Theoretical Study of σ - π Conjugated Semiconductors Based on *cis*- and *trans*-Cyclopropane Derivatives

Yuyu Liu,^{†,a} Lei Yang,^{†,a} Xiaofei Zhang,^b Jiwei Li,^a Linghai Xie,^{*,a}
Mingdong Yi,^a and Wei Huang^{*,c}

^a Institute of Advanced Materials, Nanjing University of Posts & Telecommunications, Nanjing, Jiangsu 210023, China

^b College of Mathematics and Information Science, Guangxi University, Nanning, Guangxi 530004, China

^c Institute of Advanced Materials, Nanjing Tech University, Nanjing, Jiangsu 211816, China

The high strain cyclopropane as σ block model inserted in organic semiconductors to tune the structures and optical properties was investigated by the density functional theory method. The band gaps and absorption peaks of 1,2-disubstituted cyclopropanes were between the corresponding alkanes and olefins. The *cis*-isomers had higher steric strain between two substituents and lower symmetry than the *trans*-isomers in ground-state structures. The electronic transitions ($S_0 \rightarrow S_1$) were mainly on the aryl parts, which were stronger coherence with surrounding atoms in *cis*-isomers, while the *trans*-isomers were on the cyclopropyl. Furthermore, 1,2-disubstituted cyclopropanes (**1A**, **1B**, **2A**, **4B**) could respond to the charge stimulation, which are potential materials for organic electronics and mechatronics.

Keywords cyclopropane, σ block, density functional theory, structures and optical properties, electronic transition

Introduction

Since doped polyacetylene with high electrical conductivity was discovered in 1977^[1,2] as new electronic materials, organic/polymer semiconductors have attracted scientific and industrial interests. Organic electronic devices have attractive advantages including low costs, flexibility, light weight, large size over conventional inorganic devices.^[3] The essential characteristic of organic semiconductors was the mobility of charge in the electron system.^[4] According to the four-element design principle of organic/polymeric semiconductors,^[3,5] the modification of molecular electric structure was the most basic tool to modulate the performance of devices by means of inserting various building blocks into the π -electron system, such as π block,^[6,7] heteroatom block,^[8,9] metal block,^[10,11] and σ block.^[12,13] Among them, σ electrons could not only delocalize in π -conjugated system through σ - π interactions to tune the electric structure, but also improve the solubility, thermal and optical stability. These σ - π conjugated semiconductors were potential candidates for application in organic field-effect transistors (OFETs)^[14] and organic light-emitting diodes (OLEDs).^[15,16] In this regard, the quest for new σ block based conjugated materials can be attributed to deeply uncovering physical organic properties of σ - π conjugated semiconductors and further ex-

ploring their novel properties and applications via theoretical and experimental study.

As the smallest archetypal cyclic hydrocarbons, cyclopropane with the conventional strain energy (27.5 kcal/mol)^[17] and short C—C bond (1.510 Å), not only exhibited unusual magnetic properties,^[18,19] but also had special photo-physical characteristics.^[20] During the past several decades, many efforts have been devoted to experimentally^[21,22] and theoretically^[23,24] exploring cyclopropane and their derivatives to elaborate these special properties. But the cyclopropane as the building block has rarely been found in organic/polymeric semiconductors. Fluorene exhibits inherent larger exciton binding energies and excellent charge delocalization, enabling it to be the most extensive building block in the molecular design of organic/polymer semiconductors.^[3] Herein, cyclopropane as a σ block was introduced into π conjugated benzene, naphthalene, anthracene and fluorene motifs to construct the σ - π conjugated semiconductors (Scheme 1). All calculations were performed at an integrated approach B97D (WB97XD)/TZVP level.^[25,26] The geometric/electronic structures, optical properties and effective substituent conjugation length of the *cis*- and *trans*-isomers were investigated. The relevant parameters of electronic structures and optical properties such

*E-mail: iamhxie@njupt.edu.cn, iamwhuang@njupt.edu.cn; Tel.: 0086-025-58139001; Fax: 0086-025-58139988

Received June 22, 2015; accepted June 26, 2015; published July 14, 2015.

Supporting information for this article is available on the WWW under <http://www.gchemistry.org>.

