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Spin transport of dibenzotetraaza[14]annulene complexes with first row transition metals

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Based on spin-polarized first-principles density functional theory in conjunction with nonequilibrium Green's function method, the spin transport properties of transition metal (TM)-dibenzotetraaza[14]annulene (DBTAA) complexes (TM = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) sandwiched between two Au electrodes are investigated. The results show that Fe- and Co-DBTAA can display perfect spin filtering behavior in a wide bias voltage region. Moreover, it is found that the connected position of anchoring group on the complexes affect significantly the spin filtering efficiency. The observed spin filtering behavior is explained by the spin-resolved transmission spectrum and molecular projected self-consistent Hamiltonian state analyses.

1. Introduction

Molecular electronics has been a very active field of research since it offers a promising possibility to solve the miniaturization problem of traditional silicon-based devices^{1,2}. Many novel and promising physical properties, including single-electron characteristics³, rectifying^{4,5}, switching^{6,7}, negative differential resistance (NDR)^{8,9}, field effect transistors¹⁰, *etc.*, have been demonstrated in various kinds of molecular systems. On the other hand, spintronic devices (the study of them is called spintronics) have many excellent properties such as decreasing the power consumption, increasing data processing speed, enhancing integration densities^{11,12}. Generally, a pure and coherent spin state is required for the operation of these spintronic devices. Such a spin state can be achieved by the use of half metals-based spin filters, in which one spin transport channel is conducting and the opposite one is insulating. Compared with their inorganic counterparts, half-metals based on magnetic molecules are preferable for spintronic device applications due to the fact that they typically have weak spin-orbit interactions, weak hyperfine interactions, and consequently long spin-relaxation times as well as their mechanical flexibility and chemical versatility^{13,14}. In this context, an invigorated research field of molecular spintronics, uniting the advantages of molecular electronics with the benefits of spintronics, emerges.

Among many potential magnetic molecules, the transition metal (TM)-coordination complexes have been of special interest due to their geometric, electronic, and magnetic properties can be effectively modulated by varying the central TM atoms and noninnocent ligands^{15,16}. Shen *et al.* investigated

the spin transport properties of TM-phthalocyanine molecules (TM = Mn, Fe, Co, Ni, Cu, and Zn) connected to two armchair carbon nanotube (ACNT) electrodes and found that only Mn- and Fe-phthalocyanine can function as good spin filters¹⁷. Cho *et al.* demonstrated that a one-dimensional Cr-porphyrin array sandwiched between two gold electrodes has the potential to be a spin filter¹⁸. Zeng and Chen investigated the spin transport properties of multifunctional Mn-porphyrin-based molecular spintronic devices constructed by two Mn-porphyrin molecules linked by *p*-phenylene-ethynylene group with gold electrodes, and found spin-filtering, magnetoresistance, and NDR behaviors¹⁹. Huang *et al.* found that three kinds of planar four-coordinate Fe complexes with different noninnocent ligands couple to two ACNT electrodes can act as good spin filters²⁰. Peng *et al.* investigated the spin transport properties of TM-salophens (TM = Co, Fe, Mn, Ni) sandwiched between two gold electrodes, and demonstrated that only Co-salophen can function as an efficient spin filter²¹.

Recently, dibenzotetraaza[14]annulene (DBTAA) molecule attracts considerable attention.^{22,23} Similar to porphyrin and phthalocyanine, the cavity in DBTAA can readily bind various metal atoms. Van der Putten *et al.* tested Co-DBTAA as molecular oxygen reduction catalyst and found its catalytic activities²⁴. Sun *et al.* demonstrated Fe-DBTAA was more active than Fe-porphyrin and Fe-phthalocyanine in relation to the molecular oxygen bond²⁵. Especially, Whyte *et al.* prepared a series of planar Co-, Ni-, and Cu-DBTAA complexes, and studied their electronic and magnetic properties²⁶. However, up to now, the possibility of adopting TM-DBTAA for spintronic device applications has rarely been reported. In the present work, by using the nonequilibrium Green's function (NEGF) formalism combined with density functional theory (DFT), we investigate systematically the spin transport properties of DBTAA complexes involving first row TMs (TM = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu), which are coupled to two semi-

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infinite gold electrodes. The results show that only Fe- and Co-DBTAA can function as perfect spin filters in a wide bias voltage region. Moreover, the spin filtering efficiency is found to be dependent significantly upon the connected position of anchoring group on the complexes.

