Enhancement of electron correlation due to the molecular dimerization in organic superconductors $\beta$-(BDA-TTP)$_2X$ ($X$=I$_3$, SbF$_6$)

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We perform a first principles band calculation for quasi-two-dimensional organic superconductors $\beta$-(BDA-TTP)$_2$I$_3$ and $\beta$-(BDA-TTP)$_2$SbF$_6$. The first principles band structures between the I$_3$ and SbF$_6$ salts are apparently different. We construct a tight-binding model for each material which accurately reproduces the first principles band structure. The obtained transfer energies give the differences such as (i) larger dimerization in the I$_3$ salt than the SbF$_6$ salt, and (ii) different signs and directions of the inter-stacking transfer energies. To decompose the origin of the difference into the dimerization and the inter-stacking transfer energies, we adopt a simplified model by eliminating the dimerization effect and extract the difference caused by the inter-stacking transfer energies. From the analysis using the simplified model, we find that the difference of the band structure comes mainly from the strength of dimerization. To compare the strength of the electron correlation having roots in the band structure, we calculate the physical properties originated from the effect of the electron correlation such as the spin susceptibility applying two particle self-consistent (TPSC) method. We find that the maximum value of the spin susceptibility of the I$_3$ salt is larger than that of the SbF$_6$ salt. Hypothetically decreasing the dimerization within the model of the I$_3$ salt, the spin susceptibility takes almost the same value as that of the SbF$_6$ salt for the same magnitude of the dimerization. We expect that the different ground state between the I$_3$ and SbF$_6$ salt mainly comes from the strength of the dimerization which is apparently masked in the band calculation along a particular $k$-path.

I. INTRODUCTION

There have been attempts to synthesize strongly correlated electron systems in organic conductors by applying chemical modification to stable metallic donor molecules. For example, there are ($S,S$)-DMBEDT-TTF and meso-DMBEDT-TTF, where two methyl groups are attached to BEDT-TTF, and they are pressure-induced superconductors. In the present article, we theoretically study superconductors based on BDA-TTP molecule, which is extended to six-membered-ring from five-membered-ring in the $\sigma$-bond framework of BDH-TTP molecule. The actual materials are $\beta$-(BDA-TTP)$_2$I$_3$ and $\beta$-(BDA-TTP)$_2$SbF$_6$, which will be abbreviated as I$_3$ and SbF$_6$ salts, respectively. In both materials, conductive layer is the BDA-TTP layer, and the anion layer separates the adjacent conductive layers as shown in Fig. 1 (a). Molecular configuration in the conductive layer is the $\beta$-type as shown in Fig. 1 (b). Both materials consist of the stacking structure of the BDA-TTP molecules. However, they are somewhat different in that the inter-stacking direction is slightly tilted in the I$_3$ salt, but almost side-by-side for the SbF$_6$ salt, which will be shown later.

The I$_3$ salt is an insulator at ambient pressure, and the superconductivity appears around 10 K under hydrostatic pressure of above 10 kbar. Recently, applying uniaxial strain along the $c$-axis has given higher $T_c$. Applying the uniaxial compression once increases the $T_c$ and takes a maximum before it decreases. It is considered that applying the pressure in the I$_3$ salt increases the overlap between the upper and lower bands, which gradually changes the character of the system from a strongly correlated half-filled system to a moderately correlated...
quarter filled system. The c-axis strain more efficiently increases the band-width of the overlap. As the electron correlation is reduced to some extent by pressure, the insulating nature of the material is lost, and superconductivity appears. Theoretically, Nonoyama et al. have studied the nature of the charge ordering state and the pairing mechanisms in the model of the I$_3$ salt derived from the extended Hückel band structure.

