Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Fano Resonance in molecular junctions of spin crossover complexes

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S1. Details for geometries of molecular junctions

For a two-probe molecular junction, the distance d_{MJ} between two electrode surfaces is one of the important parameters. It is optimized based on a slab-like model and only a low-spin complex is taken into account in this model, as shown in Fig. S1. Additionally, rigid constraints are applied for atoms of the electrode surface (marked by red-dashed lines in Fig. S1), while other atoms are fully relaxed without any constraints. In other words, in the optimizing simulation, these Au atoms are regarded as a rigid body with only translational motions, which is determined by the force on the center-of-mass of the rigid body atoms. When the considered complex is switched into the high-spin state, d_{MJ} is fixed to be the same as that for the low-spin complex. This requirement is reasonable for common molecular devices of good robustness. The force criterion for geometry optimizations is less than 0.04 eV/Å. Considering the periodic boundary condition, the thickness of the vacuum layer d_{VM} between two electrode surfaces is set to be 15 Å, which is large enough to avoid possible interactions between these two surfaces.

In addition, it is pointed out that the energy difference $\Delta E_{HL} = E_{\mathrm{HS}} - E_{\mathrm{LS}}$ of M2 in MJ1 (MJ2) is calculated just based on the above optimized slab-like model.

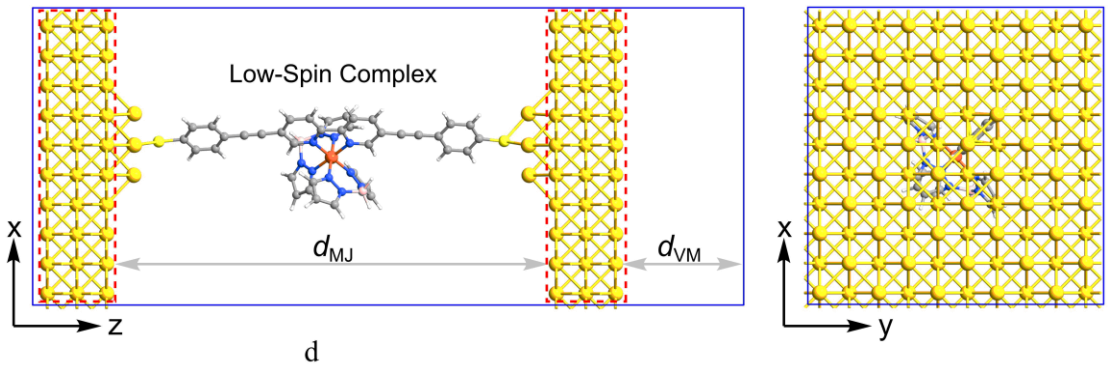

Fig. S1. The slab-like model for optimizing the distance between two electrode surfaces (d_{MJ}) of molecular junctions. A low-spin complex is considered for these optimizations. The blue rectangles mark the simulation cell of the slab model. The vacuum layer is only considered in the z direction, and d_{VM} denotes the thickness of this vacuum layer, which is set to be 15 Å. The red dashed lines mark atoms with rigid constraints for optimizing simulations.

