

Supplementary Information

New wide bandgap dithieno[3',2':5,6;2'',3'':7,8]naphtho[2,3-*d*]imidazole-9(10*H*)-one containing polymers and ternary composites with fullerene and non-fullerene acceptor: mobility of charge carriers

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3.1. Instruments

¹H NMR spectra were obtained on an Agilent 600 MHz DD2 nuclear magnetic resonance (NMR) spectrometer, using CDCl₃ as solvent at resonance frequency of 600 MHz at room temperature. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. The number-average molecular weight (M_n) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using chlorobenzene as the eluent and polystyrene as the internal standard. The elemental analysis was carried out with an “Elementar Vario EL III” element analyzer. The thermal characteristics of the polymers were investigated by thermogravimetric analysis (TGA) using a “Perkin Elmer-7” unit at a rapid heating of 10°C/min in argon.

Oxidation and reduction potentials of the compounds were determined by cyclic voltammetry (CVA). An “Autolab type III” potentiostat was used. A platinum electrode, Ag wire with AgCl coating (Ag/AgCl), and a platinum plate were used as the working electrode, reference electrode and counter electrode, respectively. Measurements were performed in a nitrogen-saturated tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) solution (0.1 M in anhydrous acetonitrile) at a scan rate of 50 mVs⁻¹. Reference electrode was calibrated using ferrocene solution in acetonitrile. Oxidation-reduction potential of Fc/Fc⁺ was equal to 0.36 V relative to the reference electrode. Assuming the absolute energy level of Fc/Fc⁺ to be -4.8 eV versus vacuum level, thus the HOMO and LUMO energy levels were obtained from the equation of

$E_{\text{HOMO}}/E_{\text{LUMO}} = -e(E_{\text{ox}}/E_{\text{red}}+4.44)$ (eV), where oxidation/reduction onset potential ($E_{\text{ox}}/E_{\text{red}}$) were determined from the position at which the current raised initially from the baseline (E_{onset}).

3.2. Materials

All of the reagents and chemicals were purchased from Aldrich, Acros, TCI and used without further purification. Toluene was dried and purified by fractional distillation over sodium/benzophenone under argon. M1 [30], M2 [31], M3[32],M4[32], and M5[33] were synthesized according to the literature procedures.

Synthesis of polymer P98. A mixture M1 (0.5076g, 0.5 mmol), M3(0.2049g, 0.5 mmol) and palladium catalyst $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.027g) were dissolved in dry toluene (16 ml) and refluxed under argon for 48 h while stirring. After cooling to room temperature, the reaction mixture was added dropwise with vigorous stirring to methanol to remove low molecular weight residues and oligomers. The resulting crude product was extracted in a Soxhlet apparatus with methanol, hexane and chloroform in succession. The polymer was then isolated from the chloroform fraction using a rotary evaporator as a solid black product in high yield (0.41g, 87%). Elem. Anal. Calcd for $(\text{C}_{59}\text{H}_{88}\text{N}_2\text{OS}_3)$: C, 75.58; H, 9.46; N, 2.99; S, 10.26. Found: C, 75.19; H, 9.30; N, 2.71, S, 9.89%. ^1H NMR (CDCl_3 , 400 MHz, δ /ppm):7.98-7.31 (m, 4H), 7.25-6.79 (m, 2H), 4.26-3.3.59 (m, $\text{CH}_2\text{-N}$, 4H), 2.34-1.96 (m,CH, 2H), 1.94-0.94(m,64H), 0.93-0.6(m,CH₃,12H)

