Supporting information

Controlling n-Type Molecular Doping via Regiochemistry and Polarity of Pendant Groups on Low Bandgap Donor-Acceptor Copolymers

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1. Materials synthesis and characterization

Reagents: All reagents and solvents were commercial and were used as received. 4,9-dibromo-2,7-bis(2-octyldodecyl) benzo[lmn] [3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (NDI-OD) and 4,9-dibromo-2,7-bis(2-(2-ethoxyethoxy)ethoxy)ethyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NDI-TEG) were synthesized according to literature procedures.\(^1\)\(^2\) (4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl)dimethylamine (n-DMBI), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide[EMIM][TFSI] were purchased from Sigma Aldrich.

Characterization: \(^1\)HNMR and \(^{13}\)CNMR were performed on a Varian Unity Plus (400 MHz) instrument at 25 °C, using tetramethylsilane (TMS) as an internal standard. NMR shifts are reported in ppm, relative to the residual protonated solvent signals of CDCl\(_3\) (\(\delta = 7.26 \text{ ppm}\)) or at the carbon absorption in CDCl\(_3\) (\(\delta = 77.23 \text{ ppm}\)). Multiplicities are denoted as: singlet (s), doublet (d), triplet (t) and multiplet (m). High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer. IR measurements were performed on a Nicolet iS50 FT-IR spectrometer. FT-IR spectra were recorded on a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler. GPC measurements were done on a GPC-PL220 high temperature GPC/SEC system at 150 °C vs polystyrene standards using trichlorobenzene as eluent. Thermal properties of the polymers were determined on a TA Instruments DSC Q20 and a TGA Q50. DSC measurements were executed with two heating-cooling cycles with a scan rate of 10 °C min\(^{-1}\), and from each scan, the second heating cycle was selected. TGA measurements were done from 20 to 800 °C with a heating rate of 10 °C min\(^{-1}\). Cyclic voltammetry (CV) was carried out with a Autolab PGSTAT100 potentiostat in a three-electrode configuration where the working electrode was glass carbon electrode, the counter electrode was a platinum wire, and the pseudo-reference was an Ag/AgCl wire that was calibrated against ferrocene (Fc/Fc\(^+\)). Cyclic voltammograms for NDI-Based polymers film deposited on the glass carbon working electrode in CH\(_3\)CN solution containing Bu\(_4\)NPF\(_6\) (0.1 molL\(^{-1}\)) electrolyte at a scanning rate of 100 mVs\(^{-1}\).
**Scheme S1. Synthetic route to the monomer T2DEG.**

3-(2-(2-methoxyethoxy) ethoxy)thiophene 2

In a dry three-neck round-bottom flask, 60% NaH (1200 mg, 30 mmol) was mixed with anhydrous DMF (20 mL) under a nitrogen atmosphere. 2-(2-ethoxyethoxy) ethanol (12 g, 11.68 mL, 100 mmol) was added drop-wise over a period of 30 minutes at 0 °C. The solution was allowed to stir for additional one hour. To this reaction mixture, 3-bromothiophene (3.2 g, 1.84 mL, 20 mmol) and CuBr (280 mg, 2 mmol) were added. The ice bath was replaced with an oil bath and the solution was heated up to 110 °C for another one hour. After cooling to the room temperature, the mixture was then poured into NH₄Cl aqueous solution and stirred for 10 minutes. The organic phase was extracted with n-hexane, dried over anhydrous Na₂SO₄. Then, the solvent was evaporated by rotary evaporation. The crude solid was purified by column chromatography (silica gel) by using ethyl acetate: hexane (1:2) as eluent to give pure target product 2 (3.6 g, 90%). ¹HNMR (400 MHz, CDCl₃) δ: 7.15 (dd, J = 5.2, 3.2 Hz, 1H), 6.76 (dd, J = 5.2, 1.3 Hz, 1H), 6.24 (dd, J = 3.2, 1.5 Hz, 1H), 4.11 (t, J = 4.8 Hz, 2H), 3.83(t, J = 4.8 Hz, 2H), 3.69 (t, J = 4.8 Hz, 2H), 3.56 (t, J = 4.8 Hz, 2H), 3.37 (s, 3H). ¹³CNMR (101 MHz, CDCl₃) δ: 157.43, 124.52, 119.43, 97.31, 71.77, 70.51, 69.53, 69.37, 58.87.

