

Supporting Information

Theoretical Studies on the Effects of π -Bridge Engineering on the Photoelectric Performance of Y6

Meizhen Tao ^{a,b}, Liang Peng ^{b,c,d*}, Feng Long Gu ^{b,c,d*}

^a School of Chemistry, South China Normal University, Guangzhou 510006, China

^b MOE Key Laboratory of Environmental Theoretical Chemistry, South China Normal University, Guangzhou 510006, China

^c SCNU Environmental Research Institute, Guangdong Provincial Key Laboratory of Chemical Pollution and Environmental Safety, South China Normal University, Guangzhou 510006, China

^d School of Environment, South China Normal University, Guangzhou 510006, China

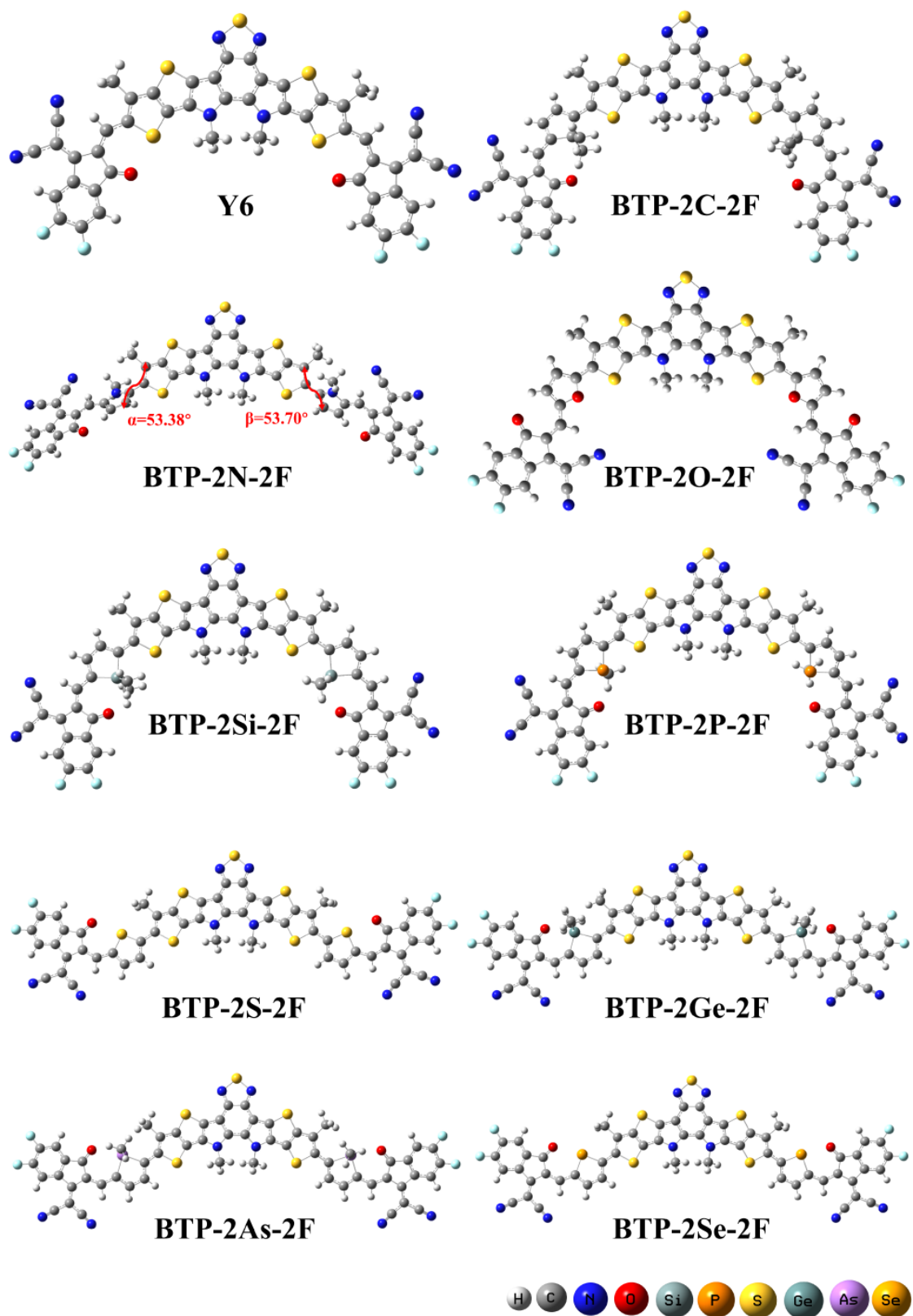


Figure S1. Molecular configurations of Y6 and its different types of π -bridge derivatives after optimization are obtained at the level of B3LYP/6-31+G (d).

