Electronic Supplementary Information

Benzene-fused BODIPYs: Synthesis and The Impact of Fusion Mode

Yong Ni,^a Wangdong Zeng,^a Kuo-Wei Huang,^b Jishan Wu^{a,c}*

^aDepartment of Chemistry, National University of Singapore 3 Science Drive 3, 117543 (Singapore). Fax: 65-67791691; Tel: 65-65162677; E-mail: <u>chmwuj@nus.edu.sg</u> ^bKing Abdullah University of Science and Technology (KAUST), Division of Physical Sciences and Engineering and KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia ^cInstitute of Materials Research and Engineering, A*Star, 3 Research Link, Singapore, 117602

Table of Contents

1. Experimental section	S 3
2. Summary of electrochemical properties	S9
3. TD-DFT calculations	S10
4. References	S 14
5. Appendix: ¹ H (¹³ C) NMR spectra and HR EI mass spectra	S15

1. Experimental section

1.1 General

All reagents were purchased from commercial suppliers and used as received without further purification. Anhydrous dichloromethane (DCM), N, N-dimethylformaldehyde (DMF) was distilled from CaH₂. Toluene and THF were distilled from sodium-benzophenone immediately prior to use. The ¹H NMR and ¹³C NMR spectra were recorded on Bruker DPX 300 or DRX 500 NMR spectrometer with tetramethylsilane (TMS) as the internal standard. The chemical shift was recorded in ppm and the following abbreviations were used to explain the multiplicities: s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet. EI-mass spectra were recorded on Agilent 5975C DIP/MS mass spectrometer. MALDI-TOF mass spectra were measured on a Bruker Autoflex MALDI-TOF instrument using 1,8,9trihydroxyanthracene as a matrix. UV-vis absorption and fluorescence spectra were recorded on Shimadzu UV-1700 spectrometer and RF- 5301 fluorometer, respectively. The solvents used for UV-vis and fluorescence measurements are of HPLC grade. The electrochemical measurements were carried out in anhydrous and degassed DCM containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte at a scan rate of 0.05 V/s at room temperature. A gold disk was used as working electrode, platinum wire was used as counting electrode, and Ag/AgCl (3 M KCl solution) was used as reference electrode. The potential was calibrated against the ferrocene/ferrocenium couple.

1.2 Synthetic procedure and characterization data

Compounds 4^{1} , 5^{2} and 7^{3} were synthesized according to a literature procedure.

ChemCommun



To a solution of 5 (297 mg, 1 mmol) and 2,4-dimethylpyrrole (114 mg, 1.2 mmol) in degassed anhydrous DCM (40 mL) was added POCl₃ (0.2 mL, 2.1 mmol) under Ar atmosphere. The solution was stirred at room temperature for 24 h until the completed consumption of 5 (monitored by TLC), then poured into 100 mL of a saturated NaHCO₃ solution. The organic layer was wash with brine and water, dried over anhydrous Na₂SO₄. The solvent was removed under vacuum to afford a crude product 6 as a brown solid. The crude product 6 was then dissolved in degassed anhydrous DCM (30 mL) and Et₃N (0.8 mL, excess), and then BF₃ OEt₂ (0.9 mL, excess) were successively added under argon atmosphere. The resulting mixture was stirred at room temperature for 2 h. After removing the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, DCM: hexane = 1: 3) to afford pure product **1** (176 mg, 42%) as a deep-red solid. ¹H NMR(CDCl₃, 300 MHz): δ 7.83 (d, J = 8.6 Hz, 1H), 7.36 (m, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.10 (m, 1H), 7.04 (m, 4H), 6.97 (m, 4H), 6.84 (m, 2H), 6.25 (s, 1H), 2.76 (s, 3H), 1.38 (s, 3H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 166.2, 149.8, 145.5, 145.1, 138.2, 136.6, 134.7, 133.4, 132.4, 130.9, 130.2, 129.7, 128.7, 127.9, 126.8, 126.5, 123.0, 121.8, 115.6, 30.4, 16.3. HR MS (EI): $m/z = 422.1759 [M^+]$ and 402.1696 [M⁺-F]; calcd. for $C_{27}H_{21}BF_2N_2$: 422.1766 (error: -1.62 ppm).



