Electronic Supplementary Information for:

Enhancement of intra- and inter-molecular π-conjugated effects for the non-fullerene acceptor to achieve high-efficiency organic solar cells with extended photoresponse range and optimized morphology

Ning Wang,‡[a] Lingling Zhan,‡[a] Shuixing Li,[a] Minmin Shi,*[a] Tsz-Ki Lau,[b] Xinhui Lu,[b] Rafi Shikler,[c] Chang-Zhi Li[a] and Hongzheng Chen*[a]

[a]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, State Key Laboratory of Silicon Materials, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China.
[b]Department of Physics, Chinese University of Hong Kong, New Territories, Hong Kong, P. R. China
[c]Department of Electrical and Computer Engineering, Ben-Gurion University of the Negev, Beer-Sheva 8410501, Israel

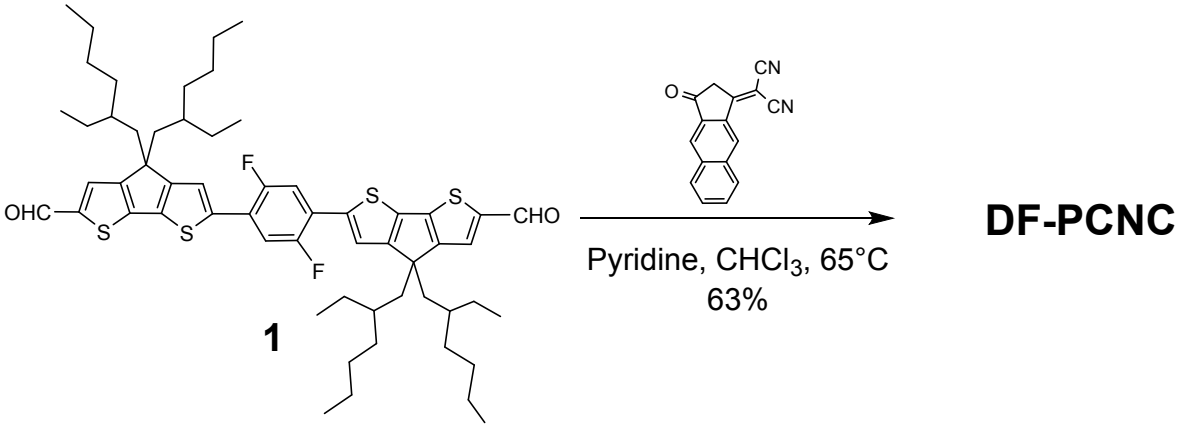
‡N. Wang and L. Zhan contributed equally to this work.

Materials and Methods

All reagents and solvents, unless otherwise specified, were purchased from J&K Scientific, Suna Tech, Aldrich and Solarmer Materials Inc., and were used without further purification. ^{1}H NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometer. Elemental analyses were carried out on a LECO 932 CHNS elemental analyzer. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 10 ^{o}C/min. Differential scanning calorimetry (DSC) was recorded on a Pekin-Elmer Pyris 1 differential scanning calorimeter under protection of nitrogen at a heating rate of 10 ^{o}C/min. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt wire and standard calomel electrode (SCE) as the working electrode, counter electrode and reference electrode, respectively, in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) CH_2Cl_2 solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^{+}) redox couple (4.8 eV below the vacuum level). Topographic images of the films were obtained on a VeecoMultiMode atomic force microscope (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of ~ 2 nN, and the scanning rate for a 10 μm×10 μm image size was 1.5 Hz. TEM images were performed on a JEOL-1010 transmission electron microscope at 80 KV accelerating voltage in bright field mode. Grazing-incidence wide-angle/small-angle X-ray scattering

(GIWAXS/GISAXS) measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2^{o}.