As can be seen from Figure S1, the introduction of nine different types of π -bridge units between the TPBT unit and 2FIC unit of Y6 has an important effect on the configuration of Y6. For instance, the 2FIC unit of BTP-2O-2F, BTP-2S-2F, BTP-2Ge-2F, BTP-2As-2F, and BTP-2Se-2F are flipped compared with Y6, which may be attributed to the different interactions of the heteroatoms in the five-membered ring π -bridges with the sulfur atom in the TPBT unit and the oxygen atom in the 2FIC unit. Among them, the oxygen atom of the π -bridge in BTP-2O-2F has a non-covalent interaction with the sulfur atom in the TPBT unit but repulsion with the oxygen atom in the 2FIC unit, so that BTP-2O-2F exhibits the conformation in Figure S1. In addition, the molecular backbone of BTP-2N-2F is deformed and distorted with poor planarity (53° - 54° out of plane) due to certain repulsion of the nitrogen atom of the π -bridge in BTP-2N-2F with both the sulfur atom in the TPBT unit and the oxygen atom in the 2FIC unit. Based on the above analysis, the effects of the introduction of different types of π -bridges on the conformation and planarity of the molecule are indeed non-negligible, and the changes in conformation and planarity may eventually affect the dipole moment and light absorption properties of the molecule.

