Electronic Supplementary Material (ESI) for Analytical Methods.

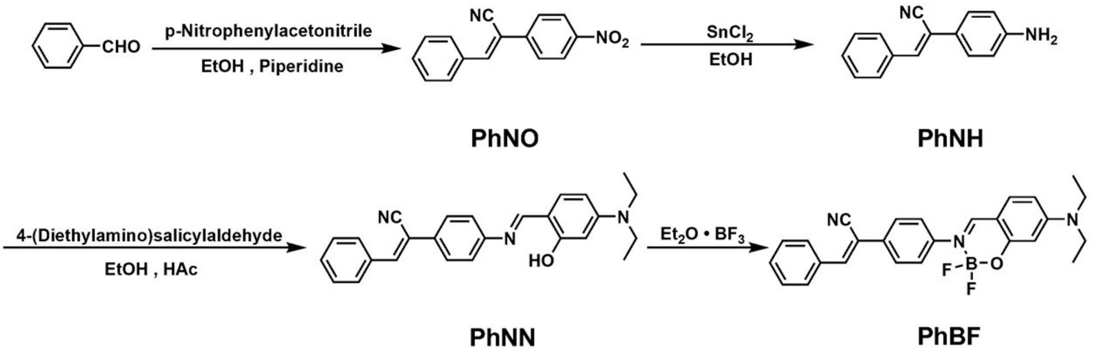
Dual-State Emission Difluoroboron Derivatives for Selective Detection of Picric Acid and Reversible Acid/Base Fluorescence Switching

Yingyong Ni, Shuaishuai Zhang, Xuan He, Jianyan Huang, Lin Kong, Jianjun Yang* and Jiaxiang Yang*

College of Chemistry & Chemical Engineering, Anhui University, Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functional Materials, Hefei 230601, P. R. China.

**Corresponding authors: Jianjun Yang: andayjj@163.com, Jiaxiang Yang: jxyang@ahu.edu.cn.*

E-mails: jxyang@ahu.edu.cn



Scheme S1. Synthetic route of compound **PhBF** and the illustration of the design.

The 4-nitroacetonitrile (458 mg, 2.82 mmol), benzaldehyde (300 mg, 2.83 mmol) and catalytic amount of piperidine were dissolved in 15 mL ethyl alcohol. The mixture was heated to reflux for 4 h. Then, the solvent was removed under vacuum to obtain the solid **PhNO** (460 mg, 1.84 mmol), yield: 65%. FT-IR (KBr, cm^{-1}): 3114， 3080, 3060, 3021, 2927, 2845, 2216, 1588, 1517, 1343, 852. ^1H NMR ($CDCl_3$, 400 MHz): 7.50-7.52 (m, 3H), 7.69 (s, 1H), 7.85 (d, 2H, J = 8.86 Hz), 7.93-7.96 (m, 2H), 8.31 (d, 2H, J = 8.86 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): 109.54, 117.19, 124.39, 126.78, 129.24, 129.77, 131.74, 132.90, 140.60, 145.58, 147.92。

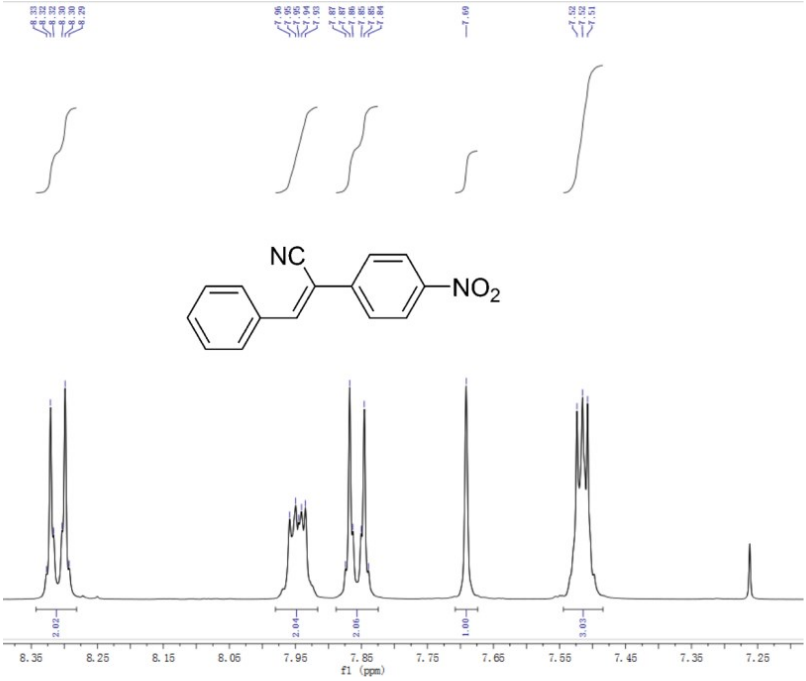


Fig. S1. The ^1H NMR spectra of **PhNO** in $CDCl_3$.

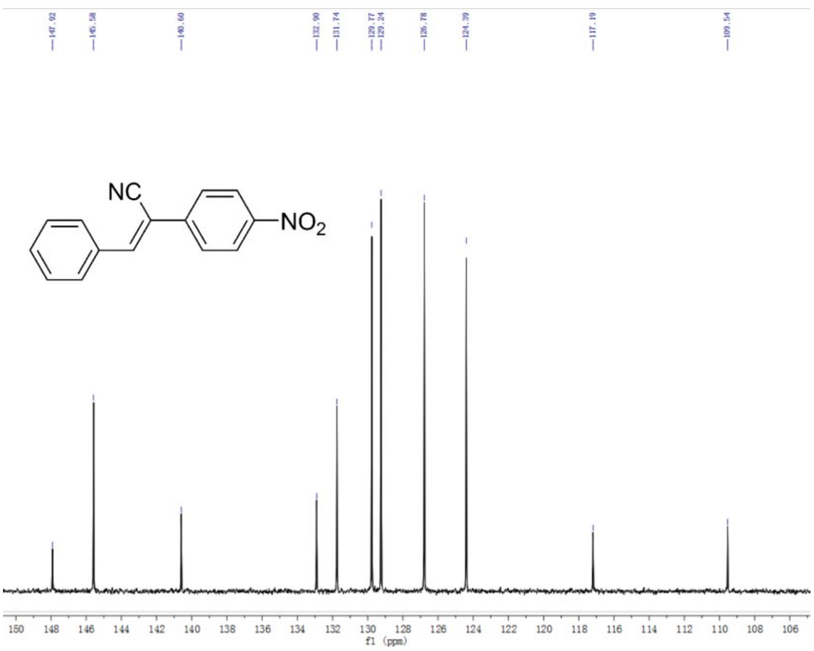


Fig. S2. The ^{13}C NMR spectra of **PhNO** in $CDCl_3$.

