Electronic Supplementary Information

High-performance molecular spin filters based on a square-planar four-coordinate Fe complex and covalent pyrazine anchoring groups

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Section 1: Detailed comparisons between the atomic and electronic structures of three isolated molecules calculated with the SIESTA code and those with the Gaussian16 package

Fig. S1 (a) Optimized atomic structures, (b) spin density, (c) energy level arrangements and spatial distribution of the frontier molecular orbitals (FMOs) for the isolated FeN₄ molecule. The left panels show the results calculated by using the Gaussian16 package at the PBE/6-311+G(d,p) level, while the right ones display the results obtained with the SIESTA code at the same PBE GGA level with the user-defined pseudopotentials and basis sets.



Fig. S2 (a) Optimized atomic structures, (b) spin density, (c) energy level arrangements and spatial distribution of the FMOs for the benzene-FeN₄ molecule in the gas phase. Results calculated by using the Gaussian16 package and the SIESTA code are shown in the left and right panels, respectively.



Fig. S3 (a) Optimized atomic structures, (b) spin density, (c) energy level arrangements and spatial distribution of the FMOs for the pyrazine-FeN₄ molecule in the gas phase. Results obtained with the Gaussian16 package and the SIESTA code are shown in the left and right panels, respectively.

Clearly, for all the three isolated molecules involving FeN_4 , benzene- FeN_4 , and pyrazine- FeN_4 , differences in the bond lengths calculated with the two software packages are not more than 0.01 Å. In addition, differences in the HOMO-LUMO gaps for both spin types are not more than 0.03 eV. All of these results shown in Fig. S1-S3 demonstrate that the results calculated by using the SIESTA code are in good agreement with those calculated by the Gaussian16 package, indicating the reliability of the pseudopotentials and basis sets built for this work.





Fig. S4 Spin-resolved equilibrium transmission spectra of the SWCNT-pyrazine-FeN₄-SWCNT junction calculated with the PBE GGA functional and with the GGA+U method. Here, J = 0.9 eV and various U values between 3 and 5 eV are employed for the Fe 3d atomic orbitals.

According to previous studies by Denawi and coworkers,¹⁻³ the value of J = 0.9 eV is fixed and different U values, between 3 and 5 eV, are employed for the Fe 3d atomic orbitals. As we can see, although the values of U affect the spin-resolved transmission spectra away from the Fermi level, these transmission spectra are similar over a broad energy range from around -0.5 to 0.6 eV. In particular, a spin polarization of 99.4% is obtained for all the applied U values, which is almost identical to that of 99.3% with the PBE GGA functional. Therefore, we can conclude that the PBE GGA functional is rather accurate for the low-bias spin-polarized transport calculations of these FeN₄-based molecular junctions.

Section 3: Reliability of our junction models to describe single-molecule transport properties



Fig. S5 Optimized atomic structures of the SWCNT-pyrazine-FeN₄-SWCNT junction, as well as the SWCNT-pyrazine-FeN₄-SWCNT-buffer and SWCNT-pyrazine-FeN₄-SWCNT-buffer' junctions with longer buffer regions together with their corresponding spin-resolved equilibrium transmission spectra. The green squares denote the principal layers of the SWCNT electrodes.

Within the NEGF+DFT approach, some parts of the electrodes should be included in the junction models for simulating their electronic transport properties. These parts of the electrodes should be large enough to guarantee that both the density matrix and the Hamiltonian matrix of the outermost layers of the electrodes (that is, the principal layer) are the same as those of bulk electrodes.⁴ Therefore, we increase the portions of the electrodes in the extended molecule region to examine the reliability of our junction models constructed in the main text. As we can see, for all transmission peaks shown in Fig. S5, the energy separation between different transmission curves is less than 0.025 eV. Furthermore, the three transmission spectra around E_F almost coincide, demonstrating that junction models reported in our manuscript can be reliably employed to describe the spin-resolved transport properties of single-molecule junctions.

Section 4: Spin density for the SWCNT-benzene-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT molecular junctions



Fig. S6 Spin density for the SWCNT-benzene-FeN₄-SWCNT (a) and SWCNT-pyrazine-FeN₄-SWCNT junctions (b).

Section 5: PDOS spectra of Fe 3d atomic orbitals in the SWCNT-benzene-FeN₄-SWCNT junction



Fig. S7 PDOS spectra of Fe 3d atomic orbitals in the SWCNT-benzene-FeN₄-SWCNT junction.

Section 6: Spin-resolved transport properties of the SWCNT-FeN₄-SWCNT junction



Fig. S8 (a) Top and side views of the optimized atomic structure of the SWCNT-FeN₄-SWCNT junction. H, C, N, and Fe atoms are represented with light grey, dark gray, blue and purple spheres, respectively. (b) Spin-resolved equilibrium transmission spectra for the spin-up (the red line) and spin-down (the blue line) electrons together with the eigenchannels for selected transmission peaks of the SWCNT-FeN₄-SWCNT junction.



