Gate-Induced Band Ferromagnetism in an Organic Polymer

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We propose that a chain of five-membered rings (polyaminotriazole) should be ferromagnetic with an appropriate doping that is envisaged to be feasible with a field-effect transistor structure. The ferromagnetism is confirmed by a spin density functional calculation, which also shows that ferromagnetism survives the Peierls instability. We explain the magnetism in terms of the Mielke and Tasaki flatband ferromagnetism with the Hubbard model. This opens a new possibility of *band ferromagnetism* in purely organic polymers.

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Since the discovery of conducting organic polymers [1,2], a great variety of studies have been performed to pave a new way to further employ polymers or oligomers in realizing various functions, such as field-effect transistors (FETs) [3] or electroluminescent diodes [4]. This is most recently highlighted by a series of works by Batlogg and co-workers [5,6], where they have demonstrated that some molecular crystals (anthracene, etc.) and polymers (polythiophene) can not only be metallized but even exhibit superconductivity.

If a gate-induced superconducting plastic is possible, a gate-induced ferromagnetic plastic is of no less interest. Ferromagnetism is usually a feature of d or f electron systems, so that π electron ferromagnetism has indeed been a theoretical and experimental challenge, for which an enormous amount of studies have been carried out. In particular, purely organic ferromagnets are interesting. A theoretical proposal was made by Shima and Aoki [7], where graphites with superhoneycomb structures are considered, but this has to do with Lieb's ferrimagnetism [8], a kind of antiferromagnetism for unbalanced numbers of sublattice sites. Organics exhibiting (single-)band ferromagnetism have yet to be synthesized [9].

Here we propose a novel possibility for a *band ferromagnetism* in a *purely* organic polymer that realizes another class of flatband ferromagnetism due to the Mielke and Tasaki mechanism [10]. We first find that a chain of five-membered rings with the right choice of the functional group (polyaminotriazole) has a flatband. We then show that, when this band is made half-filled, where the doping is envisaged to be realized in an FET structure, the ground state is ferromagnetic. The spin density functional calculation also shows that the magnetism overcomes the Peierls instability. We finally confirm that the magnetism really has to do with the Mielke-Tasaki mechanism by mapping the π-orbital system to a tight-binding model with the Hubbard repulsion.

The problem of ferromagnetism in the Hubbard model, despite a long history since the 1960s [11–13], is still some way from a full understanding. One sensible way to study the problem is to take some characteristic situation where ferromagnetism may be rigorously proved. In fact, Mielke and, independently, Tasaki have proposed classes of flatband models [10], and have proved rigorously for the Hubbard model that the ground state is fully spin polarized when the flatband is half-filled. When the flatband lies in between dispersive bands rather than at the bottom, the rigorous proof becomes inapplicable, but ferromagnetism is still expected when what is called the local connectivity condition for the basis functions in the flatband is satisfied. This amounts to a condition that adjacent "Wannier" orbitals *have to* overlap, despite the flat dispersion, no matter how they are combined to minimize the orbit size, which is why spins tend to align due to Pauli's principle. The case of a middle flatband has been studied in the context of a model atomic quantum wire [14], where the ferromagnetism is shown to be realized if the repulsive interaction is below a critical value.

The Mielke-Tasaki flatbands are constructed from interferences between nearest-neighbor and second-neighbor transfers, which require special lattice structures, especially in spatial dimensions greater than two. On the other hand, in quasi-one-dimensional chains we can conceive lattices having flatbands relatively easily [14], since it is easier to satisfy the connectivity condition in a chain than in a network. This is why we focus on organic polymers here. Although we will have to consider weak three-dimensional couplings to estimate the precise T_c [15], the possibility of band ferromagnetism in organic polymers should be an intriguing avenue to explore. Here we propose that one such system does have a flatband. We then show from both a band calculation and an exact diagonalization for the Hubbard model that the system should be indeed ferromagnetic when the band is made half-filled.

We first note that polymers comprising five-membered rings should be promising. This is because we find it empirically easier to realize flatbands in chains of odd-membered rings. Intuitively, odd-membered rings incorporate frustrations for electron transfers, while even-membered (i.e., bipartite) rings have an obvious disadvantage of a tendency toward antiferromagnetism when the electron-electron repulsion is turned on, which should compete with ferromagnetism. As we shall find below, the tight-binding model on the chain of five-membered rings can have dispersionless bands in appropriate, realistic conditions, where the eigenstate on the flatband indeed satisfies the local connectivity condition (i.e., overlapping orbitals, Fig. 1).

