2500 *J. Phys. Chem. A* **2009,** *113,* 2500–2506

Density Functional Theory Study on the Semiconducting Properties of Metal Phthalocyanine Compounds: Effect of Axially Coordinated Ligand

Xue Cai,[†,‡,§] **Yuexing Zhang,**[†,‡] **Dongdong Qi,**[†,‡] **and Jianzhuang Jiang***[,†,‡]

Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China, Department of Chemistry, Shandong University, Jinan 250100, China, and Department of Chemistry, Mudanjiang Normal College, Mudanjiang 157012, China

Received: July 16, 2008; Revised Manuscript Received: December 29, 2008

To investigate the effect of axially coordinated ligand(s) on the semidconducting properties of metal phthalocyanine complexes, density functional theory (DFT) calculations were carried out in terms of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy, ionization energy (IE), electronic affinity (EA), and reorganization energy (λ) of F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc. For the purpose of comparative studies, calculation on SnPc without axially coordinated ligand has also been conducted. The electronic couplings (V) and the charge transfer mobilities for the electron of metal phthalocyanine compounds with reported single crystal structures for Cl_2SnPc, I_2SnPc, and Cl_2TiPc are also calculated. Comparison of the calculated results of SnPc with F_2SnPc, Cl_2SnPc, I_2SnPc, and OSnPc indicates that introduction of axially coordinated ligand(s) obviously lowers the HOMO and LUMO energies of metal phthalocyanine complexes but does not change their energy difference, which results in an increase in their electronic affinity and ionization energy for metal phthalocyanine complexes containing axially coordinated ligand(s). This result is responsible for the decrease in the electron injection barrier and increase in the hole injection barrier of metal phthalocyanine complexes containing axially coordinated ligand(s) in comparison with metal phthalocyanine complexes without axially coordinated ligand, leading to the change in the nature of semiconductivity from p-type for SnPc to n-type for F_2SnPc, Cl_2SnPc, I_2SnPc, and OSnPc. Because of the smaller electronegativity of V^{IV} than that of Sn^{IV}, OVPc is revealed to display p-type semiconductivity in terms of electronic affinity (EA_v). In contrast, Cl_2TiPc is revealed to show n-type semiconductivity because of its large electronic affinity (EA_v). The present work, representing the first theoretical effort toward understanding the effect of axially coordinated ligand(s) on the semiconducting properties of metal phthalocyanine complexes, will be helpful for designing and preparing novel phthalocyanine semidconductors with good organic field effect transistor (OFET) performance.

Introduction

Organic field effect transistors (OFETs) have attracted increasing research interest due to their great potential applications in the field of flexible displays, integrated circuits, and low-cost electronic devices since their first report in 1986.[1,2] In recent years, many organic semiconductors with good OFET performance have been developed, and significant progress in OFET fabricating techniques has been made.[3]

Phthalocyanines have been among the most intensively studied small molecules with excellent semiconductivity.[4−13] A series of phthalocyanine compounds have been fabricated into the OFET devices, and their OFET performance has been studied. The charge carrier mobility for holes of CuPc and TiOPc single crystal-based OFETs was revealed to reach up to 1 and 3.31 $cm^2\ V^{-1}\ s^{-1}$, respectively, at room temperature.[14,15] Extensive studies revealed that sandwich-type bis(phthalocyaninato) and tris(phthalocyaninato) rare earth complexes also exhibited promising semiconducting properties for OFET applications.[7,8,16] In addition to the intensive experimental studies over the preparation and fabrication of OFETs in the past two decades, theoretical and computational efforts have been paid toward understanding and designing novel molecular semiconducting materials with good OFET performance.[17−21] Lately, the semiconducting properties of the sandwich-type bis(phthalocyaninato) $M(Pc)_2$ ($M = Y$, La) have been investigated using DFT method by this group.[22]

In the present Article, the semiconducting properties in terms of the HOMO and LUMO energy, ionization energy, electronic affinity, reorganization energy, transfer integral, and charge transfer mobility of a series of phthalocyanine compounds with axially coordinated ligand(s) including F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc have been investigated by density function theory (DFT) calculations. To understand the effect of the axially coordinated ligand(s) on the semiconducting properties, calculation on SnPc without axially coordinated ligand was also carried out. In line with the experimental findings, the calculated results reproduce the change in the nature of semiconductivity from p-type for SnPc to n-type for F_2SnPc, Cl_2SnPc, I_2SnPc, and OSnPc upon axial coordination. The present work should be helpful in understanding the nature of phthalocyanine semiconductor, and designing and preparing novel phthalocyanine semidconducting materials with good OFET performance.

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* Corresponding author. E-mail: jianzhuang@ustb.edu.cn, jzjiang@sdu.edu.cn.

[†] University of Science and Technology Beijing.

[‡] Shandong University.

[§] Mudanjiang Normal College.

