Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

On the relations between backbone thiophene functionalization and charge carrier mobility of A-D-A type of small molecules

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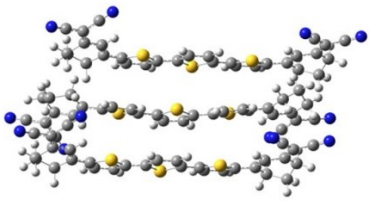
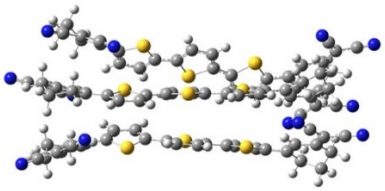
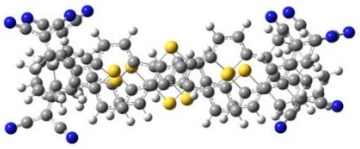
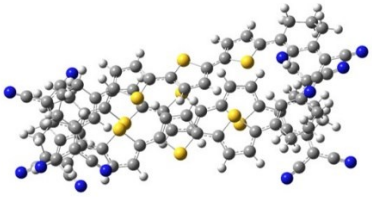
	before optimization	after optimization
Top view		
Side view		

Figure S1. Trimer configuration of DCC3T-H based on B3LYP(GD3)/6-31G(d) level of theory.

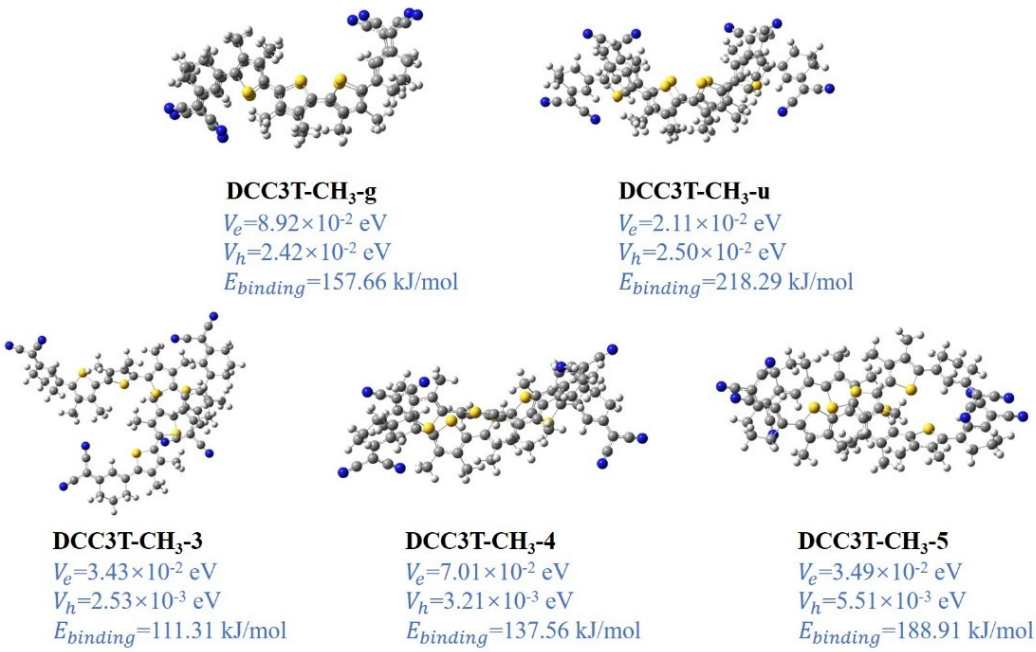


Figure S2. Optimized structures of probable dimer configurations of the double substituted DCC3T-CH_3 after geometric optimization, with the electronic coupling for electron transfer (V_e) and hole transfer (V_h) and the binding energy.

