PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

PCCP RSCPublishing

ARTICLE

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

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

*Tzu-Jen Lin and Shiang-Tai Lin**

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

Side chain and substituent engineering of conjugated polymers are important to their backbone design. Of particular interest here is how side chains and substituents influence the coplanarity of conjugated backbones. Steric hindrance is usually considered as the principal factor to the coplanarity. In this study, we used proper first-principle density functional theories to analyze the change in the torsional potentials of substituted bithiophene with substituents of varying degree of electron donating/accepting capabilities. Besides steric hindrance, the torsional potential of substituted bithiophene is also determined by other factors such as the position of substitution, non-covalent interactions between the substituents and thiophene ring, and electron conjugation in the backbone. There is no significant change in the torsional potential unless the substituent group is located at the head position of bithiophene. The bulkiness of the substituent group increases the torsional barrier at 0 and 180 degree (planar bithiophene), while the weak noncovalent interaction (such as CH-π, NH-π, and dispersion interactions) stabilizes the transition structure and decreases the barrier at 90 degree (two thiophene rings in perpendicular). Strong electron-withdrawing substituent groups (e.g., formyl or nitro groups) are found to reduce backbone conjugation resulting in reduced internal rotation barrier at 90 degree. Any of these factors deteriorates the coplanarity of bithiophene. On the other hand, the backbone conjugation can be enhanced by introducing electron-donating groups (e.g., methoxy) resulting in increased internal rotational barrier and stabilized planar structure. The influence of through-space interactions such as S···O, S···N and CH···O interactions are found to play a minor role to the coplanarity of substituted bithiophene.

1. Introduction

π-conjugated polymers have been applied in many fields such as organic light emitting diodes[1-3] (OLEDs), organic photovoltaic cells[4-8] (OPVs), and organic thin film transistors[9-13] (OTFTs). They have advantages over conventional inorganic semiconductors in many aspects, such as solution processibility, low cost, flexibility, and tunable band gap. The performance of π-conjugated polymers in optoelctronic devices has been improved rapidly in last two decades, which relies on molecular engineering on backbone repeating units, side chains, and substituent of π-conjugated polymers.[14-16]

High-performance conjugated polymers need longer effective conjugation length leading to higher charge carrier mobility and ordered close packing to enhance charge transport characteristic. In this regard, the coplanarity of the conjugated backbone is an important issue in the backbone design. Deviations to planar structure produce bends and kinks which interrupt the extent of π conjugation and diminish charge carrier mobility in a given polymer chain. In addition, high-performance conjugated polymers also require low energy for charge-transfer, low optical gaps, and large short-circuit currents. Therefore, donor-acceptor is now a popular scheme to design conjugated polymers. Various heterocyclic compounds such as bithiazole, benzothiadiazole, isoindigo, diketopyrrolopyrrole (DPP), and thieno[3,4-c]pyrrole-4,6-dione (TPD) units are incorporated into conjugated backbones as an acceptor.[17-22]

Side chain engineering on π-conjugated polymers in early days focused on the solubility in a given solvent, but recently many researches have shown that it has great potential to improve or tune the performance of π-conjugated polymers.[16] Alkyl side chains with different positioning on the backbone alter band gap, charge carrier mobility, open-circuit voltage, power conversion efficiency in bulk heterojunction (BHJ) polymer solar cell, and optical behavior.[23-28] The donor and acceptor substituents are usually used to modulate the band gap, and they also influence thermal stability, emission energy of luminescent, and photochemical stability.[29-40] However, how the side chains or substituents influence the conformation of conjugated polymers is difficult to be examined in detail by experiments. For example, the influence of alkyl side chains to individual backbone of alkyl-substituted polythiophene where inter-chain interactions are absent is still in debate. Some studies argue that polymer chain is still rigid,[41-43] while others claim that the chain is flexible and folding.[44-46] Furthermore, the influence of electron-donating and electron-withdrawing substituents to the conformation of π-conjugated polymers has rarely been addressed in either experimental or theoretical studies.

Modern computational chemistry is a powerful tool for the study of the influence of various substituents to the backbone conformation.[47-50] However, the conclusion may sometimes depend on the choice of theoretical method used. For example, some theoretical studies argue that the weak noncovalent interactions do not have substantial impacts[51-55], but recent studies done by Famulari[56, 57] on alkyl-substituted thiophene shows that the alkyl chain would interact with the backbone ring through CH-π interaction. In addition, many theoretical efforts were made to justify "intramolecular lock" such as S···O lock or S···N lock that keeps the conjugated polymers in planar conformations.[20, 58-68] We suspect that some of the arguments may be misled by the use of low level theoretical methods or methods lacking of weak noncovalent interactions.

The aim of this study is to apply proper theoretical methods on a variety of modeled bithiophene molecules in order to study the influence of substituent groups on the torsional potential of substituted bithiophenes. Methyl ($-CH_3$) and ethyl ($-C_2H_5$) functional groups are selected to represent conjugated polymers substituted with alkyl side chains. Several electron-donating and electron-withdrawing substituents are also selected including methoxy ($-OCH_3$), amino ($-NH_2$), cyano (-CN), formyl (-CHO), and nitro ($-NO_2$) group. The methoxy substituted bithiophene is chosen to represent poly(3-decyloxythiophene) (P3DOT)[33] and a series of poly(alkylenedioxythiophene).[69] The amino, cyano, and nitro substituents are often used for tuning band gaps of conjugated polymers.[35, 70-73] The formyl-substituted bithiophene represent similar bonding situation in DPP and TPD units frequently used in donor-acceptor conjugated polymers.[20, 21] The key factors that influence the coplanarity of conjugated systems are derived from a careful analysis of the torsional potential of these molecules (summarized in **Figure 1**). The results of this work would be useful for the design of conjugated polymers based on substituent engineering and developments of force fields for substituted conjugated oligomers.

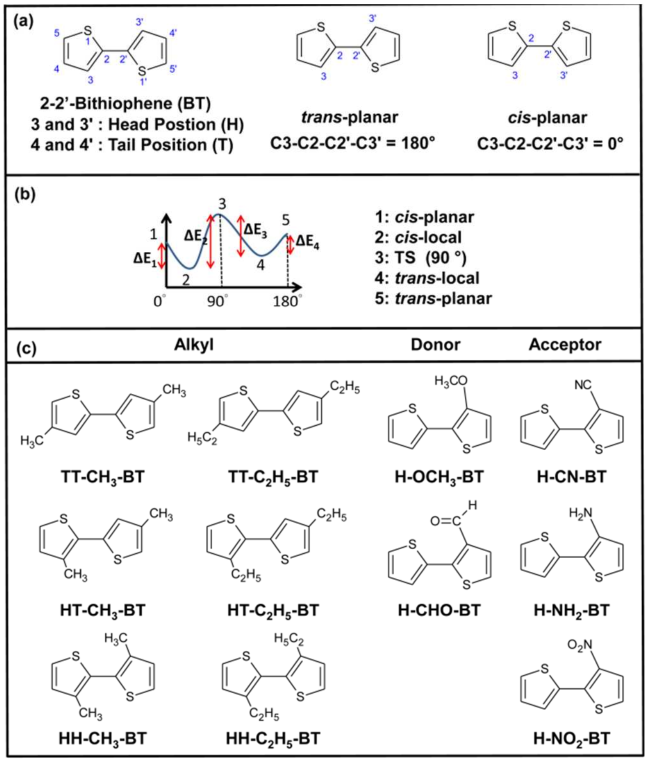


Figure 1 (a) Definition of substitution position and dihedral angle. (b) Definition of selected positions and energy barriers of substituted bithiophenes. ΔE_1 is the barrier between *cis*-local and *cis*-planar; ΔE_2 is the barrier between *cis*-local and transition state; ΔE_3 is the barrier between *trans*-local and transition state; ΔE_4 is the barrier between *trans*-local and *trans*-planar. (c) Abbreviation of substituted-bithiophene in this study. These selected molecules represent polymers (summarized in **Figure S1**) commonly used in optoelectronic device.