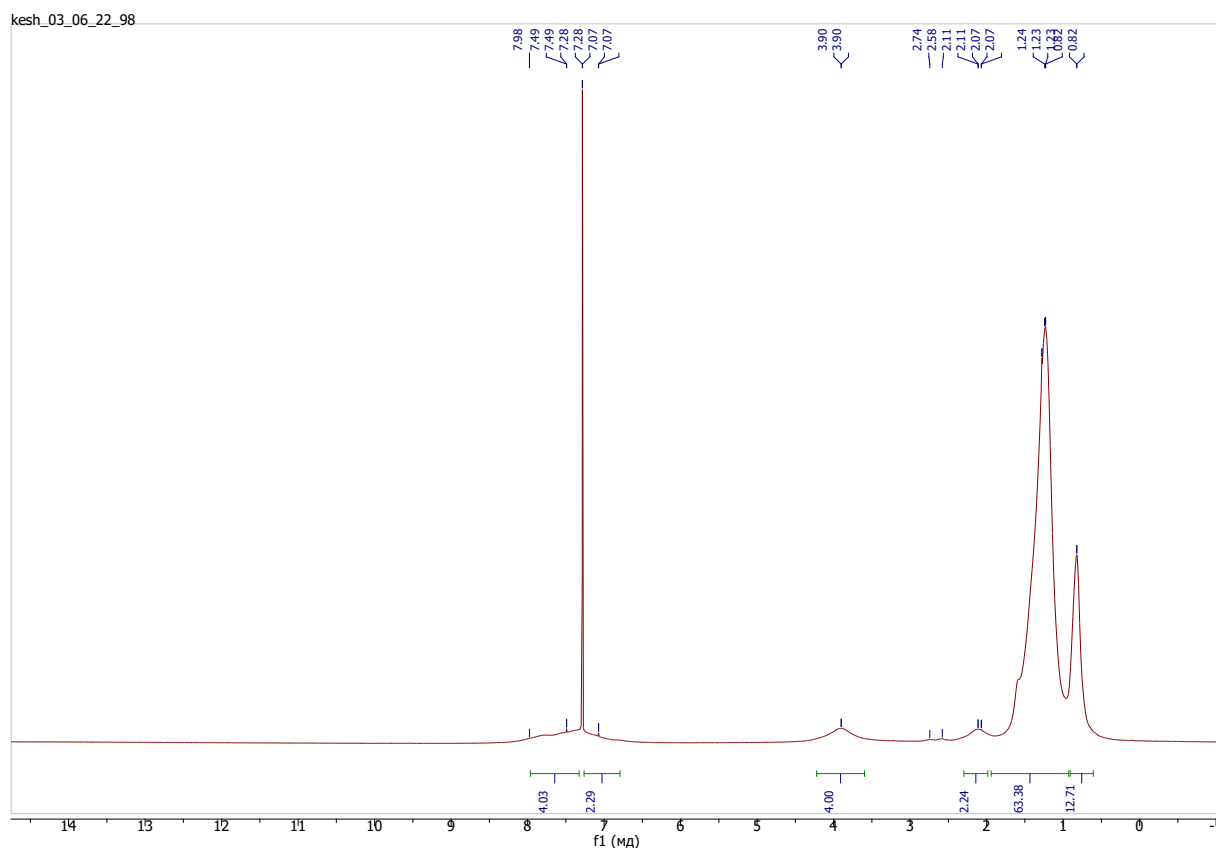


Fig.S1. ^1H NMR spectrum of random polymer **P98** in CDCl_3

Synthesis of polymer P99 was carried out similarly to polymer P98. Mixture M1 (0.5076g, 0.5 mmol), M4 (0.2459g, 0.5 mmol) and palladium catalyst Pd(Ph₃P)₄ (0.027g) was polymerized for 48h to give P99 (0.46g, yield 90%). Elem. Anal. Calcd for (C₆₃H₉₀N₂OS₄): C, 74.21; H, 8.90; N, 2.75; S, 12.58. Found: C, 73.821; H, 8.73; N, 2.57; S, 12.03%. ¹H NMR (CDCl₃, 600 MHz, δ / ppm): 8.67-7.32 (m, 4H), 4.34-3.54 (m, CH₂-N, 4H), 2.78-0.18 (m, 78H).

