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A Radical Polymer as a Two-Dimensional Organic Half Metal

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Abstract: Given that half-metals are promising futuristic materials for spintronics, organic materials showing half-metal character are highly desirable for spintronic devices, not only owing to their weak spin-orbit and hyperfine interactions, but also their light and flexible properties. We predict that a two-dimensional organic 2,4,6-tri-(1,3,5-triazinyl)methyl radical polymer has half-metallic properties as well as a spontaneous magnetic ordering at ambient temperature. The quantum transmission is studied based on the nonequilibrium Green function theory coupled with density functional theory. The half-metallic property in the triazine-based polymer depends mainly on the nature of the p-band in contrast to of conventional half metals in which the nature of the d-band is more important.

Keywords: graphene • molecular modeling • organic half metals • organic electronics • radicals

Introduction

As spintronics is a most promising subject for quantum electronic devices,[1] molecular spintronics has been an important topic in chemistry.[2] One of the key issues is to find suitable materials for spintronic devices, such as spintronic quantum dots, ferromagnetic nanowires, and two- (2D) or three-dimensional (3D) half metals.[3] A complete spin-polarized current is possible in a half metal (HM),[4] which has only one type of conduction electron, either spin up or spin down.[5] Therefore, half metals have received attention as candidates of new materials with large spin-polarized carrier sources. A complete spin polarization in the electric current of HMs is probably better than that of ferromagnetic (FM) semiconductors.[1,4,6] However, most HMs are 3D inorganic systems. There have been some reports on one-dimensional (1D) and 2D HMs, such as graphene nanoribbon (GNR), under strong electric field,[4a,7] edge-modified zigzag GNR,[8] hybrid BCN nanoribbons,[9] and organometallic HMs.[3e,10] The advantage of using organic materials for spin-based electronic (spintronic) devices is that the spin relaxation length and spin lifetime are considerably longer, because of weak spin-orbit and hyperfine interactions. In addition, organic materials would be good candidates for flexible devices.[11]

High-spin organic materials (usually radicals) should be considered as candidates of organic HM materials. Mataga suggested a hypothetical high-spin triphenylmethyl radical polymer (Figure 1c).[12] However, this system is unstable because of large steric hindrance among three clustered H atoms of CH moieties. As an extension, Rajca synthesized high-spin polymers. However, such polymers were not stable under atmospheric oxygen; then, Rajca synthesized high-spin aminyl diradicals in which carbon radicals were superseded by nitrogen radicals.[13] These radicals are stable in solution and do not react with oxygen at low temperature. Recently, Bieri et al. fabricated porous graphene of 2D polyphenylene networks.[14]

Modifying the above polymers, we have predicted that a new 2D organic material, 2,4,6-tri-(1,3,5-triazinyl)methyl radical polymer, which will be abbreviated as the triazine-based radical polymer (Figure 1a and b), is stable and be ferromagnetic. The structure of the system is similar to the g-C_3N_4 polymer (a graphitic carbon nitride material).[15] In our system, the exchange interaction between spins of itinerant electrons through the conjugated system is mainly due to the Pauli exclusion principle. Then, spins between *meta*-radicals of the arene tend to be parallel, while spins between

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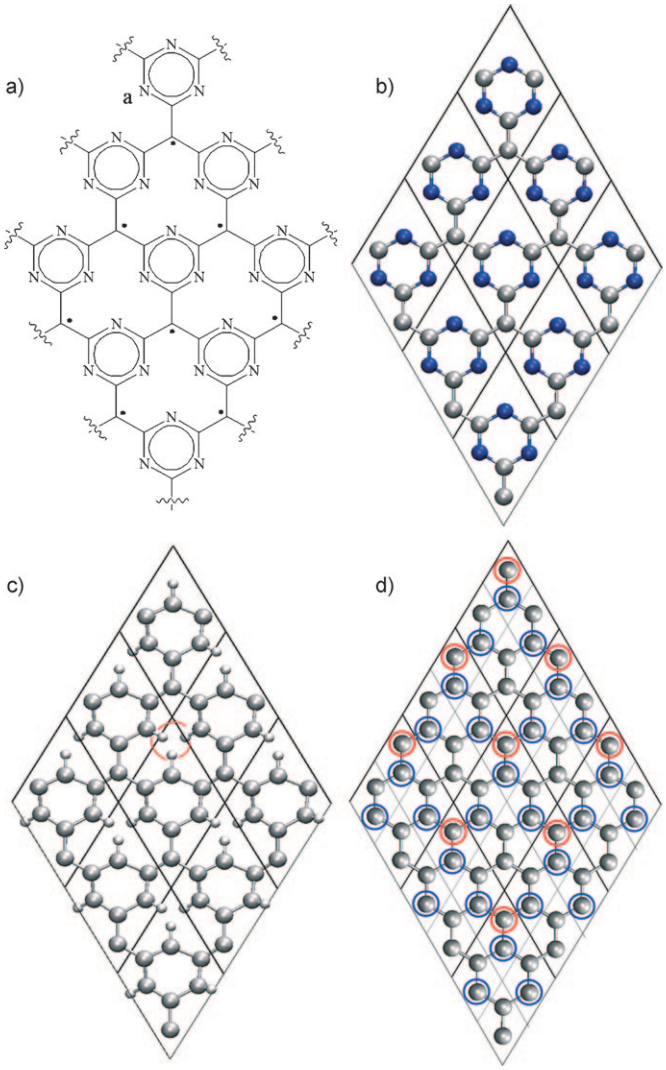

