Electronic Supplementary Material (ESI) for RSC Advances.

Theoretical Investigations of the Small Molecule Acceptor Materials Based on Oligothiophene - Naphthalene Diimide in Organic Solar Cells

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Table S1 The test HOMO energy levels of **NDI-2T$_3$Me** at the **6-31G**** and **6-311G**** basis set levels. All energies are in eV.

Opt test	B3LYP	M06	PBE0	PBE0	Exp
		6-31G**		6-311G**	
HOMO	-5.18	-5.47	-5.43	-5.64	-5.6

Table S2 The test electronic absorption spectra of **NDI-2T$_3$Me** at the **6-311G**** basis set levels based on the optimization structure.

Absorption test	**B3LYP**	**PBE0**	**BMK**	**CAM-B3LYP**	**Exp**
λ/nm	**778**	**718**	**599**	**521**	**607**

Table S3 The calculated spectroscopic properties of **NDI-T_1Me**—**NDI-T_4Me**. All absorption wavelengths are in nm. (Assignment: H=HOMO, L=LUMO, L+2=LUMO+2.)

Oligomers	Transition	λ_{max}	*f*	Main configuration	λ_{EXP}
NDI-2T_1Me	S_0-S_1	497	0.4836	H→L (96%)	525
	S_0-S_9	292	0.4365	H→L+2 (49%)	
NDI-2T_2 Me	S_0-S_1	576	0.8875	H→L (95%)	604
	S_0-S_4	340	1.4851	H→L+2 (64%)	
NDI-2T_3 Me	S_0-S_1	614	1.1813	H→L (92%)	632
	S_0-S_4	376	2.1228	H→L+2 (63%)	
NDI-2T_4 Me	S_0-S_1	631	1.4124	H→L (86%)	638
	S_0-S_4	407	2.7418	H→L+2 (54%)	

Table S4 Electron density difference plots of electronic transition $S_0 \rightarrow S_1$ for **NDI-T_1Me** — **NDI-T_4Me**. ΔD is the electron transfer distance, Δq is the fraction of electron exchange, Ω is the overlap (normalization to the exchanged charge) between the regions of density depletion and increment.

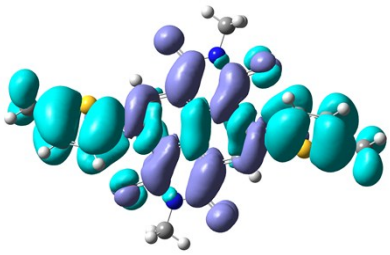
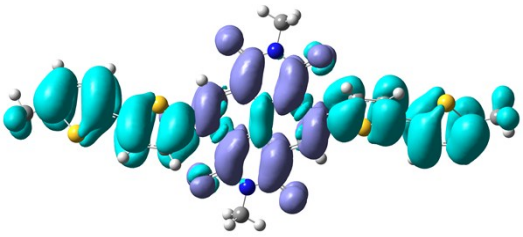
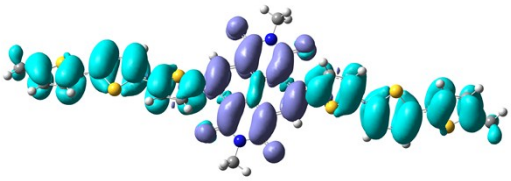
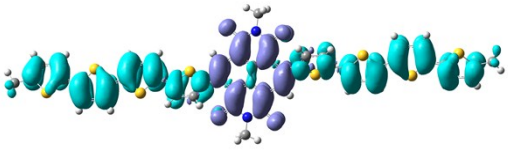
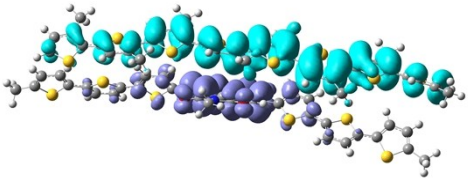
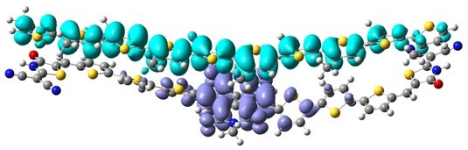
Oligomers	Electronic differential density plots	Data analysed
NDI-2T_1Me		ΔD=0.202Å Δq=1.0148 Ω=0.6016 $S_0 \rightarrow S_1$
NDI-2T_2 Me		ΔD=0.269Å Δq=1.1073 Ω=0.5797 $S_0 \rightarrow S_1$
NDI-2T_3 Me		ΔD=0.497Å Δq=1.1352 Ω=0.5246 $S_0 \rightarrow S_1$
NDI-2T_4 Me		ΔD=0.817Å Δq=1.1017 Ω=0.4201 $S_0 \rightarrow S_1$

