Supporting information for

Triphenylamine-Based Benzoxazole Derivate as a High-Contrast Piezofluorochromic Material Induced by Protonation

Pengchong Xue,*[a,b] Peng Chen,[c] Junhui Jia,[a] Qiuxia Xu,[a] Jiabao Sun,[a] Boqi Yao,[a] Zhenqi Zhang,[a] and Ran Lu *[a]

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

[b] State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, P. R. China

c Key Laboratory of Functional Inorganic Material Chemistry (MOE), School of Chemistry and Materials Science, Heilongjiang University, Harbin, P. R. Chin)

Email: xuepengchong@jlu.edu.cn luran@mail.jlu.edu.cn

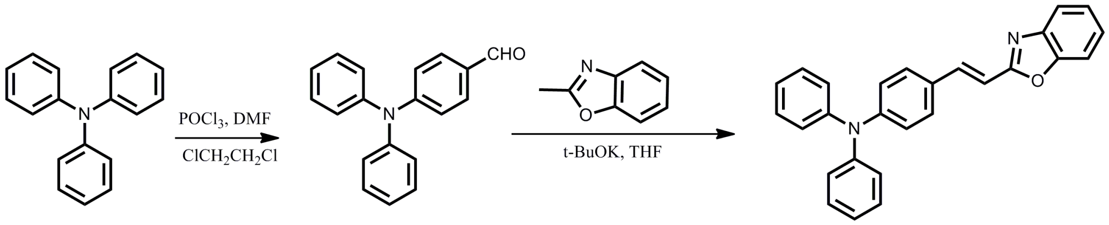
Experimental section

General information

All the raw materials were used without further purification. All the solvents as analytical reagent were purchased from Beijing Chemical Works (Beijing, China), and were used without further purification. Water used throughout all experiments was purified with the Millipore system. The UV-vis absorption spectra were obtained using a Mapada UV-1800pc spectrophotometer. Photoluminescence measurements were taken on a Cary Eclipse Fluorescence Spectrophotometer. The fluorescence quantum yields of **BVDP** in solvents were measured by comparing to a standard (9,10-diphenyl anthracene in benzene, $\Phi_F = 0.85$). The excitation wavelength was 370 nm. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass spectrometers. C, H, and N elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. Fluorescence microscopy images were taken on a fluorescence microscope (XSP-BM21AY, SOIF6, China). Excitation wavelength for fluorescence microscopy measurements is 330-385 nm. XRD patterns were obtained on an Empyrean X-ray diffraction instrument equipped with graphite-monochromatized CuKα radiation (λ=1.5418 Å), by employing a scanning rate of $0.026^{\circ}\ s^{-1}$ in the 2θ range from 5 to 30°. The samples were prepared by casting crystal powders, ground solid and fuming samples on glass slides at room temperature. Single crystal was obtained in the mixture of CH_2Cl_2 and n-hexane by slow solvent diffusion method. The molecular configuration in crystal was used to obtained frontier orbitals of **BVDP** by density functional theory (DFT) calculations at B3LYP/6-31G level with the Gaussian 09W program package.[1]

Single crystal of **BVDP** was selected for X-ray diffraction analysison in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystals were kept at room temperature during data collection. The structures were solved by the direct methods and refined on F2 by full-matrix least-square using the SHELXTL-97 program.[2] The C, N, O and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically. CCDC 973275 contains the supplementary crystallographic data for this paper.

Synthesis, Procedures, and Characterization



Scheme S1. Synthesis route of **BVDP**.

BVDP could be easily obtained by two-step reactions, as shown in Scheme S1. The detailed experimental procedures were as follows:

4-(diphenylamino)benzaldehyde

$POCl_3$ (8.1 mL) was dropped slowly into DMF (24 mL) at 0 ºC and stirred for another 2 h at room temperature. To the above solution was added a dichloromethane (CH_2Cl_2) solution of triphenylamine (15 g, 61.2 mmol). After the mixture was refluxed for 10 h CH_2Cl_2 was removed. The residue was poured into water (500 mL) and the yellow solid was collected by suction filtration. Product was obtained by recrystallization in ethanol (95% yield). Element analysis (%): calculated for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12; Found: C, 83.45; H, 5.49; N, 5.21. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.00$ (d, J = 8.9, 2H), 7.30–7.36 (t, J = 7.8, 4H), 7.15–7.18 (m, 6H), 7.67 (d, J = 8.9, 2H), 9.79 (s, 1H).