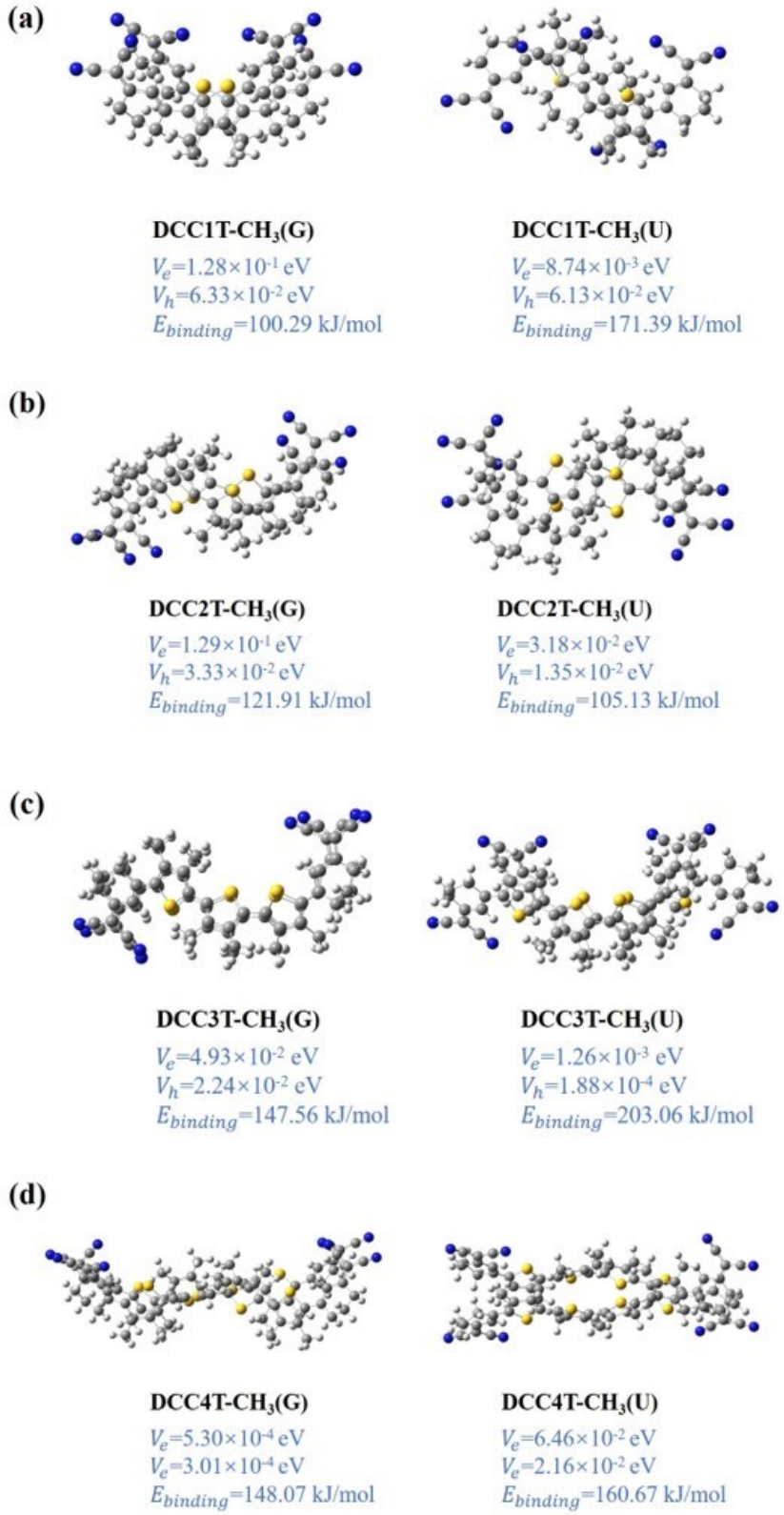


Figure S3. Dimer configurations of DCCnT-CH_3 (n=1, 2, 3, 4), with the electronic coupling for electron transfer (V_e) and hole transfer (V_h) and the binding energy. G means parallel packing and U means anti-parallel packing. The binding energy of U configurations are larger than G configurations, except for DCC2T-CH_3.

