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

Supporting Information

Transmission mechanism and quantum interference in fused thienoacenes coupling to Au electrodes through the thiophene rings

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Table S1 Au-S distance and binding energy of A1 coupling to Au_3 cluster calculated by different functionals.

basis set	functional	d_{Au-S} (Å)	$E_{binding}$ (eV)
C, H, S: 6-31G(d,p) Au: def2-SZP	M06	2.45	0.886
	B3LYP	2.42	0.828
	CAM-B3LYP	2.40	0.937
	PBE0	2.37	0.992
DZP	PBE	2.37	1.085

* The first four lines are calculated by the Gaussian 09 package and the last line is calculated by the SIESTA package.

Table S2 Au-S distance and binding energy of molecules coupling to an Au adatom on the Au(111) surface .

	d_{Au-S} (Å)	$E_{binding}$ (eV)
A1	2.509	0.41
B1	2.526	0.38
A2	2.509	0.41
B2	2.517	0.42
C2	2.517	0.37
D2	2.539	0.34
E2	2.503	0.37
A3	2.510	0.42
B3	2.533	0.41
C3	2.510	0.39
D3	2.585	0.28
E3	2.493	0.37
TT[a]	2.524	0.34
BT[b]	2.511	0.39
A3'	2.492	0.51
B3'	2.519	0.46
C3'	2.478	0.54
D3'	2.525	0.50

[a] thieno[3,2-b]thiophene

[b] benzothiophene

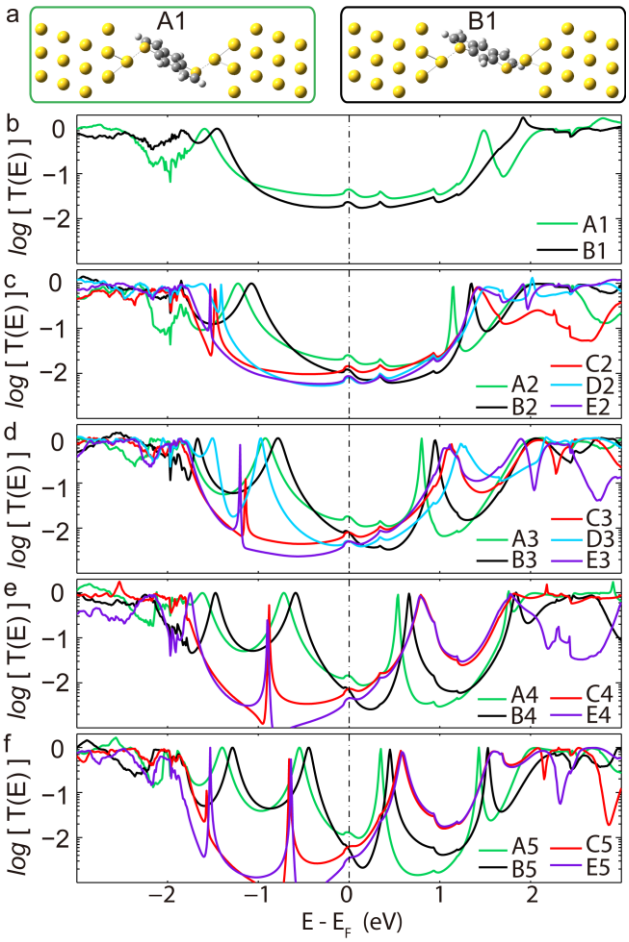

Fig. S1 (a) Structural models of A1 and B1 coupled to Au electrodes through Au-S donor-acceptor interactions. (b-f) Equilibrium transmission spectra corresponding to thienoacenes in Chart 1.