The **PhNO** (204 mg, 0.81 mmol) and stannous chloride dehydrate (1.26 g, 5.59 mmol) were dissolved in 25 mL EtOH. The mixture solution was heated to 85 ° C for 4 h. Then, the reaction was quenched by cold saturated salt water (200 mL). The solution was neutralized with $NaHCO_3$ and extracted by ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4. Then, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (1 : 1, V/V) mixture solution as eluent to obtain the yellow compound **PhNH** (147 mg, 0.67 mmol), yield: 82%. FT-IR (KBr, cm^{-1}): 3448, 3359, 3218, 3060, 3032, 2924, 2212, 1626, 1607, 1513, 1295, 1186, 831. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.87 (s, 2H), 6.70 (d, 2H, J = 8.64 Hz), 7.36 (s, 1H), 7.37-7.40 (m, 1H), 7.41-7.45 (m, 2H), 7.47 (d, 2H, J = 8.64 Hz), 7.80-7.84 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): 111.70, 115.12, 118.36, 124.52, 127.25, 128.86, 128.95, 129.81, 134.27, 138.44, 147.61。

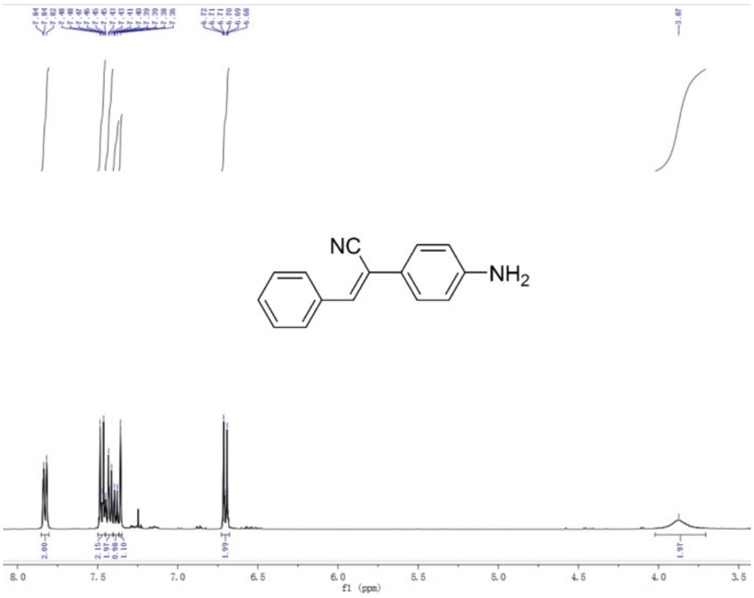


Fig. S3. The ^{1}H NMR spectra of **PhNH** in $CDCl_3$.

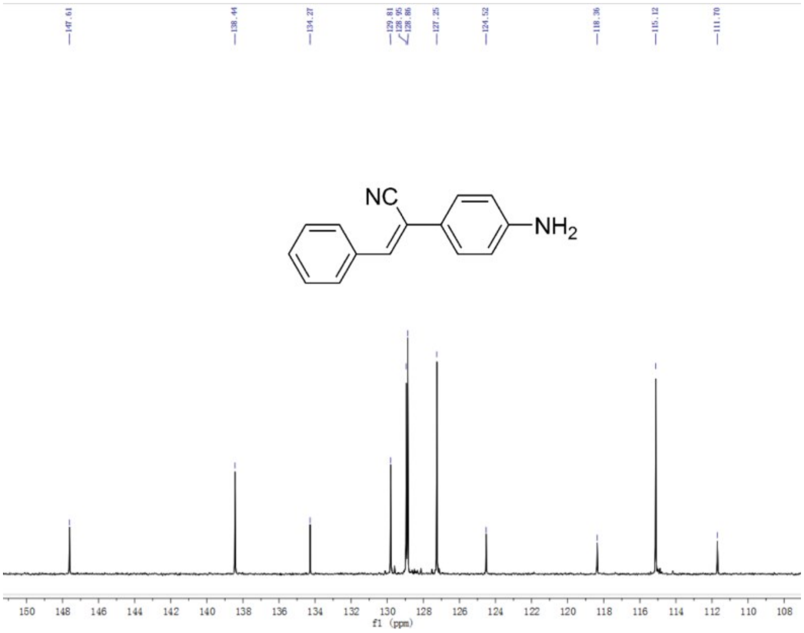


Fig. S4. The ^{13}C NMR spectra of **PhNH** in $CDCl_3$.

The **PhNH** (856 mg, 3.89 mmol), 4-(diethylamino)salicyl-aldehyde (874 mg, 4.52 mmol) were dissolved in methanol (15 mL). And then, two drops of acetic acid were added to the mixture. The solution was heated to 70 ° C for 4 h. Then, the precipitated product was obtained by filtration. The pure **PhNN** was acquired by washing with

EtOH for several times (yellow solid, 1.27 g, 3.20 mmol), yield: 82%. FT-IR (KBr, cm^{-1}): 3445, 3051, 3025, 2968, 2929, 2887, 2210, 1626, 1575, 1519, 1421, 1347, 1133, 820, 752, 705, 531。^{1}H NMR ($CDCl_3$, 400 MHz): δ= 1.21 (t, 6H, J = 7.09 Hz), 3.40 (q, 4H, J = 7.09 Hz), 6.19 (s, 1H), 6.26 (d, 1H, J = 8.78 Hz), 7.17 (d, 1H, J = 8.78 Hz), 7.29 (d, 2H, J = 8.52 Hz), 7.40-7.49 (m, 3H), 7.52 (s, 1H), 7.68 (d, 2H, J = 8.52 Hz), 7.87-7.90 (m, 2H), 8.43 (s, 1H), 13.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 12.73, 44.67, 97.75, 104.14, 109.09, 111.21, 118.02, 121.41, 126.97, 128.96, 129.25, 130.41, 131.41, 133.86, 134.11, 141.10, 149.59, 152.21, 160.65, 164.26。

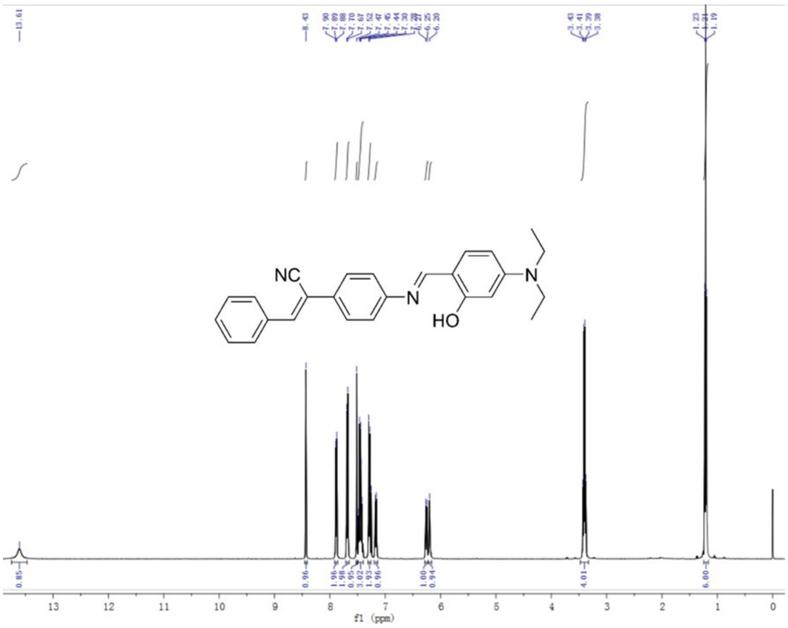


Fig. S5. The ^{1}H NMR spectra of **PhNN** in $CDCl_3$.

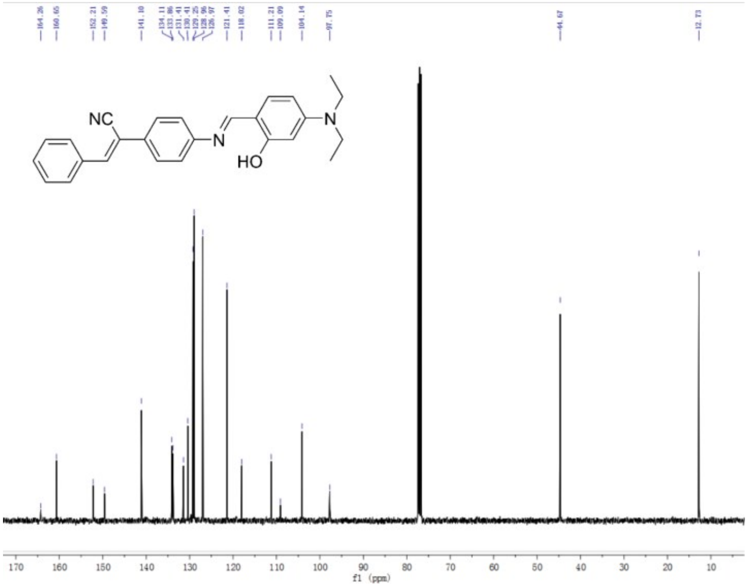


Fig. S6. The ^{1}H NMR spectra of **PhNN** in $CDCl_3$.

