# **Electronic Supplementary Information (ESI) for Dalton. Trans.**

# Discovery of polymorphism-dependent emission for crystalline boron-dipyrromethene dye

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## 1. Materials and instrumentations

All reactions were performed under nitrogen in oven-dried glassware using standard Schlenk technique and monitored by thin-layer chromatography (TLC). Column chromatography was performed using silica gel (300 mesh). All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Dichloromethane was freshly distilled from CaH<sub>2</sub> under nitrogen. Triethylamine was obtained by simple distillation. Electrochemical experiments were performed using a three-electrode system. The working electrode was 2 mm Pt with a Pt wire as auxiliary electrode and a 0.01M Ag/AgNO<sub>3</sub> solution reference electrode. The sample solution contained a BODIPY (1.0×10<sup>-3</sup> M) and 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as a supporting electrolyte in dry acetonitrile. Determined potentials (vs Ag/Ag<sup>+</sup>) were converted to those vs SCE by adding 0.29 V.<sup>1</sup> <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C. <sup>1</sup>H NMR spectra were referenced to tetramethylsilane (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet. <sup>13</sup>C NMR spectra were referenced to the CDCl<sub>3</sub> (77.67) ppm) single. Mass spectrometry (MS) experiment was carried out in the positive ion made on a Bruker Esquire HCT ion trap mass spectrometer (Billerica, MA) coupled with a homemade electrospray ionization (ESI) device. Parameters of the ESI source were optimized to enhance the signal intensity. The pressure of nebulizing nitrogen, the flow

rate of desolvation gas, and the temperature of desolvation gas were set to 8 psi, 1L/min, and 250 °C, respectively. C, H, and N microanalyses were carried out with a CE instruments EA 1110 analyzer. The experimental powder X-ray diffraction patterns of all the polymorphs were measured on a Panalytical X-Pert Pro diffractometer with Cu Kα radiation equipped with an X'Celerator detector. Differential scanning calorimetry (DSC) data were measured on a Netzsch-DSC-200F3 instrument at the heating rate of 10 °C/min from 30 to 240 °C. Samples were heated in open aluminum pans under a nitrogen gas flow of 20 mL/min. The CIE coordinates (x,y) of the emission of the polymorphs were derived from the emission spectra with the software of CIE color Matching linear Algebra. 1. C. K. Mann, K. K. Barnes, *Electrochemical Reactions in Non-aqueous System;* Marcel Dekker: New York, 1970.

2. Synthesis and characterization of (4-methoxycarbonylphenyl)BODIPY Scheme S1 Synthesis route of (4-methoxycarbonylphenyl)BODIPY (1)



**Preparation of (4-methoxycarbonylphenyl)BODIPY (1)**.<sup>2</sup> In a 250 mL reaction flask, 4-methoxycarbonyl benzaldehyde (328 mg, 2 mmol), 2,4-dimethylpyrrole (380 mg, 4 mmol) and dry dichloromethane (50 mL) were added. The mixture was stirred for 20 min at room temperature under nitrogen. One drop of trifluoroacetic acid (TFA) was added and stirred overnight. To the reaction mixture 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 454 mg, 2 mmol) in dry dichloromethane (20 mL) was added with continuous stirring. After 1h, triethylamine (6 mL) was added and stirred for 30 min. Boron trifluoride (6 mL) was added and stirred for another 2 h. The solution became fluorescent under a UV lamp, indicating the formation of the final product. The mixture was diluted with water (3×20 mL) and extracted with dichloromethane (3×20 mL). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent of the filtrate was removed *via* 

