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Synthesis and properties investigation of π-bridged 9,9’-bifluorenylidene ladder as electron acceptors

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Experimental section

General procedures. NMR spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer by using tetramethylsilane (0 ppm for ^{1}H NMR) as an internal standard. MALDI/TOF–MS measurements were performed on an AXIMA-CFR Plus (Shimadzu), with dithranol as a matrix. UV-vis absorption spectra were recorded on a JASCO V-670 spectrophotometer in a quartz cuvette of 1 cm path length. Absolute fluorescence quantum yield was recorded on a Hamamatsu absolute PL quantum yield spectrometer C11347. Cyclic voltammetry and differential pulse voltammetry were performed with an Eco Chemie AUTOLAB PGSTAT12 potentiostat in a deaerated CH_2Cl_2 containing 0.1 M $TBAPF_6$ as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as a counter electrode. The redox potentials were measured with respect to an $Ag/AgNO_3$ (1.0×10^{-2} M) reference electrode. The oxidation potential of ferrocene as an external standard was 0.21 V (*vs* $Ag/AgNO_3$) in CH_2Cl_2.

Quantum chemical calculation. Computational analysis and geometry optimization for **BBF** in the ground state was performed using the Spartan'14 software or Gaussian 09, revision D.01 and Gauss View software program (version 5), respectively.[1] Molecular orbitals were obtained by B3LYP or M06-2X functional with the 6-31G** basis set.

Materials. All chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry, Kanto Chemical, or Wako Pure Chemical Industries and used unless otherwise noted. Ferrocene and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were purified according to the literature.[2] Key compounds were purified by a recycling preparative HPLC (ChromNAV system equipped with a PU-2086 Plus pump and a RI-2031 Plus detector, JASCO Corporation) equipped with gel permeation chromatography (GPC) columns (YMC-GPC T4000). Air and water sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques.

The synthesis of compound 1.

A 50 mL two-necked round bottom flask was charged with **IFO** (640.2 mg, 0.676 mmol), which was refluxed in mixture of ethanol/THF (v/v = 10/1, 11 mL) solution in the excess presence of anhydrous hydrazine monohydrate (80%) (338.3 mg, 6.76 mmol). After 4-5 h, the suspension appeared, then the reaction solution was cooled down to room temperature and filtered to collect the bis-hydrazone **1** that precipitated out. The reaction yield is 85%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 0.88–0.91 (m, 24H), 1.26–1.34 (m, 96H), 1.84–1.86 (m, 16H), 4.03–4.10 (m, 16H), 6.50 (d, 4H, J = 3.2 Hz), 6.62 (d, 4H, J = 2.8 Hz), 6.94–7.00 (m, 4H), 7.15–7.17 (m, 4H), 7.20–7.22 (m, 4H), 7.57 (d, 2H, J = 8 Hz), 7.63 (d, 2H, J = 8 Hz), 7.70–7.72 (m, 2H), 7.83 (dd, 2H, J = 8 Hz, J = 1.6 Hz), 7.94 (dd, 2H, J = 8 Hz, J = 1.6 Hz), 8.02 (s, 1H), 8.06 (s, 2H), 8.12 (s, 1H), 8.21 (s, 1H), 8.28 (s, 1H). The poor solubility precluded the carbon NMR characterization. MALDI/TOF–MS: m/z calcd 974.66; found 973.09.

The synthesis of compound 2.

A solution of bis-hydrazone **1** (300 mg, 0.308 mmol) was dissolved in 8 mL of anhydrous THF. The activated MnO_2 (147 mg, 1.69 mmol) was added in one portion. Stirring was continued for 30 min, and then the mixture was filtered through a plug of Celite® pad and washed with $CHCl_3$. After removal of solvent under reduced pressure, the crude product was obtained quantitatively (299 mg, quantitatively). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 0.87–0.91 (m, 12H), 1.26–1.37 (m, 48H), 1.84–1.89 (m, 8H), 4.05–4.13 (m, 8H), 6.98 (d, 2H, J = 8 Hz), 7.22–7.30 (m, 4H), 7.54 (dd, 2H, J = 8 Hz, J = 1.6 Hz), 7.67 (s, 2H), 8.01 (d, 2H, J = 8 Hz), 8.05 (s, 2H). MALDI/TOF–MS: m/z calcd 970.63; found 968.92.

