First-principles study of ferromagnetism predicted for an organic polymer dimethylaminopyrrole — a realization of organic periodic Anderson model

Yuji Suwa, Ryotaro Arita, Kazuhiko Kuroki, and Hideo Aoki

Advanced Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185-8601, Japan
Department of Applied Physics, University of Tokyo, Hongo, Tokyo 113-8656, Japan
Department of Applied Physics and Chemistry, University of Electro-Communications, Chofu, Tokyo 182-8585, Japan
Department of Physics, University of Tokyo, Hongo, Tokyo 113-0033, Japan

(Dated: July 15, 2009)

Ferromagnetism in purely organic materials is predicted for polymer and oligomers of dimethylaminopyrrole. First-principles calculations with the spin-density functional theory show that oligomers larger than tetramer as well as a polymer should have spin polarizations when the density of doped holes exceeds 1/2 hole per five-membered ring. We suggest that the mechanism for the ferromagnetism is, unlike the flat-band ferromagnetism predicted previously for polyaminotriazole, related to the periodic Anderson model, so that the present system amounts to an organic realization of the periodic Anderson model.

PACS numbers: 71.20.Rv, 71.10.Fd, 75.50.Xx

I. INTRODUCTION

Realizing organic ferromagnets consisting entirely of non-magnetic elements is a challenging target in condensed-matter physics and chemistry. To stabilize spin polarization in a p-electron organic material, interatomic electron-electron interactions such as an intramolecular coupling or an intra-polymer coupling can play an important role besides the intra-atomic direct and Hund’s couplings. In usual organic materials, however, such interactions is usually not enough to guarantee spin polarizations.

In an entirely different approach to overcome this difficulty, the present authors have theoretically proposed to utilize the “flat-band ferromagnetism”, originally proposed by Mielke and by Tasaki, to design an organic ferromagnet. This mechanism for ferromagnetism is distinct from the usual band magnetism in that this is outside the conventional Stoner picture, but instead arises from an electron correlation effect exerted on the flat (dispersionless) band where the flat band is an outcome of a quantum mechanical interference rather than a narrow-band limit. However, a flat band has to satisfy what is called the local connectivity condition for the ferromagnetism to be realized. This is a special condition in which the adjacent “Wannier” orbits have to overlap with each other no matter how they are combined to minimize their size. Intuitively, the Bloch states on the flat band are something like non-bonding molecular orbitals in the language of organic chemistry, and the “generalized Hund’s coupling” i.e., Hund’s coupling in k-space acts to realize the spin alignment when the condition is met. Since the flat-band model has eluded an unambiguous realization in real materials so far, we started from a materials-design viewpoint that it should be easier to satisfy the connectivity condition if we consider chains of odd-membered rings. So polymers of five-membered rings are candidates, but chains of odd-membered rings are by no means a sufficient condition for the flat band, so that we have examined a vast number of compounds. As a candidate for the realization of the magnetism, we have proposed polymers of five-membered aminotriazole, which is commercially available, has turned out to be difficult, presumably due to a quantum chemical reason. In the course of our attempts, however, we have found that monomers of dimethylaminopyrrole can be polymerized more easily, where triazole part, presumably the difficult ingredient, is absent while the amino group is replaced with dimethylamino group. Thus we have started with obtaining the electronic structure of polymer and oligomers of dimethylaminopyrrole from first principles to examine the possibility of ferromagnetism (for the polymer) and high-spin states (for the oligomers). We have employed the generalized gradient approximation (GGA).

New findings here are two-fold: we shall first show for the polymer that the materials will be indeed spin polarized if holes are sufficiently doped (i.e., more than 1/2 hole per five-membered ring). Oligomers are also shown to have high-spin states if holes are doped enough. For n-mers of dimethylaminopyrrole, we conclude that n/2 + 2 or n/2 + 3 holes are necessary to be ferromagnetic depending on whether n/2 is even or odd, respectively.

