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

Supporting Information

Tuning the Polarity of Charge Carriers in N-Heterocyclic Carbene-base Single-molecule Junctions via Atomic Manipulation

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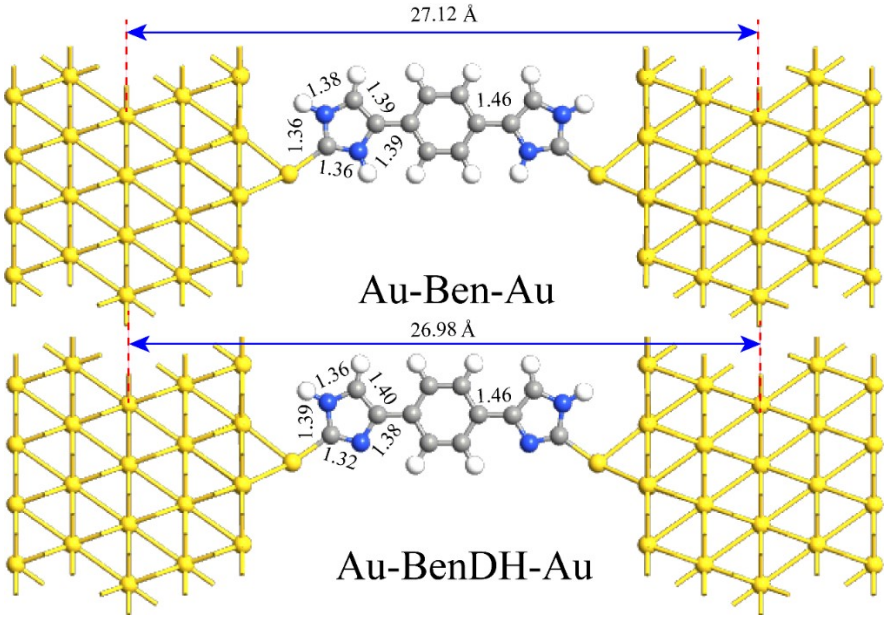

Figure S1. Optimized atomic structures for Au–Ben–Au and Au–BenDH–Au junctions with typical bond lengths.

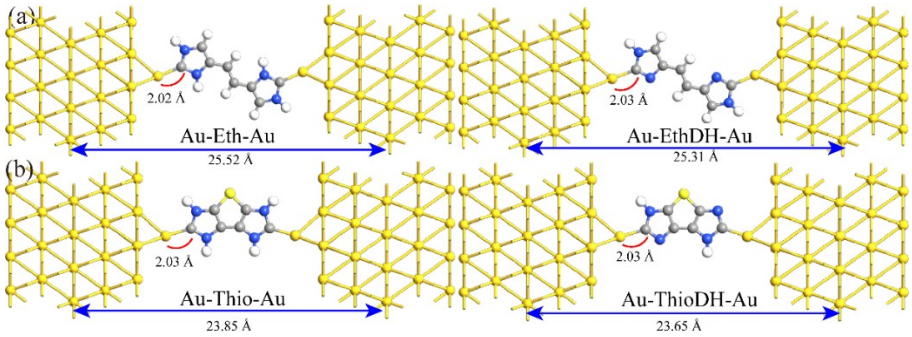

Figure S2. Optimized atomic structures for (a) Au-Eth(DH)-Au and (b) Au-Thio(DH)-Au junctions.