(E)-4-(2-(benzo[d]oxazol-2-yl)vinyl)-N,N-diphenylaniline (BVDP)

To a suspension of *t*-BuOK (0.98 g, 8.8 mmol) was added a THF solution of 2-methyl benzoxazole (0.57 mL, 4.8 mmol) at 0 ºC and the mixture was further stirred for 30 min at this temperature. A THF solution of 4-(diphenylamino)benzaldehyde was dropped slowly into the above solution at 0 ºC. After stirred for 1 h, the mixture was poured into water (200 mL) and yellow solid was collected by filtration. The crude product was purified by a silca gel column using a CH_2Cl_2/petroleum ether mixture (5:1 by vol) as the eluent. Yellow powder was obtained in a yield of 86 % (1.7 g). Element analysis (%): calculated for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21; Found: C, 83.40; H, 5.25; N, 7.27. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.78$ (d, $J = 16.2$ Hz, 1H), 7.75 – 7.68 (m, 1H), 7.58 – 7.51 (m, 1H), 7.48 (d, $J = 8.7$ Hz, 2H), 7.40 – 7.29 (m, 6H), 7.19 (m, 4H), 7.12 (t, $J = 7.3$ Hz, 2H), 7.07 (d, $J = 8.7$ Hz, 2H), 6.96 (d, $J = 16.2$ Hz, 1H). MALDI-TOF MS: m/z: calcd for $C_{27}H_{20}N_2O$: 388.2; found: 389.1 $(M+H)^+$.

References:

1. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E.

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2. Sheldrick, G. M. *SHELXL-97. Program Crystal Structure Refinement.* University of Göttingen, Germany, 1997

Table S1 Emission peaks and fluorescence quantum yields in different solvents for **BVDP**.

solvents	n-hexane	cyclohexane	toluene	THF	$CHCl_3$	CH_2Cl_2	acetone
Emission peak (nm) [a]	428, 448	430, 451	456	483	490	501	510
Fluorescence quantum yield (Φ)[b]	0.18	0.18	0.25	0.29	0.19	0.25	0.28

[a] excitation wavelength is 370 nm. [b] Φ was obtained by compared with 9,10-diphenyl anthracene (Φ = 0.85 in benzene) as a standard

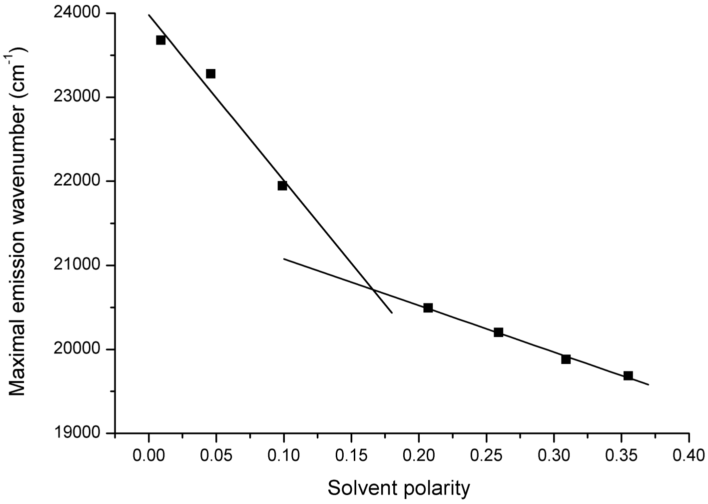

Fig. S1 Lippert–Mataga plot: fluorescence emission maximum energy of **BVDP** as a function of solvent polarity.

