Supporting Information

Density Functional Study on the Effect of a New Ladder-type Structure with Different Substituent Groups (R = H, CH_3, OCH_3 and CN) for Donor-Acceptor Copolymers

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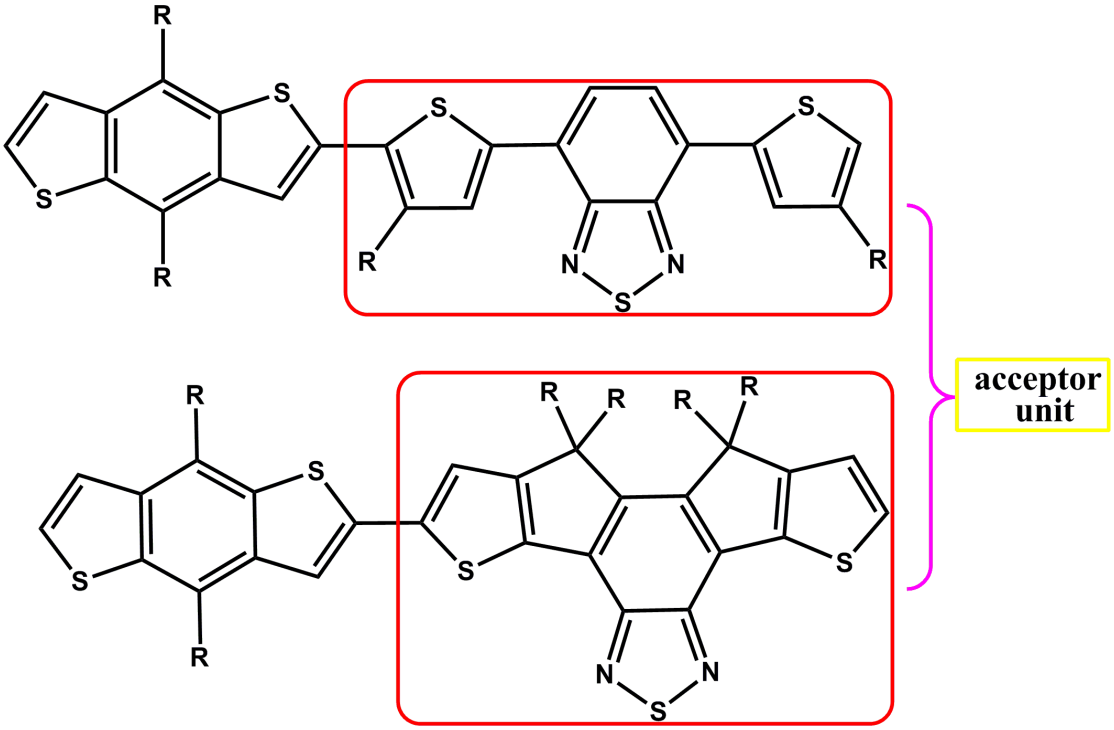
Table S1 HOMO energy (in eV), $\Delta E_{LU\text{-}HO}$ (in eV), absorption peaks: λ (in nm) and vertical transition energies of $S_0 \rightarrow S_1$: $E_{g,TD}$ (in eV) of P1 obtained in the gas phase with PBE0, B3LYP and BHandHLYP methods at 6-31G** basis set.

Method	Oligomer	HOMO	$\Delta E_{LU\text{-}HO}$	λ	$E_{g,TD}$	HOMO[a]	λ[a]
PBE0	M1	-5.22	2.64	566 381	2.19	-5.40	625 425
	D1	-5.05	2.35	649 426	1.91		
B3LYP	M1	-4.99	2.33	612 401	2.02		
	D1	-4.82	2.04	708 456	1.75		
BHand-HLYP	M1	-5.92	4.26	447 314	2.77		
	D1	-5.74	3.96	483 329	2.56		

[a]experimental values (from reference15) "M" and "D" denote monomer and dimer, respectively.