Fig. S9 A detailed comparison of the geometric structures of the benzene rings adjacent to the Hpassivated SWCNT electrode edges between the SWCNT-FeN₄-SWCNT junction (a) and the SWCNT-benzene-FeN₄-SWCNT junction (c). A detailed comparison of the geometric structures of the terminal benzene rings between the isolated FeN₄ (b) and benzene-FeN₄ (d) molecules.



SWCNT-FeN₄-SWCNT

Fig. S10 Spin density for the SWCNT-FeN₄-SWCNT junction.



Fig. S11 (a) PDOS spectra of Fe 3d atomic orbitals in the SWCNT-FeN₄-SWCNT junction. The inset shows the side view of the eigenchannel associated with the transmission peak located at -0.54 eV, which has a high weight on the C atoms of the two benzene rings in the central FeN₄ region and displays a distinctive feature of π -type orbitals on these benzene rings. This indicates that both the σ -type orbitals distributed on the central square-planar four-coordinate motif and the π -type orbitals positioned on the two adjacent benzene rings make contributions to the transmission peak at -0.54 eV. (b) PDOS spectra for the sum of all C 2p orbitals of the two terminal benzene rings in the central molecular region of the SWCNT-FeN₄-SWCNT junction.

Similar to the previous study,⁵ here we also covalently attach FeN₄ shown in Fig. 1 to two semiinfinite (5,5) armchair SWCNT electrodes through two C-C bonds on each side and the resultant molecular junction is denoted by SWCNT-FeN₄-SWCNT whose optimized atomic structure is displayed in Fig. S8a. It is worth mentioning that in order to find the equilibrium geometric structure of this junction, we also systematically vary the separation between the two SWCNT electrodes and optimize the positions of the central FeN₄ molecule and the adjacent several layers of the left and right SWCNT electrodes until the total energy reaches a local minimum. In analogy to the SWCNTbenzene-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT junctions, the optimized bond lengths in the central FeN₄ molecule. For example, the Fe-N bond length is optimized to be 1.87 Å in the SWCNT-FeN₄-SWCNT junction, the same as that in the isolated FeN₄ molecule. The adjacent C-N bond length is calculated to be 1.36 Å in the SWCNT-FeN₄-SWCNT junction, which is 1.37 Å in the isolated FeN₄ molecule. Despite the marginal change in the optimized bond length, in stark contrast to the still planar configuration in the central benzene-FeN₄ and pyrazineFeN₄ regions (see Fig. 3a and Fig. 3c), FeN₄ becomes distorted from the planarity, that is, its terminal benzene rings are significantly deviated from the *x*-*z* plane (considering that the central squareplanar four-coordinate motif is placed in the *x*-*z* plane by definition). This is mainly due to the steric hindrance between the terminal benzene rings in FeN₄ and the H-passivated electrode edges. In contrast, since the outermost benzene rings in the central benzene-FeN₄ region is further stretched along the *z*-axis in the SWCNT-benzene-FeN₄-SWCNT junction (see Fig. S9), the steric hindrance has less effect on the planarity of the central benzene anchors resulting in the SWCNT-pyrazine-FeN₄-SWCNT junction, the steric hindrance can be neglected due to the relatively long distance between the pyridinic N atoms and the adjacent H atoms at the electrode edges being almost 2.50 Å.

In analogy to the SWCNT-benzene-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT junctions, we also find that FeN₄ can well preserve its unique magnetic properties in the two-probe systems. Since the spin density is mostly distributed at the central Fe ion (see Fig. S10), the magnetism of this molecular junction is also mainly generated by the central Fe ion.