The remainder of this paper is organized as follows. In Section 2, we briefly describe the simulation model and the computational method. In Section 3, we present the results with associated discussions, and finally a short summary is given in Section 4.

2. Model and method

We first optimize the structures of free thiol (SH) group capped TM-DBTAA (TM = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) complexes by using the DFT method. These optimized complexes are then bonded to two (4×4) Au(111) electrodes *via* terminal sulfur atom since the SH group would lose its hydrogen atom upon adsorption to metal surface²⁷. The sulfur atom is chosen to be located at the hollow site of each Au surface as this is more energetically favorable than the other absorption sites²⁸, and the initial perpendicular distance (*d*) between the sulfur atom and the Au surface is set to 1.9 Å, which is a typical Au-S distance^{29,30}. Thus, we obtain eight molecular junctions M1, M2, M3, M4, M5, M6, M7 and M8 with TM = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, respectively. As shown in Fig. 1, all these molecular junctions can be divided into three regions: the left electrode, the scattering region and the right electrode. Each electrode contains three Au(111) layers, while the scattering region includes the TM-DBTAA complexes and portions of two electrodes to take into account of the molecule-electrode coupling and the electrode screening effect. All the structures are then fully relaxed until the force tolerance on each atom of 0.05 eV/Å is achieved while the electrode Au atoms are kept fixed in their bulk positions.

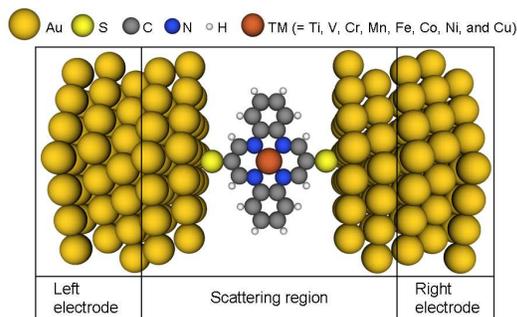


Fig. 1 Schematic illustration of the molecular junction under study, in which the TM-DBTAA complex is sandwiched between two Au electrodes through terminal S atoms symmetrically. TM = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu corresponds to models M1-M8, respectively. Atomic species are shown in golden for Au, yellow for S, gray for C, blue for N, white for H, and brown for TM atom.

The geometric optimizations of considered isolated molecules and junctions and the sequent spin-resolved electron transport properties are performed by a developed first-principles software package Atomistix Toolkit (ATK)³¹⁻³⁴, which is based on the spin-polarized DFT combined with NEGF method. In our calculations, the single- ζ

plus polarization (SZP) basis set for the valence electrons of Au atoms and the double- ζ plus polarization (DZP) basis set for the valence electrons of all the other atoms are adopted to achieve a balance between the calculation efficiency and accuracy. The core electrons are described by the norm-conserving Troullier-Martins pseudopotentials³⁵ and the exchange-correlation potential is treated at the level of spin-polarized generalized gradient approximation (GGA), with the form of Perdew-Burke-Ernzerhof (PBE)³⁶. Moreover, the Brillouin zone is sampled using a Monkhost-Pack³⁷ *k*-mesh of (3, 3, 100) and the cutoff energy is set to 200 Ry. The spin-resolved current through the system is calculated using the Landauer-Büttiker formula³⁸

$$I_{\sigma} = \frac{e}{h} \int T_{\sigma}(E, V) [f_L(E - \mu_L) - f_R(E - \mu_R)] dE, \quad (1)$$

where σ represents α - (spin-up) and β -spin (spin-down), e is the electron charge, h is the Planck's constant, $f_{L/R}$ is the Fermi-Dirac distribution function for the left/right electrode, $\mu_{L/R} = E_F \pm eV/2$ is the electrochemical potential of the left/right electrode, E_F is the Fermi level of the system which has been set to be zero in our calculations, and the energy region $[\mu_L, \mu_R]$ contributing to the current integral is referred to as the bias window. $T_{\sigma}(E, V)$ is the spin-resolved transmission function defined as

$$T_{\sigma} = \text{Tr}[\Gamma_L G^R \Gamma_R G^A]_{\sigma}. \quad (2)$$

where $G^{R/A}$ is the retarded/advanced Green's function of the central region and $\Gamma_{L/R}$ is the coupling matrix of the left/right electrode.

