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Theoretical Investigation on Structures and Second-order Nonlinear Optical Properties of (Thiophene) Manganese Tricarbonyl Cations

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Abstract: The structures of several recently reported organometallic NLO chromophores, (thiophene) manganese tricarbonyl cations, were fully optimized at the DFT non-local (GGA) level. The calculated results show that the fragments 2-$SC_4H_3CH=CHC_6H_4$-R in these organometallic chromophores are not planar with dihedral angles of 42.2~59.8° between two aromatic rings, which are different from those of uncoordinated counterparts. Based on the DFT geometry optimization, the second-order nonlinear optical polarizabilities were calculated by using RPA method. The calculated results indicate that incorporation of $Mn(CO)_3^+$ unit with thiophene leads to a substantial increase in the second-order polarizability (*b*).

Keywords: Organometallic chromophore, nonlinear optical properties, DFT method, ZINDO, (thiophene) manganese tricarbonyl cation.

There is a growing interest in the study of organometallic nonlinear optical (NLO) materials because of their potential applications in optical data storage, telecommunications and optical processing[1]. Now extensive research efforts are devoted to disclosing the structure-properties relationships, which are the basis for designing and producing novel materials[2]. Theoretical computing can play an important role in understanding the origin of NLO response of such molecules.

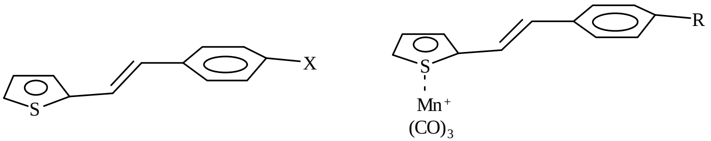
Incorporation of metal moieties with oligothiophene or thienyl entities in the conjugation chain has been used to improve the NLO properties[3,4]. In 1999, Lee[5] *et al.* synthesized a series of new organometallic NLO materials, (thiophene) manganese tricarbonyl cations, and determined their second-order polarizabilities by the HRS method. Their experimental results show that these organometallic compounds exhibit more optical nonlinearities than corresponding uncoordinated organic molecules. In order to explore the electron origin of the enhanced NLO response, in this letter, we carry out a density functional calculation on the structures of these organometallic chromophores. The optimized geometries have been found roughly in agreement with the X-ray experimental data. Basis on the optimized geometries, the second-order polarizabilities were calculated by using RPA[6,7] (Random Phase Approximation, equivalent to the CPHF method[8]) method distributed by ZINDO program package.

Results and Discussion

Optimization of the structures

The structures of the studied molecules are shown in **Figure 1**. Their geometries were fully optimized at the DFT non-local (GGA) level. In practical computation, VWN[9] functional was used for the local (LDA) calculation and the non-local gradient corrections to the exchange-correlation energy for the LDA energy were performed with Perdew 91[10,11] functional. For C, H, O and N orbitals we used double-ζ STO basis sets with 1s orbital kept frozen. For S orbitals we used double-ζ STO basis sets extended with a polarzation function and 2p orbitals kept frozen. For Mn orbitals we used triple-ζ STO basis sets extended with a polarzation function and 2p orbitals kept frozen. The calculations reported in this letter are based on the ADF (Amsterdam Density Functional) program package.

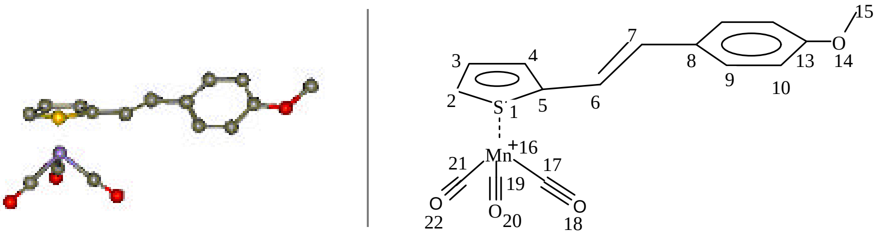
Figure 1 The structures of the studied chromophores



