Supporting Information

Bulky 4-tritylphenylethynyl substituted boradiazaindacene: Pure red emission, relatively large Stokes shift and inhibition of self-quenching

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General methods: The 400 (^{1}H) MHz NMR and 100 (^{13}C) MHz NMR spectra were measured at room temperature on a Bruker 400MHz spectrometers using perdeuterated solvents as internal standard: δ (H) in ppm relative to residual protiated solvent; δ (C) in ppm relative to the solvent. Melting points were obtained with a capillary melting point apparatus in open-ended capillaries and are uncorrected. Chromatographic purification was conducted with silica gel. All solvent mixtures are given as volume/volume ratios.

Spectroscopic measurements: Absorption spectra were recorded in CH_2Cl_2 on a US-HP8453 UV-Visible absorption spectrometer and emission spectra were recorded by using a PTI–700 instrument. All studies were made at 20 °C. Excitation and emission spectra were fully corrected by reference to a standard lamp. Solutions were deoxygenated by purging with dried Argon prior to recording the spectrum. The reference systems used were Rhodamine 6G in ethanol ($\Phi_F = 0.95$).

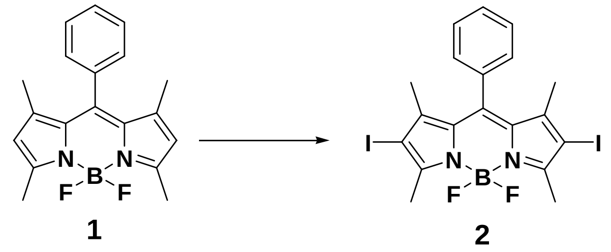
Electrochemical measurements: Electrochemical studies made use of cyclic voltammetry with a conventional 3-electrode system using a BAS 100W electrochemical analyzer in deoxygenated and anhydrous CH_2Cl_2 at room temperature. The potentials are reported vs ferrocene as internal standard and potentials are calculated relative to SCE assuming $E_{1/2}$ (Fc/ Fc$^+$) = +0.38 V (ΔEp = 70 mV) vs SCE using a scan rate of 100 m Vs^{-1}, glassy carbon working electrode, Ag/$AgNO_3$ reference electrode, platinum counter electrode, and the sample solutions contained 1.0×10^{-3} M sample and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Argon was bubbled for 10min before each measurement.

Experimental procedure for X-ray crystallographic analysis: Single crystals of compound **4** suitable for X-ray analysis were obtained by recrystallization from dichloromethane-hexane. Crystallographic data were collected on an SMART APEX diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073Å) at 273K. Data processing was accomplished with SAINT processing program. Intensity data were corrected for absorption by the SADABS program. The structures were solved by direct methods and refined on F_o^2 against full-matrix least-squares methods using the SHELXTL97 program. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation, but their positions and thermal parameters were fixed during the structure refinement.

Quantum-Chemical Calculation Details: All calculations were performed with the Gaussian 03 package[1] for Computational Chemistry, CAS at the B3LYP level. The basis sets 3-21G was used for the calculation of HOMO and LUMO level energy. The contour plots of MOs were obtained with the GaussView 3.07 program.

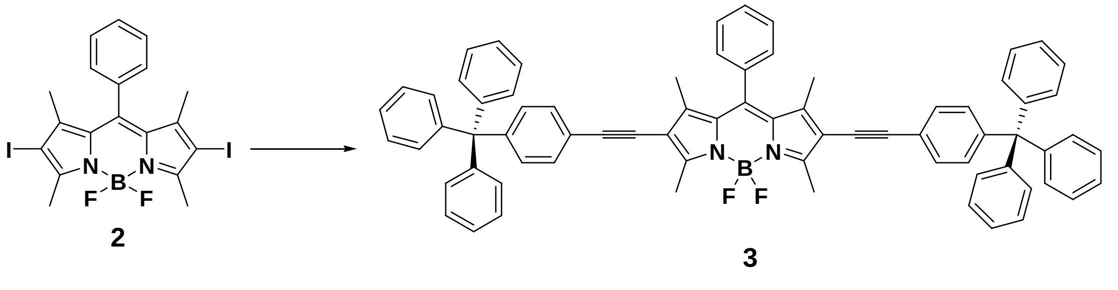
Materials: The phenylaceylene were obtained from commercial sources and used without further purification. Pd $(pph_3)_4$,[2] NIS[3] were prepared and purified according to literature procedures. DMF, Et_3N were dried over suitable reagents and distilled under argon immediately prior to use.