10.1021/jp806279u CCC: $40.75

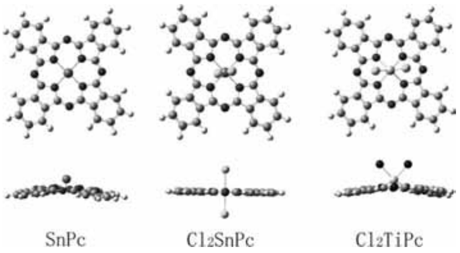

Figure 1. Molecular structures of phthalocyanine complexes SnPc, Cl_2SnPc, and Cl_2TiPc (top, top view; bottom, side view).

Computational Method and Details

According to the Marcus theory, the charge transfer can be described as a self-exchange electron transfer reaction between a neutral molecule and a neighboring cation or anion. In this situation, the charge transport can be described as a sequential electron hopping process between consecutive molecules. As a result, the hopping rate can be modeled by classical Marcus theory:

$$W_i = (V^2/\hbar)(\pi/\lambda_{\pm}k_BT)^{1/2}\exp(-\lambda_{\pm}/4k_BT) \quad (1)$$

where $\lambda_{\pm}$ is the reorganization energy, V the transfer integral, k_B the Boltzmann constant, $\hbar$ the Planck constant, and T the temperature.

The reorganization energy reflects the geometric changes in the molecule when going from neutral state to the ionized one and vice versa, which can be estimated from the sum of the relaxation energies when molecular geometry changes from the neutral to the ionized state and the vice versa process.

The transfer integral t depends on the relative arrangement of the molecules in the solid state and describes the intermolecular electronic coupling, which needs to be maximized to achieve high charge carrier mobility. In all calculations, one molecule is randomly chosen from the crystal structure as the starting point for a charge to diffuse, and the transfer is restricted between the nearest neighboring molecules. All possible intermolecular hopping pathways were generated. The electronic coupling for hole/electron transfer in the direct scheme can be written as:

$$t = \langle \Phi^{0,\mathrm{site1}}_{\mathrm{HOMO/LUMO}} | F^0 | \Phi^{0,\mathrm{site2}}_{\mathrm{HOMO/LUMO}} \rangle$$

where $\Phi^{0,\mathrm{site1}}_{\mathrm{HOMO/LUMO}}$ and $\Phi^{0,\mathrm{site2}}_{\mathrm{HOMO/LUMO}}$ represent the HOMO or LUMO of isolated molecules 1 and 2, respectively, and F^0 is the Fock operator for the dimer for a fixed pathway, in which the suffix of zero indicates that the molecular orbitals appearing in the operator (the density matrix, for instance) are unperturbed. The Fock matrix is evaluated as:

$$F^0 = SC\varepsilon C^{-1}$$

where S is the overlap matrix for the dimer taken from the crystal structure, and the C and ε are the molecular orbital coefficients and energies from one-step diagonalization without iteration. The direct method in calculating transfer integral has been proved simple, efficient, and reliable[23] in comparison with the site energy and overlap corrected splitting scheme of Valeev and co-workers.[24]

Given the hopping rate between two neighboring molecules, the diffusion coefficient can be evaluated from the hopping rates as:[25]

$$D = (1/2n)\sum_i r_i^2 W_i P_i \quad (2)$$

where n is the spatial dimension, which is equal to 3 for the crystal, W_i is the hopping rate due to charge carrier to the ith neighbor, r_i is the center mass distance in a dimer, and P_i is the relative probability for charge carrier to a particular ith neighbor.

$$P_i = W_i \Big/ \sum_i W_i \quad (3)$$

The drift mobility of hopping μ is evaluated from the Einstein relaxation:

$$\mu = eD/k_BT \quad (4)$$

Figure 1 shows the molecular structures of phthalocyanine complexes SnPc, Cl_2SnPc, and Cl_2TiPc. The molecular symmetries (C_{4v} for SnPc and OSnPc, D_{4h} for F_2SnPc, Cl_2SnPc, and I_2SnPc, and C_2 for Cl_2TiPc) of the neutral molecules are kept during structure optimization, while no symmetry constraint is enforced for the optimization of cation and anion. All calculations for the neutral molecules, cations, and anions were carried out with the density functional theory (DFT) method at the B3LYP/LANL2DZ and B3LYP/(6-31+G*, LANL2DZ) level, which have been proved feasible for calculating large molecules.[15,26] No imaginary vibration is predicted in the following frequency calculations of the IR vibration spectroscopy. All of the calculations were performed using the Gaussian 03 program[27] in the IBM P690 system at the Shandong Province High Performance Computing Centre.