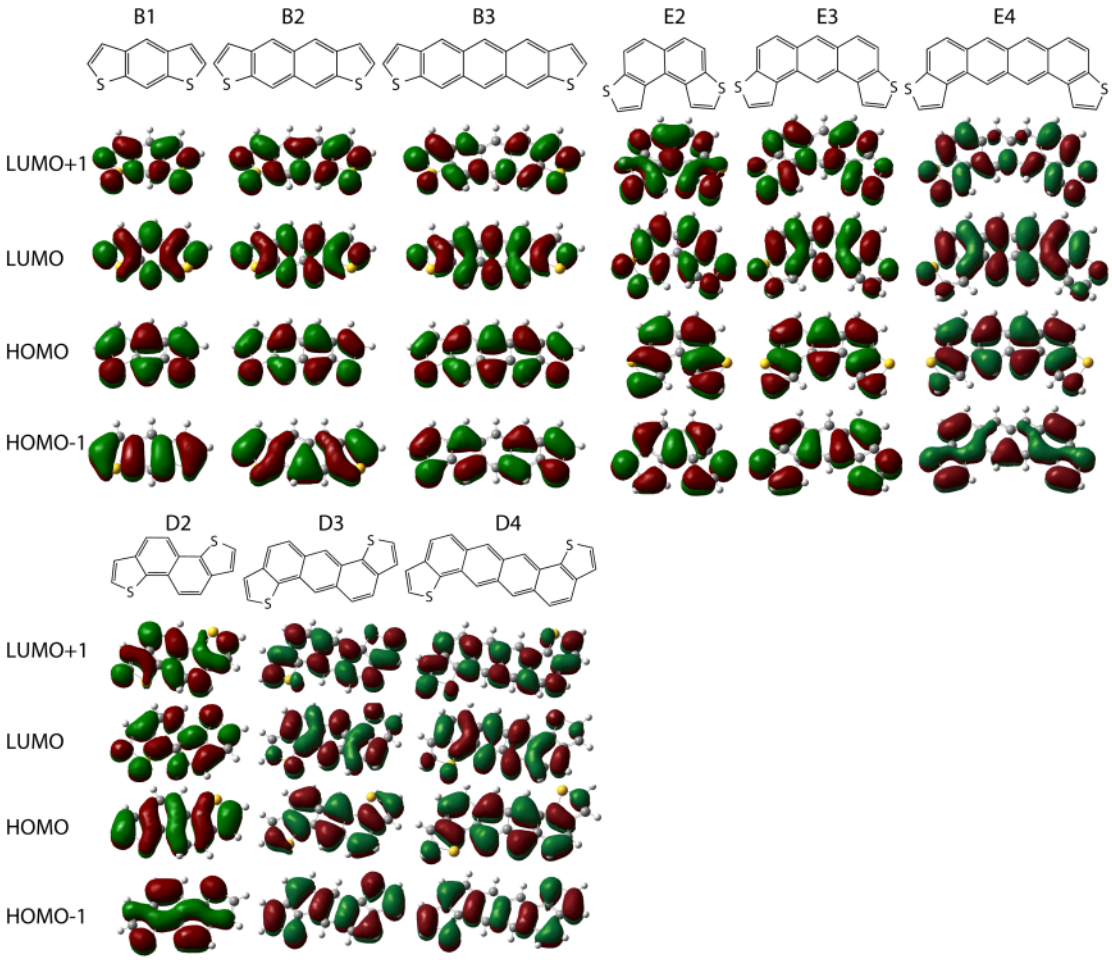

Fig. S2 Isosurface maps of the frontier molecular orbitals.

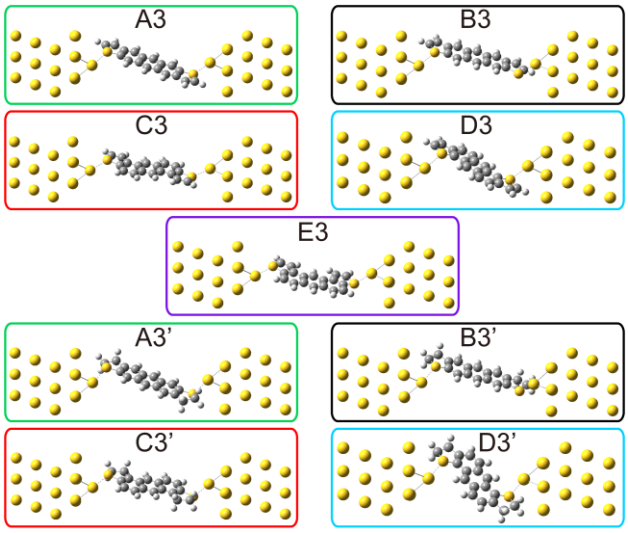

Fig. S3 Structural models of nine molecules coupled to Au electrodes through Au-S donor-acceptor interactions.

