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REGULAR ARTICL

Spin polarization properties of benzene molecule adsorbed at Fe(100) surface: first principles calculations

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Abstract: Based on density functional theory (DFT), the spin polarization properties of a benzene molecule which is adsorbed at Fe (100) surface are discussed. A variety of horizontal and vertical adsorption configurations as well as their influences on the spin density distributions is detailed studied. It is found that the interfacial orbital hybridization occurred between the 3d orbital of Fe atoms and the 2p hybridized orbital of carbon atoms. The appearance of the new interfacial coupling state make the two spin state near Fermi level no longer equal to each other. After adsorbed at Fe (100) surface, the benzene molecule is no longer spin degeneracy, an obvious spin polarization appeared. It is also found that the interfacial spin polarization for the horizontal adsorption is bigger than that of the vertical adsorption. The biggest spin polarization will be obtained when the center of the benzene ring is directly placed above the Fe atom.

AMS subject classifications: 37J55, 78A25

Key words: Organic spintronics; Spinterface; Spin polarization; Adsorption

1. Introduction

In the past few decades, a significant progress in the study of organic semiconductors is their applications in spintronics. Organic semiconductors have weak spin orbit coupling and weak hyperfine interactions, which are contributed to the spin polarized injection and transportation. Due to the size diversity and the variety of organic molecules, it is possible to

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produce high quality and low cost information equipments. Based on organic molecular devices, the study of its spin injection, spin polarized transportation, spin storage and spin detection have become hot topics in today's research field of spintronics[1-4].

The properties of ferromagnetic/organic interface and its influence on the device functionalities have attracted people's interest in organic spintronics[5-16]. In 2002, Dediu *et al.* used $La_{0.3}Sr_{0.7}MnO_3$ (LSMO) as spin polarized electron donors and they studied the spin polarized injection and transportation in the structure of LSMO/T6/LSMO system[5]. Xiong *et al.* made an organic spin valve device of Co/Alq3/LSMO in 2004, in which the magnetic resistance reached to 40% at low temperature[6]. From then on, people widely studied the properties of organic magnetic devices both theoretically and experimentally. The influence of different electrodes, different organic materials and different external conditions on the spin polarization properties as well as the mechanisms are discussed[7]. For example, Sun *et al*. studied the adsorption properties of pentacene on the Fe(100) surface experimentally and theoretically.The spin density distributions and the plane-averaged density of states at the vacuum side are computed, from which they concluded that the spin polarization is negative at the donated molecular orbital and positive at the back donated orbital close to the Fermi level[8,9]. Nicolae Atodiresei *et al.* designed the local spin polarization by adsorbing organic molecules contain $\pi(p_z)$ electrons onto a magnetic surface[10]. Souraya Goumri-Said *et al*. investigated the spin polarization at the interface between Fe(100) and a benzene for two positions of the organic molecule, which is planar and perpendicular respecting to the substrate[11]. Xuhui Wang *et al*. investigated the spin polarization properties at the interface between a thiophene molecule and Co substrate by using the ab initio calculations. They found that the reduced symmetry in the thiophene molecule leads to a strong spatial dependence of the spin polarization[12]. Ding Yi *et al.* also selected some typical adsorption configurations in benzene/Co system to reveal the spin polarization properties by using first-principles calculations [13].

In experiments, the molecular beam epitaxial and chemical vapor deposition methods are usually used to fabricate organic devices, so there are randomness between the organic molecules and metal electrode contacts. On the other hand, there are plenty of experimental evidences had already showed that the organic molecules can be spin polarized when they are adsorbed to the metal contacts, and also the spin polarization properties can be modified by changing the different contact configurations[14-16]. Therefore, it is interesting to make clear why the different adsorption configurations can affect the spin polarization properties between the organic molecules and the ferromagnetic contacts. In this article, benzene molecule/Fe electrode organic component is selected as the model system to study the interface spin polarization properties. The benzene molecule is one of the most popular small organic molecules which are used in the research field of spinterface[17-25].

