DFT and TD-DFT Study of Structure and Properties of Semiconductive Hybrid Networks Formed by Bismuth Halides and Different Polycyclic Aromatic Ligands

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Abstract: The structure and spectroscopic properties of polycyclic aromatic ligands of 2,3,6,7,10,11-hexakis (alkylthio) triphenylene (alkyl: methyl, ethyl, and isopropyl; corresponding to the abbreviations of the molecules: HMTT, HETT and HiPTT) were studied using density functional theory (DFT) and time dependent density functional theory (TD-DFT) methods with triple-zeta valence polarization (TZVP) basis set. It was shown that the type of functional theory used, Becke-Perdew (BP) and Leeuwen-Baerends (LB94) implemented in Amsterdam Density functional (ADF) program package, does not have essential influence on the geometry of studied compounds in both ground and excited states. However, significant differences were obtained for the band gap values with relativistic effects of the zero order regular approximation scalar corrections (ZORA) and LB94 functional seems to reproduce better the experimental optical band gap of these systems.

Keywords: Semiconductive hybrid networks, Electronic structure, DFT, Band gap

Introduction

Molecular conductors based on radical cations of tetrathiafulvalene (TTF)¹ and its derivatives have been of major interest in the last decades². The structures of molecular materials type donor-acceptor³, are built on stacks of organic cation with large transfer integrals between nearest neighbours to result in band formation, where partial filling due to removal of some

electrons provide superconducting, metallic, spin density wave⁴, charge density wave and semiconducting states. The properties of these salts depend on structures of chemical modification of the organic cation or inorganic anion. The charge transport pathway in organic semiconductors⁵⁻⁷ is considered to be along the direction of maximum π orbital overlap between the organic molecules subsystems. Some semi-empirical theoretical studies⁸ have been done on the dimensionality of these salts, which is generally imposed by the overlap mode developed in the organic subsystems. Among the numerous TTF ligand systems investigated in these last twenty years, the most extensively studied are those containing pyridine and bipyridine for the elaboration of metal complexes⁹. Like the first cobalt complex containing TTF-pyridines based on the coordination of the CoBr_2 fragment by tetradentate 4,5 bis(2-pyridyl-methylsulfanyl)-4',5'-ethylenedithio-TTF^{10,11}. A variety of such class of compounds have been prepared by varying the included guest organic molecule, which leads to a new family of hybrid semiconductive coordination network¹²⁻¹⁵.

These extended structures based on organic-inorganic hybrids have been synthesized and reported by zhengtao Xu¹⁶. They are based on the coordination between bismuth trichloride and tribromide (BiX_3 , $\text{X} = \text{Cl}, \text{Br}$) and the different polycyclic aromatic ligands within multiple chelating thioether groups, that leads to the corresponding abbreviations: HMTT, HETT and HiPTT (Scheme 1).

Scheme 1. Structure of the organic ligands with atom labelling

Do the solid-state electronic properties depend on nature of bond coordination of Bi-S and Bi-X of such systems. What is the correlation between band gap and dimensionality¹⁷. A large number of density functional theory (DFT) studies have treated excited state properties based on the time-dependent (TD) method. Most of these studies employ the geometric structure of the electronic ground state^{18,19}. DFT and TD-DFT methods are the most widely used tool for theoretically evaluating excited state energies and simulating the UV-vis spectra of organic and hybrids compounds in molecular and solid state level²⁰. In this paper we present results of our studies of structure of polycyclic aromatic ligands of 2,3,6,7,10,11-hexakis (alkylthio) triphenylene in the molecular level with ADF.

Experimental

The problem of large organic materials is the inefficient predicting of the band gap. The π - π interactions are one of the important noncovalent intermolecular forces especially when they involve aromatic rings, these weak bonds are problematic for DFT calculations and commonly used exchange-correlation functionals do not include effects such as dispersion interactions. The studied compounds are large systems and the electron correlation methods such as MP2 and CCSD(T) generally treat such interactions accurately, but these computations are difficult due to their high computational cost. DFT based methods, provide reasonable approximations with better computational efficiency. DFT method²¹ for ground state and TD-DFT²²⁻²⁴ for excited states calculations have been carried out with the Amsterdam Density Functional (ADF) program package^{25,26}. Several pure and hybrid functionals were used but globally pure functionals (BP and LB94) gave better results.