2. Computational detail

2.1 Abbreviation and Nomenclature

2,2′-bithiophene, referred to as BT, is the base molecule in this study. The abbreviation of substituted bithiophene is based on the following format: substituted position - substituent - BT. The 3 and 4 (or 3′ and 4′) positions of bithiophene are named "head" (H) and "tail" (T) position, respectively, as indicated in Figure 1. For instance, 3-methyl-2,2′-bithiophene and 4-methyl-2,2′-bithiophene are abbreviated as H-CH_3-BT and T-CH_3-BT respectively. If bithiophene is double substituted such as 4,4′-dimethyl-2,2′-bithiophene, 3,4′-dimethyl-2,2′-bithiophene, and 3,3′-dimethyl-2,2′-bithiophene, they are denoted as TT-CH_3-BT, HT-CH_3-BT, and HH-CH_3-BT respectively. The same rule also applies to other donor or acceptor-substituted bithiophene. The methoxy, amino, cyano, formyl, and nitro groups are denoted as OCH_3, NH_2, CN, CHO, and NO_2 respectively. The torsional potential of substituted bithiophene is based on the rotation of the central C-C partial double bond. We define *trans*-planar as C3-C2-C2′-C3′ is 180 degree, and *cis*-planar as C3-C2-C2′-C3′ is 0 degree (see **Figure 1**). All theoretical calculation in this study is done by G09 D.01.[74]

2.2 Choice of Model and Density Functional

Theoretical calculations based on density functional theory (DFT) have been used for the electronic structure and properties of conjugating copolymers because of its accuracy and computational efficiency. Since the exact form of exchange-correlation functional is unknown, there have been many density functionals developed with varying degree of success. In regards to the modeling of conjugated molecules, special attention should be paid for the delocalization error (sometimes referred to as Many-electron self-interaction error),[75-78] strong static correlation, and dispersion interactions. For conjugated molecules, functionals with reduced delocalization error should be used.[75, 79-81] Karpfen pointed out that conventional GGA and hybrid functional does not correctly describe partial double bond rotation of conjugated molecules,[82, 83] because these functionals suffer from delocalization error which overestimates torsional barriers and results in overstabilized planar structure of conjugated molecules. Furthermore, static correlation arises from degenerated ground state that cannot be fully described by a single Slater determinant.[84, 85] Conjugated polymers having a small energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are subjected to strong static correlation. The interaction between thiophene ring and substituents could be attributed to dispersion interaction which is not included in many functionals. Therefore, it is necessary to identify the proper DFT methods that have minimal error due to electron delocalizarion and dispersion interactions. To avoid strong static correlation, which would require more elaborated theory with multi-Slater determinants, we limit the systems to substituted bithiophene molecules, and not extending oligomers. Several functionals are validated by the torsional potential of BT, T-CH_3-BT, and H-CH_3-BT (see **S2** and **S3** in the Supporting Information). The wB97x functional with 6-311+G(2df,p) basis set shows best agreement to the CCSD(T)/cc-pVTZ on the torsional potential and dispersion interaction.

2.3 Binding Energy Calculation

To understand weak noncovalent interaction between substituents and thiophene ring, the binding energy of thiophene-methane and thiophene-ammonia dimers were computed. The binding energy were determined (with corrections for basis set superposition error (BSSE) based on counterpoise correction proposed by Boys/Bernardi[86, 87]) and compared by using DFT methods such as B3LYP, wB97x, and wB97xd and Post Hartree-Fock methods such as MP2 and CCSD(T).

2.4 Natural Bond Orbital (NBO) and Charge Analysis

To characterize intramolecular interactions on the backbone of substituted bithiophene, population analysis such as natural bond orbital (NBO)[88] and CM5[89, 90] were performed. NBO analysis allows for the analysis of donor-acceptor interaction between the substituent group and the thiophene ring. CM5 provides the partial atomic charges by mapping from Hirshfeld population analysis of electronic charge distributions.[89, 90] Since the diffuse function augmentation would strongly impact the conclusions in NBO analysis,[91 92] the cc-pVTZ basis set was used. For the consistency in the population analysis, CM5 charge analysis also uses the same basis set in NBO analysis.

3. Result and Discussions

3.1 Alkyl-substituted Bithiophenes

Torsional potentials of double alkyl-substituted bithiophenes (TT-CH_3-BT, HT-CH_3-BT, and HH-CH_3-BT; TT-C_2H_5-BT, HT-C_2H_5-BT, and HH-C_2H_5-BT) and their details are presented in and **Table 1** and **Figure 2**. The reference energy (0 kcal/mol) is set to be that of *trans*-planar TT isomer. In TT-CH_3-BT the positions of local minima around 34 and 153.2 degree are similar to those of BT. In HT-CH_3-BT and HH-CH_3-BT, the positions of local minima are shifted toward 90 degree (41.3 and 139.6 degree, and 57.3 and 110.2 degree, respectively). The same trend is also found in the ethyl-substituted bithiophene. The positions of local minima in HT-C_2H_5-BT are closer to the 90 degree compared with HT-CH_3-BT, because stronger steric repulsions created by the larger ethyl group at the head position. The steric repulsion increases the barrier at 0 and 180 degree (ΔE_1 and ΔE_4) and pushes the local mimina towards 90 degree, resulting in worse coplanarity.

Table 1 The relative energy (kcal/mol) of selected points, planar, transition state, and local minima, in the torsional potential of alkyl-substituted bithiophene. The values in the parenthesis are the dihedral angle C3-C2-C2′-C3′ at local minima.

	cis-planar	*cis*-local	TS	*trans*-local	*trans*-planar
BT	0.82	0.28 (34.8°)	1.62	-0.18 (151.9°)	0
		$-CH_3$			
TT	0.90	0.37 (34.0°)	1.81	-0.14 (153.2°)	0
HT	1.75	0.57 (41.3°)	1.33	0.62 (139.6°)	0.95
HH	9.34	0.16 (57.3°)	0.79	0.74 (110.2°)	3.13
		$-C_2H_5$			
TT	0.91	0.37 (34.2°)	1.80	-0.15 (153.0°)	0
HT	2.42	0.99 (50.6°)	1.13	0.36 (133.6°)	1.49
HH	10.76	0.24 (69.7°)	0.45	--	4.83

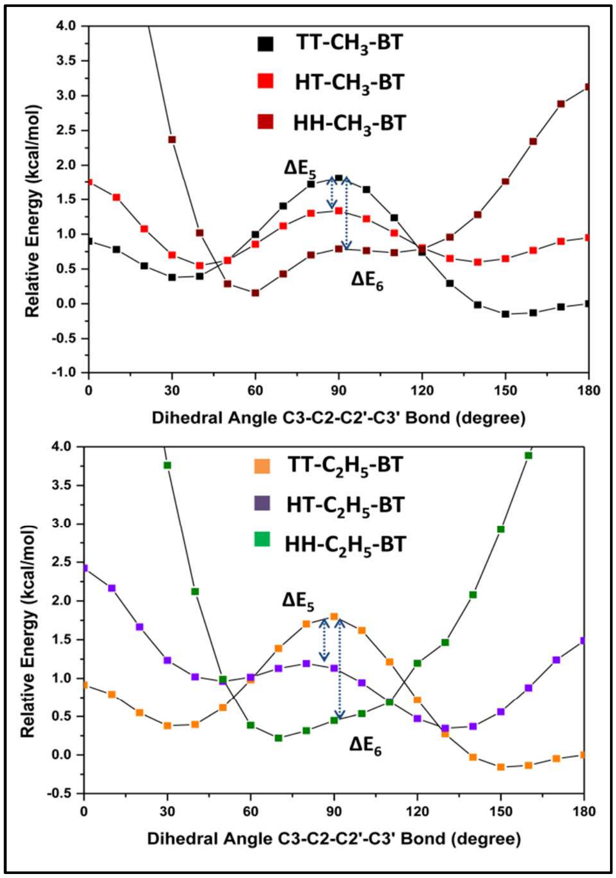


Figure 2 The torsional potential of alkyl-substituted bithiophene. ΔE$_5$ indicates the energy difference between TT and HT transition state structures (C3-C2-C2′-C3′ 90 degree), and ΔE$_6$ indicated that between TT and HH transition state structures. The relative energy over 4.0 kcal/mol is not shown.