Thus we start with a search for the case of flatbands by scanning various five-membered polymers, i.e., polypyrrole, polythiophene, polytriazole, etc. The band structure is obtained with first principles calculations within the framework of the generalized gradient approximation based on the density functional theory (which we call GGA-DFT) [16]. We adopt the exchange-correlation functional introduced by Perdew *et al.* [16] and ultrasoft pseudopotentials [17,18] in a separable form. The wave functions are expanded by plane waves up to a cutoff energy of 20.25 Ry. As for the unit cell, five-membered rings usually alternate their directions in a chain (see Fig. 2), so that there are two rings in a unit cell with the Brillouin zone folded. In directions perpendicular to the chain we take a repeated-chain model with a sufficiently large repeat distance. The atomic configuration as well as the unit cell size along the chain are optimized to minimize the ground state energy with the conjugate gradient scheme [19].

It turns out that the flatband is rather hard to realize even for five-membered chains, which is not too surprising since an odd-membered ring is by no means a sufficient condition for a flatband. However, attaching a functional group to each ring helps since this changes site energies and transfer integrals, and we have found among the polymers investigated here that polyaminotriazole [poly(4-amino 1,2,4triazole) to be precise, see inset of Fig. 2; PAT hereafter] hits the right condition. Figure 2 shows that the top valence band (with two branches due to the above-mentioned band folding) has little dispersion [$\sim$O(0.1 eV)].

To induce the flatband ferromagnetism, this band has to be half-filled, while the band is fully filled when undoped. To assess the possibility of the spin polarization in the hole-doped case, we have carried out a GGA calculation for doped polyaminotriazole [20] including the spin degrees of freedom based on the spin density functional theory (which we call GGA-SDFT) [16]. We have focused on the situation where the highest valence band is hole doped to be half-filled (i.e., the upper branch arising from the band folding is empty). Figure 3 shows the band structure in which we have taken a polarized state as the initial state. The optimized state remains polarized, where the splitting between the majority-spin and minority-spin bands is $\sim$1 eV. This is similar to the exchange splitting estimated in [21] for the atomic quantum wire [14].

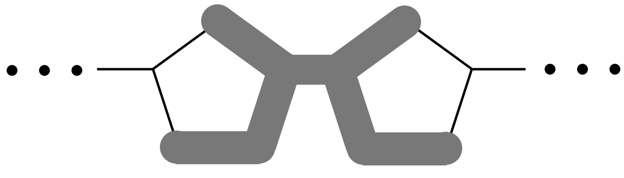

FIG. 1. The chain of five-membered rings, where the shading indicates a Wannier orbital that satisfies the local connectivity condition.

We have to be careful when we dope the band, since one-dimensional metals are, in general, unstable against the Peierls instability, where the electronic energy is lowered at the cost of the lattice distortion. So we have checked whether the energy gained due to the spin polarization overcomes the Peierls instability. The left panel in Fig. 4 is the band structure of the Peierls distortion-allowed, spin-unpolarized state obtained by the GGA-DFT. We can see that the Peierls splitting at X is negligibly small. Physically, this should be because σ electrons which form the backbone of the structure have a rigid enough bonding that can cope with the Peierls instability [22]. The total energy of the global minimum in the GGA-DFT calculation is higher than that of the polarized optimized state in the GGA-SDFT calculation by $\simeq$400 meV.

If we allow the spatial distributions of up and down spins to be different in the GGA-SDFT starting from an initially unpolarized state, the resulting band structure has a wide gap at the Fermi level (right panel in Fig. 4), which we attribute to an antiferromagnetic gap. Although the total energy of the antiferromagnetic state is lower than that for the uniformly zero spin density (the left panel in Fig. 4), the energy is higher than that of the optimized polarized state (Fig. 3) by $\simeq$ 50 meV. Thus we can conclude that the true ground state in the GGA-SDFT is the polarized one.