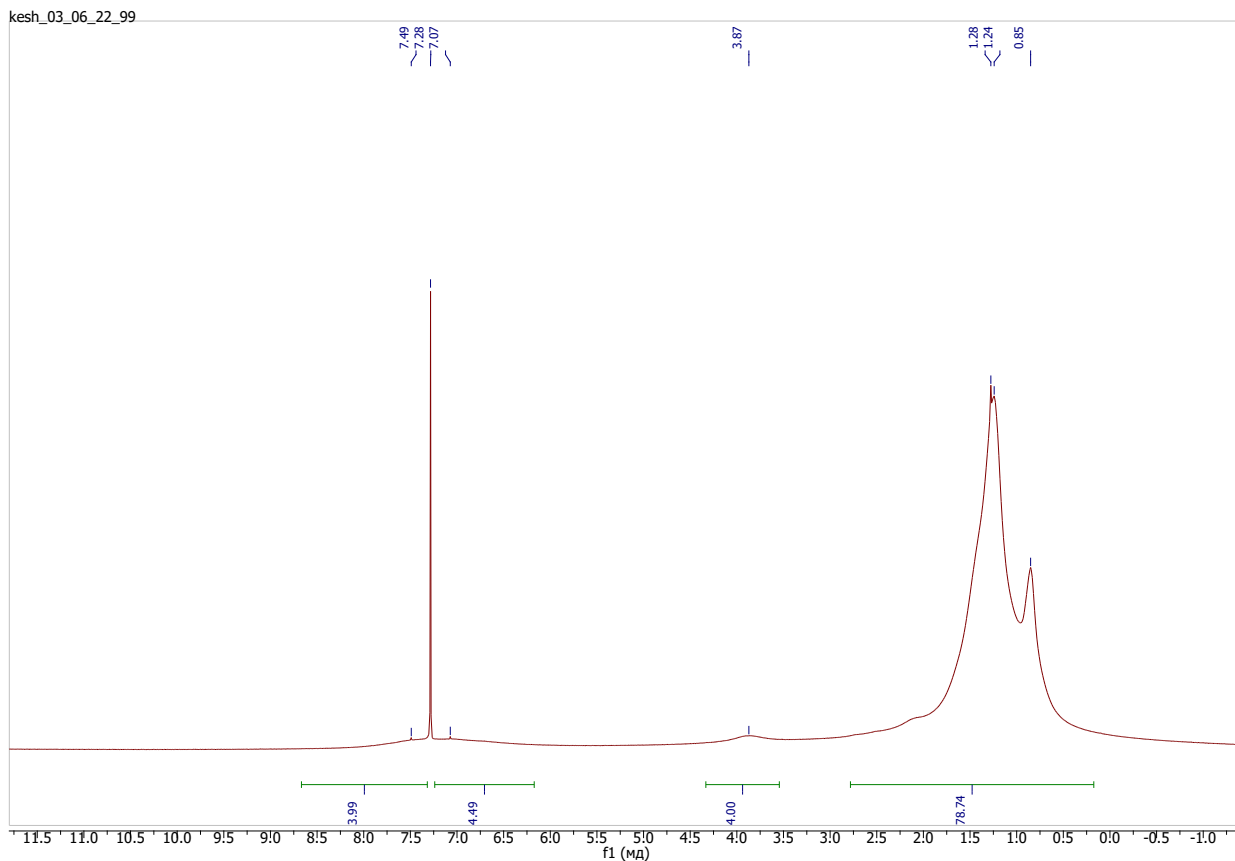


Fig.S2. ¹H NMR spectrum of random polymer **P99** in CDCl₃

The synthesis of polymer P100 was carried out similarly to polymer P98. Mixture M1 (0.5076g, 0.5 mmol), M5 (0.3722g, 0.5 mmol) and palladium catalyst Pd(Ph₃P)₄ (0.0125g) was polymerized for 48h to give P100 (0.56g, yield 88%). Elem. Anal. Calcd for (C₇₉H₁₂₂N₂OS₄Si): C, 74.58; H, 9.67; N, 2.20; S, 10.08; Si, 2.21. Found: C, 74.31; H, 9.43; N, 2.07; S, 9.84; Si, 2.00%. ¹H NMR (CDCl₃, 600 MHz, δ / ppm): 8.16-7.33 (m, br, 6H), 4.27-3.74 (br, m, CH₂-N, 4H), 2.28-2.039 (m, CH, 2H), 1.95-0.13 (m, br, 110H)