3. Results and discussion

First we investigate the atomic and electronic structure of the TM-DBTAA complexes. Table 1 presents the optimized average bond length between TM atom and the adjacent four N atoms ($d_{\text{TM-N}}$), the distance between TM atom and the N_4 plane of DBTAA ($d_{\text{TM-N}_4}$), as well as the calculated eigenenergies of HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), and HOMO-LUMO gap (HLG) for α - and β - electrons. Clearly, all TM atoms are found to be in the same N_4 plane of DBTAA, except for the case of Ti-DBTAA in which the Ti atom is pushed out of the N_4 plane with a distance of ~ 0.43 Å. Moreover, one can see that the energy levels of all TM-DBTAA complexes except Ni-DBTAA are spin-split.

Table 1 Optimized average bond length between TM atom and the adjacent four N atoms ($d_{\text{TM-N}}$), the distance between TM atom and the N_4 plane of DBTAA ($d_{\text{TM-N}_4}$). The length unit is Å. Calculated eigenenergies of HOMO, LUMO, and HOMO-LUMO gap (HLG) for α and β - electrons. The energy unit is eV.

Complex	$d_{\text{TM-N}}$	$d_{\text{TM-N}_4}$	α -HOMO	α -LUMO	α -HLG	β -HOMO	β -LUMO	β -HLG
Ti-DBTAA	2.045	0.43	-0.270	0.271	0.541	-1.415	0.410	1.825
V-DBTAA	1.995	0.00	-0.377	0.377	0.754	-1.107	0.594	1.701
Cr-DBTAA	1.985	0.00	-0.760	0.760	1.520	-0.872	0.842	1.714
Mn-DBTAA	1.933	0.00	-1.247	0.688	1.935	-0.314	0.314	0.628
Fe-DBTAA	1.904	0.00	-1.142	0.844	1.986	-0.512	0.512	1.024
Co-DBTAA	1.875	0.00	-0.830	0.841	1.671	-0.250	0.250	0.500
Ni-DBTAA	1.880	0.00	-0.597	0.595	1.192	-0.597	0.595	1.192
Cu-DBTAA	1.983	0.00	-0.629	0.893	1.522	-0.863	0.629	1.492

Table 2 presents the spin multiplicities ($2S+1$) of all TM-DBTAA complexes and the excess α -electrons in TM-DBTAA complexes (N_{complex}), in TM atoms (N_{TM}), and in $3d$ orbitals of TM atoms (N_{3d}). As one can see, the optimized isolated Cr-DBTAA has the quintet ground state (GS), V- and Mn-DBTAA have the quartet GS, Ti- and Fe-DBTAA have the triplet GS, Co- and Cu-DBTAA have the doublet GS, and Ni-DBTAA has the singlet GS, respectively. Since there is no any unpaired electron, it is difficult for Ni-DBTAA to give rise to good spin filtering behavior. Besides, it is evident that the spin multiplicities are determined by the N_{TM} , especially by the N_{3d} , *i.e.*, the filling of $3d$ orbitals of those TM atoms.

Table 2 Calculated spin multiplicities ($2S+1$) of all TM-DBTAA complexes and the excess α -electrons in TM-DBTAA complexes (N_{complex}), in TM atoms (N_{TM}), and in $3d$ orbitals of TM atoms (N_{3d}).

Complex	$2S+1$	N_{complex}	N_{TM}	N_{3d}
Cr-DBTAA	5	4.00	4.08	3.73
V-DBTAA	4	3.00	2.82	2.48
Mn-DBTAA	4	3.00	3.41	3.12
Ti-DBTAA	3	2.00	1.68	1.39
Fe-DBTAA	3	2.00	2.21	1.97
Co-DBTAA	2	1.00	1.01	1.00
Cu-DBTAA	2	1.00	0.47	0.51
Ni-DBTAA	1	0.00	0.00	0.00

Then we investigate the spin transport properties of those complexes. Fig. 2(a)-2(h) plot the spin-resolved zero-bias transmission spectra for M1-M8, respectively, which are the most intuitive representation of electron transport behaviors. For an efficient spin filter, it is generally accepted that the transmission spectrum should show distinct difference between the α - and β -spin over a range of energy close to the E_F . As one can see, except for the case of M7 (Fig. 2(g)) where the α -spin transmission mirrors the β -spin one exactly, the transmission spectra of M1-M6 and M8 exhibit asymmetric feature to different extent between the α - and β -spin (Fig. 2(a)-2(f), and Fig. 2(h)). Especially, this kind of asymmetry is prominent in M5 and M6 (Fig. 2(e) and Fig. 2(f), respectively): there are obvious β -spin transmissions above and under the E_F , in contrast, the α -spin transmission almost disappears in the whole energy region except for some very weak transmissions around -0.5 eV. All these features portend that Fe- and Co-DBTAA can display the best spin filtering behavior, while the current of Ni-DBTAA cannot be polarized.