3,3’-bis(2-(2-methoxyethoxy) ethoxy)-2,2’-bithiophene 3

To a solution of 3-(2-methoxyethoxy) thiophene 2 (1.8 g, 8.91 mmol) in anhydrous THF (20 mL) at ice bath, the n-butyllithium (8.91 mmol, 5.57 mL, 1.6M in Hexane) were added dropwise over 10 min at 0 °C under N₂ condition. The mixture was kept stirring at this temperature for 2 hours before the solution was transferred to another dry flask with Fe(acac)₃ (3.15 g, 9.8 mmol) in THF (70 mL), the reaction mixture was then heated under reflux for 3 hours. After cooling to room temperature, the precipitate was filtered off through short silica plug eluting with 5 %CH₃OH in CH₂Cl₂. The filtrate was washed with saturated NH₄Cl solution and the aqueous phases were combined and extracted with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄ and the solvent was evaporated by rotary evaporation. The crude solid was purified by column chromatography (silica gel) by using ethyl acetate: hexane (1:1) as eluent to give target product 3.
with some little red color impurities. The crude product was then purified by recrystallization in Et₂O to give pure product 3 (900 mg, 50 %). ¹HNMR (400 MHz, CDCl₃) δ: 7.05 (d, J = 5.2 Hz, 2H), 6.83 (d, J = 5.2 Hz, 2H), 4.24 (t, J = 4.8 Hz, 4H), 3.89 (t, J = 4.8 Hz, 4H), 3.72 (t, J = 4.8 Hz, 4H), 3.55 (t, J = 4.8 Hz, 4H), 3.37 (s, 6H). ¹³CNMR (101 MHz, CDCl₃) δ: 143.99, 121.89, 116.54, 114.72, 71.99, 71.36, 70.80, 70.01, 59.05.

(3,3'-bis(2-(2-methoxyethoxy)ethoxy)-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane)

Monomer T2DEG

Compound 3,3'-bis(2-methoxyethoxy)-2,2'-bithiophene 3 (402 mg, 1 mmol) was dissolved in anhydrous THF (10 mL) under an atmosphere of N₂, cooled to -78 °C and n-butyllithium (2.15 mmol, 1.35 mL, 1.6 M in hexane) was added dropwise. The solution was stirred for 2 hours in the cold bath at -78 °C before being warmed to room temperature and stirred for an additional 15 minutes. The mixture was cooled to -78 °C again. Then, trimethyltin chloride (3 mL, 3 mmol, 1.0 M in THF) was added. After that, the solution was stirred at room temperature overnight. Water was added to quench the reaction, and the solution was extracted with n-hexane. The organic phase was dried over Na₂SO₄ and the solvent was removed by rotary evaporation leading to the crude compound as a yellow oil which was purified by recrystallization in isopropanol. The pure monomer T2DEG (518 mg) was obtained in 71 % yield. ¹HNMR (400 MHz, CDCl₃) δ: 6.90 (s, 2H), 4.28 (t, J = 4.8 Hz, 4H), 3.92 (t, J = 4.8 Hz, 4H), 3.76 (t, J = 4.8 Hz, 4H), 3.57 (t, J = 4.8 Hz, 4H), 3.39 (s, 6H), 0.36 (s, 18H). ¹³CNMR (101 MHz, CDCl₃) δ: 153.77, 134.09, 124.40, 120.84, 72.29, 71.72, 71.12, 70.38, 59.31, -8.08.

Scheme S2. Synthetic route to the monomer T2DO.

Monomer T2DO was synthesized according to the literature with a slight modification.

3-(dodecyloxy) thiophene 5

Compound 5 was prepared and purified as a colorless solid using the same procedure as literature. ¹HNMR (400 MHz, CDCl₃) δ: 7.18 (dd, J = 5.2, 3.2 Hz, 1H), 6.77 (dd, J = 5.2, 1.3 Hz, 1H), 6.28 -
6.18 (m, 1H), 3.95 (t, J = 6.6 Hz, 2H), 1.87-1.73 (m, 2H), 1.52-1.41 (m, 2H), 1.40-1.20 (m, 16H), 0.91 (t, J = 6.7 Hz, 3H). 13CNMR (101 MHz, CDCl3) δ: 158.27, 124.68, 119.74, 97.14, 70.48, 32.15, 29.89, 29.86, 29.82, 29.80, 29.62, 29.58, 29.50, 26.28, 22.92, 14.34.