The SbF$_6$ salt exhibits superconductivity at 7.5 K at ambient pressure. As for the SbF$_6$ salt, there have been some controversies regarding both the anisotropy of the Fermi surface and the directions of the nodes in the superconducting gap. In our previous study for the $\beta$-(BDA-TTP)$_2$MF$_6$ (M=As, Sb and Ta), we have obtained the band structure from the first principles band calculation, and suggested the origin of the differences from the extended Hückel band structure. Also, there have been some studies on pairing mechanisms mediated by spin and/or charge fluctuations in the model of $\beta$-(BDA-TTP)$_2$X. As for the MF$_6$ (M=As, Sb) salts, adopting models derived from the extended Hückel calculation, Nonoyama et al. have applied random phase approximation (RPA) to the two band model, while Suzuki et al. have applied the fluctuation exchange (FLEX) approximation to the original two-band model and the single-band dimer model. Recently, we have constructed the tight-binding model derived from the first principles band calculation, studied the pairing symmetry of the gap function within the spin fluctuation mediated pairing.

In the present study, given the difference in the ground state between the I$_3$ salt and the SbF$_6$ salt, we focus on the difference in the electronic structure between the two salts. In fact, despite the similar lattice structure, the band structure of the I$_3$ salt and that of the SbF$_6$ salt obtained by the extended Hückel method are known to be very different. Here, we perform the first principles band calculation for $\beta$-(BDA-TTP)$_2$I$_3$ and construct an effective tight-binding model that reproduces the first principles band structure. We compare the band structure of the I$_3$ salt to that of the SbF$_6$ salt obtained in our previous study, and pin down the origin of the apparently large differences. In particular, we study the relation between the strength of the electron correlation and the molecular dimerization. We consider the Hubbard model by introducing repulsive interaction between the electrons on the same BDA-TTP molecule. Then, we study the effect of the electron correlation by applying the two particle self-consistent (TPSC) method, and present quantities such as the spin susceptibility against the temperature and dimerization strength, which reflect physical properties originating from the electron correlation. We conclude that the ground state of the I$_3$ salt differs from that of the SbF$_6$ salt due to the strength of the dimerization.

II. METHOD

A. first principles band calculation and model construction

We perform first principles band calculation using all-electron full potential linearized augmented plane-wave (LAPW) + local orbitals (lo) method within the framework of WIEN2k. This implements the density functional theory (DFT) with different possible approximation for the exchange correlation potentials. The exchange correlation potential is calculated using the generalized gradient approximation (GGA).

The single-particle wave functions in the interstitial region are expanded by plane waves with a cut-off of $R_{MT}K_{\text{max}} = 3.0$ due to the presence of the hydrogen atom, where $R_{MT}$ denotes the smallest muffin-tin radius and $K_{\text{max}}$ is the maximum value of $K$ vector in the plane wave expansion. In the I$_3$ salt, the muffin-tin radii are assumed to be 2.50, 1.62, 1.15, and 0.62 atomic units (a.u.) for I, S, C, and H, respectively. $K_{\text{max}}$ is taken as 4.8, and the plane wave cutoff energy is 318.6 eV. In the SbF$_6$ salt, the muffin-tin radii are assumed to be 1.74, 1.74, 1.62, 0.83, and 0.45 a.u. for Sb, F, S, C, and H, respectively. $K_{\text{max}}$ is taken as 6.7, and the plane wave cutoff energy is 604.7 eV. Calculations were performed using $6 \times 3 \times 9$ $k$-points for the I$_3$ salt and $7 \times 3 \times 9$ $k$-points for the SbF$_6$ salt in the irreducible Brillouin zone. We adopt the lattice structure determined experimentally for each material, and we do not relax the atomic positions in the calculation.

Having done the first principles band calculation, we then construct a tight-binding model which accurately reproduces the first principles band structure. From the lattice structure of the two materials, we regard one molecule as a site and consider a two-band (two sites per unit cell) tight-binding model to fit the first principles band structure. The tight-binding Hamiltonian, $H_0$, is written in the form

$$H_0 = \sum_{\langle i \alpha : j \beta \rangle, \sigma} \left\{ t_{i \alpha \beta} c^\dagger_{i \alpha \sigma} c_{j \beta \sigma} + \text{H.c.} \right\},$$

(1)

where $i$ and $j$ are unit cell indices, $\alpha$ and $\beta$ specifies the sites in a unit cell, $c^\dagger_{i \alpha \sigma}$ ($c_{i \alpha \sigma}$) is a creation (annihilation) operator with spin $\sigma$ at site $i$ in the $i$-th unit cell, $t_{i \alpha \beta}$ is the electron transfer energy between $(i, \alpha)$ site and $(j, \beta)$ site, and $\langle i \alpha : j \beta \rangle$ represents the summation over the bonds corresponding to the transfer.

