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Supporting Information

Even and Odd Oligothiophene-bridged bis-Naphthalimides for n-type and Ambipolar Organic Field Effect Transistors

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General Information

Materials and instruments

All the chemicals were purchased from commercial suppliers and used without further purification.

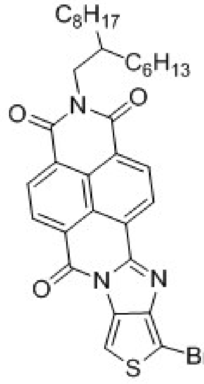
^{1}H NMR and ^{13}C NMR spectra were recorded on BrukerAvance 300 and AMX 500 MHz spectrometers. Chemical shifts are reported in ppm and referenced to the residual non-deuterated solvent frequencies ($CDCl_3$: δ 7.26 ppm for ^{1}H, δ 77.0 ppm for ^{13}C, $C_2D_2Cl_4$: δ 5.90 ppm for ^{1}H, δ 73.8 ppm for ^{13}C). UV–vis absorption spectra of the molecules in HPLC dichloromethane solutions at 20 ºC were recorded on a Varian Cary 50 UV–vis spectrophotometer. Mass spectra were recorded on a MAT95 XP (FAB) or Bruker Reflex 2 (MALDI-TOF). Cyclic voltammograms were recorded in an inert atmosphere in electrochemical workstation at a scan rate of 100 mV·s-1 at 83 ºC using tetrabutylammoniumhexafluoro phosphate (TBAHFP, 0.05 mol L^{-1}) as supporting electrolyte in o-dichlorobenzene. Polymer-precoated platinum electrodes, platinum–wire electrodes, and Ag/Ag+ electrodes were used as the working electrode, an auxiliary 3 electrode, and the reference electrode, respectively. Potentials were recorded versus Fc/Fc^+.

Theoretical calculations were carried out in the frame of density functional theory (DFT) using the B3LYP functional[6-8] and the 6-31G** basis set[9, 10] as implemented in the Gaussian 09 program.[11] The geometry optimizations were performed without any symmetry constraints. On the basis of the resulting ground-state geometries, harmonic vibrational frequencies were calculated analytically at the same theoretical level. The reorganization energies were calculated directly from the relevant points on the potential energy surfaces using the standard procedure detailed in the literature.[12,13]

FT-Raman spectra with 1064 nm excitation were recorded using a FT Raman accessory kit (RamII) of a Bruker Vertex 70 FT-IR interferometer and a continuous-wave Nd:YAG laser. A germanium detector operating at liquid-nitrogen temperature was used and the Raman scattering radiation was collected in a back-scattering configuration with a 4 cm^{-1} spectral resolution. An average of 1000 scans was used in the reported spectra.

OFET Fabrication and Characterization. Heavily doped Silicon substrates with a 300 nm thick thermally grown SiO_2 layer were coated with an octadecyltrichlorosilane(OTS) monolayer. Around 150 µL were drop casting on the treated substrates from 0.5 mg/mL semiconductor solutions in chlorobenzene at 80 ºC. Thin film AFM images were recorded in the tapping mode on a Veeco ICON PT system. The crystallinity and long range packing order of the thin films were studied by out of planediffraction of grazing incidence X-ray (GI-XRD) in a Rigaku ATX-G diffractometer with monochromatedCuKα radiation. Top Au contacts (50 nm) were then deposited by thermal evaporation through a shadow mask to complete bottom-gate, top contact OFET devices. The resulting devices had channel lengths and widths of 50 and 1000 µm, respectively. Devices were tested in the dark and under vacuum using an Agilent B1500 semiconductor parameter analyzer. Hole and electron mobilities were extracted from saturated regimes from at least three separate devices from each substrate.

NDI-1T-Br (R = 2-hexyldecyl)



To a solution of **NDI-1T**(2-hexyldecyl)[1] (422 mg, 0.74 mmol) in 150 mL of THF was very slowly added NBS (131 mg, 0.74 mmol) at 0ºC solved in 10 mL. The mixture was stirred overnight in the dark. The solvent was removed under reduced pressure and the crude reaction was chromatographed on silica gel (dichloromethane) to obtain 380 mg (79%) of a red solid.

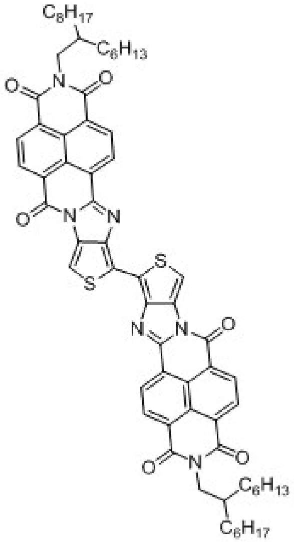
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.82 (m, 4H), 7.50 (s, 1H), 4.13 (d, 2H, J = 7.2 Hz), 2.00 (bs, 1H), 1.50-1.15 (bs, 24H), 0.85 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 162.8, 162.7, 157.3, 155.1, 148.1, 132.7, 131.2, 131.0, 130.9, 127.6, 127.5, 127.4, 126.8, 126.4, 125,4, 104.8, 97.1, 77.2, 45.1, 36.8, 32.0, 31.9, 30.2, 29.9, 29.7, 29.4, 26.6, 22.8, 14.3, 14.2.