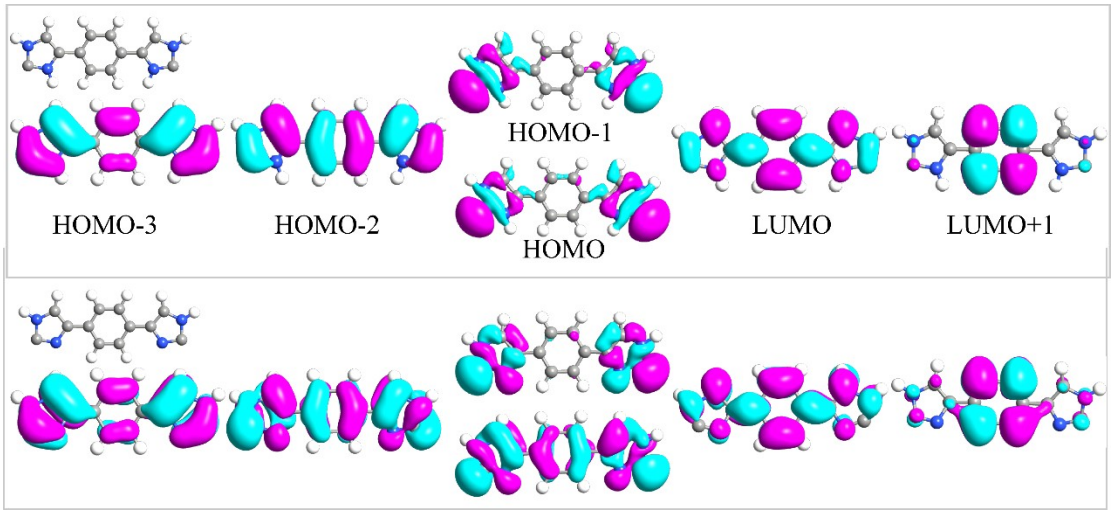

Figure S3. Frontier molecular orbitals of isolated Ben and BenDH molecules.