Compared with other small organic molecules, the benzene molecule is more easily to be obtained in experiments, and it is relatively stable. The benzene molecule has high symmetry, and the interactions of the carbon *p* orbital form a domain large π bond in the direction of the z axis, which make benzene molecule easy to interact with electrode atoms and easy to adsorption[26]. For the electrode, the spin polarization of the Fe is higher than that of Co and Ni, and also the benzene molecule/Fe surface system has been achieved experimentally[27,28], so Fe is chosen as the electrode in our study. Detailed research are needed for the influences of the different horizontal and vertical adsorption configurations on the spin density distribution at the surface of benzene/Fe structure. All possible structures are optimized[29-34] and the spin polarization properties are discussed based on the density functional theory. The organization of the article are as follows: section 2 gives the theoretical model and calculation method, results and discussions are shown in section 3, and finally a summary is given in section 4.

2. Computational Methods

The structure is shown in **Figure. 1**. Seven layers of Fe atoms are chosen as the electrode and a benzene molecule is placed on the Fe(100) surface. The top view and the side view after adsorption are all included in the figures. Diagram mainly includes five kinds of configurations. In **Figure.1 (a)**, the center of the benzene ring is directly placed above the Fe atom. In **Figure (b)**, one of the carbon atoms in the benzene ring is placed at the top of Fe atoms. **In Figure (c)**, one of the hydrogen atoms in the benzene ring is placed at the top of Fe atoms. **In Figure (d)** and **(e)**, the hydrogen atom is adsorbed at the top site and the bridge site of the Fe atoms, respectively.

We adopt VASP package which based on density functional theory to pursue the first principles calculations[35]. A 15Å vacuum space is introduced in the vertical direction [10]. The interactions between electron and nucleus are described by the projector augmented wave pseudo-potential method (PAW). The exchange correlation potential is considered by using Perdew-Burke-Ernzerhof generalized gradient approximation (GGA), which is widely used in the calculation of molecular adsorption on metal surfaces[36]. The energy cutoff is set to 500eV in each calculation. The structural relaxations continue until the forces on each atom are less than 0.02eV/A [10]. K-point samples are 3*3*1. We first relax the five kinds of structures to get the ground states. During the relaxation, all of the atoms are set to free. After the structure optimizations, the spin-dependent density of states (DOS) will be calculated. The charge density distributions and the spin density distributions will also be presented and analyzed.

