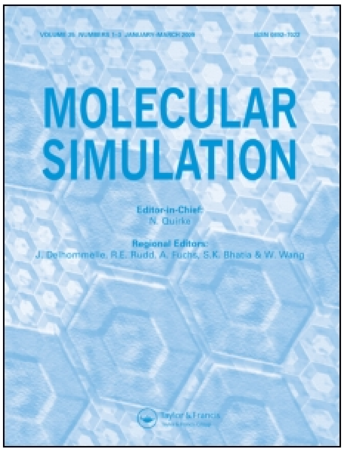

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A Hybrid DFT Study on the Mechanism of the Electron Conductivity of Molecular Devices Composed of Metal and Carbonyl Compounds

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A Hybrid DFT Study on the Mechanism of the Electron Conductivity of Molecular Devices Composed of Metal and Carbonyl Compounds

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Density functional theory (DFT) calculation at the B3LYP/6-311++G(d,p) level has been applied to one of the high-performance molecular devices, magnesium–naphthalene tetracarboxylic dianhydlide (NTCDA) complex expressed by Mg_4NTCDA. The electronic state of the complex at the ground state is consisted of a slight ion-pair state expressed by $(Mg_4)^{\delta+}(NTCDA)^{\delta-}$. The magnitude of the charge transfer (CT) is estimated to be $\delta = 0.56e$. The first and second excitation energies of free NTCDA were calculated to be 3.40 and 3.42 eV, respectively. By the interaction of NTCDA with the Mg atom, a new energy band is generated at low energy region: the excitation energies of Mg_4NTCDA are calculated to be 0.17 and 1.37 eV, respectively. These bands are assigned to a CT band. The mechanism of the electron conductivity was discussed on the basis of theoretical results.

Keywords: Naphthalene tetracarboxylic dianhydlide; Density functional theory; Charge-transfer band; Perylenetetracarboxylic dianhydride

INTRODUCTION

Recently, molecular devices have widely used as semiconductor, electroluminescence (EL) and photoconductivity materials [1,2] In particular, metal–organic compounds have attracted considerable attention over the past decade in view of their potential applications in electronic and optelectronic devices [3–11].

1,4,5,8-naphthalene tetracarboxylic dianhydlide (NTCDA) is one of the high-performance molecular devices utilized as photo-current multiplications and organic semi-conductors (Scheme 1). It is known that electron conductivity increases significantly by doping of metal atoms. For example, electron conductivity of free NTCDA ($\sigma = 10^{-8}$ S/cm) is drastically changed to $\sigma = 10^{-5}$ S/cm (Mg) and $\sigma = 10^{-2}$ S/cm (In) when doped by magnesium and indium atoms, respectively, indicating that the electron conductivity increases about 3–5 orders of magnitude by doping of metal atoms [4]. This increase is remarkably large for organic semiconductors. Although this is an interesting point in NTCDA, the mechanism of the electron conductivity in NTCDA–metal system is not clearly understood.

In previous works [12–16], we investigated the structures and electronic states of the complex of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) with In atoms, and suggested that the In atom can bind strongly to the carbonyl group of PTCDA [12]. The binding energy is calculated to be 178 kJ/mol for each atom in In_4PTCDA. This energy is strong and is almost equivalent to a covalent bond. Also, we investigated mechanism of electron and hole conductivities in molecular devices, such as poly-vinylbiphenyl (PVB) [13] and poly silanes [14,15], by means of *ab initio* DFT and *ab initio* molecular dynamics (MD) methods [16]. The origins of the conductivity in several organic and organometallic molecules have been elucidated on the basis of theoretical results.

