Supporting Information

Theoretical study on the charge transport properties of three series dicyanomethylene quinoidal thiophene derivatives

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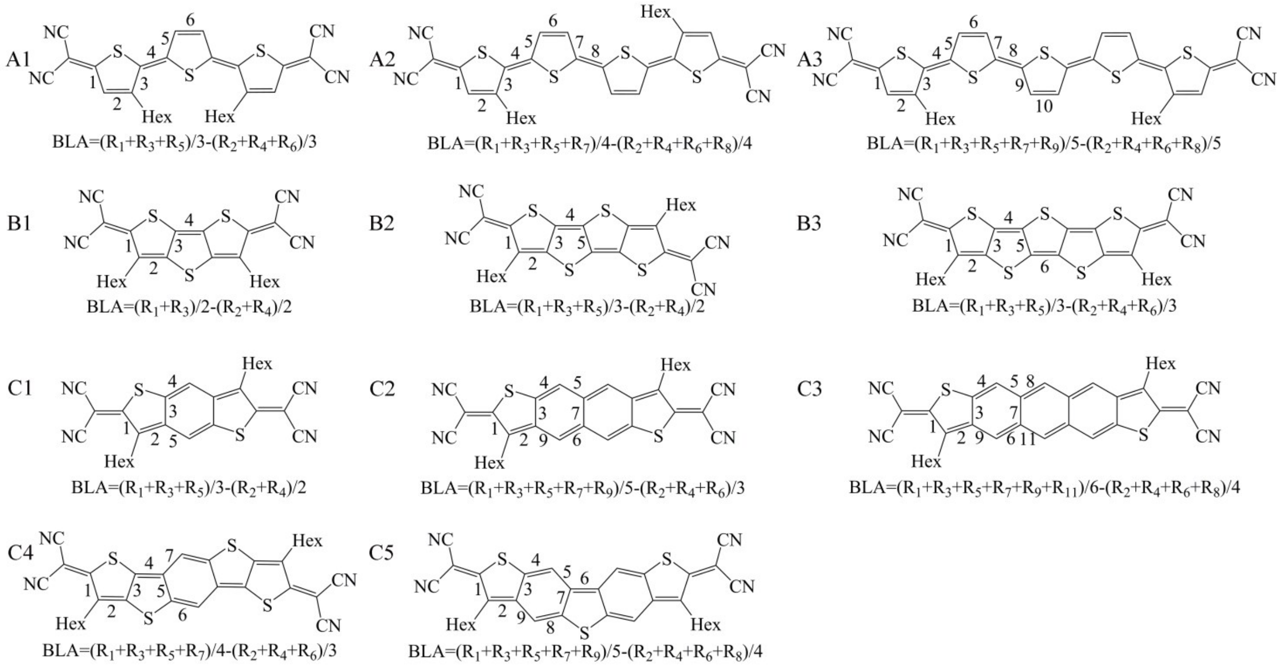

Fig.S1. Definition the bond length alternation in this study.