TABLE 1: Calculated Energies of Frontier Orbitals and HOMO−LUMO Gaps (in eV) for SnPc, F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc at the DFT/B3LYP/LANL2DZ Level[a]

	SnPc	F_2SnPc	Cl_2SnPc	I_2SnPc	OSnPc	OVPc	Cl_2TiPc
E_{HOMO}	−5.367	−5.689	−5.791	−5.849	−5.609	−5.454	−5.612
	(−5.244)	(−5.567)	(−5.669)	(−5.747)	(−5.549)	(−5.333)	(−5.457)
E_{LUMO}	−3.242	−3.546	−3.673	−3.747	−3.560	−3.309	−3.608
	(−3.172)	(−3.452)	(−3.578)	(−3.677)	(−3.475)	(−3.224)	(−3.467)
gap	2.125	2.143	2.118	2.102	2.050	2.145	2.004
	(2.072)	(2.115)	(2.091)	(2.069)	(2.074)	(2.109)	(1.990)

[a] The values calculated at the B3LYP/(6-31+G*, LANL2DZ) level are also given in parentheses.

Results and Discussion

HOMO and LUMO Energy Levels. Experimental investigations have revealed that introduction of electron-withdrawing groups onto the peripheral positions of conjugated molecules is an effective method to induce the change in the nature of semiconductivity from p-type into n-type, which is exemplified by the change from p-type for CuPc to n-type for $Cu[Pc(F)_{16}]$ after perfluorination.[28] To get the effect of axially coordinated ligand(s) on the semiconductor nature, calculations on a series of tin phthalocyanine complexes with and without axially coordinated ligand(s) were carried out. Table 1 compares the energies of the HOMO and LUMO as well as the HOMO−LUMO gap of F_2SnPc, Cl_2SnPc, I_2SnPc, and OSnPc with those of SnPc. The calculated results for Cl_2TiPc and OVPc are also included. As can be found, introduction of halogen and oxygen atoms onto the tin phthalocyanine molecules as axially coordinated ligand(s) leads to a significant decrease in the HOMO and LUMO energies, from −5.244 and −3.172 eV for SnPc to −(5.747−5.549) and −(3.677−3.452) eV for X_2SnPc (X_2 = F_2, Cl_2, I_2, O) but does not change their HOMO−LUMO gap. The significantly lowered LUMO energy level for the tin phthalocyanine complexes upon axial coordination with halogen and oxygen not only benefits the injection of electron from the source gold electrode but also makes these phthalocyanine complexes unsusceptible to oxidation in air. This is considered

TABLE 2: Vertical and Adiabatic Ionization Energies and Electronic Affinities (in eV) for SnPc, F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc at the DFT/B3LYP/LANL2DZ Level[a]

	SnPc	F_2SnPc	Cl_2SnPc	I_2SnPc	OSnPc	OVPc	Cl_2TiPc
IE_{vert}	6.422	6.731	6.8429	6.863	6.727	6.513	6.667
	(6.283)	(6.602)	(6.694)	(6.746)	(6.593)	(6.337)	(6.482)
IE_{adia}	6.398	6.722	6.813	6.847	6.699	6.482	6.631
	(6.265)	(6.581)	(6.669)	(6.698)	(6.550)	(6.369)	(6.457)
EA_{vert}	2.158	2.491	2.572	2.685	2.444	2.186	2.566
	(2.096)	(2.372)	(2.514)	(2.647)	(2.396)	(2.140)	(2.638)
EA_{adia}	2.245	2.536	2.678	2.783	2.547	2.289	2.845
	(2.218)	(2.480)	(2.626)	(2.774)	(2.514)	(2.249)	(2.928)

[a] The values calculated at the DFT/B3LYP/(6-31+G*, LANL2DZ) level are also given in parentheses.

TABLE 3: Reorganization Energies (in eV) of Hole- and Electron-Transport Processes for SnPc, F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc at the DFT/B3LYP/LANL2DZ Level[a]

	SnPc	F_2SnPc	Cl_2SnPc	I_2SnPc	OSnPc	OVPc	Cl_2TiPc
λ_1	0.024	0.024	0.022	0.078	0.026	0.022	0.035
	(0.038)	(0.018)	(0.021)	(0.020)	(0.025)	(0.012)	(0.025)
λ_2	0.024	0.009	0.029	0.015	0.027	0.030	0.036
	(0.018)	(0.021)	(0.024)	(0.048)	(0.042)	(0.032)	(0.025)
λ_3	0.087	0.044	0.11	0.097	0.10	0.10	0.28
	(0.12)	(0.11)	(0.11)	(0.13)	(0.11)	(0.11)	(0.29)
λ_4	0.10	0.13	0.057	0.10	0.10	0.11	0.31
	(0.095)	(0.10)	(0.10)	(0.088)	(0.11)	(0.090)	(0.31)
λ_+	0.048	0.034	0.051	0.093	0.053	0.052	0.071
	(0.056)	(0.039)	(0.045)	(0.068)	(0.067)	(0.044)	(0.050)
λ_-	0.19	0.18	0.16	0.20	0.21	0.22	0.59
	(0.22)	(0.21)	(0.21)	(0.21)	(0.22)	(0.20)	(0.60)

[a] The values calculated at the DFT/B3LYP/(6-31+G*, LANL2DZ) level are also given in parentheses.

to be responsible for the change in the semiconducting nature from p-type for SnPc to n-type for OSnPc and Cl_2SnPc as revealed by experimental measurements.[29] As a consequence, in a manner similar to incorporating electron-withdrawing groups onto the peripheral positions, introduction of axially coordinated electron-withdrawing ligand(s) onto the metal phthalocyanine complexes is also effective to induce the change in the semiconducting nature from p-type to n-type.