FT-IR (CH_2Cl_2) ν (cm^{-1}): 2925, 2854, 1702, 1664, 1387, 1334, 1236, 762.

EM (FAB) (*m/z*): 647 (M^+)

2NDI-2T



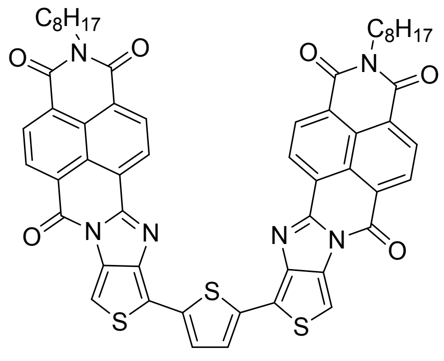
A mixture of **NDI-1T-Br**(2-hexyldecyl)(119 mg, 0.183 mmol), bis-tributyltin (75 mg, 0.128 mmol) and catalytic amount of $Pd(PPh_3)_4$ (10%) in 30 mL of degassed anhydrous DMF was refluxed under stirring for 24 h under argon. Then, the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the crude reaction was filtered and washed with hot methanol to yield 35 mg (35%) of a dark green solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.75 (m, 6H), 8.60 (d, 2H, 7.6 Hz), 7.52 (s, 2H), 3.98 (d, 4H, 7.3 Hz), 1.89 (bs, 2H), 1.45-1.00 (bs, 48H), 0.85 (m, 12 H).

MALDI-HRMS (m/z): calculated 1136.5268; found ($M+H^+$) 1137.5317.

FT-IR ($CHCl_3$) ν (cm^{-1}): 2924, 2853, 1697, 1661, 1583, 1394, 1335, 759.

2NDI-3Ta



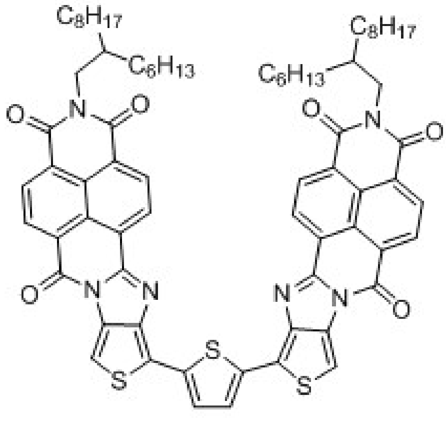
A solution of NDI-1T-Br (83 mg, 0.154 mmol), 2,5-bis(trimethylstannyl)thiophene (30 mg, 0.07 mmol) and Pd(PPh_3)$_4$ (10 %) was stirred in 25 mL of DMF at 90 ºC under argon atmosphere for 17 h. The solvent was removed under reduced pressure and the crude was filtered and washed with hot methanol and THF obteining 50 mg (83%) of a dark green solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.37-9.02 (m, 8H), 8.06 (s, 2H), 7.53 (s, 2H), 4.26 (m, 4H), 1.78 (bs, 4H), 1.52-1.20 (bs, 20H), 0.88 (m, 6H).

MALDI-HRMS (m/z): calculated 994.2641; found (M^+) 994.2595.

FT-IR ($CHCl_3$) ν (cm^{-1}): 2921, 2853, 1695, 1659, 1339, 1288, 759.

2NDI-3Tb

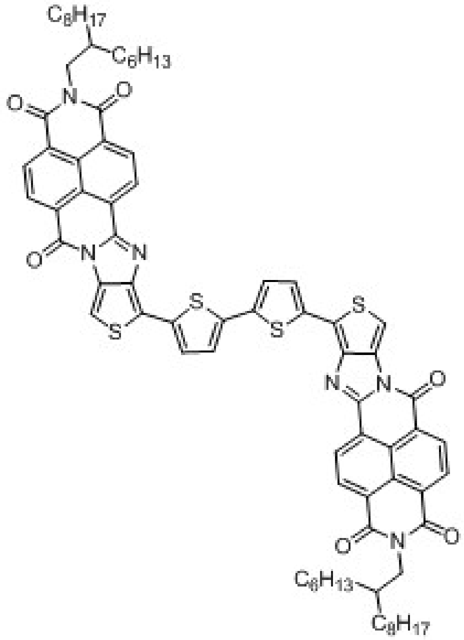


A solution of **NDI-1T-Br** (62 mg, 0.096 mmol), 2,5-bis(trimethylstannyl)thiophene (30 mg, 0.07 mmol) and Pd(PPh_3)$_4$ (10 %) was stirred in 25 mL of DMF at 90 ºC under argon atmosphere for 17 h. The solvent was removed under reduced pressure and the crude was filtered and washed with hot methanol and THF obteining 24 mg (41%) of a dark green solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.37 (bs, 2H), 8.29 (bs, 2H), 8.16 (bs, 2H), 8.01 (bs, 2H), 6.71 (bs, 2H), 6.62 (bs, 2H), 3.61 (bs, 4H), 1.75-0.55 (62H).