The **PhNN** (103 mg, 0.26 mmol) and N,N-diisopropylethylamine (DIPEA, 233 mg, 1.81 mmol)) were dissolved in dichloromethane (5 mL), and the mixture solution was stirred for 2 h at room temperature. BF_3 • Et_2O (360 mg, 2.53 mmol) was dropwise added into the mixture solution. The reaction was traced by TLC until completed. Then, the mixture was poured into cold water (100 mL), and extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$. After solvent was removed under reduced pressure, the rude product was purified by flash chromatography using dichloromethane as eluent to give yellow solid **PhBF** (107 mg, 0.24 mmol), yield: 93%. FT-IR (KBr, cm^{-1}): 3445, 3051, 3025, 2968, 2929, 2887, 2210, 1626, 1575, 1519, 1421, 1347, 1133, 820, 752, 705, 531. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.21 (t, 6H, J = 7.09 Hz), 3.40 (q, 4H, J = 7.09 Hz), 6.19 (s, 1H), 6.26 (d, 1H, J = 8.78 Hz), 7.17 (d, 1H, J = 8.78 Hz), 7.29 (d, 2H, J = 8.52 Hz), 7.40-7.49 (m, 3H), 7.52 (s, 1H), 7.68 (d, 2H, J = 8.52 Hz), 7.87-7.90 (m, 2H), 8.43 (s, 1H), 13.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.73, 44.67, 97.75, 104.14, 109.09, 111.21, 118.02, 121.41, 126.97, 128.96, 129.25, 130.41, 131.41, 133.86, 134.11, 141.10, 149.59, 152.21, 160.65, 164.26. MS (m/z): $[M]^+$, cal. 443.1975, found 443.1958.

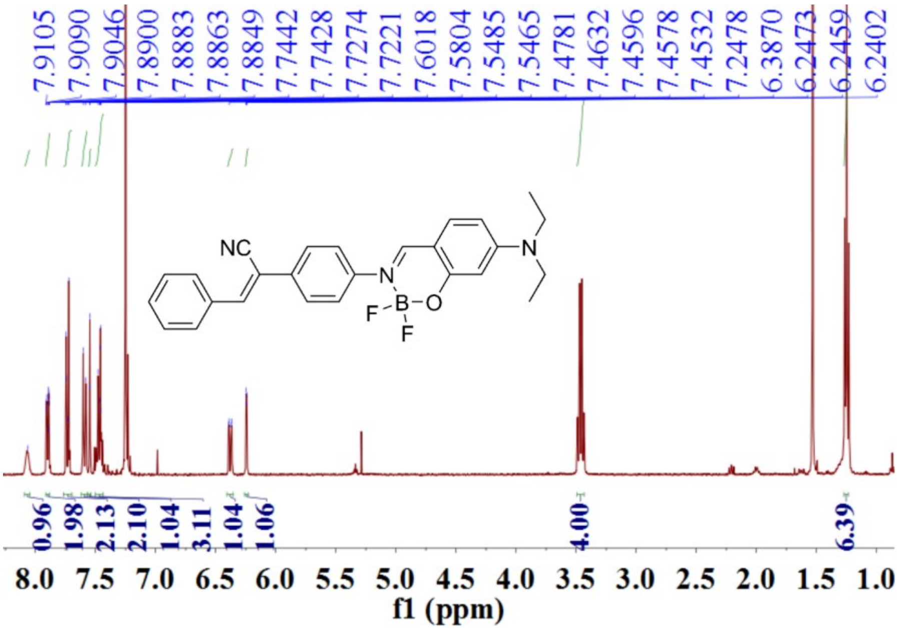


Fig. S7. The ^1H NMR spectra of **PhBF** in $CDCl_3$.

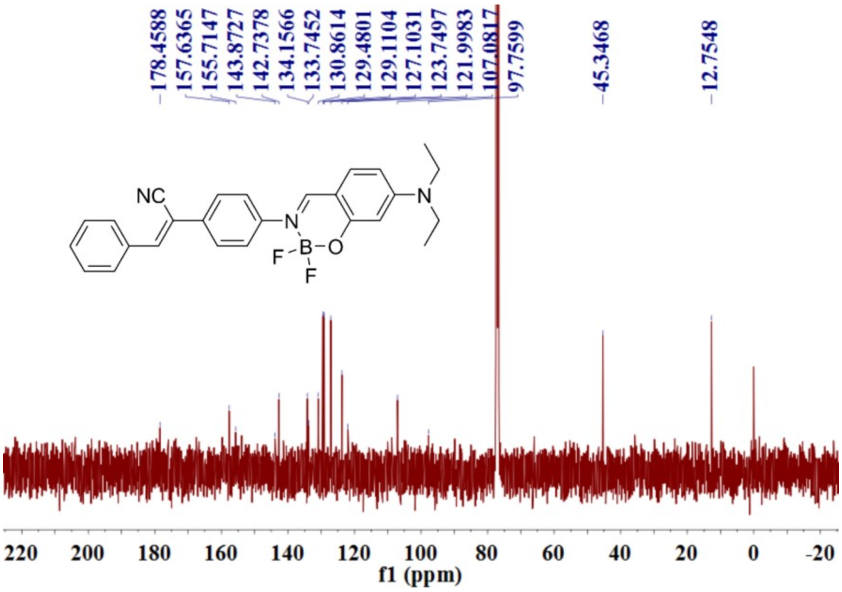


Fig. S8. The ^{13}C NMR spectra of **PhBF** in $CDCl_3$.

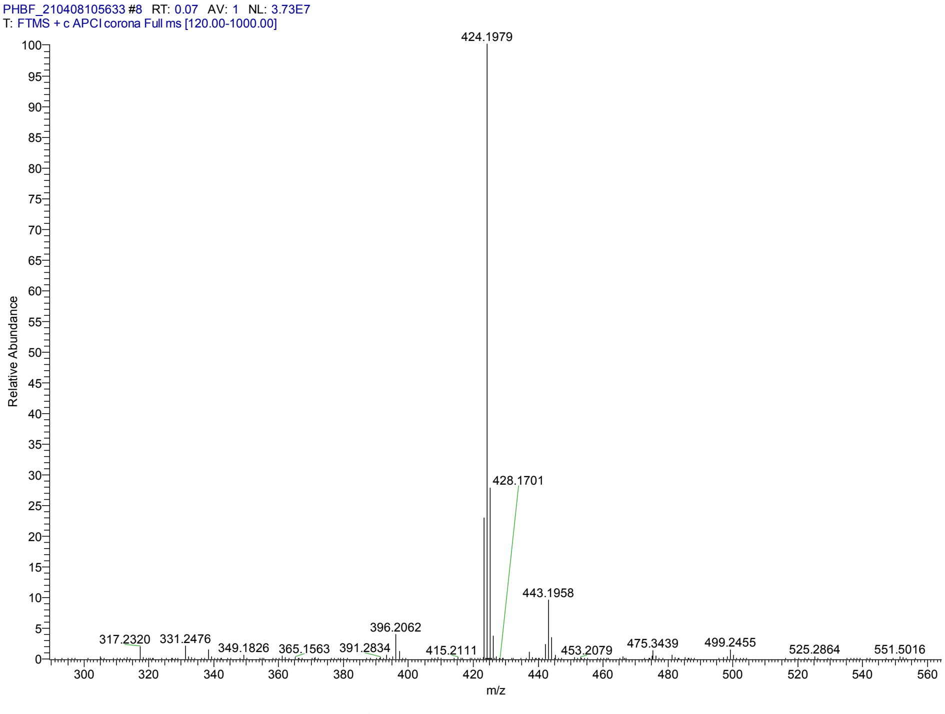


Fig. S9. The HR-MS spectra of **PhBF**.

