (calculated, 642.79, found, 642.29).

Fabrication of thin films

PEG8000 (1.8 g) was dis-solved in CH_2Cl_2 (100 mg/mL). Then, BPPA (10 mg) and $Zn(ClO_4)_2$•$6H_2O$ (5.8 mg) were mixed and dissolved in CH_2Cl_2 ($1x10^{-3}$ mol/L). Various emission color solutions can be obtained by doping the above two solution at a certain mass ratios. The glass slides were treated under UV light for 30 minutes. The films were prepared by spin coating with 45 μL doped solution at speed of 3000 r/min.

Humidity environment and determine the RHs

Concentrated H_2SO_4 (98%) and saturated salt aqueous solution (KBr) were used to establish a humidity environment and electronic hygrometer was employed to determine the RHs. By preparation the mixture with different proportion of H_2SO_4 and saturated salt aqueous solution according to the below table, different RHs can be obtained after sealing the container for 3 days.

Table S1: Proportion of prepared solution

RH (%)	18	32	47	65	72	88	95
H_2SO_4/mL	50	34	25	17	13.4	5.4	0
H_2O/mL	47.5	50	50	50	50	50	50

RH (80%): 50mL saturated KBr solution.

Reversibility experiment.

For the reversibility experiment, the prepared film was first placed in 18% RH for 2h before the measurement of PL spectrum. After that, this film was placed in 88% RH for another 2h before next PL emission recording. In this experiment, above-mentioned procedure was repeated for 10 times. The release and uptake water in the prepared film was autonomically occurred under different environment.

Additional Figures

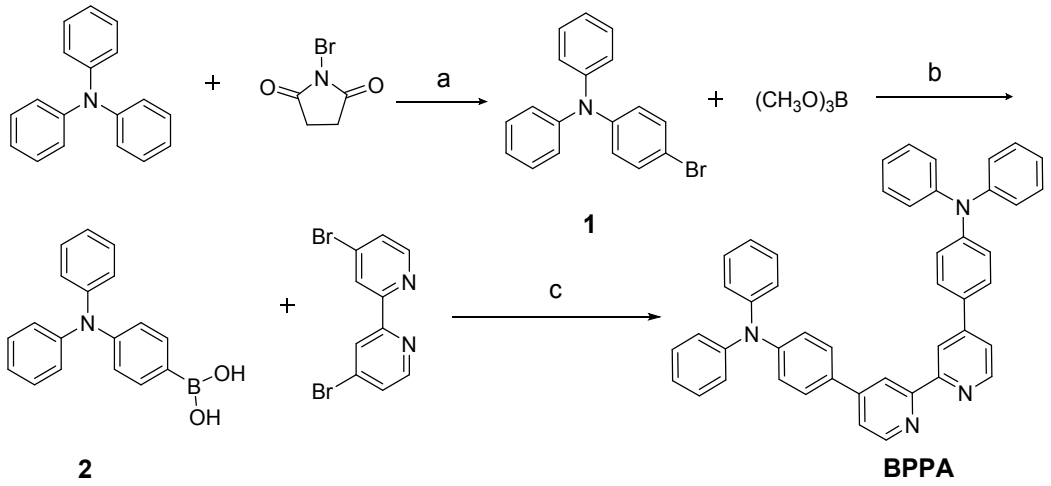

Fig. S1 Synthetic route of ligand BPPA. Reagents and conditions: (a) trichloromethane, 0 ℃, 2 h, 25 ℃, 12 h, 96%; (b) N2 atmosphere, THF, n-BuLi, -78 ℃, 1 h, 25 ℃, 12 h, 96%; (c) N_2 atmosphere, V_{PhMe} : V_{EtOH} : V_{wate}r = 3 : 1 : 1, 65 ℃, 40 h, 55%.