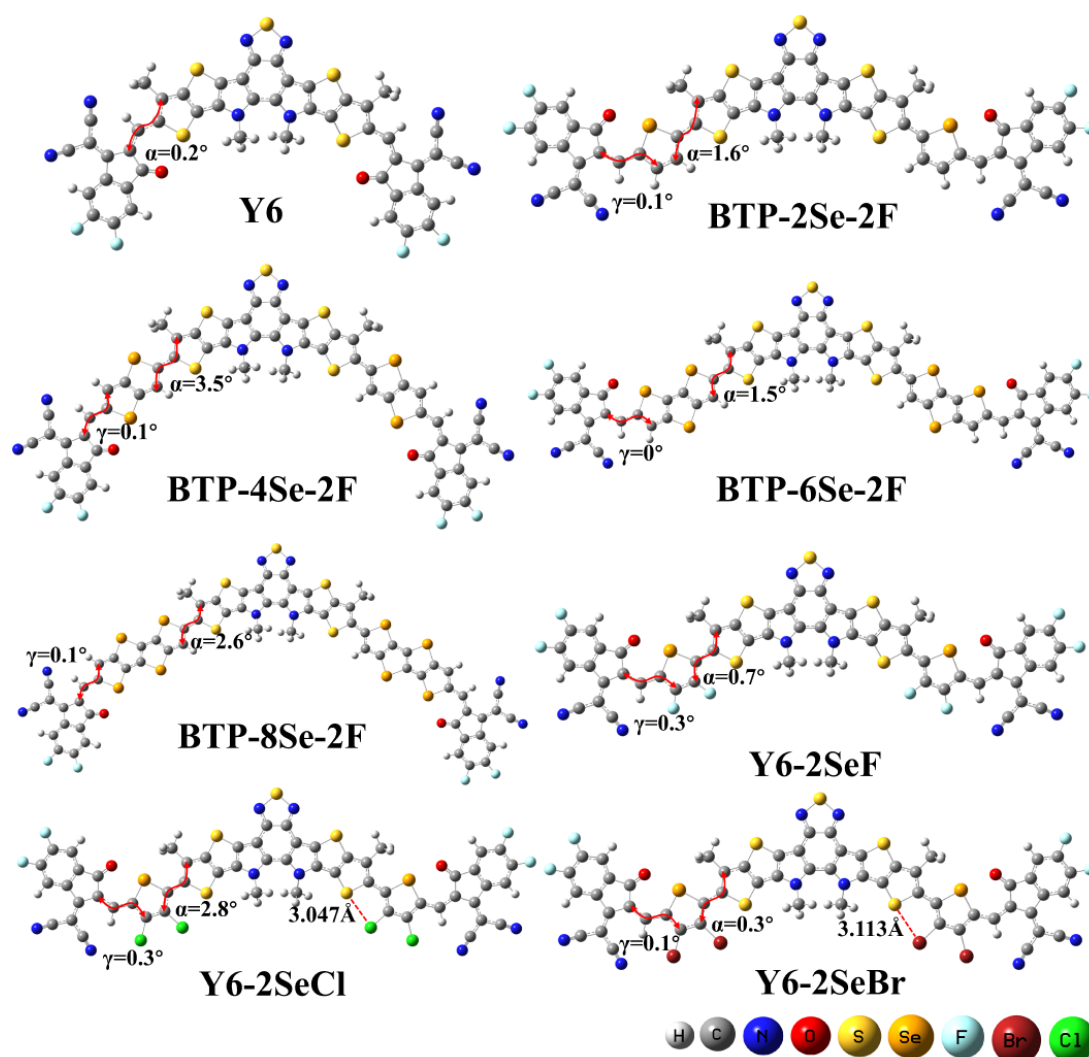


Figure S2. Molecular configurations of Y6 and its seven selenophene π -bridge derivatives after optimization are obtained at the level of B3LYP/6-31+G (d)/PCM.

The geometry structures of Y6 and its seven selenophene π -bridge derivatives optimized at the level of B3LYP/6-31+G (d)/PCM are illustrated in Figure S2. The BTP-4Se-2F and BTP-8Se-2F show no significant change in the orientation of the 2FIC unit compared to the Y6, but the 2FIC units of BTP-2Se-2F and BTP-6Se-2F are flipped. It may be due to the repulsion between the selenium atoms in π -bridge and the sulfur atom in the TPBT unit, and the attraction of the other selenium atoms in π -bridge to the oxygen atom in the 2FIC unit, so the selenium atoms in selenophene tend to be on the opposite side from the sulfur atom in the TPBT unit and on the same side as the oxygen atom in the 2FIC unit. As a result, the configurations of BTP-2Se-2F and BTP-6Se-2F alter from the original "banana" of Y6 to "W". Judging from the dihedral angle between the

optimized π -bridge unit and the TPBT unit, the larger atomic radius and size of chlorine atom cause a spatial site resistance effect, so the TPBT unit and π -bridge unit of BTP-2SeCl-2F have a certain twist compared with BTP-2Se-2F.^{1,2} BTP-2SeF-2F and BTP-2SeBr-2F form better planar structures than BTP-2Se-2F due to the non-covalent interaction of the fluorine atoms in the selenophene π -bridge with the sulfur atom in the TPBT unit and the sulfur atom in the outermost thiophene of the TPBT unit is farther away from the bromine atom compared to the chlorine atom.² In conclusion, the π -bridge units of all derivatives maintain good co-planarity with the TPBT unit and 2FIC unit, which is beneficial for enhancing the intramolecular charge transfer (ICT) effects of the derivatives.

Table S1. The excitation energies (eV), oscillator strength, major orbital transition contribution, and the maximum absorption wavelength (λ_{max} (nm)) of Y6 and its selenophene π -bridge derivatives. The results are obtained at the level of CAM-B3LYP/6-31+G(d)/PCM.

Acceptors	States	Energy(eV)	λ_{max} (nm)	Oscillator strength	Transitions
Y6	$S_0 \rightarrow S_1$	2.04	598	2.79	H -> L 81.1%
BTP-2Se-2F	$S_0 \rightarrow S_1$	1.92	638	4.02	H -> L 66.9%
BTP-4Se-2F	$S_0 \rightarrow S_1$	1.92	626	3.51	H -> L 60.0%
BTP-6Se-2F	$S_0 \rightarrow S_1$	1.93	638	4.81	H -> L 52.5%
BTP-8Se-2F	$S_0 \rightarrow S_1$	1.94	628	4.24	H -> L 45.1%
BTP-2SeF-2F	$S_0 \rightarrow S_1$	1.89	650	4.04	H -> L 69.1%
BTP-2SeCl-2F	$S_0 \rightarrow S_1$	1.89	654	3.91	H -> L 68.2%
BTP-2SeBr-2F	$S_0 \rightarrow S_1$	1.89	654	3.87	H -> L 68.2%

Table S2. The electron recombination energies λ_e (eV) and hole recombination energies λ_h of Y6 and its selenophene π -bridge derivatives are obtained at the level of CAM-B3LYP/6-31+G(d)/PCM..