Additionally, the HOMO and LUMO energies for Cl_2TiPc are calculated to be −5.457 and −3.467 eV, respectively, which correspond well with those for OSnPc, suggesting the n-type semiconducting nature of this compound. However, the HOMO and LUMO energies for VOPc, −5.333 and −3.224 eV, respectively, are more close to those for SnPc, revealing its p-type semiconducting nature. This is also in line with the experimental findings.[30]

Ionization Energy and Electronic Affinity. To give more information about the ease for the injection of hole or electron from the Au source electrode into semiconductor layer in the OFET devices, the adiabatic and vertical ionization energies (IE_a and IE_v) and the adiabatic and vertical electronic affinities (EA_a and EA_v) for the series of metal phthalocyanine complexes SnPc, F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc are calculated, and the results are organized in Table 2. As revealed previously,[22] molecular compounds with large vertical electronic affinity EA_v will show advantage as n-type organic semiconductor in terms of charge injection, while those with small IE_v favor p-type semiconductor. In particular, according to Newman and co-workers,[31] molecular materials with the electronic affinity locating in the range of 3.0−4.0 eV, which is close to the work function of gold electrode (around 5.1 eV), can ensure efficient electron injection from gold electrode and therefore act as good n-type semiconductor for OFETs. As tabulated in Table 2, the calculated vertical ionization energy (IE_v) and vertical electronic affinity (EA_v) for SnPc are 6.283 and 2.096 eV, respectively. Obviously, the vertical ionization energy of this compound is much closer to the work function of gold electrode (around 5.1 eV) than is its vertical electronic affinity, indicating the easier hole injection but harder electron injection from the gold source electrode into semiconductor layer composed of SnPc when being fabricated into OFETs. This in turn suggests the better p-type semiconducting property over n-type of this compound. This result corresponds well with the experimental findings that SnPc displays good OFET performance for hole.[6]

In line with the change in the energy of their HOMO and LUMO, introduction of axially coordinated electron-withdrawing ligand(s) onto the SnPc molecule induces the increase in both the vertical ionization energy (IE_v), 6.593−6.746 eV for X_2SnPc (X_2 = F_2, Cl_2, I_2, O) versus 6.283 eV for SnPc, and vertical electronic affinity (EA_v), 2.372−2.647 eV for X_2SnPc (X_2 = F_2, Cl_2, I_2, O) versus 2.096 eV for SnPc, Table 2. These results indicate the increased injection barrier for hole and decreased injection barrier for electron after axial coordination with electron-withdrawing ligand(s). As can be found, the vertical electronic affinitiy (EA_v) of the series of tin phthalocyanine complexes with axially coordinated ligand(s) becomes closer to the work function potential of gold electrode and the vertical electronic affinity range of good n-type semiconductors, 3.0−4.0 eV, in comparison with that of SnPc.[31] As a result, the axially coordinated tin phthalocyanine complexes with electron-withdrawing atoms X_2SnPc (X_2 = F_2, Cl_2, I_2, O) are of good n-type semiconductor in terms of electron injection barrier. Indeed, OFETs fabricated from OSnPc were experimentally revealed to display good n-type semiconducting property.[29] The calculated results indicate that functionalizing p-type metal phthalocyanine semiconductors with axially coordinated electron-withdrawing ligand(s) is a promising way toward n-type semiconductor molecular materials.

The vertical and adiabatic ionization energies and electronic affinities of OVPc and Cl_2TiPc are also listed in Table 2. The vertical electronic affinity (EA_v) for Cl_2TiPc, 2.638 eV, locates at the same range as for X_2SnPc (X_2 = F_2, Cl_2, I_2, O), indicating the potential n-type semiconducting property of this compound in terms of electronic affinity. In good contrast, the vertical ionization energy (IE_v) and vertical electronic affinity (EA_v) for OVPc are 6.337 and 2.140 eV, respectively, indicating the p-type semiconducting property of this compound. This is also in accordance with the experimental findings.[30]

