Supporting Information

Two Dimensional Directed π - π Interactions in A Linear Shaped Bi-1,3,4-oxadiazole Derivative to Achieve Organic Single Crystal with Highly Polarized Fluorescence and Amplified Spontaneous Emissions Songnan Qu, Qipeng Lu, Shaohang Wu, Lijun Wang^{*}, and Xingyuan Liu^{*}

State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

EXPERIMENTAL SECTION

PL spectra were collected using a Hitachi F-4500 spectrometer and UV-visible absorption spectra were recorded on a Shimazu UV-3101PC spectrophotometer. Photoluminescence quantum yields are obtained in a calibrated integrating sphere (excitation wavelength: 330nm) in FLS920 spectrometer. Fluorescence lifetimes were measured using FLS920 time-corrected single photon counting (TCSPC) system. The optical, POM and fluorescence microscopy images were carried out with an Olympus BX51TRF microscope. The light source for fluorescence microscopy observation was a mercury lamp with a fluorescent filter cube, which provides excitation in the range of 330-385 nm, and collects the emission longer than 420 nm. Intensity of the fluorescence emission was measured using the built-in CCD camera along with the associated software. The emission spectra were collected using an Ocean Optics Maya2000 Pro Fiber Optic Spectrometer. ASE investigations were performed using a Nd:YAG laser with a repetition rate of 1 Hz and pulse duration of about 10 ns. The laser power was detected by Newport 2936C laser power meter. Theoretical calculations were performed with the Gaussian 09 Program package and the Dmol³ suite of MS Modeling 5.5. The crystal structure data were collected at 293 K on a Rigaku R-AXIS-RAPID diffractometer equipped with Mo K α radiation ($\lambda = 0.71070$ Å) and Control Software using the RAPID AUTO at 293 (± 2) °C. Empirical absorption corrections were applied automatically. The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXL-97 programs. The space groups were determined from the systematic absences and their correctness was confined by successful solution and refinement of structures. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The hydrogen atoms were added in idealized position and refined with isotropic displacement. Crystal date refinement conditions and experimental details are tabulated in Table S3. The face-to-face interaction s were estimated by calculating the energy difference between two nearest BOXD-4 molecules in a stack (Figure2c) and two isolated BOXD-4 molecules. And the estimate of edge-to-edge interactions were obtained by calculating the energy difference between two nearest BOXD-4 molecules in adjacent stacks (Figure 2d) and two isolated BOXD-4 molecules. Both values were obtained by the accurate DFT method.



Figure S1. Fluorescent emission spectra of BOXD-1 in chloroform (red line) and BOXD-4 in chloroform (blue line) (excitation wavelength: 330 nm).



Figure S2. Fluorescent emission spectra of BOXD-1 single crystal (green line), BOXD-4 single crystal (red line) (excitation wavelength: 330 nm).



Figure S3. Fluorescent emission spectra of BOXD-1 powders (red line), BOXD-4 vacuum evaporated film (blue line), and BOXD-4 powders (purple line) (excitation wavelength: 330 nm).



Figure S4 (a) Polarized PL spectra of BOXD-1 single crystal taken with maximal and minimal intense (excitation in the range of 330-385 nm, and collected the emission longer than 420 nm), (b) relationship between the PL intensity and the polarization angle (angle between collection polarizer and the long axis of BOXD-1 single crystal).



Figure S5. POM image of BOXD-4 vacuum evaporated film on glass (white crossed arrows illustrated the crossed-polarizers).



Figure S6. (a) X-ray diffraction patterns of BOXD-4 vacuum evaporated film at room temperature; (b) Schematic representation of BOXD-4 molecules packing in its vacuum evaporated film.

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Figure S7. Single crystal structure of BOXD-1 (a) in a unit cell viewed along a-axis, (b) side viewed two nearest molecules in stack, (c) top viewed two nearest molecules in stack, and (d) top viewed of two nearest molecules in adjacent stacks.



Figure S8. (a) Optical and (b), (c), (d) POM images of BOXD-1 single crystal (white crossed arrows illustrated the crossed-polarizers, crystal shape was outlined in white line); (e), (f) polarized photoluminescence microscopy images of BOXD-4 single crystal (white arrow shows the direction of the emission polarizer); (g) single crystal structure of BOXD-1 view along *c*-axis (hydrogen atoms are not shown).

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Table S1. Main geometrical parameters of BOXD-4 obtained with B3LYP methods for ground state and CI-singles method for excited state together with 6-311+G** basis set; LUMO and HOMO levels of BOXD-4 in ground state with B3LYP methods and in excited state with 6-311+G** basis set.