Now we come to the key question of whether the ferromagnetism obtained in the band calculation can be identified as the flatband ferromagnetism for the Hubbard model *a lá* Mielke-Tasaki. For that we have to first map the π electron system to a tight-binding model (see the right panel in Fig. 5). We have estimated the values of transfer integrals (t_{CC}, etc.) by first identifying π bands, and then

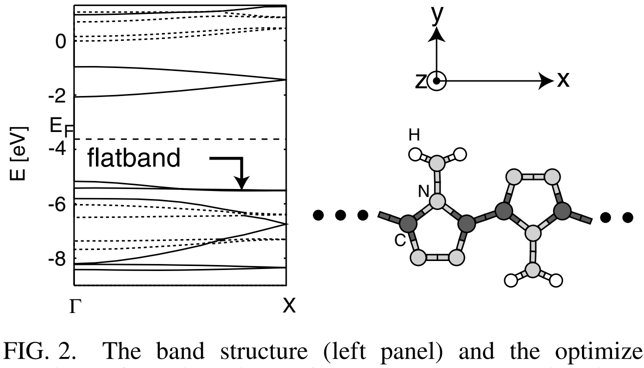

FIG. 2. The band structure (left panel) and the optimized atomic configuration (right) of the (undoped) polyaminotriazole obtained by the GGA-DFT. The solid (dotted) lines represent bands having π (σ) character.

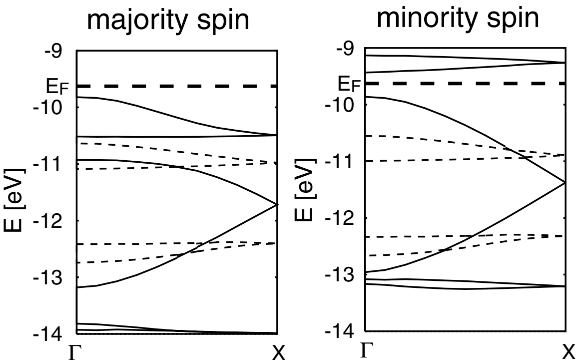

FIG. 3. The band structure of the *doped* system with an optimized structure obtained with the GGA-SDFT. The solid (dotted) lines represent bands having π (σ) character.

identifying the bonding and antibonding states for the relevant t at Brillouin zone center and edges. The nitrogen site energies (ϵ's) as measured from that for C are taken from the energy levels of isolated atoms. The obtained figures are $t_{CN} \simeq t_{CC} \simeq t_f = 2.5$ eV, $t_{NN} = 3 \sim 4$ eV, $\epsilon_0 \simeq \epsilon_1 = -1 \sim -2$ eV. The band structure for this tight-binding model, depicted in the left panel of Fig. 5, indeed reproduces the features of that for π electrons in PAT (Fig. 1). Figure 6 shows that the wave functions at Γ on the flatband in the tight-binding model capture the features of those on the flatband in the GGA-DFT result for PAT.

We can then proceed to the question of whether the ground state is spin polarized in the presence of the Hubbard interaction, $\mathcal{H}_U = U \sum_i n_{i\uparrow} n_{i\downarrow}$. In Fig. 7 we show the phase diagram against U and ϵ_1 obtained with an exact diagonalization calculation for a 12-site (two-unit cell) Hubbard model for $t_0 = 2.5$ eV and various values of $t_{NN} = 3.0$–4.0 eV. As indicated by the inset, ϵ_0 is chosen throughout to satisfy the condition for the flatband,

$$\varepsilon - \epsilon_1 = (1 - \varepsilon)[t_{NN}^2 - (\varepsilon - \epsilon_1)^2] - t_{NN},$$
$$(\varepsilon - \epsilon_1 + t_{NN})/(1 - \varepsilon) = -t_{NN}/(\epsilon_0 - \varepsilon) - t_{NN}(\varepsilon - \epsilon_0),$$

where ε is the eigenenergy of the flatband and $t_{CN} = t_{CC} = t_0$ (= 1 here) is assumed for simplicity. We can see that we have indeed a ferromagnetic phase unless the repulsion is too strong (i.e., $U < U_c$ with $U_c = 2 \sim 5$ eV). The presence of a U_c is as expected from the above discussion for a flatband lying in between dispersive ones. Our preliminary quantum Monte Carlo calculation confirms that the two-unit cell is sufficient to roughly determine the ferromagnetic phase boundary.

