



A study on the electronic and charge transfer properties in tin phthalocyanine (SnPc) derivatives by density functional theory

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ABSTRACT

The carrier transport properties of tin phthalocyanine (SnPc) derivatives have been investigated at DFT/B3LYP/(6-31G*, LANL2DZ) level. Contributions from the Boron and Nitrogen atoms are found to be predominant in the HOMOs. Moreover, the systems SnPcBN3, SnPcBN4 and SnPcBN5 have lower LUMO energy in comparison to SnPc. Introduction of BH (at position 1, 2 and 3) and NH (at position 4) onto the SnPc molecule induces the increase in both the vertical ionization potential (IP_v) and vertical electronic affinity (E_{av}) for SnPcBN3, SnPcBN4, SnPcBN5 versus SnPc. These results indicate the increased injection barrier for hole and decreased injection barrier for electron transfer. On the other hand, both IP_v and E_{av} for SnPcBN1, SnPcBN2 are decreased to SnPc revealing the decreased and increased injection barrier for hole and electron transport, respectively. It has been predicted that SnPcBN3, SnPcBN4, SnPcBN5 would be better electron transfer materials while SnPcBN1, SnPcBN2 behave as better hole transporter.

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1. Introduction

Organic devices, such as photovoltaic cells (OPVs) and field-effect transistors (OFETs), produced by solution processes own certain advantages such as large area, flexibility, lower temperatures and cost effective route for the device fabrication. In general, organic semiconductors are known to possess small carrier mobility compared to inorganic ones, because of the molecular nature of organic materials. Recently, the performance of organic devices has been improved [1–3]. Some small molecular compounds with a large π -conjugated ring structure, such as phthalocyanines, pentacene, rubrene, and porphyrins have been demonstrated as good semiconductors [4–7]. Many organic semiconductors reported so far are unipolar and exhibit p-type transport properties, whereas more efforts have been devoted to the design and synthesis of n-channel materials in recent years. Few organic semiconductors have been found to exhibit ambipolar properties [8]. Moreover, very few organic

semiconductors exhibit balanced hole and electron transport characteristics [9–11].

Ambipolar materials are strongly desirable for logic circuit design because they enable the simple fabrication of complementary circuits like inverters without advanced patterning techniques to deposit p- and n-channel materials separately. Moreover, ambipolar materials work for both positive and negative voltages which streamlines the circuit design. An ideal ambipolar material is expected to give balanced performance in both negative and positive voltage regimes; therefore, it is strongly desired that the ambipolar materials should possess balanced n- and p-channel performance.

Phthalocyanines have gained attention in OFETs for many years because of their remarkably high chemical and thermal stabilities, as well as non-toxicity and better field-effect properties [12,13]. The unique properties of phthalocyanine dyes and pigments enables them to be the colorant of choice for most blue and green colors. Phthalocyanines are also finding extensive use in modern hi-tech areas [14].

The tin phthalocyanine (SnPc) is typical phthalocyanine using in OFETs [15,16]. Previous quantum chemical studies revealed that boron-substituted hetroacene is good to design electron transport and ambipolar materials while the nitrogen-substituted hetroacene revealed improved hole injection [17–19]. Thus five SnPc

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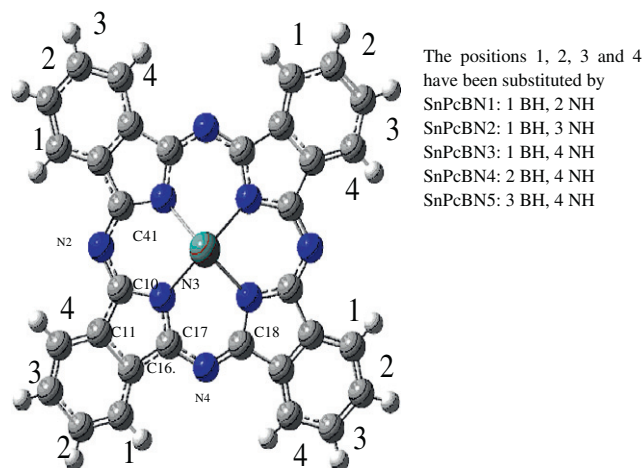


Fig. 1. The SnPc and its investigated derivatives.

derivatives have been obtained by introducing boron and nitrogen at different positions to peripheral rings of SnPc (Fig. 1). This theoretical study is to investigate the structure–property relationship, their characteristics for OFET application by calculating the ionization potential, electron affinity and reorganization energies. The obtained results have been used to explain the charge carrier behavior of the newly designed systems of SnPc, which may provide useful information to design novel OFET materials for future applications.