We also used pure meta-GGA functional M06-L for noncovalent interactions. The electronic configurations of all atoms were described by a valence-triple-polarized Slater-type orbitals (TVZP-STO) basis set²⁷. For systems containing Bismuth atoms, the scalar relativistic effects of zero order regular approximation (ZORA)^{28,29} are considered. The core electrons were kept frozen. The geometries of studied compounds based on experimental X-ray were optimized in solid state and calculated at LB94 and BP level theory without any symmetry constraints.

Results and Discussion

Structural studies

These compounds¹⁶ (Figure 1) feature different dimensionalities^{30,31} architectures framework from 0D to 2D. The experimental measurements of the electronic band gap of all compounds vary between 1.64 eV for the 2D network of 3-HMTT•2BiBr₃ to 2.98 eV for the isolated (0D) HMTT, suggesting that Bi-S and Bi-X bonds improve the electronic interactions rather than π - π stacks interactions between organic molecules.

Figure 1. Molecular structure of compounds; 0-HMTT, 1-HMTT·BiCl₃, 2-HMTT·BiBr₃, 3-HMTT·2BiBr₃, 4-HETT·2BiBr₃. (Hydrogen atoms were omitted for clarity)

We notice, in all structures, the intermolecular packing of columns of organic ligands which is dominated by π - π stacking³² of the large aromatic molecules. The calculated bond lengths from optimized structures, are listed in Table 1 and compared with the corresponding values from the X-ray data.

Table 1. Structural and electronic parameters of all described compounds

Compounds	Optical band gap [e.V]	Bi-S distances (Å) X-Ray data	Bi-X distances (Å) X-Ray data	Bi-S distances (Å) Calculated	Bi-X distances (Å) Calculated
0-HMTT	2.98	None	None	None	None
1-HMTT·BiCl ₃	1.82	3.01, 3.25	2.47, 2.58, 2.67, 2.92 3.27	2.98, 3.13	2.55, 2.69, 2.77, 2.79 3.02
2-HMTT·BiBr ₃	1.75	3.03, 3.30	2.62, 2.72 2.80, 3.07 3.48	2.93, 3.17	2.68, 2.82 2.91, 2.95 3.35
3- HMTT·2BiBr ₃	1.64	3.10, 3.12 3.31, 3.45	2.62, 2.64 2.65, 2.72 2.72, 2.75 3.26 3.29 3.30, 3.40	3.08, 3.09 3.23, 3.39	2.67, 2.68 2.73, 2.77 2.80, 2.83 3.13, 3.18 3.18, 3.26
4-HETT·2BiBr ₃	1.97	2.91, 3.04	2.67, 2.68 2.85, 3.11	2.86, 2.96	2.73, 2.73 2.94, 3.01

DFT calculations

At non-relativistic level using BP³³ and LB94³⁴ functionals, we notice that BP functional gives good estimation of the gap, as mentioned in Table 2. The relativistic effects of the ZORA scalar corrections doesn't influence substantially the band gap values obtained, except for 3-HMTT•2BiBr₃. For the compounds 0-HMTT, 2- HMTT•BiBr₃ and 4-HETT•2BiBr₃, the deviations from experimental values are 0.23 eV, 0.18 and 0.17 respectively. The use of LB94 functional at relativistic level, provide a better agreement with experimental values. LB94 functional satisfy the asymptotic conditions and improves the performance of computing long range behaviour.

Table 2. Band gap calculated energies at DFT molecular level

Compound	Gap _{exp} [eV]	Calculated gaps (ADF) [eV]			
		GGA-BP ^a X-ray data	GGA-BP ^a calculated	GGA-BP ^b calculated	GGA-LB94 ^b calculated
0-HMTT	2.98	2.77	2.75	2.75	2.53
1-HMTT·BiCl ₃ (1-A)	1.82	2.10	1.87	1.83	1.70
2-HMTT·BiBr ₃ (2-A)	1.75	2.13	1.98	1.93	1.87
3-HMTT·2BiBr ₃	1.64	2.09	1.82	1.76	1.66
4-HMTT·2BiBr ₃	1.97	2.19	2.04	2.14	2.05

a: The energy gaps were calculated using the DFT theory and triple-zeta polarized (TZP) basis.

b: The energy gaps were calculated using the DFT theory and triple-zeta polarized (TZP) basis with the addition of relativistic scalar ZORA correction

We also carried out calculations on first compound (0-HMTT) using the M06-L³⁵ functional, which yields good results, but M06³⁶ family of functionals is not well tested for large systems containing heavy elements. Therefore, the results obtained for other compounds are not reliable.