By Fourier transformation, eq. (1) is rewritten as

$$H_0 = \sum_{\mathbf{k}, \sigma, \alpha, \beta} \varepsilon_{\alpha \beta}(\mathbf{k}) c^\dagger_{\mathbf{k} \alpha \sigma} c_{\mathbf{k} \beta \sigma},$$

(2)

where $\varepsilon_{\alpha \beta}(\mathbf{k})$ is the site-indexed kinetic energy represented in $\mathbf{k}$-space. The band dispersion is given by diagonalizing the matrix $\varepsilon_{\alpha \beta}(\mathbf{k})$,

$$\varepsilon_{\alpha \beta}(\mathbf{k}) = \sum_\gamma d_{\alpha \gamma}(\mathbf{k}) d^\dagger_{\beta \gamma}(\mathbf{k}) \xi_{\gamma}(\mathbf{k}),$$

(3)
Green’s function given as
\[ \xi_{\gamma}(k) \] gives the band dispersion of the \( \gamma \)-th band measured from the chemical potential, and \( d_{\alpha\gamma}(k) \) is the unitary matrix that gives the unitary transformation.

We adopt the two-band Hubbard model obtained by adding the on-site (intra-molecule) repulsive interaction to the tight-binding model derived from the fitting of the first principles band structure. The Hubbard Hamiltonian, \( H \), is
\[ H = H_0 + \sum_{i\alpha} U_0 n_{i\alpha\uparrow} n_{i\alpha\downarrow} \] (4)
where \( U_0 \) is the bare on-site interaction and \( n_{i\alpha\sigma} \) is the number operator of the electron on the \( \alpha \)-site in the \( i \)-th unit cell. Since both salts are configured as a form of \( D_2X \) where \( D \) is the donor molecule and \( X^{-1} \) is the anion, the band-filling is 1/4-filled in the hole representation (3/4-filled in the electron representation).

B. Two particle self consistent method

To deal with the electron correlation effect arising from the on-site repulsion, we apply TPSC to the multi-site Hubbard model given by eq. (4) as follows. The bare susceptibility in the site-representation is given by
\[ \chi_{\alpha\beta}^0(q) = -\frac{T}{N_c} \sum_k G_{\alpha\beta}^0(k+q) G_{\beta\alpha}^0(k), \] (5)
where \( T \) and \( N_c \) are the temperature and the total number of unit cells, respectively, and \( G_{\alpha\beta}^0(k) \) is the bare Green’s function given as
\[ G_{\alpha\beta}^0(k) = \sum_{\gamma} d_{\alpha\gamma}(k) d_{\beta\gamma}^*(k) \frac{1}{i\epsilon_n - \xi_{\gamma}(k)} \] (6)
Here, we introduce the abbreviations \( k = (k, i\epsilon_n) \) and \( q = (q, i\omega_m) \) for the fermionic and bosonic Matsubara frequencies. The indices \( \alpha\beta \) means \( (\alpha \beta) \)-element of the matrix such as \( \chi_{\alpha\beta}(q) \).