Synthesis of DF-PCNC



Under the protection of argon, to a solution of compound **1** (350 mg, 0.36 mmol) and NC (440 mg, 1.8 mmol) in 30 mL chloroform, 0.1 mL pyridine was added dropwise. The mixture was heated to 65 °C and stirred overnight. Then the mixture was cooled to room temperature and poured in 100 mL methanol. The precipitate was collected by filtration and further purified by silica gel column chromatography with chloroform as the eluent to give a blue-green solid (323 mg, yield 63%) ^{1}H NMR (400 MHz, $CDCl_3$, *δ*/ppm): δ = 9.07-8.99 (m, 2H), 8.98-8.92 (m, 2H), 8.33 (s, 2H), 8.12-8.03 (m, 4H), 7.77-7.67 (m, 6H), 7.54 (s, 2H), 7.42-7.33 (m, 2H), 2.11-2.00 (m, 8H), 1.15-0.95 (m, 32H), 0.86-0.74 (m, 16H), 0.73-0.66 (m, 12H). MS (MALDI-TOF): Calcd for $C_{90}H_{88}F_2N_4O_2S_4$, 1422.58; found: 1423.36 $(M+1)^+$. Elem. Anal. Calcd for $C_{90}H_{88}F_2N_4O_2S_4$ (%): C, 75.91, H, 6.23, N, 3.93; found: C, 75.96, H, 6.16, N, 3.76.

Device fabrication and characterization

OSCs were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO) using an inverted structure of ITO/ZnO/ /PBDB-T:DF-PCNC/MoO_3/Ag. Prior to fabrication, the substrates were cleaned with detergent, deionized water, acetone and isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 20 min. A thin layer of ZnO was spin-coated onto precleaned ITO-coated glass substrates at 3500 rpm for 60 s and then annealed at 170 °C for 20 min.

After the substrates were transferred to a glovebox, a solution of PBDB-T and DF-PCNC in chloroform with the total concentration of 20 mg/mL was spin-coated at 2000 rpm for 60 s on the ZnO layer, giving the PBDB-T:DF-PCNC active layer with the thickness of ~ 100 nm, which was calibrated by an Ambios Technology XP-2 profilometer. For the optimization of the photovoltaic performances, a certain amount of 1-chloronaphthalene (CN) was added into the PBDB-T:DF-PCNC solution, and an extra annealing of the active layer at 100 ^{o}C for 10 min was performed. Finally, a layer of MoO_3 (10 nm) and the Ag (100 nm) electrode were deposited by thermal evaporation to complete the device with an active area of 6 mm^2.

Keithley 236 measurement source units were used to measure the current density-voltage (*J-V*) curves of OSCs under 1 sun, AM 1.5 G spectra from a solar simulator (Taiwan, Enlitech). The light intensity was calibrated with a standard Si-based photovoltaic (PV) reference cell. A Stanford lock-in amplifier 8300 unit was used to measure the external quantum efficiency (EQE) spectra.

The charge carrier mobilities of the PBDB-T:DF-PCNC films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/PBDB-T:DF-PCNC(1:1.2, by wt.)/MoO_3/Ag, and electron-only devices were fabricated in a structure of ITO/ZnO/PFN/PBDB-T:DF-PCNC(1:1.2, by wt.)/PFN/Al. Here, PEDOT:PSS (Baytron P 4083, Germany) was the mixture of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate), and PFN (M_w > 20,000, PDI < 3.0, Derthon Optoelectronic Materials Co.) was poly[9,9-bis(3'-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-*alt*- 2,7-(9,9-ioctylfluorene)]. The fabricated method was similar as that of OSCs. Then device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

where ε_γ was the average dielectric constant of the blended film, ε_0 was the permittivity

of the free space, μ was the charge carrier mobility, L was the thickness of the blended film (~ 100 nm).