MALDI-HRMS (m/z): calculated1218.5145; found (M^+) 1218.5155.

2NDI-4T



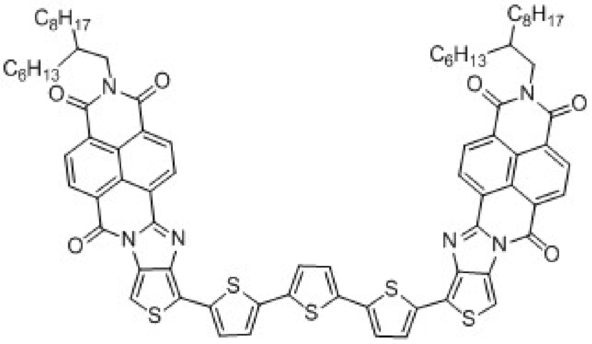
A solution of **NDI-1T-Br** (100 mg, 0.154 mmol), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene[4] (38 mg, 0.077 mmol) and $Pd(PPh_3)_4$ (10 %) was stirred in 25 mL of DMF at 90 ºC under argon atmosphere for 18h. The solvent was removed under reduced pressure and the crude was filtered and washed with hot methanol, acetone and diethyl ether obtaining 40 mg (40%) of a dark green solid.

^1H NMR (500 MHz, $C_2D_2Cl_4$, 50 ºC) δ (ppm): 8.86 (bs, 2H), 8.68 (m, 6H), 7.43 (bs, 2H), 7.29 (bs, 2H), 7.14 (bs, 2H), 4.02 (m, 4H), 1.94 (bs, 2H), 1.80-1.00 (bs, 48H), 0.80 (bs, 12H).

MALDI-HRMS (m/z): calculated 1300.5022; found ($M+H^+$) 1301.5105.

FT-IR ($CHCl_3$) ν (cm^{-1}): 2921, 2851, 1700, 1660, 1587, 1291, 758.

2NDI-5T



A solution of **NDI-1T-Br** (150 mg, 0.231 mmol), 5,5´´-bis(trimethylstannyl)-2,2′:5′,2″-terthiophene[5] (75 mg, 0.139 mmol) and $Pd(PPh_3)_4$ (10 %) was stirred in 35 mL of DMF at 90 ºC under argon atmosphere for 18h. The solvent was removed under reduced pressure and the crude was filtered and washed with hot methanol, acetone and hexane. Finally the crude was washed several folds with chloroformto yield30 mg (19%) of a dark green solid.

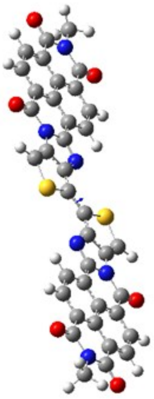
MALDI-HRMS (m/z): calculated 1382.4899; found (M^+) 1382.4936.

FT-IR ($CHCl_3$) ν (cm^{-1}): 2924, 2854, 1738, 1703, 1591, 1292, 760.

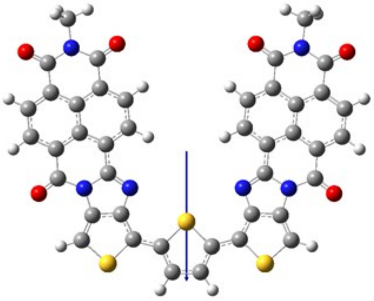
Differential scanning calorimetry

	2NDI-2T	**2NDI-3Tb**	**2NDI-4T**	**2NDI-5T**
Melting point,Tm (ºC)	335	276	346	334
Crystallization point,T_C (ºC)		254		319

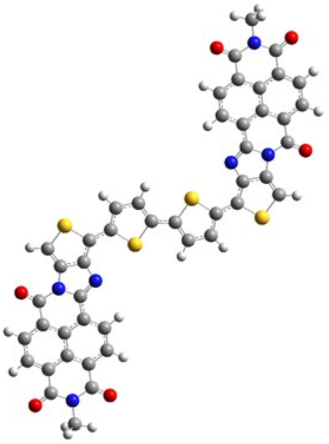
No transition was observed for **2NDI-3Ta.**



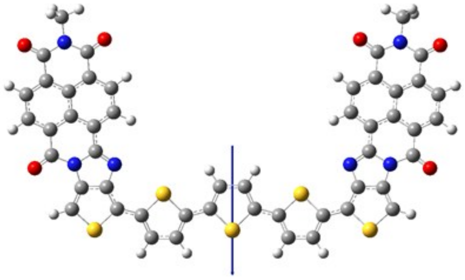
2NDI-2T μ= 0.1664 D



2NDI-3T μ = 2.1504 D



2NDI-4T $\mu = 5\cdot10^{-4}$ D



2NDI-5T μ = 2.4568 D

Figure S1. B3LYP/6-31G** optimized geometries and calculated molecular dipole moments.

