Effect of Internal BN Substitution on Electronic Properties of Pyrene Derivatives

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Abstract. Pyrene as an important chemical building block has found wide applications in the field of organic electronics. In solution, pyrene and its derivatives are well-known examples for excimer formation. Here, we studied the boron-nitrogen (BN)-substituted pyrene, decorated with thiophene side chain. From density-functional theory (DFT) calculation, this isoelectronic BN substitution maintains the coplanarity of the central motif and the delocalized π-electron distribution, but additionally induces a much stronger permanent dipole moment. Time-dependent DFT indicates a much-reduced oscillator strength for low energy transitions, and surprisingly a forbidden π-π* transition, therefore resulting in a much red-shifted absorption spectrum. Our simulation results call for future experiments to study the photo-excited properties of BN-substituted pyrene and molecular self-assembly through dipole-dipole interaction and π-π* interaction.

1. Introduction
The study of organic electronics has long been viewed as an essential determinant in the field of display technology, renewable energy and flexible electronics.[1] In the past 50 years, photochemists have been devoting continuous efforts in researching organic semi-conductors[2], and their integration into high-performance organic electronic devices. Pyrene is one of the simplest π-conjugated molecules which has shown electrical conductivity undergoing electrochemical doping.[3] This feature, together with pyrene’s unique radiometric properties[4] and its concentration-dependent excimer[5] gives rise to the multiple applications including luminescence-switching chemical sensing[4] and membrane biophysics.[5]

Owing to its outstanding optical and electronic properties, pyrene has represented an important building block in optoelectronic devices, such as organic light-emitting diodes (OLEDs)[6], organic field effect transistors (OFETs)[7], and organic photovoltaics (OPVs).[8] In OLEDs, pyrene’s high charge carrier mobility and prominent hole injection ability, together with its high photoluminescence efficiency, is particularly suitable for deep blue OLEDs[9] compared with other chromophores[10] A
high carrier mobility is also assured to fabricate OFET.[10], [11] OPVs based on pyrene molecules have showed a decent power conversion efficiency partly due to its high fill factor benefiting from the strong molecular self-assembly.[3]

Excimer formation from traditional pyrene has its unique applications in biology.[12],[13] However, the excimer formation is not always advantageous in organic electronics, given that photoluminescence efficiency of pyrenes notably decreases in thin films.[10] BN substitution has then been introduced as a tool to modulate the electronic properties of conjugated molecules, and there are isoelectronic analogues like naphthalene[14], PAHs pyrene[15], and phenanthrene.[16], [17] One further note is that unlike the common central substitution cases, in certain cases of C/BN hybrid fullerene, the BN substitution takes place out of the central area.[18]

Here, we use a DFT method to simulate the electronic properties of pyrene and its BN-substituted derivatives with thiophene as the side chain. Frontier orbital electron distribution and their energy levels are calculated. Furthermore, we use time-dependent DFT to calculate the excited state properties such as the absorption spectrum. Finally, we discuss our results in the context of excimer formation.

2. Results and Discussion

![Figure 1. The skeletal structure of a) pyrene. b) BN substituted pyrene with thiophene sidechain. c) CC pyrene with thiophene sidechain.](image)

The skeletal formula of pyrenes are shown in Figure 1 and rough Cartesian coordinates are then obtained before carrying out geometry optimization in Orca, an open-source DFT calculation software. Further notes concerning method is described in later sections. On exploring the electronic properties of BN pyrene (BNP) and CC pyrene (CCP), thiophene end group is covalently connected to pyrene to increase the solubility of the molecule for solution processing.

2.1 Geometry optimization

Though the pyrene center is coplanar, the thiophene substition is not in the same plane as the coplanar backbone in Figure 2, forming an angle to the central pyrene with approximately 120º on both sides. The substituted BN pyrene also formed an angle around 120º on both sides, but in this scenario the left and right C-C-S angles connecting pyrene and thiophene differ slightly less (see Table 1). Reason of this difference might be increased structural sustainability after substitution, which to a certain extent reduces the induced dipole moments in thiophene’s rotation around the centre when in motion. Since the planarity is related to the charge delocalization, and HOMO/LUMO, it could be deduced that thiophene sidechain will not significantly change pyrene’s electronic properties, but mainly increases its solubility in solution. However, the side-chain has a significant consequence in the solid state through the molecular packing.
Figure 2. The molecular geometry visualization of a) CC pyrene. B) BN pyrene.

Table 1. The bond angles and bond lengths of CCP and BNP.

| Molecule | Left C-C-S angle (º) | Right C-C-S angle (º) | R_{12} (Å) | R_{23} (Å) | R_{34} (Å) | Total dipole moment (Debye) |
|----------|----------------------|----------------------|------------|------------|------------|-----------------------------|
| CCP      | 120.5                | 121.7                | 1.435      | 1.420      | 1.419      | 0.300                       |
| BNP      | 120.9                | 122.1                | 1.468      | 1.511      | 1.511      | 2.694                       |

*Note: Left and Right C-C-S angles are marked in Figure 2. R_{ij} represents the distance between atom i and j labelled in Figure 2.