Supporting Figures and Tables

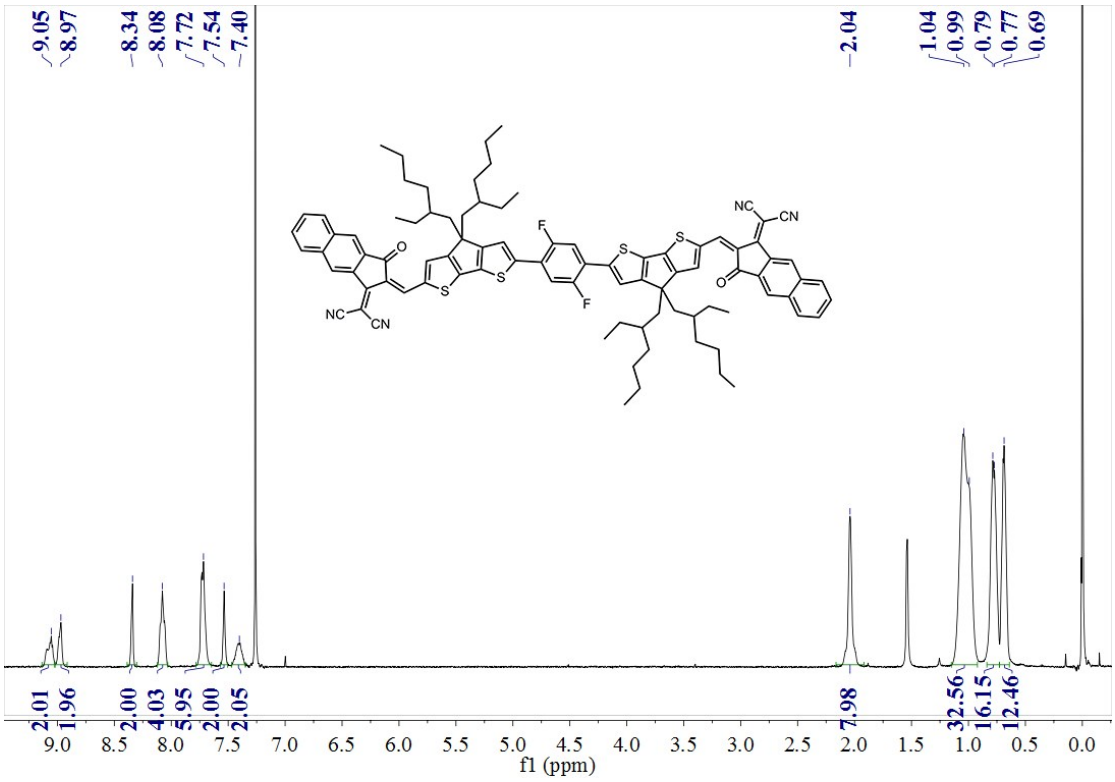


Fig. S1 ^{1}H NMR spectrum of DF-PCNC in $CDCl_3$.