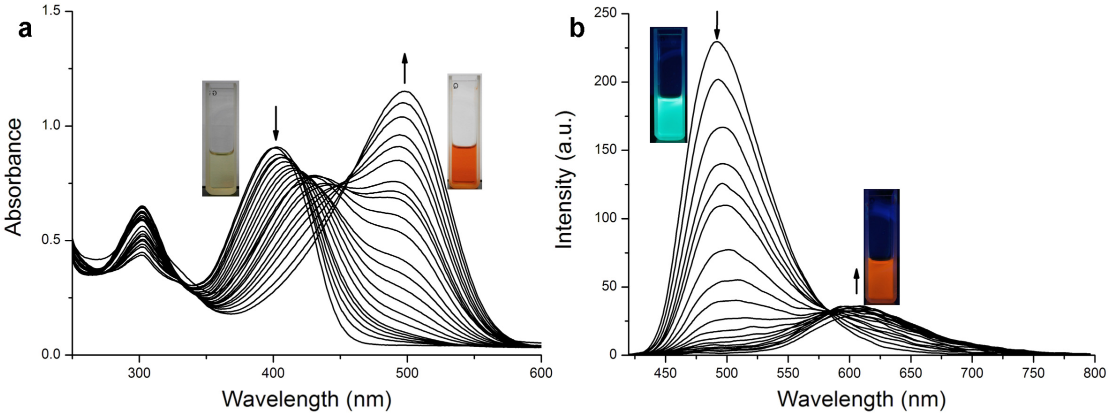

Fig. S2 Absorption (a) and emission spectral change of **BVDP** in $CHCl_3$ (10^{-4} M) upon addition of TFA from 0 to 300 equiv. Excitation wavelength is 400 nm.

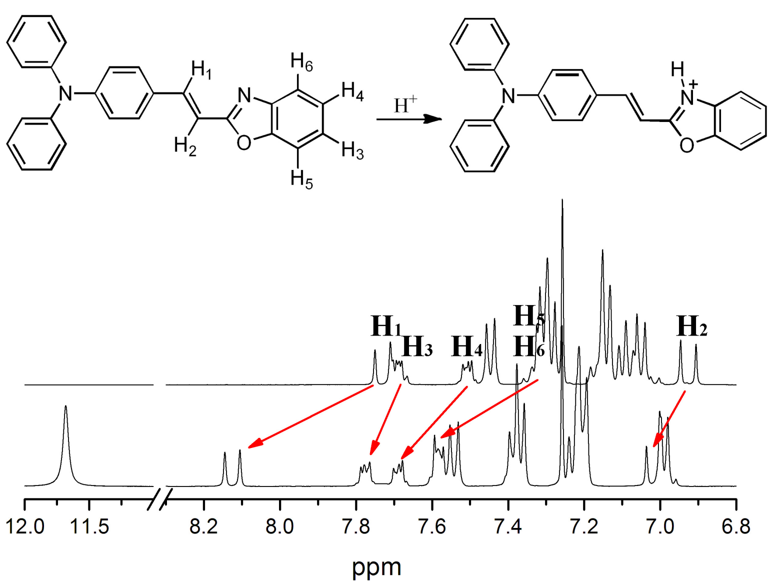

Fig. S3 ^{1}H NMR spectra of **BVDP** before (top) and after (down) adding 10 equv. TFA in $CDCl_3$. Concentration of **BVDP** is 0.021 M.