2-bromo-3-(dodecyloxy) thiophene 6

Compound 6 was prepared and purified as a colorless solid using the same procedure as literature52. 1HNMR (400 MHz, CDCl3) δ: 7.17 (d, J = 5.9 Hz, 1H), 6.74 (d, J = 5.9 Hz, 1H), 4.03 (t, J = 6.6 Hz, 2H), 1.82-1.69 (m, 2H), 1.52-1.41 (m, 2H), 1.40-1.20 (m, 16H), 0.91 (t, J = 6.8 Hz, 3H). 13CNMR (101 MHz, CDCl3) δ: 154.40, 123.90, 117.30, 91.37, 72.04, 31.81, 29.56, 29.54, 29.48, 29.45, 29.37, 29.25, 29.23, 25.71, 22.58, 14.00.

3,3'-bis(dodecyloxy)-2,2'-bithiophene 7

2-bromo-3-(dodecyloxy) thiophene 6 (1000 mg, 3.13 mmol, 1eq), BiPi (800 mg, 3.13 mmol, 1eq) and K2PO4 (2.6 g, 12.26 mmol, 4eq) were dissolved in anhydrous DMF (20 mL). After degassing with dry N2, the catalysts Pd(dppf)2Cl2 (20 mg, 0.027 mmol) was added. The reaction mixture was heating at 110 °C overnight under N2. The reaction mixture was poured into water, then the product was extracted with CH2Cl2, washing with saturated NaHCO3, water and then brine. The organic phase was then collected and dried over Na2SO4 and the solvents removed by rotary evaporation. The crude solid was purified by column chromatography to give product 7 (540 mg, 70 %). 1HNMR (400 MHz, CDCl3) δ: 7.07 (d, J = 5.5 Hz, 2H), 6.83 (d, J = 5.6 Hz, 2H), 4.09 (t, J = 6.5 Hz, 4H), 1.91-1.78 (m, 4H), 1.57-1.45 (m, 4H), 1.40-1.19 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H). 13CNMR (101 MHz, CDCl3) δ: 152.17, 121.82, 116.28, 114.35, 77.55, 77.23, 76.91, 72.22, 32.15, 29.94, 29.90, 29.88, 29.84, 29.79, 29.60, 29.58, 26.28, 22.92, 14.35.

(3,3'-bis(dodecyloxy)-[2,2'-bithiophene]-5,5'-diyl) bis(trimethylstannane), Monomer T2DO

Compound 3,3'-bis(dodecyloxy)-2,2'-bithiophene 7 (540 mg, 1 mmol) were dissolved in anhydrous THF (10mL) under an atmosphere of N2, cooled to −78 °C and n-butyllithium (2.5 mmol, 1 mL, 2.5 M in hexane) was added drop-wise. The solution was stirred for 2 hours in the cold bath at −78 °C before being warmed to room temperature and stirred for an additional 1 hour. The mixture was cooled to −78 °C again. Then, trimethyltin Chloride (2.6 mL, 2.6 mmol, 1.0 M in THF) was added. After that, the solution was stirred at room temperature overnight. Water was added to quench the reaction, and the solution was extracted with n-hexane. The organic phase was then collected and dried over Na2SO4 and the solvent was removed by rotary evaporation provide crude compound which was purified by recrystallized using ethanol to give pure product monomer T2DO (490 mg, 57 %). 1HNMR (400 MHz, CDCl3) δ: 6.87 (s, 2H), 4.11 (t, J = 6.5 Hz, 4H), 1.84(t, J = 6.5 Hz, 4H), 1.45-1.14 (m, 36H), 0.88 (t, J = 6.8 Hz, 6H), 0.36 (s 18H). 13CNMR (101 MHz, CDCl3) δ 152.17, 121.82, 116.28, 114.35, 77.55, 77.23, 76.91, 72.22, 32.15, 29.94, 29.90, 29.88, 29.84, 29.79, 29.60, 29.58, 26.28, 22.92, 14.35.
General synthetic procedures for the NDI based polymers