A mixture of compound 7 (1.59 g, 4 mmol), phenylboronic acid (585 mg, 4.8

mmol), toluene (80 mL), and Na₂CO₃ aqueous solution (2 M, 8 mL) was degassed by bubbling through argon stream for 15 min. Then Pd(PPh₃)₄ (231 mg, 0.20 mmol) was added and the mixture was further degassed for 10 min. The reaction was heated at 110 °Cfor 24 h. After cooling down to room temperature, the mixture was poured into water and extracted with DCM. The organic layer was washed by water and brine, dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, EA: hexane = 1: 10) to afford pure product **8** (1.22 g, 88%) as a white solid. ¹H NMR (CDCl₃, 300 MHz): δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.9 Hz, 3H), 7.70 (s, 1H), 7.61 (m, 2H), 7.46 (m, 2H), 7.39-7.21 (m, 5H), 2.3 (s, 3H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 145.7, 136.2, 133.7, 130.6, 130.0, 129.6, 128.6, 128.2, 127.6, 125.6, 124.7, 124.2, 123.7, 121.1, 114.5, 22.2. MS (ESI): *m/z* = 347.24 [M⁺]; calcd. for C₂₁H₁₇NO₂S: 347.10.



To a solution of **8** (695 mg, 2.0 mmol) in EtOH (100 mL) and DMSO (12.5 mL), 10% aq. NaOH (5.0 mL) was added slowly. The reaction mixture was stirred at 50 °C for 100 min until no more starting material existing (monitored by TLC), the solution was concentrated under vacuum, poured into water (100 mL), and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄, the solvent was removed under reduced pressure to give the crude product **9** (360 mg, 94%) as s white solid. TLC analysis shows that the product obtained was sufficiently pure to be used without further purification. To a solution of compound **9** (150 mg, 0.78 mmol) and benzaldehyde (41 mg, 0.39 mmol) in 15 mL of methanol, ethanol (2.6 mL) and concentrated hydrochloride acid (1.0 mL) were successively added at 0 °C under argon atmosphere.⁴ The resulting mixture was allowed to slowly warm to room temperature,

and stirred at this temperature overnight. The mixture was concentrated under vacuum and poured into ice-water (40 mL), the white precipitate was isolated by filtration, dried under vacuum, and then dissolved in degassed anhydrous DCM (30 mL). After an addition of DDQ (106 mg, 0.47 mmol), the solution was stirred under refluxing condition for 2 h under argon atmosphere. After cooling, Et₃N (1.0 mL, excess) and BF₃ OEt₂ (1.2 mL, excess) were successively added. The mixture was then stirred at room temperature for 2h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, DCM: hexane = 1:6 to 1:2) to afford pure product **2** (40 mg, 20%) as a deep blue solid. ¹H NMR (CDCl₃, 500 MHz): δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.46 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.94-6.87 (m, 10H), 6.80 (m, 4H), 6.69 (m, 1H), 6.49 (m, 2H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 153.4, 149.6, 144.4, 136.6, 133.7, 133.6, 132.7, 132.0, 131.0, 129.7, 129.3, 127.5, 126.8, 126.7, 123.9, 123.1, 116.5. HR MS (EI): *m*/*z* = 520.1939 [M⁺] and 501.1935 [M⁺-F]; calcd. for C₃₅H₂₃BF₂N₂: 520.1922 (error: 3.22 ppm).



LDA (4.55 mL, 2M solution in heptane/THF/ethylbenzene, 9.07 mmol, 1.2 eq) was slowly added to a well-stirred solution of compound **7** (3.0 g, 7.56 mmol) in dry THF at -78 °C under a nitrogen atmosphere. The solution was stirred for 1.5 h and after that a solution of 2-*iodo*-benzoyl chloride (2.41g, 9.06mmol) in dry THF (3 mL) was added dropwise.⁵ The reaction mixture was allowed to slowly warm to room temperature and the stirring was proceeded until no more starting material **7** was detectable by TLC. Then the reaction mixture was concentrated under vacuum, poured into water (40 mL), and extracted with DCM. The combined organic layer was dried over anhydrous Na₂SO₄, the solvent was removed under reduced pressure and the crude product **us** purified by column chromatography (silica gel, DCM: hexane = 4:1) to give pure product **11** (1.95 g, yield 21%) as a light yellow solid. ¹H NMR

(CDCl₃, 300 MHz): δ 8.02 (m, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.46-7.09 (m, 8H), 2.28 (s, 3H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 188.8, 146.2, 142.8, 140.5, 137.8, 136.8, 134.9, 133.7, 132.5, 130.5, 128.7, 128.5, 128.3, 125.5, 124.1, 115.6, 95.6, 22.3 ppm. MS (ESI): m/z = 649.70 [M⁺+Na]; calcd. for C₂₂H₁₅I₂NO₃S: 626.89.



