# Excited State Electronic Structures and Photochemistry of Heterocyclic Annulated Perylene (HAP) Materials Tuned by Heteroatoms: S, Se, N, O, C, Si, and B[†]

**Guang-Jiu Zhao and Ke-Li Han***

*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

*Received: September 20, 2008; Revised Manuscript Received: October 27, 2008*

Time-dependent density functional theory (TDDFT) method was performed to investigate the excited state electronic structures and photochemistry of a variety of heterocyclic annulated perylene (HAP) materials. The calculated electronic structures and photochemical properties of the newly synthesized S-, Se-, and N-heterocyclic annulated perylenes were in good agreement with the experimental results. Moreover, the O-, C-, Si-, and B-heterocyclic annulated perylenes were also theoretically designed and investigated by using the same computational methods in this work. As a result, we found that the electronic structures and photochemical properties of S-, Se-, N-, O-, and C-heterocyclic annulated perylenes are similar to each other. The energy levels of the LUMO orbital for the S-, Se-, N-, O-, and C-heterocyclic annulated perylenes become higher than those of unsubstituted perylene. At the same time, the energy gaps between LUMO and HOMO for these heterocyclic annulated perylenes are also increased in comparison with those of unsubstituted perylene. Hence, both absorption and fluorescence spectra of S-, Se-, N-, O-, and C-heterocyclic annulated perylenes are correspondingly blue-shifted relative to those of unsubstituted perylene. In addition, two bonds formed by heteroatoms with perylene are lengthened in the electronic excited state of S-, Se-, N-, O-, and C-heterocyclic annulated perylenes. On the contrary, these bonds formed by heteroatoms with perylene are shortened in the electronic excited state of Si- and B-heterocyclic annulated perylenes. Furthermore, energy levels of the LUMO orbital for Si- and B-heterocyclic annulated perylenes become significantly lowered in comparison with that of unsubstituted perylene. At the same time, energy gaps between LUMO and HOMO for Si- and B-heterocyclic annulated perylenes become decreased relative to those of unsubstituted perylene. Thus, both absorption and fluorescence spectra of Si- and B-heterocyclic annulated perylenes are significantly red-shifted in comparison with those of unsubstituted perylene. The differences of electronic structures and photochemistry of these heterocyclic annulated perylene materials can be ascribed to the electron delocalization of LUMO orbital from heteroatom into the perylene skeleton for Si- and B-heterocyclic annulated perylenes, because the electron of the LUMO orbital for S-, Se-, N-, O-, and C-heterocyclic annulated perylenes is localized on the heteroatoms.

## 1. Introduction

Perylenes as pigments and fluorescent dyes have found wide ranging applications in very diverse fields of current research.[1−71] These range from uses as laser dyes,[1] photochemical sensitizers,[2] and absorbers for sunlight collectors[3−5] to applications in liquid-crystalline phases[6] and organic semiconductors.[7] Recently, De Schryver and co-workers have used a facile method to synthesize a series of polyphenylene−dendronized perylenes and investigate their physical and mesoscopic properties.[8−11] The functionalization of perylenes with polyphenylene dendrons allows the preparation of films by spin-coating. Gade and co-workers have synthesized a New Class of tetra-N-substituted perylenes.[12−14] At the same time, they have shown that their chosen synthetic approach to the tetra-N-substituted derivatives opens up the possibility of a wide range of further modifications of the chromophores, in particular their use in extended functional supramolecular arrays based on well-defined building principles, such as nanoscopic rods. It is known that perylene diimide-based organic semiconductor materials have been the subject of investigation due to their advantageous photophysical and photochemical properties. Driving these studies are potential applications of perylene diimide derivatives in organic photorefractive media for optical signal processing,[15] electron-transporting components in organic light-emitting diodes,[16] semiconducting materials for electrophotography,[17] n-type photovoltaic materials for solar energy conversion,[18−20] and fluorescent and near-infrared (NIR) dyes.[21−31] Belfield et al. have investigated the steady state linear photophysical properties, two-photon absorption (2PA) spectra, and optical limiting behavior of fluorenylperylene diimide-based derivatives.[32−34] In addition, perylene and its derivatives, especially perylene-3,4,9,-10-tetracarboxdiimides, are well-known for their versatility as dyes for dye-sensitized solar cells (DSSCs) because of their high photostability and chemical stability.[35−49] Unsubstituted perylene shows strong fluorescence and is a key chromophore in fields such as dye lasers and light emitting diodes (LEDs).[50,51] However, the poor solubility of unsubstituted perylene in organic solvents and the low fluorescence quantum yield in the solid state, attributable to its aggregation, limit the applications of perylene. Efforts have been made to attach solubilizing and shielding side chains to the molecules, thereby improving their performances.[52−57]

Heterocyclic annulated perylenes (HAPs), which contain chalcogen, nitrogen, etc. in fused aromatic rings, are the subjects of considerable current research interest due to their fundamental

---

[†] Part of the “George C. Schatz Festschrift”.

* Corresponding author. Phone: +86-411-84379293. Fax: +86-411-84675584. E-mail: klhan@dicp.ac.cn.

10.1021/jp8083666 CCC: $40.75

optoelectronic properties and their potential applications such as organic field-effect transistors (OFETs), light emitting diodes (LEDs), photovoltaic devices, and other organic optoelectronic devices.[58−71] Incorprating heteroatoms into the perylene skeleton is an intriguing target because the introduction of heteroatoms can dramatically change the electronic structures and photochemical properties of these heterocyclic annulated perylenes. Furthermore, it would also induce a variety of intermolecular interactions, such as van der Waals interactions and heteroatom−heteroatom interactions, which is essential to achieve highly ordered supramolecular self-assembled structure and eventually excellent device performance.[66−71]