The synthesis of compound 3.

The compound **FO** (500 mg, 0.592 mmol) and Lawesson's reagent (238.98 mg, 0.592 mmol) were dissolved in anhydrous toluene (10 mL) under agron atmosphere. The mixture was heated at 90 °C for around 4h. The color of mixture gradually turned to red. The reaction was monitored by TLC until the starting material was completely reacted. Then solvent was evaporated under reduced pressure. The crude compound **3** was used for next step without any purification due to its instability.

The synthesis of BBF.

The compound **FO** (200 mg, 0.237 mmol) and Lawesson's reagent (143.76 mg, 0.356 mmol) were dissolved in anhydrous toluene (5 mL) under agron atmosphere, and the mixture was heated at 90 °C for 4h. The color of mixture gradually turned to dark grey. The TLC was employed to monitored the reaction until the **FO** was completely reacted. The compound **2** (104.64 mg, 0.108 mmol) was dissolved in 2 mL of anhydrous toluene and added into the reaction mixture and kept the mixture under refluxing under agron atmosphere. After the stirring overnight, the mixture was then allowed to cool down to room temperature and solvent was evaporated under reduced pressure. Water was poured into the reaction mixture and extracted with $CHCl_3$ for three times, the combined organic layer was washed with brine and aqueous K_2CO_3 then dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography (silica gel) with hexane: $CHCl_3$ (1:1) as the eluent, affording the pure product as dark purple powder (65.2 mg, 12%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 0.73 (t, 6H, J = 6 Hz), 0.80–0.88 (m, 44H), 1.21–1.44 (m, 130H), 1.71–1.75 (m, 12H), 1.76–1.82 (m, 12H), 3.72 (t, 4H, J = 8 Hz), 3.82 (t, 4H, J = 6 Hz), 3.72 (t, 4H, J = 6 Hz), 3.90-3.96 (m, 12H), 6.72 (d, 4H, J = 8 Hz), 6.84 (d, 2H, J = 8 Hz), 6.98 (d, 4H, J = 8 Hz), 7.08 (d, 4H, J = 8 Hz), 7.16-7.19 (m, 4H), 7.48 (d, 2H, J = 8 Hz), 7.58 (d, 2H, J = 8 Hz), 7.63-7.69 (m, 4H), 7.76-7.79 (m, 4H), 8.75 (s, 4H), 8.81 (s, 2H), 8.88 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ (ppm) 13.32, 13.80, 13.87, 15.01, 19.47, 22.43, 29.05, 29.11, 29.18, 29.44, 31.59, 31.68, 36.84, 37.13, 37.88, 59.27, 68.94, 69.00, 69.16, 69.26, 82.37, 83.17, 90.86, 111.71, 111.83, 112.04, 112.25, 113.69, 114.01, 119.08, 119.60, 120.33, 125.20, 127.52, 133.13, 133.30, 133.47, 139.10, 139.41, 139.48, 139.67, 148.52, 148.63, 149.07, 149.25. MALDI/TOF–MS: m/z calcd 2571.83; found 2567.84.

