Electronic supplementary information for

A surprising way to control the charge transport in molecular electronics: the subtle impact of the coverage of self-assembled monolayers of floppy molecules adsorbed on metallic electrodes

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S1 List of acronyms

The acronyms used to indicate the various levels of theory employed to obtain the results presented in the paper are listed below:

- PBE/cc-pVDZ: DFT calculations [1] to isolated molecules using the PBE exchange correlation functional and cc-pVDZ Dunning double-ζ basis sets;

- B3LYP/cc-pVDZ: DFT calculations [1] to isolated molecules using the hybrid B3LYP exchange correlation functional and cc-pVDZ Dunning double-ζ basis sets;

- PBE/cc-pVDZ/-PP: DFT calculations [1] to isolated molecules using the PBE exchange correlation functional and cc-pVDZ Dunning double-ζ basis sets for non-metal atoms and with relativistic core potential (cc-pVDZ-PP [2]) for gold;

- MP2/cc-pVDZ: calculations for isolated molecules at second order Møller-Plesset level [1] using cc-pVDZ basis sets;

- CCSD/cc-pVDZ: CCSD (coupled cluster singles and doubles) calculations [1] for isolated molecules using cc-pVDZ basis sets;

- 0.02: GGA-PBE SIESTA calculations for isolated molecules or SAMs adsorbed on fcc Au (111) surfaces; SZP basis set for gold, DZP basis sets for non-metal atoms; relaxation until forces on all atoms were smaller than 0.02 eV/Å; slab includes three fcc Au (111) layers. Unless otherwise specified, metal layers were always frozen at the periodicity defined by the experimental lattice constant $a = 4.078\text{Å}$ of gold;

- 0.01: GGA-PBE SIESTA calculations for SAMs adsorbed on fcc Au (111) surfaces; SZP for gold, DZP for non-metal atoms; relaxation until forces on all atoms

were smaller than 0.01 eV/Å; slab includes three fcc Au (111) layers;

- 0.005: GGA-PBE SIESTA calculations; SZP for gold, DZP for non-metal atoms; relaxation until forces on all atoms were smaller than 0.005 eV/Å; slab includes three fcc Au (111) layers;

- DZP-TZP: GGA-PBE SIESTA calculations for SAMs adsorbed on fcc Au (111) surfaces; DZP for gold, TZP for non-metal atoms; relaxation until forces on all atoms were smaller than 0.02 eV/Å; slab includes three fcc Au (111) layers;

- VDW-DRSLL: VDW-DRSLL SIESTA calculations for SAMs adsorbed on fcc Au (111) surfaces including dispersion corrections [3]; SZP for gold, DZP for non-metal atoms; relaxation until forces on all atoms were smaller than 0.02 eV/Å; slab includes three fcc Au (111) layers;

- CABCAB: GGA-PBE SIESTA calculations; SZP for gold, DZP for non-metal atoms; relaxation until forces on all atoms were smaller than 0.02 eV/Å; slab includes six fcc Au (111) layers;

- CAB-R: GGA-PBE SIESTA calculations for SAMs adsorbed on fcc Au (111) surfaces; SZP for gold, DZP for non-metal atoms; relaxation until forces on all atoms were smaller than 0.02 eV/Å; slab includes three fcc Au (111) layers, wherein the top layer *was* allowed to relax;

- CABCAB-R: GGA-PBE SIESTA calculations for SAMs adsorbed on fcc Au (111) surfaces; SZP for gold, DZP for non-metal atoms; relaxation until forces on all atoms were smaller than 0.02 eV/Å; slab includes six fcc Au (111) layers, wherein the top layer *was* allowed to relax.

In the various tables presented in this ESI, the methods utilized are indicated in the first column.

S2 Remarks on the various methods employed

For the benefit of a reader who is not expert in computational chemistry, a brief justification on the usage of the various

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methods will be given below.

Whenever possible, from a fundamental perspective, *ab initio* methods are preferable to DFT approaches: ultimately, they are based on the Schrödinger equation, which they approximate in a certain way. Unlike the DFT approaches, their accuracy can be systematically improved. Unfortunately, *ab initio* approaches are very demanding computationally. For the cases considered in this paper, they can be only applied for isolated molecules (Sec. 3.1) or molecules containing a metal atoms (Sec. 3.2). MP2 and CCSD utilized there are *ab initio* methods.

In general, DFT approaches based on hybrid exchange-correlation functionals — B3LYP[4,5] is a popular example — are more accurately for chemical studies, but they are computationally more costly than DFT approaches based on generalized gradient approximations (GGA)[6] — like PBE[7] functional — ubiquitously used in material sciences.

Table S1, S2, S3 and S4, aim at justifying the fact that the results obtained at the DFT/PBE level of theory (especially the value of the torsional angle φ) can be trusted; they are comparable both with those based on *ab initio* approaches and with those obtained with the aid of the hybrid B3LYP functional. From a pragmatic standpoint this comparison is important because hybrid functionals (like B3LYP) are not implemented in SIESTA, the package used in this paper to investigate SAMs; in SIESTA's nomenclature, "hybrid" functionals represent nothing but mixing of GGA and LDA (local density approximation) functionals, and the latter is known to be very crude in describing chemical properties.

In all quantum chemical approaches basis sets are needed in calculations; the richer the basis sets, the better is the quality of the results, but employing larger basis sets is also more demanding computationally. The comparison of the results obtained with different basis sets (SZP, DZP, TZP) illustrates that using SZP for gold and DZP for non-metal atoms represents a reliable choice.