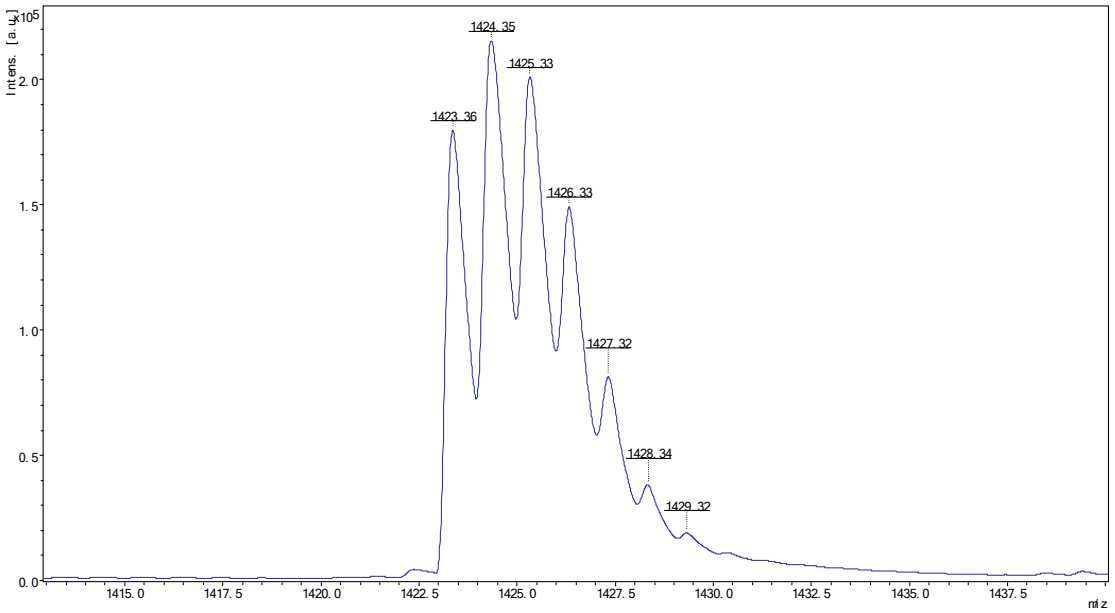


Fig. S2 MALDI-TOF MS spectrum of DF-PCNC.

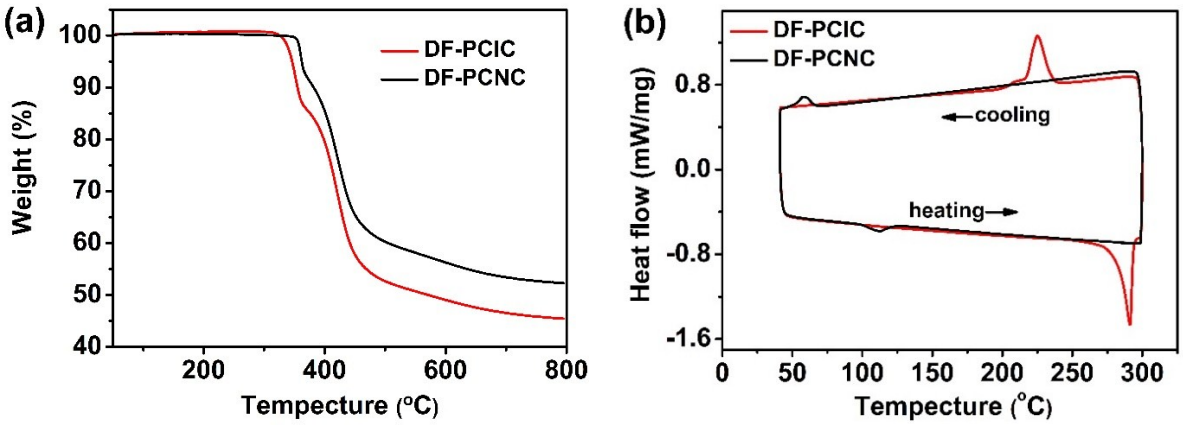


Fig. S3 TGA (a) and DSC (b) curves of DF-PCNC and DF-PCIC.