Table S5 The hole mobility (μ_h) and its relative parameters (r is the intermolecular stacking distance, t_+ is the charge transfer integral, $k_{CT\text{-}h}$ is the charge transfer rate) for **NDI-T$_1$DCRD**, **NDI-T$_4$DCRD** and **NDI-T$_3$Me**.

Oligomers	λ_h/eV	r/eV	V_+/eV	$K_{CT\text{-}h}/S^{-1}$	$\mu_h/cm^2\cdot(V\cdot S)^{-1}$
NDI-2T$_3$Me	0.257	4.950	0.0044	5.32×10^{10}	2.54×10^{-3}
NDI-2T$_3$DCRD	0.181	4.825	0.0129	1.14×10^{12}	5.15×10^{-2}
NDI-2T$_4$DCRD	0.182	4.825	0.0021	2.98×10^{10}	1.35×10^{-3}

Table S6 Electron density difference plots of electronic transition $S_0 \rightarrow S_1$ for active blend layers **P3HT/Acceptor**. ΔD is the electron transfer distance, Δq is the fraction of electron exchange, Ω is the overlap (normalization to the exchanged charge) between the regions of density depletion and increment.

Oligomers	Electronic differential density plots	Data analysed
P3HT/NDI-2T$_3$ Me		S1:ΔD=5.342Å Δq=1.4357 Ω=0.0987
P3HT/NDI-2T$_3$ DCRD		S1:ΔD=5.924Å Δq=1.3537 Ω=0.0168