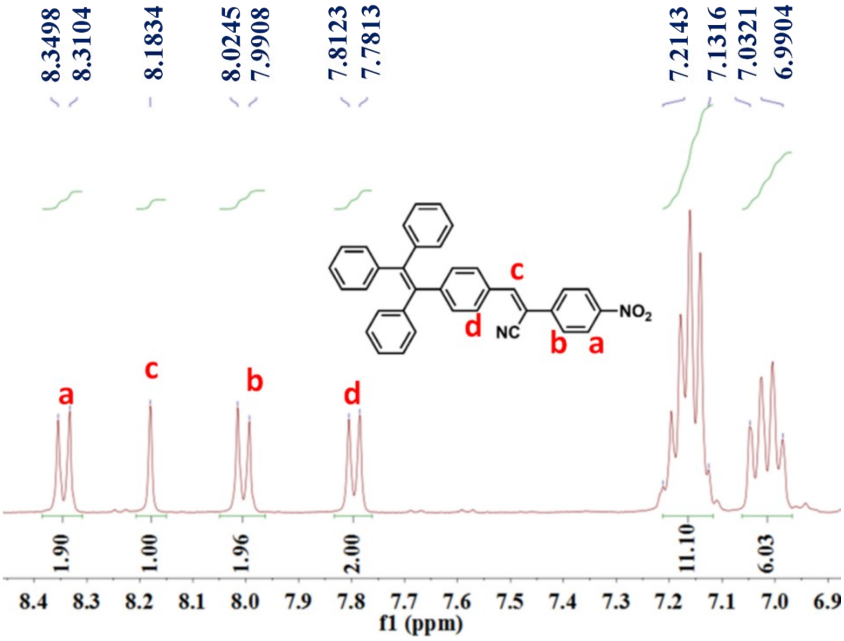


Fig. S10. The ^{1}H NMR spectra of **TPEN** in DMSO-d_6.

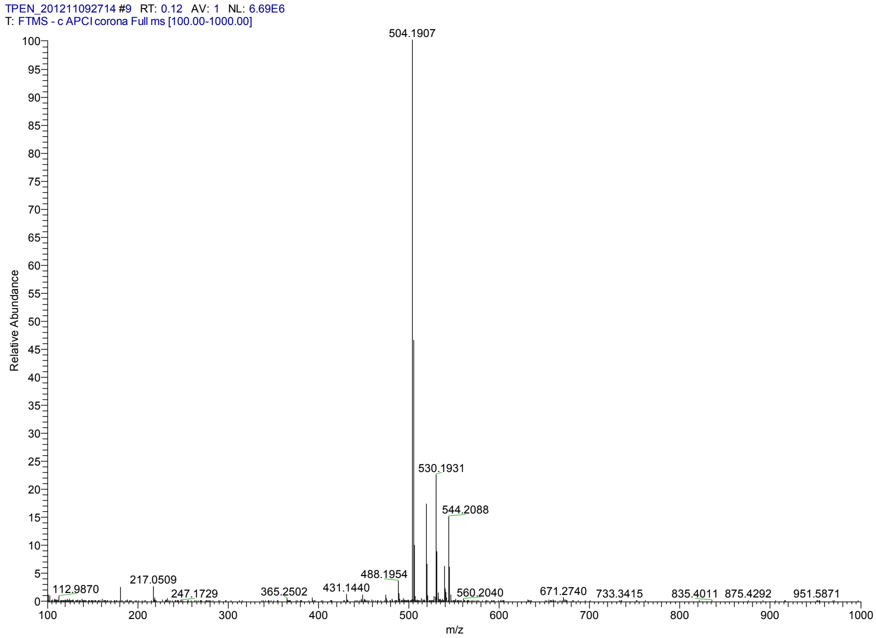


Fig. S11. The HR-MS spectra of **TPEN**.

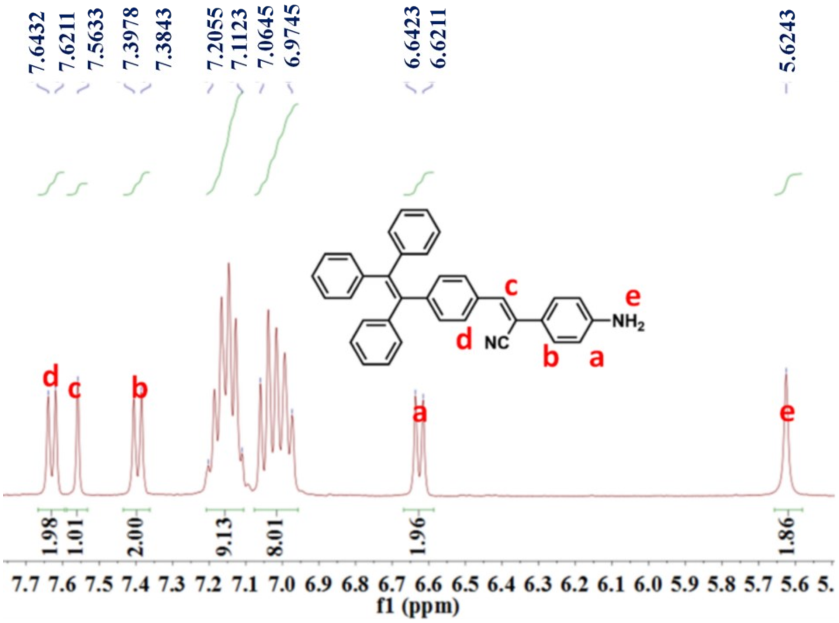


Fig. S12. The ^{1}H NMR spectra of **TPEA** in DMSO-d_6.

Fig. S13. The HR-MS spectra of **TPEA**.

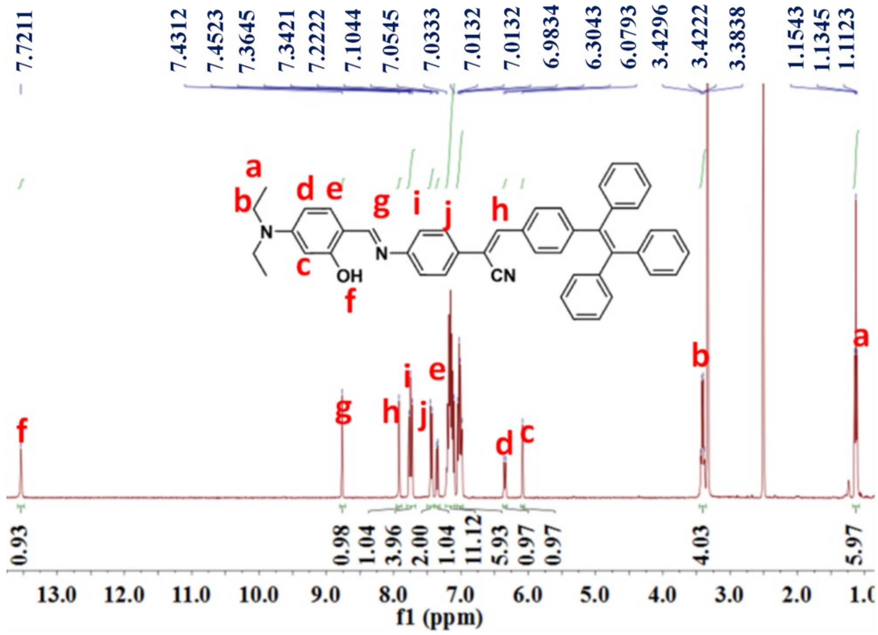


Fig. S14. The ^{1}H NMR spectra of **TPEEA** in DMSO-d_{6}.