Reorganization Energy. The reorganization energy is the sum of the relaxation energies when molecular geometry changes from the neutral to the ionized state and the vice versa process. Table 3 tabulates the calculated reorganization energies for hole (λ_+) and electron (λ_-) transfer processes, respectively, of the metal phthalocyanine complexes SnPc, F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc. For unsubstituted SnPc, the calculated reorganization energy for the hole transfer process, 0.056 eV, is much smaller than that for the electron transfer process, 0.22 eV, which is even smaller than that calculated for pentacene at the DFT/B3LYP/(6-31G*, LANL2DZ) level, 0.082 eV.[15] This result suggests the possible large charge transfer mobility of SnPc in terms of reorganization energy and rationalizes the experimentally revealed p-type semiconducting

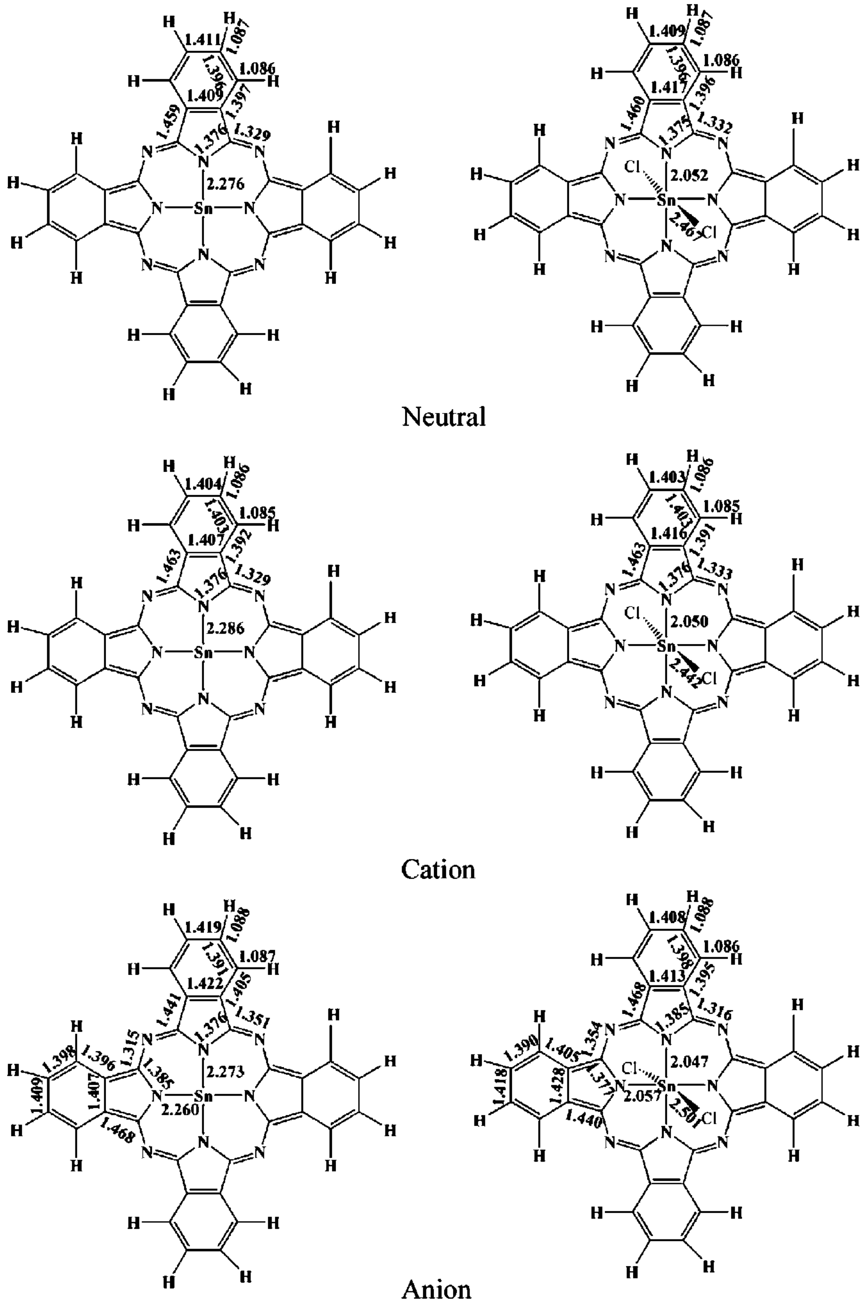

Figure 2. DFT/B3LYP/(6-31G+*, LANL2DZ)-optimized geometries of neutral, cation, and anion of SnPc and Cl_2SnPc.

property of this compound.[6] As is also organized in Table 3, the reorganization energies for the hole transfer process and the electron transfer process for X_2SnPc ($X_2 = F_2, Cl_2, I_2$, O) are comparable to those of SnPc, in the range of 0.039−0.068 and 0.21−0.22 eV, respectively. Obviously, incorporation of the axially electron-withdrawing ligands including F, Cl, I, and O onto SnPc does not lead to a significant change in the reorganization energy for either the hole transfer process or the electron transfer process. The axially electron-withdrawing ligand(s) such as two chlorine atoms located perpendicular to the conjugated system does not contribute to the HOMO and contributes a little to the LUMO of Cl_2SnPc. As a consequence, these axially coordinated electron-withdrawing ligands in X_2SnPc ($X_2 = F_2, Cl_2, I_2$, O) have little effect on their reorganization energy. In addition, despite the n-type nature revealed experimentally for OSnPc, the calculated reorganization energy (λ_+) for hole transfer process, 0.067 eV, is still