Experimental details:



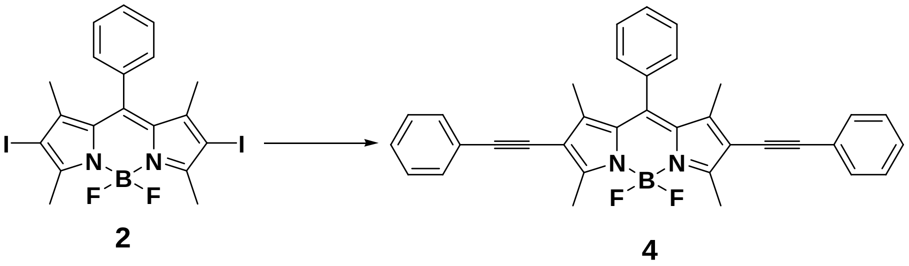
2, 6-diiodo-1, 3, 5, 7-tetramethyl-8-phenyl-4, 4-difluoroboradiazaindacene (2): To a solution of 1, 3, 5, 7-tetramethyl-8-phenyl-4, 4-difluoroboradiazaindacene (1, 170 mg, 0.51 mmol) in anhydrous CH_2Cl_2 (25 mL) was added excess NIS (459 mg, 2.04 mmol). The mixture was stirred at room temperature until total consumption of the starting material (1.5 h, as monitored by TLC). Crude product was then concentrated under vacuum, and purified by silica gel column chromatography (hexane/CH_2Cl_2, 2:1). The red colored fraction was collected and the solvent was removed under reduced pressure to yield the desired compound. Yield: 205 mg (70%); M. p. 194.3-194.9 °C ^{1}H NMR (400 MHz, $CDCl_3$): 1.37 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 7.15–7.20 (m, 2H, Ar–H), 7.42–7.48 (m, 3H, Ar–H). IR (KBr) 3435, 2922, 1530, 1464, 1121, 931cm^{-1} TOF MS EI+ calcd for $C_{19}H_{17}BF_2I_2N_2$ 575.9542, found 575.9543.

General Experimental Procedures for Sonogashira coupling reaction: In a Schlenk flask, 2, 6-diiodobodipy (100 mg, 0.207 mmol), Pd $(PPh_3)_4$ (8 mg, 0.0125 mmol) were added. DMF was added after the flask degassed several times. Alkyne reagent (0.497 mmol) and Et_3N (2 mL, 14.4 mmol) were added to the flask by using the syringe. The mixture was stirred at 65 °C under argon. The solution was observed by TLC. Water was added, and the solution was extracted with CH_2Cl_2. After evaporation, the organic layer was purified by column chromatography.



2,6-di-(4-tritylphenylethynyl)-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiaza indacene (3): Prepared according to the general procedure with 4-tritylphenylethyne (171 mg, 0.497 mmol), **2** (100 mg, 0.207 mmol) in DMF (4 mL). Complete consumption of the starting material was observed after 12 h. The chromatography was performed on silica (CH_2Cl_2/hexane, 1:3). The purple colored fraction was collected to get the compound. Yield: 148 mg (71%). R$_f$ value 0.60. M. p. >300 °C ^{1}H NMR (400 MHz, $CDCl_3$): 7.51–7.52 (m, 5H, Ar–H), 7.35–7.38 (m, 3H, Ar–H), 7.28–7.32 (m, 3H, Ar–H), 7.19–7.26 (m, 34H, Ar–H), 2.69 (s, 6H, CH_3), 1.25 (s, 6H,

CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ =158.6, 147.1, 146.4, 143.9, 142.4, 134.5, 131.1, 131.0, 130.5, 127.6, 126.1, 120.9, 96.4, 81.6, 64.9, 13.4, 12.7. IR (KBr) 3420, 2913, 2204, 1537, 1110 cm^{-1} TOF MS LD+ calcd for $C_{35}H_{27}BF_2N_2$ 1008.4426, found 1008.4426.



2,6-di-(phenylacetylenyl)-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (4): Prepared according to the general procedure with phenylaceylene (54.5 μL, 0.497 mmol), **2** (100 mg, 0.207 mmol) in DMF (4 mL). Complete consumption of the starting material was observed after 6 h. The chromatography was performed on silica (CH_2Cl_2/hexane, 1:2), the purple colored fraction was collected to get the compound. Yield: 71 mg (76%). R_f value 0.65. M. p. >300 °C ^{1}H NMR (400 MHz, $CDCl_3$): 7.65–7.67 (d, 4H, Ar–H), 7.52–7.53 (m, 4H, Ar–H), 7.35–7.37 (m, 3H, Ar–H), 7.26–7.30 (d, 4H, Ar–H), 2.55 (s, 6H, CH_3), 1.35 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ =158.4, 144.0, 142.5, 134.5, 131.3, 129.4, 128.4, 128.1, 127.8, 123.4, 116.2, 96.5, 81.6, 13.7, 13.4. IR (KBr) 3422, 2917, 2207, 1536, 1112 cm^{-1} TOF MS EI+ calcd for $C_{35}H_{27}BF_2N_2$ 524.2235, found 524.2235.