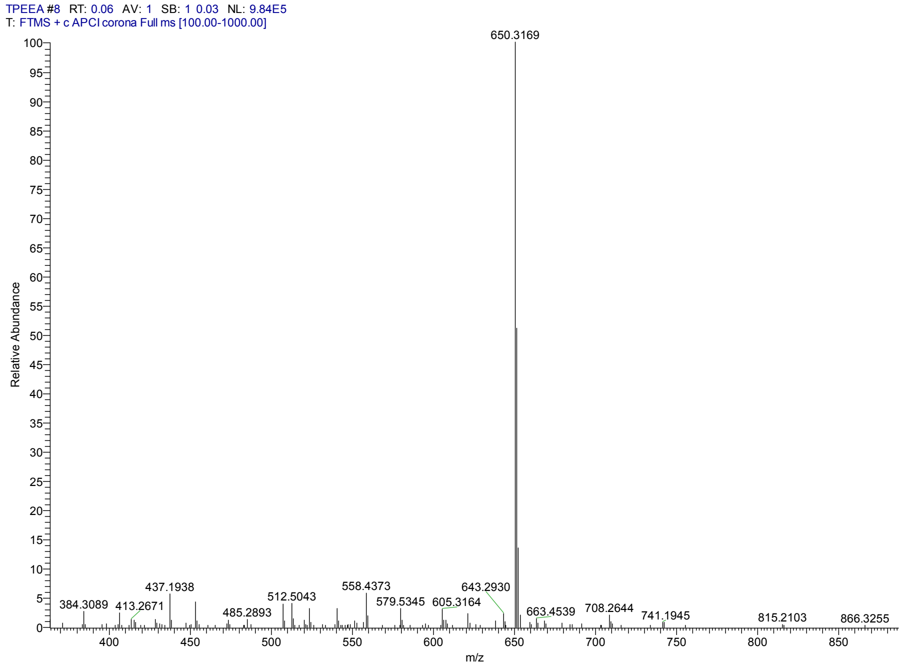


Fig. S15. The HR-MS spectra of **TPEEA**.

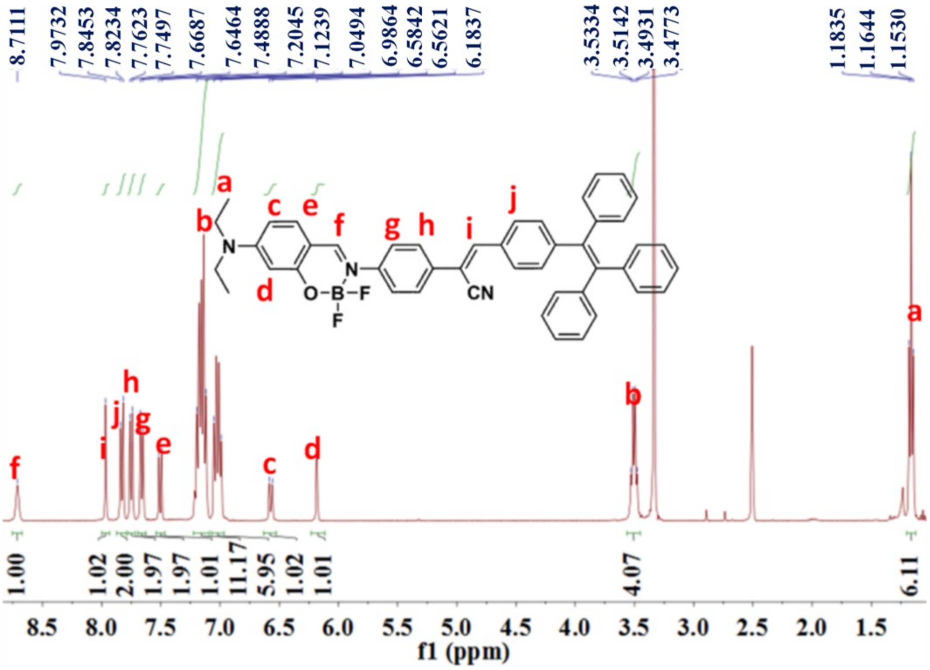


Fig. S16. The ^{1}H NMR spectra of **TPEBF** in DMSO-*d*$_6$.

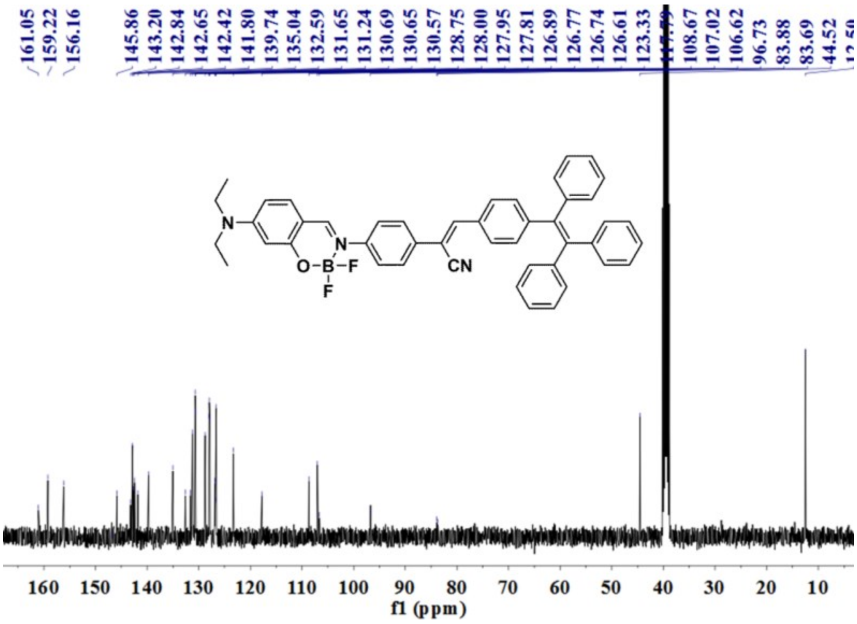


Fig. S13. The ^{13}C NMR spectra of **TPEBF** in DMSO-*d*$_6$.

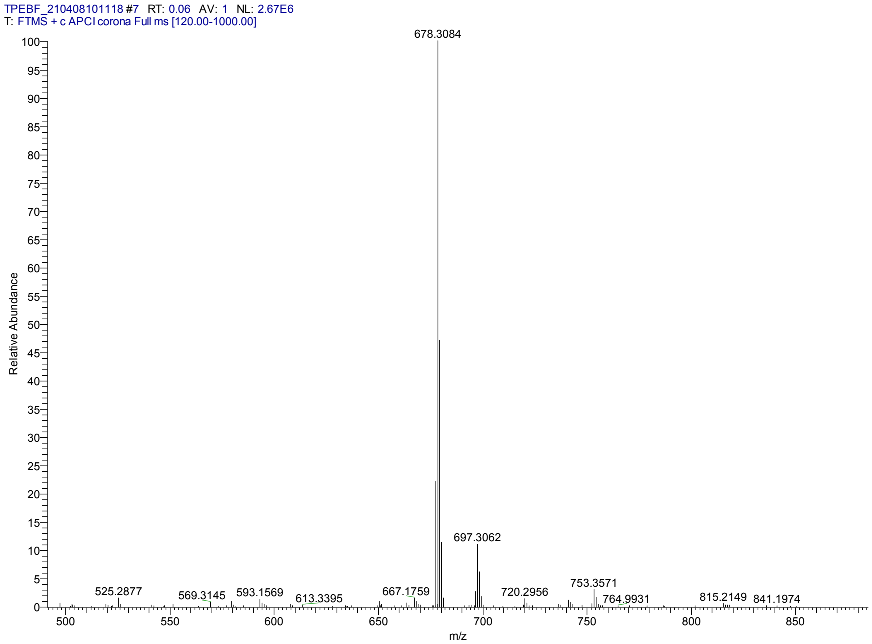


Fig. S17. The HR-MS spectra of **TPEBF**.