Figure 1. Schematic structures of a) the triazine-based polymer, b) its optimized lattice structure, c) the triphenylmethyl radical polymer structure, and d) graphene. Gray, white, and blue balls are carbon, hydrogen, and nitrogen atoms, respectively. The black borderlines are used to denote unit cells. Three H atoms in a red circle in c) indicate the steric hindrance between them. The triazine based polymer is on a plane, while the triphenylmethyl radical polymer has a large torsional angle due to the large steric hindrance between three clustered CHs, resulting in highly nonplanar sructure. For the triazine-based polymer, the DFT-optimized bond lengths are 1.43 Å for C−C and 1.35 Å for C−N; the bond angles are 120.8° for C-C-N, 121.6° for C-*N*-C, and 118.4° for N-C-N.

ortho/*para*-radicals are antiparallel.[16] Thus, this polymer would be a FM material and a good target material for an organic HM.

The triazine-based radical polymer can be compared with graphene, a carbon-based material, which has been a hot research topic because of its great potentials for possible applications to electronic and spintronic devices.[17] The radical polymer can be designed from graphene by making a defect of C atoms (marked in red in Figure 1 d), followed by substitution of some of C atoms for N atoms (marked in blue in Figure 1 d).

Computational Methods

To understand the triazine-based magnetic polymer, the band structure and the density of states (DOS) were analyzed by using the spin-polarized plane-wave density functional theory (DFT). The ultrasoft Vanderbilt pseudopotentials and the generalized gradient approximation (GGA) in the Vasp program[18] were used. A 7×7 k-point grid with automatic mesh for the first Brillouin zone of the unit cell and the cut off energy of 400 eV were used for geometry optimization. For the plot of DOS, we used a 45×45 k-point grid with automatic mesh using the tetrahedron method with Blöchl corrections. The band structure was drawn with 100 k-point line grids through M-Γ and Γ-K, respectively. Molecular orbital (MO) analyses were performed under the periodic boundary condition by using the Gaussian 03 suite of programs.[19] The transport phenomena of spins were studied using the Postrans program,[20] in which the non-equilibrium Green's function (NEGF) was implemented in the Siesta[21] DFT code. The graphical analysis was carried out by visual molecular dynamics[22] and the Posmol package.[23]

Results and Discussion

Upon optimizing a structure of the triazine-based radical polymer in a completely symmetry relaxed condition by using ab initio calculations, we find that the polymer is on a plane without distortion as the polymer size becomes larger, except that the edges are slightly distorted, since a small size polymer is also slightly distorted at the edges. It seems that as the system is polymerized, the steric hindrance by lone pair electrons of nitrogen atoms is reduced by delocalization.

Figure 2 shows clear half-metallic behavior in the band structure and DOS of the triazine-based radical polymer. The majority spin shows the non-metallic nature with the band gap of 2.13 eV, but the minority spin shows the conducting behavior without band-gap features. When we apply LDA + U,[24] the half metallic property is retained as long as the effective U value ($U_{\text{eff}} = U - J$, in which U and J are the effective on-site Coulomb and exchange interaction parameters, respectively) is up to 7 eV. This is owing to the fact that the band for the minority spin is very wide (larger than 3.5 eV). On the other hand, in the case of the 1,3,5-tridehydrobenzene triradical system, both majority and minority electrons are conducting. Although the radical polymer helps delocalize both majority and minority spins, the substitution of some of carbon atoms for nitrogen atoms enhances the localization of the majority spins because of the stronger interaction of electrons by the more positive charge on N than on C.

