Supporting Information

**Understanding the Effect of Chlorine Substitution in All-Polymer Solar Cells**

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## 1. Materials

All the monomers used for the synthesis of PBDB-T, Cl-PBDB-T, N2200, and Cl-N2200 were purchased from Suna Tech Inc. and Solarmer Beijing, and the Pd catalyst was purchased from Strem Chemical Industry and used without further purification. The solvents used in this experiment were freshly dried using standard distillation methods.

## 2. Characterizations

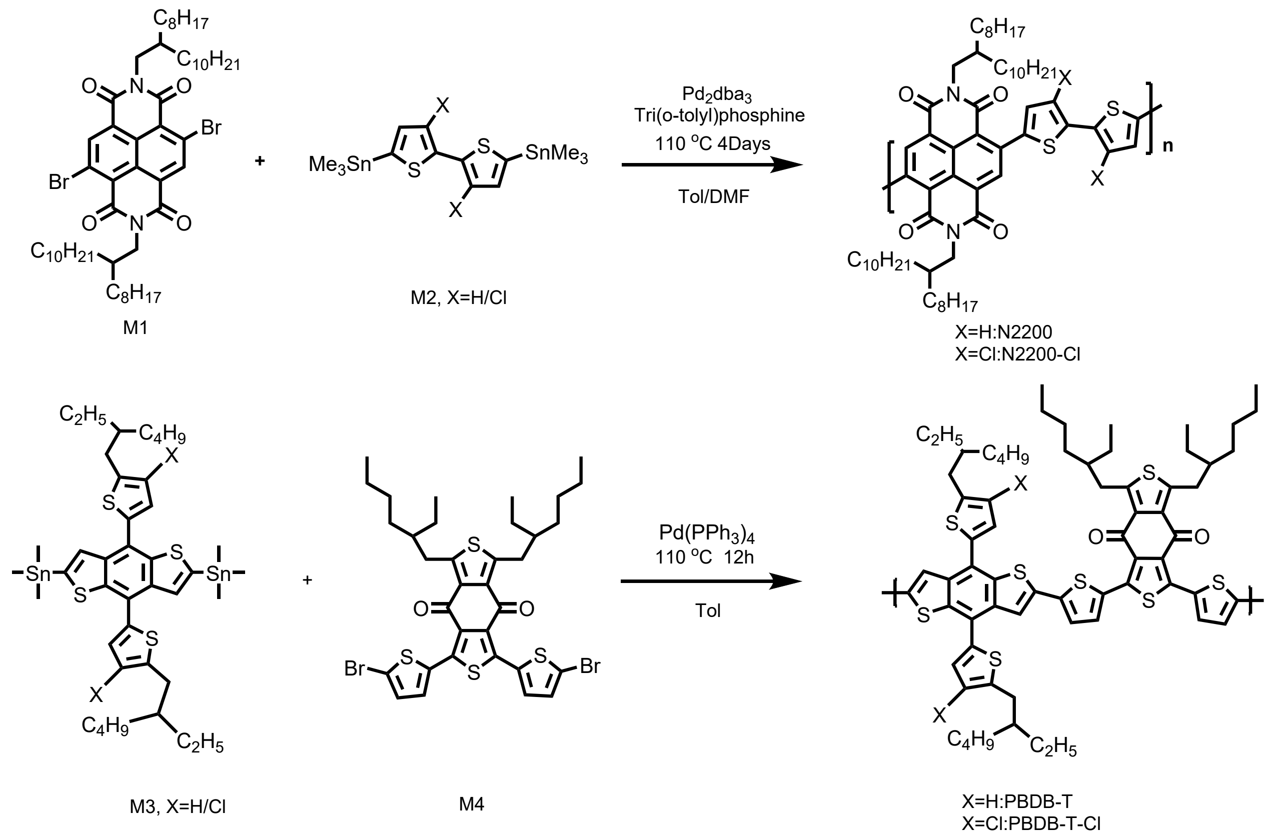
UV-vis-NIR spectra were recorded on a Perkin Elmer model Lambda 950. Steady-state photoluminescence spectra were obtained through a FluoroMax-4 spectro fluorometer (HORIBA Scientific). UPS measurements were performed using a custom-built ultrahigh vacuum apparatus equipped with a He-I UV-light source (21.22 eV) and a hemispherical electron energy analyzer (Scienta R3000). The AFM images of the films were obtained from Bruker MultiMode V AFM microscope in tapping-mode. TEM images were characterized by Tecnai G2 F20 S-Twin transmission electron microscope.

