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# Supporting Information

## Efficient and thermally stable all-polymer solar cells based on a fluorinated wide bandgap polymer donor with high crystallinity

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### Materials

The polymer donor PFBZ[1] and polymer acceptor N2200[2] were synthesized according to the procedure reported in the literatures.

### Experimental Section

*Measurements:* UV-vis absorption spectrum was recorded on a UV-Vis-NIR Spectrophotometer of Agilent Technologies Cary Series. The electrochemical cyclic voltammetry (CV) was taken on a Electrochemical Workstation of Zahner Ennium IM6 in a acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$), where glassy carbon disk, $Ag/Ag^+$ electrode, and Pt wire as working electrode, reference electrode and counter electrode, respectively. Photoluminescence (PL) spectra were taken on an Edinburgh Instrument FLS 980. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage. TEM was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, in which the blend films were prepared using a processing technique, as following: first, the blend films were spin-cast on the ITO/PEDOT:PSS substrates; second, the resulting ITO/PEDOT:PSS/blend film substrates were submerged in deionized water to make these blend films float onto the air-water interface; finally, the floated blend films were taken up on unsupported 200 mesh copper grids for a TEM measurement. GIWAXS experiment was performed at beamline 7.3.3[3] at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA. Samples were prepared using identical blend solutions as those used in devices on a PSS pre-coated Si substrate. The 10 keV X-ray beam was incident at a grazing angle of 0.14°, which maximized the scattering intensity from the samples. The scattered intensity was detected with a Pilatus detector. The crystal coherence length (CCL) was defined as CCL = 0.9 × (2π/FWHM) (Å), where FWHM is the full width at half maximum of the corresponding diffraction peak.

**Fabrication and characterization of all-polymer solar cells.** All-polymer solar cell devices with a device structure of glass/ITO/PEDOT:PSS/PFBZ:N2200/PDINO/Al were fabricated under conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 15 min, then a 30 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 °C for 15 min. The active layer was then deposited on top of the PEDOT:PSS layer by spin-coating a chlorobenezene (CB) solution (9 mg $mL^{-1}$, dissolved 20 h under 100 °C and then cooled to 65 °C for 15 min) of PFBZ:N2200. The thickness of active layer is measured on a KLA Tencor D-100 profilometer. The *N*,*N*'-bis(dimethylaminopropyl-*N*'''-oxide)-perylene-3,4:9,10-tetracarboxidiimide (PDINO) was then deposited on top of the active layer by spin-coating a methanol solution with a concentration of 1 mg/mL. Finally, 80 nm Al were successively deposited on the photosensitive layer under vacuum at a pressure of ca. $4 \times 10^{-4}$ Pa, and through a shadow mask to determine the active area of the devices (0.2 $cm^2$). The PCE values of the PSCs were measured under a illumination of AM 1.5G (100 $mW/cm^2$) using a SS-F5-3A solar simulator (AAA grade, $50 \times 50$ $mm^2$ photobeam size) of Enli Technology CO., Ltd.. A $2 \times 2$ $cm^2$ monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd. PCE statistics were obtained using 10 individual devices fabricated under the same conditions. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 of Enli Technology CO., Ltd. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell. To study the charge generation and dissociation processes of the PFBZ:N2200-based PSCs, plots of the photocurrent ($J_{ph}$) *versus* effective voltage ($V_{eff}$) of the PSCs were measured. Here, $J_{ph}$ and $V_{eff}$ are defined as $J_{ph} = J_L - J_D$ and $V_{eff} = V_0 - V_{appl}$, respectively, where $J_D$ and $J_L$ are the photocurrent densities in the dark and under the illumination, and $V_{appl}$ is the applied bias voltage and $V_0$ is the voltage at which $J_{ph} = 0$, respectively.[4] The $J_{ph}$ reaches the saturation current density ($J_{sat}$) at high $V_{eff}$ ($\geq 2$ V in this case).