Very recently, Jiang et al. have developed a practical synthetic procedure for the synthesis of a series of heterocyclic annulated perylenes (HAPs) in good yields.[66] All the S-, Se-, and N-heterocyclic annulated perylenes (here denoted as S-Perylene, Se-Perylene, and N-Perylene, respectively) are prepared from the readily available 1-nitroperylene.[66] Moreover, the detailed investigations of photochemical properties of these heterocyclic annulated perylenes have been presented to fully explore the influence of different heteroatoms on the inherent electronic structures. All these heterocyclic annulated perylenes exhibit well-defined vibronic $\pi-\pi^*$ transition absorption bands from the UV−vis absorption spectra with the longest maximum absorption at 412.0, 416.5, and 425.0 nm for S-Perylene, Se-Perylene, and N-Perylene, respectively.[66] It is distinct that the absorption spectra of all of these heterocyclic annulated perylenes are blue-shifted in comparison with those of unsubstituted perylene ($\lambda_{max} = 438.5$ nm). In addition, the fluorescence spectra of Perylene, S-Perylene, Se-Perylene, and N-Perylene have also been given in the experimental works.[66] It can be found that the vibrationally structured fluorescence spectra mirror the well-defined vibronic $\pi-\pi^*$ absorption bands. Moreover, the fluorescence spectra of S-Perylene, Se-Perylene, and N-Perylene are also blue-shifted relative to that of Perylene. Therefore, both the absorption and fluorescence spectra of the S-, Se-, and N-heterocyclic annulated perylenes are blue-shifted in comparison with those of unsubstituted perylenes. This means that the energy gap between the electronic excited state and the ground state of perylene can be tuned to increase by introduction of the S, Se, and N heteroatoms into the perylene skeleton.

At the same time, the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for heterocyclic annulated perylenes (HAPs) molecular materials can also be tuned by incorporating heteroatoms into the perylene skeleton. In the previous works, Jiang et al. found that cyclic voltammetry of these heterocyclic annulated perylenes shows a reversible oxidation wave.[66] The oxidation peaks ($E^{1/2}$ values) of Perylene, S-Perylene, Se-Perylene, and N-Perylene are found at 1.05, 1.12, 1.08, and 0.89 V vs Ag/AgCl, respectively. Given the silver wire as a quasireference electrode and the ferrocene/ferrocenium ($Fc/Fc^+$) couple as the internal potential standard, HOMO levels for Perylene, S-Perylene, Se-Perylene, and N-Perylene can be estimated by oxidation onset at −5.38, −5.42, −5.39, and −5.18 eV, respectively.[66] However, the LUMO energy levels of these heterocyclic annulated perylene materials have not been given in their studies. It is well-known that the energy gaps between LUMO and HOMO orbitals are of fundamental importance for the photochemistry of molecular materials. Hence, energy levels of LUMO orbitals for all the heterocyclic annulated perylenes are also very important data for these molecular materials. As a result, the quantum chemistry computations on the electronic structures are very useful and helpful for understanding the electronic structures and photochemical properties of the heterocyclic annulated perylene materials.

It should be mentioned that the ground state electronic structures for these types of molecular materials can be conveniently obtained by using various quantum chemistry computation methods. However, it is difficult to calculate the electronic structures of the electronic excited state for complex molecular materials. Nowadays, the configuration interactions with single substitute (CIS),[72,73] complete active space self-consistent field (CASSCF),[74,75] etc. methods are very popular excited state computational methods. It is noted that the CAASCF method can give very accurate results but is quite expensive for the large molecular materials. On the contrary, the CIS method is less expensive but gives less accurate results. And then, the time-dependent density functional theory (TD-DFT) method becomes a good candidate for computing the electronic excited states of complex molecular materials systems due to its moderate efficiency and accuracy. We have done a variety of work about the theoretical studies on the excited state electronic structures and photochemistry of complex molecular systems using the TDDFT method.[22−29]

Although some information on electronic structures and photochemical properties of S-, Se-, and N-heterocyclic annulated perylenes has been experimentally obtained in the previous studies, we can further obtain more detailed information on the excited state electronic structures and photochemical properties of these heterocyclic annulated perylenes by the quantum chemistry methods. Furthermore, the electronic structures and photochemical properties of some newly designed heterocyclic annulated perylene materials by incorporating other heteroatoms into the perylene skeleton are also theoretically studied. In this work, some other heteroatoms, such as O, C, Si, and B, are also introduced into the perylene skeleton. Herein, they are denoted as O-Perylene, C-Perylene, Si-Perylene, and B-Perylene, respectively. The density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods are performed to investigate the ground state and electronic excited state of the unsubstituted perylene and all the S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes, respectively. As a result, we found that our theoretical results for Perylene, S-Perylene, Se-Perylene, and N-Perylene are in good agreement with experimental results in the previous works. Moreover, the electronic structures and photochemical properties of O-Perylene and C-Perylene are similar to those of S-, Se-, and N-heterocyclic annulated perylenes. Both the absorption and fluorescence spectra of the S-, Se-, N-, O-, and C-heterocyclic annulated perylenes are blue-shifted in comparison with that of the unsubstituted perylene. However, it is very interesting that both the absorption and fluorescence spectra of Si-Perylene and B-Perylene are shifted to the red relative to that of the unsubstituted perylene.

## 2. Theoretical Methods

All the quantum chemistry calculations are carried out using the TURBOMOLE program suite.[76−80] The ground state geometry optimizations of the unsubstituted perylene and various heterocyclic annulated perylenes (HAPs) are performed by using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with the Lee−Yang−Parr gradient-corrected correlation functional (B3-LYP functional).[76,77] The triple-$\zeta$ valence quality with one set of polarization functions (def-TZVP) is chosen as the basis set throughout.[78] The time-dependent density functional theory (TD-DFT) method with B3-