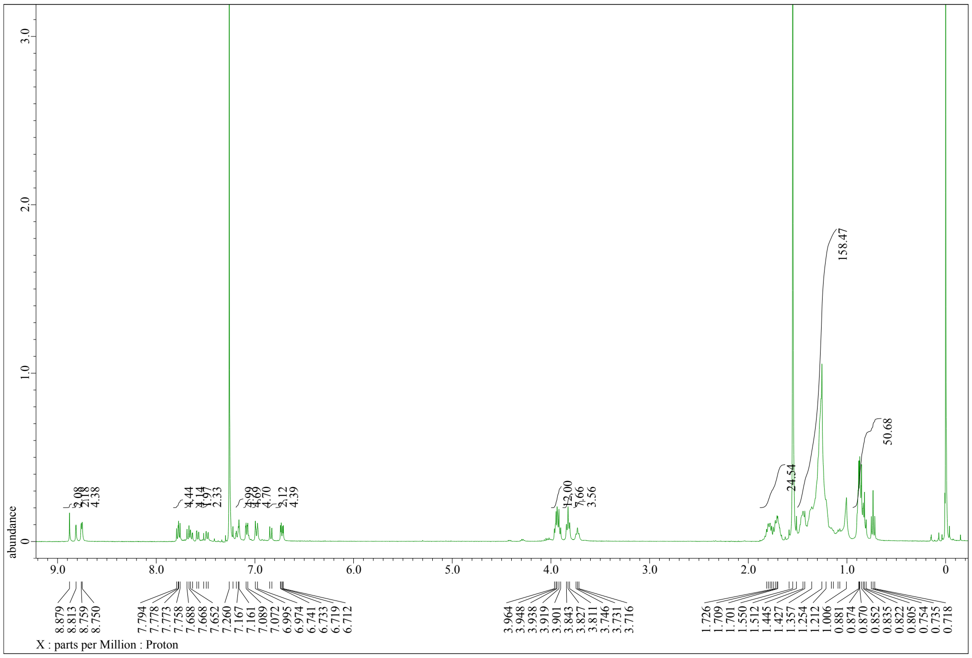

Figure S1 ^{1}H NMR spectrum of **BBF** (400 MHz, in $CDCl_3$) at 298 K.

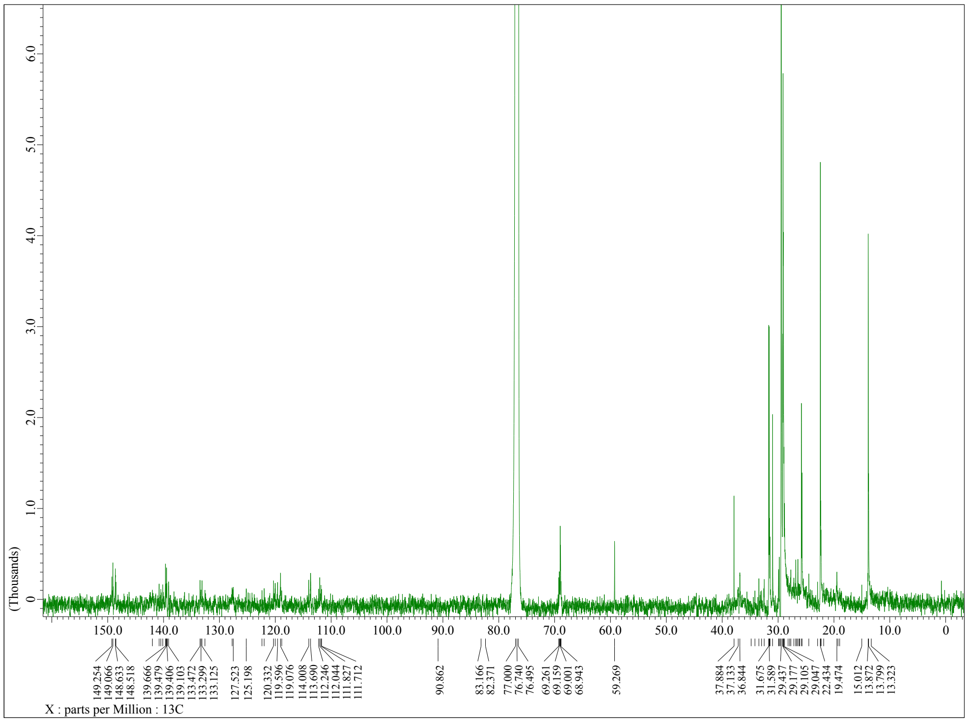

Figure S2 ^{13}C NMR spectrum of **BBF** (100 MHz, in $CDCl_3$) at 298 K.