The polymer shows the half-metallic nature with a 100 % spin-polarized carrier source.[25] This is in good agreement with the quantum transmission analysis of the model system (Figure 3). The numbers of transmission channels for the majority and minority spins are 0 and 2 or 3, respectively, near the Fermi energy.

To understand the nature of the HM property and to stabilize the system, we analyzed the frontier MOs in a unit cell in Figure 4. For α-MOs (majority spin bands), the energy gap between the lowest unoccupied MO (LUMO)

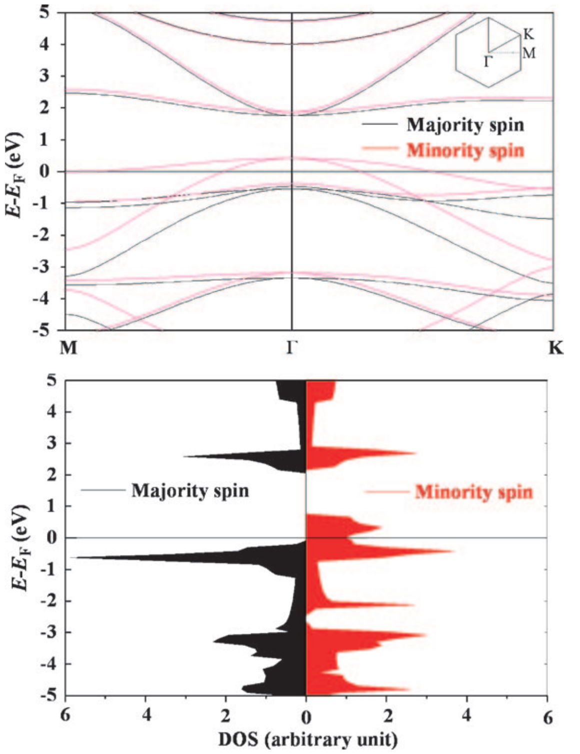

Figure 2. Band structure (top) drawn through M-Γ and Γ-K at the Brillouin zone boundary using 100 k-point line grids and DOS (bottom) carried out using a 45×45 k-point grid and a cut off energy 400 eV. The vertical axes denote the energy relative to the Fermi energy (−4.49 eV). The majority and minority spins are shown in black and red, respectively.

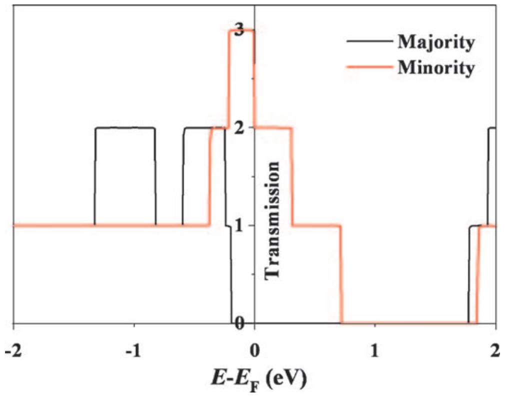

Figure 3. Quantum transmission of the triazine based polymer with respect to the energy ($E-E_F$). The black and red lines in the transmission curve denotes the majority and minority spins, respecitvely.