TD-DFT calculations

Single point time dependent density functional theory³⁷⁻³⁹ calculations including ten lowest singlet-singlet transitions were performed by employing the GGA-BP functional at non relativistic level, in order to obtain the character of electronic transition and oscillator strength of 0-HMTT, 1-HMTT•BiCl₃ (1-A). The results are listed in Table 3. Only the singlet-singlet transitions are mentioned, singlet-triplet transitions are not optically forbidden but they correspond to zero strength oscillator. We can notice that the calculated energies of S₀ state which correspond to the lowest excitation energy occur at equivalent energies with those of DFT level. The highest occupied molecular orbital (HOMO) of the system involved in the transition is mainly localized on the organic part, while the lowest unoccupied molecular orbital (LUMO) is entirely confined by the BiCl₃ entity as illustrated in the molecular orbital (MO) plots and displayed in Figure 2. Similar conclusions are obtained for compound 1-HMTT•BiBr₃ (1-A). Two major electronic transitions for the compound 0-HMTT exhibiting a large oscillator strength and assigned to S₀→S₄ and S₀→S₅ correspond essentially to HOMO-LUMO+1, HOMO-1-LUMO, and HOMO-1-LUMO+2, HOMO-LUMO and their energies are close to the experimental gap. These excitations are local type within 0-HMTT. The visibility of the S₀→S_{1,2,3} transitions seems highly improbable, since the oscillator strength is very weak. However, for 1-HMTT•BiCl₃ (1-A), the S₀→S₁ transition which correspond to HOMO-LUMO excitation, is pure charge transfer type.

Table 3. TDDFT calculation of excitation energies (E) and oscillator strengths (f) of the lowest excited singlet-singlet states

0-HMTT ^[a]			1-HMTT•BiCl ₃ (1-A) ^[a]		
TD-DFT state	E[ev]	f	TD-DFT state	E[ev]	f
S ₀	2.80	0.000007	S ₀	1.88	0.00592
S ₁	2.87	0.000266	S ₁	2.03	0.09055
S ₂	2.90	0.002620	S ₂	2.24	0.02133
S ₃	2.97	0.001608	S ₃	2.38	0.02888
S ₄	3.19	0.286500	S ₄	2.46	0.00040
S ₅	3.21	0.294900	S ₅	2.52	0.00120
S ₆	3.45	0.076080	S ₆	2.56	0.09946
S ₇	3.47	0.031130	S ₇	2.62	0.01436
S ₈	3.48	0.007941	S ₈	2.64	0.01972
S ₉	3.49	0.120800	S ₉	2.65	0.02037

a: The energy gaps were calculated using the DFT-BP functional at non relativistic level

The frontier orbitals⁴⁰ of the studied compounds, calculated at the GGA-LB94^{41,42}/TZP and relativistic level of theory are shown in Figure 2. The HOMO's show contributions exclusively from the organic ligands in almost constant percentage and are generally of bonding character, while the LUMO's are most of antibonding character and essentially delocalized over the inorganic chain. It is interesting to notice that the frontier orbitals of compound 1-HMTT•BiCl₃ and 2-HMTT•BiBr₃ are quite the same, producing a similar band gap, 1.82 and 1.75 respectively and similar electronic transitions. The interactions between orbitals of Bi and S atoms are of antibonding character, they increase the band gap value whereas major interactions between Bi and Br atoms of bonding character are getting shorter and decrease the band gap.

Figure 2. Contour plots of the frontier molecular orbitals of compounds 0-HMTT, 1-HMTT·BiCl₃ and 2-HMTT·BiBr₃

Conclusion

In this paper, the structural and band gap of a semiconductive network hybrid compounds were computationally explored. Their vertical singlet-singlet electronic excitations were calculated and characterized by employing TD-DFT methods. We have assessed the efficiency of different methods and functionals for calculating the optical band gaps. It was found that theoretical calculations at molecular level were adequate to provide a reliable accuracy for estimation of the band gap, notably when using rationalized functionals such

LB94 in the aim of reproducing the experimental values. The TD-DFT calculations point out that the most probable two transitions of HMTT belong to the local excitations, and the $S_0 \rightarrow S_1$ transitions for 1-HMTT•BiCl₃ and 2-HMTT•BiBr₃ belong to the charge transfert excitations. For the present structures, the LUMO, which consists essentially of Bi-X bonds of the inorganic networks, is the key issue in determining the band gap, and the variations of the frontier orbital energies resulting in reduced band gaps correlates well with the increase of dimensionality.

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