Electronic Supplementary Information

The effects of positional isomer, protonation and solvent on the morphologies and photophysical properties of boron-difluoride complex microcrystals

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Experimental procedures and measurements

Measurements

Microanalytical data (C, H, N) were collected on Vario ELIII elemental analyzer. The solid-state UV/Vis/NIR absorption spectra were recorded at room temperature on a DUV–3700 UV/Vis/NIR spectrometer. The solid-state photoluminescence spectra and the decay lifetimes were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The solid-state quantum yields were measured also on a Fluorolog-3-TAU fluorescence spectrophotometer equipped with a $BaSO_4$-coated integrating sphere, upon excitation at 365 nm. The experimental uncertainties were 1 nm for the band maxima for the luminescence spectra and 10 % for quantum yield. Powder X-ray diffraction (PXRD) patterns were collected on a Philips X'pert PRO SUPER diffractometer operating with nickel-filtered Cu-Kα radiation (λ = 1.540598 Å) at 40 kV and 200 mA. Field-emission scanning electron microscopy (FE-SEM) measurements were performed with a FEI Sirion 200 field emission scanning electronic microanalyser operated at an accelerating voltage of 5 kV.

Experimental procedures

All reagents were commercially available and used without further purification. 7,7' (or 8,8')-Dimethyl-2,3'-biimidazo[1,2-*a*]pyridin]-2'-one radical (7,7' (or 8,8')-Hdmbipo$^{-\bullet}$) was synthesized by similar procedure to synthesis of 2,3'-biimidazo [1,2-*a*]pyridin-2'-one radical.[S1]

Synthesis of BF_2-7,7'-dmbipo (microcrystal **A**) and BF_2-8,8'-dmbipo (microcrystal **B**): 0.50 mL of $BF_3{\cdot}OEt_2$ (4.00 mmol) was slowly injected into 10 mL of DMF containing 0.56 g (2.01 mmol) of 7,7' (or 8,8')-Hdmbipo$^{-\bullet}$. The reaction system was stirred at 100 °C for one day, resultant solid was collected by filtration and washed with DMF and water, and then dried in air at 75°C for 8 h, leading to microcrystals **A**

or **B** (75.26% or 62.11% yield). Anal. calcd for $C_{16}H_{13}BF_2N_4O$: C 58.93%, H 4.02%, N 17.18%; found: C 58.17%, H 3.93%, N 16.92% for microcrystal **A** or C 58.05%, H 3.96%, N 16.85% for microcrystal **B**.

Fabrication of BF_2-7,7'-dmbipoHCl (microcrystal **C**) and BF_2-8,8'-dmbipoHCl (microcrystal **D**): At room temperature, 0.65 g (2.00 mmol) of BF_2-7,7'-dmbipo or BF_2-8,8'-dmbipo was dissolved in 15 mL of DMF-HCl solution (DMF:HCl (36 %) = 1:1, v/v), and made to stand at room temperature for 3 days, giving rise to microcrystals **C** or **D**, which then was collected by filtration and dried in air at 75°C for 8 h (~60.00% yield). Anal. calcd for $C_{16}H_{14}BClF_2N_4O$: C 53.00%, H 3.89%, N 15.45%; found: C 53.58%, H 3.76%, N 15.81% for microcrystal **C** or C 53.37%, H 3.80%, N 15.76% for microcrystal **D**.

Fabrication of BF_2-8,8'-dmbipoHCl (microcrystal **E**): At room temperature, 0.65 g (2.00 mmol) of BF_2-8,8'-dmbipo was dissolved in 15 mL of DMSO-HCl solution (DMSO:HCl (36 %) = 1:1, v/v), and made to stand at room temperature for 3 days, giving rise to microcrystal **E**, which then was collected by filtration and dried in air at 75°C for 8 h (~50.00% yield). Anal. calcd for $C_{16}H_{14}BClF_2N_4O$: C 53.00%, H 3.89%, N 15.45%; found: C 53.62%, H 3.78%, N 15.90%.