S2. Details for electronic and transport properties of M1

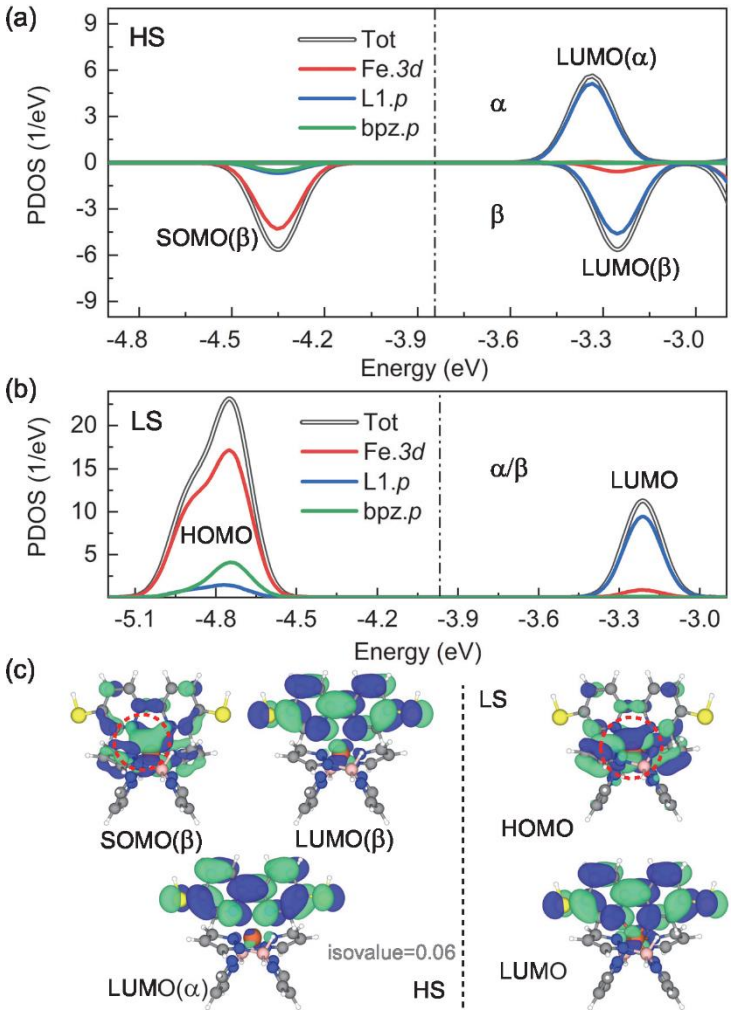

Fig. S2. The PBE+U calculated partial density of states (PDOS) for the high-spin M1 (a) and the low-spin M1 (b). `Tot' in (a) and (b) denotes the total density of states for the whole complex. `Fe.*3d*', `L2.*p*', and `bpz.*p*' denote *3d* states of the Fe(II) ion, *p* states of the L2 ligand, and *p* states of the bpz group. The α(β)-spin channel is identified by positive (negative) values of longitudinal axes in (a). α/β means the spin degeneracy in (b). The Fermi level, defined as the middle position of HOMO and LUMO levels, is marked by the dash-dotted lines. (c) Orbital profiles of some FMOs in the two spin states. The red-dashed lines highlight notable *3d* states of the Fe(II) ion.

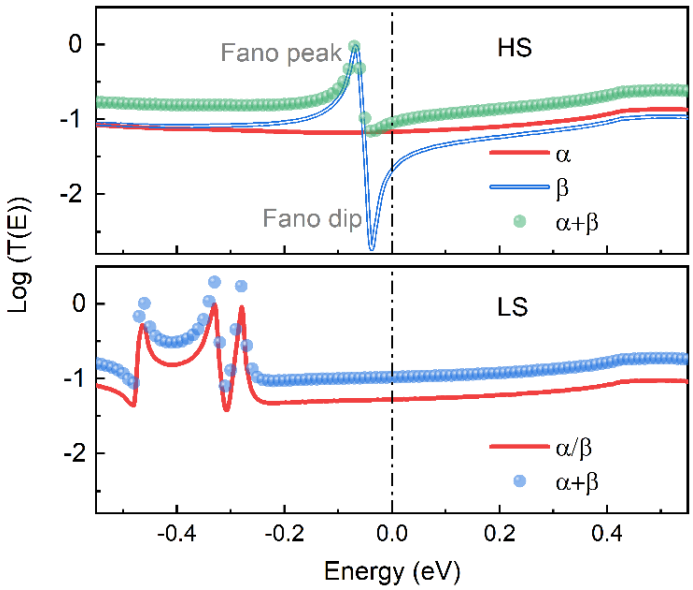

Fig. S3. Transmission spectra of MJ1 with M1 sandwiched between two electrodes. The electrodes and the tips are the same as those of MJ1 with M2. The distance between two electrode surfaces is re-optimized based on the method mentioned in Section S1. The Fano effect is clearly seen in the high-spin state as well, but absent in the low-spin state.