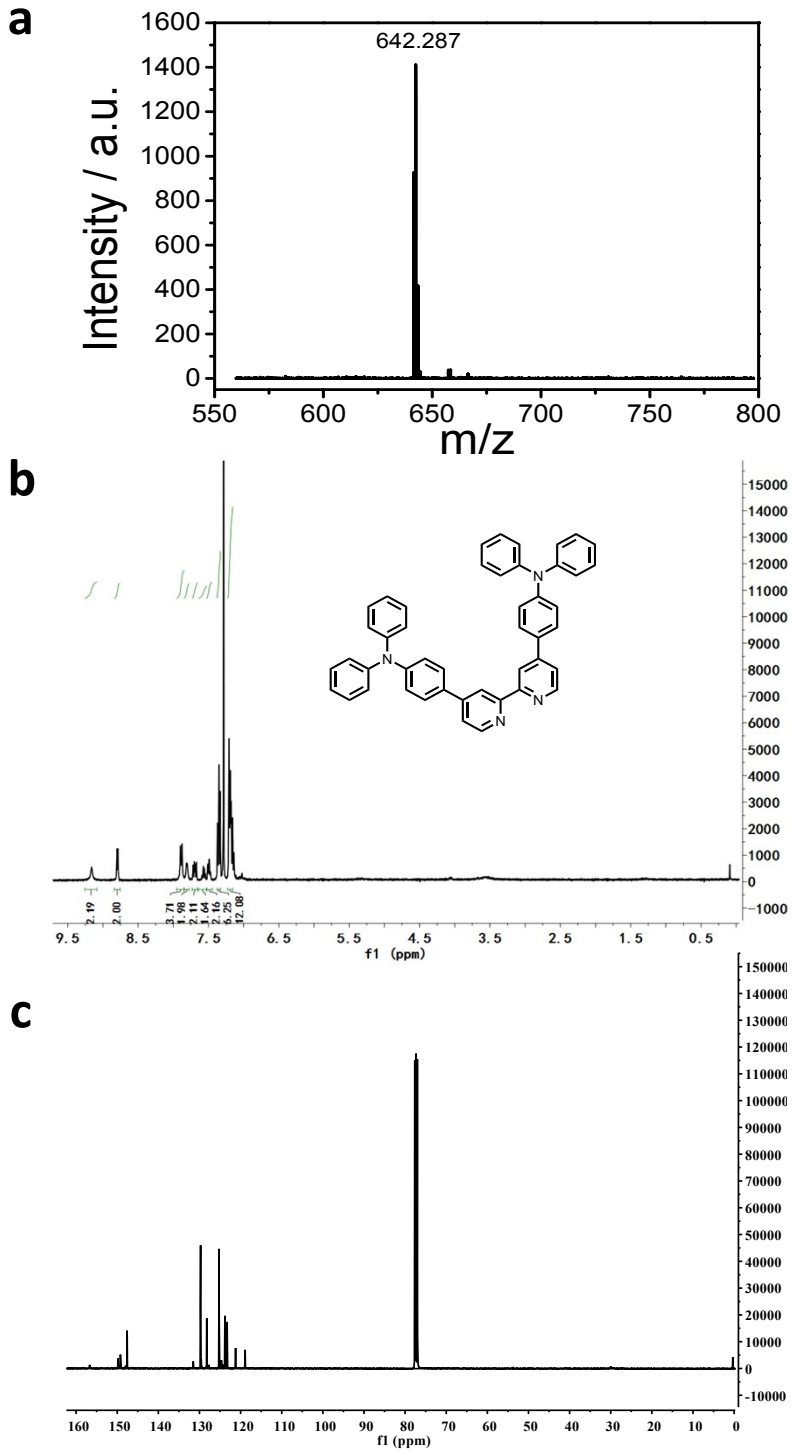

Fig. S2 (a) MALDI-TOF MS. [m/z]: (calculated, 642.79, found, 642.29). (b) 1H NMR (400 MHz) ^{1}H NMR (400 MHz, CD3Cl) δ (ppm): 9.16 (s, 2H), 8.80 (d, J = 4.0 Hz, 2H), 7.9 (d, J = 8.0 Hz, 4H), 7.81 (d, J = 4.0 Hz, 2H), 7.7 (m, 2H), 7.58 (m, 2H), 7.49 (m, 2H), 7.35 (t, J = 16.0 Hz, 6H), 7.21 (m, 12H). (c) ^{13}C NMR (100 MHz, (chloroform-*d*, 25℃, TMS): δ = 156.71, 149.59, 149.23, 148.04, 147.59, 131.60, 129.72, 128.23, 17.78, 125.78, 125.22, 124.49, 124.37, 123.82, 123.27, 121.22, 118.89.