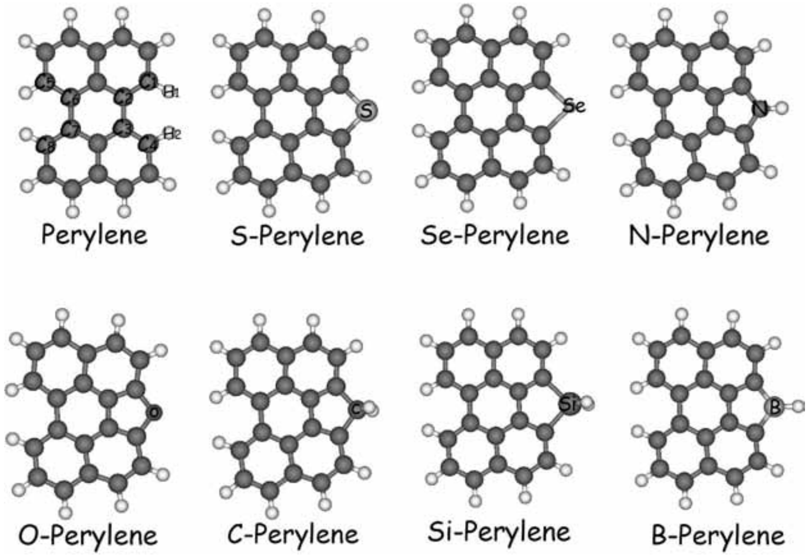

**Figure 1.** Optimized ground state geometric conformations of unsubstituted perylene and S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes. Some important atoms are labeled.

**TABLE 1: Computed Bond Lengths *L* (in Å) and Bond Angles *A* (in deg) for the Ground State Geometric Conformations of Unsubstituted Perylene and Heterocyclic Annulated Perylenes**[a]

| | Perylene | S-Perylene | Se-Perylene | N-Perylene | O-Perylene | C-Perylene | Si-Perylene | B-Perylene |
|---|---|---|---|---|---|---|---|---|
| $L_{C1-C4}$ | 2.952 | 2.551 | 2.646 | 2.297 | 2.241 | 2.409 | 2.732 | 2.516 |
| $L_{C2-C3}$ | 1.475 | 1.407 | 1.418 | 1.383 | 1.381 | 1.412 | 1.457 | 1.443 |
| $L_{C6-C7}$ | 1.475 | 1.485 | 1.482 | 1.496 | 1.501 | 1.494 | 1.481 | 1.493 |
| $L_{C5-C8}$ | 2.952 | 3.062 | 3.036 | 3.135 | 3.156 | 3.091 | 3.003 | 3.060 |
| $L_{C1\text{-}X}$ | | 1.781 | 1.915 | 1.407 | 1.404 | 1.537 | 1.894 | 1.589 |
| $L_{C4\text{-}X}$ | | 1.781 | 1.915 | 1.407 | 1.404 | 1.537 | 1.895 | 1.588 |
| $A_{C1C2C3}$ | 122.2 | 114.4 | 116.3 | 109.3 | 108.3 | 111.2 | 117.2 | 112.7 |
| $A_{C2C3C4}$ | 122.2 | 114.4 | 116.3 | 109.3 | 108.3 | 111.2 | 117.2 | 112.7 |
| $A_{C5C6C7}$ | 122.2 | 124.6 | 124.0 | 126.1 | 126.5 | 125.2 | 123.3 | 124.6 |
| $A_{C6C7C8}$ | 122.2 | 124.5 | 124.0 | 126.1 | 126.6 | 125.2 | 123.3 | 124.6 |
| $A_{C1XC4}$ | | 91.49 | 87.40 | 109.4 | 105.9 | 103.1 | 92.26 | 104.8 |

[a] X refers to the heteroatom in various heterocyclic annulated perylenes.

**TABLE 2: Computed Energy Levels *E* (in eV) of the LUMO and HOMO Orbitals As Well As the Energy Gap Δ*E* (in eV) between LUMO and HOMO for the Unsubstituted Perylene and All the Heterocyclic Annulated Perylenes**

| | Perylene | S-Perylene | Se-Perylene | N-Perylene | O-Perylene | C-Perylene | Si-Perylene | B-Perylene |
|---|---|---|---|---|---|---|---|---|
| $E_{LUMO}$ | −2.16 | −2.08 | −2.09 | −1.81 | −2.09 | −2.03 | −2.28 | −2.99 |
| $E_{HOMO}$ | −5.18 | −5.34 | −5.32 | −5.07 | −5.31 | −5.09 | −5.23 | −5.18 |
| $\Delta E_{L-H}$ | 3.02 | 3.26 | 3.23 | 3.26 | 3.22 | 3.06 | 2.95 | 2.19 |

LYP hybrid functional and the def-TZVP basis set is used to investigate the excited state electronic structures. All the electronic excited state geometric conformations are fully optimized by using the TDDFT method. Fine quadrature grids 4 were also employed.[79,80] The convergence thresholds for both the ground state and excited state optimization were set to be $10^{-6}$.

## 3. Results and Discussion

Optimized ground state geometric conformations of unsubstituted perylene and S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes are shown in Figure 1. In addition, some important atoms are labeled in Figure 1. It is distinct that all molecules are of planar conformations. Some bond lengths and bond angles for the optimized geometric conformations of unsubstituted perylene and heterocyclic annulated perylenes are listed in Table 1. From the listed bond lengths and bond angles for Perylene, one can find that perylene is of good symmetry. The two naphthalene moieties of perylene are completely the same. It is noted that the introduction of heteroatom into the perylene skeleton breaks down the original symmetry of Perylene. The original conformation of the perylene skeleton is changed due to the introduction of heteroatoms. One can find that the distance between $C_1$ and $C_4$ atoms and the bond length of $C_2-C_3$ for all the heterocyclic annulated perylenes are decreased in comparison with those of unsubstituted perylene. On the contrary, the distance between the $C_5$ and $C_8$ atom and the bond length of $C_6-C_7$ are distinctly increased. At the same time, the angles formed by $C_1C_2C_3$ and $C_2C_3C_4$ for all the heterocyclic annulated perylenes are decreased in comparison with those of unsubstituted perylene. Moreover, the angles formed by $C_5C_6C_7$ and $C_6C_7C_8$ are correspondingly increased for all the heterocyclic annulated perylenes. Moreover, it is noted that the $C_1C_2C_3$ and $C_5C_6C_7$ angles for all the heterocyclic annulated perylenes are the same as the $C_2C_3C_4$ and $C_6C_7C_8$ angles, respectively. The bond lengths of $C_1-X$ and $C_4-X$ (X refers heteroatoms) are also the same for each.

