Supporting Information

for

An Organoboron Compound with Wide Absorption Spectrum for Solar Cell Application

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1. Materials and synthesis

Materials. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Toluene and tetrahydrofuran were purified by distillation under Argon prior to use. PTB7-Th was purchased from 1-Material Chemscitech Inc. (Canada). 5,5′-dibromo-2,2′-bipyridine)-3,3′-diamine, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbaldehyde, and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile were prepared according to the literature methods.\[1,2\]

Scheme 1. Synthetic route of M-BNBP4P-1.

Synthesis of 5,5′-dibromo-N3,N3′-di-2-hexyldecyl-[2,2′-bipyridine]-3,3′-diamine (2): Under argon, to a solution of 5,5′-dibromo-2,2′-bipyridine-3,3′-diamine (1) (1.00 g, 2.92 mmol) in THF (45 mL) was added n-BuLi (2.4 M in hexane, 2.7 mL, 6.43 mmol) dropwise at −78 °C. After the mixture being stirred at −78 °C for 1 h, 1-iodine-2-butyloctane (1.90 g, 6.43 mmol) was added and the resulting mixture was stirred for 10 h at 75 °C. After removal of the solvents in reduced pressure, the residual was purified by silica gel column chromatography with CH2Cl2/hexane=1/5 as the solvent to give 2 as light yellow oil. Yield: 798 mg, 55%. 1H NMR (400 MHz, C6D6, 25 °C): δ 10.24 (t, J = 3.6 Hz, 2H), 8.01 (d, J = 1.6 Hz, 2H), 7.08 (d, J = 1.6 Hz, 2H), 2.74 (m, J = 4.0 Hz, 4H), 1.57 (m, 2H), 1.43-1.17 (m, 32H), 0.97-0.87 (m, 12H). 13C NMR (400 MHz, C6D6, 25 °C): δ 147.41, 138.20, 132.17, 120.37, 119.13, 46.08, 37.66, 32.91, 32.64, 32.27, 30.17, 29.43, 27.21, 23.49, 23.15, 14.42, 14.36. Anal. Calc. for C34H56Br2N4: C, 60.00; H, 8.29; Br, 23.48; N, 8.23. Found: C, 60.53; H, 8.01; Br, 23.22; N, 8.24
**Synthesis of 3:** A mixture of 2 (750 mg, 1.10 mmol), BPh₃ (1.330 g, 5.51 mmol) and toluene (30 mL) was stirred at 120 °C for 8 h. After removal of the solvents under reduced pressure, the residual was purified by silica gel column chromatography with CH₂Cl₂/hexane=1/5 as the eluent. The compound 3 was obtained as a red solid. Yield: 930 mg, 84%. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 7.83 (s, 2H), 7.53 (s, 2H), 7.25-7.10 (m, 20H), 3.24 (d, J = 5.8 Hz, 4H), 1.72 (m, J = 5.2 Hz, 2H), 1.36-0.97 (m, 32H), 0.96-0.76 (m, 12H). ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ 149.80, 134.65, 132.10, 131.03, 127.91, 127.05, 126.14, 121.23, 52.76, 36.21, 32.40, 32.19, 32.11, 30.03, 29.04, 26.88, 23.36, 23.06, 14.37, 14.24. Anal. Calc. for C₅₈H₇₄B₂Br₂N₄: C, 69.06; H, 7.39; B, 2.14; Br, 15.84; N, 5.55. Found: C, 68.81; H, 7.67; B, 2.33; Br, 15.53; N, 5.66

**Synthesis of 4:** A mixture of 3 (441 mg, 0.437 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carbaldehyde (261 mg, 1.093 mmol), Pd(PPh₃)₄ (51 mg, 0.044 mmol), THF (30 ml), aqueous K₂CO₃ (2M, 0.66 mL, 1.311 mmol) was stirred under argon at 75 °C overnight. After cooled to room temperature, the reaction mixture was extracted with CH₂Cl₂. The organic phase was washed with water, dried over anhydrous Na₂SO₄, filtered and concentrated. The residual was purified by silica gel column chromatography with CH₂Cl₂/hexane=1/2 as the eluent to afford 4 as blue solid. Yield: 388 mg, 82%. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 9.30 (s, 2H), 8.02 (d, J = 1.2 Hz, 2H), 7.68 (d, J = 1.2 Hz, 2H), 7.50-7.25 (m, 20H), 6.63 (d, J = 3.2 Hz, 2H), 6.51 (d, J = 3.2 Hz, 2H), 3.50 (d, J = 2.4 Hz, 4H), 1.89 (m, 2H), 1.52-1.00 (m, 32H), 0.99-0.70 (m, 12H). ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ 181.85, 149.50, 144.81, 136.59, 135.08, 131.94, 130.57, 129.33, 127.31, 125.85, 120.36, 53.17, 36.71, 33.02, 32.69, 32.47, 30.42, 29.66, 27.53, 27.45, 23.75, 23.32, 14.62, 14.56. Anal. Calc. for C₆₈H₇₀B₂N₄O₂S₂: C, 76.25; H, 7.53; B, 2.02; N, 5.23; O, 2.99; S, 5.99. Found: C, 75.96; H, 7.83; B, 2.22; N, 5.20; O, 3.43; S, 5.36.