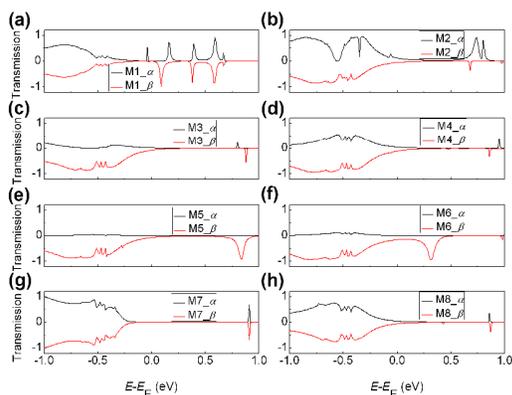


Fig. 2 (a)-(h) Calculated spin-resolved zero-bias transmission spectra for M1-M8, respectively.

Fig. 3(a)-3(h) show the spin-resolved I - V curves of M1-M8 at a bias up to 2.0 V in steps of 0.1 V, respectively. As shown in Fig. 3(a) and Fig. 3(h), there is only a little distinction between the α -spin current (I_α) and β -spin current (I_β) in M1 and M8. As shown in Fig. 3(b)-3(f), the I - V curves of M2-M6 are obviously polarized. In particular, for the case of M5 and M6, the I_β is significantly larger than I_α , where the latter is nearly close to zero in most of the bias range, indicating a perfect spin filtering behavior in Fe- and Co-DBTAA. On the contrary, for the case of M7, as shown in Fig. 3(g), the I_α completely coincides with I_β , indicating there is no any spin filtering effect in Ni-DBTAA. To further quantify the different spin filtering effect just by changing the central TM atoms in DBTAA molecule, we define the spin filtering efficiency (SFE) as follows: $\text{SFE} = |(I_\alpha - I_\beta)/(I_\alpha + I_\beta)| \times 100\%$. At zero bias, when all the currents vanish, we calculate the SFE using the corresponding zero-bias transmission coefficients at the E_F of two spin states, *namely*, $T_\alpha(E_F)$ and $T_\beta(E_F)$. As shown in Fig. 4, Ni-DBTAA cannot exhibit any spin filtering behavior, and the SFE of Ti- and Cu-DBTAA is also very low. V-, Cr- and Mn-DBTAA give rise to moderate SFE around 60%. Interestingly, Fe- and Co-DBTAA exhibit perfect spin filtering behavior: the SFE of Fe- and Co-DBTAA is higher than 97% before 1.9 V with a maximum value of $\sim 99.5\%$ at 1.1 V, and higher than 94% before 1.2 V with a maximum value of $\sim 99.9\%$ at 0.3 V, respectively. Such a significant SFE in such a wide bias range (especially for Fe-DBTAA) is desirable for real applications.

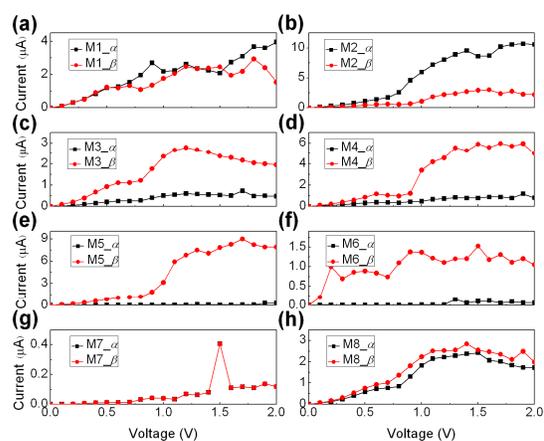


Fig. 3 (a)-(h) Calculated spin-resolved I - V curves for M1-M8, respectively.

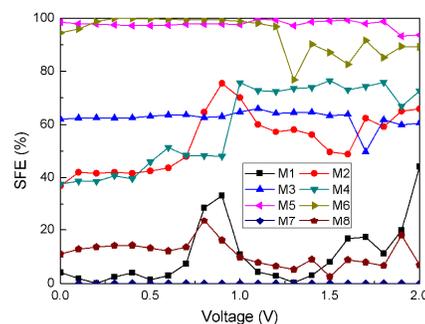


Fig. 4 Calculated spin filtering efficiency (SFE) curves for M1-M8, respectively.

