# *Supporting Information:*

# Reversible Luminescence Switching between Single and Dual Emission of a Bipyridinium-type Organic Crystals

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## 1. Materials and General Procedures

All of the chemicals were obtained from commercial sources and used without further purification. Fluorescence measurements were carried out on a FLS920 Luminescence Spectrometer at room temperature. The elemental analyses (C, H, N) were determined using a Vario EL III CHNOS elemental analyze. X-ray powder diffraction data were recorded on an X-ray diffractometer (MiniFlex II goniometer).

Data collections of **Form1** and **Form2** were performed respectively on Rigaku Mercury CCD and Saturn 70 diffractometers by using graphite-monochromated Mo Kα (λ = 0.71073 Å) at 293(2) K. All absorption corrections were performed by using the multi-scan program and all structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares methods using the SHELXL-97 program package.

## 2. Experimental Section

**HBCbpyCl and BCbpy:** HBCbpyCl salt was synthesized by the reaction of 4,4'-bipyridine and 4-(chloromethyl) benzoic acid in a molar ratio of 1.5:1 according to a similar procedure that described previously (Published in CrysEngCommun. 2008, 10, 1299). HBCbpyCl salt (0.1 g, 0.3 mmol) was dissolved in 6 mL of water, and then the pH value of the solution was adjusted to 7 with 1 mol/L NaOH solution. After filtration, the filtrate was left in a refrigerator at 5 ºC. Column-like crystals of BCbpy were obtained after three days (Yield: > 50%). X-ray powder diffraction analysis reveals that they possess the same structure as that of **Form1**.

**Form1 (**BCbpy·6H$_2$O**):** The crystals with good quality for X-ray diffraction analysis can be obtained at room temperature by slow evaporation over two weeks in low yield. Elemental analysis (%) Calcd for $C_{18}H_{26}N_2O_8$: C, 54.26; H, 6.57; N, 7.03; Found: C, 53.90; H, 6.32; N, 6.96.

**Form2 (**BCbpy·2H$_2$O**):** Crystals of **Form1** (0.1 g, 0.25 mmol) were dissolved in 0.5 mL water at 40 ºC and then 6 mL of DMSO were added. After filtration, the filtrate was left for slow evaporation at room temperature in a desiccator with silica gel absorbent. Block-like crystals were obtained after about one month in 29% yield. Elemental analysis (%) Calcd for $C_{18}H_{18}N_2O_4$: C, 66.24; H, 5.56; N, 8.58; Found: C, 66.93; H, 5.42; N, 8.46. The small deviation is probably related to the account of disordered water molecules in the **Form2**. The experimental value corresponds well to the calculated one for BCbpy·$1.8H_2O$: C, 66.99; H, 5.50; N, 8.68.

**Crystal data for Form1:** Crystal data for $C_{18}H_{26}N_2O_8$ (BCbpy·$6H_2O$): $M_r$ = 398.41, monoclinic, space group $P2_1/n$, $a$ = 7.1632(18), $b$ = 18.563(4), $c$ = 15.136(4) Å, $\beta$ = 90.10(2)°, $V$ = 2012.6(8) $Å^3$, $Z$ = 4, $D_c$ = 1.315 g·cm$^{-3}$, $\mu$ = 0.104 mm$^{-1}$, $F_{000}$ = 848, $T$ = 293(2) K, 15322 reflections collected, 4439 unique ($R_{int}$ = 0.0285). Final $GOF$ = 1.098, $R1$ = 0.0593, $wR2$ = 0.1692, $R$ indices based on 3574 reflections with $I > 2\sigma(I)$, 253 parameters.

**Crystal data for Form2:** Crystal data for $C_{18}H_{16}N_2O_3$ (BCbpy·$H_2O$): $M_r$ = 308.33, monoclinic, space group $P2_1/c$, $a$ = 7.338(7), $b$ = 23.989(19), $c$ = 9.246(8) Å, $\beta$ = 110.977(16)°, $V$ = 1520(2) $Å^3$, $Z$ = 4, $D_c$ = 1.348 g·cm$^{-3}$, $\mu$ = 0.093 mm$^{-1}$, $F_{000}$ = 648, $T$ = 293(2) K, 11684 reflections collected, 3469 unique ($R_{int}$ = 0.0513). Final $GOF$ = 1.041, $R1$ = 0.0514, $wR2$ = 0.1289, $R$ indices based on 2331 reflections with $I > 2\sigma(I)$, 210 parameters. Only one lattice water molecule can be located from the difference Fourier map. CCDC-822542 and 822543 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif