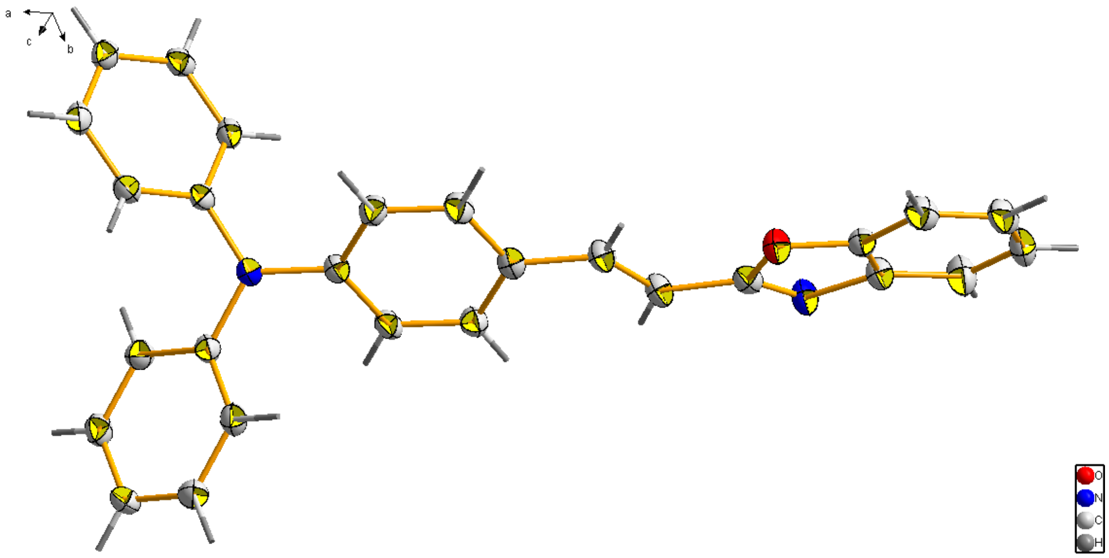

Table S2 Crystal data

Formula sum	$C_{27} H_{20} N_2O$
Formula weight	388.45
Crystal system	monoclinic
Space group	P 121/c1 (no. 14)
Unit cell dimensions	a = 8.1562(16) Å
	b = 14.302(3) Å
	c = 16.983(3) Å
	β = 97.22(3) °
Cell volume	965.36(70) $Å^3$
Z	4
Density, calculated	1.313 g/cm^3
R_{All}	0.062
Pearson code	mP200
Formula type	NO2P20Q27
Wyckoff sequence	e50

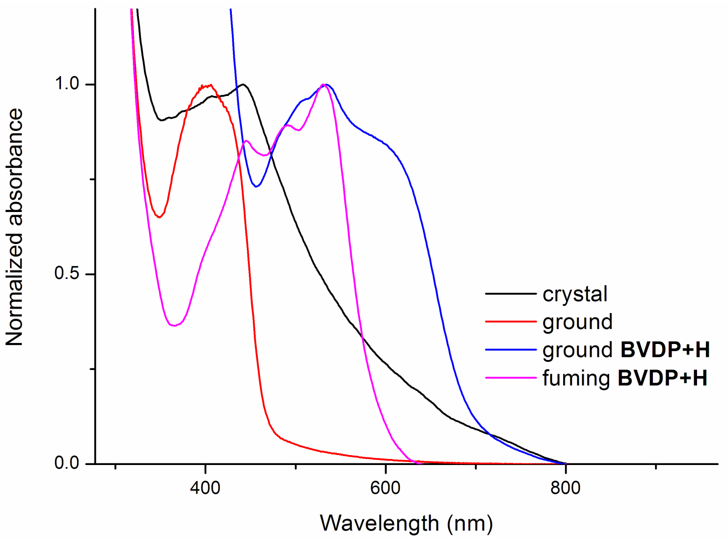

Fig. S4 Normalized absorption spectra of **BVDP** in different states.