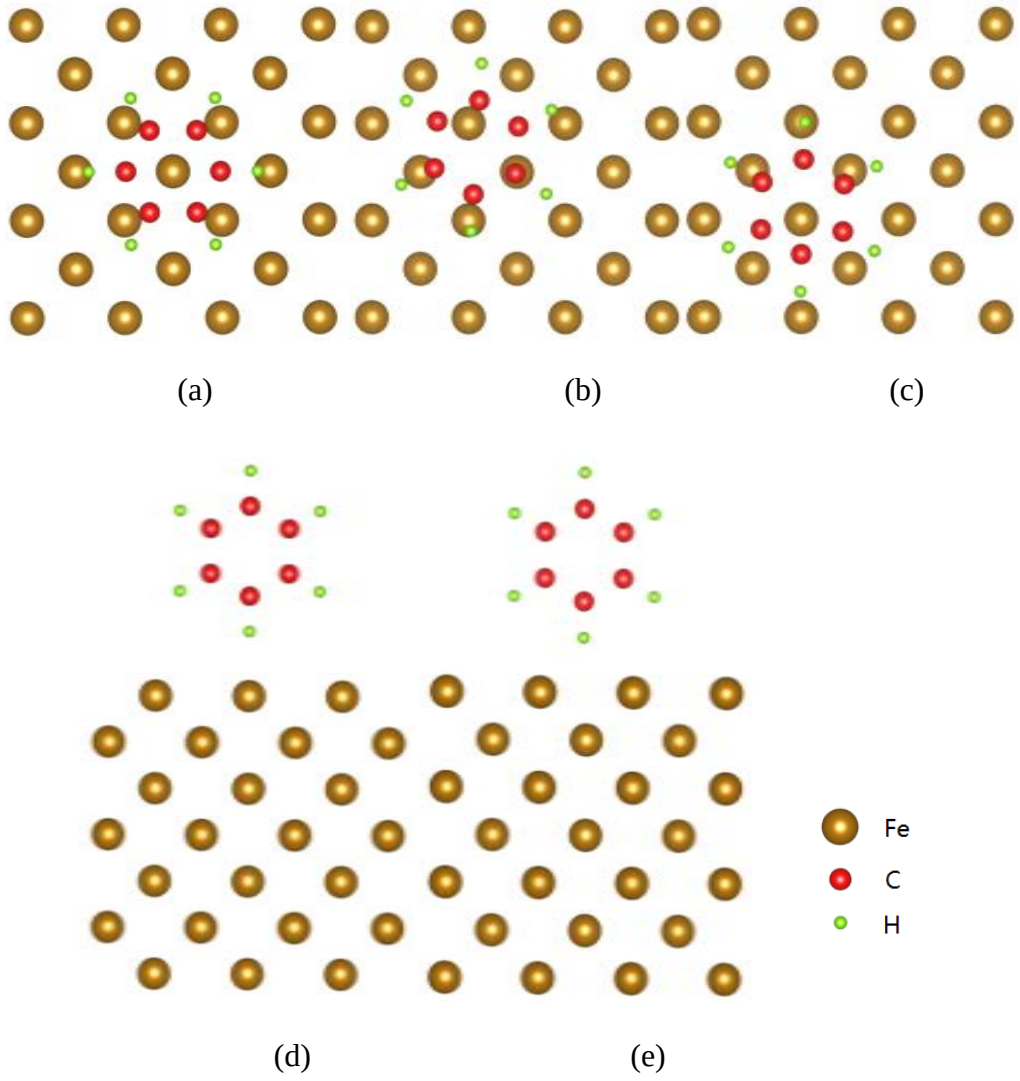

Figure 1: Schematics of the benzene molecule/Fe contact configurations. (a), (b), and (c) are the top views of horizontal adsorptions, whereas (d) and (e) are the side views of vertical adsorptions.

3. Results and discussion

Figure 1 shows the original structure of the five types of adsorption configurations. After structure optimizations are completed, the benzene molecule deformations occurred in the case of the horizontal adsorptions. By calculating the total energy of the system, we found that the horizontal adsorption structures are more stable than those of the vertical structures. The benzene molecule is more likely to interact with the electrode in the case of horizontal

adsorptions than that of the vertical adsorptions, and so the spin polarization properties will different which also can be seen from the density of states (DOS) in **Figure 2**. It is well known that the isolated benzene molecule is spin degeneracy. After contacted with the Fe electrode, the benzene molecules become spin polarized. Figure 2 gives the projected density of states (PDOS) of the carbon atoms in the benzene ring for the five different configurations. From the data near the Fermi energy in **Figure 2 (a), (b)**, and **(c)**, it is clear that the PDOS of the two spin species are not the same; rather, there is splitting between spin-up and spin-down carriers, which means that the benzene molecules are spin-polarized. The spin polarization is come from the *p-d* orbital coupling between the benzene molecule and the electrode. Also we can find that it is the p_z orbital which contributes the most to the spin polarization. Among the three configurations, we can see that the case of **Figure 2 (a)** has the biggest splitting, which means that people will get the biggest spin polarization when the center of the benzene ring is directly placed above the Fe atoms, although this is not the most stable structure. Near the Fermi level the achieved spin polarization is about 47%, in which the spin polarization is defined as : $P=(n_{\uparrow}-n_{\downarrow})/(n_{\uparrow}+n_{\downarrow})$, where $n_{\uparrow}$ and $n_{\downarrow}$ are the numbers of the carriers for spin up and spin down, respectively. For vertical adsorptions of **Figure (d)** and **(e)**, the spin splitting near the Fermi energy are small, which means that the benzene molecules in these two cases are not obviously spin polarized. So it is better to get spin polarization for benzene molecules when they are horizontally adsorbed at Fe(100) surface than those of the vertical adsorptions.