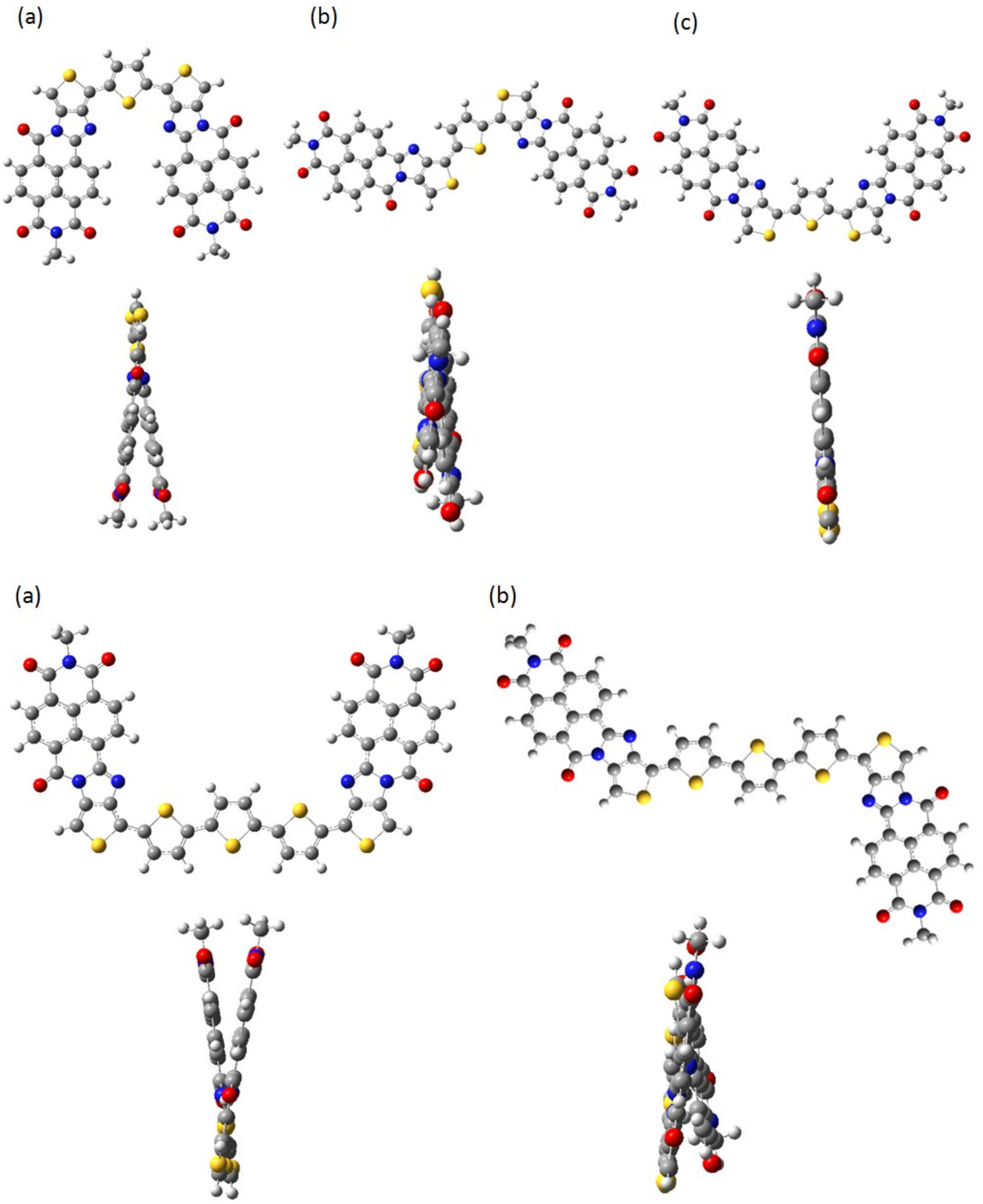


Figure S2. Top: DFT/M062X predicted **2NDI-3T** conformers in: (a) all-trans conformation, (b) trans-cis conformation and (c) all-cis conformation. Bottom: DFT/M062X predicted **2NDI-5T** conformers in: (a) all-trans conformation and (b) cis-trans-trans-trans conformation.

