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

Electronic Supplementary Information (ESI)

An approach to the electronic structure of molecular junctions with metal clusters of atomic thickness

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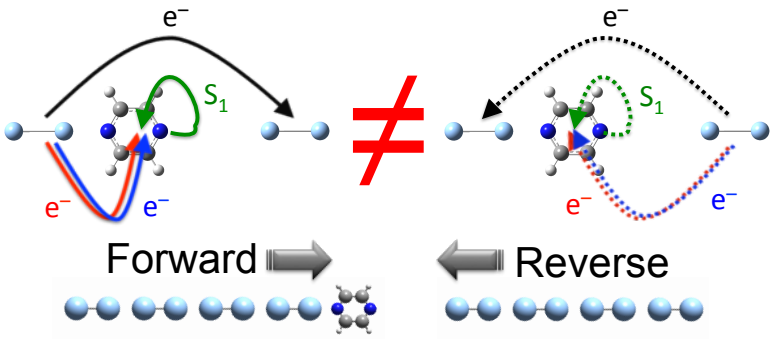

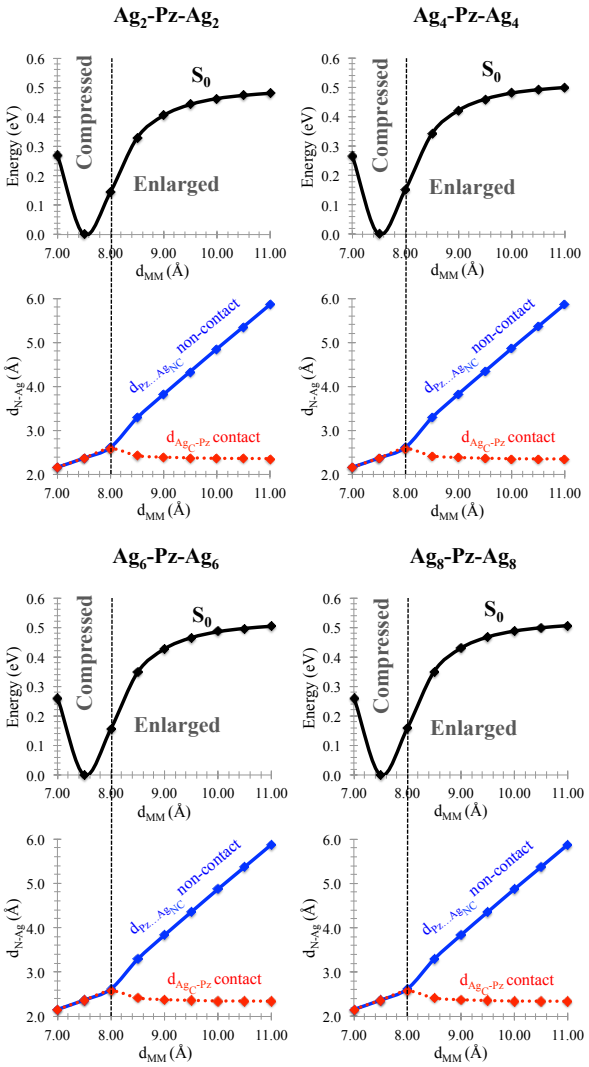

Figure S1 Effect of the inter-cluster distance (d_{MM}) on the M06-HF/LanL2DZ stabilization energy of the bond formed between pyrazine and the non-contact silver cluster in the ground electronic state S_0 (top) of Ag_n-Pz-Ag_n junctions. N-Ag bond lengths of pyrazine linked to the contact (d_{AgC-Pz}) and non-contact ($d_{Pz...AgNC}$) silver clusters versus the intercluster distance (bottom).