## 3. Figures

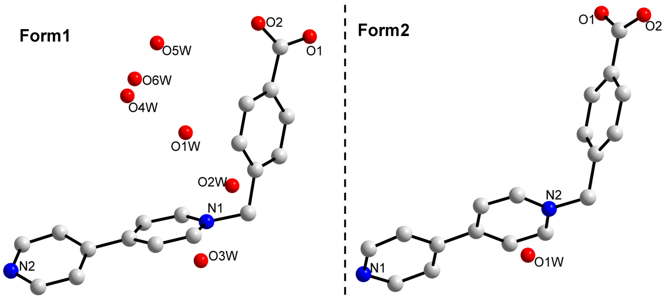

**Fig. S1** The asymmetric units of **Form1** and **Form 2** with atomic labeling.

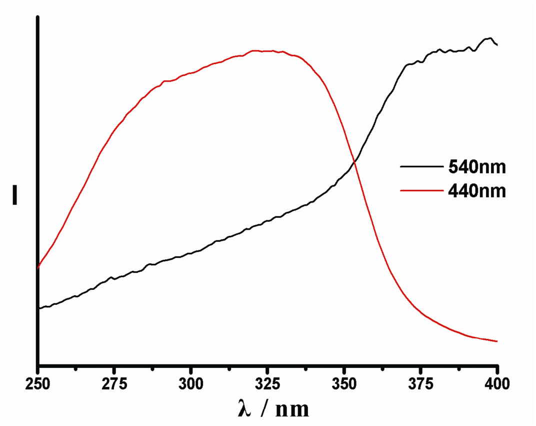

**Fig. S2** The excitation spectra of **Form1** monitored at 440 and 540 nm respectively.

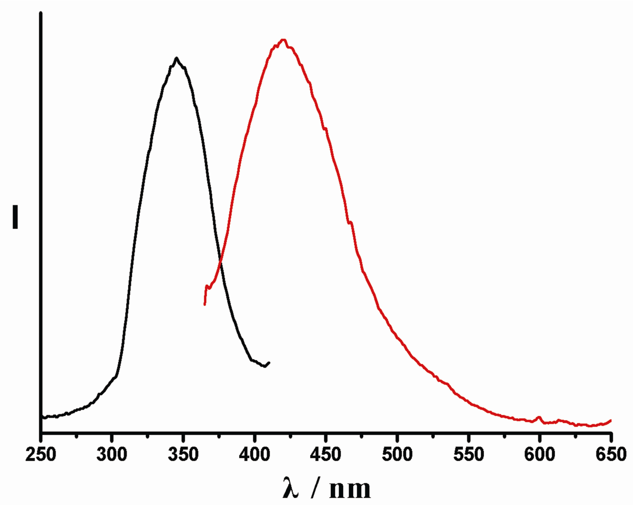

**Fig. S3** Solid-state excitation (black line) and emission spectra (red line) of 4,4′-bipyridine.

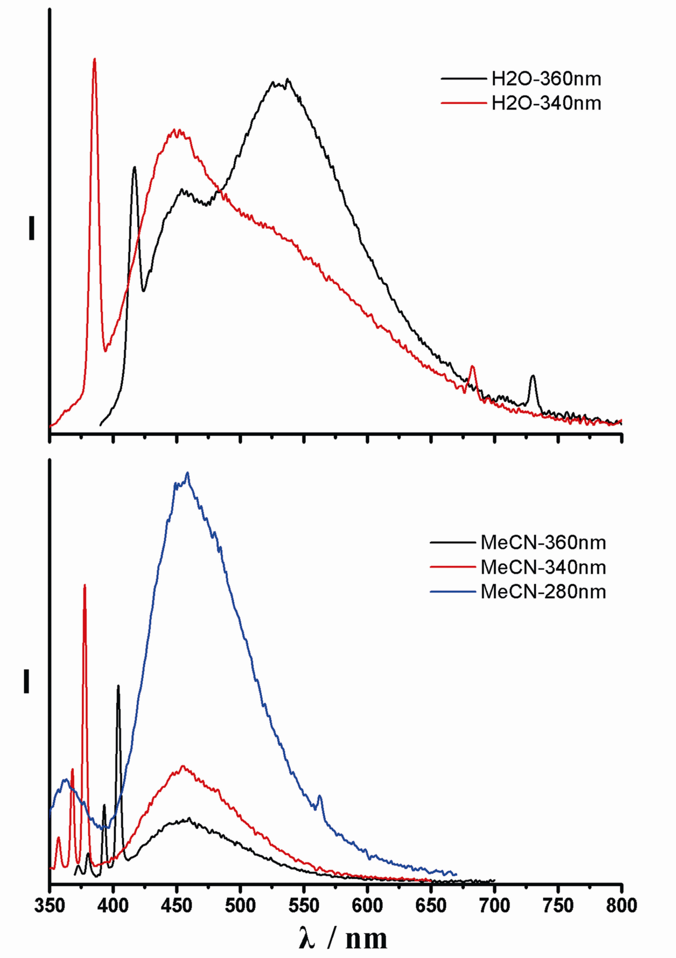

**Fig. S4** The emission spectra of BCbpy in aqueous or MeCN solution at different excitation wavelengths. The sharp peaks in are Raman lines.