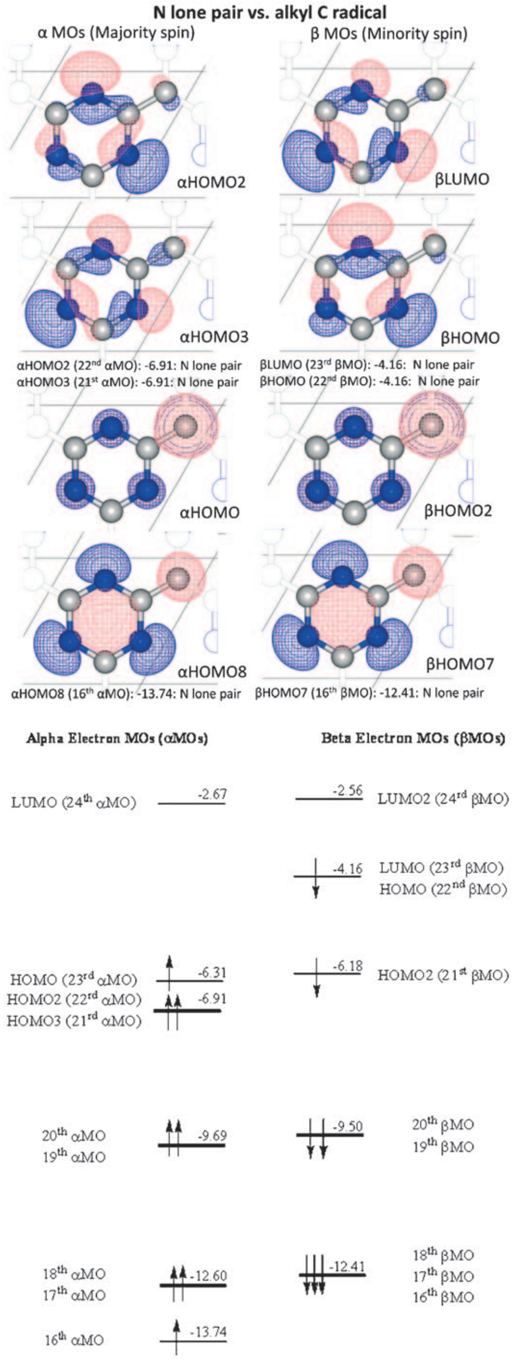

Figure 4. Frontier MOs with occupied up or down spins and unoccupied states. All energies are in eV. Gray and blue balls are C and N, respectively.

and the highest occupied MO (HOMO) is large (3.64 eV), while for β-MOs (minority spin bands) the energy gap is zero. The degenerate β-LUMO and β-HOMO (energy $E=-4.16$ eV) and two degenerate α-HOMO2 and α-HOMO3 ($E=-6.91$ eV) have the character of the N lone pairs with one nodal plane among the three p_z orbitals of three N atoms (here, HOMO*n* denotes *n*-th HOMO). One of two degenerate α-HOMO2 and α-HOMO3 or its combination forms a lone pair with β-HOMO, while the remaining orbital remains as a radical in a singly occupied α-MO (SOMO) unless the complementary β-LUMO is occupied. The character of β-LUMO indicates that the SOMO should have the same character of the N lone pairs, instead of the alkyl radical on the alkyl C atom, which is expected in this polymer system from the general chemistry concept. Indeed, the two nearly degenerate α-HOMO ($E=-6.31$ eV) and β-HOMO2 ($E=-6.18$ eV), which show the character of alkyl radical on the C atom, combine to form a lone pair in the p_z orbital of C, losing the radical property. Among three N lone pairs, one was a SOMO and one was a lone pair, both of which have the character of the N lone pairs with one nodal plane among three p_z orbitals of the three N atoms. The remaining one, which is composed of three p_z orbitals of the three N atoms without a nodal plane, should have lower energy than the other two. This one is noted from the combination of α-HOMO8 (16th α-MO, $E=-13.74$ eV) and β-HOMO7 (16th β-MO, $E=-12.41$ eV). Thus, one electron in the β-LUMO is missing, so the α-SOMO should show the complementary character of β-LUMO with an α electron. Thus, a radical with an α spin is not on an alkyl C atom, but appears with fractional density on three N atoms.

In general, radicals are localized on alkyl C atoms than on N atoms, while lone pairs of electrons are on N atoms. However, in the triazine polymer, some fractional electron density of three N atoms moves to an alkyl C atom, resulting in the closed shell of the p_z orbital of the alkyl C atom and a radical on the SOMO, composed of three p_z orbitals on three N atoms. Therefore, a radical electron is stabilized by N atoms, similar to an aminyl diradical to a certain extent.[14] In addition, the steric hindrance by the lone-pair of electrons on the N atoms is reduced as the dense electron density on the N atoms shifts to an alkyl C atom, which results in the stabilization of the polymer. The β electrons are delocalized among the N atoms through degenerate β-HOMOs and β-LUMOs, making the system electro-conductive. The MO analysis agrees with the density difference map for α and β spins in Figure 5. The majority spin density is mainly localized on N atoms (and only partly on alkyl C atoms). The minority spin density is more on the aromatic carbon atoms as compared to the majority spin density. In a more strict analysis, the HOMO–LUMO concept would not work properly for 2D polymers, owing to the band structure characteristics for which fractional occupancies of electrons would be possible. Nevertheless, the HOMO–LUMO concept is useful for the understanding of the radical stability for the polymer systems.