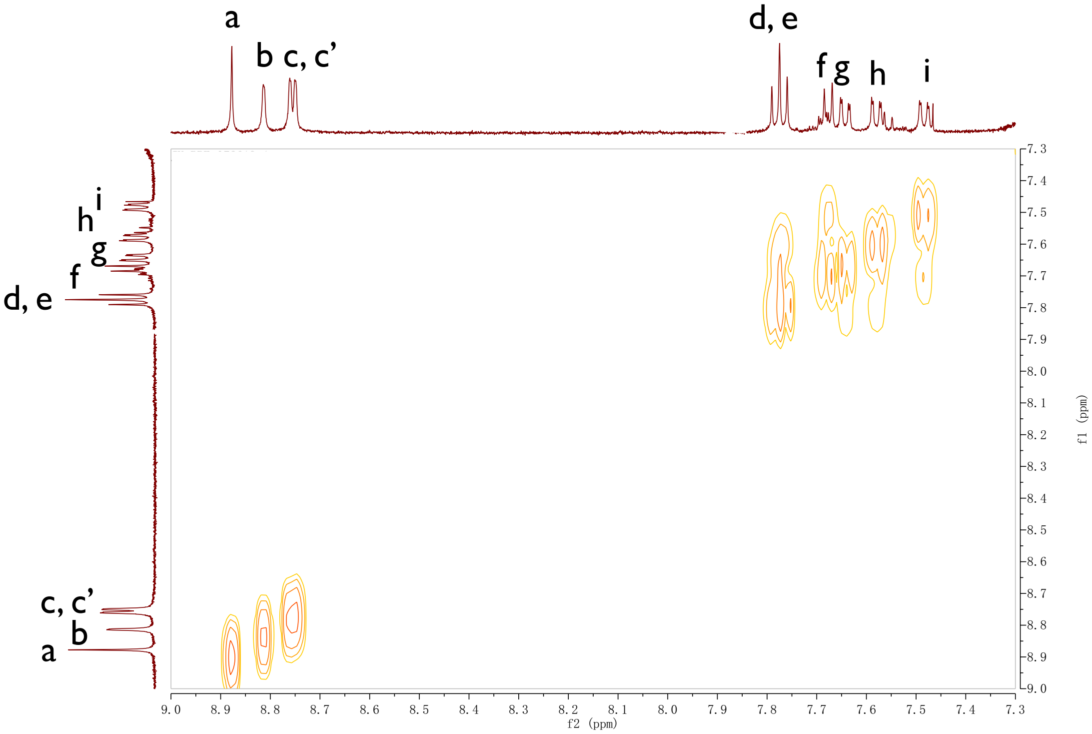

Figure S3 Partial ^{1}H,^{1}H COSY NMR spectrum of **BBF** (500 MHz, in CDCl$_3$) at 298 K.