[†] These authors contributed equally to this work.

as dipole moment, electrostatic potential (ESP), the visualization of the weak interactions in real space and frontier molecular orbitals were estimated. The absorption spectra and transition density matrix (TDM) ($S_0 \rightarrow S_1$) of these materials were predicted and discussed. The structure and photoelectronic properties of the *cis*- and *trans*-isomers of 1,2-disubstituted cyclopropanes were also compared with corresponding alkanes, olefins and 1,1-disubstituted (Figure S1).

Scheme 1 Chemical structures of 1,2-disubstituted cyclopropanes. Some important atoms are labeled.

Theoretical evidence and computational details

The absorption spectrum of **1B** as a benchmark for this σ - π conjugation system was employed to choose the suitable methods. The ground-state geometry of **1B** was fully optimized by using density functional theory (DFT) with B3LYP and B97D at different basis sets (Figure S2). The electronic absorption spectra of **1B** were calculated by TD-DFT-B3LYP (-B97D) with 25 lowest singlet states. The calculated wavelengths of main UV-*vis* absorption peaks (simulated by B97D, about 277.58 and 217.88 nm) were only about 1 and 12 nm differences compared to the experimental results,^[27,28] which demonstrated that B97D was a suitable method for cyclopropane derivatives. However, B3LYP overestimated the excitation energies. Therefore, B97D/TZVP was implemented to investigate the geometry/electronic structures and optical properties of σ - π conjugated cyclopropane derivatives, including population charge distributions (by NBO method), UV-*vis* absorption, and so on. The analysis of Mayer bond order, weak interactions and the transition density matrix was performed by Multiwfn 3.3 software^[29] based on the wave function generated at B97D/TZVP level. The visualization of weak interactions in real space was drawn by VMD1.9.^[30]

Transition density matrix (TDM) between electronic state K and state L denoted by P^{KL} is generated by Gaussian 09 software^[31] during excited state calculation. This matrix outputted in the form of expansion by

atomic-center basis functions was defined by the following equation:

$$P_{A,B}^{KL} = \sum_{\mu \in A} \sum_{\nu \in B} (P_{\mu\nu}^{KL})^2$$

where μ and ν denote the basis functions centered at atom A and B, respectively.

Diagonal terms represent the magnitude of induced charge on atom A when the system undergoes electron transition from state K to L. Off-diagonal terms display the strength of electron-hole coherence between atom A and B when electron transits. When TDM is plotted as a color-filled map, hydrogens are omitted.^[29]

Considering the accurate description of charge state of compounds, the charged geometries of **1A**, **1B**, **2A** and **4B** were optimized at the UWB97Xd/TZVP level. All calculations of quantum chemistry are carried out in Gaussian 09 software.

Results and Discussion

Optimized ground-state geometries

The chemical structures of cyclopropane molecules with different π -conjugated substituent groups in their ground states were fully optimized using the DFT method (Scheme 1 and Figure S1). Some key bond lengths, bond angles, dipole moments, 2-center and 3-center Mayer bond-order for the fully optimized geometric conformations of cyclopropane derivatives in the S_0 states are listed in Table 1. The *trans*-1(R), 2(R)-disubstituted cyclopropanes were used as the example of *trans*-isomers (Figure S3). Compared with cyclopropane (1.510 Å),^[32] the bond lengths of C(1)—C(2) increased and were close to ethane 1.535 Å, but much longer than 1.332 Å in ethylene, while the bond lengths of C(2)—C(3) and C(1)—C(3) decreased in all employed molecules. It was also found that the C—H bonds [C(1)—H(1)] in cyclopropyl were around 1.090 Å, which were close to those of ethane (1.094 Å), ethylene (1.090 Å) and the experimental data (1.089 Å).^[32] The calculated H—C—C (π) bond [H(1)—C(1)—C(10)] angles were about 117.1° in ethylene, but slightly larger than 107.7° in ethane. The bond angles of C(3)—C(1)—C(2) and C(1)—C(2)—C(3) were smaller than those in cyclopropane (60°). According to the knowledge of mathematics, the bond angles of C(1)—C(3)—C(2) would be larger than 60° and the values were around 61°. It is well known that the symmetry of cyclopropane geometry structure is D_{3h} . After contrastive analysis of cyclopropane and employed molecules, it was found that when 1,2-H was replaced by π conjugation group in cyclopropane, such as phenyl, the symmetry of molecule was broken in *cis*-isomers and reduced in *trans*-isomers. The dipole moments (μ) were calculated and listed in Table 1. It could be seen that the values of μ in *cis*-isomers were larger than those in *trans*-isomers. The energies