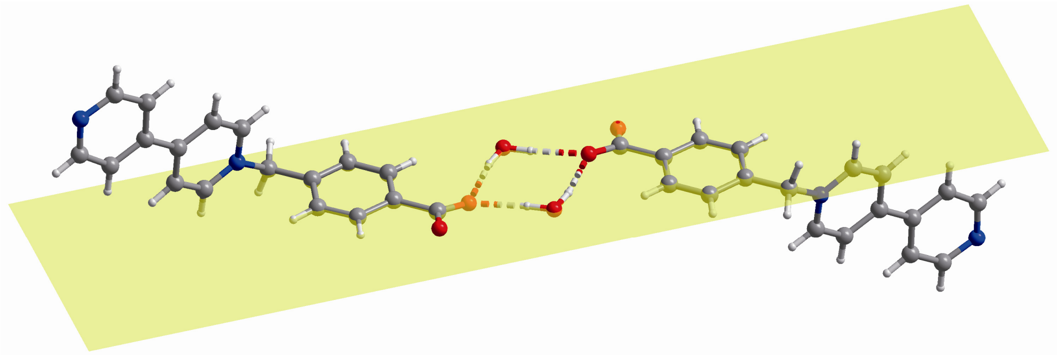

**Fig. S5** A bimolecular unit with a O-H···O hydrogen-binding interaction in a $R_4^2(8)$ type graph-set motif in **Form2**.

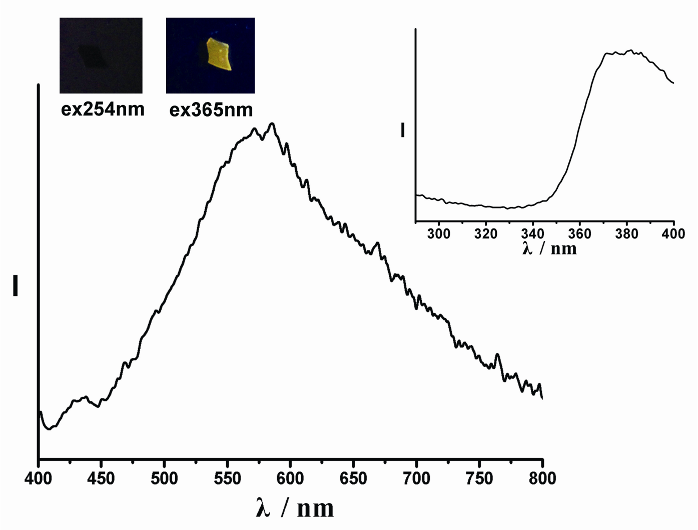

**Fig.** S6 The emission spectrum of **Form2** at an excitation wavelength of 385 nm. Insert: the photographs showing fluorescent emissions of the single crystal **Form2** under a UV lamp with the wavelength of 254 nm or 365 nm (left); the excitation spectrum of **Form2** (right).