TPSC has been applied to single-site systems,23,24 multi-site systems,25 and multi-orbital systems.26 By applying TPSC, we can consider the local vertex correction in both spin and charge channels within a self-consistent procedure. In the TPSC, using the bare susceptibility given by eq. (6), the spin and charge susceptibilities are obtained as
\[ \tilde{\chi}^{sp}(q) = \left[ \hat{I} - \hat{\chi}^0(q) \hat{U}^{sp} \right]^{-1} \hat{\chi}^0(q) \],
\[ \tilde{\chi}^{ch}(q) = \left[ \hat{I} + \hat{\chi}^0(q) \hat{U}^{ch} \right]^{-1} \hat{\chi}^0(q) \],
where \( \hat{U}^{sp} \) (\( \hat{U}^{ch} \)) is the local spin (charge) vertex and \( \hat{I} \) is the unit matrix. The local vertices are determined by satisfying two sum rules for the local moment such as
\[ \frac{2T}{N_c} \sum_q \chi_{\alpha\alpha}^{sp}(q) = n_{\alpha} - 2 \langle n_{\alpha\uparrow} n_{\alpha\downarrow} \rangle, \] (9)
\[ \frac{2T}{N_c} \sum_q \chi_{\alpha\alpha}^{ch}(q) = n_{\alpha} + 2 \langle n_{\alpha\uparrow} n_{\alpha\downarrow} \rangle - n_{\alpha}^2, \] (10)
where \( n_{\alpha} \) is the particle number at the site \( \alpha \). We have used the relations \( n_{\alpha\uparrow} = n_{\alpha\downarrow} = n/2 \) and \( n_{\alpha\sigma} = n_{\alpha\sigma}^2 \) from the Pauli principles.

The local spin vertex \( \hat{U}^{sp} \) is related with the double occupancy \( \langle n_{\alpha\uparrow} n_{\alpha\downarrow} \rangle \) by the following ansatz
\[ \hat{U}_{\alpha\alpha}^{sp} = \frac{n_{\alpha\uparrow} n_{\alpha\downarrow}}{\langle n_{\alpha\uparrow} \rangle \langle n_{\alpha\downarrow} \rangle} U_{\alpha\alpha}^0, \] (11)
where \( U_{\alpha\alpha}^0 \) is the \( (\alpha \alpha) \)-element of the on-site interaction matrix \( U_0 \). Equation (11) breaks the particle-hole symmetry and should be used for \( n_{\alpha} \leq 1 \). When \( n_{\alpha} > 1 \), that can be applied through the particle-hole transformation, then the double occupancy \( D_{\alpha} = \langle n_{\alpha\uparrow} n_{\alpha\downarrow} \rangle \) is given by
\[ D_{\alpha} = \frac{U_{\alpha\alpha}^0 n_{\alpha}^2}{4} + \left( 1 - \frac{U_{\alpha\alpha}^0}{U_{\alpha\alpha}^0} \right) (n_{\alpha} - 1) \theta (n_{\alpha} - 1), \] (12)
where \( \theta (x) \) is Heaviside step function. Equations (7)-(11) give a set of the self-consistent equations for the TPSC method. Obtaining the \( \hat{U}_{sp} \) and \( \hat{U}_{ch} \), the interaction for the self-energy is obtained as
\[ \hat{\Sigma}^\Sigma(q) = \frac{1}{2} \left[ \hat{U}_{sp}^{ch} \hat{\chi}^{sp}(q) \hat{U}_{sp}^0 + \hat{U}_{ch}^{ch} \hat{\chi}^{ch}(q) \hat{U}_{ch}^0 \right]. \] (13)
Using the eq. (13), the self-energy is given by
\[ \hat{\Sigma}_{\alpha\beta}(k) = -\frac{T}{N_c} \sum_q V_{\alpha\beta}^0(q) G_{\alpha\beta}(k-q), \] (14)
and the dressed Green’s function is obtained as
\[ \hat{G}(k) = \hat{G}^0(k) + \hat{G}^0(k) \hat{\Sigma}(k) \hat{G}(k). \] (15)
Since we need two sites per unit cell, \( \hat{U}_{sp}^0, \hat{U}_{sp}^{ch}, \hat{U}_{ch}^{ch} \), \( \hat{\chi}^{sp}(q) \), \( \hat{\chi}^{ch}(q) \), \( \chi^{\Sigma}(q) \), \( \hat{\Sigma}(k) \), \( \hat{G}^0(k) \) and \( \hat{G}(k) \) all become \( 2 \times 2 \) matrices. In the present study, the spin susceptibility is obtained as the larger eigenvalue of the \( 2 \times 2 \) spin susceptibility matrix. We consider not only the spin susceptibility, but also other physical values such as the local spin vertex and the double occupancy. In the present calculation, we take the system size as \( 64 \times 64 \) \( k \)-meshes and 16384 Matsubara frequencies.