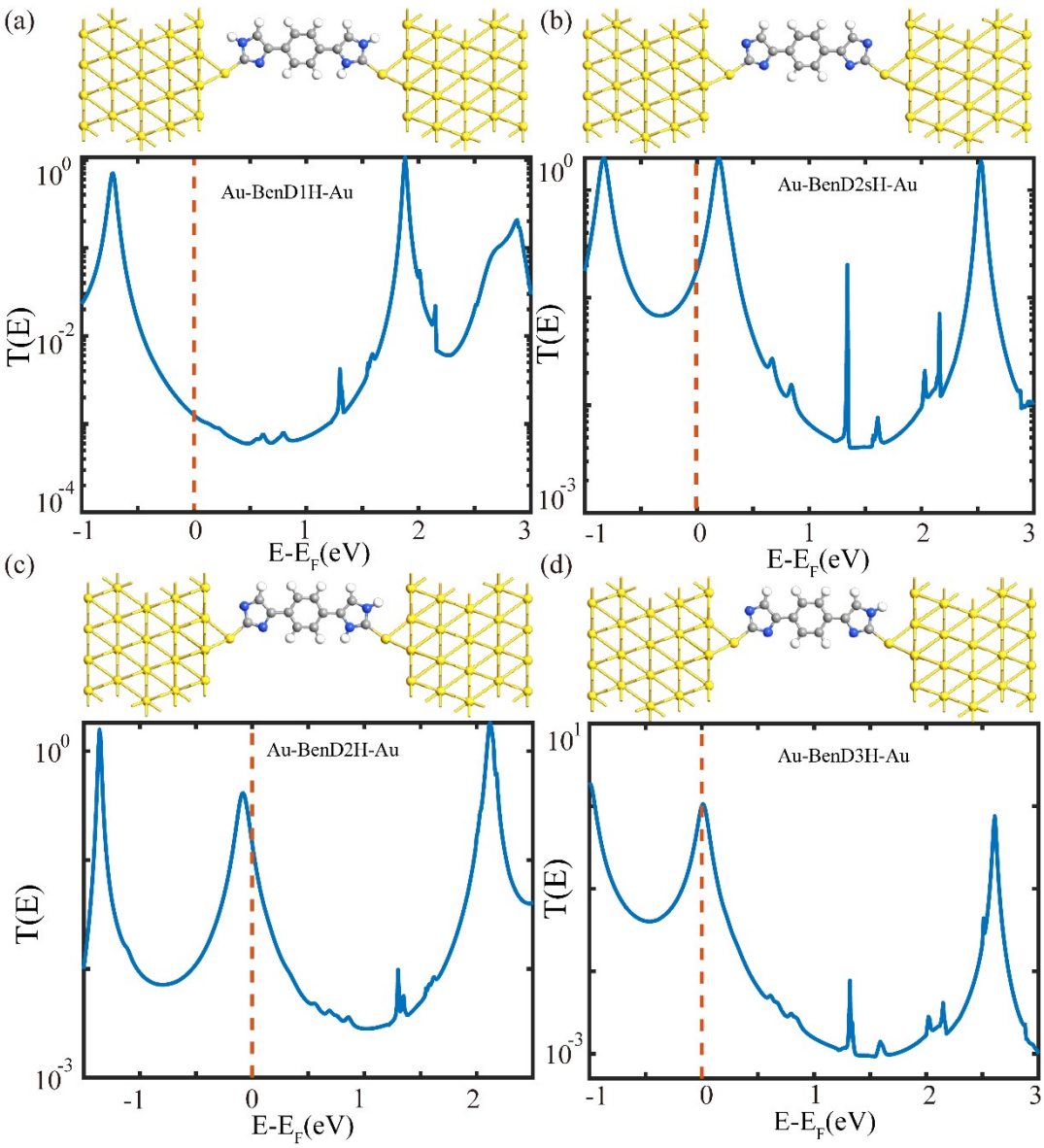

Figure S4. Optimized atomic structures (upper panel) and equilibrium transmission spectra (lower panel) for: (a) Au–BenD1H–Au, (b) Au–BenD2sH–Au, (c) Au–BenD2H–Au, and (d) Au–BenD3H–Au.