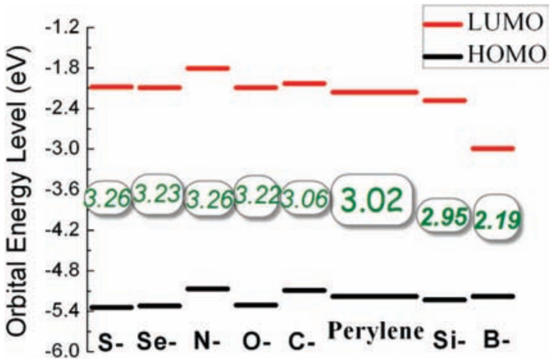

**Figure 2.** The calculated energy levels of LUMO and HOMO orbitals for unsubstituted perylene and S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes.

Table 2 lists the computed energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) as well as their energy gap between LUMO and HOMO orbitals. The calculated energy level of the HOMO orbital for the unsubstituted perylene is at −5.18 eV, which is in good agreement with the experimental value of −5.38 eV.[66] Furthermore, the energy level of the LUMO orbital for perylene is calculated to be at −2.16 eV. Hence, the calculated energy gap between LUMO and HOMO is 3.02 eV. One can find that the energy levels of HOMO and LUMO orbitals as well as their energy gap can be tuned by heteroatoms. The energy levels of the HOMO orbital for S-Perylene, Se-Perylene, O-Perylene, and Si-Perylene are lowered relative to that of unsubstituted perylene, while the HOMO energy level of N-Perylene and C-Perylene is highered slightly. In addition, the energy level of the HOMO orbital for B-Perylene is nearly unchanged. Our calculated energy level of the HOMO orbital for S-Perylene, Se-Perylene, and N-Perylene is −5.34, −5.32, and −5.07 eV, respectively. Therefore, they are in good agreement with the experimental values of −5.42, −5.39, and −5.18 eV, respectively.[66] Moreover, it should be noted that the introduction of S, Se, N, O, and C heteroatoms can raise the energy level of the LUMO orbital. However, the energy levels of the LUMO orbital for Si-Perylene and B-Perylene are lowered in comparison with that of unsubstituted perylene. Especially, the LUMO energy level of B-Perylene is lowered significantly from −2.16 to −2.99 eV.

The calculated energy levels of LUMO and HOMO orbitals for unsubstituted perylene and S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes are also shown in Figure 2. One can clearly find that the energy gap between LUMO and HOMO is enlarged for S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene. This is consistent with the blue-shift of the electronic spectra for these heterocyclic annulated perylenes in comparison with that of unsubstituent perylene.[66] It is very interesting that the energy gap between LUMO and HOMO orbitals of Si-Perylene and B-Perylene is significantly decreased in comparison with that of unsubstituted perylene. Especially, the energy gap between LUMO and HOMO orbitals of B-Perylene is decreased drastically from 3.02 to 2.19 eV. Therefore, it can be expected that the electronic spectra of Si- and B-heterocyclic annulated perylenes would be red-shifted relative to that of the unsubstituted perylene.

The calculated electronic excitation energies and the corresponding oscillator strengths of Perylene, S-Perylene, Se-Perylene, N-Perylene, O-Perylene, C-Perylene, Si-Perylene, and B-Perylene are shown in Table 3. The calculated $S_1$ state absorption wavelengths with the maximum oscillator strength are at 440, 409, 414, and 411 nm for Perylene, S-Perylene, Se-Perylene, and N-Perylene, respectively. It is noted that our calculated $S_1$ state absorption wavelengths are in good agreement with experimental results (438.5, 412.0, 416.5, and 425.0 nm for Perylene, S-Perylene, Se-Perylene, and N-Perylene, respectively).[66] So our calculated electronic spectra of these heterocyclic annulated perylenes (HAPs) materials can be demonstrated to be reliable. In addition, the $S_1$ state absorption wavelengths of O-Perylene and C-Perylene are calculated to be at 413 and 438 nm, respectively. Thus, it can be predicted that the electronic absorption spectrum of C-Perylene is very similar to that of perylene. The electronic absorption spectrum of O-Perylene is similar to that of S-Perylene and Se-Perylene. As the calculated energy gap between LUMO and HOMO orbitals suggested, the $S_1$ state absorption wavelengths of all the S-, Se-, N-, O-, and C-heterocyclic annulated perylenes are blue-shifted in comparison with those of unsubstituted perylene. On the contrary, the calculated $S_1$ state absorption with the maximum oscillator strength is red-shifted to 465 nm for the Si-heterocyclic annulated perylene. The $S_1$ state absorption wavelength for B-Perylene is also drastically red-shifted to 799 nm from 440 nm for perylene. These indicate that the introduction of the B atom into the Perylene skeleton can significantly change the photochemistry of heterocyclic annulated perylenes. However, the Si-, and B-heterocyclic annulated perylenes with red-shifted electronic absorption spectra have not been synthesized and observed in experiments to our best knowledge. On the other hand, experimental chemists can be inspired from our theoretical results to obtain electronic spectral red-shifted heterocyclic annulated perylenes (HAPs) molecular materials by introduction of Si and B heteroatoms into the molecular skeleton.

The molecular orbital transition contributions for the $S_1$ state of unsubstituted perylene and the S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes are also listed in Table 3. It is distinct that the $S_1$ states of all the molecular materials are dominatively contributed by the orbital transition from HOMO to LUMO. Therefore, the $S_1$ state electronic absorption spectra for these molecular materials are dominated by the energy gap