III. RESULTS

A. first principles band calculation

Figures 2 (a) and (c) show the first principles band structures for the I\(_3\) and the SbF\(_6\) salts. For both materials, the experimental lattice structure at an ambient pressure and room temperature are used. In both of the materials, it can be seen that the highest-occupied molecular orbital (HOMO) is isolated from the lowest-unoccupied molecular orbital (LUMO). Considering this and also the number of donor molecules in a unit cell, we adopt the HOMO and HOMO–1 bands as the target bands to construct an effective tight-binding model.
Although the difference is only the anion, the band structures of the two materials are apparently very different. In order to reveal the origin of this difference in the band structure, in the following we focus on the following two differences of the two salts. One is the magnitude of the molecular dimerization, namely the dimerization of the donor molecule in the I$_3$ salt is larger than that in the SbF$_6$ salt resulting in a larger gap between HOMO and HOMO−1 in the former. The other is the anisotropy of the band structure, namely, there are two flat portions near the Fermi level around the Z and the X-points in the I$_3$ salt, while there is only one flat portion around the B-point in the SbF$_6$ salt.

Figure 2 (b) shows the Fermi surface of the first principles band calculation for the I$_3$ salt, where the high symmetry points in the Brillouin zone are presented only on the $k_Y(k_x) = 0$ plane. The Fermi surface of the I$_3$ salt is disconnected, namely quasi-one-dimensional, but it is actually close to two dimensional because a slight shift of the band structure around the Z-point would give a closed (i.e. 2D) Fermi surface. Figure 2 (d) shows the Fermi surface of the SbF$_6$ salt. The Fermi surface is cylindrical, reflecting the two-dimensionality of this salt as shown in our previous work.$^{15}$}

### B. Effective tight-binding model

Figure 3 shows the effective tight-binding model adopted to fit the first principles band. The nearest-neighbor transfers are shown in the left panel of Fig. 3, and in addition we also need to introduce the next-nearest-neighbor transfers shown in the right panel of Fig. 3 to reproduce the first principles band structure more accurately. Note that the stacking direction of the BDA-TTP molecules is taken in the $a$-direction$^{27}$. The band dispersions of the tight-binding model are shown as blue solid curves in Fig. 2 (a) for the I$_3$ salt and Fig. 2 (c) for the SbF$_6$ salt.

The transfer energies for the two salts are summarized in Table I. The bottom three lines represent the magnitude of the dimerization which is measured by the ratio $t_{p2}/t_{p1}$, and the transfer between the inter-stacking direction normalized by the average value of intra-stacking transfer energies, $(t_{q1}+t_{q2})/(t_{p1}+t_{p2})$ and $2t_c/(t_{p1}+t_{p2})$. From Table I it can be seen that there are two major differences between the two salts. One is the strength of the molecular dimerization, namely the dimerization in the I$_3$ salt is larger than that in the SbF$_6$ salt. Another difference is the transfers in the inter-stacking direction namely, the magnitudes as well as the sign of the inter-stacking transfers are different between the two salts, that is in $c(q)$-direction in the I$_3$ (SbF$_6$) salt.

To clarify the origin of the differences between the two salts, we consider the alignments of the donor molecules in the conducting $c$-$a$ plane for the two salts. The conducting $c$-$a$ plane for each salt is shown in Fig. 4. We find that the tilting angle of the donor molecules from the $c$-axis is different between the two salts. In the I$_3$ salts shown in Fig. 4 (a), the tilting angle is larger than that in the SbF$_6$ salts shown in Fig. 4 (b). The difference in the tilting angle gives rise to differences in both the magnitude and the sign of the main inter-stacking transfers, which is $t_c$ in the I$_3$ salt shown in the lower panel of Fig. 4 (a), while they are $t_{q1}$ and $t_{q2}$ in the SbF$_6$ salt shown in the lower panel of Fig. 4 (b).