Table S1: Crystallographic data for compounds **4**

	4
Formula	$C_{35}H_{27}BF_2N_2$
M_r	524.40
crystal system	Orthorhombic
space group	Fdd2
a [Å]	28.6219 (16)
b [Å]	6.9589 (4)
c [Å]	28.2896 (16)
α [°]	90.00
β [°]	90.00
γ [°]	90.00
V [Å^3]	5634.6 (6)
Z	8
F (000)	2192
ρ_{calcd} [Mg m^{-3}]	1.236
crystal size [mm]	0.360×0.270×0.150
Flack parameter	10(10)
Reflns collected	9043
Independent reflns	1721
R_{int}	0.0566
Reflns with $I>2\sigma(I)$	1169
Parameters refined	183
GOF on F^2	1.094
$R1^a$ ($I>2\sigma(I)$)/$w R2^b$	0.0455/0.1031
$R1^a$ (*all data*)/$w R2^b$	0.0759/ 0.1169
Residue electron density/e Å^{-3}	0.138/ - 0.161

CCDC-650117 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via deposit@ccdc.cam.uk.

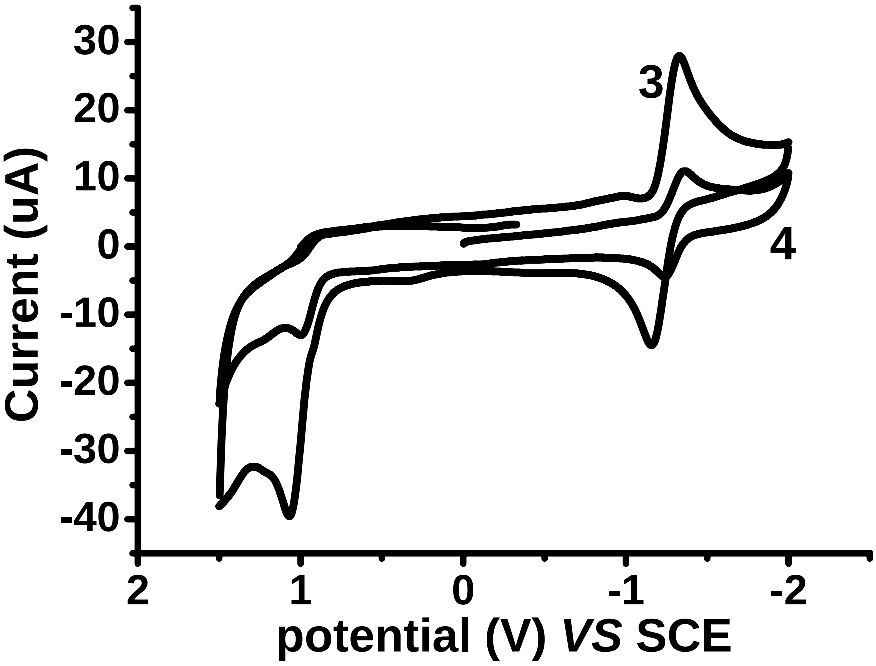


Figure S1.Cyclic voltammograms of compounds **3** and **4** measured in CH_2Cl_2 solution, containing 0.1 M $TBAPF_6$ at 20 °C.

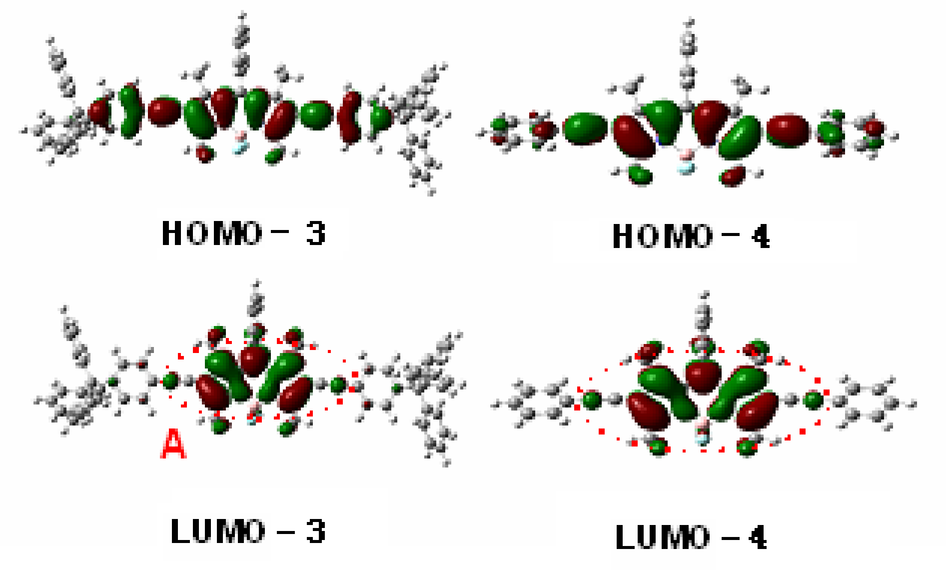


Figure S2. Diagrams showing the HOMO and LUMO levels of **3** and **4**. The electron density in the LUMO of these two compounds was mainly distributed over part A, almost the same.