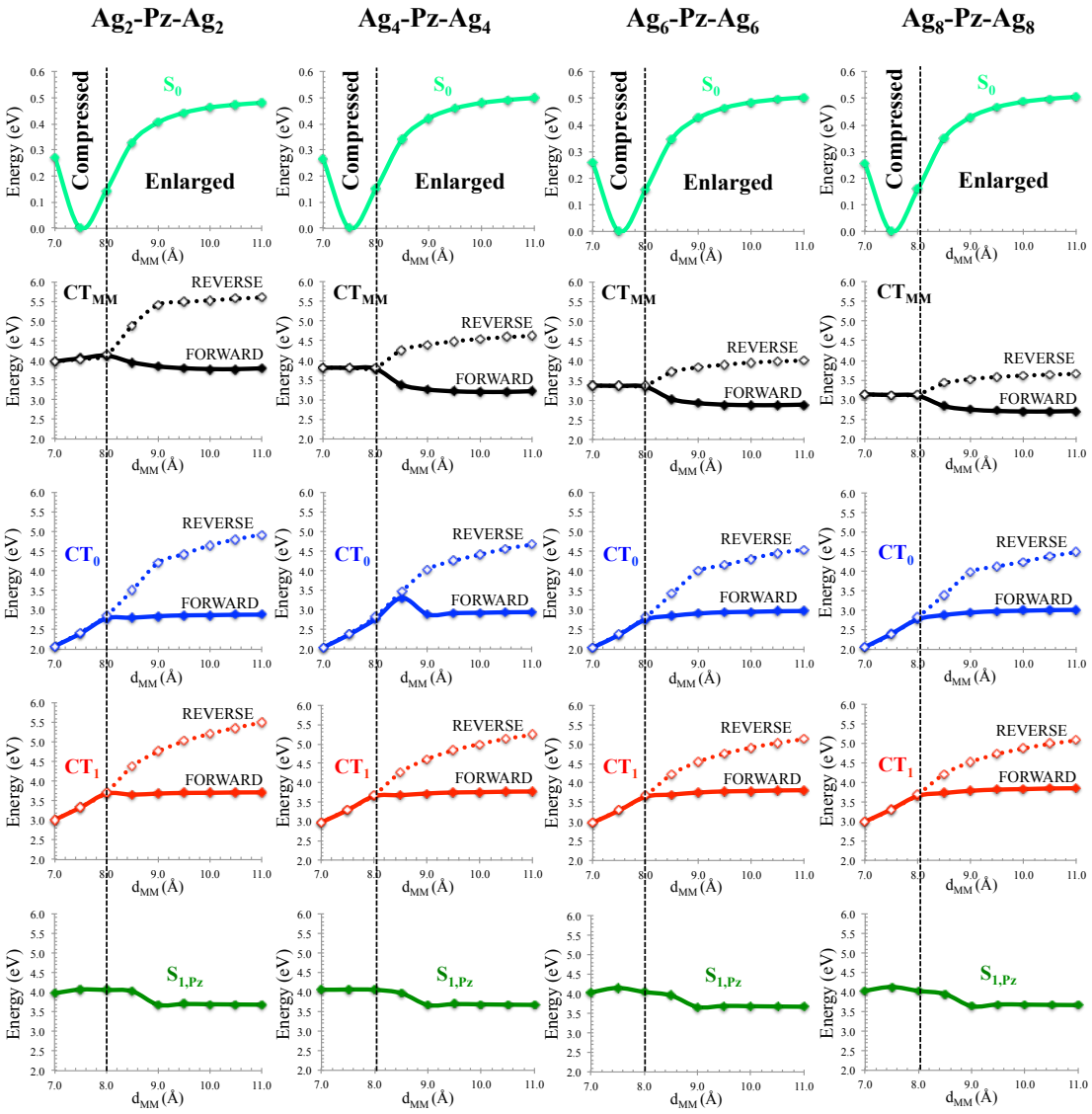

Figure S2 Effect of the inter-cluster distance (d_{MM}) on the M06-HF/LanL2DZ stabilization energy of the bond formed between pyrazine and the non-contact silver cluster in the ground electronic state S_0 (top) and on the corresponding vertical energies of the metal-metal (CT_{MM}), metal-molecule ($CT_{0,1}$) and molecular ($S_{1,Pz}$) excited states of Ag_n-Pz-Ag_n junctions.