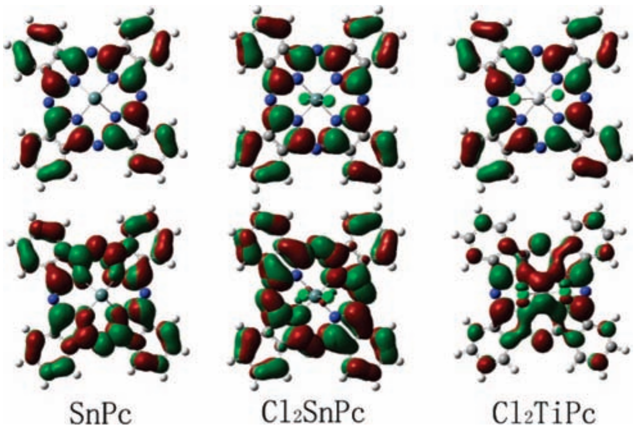

Figure 3. Molecular orbital maps of HOMO (top) and LUMO (bottom) for SnPc, Cl_2SnPc, and Cl_2TiPc.

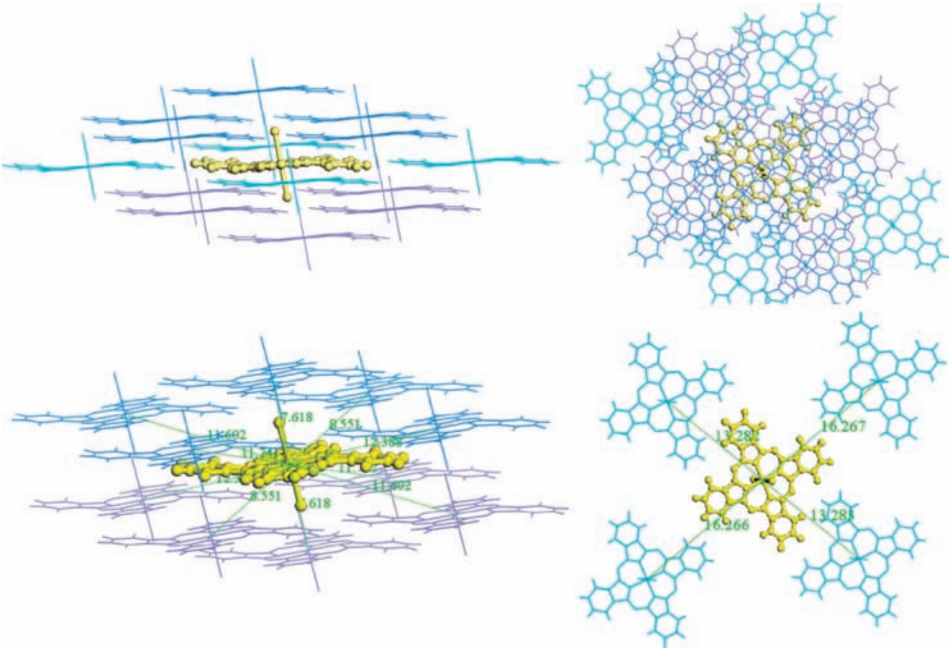

Figure 4. The crystal structure of I_2SnPc with space group $P\bar{1}$ (top) and hopping routes in the crystal (bottom). Left, side view; right, top view.

TABLE 4: Hopping Pathways, Center Mass Distance, Electronic Coupling, and Mobility in the Crystal of Cl_2SnPc, I_2SnPc, and Cl_2TiPc at the B3LYP/LANL2DZ Level

	Cl_2SnPc ($P\bar{1}$)		I_2SnPc ($P\bar{1}$)		I_2SnPc ($C/2c$)		Cl_2TiPc ($P\bar{1}$)	
pathway	distance/Å	V^- (in meV)	distance/Å	V^- (in meV)	distance/Å	V^- (in meV)	distance/Å	V^- (in meV)
1	13.50	0.40	7.62	0.70	8.03	44.09	8.74	1.43
2	11.81	8.34	11.60	13.13	10.98	17.50	12.58	4.22
3	12.20	8.90	11.74	13.00	8.03	12.51	13.31	0.82
4	7.36	2.87	12.39	12.13	11.14	11.45	7.35	50.99
5	11.05	5.06	16.27	0.57	10.98	17.50	12.24	0.49
6	8.68	16.49	8.55	28.45	8.03	12.54	16.19	2.38
7	13.50	0.41	12.39	12.14	8.03	44.72	16.19	2.38
8	11.81	8.32	8.55	28.52	11.14	11.45	13.04	0.95
9	12.20	8.90	13.28	0.24			13.31	0.82
10	7.36	2.87	16.27	0.57			8.17	50.40
11	11.05	5.06	7.62	0.68			11.15	18.23
12	8.68	16.59	11.60	13.13			11.65	15.77
13			11.74	13.00			11.18	4.94
14			13.28	0.24			12.24	0.49
15							8.74	1.43
mobility, μ, $cm^2 V^{-1} s^{-1}$		$\mu^- = 0.045$		$\mu^- = 0.13$		$\mu^- = 0.30$		$\mu^- = 0.0056$