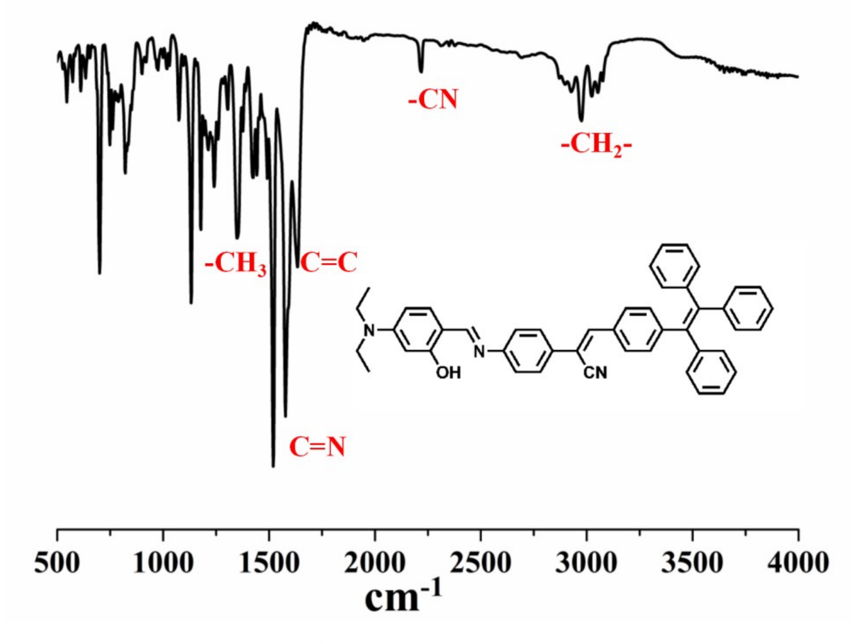


Fig. S18. The FT-IR spectra of **TPEEA**.

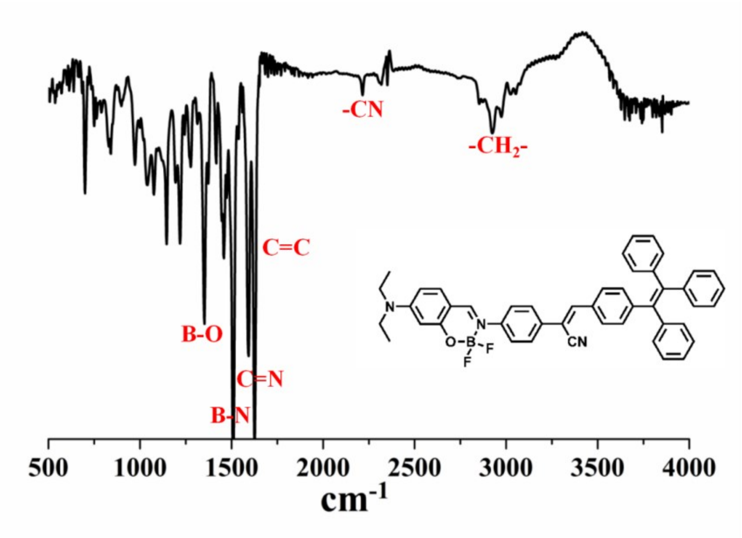


Fig. S19. The FT-IR spectra of **TPEBF**.

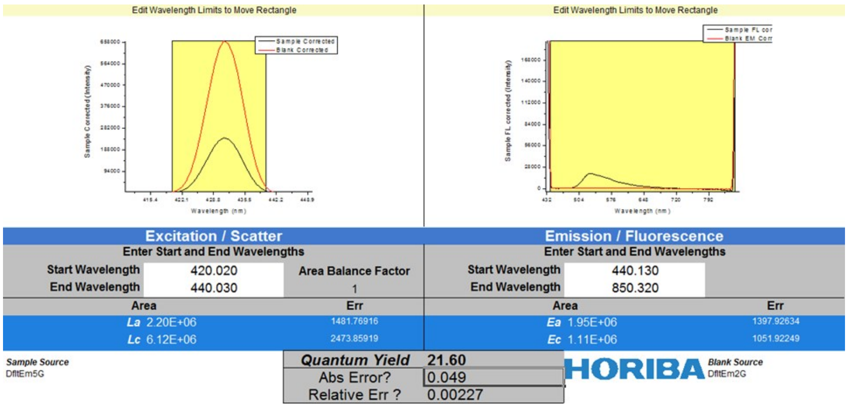


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Fig. S20. The fluorescence quantum yield information of PhBF.

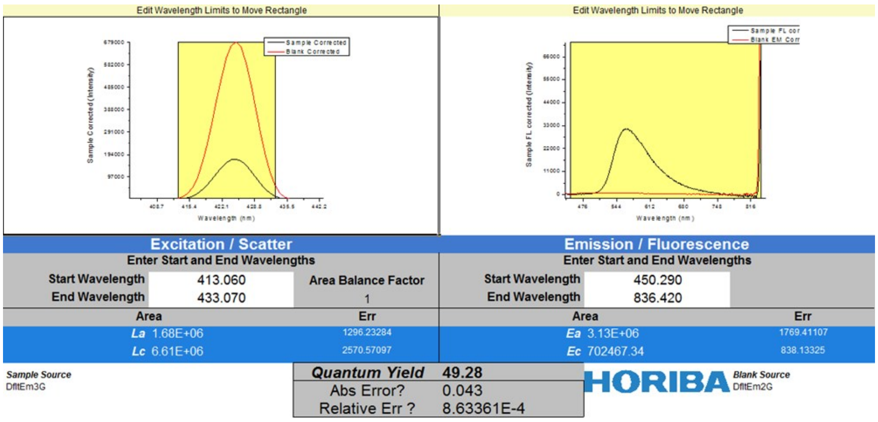

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Fig. S21. The fluorescence quantum yield information of **TPEBF**.

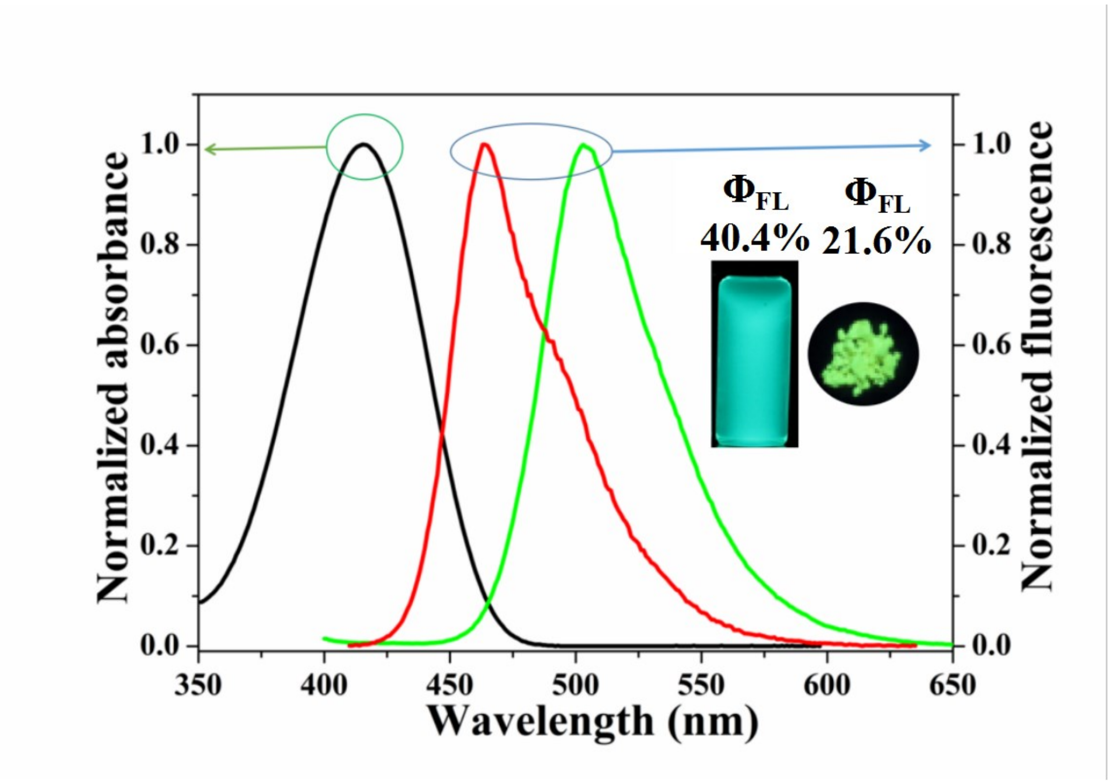

Fig. S22. The normalized UV-vis (blank line) and FL spectra of **PhBF** in THF solution (red line), solid state(green line); Inset: photographs of **PhBF** in THF and in solid state taken under 365 nm UV light.