**Synthesis of M-BNBP4P-1:** A mixture of 4 (150 mg, 0.140 mmol), 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (82 mg, 0.420 mmol), pyridine (0.5 mL) and toluene (15 mL) was stirred at 75 °C for 6 h. After cooled to room temperature, the mixture was poured into methanol (100 mL) and filtered. The solid was purified by silica gel column chromatography with CH₂Cl₂/hexane=2/1 as the eluent. Yield: 169
mg, 85%. $^1$H NMR (400 MHz, C$_6$D$_6$, 25 ºC): δ 8.43-8.40 (m, 4H), 8.15 (d, $J$ = 1.2 Hz, 2H), 7.97 (d, $J$ = 1.2 Hz, 2H), 7.58 (m, 2H), 7.43 (s, 8H), 7.26 (m, 12H), 6.96 (t, $J$ = 2.8 Hz, 2H), 6.86 (m, 4H), 6.60 (d, $J$ = 3.2 Hz, 2H), 3.64 (d, $J$ = 5.2 Hz, 4H), 2.08 (m, $J$ = 5.2 Hz and 4.4 Hz, 2H), 1.57-1.15 (m, 32H), 1.05-0.81 (m, 12H).

$^{13}$C NMR (400 MHz, C$_6$D$_6$, 25 ºC): δ 187.81, 159.35, 152.80, 149.63, 145.24, 140.44, 138.20, 137.30, 136.69, 135.16, 134.33, 132.07, 130.74, 129.80, 128.54, 128.45, 128.35, 128.25, 128.16, 128.06, 127.36, 126.36, 125.51, 125.00, 123.76, 120.20, 114.84, 114.59, 72.19, 53.39, 36.89, 33.17, 32.84, 32.46, 30.51, 29.69, 27.49, 23.85, 23.39, 14.61, 14.59. Anal. Calc. for C$_{86}$H$_{88}$B$_2$N$_4$O$_4$S$_2$: C, 77.82; H, 6.68; B, 1.63; N, 4.22; O, 4.82; S, 4.83. Found: C, 77.12; H, 6.77; B, 1.98; N, 4.56; O, 4.32; S, 5.25.

Characterization. $^1$H and $^{13}$C NMR spectra were measured with a Bruker AV-400 (400 MHz for $^1$H NMR and $^{13}$C NMR) spectrometer with C$_6$D$_6$ as the solvent and TMS as an internal standard. Elemental analyses were carried out using a VarioEL elemental analyzer. UV-vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer. Thermogravimetric analysis (TGA) measurement was performed using a Perkin-Elmer 7 instrument under nitrogen flow at a heating rate of 10 ºC min$^{-1}$. Differential scanning calorimetry (DSC) was performed at the heating/cooling rate of 10 ºC min$^{-1}$ with a TA Instruments Q2000. X-ray diffraction (XRD) measurement was performed using a Bruker D8 Discover reflector, and the sample was prepared by dropcasting with chlorobenzene solution (10 mg mL$^{-1}$) on silicon substrate. Atomic force microscopy (AFM) was recorded with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. Cyclic voltammetry (CV) was performed using an CHI660a electrochemical workstation with a standard three-electrode system consisting of a cylindrical platinum working electrode, platinum mesh counter electrode and Ag/Ag$^+$ reference electrode. CV measurements were carried out with the solution in anhydrous and deoxygenated dichloromethane with the concentration of 0.3 mM containing $n$-Bu$_4$NCIO$_4$ (0.1 M) as the electrolyte at a scan rate of 100 mV s$^{-1}$. Ferrocene (Fc) was used as the standard. LUMO and HOMO energy levels were calculated from the equations: $E_{\text{LUMO}} = -(E_{\text{red}} + 4.8)$ eV and $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV, where $E_{\text{red}}$ and $E_{\text{ox}}$ are the onset potentials vs. Fc/Fc$^+$ of the reduction and oxidation processes,
respectively.