Table 1. DFT optimized energies (in kcal/mol) for the different predicted **2NDI-3T** conformers.

2NDI-3T (kcal/mol)	All-trans	Trans-cis	All-cis
CAM-B3LYP	-2249455.5859	-2249455.8719	-2249455.6287
M062X	-2249577.7536	-2249577.6958	-2249577.1965
B3LYP	-2250199.7352	-2250200.0870	-2250199.8519

Table 2. DFT optimized energies (in kcal/mol) for the different predicted **2NDI-5T** conformers.

2NDI-5T (kcal/mol)	All-trans	Cis-Trans-Trans-Trans
CAM-B3LYP	-2241879.0070	-2241878.8156
M062X	-2942003.0023	-2942002.4615
B3LYP	-2942743.1860	-2942743.0217

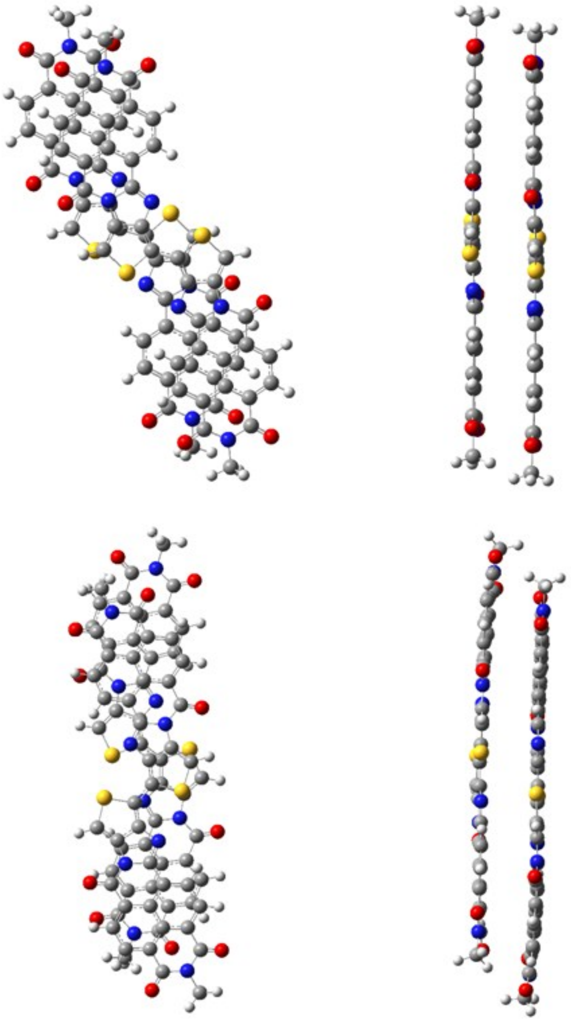
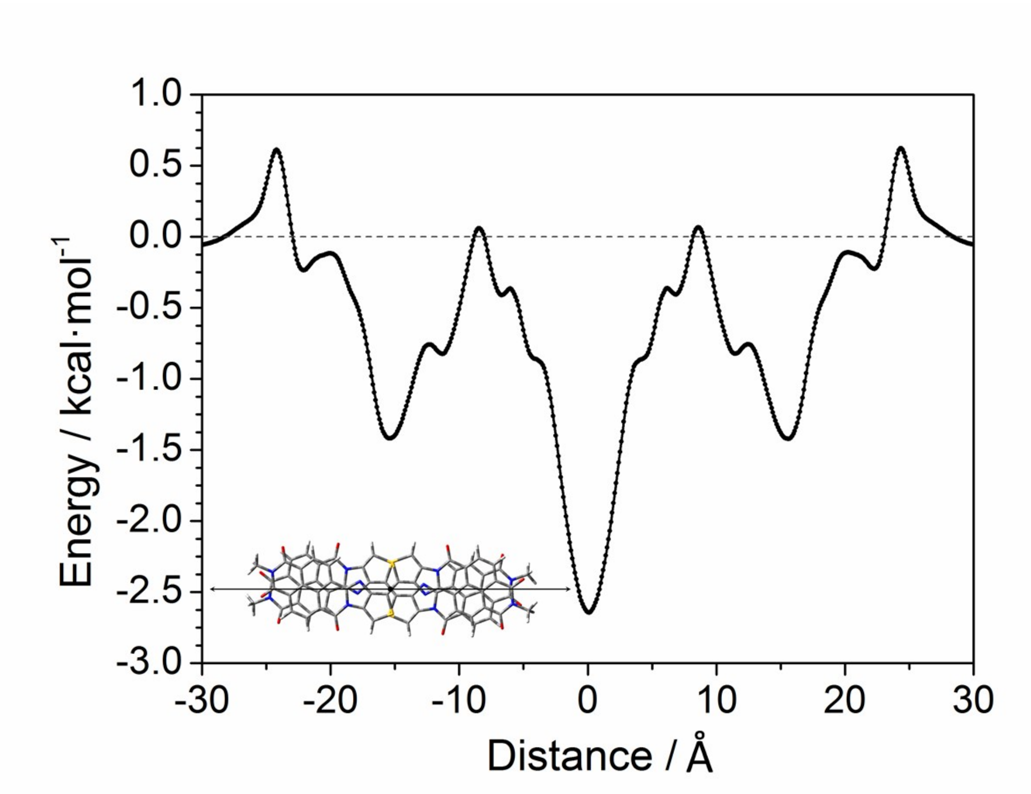