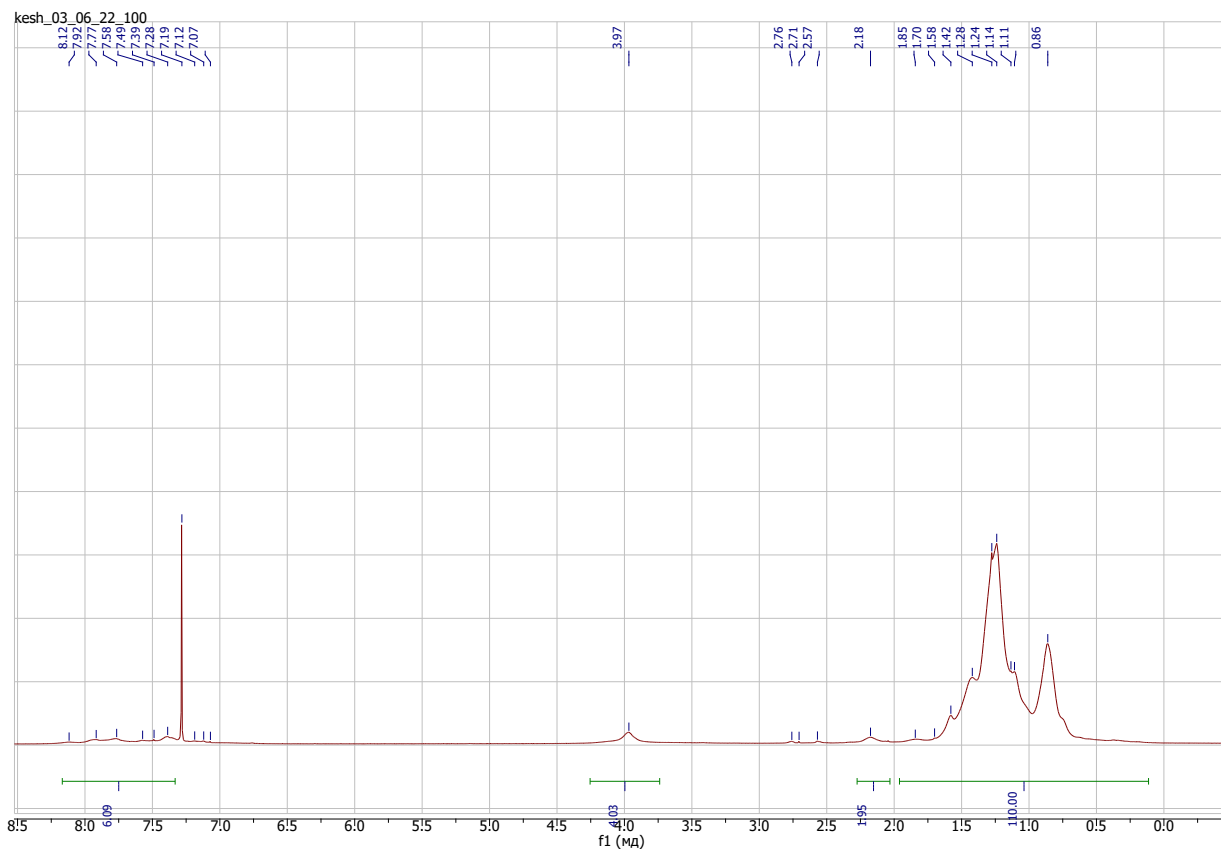


Fig.S3. ^1H NMR spectrum of random polymer **P100** in CDCl_3

Synthesis of polymer P101 was carried out similarly to polymer P98. Mixture M1 (0.5076g, 0.5 mmol), M2 (0.4423g, 0.5 mmol) and palladium catalyst $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.027g) was polymerized for 48h to give P101 (0.25g, yield 95%). Elem. Anal. Calcd for $(\text{C}_{90}\text{H}_{141}\text{N}_2\text{O}_3\text{S}_4)$: C, 75.69; H, 9.85; N, 1.98; S, 9.08. Found: C, 75.41; H, 9.69; N, 1.77; S, 8.84%. ^1H NMR (CDCl_3 , 600 MHz, δ / ppm): 7.97-7.32 (br, m, 4H), 7.26-6.72 (br, m, 2H), 4.95-3.76 (br, m, 8H), 2.98-1.00 (br, m, 106H), 0.96-0.63 (m, CH_3 , 18H)

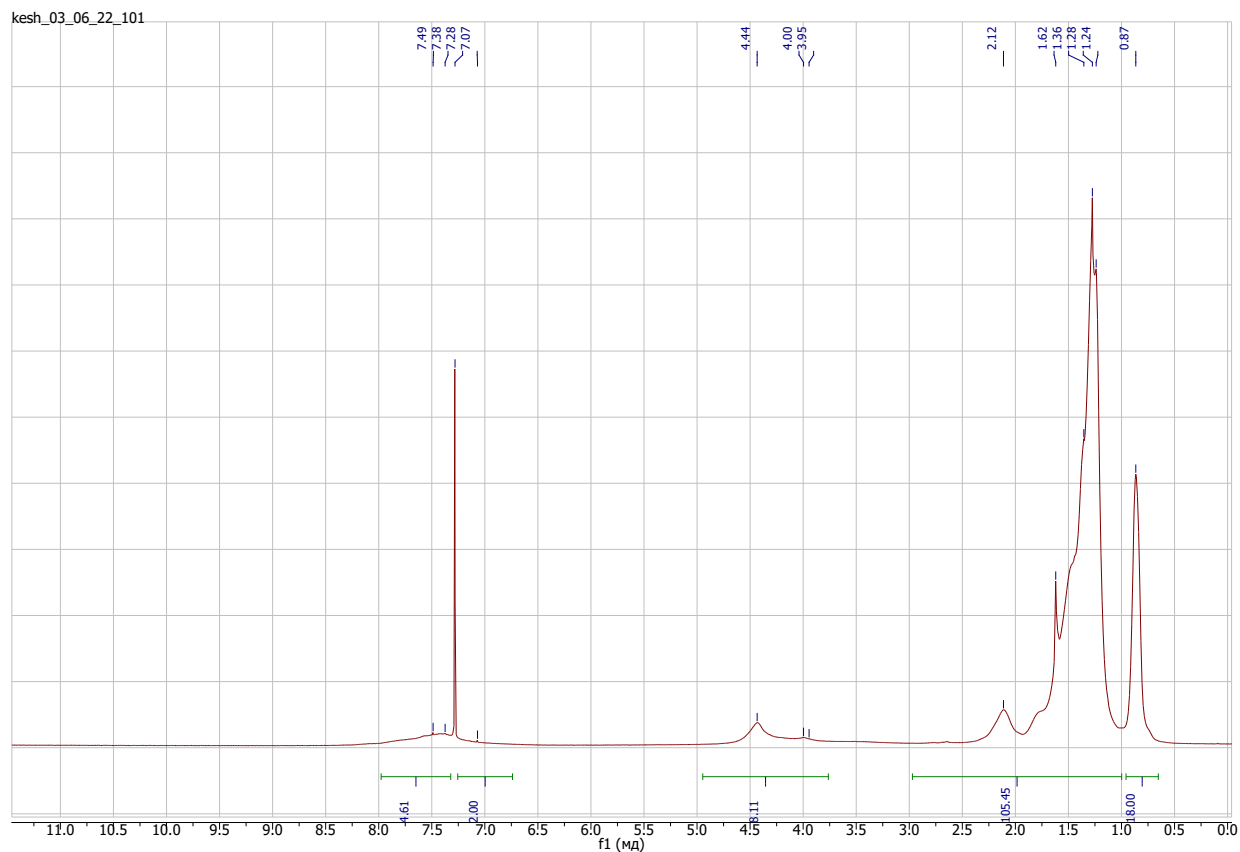
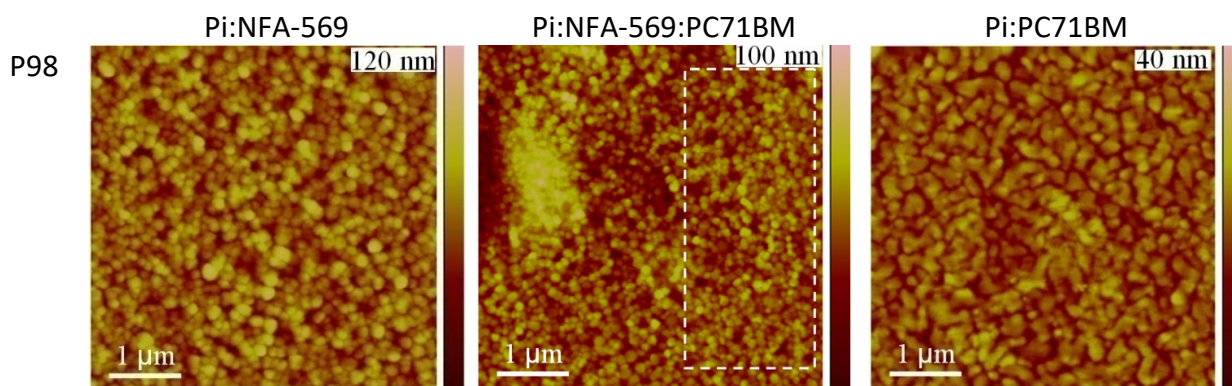