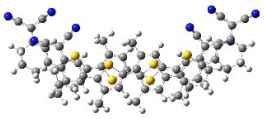
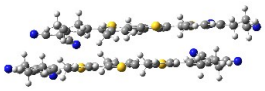
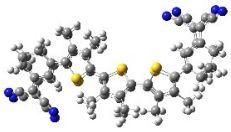
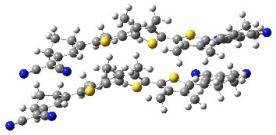
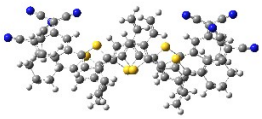
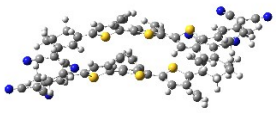
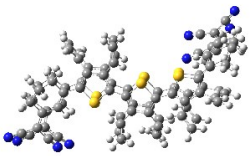
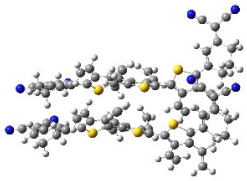
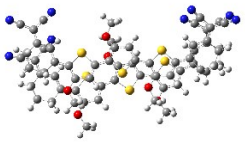
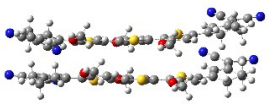
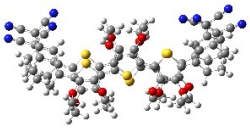
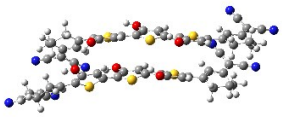
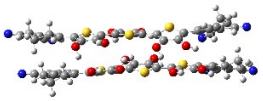
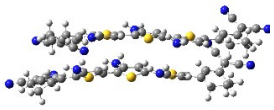
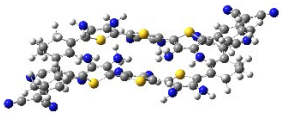
G configurations	substitution	Top	Side
DCC3T-CH_3	*single*		
	double		
DCC3T-$CHCH_2$	*single*		
	double		
DCC3T-OCH_3	*single*		
	double		
DCC3T-OH	*single*		
	double		
DCC3T-NH_2	*single*		
	double		

Figure S4. The optimized parallel (G) dimer configurations of DCC3T-X (X= H, $CHCH_2$, OCH_3, OH, NH_2) based on B3LYP(GD3)/6-31G(d) theory level.

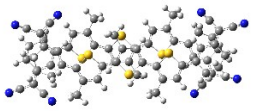
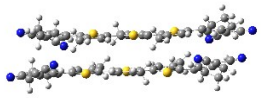
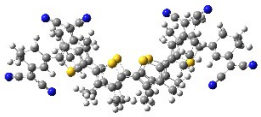
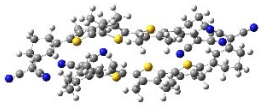
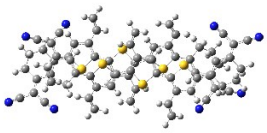
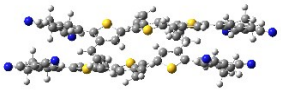
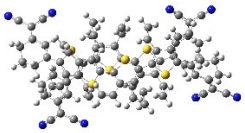
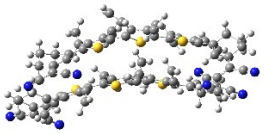
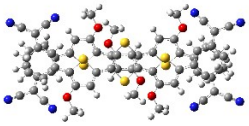
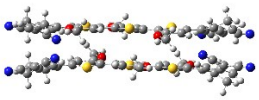
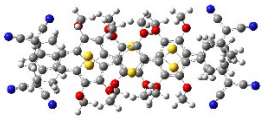
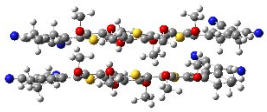
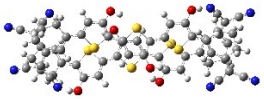
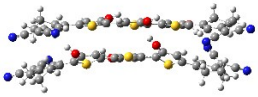
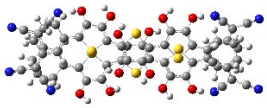
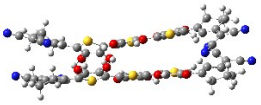
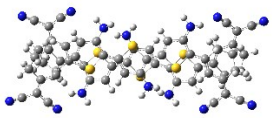
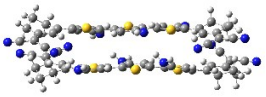
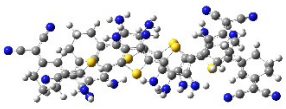
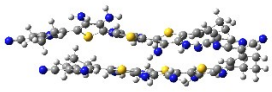
U configurations	substitution	Top	Side
DCC3T-CH_3	*single*		
	double		
DCC3T-$CHCH_2$	*single*		
	double		
DCC3T-OCH_3	*single*		
	double		
DCC3T-OH	*single*		
	double		
DCC3T-NH_2	*single*		
	double		