vacuum evaporation. The compound was purified by column chromatography (SiO<sub>2</sub>, 6:1 n-hexane/ethyl acetate) to provide (4-methoxycarbonylphenyl)BODIPY (**1**) (44% yield) as a red colored solid. Anal. calcd (%) for  $C_{21}H_{21}BF_2N_2O_2$ : C 65.99, H 5.54, N 7.73%. Found: C 66.43, H 5.40, N 7.65. <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>):  $\delta$  8.21 (d, 2H, J = 8.0 Hz, ArH); 7.44 (d, 2H, J = 8.0 Hz, ArH); 6.01 (s, 2H, H2 and H6); 3.99 (s, 3H, COOCH<sub>3</sub>); 2.58 (s, 6H, CH<sub>3</sub>); 1.38 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR(75 MHz, CDCl<sub>3</sub>):  $\delta$  14.6, 14.5, 52.4, 122.1, 128.4, 130.4, 130.8, 130.9, 139.8, 140.2, 142.9, 156.0, 166.5. MS (ESI) calcd for  $C_{21}H_{21}BF_2N_2O_2$  [M+Na]<sup>+</sup> 405.2, found 405.1.

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### 3. Crystallization experiments

All crystallization experiments were carried out under nearly identical conditions. Vials containing solutions of the compound were covered with parafilm and allowed to crystallize and/or evaporate under ambient conditions in a fume hood. Vaporizing mix solvents of chloroform and n-hexane under exclusion of lights affords crystals of both the orange (I) and deep red (II) phases. The two forms were obtained separately by modifying the crystallization conditions: fast evaporation from chloroform solution afforded pure II, whist very slow diffusion of n-hexane into the concentrated chloroform gave pure I. Crystallization from ethyl acetate yielded two different types of crystal phases including the orange-red (III) and aforementioned deep red crystals (II), and the proportion of form III is larger than that of form II.

## 4. Spectroscopic measurements

The solvents used for photophysical measurement were of spectroscopic grade and used without further purification. UV-vis spectra in solution were recorded on an Unic UV-2800H spectrophotometer. Steady-state fluorescence spectroscopic studies in solution were performed on a Hitachi F-7000 spectrophotometer with a xenon arc lamp as light source. Samples for absorption and emission measurements were contained in 1 cm × 1 cm

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quartz cuvettes. Solid state emission spectra were recorded on an Edinburgh FLSP920 fluorescence spectrophotometer. Fluorescence decay curves of the samples were measured with the time-correlated single-photon-counting (TCSPC) method on FLSP920 Lifespec-ps (Edinburgh) and the data were analyzed by Edinburgh software. The goodness of the fit of the decays as judged by reduced chi-squared ( $\chi^2_R$ ) and autocorrelation function C(j) of the residuals was below  $\chi^2_R < 1.1$ . The fluorescence decay time ( $\tau$ ) was obtained from the slope. The rate constants for the radiative ( $k_r$ ) and nonradiative ( $k_{rr}$ ) deactivation processes can be calculated from the measured fluorescence quantum yield ( $\phi_i$ ) and mean fluorescence lifetime ( $\tau$ ) as  $k_r = \phi_i / \tau_r$  and  $k_{rr} = (1-\phi_i)/\langle \tau_r \rangle$ . The average fluorescence lifetime ( $\tau_r$ ) was calculated from  $\tau_r = \sum_{i=1}^{2} a_i \times \tau_i / \sum_{i=1}^{2} a_i$ , where  $a_i$  and  $\tau_i$ , respectively, represent the individual exponential decay time constant and

the corresponding pre-exponential factor.

#### 5. X-ray Single-crystal diffraction

Intensity data for polymorphs I and II were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer using graphite-monochromated Mo K $\alpha$  radiation source ( $\lambda = 0.71073$  Å). A superNova Dual equipped with an Atlas detector and employing mirror monochromated Cu K $\alpha$  radiation from a micro-source was used for the data collection of polymorph III. Single crystals of these polymorphs I-III with appropriate dimensions were chosen under an optical microscope and mounted on a glass fiber for data collection. Unit cell determinations were carried out both at ambient temperature (294 ± 2K) as well as low temperature (173 ± 2K) in order to test whether there were any phase changes during the cooling process, and none was observed. For I and II, absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.<sup>3</sup> For III the data processing was undertaken with CrysAlis Pro<sup>4</sup> and a multi-scan absorption correction was applied<sup>4</sup> to the data. In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97<sup>5</sup> and refined by full-matrix least-squares on  $F^2$  using SHELXL-97<sup>6</sup> via the program interface X-Seed.<sup>7</sup> Non-hydrogen atoms were refined anisotropically and H atoms isotropically in a riding