More importantly, from the viewpoint of mechanism of ferromagnetism, the second finding is that the band on which the spin polarization resides does not satisfy the local connectivity condition although it is quite dispersionless, so that the mechanism of the ferromagnetism should indeed be outside the flat-band ferromagnetism. We shall then discuss that the magnetism can be explained by the mechanism proposed by Batista et al based on the periodic Anderson model. In this theory, coexistence of a
FIG. 1: A top view(a) and side view(b) of the optimized atomic structure of polydimethylaminopyrrole in a unit cell. (c) Band structure of undoped polydimethylaminopyrrole. Thick solid (dashed) lines represent $\sigma$-bands ($\pi$-bands).

II. DIMETHYLAMINOPYRROLE POLYMER

Let us start with the polymer of dimethylaminopyrrole. Figure 1(a,b) depicts the atomic structure of polydimethylaminopyrrole in a unit cell. We have studied both the spin-unpolarized cases based on the density-functional theory (GGA-DFT) and the spin-polarized ones based on the spin-density functional theory (GGA-SDFT). We have used the plane-wave based ultrasoft pseudopotentials$^{10,11}$ with the energy cutoff at 20.25 Rydberg. The convergence criterion of the geometry optimization was that all of the forces acting on each atom were within $1 \times 10^{-3}$ $\text{H/au}$. We have first optimized the structure. While we have started, in our materials design, from a planar configuration of rings, the structure-optimized polydimethylaminopyrrole has dimethylamino bases somewhat twisted out of the plane. This makes the $\pi$-orbital of the nitrogen atom in the amino base lying in the molecular plane, that is, the angle between the $\pi$-orbitals of the nitrogen atom in the amino base and the neighboring nitrogen atom in the five membered ring becomes nearly 90 degrees, leading to a very small $\pi$-bonding between them.

The band structure of undoped polydimethylaminopyrrole is shown in Fig. 1(c). We can see that there exist flat bands (labeled as (B)-(E) and (C)-(F) in Fig. 1(c)), but they lie well below the Fermi energy, unlike the case of polyaminotriazole$^{3,4,5,6}$ where the flat band sits around $E_F$. In the band structure, a band folding of the quasi-one-dimensional band is due to the alternating directions of the pyrrole molecules.

Figure 2(A-H) shows the wave functions in the highest four valence (occupied) bands at $\Gamma$ and $X$ points. The wave functions of the flat bands (B, C, E and F in Fig. 1(c)) are mixtures of the $\pi$-orbitals of the nitrogen atoms and $\sigma$-orbitals of the carbon atoms, while the other wave functions consist almost entirely of $\pi$-orbitals. We can thus call the flat bands (B)-(E) and (C)-(F) (thick solid lines in Fig. 1(c)) as $\sigma$-bands, and the top valence band (A)-(G) (uppermost thick dashed line in Fig. 1) as a $\pi$-band.

While in polyaminotriazole$^{3,4,5,6}$ the $\pi$-band is flat, for which the “flat-band ferromagnetism” is expected to be realized, this is no longer the case with polydimethylaminopyrrole, since the $\pi$-band is considerably dispersive. On the other hand the $\sigma$-bands are flat, and one might expect that the flat-band ferromagnetism may occur. This does not apply either, since the bands do not satisfy the local connectivity condition$^1$ mentioned above, but they are flat simply because the transfer between five-membered rings is small, as seen in Figs. 2(B), (C), (E) and (F) where $\sigma$-bands are absent between those two carbon atoms connecting the adjacent five-membered rings. Although small $\pi$-like orbitals can be seen there, they are negligibly small compared to those of $\pi$-bands in Figs. 2(G) and (H).

Does this imply that we have no ferromagnetism? If we look at the band structures of the hole-doped polydimethylaminopyrrole calculated with GGA-SDFT for various values of the hole concentration in Fig. 3, while there is no spin polarization for the number of holes per unit cell $n_h = 0.5$ or 1.0, spin polarization does appear when $n_h$ exceeds 1.0. The differences between the num-
FIG. 2: Wave functions in the highest four valence bands of undoped polydimethylaminopyrrole at Γ (A–D) and X (E–H) as depicted by isosurfaces with different colors representing the signs of the wave function. See Fig. 1(c) for labels of the energy levels. We have chosen the wave function to be real at Γ.