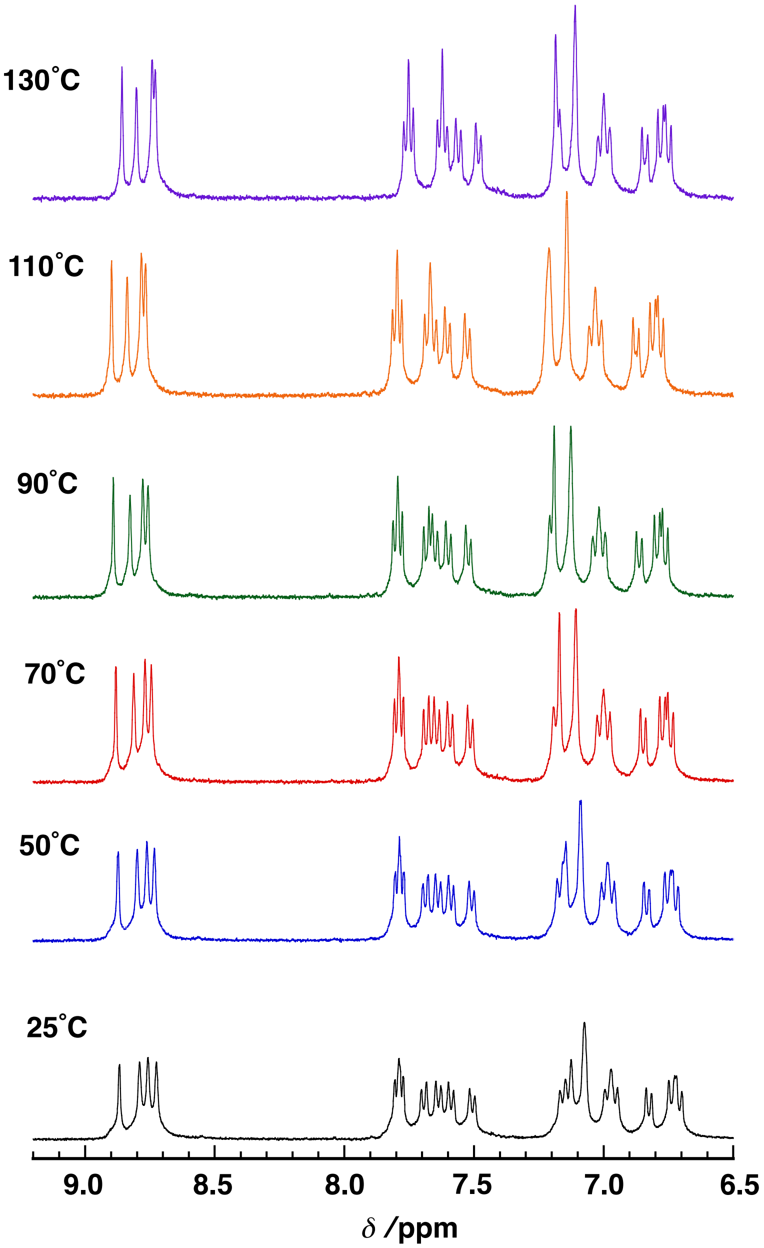

Figure S4 Variable-temperature ^{1}H NMR spectra of **BBF** in 1,1,2,2-tetrachloroethane-d_2.

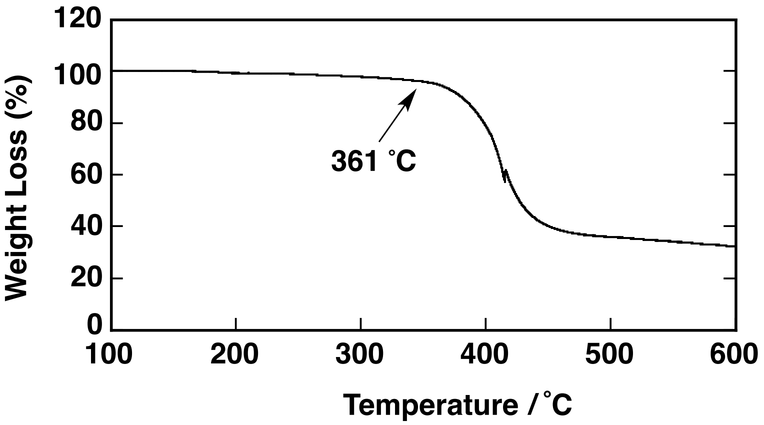

Figure S5 Thermal gravity analysis (TGA) of **BBF** under flowing argon gas. The arrow indicates the temperature where 5% of the sample weight is lost.

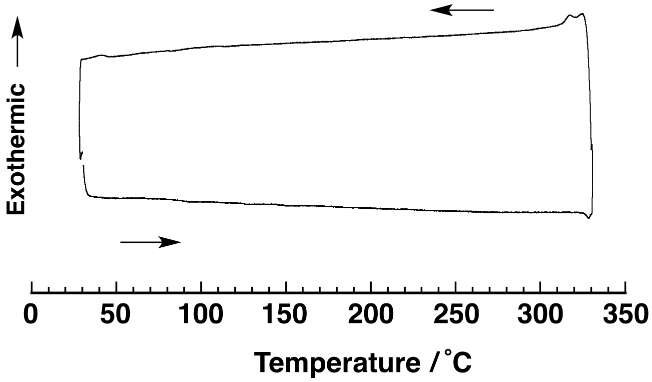

Figure S6 Differential scanning calorimetry (DSC) traces of **BBF** at 2nd heating and 1st cooling processes at a scanning rate of 10 °C /min.