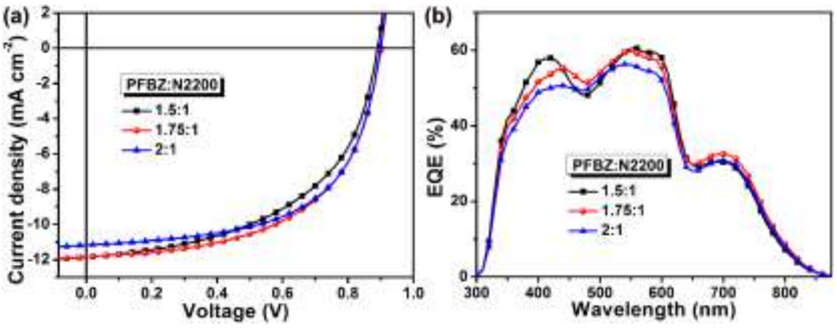

**Fig. S1.** The *J*-*V* plots of the all-PSCs based on PFBZ:N2200 with different D:A weight ratios.

**Table S1.** Photovoltaic data of the all-PSCs based on PFBZ:N2200 with different D:A weight ratios.

| D:A [w/w] | $V_{oc}$ [V] | $J_{sc}{}^{a}$ [mA cm$^{-2}$] | FF [%] | PCE$^{b}$ [%] |
|---|---|---|---|---|
| 1.5:1 | 0.89 | 11.9 (11.3) | 52.5 | 5.5 (5.2) |
| 1.75:1 | 0.90 | 11.9 (11.5) | 56.7 | 6.1 (5.9) |
| 2:1 | 0.90 | 11.2 (10.8) | 59.5 | 6.0 (5.7) |

[a] The integral $J_{sc}$ in parentheses from the EQE curves. [b] The average PCEs in parentheses from 10 devices.

**Table S2.** Photovoltaic data of the PFBZ:N2200-based all-PSCs with different storage times in the $N_2$-filled glovebox.

| Storage time [h] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | PCE$^{a}$ [%] |
|---|---|---|---|---|
| 0 | 0.90 | 13.5 | 67.3 | 8.1 (7.8) |
| 120 | 0.89 | 13.1 | 66.0 | 7.7 (7.4) |
| 240 | 0.89 | 12.9 | 65.2 | 7.5 (7.2) |
| 600 | 0.89 | 12.7 | 64.0 | 7.2 (6.8) |
| 1080 | 0.89 | 12.6 | 62.2 | 7.0 (6.4) |

[a] The average PCEs in parentheses from 10 devices.

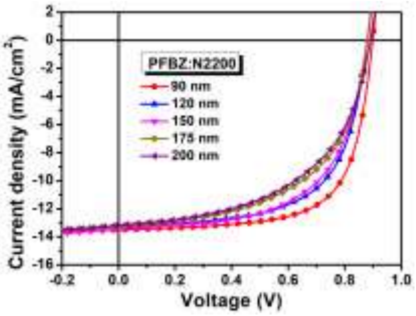

**Fig. S2.** The *J-V* plots of the all-PSCs based on PFBZ:N2200 with different active layer thicknesses.

**Table S3.** Photovoltaic data of the all-PSCs based on PFBZ:N2200 with different active layer thicknesses

| thickness [nm] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | PCE$^a$ [%] |
|---|---|---|---|---|
| 90 | 0.90 | 13.5 | 67.3 | 8.1 (7.8) |
| 120 | 0.88 | 13.6 | 61.7 | 7.4 (7.1) |
| 150 | 0.88 | 13.5 | 60.3 | 7.2 (7.0) |
| 175 | 0.88 | 13.3 | 55.7 | 6.5 (6.1) |
| 200 | 0.89 | 13.2 | 53.6 | 6.3 (6.0) |

$^a$The average PCEs in parentheses from 10 devices.

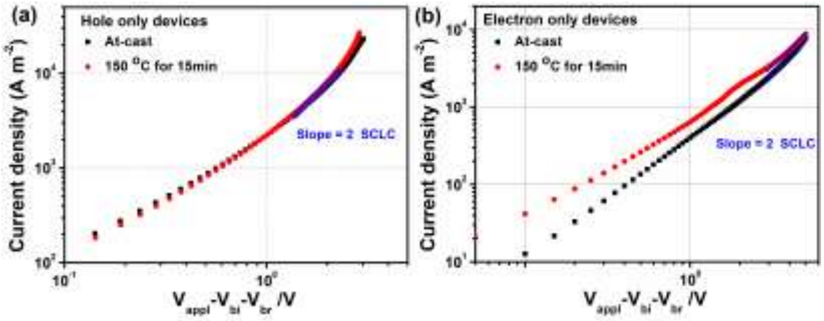

**Fig. S3.** The *J-V* curves of (a) the hole-only devices with the structure of ITO/PEDOT:PSS/PFBZ:N2200/$MoO_3$/Al; and (b) the electron-only devices with the structure of ITO/ZnO/PFBZ:N2200/PFN-Br/Al according to the SCLC model.

## References

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