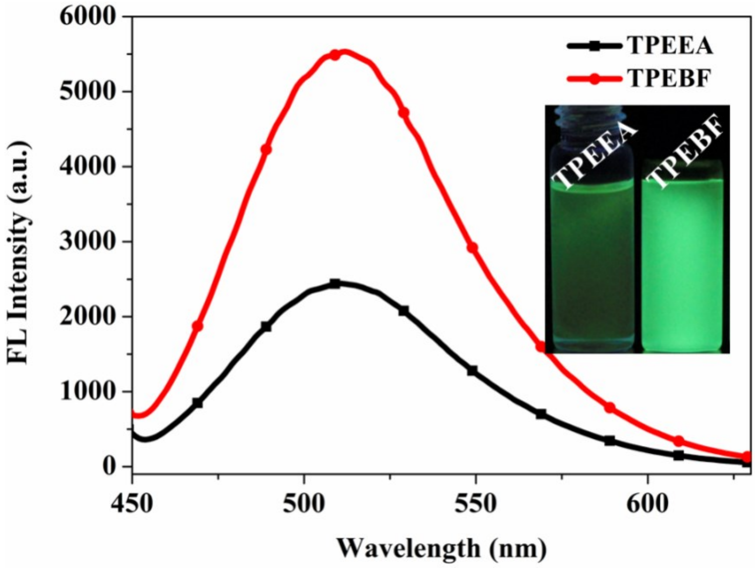

Fig. S23. The fluorescence spectra of **TPEEA** and **TPEBF** (1.0×10^5 M) in THF solution.

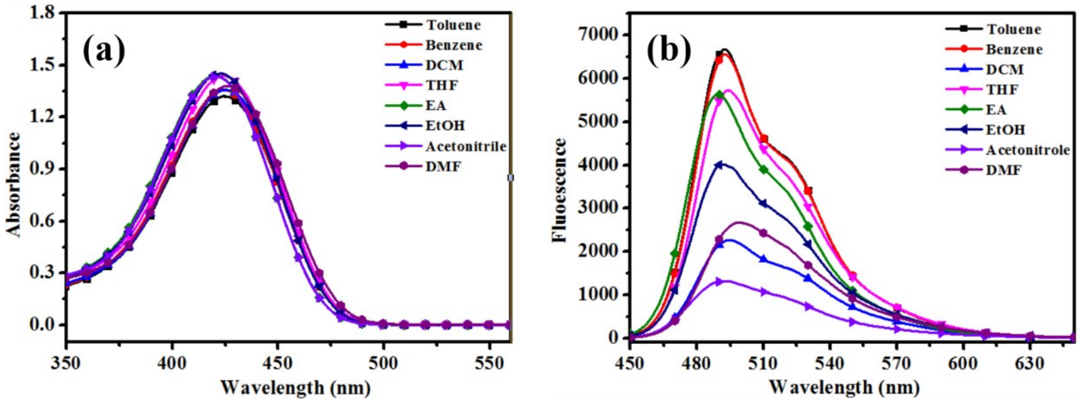

Fig. S24. UV-vis spectra (a) and (b) fluorescence spectra of **TPEBF** in different solvents

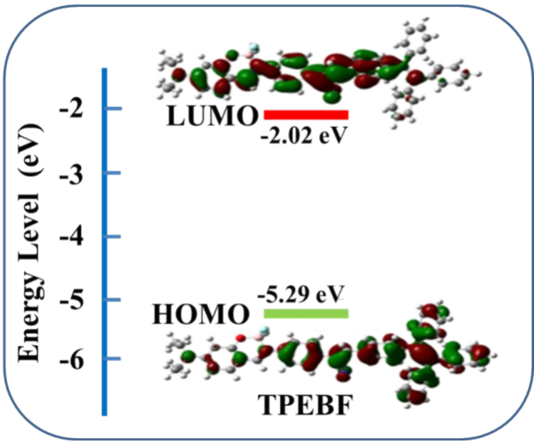

Fig. S25. The molecular orbital surfaces of the HOMOs and LUMOs of **TPEBF** obtained at the B3LYP/6-31G* level

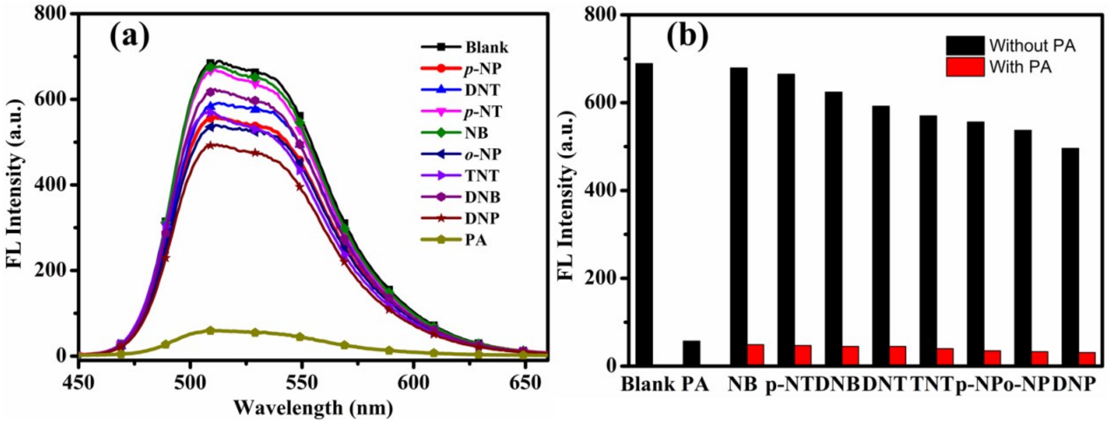

Fig. S26. (a) Fluorescent spectra of **TPEBF** (10 uM) in THF/H_2O solution (1 : 9, v/v) upon the different NACs. (b) Quenching percentages of compound **TPEBF** (10 uM) with different analytes (200 ppm) before (black) and after (red) the addition of 100 ppm PA.