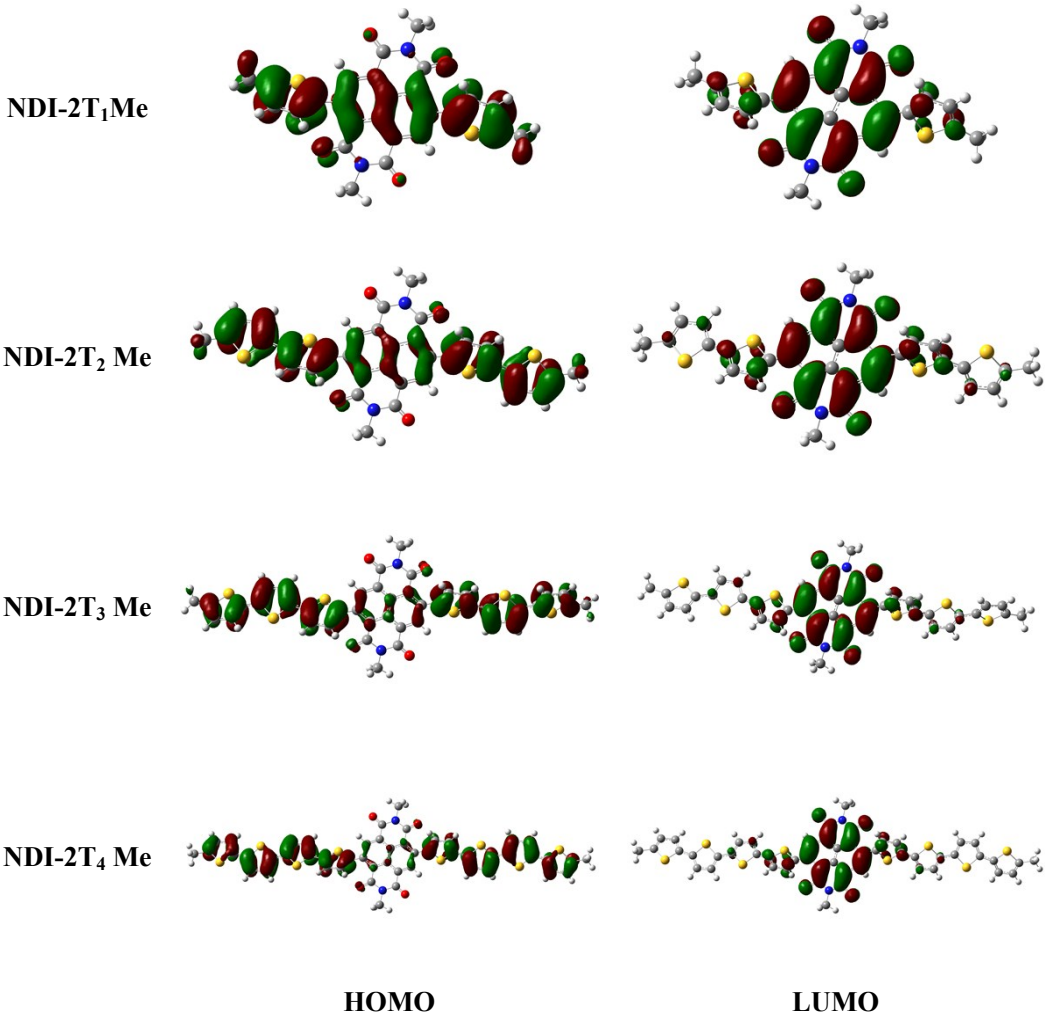


Fig. S1 The distributions of Frontier Molecular Orbitals of **NDI-T$_1$Me**—**NDI-T$_4$Me**.