To a dry three-neck flask, NDI based monomer (0.1 mmol) and thiophene based monomer (0.1 mmol) were added under argon followed by tris(dibenzylideneacetone) dipalladium \([\text{Pd}_2(\text{dba})_3]\)(8 mg) and tri(o-tolyl)phosphine \([\text{P}(\text{o-tolyl})_3]\)(12 mg). The flask and its contents were subjected to 3 pump/purge cycles with N\(_2\) followed by addition of anhydrous, degassed toluene or chlorobenzene (5 mL) via syringe. The reaction mixture was stirred at 110 °C for three days. After cooling to room temperature, the deeply green colored reaction mixture was dropped into 100 mL vigorously stirred methanol (containing 5 mL 12 M hydrochloride acid). After stirring for 4 hours, the precipitated solid was collected by filtration. The solid polymers were re-dissolved in chloroform and reprecipitated into methanol. After filtration, the polymers were subjected to sequential Soxhlet extraction. The sequential solvents were methanol, hexane and chloroform. Impurities and low-molecular-weight fraction were removed by methanol. Finally, the polymer solution in hexane or chloroform was concentrated to give the polymer as a dark green solid.

**Scheme S3.** Synthetic route to the polymer of PNDI2OD-T2DO and PNDI2OD-T2DEG.

**PNDI2OD-T2DO** Synthesis according to the general polymerization procedure: monomer NDI-OD (98.5 mg, 0.1 mmol), monomer T2DO (86 mg, 0.1 mmol), dry chlorobenzene (5 mL). The polymer was obtained as a green solid (103 mg, 74%). \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\): 9.08-7.34 (m, 2H), 7.26-6.79 (m, 2H), 4.61-3.03 (m, 8H), 2.18-1.69 (m, 6H), 1.67-0.99 (m, 104H), 0.92-0.73 (m, 18H). IR (cm\(^{-1}\)): 717, 792, 1060, 1180, 1245, 1309, 1439, 1565, 1660, 1702, 2851, 2920.

**PNDI2OD-T2DEG** Synthesis according to the general polymerization procedure: monomer NDI-OD (98.5 mg, 0.1 mmol), monomer T2DEG (73 mg, 0.1 mmol), dry toluene (5 mL). The polymer was obtained as a green solid (110 mg, 87%). \(^1\)HNMR (400 MHz, CDCl\(_3\)) \(\delta\): 9.15-7.30 (m, 2H), 7.25-6.67 (m, 2H), 5.05-2.69 (m, 20H), 2.25-1.74 (m, 2H), 1.70-1.05 (m, 70H), 0.99-0.62 (m, 12H). IR (cm\(^{-1}\)): 716, 792, 823, 853, 927, 1072, 1108, 1140, 1177, 1242, 1310, 1409, 1436, 1523, 1563, 1661, 1701, 2851, 2920.
Scheme S4. Synthetic route to the polymer of PNDI2TEG-T2DO and PNDI2TEG-T2DEG.

**PNDI2TEG-T2DO** Synthesis according to the general polymerization procedure: monomer NDI-TEG (74 mg, 0.1 mmol), monomer T2DO (86 mg, 0.1 mmol), dry chlorobenzene (5 mL). The polymer was obtained as a green solid (40 mg, 35%). $^1$HNMR (400 MHz, CDCl$_3$) δ: 9.30-7.33 (m, 2H), 7.25-6.57 (m, 2H), 4.85-2.69 (m, 28H), 2.05-1.76 (m, 4H), 1.61-1.03 (m, 44H), 0.99-0.68 (m, 6H). IR (cm$^{-1}$): 656, 720, 764, 791, 928, 1057, 1109, 1176, 1206, 1249, 1314, 1376, 1439, 1567, 1663, 1702, 2852, 2920.

**PNDI2TEG-T2DEG** Synthesis according to the general polymerization procedure: monomer NDI-TEG (74 mg, 0.1 mmol), monomer T2DEG (73 mg, 0.1 mmol), dry toluene (5 mL). The polymer was obtained as a green solid (43 mg, 42%). $^1$HNMR (400 MHz, CDCl$_3$) δ: 9.18-7.33 (m, 2H), 7.25-6.59 (m, 2H), 4.47-2.82 (m, 44H), 1.47-0.79 (m, 12H). IR (cm$^{-1}$): 660, 713, 734, 765, 790, 858, 929, 945, 1012, 1069, 1174, 1205, 1247, 1311, 1329, 1407, 1436, 1520, 1564, 1664, 1700, 2866.
2. $^1$HNMR spectra of NDI-based copolymers

Figure S1. $^1$HNMR spectrum of PNDI2OD-T2DO.