significantly smaller than its electron transfer reorganization energy (λ_-), 0.22 eV. This result, again, indicates that the reorganization energy (λ) is not a major factor in determining the nature of the molecular semiconductor.

For Cl_2TiPc, the reorganization energies for the hole and electron transfer processes are calculated to be 0.050 and 0.60 eV, respectively, the former of which is very close to that obtained for TiOPc at the DFT/B3LYP/(6-31G*, LANL2DZ) level, 0.079 eV.[15] The reorganization energies for hole and electron transfer processes for VOPc are 0.044 and 0.20 eV, respectively.

On the basis of previous research results, the reorganization energy of a π-conjugated system correlates directly with the change in the geometric structure associated with the change in the electronic structure upon removing an electron from the HOMO or adding an electron into the LUMO.[32] As a result, to further understand the change in internal reorganization energy of metal phthlocyanine complexes upon introduction of axially coordinated ligand(s), the geometry deformation during oxidation and reduction for SnPc and Cl_2SnPc has been comparatively studied. Figure 2 shows the optimized structures of neutral, monocation, and monoanion for SnPc and Cl_2SnPc. Figure 3 describes the map of HOMO and LUMO of SnPc and Cl_2SnPc. As can be seen from this figure, the HOMO of SnPc distributes over all of the carbon atoms in the phthalocyanine ring without any contribution from tin(II) ion, nitrogen, and hydrogen atoms. In contrast, in addition to all of the carbon atoms, the nitrogen atoms also contribute to the LUMO of SnPc. This is also true for Cl_2SnPc. However, in addition to all of the carbon and nitrogen atoms, the two axially coordinated chlorine atoms also contribute a little to the LUMO of Cl_2SnPc. As a total result, oxidation leads to change mainly in the C−C bond length for SnPc and Cl_2SnPc, while reduction induces change mainly in the C−C, C−N, and Sn−N bond lengths for SnPc and C−C, C−N, Sn−N, and Sn−Cl bond lengths for Cl_2SnPc. Upon oxidation, the largest C−C bond-length modification in comparison with neutral species for SnPc and Cl_2SnPc is about 0.007 Å, Figure 2. As expected, variation in the C−H and C−N bond lengths for both SnPc and Cl_2SnPc, 0.001 Å, is negligible. Similar to the situation upon oxidation, addition of one electron to the LUMO also induces some degree of change in the C−C, C−N, and Sn−N bond lengths of SnPc and in the C−C, C−N, Sn−N, and Sn−Cl bond lengths of Cl_2SnPc. The largest C−N bond-length modification is about 0.10 Å for SnPc and Cl_2SnPc. The Sn−Cl bond-length modification between neutral and anion state is 0.034 Å. As a consequence, the calculation results indicate that geometric change for both SnPc and Cl_2SnPc upon oxidation is very small, which in turn induces a very small reorganization energy for the hole transfer process. In contrast, the larger geometric change for these two tin phthalocyanine complexes upon reduction results in a larger reorganization energy for the electron transfer process. This is also true for F_2SnPc, I_2SnPc, and OSnPc.

As for Cl_2TiPc with two axially coordinated *cis*-chlorine atoms, its LUMO distributes over all the atoms in the molecule with contribution also from the central metal titanium(IV) ion and two axially coordinated chlorine atoms. Upon reduction, the Ti−Cl and Ti−N bond-length modification reaches 0.102 and 0.057 Å, respectively, indicating the large geometry deformation during reduction for Cl_2TiPc, Figure S1 (Supporting Information). This in turn results in the large reorganization energy for the electron transfer process for this compound, Table 3.