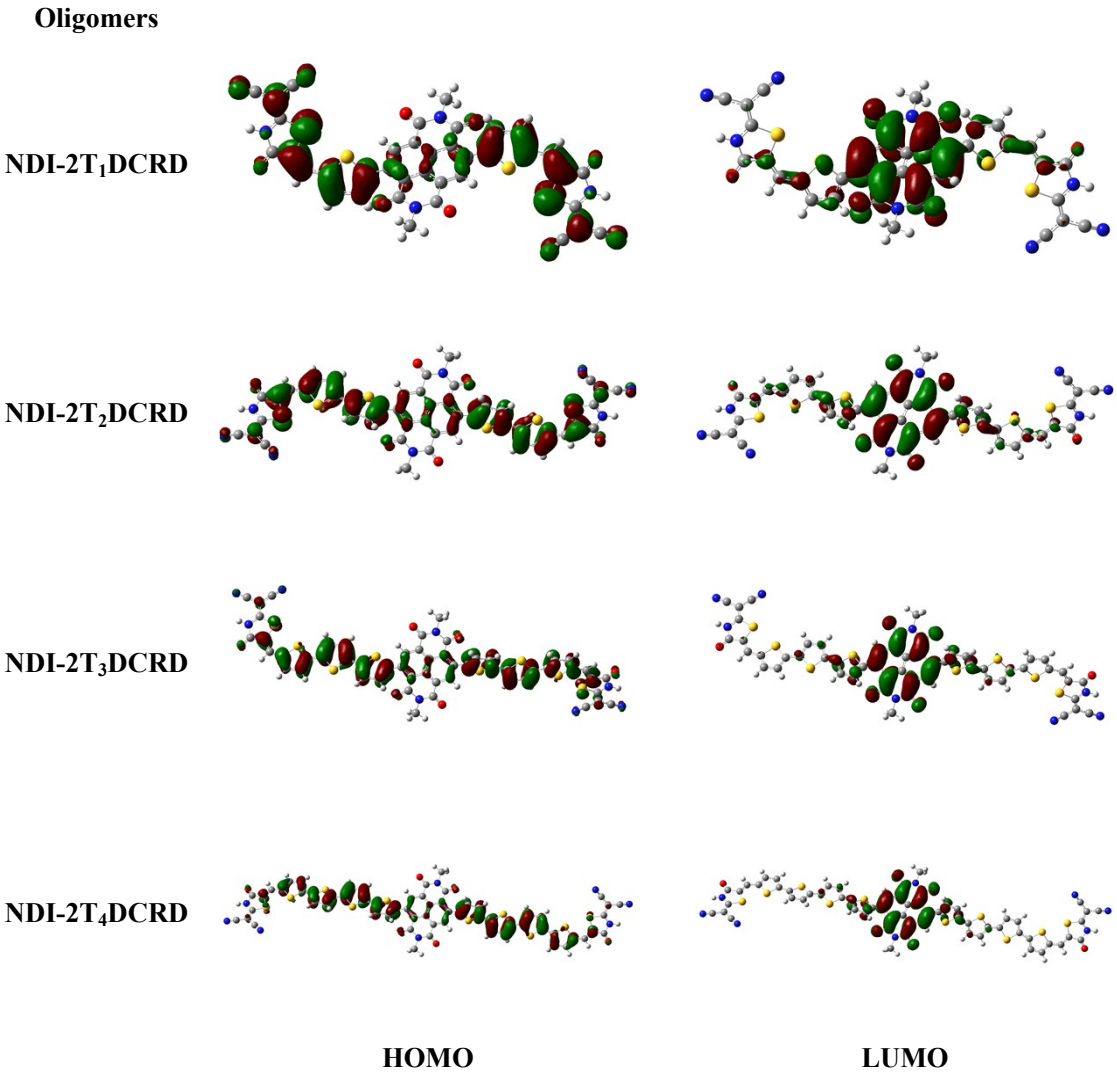


Fig. S2 The distributions of Frontier Molecular Orbitals.

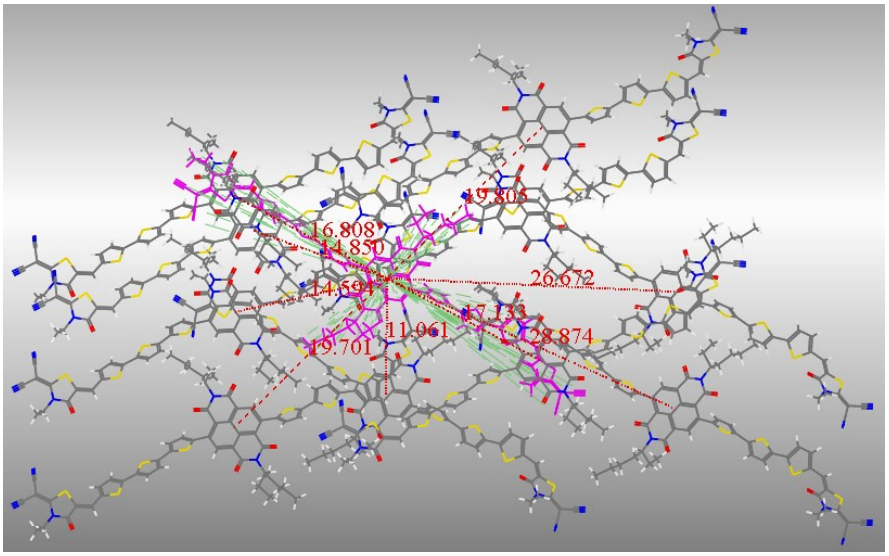


Fig. S3 The possible transfer paths of **NDI-2T$_3$DCVRD** in a supercell.