Fig.S4. ^1H NMR spectrum of random polymer **P101** in CDCl_3

3.3. AFM experimental data

AFM measurements were performed on an EnviroScope microscope with a Nanoscope-V controller (Veeco) in semi-contact mode under ambient conditions. Silicon cantilevers with force constants of 5–40 N/m and resonance frequencies of 150–350 kHz were used. It was checked that the static electric charge did not smooth the images.



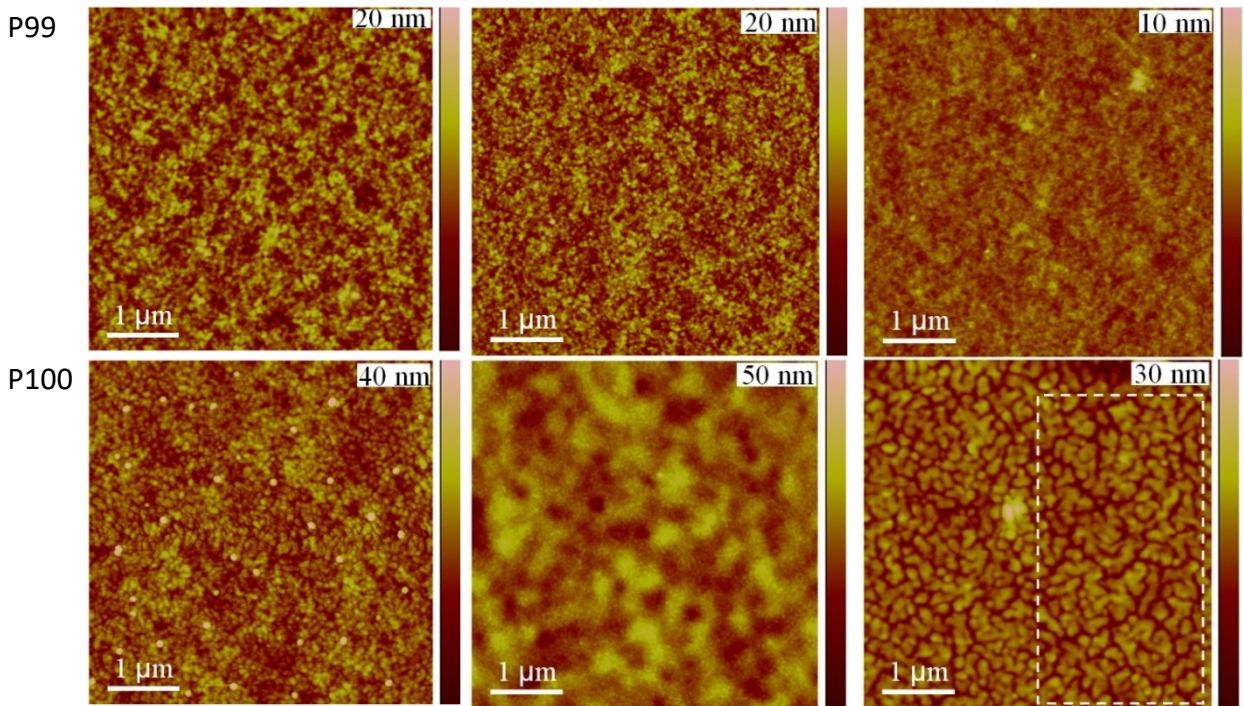


Fig. S5. AFM images of the surface topography of the composite films based on P98-P100. As an example, the rectangle shows the area for calculating RMS.

3.4. Thin film formation and SCLC measurements

The electron-only and hole-only devices with the structure of Al/composite layer/Al and ITO/composite layer/MoO₃/Al, respectively, were prepared for the measurements. PC71BM component, purity 99%, was purchased from SES Research, Inc. Composite films were deposited from a solution in chlorobenzene at the concentration of 20 mg/ml by spin coating of the substrate at 1000 rpm and dried at 70°C for 10 min. Al (60 nm thick) and MoO₃ (7 nm thick) layers were deposited by thermal evaporated at a vacuum of 2×10^{-6} mbar. In the devices of the polymer composites, the charge carrier mobility μ was obtained by measuring current–voltage (j - V) characteristics of the steady-state current j . At the space charge-limited current (SCLC) regime, the j - V curves reflect the non-trapping mode which obeys the Mott–Gurney equation:^{S1}

$$j = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{V^2}{d^3}$$

where d is the thickness of the film, ϵ_0 is the vacuum permittivity, and ϵ is the relative dielectric constant of the material. The constant $\epsilon = 3$ was used for the composites. The j - V measurements were carried out within a dry argon-filled MBraun glove box at r.t. The 90% confidence interval calculated from 10 replicates.

3.5. Grazing Incidence Diffraction measurements

Grazing incidence diffraction measurements were carried out at Rigaku SmartLab diffractometer with rotating Cu-anode. The incident beam was formed with multilayer parabolic mirror that provide X-ray beam with angular divergence $\approx 0.01^\circ$ in a scattering plane. X-ray diffractometry patterns were obtained by two-dimensional detector HyPix-3000 positioned at 0 and 16 2θ degrees in plane positions. The slit before samples was 1 mm, slits between samples and detector – 0.5 mm, exposure was chosen from experimental data and signal-noise ratio around 3000-10000 s, incidence angle α was varied 0.3 – 1 degree.