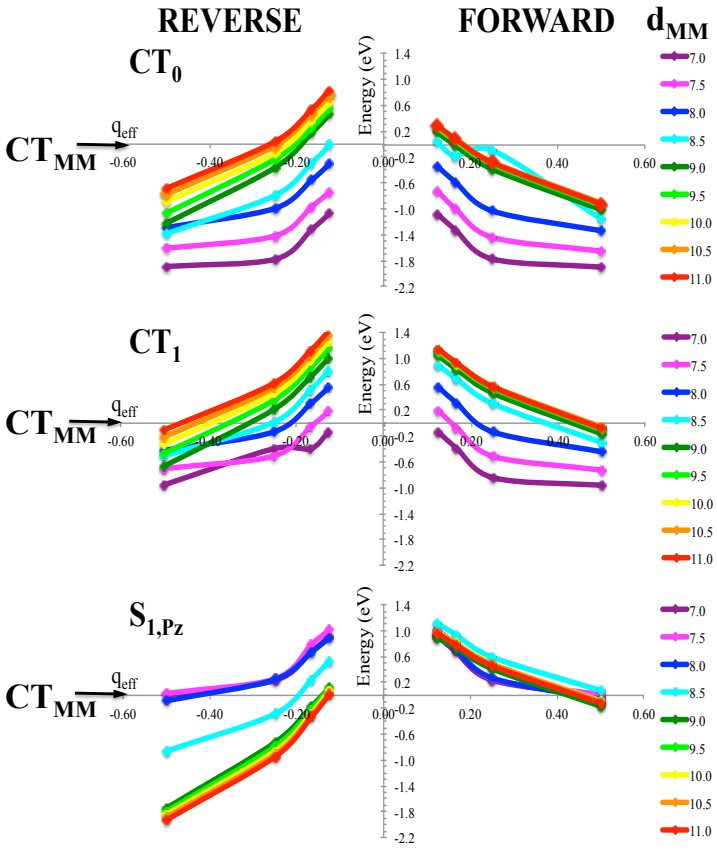

Figure S3 M06-HF/LanL2DZ relative energies of the $CT_{0,1}$ and $S_{1,Pz}$ states referred to the corresponding forward (q=+1) and reverse (q=-1) CT_{MM} polarized states plotted versus the density of charge (q_{eff}=q/n) of the silver clusters in charged Ag_n^{q}-Pz-Ag_n^{-q} junctions at different inter-cluster distances (d_{MM}).