FIG. 3: Spin-resolved band structures of the hole-doped polydimethylaminopyrrole for the concentration of holes per unit cell (a) \( n_h = 0.5 \), (b) \( n_h = 1.0 \), (c) \( n_h = 1.5 \), (d) \( n_h = 2.0 \).

numbers of up and down spins per unit cell are 0.17, 0.45 and 0.97 for \( n_h = 1.25, 1.5, 2.0 \), respectively. This shows that more than half-filled holes (\( n_h \geq 1.0 \)) make the system ferromagnetic. This is the first key result.

III. ORIGIN OF THE MAGNETISM: PERIODIC ANDERSON MODEL

So the natural question is what is the mechanism of the spin polarization observed in the present calculation, which should be other than the flat-band mechanism. We can evoke ferromagnetism in the periodic Anderson model as a possible scenario. Indeed, here we have narrow \( \sigma \) bands embedded in wide \( \pi \) bands which hybridize with each other. Theoretically, it has been well known that the periodic Anderson model can have a ferromagnetic ground state in a variety of conditions. One famous example is the situation when the model can be mapped to the Kondo lattice model, i.e., when there is one electron in each localized orbital. On the other hand, Batista et al. recently proposed another mechanism which can work when the particle density of the localized state is not close to unity. The basic idea of Batista et al. may be recapitulated as follows. Let us consider the periodic Anderson model whose Hamiltonian is defined as

\[
H = H_0 + H_U, \\
H_0 = -t_c \sum_{r,r',\sigma} (c_{r,\sigma}^\dagger c_{r',\sigma} + \text{h.c.}) \\
- t_f \sum_{r,r',\sigma} (f_{r,\sigma}^\dagger f_{r',\sigma} + \text{h.c.}) + \varepsilon_f \sum_{r,\sigma} n_{r,\sigma}^f \\
+ V \sum_{r,\sigma} (\epsilon_{r,\sigma} f_{r,\sigma} + \text{h.c.}), \\
H_U = -U \sum_r n_{r,\uparrow}^f n_{r,\downarrow}^f,
\]

where the conduction electrons (created by \( c_{r,\sigma}^\dagger \)) hybridize with localized electrons (created by \( f_{r,\sigma}^\dagger \)) with \( r \) representing the site and \( \sigma \) the spin. Here \( t_c, t_f \) are the respective hopping energies, \( \varepsilon_f \) (assumed to be \( |\varepsilon_f| < t_c \)) the energy level of the localized orbital, \( V \) the hybridization, and \( U \) is the repulsive interaction within the localized orbital. We can diagonalize the one-body part of the two-band Hamiltonian \( H_0 \) to obtain the band representation as

\[
H_0 = \sum_{k,\sigma} \left( E_k^+ \beta_{k,\sigma}^\dagger \beta_{k,\sigma} + E_k^- \alpha_{k,\sigma}^\dagger \alpha_{k,\sigma} \right),
\]

where \( E_k^+ > E_k^- \) (see Fig. 3).
Let us introduce two kinds of Wannier orbitals, one dominantly localized,
\[
\phi_{r,\sigma} = \frac{1}{N} \sum_k K^> \phi_{kr,\sigma} + \frac{1}{N} \sum_k K^< \phi_{kr,\sigma}, \tag{5}
\]
and another dominantly conductive,
\[
\psi_{r,\sigma} = \frac{1}{N} \sum_k K^< \psi_{kr,\sigma} + \frac{1}{N} \sum_k K^> \psi_{kr,\sigma}, \tag{6}
\]
where we have decomposed the k-space into \(K^>\) (\(K^<\)) for which the localized (conduction) electrons are the dominant in the \(\beta_{k,\sigma}\) band (Fig. 3).