Acceptors	λ_e	λ_h
Y6	0.327	0.309
BTP-2Se-2F	0.174	0.314
BTP-4Se-2F	0.242	0.517
BTP-6Se-2F	0.608	0.317
BTP-8Se-2F	0.170	0.320
BTP-2SeF-2F	0.201	0.311
BTP-2SeCl-2F	0.869	0.362
BTP-2SeBr-2F	0180	0.304

The electron recombination energies λ_e (eV) and hole recombination energies λ_h of Y6 and its selenophene π -bridge derivatives are analyzed at the level of CAM-B3LYP/6-31+G(d)/PCM, as shown in Table S2. The calculation method B3LYP is used to calculate the recombination energies of Y6 and its derivatives for the following reasons: First, the electronegativity of chlorine atom is close to that of fluorine atom and bromine atom, but the λ_e and λ_h of BTP-2SeCl-2F are too different from those of BTP-2SeF-2F and BTP-2SeBr-2F; furthermore, the λ_e and λ_h of the BTP-4Se-2F and BTP-6Se-2F are also different from those of BTP-8Se-2F and BTP-2Se-2F. The difference is too large; finally, Y6 is used as the acceptor material, but the λ_e of Y6 is larger than λ_h , so based on the above data analysis, we think this may be attributed to the fact that the computational method of CAM-B3LYP may not be suitable for calculating the recombination energies of Y6 and its derivative materials. Based on the previous reports,^{3, 4} the method B3LYP is suitable for calculating the recombination energies of Y6 and its derivative. Therefore, the calculation of the recombination energy is performed at the level of B3LYP/6-31+G(d). We think this may be attributed to the fact that the computational method of CAM-B3LYP may not be suitable for calculating the recombination energies of Y6 and its derivative materials.

Table S3. The amounts of net charge transfer between the TPBT, π -bridge, and 2FIC molecular fragments of Y6 and its selenophene π -bridge derivatives (Net transfer is the amount of total charge transferred from fragments 1 and 2 to fragment 3). The results are obtained at the program of Multiwfn 3.8(Dev).

Acceptors	Net 1 \rightarrow 2/e	Net 1 \rightarrow 3/e	Net 2 \rightarrow 3/e	Net transfer/e
Y6	-	0.180	-	0.180
BTP-2Se-2F	0.089	0.145	0.026	0.234
BTP-4Se-2F	0.093	0.128	0.051	0.221
BTP-6Se-2F	0.091	0.104	0.068	0.195
BTP-8Se-2F	0.079	0.087	0.089	0.166
BTP-2SeF-2F	0.104	0.165	0.027	0.269
BTP-2SeCl-2F	0.107	0.171	0.035	0.278
BTP-2SeBr-2F	0.105	0.171	0.038	0.276

Table S4. The Multiwfn3.8 program is used to calculate the D index (Å), S_r index (eV), H index (Å), t index (Å), HDI index (eV), EDI index (eV), and E_{coul} index (eV) of $S_0 \rightarrow S_1$ of Y6, BTP-2Se-2F, BTP-4Se-2F, BTP-6Se-2F, BTP-8Se-2F, BTP-2SeF-2F, BTP-2SeCl-2F, and BTP-2SeBr-2F. The results are obtained at the program of Multiwfn 3.8 (Dev).

Acceptors	D(Å)	S_r (eV)	H(Å)	t(Å)	HDI(eV)	EDI(eV)	E_{coul} (eV)
Y6	0.694	0.742	7.114	-1.492	4.520	4.200	2.740
BTP-2Se-2F	0.940	0.740	9.389	-1.191	3.940	3.790	2.282
BTP-4Se-2F	1.466	0.743	10.225	-1.748	3.710	3.610	1.969
BTP-6Se-2F	1.170	0.747	11.785	-1.420	3.500	3.450	1.905
BTP-8Se-2F	1.628	0.748	12.895	-1.890	3.330	3.340	1.681
BTP-2SeF-2F	1.028	0.732	9.286	-1.032	4.010	3.840	2.312
BTP-2SeCl-2F	0.886	0.735	9.380	-1.058	3.940	3.810	2.348
BTP-2SeBr-2F	0.846	0.734	9.381	-1.096	3.940	3.790	2.349

