Electronic Supplementary Information

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

Cong Zhang, Chen Shen and Guo-Ping Yong*

Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China
E-mail: gpyong@ustc.edu.cn

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 BaSO₄-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•) was synthesized by similar procedure to synthesis of 2,3'-biimidazo [1,2-a]pyridin-2'-one radical. S1

Synthesis of BF₂-7,7'-dmbipo (microcrystal A) and BF₂-8,8'-dmbipo (microcrystal B): 0.50 mL of BF₃·OEt₂ (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•. 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_{2}N_{4}O: 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\textsubscript{2}-7,7'-dmbipoHCl (microcrystal C) and BF\textsubscript{2}-8,8'-dmbipoHCl (microcrystal D): At room temperature, 0.65 g (2.00 mmol) of BF\textsubscript{2}-7,7'-dmbipo or BF\textsubscript{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_{2}N_{4}O: 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\textsubscript{2}-8,8'-dmbipoHCl (microcrystal E): At room temperature, 0.65 g (2.00 mmol) of BF\textsubscript{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_{2}N_{4}O: 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 ($\tau$) is defined as the time in which the emission intensity decays to $1/e$ of the initial intensity ($I_0$), where $e$ is the natural log constant and is equal to 2.718. ($I = I_0 e^{(-t/\tau)} \Rightarrow \tau = t \Rightarrow I = (1/e) I_0$). 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