**Supporting Information for "Theoretical Study on the Torsional Potential of Alkyl, Donor, and Acceptor Substituted Bithiophene: The Hidden Role of Noncovalent interaction and Backbone Conjugation"**

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## S1. The structure of conjugating polymers relevant to the bithiophene molecules in this study
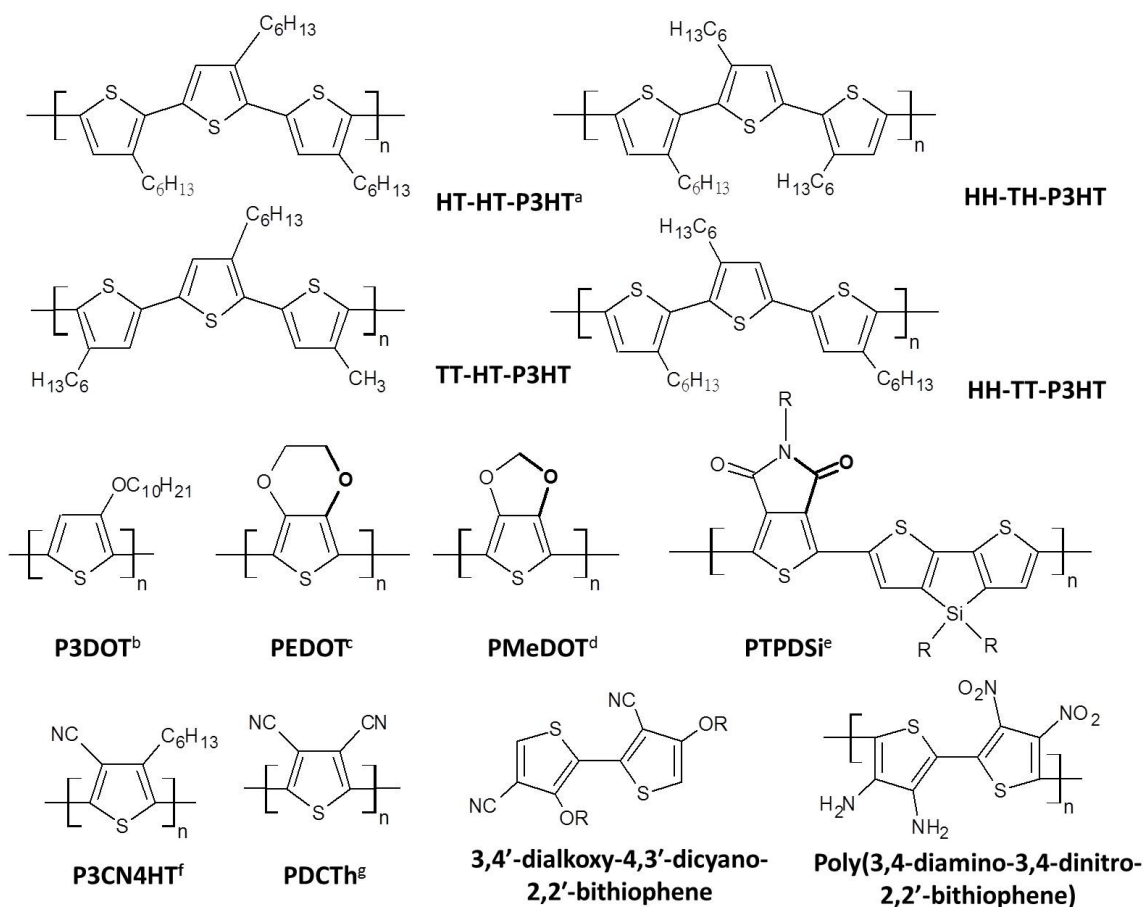


**Figure S1.** The list of commonly used π-conjugated polymers similar to the modeled bithiophenes in this study. The bolded bond in PEDOT, PMeDOT, and PTPDSi indicates the similar bonding situation in H-OCH$_3$-BT and H-CHO-BT. [a] P3HT stands for poly(3-hexylthiophene), [b] P3DOT for poly(3-decyloxythiophenel), [c] PEDOT for poly(ethylenedioxythiophene), [d] PMeDOT for poly(methylenedioxythiophene), [e] PTPDSi for Thieno[3,4-c]pyrrole-4,6-dione and dithienosilole copolymer, [f] P3CN4HT for poly(3-cyano-4-hexylhiophene), and [g] PDCTh for poly(3,4-dicyanothiophene).

