Supporting Information for

Remarkable Fluorescence Change Based on the Protonation/Deprotonation Control in Organic Crystals

Jibo Zhang, Jinlong Chen, Bin Xu*, Lijuan Wang, Suqian Ma, Yujie Dong, Bao Li, Ling Ye and Wenjing Tian*

State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, 130012, Jilin, P. R. China

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1. General Information

All solvents and materials were used as received from commercial suppliers without further purification. ¹H NMR spectra were recorded on Bruker AVANCE III 500MHz spectrometer with tetramethylsilane as the internal standard. The time of flight mass spectra were recorded using a Kratos MALDI-TOF mass system. UV-vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded by Shimadzu RF-5301 PC spectrometer and Maya2000Pro optical fiber spectrophotometer. Crystalline state PL efficiencies were measured using an integrating sphere (C-701, Labsphere Inc.), with a 405 nm Ocean Optics LLS-LED as the excitation source, and the light was introduced into the integrating sphere through optical fiber. The fluorescence microscopy images were obtained on an Olympus BX51 fluorescence microscope. The ground state geometries were fully optimized by the density functional theory (DFT) method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G* basis set using the Gaussian 03 software package.

The single crystal of BP3VA was prepared by vaporizing mixed solvent of chloroform and ethanol (3:1 v/v) slowly at room temperature. And the single crystal of BP3VA-HCl was prepared in the same way except for the slightly excess hydrochloric acid added into the mixed solvent. Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphite-monochromator Mo·Ka radiation. The structures were solved with direct methods using SHELXTL and refined with full-matrix least-squares on F². Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The powder X-ray diffraction patterns were recorded by Rigaku SmartLab X-ray diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å).

CCDC 919148 and 919149 contain the supplementary crystallographic data for this paper. These date can be obtained free of charge from the Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request /cif.

2. Synthesis of BP3VA



Scheme S1 Synthesis route of BP3VA

Synthesis of (1)9,10-bis(dichloromethyl)anthracene

A two-necked bottle (500 mL) was oven-dried, anthracene (18 g, 0.1 mol) was dissolved in 1,4-dioxane (144 ml) and HCl (24 mL). Paraformaldehyde (15.2 g) was added to the solution and the mixture was stirred for 2 h at 110 °C under HCl atmosphere. After removing the HCl atmosphere, the reaction went on stiring for 4 h at this temperature. The reaction mixture was cooled to room temperature and washed by 1,4-dioxane and neutralized by water to give compound as yellow powder 12.3 g (40% yield). ¹H NMR (500MHz CDCl₃) δ 8.366-8.346 (m, 4H, Ar), 7.638-7.618 (m, 4H, Ar), 5.580 (s, 4H, CH₂).

Synthesis of (2) tetraethyl anthracene-9,10-diylbis(methylene)diphosphonate

Compound (1) (17g, 50mmol) was dissolved in P(OC₂H₅)₃(86.5ml,0.5mol). The reaction mixture was heated to 150 °C in an oil bath and stirred for 18 h at this temperature under N₂ atmosphere. After being cooled to room temperature, the reaction mixture was poured into petroleum ether and filtered to give 18 g of compound (2) as a light yellow solid (75% yield).^[1,2] ¹H NMR (500MHz CDCl₃) δ 8.388-8.354 (m, 4H, Ar), 7.582-7.548 (m, 4H, Ar), 4.263 (s, 2H, CH₂), 4.196 (s, 2H, CH₂), 3.931-3.777 (m, 8H, CH₂), 1.080-1.033 (t, 12H, CH₃).

Synthesis of (BP3VA) 9,10-bis((E)-2-(pyridin-3-yl)vinyl)anthracene

Compound (2) tetraethylanthracene-9,10-diylbis(methylene)diphosphonate (0.500 g, 1.04mmol) was stirred with Bu^tOK (0.468 g, 4.17mmol) in THF (70 mL) under nitrogen. Compound nicotinaldehyde (0.24 mL, 2.53mmol) in THF (70 mL) was added to the solution that was kept in an ice-bath and the mixture was stirred for 12 h at room temperature. The resultant precipitate was washed successively with MeOH and filtered off to give compound as yellow powder (45% yield). ¹H NMR (500MHz CDCl₃) δ 8.894-8.890 (m, 2H, Ar), 8.620-8.608 (m, 2H, Ar), 8.380-8.360 (m, 4H, Ar), 8.062-8.042 (m,2H, Ar), 8.042-8.009 (d, *J* = 16.5Hz, 2H, CH=CH), 7.530-7.510 (m, 4H, Ar), 7.425-7.400 (m, 2H, Ar), 6.965-6.932 (d, *J* = 16.5Hz, 2H, CH=CH). VMALDI/TOF MS: Calcd for C₂₈H₂₀N₂: 384.16, Found: 384.87. Anal. Calcd for C₂₈H₂₀N₂: C, 87.47; H, 5.24; N, 7.29, Found: C, 86.63; H, 5.98; N, 7.39.