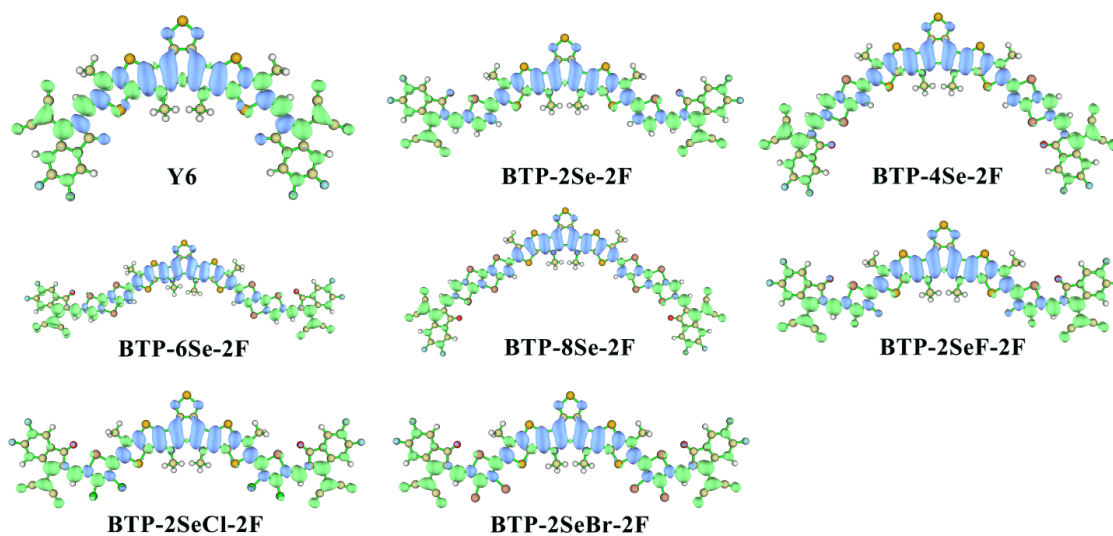


Figure S3. Charge density difference (CDD) of $S_0 \rightarrow S_1$ of Y6 and its selenophene π -bridge derivatives are obtained by the Multiwfn3.8 (Dev) program (Green indicates an increase in charge density, while blue indicates a decrease; isosurface = 0.0005 au).

The hole-electron distribution indexes of selenophene π -bridge derivatives are analyzed, as shown in Table S4. The D index can be used to characterize the degree of exciton separation in the CT (charge transfer) direction. The S_r index can estimate the difficulty of hole-electron separation. The greater the S_r index, the harder hole-electron separation is. The S_r indexes of Y6 and BTP-2Se-2F are larger than 0.6 eV (the upper limit is 1.0 eV), which means that the electrons and holes

overlap. The S_0 - S_1 excitation of Y6 and BTP-2Se-2F are estimated from the D index, S_r index, and the charge density difference (CDD) (see Figure S3) diagrams as localized excitation. The H index represents the overall average extension degree of electrons and holes. HDI (EDI) represents the degree of hole (electron) delocalization, and the smaller the HDI (EDI) index, the higher the degree of hole (electron) delocalization. The t index and E_{coul} index can estimate the difficulty of exciton separation in NFAs. The larger the t index and smaller E_{coul} index, the easier the exciton separation for NFAs. From Table S4, it can be seen that with the extension of the selenophene π -bridge from Y6 to BTP-8Se-2F, the D index, H index, and t index of Y6 increase; and the S_r index and HDI/EDI index gradually decrease. This means that as the conjugate bridge is extended, the overall average extension of electrons and holes is larger, and the separation of excitons is easier. In addition, it can be found from Table S4 that BTP-2SeF-2F, BTP-2SeCl-2F and BTP-2SeBr-2F have larger D index, t index and H index and smaller HDI (EDI) index and E_{coul} index than Y6, which indicates that the selection of halogen atoms to modify the selenophene π -bridge side chains is beneficial to increase the overall average extension of electron holes and the dissociation of excitons.

References:

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