Now, let us try to decompose these differences. We consider a case where we hypothetically eliminate the dimerization effect. Namely, we simplify the model by considering only the nearest neighbor transfer energies,
and replace the hopping in the $p$- and $q$-directions by taking their averages. The band structure of the simplified model is given by

$$
\varepsilon (\mathbf{k}) = 2t_c \cos (k_c) + 2t_p \cos (k_a) + 2t_q \cos (k_c + k_a/2)
$$

where the transfer energies are $t_p = -0.138$ eV, $t_q = 0.030$ eV, $t_c = 0.062$ eV for the I$_3$ salt, and $t_p = -0.140$ eV, $t_q = -0.063$ eV, $t_c = 0.007$ eV for the SbF$_6$ salt. Eliminating the dimerization effect enables us to take the unit cell reduced along the $a$-direction. By comparing the band structure of the simplified model, we can extract the difference caused by the inter-stacking transfer.

We compare the band structure of the two salts in the $(k_X, k_Y)$ plane, where $k_Y$ is taken in the molecular stacking direction and $k_X$ is taken in the direction of the main inter-stacking transfer, namely, $c$-direction in the I$_3$ salt (Fig. 4(a)) and $a/2 + c$-direction in the SbF$_6$ salt as seen in Fig. 4(b). Also, we shift the wave-number by $(\pi, 0)$ for the SbF$_6$ salt considering the sign difference in the main transfer energies along the inter-stacking direction. By such a transformation, we find that the band structures between the I$_3$ salt and the modified SbF$_6$ salt become very similar as shown in Fig. 5(c). Since the simplified model eliminates the dimerization effect, the difference in the original band structure between the two salts comes mainly from the dimerization, and the differences coming from the inter-stacking transfer are not essential.

### C. Effect of electron correlation cooperating with dimerization

A quarter-filled system effectively becomes a half-filled system by increasing the dimerization, so that the electron correlation is strengthened. Since we now know that the strength of the dimerization is the essential difference between the I$_3$ and SbF$_6$ salts, we expect that the difference of the ground state physical properties between the two salts is caused by the strength of the electron correlation originating from the difference in the strength of the dimerization.

The strength of the electron correlation can be measured by calculating the spin susceptibility. We apply the TPSC scheme to the Hubbard model of the I$_3$ salt. From the first principles calculation of the I$_3$ salt, the band width $W$ is about 0.77 eV, so we take the on-site interaction $U_0 = 0.8$ eV as same as the band width. The bare on-site interaction $U_0$ is estimated in the other strongly correlated organic conductors applying the first-principles method.

### TABLE I: List of the transfer energies in the unit of eV for $\beta$-(BDA-TTP)$_2X$.

| $X$    | I$_3$ | SbF$_6$ |
|--------|-------|---------|
| $t_{p1}$ (eV) | -0.174 | -0.153 |
| $t_{p2}$  | -0.102 | -0.126 |
| $t_{q1}$   | 0.018  | -0.071 |
| $t_{q2}$   | 0.041  | -0.055 |
| $t_c$    | 0.062  | 0.007  |
| $t_{2c}$  | 0.002  | 0.005  |
| $t_{2p}$  | 0.006  | 0.021  |
| $t_a$    | -0.001 | 0.003  |
| $t_{q3}$  | -0.012 | 0.003  |
| $t_{q4}$  | 0.013  | 0.006  |
| $t_{r1}$  | 0.002  | 0.014  |
| $t_{r2}$  | 0.009  | 0.008  |
| $t_{p2}/t_{p1}$ | 0.586  | 0.824  |
| $t_{q1}+t_{q2}$ | -0.214 | 0.452  |
| $t_{p1}+t_{p2}$ | -0.449 | -0.050 |

FIG. 4: (color online) The lattice structures of (a) the I$_3$ and (b) the SbF$_6$ salt. Blue solid lines represent the tilting angles of the donor molecules, which is measured from the $c$-direction taken in the horizontal direction. In the lower panel, the ellipses represent the donor molecules, the black solid lines show the intra-stacking transfer, and the red solid (black dotted) lines represent the main (not main) inter-stacking transfer.