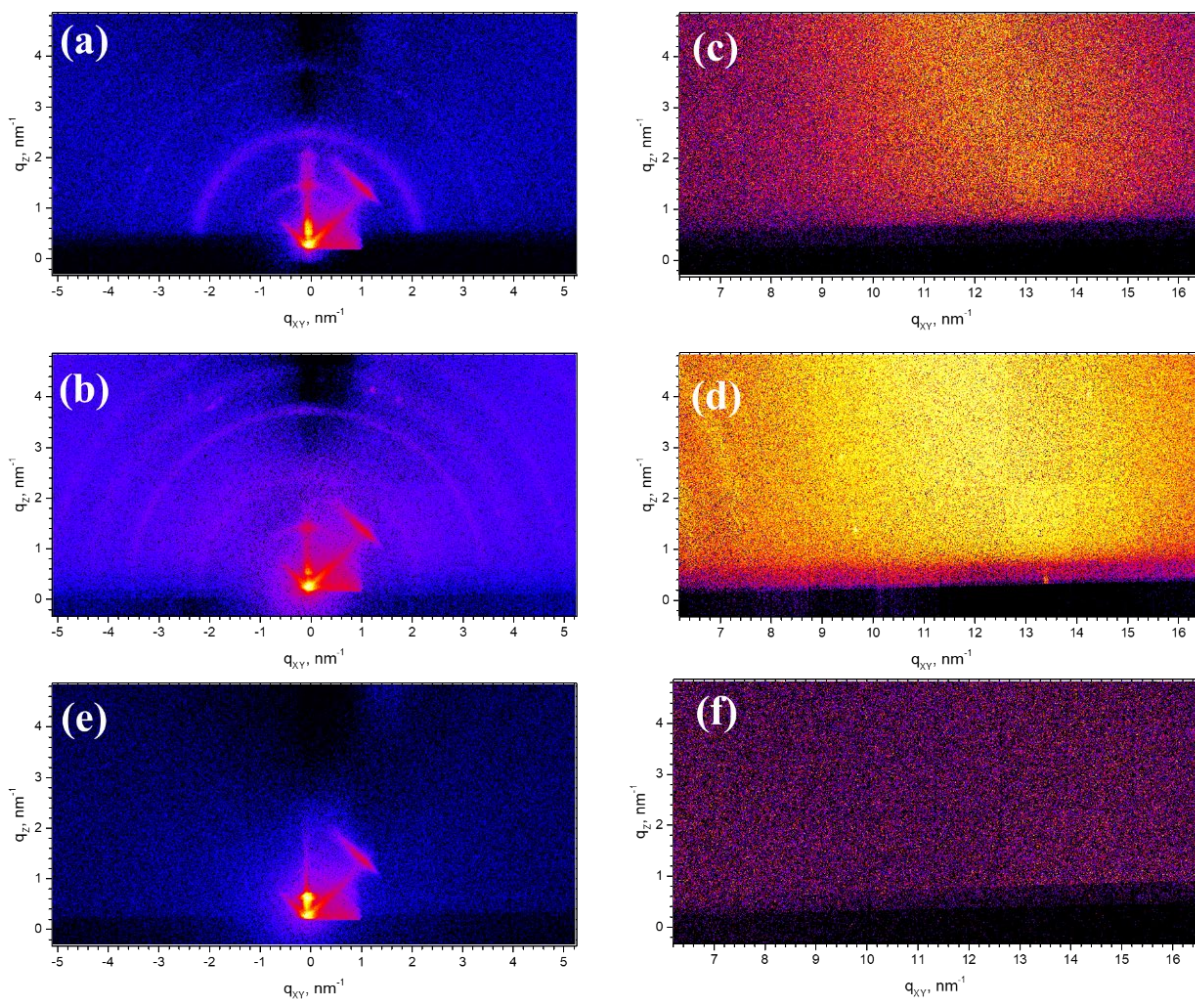


Fig. S6. (a)-(b) GISAXS images for P98:NFA-569:PCBM70 and P100:NFA-569:PCBM70 at 0.3 incident angle. (c)-(d) GIWAXS images for P98:NFA-569:PCBM70 and P100:NFA-569:PCBM70. (e)-(f) background GISAXS and GIWAXS images. Logarithmic intensity shown for all GID data for clarity.

Reference

S1. M. A. Lampert and P. Mark, Current Injection in Solids; Academic: New York, 1970.