The most intriguing part is the central region (C3-C2-C2′-C3′ between 60 to 120 degree) of torsional potential when the alkyl group is substituted at the head position. It is obvious that CH-π interaction between the alkyl group and its neighboring thiophene ring stabilizes the twisted structures in HT-CH$_3$-BT, HH-CH$_3$-BT, HT-C$_2$H$_5$-BT, and HT-C$_2$H$_5$-BT (**Figure 2**). The interaction is identified by the thiophene-methane dimer calculation (**S4** in Supporting Information). The CH-π interaction reduces the internal rotation barriers, ΔE$_2$ and ΔE$_3$, from 1.44 and 1.95 kcal/mol in TT-CH$_3$-BT, to 0.76 and 0.71 kcal/mol in HT-CH$_3$-BT, and to 0.63 and 0.05 kcal/mol in HH-CH$_3$-BT. The energy difference between the transition structures of HT-CH$_3$-BT and TT-CH$_3$-BT (ΔE$_5$ in **Figure 2**) is 0.48 kcal/mol, and that between HH-CH$_3$-BT and TT-CH$_3$-BT (ΔE$_6$ in **Figure 2**) is 1.02 kcal/mol. The higher value of ΔE$_6$ compared to ΔE$_5$ is a result of increased CH-ring interactions, i.e., two thiophene-methyl interactions in HH-CH$_3$-BT instead of one in HT-CH$_3$-BT. For the double ethyl-substituted BT, ΔE$_5$ is 0.57 kcal/mol which is only 0.09 kcal/mol higher than the double methyl-substituted BT, and ΔE$_6$ is 1.35 kcal/mol which is 0.33 kcal/mol higher than the double methyl-substituted BT. Since the tail of the ethyl group is distant from the thiophene ring, the enhanced stabilization of transition structure in HH-C$_2$H$_5$-BT should be a result of the interaction between the alkyl groups. With such additional weak noncovalent interaction, the internal rotation barrier in HH-C$_2$H$_5$-BT disappears, and the torsional potential contains only one local minimum at around 80 degree. The weak noncovalent interaction between the alkyl substitutions also explains the lower relative energy of HH-CH$_3$-BT in *cis*-local conformation compared to its *trans*-local conformation. At *cis*-local, the two methyl group is in 2:2 staggered configuration which is one of stable configurations validated by other theoretical studies.[93]

The shape of torsional potentials does not show significant differences predicted from B3LYP or wB97x; however, the relative position of torsional potential between isomers shows large discrepancies (**Figure S5**). Since B3LYP cannot describe CH-π interaction from the thiophene-methane dimer (shown in **Figure S4(b))**, there is no stabilization energy for the twisted structure of alkyl-substituted bithiophene. B3LYP gives the reduced internal rotation barrier when more alkyl groups are attached at the head position of bithiophene simply because of the elevation of the torsional potential at two flanks.

In summary, steric repulsion (increases with the size of the substituent group) increases the barrier at 0 and 180 degree (planar structure) that drives the substituted bithiophene deviate from the planar conformations. The weak noncovalent interactions (including CH-π interaction and dispersion interactions between alkyl substituents) reduce the barrier at 90 degree (transition structure). The stabilization of the transition structure by CH-π and weak noncovalent interactions leads to the reduced internal rotation barrier of alkyl-substituted bithiophene, and facilitates conformation transitions from *trans*-local to *cis*-local, or vice versa. Thus, the coplanarity is destroyed.

It is worth to note that early experimental studies had speculated the influence of weak noncovalent interactions in alkyl-substituted oligothiophene. NMR and X-ray studies done by Giovanna suggest that the presence of segments with adjacent heat-to-tail/head-to-head linkages is the result of the stabilization via side chain interaction.[94-97] Our study shows that the stabilization is not only realized by weak noncovalent interactions between the alkyl groups but also the CH-π interaction between the alkyl groups and thiophene ring. Our results also support the thermochromism study of poly(3-hexylthiophene) that the *trans*-planar conformation is less stable and conformation changes take place at room temperature[98-101]

3.2 Donor and Acceptor Substituted Bithiophenes

In this section the torsional potentials of bithiophenes with different donor and acceptor substituents are examined. In the comparison of torsional potentials between different compounds in **Table 2** and **Figure 3**, the reference point is the energy of *trans*-planar for each compound. **Table 3** lists the population analysis in the donor/acceptor-substituted bithiophene. The substituents at the tail position of bithiophene do not have any substantial influence to the torsional potential (see **Figure S6**), and thus they are not discussed further. Selected non-bonded distances in the donor/acceptor substituted bithiophene are collected in **Table S1**.

3.2.1 Donor-Substituted Bithiophenes

The coplanarity of H-OCH_3-BT is enhanced compared to that of BT. The local minima of H-OCH_3-BT are shifted to 0 and 180 degree, and the internal rotation barrier increases to about 2 kcal/mol (3 k_BT). This is a relatively high barrier for conformation changes at room temperature. From NBO and CM5 charge analysis, the atomic charge of C2′ (-0.066 *e* by CM5 charge; -0.277 *e* by natural charge in **Table 3**) in H-OCH_3-BT is 20 to 25% higher compared to that in BT (-0.048 *e* by CM5 charge; -0.217 *e* by natural charge). This can be attributed to the electron donation from the methoxy group at the head position. NBO analysis shows a strong donor-acceptor interaction (LPπ(Oa′)→π*(C2′C3′) 41.61 kcal/mol) from the lone pair of the methoxy oxygen to the thiophene ring. In addition, the degree of conjugation increases. The donor-acceptor interaction π(C2′C3′) → π*(C2C3) increases from 17.41 kcal/mol in BT to 18.90 kcal/mol in H-OCH_3-BT at *trans*-planar. The electron donation enhances the conjugation of backbone leading to stabilized planar structure and enhanced π character of the central partial double bond C2-C2′ (making the internal rotation more difficult).

Table 2 Relative energy (kcal/mol) of selected points, planar, transition state, and local minima, in the torsional potential of donor- and acceptor-substituted bithiophene. The value in the parenthesis is the dihedral angle C3-C2-C2′-C3′ at local minima.

	cis-planar	*cis*-local	TS	*trans*-local	*trans*-planar
BT	0.82	0.28 (34.8°)	1.62	-0.18 (151.9°)	0
Donor substituents					
-OCH3	0.54	--	2.30	--	0
-NH2	0.76	-1.29 (38.7°)	-0.07	-0.82 (143.3°)	0
Acceptor substituents					
-CN	-0.52	-0.84 (28.5°)	1.35	-0.19 (149.8°)	0
-COH	-0.37	-0.98 (35.6°)	0.60	-0.33 (150.8°)	0
-NO2	0.81	-1.25 (48.9°)	-0.61	-1.08 (141.1°)	0