With the new Wannier basis the one-body part of the Hamiltonian now reads
\[
H_0 = \sum_{r,\sigma} \tau^0_{r',r} \psi^\dagger_{r',\sigma} \phi_{r,\sigma} + \sum_{r,\sigma} \tau^0_{r',r} \phi^\dagger_{r,\sigma} \psi_{r',\sigma}, \tag{7}
\]
where \(\tau^0\)'s are new transfer energies with no off-diagonal terms like \(\psi^\dagger_{r',\sigma} \phi_{r,\sigma}\). Batista et al.\(^2\) have shown that, while the interaction term in the Hamiltonian becomes complicated in terms of \(\psi\) and \(\phi\), the dominant term is \(U_{\text{eff}} \phi_{r,\sigma} \psi_{r,\sigma}\), while the other terms can be neglected when the hybridization \(V\) is not too strong. When the system is in the mixed valence regime, namely, when the Fermi energy \(E_F\) is above \(\varepsilon_f\) in the present hole-doped case, holes first doubly-occupy the uncorrelated \(\psi_k\) states which are above \(\varepsilon_f\), and then go into \(\phi_k\) states. There \(\phi_k\)'s tend to have parallel spins, because the cost of the kinetic energy due to the spin polarization (\(\sim t_f\)) is small, while the ferromagnetic state does not feel \(U_{\text{eff}}\) because of the Pauli’s exclusion principle.

When all the \(\phi_k\)'s are singly occupied (by holes in the present case), we can construct localized \(\phi_k\)'s by using occupied states only. Because there is no interaction between the spins in this case, the ferromagnetic state and the paramagnetic state have the same energy. When \(\phi_k\)'s are only partly occupied, by contrast, we cannot construct completely localized \(\phi_k\)'s only from the occupied states. Carriers then start to feel \(U_{\text{eff}}\) through the overlap of delocalized \(\phi_r\)'s, which makes the ferromagnetic state energetically unfavorable. Therefore, the system should choose a ferromagnetic ground state when \(\phi_k\) states are less than half-filled for \(U_{\text{eff}}\) sufficiently greater than \(t_f\). This has been demonstrated numerically for the one-dimensional periodic Anderson model.\(^2\)

In this mechanism of ferromagnetism, a hybridization between narrow and dispersive bands plays an important role. In polydimethylaminopyrrole, it is clear from the band structures in Fig. 1(c) and Fig. 3 (which are summarized in Fig. 4) that the \(\sigma\)-band and \(\pi\)-band are hybridized each other. Although the two bands may seem intersecting, they are actually anticrossing with each other. So if this scenario is correct, the organic material considered in the present work amounts to the first proposal for an organic periodic Anderson system.

**FIG. 4: Band structure of polydimethylaminopyrrole in a tight-binding model.** The transfer energies and on-site energies are fitted to reproduce Fig. 1(c). Thick solid (dashed) lines correspond to \(E_k^+\) \((E_k^-)\) in Eq. 4. (A-D) on the right depict wave functions for the highest four occupied states at \(\Gamma\), where the size of each circle represents the amplitude while the different colors its sign.

**IV. TIGHT-BINDING ANALYSIS**

In order to grasp what is essentially happening in the ferromagnetism of this material, we introduce a simple tight-binding model. The model consists of five sites representing the \(\pi\)-orbitals in the five-membered ring and an additional “amino N” site. The amino N site represents the molecular orbital that consists of the \(\pi\)-orbital of the N atom in the amino base, the \(\sigma\) \((\text{sp}^3)\) orbitals of two methyl bases and \(\sigma\)-orbitals of the five-membered ring. The transfer and on-site energies are fitted to reproduce Fig. 1(c). Figure 1 shows the band structure and wave functions in the tight-binding model. In the tight-binding model the primitive cell contains only one five-membered ring, but we have folded the bands at \(X\) \((k = \pi/2a)\) to facilitate comparison with Fig. 1(c). We can see that the tight-binding fit successfully reproduces all the relevant (i.e., the thick lines in the DFT result in Fig. 1(c)) \(\pi\)-bands and \(\sigma\)-band. So the six sites considered in the tight-binding model have turned out to be sufficient for describing the relevant bands (consisting of the mainly \(\pi\) bands of the ring, plus another one whose character is not the \(\pi\) orbits of the ring). In other words, the bonding between the ring and amino N can be expressed only by the transfer between the \(\pi\)-orbital of the N atom at the apex of the ring (apex N) and that at the amino N. Because the molecular orbital that forms \(\sigma\)-band is included in the amino N site, the \(\sigma\)-band of this model has a large amplitude at the amino N. In this sense, \(\pi\)-band” (which was meant to mean those other than the \(\pi\) orbits of the
FIG. 5: Band structure of polydimethylaminopyrrole in the tight-binding model, unfolded onto an extended Brillouin zone. Solid (dashed) lines correspond to \( E^+ \) (\( E^- \)) in Eq. (4), while thick (thin) lines \( \phi \) (\( \psi \)) states in Eq. (6) (\( \sim \sigma \) (\( \pi \)) bands in the present system). Labels (A-D) refer to the band structure in Fig. 4. Arrows schematically indicate the spins of accommodated holes.