model with U<sub>iso</sub> values 1.2-1.5 times those of their parent atoms. They all were visible on difference electron density maps. All structures were examined using the Addsym subroutine PLATON<sup>8</sup> to ensure that no additional symmetry could be applied to the models. Crystal structure views were obtained using Diamond v3.1<sup>9</sup> and Mercury.<sup>10</sup> Simulated powder XRD patterns were calculated with the Material Studio program<sup>11</sup> using the single crystal data. Some crystallographic data are summarized in Table S2. Selected bond lengths and angles are listed in Table S3.

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7. L. J. Barbour, X-Seed, A software tool for Supramolecular Crystallography; *Supramol. Chem.* 2001, 1, 189-191.

8. A. L. Spek, Implemented as the *PLATON* Procedure, a Multi-purpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 1998.

K. Brandenburg, *DIAMOND*, Version 3.1f; Crystal Impact GbR: Bonn, Germany, 2008.
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11. *Materials Studio Program*, Version 4.3; Accelrys: San Diego, CA, 2008.

# 6. Hirshfeld surface analysis

Molecular Hirshfeld surfaces in the crystal structure are constructed based on the electron distribution calculated as the sum of spherical atom electron densities.<sup>12</sup> The Hirshfeld surface enclosing a molecule is defined by points where the contribution from all the other molecules. For each point on that isosurface two distances are defined:  $d_e$ , the distance from the point to the nearest nucleus external to the surface, and  $d_i$  the distance to the nearest nucleus internal to the surface. The combination of  $d_e$  and  $d_i$  in the form of a 2D fingerprint plot provides summary of intermolecular contacts in the crystal. The Hirshfeld surfaces are mapped  $d_e$ ,  $d_{norm}$ , shape index and 2D fingerprint plots presented in the supplemental material were generated using CrystalExplorer program.<sup>13</sup>

12. (a) M. A. Spackman and P. G. Byrom, *Chem. Phys. Lett.*, 1997, **267**, 215-220. (b) J. J. Mckinnon, A. S. Mitchell, M. A. Spackman and *Chem.-Eur. J.*, 1998, **4**, 2136-2141.

13. S. K. Wolff, D. J. Grimwood, J. J. McKinnon, D. Jayatilaka and M. A. Spackman, *CrystalExplorer*, *2.1 (381)*; University of Western Australia: Perth, 2005-2007.

# 7. Electronic structure calculation

DFT has proved suitable for calculating the electronic distribution and molecular orbitals of a series of BODIPY derivatives.<sup>14</sup> For DFT calculations, the hybrid B3LYP method was employed with the 6-31G(d,p) basis set was used to study of the electronic structure of **1**. The conformational search for the optimum geometry of **1** started from the X-ray crystal data. The Berny algorithm using redundant internal coordinates<sup>15</sup> was employed and the default cutoffs were used throughout. The geometry optimization was considered to be adequately converged when the analysis of the vibrational frequencies did not give any negative frequency. All calculations were carried out using the Gaussian 03 program.<sup>16</sup>