According to the Landauer-Büttiker formula, the current is determined by integrating the transmission spectrum over the bias-dependent bias window. Then, to understand the origin of the observed spin filtering behavior, we take Fe-DBTAA molecular junction as a representative system and plot the bias-dependent α - and β -spin transmission spectra, as shown in Fig. 5(a) and 5(b). The two blue dashed lines indicate the μ_L and μ_R , respectively, and the region between them is the bias-dependent bias window. It is evident that there is always significant β -spin transmission in the bias window (Fig. 5(b)), while there is no obvious α -spin transmission in the bias window except for some weak and sharp peaks at high bias voltages (Fig. 5(a)). As a result, Fe-DBTAA can exhibit perfect spin filtering behavior in a wide bias range.

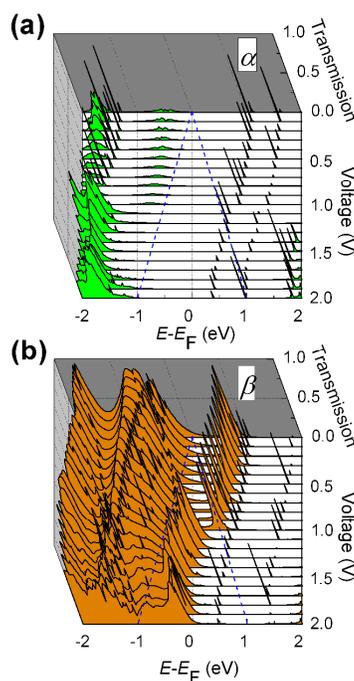


Fig. 5 (a)-(b) Calculated bias-dependent α - and β -spin transmission spectra for M5.

The distinct difference between α - and β -spin transmission spectra can be further understood by the molecular projected self-consistent Hamiltonian (MPSH) states³⁹. Taking the case of 1.1 V (which corresponds to the maximum SFE) as an example, as shown in Fig. 6(a), we mark the positions of MPSH orbitals relative to the E_F with black circles for α -spin and with red circles for β -spin. Since the scattering region contains not only the Fe-DBTAA but also portions of two electrodes, there are many MPSH orbitals with a very small spacing within the bias window. Here, for clarity, we just give those in the energy range of $[-0.7, -0.3$ eV] and $[0, 0.4$ eV]. Evidently, there are two α -spin (α_{416} and α_{417}) and three β -spin (β_{413} , β_{414} and β_{415}) MPSH orbitals within $[-0.7, -0.3$ eV], and one α -spin (α_{427}) and three β -spin (β_{425} , β_{426} and β_{427}) MPSH orbitals within $[0, 0.4$ eV], respectively. In Fig. 6(b), we plot the

spatial distribution of these MPSH orbitals. In general, the magnitude of transmission is determined by the delocalization degree of these MPSH orbitals, which can illustrate the coupling strength between molecular orbitals and electrode states. Only MPSH states that are spatially delocalized throughout the scattering region and possess significant values on the terminal sulfur atoms, overlapping with both left and right electrodes, will have contribution to the transmission^{40,41}. As one can see, the electron density of all three α -spin MPSH orbitals only localizes on part of the scattering region, which leads to a high barrier for α -spin electron transport and results in the negligible α -spin transmission in the corresponding energy range. As for the case of β -spin, β_{414} , β_{425} and β_{427} are localized orbitals, which have no contribution to the transmission. In contrast, though the electron density of β_{413} (β_{415} and β_{426}) mainly localizes on the left (right) and middle parts of the scattering region, it still extends to the opposite end somewhat. These delocalized orbitals offer better transport channels for β -spin electron and further give rise to the obvious β -spin transmission in the corresponding energy range. As a result, a very high SFE $\sim 99.5\%$ occurs. Clearly, better couplings between molecular orbitals and electrode states for β -spin than that for α -spin is the origin of perfect spin filtering behavior. This point can also be seen from the spin-resolved projected density of state (PDOS) spectra of Fe atom (solid curves) and PDOS spectra of Fe-DBTAA molecule (dashed curves) in M5. The bigger the PDOS, the stronger the coupling between the central molecule and the electrodes. As shown in Fig. 7(a) and 7(b), there is no obvious α -spin PDOS in the energy range of $[-0.7, -0.3$ eV] and $[0, 0.4$ eV], therefore, the α -spin transmission is inhibited in these energy region. On the contrary, there is strong β -spin PDOS coming mainly from the contribution of Fe atom. As a result, significant β -spin transmission occurs at corresponding energy region.