Let us finally comment on the robustness of the flatband ferromagnetism. The one-electron dispersion does not have to be exactly flat to realize ferromagnetism, as confirmed from a number of studies [23,24]. Also, electron-electron interactions extending beyond the on-site do not necessarily degrade, or in some situation even induce, the ferromagnetism as has been shown for the extended

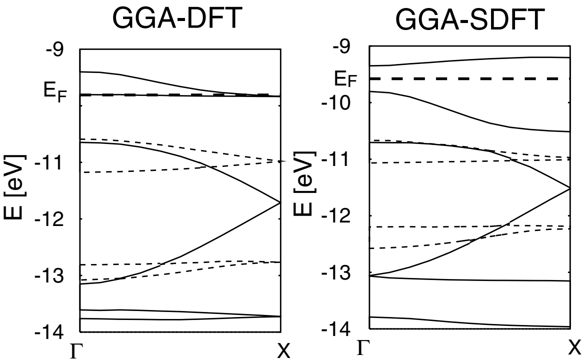

FIG. 4. Band structure of the *doped* system optimized by allowing the Peierls distortion in the GGA-DFT (left panel), and that for the antiferromagnetic state obtained with the GGA-SDFT (right panel). The solid (dotted) lines represent bands having π (σ) character.

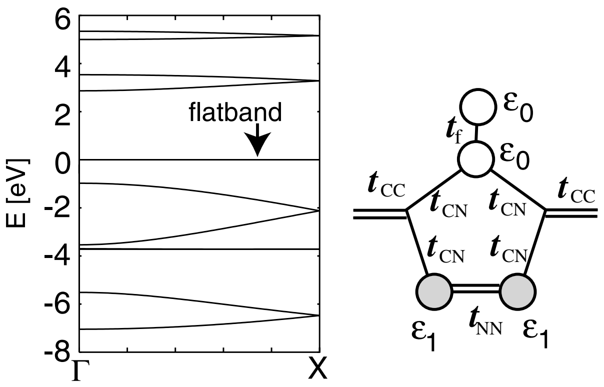

FIG. 5. The band dispersion of the tight-binding model with $\epsilon_0 = -1.43$ eV, $\epsilon_1 = -0.5$ eV, $t_{CN} = t_{CC} = t_f = 2.5$ eV, and $t_{NN} = 3.0$ eV. To facilitate comparison with Fig. 2, we have folded the band to have a two-ring unit cell.

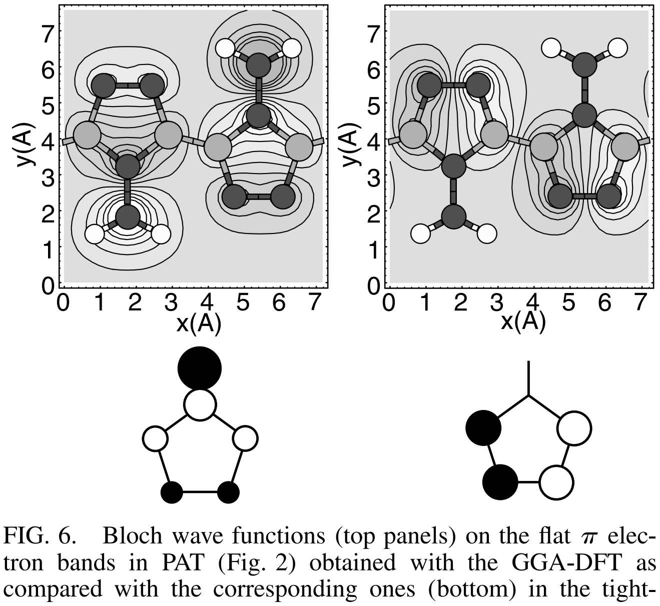

FIG. 6. Bloch wave functions (top panels) on the flat π electron bands in PAT (Fig. 2) obtained with the GGA-DFT as compared with the corresponding ones (bottom) in the tight-binding model (Fig. 5). Left/right panels correspond to the two eigenstates at Γ (which are degenerate in the folded flatband). White/black regions (or circles) represent the sign of the wave function, while the size of the circles represents the amplitude.