## 3. SCLC measurements

Hole-only and electron-only devices were fabricated to measure the hole and electron mobility using the space charge limited current (SCLC) method. The hole-only device structure is ITO/ PEDOT:PSS (40 nm)/ active layer (150~200 nm)/ $MoO_x$ (8 nm)/Ag (100 nm) and the electron-only device structure is ITO/ ZnO (40 nm)/ active layer (150~200 nm)/ PFN-Br (30 nm)/ Al (100 nm). The thickness was measured by a profilometer. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$$

Where $J$ is current, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the material, μ is the zero-field mobility, d is the thickness of the polymer layer, V is the applied voltage. Then hole and electron mobilities were calculated from the fitting slope of the $J^{1/2}$-V curves.




Scheme S1. Synthetic route of target polymers PBDB-T, Cl-PBDB-T, N2200, and Cl-N2200

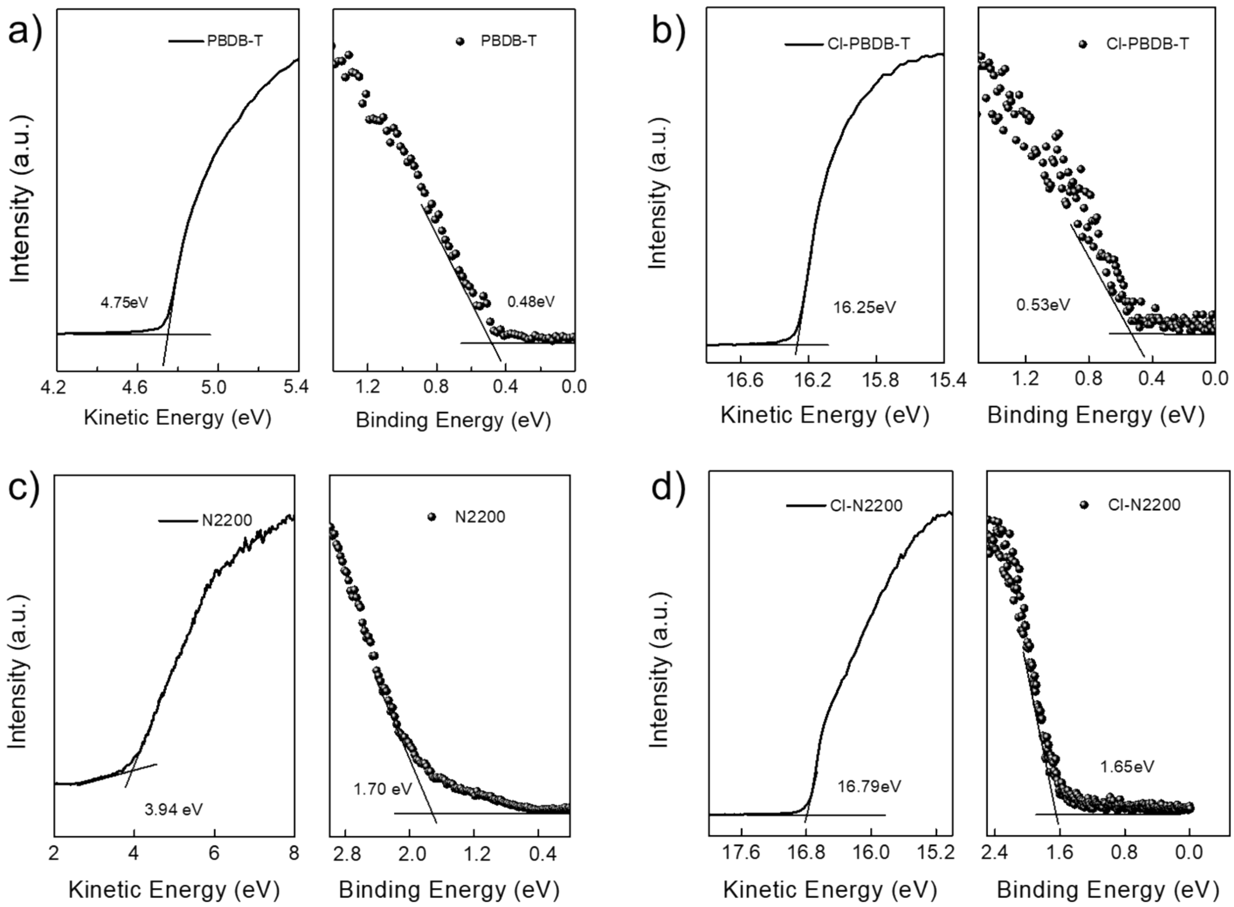



Figure S1. UPS spectra of a) neat PBDB-T, b) neat Cl-PBDB-T, c) neat N2200, and d) neat Cl-N2200 films.

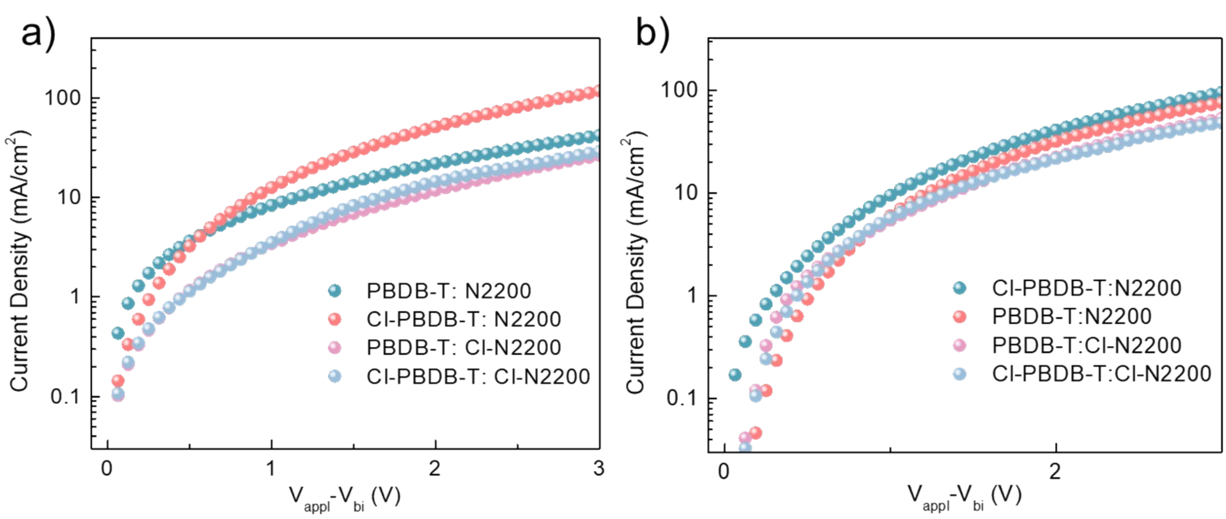



Figure S2.a) Dark *J-V* characteristics of the hole-only devices, b) Dark *J-V* characteristics of the electron-only devices.