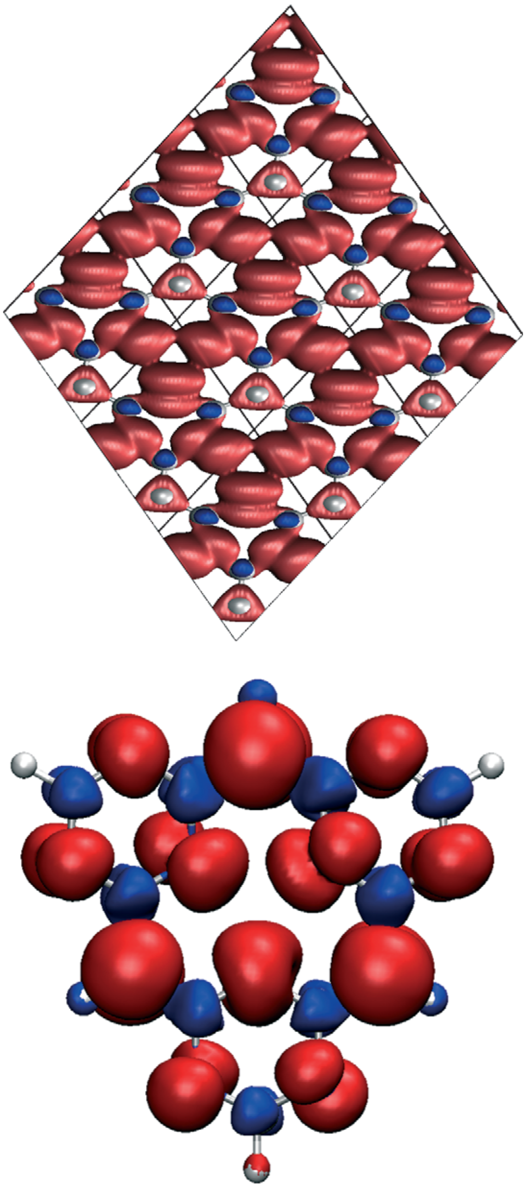

Figure 5. Density difference map for α and β spins of the 2D 2,4,6-tri-(1,3,5-triazinyl)methyl radical polymer (top) and the calix[3]triazine-6,12,18-triyl (bottom). Gray/blue/white spheres are C/N/H atoms. The black borderlines are used to denote unit cells. The isovalue scale of majority and minority spins are same. In the top panel most of the majority spin density (red) is on the N atoms and only partly on the alkyl C atoms, while the minority spin density (blue) is higher on the aromatic C atoms. The spin of a radical is delocalized over three N atoms through aromatic conjugation. The radicals form FM spin ordering. In the bottom panel the majority spin density (red) is on both alkyl C atoms and N atoms (but denser on the alkyl C atoms than on the N atoms), while the minority density is denser on the aromatic C atoms (blue). As the molecular size increases, the eventual 2D polymer (top) shows that the majority spin density is predominantly located on the N atoms rather than on the alkyl C atoms.

To compare the ferromagnetic (FM), antiferromagnetic (AM), and non-magnetic (diamagnetic, DM) ordering in the triazine-based polymer, we optimize each system of 2×2 unit cells by using a 5×5 k-point grid and a 350 eV cut off energy, and carry out single-point calculations by using the tetrahedron method with a 25×25 k-point grid. The stability is in the order of FM > AM > DM. The FM ordering is more stable than AM and DM ordering by $\approx$69.6 and 92.1 meV per unit cell, respectively. The FM ordering is still favored at room temperature (25.7 meV). Generally, it is difficult to achieve spontaneous magnetic ordering in 1D and 2D spin lattice models at finite temperature;[26] however, the triazine-based polymer should show the HM property as well as a spontaneous magnetic ordering at finite temperature. This is supported by the band analysis. The band width between the Fermi energy and the top of the first conduction band for the minority spins is $\approx$400 meV, while that between the top of the highest valence band and the Fermi energy of the majority spins is $\approx$465 meV. It means that the HM property remains unless the Fermi level shifts significantly. Thus, the HM property would be maintained at room temperature. We also estimate the Curie temperature (T_c)