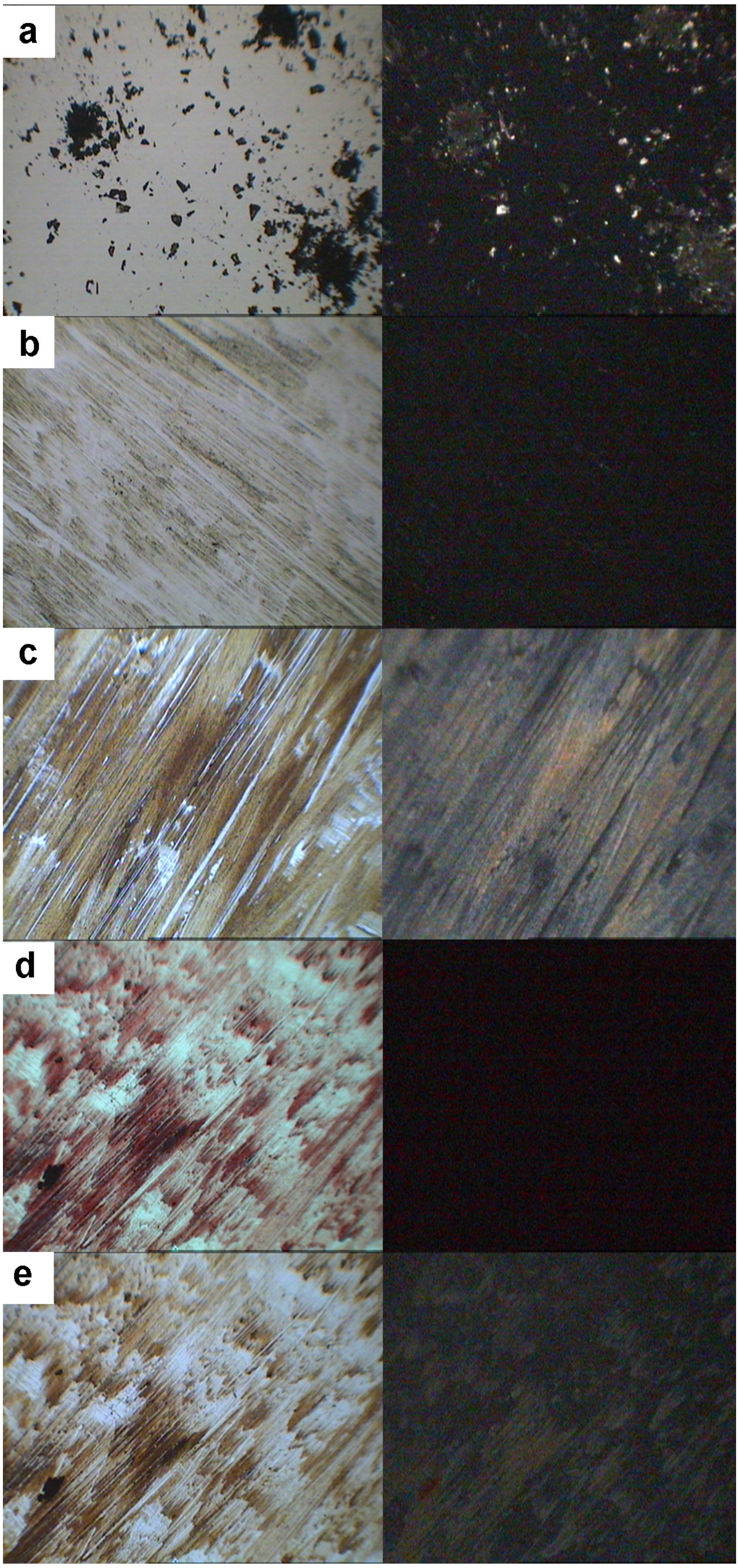

Fig. S5 light (left) and polarizing (right) microscopy images: (a) microcrystal, (b) ground film, (c) fuming film, (d) ground **BVDP+H** film and (d) fuming **BVDP+H** film.

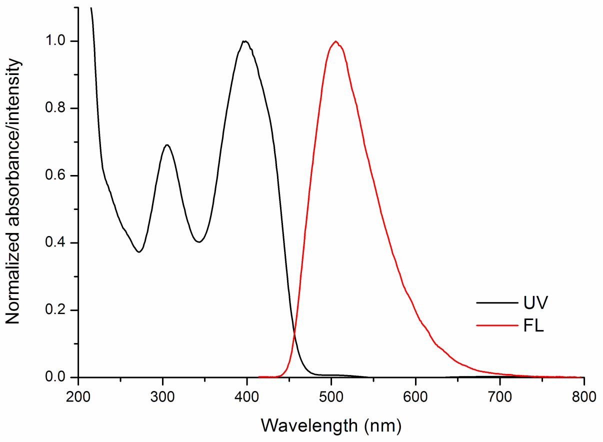

Fig. S6 Normalized absorption and emission spectra of casting film from **BVDP** CH_2Cl_2 solution. Excitation wavelength is 400 nm.

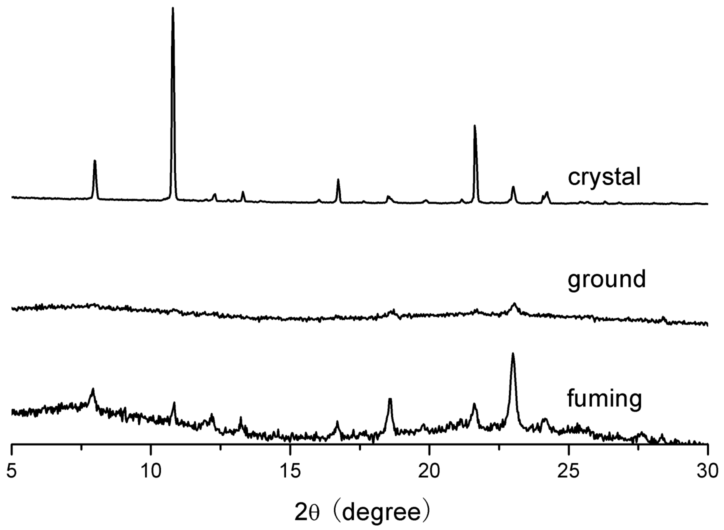

Fig. S7 XRD patterns of **BVDP** in difference states.