## S2. The performance of density functional on the torsional potential of BT

The structures were relaxed by B3LYP[1, 2] functional with 6-311+G(2df,p) basis set.[3, 4] During the structure relaxation, the dihedral angle C3-C2-C2′-C3′ was fixed and the remaining degrees of freedom optimized. The dihedral angle started from 0 to 180 degree with a 10-degree increment. The partially optimized structures were further taken out for single point calculations with different functionals and levels of correlation calculations.

From Figure S2, functionals such as wB97x and wB97xd[5, 6] show comparable performance to CCSD(T)/cc-pVTZ.[7, 8] These two range-separated functionals predict slightly lower internal rotation barrier by about 0.25 kcal/mol compared to that from CCSD(T), and outperform conventional functional such as B3LYP and M062X.[9] B3LYP and M062X predict higher internal rotation barrier than CCSD(T) because the delocalization error overstablizes planar conformation of BT. On the other hand, due to the proper mixing of exact single reference exchange energy and long-range correction, the range-separated functional has reduced delocalization error leading to comparable performance to CCSD(T).
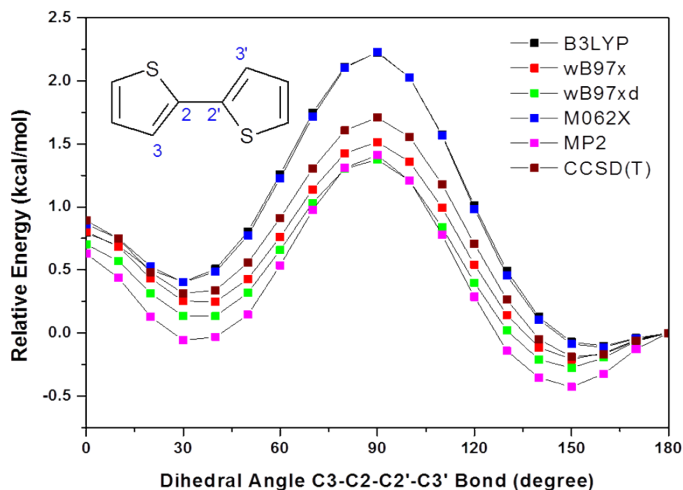


**Figure S2.** Torsional potential of BT with different density functional and levels of theoretical methods. Each torsional potential has its own reference point which is the energy of *trans*-planar structure (180⁰). 6-311+G(2df,p) basis set was implemented for DFT and MP2, and cc-pVTZ basis set was used from CCSD(T). The torsional potential of B3LYP and M062X are overlapping with each other.