Figure S5. The optimized parallel (G) dimer configurations of DCC3T-X (X= H, CHCH2, OCH3, OH, NH2) based on B3LYP(GD3)/6-31G(d) theory level.

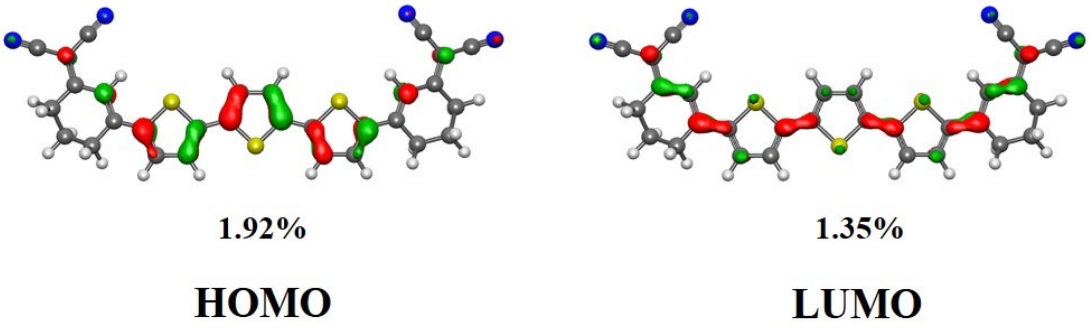
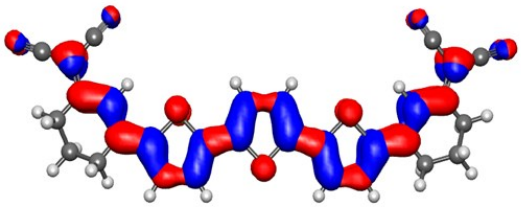


Figure S6. HOMO and LUMO orbitals of DCC3T-H with the contributions (listed percentage) of functionalized groups based on CAM-B3LYP/6-31G(d) level of theory. Isosurface=0.05.



DCC3T-H

H→L=87.2 %;
E-E_0=2.53 eV; q_{CT}=0.46

Figure S7. The CDD maps of the first singlet excited state of DCC3T-H based on TDDFT/CAM-B3LYP/6-31G(d) .Isosurface=0.001, H→L: percentage of the HOMO→LUMO transition; *E-E₀*: excitation energy; q_{CT}: the amount of transferred charge in unit of elementary charge. Color of codes: red-electron; blue-hole.