A solution of compound **11** (0.50 g, 0.80 mmol) and activated copper powder (0.150 g, 2.39 mmol) in anhydrous DMF (15 mL) was heated at 140 °Cfor 3 h. After cooling, the reaction mixture was poured into water (200 mL) and extracted with diethyl ether. The organic layer was washed with water and brine, dried over anhydrous Na₂SO₄, the solvent was removed under reduce pressure to afford **12** (283 mg, 95%) as a dark orange solid. ¹H NMR (CDCl₃, 300 MHz): δ 8.25 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.46 (m, 1H), 7.42(m, 1H), 7.37-7.11 (m, 5H), 7.07 (m, 1H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 181.0, 146.3, 143.4, 143.1, 137.6, 136.5, 136.1, 135.4, 134.3, 130.6, 129.5, 129.2, 128.0, 125.4, 124.8, 123.3, 122.4, 120.7, 116.4, 22.3 ppm. MS (ESI): *m/z* = 374.18 [M⁺+H]; calcd. for C₂₂H₁₅NO₃S: 373.08.



To a solution of **12** (150 mg, 0.402 mmol) in EtOH (20 mL) and DMSO (2.5 mL), 10% aq. NaOH (1.0 mL) was added slowly. The reaction mixture was stirred at 50 $^{\circ}$ C for 40 min, concentrated under vacuum, poured into water (100 mL), and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was recrystallized from hexane to give the pure product **13** (0.06 g, 68%) as a dark red solid. ¹H NMR

(d₆-DMSO, 300 MHz): δ 12.04 (br, 1H), 7.83 (d, J = 4.8Hz, 1H), 7.38-7.26 (m, 4H), 7.24 (d, J = 4.2Hz, 1H), 7.16 (t, J = 4.2Hz, 1H), 7.02 (t, J = 4.1Hz, 1H) ppm. ¹³C NMR (d₆-DMSO, 125 MHz): δ 183.6, 143.0, 134.2, 133.9, 126.7, 126.2, 123.12, 121.8, 121.4, 120.6, 119.3 ppm. MS (ESI): m/z = 220.01 [M⁺+H]; calcd. for C₁₅H₉NO: 219.07.



To a solution of compound 13 (40 mg, 0.183 mmol) and 2,4-dimethylpyrrole (21 mg, 0.22 mmol) in degassed anhydrous DCM (20 mL) was added POCl₃ (0.2 mL). The solution was stirred at room temperature for 24 h and then TEA (1 mL) was added to neutralize the solution. The solvent was removed under vacuum and the residue was somehow purified by column chromatography (Al_2O_3 , hex: DCM = 1:1) to give the crude product 14 as a deep brown solid. The crude product 14 was then dissolved in degassed anhydrous DCM (20 mL). Et₃N (0.8 mL, excess) and BF₃ OEt₂ (1.0 mL, excess) were successively added. The resulting mixture was further stirred for 2h, concentrated under vacuum and then purified by column chromatography (silica gel, EA: hexane = 1:9) to afford pure product 3 (15 mg, yield 24%) as a deep brown solid. ¹H NMR (CDCl₃, 500 MHz): δ 7.35 (m, 2H), 7.21 (d, J = 3.8 Hz, 1H), 7.09 (m, 1H), 6.83-6.98 (m, 3H), 6.55-6.60 (m, 1H), 6.34 (s, 1H), 2.71 (s, 3H), 2.47 (s, 3H) ppm. ¹³C NMR (CDCl₃, 125 MHz): *δ* 171.6, 148.1, 147.4, 146.5, 144.2, 138.2, 138.1, 137.4, 133.2, 129.3, 128.2, 128.1, 126.2, 125.1, 124.8, 121.9, 121.4, 115.6, 29.7, 16.7 ppm. HR MS (EI): m/z = 344.1295 [M⁺]; calcd. for C₂₁H₁₅BF₂N₂: 344.1296 (error: -0.52) ppm).