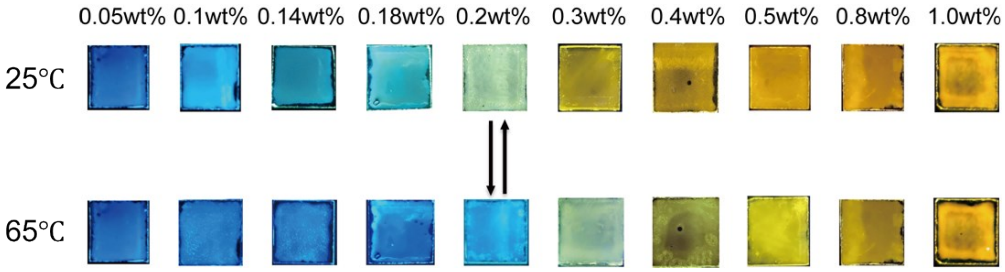

Fig. S3 PL photographs of Zn-BPPA in PEG films at different concentrations (0.05 to 1.0 wt%) upon heating to 65 °C (excitation at 365 nm).

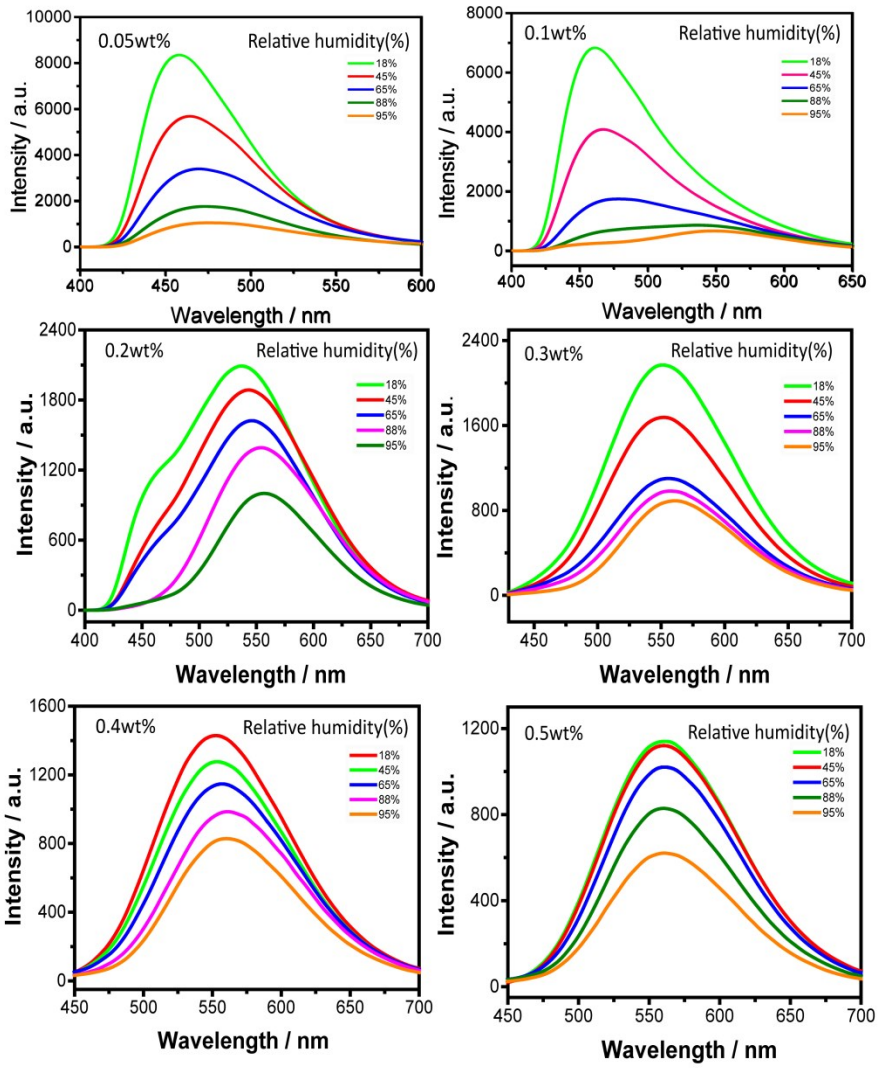

Fig. S4 The PL spectra of thin films with different mass ratios of Zn-BPPA/PEG under different RHs.