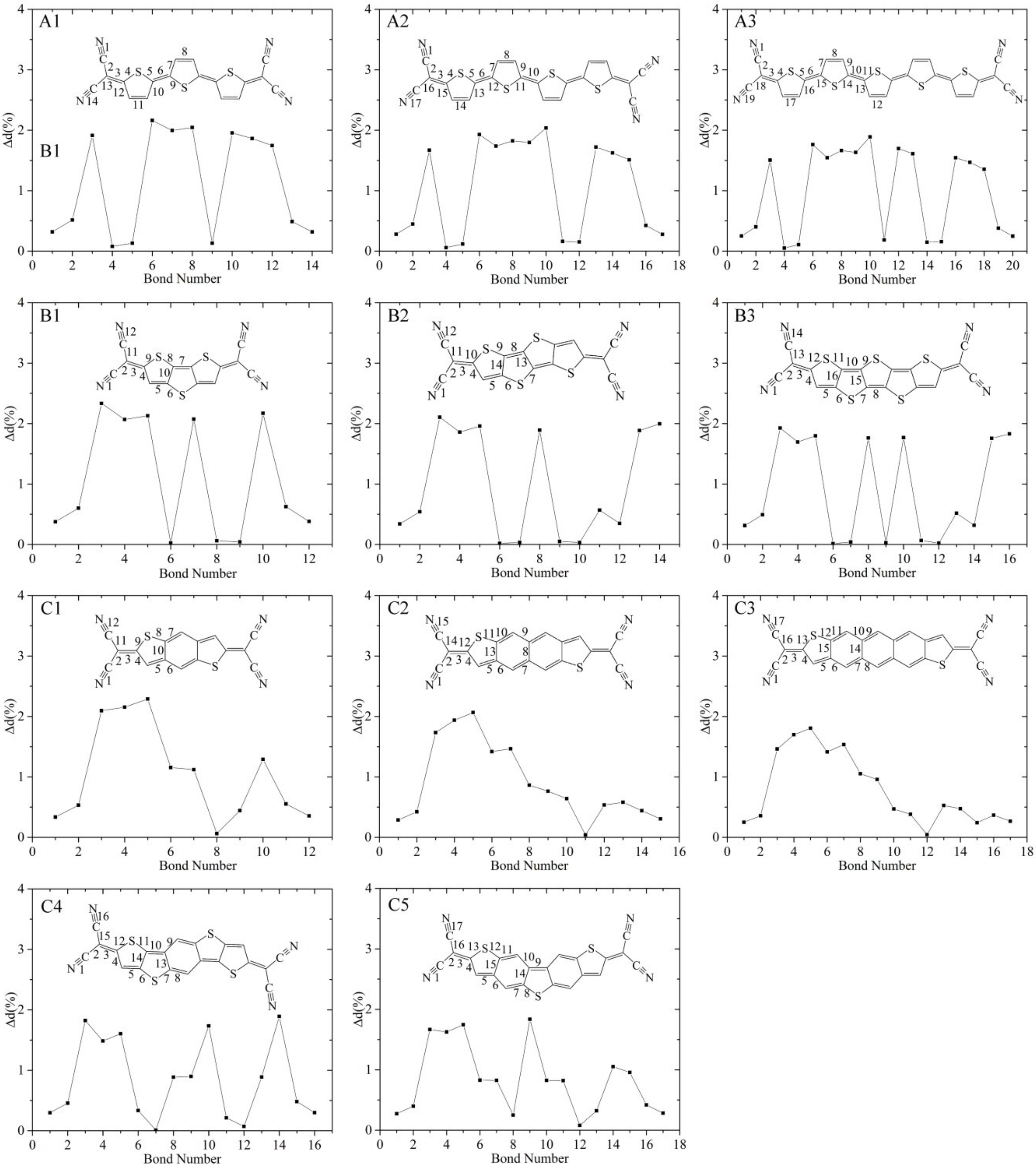

Fig. S2. Changes of bond length for all molecules from series ***A*** to series ***C*** in electron transfer process.

From the view of the specific changes of molecular geometries, the bond length changes (Δd%) of the ion geometry structure changes relative to neutral molecules during the electron transfer process and Δd_i is defined as: $\Delta d_i = \frac{\left| d_i^{anionic} - d_i^{neutral} \right|}{d_i^{neutral}} \times 100\%$, The structural parameters of the neutral and ionic states of studied molecules are shown in **Fig. S2**.