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Center	Atomic	Atomic	Coordir	nates (Angstrom	s)
Number	Number	Туре	Х	Y	Z
	~	·····	4 4 9 7 9 9 5		4 004007
1	9	0	4.107265	0.145190	-1.391007
2	9	0	4.460726	0.138794	0.847914
3	8	0	-5.834381	-0.171723	-0.905579
4	(	0	2.64/361	-1.193322	-0.021913
5	8	0	-5.858770	0.269510	1.286342
6	7	0	2.518261	1.283610	-0.009386
7	6	0	-1.728627	-0.438903	-1.047983
8	1	0	-1.229260	-0.694092	-1.970997
9	6	0	0.504964	-0.056824	0.024137
10	6	0	-3.765006	-0.098350	0.203636
11	6	0	1.246727	-1.235270	0.019801
12	6	0	-1.632498	0.159724	1.285562
13	1	0	-1.054524	0.369281	2.173555
14	6	0	1.125044	1.197825	0.005488
15	6	0	0.605535	2.523103	-0.012616
16	6	0	-5.243027	0.021297	0.280720
17	6	0	-0.983559	-0.123101	0.088490
18	6	0	-3.111946	-0.423323	-0.985979
19	1	0	-3.690202	-0.664681	-1.865601
20	6	0	1.701523	3.365355	-0.046788
21	1	0	1.665293	4.444366	-0.075621
22	6	0	2.866858	2.587643	-0.037801
23	6	0	2.024028	-3.338225	0.113735
24	1	0	2.091636	-4.414694	0.168526
25	6	0	0.851906	-2.606183	0.108385
26	6	0	3.110257	-2.457094	0.036503
27	6	0	-0.817474	3.004019	0.032400
28	1	0	-1.490198	2.146649	0.053205
29	1	0	-1.025165	3.607458	-0.851226
30	1	0	-0.969205	3.606713	0.927833
31	5	0	3.494364	0.094624	-0.138427
32	6	0	-3.011360	0.174037	1.344645
33	1	0	-3.507987	0.396896	2.277445
34	6	0	4.560425	-2.803671	0.024627
35	1	0	4.675711	-3.886094	0.080560
36	1	0	5.051592	-2.341253	0.880767
37	1	0	5.014099	-2.437022	-0.896130
38	6	0	-0.514965	-3.188441	0.221729
39	1	0	-1.254505	-2.388262	0.190215

# Table S1Cartesian coordinates for DFT optimized structure of 1.

40	1	0	-0.603106	-3.727713	1.164832
41	1	0	-0.687198	-3.875262	-0.606983
42	6	0	4.279304	3.045952	-0.054184
43	1	0	4.942219	2.180809	-0.040839
44	1	0	4.470939	3.664056	0.822926
45	1	0	4.461554	3.629436	-0.956614
46	6	0	-7.265077	-0.004847	-0.926048
47	1	0	-7.637357	-0.184605	-1.934601
48	1	0	-7.516817	1.011053	-0.621443
49	1	0	-7.723600	-0.714661	-0.237598

 Table S2
 Electrochemical data and HOMO-LUMO gaps determined from spectroscopy and DFT calculations of 1.

compound	<i>E</i> <sub>ox</sub> (vs SCE), V	<i>E</i> <sub>red</sub> (vs SCE), V	$E_{g}$	$E_{g}$	HOMO/LUMO
	BODIPY <sup>•+</sup> /BODIPY	BODIPY/BODIPY-•	(eV) <sup>a</sup>	(eV) <sup>b</sup>	(eV) <sup>c</sup>
1	1.26	-1.16	2.42	2.44	-5.71/-2.73

<sup>a</sup>Obtained from CV measurements. <sup>b</sup>Obtained from the intercept of the normalized absorption and emission spectra. <sup>c</sup>Obtained from DFT calculations; HOMO/LUMO values are with respect to vacuum.

Polymorph	l (orange)	ll (deep red)	III (orange-red)
formula	$C_{21}H_{21}BF_2N_2O_2$	$C_{42}H_{42}B_2F_4N_4O_4$	$C_{21}H_{21}BF_2N_2O_2$
formula weight	382.21	764.42	382.21
crystal system	monoclinic	triclinic	orthorhombic
space group	C2	Pī	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	32.799(2)	7.9124(13)	8.3318(13)
b (Å)	7.9896(4)	14.511(2)	12.0855(17)
<i>c</i> (Å)	7.2920(4)	17.330(3)	18.610(2)
α (deg)	90	86.939(3)	90
β (deg)	90.511(2)	77.665(3)	90
γ (deg)	90	75.267(3)	90
$Z$ , $D_{calcd}$ (g m <sup>-3</sup> )	4, 1.329	2, 1.350	4, 1.355
V (Å <sup>3</sup> )	1910.79(19)	1879.9(5)	1893.9(6)
µ (mm <sup>-1</sup> )	0.098	0.10	0.83
F (000)	800	800	800
<i>Т</i> (К)	173(2)	173(2)	173(2)
no. of refins collected	12361	9446	6851
no. of unique reflns.	3363 ( <i>R</i> <sub>int</sub> =	6491 ( <i>R</i> <sub>int</sub> =	3129 ( <i>R</i> <sub>int</sub> =
	0.0488)	0.016)	0.048)
no. of observed refins	2483	5991	2740