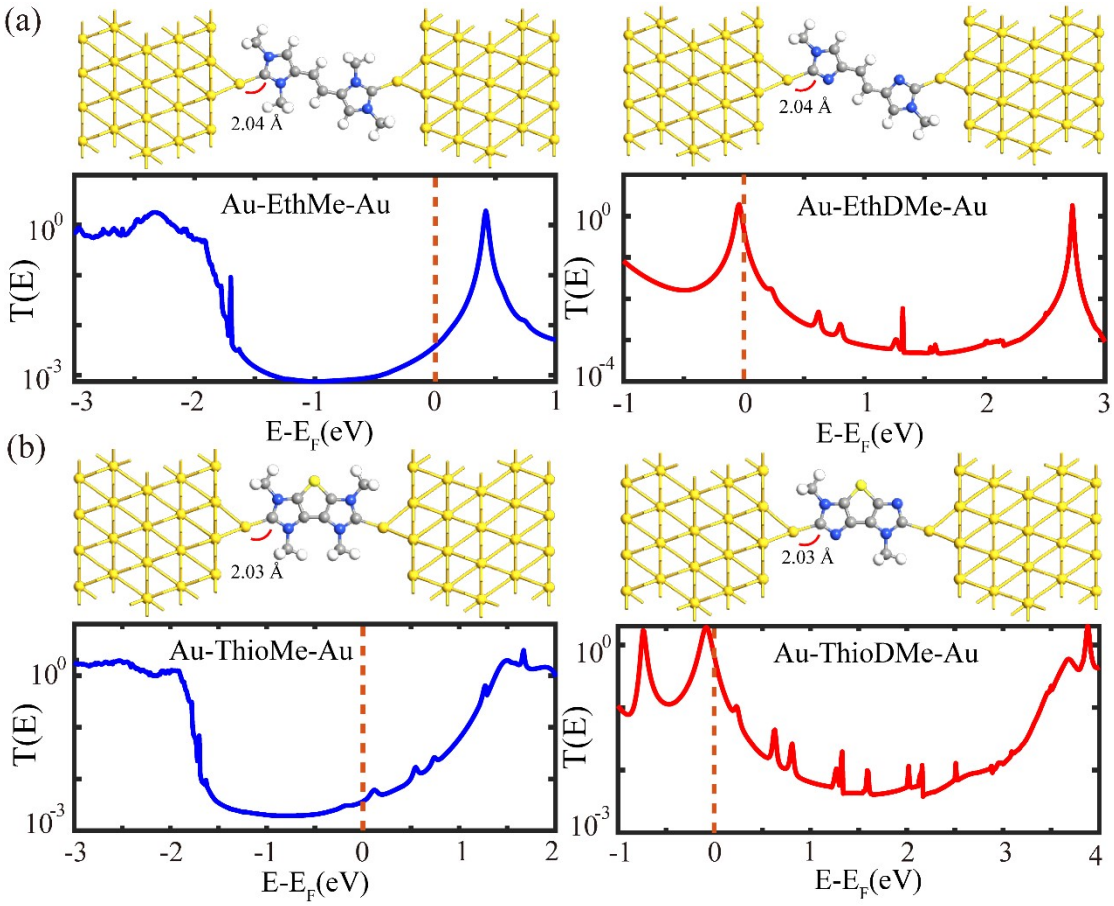

Figure S5. Optimized atomic structures (upper panel) and equilibrium transmission spectra (lower panel) for: (a) Au-Eth(D)Me-Au, and (b) Au-Thio(D)Me-Au.