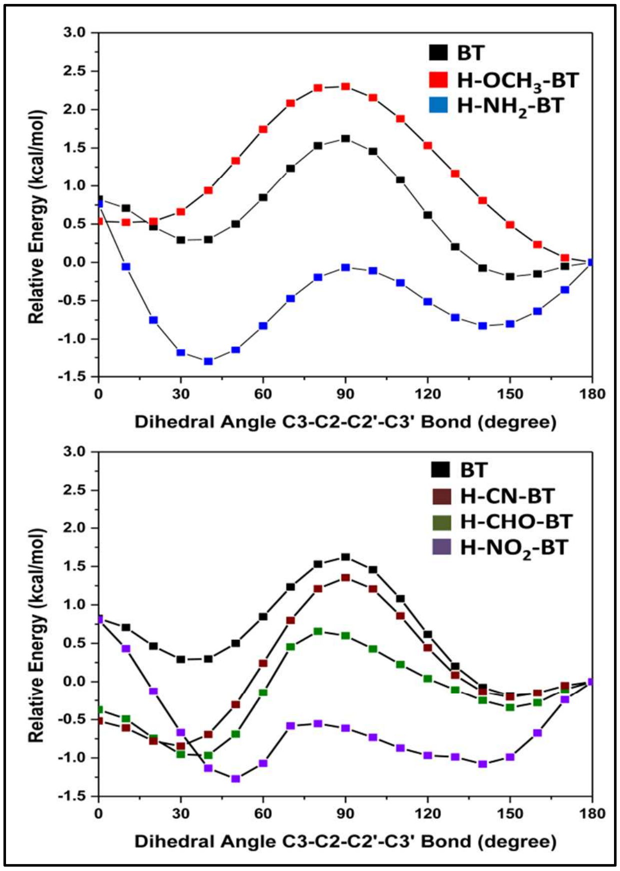
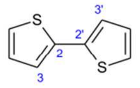
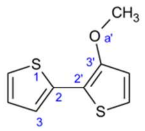
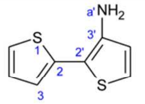
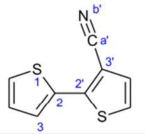
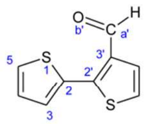
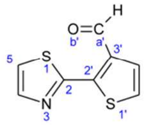
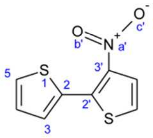


Figure 3 The torsional potential of donor/acceptor substituted bithiophene compared with unsubstituted one.

Some theoretical studies suggested that the electrostatic interaction between the negative charged oxygen (Oa′) and the positively charged sulfur atom (S1) enhances the coplanarity.[58, 59] In order to validate this argument, the torsional potential of 3′-methoxyl-2-(2′-thienyl)furan was computed (**Figure S7(a)**). In the thienylfuran the sulfur atom at the 1 position (S1) was replaced by oxygen atom. From the torsional potential of the thienylfuran, the *trans*-planar conformation is easily accessible regardless of the presence of energetically unfavourable interactions between the two negatively charged oxygen atoms, O1 and Oa′. Therefore, the coplanarity of H-OCH_3-BT is majorly contributed by the increased degree of conjugation resulting from the electron donation from the methoxy group at the head position. Theoretical studies done by Poater and Burkhardt also support this argument.[60, 69] The reduced *tans* to *cis* barrier in 3′-methoxyl-2-(2′-thienyl)furan is attributed to the energetically unfavourable interaction between O1 and Oa′ at *trans*-planar. Therefore the electrostatic interaction between S1 (0.098 *e* by CM5; 0.45 *e* by NBO) and Oa′ (-0.226 *e* by CM5; -0.496 *e* by NBO) has minor contribution in stabilizing the planar structure of H-OCH_3-BT. Although the distance between S1 and Oa′ (D1~2.9 Å shown in **Table S1**) is shorter than the summation of their van der Waals radii (~3.4 Å), the favourable electrostatic attraction seems to compensate the unfavourable steric repulsion to some extent. Some literature also proposed that the interaction between S1 and Oa′ could be originated from the lone pair of Oa′ and S1 due to hypervalence character of sulfur atom.[102, 103] However, the donor-acceptor interaction, LPσ(Oa′)→σ*(S1C5), is less than 1.5 kcal/mol at *trans*-planar, and it would die off very quickly when the molecule deviates from the planar structure. Thus, this type of interaction should not have a substantial impact compared with backbone conjugation and electrostatic interactions. At *cis*-planar the hydrogen bond interaction (CH⋯O; 2.36Å) also helps stabilize the planar conformation.

In the case of H-NH_2-BT, the atomic charge of C2′ (-0.071 *e* by CM5 charge and -0.285 *e* by natural charge) also increases over 30% compared with BT (-0.048 *e* by CM5 charge and -0.217 *e* by natural charge), and strong donor-acceptor interaction from the lone pair of the amino nitrogen to the thiophene ring (LPσ(Na′)→ π*(C2′C3′)) is identified by NBO analysis (39.93 kcal/mol at *trans*-planar). The result is similar to that of H-OCH_3-BT; however, H-NH_2-BT does not favor planar structures from its torsional potential. The local minima

Table 3 Charge and NBO analysis on the donor/acceptor substituted bithiophene. The charge analysis is done by CM5 and NBO, and the value of NBO is in parenthesis. The donor-acceptor interactoin is based on *trans*-planr conformation and the value for *cis*-planar is shown in parenthesis. LP stands for lone pair.

Donor/acceptor substituted bithiophene	Charge (e)	Donor-Acceptor Interaction (kcal/mol)
	C2 -0.050 (-0.217) C2′ -0.048 (-0.217)	π(C2′C3′)→π*(C2C3) 17.41(15.99)
	C2 -0.050 (-0.214) C2′ -0.066 (-0.277) S1 0.098 (0.450) Oa′ -0.226 (-0.496)	π(C2′C3′)→π*(C2C3) 18.90(18.43) LPπ(Oa′)→π*(C2′C3′) 41.61 (41.55) LPσ(Oa′)→σ*(S1C5) 1.47
	C2 -0.048 (-0.200) C2′ -0.071 (-0.285)	π(C2′C3′)→π*(C2C3) 21.01(20.51) LPσ(Na′)→π*(C2′C3′) 39.93 (35.56)
	C2 -0.056 (-0.251) C2′ -0.020 (-0.140)	π(C2′C3′)→π*(C2C3) 14.19(13.78) π(C2′C3′)→π*(Ca′Nb′) 20.95 (21.20)
	C2 -0.056 (-0.262) C2′ -0.010 (-0.127) S1 0.130 (0.515) Ob′ -0.301 (-0.533)	π(C2′C3′)→π*(C2C3) 14.09(13.76) π(C2′C3′)→π*(Ca′Ob′) 26.05 (25.97) LPπ(Ob′)→σ*(S1C5) 2.62
	C2 0.107 (0.002) C2′ -0.011 (-0.170) S1 0.146 (0.493) Ob′ -0.300 (-0.535) N3 -0.391 (-0.447)	π(C2′C3′)→π*(C2N3) 18.40 π(C2′C3′)→π*(Ca′Ob′) 25.11 LPπ(Ob′)→σ*(S1C5) 2.72
	C2 -0.059 (-0.268) C2′ -0.008 (-0.145) S1 0.128 (0.522) Ob′ -0.152 (-0.397)	π(C2′C3′)→π*(C2C3) 12.26(12.33) π(C2′C3′)→π*(Na′Oc′) 27.45 (21.44) LPπ(Ob′)→σ*(S1C5) 2.21

(38.7 and 143.3 degree, respectively) are shifted to the central region (90 degree) of torsional potential compared to that of BT. This is majorly attributed to the steric repulsions, which are strongest at 0 and 180 degrees, from the amino group (see D1 (S···HN) is 2.5 Å and D4 (CH···HN) 1.98 Å in **Table S1**). In addition, the electrostatic interaction between NH_2 and thiophene of H-NH_2-BT at the planar is repulsive since the hydrogen and sulfur atoms are both positively charged. Thus, the steric repulsion cannot be compensated by electrostatic interactions as in the case of H-OCH_3-BT. Similar to alkyl-substituted bithiophenes, the steric repulsions in H-NH_2-BT result in large barriers ΔE_1 and ΔE_4 (2.05 and 0.82 kcal/mol) compared to those in BT (0.54 and 0.18 kcal/mol).