The simple model shows that the \( \sigma \)-band does not satisfy local connectivity condition. The flatness of the band simply comes from localized nature of the wave function. While the tight-binding model here is the same as that for polyaminotriazole \(^5\) except for the values of parameters, a large difference is that the transfer between the amino N and apex N is very small here compared to that in polyaminotriazole, which is precisely because the \( \pi \)-orbitals of the N atoms are twisted almost 90 degrees with each other here. The twist also produces hybridization with \( \sigma \)-orbitals of the five-membered ring. The small transfer between the amino N and apex N breaks the subtle balance of parameters necessary to satisfy local connectivity condition for the flat-band ferromagnetism, but simultaneously creates narrow and dispersive bands, mutually hybridized, which is a prerequisite for the ferromagnetism based on the periodic Anderson model.

In order to make the identification of the present band structure with the periodic Anderson model clearer in terms of \( \phi \) and \( \psi \) states in Eq. (6), we show in Fig. 5 the band structure (Fig. 4) unfolded into an extended Brillouin zone. The upper band (solid line) consisting of a part of the top valence \( \pi \)-band and a part of the flat \( \sigma \)-band correspond to \( E^+_k \) in Eq. (4), while the lower band (dashed line) consisting of the other parts of \( \sigma \) and \( \pi \)-bands correspond to \( E^-_k \). In the figure, thick lines and thin lines correspond to \( \phi \) and \( \psi \)-states in Eq. (6), respectively. Simply put, \( \phi \) represents the \( \sigma \)-band and \( \psi \) the \( \pi \)-band in the present organic system.

In terms of the tight-binding model, we can explain an interesting feature in the GGA-SDFT band structure (Fig. 3) where the energy of the \( \sigma \)-band shifts relative to the other bands with the doping. For instance, as we increase the number of holes from \( n_h = 0 \) (Fig. 3(a)) to 1.0 (Fig. 3(b)), the \( \sigma \)-band goes up. When \( n_h \) is increased further (Figs. 3(c) and 3(d)), the \( \sigma \)-band of majority spins starts to go down, while that of minority spins does not. As a result, the lower limit of doping concentration necessary for the ferromagnetism becomes just half-filled (\( n_h = 1.0 \), i.e., 1/2 hole per five membered ring). Such a shift of the \( \sigma \)-band in the GGA-SDFT calculation can be reproduced by using the tight-binding model, if a Coulomb interaction of 1.4 eV between the amino N site and five-membered ring is assumed and a mean-field approximation is applied. Note that \( \pi \) orbital of the amino N is hybridized with the \( \sigma \) orbitals of the five-membered ring, so that the interaction effectively contains an intrasite interaction and can be large.

V. OLIGOMERS

We move on to the oligomers of dimethylaminopyrrole. This is practically important because synthesis of the oligomers of dimethylaminopyrrole is possible \(^7\) while the polymer may be difficult to fabricate.

As a typical case we show the result for a tetramer. Figure 6 shows the atomic structure, the energy levels of undoped and four-hole-doped tetramer of dimethylaminopyrrole. Solid (dashed) lines represent occupied (unoccupied) states. Wave functions of the states labeled as (A-L) are shown in Fig. 7 below.

FIG. 6: Atomic structure(a) and energy levels of undoped(b) and four-hole-doped(c) tetramer of dimethylaminopyrrole. Solid (dashed) lines represent occupied (unoccupied) states.