Electronic Coupling and Charge Transfer Mobility. On the basis of the single crystal X-ray diffraction analysis results for compounds Cl_2SnPc, I_2SnPc, and Cl_2TiPc, their intermolecular electronic coupling (*V*, transfer integral) is calculated. As Cl_2SnPc, I_2SnPc, and Cl_2TiP are revealed to be potential n-type semiconductors in terms of electronic affinity, only transfer integrals for electron are calculated. Table S1 (Supporting Information) lists the experimental cell parameters of Cl_2SnPc, I_2SnPc, and Cl_2TiPc obtained from the Cambridge structure database. It is worth noting that availability of two different crystal structures with different space group reported for I_2SnPc provides a good chance to investigate the effect of the intermolecular electronic coupling on charge mobility. The crystal structures and the hopping routes for I_2SnPc with space group $P\bar{1}$ and $C/2c$ are displayed in Figures 4 and S2 (Supporting Information), respectively. The hopping pathways, center mass distances between the two neighboring molecules, intermolecular transfer integrals, and charge mobilities for electron of Cl_2SnPc, I_2SnPc, and Cl_2TiPc in the crystals with just the same space group $P\bar{1}$ as well as of I_2SnPc with additional space group $C/2c$ are calculated and summarized in Tables 4. The intrinsic electron mobility (μ_-) is revealed to be 0.045, 0.13, and 0.0056 $cm^2\ V^{-1}\ s^{-1}$, respectively, for Cl_2SnPc, I_2SnPc, and Cl_2TiPc.

With the reported X-ray crystal structure of I_2SnPc ($P\bar{1}$ space group), charge transfer integrals between one randomly selected molecule and all its possible neighbors are calculated in Figure 4. As can be seen in Table 4, the largest transfer integral of I_2SnPc for electron in the crystal with $C/2c$ space group, 44.72 meV, is also larger than that with $P\bar{1}$ space group, 28.52 meV. These results indicate that the LUMO orbital coupling in the former crystal is stronger than that in the latter one. Because of the larger transfer integral of I_2SnPc with space group $C/2c$ than that with space group $P\bar{1}$, the charge transfer mobility for electron calculated for the former crystal is larger than that for the latter one, 0.30 versus 0.13 $cm^2\ V^{-1}\ s^{-1}$. As clearly revealed by X-ray analysis, the I_2SnPc molecules in the crystal with $C/2c$ space group take a herringbone packing manner, while with space group $P\bar{1}$ the parallel packing manner, so the present calculation result therefore seems to suggest the advantage of herringbone molecular packing manner over the parallel molecular packing manner in benefiting the charge transfer mobility for molecular organic semicondutors.

Cl_2TiPc is of a nonplanar molecular structure with two axially coordinated *cis*-chlorine atoms. As a result, two Cl_2TiPc molecules form concave and convex pairs with significant molecular overlap and very short intermolecular distance. The distance between two neighboring planes formed by four isoindole nitrogen atoms is 3.477 Å in the convex pair and 2.569 Å in the concave pair, indicating the surprisingly close $\pi-\pi$ molecular contact and suggesting the high charge mobility with such a packing structure due to the close $\pi-\pi$ molecular contact. The calculated transfer integrals together with the transfer distances and transfer mobilities are tabulated in Table 4. According to the calculation result, among all the possible routes in the crystal of Cl_2TiPc, the largest transfer integral for electron is 50.99 meV. Because of the significantly larger electron reorganization energy (λ_-) for Cl_2TiPc in comparison with that for I_2SnPc (P_{-1}) (vide supra), the calculated charge transfer mobility of Cl_2TiPc for electron is much smaller than that of I_2SnPc ($P\bar{1}$) for electron, 0.0056 versus 0.13 $cm^2\ V^{-1}\ s^{-1}$.

Conclusion

In summary, the semiconducting properties of a series of metal phthalocyanine complexes with axially coordinated ligand(s) including F_2SnPc, Cl_2SnPc, I_2SnPc, OSnPc, OVPc, and Cl_2TiPc have been systematically investigated by density function theory (DFT) calculations. Comparative studies with unsubstituted counterpart SnPc reveal the effect of axially coordinated electron-withdrawing ligands on the semiconducting properties. Introduction of the axially coordinated electron-withdrawing ligands onto SnPc is revealed to lower the HOMO and LUMO energy level and increase the ionization energy and electronic affinity, resulting in the change in the nature of semiconductivity from p-type to n-type. The present work, representing the first theoretical effort on studying the semiconducting properties of a series metal phthalocyanine complexes with axially coordinated ligand(s), should be helpful for understanding the OFET properties of phthalocyanine derivatives as well as designing and preparing novel phthalocyanine semiconductors with good OFET performance.

Acknowledgment. Financial support from the Natural Science Foundation of China, Ministry of Education of China, and Shandong University is gratefully acknowledged. We are also grateful to Prof. Z. Shuai (Institute of Chemistry, Chinese Academy of Sciences) for help in calculating the transfer integral.

Supporting Information Available: Experimental cell parameters of SnPc, Cl_2SnPc, I_2SnPc, and Cl_2TiPc, the hopping pathway, electronic coupling, and mobility in the crystal of I_2SnPc with $C/2c$ space group, structure changes in Cl_2TiPc upon reduction and oxidation, and hopping routes for I_2SnPc with $P\bar{1}$ and $C/2c$ space groups. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP806279U