In the present study, density functional theory (DFT) calculation was applied to the ground and low-lying excited states of the Mg–NTCDA complex

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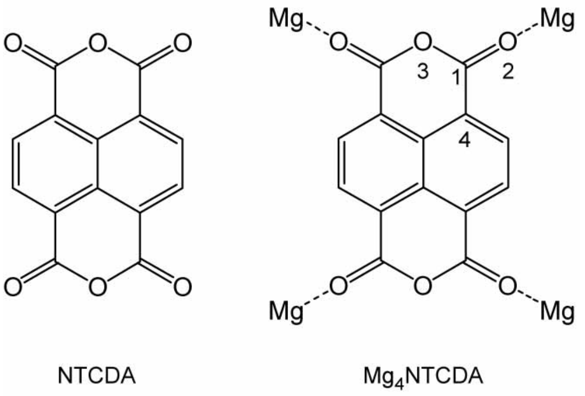

SCHEME 1

in order to elucidate the mechanism of electron conductivity. As be known, the electronic state at the excited state, especially the first excited state, strongly correlates to the electron conductivity in molecular devices. Therefore, the elucidation of the electronic structure for both ground and low-lying excited states is important in development for new molecular devices. In the present study, we extend previous our techniques [12–16] to the molecular device of Mg_4NTCDA.

COMPUTATIONAL METHODS

All hybrid DFT calculations were carried out using Gaussian 98 program package [17]. The geometries of NTCDA and its complexes with aluminum atom Mg_nNTCDA ($n = 0$ and 4) were fully optimized at the B3LYP/6-311++G(d,p) level of theory. Harmonic vibrational frequencies were calculated using the optimized structures. The excitation energies of Mg_nNTCDA ($n = 0–4$) were calculated by means of time-dependent DFT calculations at the B3LYP/6-311++G(d,p) level.

RESULTS

Structures of NTCDA and Mg_4–NTCDA Molecular Complex

The geometries of Mg_nNTCDA ($n = 0$ and 4) are fully optimized under a D_{2h} symmetry restriction. The optimized structure of Mg_4NTCDA is illustrated in Fig. 1. The selected geometrical parameters for $n = 0$ and 4 are given in Table I. The C=O bond lengths for $n = 0$ and 4 are calculated to be $r(C_1{=}O_2) = 1.1952$ and 1.2535 Å, respectively, indicating that the distance of the C=O carbonyl group of NTCDA is elongated by the interaction with the Mg atoms. This bond elongation is caused by the electron transfer from metal to the π* orbital of the C=O carbonyl group of NTCDA. For the molecular complex for $n = 4$, the Mg atom is located at the distance $R(Mg–O_2) = 2.8944$ Å and angle $< C_1–C_2–Mg$ is 115.0°.

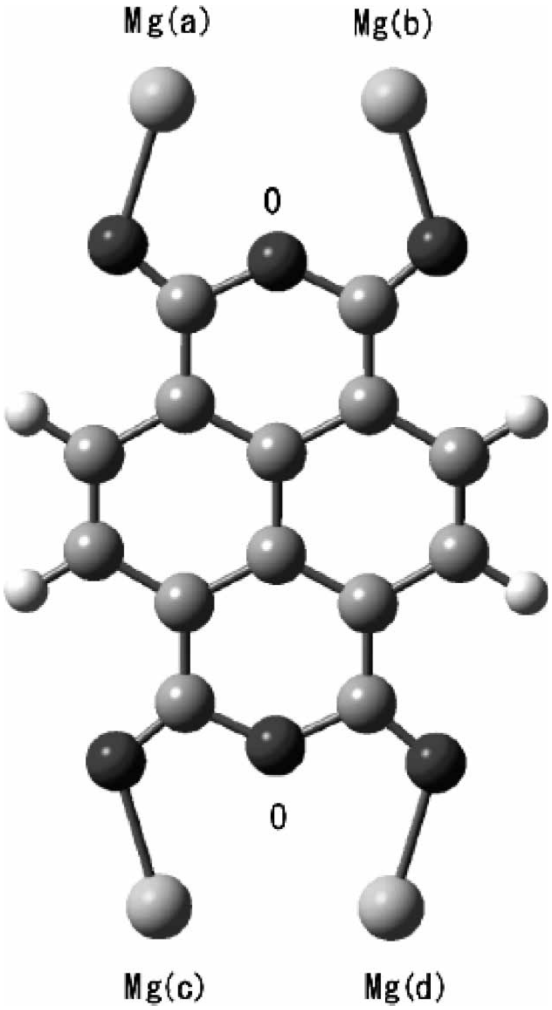

FIGURE 1 Optimized structure of Mg_4NTCDA calculated at the B3LYP/6-311++G(d,p) level.