Wave functions of the states labeled as (A-L) are shown in Fig. 7 below.
FIG. 7: Wave functions of a four-hole-doped tetramer of dimethylaminopyrrole for the energy levels labeled in Fig. 6(c) as depicted by isosurfaces with different colors representing the signs of the wave function.

energy levels than corresponding majority-spin states (C-F), while other levels are almost the same between the majority and minority spins. As a consequence the higher two states out of the four become unoccupied in the minority-spin channel.

The four states are $\sigma$-states, counterparts of the $\sigma$-band in the polymer, which can be confirmed if we look at the wave functions of the four states in Figs. 7(C-F) for majority spin and in Figs. 7(H-K) for minority spin. All these wave functions are seen to consist of nitrogen $\pi$-orbitals and carbon $\sigma$-orbitals, while the other wave functions in Figs. 7(A,B,G,L) consist only of $\pi$-orbitals.

We can relate the arrangement of energy levels of the oligomer with the band structure of the polymer. Generally, for an oligomer consisting of $n$ monomers ($n$-mer), the number of electronic states constructed from one kind of molecular orbital of the monomer is $n$. Obviously, a state in which all monomers have the same phase is one of the $n$ states, and its wave function is similar to that of the polymer at $\Gamma$-point except for the truncation of the chain. We call it $\Gamma$-state. Another linearly independent state can be constructed by introducing a node into the wave function of the $\Gamma$-state making the signs of the molecular orbitals at the opposite ends reversed. This state is similar to that of the polymer at $k = \pi/na$ ($a$: the length of the monomer) in that the phase rotates by $\pi$ per $n$ monomers. In the same way, $m$-th state of the oligomer corresponding to the polymer’s state at $k = (m-1)\pi/na$ can be constructed by introducing $m-1$ nodes (a phase rotation of $(m-1)\pi$) in the $\Gamma$-state. Because of the similarity of the wave functions, the energy level of the $m$-th state in $n$-mer can be inferred according to the band energy of the polymer at $k = (m-1)\pi/na$.

An easy way to do such an estimation is to take the intersecting points of the band with vertical lines dividing the zone in $k$-space ($k = 0$ to $\pi/a$) into $n$. For example, the energy levels of the four-hole-doped tetramer and six-hole-doped hexamer around the LUMO-HOMO can be estimated as in Figs. 8(a) and 8(b), respectively. Note again that the whole band is folded at $X$ ($k = \pi/2a$) because of two monomers in the unit cell. The band structure of Fig. 3(d) is used here because the hole density of these examples is $n_h = 2.0$. We take $n$ to be even in the following for simplicity. As shown in the following, the order of energy levels estimated in this way agrees well with the result for the oligomers. One reason why
such an estimation is valid is that the finite-size effect is not very large in the oligomers of dimethylaminopyrrole, probably due to the simple chain structure and not-too-large transfer between monomers.

With such a kind of level scheme, we can estimate how many holes should be doped to realize spin polarization in a given oligomer. For that purpose, whether the vertical line in Fig. 8 exist at $k = \frac{X}{2}$ is important, since the $\pi$-band and the flat $\sigma$-band of minority spin cross at this point. When $n/2$ is odd as in Fig. 8(b), no vertical line exists at $X/2$ and thus $n/2 + 1$ holes first enter the levels coming from the $\pi$-band whose energies are the same for both spins. Since two more holes are necessary to occupy the levels associated with the flat $\sigma$-band, $n/2 + 3$ holes are necessary in total for the state to be spin-polarized. The total spin (i.e., the difference, $\eta$, of the number of up and down spins) can be estimated to be $N - n/2 - 1$, where $N$ is the number of doped holes in an $n$-mer. When $n/2$ is even, on the other hand, one of the vertical lines passes through $X/2$ as in Fig. 8(a). At $k = X/2$, the four energy levels, two from the $\pi$-bands for both spins and two from the $\sigma$-bands for the minority spin, almost coincide when holes are doped. Depending on which level is the highest, $n/2 + 2$ or $n/2 + 4$ holes are necessary to have spin-polarizations in this case, with $\eta$ estimated to be $N - n/2$ or $N - n/2 - 2$, respectively.