## S3. The performance of density functional on the torsional potential of alkyl-substituted BT

Torsional potentials of T-CH$_3$-BT and H-CH$_3$-BT are illustrated in **Figure S3**. From the potential obtained by CCSD(T)/cc-pVTZ, the twisted structure (C3-C2-C2′-C3′ between 60 and 120 degree) of H-CH$_3$-BT is more stable than T-CH$_3$-BT. This implies certain attractive interactions between the methyl group and thiophene ring (CH-π interaction)[10, 11] which is addressed in the main text and S4. The B3LYP functional is not able to describe this type of interactions, and MP2 seems to overestimate CH-π interaction. M062X is able to capture the CH-π interaction, but it gives a higher internal rotation barrier than CCSD(T) shown in Figure S2. Both wB97x and wB97xd functionals show comparable performance to CCSD(T). The performance of wB97xd, includes empirical dispersion correction, seems to vary with different molecules. Therefore, we finally choose wB97x in this study.
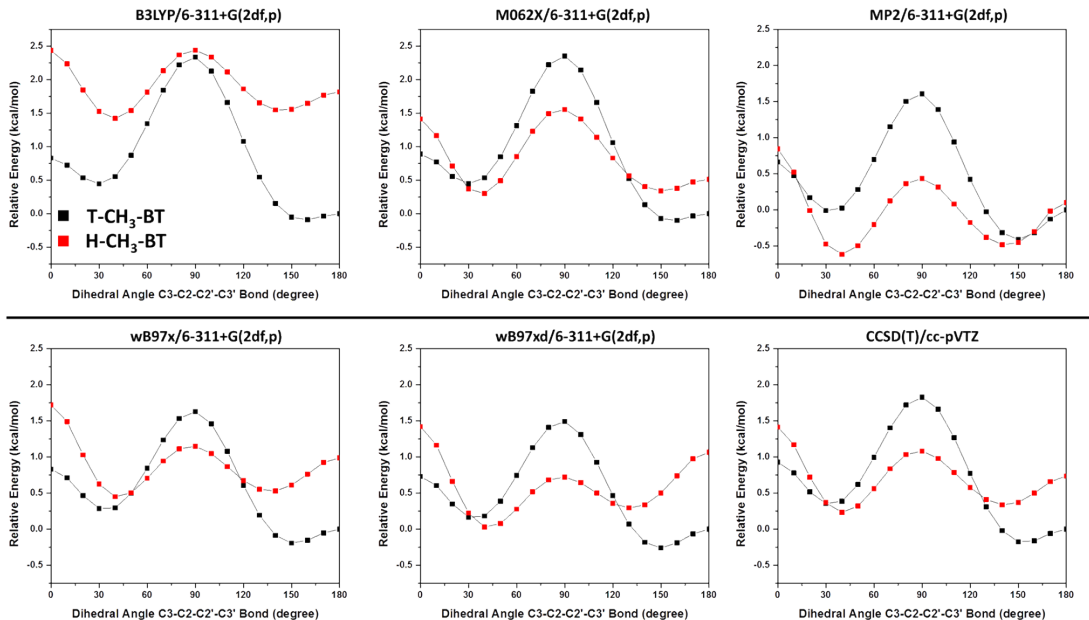


**Figure S3.** Torsional potentials of T-CH$_3$-BT and H-CH$_3$-BT with different density functionals and levels of theoretical methods. The two potential energy curves, T-CH$_3$-BT and H-CH$_3$-BT, in each graph have the same reference point, the energy of T-CH$_3$-BT at the *trans*-planar structure (180 degree).

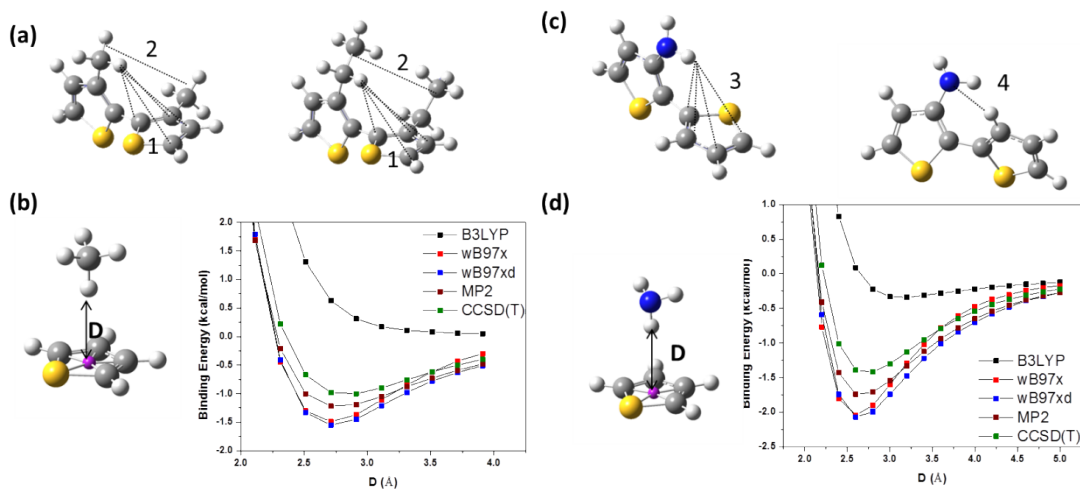## S4. The noncovalent interaction in alkyl-substituted and amino-substituted bithiophene