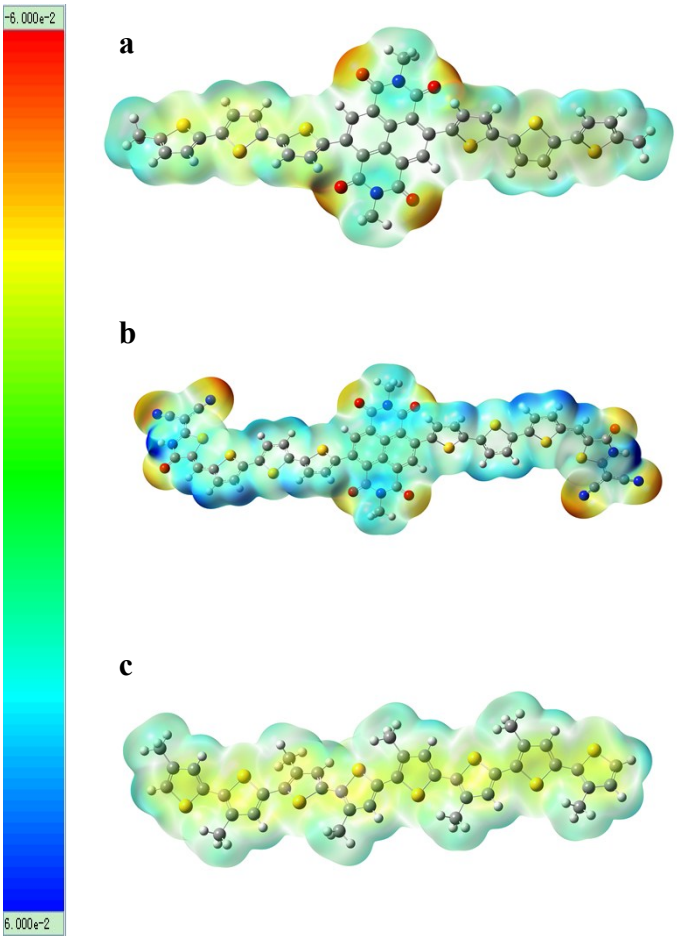


Fig. S4 The scatter diagrams of electrostatic potential of **NDI-2T$_3$Me (a)**, **NDI-2T$_3$DCRD (b)** and **P3HT (c).**