Figure S3. DFT/M062X predicted **2NDI-2T** dimers in: (top) a parallel configuration and (bottom) an antiparallel configuration. Both frontal and lateral views are shown.



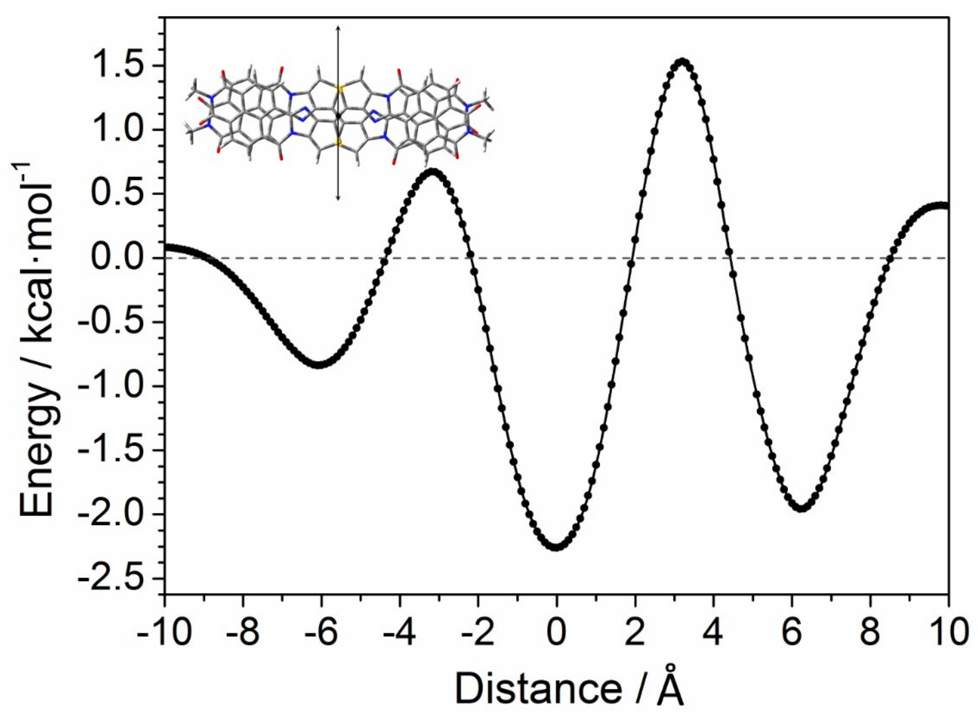


Figure S4. Potential energy curves, computed at the B3LYP/6-31G** level, for **2NDI-2T** upon (up) long-axis and (down) short-axis displacements.