**Figure S4** (a) 1 indicates the CH-π interaction between the alkyl group at the head position and its neighbor thiophene ring, and 2 indicates the interaction between the alkyl groups at transition structure. The average distance involving the CH-π interaction in the transition structure of alkyl-substituted bithiophene is 3.5 Å. (b) The potential energy curve between methane and thiophene ring. The basis set implemented for CCSD(T) is cc-pVTZ, otherwise, 6-311+G(2df,p) (c) 3 indicates the NH-π interaction between the amino hydrogen and its neighbor thiophene ring at the transition structure. Their average distance is 3.55 Å. 4 indicates the hydrogen bond between the aryl hydrogen and amino nitrogen (CH···NH), and its bond length is 2.8 Å. (d) The potential energy curve of thiophene-ammonia dimer. The basis set implemented for CCSD(T) is cc-pVTZ, otherwise, 6-311+G(2df,p).

**S5. The comparison of the torsional potential of alkyl-substituted bithiophene between B3LYP and wB97x**
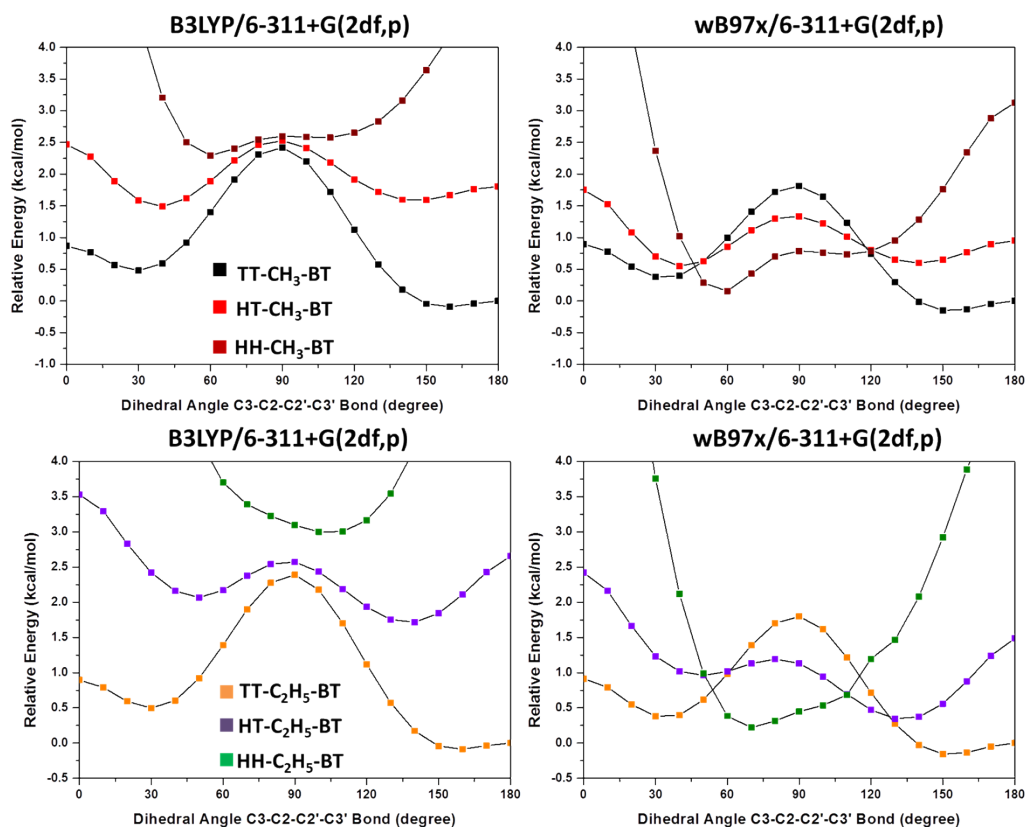


**Figure S5.** Since B3LYP fails to describe dispersion interactions, there is no stabilization interaction for the transition structure. B3LYP seems also predicts reduced internal rotation barrier when more alkyl groups are attached at the head position, but it is because of the elevation of the potential energy surface due to steric repulsion from the alkyl groups.