Table S3 Crystallographic data for polymorphs I, II and III.

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254	505	253
$R_1 = 0.0467$ ,	$R_1 = 0.0656$ ,	$R_1 = 0.0504,$
$wR_2 = 0.1169$	$wR_2 = 0.1884$	$wR_2 = 0.1372$
$R_1 = 0.0728$ ,	$R_1 = 0.0697$ ,	$R_1 = 0.0591,$
$wR_2 = 0.1547$	$wR_2 = 0.1934$	$wR_2 = 0.1479$
1.094	1.085	1.03
0.23, -0.23	0.58, -0.52	0.30, -0.31
	254 $R_1 = 0.0467,$ $wR_2 = 0.1169$ $R_1 = 0.0728,$ $wR_2 = 0.1547$ 1.094 0.23, -0.23	254505 $R_1 = 0.0467$ , $R_1 = 0.0656$ , $wR_2 = 0.1169$ $wR_2 = 0.1884$ $R_1 = 0.0728$ , $R_1 = 0.0697$ , $wR_2 = 0.1547$ $wR_2 = 0.1934$ $1.094$ $1.085$ $0.23, -0.23$ $0.58, -0.52$

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, {}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma w (F_{o}^{2})^{2}]^{1/2}$ 

Table S4 Selected bond lend	oths, bond angles a	and dihedral angles of	various forms of 1.
	<i>, , , , , , , , , ,</i>		

Form	I		F	orm <b>II</b>		Form I	II
Bond lengths		ll <sub>A</sub>		II <sub>B</sub>		Bond lengths	
B1-F1	1.397(4)	Bond lengths		Bond lengths		B1-F1	1.390(4)
B1-F2	1.395(4)	B1-F1	1.397(3)	B2-F3	1.392(3)	B1-F2	1.394(4)
B1-N1	1.535(5)	B1-F2	1.375(3)	B2-F4	1.382(3)	B1-N1	1.558(4)
B1-N2	1.538(4)	B1-N1	1.545(3)	B2-N3	1.548(3)	B1-N2	1.545(4)
O1-C1	1.199(5)	B1-N2	1.553(3)	B2-N4	1.545(3)	O1-C1	1.208(4)
O2-C1	1.333(5)	O1-C1	1.202(3)	O3-C22	1.208(3)	O2-C1	1.339(4)
O2-C2	1.448(4)	O2-C1	1.338(3)	O4-C22	1.336(3)	O2-C2	1.448(4)
N1-C14	1.348(4)	O2-C2	1.447(3)	O4-C23	1.442(3)	N1-C14	1.354(4)
N2-C13	1.347(4)	N1-C14	1.342(3)	N3-C35	1.340(3)	N2-C13	1.344(4)
N1-C17	1.405(4)	N2-C13	1.343(3)	N4-C34	1.345(3)	N1-C17	1.396(4)
N2-C10	1.398(4)	N1-C17	1.399(3)	N3-C38	1.396(3)	N2-C10	1.411(4)
Bond angles		N2-C10	1.395(3)	N4-C31	1.403(3)	Bond angles	
F1-B1-F2	108.6(3)	Bond angles		Bond angles		F1-B1-F2	109.1(3)
N1-B1-N2	107.6(3)	F1-B1-F2	109.7(2)	F3-B2-F4	109.5(2)	N1-B1-N2	106.4(2)
N1-B1-F1	110.2(3)	N1-B1-N2	106.5(2)	N3-B2-N4	106.9(2)	N1-B1-F1	110.8(3)
N1-B1-F2	109.9(3)	N1-B1-F1	109.4(2)	N3-B2-F3	108.8(2)	N1-B1-F2	109.5(3)
N2-B1-F1	110.3(3)	N1-B1-F2	111.5(2)	N3-B2-F4	110.8(2)	N2-B1-F1	111.1(3)
N2-B1-F2	110.1(3)	N2-B1-F1	108.9(2)	N4-B2-F3	109.5(2)	N2-B1-F2	109.9(3)
C1-O2-C2	116.1(3)	N2-B1-F2	110.8(2)	N4-B2-F4	110.8(2)	C1-O2-C2	114.8(3)
O1-C1-O2	124.0(4)	C1-O2-C2	115.8(2)	C22-O4-C23	115.7(2)	01-C1-O2	124.0(3)
O1-C1-C3	124.6(4)	O1-C1-O2	123.1(2)	O3-C22-O4	123.1(2)	O1-C1-C3	123.5(3)
Dihedral angle	es	O1-C1-C3	124.5(2)	O3-C22-C24	124.4(2)	Dihedral angle	es
C10-C9-C6-C5	80.3	Dihedral angle	es	Dihedral angles		C10-C9-C6-C5	81.8
O1-C1-C3-C8	5.4	C10-C9-C6-C5	80.5	C31-C30-C27-C26	75.8	O1-C1-C3-C8	28.2
		O1-C1-C3-C8	4.7	O3-C22-C24-C29	5.1		