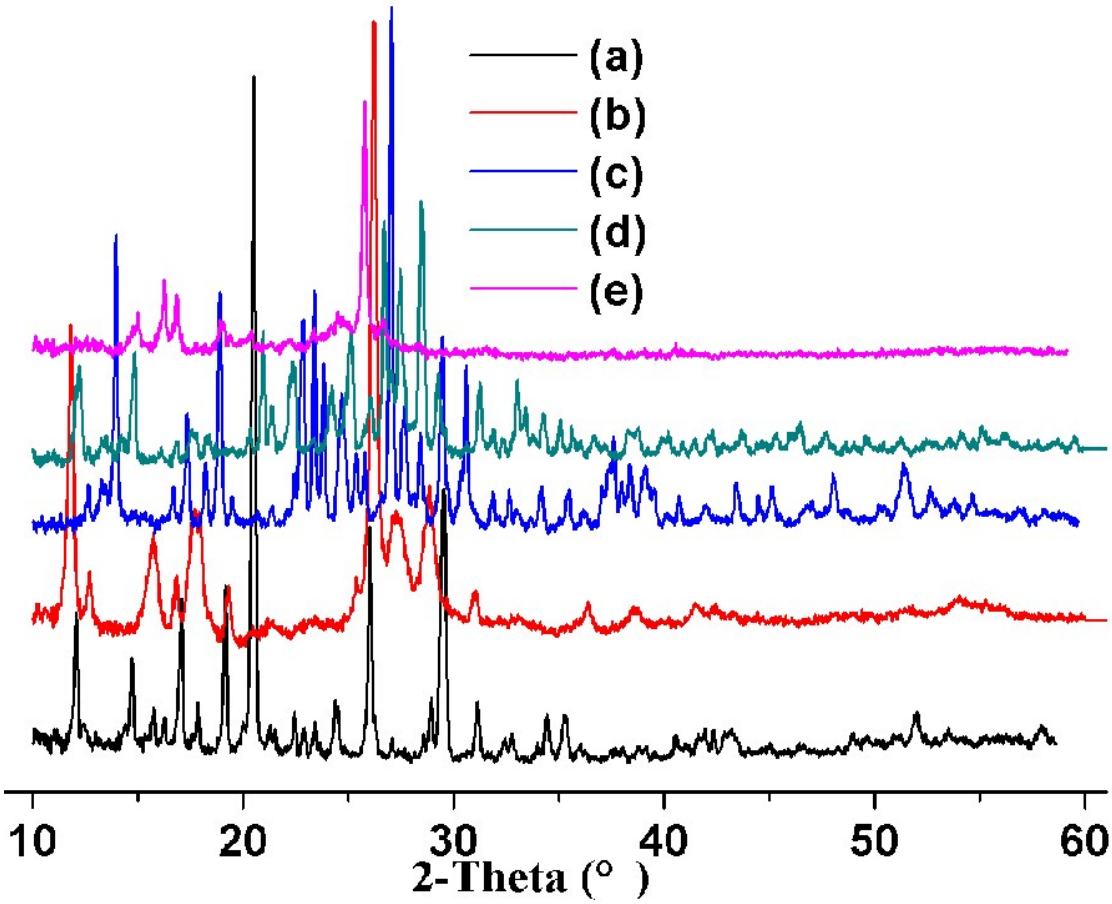

Fig. S1 The PXRD patterns of microcrystals **A** (a), **B** (b), **C** (c), **D** (d) and **E** (e).