Another interesting feature in the torsional potential of H-NH_2-BT is that the relative energy at 90 degree is lower compared to those of BT and H-OCH_3-BT. The lower transition structure energy also reduces the internal rotation barrier, e.g., the *trans* to *cis* barrier ΔE_3 (0.75 kcal/mol) compared to that of BT (1.80 kcal/mol). The *cis* to *trans* barrier ΔE_2 (1.22 kcal/mol) is not much lower compared to that of BT (1.34 kcal/mol) because of the possible hydrogen bond between the aryl hydrogen and amino nitrogen (CH···NH) shown in **Figure S4(c)**. The lower energy for the transition structure of H-NH_2-BT is caused by NH-π interaction between the amino group and its neighboring thiophene (**Figure S4(c)**). The NH-π interaction stabilizes the transition structure just like the alkyl-substituted bithiophene. This is confirmed by the thiophene-ammonia dimer calculation (**Figure S4(d))**. The destablized planar structure caused by steric repulsion and reduced internal rotation barrier caused by NH-π interaction both contribute to the deterioration of coplanarity in amino-substituted bithiophenes.

The torsional potential of donor-substituted bithiophene by B3LYP is presented in **Figure S8**. It follows the same trend with the result from wB97x. Due to delocalization error, the internal rotation barrier is higher than that of wB97x. Since B3LYP underestimates the magnitude of the NH-π interaction (See **Figure S4(d)**), the relative energy of transition structure is higher than the value by wB97x (0.54 kcal/mol by B3LYP and -0.07 kcal/mol by wB97x).

3.2.2 Acceptor-Substituted Bithiophenes

From the torsional potential of H-CN-BT (**Figure 3** and **Table 2**), the coplanarity is not much affected by the cyano group. The linear cyano group of H-CN-BT possesses reduced steric hindrance, and thus the position of the *trans*-local is close to that of BT. The energy difference between local minima and planar structures (ΔE_1 and ΔE_4) are 0.32 and 0.19 kcal/mol which are well below 1 k_BT. In addition, the *trans* to *cis* barrier ΔE_3 (1.54 kcal/mol) is lower than that of BT (1.80 kcal/mol) by about 0.3 kcal/mol, but the barrier height ΔE_3 is still reaching 3 k_BT. The *cis*-local has lower energy than the *trans*-local due to less steric hindrance between the aryl hydrogen and cyano group compared with the sulfur atom and cyano group. The lower energy of *cis* local minimum enhances the *cis* to *trans* barrier ΔE_2 to 3 k_BT (2.19 kcal/mol), making the *cis* to *trans* transition difficult at room temperatures. Easy reaching planar structure and high internal rotation barrier preserve the coplanarity of cyano-substituted bithiophene. Following the same argument, the coplanarity of PDCTh and 3,4'-dialkoxy-4,3′-dicyano-2,2′-bithiophene are still preserve, as supported by UV-vis and X-ray studies.[72, 73] In P3CN4HT, the coplanarity could be destroyed by the alkyl side chain, which has been discussed in the previous section.

The coplanarity of H-CHO-BT is not preserved because of the lower relative energy of transition structure and lower internal rotation barrier. From the charge analysis at *trans*-planar structure, the atomic charge on C2′ becomes less negative (-0.01 *e* by CM5 and -0.127 *e* by natural charge) due to the electron-withdrawing formyl group at the head position compared that of BT (-0.048 *e* by CM5 and -0.217 *e* by natural charge). The donor-acceptor interaction representing backbone conjugation, π(C2′C3′)→π*(C2C3), is also reduced to 14.09 kcal/mol compared with 17.41 kcal/mol in BT. A very strong donor-acceptor interaction π(C2′C3′)→π*(Ca′Ob′) (26 kcal/mol) is observed compared to donor-acceptor interaction π(C2′C3′)→π*(Ca′Nb′) in H-CN-BT (20.95 kcal/mol). The strong donor-acceptor interaction between the backbone and formyl group in H-CHO-BT decreases the backbone conjugation, which destabilizes planar structures and reduces the internal rotation barrier since the partial double bond C2-C2′ loses π character to a certain extent.

Many theoretical studies on molecules similar to H-CHO-BT argue that the S···O interaction between S1 and Ob′ and the CH···O interaction between H3 and Ob′ would enhance the coplanarity.[20, 63, 64] From the change of C2'-C3'-Ca'-Ob' in H-CHO-BT (**Figure S7(b)**) during potential energy scan, the dihedral angle changes widely with respect to the ring plane. When S1 moves away from the ring plane, Ob′ follows the move of S1 and deviates from the plane as well. The same trend is also found in H3 and Ob′. The result indicates that the S···O and CH···O interactions do exist. However, these interactions do not enhance the coplanarity of H-CHO-BT from the torsional potential shown in **Figure 3**. The questionable argument could have been misled by the choice of spread out basis sets or functional with delocalization error.

The influence of S···N interaction is examined by replacing the unsubstituted thiophene in H-CHO-BT with thiazole, as shown in **Figure S7(c)**. From the torsional potential, there is only one minimum at *trans*-planar, and the barrier from *trans*-planar to transition structure is nearly 4 kcal/mol. Two factors improve the coplanarity of 3′-formyl-2-(2′-thienyl)thiazole from the convention point of view. First, the nitrogen atom at the 3 position reduces the steric repulsion between the aryl hydrogen and sulfur atom in *cis*-planar H-CHO-BT. Second, the negative charge of nitrogen (-0.391 *e* by CM5; -0.447 *e* by NBO) also favors the electrostatic interaction with the positively charged neighboring sulfur atom (S1′). From the NBO analysis, we found that the backbone conjugation could also attribute to the enhanced coplanarity. The conjugation interaction π(C2′C3′)→π*(C2N3) reaches 18.40 kcal/mol, which is similar to the interaction in H-OCH$_3$-BT. The backbone conjugation is recovered by the electron negative nitrogen in 3′-formyl-2-(2′-thienyl)thiazole even if the electron-withdrawing formyl group is attached at the head position.

The torsional potential of H-NO$_2$-BT (**Figure 3**) shows very different characters compared to those of H-CN-BT and H-CHO-BT. The planar structure is becoming less stable and the relative energy of transition structure is much lower compared to H-CN-BT and H-CHO-BT. At the planar structures, the distance parameters from D1 to D4 in H-NO$_2$-BT are slightly shorter than the parameters in H-CHO-BT by about 0.05 Å (see **Table S1**). Therefore, the steric repulsions in H-NO$_2$-BT should be similar that in H-CHO-BT at the planar structures. The relative energy of local minima in H-NO$_2$-BT is lower than the energy in H-CHO-BT. One can argue that the S···O and CH···O interactions in H-NO$_2$-BT are stronger than H-CHO-BT; however, the distance parameters D1 and D4 in H-CHO-BT and H-NO$_2$-BT are similar at local minima **(Table S1)**. Therefore, we argue that the strength of through-space interactions is similar in H-CHO-BT and H-NO$_2$-BT. The different torsional potentials between H-CHO-BT and H-NO$_2$-BT can be explained by NBO analysis. Weaker backbone conjugation and stronger donor-acceptor interactions between the backbone and the electron-withdrawing nitro group in H-NO$_2$-BT are observed compared to H-CN-BT and H-CHO-BT. The π(C2′C3′)→π*(C2C3) interaction energy is reduced to 12.26 kcal/mol compared to 14.19 and 14.09 kcal/mol in H-CN-BT and H-CHO-BT respectively. The π(C2′C3′)→π*(Na′Oc′) interaction energy increases to 27.45 kcal/mol at *trans*-planar compared to 20.96 and 26.05 kcal/mol in H-CN-BT and H-CHO-BT, respectively. Although the interaction energy decreases to 21.44 kcal/mol at *cis*-planar (because the nitro group largely deviate to the ring plane about 30 degree, see **Figure S7(d)**), the backbone conjugation energy is still low (12.33 kcal/mol). The weak backbone conjugation destabilizes the planar structures of H-NO$_2$-BT and reduces the internal rotation barrier more than H-CHO-BT.