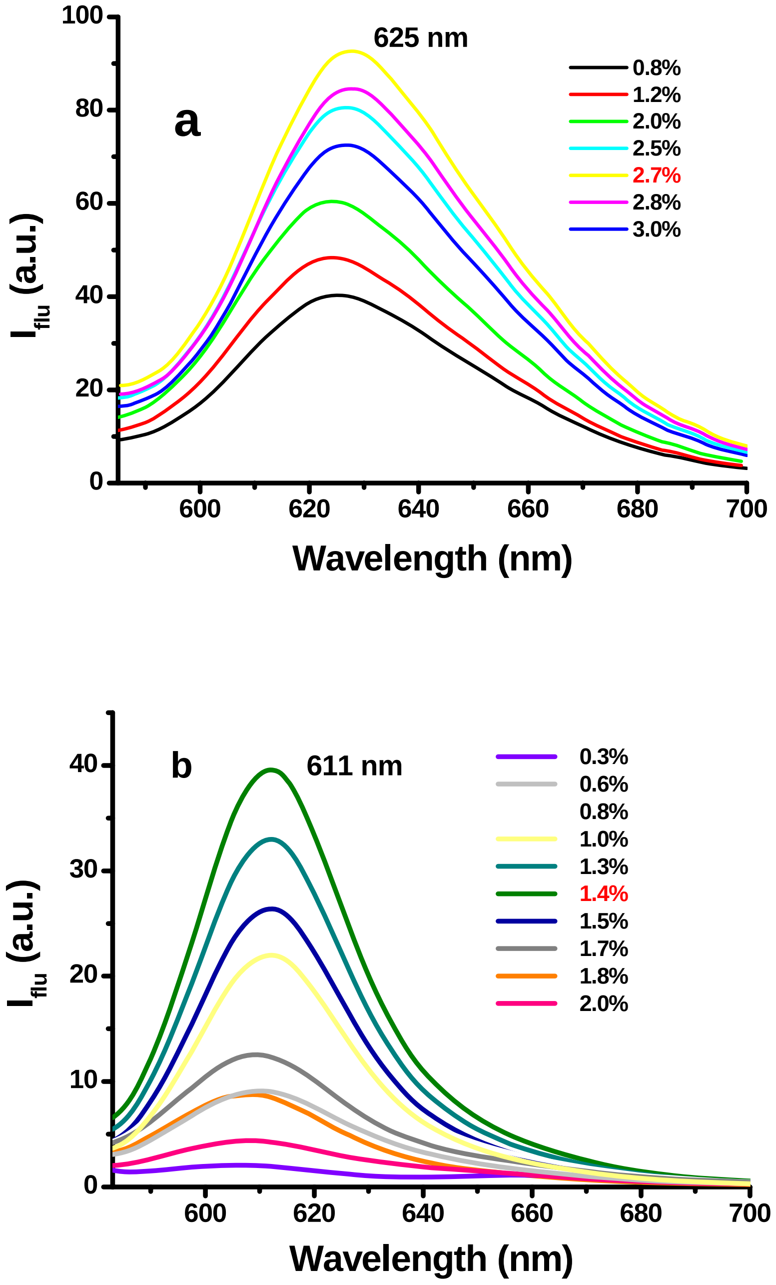
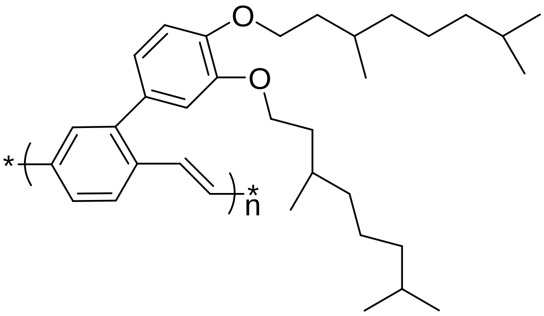


Figure S3. Emission intensity of compounds **3** (a) on films under different doped concentrations as dopants for SBS (styrene-butadiene block copolymer, M.W. = 200,000 g/mol, an inert polymer matrix, films are prepared by spin-coating) and (b) for compound **4**. The maximum doping concentrations are 2.7% (1.4%) for compound **3** (**4**).