From **Fig. S2**, it can be found that the changes (Δd%) in bond length are different for the molecules with different number of rings and different types of connection during electron transfer process. For molecules in series ***A***, the largest Δd% appears in C=C double bond between the center and adjacent thiophenes (number 6 for ***A1***, number 10 for ***A2*** and ***A3***) and the Δd% is less than 2.2%. For series ***B***, the largest Δd% occurs in C=C double bond between outboard thiophene and dicyanomethylene (number 3) with a range from 1.9% to 2.3%. For series ***C***, Δds% is less than 2.3%. From ***C1*** to ***C3*** molecules, the largest Δd% presents at the C=C double bond of the outboard thiophenes (number 5, see **Fig. 3**), while it can be found at the C-C single bond of thienothiophene for ***C4*** molecule (number 14) and at the C=C double bond of the center thiophene for ***C5*** molecule (number 9). From the results of ***C4*** and ***C5*** molecules, it is possible to speculate that the interactions of thiophene-thiophene are stronger than that of benzene-thiophene so that the structural changes of series ***B*** are greater than series ***C***.

Table S1. Calculated total electronic energies of ***A2*** and ***A3*** molecules in both closed-shell singlet, singlet biradical states and triplet biradical states, and HOMO/LUMO energies (E_{HOMO}/E_{LUMO}, in eV) and electron reorganization (λ_e, in eV) at DFT functionals with 6-31G(d,p) basis set for ***A2*** and ***A3*** in singlet biradical.

	$E_{closed\text{-}shell\text{-}singlet}$	$E_{open\text{-}shell\text{-}singlet}$	$E_{open\text{-}shell\text{-}triplet}$	E_{HOMO}	E_{LUMO}	E_{gap}	λ_e (AP)	λ_e (NM)
A2	-3126.598	-3126.599	-3126.592	-5.63	-4.09	1.54	0.087	0.089
A3	-3678.414	-3678.419	-3678.416	-5.48	-4.02	1.46	0.052	0.052

Table S2. Calculated HOMO/LUMO energies (E_{HOMO}/E_{LUMO}, in eV) using several popular DFT functionals with 6-31G(d,p) basis set for ***B1*** and ***B2***.

B1	HOMO	LUMO	E_g	*B2*	HOMO	LUMO	E_g
B3LYP	-6.32	-4.21	2.11	B3LYP	-6.07	-4.28	1.79
PBE0	-6.57	-4.27	2.30	PBE0	-6.30	-4.30	1.99
M06-2X	-7.34	-3.73	3.61	M06-2X	-7.01	-3.81	3.19
exp	-6.13	-4.22		exp		-4.3	1.8

Table S3. Calculated HOMO/LUMO energies (E_{HOMO}/E_{LUMO}, in eV) using B3LYP functional combined with different basis sets for ***B1*** and ***B2***.

B1	HOMO	LUMO	E_g	*B2*	HOMO	LUMO	E_g
6-31G(d,p)	-6.32	-4.21	2.11	6-31G(d,p)	-6.07	-4.28	1.79
6-31G+(d,p)	-6.59	-4.51	2.08	6-31G+(d,p)	-6.31	-4.53	1.79
6-311G(d,p)	-6.55	-4.46	2.09	6-311G(d,p)	-6.28	-4.48	1.80

6-311G+(d,p)	-6.63	-4.54	2.09	6-311G+(d,p)	-6.36	-4.56	1.80

We selected hybrid functionals with different Hartree-Fock exchange percentage (HF%), such as, B3LYP (20%), PBE0 (25%) and M06-2X (54%) to test the dependence with HOMO/LUMO energy and band gaps for ***B1*** and ***B2***. From Table **S2**, as the HF% increase, HOMO energies and LUMO energies are decreased continuously and the band gap increased. The experimental values of HOMO and LUMO are respectively -6.13eV and -4.22eV for ***B1***, the experimental value of LUMO is -4.3eV and the gap is 1.8eV for ***B2***. Obviously, the HOMO/LUMO energies calculated at the B3LYP/6-31G(d,p) level is in reasonable agreement with the known experimental values.