**Table S5** Hydrogen bonding parameters of the intermolecular hydrogen bonds observedin the crystal structures of various forms of 1.

Polymorph	D-H…A	D-H (Å)	<i>d</i> (H…A) (Å)	<i>d</i> (D…A) (Å)	∠D-H…A (º)	Symmetry codes
	C7-H7A…F1 <sup>i</sup>	0.95	2.349	3.152	142.00	<sup>i</sup> = x, y+1, z
Form I	C19-H19A…π	0.98	2.750	3.511	134.89	
	C15 <sup>ii</sup> -H15A <sup>ii</sup> …O1	0.95	2.619	3.520	158.71	<sup>ii</sup> = x, y+1, 1+z
	C5 <sup>i</sup> -H5A <sup>i</sup> …O1	0.95	2.596	3.545	177.69	<sup>i</sup> = x, y+1, z
	C40 <sup>i</sup> -H40A <sup>i</sup> …F1	0.98	2.658	3.270	120.73	<sup>i</sup> = x-1, y, z
	C18 <sup>i</sup> –H18C <sup>i</sup> …F1	0.95	2.654	3.578	157.39	<sup>i</sup> = x-1, y, z
	C28 <sup>ii</sup> –H28A <sup>ii</sup> …F3	0.95	2.469	3.084	122.49	<sup>ii</sup> = x+1, y, z
	C19-H19C…π	0.98	3.224	3.827	121.45	
	C20-H20B…π	0.98	3.108	3.717	121.70	
Form II	C5 <sup>II</sup> -H5A <sup>II</sup> O1	0.95	2.618	3.470	149.51	<sup>ii</sup> = x+1, y, z
	C21 <sup>i</sup> -H21C <sup>i</sup> O1	0.98	2.610	3.467	146.06	<sup>i</sup> = x-1, y, z
	C36 <sup>Ⅲ</sup> -H36A <sup>Ⅲ</sup> …O2	0.95	2.650	3.560	160.69	<sup>lii</sup> = -x+1, -y+2, -z
	C26 <sup>i</sup> -H26A <sup>i</sup> O3	0.95	2.482	3.408	165.00	<sup>i</sup> = x-1, y, z
	$B_1$ - $F_2$ ··· $\pi$	1.376	3.014	4.010	128.0	
	$B_2$ - $F_4$ ··· $\pi$	1.382	3.029	4.046	129.1	
	C15 <sup>i</sup> –H15A <sup>i</sup> …F2	0.95	2.523	3.299	138.87	<sup>i</sup> = x+1/2, -y+3/2,
Form III						-z+1
	C7 <sup>ii</sup> –H7A <sup>ii</sup> …F2	0.95	2.431	3.266	146.41	<sup>ii</sup> = x-1/2, -y+3/2,
						-z+1
	C20-H20B…π	0.98	2.605	3.575	170.23	
	C12 <sup>iii</sup> -H12A <sup>iii</sup> O1	0.95	2.499	3.304	142.48	<sup>iiii</sup> = -x+5/2, -y+2,
						z-1/2