Device 1: ITO/PEDOT (30 nm)/BDP-PPV: 2% **3** (60 nm)/Alq$_3$ (10 nm) /Al (100 nm)

Structure of BDP-PPV^4:



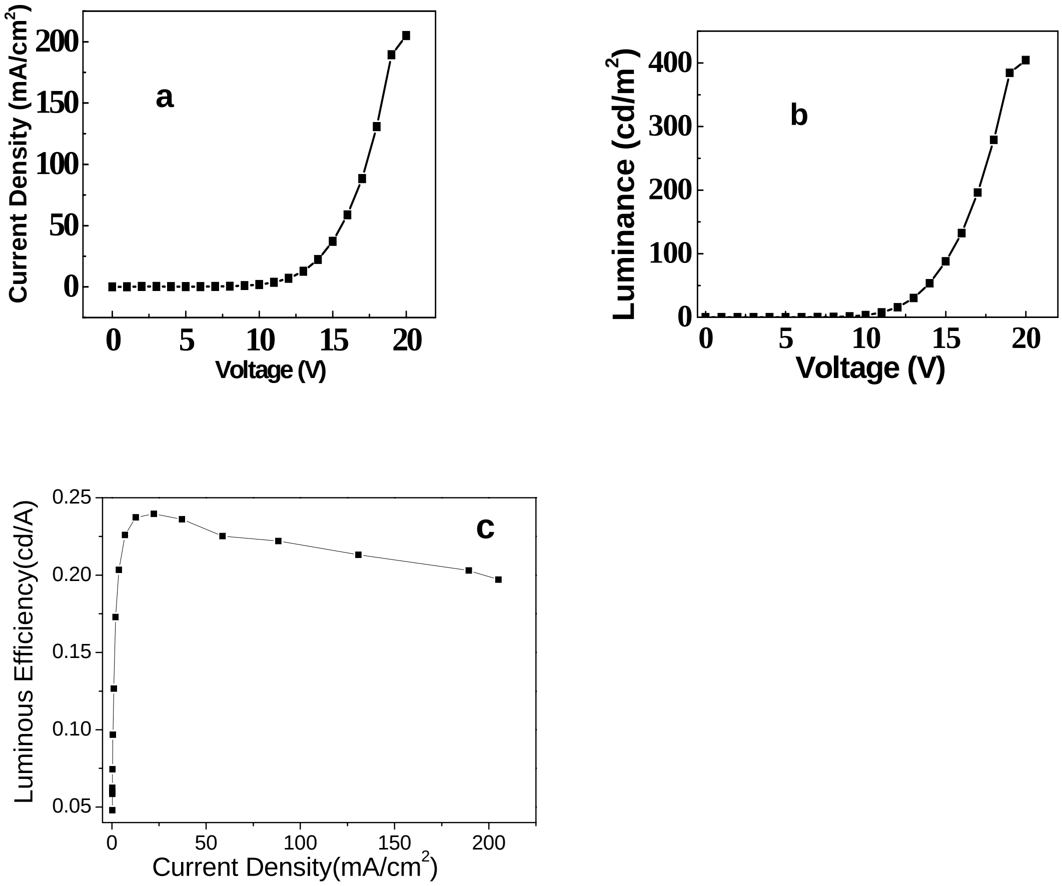


Figure S4. (a): Current–Voltage (*I*–*V*) characteristics of device 1. (b): luminance–Voltage (*L*–*V*) characteristics of device 1. (c): luminescence efficiency–Current density curve of the device 1.

Device 2: ITO/PEDOT (30nm)/BDP-PPV: 1% **4** (60 nm)/Alq$_3$ (10 nm) /Al (100 nm)