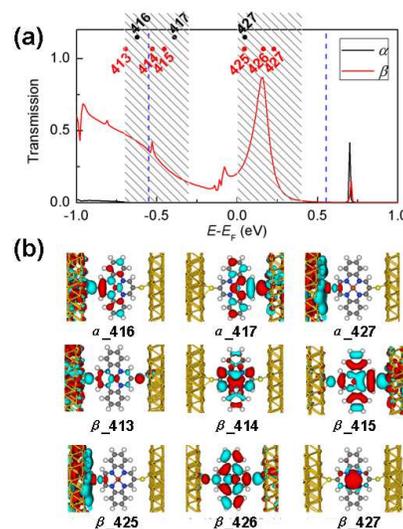


Fig. 6 (a) The spin-resolved transmission spectra at 1.1 V for M5. The positions of MPSH orbitals are marked with black circles for α -spin and with red circles for β -spin in the energy range of $[-0.7, -0.3$ eV] and $[0, 0.4$ eV] (the two energy regions in shadow). (b) The spatial distribution of MPSH orbitals within $[-0.7, -0.3$ eV] and $[0, 0.4$ eV]. The isosurface level is taken as 0.03 ($\text{\AA}^{-3} \text{eV}^{-1}$).

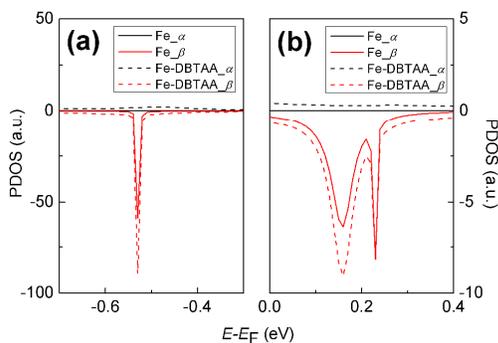


Fig. 7 The spin-resolved PDOS spectra of Fe atom (solid curves) and PDOS spectra of Fe-DBTAA (dashed curves) at 1.1 V for M5 in the energy range of (a) [-0.7, -0.3 eV] and (b) [0, 0.4 eV].

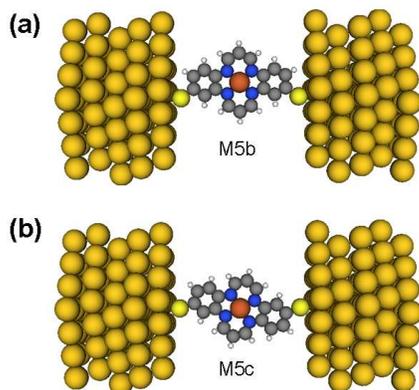


Fig. 8 (a)-(b) Two new molecular junctions named M5b and M5c to investigate the effect of connected position of anchoring group on the observed spin filtering behavior in Fe-DBTAA.

Moreover, it is well known that the connected position of anchoring group plays a significant role on the electron transport properties^{42,43}. Then an intriguing question arises: how does the connected position of anchoring group affect the observed spin filtering behavior in Fe-DBTAA? To answer this question, we construct another two molecular junctions named M5b and M5c, as shown in Fig. 8. The spin-resolved zero-bias transmission spectrum for M5b and M5c are plotted in Fig. 9(b) and 9(c), respectively. For comparison, the zero-bias transmission spectrum of M5 is also shown in Fig. 9(a). As one can see, there are always significant β -spin transmissions below and above the E_F no matter where the terminal sulfur atoms are connected. However, for the case of α -spin, obvious transmissions below the E_F and above 1.0 eV appear only in M5b and M5c, while those in M5 are very weak. The remarkable difference in α -spin transmission just by changing the connected position of anchoring group on DBTAA molecule can still be elucidated by the delocalization degree of corresponding MPSH orbitals. Taking α_{411} around -0.4 eV as an example, as shown in the insets of Fig. 9, we plot their spatial distributions for three cases. Clearly, the electron density mainly localizes on the left and middle parts of the scattering region in M5, while those in M5b and M5c delocalize throughout the whole scattering region. As a result,

obvious α -spin transmission around -0.4 eV can only be found in M5b and M5c. These α -spin transmissions will inevitably lead to a notable I_α in M5b and M5c, as shown by the spin-resolved I - V curves in Fig. 10(b) and 10(c), respectively. The spin-resolved I - V curve of M5 is also presented in Fig. 10(a) for comparison. And the corresponding SFE curves of three molecular junctions are plotted in Fig. 10(d). It is evident that the SFE of M5b and M5c are strongly deteriorated compared to the case of M5.