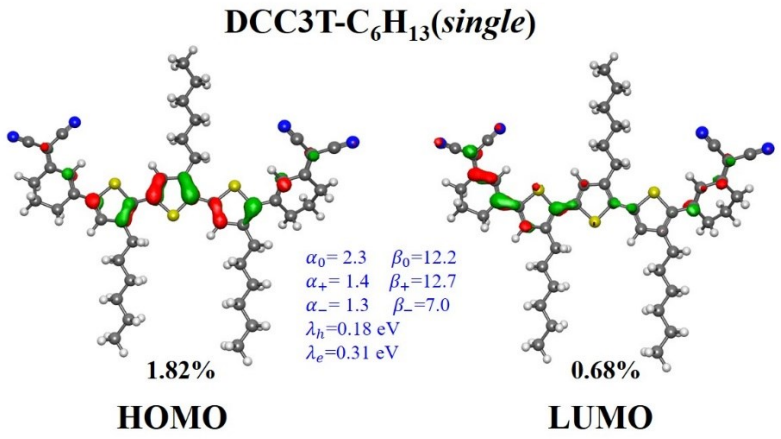


Figure S8. HOMO and LUMO orbitals of single substituted DCC3T-C_6H_{13} with the contributions (listed percentage) of functionalized groups based on CAM-B3LYP/6-31G(d) level of theory (Isosurface=0.05). The dihedral angles of neutral (α_0, β_0) and charged ($\alpha_\pm$, $\beta_\pm$) states and the inner reorganization energy of electron transfer (λ_e) and hole transfer (λ_h) based on B3LYP/6-31G(d) level of theory are also listed.

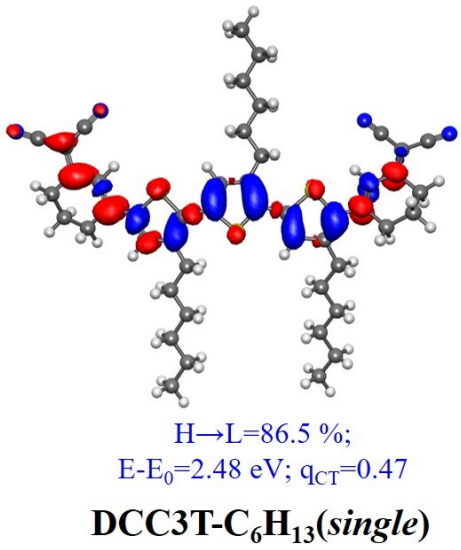


Figure S9. The CDD maps of the first singlet excited state based on TDDFT/CAM-B3LYP/6-31G(d). Isosurface=0.001, H→L: percentage of the HOMO→LUMO transition; *E-E*$_0$: excitation energy; q_{CT}: the amount of transferred charge in unit of elementary charge. Color of codes: red-electron; blue-hole.

The results of geometry, FMOs and the first excited state of DCC3T-C_6H_{13} are close to those of DCC3T-CH_3, indicating the long alkyl sidechain does little effect on the properties of monomer.