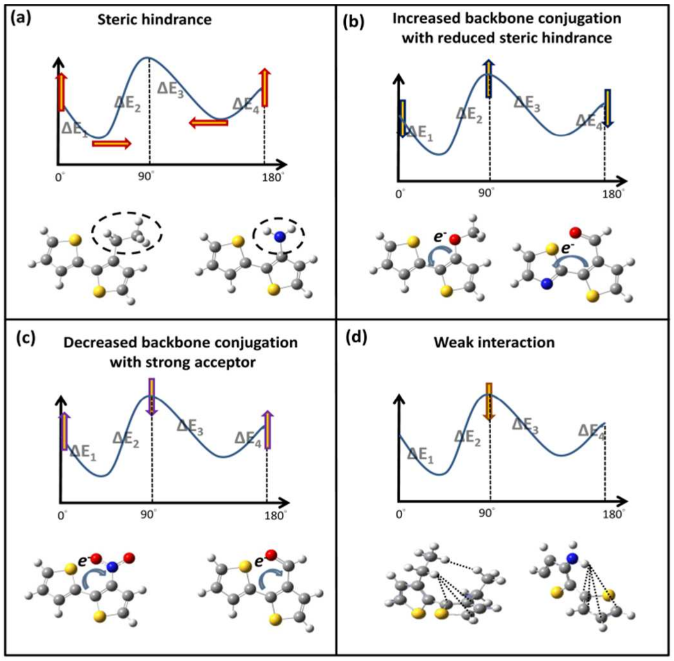


Figure 4. The influences and examples of (a) steric hindrance, (b) (c) backbone conjugation, and (d) weak noncovalent interaction to the torsional potential of the substituted bithiophene. The arrows show the tendency of the change.

Combining the torsional potential of H-NH$_2$-BT, one can infer that the coplanraity of Poly(3,4-diamino-3,4-dinitro-2,2'-bithiophene) is unfavorable due to the steric repulsion from the amino group and strong electron-withdrawing nitro group. Therefore, previous arguments that the intramolecular charge transfer keeps Poly(3,4-diamino-3,4-dinitro-2,2'-bithiophene) in planar conformation may be doubtful.[35]

3.3 Key factors influencing the coplanarity of substituted bithiophene

Based on these studies, we conclude that there are four factors governing the torsional potential of the substituted bithiophene: substitution position, steric hindrance, backbone conjugation, and weak noncovalent interaction between the substituents and thiophene rings. The substitutions at the tail positions of bithiophene have no influence on the torsional potential but those at the head positions do. **Figure 4** illustrates key factors influence the torsional potential when the substituent is attached at the head position.

Steric hindrance, resulting from bulky substituent group (e.g., alkyl-substituted bithiophene and H-NH_2-BT), increases the barrier at 0 and 180 degree (ΔE_1 and ΔE_4) and pushes the local minimum away from planar conformations.

The backbone conjugation, which can be enhanced by electron donating groups or electron negative atom on the ring (e.g, H-OCH_3-BT and 3′-formyl-2-(2′-thienyl)thiazole), increases the rotational barriers (ΔE_2 and ΔE_3) for cis-trans transition. Conversely electron withdrawing groups (e.g., H-CHO-BT and H-NO_2-BT) reduce the *cis-trans* transition barriers. More specifically, when the increased backbone conjugation $\pi(C2'C3') \rightarrow \pi^*(C2C3)$ is higher than 18 kcal/mol (with reduced steric hindrance) often results in diminished ΔE_1 and ΔE_4 and increased ΔE_2 and ΔE_3, resulting in stabilized planar structure. On the contrary, decreased backbone conjugation with strong electron-acceptor ($\pi(C2'C3') \rightarrow \pi^*(C2C3)$ lower than 14 kcal/mol and backbone→acceptor interaction higher than 25 kcal/mol) increases ΔE_1 and ΔE_4 and reduces internal rotation barriers ΔE_2 and ΔE_3.

Weak noncovalent interactions between the substituent and thiophene ring such as CH-π, NH-π, and dispersion interactions stabilize the transition structures and reduce the internal rotation barrier (eg. alkyl-substituted bithiophene and H-NH_2-BT). The reduced barrier caused by decreased backbone conjugation and weak noncovalent interaction would facilitate conformation changes at room temperature. S⋯O, N⋯O, and CH⋯O interactions contribute to the coplanairty of the substituted bithiophenes to certain extents, but they are not critical factors. The similar argument is also proposed by Jackson.[104]

Conclusions

Torsional potentials of alkyl-, donor-, and acceptor-substituted bithiophenes are examined by DFT calculations. It is found that the stable conformation of these compounds are results of competition of interactions from steric hindrance, backbone conjugation, and weak noncovalent interaction. Reduced steric hindrance and enhanced backbone conjugation (due to electron donating substituents) improve the stability of planar structures. Strong steric hindrance and reduced backbone conjugation (due to electron withdrawing substituents) destabilize the planar structures. The weak noncovalent interactions and the backbone conjugation may reduce the transition barrier of *cis-trans* conformation transitions. For the systems studied here, the importance of these factors often falls in the following order, steric hindrance > backbone conjugation > weak noncovalent interaction.

Different theoretical methods may provide quite different description on the strength of weak noncovalent interactions, and some of them may possess delocalization error which would give wrong physical pictures of conjugated molecules with different substituents. Thus, the results of the present study can provide possible new strategies for developing force field parameters of substituted oligothiophene or its similar derivatives. The functional with delocalization error and without considering dispersion interactions should be avoided. In addition, substituents with various electron withdrawing/donating capabilities should have corresponding backbone torsional potentials. It would be interesting to extend this study to longer oligomers to approach realistic situations in materials. Nevertheless, delocalization error, weak noncovalent interactions, and multi-reference character of extending conjugated system must be all taken care in future theoretical studies.

Acknowledgements

This research was partially supported by the National Science Council of Taiwan (NSC 101-2628-E-002-014-MY3) and the Ministry of Education of Taiwan (NTU-CDP-103R7815). The authors would like to thank Prof. Jeng-Da Chai, Physics Department of National Taiwan University, for discussion and testing the multi-reference character of bithiophene molecule.

Notes and references

[a] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan .
[*] stlin@ntu.edu.tw

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

Reference

1. E. Ahmed, T. Earmme and S. A. Jenekhe, *Advanced Functional Materials*, 2011, **21**, 3889-3899.
2. M. Cai, T. Xiao, E. Hellerich, Y. Chen, R. Shinar and J. Shinar, *Advanced Materials*, 2011, **23**, 3590-3596.
3. A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chemical Reviews*, 2009, **109**, 897-1091.
4. S. Ko, E. Verploegen, S. Hong, R. Mondal, E. T. Hoke, M. F. Toney, M. D. McGehee and Z. Bao, *Journal of the American Chemical Society*, 2011, **133**, 16722-16725.
5. C. Li and H. Wonneberger, *Advanced Materials*, 2012, **24**, 613-636.
6. I. Osaka, M. Shimawaki, H. Mori, I. Doi, E. Miyazaki, T. Koganezawa and K. Takimiya, *Journal of the American Chemical Society*, 2012, **134**, 3498-3507.
7. H. J. Son, F. He, B. Carsten and L. Yu, *Journal of Materials Chemistry*, 2011, **21**, 18934-18945.
8. Q. Zheng, B. J. Jung, J. Sun and H. E. Katz, *Journal of the American Chemical Society*, 2010, **132**, 5394-5404.