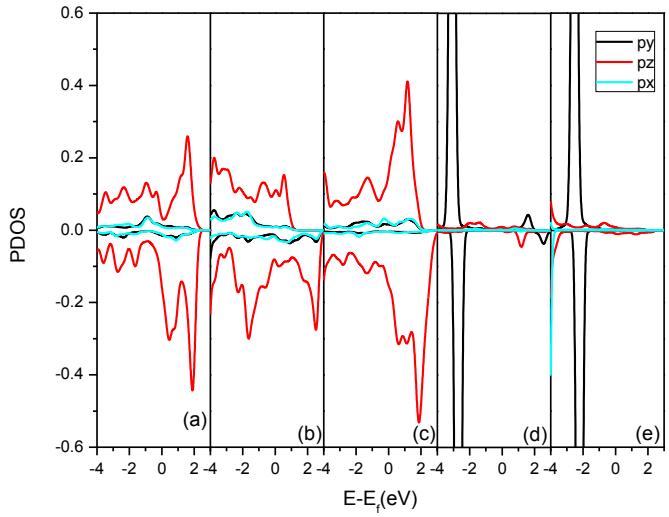

Figure 2: Projected density of states (PDOS) of the carbon atoms in the benzene ring for the five different configurations.

The spin density distributions of the system are shown in **Figure 3**. Red represents

spin up which accounts for a major role, blue corresponds to the case when spin down is the main role. It is found from the figure that the spin density is not equally distributed in the benzene molecule in **Figure (a), (b)**, and **(c)**, so there are spin polarization in the molecule. The structure is the most stable one when one of the carbon atoms in the benzene ring is placed at the top of Fe atoms, however, the spin polarization in this case is lower than that when the center of the benzene ring is directly placed above the Fe atoms, which is in consistent with the results in **Figure 2**. However, there are no obvious spin density distributions in **Figure (d)** and **(e)**, which corresponds to the vertical adsorptions. The origin of the spin polarization is the charge transfer between the benzene molecule and the electrode. Coulomb interactions between the transferred charges and the carbon atoms in benzene molecule make the molecular structure changes differently, so the benzene molecules become spin-polarized.

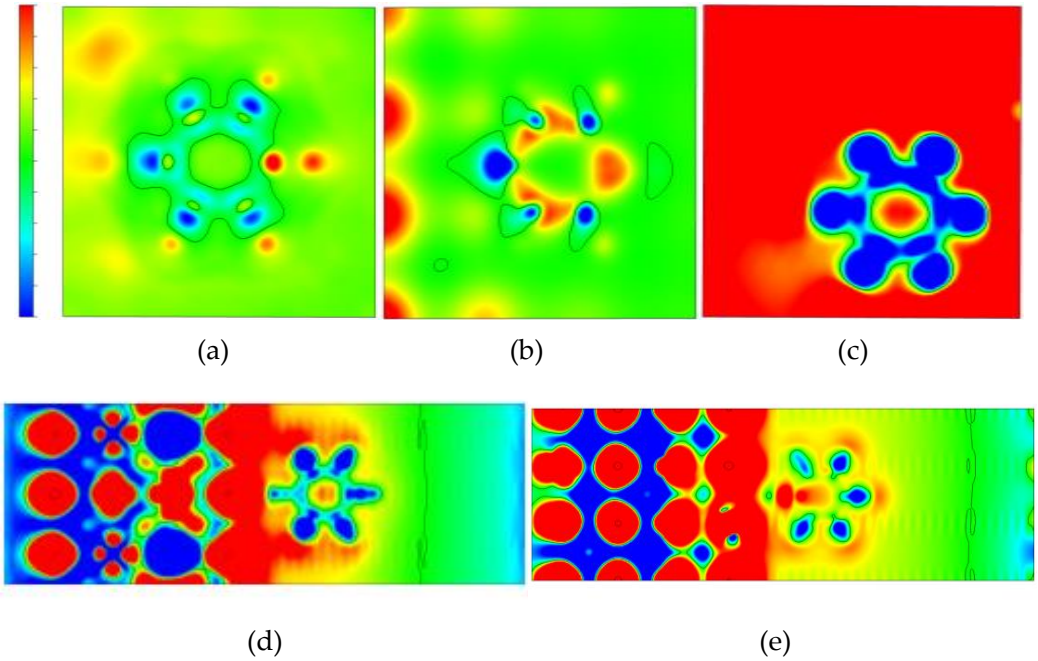

Figure 3: Spin density distributions for the five different adsorption configurations.