Table S2 The calculated NBO charge of the corresponding electron-deficient units for those monomers (M1-M3, M2a-M2c and M2a′-M2c′) at PBE0/6-311G** level are listed in the table. "**M**" means monomer.



	M1	M2	M2a	M2b	M2c	M2a′	M2b′	M2c′	M3
Charge[a]	0.012	0.017	0.019	0.002	-0.010	0.005	-0.007	-0.016	-0.039

[a] The values of charge from positive to negative denote that the electron-withdrawing ability of the electron-deficient units strengthen gradually.

Table S3 Calculated HOMO energies (eV) and electronic transitions of oligomers (monomer (M), dimer (D) and trimer (T)) obtained in the gas phase with PBE0 methods at 6-311G** basis set.

Oligomer	Excitation energy (eV and nm)		HOMO
M1	2.20	563	-5.40
	3.36	369	
D1	1.95	636	-5.24
	2.95	420	
T1	1.86	667	-5.20
	2.90	427	

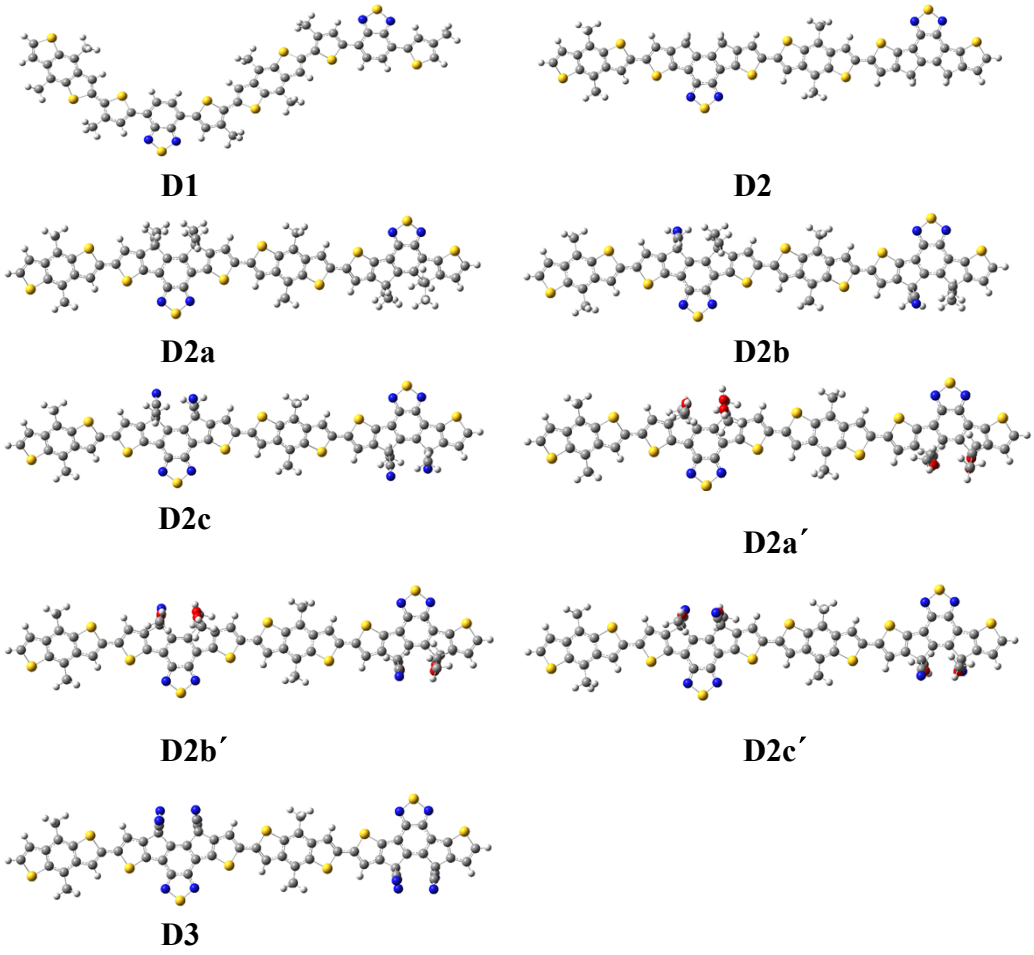


Fig. S1 The optimized geometries of all investigated monomers calculated at PBE0/6-311G**level. Color code: yellow (S), blue (N), black (C), red (O) and grey (H). In molecular structures, the alkyl (alkoxy) group has been replaced with methyl (methoxyl).