2. Computational details

The designed derivatives of SnPc in the ground states (S_0) have been optimized at the density functional theory (DFT) level using the B3LYP functional and 6-31G*(lan12dz) basis set [20,21]. To calculate the reorganization energies same theory has been applied which has been reported to be an efficient approach for SnPc [21]. In the previous study the B3LYP/6-31G* (Lan12dz) level was also used for the solvent reorganization energies of hole in acetonitrile,

dimethylsulfoxide, chloroform, toluene, acetone and tetrahydrofuran solvents, respectively, using PCM and CPCM models for SnPc. It was reported that reorganization energy is solvent independent [21].

The reorganization energy is further divided into two parts: $\lambda_{\text{rel}}^{(1)}$ and $\lambda_{\text{rel}}^{(2)}$, where $\lambda_{\text{rel}}^{(1)}$ corresponds to the geometry relaxation energy of one molecule from neutral to charged state, and $\lambda_{\text{rel}}^{(2)}$ corresponds to the geometry relaxation energy from charged to neutral state [22].

$$\lambda = \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} \quad (1)$$

In the evaluation of λ , the two terms were computed directly from the adiabatic potential energy surfaces [23,24].

$$\lambda = \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} = [E^{(1)}(X^+) - E^{(0)}(X^+)] + [E^{(1)}(X) - E^{(0)}(X)] \quad (2)$$

Here, $E^{(0)}(X)$, $E^{(0)}(X^+)$ are the ground-state energies of the neutral and charged states, $E^{(1)}(X)$ is the energy of the neutral molecule at the optimized charged geometry and $E^{(1)}(X^+)$ is the energy of the charged state at the geometry of the optimized neutral molecule. It should be noted that the polarization effects from the surrounding molecules, as well as the charge reorientation, have been neglected to minimize the complications involved in the theoretical calculations [25,26,22]. All the quantum calculations have been performed using Gaussian03 package [27].

3. Results and discussions

3.1. Geometries

The optimized geometries of SnPc and its derivatives have been tabulated in Table 1. The substitution of boron and nitrogen at different positions leads to increase or decrease the bond lengths of pyrrole rings. The major change has been observed in the bond length of C11–C16 which decreases 0.018 and 0.02 Å in SnPcBN3 and SnPcBN5, respectively. The most important change in bond lengths has been examined in Sn–N2, Sn–N4, Sn–N6 and Sn–N8 which increases in SnPcBN3, SnPcBN4 and SnPcBN5 in the range of 0.011–0.021 Å. It has been observed that the associated angles (\angle C10–N2–C41 and \angle C17–N4–C18) between pyrrole rings in SnPc

Table 1
Selected optimized bond lengths in Angstrom (Å) and bond angles ($^\circ$) for SnPc and its designed derivatives at the B3LYP/6-31G* (Lan12dz) level.

	SnPc	SnPcBN1	SnPcBN2	SnPcBN3	SnPcBN4	SnPcBN5
<i>Bond lengths</i>						
Sn–N2	3.607	3.613	3.609	3.621	3.618	3.621
Sn–N3	2.276	2.268	2.272	2.270	2.276	2.270
Sn–N4	3.607	3.609	3.609	3.623	3.619	3.619
Sn–N5	2.276	2.264	2.272	2.270	2.276	2.267
Sn–N6	3.607	3.609	3.609	3.621	3.619	3.619
Sn–N7	2.276	2.268	2.272	2.272	2.276	2.270
Sn–N8	3.607	3.612	3.609	3.624	3.618	3.622
Sn–N9	2.276	2.269	2.272	2.272	2.275	2.271
C10–C11	1.458	1.463	1.462	1.454	1.438	1.453
C11–C16	1.408	1.399	1.414	1.390	1.406	1.388
C16–C17	1.458	1.453	1.457	1.459	1.472	1.454
C10–N2	1.329	1.328	1.327	1.327	1.331	1.328
C10–N3	1.375	1.371	1.369	1.370	1.377	1.373
C17–N3	1.375	1.378	1.380	1.381	1.375	1.378
C17–N4	1.329	1.333	1.333	1.334	1.327	1.331
<i>Bond angles</i>						
C10–C11–C16	106.46	107.44	108.28	109.85	109.31	107.91
C11–C16–C17	106.46	105.45	104.27	103.47	103.90	105.57
C10–N3–C17	108.71	108.07	108.45	107.95	108.66	107.99
C10–N2–C41	123.63	123.52	123.80	123.18	123.25	122.97
C17–N4–C18	123.63	123.57	123.80	123.24	123.25	122.99
N2–C10–N3	127.77	128.72	129.15	130.36	129.15	129.11
N3–C17–N4	127.77	126.42	126.21	125.30	126.92	126.58

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