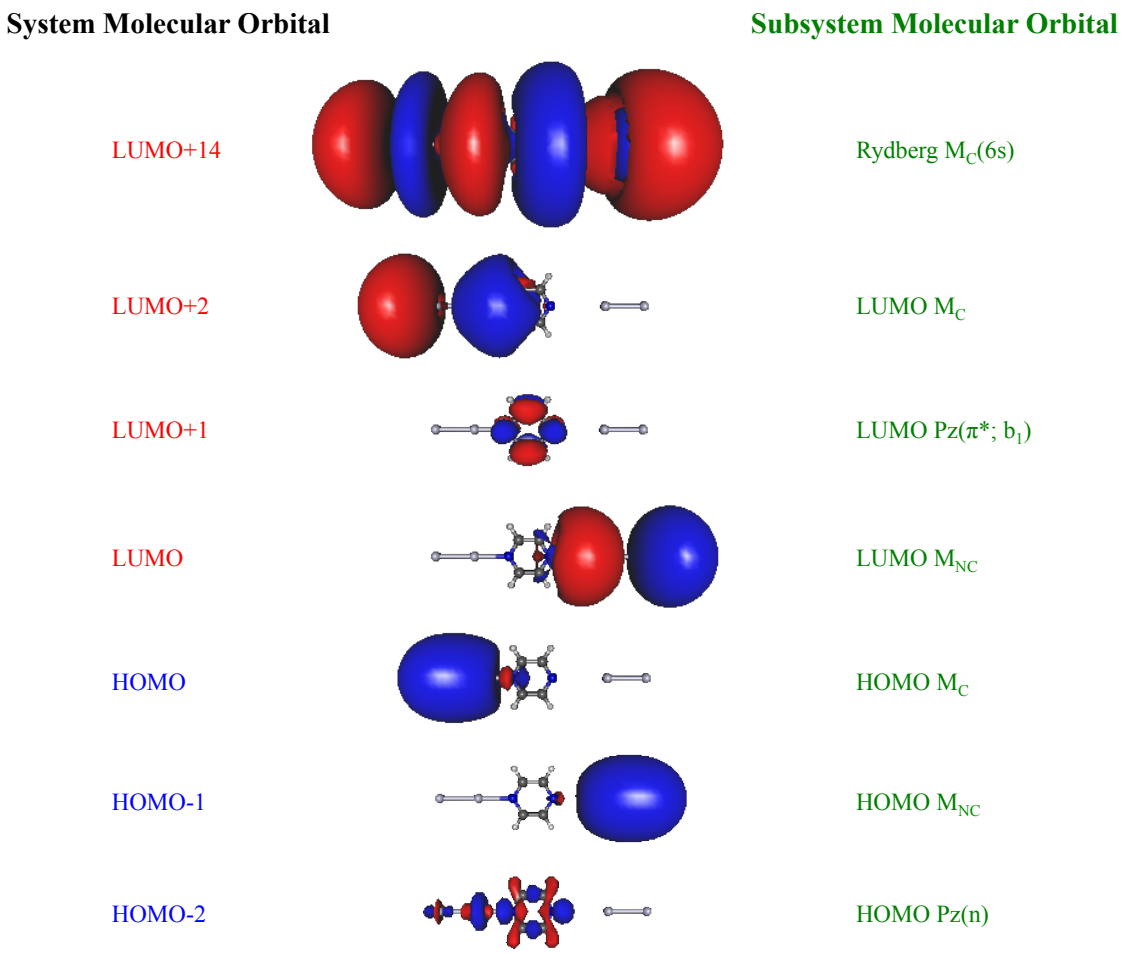

Figure S4 Relevant Kohn-Sham molecular orbitals involved in the discussed electronic states of the Ag_2-Pz…Ag_2 junction at an inter-cluster distance of 9.0 Å. Orbitals labelled according to the energies for the whole M_C-Pz…M_{NC} system (left) or for each subsystem: the contact metal (M_C), the molecule (Pz) and the non-contact metal (M_{NC}) (right) (see Table S1).