**S6. The torsional potential of donor and acceptor substituted bithiophene with the donor and acceptor substituents at the 3′ (tail) position**
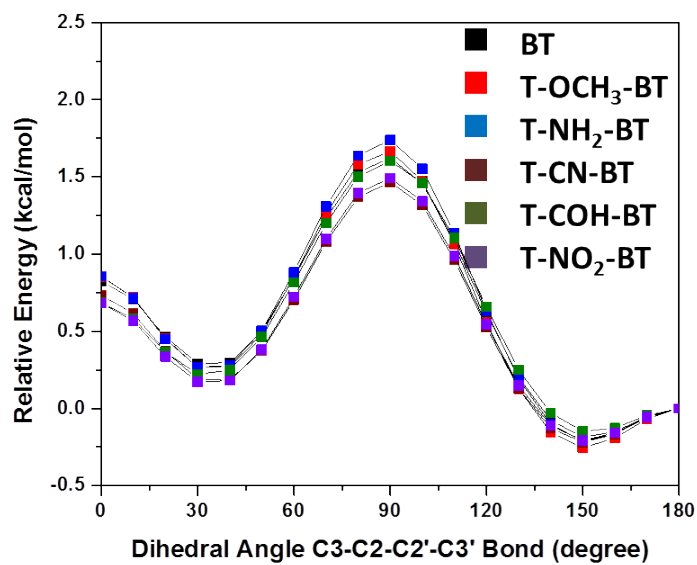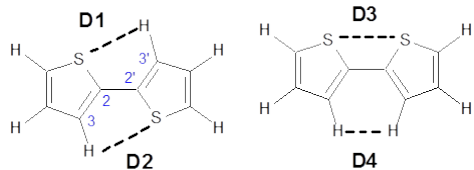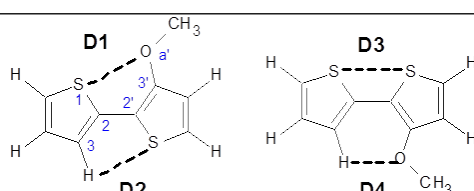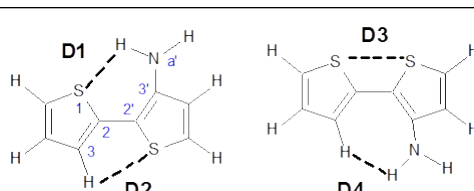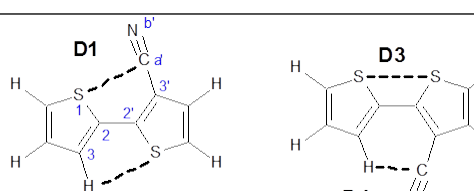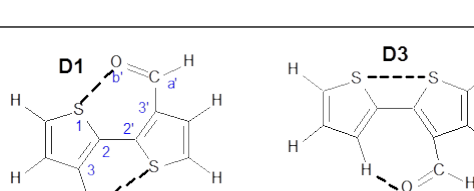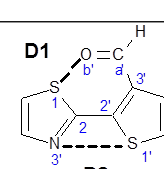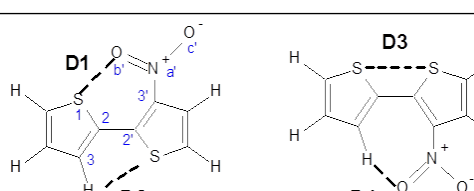