Table S1. The devices optimization process for Cl-PBDB-T:N2200.

| Control | Control | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) |
|---|---|---|---|---|---|
| Cl-PBDB-T:N2200 2:1 2000 rpm CB | 12 mg/mL | 1.00 | 6.61 | 0.48 | 3.17 |
| | 10 mg/mL | 1.00 | 7.16 | 0.50 | 3.62 |
| | 8 mg/mL | 1.01 | 6.56 | 0.52 | 3.42 |
| Cl-PBDB-T:N2200 2:1 10 mg/mL CB | 2000 rpm | 1.00 | 7.12 | 0.49 | 3.53 |
| | 2500 rpm | 1.00 | 7.07 | 0.51 | 3.60 |
| | 3000 rpm | 1.00 | 7.35 | 0.50 | 3.68 |
| Cl-PBDB-T:N2200 2:1 10 mg/mL 3000 rpm | CF | 0.98 | 8.29 | 0.48 | 3.90 |
| | CB:CF 1:1 | 0.99 | 9.21 | 0.56 | 5.13 |
| | CB | 0.98 | 8.53 | 0.56 | 4.72 |
| Cl-PBDB-T:N2200 2:1 10 mg/mL 3000 rpm CB:CF=1:1 | | 0.97 | 8.60 | 0.56 | 4.65 |
| | TA 100 | 0.97 | 8.93 | 0.59 | 5.12 |
| | 1% DIO | 0.96 | 7.89 | 0.57 | 4.28 |
| | 1% DIO TA 100 °C | 0.97 | 8.24 | 0.60 | 4.82 |
| Cl-PBDB-T:N2200 2:1 10 mg/mL 3000 rpm CB:CF=1:1 | TA 80 °C | 0.98 | 10.04 | 0.56 | 5.53 |
| | TA 100 °C | 0.97 | 10.47 | 0.56 | 5.74 |
| | TA 120 °C | 0.96 | 11.39 | 0.55 | 6.01 |
| | TA 140 °C | 0.95 | 9.77 | 0.56 | 5.30 |