Mulliken atomic charges of NTCDA and Mg_4NTCDA are given in Table II. In Mg_4NTCDA, the charge on the Mg atom is calculated to be +0.141, indicating that NTCDA has a negative charge (−0.56). These results suggest that the ground state of the complex is composed of charge separation (ion-pair) character.

For comparison, the structure and electronic states of the NTCDA anion were calculated with the same manner. The result is given in Tables I and II.

TABLE I Selected optimized geometrical parameters of NTCDA, NTCDA anion and Mg_4NTCDA, calculated at the B3LYP/6-311++G(d,p) level. Bond lengths and angles are in Å and in degrees, respectively

Molecule	*$R(C_1–O_2)$*	*$R(C_1–C_4)$*	*$R(Mg–O_2)$*	*$\angle C_1–C_2–Mg$*
NTCDA	1.1952	1.4833	–	–
NTCDA anion	1.2122	1.4538	–	–
Mg_4NTCDA	1.2535	1.4072	2.8944	115.0

TABLE II Mulliken atomic charges of C═O carbonyl and Mg atom of NTCDA, NTCDA anion and Mg_4NTCDA, calculated at the B3LYP/6-311++G(d,p) level

Molecule	C_1	O_2	*Mg*
NTCDA	0.085	− 0.208	–
NTCDA anion	0.065	− 0.309	–
Mg_4NTCDA	− 0.108	− 0.152	0.141

The C═O bond length of the NTCDA anion is calculated to be 1.2122 Å. This bond length is close to that of Mg_4NTCDA. The result supports the fact that the elongation of the C═O bond length is caused by the electron transfer from the metal to the π^* orbital of the C═O carbonyl in NTCDA.

Binding Energies of Mg to NTCDA

The geometry optimization shows that Mg can bind to NTCDA, as mentioned in previous section. The binding energies calculated are summarized in Table III. For $n = 4$, total binding energy (summation of four magnesium atoms) and binding energy of one magnesium atom are calculated to be 50.0 and 12.5 kcal/mol, respectively. The binding energy decreases to 9.90 kcal/mol for $n = 3$. These results suggest that the interaction between Mg and NTCDA is weaker than that of In–PTCDA system [12].

Excitation Energies of NTCDA and Mg_nNTCDA ($n = 4$)

To elucidate the origin of the electron conductivity in Mg_4NTCDA, the electronic structures of the excited states are determined by means of TD-DFT method. The excitation energies of free NTCDA and Mg_4 NTCDA are calculated, and the results are given in Fig. 2. The first and second excited states of NTCDA are constructed of $^1B_{1u}$ and $^1B_{2g}$ states, respectively. The excitation energies for the first and second absorption bands are calculated to be 3.40 and 3.78 eV, respectively. The electronic transition from the ground to first excited states, $^1Ag \rightarrow {}^1B_{1u}$, is “symmetry allowed” with a large transition moment ($f = 0.257$). The first excitation energy of NTCDA calculated is in reasonably agreement with the experimental value (3.20 eV) [4]. The agreement implies that TD-DFT calculation at the B3LYP/6-311++G(d,p) level would give a reasonable feature for the excitation energy and electronic structure of the excited states in the NTCDA system.

TABLE III Total energies (in a.u) and binding energies (ΔE_{bind}) of Mg to NTCDA calculated at the B3LYP/6-311++G(d,p) level. The binding energies per Mg atom are given in parentheses

Mg atom	*Binding site*	ΔE_{bind}/*kcal mol*$^{-1}$
$n = 1$	(a)	− 172.7 (− 172.7)
$n = 3$	(a,b,c)	+29.7 (+9.90)
$n = 4$	(a,b,c,d)	+49.96 (+12.5)

For the complex with $n = 4$, Mg_4NTCDA, the excitation energies for low-lying excited states are calculated to be 0.17, 1.37, 1.46, 1.51, and 1.73 eV. The lowest symmetry-allowed electronic transition is appearing at 0.17 eV whose oscillator strength is 0.023.