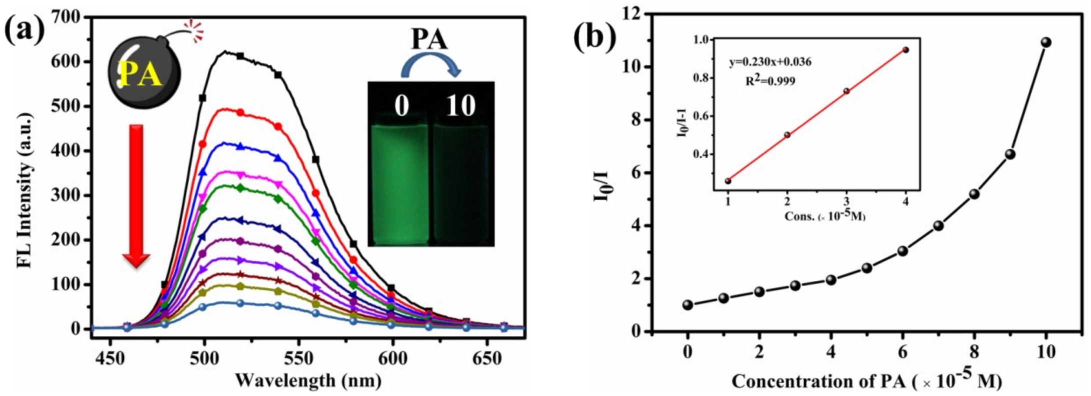

Fig. S27. (a) The fluorescent spectra of **TPEBF** (50 uM) in THF/H_2O solution (1 : 9, v/v) upon addition of incremental amount of PA (0-10 equiv.; λ_{ex} = 410 nm); Insert: photograph the emission of a solution of **TPEBF** in THF upon addition of PA (irradiation under UV lamp at 365 nm); (b) Stern-Volmer plot of **TPEBF** for PA.

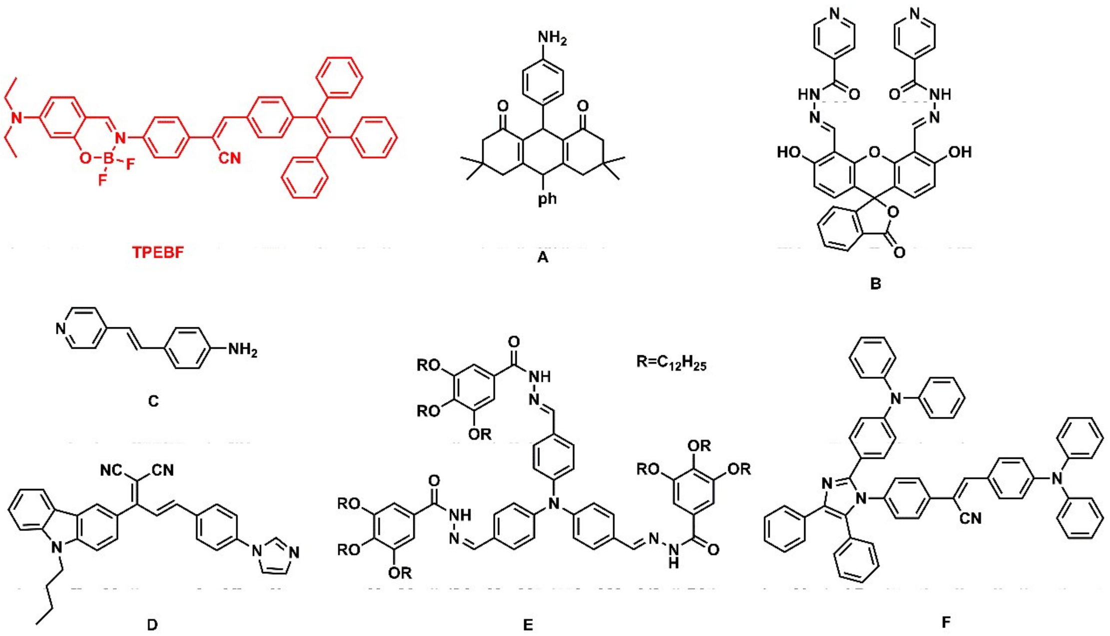

Fig. S28. Molecular structure in **Table S1**

Table. S1. Comparison of the sensing performance of some reported probes for PA

Molecular structure	Detecting goal	Detecting system	*Ksv* (M^{-1})	LOD	Ref.
TPEBF	PA	THF	1.23×10^4	497 nM	This work
		THF : H_2O=1：9	2.3×10^4	355 nM	
A	PA	CH_3OH	1.8×10^4	2.4 μM	[1]
B	PA	ethanol	2.5×10^5	0.11 μM	[2]
C	PA	THF	4.106×10^5	400 ppb	[3]
D	PA	DMF : H_2O=1：9	1.3×10^4	3.55μM	[4]
E	PA	1-octanol	6.8×10^2	0.9 nM	[5]
F	PA, DNP	THF : H_2O=1：9	5.0×10^3	5.0μM	[6]

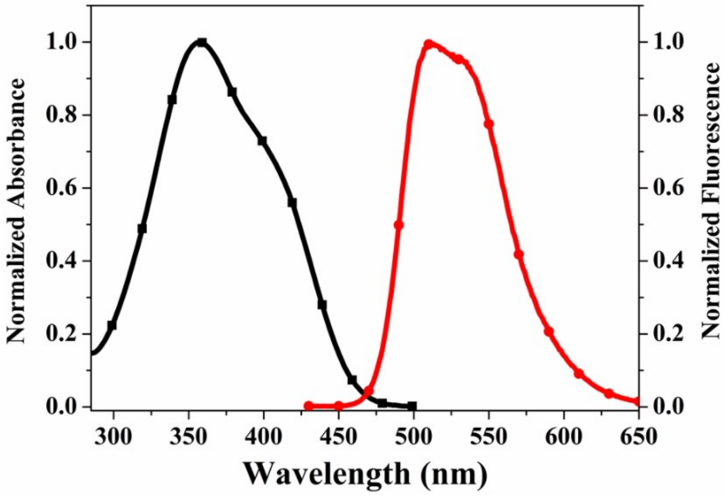

Fig. S29. Normalized absorption spectrum of PA and the fluorescence spectrum of **TPEBF** in THF/H_2O solution (1 : 9, v/v).

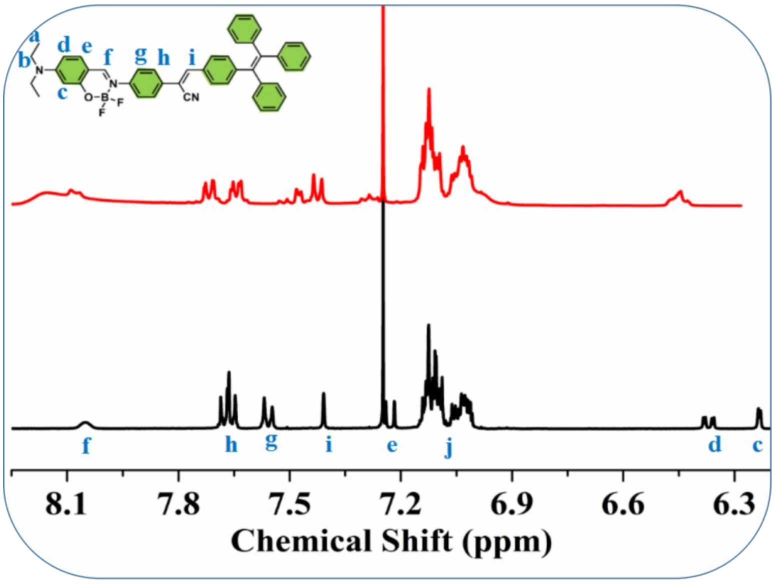

Fig. S30. Partial ^{1}H NMR spectra of **TPEBF** (blank line) and after the addition TFA (red line).

Notes and references

[1] X. C. Sun, J. K. He, Y. T. Meng, L. C. Zhang, S. C. Zhang, X. Y. Ma, S. Dey, J. Zhao and Y. Lei. *J. Mater. Chem. A*, 2016, **4**, 4161.

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[3] J. T. Pan, F. Tang, A. X. Ding, L. Kong, L. M. Yang, X. T. Tao, Y. P. Tian and J. X. Yang. *RSC Adv*., 2015, **5**, 191.

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[5] S. Mondal, P. Bairi, S. Das, P. A. K. Nandi. *Chem Eur J.* 2018, **24**, 5591.

[6] Y. Y. Zhang, J. Y. Huang, L. Kong, Y. P. Tian and J. X. Yang. *CrystEngComm*, 2018, **20**, 1237.