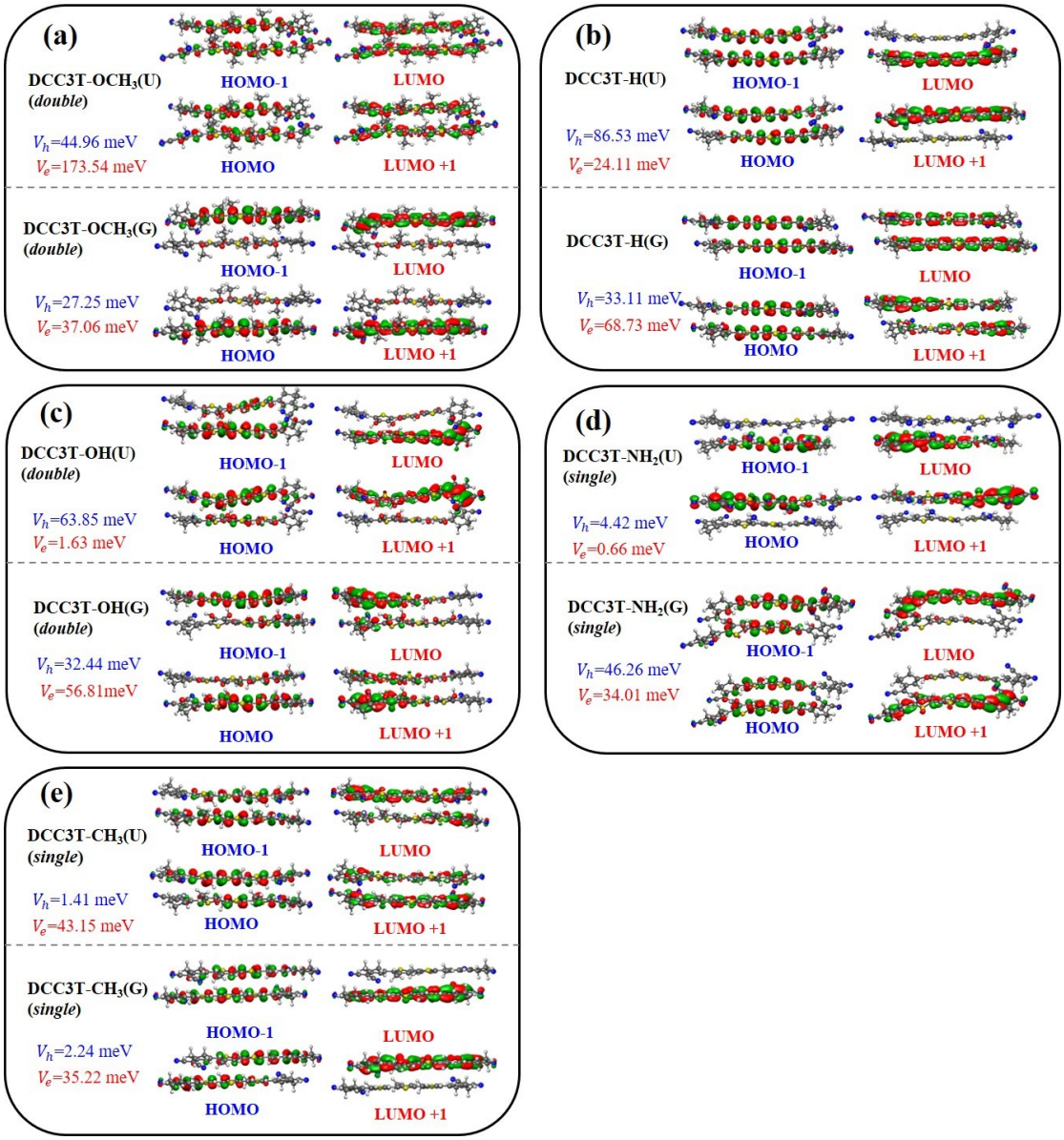


Figure S10. FMOs DCC3T-X dimers based on CAM-B3LYP/6-31G(d) theory level, with the calculated overlap integral (S_{if}) and electronic coupling ($V_{e,h}$). For clarity, the Isosurface value is set to 0.03. a: double substituted DCC3T-OCH_3; b: DCC3T-H; c: double substituted DCC3T-OH(U); d: single substituted DCC3T-NH_2; e: single substituted DCC3T-CH_3.

For single substituted DCC3T-NH_2, the FMOs are delocalized on single molecule, besides, the HOMO(LUMO+1) and HOMO-1(LUMO) are distributed on opposite sides, thus, the orbital overlap and electronic coupling are extremely small. For the

double substituted DCC3T-OCH_3(U), the FMOs are separated on two molecules with high symmetry, thus, the orbital overlap and electronic coupling are extremely large.