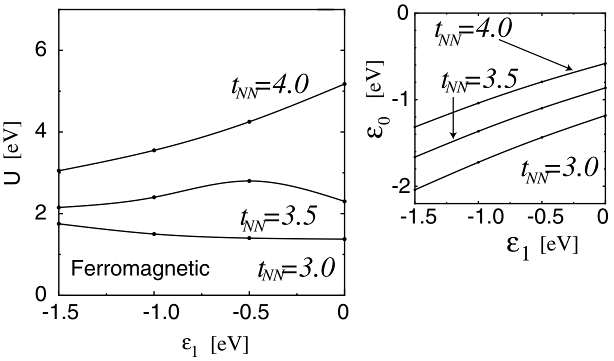

FIG. 7. Phase diagram of the Hubbard model on a lattice depicted in Fig. 5 against U and ϵ_1 for various values of t_{NN} for $t_0 = 2.5$ eV. The inset shows the relation between ϵ_1 and ϵ_0 to realize the flatband.

Hubbard model [25]. As for the doping dependence, a numerical calculation [26] indicates that the ferromagnetism survives when the flatband is shifted away from the half-filling. Therefore, we may expect that the appropriate polymers as exemplified by PAT should have ferromagnetic instabilities at low temperatures when the system is sufficiently doped in, e.g., an FET geometry. In view of a quite recent finding [6] that polythiophene may be doped with this geometry to realize superconductivity, we expect the gate-induced band ferromagnetism in plastics conceived here should be within experimental feasibility.

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[1] T. Ito, H. Shirakawa, and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. **12**, 11 (1974).

[2] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc. Chem. Commun. 578 (1977).

[3] F. Garnier, R. Hajlaoui, A. Yassar, and P. Srivastava, Science **265**, 1684 (1994).

[4] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Tailiani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, Nature (London) **397**, 121 (1999).

[5] J. H. Schön, S. Berg, C. Kloc, and B. Batlogg, Science **287**, 1022 (2000).

[6] J. H. Schön, A. Dodabalapur, Z. Bao, C. Kloc, O. Schenker, and B. Batlogg, Nature (London) **410**, 189 (2001).

[7] N. Shima and H. Aoki, Phys. Rev. Lett. **71**, 4389 (1993).

[8] E. H. Lieb, Phys. Rev. Lett. **62**, 1201 (1989).

[9] There are multiorbital ferromagnets such as TDAE-C_{60} [P.-M. Allemand *et al.,* Science **253**, 301 (1991)] or ferromagnets that exploit radicals [A. Rajca, J. Wongsri-ratanakul, and S. Rajca, Science **294**, 1503 (2001)].

[10] For reviews, see H. Tasaki, Prog. Theor. Phys. **99**, 489 (1998); A. Mielke and H. Tasaki, Commun. Math. Phys. **158**, 341 (1993).

[11] M. C. Gutzwiller, Phys. Rev. Lett. **10**, 159 (1963).

[12] J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963).

[13] J. Hubbard, Proc. R. Soc. London A **276**, 238 (1963).

[14] R. Arita, K. Kuroki, H. Aoki, A. Yajima, M. Tsukada, S. Watanabe, M. Ichimura, T. Onogi, and T. Hashizume, Phys. Rev. B **57**, R6854 (1998).

[15] Ferromagnetism will remain in a bunch of chains if the magnetic easy axis is normal to the chain.

[16] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16 533 (1996).

[17] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[18] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10 142 (1993).

[19] J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Phys. Rev. B **54**, 5586 (1996).

[20] Holes are introduced to the system with uniform negative background charge.

[21] S. Okada and A. Oshiyama, Phys. Rev. B **62**, R13 286 (2000).

[22] Note that polyaminotriazole is not a conjugated polymer, in contrast to polyacetylene, where the double bonds resonating with single bonds cause strong Peierls instability, and hence the application of DFT here is not a subtle problem. Even when the flatband is doped, holes are doped into the Mielke-Tasaki orbitals satisfying the connectivity condition, so that the localized double bonds are again absent.

[23] K. Kusakabe and H. Aoki, Phys. Rev. Lett. **72**, 144 (1994).

[24] K. Penc, H. Shiba, F. Mila, and T. Tsukagoshi, Phys. Rev. B **54**, 4056 (1996).

[25] R. Arita, Y. Shimoi, K. Kuroki, and H. Aoki, Phys. Rev. B **57**, 10 609 (1998).

[26] H. Sakamoto and K. Kubo, J. Phys. Soc. Jpn. **65**, 3732 (1996).