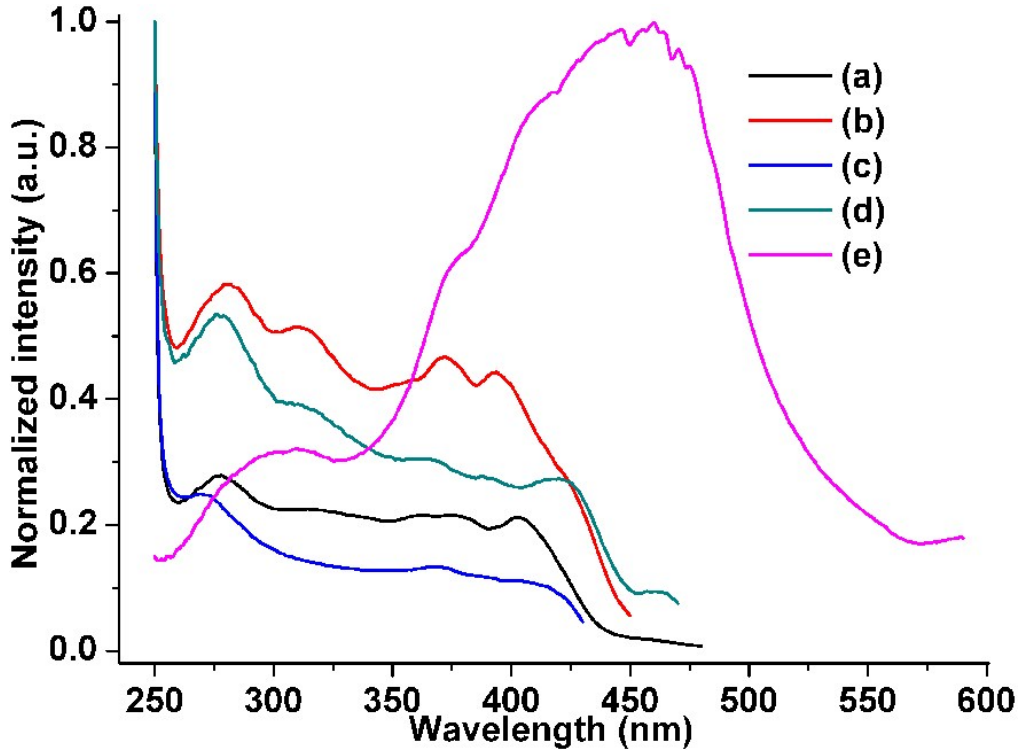

Fig. S2 Normalized excitation spectra of microcrystals **A** (a), **B** (b), **C** (c), **D** (d) and **E** (e).

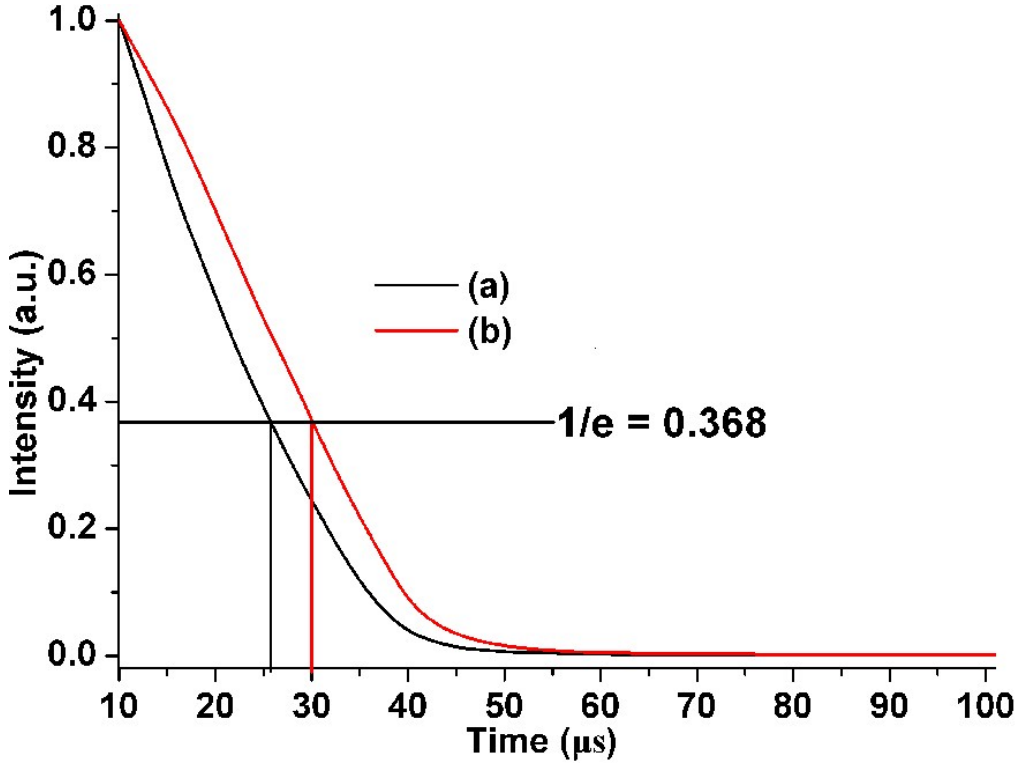

Fig. S3 The decay lifetime curves of microcrystals **C** (a) and **D** (b) at emission peak of 447 and 455 nm, respectively in solid state. The lifetime (τ) is defined as the time in which the emission intensity decays to 1/e of the initial intensity (I_o), where e is the natural log constant and is equal to 2.718. ($I = I_o e^{-(t/\tau)} \Rightarrow \tau = t \Rightarrow I = (1/e)\ I_o$).[S2]