**TABLE 3: Calculated Electronic Excitation Energies (in nm) and Corresponding Oscillator Strengths of the Unsubstituted Perylene As Well As S-, Se-, N-, O-, C-, Si-, and B-Heterocyclic Annulated Perylenes[a]**

| | Perylene | S-Perylene | Se-Perylene | N-Perylene | O-Perylene | C-Perylene | Si-Perylene | B-Perylene |
|---|---|---|---|---|---|---|---|---|
| $S_1$ | 440 (0.351)<br>H → L98.0% | 409 (0.294)<br>H → L96.8% | 414 (0.287)<br>H → L96.9% | 411 (0.295)<br>H → L96.2% | 413 (0.317)<br>H → L96.9% | 438 (0.301)<br>H → L97.4% | 465 (0.244)<br>H → L97.0% | 799 (0.030)<br>H → L97.3% |
| $S_2$ | 343 (0.000) | 350 (0.057) | 361 (0.078) | 352 (0.042) | 330 (0.023) | 347 (0.005) | 359 (0.020) | 419 (0.022) |
| $S_3$ | 314 (0.000) | 325 (0.001) | 329 (0.000) | 320 (0.000) | 322 (0.000) | 315 (0.007) | 315 (0.012) | 369 (0.095) |
| $S_4$ | 309 (0.006) | 298 (0.000) | 302 (0.000) | 293 (0.002) | 295 (0.000) | 305 (0.006) | 314 (0.009) | 356 (0.000) |
| $S_5$ | 306 (0.000) | 291 (0.010) | 301 (0.000) | 290 (0.001) | 290 (0.000) | 300 (0.020) | 310 (0.002) | 355 (0.238) |
| $S_6$ | 295 (0.000) | 286 (0.001) | 294 (0.004) | 283 (0.029) | 287 (0.036) | 295 (0.001) | 299 (0.000) | 330 (0.057) |

[a] H and L refer to HOMO and LUMO.

**TABLE 4: The Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) of the Unsubstituted Perylene as well as the S-, Se-, N-, O-, C-, Si-, and B-Heterocyclic Annulated Perylenes**

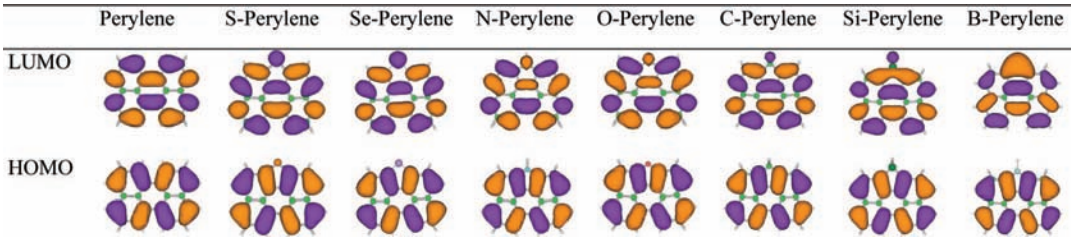

**TABLE 5: Computed Bond Lengths *L* (in Å) and Bond Angles *A* (in deg) for the Excited State Geometric Conformations of Unsubstituted Perylene and Heterocyclic Annulated Perylenes**[a]

| | Perylene | S-Perylene | Se-Perylene | N-Perylene | O-Perylene | C-Perylene | Si-Perylene | B-Perylene |
|---|---|---|---|---|---|---|---|---|
| $L_{C1-C4}$ | 2.940 | 2.562 | 2.658 | 2.305 | 2.247 | 2.399 | 2.697 | 2.462 |
| $L_{C2-C3}$ | 1.440 | 1.388 | 1.397 | 1.368 | 1.365 | 1.391 | 1.422 | 1.398 |
| $L_{C6-C7}$ | 1.440 | 1.450 | 1.447 | 1.460 | 1.464 | 1.453 | 1.445 | 1.463 |
| $L_{C5-C8}$ | 2.940 | 3.047 | 3.018 | 3.120 | 3.152 | 3.096 | 3.011 | 3.068 |
| $L_{C1-X}$ | | 1.794 | 1.928 | 1.411 | 1.408 | 1.539 | 1.887 | 1.569 |
| $A_{C1C2C3}$ | 121.8 | 114.6 | 116.4 | 109.4 | 108.4 | 111.0 | 116.4 | 111.8 |
| $A_{C5C6C7}$ | 121.8 | 124.1 | 123.5 | 125.7 | 126.4 | 125.3 | 123.5 | 124.8 |
| $A_{C1XC4}$ | | 91.13 | 87.13 | 109.5 | 105.8 | 102.5 | 91.22 | 103.4 |

[a] X refers to the heteroatom in various heterocyclic annulated perylenes.

**TABLE 6: Calculated Ground State and Excited State Dipole Moments $\mu$ (in D) As Well As the Calculated Fluorescence Wavelengths $\lambda_{Flu}$ (in nm) for Perylene, S-Perylene, Se-Perylene, N-Perylene, O-Perylene, C-Perylene, Si-Perylene, and B-Perylene**

| | Perylene | S-Perylene | Se-Perylene | N-Perylene | O-Perylene | C-Perylene | Si-Perylene | B-Perylene |
|---|---|---|---|---|---|---|---|---|
| $\mu_{GS}$ (D) | 0.0112 | 0.7391 | 0.5273 | 2.1519 | 1.0065 | 0.5670 | 0.7407 | 1.6611 |
| $\mu_{ES}$ (D) | 0.0033 | 0.0556 | 0.0463 | 3.6044 | 0.4724 | 1.9935 | 1.2125 | 4.1997 |
| $\lambda_{Flu}$(nm) | 499 | 457 | 463 | 454 | 459 | 495 | 541 | 1112 |

between LUMO and HOMO. By comparing the $S_1$ state electronic absorption spectra in Table 3 with the energy gap between LUMO and HOMO listed in Table 2, the $S_1$ state electronic absorption spectra are very consistent with the energy gaps between LUMO and HOMO for Perylene, S-Perylene, Se-Perylene, N-Perylene, O-Perylene, C-Perylene, Si-Perylene, and B-Perylene.