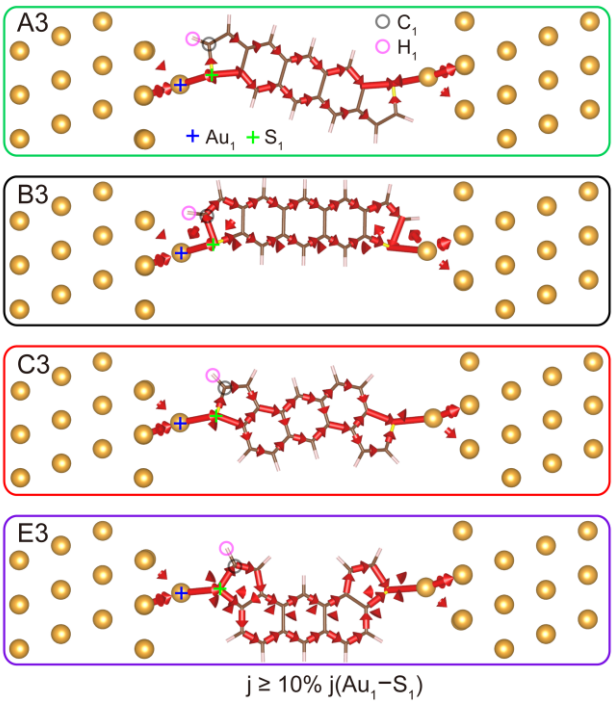

Fig. S4 Equilibrium left-to-right bond currents which are greater than 10% of the bond current between Au_1 and S_1. Lengths of the red arrows indicate the magnitudes.

Table S3 Comparison of the equilibrium left-to-right bond currents from atoms in the left electrode to H_1, C_1 and S_1 (labeled in Fig. S5) along with the distances between Au_1 and C_1, and between H_1 and the Au surface.

	d(Au_1-C_1) (Å)	d(H_1-surface) (Å)	j(left-H_1)/ j(left-S_1)	j(left-C_1)/ j(left-S_1)
A3	3.26	2.80	-0.001%	-0.052%
B3	3.16	2.45	-0.018%	-0.317%
C3	3.50	4.05	-0.001%	-0.031%
E3	3.63	4.77	-0.005%	-0.145%

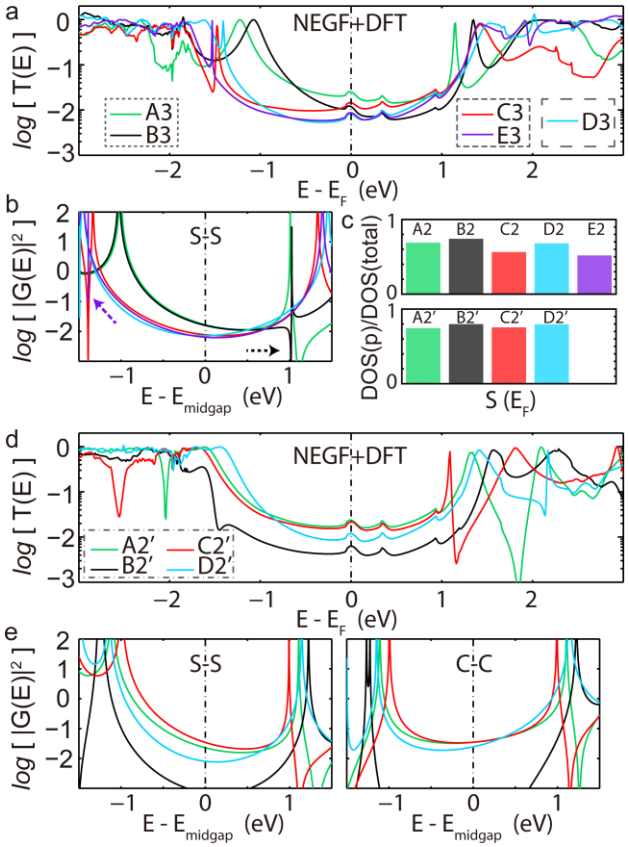

Fig. S5 (a) Equilibrium transmission spectra of A2 to E2. (b) Modulus square of zeroth Green's function between the p_z orbitals of the S atoms of A2 to E2. (c) Proportion of the p orbitals in the total DOS on the S atoms at the Fermi level. (d) Equilibrium transmission spectra of A2' to D2'. (e) Modulus square of zeroth Green's function between the p_z orbitals of the S atoms (left) and sp^2 C atoms directly bonded to S (right) of A2' to D2'.