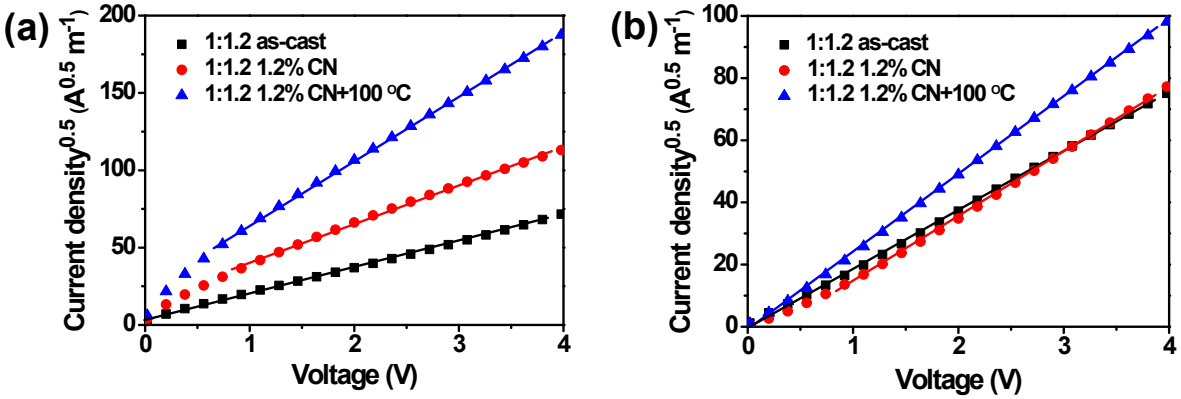


Fig. S4 $J^{0.5}$-V curves of the hole-only (a) and electron-only (b) devices based on the PBDB-T:DF-PCNC blended films obtained under different conditions.

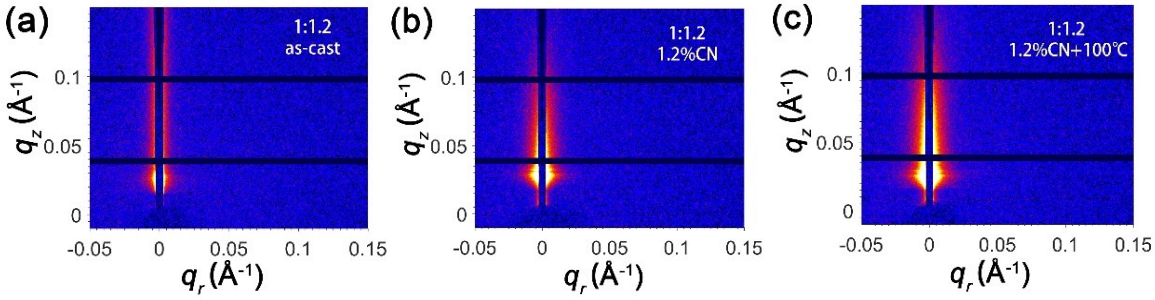


Fig. S5 The 2D GISAXS patterns of the as-cast PBDB-T:DF-PCNC blended film (a), the PBDB-T:DF-PCNC blended film processed with 1.2% CN (b), and the PBDB-T:DF-PCNC blended film processed with 1.2% CN and thermal annealing at 100 °C for 10 minutes (c).