We also give the charge density distributions, which are shown in **Figure 4**. Red stands for gaining electrons, blue represents for losing electrons. It is clear that there is charge transfer between the benzene molecule and the Fe electrode in **Figure (a), (b)** and **(c)**, which corresponds to the horizontal adsorptions. The charge density in the benzene molecule is not equally distributed, which means that different atoms in benzene molecule have different abilities to gain or lose electrons. After the charge transfer between the benzene molecule and the electrode, there exist Coulomb interactions between the transferred additional

charges and the carbon atoms in the benzene molecule, consequently the molecular structure changes will be different. For **Figure (d)** and **(e)**, there are no obvious charge transfers, so the molecular structure nearly not changed, and the benzene molecule is nearly not spin-polarized. These results are in consistent with those in the above figures.

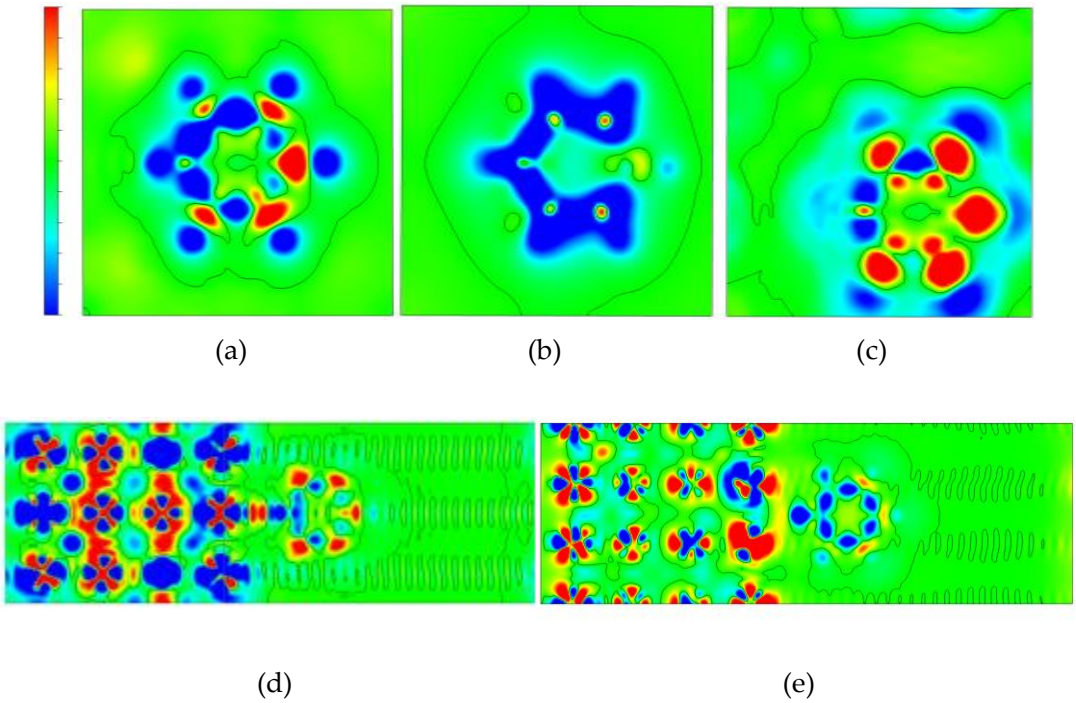

Figure 4: Charge density distributions for the five different configurations.

4. Conclusion

Different structure configurations induce different spin polarization properties when benzene molecule is adsorbed at ferromagnetic Fe (100) surface. Based on the DOS as well as the spin density distributions, it is found that the molecule's spin polarizations for horizontal adsorptions are bigger than those of the vertical adsorptions. The biggest spin polarization will be obtained when the center of the benzene ring is directly placed above the Fe atom. There are charge transfer between the benzene molecule and the Fe atoms. The spin polarization of the benzene molecule is originated from the interfacial orbital hybridization between the *3d* orbital of Fe atoms and the *2p* hybridized orbital of carbon atoms. The spin polarization properties could be tuned by changing the adsorption configurations, which is favorable for the building of molecular spintronic devices[37].