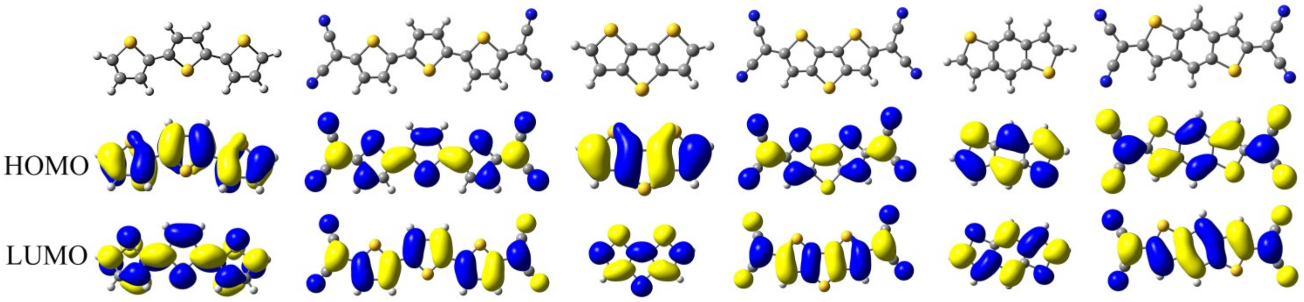

Fig S3. Electron-density contours [0.02 e bohr^{-3}] calculated for the frontier molecular orbitals of studied molecules without and with dicyanomethylene for ***a1***, ***b1*** and ***c1***.

As illustrated in **Fig S3**, the quinoidal structure with dicyanomethylene was compared with the corresponding aromatic structure, the electron-density contours of these orbitals are reversed due to the HOMO→LUMO excitation and this is the reason why quinoidal compounds have small gaps.

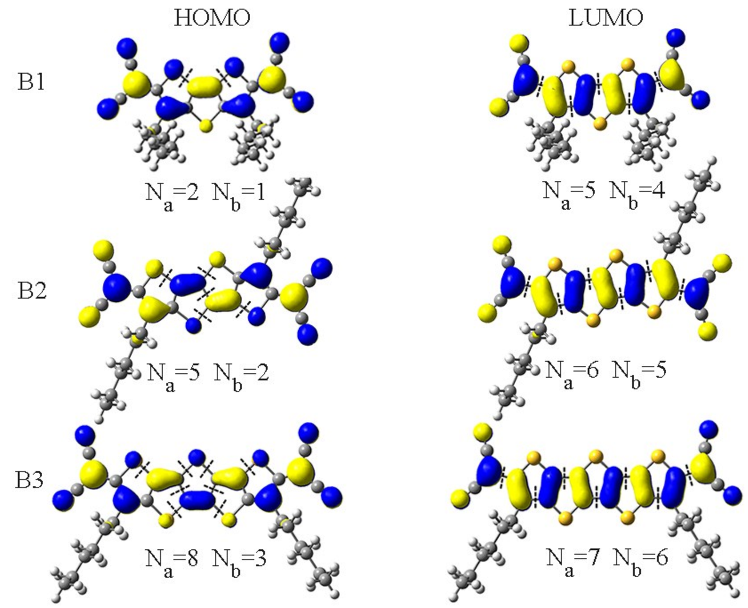

Fig. S4. Frontier molecular orbitals (0.03 a.u.) for molecules in series ***A***, the dotted line represent the antibond, N_a is the number of antibond and N_b is the number of bond.

Table S4. Calculated charge transport parameters for ***A1*** and ***A2*** dimers: intermolecular distance r (Å), hole transfer integral (meV), hole charge transport rate k (h), hopping probability p (h) and hole charge mobility μ_h ($cm^2V^{-1}s^{-1}$).