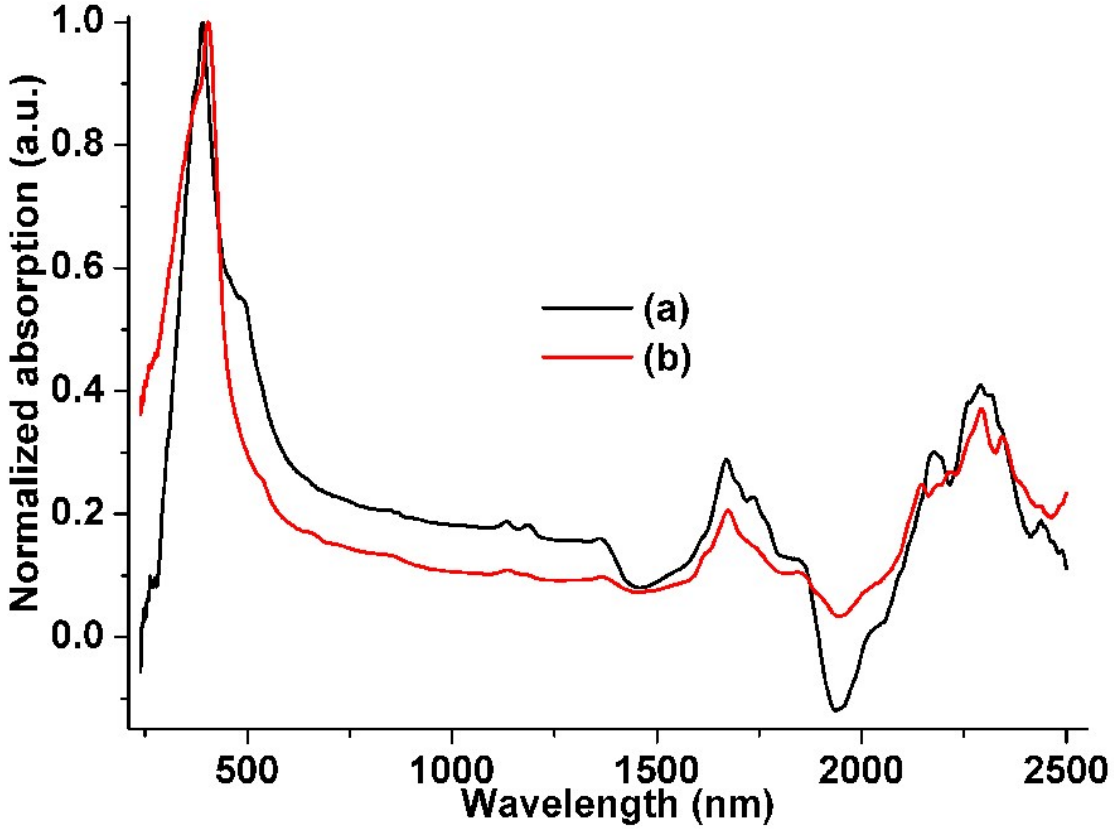

Fig. S4 UV/Vis/NIR absorption spectra of microcrystals **A** (a) and **B** (b) in solid state.