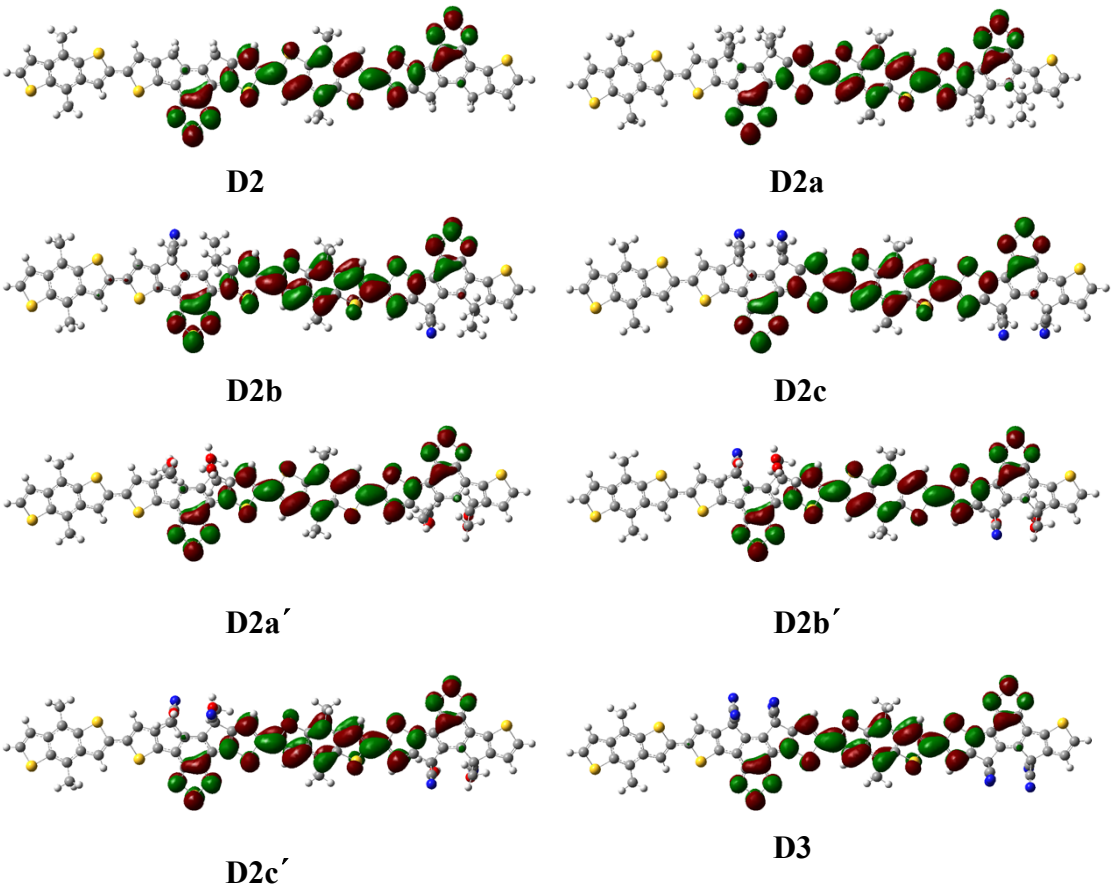


Fig. S2 Electron density plots of LUMO+2 for all the dimers (P2, P2a-P2c, P2a′-P2c′ and P3) computed at PBE0/6-311G** level.