	R(Å)	V_h(meV)	k_h	p	$\bar{\mu}_h$($cm^2V^{-1}s^{-1}$)
A1	5.34	92.11	2.37×10^{14}	0.88	3.93 (2D)
	8.48	27.50	2.12×10^{13}	0.08	
	13.21	0.62	1.07×10^{10}	0.00	
	13.54	10.27	2.95×10^{12}	0.01	
	14.51	12.48	4.35×10^{12}	0.02	
	15.46	9.92	2.75×10^{12}	0.01	
A2	6.29	80.00	1.83×10^{14}	0.99	14.31 (1D)
	8.61	3.81	4.15×10^{11}	0.00	
	15.25	6.90	1.36×10^{12}	0.01	

Table S5. Reorganization energies (λs) were calculated by four site method of the studied molecules (without dicyanomethylene) obtained in B3LYP/6-31G** theory level (in eV).

	a1*	***a2****	***a3****	***b1****	***b2****	***b3****	***c1****	***c2****	***c3****	***c4****	***c5****
λ_1	0.15	0.14	0.12	0.16	0.15	0.13	0.15	0.11	0.08	0.12	0.12
λ_2	0.20	0.18	0.15	0.16	0.15	0.14	0.15	0.11	0.08	0.12	0.12

λ	0.35	0.32	0.28	0.32	0.29	0.27	0.30	0.21	0.16	0.23	0.24

A four-point method was used to calculate the reorganization energies of aromatic oligothiophene(without dicyanomethylene) and the results are shown in **Table S5**. Compare the **Table S5** and **Table 1,** the λ_1 and λ_2 of the thienothiophenes and benzothiophenes are almost equal whether or not the dicyanomethylene is introduced, and the oligothiophenes are quite different. For quioidal oligothiophenes, the double-bond character of the inter-ring bonds restricts internal rotation around C-C single bond and the compounds are essentially planar, so the λ_1 and λ_2 are almost equal, In the case of aromatic oligothiophenes (without dicyanomethylene) is the opposite.

Table S6. Compare all predicted crystal properties

	Enthalpy(eV)	**Single molecule enthalpy(eV)**	**Density(g/cm^3)**
C1-Z-1	-396.951	-396.951	1.118
C1-Z-2	-794.203	-397.102	1.200
C2-Z-1	-441.026	-441.026	1.326
C2-Z-2	-882.164	-441.082	1.272

Because at the given temperature and pressure, the crystal structure of the known molecules should be only one (except for eutectic conditions), so Z = 1 and Z = 2(that is single unit cell has one or two molecules) crystals were compared to find the most reliable crystal, situation as Table **S6.** As can be seen from Table **S6**, the single molecule enthalpy (the enthalpy is divided by the number of molecules in a single cell) of ***C1*** and ***C2*** molecules for Z=1 and Z=2 is almost equal, there is almost no interaction between two molecules in a unit cell, same to two repeating units at Z=1 condition. Therefore, the crystal structure of ***C1*** and ***C2*** molecules should be Z = 1 and the density is close.

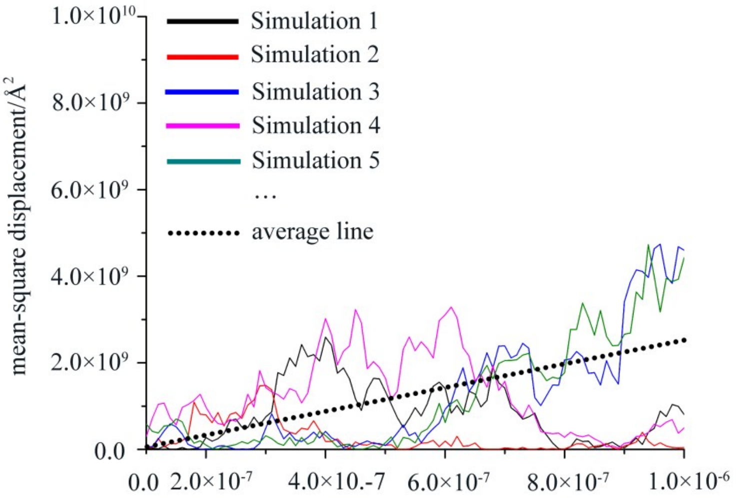

Fig S5. A typical evolution of the square displacement of five individual simulations and the mean-square displacement over two thousand simulations.