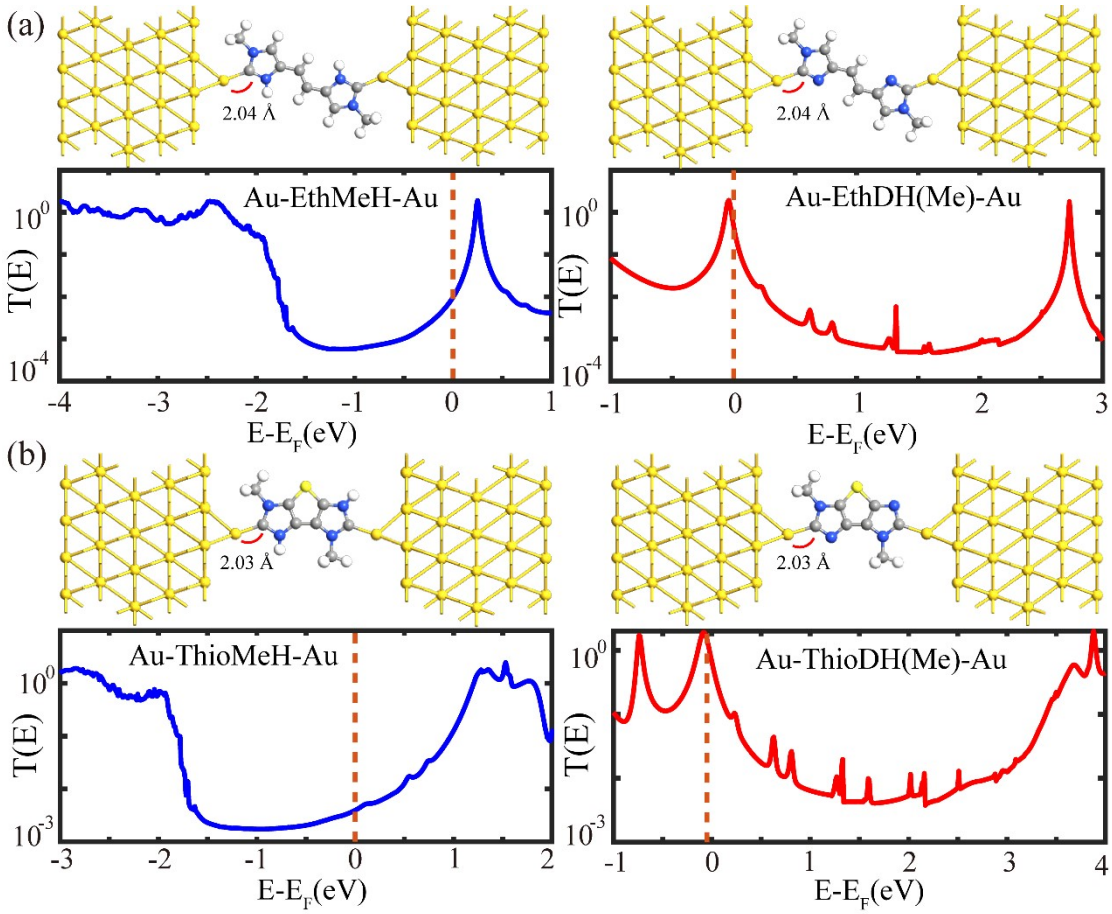

Figure S6. Optimized atomic structures (upper panel) and equilibrium transmission spectra (lower panel) for: (a) Au-EthMeH(EthDH(Me))-Au, (b) Au-ThioMeH(ThioDH(Me))-Au.

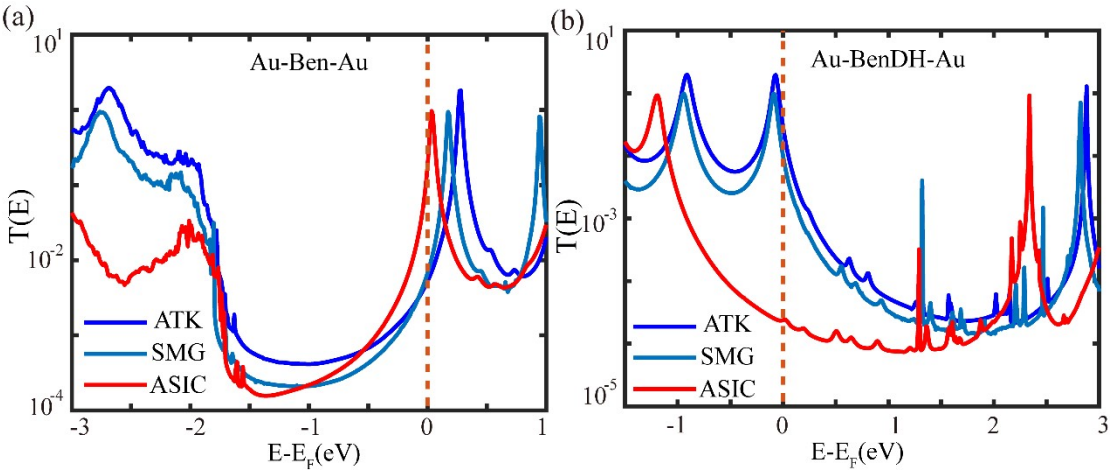

Figure S7. Comparison of the transmission spectra of (a) Au-Ben-Au and (b) Au-BenDH-Au. The blue line represents the transmission spectrum calculated using ATK with the PBE functional. The green line is the transmission spectrum calculated using SMEAGOL with the PBE functional, and the red line represents that calculated using SMEAGOL with the PBE functional and the ASIC approach.

Table S1 Binding energies of the molecular junctions considered in this study.

Energy	Au-Ben-Au -5.11 eV	Au-BenDH-Au -7.04 eV	Au-BenMe-Au -5.56 eV	Au-BenDMe-Au -7.26 eV	Au-BenMeH-Au -5.38 eV
Energy	Au-Eth-Au -4.76 eV	Au-EthDH-au -6.83 eV	Au-EthMe-Au -5.55 eV	Au-EthDMe-Au -7.22 eV	Au-EthMeH-Au -5.40 eV
Energy	Au-Thio-Au -4.55 eV	Au-ThioDH-Au -6.80 eV	Au-ThioMe-Au -5.46 eV	Au-ThioDMe-Au -7.04 eV	Au-ThioMeH-Au -5.01 eV