	Ground state	Excited state	
	B3LYP/6-311+G**	CIS/6-311+G**	
Bond lengths (Å)	I		
C1-C1	1.427	1.401	
C1-N1	1.315	1.387	
C1-01	1.396	1.397	
N1-N2	1.424	1.356	
N2-C2	1.321	1.368	
C2-01	1.402	1.383	
C2-C3	1.443	1.439	
C3-C8	1.407	1.409	
C3-C4	1.411	1.415	
C4-C5	1.388	1.368	
C8-C7	1.393	1.376	
C5-C6	1.407	1.414	
C7-C6	1.406	1.404	
C6-O2	1.381	1.386	
O2-C9	1.464 1.438		
C9-C10	1.522	1.547	
C10-C11	1.540	1.544	
C11-C12	1.540	1.541	

Angles		
01-C1-C1	118.55	120.92
01-C1-N1	112.33	111.63
C1-O1-C2	102.73	102.47
C1-N1-N2	106.45	106.23
N1-N2-C2	107.16	107.84
N1-C2-O1	111.33	111.84
01-C2-C3	119.47	120.96
C4-C3-C8	119.29	118.55
Dihedral angles		
01-C1-C1-O1	179.95	180.00
01-C2-C3-C8	180.00000	180.00
	B3LYP/6-3	11+G**
НОМО	-6.17 eV	-5.82
LUMO	-2.38 eV	-2.69 eV



Table S2. Calculated ground to excited state transition electric dipole moments (Au) of

 BOXD-4:

State	Х	у	Z	Dip. S.	Osc.
1	3.5132	0.4024	-0.0120	12.5046	1.5368
2	0.0000	0.0000	0.0000	0.0000	0.0000
3	-0.3446	-0.1799	0.0004	0.1511	0.0215
4	0.0000	0.0000	0.0000	0.0000	0.0000
5	0.5689	1.0304	0.0204	1.3858	0.2140
6	0.0000	0.0000	0.0000	0.0000	0.0000

Identification code	BOXD-1	BOXD-4	
Empirical formula	C18 H14 N4 O4	C24 H26 N4 O4	
Formula weight	350.33	434.49	
Temperature	293(2) K	293(2) K	
Wavelength	0.71073 Å	0.71073 Å	
Crystal system, space group	Monoclinic, P2 ₁ /n	Triclinic, P-1	
Unit cell dimensions	$a = 6.419(1) \text{ Å} \alpha = 90 ^{\circ}$	$a = 8.0873(16) \text{ Å} \alpha = 107.15(3)^{\circ}$	
	$b = 8.268(2) \text{ Å} \beta = 92.69(3)^{\circ}$	$b = 8.1278(16) \text{ Å} \beta = 105.03(3)^{\circ}$	
	$c = 15.213(3) \text{ Å} \gamma = 90^{\circ}$	$C = 9.3175(19) \text{ Å} \gamma = 97.99(3)^{\circ}$	
Volume	806.5(3) Å ³	549.59(19) Å ³	
Z, Calculated density	2, 1.443 Mg/m ³	1, 1.313 Mg/m ³	
Absorption coefficient	0.105 mm ⁻¹	0.091 mm ⁻¹	
F(000)	364	230	
Crystal size	0.36 x 0.16 x 0.13 mm ³	0.24 x 0.23 x 0.21 mm ³	
Theta range for data collection	3.39 to 27.47°	3.33 to 27.48°	
Limiting indices	-8≤h≤8, -10≤k≤10, -19≤l≤19	-10≤h≤10, -9≤k≤10, -12≤l≤12	
Reflections collected / unique	7435 / 1814 [R(int) = 0.0285]	5423 / 2492 [R(int) = 0.0204]	
Completeness to θ	$\theta = 27.47^{\circ}$ 97.9 %	$\theta = 27.48^{\circ}$ 99.0 %	
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9869 and 0.9634	0.9811 and 0.9785	
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	1814 / 0 / 146	2492 / 0 / 198	
Goodness-of-fit on F^2	1.087	1.079	
Final R indices [I>2o(I)]	R1 = 0.0368, wR2 = 0.0916	R1 = 0.0386, $wR2 = 0.1226$	
R indices (all data)	$R1 = 0.0580, \ wR2 = 0.0983 \qquad \qquad R1 = 0.0478, \ wR2 = 0.1270$		
Largest diff. peak and hole	0.204 and -0.123 e Å $^{\text{-3}}$	0.231 and -0.188 e. Å ⁻³	

Table S3. Crystal data and structure refinement for BOXD-1 and BOXD-4.