3. Summarized photophysical properties of BP3VA

Table S1. Photophysical properties of BP3VA in different solvents						
Solv	/ent	CHX	CF	THF	DMF	CF+TFA(excess)
λ_{Abs} (nm)		405	412	407	408	432
$\lambda_{em}(nm)$		567	585	610	635	596
Φ	a F	0.65	0.45	0.33	0.11	0.18
	$ au_1$	0.16(0.04)	0.12(0.06)	0.05(0.03)	0.07(0.09)	0.10(0.14)
τ(ns)	τ_2	5.77(0.96)	3.61(0.94)	3.53(0.97)	1.44(0.91)	1.37(0.86)
	$\tau_{\rm avr}$	5.56	3.38	3.44	1.30	1.19

^aUsing Rhodamine B as the standard reference.



Figure S1. a) Normalized UV-vis absorption and PL spectra of BP3VA in different solvents. (Abbreviation: CHX: cyclohexane; CF: chloroform; THF: tetrahydrofuran; DMF: dimethyl formamide). b) Normalized UV-vis absorption and PL spectra of BP3VA in CF with excess HCl. c) Time-resolved peak fluorescence of BP3VA in different solvents (CHX, CF, THF and DMF).

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4. ¹H NMR of BP3VA with TFA in CDCl₃



Figure S2. ¹H NMR spectra of BP3VA in (I) CDCl₃and (II) CDCl₃ with TFA expanded in 7-9 ppm region.

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5. The aggregating state of molecules in single crystals



Figure S3. The aggregating state of molecules in BP3VA single crystals. d= 6.342 (2) Å.



Figure S4. The aggregating state of molecules in BP3VA-HCl single crystals. d= 4.993 (2) Å.

C-H···Cl-

V

Table 52. Summary of the supramolecular interactions in the two erystars				
Crystal	Ori	entation of Interaction	$d(Å)^a$	$A(^{\circ})^{b}$
BP3VA	Ι	C-H···N	2.585(2)	156(1)
	II	$Pyrid^{c} \rightarrow An^{d}$	2.796(2)	163(1)
BP3VA-HC1	Ι	Vin ^e →An	2.661(1)	140(1)
	II	N-H···Cl ⁻	2.163(1)	159(1)
	III	$C-H\cdots Cl^{-}$	2.817(1)	148(1)
	IV	C-H···Cl ⁻	2.856(1)	128(1)

Table S2. Summary of the supramolecular interactions in the two crystals

^a Distance of the H…ring, N…H or the Cl⁻…H interaction. ^b Angel of the C-H…ring, C-H…N, N-H…Cl⁻ or the C-H…Cl⁻ interaction. ^cPyridine. ^dAnthracene. ^eVinyl substituent.

2.621(1)

167(1)

6. Theoretical calculated frontier orbitals contribution of BP3VA



Figure S5. The theoretical calculated frontier orbitals contribution of BP3VA and protonated BP3VA in (I) gas state and (II) crystals.

7. UV-vis absorption of BP3VA and BP3VA-HCl crystals



Figure S6. UV-vis absorption of BP3VA and BP3VA-HCl crystals performed by diffuse reflectance mode.

8. Selected Dihedral Angles (deg) in Crystals



Table S3. Selected Dihedral Angles (deg) in Crystal

Crystal	$\theta_{(1,2,3,4)}$	$ heta_{(2,3,4,5)}$	$ heta_{(3,4,5,6)}$
BP3VA	7.8	178.5	59.3
BP3VA-HCl	13.4	177.4	53.4

9. PL spectra of BP3VA powder in an atmosphere of HCl at different time



Figure S7. PL spectra of BP3VA powder in an atmosphere of HCl at different time.

10. PL spectra of spin-coated BP3VA film fumed by HCl and TEA



Figure S8. PL spectra of spin-coated BP3VA film fumed by HCl and then by TEA.



11. PL spectra and PXRD patterns of TEA fumed treated by water

Figure S9. a) PL spectra and b) PXRD patterns of TEA fumed powder treated by deionized water.

12. Crystal Data and Structure Refinements of Two Crystals

	BP3VA	BP3VA-HC1
empirical formula	$C_{28}H_{20}N_2$	$C_{28}H_{22}Cl_2N_2$
formula wt	384.46	457.38
Т, К	293(2)	291(2)
crystal system	Monoclinic	Triclinic
space group	$P 2_1/c$	P-1
<i>a</i> , Å	7.3295(15)	4.9933(10)
b, Å	6.3418(13)	7.9912(16)
<i>c</i> , Å	21.422(4)	14.017(3)
a,deg	90.00	87.95(3)
ß,deg	91.26(3)	85.51(3)
y,deg	90.00	81.56(3)
V,Å ³	995.5(4)	551.40(19)
Z	2	1
density, Mg/m^3	1.283	1.377
Absorption coefficient, mm ⁻¹	0.075	0.314
θ range, deg	3.33-27.48	3.85-27.46
no. of reflens collected	9378	5455
no. of unique reflcns	2283	2504
<i>R</i> (int)	0.0336	0.0250
Good-of-fit on F ²	1.029	1.127
$R1 [I > 2\sigma(I)]$	0.0434	0.0427
$wR2 [I > 2\sigma(I)]$	0.1109	0.1152
<i>R1</i> (all data)	0.0623	0.0549
wR2 (all data)	0.1219	0.1290

Table S4. Crystal data and	l structure refinements	of twocrystals
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Reference

(1) He, J.; Xu, B.; Chen, F.; Xia, H.; Li, K.; Ye, L.; Tian, W. J. Phys. Chem. C 2009, 113, 9892.

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