

Property Prediction of Charge Transport for Di- or Tetra-halogen-substituted Pyrene by DFT Calculation

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Abstract

A series of reorganization energy of di- or tetra-halogen-substituted pyrene were calculated by the DFT method [B3LYP/6-31++G(d,p)]. The reorganization energy decreased as the size of the halogen atom increased, and 1,3,6,8-tetrabromopyrene showed very small electron reorganization energy, implying n-type semiconductor properties.

1. Introduction

Semiconductors have been regarded as indispensable materials in modern society. Among them, organic semiconductors are expected to make new generations of electronic applications [1,2]. One of their most important parameters is charge mobility. Although the structure-mobility relationship have been studied for several decades [3,4], it has not been fully elucidated yet.

Pyrene skeleton is a hopeful candidate for organic semiconductors due to its high accessibility to peripheral modification and high charge mobility, and its derivatives are synthesized and examined [5,6]. Nevertheless, to our knowledge, there is no report on the mobilities even of simple halogen-substituted pyrenes although they are frequently used as “building blocks”. Some studies indicate halogenation of organic semiconductors results in increasing its mobilities [7,8].

Recently, charge transport properties of mono-substituted pyrene were estimated based on density functional theory (DFT) calculation [9], and strong intermolecular interactions and high mobilities are predicted. Mobility is mainly influenced by reorganization energy and transfer integral [3]. In this study, we compared the reorganization energies of di- and tetra-halogen-substituted pyrenes calculated by the DFT method and examined the possibility of elevating the mobility of pyrene derivatives.

2. Experimental methods

Computation

Geometry optimization and energy calculation of pyrene and its halogen derivatives were carried out using Gaussian 16W [10].

Calculation methods

B3LYP was used as functional and 6-31++G(d,p) was used as basis set. The use of this combination was reported to show the calculated results with a very small error compared with the experimental ones [9].

The (internal) reorganization energies λ were calculated based on “four-point method” which is expressed by eq. (1)

[9],

$$\lambda = [E^{\text{ion}}(R^0) - E^{\text{ion}}(R^{\text{ion}})] + [E^0(R^{\text{ion}}) - E^0(R^0)], \quad (1)$$

where E^{ion} and E^0 indicate the energies of ionized molecule and neutral molecule, respectively. R^{ion} and R^0 indicate the geometries of ionized state and neutral state, respectively.

The compound structures studied in this study are shown in Fig. 1. X indicates a halogen atom. Structures 1, 2, and 3 indicate 1,6-disubstituted, 1,8-disubstituted, 1,3,6,8-tetrasubstituted type pyrenes, respectively.

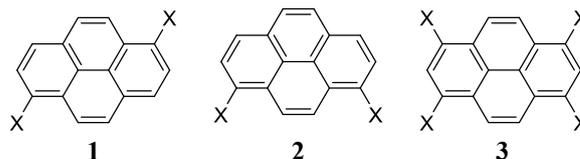


Fig. 1 Chemical structures of studied compounds.

3. Results and discussion

Table I shows the calculated reorganization energies. In the table, λ_h and λ_e indicate hole and electron reorganization energy, respectively. Structures 1 and 2 showed almost the same hole and electron reorganization energies when they have the same two halogen atoms even though one of these was placed on a different position (compare entries 2 and 5, entries 3 and 6, or entries 4 and 7). This indicates that the offsetting of dipole moments inside the molecule is not an important factor for reorganization energy. Perhaps, the resonance effect is an important factor. In other words, in resonance structure formula charges existing on 6-position and one on 8-position can mutually exchange their positions.

Focusing on the molecules with the same structure, both λ_h and λ_e decreased as the atomic number of halogen atom increases (see entries 2 to 4, 5 to 7, or 8 to 10). The present calculation presented a decrease in both the first term and the second term in eq. (1) as the size of the halogen atom increased. This is ascribed to that larger halogen atom can more stabilize charge.

Table I. Calculated reorganization energies.

Entry	Structure	X	λ_h (eV)	λ_e (eV)
1	pyrene	—	0.148	0.210
2	1	F	0.227	0.237
3	1	Cl	0.200	0.205
4	1	Br	0.185	0.194
5	2	F	0.227	0.238
6	2	Cl	0.200	0.206
7	2	Br	0.183	0.197
8	3	F	0.289	0.259
9	3	Cl	0.227	0.197
10	3	Br	0.199	0.182

In structures **1** and **2**, λ_h was smaller than λ_e (entries 2 to 7), however, in structure **3**, it was the other way around (entries 8 to 10). This implies that di-halogen-substituted pyrene compounds tend to be p-type semiconductors, while tetra-halogen-substituted pyrene compounds tend to be n-type ones. Among examined compounds, 1,3,6,8-tetrabromopyrene showed remarkably small electron reorganization energy (entry 10). This suggests it is a hopeful candidate for the n-type semiconductor material.

For further study about the advantage of 1,3,6,8-tetrabromopyrene, its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated with an isovalue of 0.02. Their distributions are depicted in Fig. 2. In both HOMO and LUMO, the orbitals on the bromine atoms stick out from the pyrene skeleton. These orbital shapes are thought to benefit charge transport because the orbitals between adjacent molecules overlap effectively [4,11].

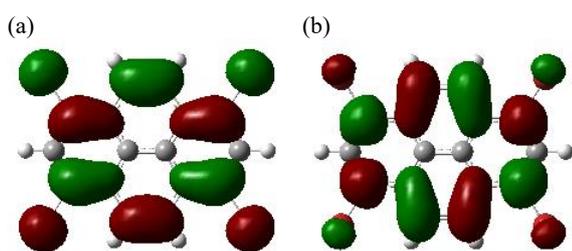


Fig. 2 Distributions of (a) HOMO and (b) LUMO of 1,3,6,8-tetrabromopyrene calculated with an isovalue of 0.02.

Although significant studies have been carried out, the number of available n-type semiconductors is still limited [12]. This study showed a possibility of new n-type materials.

4. Conclusions

The reorganization energy of di- or tetra-halogen-substituted pyrene compounds were calculated. Among halogen atoms, bromine indicated possible enhancement of the mobility of pyrene. 1,3,6,8-Tetrabromopyrene showed remarkably

small electron reorganization energy, which suggests the realization of the n-type properties.

Acknowledgements

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