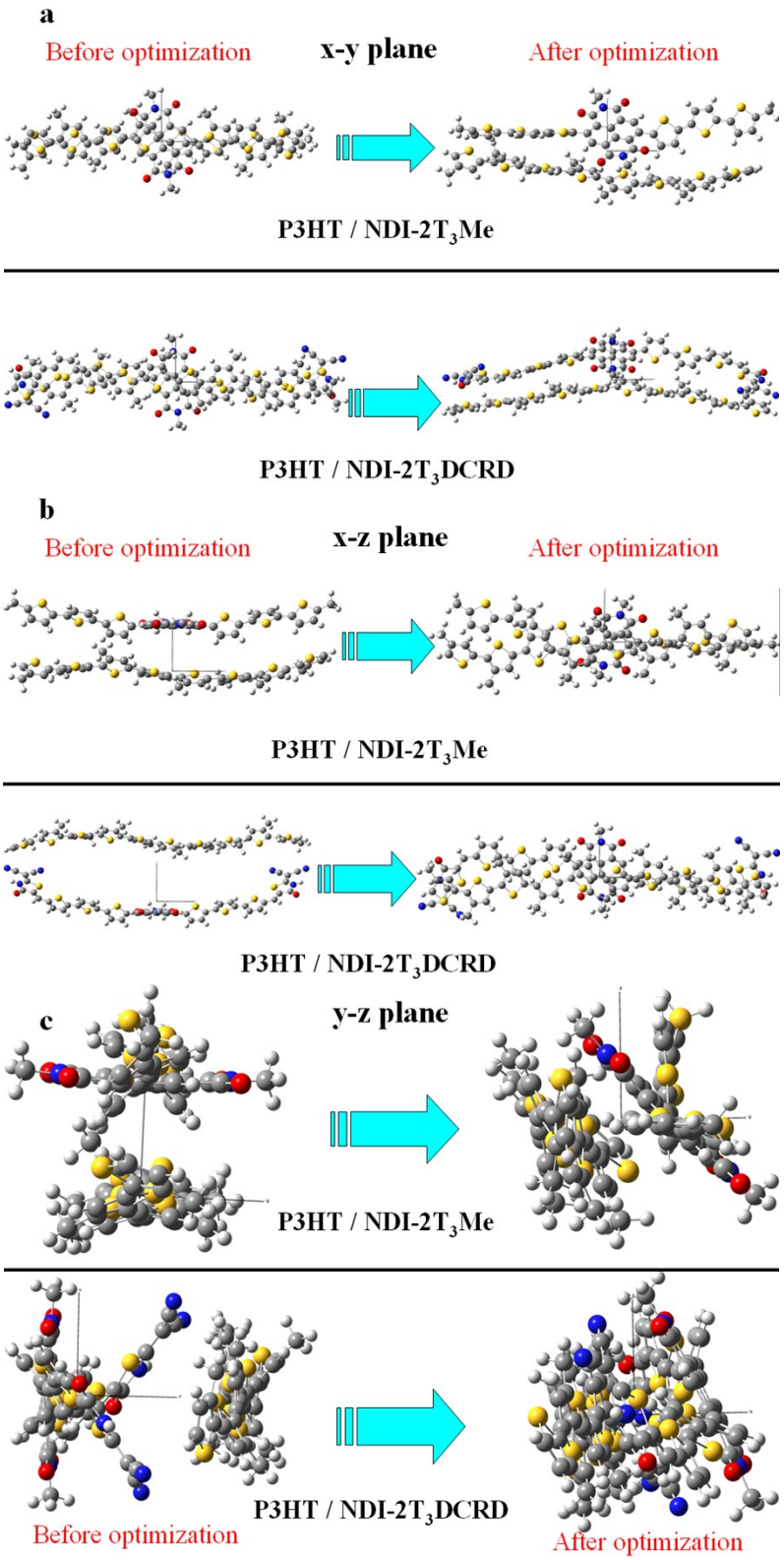


Fig. S5 The different-plane spatial structure of **P3HT/Acceptor** based on the optimized geometry.

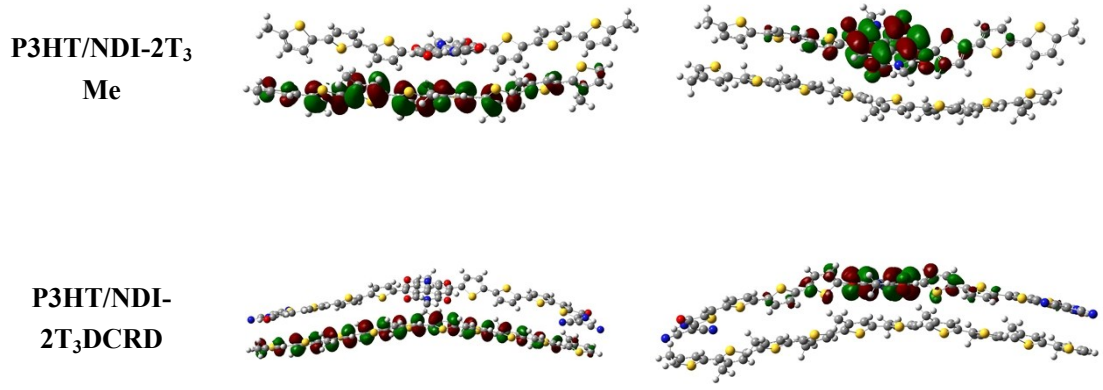


Fig. S6 The distributions of Frontier Molecular Orbitals of blend **P3HT/Acceptor**.