Table 1 Some key computed bond lengths *L* (in Å), bond angles *A* (in deg) as well as dipole moments μ (in D) for the ground-state geometric conformations of 1,2-disubstituted cyclopropanes

	1A	1B	2A	2B	3A	3B	4A	4B
$L_{C(1)-C(2)}$	1.537	1.537	1.535	1.539	1.536	1.539	1.543	1.544
$L_{C(1)-C(3)}$	1.503	1.510	1.504	1.509	1.505	1.510	1.522	1.514
$L_{C(2)-C(3)}$	1.517	1.510	1.518	1.509	1.518	1.510	1.508	1.514
$L_{C(2)-C(4)}$	1.489	1.487	1.488	1.485	1.488	1.484	1.501	1.491
$L_{C(1)-C(10)}$	1.496	1.487	1.497	1.487	1.497	1.484	1.493	1.491
$L_{C(1)-H(1)}$	1.092	1.090	1.092	1.090	1.092	1.089	1.094	1.094
$A_{C(3)-C(1)-C(2)}$	59.85	59.41	59.93	59.33	59.90	59.35	58.97	59.34
$A_{C(1)-C(2)-C(3)}$	58.94	59.41	59.02	59.35	59.05	59.35	59.81	59.36
$A_{C(1)-C(3)-C(2)}$	61.21	61.19	61.04	61.37	61.04	61.29	61.22	61.30
$A_{H(1)-C(1)-C(10)}$	114.00	114.00	114.00	114.00	114.00	114.00	113.00	114.00
$BO_{C(1)-C(2)}^a$	0.852	0.882	0.840	0.861	0.843	0.845	0.828	0.851
$BO_{C(1)-C(3)}$	0.870	0.903	0.972	0.893	0.972	0.882	0.846	0.888
$BO_{C(2)-C(3)}$	0.966	0.903	0.836	0.893	0.835	0.882	0.965	0.887
$BO_{C(2)-C(4)}$	1.136	1.099	1.153	1.108	1.153	1.128	1.083	1.135
$BO_{C(1)-C(10)}$	1.046	1.099	1.059	1.113	1.063	1.128	1.185	1.151
$BO_{C(3)-C(2)-C(10)}^b$	0.004	0.006	0.007	0.010	0.006	0.010	0.005	0.012
$BO_{C(1)-C(3)-C(4)}$	0.006	0.006	0.007	0.010	0.007	0.011	0.007	0.011
<i>E</i> (kcal/mol)	1.500	0.000	1.150	0.000	1.500	0.000	1.360	0.000
μ	0.486	0.218	0.624	0.314	0.770	0.465	1.118	0.945

^a 2-Center Mayer bond order; ^b 3-Center Mayer bond order.

of *cis*-isomers were higher than those of *trans*-isomers, which indicated that the *trans*-isomers were more stable than *cis*-isomers. This phenomenon coincided with the traditional organic chemistry. The Mayer bond orders were also calculated and listed in Table 1. It was found that the two-center bond orders of C(1)—C(2), C(1)—C(3) and C(2)—C(3) were only in the range of 0.83—0.88, 0.85—0.97 and 0.83—0.97, respectively, lower than that of the normal single bond. The two-center bond orders of C(2)—C(4) and C(1)—C(10) were between 1.04 and 1.18, higher than 1. However, the circular three-center bond orders of C(3)—C(2)—C(10) and C(1)—C(3)—C(4) were in the range of 0.0042—0.0116 and 0.0058—0.0110, respectively. The result indicated that the electron density transferred from the bond centers of the two-center bonds [C(1)—C(2), C(1)—C(3), C(2)—C(3)] in cyclopropyl group to the bond centers of the three bonds [C(3)—C(2)—C(10) and C(1)—C(3)—C(4)].^[32] When the substituent was changed from phenyl to naphthyl, anthryl and fluorenyl, a subtle change of the structure was observed.