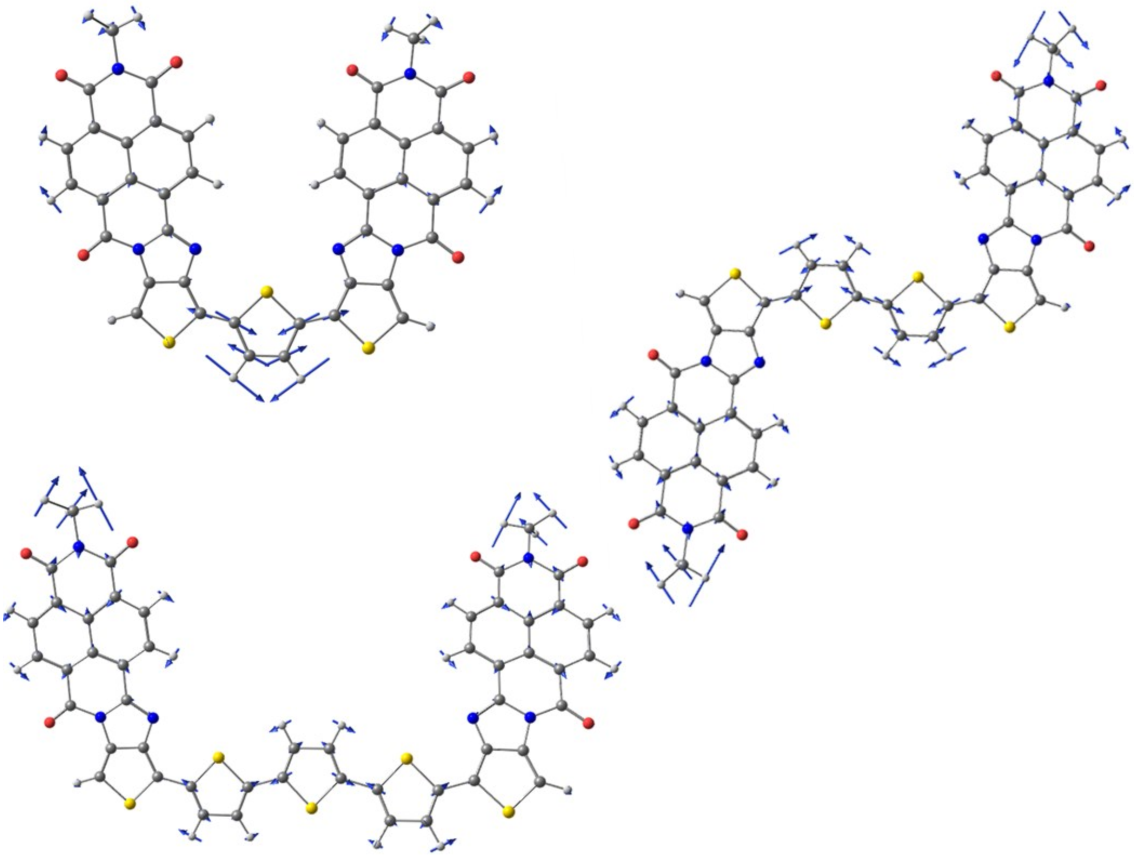


Figure S5. B3LYP/6-31G** eigenvectors for the indicated experimental Raman bands.

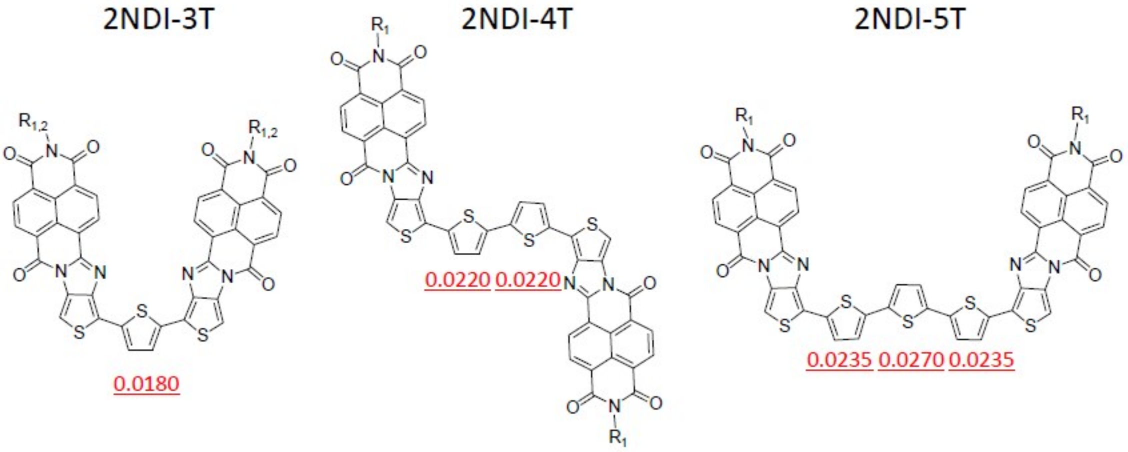


Figure S6. B3LYP/6-31G** bond length alternation parameter (BLA) calculated for the internal thiophene rings of **2NDI-3T**, **2NDI-4T**, and **2NDI-5T**.