**Figure S6.** The torsional potential of the substituted bithiophenes has no significance difference from BT.

**Table S1**. Selected nonbonded distances for donor/acceptor substituted bithiophene

| Donor- and acceptor- substituted bithiophene | Planar conformations (Å) | | Local Mins (Å) | |
|---|---|---|---|---|
| (structures) | D1 | 2.908 | D1 | 3.036 |
| | D2 | 2.908 | D2 | 3.036 |
| | D3 | 3.297 | D3 | 3.412 |
| | D4 | 2.392 | D4 | 2.719 |
| (structures) | D1 | 2.903 | | |
| | D2 | 2.871 | | |
| | D3 | 3.262 | | |
| | D4 | 2.338 | | |
| (structures) | D1 | 2.520 | D1 | 2.701 |
| | D2 | 2.834 | D2 | 3.066 |
| | D3 | 3.235 | D3 | 3.427 |
| | D4 | 1.983 | D4 | 2.346 |
| (structures) | D1 | 3.100 | D1 | 3.226 |
| | D2 | 2.810 | D2 | 2.974 |
| | D3 | 3.229 | D3 | 3.325 |
| | D4 | 2.490 | D4 | 2.658 |
| (structures) | D1 | 2.759 | D1 | 2.880 |
| | D2 | 2.655 | D2 | 2.823 |
| | D3 | 3.123 | D3 | 3.243 |
| | D4 | 2.050 | D4 | 2.299 |
| (structure) | D1 | 2.757 | | |
| | D2 | 2.861 | | |
| (structures) | D1 | 2.655 | D1 | 2.849 |
| | D2 | 2.600 | D2 | 2.892 |
| | D3 | 3.103 | D3 | 3.296 |
| | D4 | 2.119 | D4 | 2.403 |

## S7. Supporting calculations for the influence of intramolecular interactions to the torsional potential of the selected substituted bithiophene
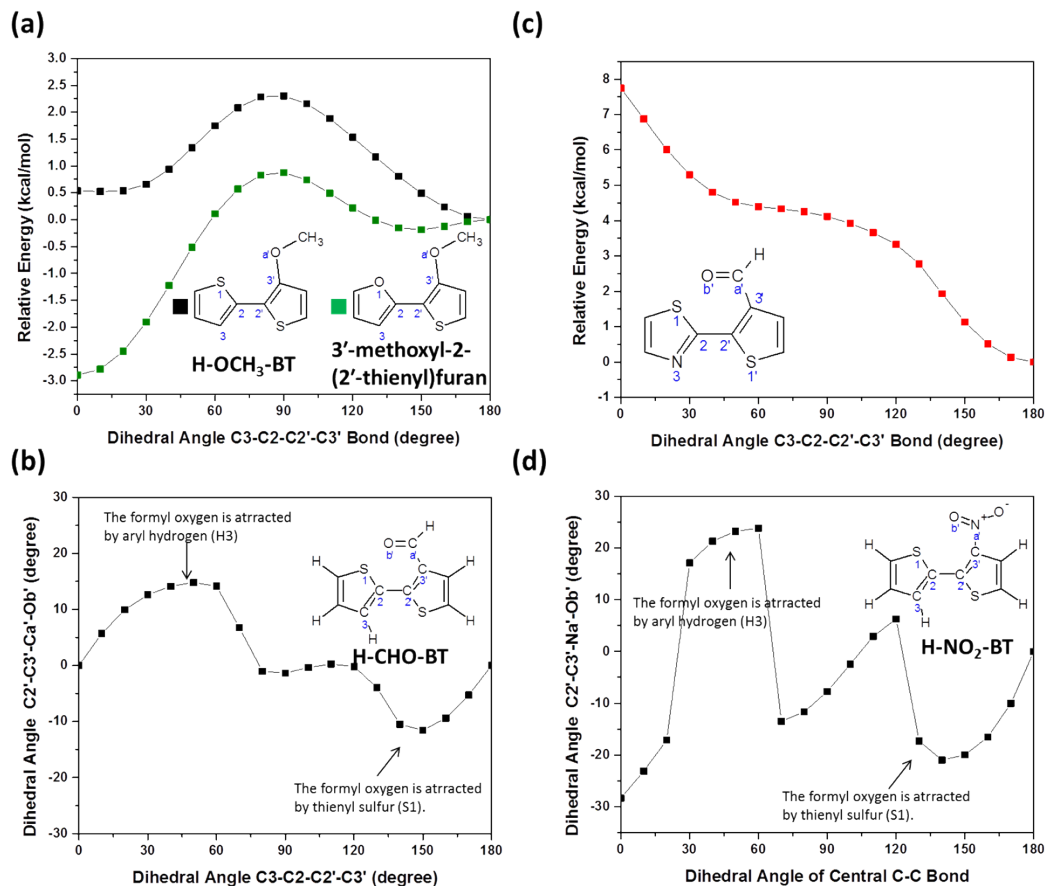