Analysis of population charge distributions, electrostatic potential and weak interactions

The analysis of population charge distributions (analyzed by the NBO method), electrostatic potential (ESP) and weak interactions was listed in Figure 1. When the structures were *cis*-isomers, the population charge distributions were asymmetric and the negative charges were concentrated in one of substituent groups, while

groups, while the population charge distributions were symmetric and the negative charges were located on two substituents with the same values in *trans*-isomers. For example, the charge values were +0.0234, −0.0245, −0.0011 eV, distributed on cyclopropyl (middle part) and phenyl (the left and right parts) in **1A**, but the values in **1B** were +0.0447 e on cyclopropyl and −0.0239 eV on phenyls. The result coincided with the geometric conformations of all cyclopropane derivatives. It was also seen that the fragment charge values on the cyclopropyl group for **1A**—**3A** and **1B**—**3B** were +0.0234, +0.0268, +0.0271 eV and +0.0447, +0.0550, +0.0533 eV, respectively, which indicated the electron density of the cyclopropyl group decreased along with the conjugated size of the substituents. When the substituent was changed from phenyl to fluorenyl, the change was inconspicuous. The electrostatic potential analysis showed that the electrostatic potential was more negative in the upper and lower parts due to the *p* orbitals of conjugation systems perpendicularly oriented to the molecular plane. The strong strain energy of ring and σ orbitals of the middle part of molecules made the electrostatic potential more negative around the cyclopropyl group. Due to the substituents located above and below cyclopropyl plane in *trans*-isomers, the red parts of cyclopropyl motifs and substituents were overlapped with each other. The obvious σ - π conjugation was observed. The visualizations of weak interactions of all employed molecules in real space were drawn by VMD 1.9 software with the scale min-max from

−0.015 (blue) to 0.015 (red), as shown in Figure 1. The obvious π - π stacking in *cis*-isomers was observed and the weak interactions of cyclopropyls and substituents were also shown in *trans*-isomers. The population charge distributions, ESP and weak interactions of corresponding 1,1-disubstituted cyclopropanes, olefins and alkanes were also calculated and listed in Figure S4–S7. The charge distributions of a series of D–F had the same trend as *trans*-isomers, but the negative charges were concentrated in cyclopropyl group. From the analysis of ESP, it was found that the negative parts of olefins (1D–4D, 1E–4E) and 1,1-disubstituted cyclopropane were linked up into a single stretch and similar to those of *trans*-isomers. The red parts of electrostatic potentials in alkanes (1F–4F) were only

Figure 1 Summary of the NBO, ESP and visualization of weak interactions in real space of 1,2-disubstituted cyclopropanes at the B97D/TZVP level. (a) The charge of middle part of molecule (unit: e); (b) The charge of left part of molecule; (c) The charge of right part of molecule; (d) The scale min-max is from −0.01 eV (red) to 0.01 eV (blue); (e) WI: visualization of weak interactions [The scale runs from −0.015 (blue) to 0.015 (red)].

located on upper and lower parts of substituents and the σ - π conjugation was not observed.

Frontier molecular orbitals and electronic properties

The energy levels of HOMO−3 to LUMO+3 orbitals for all cyclopropane derivatives were calculated and presented in Figure 2. From frontier molecular energy levels, it was found that the energy differences between the HOMOs and LUMOs of all cyclopropane derivatives were very small, which might cause a broad UV-vis spectrum. When the substituent changed from phenyl to naphthyl, anthryl, the calculated energy levels of LUMOs decreased and HOMOs increased. The energy gap became smaller. When the *cis*-isomers changed to *trans*-isomers, the energy levels of LUMOs and HOMOs changed slightly. Owing to the fluorenyl group with conjugation-interrupted conformations, the energy levels of 4A (4B) were between 2A (2B) and 3A (3B). The calculated energy level of HOMO and LUMO of 1B is 0.08 eV higher and 0.10 eV lower than that of 1A, respectively. The energy gap of 1A was 0.19 eV higher than that of 1B. The energy levels of HOMO−3 to LUMO+3 orbitals for all corresponding olefins and alkanes were calculated and listed in Figure S8. The result showed that the energy levels (HOMO−3 to LUMO+3) and the energy gaps of cyclopropane derivatives were between olefins and alkanes. When the 1,2-disubstituted cyclopropanes were transformed to 1,1-disubstituted compounds, the energy levels of LUMO and HOMO decreased and the energy gap became larger. For further information, the energy gaps of all series of compounds are drawn in Figure 2b. It was found that when the substituent was phenyl, the energy gap difference between 1A and 1D was obvious. With

Figure 2 (a) Calculated energy levels of LUMO-LUMO+3 and HOMO-HOMO−3 orbitals for 1,2-disubstituted cyclopropanes at B97D/TZVP level; (b) Calculated energy gap of all employed molecules at B97D/TZVP level.

the increasing size of conjugation length, the difference between corresponding olefins and cyclopropane derivatives decreased. The energy gaps of series 4 were similar to those of series 2.