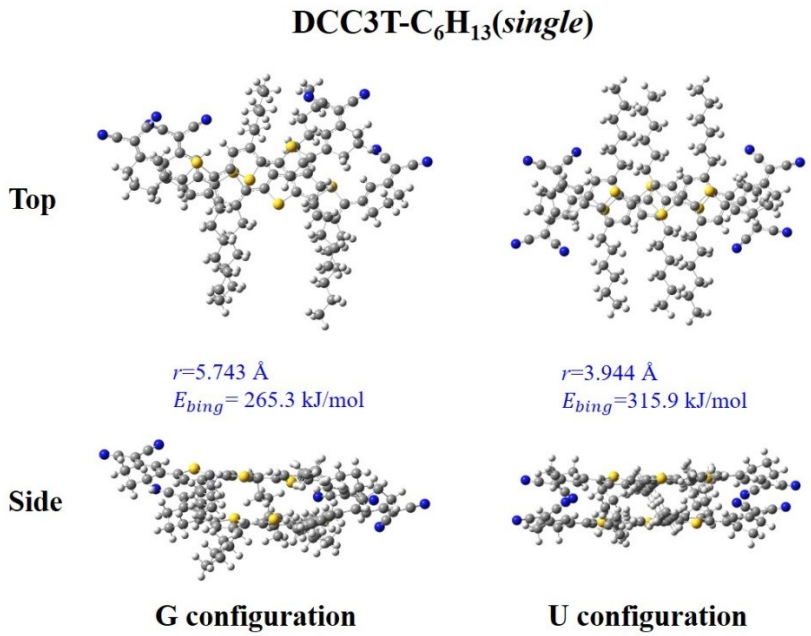


Figure S11. The optimized dimer structure of the single substituted DCC3T-C_6H_{13}, based on B3LYP(GD3)/6-31G(d) theory level. The geometry center distance (r) and binding energy ($E_{binding}$) are also listed. The results suggest U configuration is much stabler than G configuration in terms of binding energy, and the π-π stacking of U configuration is much stronger than G configuration due to smaller distance and better fitted molecular packing.

Table S1. Charge transfer distance (r, in Å), absolute value of electronic coupling ($|V_{e,h}|$in meV), charge transfer rate constant ($k_{e,h}$, in s^{-1}), inner reorganization energy (in eV) of electron transfer (λ_e) and hole transfer (λ_h), and charge carrier mobility ($\mu_{e,h}$, in $cm^2V^{-1}s^{-1}$) of dimers of the single substituted DCC3T-C_6H_{13} and DCC3T-CH_3.

			Electron transport				Hole transport			
Molecule		r	$\|V_e\|$	λ_e	k_e	μ_e	$\|V_h\|$	λ_h	k_h	μ_h
DCC3T-C_6H_{13}(U)	*single*	3.944	14.83	0.31	3.43×10^{11}	2.20×10^{-2}	26.64	0.18	5.03×10^{12}	3.23×10^{-1}
DCC3T-C_6H_{13}(G)	*single*	5.743	11.52	0.31	2.07×10^{11}	1.33×10^{-2}	15.52	0.18	1.71×10^{12}	1.10×10^{-1}
DCC3T-CH_3(U)	*single*	3.638	43.15	0.32	2.58×10^{12}	6.62×10^{-2}	1.41	0.19	1.28×10^{10}	3.29×10^{-4}
DCC3T-CH_3(G)	*single*	4.713	35.22	0.32	1.72×10^{12}	7.44×10^{-2}	2.44	0.19	3.82×10^{10}	1.65×10^{-3}

The electron mobility of DCC3T-C_6H_{13} are slightly smaller than DCC3T-CH_3, while the hole mobility of DCC3T-C_6H_{13} are about one hundred times of DCC3T-CH_3. The

differences between DCC3T-CH_3 and DCC3T-C_6H_{13} can mainly attribute to the molecular packing. In DCC3T-CH_3 dimer, the π-π stacking between the A-D-A backbones of two molecules are much weaker than DCC3T-C_6H_{13}, as shown in Figure S3-4 and Figure S10. The results indicate the presence of alkyl side chain does good to the molecular packing and charge mobility.