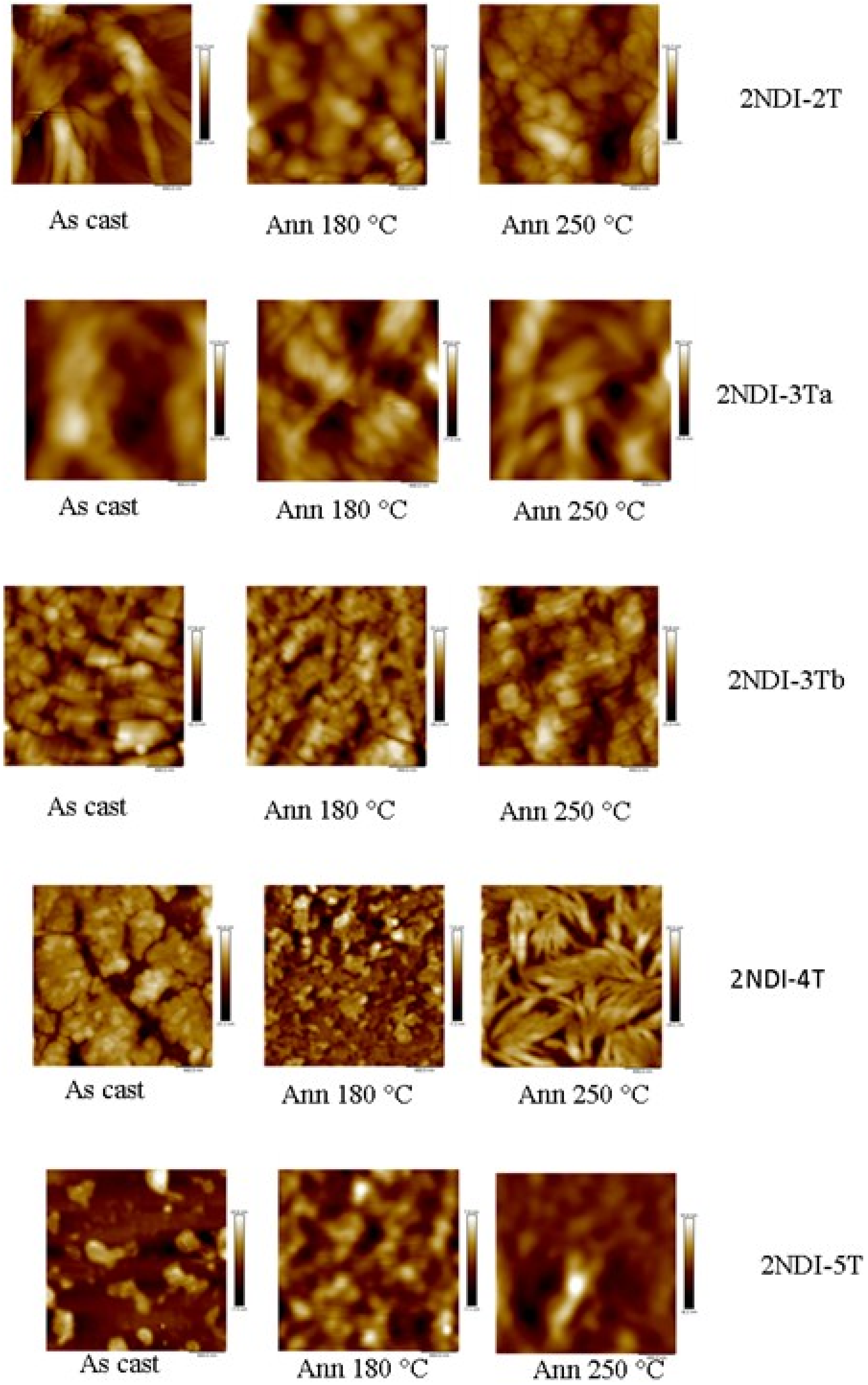


Figure S7.AFM images of thin films of the studied semiconductors deposited onto OTS-treated substrates and annealed at selected temperatures. Image size: 600x600 nm.

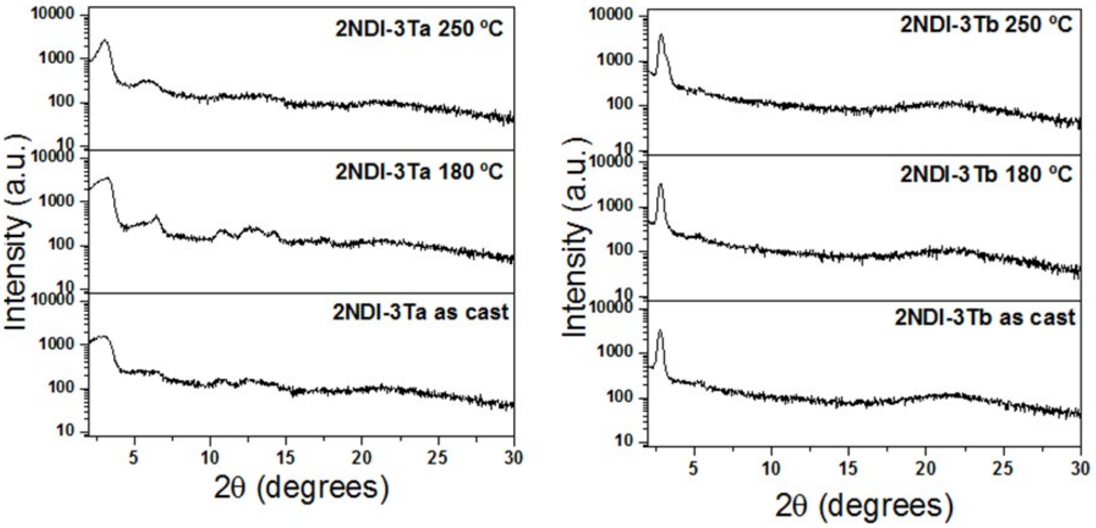


Figure S8. Comparison of the Out-of-plane XRD patterns of the two **2NDI-3T** derivatives at different annealing temperatures.

References

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