It is well known that the HOMO is represented by its bonding character, and the LUMO is characterized with antibonding. In order to elaborate the nature of the S_1 state related to the HOMO-LUMO orbitals transition from our calculated results, the isosurface of wave functions of the frontier orbitals (from HOMO-1 to LUMO+1) for all employed molecules were shown in Figure 3. The orbitals delocalized on cyclopropyl and substituents were overlapped with each other and the HOMO orbitals spread through whole molecules in all compounds. In *cis*-isomers, other orbitals (HOMO-1, LUMO, LUMO+1) were asymmetric and mainly delocalized on one of the substituents. The obvious intra-molecular π - π stacking has been observed in the HOMO-LUMO+1 orbitals of **1A**, LUMO-LUMO+1 orbitals of **2A** and LUMO+1 orbitals of **4A**, while other orbitals (HOMO-1, LUMO, LUMO+1) of *trans*-isomers were symmetric and evenly distributed on two substituents. The symmetry of the frontier orbitals of *trans*-isomers and *cis*-isomers coincided with the analysis of the structure and NBO. Compared with corresponding 1,1-disubstituted compounds, olefins and alkanes, the isosurfaces of wave functions of the frontier orbitals (from HOMO-1 to LUMO+1) of *trans*-isomers were similar, except for **4C** and **4F** (Figure S8).

Figure 3 The electronic densities of HOMO-1, HOMO, LUMO and LUMO+1 of 1,2-disubstituted cyclopropanes at B97D/TZVP level.

cis-1,2-Diphenyl cyclopropane was employed as a molding compound to investigate the process of electric transport and the result was shown in Figure 4. At first, the structure of *cis*-1,2-diphenyl cyclopropane was optimized at the WB97Xd/TZVP level and the bond length of C(1)—C(2) was 1.5236 Å. And then, a negative charge was added on the molecule. When the geometry was optimized at the UWB97Xd/TZVP level, the ring opened and the bond length of C(1)—C(2) was 1.6368 Å. When the charge was removed from the molecule, the structure returned to the first-step geometry and the ring closed. The process had two states and was similar to the procedure of electric memory. To confirm the process, it was replicated several times under the same conditions. The structure recovered to the neutral geometry. When a positive charge was added on the molecule, the structure was different from the original structure (Figure S9). All 1,2-disubstituted cyclopropanes were also investigated using these methods, only three molecules (**1B**, **2A** and **4B**) containing one positive charge could recover to the initial structures. The result may propose the alternative explanation of the photoisomerization of 1,2-disubstituted cyclopropanes.

Figure 4 The process of electric transport of *cis*-1,2-diphenyl cyclopropane at WB97DX/TZVP level.

Absorption spectra and transition density matrix analysis

In order to distinctly describe the spectral characters of cyclopropane derivatives, the absorption spectra were simulated by Gaussian functions with a half-width of 3.5 eV based on the 25 lowest singlet energies from TDDFT/B97-D/TZVP calculations and listed in Figure S9. It was noted that the conjugation size had great effects on the absorption band. When the substituents were phenyl, the absorption bands were 175–300 nm in *cis*-isomer and 170–310 nm in *trans*-isomer. When the substituents changed to naphthyl, anthryl, the absorption band became broad. The values were 200–380 nm, 240–610 nm in *cis*-isomers and 200–420 nm, 240–650 nm in *trans*-isomers. Compared with the *cis*-isomers, the wavelength of absorption peaks was red-shifted in *trans*-isomers. From Figure S9, it was found that there were many absorption peaks in the absorption spectra. These may be related to the similar energies among the frontier orbitals of all cyclopropane

derivatives. The electron easily transited from HOMOs to LUMOs. Compared with olefins and alkanes, the absorption peaks were blue-shifted and red-shifted.