Figure S2. $^1$HNMR spectrum of PNDI2OD-T2DEG.
Figure S3. $^1$HNMR spectrum of PNDI2TEG-T2DO.

Figure S4. $^1$HNMR spectrum of PNDI2TEG-T2DEG.
3. IR Spectra of NDI-based copolymers

**Figure S5.** IR spectrum of PNDI2OD-T2DO.

**Figure S6.** IR spectrum of PNDI2OD-T2DEG.
Figure S7. IR spectrum of PNDI2TEG-T2DO.

Figure S8. IR spectrum of PNDI2TEG-T2DEG.
4. GPC curves of NDI-based copolymers
Figure S9 High-temperature gel permeation chromatography traces of a) PNDI2OD-T2DO, b) PNDI2OD-T2DEG, c) PNDI2TEG-T2DO, and d) PNDI2TEG-T2DEG. The molecular weight was evaluated with 1,2,4-trichlorobenzene as eluent at 150 °C.
Figure S10. Molecular weights distribution plots measured from high-temperature gel permeation chromatography: a) PNDI2OD-T2DO, b) PNDI2OD-T2DEG, c) PNDI2TEG-T2DO, and d) PNDI2TEG-T2DEG.
5. Thermal properties of NDI-Based Copolymers

Figure S11. TGA curves of NDI-based copolymers.
Figure S12. DSC curves of NDI-based copolymers.

Table S1. Molecular weight and thermal properties of NDI-based copolymers.

| Polymer       | $M_n$ (kgmol$^{-1}$) | $M_w$ (kgmol$^{-1}$) | PDI | $T_d$ (°C) | $T_m$ (°C) |
|---------------|----------------------|----------------------|-----|------------|------------|
| PNDI2OD-T2DO  | 7433                 | 12558                | 1.689 | 334        | 248        |
| PNDI2TEG-T2DO | 8661                 | 14133                | 1.631 | 321        | ---        |
| PNDI2OD-T2DEG | 13172                | 24577                | 1.866 | 335        | ---        |
| PNDI2TEG-T2DEG| 10496                | 13204                | 1.258 | 307        | 108, 209, 274 |
6. UV-Vis-NIR absorption spectra of NDI-Based copolymers

Figure S13. UV-Vis-NIR spectrum of NDI-based copolymers in dilute chloroform and thin film state.
7. Cyclic voltammograms reduction plots of NDI-Based copolymers

![Cyclic voltammograms plots]

Figure S14. The reduction cyclic voltammograms of NDI-based conjugated polymer P(NDI2OD-T2) and PNDI2OD-T2DO, PNDI2TEG-T2DO, PNDI2OD-T2DEG and PNDI2TEG-T2DEG thin films deposited on glass carbon working electrode. The reduction waves of these polymers have a very similar shape. All the spectra are divided into the first (NDI-polymer radical anion) and second (NDI-polymer dianion) reduction.
8. Density functional theory calculation

To gain insights into the donor/acceptor character of NDI based copolymers, we carried out density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level using Gaussian 16\(^3\). To simplify the calculations, our model molecules contain only two repeating unit and the alkyl group was replaced by methyl group. As shown in the Figure S15, all the HOMO orbitals and LUMO orbitals are isolated on their donor and acceptor moieties, respectively, in all the NDI based copolymers. All the optimized model molecules present twist structure in gas phase calculations. The calculated energy levels are shown in the Table S2. The DFT calculation data show that the inclusion of glycol ethers chain seems lower the HOMO in all case. However, our experimental results reveal that the inclusion of glycol ethers chain only on donor or acceptor moiety has little effect on HOMO, but in the case, inclusion of glycol ethers chain on both monomers raise the HOMO by approximately 400 mV. The calculation results do not agree with the experimental data, implying that the solid state structure of these copolymers is different from those structure obtained from the gas phase calculation. The large red shift from the solution absorption to solid state absorption (Figure S13) also approves this differences.