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References

[1] V. A. Dediu, L. E. Hueso, I. Bergenti and C. Taliani, Spin routes in organic semiconductors, Nature Mater. 8(2009) 707.

[2] W. J. M. Naber, S. Faez, and W. G. van der Wie, Organic spintronics, J. Phys. D 40(2007) R205.

[3]S. Sanvito, and I. Tadaaki, Molecular spintronics, Chem. Soc. Rev. 40(2011) 3336.

[4] Y. H. Zheng, and F. Wudl, Organic spin transporting materials: present and future, J. Mater. Chem. A, 2 (2014) 48.

[5] V. Dediu, M. Murgia, F. C. Mataeotta, C. Taliani, and S. Barbanera, Room temperature spin polarized injection in organic semiconductor , Solid State Commun. 122(2002) 181.

[6] Z. H. Xiong, D. Wu, Z. V. Vardeny and J. Shi, Giant magnetoresistance in organic spin valves , Nature. 427(2004) 821.

[7] D. Sun, L. Yin, C. Sun H. Guo, Z. Gai, X. G. Zhang, T. Z. Ward, Z. Cheng, and J. Shen, Giant magnetoresistance in organic spin valves, Phys. Rev. Lett. 104(2010) 236602.

[8] T. Suzuki, M. Kurahashi, X. Ju and Y. Yamauchi. Adsorption structure and spin polarization of pentance on a magnetized Fe(100) substracte:SPMDS and ERDA study, Surf. Sci. 549(2004) 97.

[9] Y. Yamauchi, M. Kurahashi, Z. P. Wang, and S. Entani, Ab initio study of pentacene on the Fe(100) surface, Surf. Sci. 602(2008) 1191.

[10] N. Atodiresei, J. Brede, P. Lazić, V. Caciuc, G. Hoffmann, R. Wiesendanger, and S. Blügel, Design of the Local Spin polarization at the organic ferromagnetic interfaces, Phys. Rev. Lett. 105(2010) 066601.

[11] G. S. Souraya, B. K. Mohammed, M. Aurélien, and S. Udo, Spin-polarization reversal at the interface between benzene and Fe(100), J. Appl. Phys. 113(2013) 013905.

[12] X. Wang, Z. Zhu, A. Manchon, and U. Schwingenschlögl, Peculiarities of spin polarization inversion at a thiophene/cobalt interface, Appl. Phys. Lett. 102(2013) 111604 .

[13] D. Yi, Z. Wu, L. Yang, Y. Dai, and S. J. Xie, Spin polarization of organic molecules at the ferromagnetic surfaces, Acta Phys. Sin. 64(2015) 187305.

[14] A. Hashmi, and J. Hong, Magnetic properties of graphene/BN/Co(111) and potential spintronics, J. Magn. Magn. Mater. 355(2014) 7.

[15] M. Kepenekian, J. P. Gauyacq, and N. Lorente, Difficulties in the ab initio description of electron transport through spin filters, J. Phys. Condens. Mat. 26(2014) 104203.

[16] K. Ulman, S. Narasimhan, and A. Delin, Tuning spin transport properties and molecular

magnetoresistance through contact geometry, J. Chem. Phys. 140(2014) 044716.

[17] S. Sanvito, Molecular spintronics: The rise of spinterface science, Nat. Phys. 6(2010) 562.

[18] X. Sun, M. Kurahashi, A. Pratt, and Y. Yamauchi, First-principles study of atomic hydrogen adsorption on Fe3O4(100), Surf. Sci. 605(2011) 1067.

[19] P. Lazic, V. Caciuc, N. Atodiresei, M. Callsen, and S. Blüggel, First-principles insights into the electronic and magnetic structure of hybrid organic-metal interfaces, J. Phys. Condens. Mat. 26(2014) 263001.