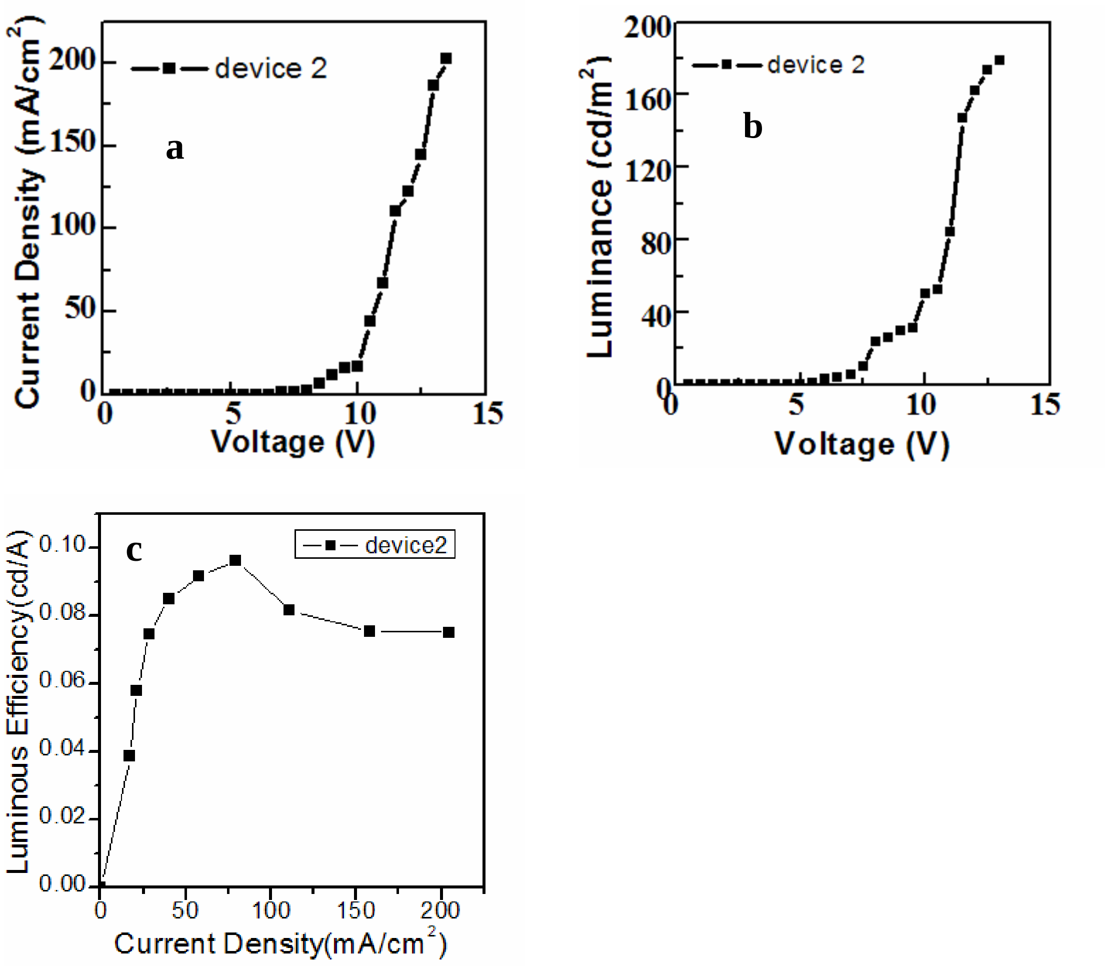


Figure S5. (a): Current–Voltage (*I*–*V*) characteristics of device 2. (b): luminance–Voltage (*L*–*V*) characteristics of device 2. (c): luminescence efficiency–Current density curve of the device 2.