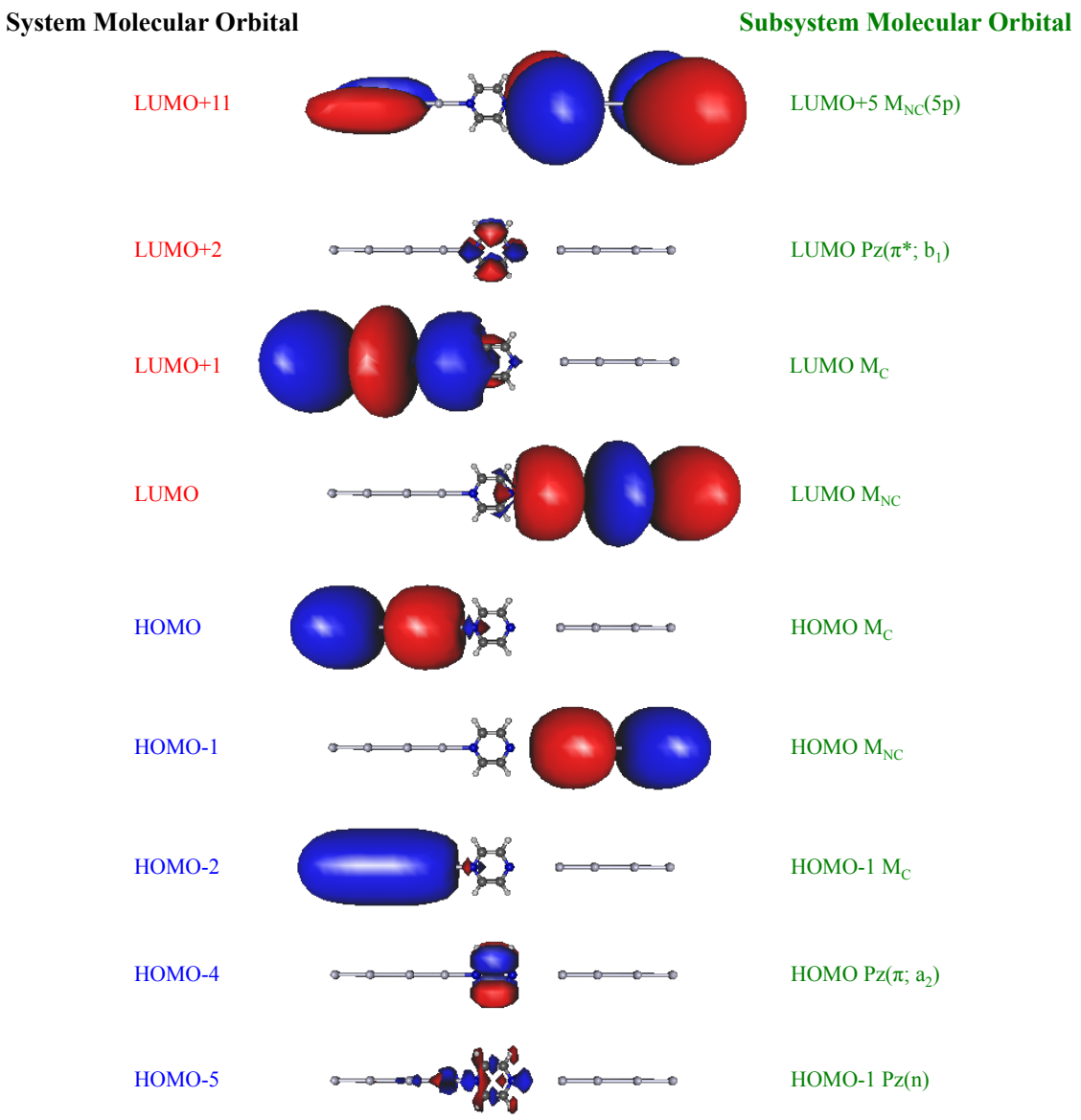

Figure S5 Relevant Kohn-Sham molecular orbitals involved in the discussed electronic states of the Ag_4-Pz…Ag_4 junction at an inter-cluster distance of 9.0 Å. Orbitals labelled according to the energies for the whole M_C-Pz…M_{NC} system (left) or for each subsystem: the contact metal (M_C), the molecule (Pz) and the non-contact metal (M_{NC}) (right) (see Table S1).