FIG. 5: (color online) The simplified model for (a) the I$_3$ salt and (b) the SbF$_6$ salt, where the line width schematically represents the magnitude of the transfer energies, and the solid (dashed) line represents the negative (positive) value of the transfer energies. (c) The band structure of the simplified model by eliminating the dimerization for each salts.
calculation. Referring to them, the on-site interaction we taken is appropriate.

Figure 6 (a) shows the temperature dependence of the local vertex of the spin part $U_{sp}$ and the critical on-site interaction of the magnetic order $U_{SDW}$ in the left scale. Above the temperature $T \approx 0.004$eV, $U_{sp}$ is almost unchanged and $U_{SDW}$ gradually decreases with lowering the temperature. Below $T \approx 0.004$eV, $U_{sp}$ takes almost the same value, but somewhat smaller value than $U_{SDW}$, which can be understood that the magnetic ordering is developed with lowering the temperature.

In the right scale of Fig. 6(a), we present the ratio $U_{SDW}/U_{sp}$ as a function of $T$. The TPSC approach satisfies the Mermin-Wagner theorem so the true magnetic ordering does not occur in the present model, but we can regard the temperature at which the line extrapolating $U_{SDW}/U_{sp}$ from high temperature reaches unity as the magnetic critical temperature in the actual three dimensional system. We estimate the magnetic critical temperature to be about 0.0038 eV. Reflecting the tendency toward the magnetic ordering, $U_{ch}$ quickly increases below $T = 0.0038$ eV as shown in Fig. 6 (b). We show the double occupancy $\langle D \rangle = \langle n_{\uparrow}n_{\downarrow} \rangle$ as a function of $T$ in Fig. 6 (c). Similarly to the local vertices, the double occupancy $\langle D \rangle$ also changes below $T = 0.0038$eV. Decreasing the temperature reduces the double occupancy, which means the tendency of the magnetic localization at each site. Figure 6(d) shows the inverse of the maximum value of the spin susceptibility against $T$. As expected from Fig. 6 (a), the inverse of the spin susceptibility extrapolates to zero around $T = 0.0038$ eV. In fact, a very recent experiment observes a magnetic transition in the Mott insulating state of the $I_3$ salt at low temperature. TPSC is not capable of directly describing the magnetic ordering of a Mott insulator, but the very fact that the material is a Mott insulator is consistent with our view that the electron correlation effect is strong due to the strong dimerization.

Figures 7 (a) and (b) show the absolute value of the Green’s function $|G|$ and the spin susceptibility $\chi_{sp}$ of the $I_3$ salt with $U_0 = 0.8$eV and $T = 0.004$eV. The absolute value of the Green’s function takes large values near the Fermi surface shown in Fig. 6 (a). The wave number at which the spin susceptibility is maximized corresponds to the nesting vector of the Fermi surface as seen in Fig. 6 (b). As shown in Fig. 6(b), the maximum value of the spin susceptibility takes a large value since its temperature is close to the critical temperature.

To clarify the relation between the electron correlation and the dimerization, we measure the strength of the dimerization by the quantity $t_{p2}/t_{p1}$. When $t_{p2}/t_{p1}$ goes to unity, the dimerization decreases. If the decrease of the dimerization results in weakening the electron correlation, we expect (i) $U_{sp}$ gradually deviates from $U_{SDW}$, (ii) the double occupancy $\langle D \rangle$ becomes large, and (iii) the maximum value of the spin susceptibility decreases within the TPSC scheme. Furthermore, if the stronger electron correlation of the $I_3$ salt originates from the stronger molecular dimerization, all the quantities should...
approach the values close to those of the SbF$_6$ salt when the dimerization is reduced hypothetically in the model of the I$_3$ salt.