Table 4 shows the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the unsubstituted perylene as well as the S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes. One can note that all the HOMO orbitals of S-Perylene, Se-Perylene, N-Perylene, O-Perylene, C-Perylene, Si-Perylene, and B-Perylene are nearly the same as the HOMO orbital of Perylene. However, the LUMO orbitals of S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes are different from that of perylene. The most important difference is the populated electron densities on heteroatoms. This also suggests that the photochemistry of heterocyclic annulated perylenes (HAPs) materials certainly can be influenced by the introduction of heteroatoms into the perylene skeleton. Furthermore, one can find that the electron densities of the LUMO orbital in the heteroatom sites for S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene are localized on the heteroatoms. However, it should be noted that the electron densities of LUMO orbitals in the heteroatom sites for Si-Perylene and B-Perylene are delocalized from heteroatom to the perylene skeleton. This may be used to explain the energy level down-shift of the LUMO orbital for Si-Perylene and B-Perylene in comparison with that of perylene. And then, the $S_1$ state electronic absorptions of Si-Perylene and B-Perylene are also red-shifted by introduction of Si and B heteroatoms into the perylene skeleton.

The excited state geometric conformations of the unsubstituted perylene as well as the S-, Se-, N-, O-, C-, Si-, and B-heterocyclic annulated perylenes are fully optimized by using the TDDFT method and some geometric informations are listed in Table 5. Herein, the bond lengths of $C_4-X$ as well as the angles formed by $C_2C_3C_4$ and $C_6C_7C_8$ are not shown due to the symmetry of all the heterocyclic annulated perylenes. In the $S_1$ state, Perylene, S-Perylene, Se-Perylene, N-Perylene, O-Perylene, C-Perylene, Si-Perylene, and B-Perylene remain in their planar geometric conformations. It is noted that the bond length of $C_1-X$ in the electronic excited state of S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene is lengthened in comparison with that in the ground state. So the $C_1C_2C_3$ bond angles for these molecular materials are slightly increased in the $S_1$ state. At the same time, the $C_5C_6C_7$ bond angles are correspondingly decreased in the electronic excited state. However, for Si-Perylene and B-Perylene, one can note that the $C_1-X$ bond length is shortened in the $S_1$ state. This may be related to the delocalized LUMO orbital from heteroatom to perylene for Si-Perylene and B-Perylene. In addition, the $C_1C_2C_3$ bond angles of Si-Perylene and B-Perylene in the $S_1$ state become smaller than that in the ground state. At the same time, the $C_5C_6C_7$ bond angles become larger in the excited state of Si-Perylene and B-Perylene.

Table 6 shows the calculated ground state and excited state dipole moments as well as the absorption and fluorescence spectral values for all the molecular materials. We can find that the dipole moment of unsubstituted perylene in the ground state is very small. In the electronic excited state of unsubstituted perylene, the dipole moment becomes smaller and gets close to zero. By introduction of heteroatoms into the perylene skeleton, the ground state dipole moments of heterocyclic annulated perylenes would become larger. In the electronic excited state, the dipole moments of S-Perylene, Se-Perylene, and O-Perylene are dramatically decreased. Moreover, the excited state dipole moments of N-Perylene, C-Perylene, Si-Perylene, and B-Perylene become larger than that in the ground state.

From Table 6, one can also find that the calculated fluorescence wavelength of unsubstituted perylene is at 499 nm. The fluorescence spectra of S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene are blue-shifted to 457, 463, 454, 459, and 495 nm, respectively. The change tendency of fluorescence spectra for these heterocyclic annulated perylenes is consistent with that of the absorption spectra and the energy gap between LUMO and HOMO. Furthermore, the calculated fluorescence spectra are in agreement with the experimental fluorescence spectra at the longest wavelength without vibrational excitations. However, the fluorescence spectra of Si-Perylene are red-shifted to 541 nm from 499 nm for the unsubstituted perylene. It is evident that introduction of Si heteroatom into the heterocyclic annulated perylene materials can markedly red-shift the fluorescence spectra. Photochemists may be inspired from this to synthesize red-shifted fluorescent molecular materials by introduction of Si heteroatom into the original molecular skeleton. Moreover, we also find that the fluorescence wavelength of B-perylene is drastically red-shifted to 1112 nm, which is located in the near-infrared (NIR) region.[21−31] Thus, the B-heterocyclic annulated perylenes may be potential NIR fluorescent materials.

## 4. Conclusion

In this work, the ground state and excited state electronic structures as well as the photochemical properties of unsubstituted perylene and a variety of heterocyclic annulated perylenes have been investigated by using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. The ground state and excited state geometric conformations for the unsubstituted perylene and various heterocyclic annulated perylenes are fully optimized by using the B3LYP/def-TZVP and the TD-B3LYP/def-TZVP methods, respectively. By incorporating heteroatoms into the perylene skeleton, the heteroatom and the perylene skeleton can form a five-membered ring. The formation of the five-membered ring induces the two naphthalene moieties to get close to each other in the site of the five-membered ring, while the two naphthalene moieties get far away in the site of the open ring. In the electronic excited state, we have noted that two bonds formed by heteroatom with perylene skeleton are lengthened in comparison with that in the ground state for S-, Se-, N-, O-, and C-heterocyclic annulated perylenes. So the five-membered rings in S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene are enlarged in the electronic excited state. At the same time, the open rings of these heterocyclic annulated perylenes are correspondingly reduced in the electronic excited state. Moreover, the electronic structures of all the heterocyclic annulated perylenes are changed due to the introduction of the heteroatoms into the perylene skeleton. Especially, the LUMO energy level of the S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene become higher than that of unsubstituted perylene. At the same time, the energy gaps between LUMO and HOMO for these heterocyclic annulated perylenes are also increased in comparison with that of the unsubstituted perylene. Hence, the absorption and fluorescence spectra of the S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene are correspondingly blue-shifted relative to that of the unsubstituted perylene. Furthermore, all the theoretical results on the newly synthesized S-Perylene, Se-Perylene, and N-Perylene are in good agreement with the experimental results in the previous studies. We also find that the electronic structures and photochemistry of our theoretically designed heterocyclic annulated perylenes, O-Perylene and C-Perylene, are similar to that of the synthesized S-Perylene, Se-Perylene, and N-Perylene.