Compounds	$E_{\rm ox}^{1}$	$E_{\rm red}^{1}$	$E_{\rm red}^{2}$	НОМО	LUMO	$E_{ m g}^{~ m a}$	$E_{\rm g}^{\ \rm b}$
	(V)	(V)	(V)	(eV)	(eV)	(eV)	(eV)
4	1.05	-1.68	-	-5.68	-3.32	2.36	2.40
1	1.11	-1.24	-	-5.79	-3.69	2.10	2.23
2	1.20	-0.70	-	-5.88	-4.19	1.69	1.76
3	0.78	-0.85	-1.61	-5.44	-4.08	1.36	1.28

2. Summary of electrochemical properties

Table S1. Summary of electrochemical properties of compounds **1**, **2**, **3** and **4**. E_{ox}^{n} and E_{red}^{n} are the half-wave potentials for respective redox waves with Fc/Fc⁺ as reference. HOMO and LUMO energy levels were calculated from the onset of the first oxidation and reduction waves according to equations: HOMO = -(4.8 + E_{ox}^{onset}) and LUMO = - (4.8 + E_{red}^{onset}).⁶ a) Obtained from cyclic voltammograms. b) Obtained from the low energy absorption onset in the absorption spectra.

3. TD-DFT calculations

Time-dependent DFT (TD-DFT) calculations have been performed at the B3LYP/6-31G* level of theory,⁷⁻¹¹ as implemented in the *Gaussian 09* program package. The geometries of **1**, **2** and **3** were fully optimized in gas phase using the default convergence criteria without any constraints and confirmed by frequency calculations. UV-vis-NIR absorption spectra were generated assuming an average UV-vis width of 4000 cm⁻¹ at half-height using the SWizard program.¹²

	Hartree	eV
LUMO+5	0.00356	0.10
LUMO+4	-0.0002	-0.01
LUMO+3	-0.00699	-0.19
LUMO+2	-0.01669	-0.45
LUMO+1	-0.01802	-0.49
LUMO	-0.10254	-2.79
НОМО	-0.19835	-5.40
HOMO-1	-0.21138	-5.75
HOMO-2	-0.24122	-6.56
HOMO-3	-0.24946	-6.79
HOMO-4	-0.25088	-6.83
HOMO-5	-0.25959	-7.06
HOMO-6	-0.26407	-7.19
HOMO-7	-0.27759	-7.55
HOMO-8	-0.28277	-7.69
HOMO-9	-0.3112	-8.47

 Table S2. Calculated energy levels of molecule 1.

calcd. (nm)	f	composition (H = HOMO, L= LUMO, L+1 = LUMO+1, etc.)
562.6	0.0528	H-0->L+0(+67%) H-1->L+0(33%)
443.6	0.6114	H-1->L+0(+64%) H-0->L+0(+33%)
336.3	0.0892	H-5->L+0(+76%) H-6->L+0(+16%)
277.1	0.1501	H-8->L+0(+57%) H-7->L+0(+14%)
		H-0->L+3(11%) H-0->L+2(+6%)

Table S3. Calculated absorption spectral data for 1.

ChemCommun



Figure S1. Calculated absorption spectrum for 1.

	Hartree	eV
LUMO+5	-0.00698	-0.19
LUMO+4	-0.0085	-0.23
LUMO+3	-0.01727	-0.47
LUMO+2	-0.01753	-0.48
LUMO+1	-0.02285	-0.62
LUMO	-0.11814	-3.21
НОМО	-0.20099	-5.47
HOMO-1	-0.21251	-5.78
HOMO-2	-0.21893	-5.96
HOMO-3	-0.23966	-6.52
HOMO-4	-0.24824	-6.75
HOMO-5	-0.2534	-6.90
HOMO-6	-0.25512	-6.94
HOMO-7	-0.25854	-7.04
HOMO-8	-0.26456	-7.20
HOMO-9	-0.28129	-7.65

 Table S4. Calculated energy levels of molecule 2.

calcd. (nm)	f	composition (H = HOMO, L= LUMO, L+1 = LUMO+1, etc.)
661.4	0.0896	H-0->L+0(+77%) H-2->L+0(23%)
484.0	0.8039	H-2->L+0(+75%) H-0->L+0(+24%)

ChemCommun

366.2	0.1375	H-7->L+0(+59%) H-8->L+0(+33%)
		H-9->L+0(+5%)

 Table S5. Calculated absorption spectral data for 2.



Figure S2. Calculated absorption spectrum for 2.

	Hartree	eV
LUMO+5	0.04563	1.24
LUMO+4	0.02938	0.80
LUMO+3	-0.00124	-0.03
LUMO+2	-0.00677	-0.18
LUMO+1	-0.01382	-0.38
LUMO	-0.11955	-3.25
НОМО	-0.19068	-5.19
HOMO-1	-0.21611	-5.88
HOMO-2	-0.24805	-6.75
HOMO-3	-0.25601	-6.97
HOMO-4	-0.26271	-7.15
HOMO-5	-0.29382	-8.00
HOMO-6	-0.30382	-8.27
HOMO-7	-0.31807	-8.66
HOMO-8	-0.33494	-9.11
HOMO-9	-0.33704	-9.17

Table S6. Calculated energy levels of molecule 3.