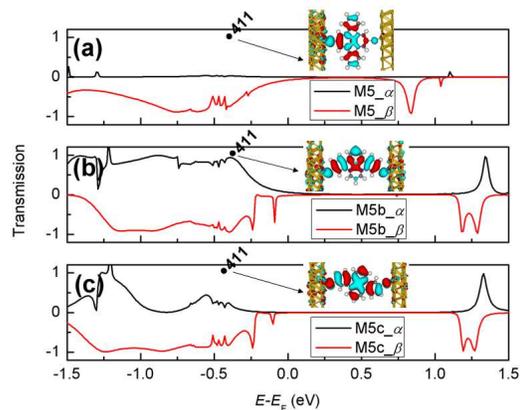


Fig. 9 (a)-(c) Calculated spin-resolved zero-bias transmission spectra for M5, M5b, and M5c, respectively. The insets show the spatial distributions of α -spin MPSH orbital 411 around -0.4 eV for three cases. The isosurface level is taken as $0.03 \text{ \AA}^{-3} \text{ eV}^{-1}$.

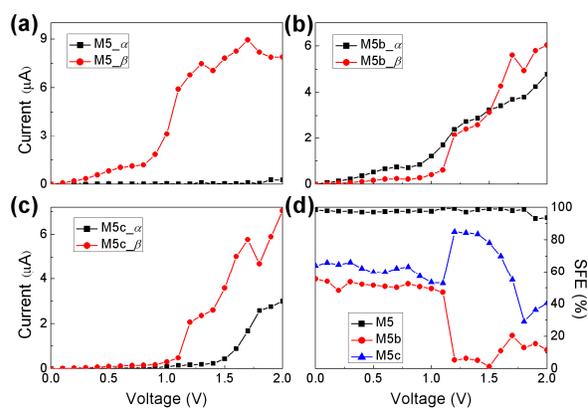


Fig. 10 (a)-(c) Calculated spin-resolved I - V curves for M5, M5b, and M5c, respectively. (d) The corresponding SFE curves for three cases.

At last, we must point out that the hybrid functionals are argued to be more appropriate to deal with TM-phthalocyanine complexes than the GGA functionals due to the mitigated self-interaction (SI) error⁴⁴⁻⁴⁶. However, Shen *et al.* have demonstrated that, at least for the Mn-phthalocyanine, the PBE GGA functional is a better choice than the hybrid functionals⁴⁵. In our calculations, the effect of SI correction (SIC) has not been considered since it has not been implemented in the ATK package currently. If SIC is included, Toher and Sanvito have shown that the energy levels will be shifted down and the E_F will be shifted upwards relatively^{48,49}. Then, in the cases of Fe- and Co-DBTAA, the I_β will be changed accordingly. However, the I_α will still keep small due to the absence of α -spin

transmission in a wide energy region (Fig. 2(e) and 2(f)). Therefore, we believe that Fe- and Co-DBTAA can still exhibit significant spin filtering effect.

Conclusions

In summary, by using spin-polarized first-principles DFT+NEGF method, we have investigated systematically the spin transport properties of DBTAA complexes involving first row TMs (TM = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) sandwiched between two Au electrodes. Our results show that Fe- and Co-DBTAA can exhibit perfect spin filtering effect in a wide bias voltage region, which can be attributed to spin-dependent coupling of molecular orbitals with electrode states. Moreover, it is found that the spin filtering efficiency is dependent significantly upon the connected position of anchoring group on the complexes. These results indicate that Fe- and Co-DBTAA are potential materials for high-performance spin filters.

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Graphical abstract

We investigate systematically the spin transport properties of DBTAA complexes involving first row transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) sandwiched between two Au electrodes. The results show that Fe- and Co-DBTAA can exhibit perfect spin filtering effect in a wide bias voltage region. And the spin filtering efficiency is dependent significantly upon the connected position of anchoring group on the complexes.