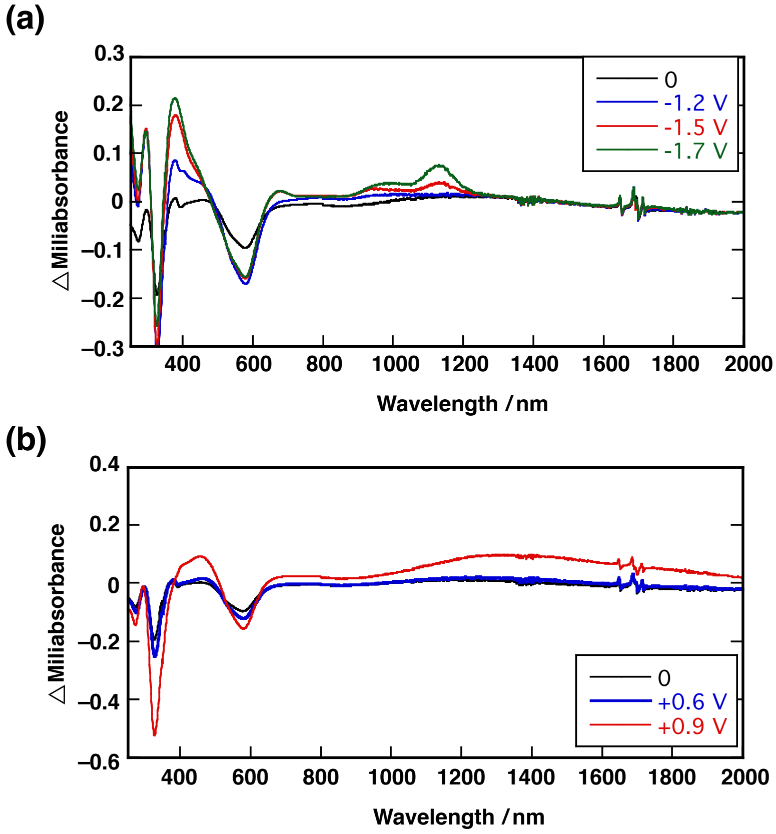

Figure S7 UV/Vis/NIR spectral changes of **BBF** during (a) the reduction at –1.2 V (blue line), –1.5 V (red line), –1.7 V (green line) and (b) the oxidation at +0.6 V (blue line) and +0.9 V (red line) in deaerated CH_2Cl_2 containing 0.1 M of $TBAPF_6$.

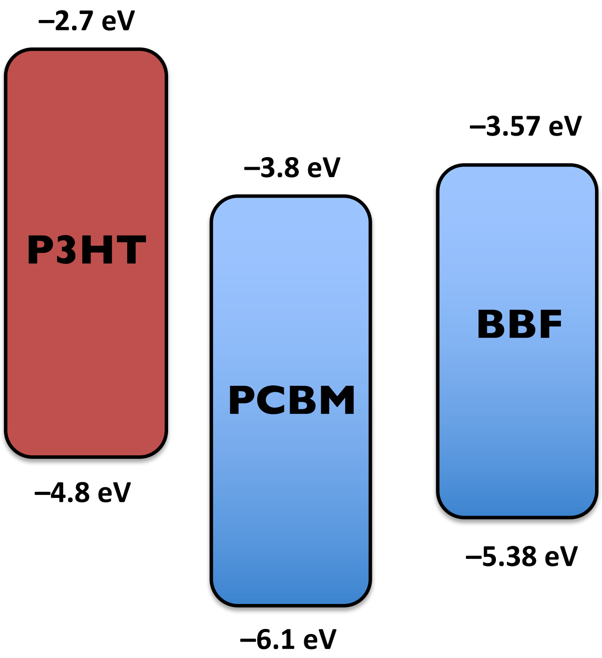

Figure S8 Electronic energy levels of P3HT, PCBM and **BBF**.

References

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