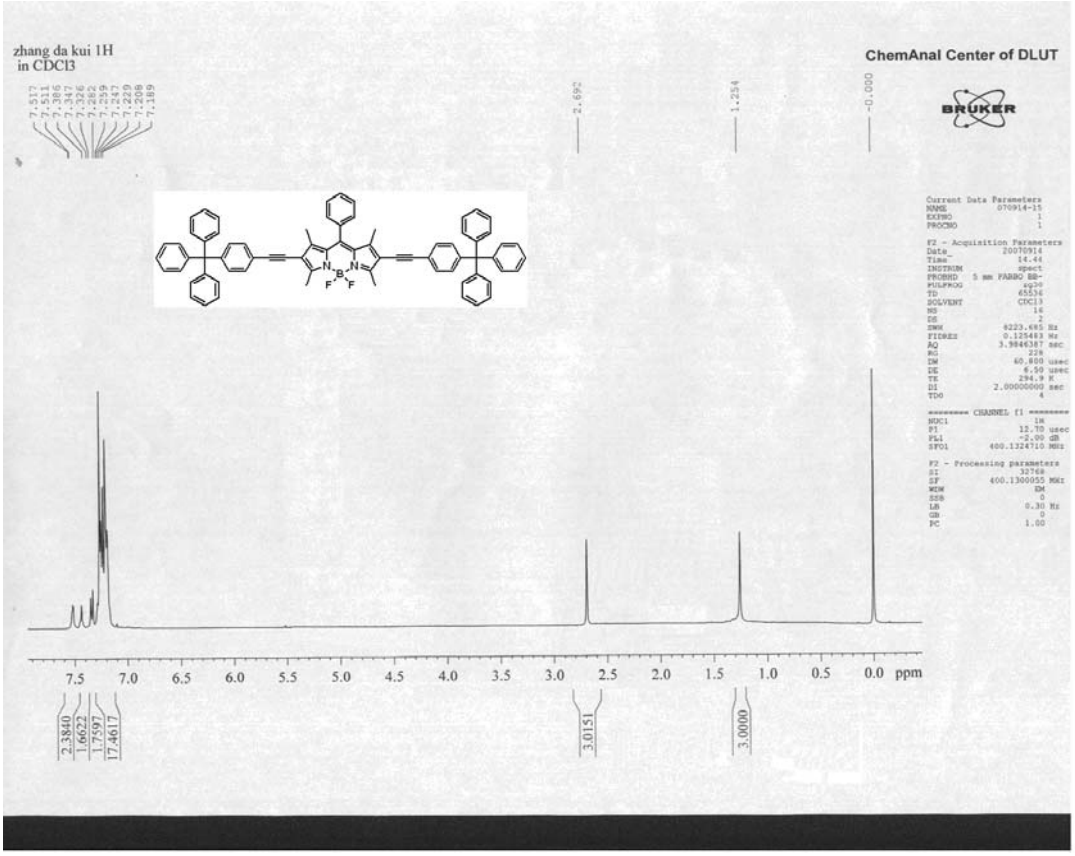


Figure S6. ^{1}H NMR for compound **3** in $CDCl_3$ at 400 MHz

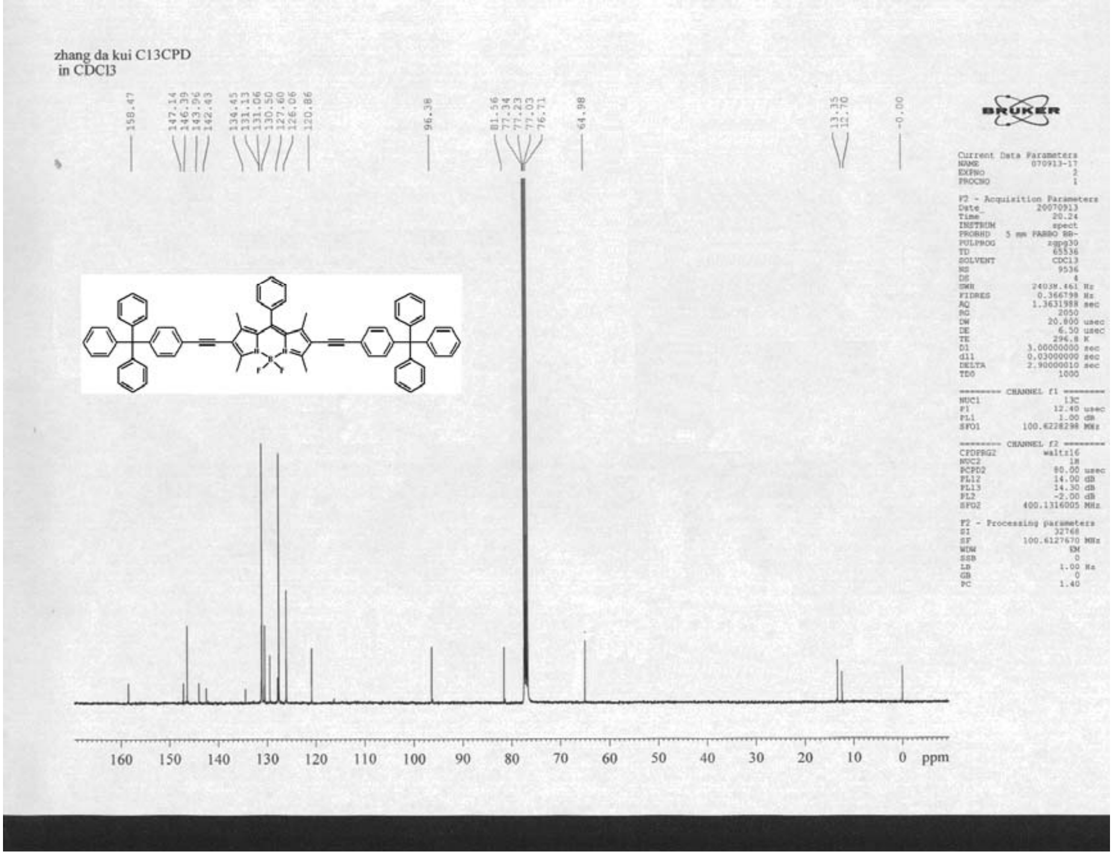


Figure S7. ^{13} C NMR for compound **3** in $CDCl_3$ at 100 MHz.