Fig. S8b shows the spin-resolved equilibrium transmission spectra for the SWCNT-FeN₄-SWCNT junction. In addition, it also shows the calculated eigenchannels associated with selected transmission peaks for the spin-up and spin-down channels around $E_{\rm F}$. As we can see, the transport properties of the two spin channels are also significantly different. For the spin-up channel, two transmission peaks appear around E_F , of which one is centered at 0.19 eV and the other is centered at -0.69 eV. By inspecting the FMOs of the isolated FeN₄ molecule, we can observe that these two transmission peaks are dominated by the spin-up LUMO and HOMO orbitals, respectively. This reveals an energy separation of 0.88 eV between these two peaks, which is significantly larger than that corresponding to the SWCNT-benzene-FeN₄-SWCNT junction (0.62 eV) indicating that the benzene anchors are effective in extending the conjugation of FeN₄ and coupling with the SWCNT electrodes. As for the spin-down channel, no evident transmission peaks can be found in an energy range going roughly from -0.4 to 0.5 eV, which is mainly due to the localization nature of the spindown LUMO orbital so that no transmission peaks present a distinct spin-down LUMO character. However, it is worth noting that the low transmission region is much narrower than that in the SWCNT-benzene-FeN₄-SWCNT junction (see Fig. 3b). Intriguingly, this is mainly because the spin-down HOMO-1 orbital plays a significant role in the appreciable transmission peak at -0.54 eV, although this orbital is localized at the central Fe and N atoms and is expected to provide a very small contribution to the transmission. As demonstrated in Fig. S8b and Fig. S11a for the top and side views of the eigenchannel corresponding to this transmission peak, we also find that the π -type orbitals, distributed on the C atoms of the two benzene rings adjacent to the central square-planar four-coordinate motif, contribute to this transmitting channel. This is further manifested by the PDOS spectra in Fig. S11, where the Fe $3d_{x^2-y^2}$ and $3d_{z^2}$ atomic orbitals together with C 2p orbitals obviously make contributions to the transmission peak located at -0.54 eV, indicating the electronic coupling between the σ -type spin-down HOMO-1 and the π -type orbitals on the adjacent benzene rings. Apparently, the nonplanar geometry in the central molecular region in the SWCNT-FeN₄-SWCNT junction results in this σ - π interaction. It is worth mentioning that such a transmission peak was not significant in Huang's work and the spin-up LUMO-dominated transmission peak in Huang's work was located at 0.33 eV which was 0.14 eV higher in energy than that in our calculations.⁵ This may be mainly ascribed to the optimized atomic structure of this junction and

the basis set.

As for the fully delocalized FMOs of the isolated FeN₄ of the spin-down electrons such as its HOMO and LUMO+1, the transmission peak at 0.60 eV matches well with the LUMO+1 orbital, whereas the one at -0.75 eV is contributed by a combination of several FMOs, namely subparts of several FMOs such as the HOMO, HOMO-1 and HOMO-2 orbitals (see Fig. S11 for further details of PDOS spectra demonstrating the contribution of a set of atomic orbitals showing characteristics of these FMOs). Consequently, we conclude that the junction transport properties around E_F are dominated by the spin-up channel, especially the transmission peak corresponding to the FeN₄ spin-up LUMO orbital, in accordance with Huang's work.⁵ Herein, $T_{\uparrow}(E_F)$ and $T_{\downarrow}(E_F)$ are calculated to be 6.4×10^{-2} and 4.7×10^{-3} , respectively, close to the results reported by Huang and coworkers,⁵ and the corresponding spin polarization is obtained to be 86.3%.

Section 7: Ratios of the spin-up current to the spin-down one as a function of the applied bias voltage for the SWCNT-benzene-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT molecular junctions



Fig. S12 Calculated R as a function of the applied bias voltage within the range of 0.1 to 0.6 V for the SWCNT-benzene-FeN₄-SWCNT junction (the upper row) and the SWCNT-pyrazine-FeN₄-SWCNT junction (the bottom row). Herein, R is defined as the ratio of the spin-up current to the spin-down one, that is, $R = I_{\uparrow}/I_{\downarrow}$.

Section 8: Spin-resolved transmission spectra within the bias range of 0.1 to 0.6 V for the SWCNTbenzene-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT molecular junctions



Fig. S13 Spin-resolved transmission spectra for the SWCNT-benzene-FeN₄-SWCNT molecular junction within the bias range of 0.1 to 0.6 V.



Fig. S14 Spin-resolved transmission spectra for the SWCNT-pyrazine-FeN₄-SWCNT molecular junction within the bias range of 0.1 to 0.6 V.

Section 9: PDOS spectra for Fe 3d atomic orbitals and the sum of all π -type orbitals distributed on the four aromatic rings in the central molecular region of the SWCNT-benzene-FeN₄-SWCNT-BS and SWCNT-pyrazine-FeN₄-SWCNT-BS junctions



Fig. S15 (a) PDOS spectra of Fe 3d atomic orbitals in the SWCNT-benzene-FeN₄-SWCNT-BS junction. The inset shows the side view of the eigenchannel associated with the transmission peak located at -0.42 eV, which gives a visual illustration of the σ - π interaction. (b) PDOS spectra for the sum of all C 2p orbitals of the four benzene rings in the central molecular region of the SWCNT-benzene-FeN₄-SWCNT-BS molecular junction.



Fig. S16 (a) PDOS spectra of Fe 3d atomic orbitals in the SWCNT-pyrazine-FeN₄-SWCNT-BS junction. (b) PDOS spectra for the sum of all C and N 2p orbitals distributed on the four aromatic rings in the central molecular region of the SWCNT-pyrazine-FeN₄-SWCNT-BS junction.