using the Heisenberg model ($U=-2JS_iS_j$ and $J=3k_BT_c/2zS(S+1)$, in which J and z are the exchange integral and the number of nearest neighbors, respectively, and S_i and S_j are the electron spins of atoms i and j).[27] The molecular orbital should be considered as a magnetization unit; hence the spin magnetic moment is 1 μ_B ($S=1/2$) per unit cell according to Figure 4. If we consider this magnetic unit as an effective single site, the system becomes triangular lattice, not a honeycomb lattice. In this model, it is estimated that J is 34.8 meV and T_c is $\approx$1212 K, under the assumption that the structure does not change significantly depending on the temperature. An actual T_c of a triangular lattice tends to be 60% of the result of the mean field theory of Heisenberg model.[28] Therefore, T_c would be $\approx$730 K scaled from the result of mean field theory; hence T_c would be at least higher than room temperature.

Conclusion

In summary, the 2,4,6-tri-(1,3,5-triazinyl)methyl radical polymer is predicted to be a ferromagnetic 2D half metal at room temperature . The HM property in the triazine-based polymer depends mainly on the nature of the p-band, while conventional HMs depend on the d-band, which is distinguished into three categories[29] by the nature of HMs related to the covalency, charge transfer, and d–d band gaps. The triazine-based polymer is a half metal, and the structure would be thermally stable at very high temperatures. The designed polymer would be a good candidate for a perfect spin filter as a large magnetoresistance material, which would be useful for flexible high density memory devices and organic/polymer-based spintronics.

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[1] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger, *Science* **2001**, *294*, 1488–1495.

[2] a) W. Y. Kim, K. S. Kim, *Acc. Chem. Res.* **2009**, *42*, 111–120; b) S. Sanvito, *Nat. Mater.* **2007**, *6*, 803–804; c) A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer, S. Sanvito, *Nat. Mater.* **2005**, *4*, 335–339; d) Z. H. Xiong, D. Wu, Z. V. Vardeny, J. Shi, *Nature* **2004**, *427*, 821–824; e) W. Y. Kim, Y. C. Choi, S. K. Min, Y. Cho, K. S. Kim, *Chem. Soc. Rev.* **2009**, *38*, 2319–2333.

[3] a) S. Pramanik, C.-G. Stefanita, S. Patibandla, S. Bandyopadhyay, K. Garre, N. Harth, M. Cahay, *Nat. Nanotechnol.* **2007**, *2*, 216–219; b) L. E. Hueso, J. M. Pruneda, V. Ferrari, G. Burnell, J. P. Valdes-Herrera, B. D. Simons, P. B. Littlewood, E. Artacho, A. Fert, N. D. Mathur, *Nature* **2007**, *445*, 410–413; c) W. Y. Kim, Y. C. Choi, K. S. Kim, *J. Mater. Chem.* **2008**, *18*, 4510–4521; d) M. Diefenbach, K. S. Kim, *Angew. Chem.* **2007**, *119*, 7784–7787; *Angew. Chem. Int. Ed.* **2007**, *46*, 7640–7643; e) H. Xiang, J. Yang, J. G. Hou, Q. Zhu, *J. Am. Chem. Soc.* **2006**, *128*, 2310–2314; f) T. Nautiyal, T. H. Rho, K. S. Kim, *Phys. Rev. B* **2004**, *69*, 193404; g) M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science* **2002**, *296*, 1443–1445; h) Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, D. D. Awschalom, *Nature* **1999**, *402*, 790–792.

[4] a) Y. W. Son, M. L. Cohen, S. G. Louie, *Nature* **2006**, *444*, 347–349; b) R. A. de Groot, F. M. Mueller, P. G. van Engen, K. H. J. Buschow, *Phys. Rev. Lett.* **1983**, *50*, 2024–2027.

[5] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, T. Venkatesan, *Nature* **1998**, *392*, 794–796.

[6] V. V. Maslyuk, A. Bagrets, V. Meded, A. Arnold, F. Evers, M. Brandbyge, T. Bredow, I. Mertig, *Phys. Rev. Lett.* **2006**, *97*, 097201.

[7] T. B. Martins, A. J. R. da Silva, R. H. Miwa, A. Fazzio, *Nano Lett.* **2008**, *8*, 2293–2298.

[8] a) O. Hod, V. Barone, J. E. Peralta, G. E. Scuseria, *Nano Lett.* **2007**, *7*, 2295–2299; b) E.-J. Kan, Z. Li, J. Yang, J. G. Hou, *J. Am. Chem. Soc.* **2008**, *130*, 4224–4225.