S3. Partial device density of states (PDDOS) for electrode surfaces tips in MJ1 and MJ2

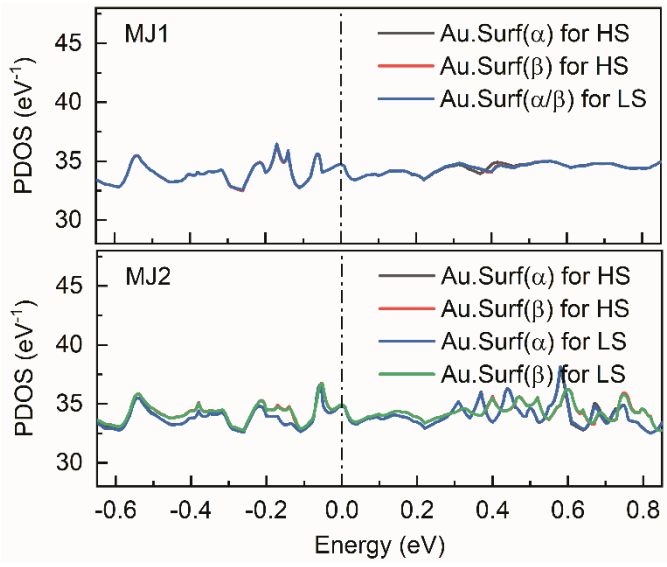

Fig. S4. Partial device density of states (PDDOS) for the electrode surfaces in MJ1 and MJ2. α(β) is the spin index. The Fermi level is marked by the dash-dotted lines.

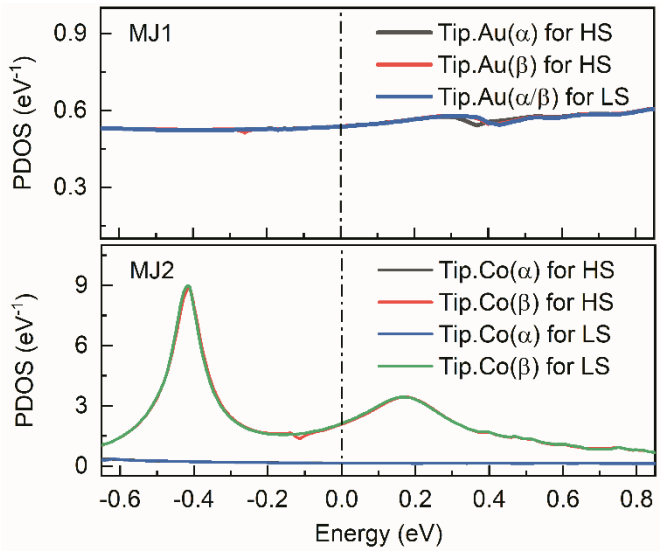

Fig. S5. Partial device density of states (PDDOS) for the tips in MJ1 and MJ2. α(β) is the spin index. The Fermi level is marked by the dash-dotted lines.

S4. Cartesian coordinates for M2 and molecular junctions MJ1 and MJ2

Molecular coordinates of the complex M2 in the high-spin and low-spin states are provided by the files named "*M2-hs.xyz*" and "*M2-ls.xyz*". For molecular junctions, only coordinates for the central scattering region are listed in the files. "*MJ1-M2.hs.xyz*" and "*MJ2-M2.hs.xyz*" are for the molecular junctions MJ1 and MJ2 with the high-spin M2, while "*MJ1-M2.ls.xyz*" and "*MJ2-M2.ls.xyz*" are for the molecular junctions MJ1 and MJ2 with the low-spin M2, respectively. The lattice parameters for these central scattering regions are:

1) For *MJ1-M2.hs.xyz*: a=20.8, b=20.8, c= 50.3495; α=90º, β=90º, γ=90º.

2) For *MJ1-M2.ls.xyz*: a=20.8, b=20.8, c= 50.3495; α=90º, β=90º, γ=90º.

3) For *MJ2-M2.hs.xyz*: a=20.8, b=20.8, c= 48.8058; α=90º, β=90º, γ=90º.

4) For *MJ2-M2.hs.xyz*: a=20.8, b=20.8, c= 48.8058; α=90º, β=90º, γ=90º.

All XYZ files are included in an attached zip file.