[20] X. Sun, B. Wang, A. Pratt, and Y. Yamauchi, Magnetic moment enhancement and spin polarization switch of the manganese phthalocyanine molecule on an IrMn(100) surface, J. Chem. Phys. 141(2014) 034703.

[21] Z. Sun, Y. Zhan, S. Shi, and M. Fahlman, Energy level alignment and interactive spin polarization at organic/ferromagnetic metal interfaces for organic spintronics, Org. Electron. 15(2014) 1951.

[22] D. Sun, E. Ehrenfreund, and Z. V. Vardeny, The first decade of organic spintronics research, Chem. Commun. 50(2014) 1781.

[23] F. J. Yang, S. X. Han, and S. J. Xie, Progress in organic spintronics, Chin. Phys. B, 23(2014) 058106.

[24] M. Galbiati, S. Tatay, C. Barraud, A. V. Dediu, and F. Petroff, Spinterface: Crafting spintronics at the molecular scale, MRS Bull. 39(2014) 602.

[25] Y. H. Zheng, and F. Wudl, Organic spin transporting materials: present and future, J. Mater. Chem. 2(2014) 48.

[26] S. Caliskan, A. Laref, Spin transport properties of n-polyacene molecules (n = 1–15) connected to Ni surface electrodes: Theoretical analysis, Sci Rep-uk. 4(2014) 7363.

[27] S. W. Shi, Z. Y. Sun,B. P. Amilcar, P. Graziosi, X. Li, X. J. Liu, L. Hueso, V. A. Dediu, Y. Luo, and M. Fahlman, Hybrid Interface States and Spin Polarization at Ferromagnetic Metal–Organic Heterojunctions: Interface Engineering for Efficient Spin Injection in Organic Spintronics, Adv. Funct. Mater. 24(2014) 4812.

[28] K. V. Raman, N. Atodireset, and J. S. Moodera, Tailoring ferromagnet-molecule interfaces: towards molecular spintronics , SPIN. 4(2014) 1440014.

[29] S. W. Jiang, P. Wang, S. C. Jing, B. B. Chen, M. Wang, Z. S. Jiang, and D. Wu, Fabrication of lateral organic spin valves based on La0.7Sr0.3MnO3 electrodes, SPIN. 4(2014) 1440008.

[30] S. Fahrendorf, F. Matthes, D. E. Bürgler, C. M. Schneider, N. Atodiresei, V. Caciuc, S. Blügel, C. Besson, and P. Kögerler, Structural integrity of single bis(phthalocyaninato)-neodymium(III) molecules on metal surfaces with different reactivity, SPIN. 4(2014) 1440007.

[31] S. W. Jiang, B. B. Chen, P. Wang, Y. Zhou, and Y. J. Shi, Voltage polarity manipulation of the magnetoresistance sign in organic spin valve devices, Appl. Phys. Lett. 104(2014) 262402.

[32] W. Fu, P. Makk, R. Maurand, and M. Brauninger, Large-scale fabrication of BN tunnel barriers for graphene spintronics, J. Appl. Phys. 116(2014) 074306.

[33] K. B. Dhungana, and R. Pati, Giant amplification of tunnel magnetoresistance in a molecular junction:

Molecular spin-valve transistor, Appl. Phys. Lett. 104(2014) 162404.

[34] S. Majumar, S. Dey, H. Huhtinen, J. Dahl, M. Tuominen, P. Laukkanen, S. V. Dijken, and H. S. Majumdar, Comparatives study of spin injection and transport in Alq3 and Co-phthalocyanine-based organic spin valves, SPIN. 4(2014) 1440009.

[35](a)G. Kresse, and J. Hafner, Ab initio molecualr dynamics for liquid metals, Phys. Rev. B, 47(1993) 558.
(b)G. Kresse, and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B, 54(1996)11169.

[36] J. F. Ren, Y. R. Zhang, X. B. Yuan et al. Density functional Theory Calculations of Charge Induced Spin Polarization in Pentacene, Chin. J. Chem. Phys. 27(2014) 617.

[37] C. Boehme, and J. M.Lupton, Challenges for organic spintronics, Nat. Nanotechnol, 8(2013) 612.