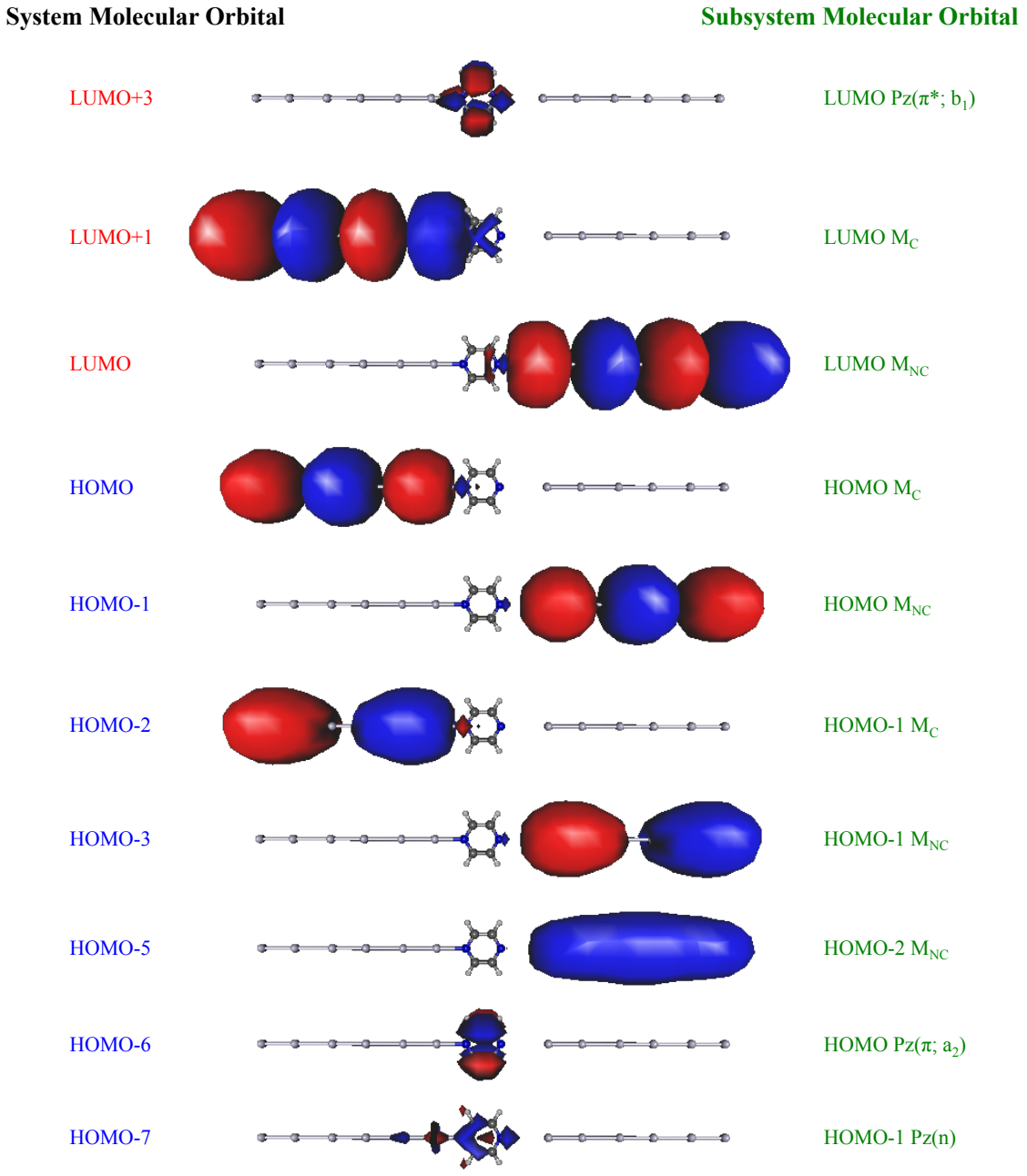

Figure S6 Relevant Kohn-Sham molecular orbitals involved in the discussed electronic states of the Ag_6-Pz…Ag_6 junction at an inter-cluster distance of 9.0 Å. Orbitals labelled according to the energies for the whole M_C-Pz…M_{NC} system (left) or for each subsystem: the contact metal (M_C), the molecule (Pz) and the non-contact metal (M_{NC}) (right) (see Table S1).