Moreover, the Si- and B-heterocyclic annulated perylenes have also been theoretically designed in the present work. The ground state and excited state electronic structures of Si-Perylene and B-Perylene materials are also investigated by using the same methods as discussed above. We have found that the two bonds formed by heteroatom with the perylene skeleton for Si-Perylene and B-Perylene are shortened in the electronic excited state in comparison with those in the ground state. As a result, the five-membered rings of Si-Perylene and B-Perylene are correspondingly reduced in the electronic excited state. This is tightly associated with the electronic structures of Si-Perylene and B-Perylene, which are different from those of S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene. The electron densities of LUMO orbitals in the heteroatom sites for S-Perylene, Se-Perylene, N-Perylene, O-Perylene, and C-Perylene are localized on the heteroatoms. However, the electron densities of LUMO orbitals are delocalized from heteroatom into the perylene skeleton for Si-Perylene and B-Perylene. This electron delocalization of the LUMO orbital from heteroatom into the perylene skeleton can contribute to the conformational changes in the electronic excited state. In addition, the energy levels of the LUMO orbital for Si-Perylene and B-Perylene are significantly lowered relative to that of the unsubstituted perylene. At the same time, the energy gaps between LUMO and HOMO for Si-Perylene and B-Perylene are correspondingly decreased in comparison with that of the unsubstituted perylene. Therefore, the absorption and fluorescence spectra of Si-Perylene and B-Perylene are dramatically red-shifted by introduction of Si and B heteroatoms into the perylene skeleton. These interesting electronic structures and photochemical properties of Si-Perylene and B-Perylene can also be ascribed to the electron delocalization of the LUMO orbital from heteroatoms into the perylene skeleton. Our studies have theoretically proposed a variety of heterocyclic annulated perylenes (HAPs) materials with red-shifted fluorescence by incorporating Si or B heteroatoms into the perylene skeleton. Especially, the B-heterocyclic annulated perylenes may be potential near-infrared (NIR) fluorescent materials. The synthesis and photochemical investigations of these potential Si- and B-heterocyclic annulated perylene materials with red-shifted fluorescence are expected in the future.

**Acknowledgment.** This work was supported by NKBRSF (2007CB815202) and NSFC (Nos. 20833008 and 20573110).

## References and Notes

(1) Sadrai, M.; Bird, G. R. *Opt. Commun.* **1984**, *51*, 62.
(2) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395.
(3) Cormier, R. A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 11004.
(4) Gregg, B. A.; Cormier, R. A. *J. Phys. Chem. B* **1998**, *102*, 9952.
(5) Cormier, R. A.; Gregg, B. A. *Chem. Mater.* **1998**, *10*, 1309.
(6) Wiederrecht, G. P.; Yoon, B. A.; Wasielewski, M. R. *Adv. Mater.* **2000**, *12*, 1533.
(7) Gama, V.; Henriques, R. T.; Bonfait, G.; Almeida, M.; Meetsma, A.; van Smaalen, S.; de Boer, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 1986.
(8) Qu, J.; Liu, D.; De Feyter, S.; Zhang, J.; De Schryver, F. C.; Müllen, K. *J. Org. Chem.* **2003**, *68*, 9802.
(9) Vosch, T.; Cotlet, M.; Hofkens, J.; Van der Biest, K.; Lor, M.; Weston, K.; Tinnefeld, P.; Sauer, M.; Latterini, L.; Müllen, K.; De Schryver, F. C. *J. Phys. Chem. A* **2003**, *107*, 6920.

(10) Herrmann, A.; Weil, T.; Sinigersky, V.; Wiesler, U. M.; Vosch, T.; Hofkens, J.; De Schryver, F. C.; Müllen, K. *Chem. Eur. J.* **2001**, *7*, 4844.

(11) Bell, T. D. M.; Stefan, A.; Masuo, S.; Vosch, T.; Lor, M.; Cotlet, M.; Hofkens, J.; Bernhardt, S.; Müllen, K.; van der Auweraer, M.; Verhoeven, J. W.; De Schryver, F. C. *ChemPhysChem* **2005**, *6*, 942.

(12) Gade, L. H.; Galka, C. H.; Williams, R. M.; De Cola, L.; McPartlin, M.; Dong, B.; Chi, L. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 2677.

(13) Gade, L. H.; Galka, C. H.; Hellmann, K. W.; Williams, R. M.; De Cola, L.; Scowen, I. J.; McPartlin, M. *Chem. Eur. J.* **2002**, *8*, 3732.

(14) Gade, L. H. *Acc. Chem. Res.* **2002**, *35*, 575.

(15) Wiederrecht, G. P.; Niemczyk, M. P.; Svec, W. A.; Wasielewski, M. R. *Chem. Mater.* **1999**, *11*, 1409.

(16) Cormier, R. A.; Gregg, B. A. *Chem. Mater.* **1998**, *10*, 1309.

(17) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449.

(18) Gregg, B. A. *Appl. Phys. Lett.* **1995**, *67*, 1271.

(19) Hiramoto, M.; Ihara, K.; Fukusumi, H.; Yokoyama, M. *J. Appl. Phys.* **1995**, *78*, 7153.

(20) Zhang, H.; Smith, S. C. *J. Theor. Comput. Chem.* **2007**, *6*, 789.

(21) Adachi, M.; Nagao, Y. *Chem. Mater.* **1999**, *11*, 2107.

(22) Zhao, G.-J.; Han, K.-L. *J. Phys. Chem. A* **2007**, *111*, 2469.

(23) Zhao, G.-J.; Han, K.-L. *J. Phys. Chem. A* **2007**, *111*, 9218.

(24) Zhou, L.-C.; Liu, J.-F.; Zhao, G.-J.; Shi, Y.; Peng, X.-J.; Han, K.-L. *Chem. Phys.* **2007**, *333*, 179.

(25) Han, K.-L.; He, G.-Z. *J. Photochem. Photobiol. C: Photochem. Rev.* **2007**, *8*, 55.

(26) Zhao, G.-J.; Han, K.-L. *J. Chem. Phys.* **2007**, *127*, 024306.

(27) Zhao, G.-J.; Han, K.-L.; Lei, Y.-B.; Dou, Y. *J. Chem. Phys.* **2007**, *127*, 094307.

(28) Zhao, G.-J.; Liu, Y.-H.; Han, K.-L.; Dou, Y. *Chem. Phys. Lett.* **2008**, *453*, 29.