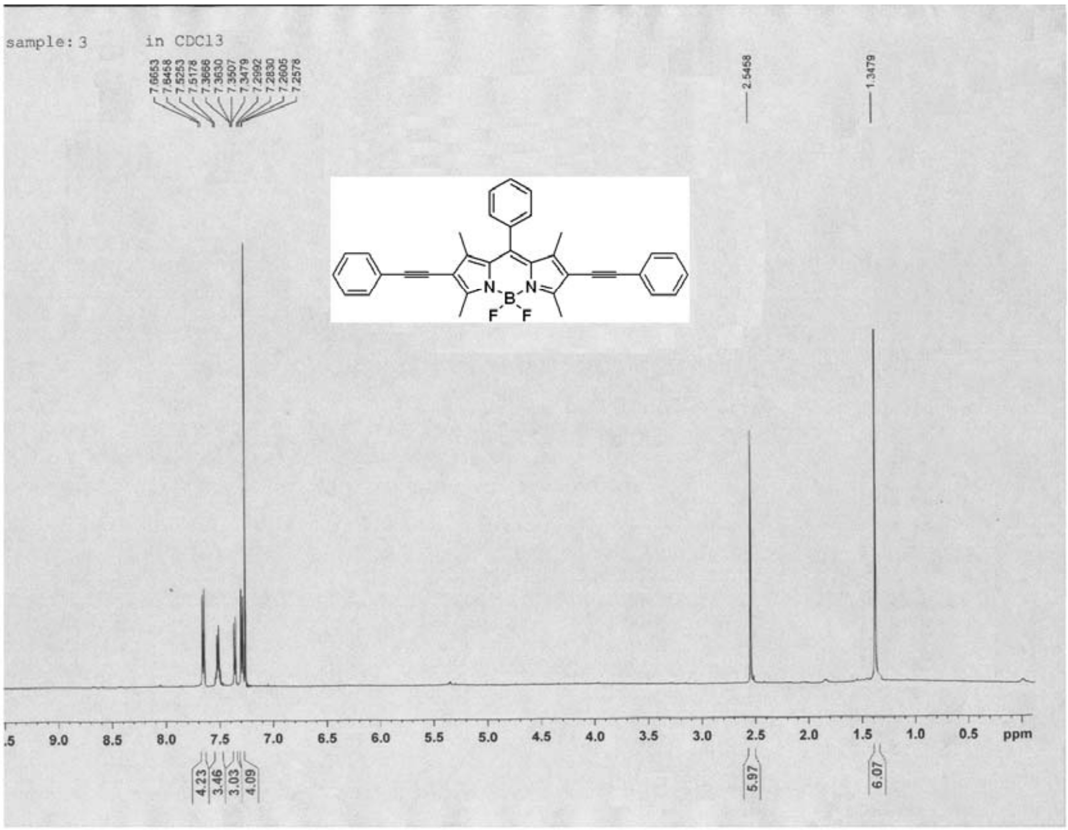


Figure S8. ^{1}H NMR for compound **4** in $CDCl_3$ at 400 MHz

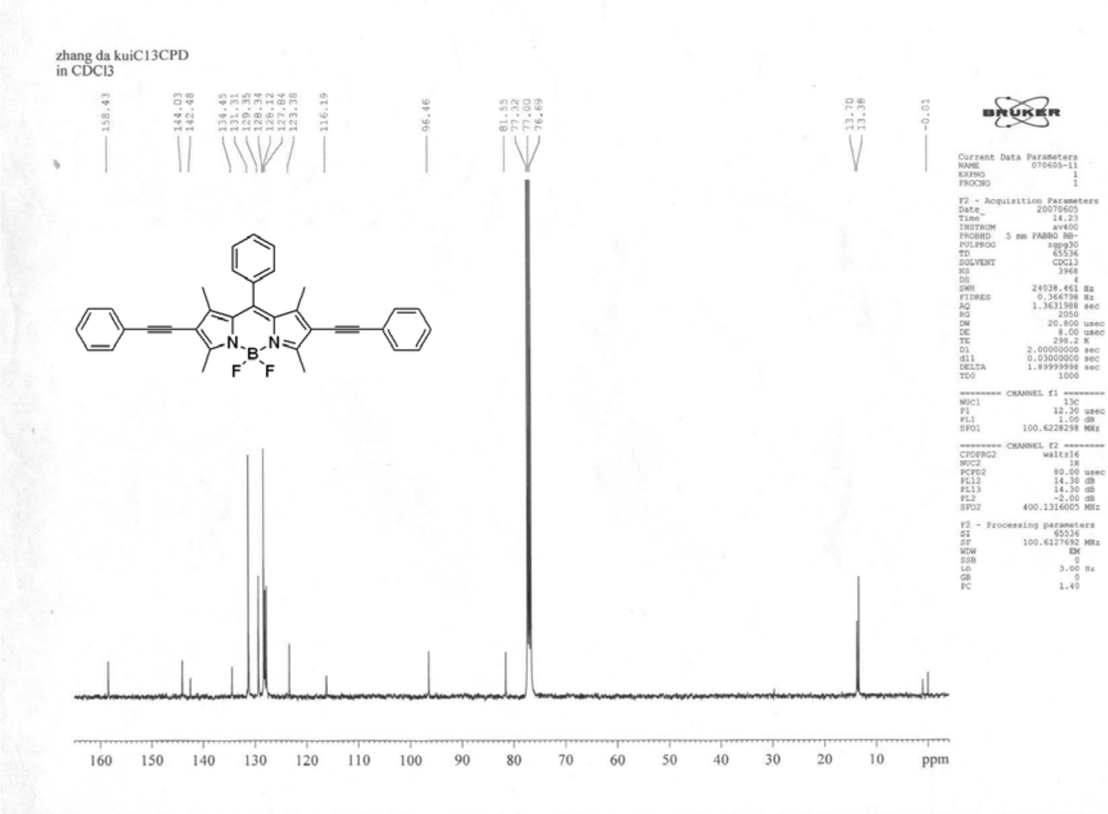


Figure S9. ^{13} C NMR for compound **4** in $CDCl_3$ at 100 MHz.

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