	Εl	lectronic	Supple	ementary	Information	า (ESI)
--	----	-----------	--------	----------	-------------	---------

ChemCommun

calcd. (nm)	f	composition (H = HOMO, L= LUMO, L+1 = LUMO+1, etc.)		
930.5	0.0207	H-0->L+0(+97%)		
536.8	0.1767	H-1->L+0(+91%) H-2->L+0(+6%)		
401.1	0.1934	H-2->L+0(+49%) H-3->L+0(44%)		
376.2	0.2463	H-3->L+0(+39%) H-2->L+0(+33%) H $_{4}$ >L+0(+17%) H $_{0}$ >L+1(+7%)		
198.5	0.1196	H-4->L+0(+17%) $H-0->L+1(+7%)H-1->L+4(+31%)$ $H-0->L+6(+18%)$		
190.4	0.1435	H-3->L+3(+17%) H-4->L+1(+14%) H-3->L+2(7%) H-3->L+1(+30%) H-2->L+2(+15%) H-5->L+1(13%) H-17->L+0(+13%)		
185.1	0.1320	H-0->L+6(8%) H-4->L+3(+7%) H-4->L+3(+33%) H-19->L+0(+24%) H-1->L+5(17%) H-3->L+3(6%)		

 Table S7. Calculated absorption data for 3.



Figure S3. Calculated absorption spectrum for 3.

4. Reference

- Y. Gabe, Y. Urano, K. Kikuchi, H. Kojima, T. Nagano, J. Am. Chem. Soc. 2004, 126, 3357-3367.
- (2) C. Jones, T. Arez, J. Org. Chem., 1979, 37, 3622-3623.
- (3) B. Witulski, N. Buschmann, U. BergstraÈûer, *Tetrahedron*, 2000, 56, 8473-8480.
- (4) K. Dittmann, U. Pindur, Arch. Pharm. (Weinheim) 1985, 318, 340-350.
- (5) G. Abbiati, V. Canevari, E. Rossi, A. Ruggeri, Synth. Commun., 2005, 35, 1845–1850.
- (6) C. Chi, G. Wegner, Macromol. Rapid Commun. 2005, 26, 1532-1537.
- (7) A. D. Becke, J. Chem. Phys., 1993, 98, 5648.
- (8) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B: Condens. Matter, 1988, 37, 785.
- (9) R. W. Ditchfie, J. Hehre, J. A. Pople, J. Chem. Phys., 1971, 54, 724.
- (10) W. J. Hehre, R. Ditchfie J. A. Pople, J. Chem. Phys., 1972, 56, 2257.
- (11) P. C. Harihara, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
- (12) S. I. Gorelsky, , *SWizard program*, http://www.sg-chem.net/, University of Ottawa, Ottawa, Canada, **2010**.

5. Appendix: ¹H NMR and ¹³CNMR spectra and HR-EI mass spectra

5.1 ¹H NMR and ¹³CNMR spectra

¹H NMR spectrum of **4** (500 MHz, CDCl₃, RT):



¹³C NMR spectrum of **4** (125 MHz, CDCl₃, RT):



15 / 22

ChemCommun





¹³C NMR spectrum of **5** (75 MHz, CDCl₃, RT):



ChemCommun

¹H NMR spectrum of **1** (300 MHz, CDCl₃, RT):



¹³C NMR spectrum of **1** (75 MHz, CDCl₃, RT):





ChemCommun

¹H NMR spectrum of **2** (500 MHz, CDCl₃, RT):



(t1) maa

¹³C NMR spectrum of **2** (125 MHz, CDCl₃, RT):



ChemCommun





¹³C NMR spectrum of **12** (75 MHz, CDCl₃, RT):



ChemCommun





¹³C NMR spectrum of **13** (125 MHz, d₆-DMSO, RT):



ChemCommun



¹³C NMR spectrum of **3** (125 MHz, CDCl₃, RT):



5.2 HR-EI mass spectra



Compound 2:



1024wu-ny: T: + c Ful m/z= 520.	1002-c1-AV# 1 ms [500 04-520.36	1 RT: 4.8 .19-533.98	7 3]			
m/z	Intensity	Relative	Theo.	Delta	RDB	Composition
520.1939	2190730.0	100.00	520.1939	-0.08	29.0	C 39 H 24 N 2
			520.1922	3.22	24.5	C ₃₅ H ₂₃ N ₂ ¹¹ B ₁ F ₂

Compound 3:

