Supporting Information

Theoretical Study of Long-Ranged Electron Transport in Molecular Junctions

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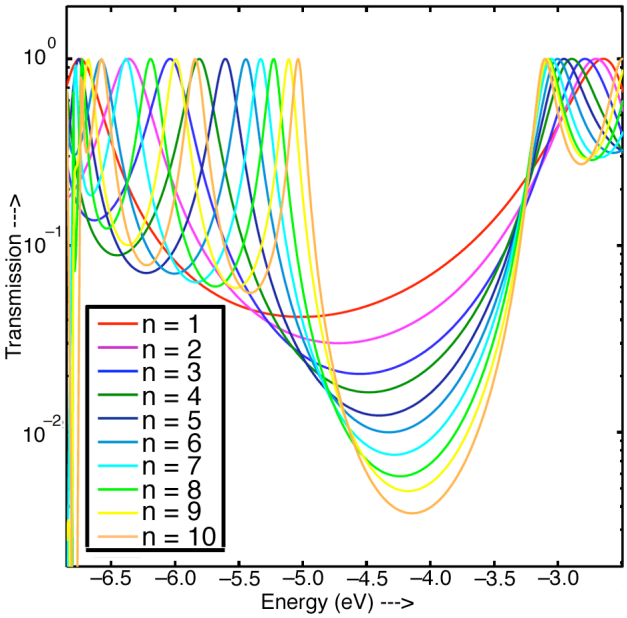

Figure S1. Coherent transmission spectra, between two outermost p-orbitals on sulfer atoms, in PD-based junctions having even-number of carbon atoms calculated with the Newns-Anderson approximation. Other parameters are shown in the text.

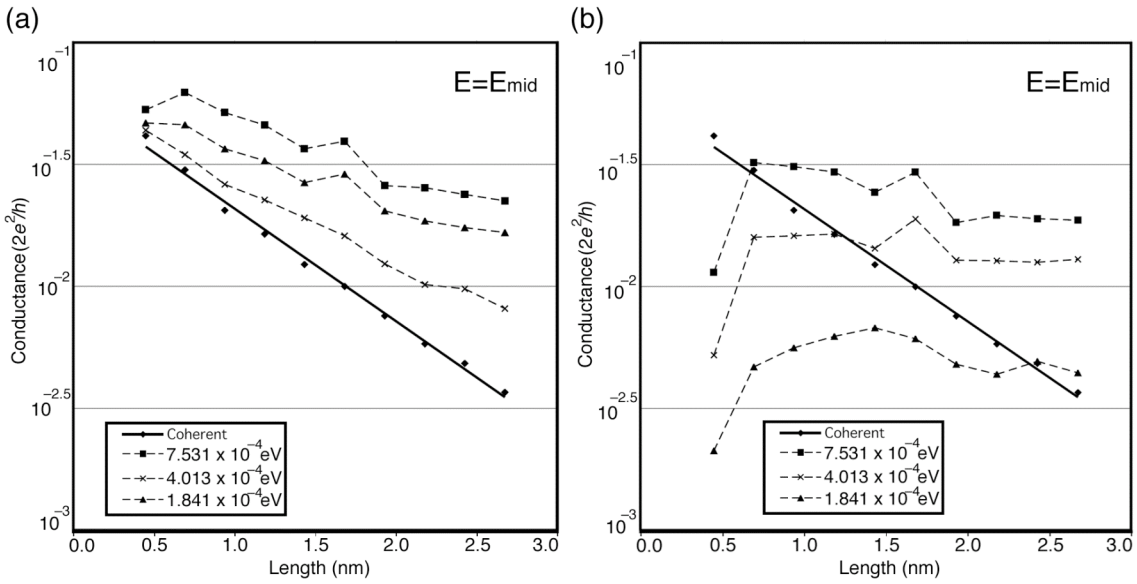

Figure S2. Molecular length dependence of electron conduction including incoherent scattering effects in PD-based junctions having even-number carbon atoms calculated using the ab initio approach. The electron injection energy is chosen at the mid-gap. (a) Total conductivities are depicted in dashed lines. Coherent components are depicted in solid lines for comparison. Dephasing strengths are parameterized in terms of the broadening energies shown in inset. It corresponds to changing the distances between the dephasing probes and atomic orbitals from 3.0 to 3.6 Å in at intervals of 0.3 Å. (b) Incoherent components and coherent component are depicted in dashed lines and solid line, respectively. Details for the dephasing parameters are shown in Table S3.

Table S1. Molecular energy levels of (a) PDs having even-number and (b) odd-number of carbon atoms without (with) 2 gold atoms, and (c) OPEDs without (with) 2 gold atoms calculated within the extended Hückel method.

(a) PDs having even number carbon atoms without (with) 2 gold atoms

$(CH)_{2n}$-$(SH)_2$ ($(CH)_{2n}$-$(SAu)_2$)	n=1	n=2	n=3	n=4	n=5
LUMO+4	6.7487	1.9013	–0.6963	–0.8709	–5.3257
	(–5.4315)	(–5.4765)	(–5.7435)	(–6.5506)	(–8.23357)
LUMO+3	2.2128	–0.4456	–0.9737	–5.4510	–6.0693
	(–5.5082)	(–6.2721)	(–7.2683)	(–7.8788)	(–8.65993)
LUMO+2	0.1879	–1.2462	–5.6828	–6.4915	–7.1414
	(–7.4838)	(–8.2427)	(–8.4743)	(–8.5841)	(–8.2336)
LUMO+1	–2.1010	–6.1740	–7.2078	–7.8965	–8.3695
	(–8.6290)	(–8.6857)	(–8.7674)	(–8.8657)	(–9.0026)
LUMO	–7.4112	–8.4661	–9.0080	–9.3383	–9.5626
	(–8.9455)	(–9.2446)	(–9.5247)	(–9.7483)	(–9.9094)
HOMO	–10.346	–10.463	–10.543	–10.600	–10.642
	(–10.649)	(–10.620)	(–10.670)	(–10.680)	(–10.695)
HOMO-1	–11.432	–11.299	–11.213	–11.153	–11.109
	(–10.821)	(–10.854)	(–10.802)	(–10.791)	(–10.771)
HOMO-2	–12.247	–12.278	–12.301	–12.238	–12.055
	(–11.544)	(–11.497)	(–11.440)	(–11.383)	(–11.337)
HOMO-3	–12.552	–12.452	–12.410	–12.320	–12.330
	(–12.062)	(–12.033)	(–11.918)	(–11.855)	(–11.788)
HOMO-4	–13.529	–12.882	–12.494	–12.383	–12.369
	(–12.658)	(–12.465)	(–12.575)	(–12.331)	(–12.250)

$(CH)_{2n}$-$(SH)_2$ ($(CH)_{2n}$-$(SAu)_2$)	n=6	n=7	n=8	n=9	n=10
LUMO+4	–5.8042	–6.2838	–6.7145	–7.0875	–7.4077
	(–7.65267)	(–7.9940)	(–8.2368)	(–8.40734)	(–8.5188)
LUMO+3	–6.6338	–7.1076	–7.4983	–7.8214	–8.0905
	(–8.4341)	(–8.5515)	(–8.6313)	(–8.6984)	(–8.7618)
LUMO+2	–7.6408	–8.0287	–8.3349	–8.5815	–8.7841
	(–8.7286)	(–8.8100)	(–8.8977)	(–8.9957)	(–9.1117)
LUMO+1	–8.7105	–8.9675	–9.1680	–9.3286	–9.4601
	(–9.1550)	(–9.3251)	(–9.4672)	(–9.5820)	(–9.6904)
LUMO	–9.7257	–9.8499	–9.9481	10.028	–10.093
	(–10.014)	(–10.114)	(–10.182)	(–10.229)	(–10.280)
HOMO	–10.674	–10.701	–10.722	–10.739	–10.754
	(–10.699)	(–10.705)	(–10.708)	(–10.711)	(–10.713)
HOMO-1	–11.074	–11.047	–11.025	–11.006	–10.991
	(–10.774)	(–10.756)	(–10.750)	(–10.759)	(–10.749)
HOMO-2	–11.912	–11.811	–11.725	–11.654	–11.595
	(–11.315)	(–11.279)	(–11.258)	(–11.247)	(–11.225)
HOMO-3	–12.337	–12.341	–12.332	–12.211	–12.109
	(–11.737)	(–11.688)	(–11.642)	(–11.606)	(–11.565)
HOMO-4	–12.360	–12.355	–12.344	–12.345	–12.346
	(–12.143)	(–12.072)	(–12.004)	(–11.946)	(–11.893)

(b) PDs having odd-number carbon atoms without (with) 2 gold atoms

$(CH)_m$-$(SH)_2$ ($(CH)_m$-$(SAu)_2$)	m=5	m=7	m=9	m=11	m=13
LUMO+4	1.91631	–0.733831	–0.776043	–5.30581	–5.73109
	(–5.47346)	(–5.61393)	(–6.31642)	(–6.91622)	(–7.38933)
LUMO+3	–0.635874	–0.77499	–5.40928	5.95193	6.47379
	(–5.96508)	(–6.87201)	(–7.52252)	(–7.96277)	(–8.25146)
LUMO+2	–0.82596	–5.58941	–6.29431	–6.90228	–7.39224
	(–7.77755)	(–8.26434)	(–8.47575)	(–8.58885)	(–8.66228)
LUMO+1	–5.94233	–6.8566	–7.53368	–8.02703	–8.39643
	(–8.64606)	(–8.71482)	(–8.76768)	(–8.84084)	(–8.94488)
LUMO	–7.83777	–8.47766	–8.89121	–9.17866	–9.39643
	(–8.93019)	(–9.08354)	(–9.29849)	(–9.47948)	(–9.64667)
SOMO	–9.88251	–10.0627	–10.1875	–10.2784	–10.3484
	(–10.1489)	(–10.2734)	(–10.3956)	(–10.4464)	(–10.5079)
SOMO–1	–10.8687	–10.8669	–10.8667	–10.866	–10.8656
	(–10.7631)	(–10.7513)	(–10.7494)	(–10.7500)	(–10.7435)
SOMO–2	–11.8017	–11.638	–11.521	–11.4359	–11.3698
	(–11.1294)	(–11.099)	(–11.0157)	(–11.0037)	(–10.9626)
SOMO–3	–12.3375	–12.3081	–12.3098	–12.2202	–12.1102
	(–11.7397)	(–11.6854)	(–11.6196)	(–11.5756)	(–11.5266)
SOMO–4	–12.4122	–12.4205	–12.3437	–12.3687	–12.3368
	(–12.1991)	(–12.1204)	(–12.0234)	(–11.9556)	(–11.8955)

$(CH)_m$–$(SH)_2$ ($(CH)_m$–$(SAu)_2$)	m=15	m=17	m=19
LUMO+4	–6.17368	–6.58205	–6.94267
	(–7.75591)	(–8.03736)	(–8.24873)
LUMO+3	–6.92697	–7.31119	7.63387
	(–8.42943)	(–8.54492)	(–8.62613)
LUMO+2	–7.78406	–8.10171	–8.36076
	(–8.72974)	(–8.79692)	(–8.87307)
LUMO+1	–8.68082	–8.90706	–9.08893
	(–9.08369)	(–9.21616)	(–9.3434)
LUMO	–9.55298	–9.68296	–9.78725
	(–9.79405)	(–9.89645)	(–9.98088)
SOMO	–10.4032	–10.4492	–10.486
	(–10.5741)	(–10.5991)	(–10.619)
SOMO–1	–10.8654	–10.8649	–10.8649
	(–10.7320)	(–10.7312)	(–10.7300)
SOMO–2	–11.3174	–11.2729	–11.2379
	(–10.9034)	(–10.8922)	(–10.8838)
SOMO–3	–12.0025	–11.9065	–11.8276
	(–11.4743)	(–11.4376)	(–11.40494)
SOMO–4	–12.3332	–12.3062	–12.2635
	(–11.844)	(–11.7936)	(–11.7478)

(c) OPEDs without (with) 2 gold atoms

Tour–wire–$(SH)_2$ ($(Tour–wire–(SAu)_2$)	n=2	n=3	n=4	n=5	n=6
LUMO+4	–5.9599	–8.3207	–8.34524	–8.34547	–8.34558
	(–7.73304)	(–8.3626)	(–8.36229)	(–8.36252)	(–8.58303)
LUMO+3	–6.56274	–8.34513	–8.34542	–8.34557	–8.34953
	(–8.3627)	(–8.3626)	(–8.36229)	(–8.77807)	(–9.05448)
LUMO+2	–7.71742	–8.34533	–8.34556	–8.54336	–8.83993
	(–8.3629)	(–8.59884)	(–9.0559)	(–9.31473)	(–9.47688)
LUMO+1	–8.36479	–8.34553	–8.82155	–9.1052	–9.28179
	(–9.05903)	(–9.46883)	(–9.65384)	(–9.75173)	(–9.80921)
LUMO	–9.05222	–9.24546	–9.45762	–9.56775	–9.63101
	(–10.7219)	(–10.7219)	(–10.7218)	(–10.7217)	(–10.7217)
HOMO	–10.747	–10.194	–10.7354	–10.7829	–10.7876
	(–10.7223)	(–10.7219)	(–10.7218)	(–10.7217)	(–10.7217)
HOMO–1	–10.9806	–10.8458	–10.8107	–10.7978	–10.7931
	(–10.7402)	(–10.8130)	(–10.8412)	(–10.8524)	(–10.8569)
HOMO–2	–12.1543	–11.5892	–11.5894	–11.5894	–11.5894
	(–10.9815)	(–10.9072)	(–10.8786)	(–10.8673)	(–10.8628)
HOMO–3	–12.1858	–11.5896	–11.5894	–11.5894	–11.5894
	(–12.2805)	(–11.9784)	(–11.833)	(–11.7536)	(–11.7062)
HOMO–4	–12.2871	–12.0411	–11.8787	–11.7914	–11.7405
	(–12.3524)	(–12.3788)	(–12.2705)	(–12.0860)	(–11.9653)

Tour–wire–$(SH)_2$ ($(Tour–wire–(SAu)_2$)	n=7	n=8
LUMO+4	–8.34559	–8.48334
	(–8.85579)	(–9.05384)
LUMO+3	–8.63917	–8.84921
	(–9.24355)	(–9.37902)
LUMO+2	–9.04238	–9.18695
	(–9.58522)	(–9.66106)
LUMO+1	–9.39883	–9.48005
	(–9.84548)	(–9.86964)
LUMO	–9.67021	–9.69598
	(–10.7216)	(–10.7216)
HOMO	–10.7894	–10.790
	(–10.7216)	(–10.7216)
HOMO–1	–10.7914	–10.7908
	(–10.8586)	(–10.8592)
HOMO–2	–11.5894	–11.5894
	(–10.8609)	(–10.8602)
HOMO–3	–11.5894	–11.5894
	(–11.6761)	(–11.656)
HOMO–4	–11.7087	–11.6877
	(–11.8823)	(–11.8231)

Table S2. Molecular energy levels of PDs having even-number carbon atoms without (with) 2 gold atoms calculated at the B3LYP/LANL2DZ level.

$(CH)_{2n}$–$(SH)_2$ ($(CH)_{2n}$–$(SAu)_2$)	n=1	n=2	n=3	n=4	n=5
LUMO+4	2.13691	1.20682	1.33036	1.26805	0.88355
	(–0.31456)	(–0.49525)	(–0.48191)	(–0.46178)	(–0.43457)
LUMO+3	0.92491	1.16002	0.66559	0.62341	0.60899
	(–0.63430)	(–0.56926)	(–0.56681)	(–0.60681)	(–0.85580)
LUMO+2	0.53062	0.67539	0.63291	0.59974	0.60600
	(–0.88274)	(–1.39295)	(–1.82724)	(–2.13473)	(–2.33392)
LUMO+1	0.42531	0.56981	0.49661	–0.03537	–0.50178
	(–3.63326)	(–3.58401)	(–3.57639)	(–3.54673)	(–3.52605)
LUMO	–0.58259	–1.19975	–1.63377	–1.91976	–2.12167
	(–4.00605)	(–3.96306)	(–3.89884)	(–3.84279)	(–3.79489)
HOMO	–6.29806	–5.75465	–5.46295	–5.26240	–5.11301
	(–6.31031)	(–6.08582)	(–5.87574)	(–5.71737)	(–5.57071)
HOMO–1	–7.42543	–7.12230	–6.77590	–6.49018	–6.24772
	(–6.81426)	(–6.71984)	(–6.57344)	(–6.50188)	(–6.40501)
HOMO–2	–8.75960	–8.28041	–7.81727	–7.44230	–7.14461
	(–7.15577)	(–6.93046)	(–6.79249)	(–6.66161)	(–6.56746)
HOMO–3	–9.18437	–9.21512	–8.81348	–8.34898	–7.95524
	(–7.87088)	(–7.59305)	(–7.32529)	(–7.07740)	(–6.85236)
HOMO–4	–10.21949	–9.26410	–9.27934	–9.06056	–8.71443
	(–8.70464)	(–8.31796)	(–7.97755)	(–7.70407)	(–7.47686)

$(CH)_{2n}$–$(SH)_2$ ($(CH)_{2n}$–$(SAu)_2$)	n=6	n=7	n=8	n=9	n=10
LUMO+4	0.62913	0.62450	0.61362	0.61008	0.60790
	(–0.43375)	(–0.46613)	(–0.61606)	(–0.82124)	(–1.01798)
LUMO+3	0.61606	0.61035	0.58913	0.37035	0.09660
	(–1.15784)	(–1.41472)	(–1.61744)	(–1.77472)	(–1.90915)
LUMO+2	0.42205	0.05333	–0.26640	–0.53906	–0.77335
	(–2.47433)	(–2.58372)	(–2.66181)	(–2.71841)	(–2.76984)
LUMO+1	–0.86206	–1.14641	–1.37009	–1.55350	–1.70806
	(–3.51598)	(–3.50645)	(–3.49639)	(–3.50836)	(–3.49475)
LUMO	–2.26807	–2.38262	–2.46888	–2.53991	–2.60059
	(–3.75190)	(–3.72333)	(–3.69122)	(–3.67925)	(–3.65040)
HOMO	–4.99464	–4.90158	–4.82158	–4.75709	–4.70511
	(–5.42376)	(–5.32880)	(–5.23709)	(–5.12526)	(–5.05832)
HOMO–1	–6.03956	–5.86296	–5.70676	–5.57343	–5.46077
	(–6.28718)	(–6.17453)	(–6.04445)	(–5.88989)	(–5.77425)
HOMO–2	–6.89481	–6.67984	–6.48800	–6.31793	–6.16854
	(–6.51712)	(–6.43766)	(–6.38596)	(–6.35385)	(–6.29806)
HOMO–3	–7.64013	–7.37835	–7.15604	–6.96066	–6.78678
	(–6.71576)	(–6.55821)	(–6.47331)	(–6.46514)	(–6.40256)
HOMO–4	–8.35198	–8.03660	–7.77210	–7.54326	–7.34108
	(–7.27386)	(–7.07903)	(–6.89835)	(–6.75658)	(–6.60338)

Table S3. Dephasing parameters for $pp\pi$ coupling between outermost p-orbitals in the terminal of phase-breaking probes and carbon outermost p-orbitals in a molecular wire calculated from the ab initio approach. Escape rate and interval of each escape processes are determined from eq (2.12) with E = –4.145 eV. Dephasing strengths in PD-based junctions are parameterized from 6.5 Å to 7.1 Å at an interval of 0.3 Å.

Length between atom and probe (Å)	Resonant integral (eV)	Broadening (eV)	Energy shift (eV)	Escape rate (s^{-1})	Interval of escape process (s)
6.5	-4.758×10^{-2}	7.531×10^{-4}	-5.848×10^{-4}	1.139×10^{12}	8.780×10^{-13}
6.8	-3.427×10^{-2}	4.013×10^{-4}	-3.116×10^{-4}	6.067×10^{11}	1.648×10^{-12}
7.1	-2.322×10^{-2}	1.841×10^{-4}	-1.430×10^{-4}	2.784×10^{11}	3.592×10^{-12}