To assign the absorption band appearing at 0.17 eV, weight of the reference function is analyzed in detail. The TD-DFT calculation indicates that the main configuration is expressed by a transition HOMO → LUMO + 1, and its weight of the reference function is 0.64, where HOMO and LUMO mean highest occupied and lowest unoccupied molecular orbitals, respectively. The HOMO of the complex is mainly composed of HOMO of free-NTCDA and π-orbital of the Mg atoms, indicating that the electron of Mg is slightly diffused into the HOMO of free-NTCDA. Hence the Mg atom has a slight positive charge. On the other hand, the orbital is localized on the Mg atom in LUMO + 1. These results suggest that the “symmetry allowed” electronic transition is attributed to a charge transfer (CT) band between Mg and carbonyl group.

Thus, it can be summarized that band structure of NTCDA is significantly changed by the interaction with magnesium atoms. The new energy band is appeared at very low energy region below 0.3 eV.

Harmonic Vibrational Frequency

All vibrational frequencies for free NTCDA and Mg_4NTCDA are illustrated in Fig. 3. The frequencies are widely distributed in the range up to 3200 cm^{-1}. The higher two frequencies (3211 and 3200 cm^{-1}: each mode doubly degenerates) are assigned to C–H stretching modes of the benzene rings of NTCDA. The frequencies in middle region (1000–2000 cm^{-1}) are corresponding to C–C or C═O stretching modes. The peaks with large intensities are assigned to be the C═O stretching modes of NTCDA. For example, the C═O stretching modes of free NTCDA are calculated to be 1846 (a_g), 1838 (b_{1u}), 1809 (b_{3g}) and 1809 cm^{-1} (b_{2u}). These frequencies are red-shifted by the interaction with the Mg atom, while the intensities of IR bands decrease. The frequencies for the C═O stretching modes of Mg_4NTCDA are calculated to be 1707 (a_g), 1635 (b_{1u}), 1537 (b_{3g}) and 1517 cm^{-1} (b_{2u}). This red-shift is caused by the change of the bonding nature of the C═O carbonyl by the interaction with Mg atom: the C═O double bond is changed to single bond-like.

DISCUSSION

Summary of the Present Study

In the present study, the structure and electronic states of the Mg_4NTCDA complex were calculated at