9. G. Giri, E. Verploegen, S. C. B. Mannsfeld, S. Atahan-Evrenk, D. H. Kim, S. Y. Lee, H. A. Becerril, A. Aspuru-Guzik, M. F. Toney and Z. Bao, *Nature*, 2011, **480**, 504-508.
10. B. J. Jung, N. J. Tremblay, M.-L. Yeh and H. E. Katz, *Chemistry of Materials*, 2010, **23**, 568-582.
11. T. Lee, C. A. Landis, B. M. Dhar, B. J. Jung, J. Sun, A. Sarjeant, H.-J. Lee and H. E. Katz, *Journal of the American Chemical Society*, 2009, **131**, 1692-1705.
12. K. Takimiya, S. Shinamura, I. Osaka and E. Miyazaki, *Advanced Materials*, 2011, **23**, 4347-4370.
13. H. Usta, A. Facchetti and T. J. Marks, *Accounts of Chemical Research*, 2011, **44**, 501-510.
14. H. Zhou, L. Yang and W. You, *Macromolecules*, 2012, **45**, 607-632.
15. A. Facchetti, *Chemistry of Materials*, 2010, **23**, 733-758.
16. J. Mei and Z. Bao, *Chemistry of Materials*, 2013, **26**, 604-615.
17. B. Balan, C. Vijayakumar, A. Saeki, Y. Koizumi and S. Seki, *Macromolecules*, 2012, **45**, 2709-2719.
18. M. S. Chen, J. R. Niskala, D. A. Unruh, C. K. Chu, O. P. Lee and J. M. J. Fréchet, *Chemistry of Materials*, 2013, **25**, 4088-4096.
19. A. A. El-Shehawy, N. I. Abdo, A. A. El-Barbary and J.-S. Lee, *European Journal of Organic Chemistry*, 2011, **2011**, 4841-4852.
20. X. Guo, N. Zhou, S. J. Lou, J. W. Hennek, R. Ponce Ortiz, M. R. Butler, P.-L. T. Boudreault, J. Strzalka, P.-O. Morin, M. Leclerc, J. T. López Navarrete, M. A. Ratner, L. X. Chen, R. P. H. Chang, A. Facchetti and T. J. Marks, *Journal of the American Chemical Society*, 2012, **134**, 18427-18439.
21. C. Kanimozhi, M. Naik, N. Yaacobi-Gross, E. K. Burnett, A. L. Briseno, T. D. Anthopoulos and S. Patil, *The Journal of Physical Chemistry C*, 2014, **118**, 11536-11544.
22. H.-J. Song, D.-H. Kim, E.-J. Lee, S.-W. Heo, J.-Y. Lee and D.-K. Moon, *Macromolecules*, 2012, **45**, 7815-7822.
23. J. C. Speros, H. Martinez, B. D. Paulsen, S. P. White, A. D. Bonifas, P. C. Goff, C. D. Frisbie and M. A. Hillmyer, *Macromolecules*, 2013, **46**, 5184-5194.
24. S. Ko, E. T. Hoke, L. Pandey, S. Hong, R. Mondal, C. Risko, Y. Yi, R. Noriega, M. D. McGehee, J.-L. Brédas, A. Salleo and Z. Bao, *Journal of the American Chemical Society*, 2012, **134**, 5222-5232.
25. Z.-G. Zhang, J. Min, S. Zhang, J. Zhang, M. Zhang and Y. Li, *Chemical Communications*, 2011, **47**, 9474-9476.
26. S. K. Lee, S. Cho, M. Tong, J. Hwa Seo and A. J. Heeger, *Journal of Polymer Science Part A: Polymer Chemistry*, 2011, **49**, 1821-1829.
27. L. Biniek, S. Fall, C. L. Chochos, D. V. Anokhin, D. A. Ivanov, N. Leclerc, P. Lévêque and T. Heiser, *Macromolecules*, 2010, **43**, 9779-9786.
28. M. R. Andersson, O. Thomas, W. Mammo, M. Svensson, M. Theander and O. Inganas, *Journal of Materials Chemistry*, 1999, **9**, 1933-1940.
29. Y. Huang, M. Zhang, L. Ye, X. Guo, C. C. Han, Y. Li and J. Hou, *Journal of Materials Chemistry*, 2012, **22**, 5700-5705.
30. R. Qin, W. Li, C. Li, C. Du, C. Veit, H.-F. Schleiermacher, M. Andersson, Z. Bo, Z. Liu, O. Inganäs, U. Wuerfel and F. Zhang, *Journal of the American Chemical Society*, 2009, **131**, 14612-14613.
31. S. Vandeleene, K. Van den Bergh, T. Verbiest and G. Koeckelberghs, *Macromolecules*, 2008, **41**, 5123-5131.
32. T. Okamoto and Z. Bao, *Journal of the American Chemical Society*, 2007, **129**, 10308-10309.
33. C. Shi, Y. Yao, Yang and Q. Pei, *Journal of the American Chemical Society*, 2006, **128**, 8980-8986.
34. A. P. Monkman, L.-O. Pålsson, R. W. T. Higgins, C. Wang, M. R. Bryce, A. S. Batsanov and J. A. K. Howard, *Journal of the American Chemical Society*, 2002, **124**, 6049-6055.
35. Q. T. Zhang and J. M. Tour, *Journal of the American Chemical Society*, 1998, **120**, 5355-5362.
36. M. Banno, T. Yamaguchi, K. Nagai, C. Kaiser, S. Hecht and E. Yashima, *Journal of the American Chemical Society*, 2012, **134**, 8718-8728.
37. M. Manceau, E. Bundgaard, J. E. Carle, O. Hagemann, M. Helgesen, R. Sondergaard, M. Jorgensen and F. C. Krebs, *Journal of Materials Chemistry*, 2011, **21**, 4132-4141.
38. Y. Huang, L. Huo, S. Zhang, X. Guo, C. C. Han, Y. Li and J. Hou, *Chemical Communications*, 2011, **47**, 8904-8906.
39. H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat Photon*, 2009, **3**, 649-653.
40. H. Li, A. Sundararaman, K. Venkatasubbaiah and F. Jäkle, *Journal of the American Chemical Society*, 2007, **129**, 5792-5793.
41. Y. Terada, B.-K. Choi, S. Heike, M. Fujimori and T. Hashizume, *Nano Letters*, 2003, **3**, 527-531.
42. Z. Hu, J. Liu, L. Simón-Bower, L. Zhai and A. J. Gesquiere, *The Journal of Physical Chemistry B*, 2012, **117**, 4461-4467.
43. B. McCulloch, V. Ho, M. Hoarfrost, C. Stanley, C. Do, W. T. Heller and R. A. Segalman, *Macromolecules*, 2013, **46**, 1899-1907.
44. T. Adachi, J. Brazard, R. J. Ono, B. Hanson, M. C. Traub, Z.-Q. Wu, Z. Li, J. C. Bolinger, V. Ganesan, C. W. Bielawski, D. A. Vanden Bout and P. F. Barbara, *The Journal of Physical Chemistry Letters*, 2011, **2**, 1400-1404.
45. E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer and P. Bäuerle, *Angewandte Chemie International Edition*, 2000, **39**, 2679-2684.
46. F. Nishiyama, K. Ogawa, S. Tanaka and T. Yokoyama, *The Journal of Physical Chemistry B*, 2008, **112**, 5272-5275.
47. G. Raos, A. Famulari and V. Marcon, *Chemical Physics Letters*, 2003, **379**, 364-372.
48. H. A. Duarte, H. F. Dos Santos, W. R. Rocha and W. B. De Almeida, *The Journal of Chemical Physics*, 2000, **113**, 4206-4215.
49. P. M. Viruela, R. Viruela and E. Orti, *International Journal of Quantum Chemistry*, 1998, **70**, 303-312.
50. E. Orti, P. M. Viruela, J. Sanchez-Marin and F. Tomas, *The Journal of Physical Chemistry*, 1995, **99**, 4955-4963.
51. C. Alemán and L. Julia, *The Journal of Physical Chemistry*, 1996, **100**, 1524-1529.
52. R. S. Bhatta, Y. Y. Yimer, M. Tsige and D. S. Perry, *Computational and Theoretical Chemistry*, 2012, **995**, 36-42.
53. S. B. Darling and M. Sternberg, *The Journal of Physical Chemistry B*, 2009, **113**, 6215-6218.
54. V. Hernandez and J. T. Lopez Navarrete, *The Journal of Chemical Physics*, 1994, **101**, 1369-1377.
55. G. Raos, A. Famulari, S. V. Meille, M. C. Gallazzi and G. Allegra, *The Journal of Physical Chemistry A*, 2004, **108**, 691-698.
56. A. Baggioli and A. Famulari, *Physical Chemistry Chemical Physics*, 2014, **16**, 3983-3994.
57. A. Baggioli, S. V. Meille, G. Raos, R. Po, M. Brinkmann and A. Famulari, *International Journal of Quantum Chemistry*, 2013, **113**, 2154-2162.
58. X. Guo, J. Quinn, Z. Chen, H. Usta, Y. Zheng, Y. Xia, J. W. Hennek, R. P. Ortiz, T. J. Marks and A. Facchetti, *Journal of the American Chemical Society*, 2013, **135**, 1986-1996.
59. H. Huang, Z. Chen, R. P. Ortiz, C. Newman, H. Usta, S. Lou, J. Youn, Y.-Y. Noh, K.-J. Baeg, L. X. Chen, A. Facchetti and T. Marks, *Journal of the American Chemical Society*, 2012, **134**, 10966-10973.
60. J. Poater, J. Casanovas, M. Solà and C. Alemán, *The Journal of Physical Chemistry A*, 2009, **114**, 1023-1028.
61. N. Hergue, P. Leriche, P. Blanchard, M. Allain, N. Gallego-Planas, P. Frere and J. Roncali, *New Journal of Chemistry*, 2008, **32**, 932-936.
62. C. Alemán and J. Casanovas, *The Journal of Physical Chemistry A*, 2004, **108**, 1440-1447.
63. M. Pomerantz, *Tetrahedron Letters*, 2003, **44**, 1563-1565.
64. M. Pomerantz and Y. Cheng, *Tetrahedron Letters*, 1999, **40**, 3317-3320.
65. N. DiCésare, M. Belletête, M. Leclerc and G. Durocher, *Journal of Molecular Structure: THEOCHEM*, 1999, **467**, 259-273.
66. G. C. Welch, R. C. Bakus, S. J. Teat and G. C. Bazan, *Journal of the American Chemical Society*, 2013, **135**, 2298-2305.
67. Y.-H. Tian and M. Kertesz, *Macromolecules*, 2009, **42**, 2309-2312.
68. A. S. Özen, C. Atilgan and G. Sonmez, *The Journal of Physical Chemistry C*, 2007, **111**, 16362-16371.

