DFT calculations for the high-temperature structure of \((\text{EDO-TTF})_2\text{PF}_6\): Identification of an electronic molecular dimer

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Abstract. Density-functional theory (DFT) calculations are performed based on the high-temperature structure of \((\text{EDO-TTF})_2\text{PF}_6\), a quasi-one-dimensional molecular compound that shows both thermal and photoinduced phase transitions. In this structure, the EDO-TTF molecules are one-dimensionally aligned, accompanied with weak dimerization. Contrary to a common sense, our DFT calculations reveal that the pair having a shorter mutual distance has a weaker intermolecular coupling than the pair with a longer one; the latter is appropriate to be called an electronic dimer. We also estimate the corresponding transfer energies and discuss their relevance to spin correlations and optical excitations.

1. Introduction

Among many molecular solid compounds, \((\text{EDO-TTF})_2\text{PF}_6\) is a unique material that shows \((0110)\) type of charge ordering in the low-temperature phase [1]. Here, \(0\) or \(1\) means the number of holes residing at each EDO-TTF molecule of its tetramer structure. This type of charge ordering makes striking contrast to another type of charge ordering, namely, \((0101)\) type, suggesting a mechanism not originating from nearest-neighbor Coulombic repulsion [2]. This charge ordering of \((\text{EDO-TTF})_2\text{PF}_6\) can be melted by light irradiation, giving a good example of photoinduced phase transition (PIPT) [3, 4]. In the previous paper, we have proposed a new mechanism for the \((0110)\) type of charge ordering, which is the potential bias due to long-range Coulombic potentials from surrounding molecules [5, 6]. Using this mechanism, we have succeeded in the quantitative reproductions of both the actual degree of charge ordering and the optical absorption spectrum of \((\text{EDO-TTF})_2\text{PF}_6\), and further discussed its possible role in the PIPT.

To understand the phase transitions in this compound, it is necessary to reveal the nature of its high-temperature phase. As is already known, this is a metallic phase in which the aforementioned tetramer structure disappears [1]. This might suggest that this is a simple metal that develops after the structural change. However, its absorption spectrum has a feature in the mid-IR region [7], which seems to mean the importance of electron correlation even in the...
metallic phase. Based on this prospect, we here investigate electronic properties of its most basic units, namely, the two types of EDO-TTF pairs aligning alternatively along the chain, using density-functional theory (DFT) calculations. The purposes of this investigation are, firstly, the clear identification of a dimer based on electronic coupling and, secondly, the evaluations of the parameter values required for a further modeling.

2. Results of calculations

Figure 1 shows the chain structure in the high-temperature phase of (EDO-TTF)$_2$PF$_6$ determined by X-ray measurement. All the molecules are structurally equivalent, although there are two kinds of relationship between the nearest neighbor molecules. We call them Pair A and Pair B as shown in Figure 1. When we look at the bending of the molecules, we can easily distinguish Pair A and Pair B. In other words, the chain structure is accompanied with weak dimerization. From a structural viewpoint, Pair A is regarded as a dimer and Pair B is as an interdimer, since the distances between the sulfur (S) atoms are shorter in Pair A than in Pair B by 0.04∼0.05Å. We examine whether Pair A has an stronger electronic coupling between the molecules than Pair B as expected from a structural viewpoint. For this purpose, we analyze the two types of isolated pairs and perform DFT calculations with the B3LYP functional using the Gaussian 03 package [8]. As a result, we obtain level diagrams as shown in the right part of Figure 2. Here, the pairs with (+2)$|e|$ charge are taken as examples. Among these levels, the HOMO and LUMO ones originate from the same molecular orbital and are split due to dimer hybridization as shown in the left part.

![Figure 1. A segment of the EDO-TTF chain in the high-temperature structure.](image1)

![Figure 2. (Right) Level diagrams around the Fermi energy in the case of Pairs A and B. The levels specified as “HOMO” and “LUMO” originate from the same molecular orbital. (Left) Splitting of the above levels due to dimer hybridization.](image2)

While the magnitude of splitting depends on valency, it is larger in Pair B than in Pair A, in all the cases we examine. This indicates that larger electronic coupling in Pair B. We summarize the splitting for different kinds of valency in Table 1. This valency dependency of the splitting is not surprising, since the splitting, or the transfer energies between the molecules in other
Table 1. Degree of energy splittings in units of eV for various valencies which are specified in the parentheses. Note that the (+1) means the case with one spin-up electron at the upper level.

|       | ∆ (+0) | ∆ (+2) | (∆(+0)+∆(+2))/2 | ∆₁(+1) | ∆₂(+1) | (∆₁(+1) + ∆₂(+1))/2 |
|-------|--------|--------|------------------|--------|--------|----------------------|
| Pair A| 0.498  | 1.091  | 0.795            | 0.461  | 1.136  | 0.798                |
| Pair B| 0.584  | 1.167  | 0.875            | 0.567  | 1.202  | 0.884                |

Figure 3. Wave function profiles of the bonding (lower) levels in the pairs with the (+2) valency. The intermolecular overlap of the molecular orbitals is larger in Pair B, compared with that in Pair A.

Words, receives bond-charge contributions in exchange terms and this bond charge depends on the valency. We therefore perform suitable averagings as shown in the third and sixth columns of Table 1, keeping in mind that the pairs have the (+1) valency in the bulk system. Note that a (+1) pair is an open-shell system and that the spin symmetry is broken within the spin-polarized DFT method. We hence must average the splitting between the two spins in this case. We emphasize that the two ways of averaging give quantitatively almost the same result, validating our procedure.

To understand this unexpected result, we closely check the wave functions of the relevant levels. In Figure 3, we compare those for the bonding (lower) levels in the pairs with the (+2) valency and notice a stronger bonding in Pair B. Meanwhile, we recognize a larger degree of vertical misfit of π lobes in the S-S contacts of Pair A and conclude that this is the reason for the weakened bonding in the same pair. The feature of the stronger intermolecular coupling in Pair B can be seen also in the wave function profile of the anti-bonding (upper) levels.

3. Concluding remarks
The results in the previous section tell us that Pair B is appropriate to be called the electronic dimer, in contrast to the expectation from the crystal structure. Furthermore, we deduce the values of nearest-neighbor transfer-energies assuming that the splitting is equal to twice that energy. Defining $t_1$ and $t_2$ as those energies for Pairs A and B, respectively, we determine $t_1=0.40$ eV and $t_2=0.44$ eV. These values are consistent with the calculations of a cluster consisting of six dimers: The full band width of the cluster, 1.63 eV, is slightly smaller than the expected one, i.e., 2($t_1 + t_2$), because of an open boundary condition.

According to the result based on a one-dimensional Hubbard model [9], such alternating transfers will lead to mid-IR absorptions. Actually, a strong mid-IR absorption band above the critical temperature is observed in this material [7]. Since the existence of such absorption is a feature of strong mutual electron repulsion particularly in the same molecule, we claim that this material also has such nature. Furthermore, we expect spin correlations of a dimer-
Mott type [2], that is, the situation where one spin residing in each dimer is coupled with the neighboring spins antiferromagnetically. We hope that these findings and the prospect will lead to better understanding of this material, including the nature and the mechanism of the photoinduced phase transition.

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