R = CH_3O, CH_3, H, NO_2
1 2 3 4

R = CH_3O, CH_3, H, NO_2
5 6 7 8

Figure 2 The atom serial number and optimized geometry of chromophore **5**

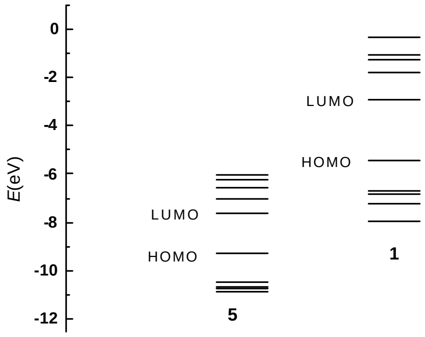


The calculated results on uncoordinated chromophores **1~4** indicate that the thiophene ring, bridging ethylene and benzene ring are coplanar. But for organometallic chromophores **5~8**, the fragments $2\text{–}SC_4H_3CH{=}CHC_6H_4\text{–}R$ are not planar with dihedral angles of 42~60° between two aromatic rings. **Figure 2** shows the optimized structure of chromophores **5**. The dihedral angle between thiophene and benzene rings in chromophore **5** is 42.2°, which does not agree with the crystal structural data (5.9°)[5]. The great difference was possibly ascribed to the intense π-π interaction between molecules in crystal. X-ray structural measurement of chromophore **5** confirmed that the two molecules A and B are π-stacked. The thiophene ring of A is roughly parallel to the arene ring of B with a distance of 3.60 Å between the centroids of the two rings[5]. But in a single molecule, there is no such π-π interaction and each fragment is "free", so the calculated dihedral angle between the two aromatic rings becomes large.

Electron structures

Figure 3 shows the frontier orbital energies of chromophores **1** and **5**. We can see that the introduction of $Mn(CO)_3^+$ moiety leads to a substantial decrease in the energies difference between the highest occupied orbital and the lowest unoccupied orbital. In addition, we have calculated the net charge on each fragment of chromophores **1** and **5~8**. For chromophores **5~8**, the intramolecular electron transfer is strong. The unit positive charge was distributed in thiophene ring, benzene ring and $Mn(CO)_3^+$ fragment, respectively, which indicates that the unit positive charge centered originally in $Mn(CO)_3^+$ moiety transfers partly to thiophene and benzene rings. And the extent of electron transfer depends on the electron-donating power of the substituent appended to the arene ring. The stronger the electron-donating power, the larger the extent of the electron transfer and the less the positive charge distributed to $Mn(CO)_3^+$.

Figure 3 The frontier orbital energies of chromophores **1** and **5**



Second-order polarizabilities

Our effort is to investigate the influence on second-order polarizabilities of incorporation of $Mn(CO)_3^+$ with thiophene and the structure-activity relationship but not to calculate the absolute values of hyperpolarizabilities, so, in this letter, we used semiempirical ZINDO-PRA method to calculate the second-order polarizabilities b_0 and b_m ($\omega = 0.65$ or 1.17 eV). The calculated results are shown in **Table 1**.

Table 1 shows that the second-order polarizabilities of chromophores **1~3** are very little but those of **5~7** are relatively large, which indicates that the introduction of $Mn(CO)_3^+$ fragment enhances strongly the optical nonlinearity. It is ascribed to the strong nonbond interaction between thiophene and $Mn(CO)_3^+$ moiety. Incorporation of $Mn(CO)_3^+$ moiety with thiophene increases the intramolecular electron transfer motion of the NLO chromophore. In these organometallic chromophores $Mn(CO)_3^+$ fragment functions as an electron-withdrawing group. Thus, chromophores **5~7** can be taken as A-π-D type molecules. The hyperpolarizability (b_0 and b_m) values of chromophores **5~7** decrease in the order **5** > **6** > **7**, similar to the electron-donating power of the substituent (MeO > CH_3 > H) appended to arene. But when $Mn(CO)_3^+$ coordinate to chromophore **4**, the hyperpolarizability b_0 and b_m values of corresponding complex decease substantially (see **Table 1**).

For comparison, **Table 1** also shows some experimentally b_0 and b_m data measured by the HRS method. One can see from **Table 1** that our calculated results are quite different from Lee′s experimental ones. This possibly because the calculated results were obtained for an isolated molecule and did not include the effect of anion BF^-_4, and the experimental ones were measured in solvent and include the intermolecular interaction. On the other hand, the theoretical computing of hyperpolarizability b is based on the optimized geometries, which are different from X-ray crystal structures.

The results of this letter might be useful for optimizing nonlinear optical materials from the viewpoint of molecular structures.

Table 1 The second-order polarizabilities b_0 and b_m (10^{-30}esu)

chromophore	b_0	b_m (0.65 eV)	b_m (1.17 eV)	$b^a_{m,\,exp}$(1.17 eV)
1	1.16	1.54	3.37	
2	0.20	0.18	0.06	
3	0.17	0.15	0.01	
4	21.0	27.8	64.5	326
5	24.7	35.6	127.5	252
6	21.3	29.1	75.9	355
7	14.3	19.0	43.2	413
8	10.8	14.0	29.7	613

[a] Experimental b_m values measured by HRS method from reference 5.

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