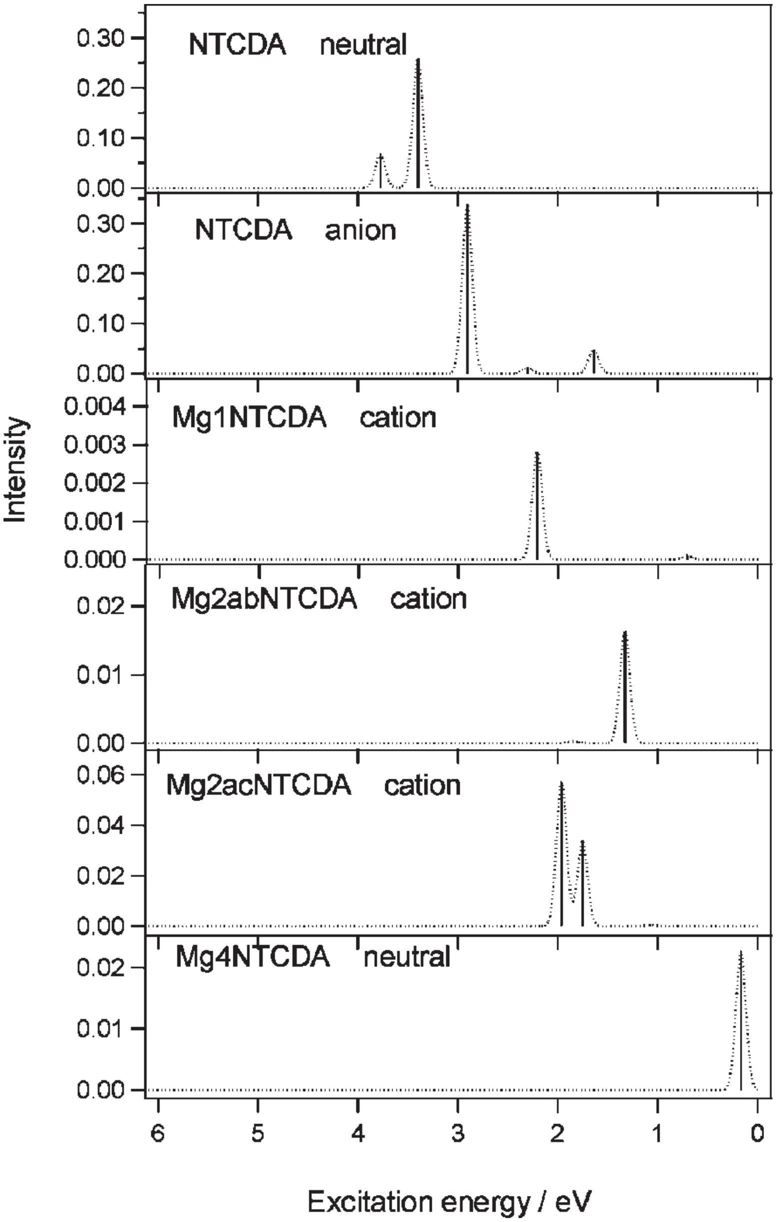

FIGURE 2 Simulated absorption spectra of Mg_4NTCDA at the B3LYP/6-311++G(d,p) level. Notation (*m*,*n*) means the position of the Mg atom around NTCDA (see, Scheme 1). Relative oscillator strengths are in arbitrary unit.

the B3LYP/6-311++G(d,p) level. The calculations showed that the ground state of the complex is expressed by $(Mg_4)^{\delta+}(NTCDA)^{\delta-}$. The NTCDA moiety has a negative charge ($\delta^- = -0.56$). Thus, solid of NTCDA behaves as *n*-type semi-conductor. This feature is the same as previous experiment [4].

By the electronic excitation of Mg_4NTCDA, the electron is transferred from NTCDA to the magnesium atoms, which is schematically expressed by

$$(Mg_4)^{\delta+}(NTCDA)^{\delta-} + h\nu \rightarrow (Mg_4)(NTCDA).$$

The present calculations predict that the new band appears at near IR region. Also, it is found that the C=O stretching mode of NTCDA is red-shifted.

Doping Effects on the Electronic States

As mentioned in the result section, the electronic states of NTCDA are significantly changed by the interaction with magnesium atoms. And then, new energy level is appeared as low-lying electronic states. When the complexes are aggregated as amorphous solid or solid film, this new electronic state contributes the electron conductivity because the energy level of the excited state in the complex is significantly low.

Thus, the present calculations strongly indicate that the low-lying energy state is appeared as a new energy band in solid film. NTCDA becomes negative after the interaction with Mg in the solid film.