The transition density matrix (TDM) plotted as color-filled maps between electronic state S_0 and S_1 in cyclopropane derivatives were shown in Figure 5 to give further insight into the optical transitions. The x and y axes represented the number of C atom in the molecule. The molecule contained two fragments, cyclopropyl [C(1)—C(3)] and aryl. The individual matrix elements were depicted in various colors. The density-matrix delocalization patterns in each system were considerably different. From Figure 5, it was clearly found that the transition corresponding to $S_0 \rightarrow S_1$ transition involved mainly cyclopropyl parts in *trans*-isomers and most C atoms in cyclopropyl were evidently coherent with surrounding atoms, while in *cis*-isomers the transition was mainly on the aryl parts except **1A** and the coherence between atoms in each aryl and cyclopropyl ring was stronger than *trans*-isomers. This might be explained from the distance among atoms in *cis*-isomers, which was smaller than that in *trans*-isomers. Obviously, when the substituent conjugation length increased, the coherence between atoms of the lowest excitation energy ($S_0 \rightarrow S_1$) in **3A—3B** and

4A—4B was weaker than that of other cyclopropane derivatives. Due to the instability of cyclopropyl group, the ring opened when excited-state geometries were optimized. So the emission spectra were not calculated in this paper.

Conclusions

In summary, organic semiconductors allowed for tuning electronic structures by means of sp^3 C, providing state-of-the-art models in organic electronics. The cyclopropyl group as a σ block inserted into the π -electron system had many effects on the electronic structures and optical properties. The obvious σ - π conjugation was observed from the analysis of red parts of electrostatic potentials and overlapped frontier molecular orbitals. The energy gaps of 1,2-cyclopropane derivatives between the corresponding alkanes and olefins were larger than 1,1-disubstituted cyclopropane. When the substituent changed from phenyl to naphthyl and fluorenyl, the energy gap decreased and the absorption bands became broad. The *trans*-isomers had higher symmetry than *cis*-isomers in ground-state geometry and electronic structures. The wavelengths of absorption peaks were red-shifted in *trans*-isomers compared to the *cis*-isomers. The electronic transitions ($S_0 \rightarrow S_1$) were mainly on the aryl parts and were strongly coherent with surrounding atoms in *cis*-isomers, while the *trans*-isomers were on the cyclopropyl. When a negative/positive charge was added and removed on the **1A**, **1B**, **2A**, and **4B**, the ring opened and closed. The geometry could return to the original structure. The series of cyclopropane-based π -systems might be applied in organic electronics and mechatronics. Our group will conduct further study in this field.

Acknowledgement

This work was partially supported by the National Natural Science Funds for Excellent Young Scholar (No. 21322402), the National Key Basic Research Program of China (973) (No. 2015CB932200), the National Natural Science Foundation of China (Nos. U1301243, 21274064), the Program for New Century Excellent Talents in University (No. NCET-11-0992), Doctoral Fund of Ministry of Education of China (No. 20133223110007), the Natural Science Foundation of Jiangsu Province of China (No. BM2012010), the Synergetic Innovation Center for Organic Electronics and Information Displays and Excellent science and technology innovation team of Jiangsu Higher Education Institutions (2013) and Open Project from State Key Laboratory of Supramolecular Structure and Materials at Jilin University (No. sklssm2015022). The project was funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Figure 5 Plot transition density matrix as color-filled map for the lowest excitation energy ($S_1 \leftarrow S_0$) in the 1,2-disubstituted cyclopropanes. The x - and y -axis labels represent the number of C atom in the molecule [C(1)—C(3) were in cyclopropyl units, and the others were in substitution groups].