We assume that introducing glycol ethers chain on the polymer could promote the planarity of polymer backbone in the solid state especially for PNDI2TEG-T2DEG due to the force via dipole-dipole interactions between interdigitating glycol ethers chains\(^4\). Therefore, we further did the calculation by reducing the dihedral angle between NDI unit and bithiophene unit in PNDI2TEG-T2DEG. Figure S16 shows that HOMO and LUMO are more delocalized in the all planar model molecule. The energy of HOMO is increasing while that of LUMO is decreasing when gradually reducing the dihedral angle between NDI unit and bithiophene unit (more planar a polymer), which results in a smaller bandgap.

Table S2. The calculated energy level and band gap of NDI-based copolymers.

| Polymer          | HOMO  | LUMO  | Gap  |
|------------------|-------|-------|------|
| PNDI2OD-T2DO     | -4.87 | -3.27 | 1.60 |
| PNDI2TEG-T2DO    | -4.91 | -3.35 | 1.56 |
| PNDI2OD-T2DEG    | -4.91 | -3.28 | 1.62 |
| PNDI2TEG-T2DEG   | -4.95 | -3.32 | 1.63 |
| (twist)          |       |       |      |
| PNDI2TEG-T2DEG   | -4.88 | -3.37 | 1.51 |
| (planar)         |       |       |      |
Figure S15. DFT-optimized molecular orbitals of (a) PNDI2OD-T2DO, (b) PNDIOD-T2DEG, (c) PNDI2TEG-T2DO and (d) PNDI2TEG-T2DEG copolymers in gas phase.
Figure S16. DFT-optimized molecular orbitals of PNDI2TEG-T2DEG model molecule in twist and planar structure and corresponding energy levels.
Figure S17. UV-Vis-NIR absorption spectra of pristine and doped PNDI2OD-T2DEG films.

9. Device fabrication and characterization.

Clean borosilicate glass substrates were treated with UV-ozone for 20 minutes. The doped films were prepared by spin-coating conjugated polymer solution (10 mg/mL in chloroform) mixed with different amounts of n-DMBI solution (20 mg/mL in chloroform) in a glovebox with nitrogen atmosphere. The resultant films were annealed at 120 °C for one hour. For the electrical conductivity measurements, parallel line-shape Au electrodes with a width (w) of 13 mm and a channel length (L) of 100-300 µm were deposited as the bottom contact before spin-coating. Voltage-sourced two-point conductivity measurements were conducted with a probe station in a N₂ glovebox. The electrical conductivity (σ) was calculated based on the formula: $\sigma=(J/V) \times L/(w \times d)$. The conductivity reported in this work were averaged from 6 devices. The Seebeck coefficient values for various doped D-A copolymer films were measured in vacuum by a home-built setup, which was reported by our previous work. The charge carrier densities (n) in doped films were measured from admittance spectroscopy of metal-insulator-semiconductor architecture (ITO/insulator/doped active layer/Al) combined with Mott-Schottky analysis:

$$n = \frac{2}{e\varepsilon_0 \varepsilon_r \frac{\partial c_p^2}{\partial V}}$$  \hspace{1cm} (1)
where $\varepsilon_r$ and $C_p$ are dielectric constant of active layer and capacitance of MIS devices. PVDF-HFP: [EMIM][TFSI] (2.76:1 in weight) blend solution in cyclohexanone was spin-coated on ITO substrate to form 150-300 nm ion gel thin film as the insulator layer in MIS architecture. The capacitance-voltage ($C_p$-V) measurements were conducted at a frequency of 10 Hz for the ion gel based MIS devices. The UV-vis-NIR spectra of different thin films coated on quartz substrates were recorded on Shimadzu UV 3600. The AFM topographical images were recorded in the Peak Force Tapping mode using a Bruker MultiMode 8 microscope with ScanAsyst-Air probes. Cyclic voltammetry (CV) was carried out with a Autolab PGSTAT100 potentiostat in a three-electrode configuration where the working electrode was glass carbon electrode, the counter electrode was a platinum wire, and the pseudo-reference was an Ag/AgCl wire that was calibrated against ferrocene (Fc/Fc$^+$). Cyclic voltammograms for NDI-Based polymers film deposited on the glass carbon working electrode in CH$_3$CN solution containing Bu$_4$NPF$_6$ (0.1 mol L$^{-1}$) electrolyte at a scanning rate of 100 mV s$^{-1}$.