Table S2. The devices optimization process for PBDB-T:Cl-N2200.

| Control | Control | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) |
|---|---|---|---|---|---|
| PBDB-T:Cl-N2200 2:1 2000 rpm CB | 8 mg/mL | 0.75 | 6.03 | 0.52 | 2.39 |
| | 10 mg/mL | 0.75 | 7.40 | 0.526 | 2.92 |
| | 12 mg/mL | 0.79 | 4.06 | 0.67 | 2.18 |
| PBDB-T:Cl-N2200 2:1 2000 rpm 10 mg/mL | CB | 0.80 | 5.12 | 0.59 | 2.43 |
| | CB:CF=1:1 | 0.81 | 6.94 | 0.63 | 3.54 |
| | CF | 0.81 | 8.36 | 0.61 | 4.14 |
| PBDB-T:Cl-N2200 2:1 2000 rpm 10 mg/mL CF | | 0.79 | 9.02 | 0.60 | 4.34 |
| | TA | 0.77 | 9.02 | 0.533 | 3.68 |
| | 1% DIO | 0.81 | 8.7 | 0.52 | 3.71 |
| | 1% DIO TA | 0.81 | 8.99 | 0.67 | 4.88 |

Table S3. The devices optimization process for Cl-PBDB-T:Cl-N2200

| Control | Control | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | Fill Factor | PCE (%) |
| --- | --- | --- | --- | --- | --- |
| Cl-PBDB-T:Cl-N2200 2:1 8 mg/mL CB | 1000 rpm | 0.93 | 5.58 | 0.43 | 2.22 |
| | 1500 rpm | 0.93 | 5.30 | 0.47 | 2.41 |
| | 2000 rpm | 0.93 | 5.19 | 0.40 | 1.97 |
| Cl-PBDB-T:Cl-N2200 2:1 1500 rpm CB | 10 mg/mL | 0.91 | 7.21 | 0.47 | 3.11 |
| | 12 mg/mL | 0.92 | 7.66 | 0.49 | 3.45 |
| | 15 mg/mL | 0.93 | 8.02 | 0.52 | 3.89 |
| | 20 mg/mL | 0.80 | 8.38 | 0.44 | 2.96 |
| Cl-PBDB-T:Cl-N2200 2:1 15 mg/mL 1500 rpm CB | 1% DIO | 0.94 | 8.97 | 0.60 | 5.06 |
| | 1% DIO TA | 0.92 | 8.92 | 0.53 | 4.39 |
| | | 0.92 | 7.82 | 0.54 | 3.90 |

Table S4. Charge carrier mobilityof the blend films.

| Condition | $\mu_h$ (cm$^2$ v$^{-1}$ s$^{-1}$) | $\mu_e$ (cm$^2$ v$^{-1}$ s$^{-1}$) |
| --- | --- | --- |
| PBDB-T:N2200 | $1.27\times10^{-4}$ | $2.24\times10^{-4}$ |
| Cl-PBDB-T:N2200 | $1.93\times10^{-4}$ | $1.02\times10^{-4}$ |
| PBDB-T:Cl-N2200 | $1.75\times10^{-5}$ | $2.62\times10^{-5}$ |
| Cl-PBDB-T:Cl-N2200 | $9.07\times10^{-6}$ | $1.67\times10^{-5}$ |