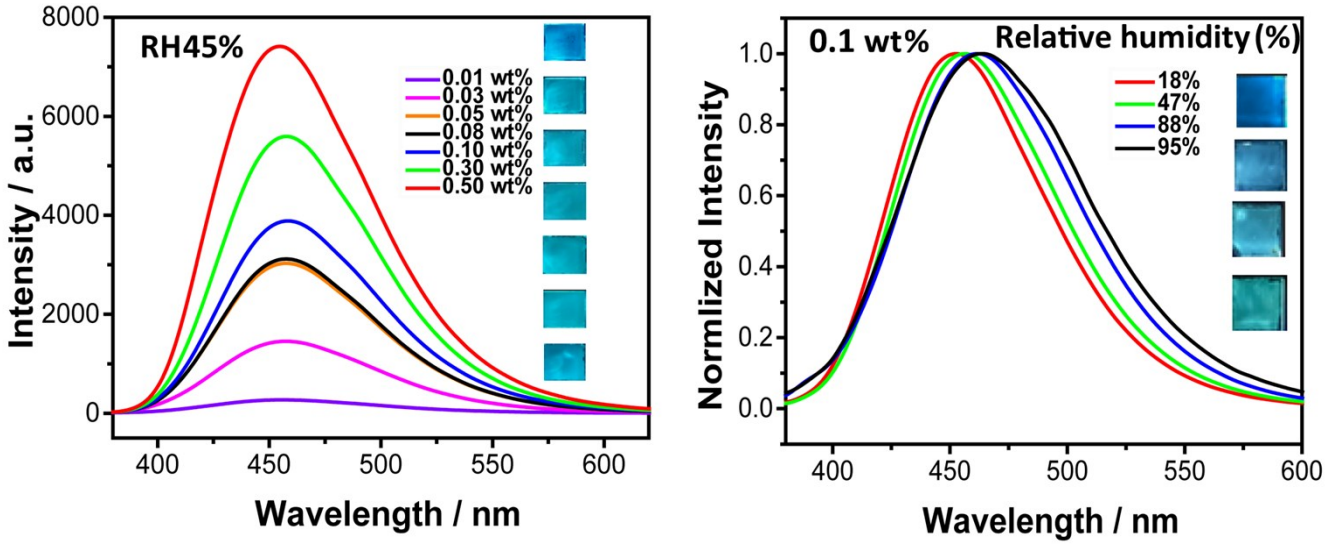

Fig. S5 The PL spectra of various mass ratios of BPPA/PEG thin films and Zn-BPPA/PEG under different RHs.