Figure S1. a) $^1$H NMR and b) $^{13}$C NMR spectra of M-BNBP4P-1.
2. OSCs device fabrication and measurement

OSC device was fabricated with an architecture of indium tin oxide (ITO)/ poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS)/PTB7-Th:M-BNBP4P-1/Ca/Al. Patterned ITO glass substrates were cleaned by sequential ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol, followed by heating at 120 °C for 30 min and UV-ozone treatment for 30 min. PEDOT:PSS (Clevios PVP Al4083 from H. C. Starck Inc.) with the thickness of 40 nm was spin-coated on the ITO substrates and annealed at 120 °C for 30 min. The active layer was spin-coated from the solution of PTB7-Th and M-BNBP4P-1 in chlorobenzene (20 mg mL⁻¹) at 2000 rpm, which resulted in the active layer thickness of 110 nm. Then the active layer was heated at 100 °C for 10 minutes. Finally, the device was transferred to a vacuum chamber and Ca (20 nm)/Al (100 nm) was sequentially deposited by thermal evaporation at the pressure of about 2×10⁻⁴ Pa. The active area of each device was 8.0 mm².

The current density (J-V) curves of the OSC devices were measured using a computer-controlled Keithley 2400 source meter under 100 mW cm⁻² AM 1.5G simulated solar light illumination provided by a XES-40S2-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd.). The EQE was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.), which was calibrated with a crystal silicon photovoltaic cell before use.

3. TGA

![Figure S2. TGA plot of M-BNBP4P-1. In N₂ atmosphere, M-BNBP4P-1 has good thermal stability with decomposition temperature (T_d) at 5% weight loss of 288 °C.](image_url)
4. DSC and XRD

![DSC and XRD Diagram]

**Figure S3.** a) DSC curves and b) XRD pattern of M-BNBP4P-1. The second cycle of DSC measurement is shown.

5. DFT calculation results

All calculations were carried out using Gaussian 09. The geometry structure of M-BNBP4P-1 were optimized by using DFT calculations (B3LYP/6-31G*) and the alkyl chains have been replaced by methyl for clarity. Time-dependent DFT (TD-DFT) calculations were performed at the B3LYP/6-31G* level of theory to more precisely elucidate the absorption of M-BNBP4P-1. TD-DFT calculation for the S₀→Sₙ transitions using the same functional and basis set were then performed based on the optimized structure at ground state.

**Excitation energies and oscillator strengths (Oscillator strength exceeding 0.1):**

**Excited State 1:** Energy: 1.4610 eV Wavelength: 848.6 nm Oscillator strength: 0.5406 Configurations: HOMO→LUMO (0.70516);

**Excited State 6:** Energy: 2.3050 eV Wavelength: 537.9 nm Oscillator strength: 0.2454 Configurations: HOMO→LUMO+1 (0.69991);
Excited State 7: Energy: 2.4336 eV Wavelength: 509.5 nm Oscillator strength: 0.8902 Configurations: HOMO-4→LUMO (0.16303); HOMO-2→LUMO (0.57666); HOMO→LUMO+4 (-0.34843);

Excited State 10: Energy: 2.5472 eV Wavelength: 486.8 nm Oscillator strength: 0.4766 Configurations: HOMO-8→LUMO (0.15556); HOMO-6→LUMO (-0.11425); HOMO-4→LUMO (0.56391); HOMO-2→LUMO (-0.28798); HOMO→LUMO+4 (-0.22390);

Excited State 14: Energy: 2.6496 eV Wavelength: 467.9 nm Oscillator strength: 0.1388 Configurations: HOMO-8→LUMO (0.67600); HOMO-4→LUMO (-0.10907);

Excited State 27: Energy: 3.0073 eV Wavelength: 412.3 nm Oscillator strength: 0.1695 Configurations: HOMO-12→LUMO (0.13025); HOMO-9→LUMO+1 (0.51556); HOMO-7→LUMO+1 (-0.23619); HOMO-5→LUMO+1 (0.12836); HOMO-2→LUMO+2 (0.24602); HOMO-1→LUMO+2 (0.13538).

The transition energies and oscillator strengths simulated by the TD-DFT (B3LYP/6-31G*) calculations resulted in two absorption bands for M-BNBP4P-1. The calculation results agree well with the measured absorption spectrum (Figure S4), and explain the relation between the molecule structure and absorption spectra. The electronic transition HOMO→LUMO (Excited State 1) corresponding to the energy of 1.4610 eV (wavelength at 848.6 nm) results in the low-energy absorption band in the absorption spectrum. The high-energy absorption band around 500 nm is attributed to six types of electronic transitions, HOMO-8→LUMO, HOMO-6→LUMO, HOMO-4→LUMO, HOMO-2→LUMO, HOMO→LUMO+1 and HOMO→LUMO+4 (illustrated by Excited State 6, 7 and 10). The main orbital configurations and electronic transitions of M-BNBP4P-1 mentioned above were shown in Figure S5.
Figure S4. UV/Vis absorption spectra of **M-BNBP4P-1** in chlorobenzene solution and in thin film. The green bar shows the transition energies and oscillator strengths simulated by the TD-DFT (B3LYP/6-31G*) calculations.