Table I shows the result of GGA-SDFT calculations for a series of oligomers of dimethylaminopyrrole with various numbers of doped holes. The number of holes necessary for spin polarization almost fully agree with the above estimate in terms of the polymer’s band structure. The only exception in this table is the existence of a spin polarization in the six-hole doped decamer, but the spin polarization of 0.32 there is rather small. For the $n$-mers with odd $n/2$, i.e., hexamer and decamer, the values of the spin polarization agree accurately with the above estimate, which should reflect the fact that no energy levels associated with the $\pi$-band exist near the Fermi energy when spin polarization emerges, as shown in Fig. 8(b). For the oligomers with even $n/2$, i.e., octamer and dodecamer, the spin polarization takes the value somewhere between the two estimations, $N - n/2$ and $N - n/2 - 2$. In reality, $\eta$ is expected to take either of those two values, depending on the order of almost degenerated energy levels of $\pi$-band and $\sigma$-band. The calculated values between the two estimations should come from fractional occupations of these energy levels on the assumption of a finite temperature introduced to ensure the convergence of the electronic states.

### VI. CONCLUSION

We have used a first-principles calculation to examine magnetism in a polymer and oligomers of dimethylaminopyrrole from a viewpoint of materials design for ferromagnetism without magnetic atoms. We have found that polydimethylaminopyrrole should be ferromagnetic if density of doped holes are more than one hole per unit cell ($n_h > 1.0$). For $n$-mers of dimethylaminopyrrole, we conclude that $n/2 + 2$ or $n/2 + 3$ holes are necessary to be spin-polarized depending on whether $n/2$ is even or odd, respectively. While polydimethylaminopyrrole belongs to the same category (chains of five-membered rings) as the previously proposed polyaminotriazole, which has theoretically shown to realize the flat-band ferromagnetism, we suggest that the present ferromagnetism is distinct from the flat-band ferromagnetism, but has instead the mechanism proposed by Batista et al. based on the periodic Anderson model.

So the present work gives an interesting instance of material design where control of the parameters of electronic states even leads to a different mechanism for the many-body effects, namely organic periodic Anderson model and associated ferromagnetism. An important future problem is whether the SDFT calculations can capture the ferromagnetism à la Batista. Another future problem is how the present concept of the organic periodic Anderson model can be extended to wider materials beyond those considered here. As for the doping the material, we can consider various chemical dopants as discussed for in Ref. [4].

#### Acknowledgments

We would like to thank Hiroshi Nishihara, Yoshinori Yamanoi and Norikazu Olishima for extensive discussions.
on the chemistry of polymers and oligomers, and also for the collaboration in fabricating the materials. This work was partly supported by a Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science. The first-principles calculations were performed with TAPP (the Tokyo Ab-initio Program Package).

1 For reviews, A. Mielke and H. Tasaki, Commun. Math. Phys. 158, 341 (1993), H. Tasaki, Prog. Theoer. Phys. 99, 489 (1998).
2 K. Kusakabe and H. Aoki, Phys. Rev. Lett. 72, 144 (1994).
3 R. Arita, Y. Suwa, K. Kuroki, and H. Aoki, Phys. Rev. Lett. 88, 127202 (2002).
4 R. Arita, Y. Suwa, K. Kuroki, and H. Aoki, Phys. Rev. B 68, 140403 (2003).
5 Y. Suwa, R. Arita, K. Kuroki, and H. Aoki, Phys. Rev. B 68, 174419 (2003).
6 Y. Suwa, R. Arita, K. Kuroki, and H. Aoki, e-J. Surf. Sci. Nanotech. 2, 38 (2004).
7 Y. Yamanoi, T. Hamada, K. Ohshima, and H. Nishihara, unpublished.
8 J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B 54, 16533 (1996).
9 C. D. Batista, J. Bonda, and J. E. Gubernatis, Phys. Rev. B 68, 214430 (2003).
10 D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
11 K. Laasonen et al., Phys. Rev. B 47, 10142 (1993).
12 For recent exact results, see e.g., Z. Gulácsi and D. Vollhardt, Phys. Rev. Lett. 91 186401 (2003), Phys. Rev. B 72, 075130 (2005).
13 For review, H. Tsunetsugu, M. Sigrist, and K. Ueda, Rev. Mod. Phys. 69, 809 (1997).