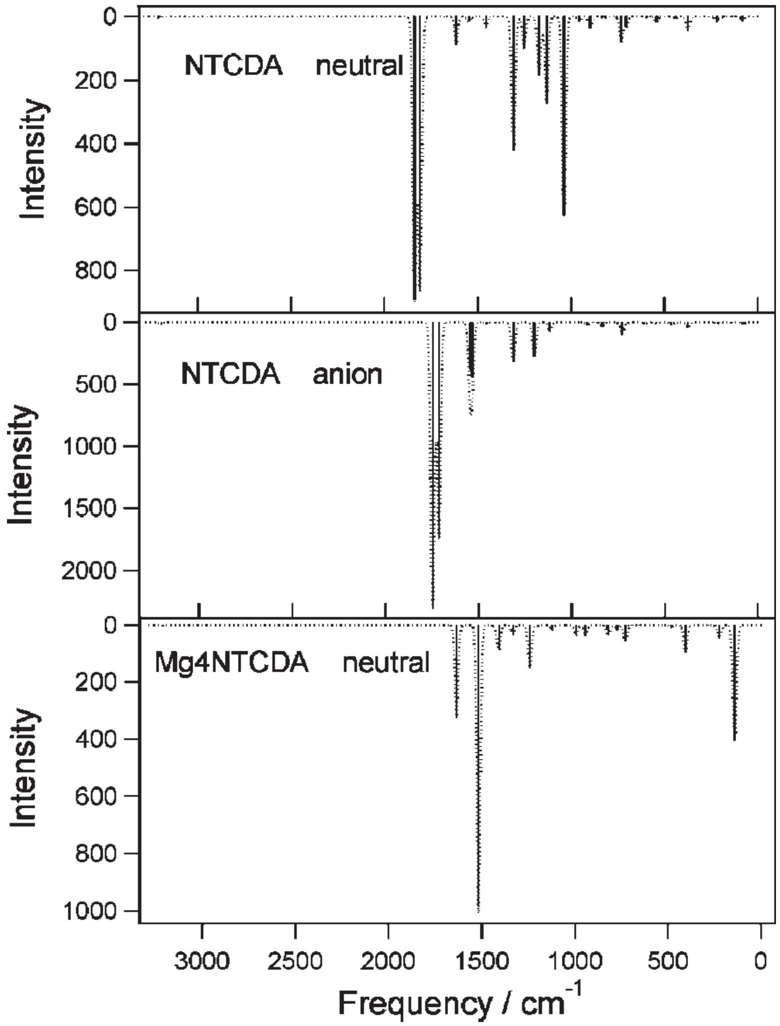

FIGURE 3 Harmonic vibrational frequencies of free NTCDA (upper panel), NTCDA anion (middle) and Mg_4NTCDA (lower panel). Relative intensity of IR band is in arbitrary unit.

Therefore, the excess electron on NTCDA can easily move along the molecular sheets composed of NTCDA molecules. This is the origin of the electron conductivity in the molecular device of the Mg–NTCDA system

Comparison with Previous Studies

The metal–organic complexes of 3,4,9,10-PTCDA, which is a very similar molecule to NTCDA, have been investigated from theoretical and experimental points of view [4–11]. In a previous paper [12], we calculated energy bands of $(In)_n$(PTCDA) complexes ($n = 1–4$) using B3LYP and configuration interaction (CI) methods with LANL2DZ base and suggested that the ground state is composed of ion-pair state expressed by $(In_4)^{\delta+}(PTCDA)^{\delta-}$. On the basis of MO characters, Kera *et al.* suggested that the new state of In_4PTCDA [10] is composed of a π-state containing In(5pz) orbital. The present calculations for Mg_4 NTCDA show the similar tendency for the electronic states at the ground state. However, the magnitude of the CT from metal to the organic molecule in Mg_4NTCDA is smaller than that of In_4PTCDA.

In order to clarify the properties of organic/metal interface, Nakayama *et al.* investigated experimentally the electronic interaction between In and NTCDA using spectroscopic techniques [4]. The C═O and C–O stretching modes of NTCDA are measured to be 1770 and 1550 cm^{-1}, respectively. By the interaction with In atom, the C═O stretching mode is red-shifted to be 1517 cm^{-1}. The present calculations showed that the C═O stretching mode of NTCDA is red-shifted by the interaction of C═O carbonyl with the Mg atom.

An ion-pair state is usually appeared in the reaction of the carbonyl compounds with alkali–metal atoms (M═Na and K) [18–23]. For example, acetone–M and benzophenone–M complexes have been extensively investigated from theoretical and experimental points of view. From theoretical calculations, it was suggested that the ground state of C═O–M moiety is ion-pair state expressed by C═O$^{\delta-}$–M$^{\delta+}$. On the other hand, the first excited state is composed of van der Waals (vdW) interaction expressed by C═O·M. This feature is much similar to that of the present system. This would be nature of bonding between the carbonyl compounds and metal atoms.

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