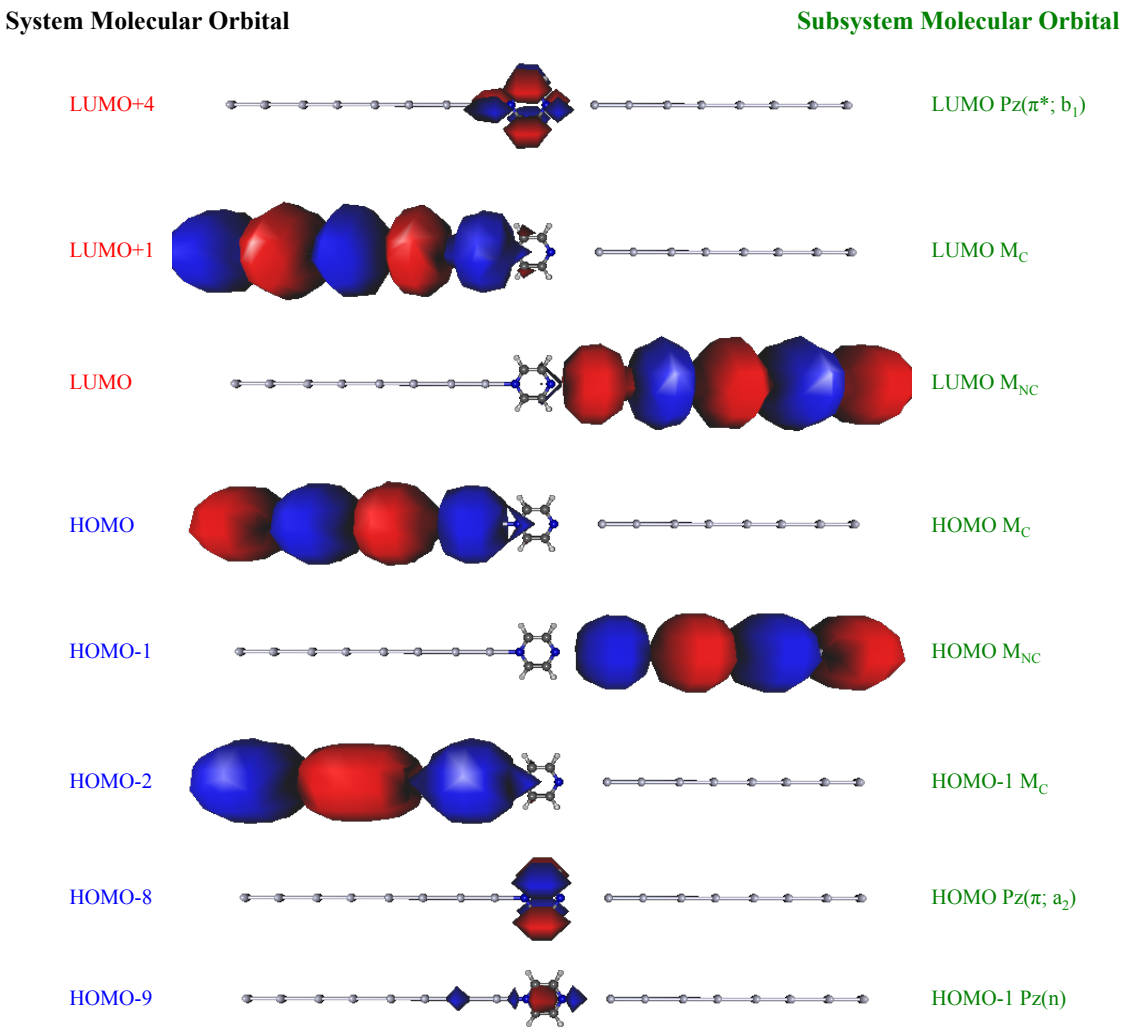

Figure S7 Relevant Kohn-Sham molecular orbitals involved in the discussed electronic states of the Ag_8-Pz…Ag_8 junction at an inter-cluster distance of 9.0 Å. Orbitals labelled according to the energies for the whole M_C-Pz…M_{NC} system (left) or for each subsystem: the contact metal (M_C), the molecule (Pz) and the non-contact metal (M_{NC}) (right) (see Table S1).