69. S. E. Burkhardt, G. G. Rodríguez-Calero, M. A. Lowe, Y. Kiya, R. G. Hennig and H. c. D. Abruña, *The Journal of Physical Chemistry C*, 2010, **114**, 16776-16784.
70. C. L. Chochos, S. P. Economopoulos, V. Deimede, V. G. Gregoriou, M. T. Lloyd, G. G. Malliaras and J. K. Kallitsis, *The Journal of Physical Chemistry C*, 2007, **111**, 10732-10740.
71. C. L. Chochos, N. Tagmatarchis and V. G. Gregoriou, *RSC Advances*, 2013, **3**, 7160-7181.
72. Y. Greenwald, X. Xu, M. Fourmigué, G. Srdanov, C. Koss, F. Wudl and A. J. Heeger, *Journal of Polymer Science Part A: Polymer Chemistry*, 1998, **36**, 3115-3120.
73. N. m. Hergué, C. Mallet, G. Savitha, M. Allain, P. Frère and J. Roncali, *Organic Letters*, 2011, **13**, 1762-1765.
74. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, (2009) Gaussian, Inc., Wallingford, CT, USA.
75. J. Autschbach and M. Srebro, *Accounts of Chemical Research*, 2014.
76. A. J. Cohen, P. Mori-Sánchez and W. Yang, *Chemical Reviews*, 2011, **112**, 289-320.
77. P. Mori-Sánchez, A. J. Cohen and W. Yang, *The Journal of Chemical Physics*, 2006, **125**, -.
78. Y. Zhao and D. G. Truhlar, *The Journal of Physical Chemistry A*, 2006, **110**, 10478-10486.
79. J. C. Sancho-García, *The Journal of Physical Chemistry A*, 2005, **109**, 3470-3475.
80. J. S. Sears, R. R. Chance and J.-L. Brédas, *Journal of the American Chemical Society*, 2010, **132**, 13313-13319.
81. C. Sutton, T. Körzdörfer, M. T. Gray, M. Brunsfeld, R. M. Parrish, C. D. Sherrill, J. S. Sears and J.-L. Brédas, *The Journal of Chemical Physics*, 2014, **140**, 054310.
82. C. H. Choi, M. Kertesz and A. Karpfen, *Chemical Physics Letters*, 1997, **276**, 266-268.
83. A. Karpfen, C. H. Choi and M. Kertesz, *The Journal of Physical Chemistry A*, 1997, **101**, 7426-7433.
84. J.-D. Chai, *The Journal of Chemical Physics*, 2012, **136**, 154104.
85. J.-D. Chai, *The Journal of Chemical Physics*, 2014, **140**, 18A521.
86. S. F. Boys and F. Bernardi, *Molecular Physics*, 1970, **19**, 553-566.
87. S. Simon, M. Duran and J. J. Dannenberg, *The Journal of Chemical Physics*, 1996, **105**, 11024-11031.
88. E. D. Glendening, C. R. Landis and F. Weinhold, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2012, **2**, 1-42.
89. F. L. Hirshfeld, *Theoret. Chim. Acta*, 1977, **44**, 129-138.
90. A. V. Marenich, S. V. Jerome, C. J. Cramer and D. G. Truhlar, *Journal of Chemical Theory and Computation*, 2012, **8**, 527-541.
91. L. Goodman and R. R. Sauers, *Journal of Computational Chemistry*, 2007, **28**, 269-275.
92. F. Martin and H. Zipse, *Journal of Computational Chemistry*, 2005, **26**, 97-105.
93. J. Echeverría, G. Aullón, D. Danovich, S. Shaik and S. Alvarez, *Nat Chem*, 2011, **3**, 323-330.
94. G. Barbarella, A. Bongini and M. Zambianchi, *Macromolecules*, 1994, **27**, 3039-3045.
95. G. Barbarella, M. Zambianchi, L. Antolini, U. Folli, F. Goldoni, D. Iarossi, L. Schenetti and A. Bongini, *Journal of the Chemical Society, Perkin Transactions 2*, 1995, 1869-1873.
96. G. Barbarella, M. Zambianchi, A. Bongini and L. Antolini, *Advanced Materials*, 1992, **4**, 282-285.
97. G. Barbarella, M. Zambianchi, A. Bongini and L. Antolini, *Advanced Materials*, 1993, **5**, 834-838.
98. O. Inganäs, G. Gustafsson, W. R. Salaneck, J. E. Österholm and J. Laakso, *Synthetic Metals*, 1989, **28**, 377-384.
99. W. R. Salaneck, O. Inganäs, J. O. Nilsson, J. E. Österholm, B. Thémans and J. L. Brédas, *Synthetic Metals*, 1989, **28**, 451-460.
100. M. J. Winokur, D. Spiegel, Y. Kim, S. Hotta and A. J. Heeger, *Synthetic Metals*, 1989, **28**, 419-426.
101. C. Yang, F. P. Orfino and S. Holdcroft, *Macromolecules*, 1996, **29**, 6510-6517.
102. M. Iwaoka and N. Isozumi, *Molecules*, 2012, **17**, 7266-7283.
103. C. Rethore, A. Madalan, M. Fourmigue, E. Canadell, E. B. Lopes, M. Almeida, R. Clerac and N. Avarvari, *New Journal of Chemistry*, 2007, **31**, 1468-1483.
104. N. E. Jackson, B. M. Savoie, K. L. Kohlstedt, M. Olvera de la Cruz, G. C. Schatz, L. X. Chen and M. A. Ratner, *Journal of the American Chemical Society*, 2013, **135**, 10475-10483.