Figure S5. Schematic diagrams showing the main orbital configurations and electronic transitions of **M-BNBP4P-1** based on the TD-DFT (B3LYP/6-31G*) calculation.
6. AFM images

![AFM images](image)

**Figure S6.** a) AFM height image, b) phase image and c) TEM image of the PTB7-Th:M-BNBP4P-1 blend film.

7. Charge mobility measurement

![J-V curves and SCLC fitting](image)

**Figure S7.** J-V curves and SCLC fitting of a) the hole-only device and b) electron-only device of the PTB7-Th:M-BNBP4P-1 blend film.

Charge carrier mobilities of the PTB7-Th:M-BNBP4P-1 blend were measured based on the SCLC method with the hole-only device (ITO/PEDOT:PSS/active layer/Al) and electron-only device (ITO/PEIE/active layer/Ca/Al). The J-V curves were fitted to a space-charge-limited function:

\[
J = \frac{9 \varepsilon_0 \varepsilon_r \mu_0 V^2}{8L^3} \exp \left( \frac{0.89}{\beta} \sqrt{\frac{V}{L}} \right)
\]

where \(J\) is the current density, \(L\) is the film thickness of the active layer, \(\mu_0\) is the charge mobility, \(\varepsilon_r\) is the relative dielectric constant of the transport medium, \(\varepsilon_0\) is the permittivity of free space, \(V(V_{\text{appl}} - V_{\text{bi}})\) is the internal voltage in the device, where \(V_{\text{appl}}\)
is the applied voltage to the device and $V_{bi}$ is the built-in voltage due to the relative work function difference of the two electrodes. The hole and electron mobilities are estimated to be $6.87 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $1.47 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The high and balanced hole/electron mobilities of the blend are in agreement with the high OSCs performance.

8. $J_{sc}$ versus light intensity

The dependence of short-circuit current on the light intensity was measured to study charge recombination in the OSC devices. As reported, the $J_{sc}$ follows a power-law dependence on the illumination intensity ($J_{sc} \propto P_{light}^\alpha$, where $P_{light}$ is light intensity and $\alpha$ is the calculated power-law exponent). If all free carriers are swept out and collected at the electrodes prior to recombination, $\alpha$ should be equal to 1. In this work, the current density shows a linear dependence on the light intensity in logarithmic coordinates with a slope ($\alpha$) of 0.98, indicating efficient sweep-out of carriers and well suppressed bimolecular recombination.

![Figure S8. $J_{sc}$ versus light intensity characteristic of the OSC device based on PTB7-Th:MNBP4P-1 blend.](image)
9. $J_{\text{ph}}$ versus effective voltage

Figure S9. Photocurrent density ($J_{\text{ph}}$) versus effective voltage ($V_{\text{eff}}$) characteristic of the OSCs device based on PTB7-Th:M-BNPB4P-1 blend.

The photocurrent density ($J_{\text{ph}}$) versus the effective voltage ($V_{\text{eff}}$) was measured to study the charge generation and extraction properties. $J_{\text{ph}}$ can be defined as $J_{\text{ph}} = J_L - J_D$, where $J_L$ and $J_D$ are the photocurrent densities under illumination and in the dark, respectively. $V_{\text{eff}}$ can be defined as $V_{\text{eff}} = V_{\text{oc}} - V_{\text{bias}}$, where $V_{\text{oc}}$ is the voltage at which the photocurrent is zero and $V_{\text{bias}}$ is the applied voltage. Therefore, $V_{\text{eff}}$ determines the electric field in the bulk region and thereby affects the carrier transport and the photocurrent extraction. The plot of $J_{\text{ph}}$ versus $V_{\text{eff}}$ is presented in Figure S7. At high $V_{\text{eff}}$ values, mobile charge carriers rapidly move toward the corresponding electrodes with minimal recombination. $J_{\text{ph}}$ reaches saturation (15.58 mA cm$^{-2}$) at $V_{\text{eff}} \geq 2.5$ V, suggesting that all photogenerated excitons are dissociated into free charge carriers and charge carriers are collected at the electrodes very efficiently. Under short-circuit condition, $J_{\text{ph}}$ is 14.62 mA cm$^{-2}$, which is $\sim$94% of all photogenerated carriers collected by the electrodes, indicating efficient photogenerated exciton dissociation and charge collection for PTB7-Th:M-BNPB4P-1 device.
10. Chemical structure of PTB7-Th

\[
\text{PTB7-Th} \\ R = \text{ethylhexyl}
\]

11. The absorption spectrum of blend film

![Absorption Spectrum](image)

**Figure S10.** The absorption spectrum of PTB7-Th:M-BNBP4P-1 blend film.

12. References