Table S1 M06-HF/LanL2DZ vertical energies (VE/eV) and wave functions for CT_{MM} metal-to-metal and CT_0 metal-to-molecule forward and reverse charge transfer states of Ag_n-Pz-Ag_n junctions (n=2,4,6 and 8) at 9.0 Å inter-cluster distance (d_{MM}).

CT_{MMF} : M_C^+-A…M_{NC}^-			
n[a]	**Configurations**[b]	**Coeff.**[c]	**VE**[d]
2	HOMO(M_C) → LUMO(M_{NC})	0.66	3.85
4	HOMO(M_C) → LUMO(M_{NC})	0.68	3.26
6	HOMO(M_C) → LUMO(M_{NC}) HOMO-2(M_{NC}) → LUMO(M_{NC})	0.55 -0.41	2.92
8	HOMO(M_C) → LUMO(M_{NC})	0.67	2.75
CT_{MMR} : M_C^--A…M_{NC}^+			
n[a]	**Configurations**[b]	**Coeff.**[c]	**VE**[d]
2	HOMO(M_{NC}) → LUMO(M_C) HOMO(M_{NC}) → Rydberg(M_{NC}; 6s)	0.50 -0.37	5.42
4	HOMO(M_{NC}) → LUMO(M_C)	0.68	4.40
6	HOMO(M_{NC}) → LUMO(M_C)	0.67	3.84
8	HOMO(M_{NC}) → LUMO(M_C)	0.69	3.52
CT_{0F} : M_C^+-A^-…M_{NC}			
n[a]	**Configuration**[b]	**Coeff.**[c]	**VE**[d]
2	HOMO(M_C) → LUMO(Pz; π*, b_1)	0.68	2.85
4	HOMO(M_C) → LUMO(Pz; π*, b_1) HOMO-1(M_C) → LUMO(Pz; π*, b_1)	0.61 -0.29	2.88
6	HOMO(M_C) → LUMO(Pz; π*, b_1) HOMO-1(M_C) → LUMO(Pz; π*, b_1)	0.55 -0.36	2.92
8	HOMO(M_C) → LUMO(Pz; π*, b_1) HOMO-1(M_C) → LUMO(Pz; π*, b_1)	0.49 0.38	2.94
CT_{0R} : M_C-A^-…M_{NC}^+			
n[a]	**Configurations**[b]	**Coeff.**[c]	**VE**[d]
2	HOMO(M_{NC}) → LUMO(Pz; π*, b_1)	0.64	4.21
4	HOMO(M_{NC}) → LUMO(Pz; π*, b_1) HOMO(M_{NC}) → LUMO+5(M_{NC}; 5p, b_1) HOMO-1(Pz; n, a_1) → LUMO(Pz; π*, b_1)	0.48 0.30 -0.26	4.04
6	HOMO(M_{NC}) → LUMO(Pz; π*, b_1) HOMO-1(Pz; n, a_1) → LUMO(Pz; π*, b_1) HOMO-1(M_{NC}) → LUMO(Pz; π*, b_1)	0.51 -0.32 0.27	4.00
8	HOMO(M_{NC}) → LUMO(Pz; π*, b_1) HOMO-1(Pz; n, a_1) → LUMO(Pz; π*, b_1)	0.39 0.28	3.98

[a]Number of silver atoms of each silver cluster; [b]Configurations with weights larger than 7%. Molecular orbitals are labelled for the contact metal (M_C), the molecule (Pz) and the non-contact metal (M_{NC}) subsystems (see Figs. S4-S7); [c]Coefficient of the corresponding configuration; [d]Vertical excitation energies (eV) at S_0 geometries.