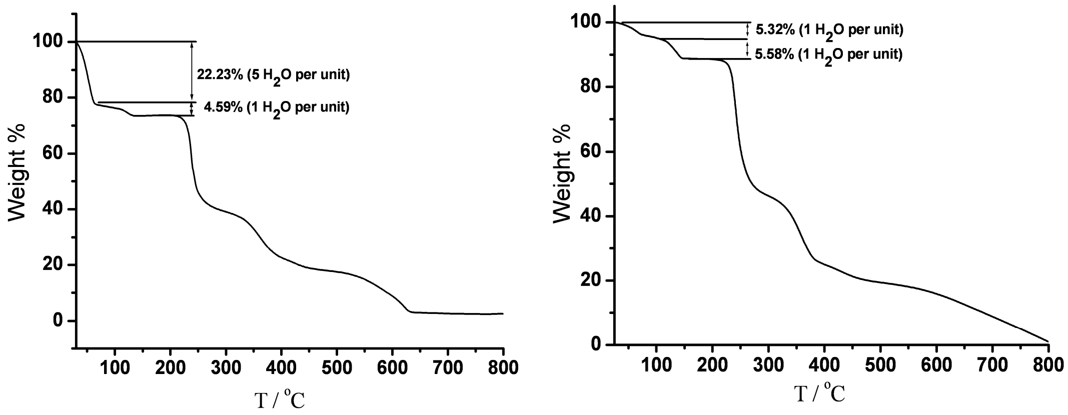

**Fig. S7**. The TG Plots of **Form1** (left) and **Form2** (right).

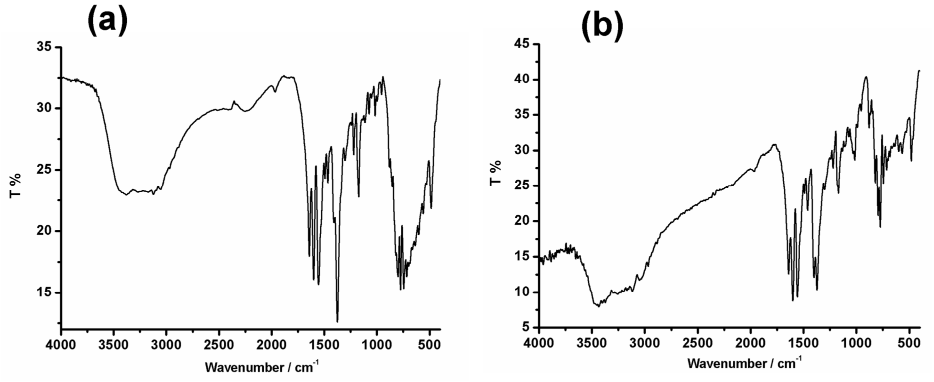

**Fig. S8.** The IR spectra of **Form1** (a) and **Form2** (b).

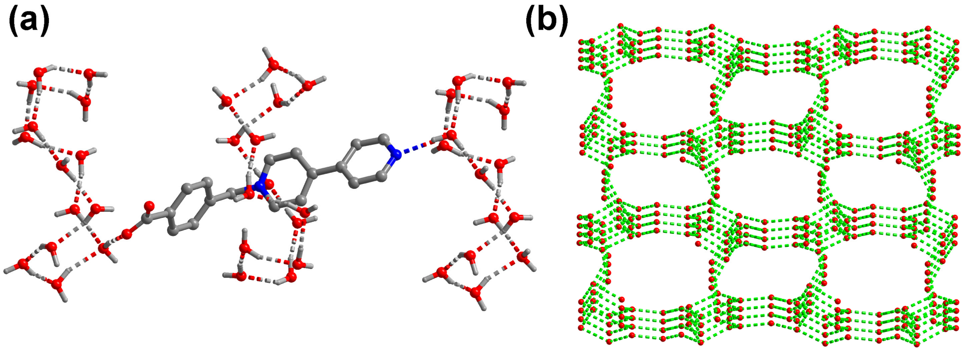

**Fig. S9** (a) The incorporation of the BCbpy molecules in the 14-membered water rings in **Form1**. (b) 3D hydrogen-bonded water layers are pillared by the carboxylate groups to form porous framework.

Water aggregates held by hydrogen bonds have been extensively investigated both experimentally and theoretically due to their importance in gas hydrate and life-sustaining processes.[1] Different from the most commonly reported water aggregates, which are located within the host cavities or channels generated by organic or inorganic moieties, the water layer in **Form1** can be viewed as a porous host network that can accommodate guest molecules. Such an encapsulation of organic molecules in water aggregates is still rarely reported.

**Ref.1:** a) S. Liang, P. G. Kusalik, *J. Am. Chem. Soc.* **2011**, 133, 1870; b) B. Q. Ma, H. L. Sun, S. Gao, *Angew. Chem. Int. Ed.* **2004**, 43,1374; c) L. S. Long, Y. R. Wu, R. B. Huang, L. S. Zheng, Inorg. Chem. **2004**, 43, 3798; d) B. Sreenivasulu, J. J. Vittal, *Angew. Chem. Int. Ed.* **2004**, 43, 5769; e) C. Massera, M. Melegari, F. Ugozzoli, E. Dalcanale, *Chem. Commun.* **2010**, 46, 88-90; f) C. C. Wang, C. C. Yang, W. C. Chung, G. H. Lee, M. L. Ho, Y. C. Yu, M. W. Chung, H. S. Dheu, C. H. Shih, K. Y. Cheng, P. J. Chang, P. T. Chou, Chem. Eur. J. 2011, 17, 9232.