References

- [1] Chiang, C. K.; Fincher Jr, C.; Park, Y.; Heeger, A.; Shirakawa, H.; Louis, E.; Gau, S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.
- [2] Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J., *J. Chem. Soc., Chem. Commun.* **1977**, 578.
- [3] Xie, L.-H.; Yin, C.-R.; Lai, W.-Y.; Fan, Q.-L.; Huang, W. *Prog. Polym. Sci.* **2012**, *37*, 1192.
- [4] Basescu, N.; Liu, Z.; Moses, D.; Heeger, A.; Naarmann, H.; Theophilou, N. *Nature* **1987**, *327*, 403.
- [5] Xie, L.-H.; Chang, Y.-Z.; Gu, J.-F.; Sun, R.-J.; Li, J.-W.; Zhao, X.-H.; Huang, W. *Acta Phys-Chim. Sin.* **2010**, *26*, 1784.
- [6] Beaujuge, P. M.; Fréchet, J. M., *J. Am. Chem. Soc.* **2011**, *133*, 20009.
- [7] Guo, X.; Baumgarten, M.; Müllen, K. *Prog. Polym. Sci.* **2013**, *38*, 1832.
- [8] Lee, C. W.; Lee, J. Y. *Adv. Mater.* **2013**, *25*, 596.
- [9] An, Z.; Zheng, C.; Tao, Y.; Chen, R.; Shi, H.; Chen, T.; Wang, Z.; Li, H.; Deng, R.; Liu, X. *Nature Mater.* **2015**.
- [10] Talin, A. A.; Centrone, A.; Ford, A. C.; Foster, M. E.; Stavila, V.; Haney, P.; Kinney, R. A.; Szalai, V.; El Gabaly, F.; Yoon, H. P. *Science* **2014**, *343*, 66.
- [11] Sun, H.; Liu, S.; Lin, W.; Zhang, K. Y.; Lv, W.; Huang, X.; Huo, F.; Yang, H.; Jenkins, G.; Zhao, Q. *Nature Commun.* **2014**, *5*, 3601.
- [12] Tibbelin, J.; Wallner, A.; Emanuelsson, R.; Heijkenskjöld, F.; Rosenberg, M.; Yamazaki, K.; Nauroozi, D.; Karlsson, L.; Feifel, R.; Pettersson, R. *Chem. Sci.* **2014**, *5*, 360.
- [13] Chang, Y. Z.; Shao, Q.; Bai, L. Y.; Ou, C. J.; Lin, J. Y.; Xie, L. H.; Liu, Z. D.; Chen, X.; Zhang, G. W.; Huang, W. *Small* **2013**, *9*, 3218.
- [14] Chou, Y.-H.; You, N.-H.; Kurosawa, T.; Lee, W.-Y.; Higashihara, T.; Ueda, M.; Chen, W.-C. *Macromolecules* **2012**, *45*, 6946.
- [15] Wang, L.; Zhang, G.-W.; Ou, C.-J.; Xie, L.-H.; Lin, J.-Y.; Liu, Y.-Y.; Huang, W. *Org. Lett.* **2014**, *16*, 1748.
- [16] Méhes, G.; Nomura, H.; Zhang, Q.; Nakagawa, T.; Adachi, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 11311.
- [17] Greenberg, A.; Liebman, J. *Academic*, New York, **1978**.
- [18] Friebolin, H.; Beconsall, J. K. *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH, Weinheim, **1993**.
- [19] Lambert, J. B.; Mazzola, E. P. *Nuclear Magnetic Resonance Spectroscopy: an Introduction to Principles, Applications, and Experimental Methods*, Pearson Education, New York, **2004**.
- [20] Goldstein, E.; Vijaya, S.; Segal, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 6198.
- [21] Cavitt, M. A.; Phun, L. H.; France, S. *Chem. Soc. Rev.* **2014**, *43*, 804.
- [22] Qian, D.; Zhang, J. *Chem. Soc. Rev.* **2015**, *44*, 677.
- [23] Dewar, M.; McKee, M. *Pure Appl. Chem.* **1980**, *52*, 1431.
- [24] Dewar, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 669.
- [25] Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
- [26] Hu, C.-P.; Liu, Y.-Y.; Xie, L.-H.; Li, J.-W.; Li, Y.-R.; Tai, Q.; Yi, M.-D.; Huang, W. *Chem. Phys. Lett.* **2013**, *578*, 150.
- [27] Curtin, D. Y.; Gruen, H.; Hendrickson, Y. G.; Knipmeyer, H. *J. Am. Chem. Soc.* **1961**, *83*, 4838.
- [28] Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffin, G. J. *Am. Chem. Soc.* **1972**, *94*, 6584.
- [29] Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33*, 580.
- [30] Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graph.* **1996**, *14*, 33.
- [31] Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. *Gaussian 09*, Revision A. 02, Gaussian, Inc., Wallingford CT, **2009**.
- [32] Qi, D.; Zhang, L.; Zhao, L.; Cai, X.; Jiang, J. *ChemPhysChem* **2012**, *13*, 2046.