**Figure S7.** (a) The torsional potential of H-OCH3-BT and 3′-methoxyl-2-(2′-thienyl)furan. The potential of 3′-methoxyl-2-(2′-thienyl)furan from wB97x shows a very shallow local minimum around 150 degree, but we think the furan still can reach planar structure very easily. (b) The change of dihedral angle C2'-C3'-Ca'-Ob' during potential energy surface scan in H-CHO-BT. (c) The torsional potential of 3′-formyl-2-(2′-thienyl) thiazole. The reference point is the energy at 180 degree. (d) The change of dihedral angle C2'-C3'-Na'-Ob' during potential energy surface scan in H-NO$_2$-BT.

## S8. Comparisons of the torsional potential of donor and acceptor substituted bithiophene between B3LYP and wB97x
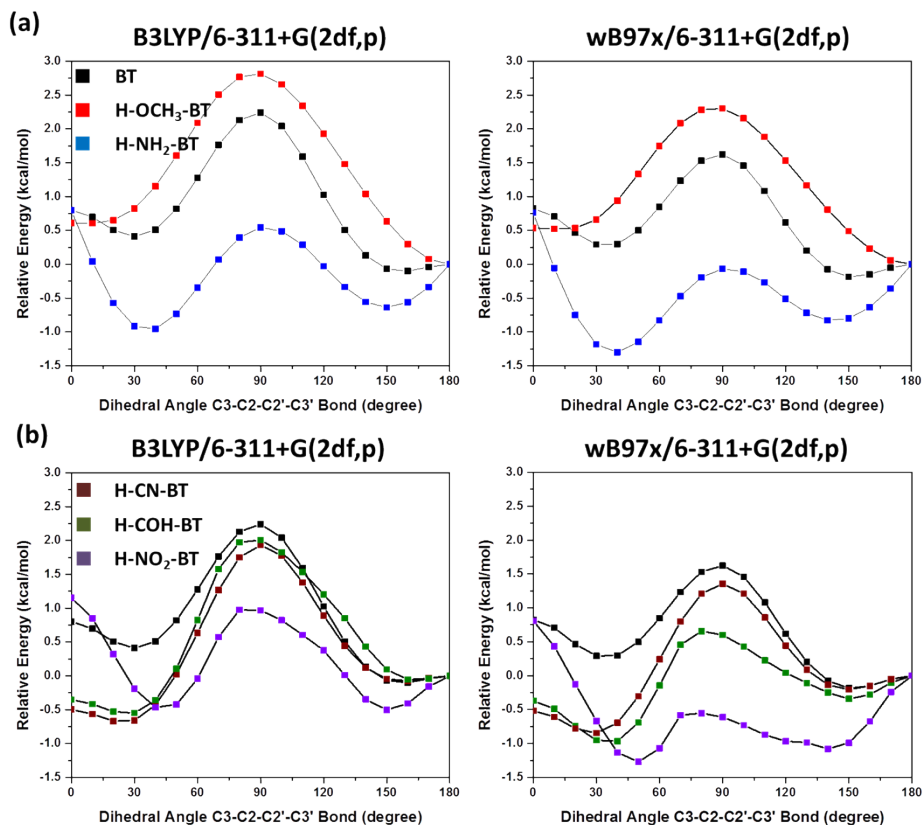


**Figure S8**. The torsional potential obtained by B3LYP follows the trend by wB97x in general. The major differences are taken place in H-NH$_2$-BT and H-CHO-BT. Since B3LYP fails to describe NH-$\pi$ interaction the internal rotation barrier is higher than that of wB97x. The torsional potential of H-CHO-BT is almost identical with H-CN-BT, and the coplanarity is still preserved by B3LYP. We believe that this is due to the delocalization error from B3LYP functional, which makes the pi electron interact on the backbone rather than with the electron-withdrawing formyl group.

**References**

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