Section 10: A comparison of LDOS of C atoms at the connecting sites corresponding to the SWCNT-pyrazine-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT-BS junctions



Fig. S17 Local density of states (LDOS) of C atoms at the connecting sites denoted by C_a (blue) and C_b (red) corresponding to the SWCNT-pyrazine-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT-BS junctions. The insets show the enlarged connecting sites of the C_a and C_b atoms.

According to the NEGF theory,⁶ the real part and the imaginary part of the electrode selfenergies dictate the energy shift and the broadening of the transmission peaks, respectively. Considering that the atomic structures of the two pyrazine-linked junctions are very similar, the molecule-electrode coupling due to the pyrazine anchors should be almost the same. Therefore, the large differences between the spin-dependent transport properties of these two junctions might be attributed to the differences of the surface's Green functions of the SWCNT electrodes, whose imaginary part is proportional to the LDOS of the C atoms at the connecting sites. Therefore, we plot the LDOS of C atoms connecting the SWCNT electrode to the pyrazine-FeN₄, which are denoted by C_a and C_b corresponding to the SWCNT-pyrazine-FeN₄-SWCNT and SWCNT-pyrazine-FeN₄-SWCNT-BS junctions respectively. As we can see, the LDOS of C_b atoms around E_F is much higher than that of the C_a atoms, demonstrating an enhanced imaginary part of the electrode selfenergy for the SWCNT-pyrazine-FeN₄-SWCNT-BS junction and an increase in the broadening of their transmission peaks. **Section 11:** Spin-resolved transmission spectra within the bias range of 0.1 to 0.6 V for the SWCNTbenzene-FeN₄-SWCNT-BS and SWCNT-pyrazine-FeN₄-SWCNT-BS junctions



Fig. S18 Spin-resolved transmission spectra for the SWCNT-benzene-FeN₄-SWCNT-BS molecular junction within the bias voltages from 0.1 to 0.6 V.



Fig. S19 Spin-resolved transmission spectra for the SWCNT-pyrazine-FeN₄-SWCNT-BS molecular junction within the bias voltages from 0.1 to 0.6 V.

Section 12: Effects of the edge passivation on the spin-polarized transport properties of the molecular junction based on pyrazine-FeN₄



Fig. S20 Optimized atomic structures of FeN₄ sandwiched between two (5,5) armchair SWCNT electrodes with F (a) or OH (c) termination through the pyrazine anchors. H, C, N, O, F, and Fe atoms are represented with light grey, dark grey, blue, red, cyan, and purple spheres, respectively. The right-hand side plots display the corresponding spin-resolved equilibrium transmission spectra for the spin-up (red lines) and spin-down (blue lines) electrons together with the eigenchannels for selected transmission peaks of the junction with F-terminated SWCNT electrodes (b) and the junction with OH-terminated SWCNT electrodes (d).

Section 13: A comparison of LDOS of C atoms at the connecting sites considering different edge passivation



Fig. S21 The LDOS of C atoms at the connecting sites denoted by C_a (blue), C_c (green), and C_d (yellow) corresponding to the FeN₄-based and pyrazine-linked molecular junctions constructed with the H-terminated, F-terminated, and OH-terminated SWCNT electrode edges respectively. The insets show the enlarged connecting sites of the C_a , C_c , and C_d atoms.





Fig. S22 Optimized atomic structures of the molecular junctions based on pyrazine-FeN₄ constructed with two semi-infinite armchair (4,4) (a), (5,5) (b), (6,6) (c), and (8,8) (d) SWCNT electrodes, and their corresponding spin-resolved equilibrium transmission spectra are shown in (e).

Section 15: A comparison of DOS between SWCNT and N-doped graphene electrodes



Fig. S23 Unit cell (a) and the total DOS (c, red) of the principal layer of the N-doped graphene electrode with a doping concentration level of 2.5%. The unit cell (b) and the total DOS (c, blue) of the principal layer of the armchair (5,5) armchair SWCNT electrode.

Section 16: Spin-resolved transport properties of the molecular junction based on pyrazine-FeN₄ constructed with N-doped graphene electrodes



Fig. S24 The optimized atomic structure (a) and the corresponding spin-resolved equilibrium transmission spectra for the spin-up (the red line) and spin-down (the blue line) channels (b) of the FeN₄ molecule sandwiched between two N-doped graphene electrodes through the pyrazine anchors, together with the eigenchannel for the spin-up LUMO-dominated transmission peak.

In our calculations, the N-doped graphene electrodes are placed in the *y-z* plane and periodic boundary conditions are considered along the *y*-axis. The distance between the neighboring graphene sheets is set to be 15 Å in order to model isolated two-dimensional N-doped graphene electrodes. In addition, the k-point grid of $1 \times 200 \times 1$ is chosen to obtain smooth transmission curves.

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