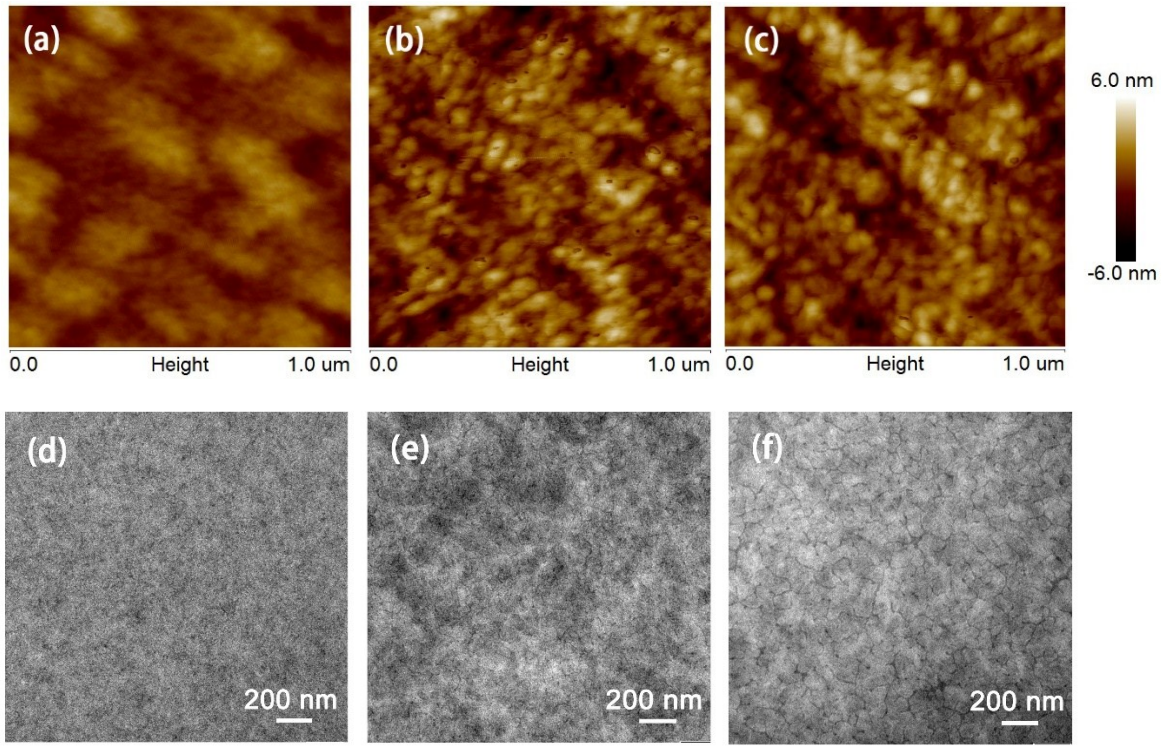


Fig. S6 AFM (a-c) and TEM (d-f) images of the as-cast PBDB-T:DF-PCNC blended film (a, d), the PBDB-T:DF-PCNC blended film processed with 1.2% CN (b, e), and the PBDB-T:DF-PCNC blended film processed with 1.2% CN and thermal annealing at 100 °C for 10 minutes (c, f).

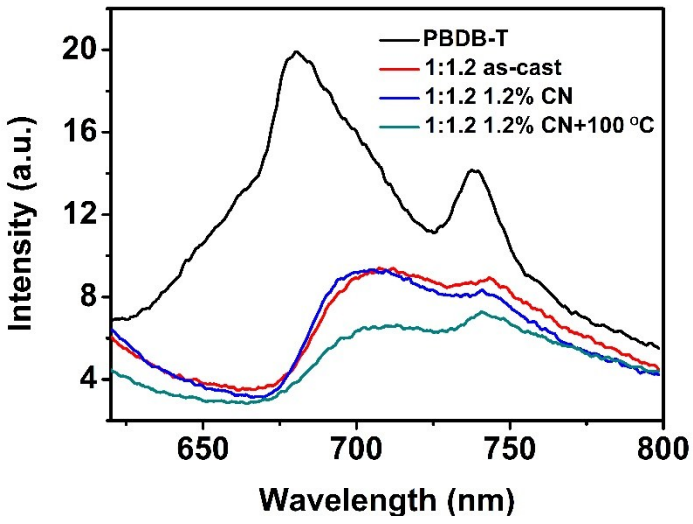


Fig. S7 The fluorescence spectra of the pure PBDB-T film and the PBDB-T:DF-PCNC blended films obtained under different conditions.

Table S1 Photovoltaic parameters of the OSCs based on the PBDB-T:DF-PCNC blended films under the illumination of AM 1.5 G, 100 mWcm^{-2}

D:A	CN (%)	Thermal annealing[a]	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{max} (%)
1:1	/	/	0.91	14.34	42.26	5.52
1:1.2	/	/	0.90	14.36	44.98	5.94
1:1.2	0.8	/	0.86	17.18	65.01	9.63
1:1.2	1.0	/	0.85	18.64	67.60	10.74
1:1.2	1.2	/	0.87	17.63	69.91	10.85
1:1.2	1.2	100 °C	0.86	18.16	72.62	11.63
1:1.2	1.5	/	0.86	17.50	68.14	10.26
1:1.5	/	/	0.89	15.07	43.11	5.79

[a]Annealing for 10 minutes.