**Fig. S1** a) Absorption spectra, b) fluorescence emission spectra of **1** in several solvents. All intensities have been normalized to the same value at the wavelength of maximum intensity.



(b)



**Comments**: The absorption spectra of **1** show the typical BODIPY features with a very strong  $S_0 \rightarrow S_1 (\pi - \pi^*)$  transition centered at 502 ± 3 nm and a much weaker and broader  $S_0 \rightarrow S_2 (\pi - \pi^*)$  transition around 375 nm. In addition, a shoulder at the short wavelength (high-energy) side, is centered at about 470 nm, and is attributed to the 0-1 vibrational band of the same transition. The position of the  $S_0 \rightarrow S_1$  absorption band is barely affected by solvent polarity; the maximum is slightly shifted hypsochromically (~7 nm) when the

solvent is changed from toluene to acetonitrile (MeCN, 498 nm) or methanol (MeOH, 499 nm), which is in accordance with the general behavior of BODIPY chromophores. **1** also showed the characteristic emission features of BODIPY in all solvents studied: that is a narrow, slightly stokes-shifted band of mirror-image shape, and fluorescence bands that shifted hypsochromically (from in toluene to in acetonitrile) with increasing solvent polarity.

**Fig. S2** Schematic representation of the frontier orbitals (left: HOMO, right: LUMO) of the dye **1** computed at the B3LYP/6-31+G(d,p) level of theory.



HOMO

LUMO

**Comments**: DFT calculations suggest that the  $S_0$ - $S_1$  transition is a nearly pure HOMO-LUMO transition. The electronic density contour map of these states indicates an important increase in the electronic density at the 8-position in the LUMO ( $S_1$ ) with respect to the HOMO ( $S_0$ ) state.

**Fig. S3** Comparison between the calculated powder X-ray diffractions and the experimental powder X-ray diffractions of polymorphs I (top), II (middle) and III (bottom) at room temperature.





**Comments:** For each polymorph, the *experimental* powder X-ray diffraction pattern and the powder X-ray diffraction pattern *calculated* for the crystal structure determined from single-crystal X-ray diffraction data. In each case, the *calculated* powder X-ray diffraction pattern clearly matches the experimental powder X-ray diffraction pattern, thus confirming that, in each case, the single crystal used in the single-crystal X-ray diffraction experiment was representative of the bulk polycrystalline sample from which it was selected. We emphasize the importance of carrying out this test in making structural assignments of polymorphic systems from single-crystal X-ray diffraction data. These diffraction patterns provide an unambiguous proof for the existence of three polymorphs **I**, **II** and **III**.

**Fig. S4** ORTEP with atom numbering scheme of polymorphs **I**, **II** and **III** with displacement ellipsoids at the 50% probability level.