BN substitution was observed to change the bond length. As in the Table 1, the BN substitution increases the center C-C bond length, while also enlarging the difference between central bond and bonds connecting to the substitution area. Reason for such extension might due to change in the hybrid method (HF) caused by the substitution. The substitution also introduces a clear increase in total dipole moment, demonstrating a change in pyrene’s polarity with BN replacing CC.

2.2 HOMO and LUMO analysis

Figure 3. The frontier orbitals of pyrenes from DFT calculation. a) HOMO of BNP. b) LUMO of BNP. c) HOMO of CCP. d) LUMO of CCP.
Table 2. HOMO/LUMO specific data.

| Molecule | HOMO-1 (eV) | HOMO (eV) | LUMO (eV) | LUMO+1 (eV) |
|----------|-------------|-----------|-----------|-------------|
| BNP      | -7.064      | -7.036    | 1.217     | 1.501       |
| CCP      | -8.262      | -7.268    | 1.541     | 2.443       |

This part is about the molecular orbital analysis of BN-CC pyrenes with thiophene groups. The frontier orbital distributes in an approximately symmetrical way relative to the center substitution area, where there almost none electron distribution exists. Band gaps (see Table 2) of 8.253 eV (or equivalently, 150.2 nm) and 8.809 eV (140.7 nm) are observed respectively in BNP and CCP. The abridged band gap value is largely due to the decrease in LUMO, which gives the CCP a stronger tendency to deduct electricity and a more violet-shift nature to the end of absorption.

2.3 Molecular absorption spectrum

It is worth noting that redshift occur when undergoing the BN substitution, the main highest absorption peak in Figure 4 which is locating around 5.5 eV, has moved leftward by 0.1 eV. The red shift indicates a decrease in BN band gap, a result perfect consistent with previous works done in the field with graphdiyne. Moreover, the substitution introduces a new lower peak absorption situated at 4.95 eV with an intensity peak of 0.571, despite the approximation attempt of set Gaussian width.

![Normalized absorption spectrum of a) BNP-T, Gaussian width set as 0.1. b) CCP-T, Gaussian width set as 0.09.](image)

Table 3. Transition dipole moment at the transitions with the lowest energies. a) CCP. b) BNP

| Molecule | Wavelength (nm) | Intensity |
|----------|----------------|-----------|
| CCP      | 330.20          | 0.053     |
|          | 327.30          | 0.212     |
The transition dipole in Table 3 moment results surprisingly reveal a forbidden $\pi-\pi^*$ transition in substituted pyrene, as the data extracted shows that at a wavelength of 428.50 nm where HOMO to LUMO transition occur, the intensity is zero. The transition from HOMO-1 to LUMO and HOMO to LUMO+1 also just weakly allowed with 0.031 and 0.346 intensity respectively.

3. Method
The numerical calculation is performed using Orca 4.0,[20],[21] Orca, developed by Max Planck Institute, could conduct ab initio, DFT, and semi-empirical molecular orbital calculation. For the geometrical optimisation, the basic set is def2-TZVP. B3LYP. In TDDFT calculation, the Coulomb and exchange integral are approximated by RIJCOSX in Orca. Calculated results are visualized via Avogadro for molecular orbitals and Gabedit[22] for UV-Vis spectrum.

3.1 Input Block
In this section, we use RHF, B3LYP and TightSCF as the main input blocks for calculating pyrene’s electronic molecular properties.

3.2 Basis Set
The basis sets applied in the simulation mostly diffuse from the Rappoport property-optimized def2 basis set. The def2-SVP basis is used in geometry optimization of pyrenes as to split valence polarization, on which the new polarization functions modify the expression of the zeta function’s expression on the def2 basis set. In the later part of excited states geometry optimization, def2/J is exercised with the Weigend’s universal Coulomb fitting. The presence of ECPs beyond Kr is assumed. Despite longer time needed (see figure 4), an updated triple-zeta polarization function diffused from def2 basis set is applied to the PES scan, as the TZ polarization function better suits intercorrelation between H, S, C.

4. Conclusion
To sum up the research, we numerically compared the electronic properties of pyrene and BN-substituted derivative. Due to the isoelectronic nature, the coplanarity and the pi-conjugation is maintained, despite prolonged substituted area bond length. After substitution, the bandgap is smaller from the red-shifted onset of the UV-Vis spectrum, with changes occur in the electron clouds distribution. Surprisingly, we find the lowest energy transition is forbidden, probably due to symmetrical constrains. The introduced permanent dipole moment might significantly change the intermolecular interaction. Our single molecule calculation indicates that the excimer formation, traditionally popular in pyrene molecules, might change in the BN pyrene. Future experimental studies
should focus on studying its photo-excited properties and molecular self-assembly in the solid state phase.

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