Let us now investigate the relation between the electron correlation and the dimerization. Figure 8(a) shows the local vertex of the spin part $U_{sp}$ and the critical on-site interaction for the magnetic order $U_{SDW}$ as a function of $t_{p2}/t_{p1}$ in the model of the I$_3$ salt, also shows them for the SbF$_6$ salt at the point corresponding $t_{p2}/t_{p1}$, where we take $T = 0.004$ eV. Decreasing the dimerization (increasing $t_{p2}/t_{p1}$), $U_{sp}$ gradually differs from $U_{SDW}$, which expects that increasing the $t_{p2}/t_{p1}$ suppresses the maximum value of the spin susceptibility. In contrast to the temperature dependence, decreasing the dimerization increases $U_{ch}$ as seen in Fig. 8(b), although $U_{sp}$ differs from the $U_{SDW}$. In Fig. 8(c), the double occupancy $\langle D \rangle$ monotonically increases with decreasing the dimerization, which can be understood as the suppression of the magnetic localization. This tendency is confirmed by the deviation of $U_{sp}$ from $U_{SDW}$. Figure 8(d) shows the maximum value of the spin susceptibility as a function of $t_{p2}/t_{p1}$. Decreasing the dimerization from the actual value of the I$_3$ salt quickly suppresses the spin susceptibility, and that of the I$_3$ salt takes almost the same value as that of the SbF$_6$ salt around the same strength of the dimerization.

From the $t_{p2}/t_{p1}$ dependence in Fig. 8 we can say that the electron correlation in the I$_3$ salt is stronger than in the SbF$_6$ salt due to the strong dimerization. We therefore conclude that the difference of the ground state between the two salts, namely, insulating for the I$_3$ salt and superconducting for the SbF$_6$ salt, originates from the strength of the dimerization, which affects the electron correlation. Applying the pressure to the I$_3$ salt reduces the dimerization, resulting in the metallicity, and hence the superconductivity appears.

**IV. CONCLUSION**

In the present study, we have performed first principles band calculations and have derived the effective tight-binding models of $\beta$-(BDA-TTP)$_2$I$_3$ and $\beta$-(BDA-TTP)$_2$SbF$_6$. The band structures and the Fermi surface between the I$_3$ and SbF$_6$ salts are apparently different although only the anion differs. The derived tight-binding models, which accurately reproduce the first principles band structures of the two salts, show that the differences between the two salts comes mainly from the strength of the dimerization.

As for the effect of the electron correlation, we have presented the TPSC results for quantities such as the spin susceptibility in the Hubbard model for the two salts. The TPSC results show that the electron correlation becomes stronger upon lowering the temperature and/or increasing the dimerization strength. Then, we have hypothetically reduced the strength of the dimerization in the I$_3$ salt to that of the SbF$_6$ salt, where all the calculated quantities tend to become similar to those of the SbF$_6$ salt. Thus, we conclude that the electron correlation in the I$_3$ salt is stronger than the SbF$_6$ salt due to the strong dimerization. The expected stronger correlation in the I$_3$ salt is at least qualitatively consistent with a recent experimental observation that the material is a Mott insulator, which is a hallmark of strong correlation, and exhibits a magnetic transition at low temperature $T$. Applying the pressure to the I$_3$ salt reduces the dimerization, which weakens the electron correlation, and hence the superconductivity appears as in the SbF$_6$ salt.

In the present study, we have considered only the on-site (intra-molecular) electron-electron interaction. It remains an interesting future problem to study the effect of the off-site interactions. In fact, it has been known that in organic conductors having quarter-filled bands, the Mott insulating state often competes with the charge...
ordering and/or charge-density-wave states. It is an interesting issue to investigate how such interactions would affect the insulating properties as well as the mechanism of the superconductivity.

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