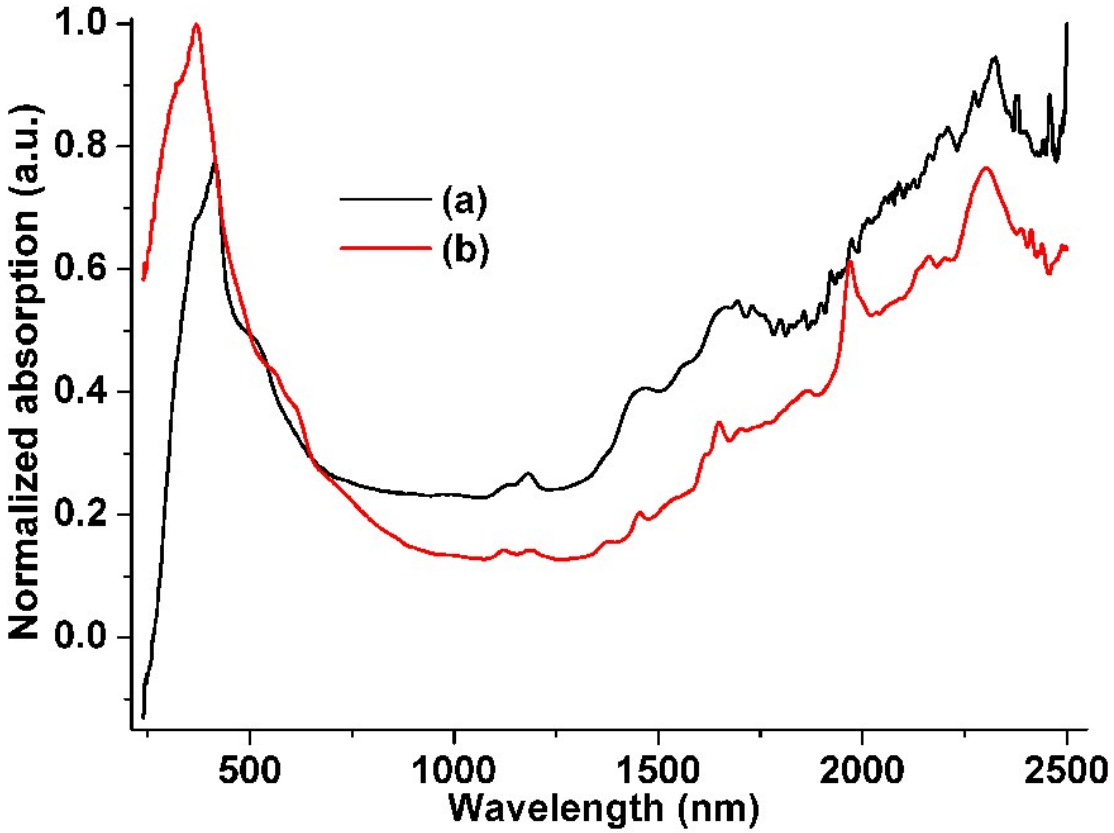

Fig. S5 UV/Vis/NIR absorption spectra of microcrystals **C** (a) and **D** (b) in solid state.

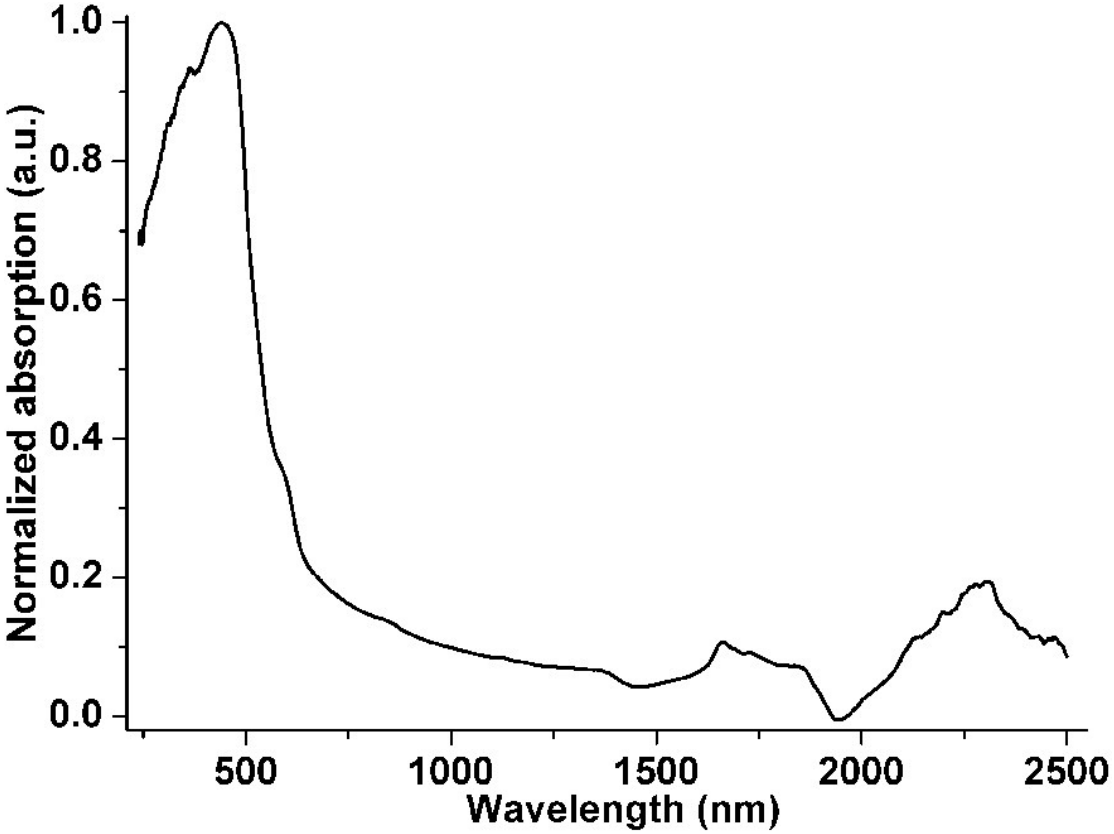

Fig. S6 UV/Vis/NIR absorption spectra of microcrystal **E** in solid state.

Reference

S1 G. P. Yong, C. F. Li, Y. Z. Li and S. W. Luo, *Chem. Commun.*, 2010, **46**, 3194.

S2 K. C. Stylianou, R. Heck, S.Y. Chong, J. Bacsa, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2010, **132**, 4119.