[9] E.-J. Kan, X. Wu, Z. Li, X. C. Zeng, J. Yang, J. G. Hou, *J. Chem. Phys.* **2008**, *129*, 084712.

[10] a) L. Wang, Z. Cai, J. Wang, J. Lu, G. Luo, L. Lai, J. Zhou, R. Qin, Z. Gao, D. Yu, G. Li, W. Ning Mei, S. Sanvito, *Nano Lett.* **2008**, *8*, 3640–3644; b) P. Luo, J. Y. Lee, *J. Phys. Chem. C* **2009**, *113*, 12637–12640.

[11] a) K. Tsukagoshi, B. W. Alphenaar, H. Ago, *Nature* **1999**, *401*, 572–574; b) J. M. Kikkawa, D. D. Awschalom, *Nature* **1999**, *397*, 139–141.

[12] N. Mataga, *Theor. Chim. Acta* **1968**, *10*, 372–376.

[13] a) A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* **2001**, *294*, 1503–1505; b) A. Rajca, K. Shiraishi, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2007**, *129*, 7232–7233.

[14] N. Bieri, M. Treier, J. Cai, K. Aït-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, X. Feng, *Chem. Commun.* **2009**, 6919–6921.

[15] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J. O. Müller, R. Schlögl, J. M. Carlsson, *J. Mater. Chem.* **2008**, *18*, 4893–4908.

[16] A. Rajca, *Chem. Rev.* **1994**, *94*, 871–893.

[17] a) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666–669; b) Y. Zhang, Y.-W. Tan, H. L. Stormer, P. Kim, *Nature* **2005**, *438*, 201–204; c) Y. J. Yu, Y. Zhao, S. Ryu, L. E. Brus, K. S. Kim, P. Kim, *Nano Lett.* **2009**, *9*, 3430–3434; d) N. Tombros, C. Jozsa, M. Popinciuc, H. T. Jonkman, B. J. van Wees, *Nature* **2007**, *448*, 571–574; e) W. Y. Kim, K. S. Kim, *Nat. Nanotechnol.* **2008**, *3*, 408–412; f) K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706–710; g) S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, *5*, 574–578.

[18] a) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186; b) G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558–561; c) G. Kresse, J. Furthmüller, *Comp Mater Sci* **1996**, *6*, 15–50; d) G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251–14269.

[19] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[20] W. Y. Kim, K. S. Kim, *J. Comput. Chem.* **2008**, *29*, 1073–1083.
[21] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, D. Sanchez-Portal, *J. Phys. Condens. Matter* **2002**, *14*, 2745–2779.
[22] W. Humphrey, A. Dalke, K. Schulten, *J Mol Graphics* **1996**, *14*, 33–38.
[23] S. J. Lee, H. Y. Chung, K. S. Kim, *Bull. Korean Chem. Soc.* **2004**, *25*, 1061–1064.
[24] a) V. I. Anisimov, J. Zaanen, O. K. Andersen, *Phys. Rev. B* **1991**, *44*, 943–954; b) A. I. Liechtenstein, V. I. Anisimov, J. Zaanen, *Phys. Rev. B* **1995**, *52*, R5467–R5470; c) I. V. Solovyev, A. I. Liechtenstein, K. Terakura, *Phys. Rev. Lett.* **1998**, *80*, 5758–5761; d) S. K. Kwon, B. I. Min, *Phys. Rev. Lett.* **2000**, *84*, 3970–3973; e) S. J. Youn, B. R. Sahu, K. S. Kim, *Phys. Rev. B* **2002**, *65*, 052415.
[25] J. M. De Teresa, A. Barthélémy, A. Fert, J. P. Contour, R. Lyonnet, F. Montaigne, P. Seneor, A. Vaurès, *Phys. Rev. Lett.* **1999**, *82*, 4288–4291.
[26] N. D. Mermin, H. Wagner, *Phys. Rev. Lett.* **1966**, *17*, 1133–1136.
[27] C. Kittel, *Introduction to Solid State Physics*, 7th ed., Wiley, New York, **1996**, p. 446.
[28] N. W. Ashcroft, N. D. Mermin, *Solid State Physics*, Thomson Learning, Andover, **1976**, p. 717.
[29] C. M. Fang, G. A. de Wijs, R. A. de Groot, *J. Appl. Phys.* **2002**, *91*, 8340–8344.

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