(29) Zhao, G.-J.; Han, K.-L. *ChemPhysChem* **2008**, *9*, 1842.

(30) Zwier, T. S. *Annu. Rev. Phys. Chem.* **1996**, *47*, 205.

(31) Dian, B. C.; Longarte, A.; Zwier, T. S. *J. Chem. Phys.* **2003**, *118*, 2696.

(32) Belfield, K. D.; Schafer, K. J.; Alexander, M. D., Jr. *Chem. Mater.* **2000**, *12*, 1184.

(33) Belfield, K. D.; Bondar, M. V.; Przhonska, O. V.; Schafer, K. J. *J. Photochem. Photobiol. A* **2002**, *151*, 7.

(34) Belfield, K. D.; Bondar, M. V.; Hernandez, F. E.; Przhonska, O. V. *J. Phys. Chem. C* **2008**, *112*, 5618.

(35) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L.; Wasielewski, M. R. *Science* **1992**, *257*, 63.

(36) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; Mackenzie, J. D. *Science* **2001**, *293*, 1119.

(37) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267.

(38) Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. Y. *J. Phys. Chem. B* **2003**, *107*, 6668.

(39) Sudeep, P. K.; Takechi, K.; Kamat, P. V. *J. Phys. Chem. C* **2007**, *111*, 488.

(40) Kamat, P. V. *J. Phys. Chem. C* **2007**, *111*, 2834.

(41) Robel, I.; Bunker, B. A.; Kamat, P. V. *Adv. Mater.* **2005**, *17*, 2458.

(42) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.

(43) Zheng, Y.; Long, H.; Schatz, G. C.; Lewis, F. D. *Chem. Commun.* **2005**, *38*, 4795.

(44) Drukker, K.; Schatz, G. C. *J. Phys. Chem. B* **2000**, *104*, 6108.

(45) Zhao, L.; Jensen, L.; Schatz, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 2911.

(46) Zhao, G.-J.; Chen, R.-K.; Sun, M.-T.; Liu, J.-Y.; Li, G.-Y.; Gao, Y.-L.; Han, K.-L.; Yang, X.-C.; Sun, L. *Chem. Eur. J.* **2008**, *14*, 6935.

(47) Zhao, G.-J.; Han, K.-L. *Biophys. J.* **2008**, *94*, 38.

(48) Zhao, G.-J.; Liu, J.-Y.; Zhou, L.-C.; Han, K.-L. *J. Phys. Chem. B* **2007**, *111*, 8940.

(49) Zhao, G.-J.; Han, K.-L. *J. Comput. Chem.* **2008**, *29*, 2010.

(50) Kozlov, V. G.; Parthasarathy, G.; Burrows, P. E.; Forrest, S. R.; You, Y.; Thompson, M. E. *Appl. Phys. Lett.* **1998**, *72*, 144.

(51) Kim, C.-H.; Shinar, J. *Appl. Phys. Lett.* **2002**, *80*, 2201.

(52) Shortreed, M. R.; Swallen, S. F.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Devadoss, C.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **1997**, *101*, 6318.

(53) Melinger, J. S.; Pan, Y.; Kleiman, V. D.; Peng, Z.; Davis, B. L.; McMorrow, D.; Lu, M. *J. Am. Chem. Soc.* **2002**, *124*, 12002.

(54) Elemans, J. A. A. W.; van Hameren, R.; Nolte, R. J. M.; Rowan, A. E. *Adv. Mater.* **2006**, *18*, 1251.

(55) Langhals, H.; Jaschke, H.; Ring, U.; von Unold, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 201.

(56) Dotcheva, D.; Klapper, M.; Müllen, K. *Macromol. Chem. Phys.* **1994**, *195*, 1905.

(57) Quante, H.; Schlichting, P.; Rohr, U.; Geerts, Y.; Müllen, K. *Macromol. Chem. Phys.* **1996**, *197*, 4029.

(58) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.

(59) Takimiya, K.; Jigami, T.; Kawashima, M.; Kodani, M.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **2002**, *67*, 4218.

(60) Langhals, H.; Kirner, S. *Eur. J. Org. Chem.* **2000**, 365.

(61) Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847.

(62) Shkrob, I. A. *J. Phys. Chem. A* **1998**, *102*, 4976.

(63) Wang, Z.; Enkelmann, V.; Negri, F.; Müllen, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1972.

(64) Qian, H.; Liu, C.; Wang, Z.; Zhu, D. *Chem. Commun.* **2006**, 4587.

(65) Sun, Y.; Tan, L.; Jiang, S.; Qian, H.; Wang, Z.; Yan, D.; Di, C.; Wang, Y.; Wu, W.; Yu, G.; Yan, S.; Wang, C.; Hu, W.; Liu, Y.; Zhu, D. *J. Am. Chem. Soc.* **2007**, *129*, 1882.

(66) Jiang, W.; Qian, H.; Li, Y.; Wang, Z. *J. Org. Chem.* **2008**, *73*, 7369.

(67) Briseno, A. L.; Miao, Q.; Ling, M.; Reese, C.; Meng, H.; Bao, Z.; Wudl, F. *J. Am. Chem. Soc.* **2006**, *128*, 15576.

(68) Wu, Y.; Li, Y.; Gardner, S.; Ong, B. S. *J. Am. Chem. Soc.* **2005**, *127*, 614.

(69) Zhou, Y.; Liu, W.; Ma, Y.; Wang, H.; Qi, L.; Cao, Y.; Wang, J.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 12386.

(70) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224.

(71) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034.

(72) Krishnan, R.; Schlegel, H. B.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4654.

(73) Foresman, J. B.; Head-Gordon, M.; Pople, J. A. *J. Phys. Chem.* **1992**, *96*, 135.

(74) Malmqvist, P.-A.; Roos, B. O. *Chem. Phys. Lett.* **1989**, *155*, 189.

(75) Stalring, J.; Bernhardsson, A.; Lindh, R. *Mol. Phys.* **2001**, *99*, 103.

(76) Ahlrichs, R.; Bär, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(77) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(78) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(79) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.

(80) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117*, 7433.

JP8083666