Supporting Information.

Organic Phosphorescent Polymorphs Induced by Various Halogen Bonds with Stimuli-Responsive Single/Dual Phosphorescence Switching

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1. General Information

Emission spectra were measured by maya2000 pro range from 200 nm to 1100 nm and a Fluoromax-4 spectrometer. Lifetimes and temperature-dependent spectra were measured by an Edinburgh FLS980 spectrometer with μ F9200-300. Mass spectrum was recorded on a Thermo Fisher ITQ1100 mass spectrometer. Elemental analysis was performed on an Elementar Vario Micro Cube analyzer. Powder X-ray diffractions were performed on an Empyrean diffractometer. Differential scanning calorimetric (DSC) measurements were performed on a TA DSC Q20 instrument.

Cry-A was grown by solvent diffusion method. 50 mg **BrTA-F** was dissolved in a test tube, and then the test tube was put in a jar with enough methanol. After few days, white crystals were obtained in the bottom of test tube. **Cry-B** was obtained by vacuum thermal deposition with different temperature range (220 °C for sublimation and 100 °C for the cooling of **BrTA-F** compound). Single crystal X-ray diffraction data were collected on a Rigaku R-AXIS-RAPID diffractometer using the ω -scan mode with graphite-monochromator Mo·K α radiation. The structure determination was solved with direct methods using the OLEX² programs and refined with full-matrix least-squares on F². Reagents were purchased from Beijing Chemical Reagent Co.(China) as analytical grade and were added nitrogen more than 2 hours to get rid of the influence of oxyen on emission behaviors. The corresponding CCDC reference number (CCDC: 2045679 for **Cry-A** and 2045680 for **Cry-B**) and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Theoretical Calculation

(U)DFT and TD-DFT calculations were performed with Gaussian 16 programs using B3LYP-D3(BJ) hybrid functional and 6-31G (d, p) basis set. The molecules in trimer states were frozen by Gaussview 6.0. The optimized stationary point was further characterized by harmonic vibrational frequency analysis without imaginary frequencies to ensure that real local minima were reached. Spin-orbit coupling (SOC) matrix elements were calculated at the level of B3LYP/def-TZVP by ORCA programs. NTO orbits diagrams were drawn by VMD and Multiwfn programs.

3. Synthetic Details

¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker Avance 500 MHz spectrometer in DMSO- d_6 . The chemical shifts in ¹H NMR spectra are reported in δ ppm using tetramethylsilane as an internal standard, and those in ¹³C NMR spectra are reported using the solvent signal as an internal standard. Commercially available solvents and reagents were used without further purification. Compound is synthesized at list:



2,5-dibromo-N1,N4-bis(2-fluorophenyl)terephthalamide:2,5-dibromoterephthaloyl dichloride was synthesized according the literature.¹ For **BrTA-F**, to a solution of 2-fluoroaniline (1.1 g, 9.86 mmol) in CH₂Cl₂ (30 mL) and triethylamine (2 mL) was added 2,5-dibromoterephthaloyl dichloride (1 g, 2.8 mmol). The reaction mixture was stirred at room temperature overnight and a white precipitate was formed. Filtration and washing with water and ethanol afforded raw **BrTA-F** as a white solid. Vacuum thermal sublimation and deposition was performed for a further purity (1.00 g, 63%). ¹H NMR (500 MHz, DMSO) δ 10.50 (s, 2H), 7.98-7.84 (m, 4H), 7.36-7.22 (m, 6H). ¹³C NMR (126 MHz, DMSO) δ 164.76 (s), 155.99 (s), 154.03 (s), 141.09 (s), 133.13 (s), 127.12 (d, J = 6.6 Hz), 125.90 (s), 124.88 (s), 118.62 (s), 116.29 (d, J = 19.3 Hz). MS (*m/z*): 508.0 [M]⁺ Anal. calcd (%) for C₂₀H₁₂Br₂F₂N₂O₂: C, 47.09; H, 2.37; Br, 31.33; F, 7.45; N, 5.49; O, 6.27. Found: C, 47.01; H, 2.41; N, 5.50.

4. Supplementary Figures



Figure S1. Temperature-dependent emission spectra of Cry-A (a) and Cry-B (b) excited at 370 nm.



Figure S2. Temperature-dependent decay spectra of Cry-A (a) measure at 440 nm, and Cry-B measured at 430 nm (b) and 510 nm (c), respectively.



Figure S3. Photographs of **BrTA-F** in solution, thin film, and at 77 K excited by a 365 nm UV light.



Figure S4. Excitation spectra of Cry-A (a) and Cry-B (b)



Figure S5. Emission spectra of Cry-A and Cry-B under oxygen environment

Figure S6. Emission spectra of BrTA-F thin film and THF solution under 77 KFigure S7. Emission spectra of grounded Cry-A (a) and grounded Cry-B (b)





Figure S8. Natural transition orbitals (NTO) images of S_1 , S_2 , T_1 and T_2 excited states of **Cry-A**, and corresponding transition forms of different excited states.



Figure S9. Simulated energy level diagrams of Cry-A (a) and Cry-B (b).



Figure S10. DSC spectra of Cry-A insert: phase-inversion process (a), and Cry-B (b).



Figure S11. Photographs of Cry-A (a) and Cry-B (b) before and after stimuli response



Figure S12. The XRD spectra comparison of Cry-B after solvent vapor processing and Cry-A after heating (a); XRD spectra of Cry-B after solvent vapor processing and simulated by crystal structure of Cry-A (b); XRD spectra of Cry-A after heating stimulation and simulated by crystal structure of Cry-B (c).From the spectra, it could be concluded that the crystal structure of Cry-A after heating should be assign to Cry-B, while the crystal structure of Cry-B after solvent vapor processing should be ascribe to Cry-A, indicating phase-inversion processes.



Figure S14. ¹C NMR spectrum of BrTA-F.

Reference:

1. S. Y. Lee, T. Yasuda, I. S. Park, C. Adachi, Dalton Trans., 44(2015) 8356-8359.