![Figure S18](image)

**Figure S18.** The plot of $C_p$ versus $V_d$ of metal-insulator-semiconductor devices using 28 mol% doped PNDI2OD-T2DO, PNDI2TEG-T2DO, PNDI2OD-T2DEG, and PNDI2TEG-T2DEG films as the active layer and ion gel layer as the insulator.
10. CP-AFM images of NDI-based copolymers films

AFM measurements. PeakForce tapping AFM, conductive probe AFM measurements were performed on a Bruker AFM multimode MMAFM-2 equipped with a PeakForce TUNA application module (Bruker). PeakForce Tapping AFM was performed with a ScanAsyst-Air probe (resonant frequency 70 kHz, spring constant 0.4 N/m, Bruker) to characterize the surface morphology of the samples at a scan rate of 0.75 Hz and 640 samples per line. In conductive probe AFM measurements, samples were contacted with a Pt-coated silicon tip with a nominal radius of 30 nm (ANSCM-PC-20, APPNANO, resonant frequency 12 kHz, spring constant 0.2 N/m) in TUNA mode with a setpoint of 0.2 V (voltage setpoint of the photodiode to determine the force load of the tip). Samplers were scanned under a constant bias of 2 V at a scan rate of 0.7 Hz. The data were analyzed with Nanoscope Analysis 1.5 (Bruker).

Figure S19. The topographic (top panel) and current (bottom panel) AFM micrographs for 28 mol% doped (a) PNDI2OD-T2DO, (b)PNDI2TEG-T2DO, (c)PNDI2OD-T2DEG, and (d)PNDI2TEG-T2DEG thin films, respectively.

Conductance (S @2V) PNDI2OD-T2DO 5.24x10^{-12} S, PNDI2TEG-T2DO 1.25x10^{-10} S PNDI2TEG-T2DEG 3.79x10^{-10} S PNDI2OD-T2DEG 1.53x10^{-10} S
11. Spatially resolved absorption

Methods

Spatially resolved absorption measurements (Figure 5 in the main text, and Figure S20) were performed with a home-built inverted confocal microscope similar to the one described in literature\(^7\). In short, we employed a fiber Halogen light source (Thorlabs OSL1) to illuminate the sample from above, and collected the transmitted light with a high-NA oil-immersion objective (Olympus PLAPON60XOPH UIS2). The light passed a 10/90RT beamsplitter plate (Thorlabs, BSN10R) and was imaged onto the slit of an imaging spectrograph (Princeton Instruments, IsoPlane 160, 50g/mm) with an attached electron-multiplying charge-coupled device (emCCD) camera (Andor iXon Ultra 897). The captured images thus resolve the transmitted intensity \(I(\lambda)\) spectrally (along the x-axis) while maintaining spatial resolution along the y-axis (parallel to the spectrograph’s entrance slit). The sample was mounted on a piezo table (piezosystems jena, TRITOR 102CAP), allowing us to move the sample in 500 nm steps in the x-direction. We scanned 40x40\(\mu\)m areas on the sample, obtaining 6640 individual transmission spectra (80 pixels in x-direction, 83 in y-direction). Without sample, we acquired reference spectra for the incident light \(I_0(\lambda)\), and calculated the wavelength-dependent absorption \(A(\lambda)\) with Beer’s Law \(A(\lambda) = -\log \left( \frac{I(\lambda)}{I_0(\lambda)} \right)\).

Spatially resolved absorption on pristine PNDI2TOD-T2DEG films

To confirm that the observed spatial variation of the absorbance ratio \(A_{600}/A_{850}\) is indeed caused by the dopant, we analyzed a film of pristine PNDI2TOD-T2DEG. Figure S20 compares the results for a 42 mol% doped film (a, b, corresponding to figure 5c and g in the main text) and a pristine film (c, d). We note that the spectral variation is significantly smaller in the pristine film (blue shaded area in S20c), and that there are no structures visible in the map of the ratio \(A_{600}/A_{850}\) (S20d). In other words, the observed spectral variations in doped films cannot be observed in pristine films, confirming that those variations are caused by local variations of the dopant concentration.
Figure S20. Spatially resolved absorption data on a 42 mol% doped (a, b) and a pristine PNDI2TOD-T2DEG film (c, d). The left figures (a, c) show the average spectra (blue line), and the spectral variation (blue shaded area). The right figures (b, d) show maps of the absorption ratio $A_{600}/A_{850}$. 
12. References

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