Form II





**Comments:** The molecular views (*ORTEP*) of the polymorphs I-III with atom numbering scheme is shown in Figure S4. X-ray structure reveals polymorph I crystallizes in the monoclinic space group C2 and III crystallizes in the orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, both of which have one independent molecule in the asymmetric unit (Z' = 1). Whereas II crystallizes in space group P-1 with two independent molecules in the asymmetric unit (Z' = 1). Whereas II crystallizes in space group P-1 with two independent molecules in the asymmetric unit (Z' = 2, denoted as II<sub>A</sub> and II<sub>B</sub>). In the four molecules of three polymorphs (I, II<sub>A</sub>, II<sub>B</sub> and III), the C<sub>9</sub>BN<sub>2</sub> (BODIPY) framework consisting of one central six-membered and two adjacent five-membered rings is essentially flat, with the maximum deviation from the least-squares mean plan being 0.0208 Å in I, 0.0675 and 0.0367 Å in II, and 0.0742 Å in III, respectively. All of the C-C and C-N bond lengths within the C<sub>9</sub>BN<sub>2</sub> core in I, II<sub>A</sub>, II<sub>B</sub> and III. The boron atom of the BODIPY core in these compounds has the typical B-N (1.535-1.558 Å) and B-F (1.375-1.397 Å) bond lengths, comparable to those of previously reported BODIPY compounds.<sup>17,18</sup>

17. J. S. Lu, H. Fu, Y. Zhang, Z. J. Jakubek, Y. Tao and S. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 11658.

18. L. Bonardi, H. Kanaan, F. Camerel, P. Jolinat, P. Retailleau, R. Ziessel, *Adv. Funct. Mater.* 2008, **18**, 401.

**Fig. S5** The relative orientation of nearest-neighbor molecules for these polymorphs includes edge-to-face for I, face-to-face for II and arris edge-to-face (tilted *ca*. 45°) method for III.





(c)



**Fig. S6** A view of the layered structures in **I**(top), **II**(middle), and a herringbone-like pattern in **III**(bottom). Small arrows next to the molecules highlight the orientation of their macroscopic dipole moment.



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**Fig. S8** Two independent molecules in form **II** pack *via* two weak B-F $\cdots\pi$  interactions to generate a molecular dimer.



**Fig. S9** Hirshfeld surfaces for molecules I, II<sub>A</sub>, II<sub>B</sub> and III colored by  $d_e$  (a),  $d_{norm}$  (b), and shape index (c).

(a)



(b)





Form I



Form III



**Fig. S10** Fingerprint plots for **I**, **II** and **III**. Fingerprint plots are 2D graphs showing the distribution of the  $d_e$  distances as a function of  $d_i$ . Each point of the graph is colored according to the fraction of the total surface area contained by a specific data bin, ranging from blue (few points) through green (moderate number of points) to red (many points).



**Comments**: The fingerprints can be decomposed to show contacts characteristic for specific intermolecular interactions and the molecular plots for the four crystallographically independent molecules in the three structures can be readily seen to be unambiguously different, reflecting a different crystallographic environment for each. A pair of spikes are characteristic for C-H...O or C-H...F interactions. The wings seen in the plots belong to signature C-H... $\pi$  interactions. In all the forms, the contribution of the H...H contacts is higher than 50%, as listed in Table S5.

**Table S6** Percentage contribution from individual intermolecular interactions to theHirshfeld surface of the polymorphs.

	О…Н	С…Н	F…H	N…H	Н…Н
Form I	8.7	17.4	14	3.1	53.3
Form <b>II</b> A	10.9	18.2	10.3	1.5	54.1
Form II <sub>B</sub>	10.9	18.0	10.2	1.6	54.3
Form III	9.9	18.8	13	3.2	52.1

**Fig. S11** Fluorescence decay histograms of these polymorphs, **I**(top), **II**(middle) and **III**(bottom). The percentages in parentheses are relative amplitudes.









Fig. S12 CIE-1931 chromaticity diagram of these polymorphs.



Fig. S13 Polymorphs of another BODIPY, 4,4-Difluoro-8-[4-(methoxycarbonyl) phenyl]-2,6-bromo-1,3,5,7-tetramethyl-2,6-bromo-3a,4a-diaza-4-bora-s-indacene (2Br-BODIPY).



Fig. S14 <sup>1</sup>H NMR spectrum of (4-methoxycarbonylphenyl)BODIPY (1).

191	415 415 284	600	166	6.5	377	022
00 00	555	10	1	1	7	0
- V -	NZ				10	