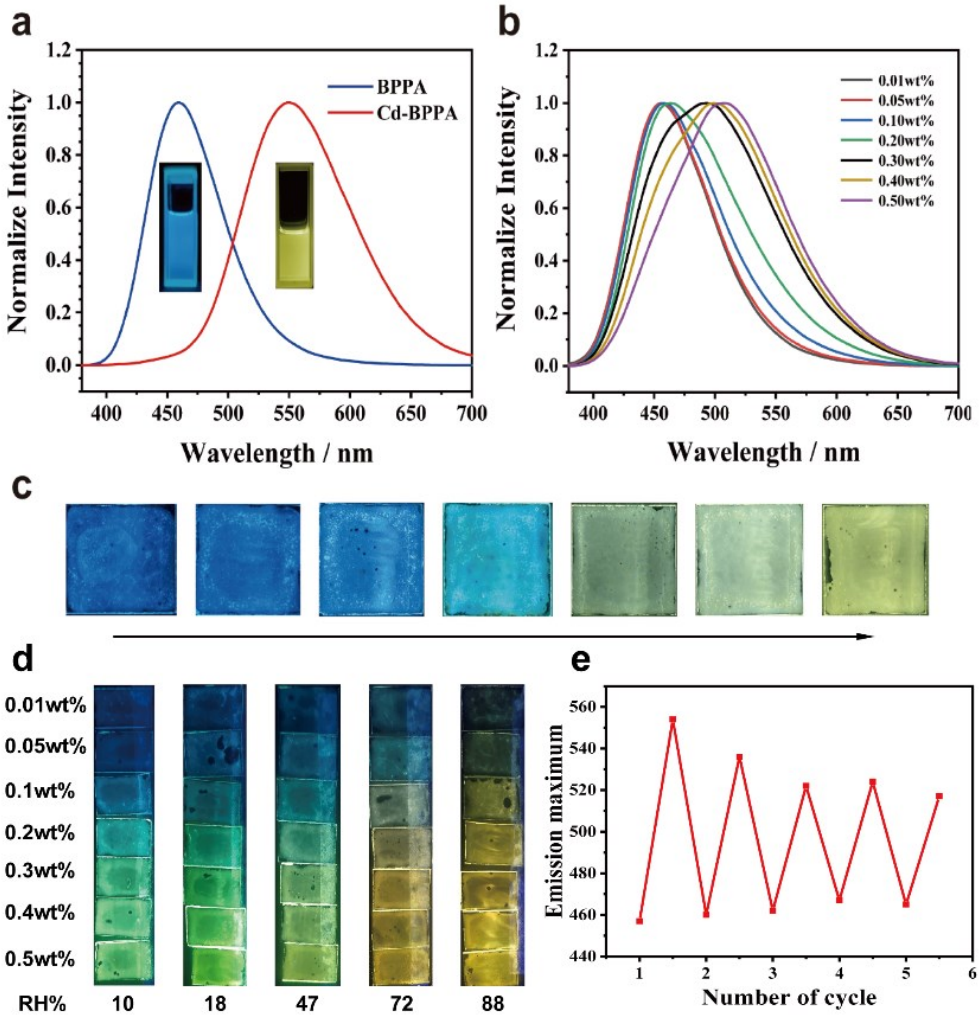

Fig. S6 (a) PL spectra of BPPA and Zn-BPPA in CH_2Cl_2 (1×10^{-5} mol/L). Insert: Photos of BPPA and Cd-BPPA under UV excitation. (b) PL spectral changes of cd-BPPA/PEG (RH 40%) at different concentrations (from 0.01 wt% to 0.5 wt%). (c)The pictures of Cd-BPPA/PEG film (from 0.01 wt% to 0.5 wt%) under 365 nm UV light irradiation. (d)The pictures of Cd-BPPA/PEG film (from 0.01 wt% to 0.5 wt%) under 365 nm UV light irradiation at various RHs (from 10% to 95 wt%). (d) Fivecycles of maxium wavelength variations measured at RH 10-95%.

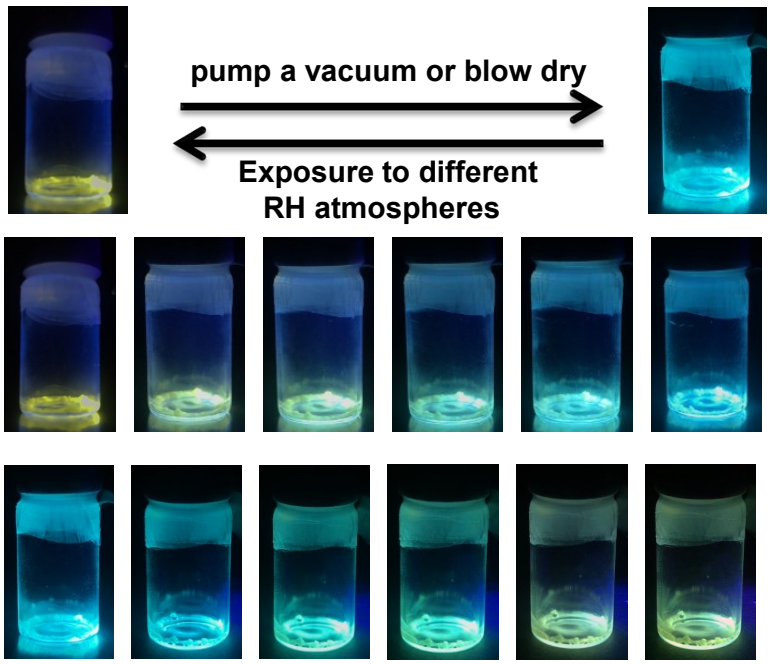

Fig. S7 the bottle emission color changed induced by the pump to vacuum process.