Last but not least, a thorny aspect of DFT approaches is often whether "dispersion corrections" substantially affect the results. By presenting results obtained by means of the VDW-DRSLL functional[3] we demonstrate that, for the presently considered systems, this is not the case.

Notes and references

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Method, BPMT	C_1C_2	C_2C_3	C_3C_4	C_4C_4'	$C_1'C_2'$	$C_2'C_3'$	$C_3'C_4'$	SC_1	SC_1'	φ
0.02	1.4173	1.4052	1.4189	1.4915	1.4105	1.4079	1.4199	1.7833	8.9871	38.855
PBE/cc-pVDZ	1.4101	1.3989	1.4135	1.4846	1.4040	1.4015	1.4143	1.7852	8.9585	36.447
B3LYP/cc-pVDZ	1.4031	1.3941	1.4069	1.4859	1.3981	1.3962	1.4079	1.7888	8.9391	37.956
MP2/cc-pVDZ	1.4101	1.4023	1.4124	1.4835	1.4059	1.4040	1.4130	1.7856	8.9424	42.010
CCSD/cc-pVDZ	1.4088	1.4029	1.4107	1.4946	1.4054	1.4044	1.4116	1.7952	8.9628	42.988

Table S1 Optimized geometry of an isolated BPMT molecule. Results obtained within various methods specified by means of the acronyms defined above for the twisting angle φ and several bond lengths XY between various atoms X and Y labeled as shown in Fig. 1. For the nearly symmetric bonds C_1-C_2 and C_1-C_6; C_2-C_3 and C_5-C_4; C_3-C_4 and C_5-C_4 we only show their length averages, which are denoted here by C_1C_2; C_2C_3; C_3C_4, respectively, and similar for the other ring whose atoms are labeled by prime. Throughout, lengths are given in angstrom and angles in degrees.

Method, BPDT	C_1C_2	C_2C_3	C_3C_4	C_4C_4'	SC_1	SC_1'	φ
0.02	1.4170	1.4050	1.4194	1.4883	1.7841	8.9995	38.823
PBE/cc-pVDZ	1.4102	1.3988	1.4139	1.4826	1.7852	8.9710	35.361
B3LYP/cc-pVDZ	1.4031	1.3940	1.4072	1.4843	1.7888	8.9058	37.092
MP2/cc-pVDZ	1.4102	1.4022	1.4127	1.4819	1.7851	8.9525	40.990

Table S2 Counterpart of Table S1 for an isolated BPDT molecule. See the caption of Table S1 and Fig. 1 for notations. Lengths in angstrom, angles in degrees.

Method, BPMT-Au	C_1C_2	C_2C_3	C_3C_4	SC_1	SC_1'	AuS
0.02	1.4213	1.4039	1.4211	1.7784	8.9750	2.3449
DZP-TZP	1.4212	1.4039	1.4211	1.7784	8.9766	2.3338
PBE/cc-pVDZ	1.4131	1.3978	1.4159	1.7873	8.9504	2.2748
B3LYP/cc-pVDZ	1.4060	1.3931	1.4089	1.7905	8.9336	2.2978
MP2/cc-pVDZ-PP	1.4115	1.4063	1.4141	1.7908	8.9374	2.2067

Method, BPMT-Au	$C_1'C_2'$	$C_2'C_3'$	$C_3'C_4'$	C_4C_4'	φ
0.02	1.4108	1.4076	1.4200	1.4897	36.976
DZP-TZP	1.4105	1.4078	1.4202	1.4895	37.067
PBE/cc-pVDZ	1.4040	1.4012	1.4145	1.4838	35.368
B3LYP/cc-pVDZ	1.3981	1.3960	1.4080	1.4853	37.044
MP2/cc-pVDT-PP	1.4059	1.4040	1.4130	1.4834	41.816

Table S3 Optimized geometry of an isolated BPMT molecule wherein the H atom of the thiol group was replaced by a gold atom. In addition to data shown in Table S1, the Au-S bond length is indicated here. See the caption of Table S1 and Fig. 3 for notations. Lengths in angstrom, angles in degrees.

Method, BPDT-Au	C_1C_2	C_2C_3	C_3C_4	C_4C_4'	SC_1	SC_1'	AuS
0.02	1.4209	1.4036	1.4223	1.4875	1.7801	8.9926	2.3472
DZP-TZP	1.4209	1.4034	1.4220	1.4867	1.7810	8.9921	2.3355
PBE/cc-pVDZ	1.4133	1.3973	1.4168	1.4808	1.7861	8.9634	2.2763
B3LYP/cc-pVDZ	1.4061	1.3928	1.4094	1.4832	1.7898	8.9454	2.2986
MP2/cc-pVDZ-PP	1.4116	1.4017	1.4144	1.4815	1.7906	8.9487	2.2068

Method, BPDT-Au	$C_1'C_2'$	$C_2'C_3'$	$C_3'C_4'$	$S'C_1'$	$S'C_1$	SS'	φ
0.02	1.4176	1.4044	1.4205	1.7821	8.9984	10.7726	34.714
DZP-TZP	1.4176	1.4040	1.4201	1.7820	8.9937	10.7720	34.704
PBE/cc-pVDZ	1.4108	1.3978	1.4147	1.7825	8.9626	10.7446	32.661
B3LYP/cc-pVDZ	1.4035	1.3934	1.4077	1.7871	8.9452	10.7313	35.431
MP2/cc-pVDZ-PP	1.4105	1.4019	1.4127	1.7838	8.9445	10.7307	40.605

Table S4 Optimized geometry of an isolated BPDT molecule wherein the H atom of a thiol group was replaced by a gold atom. In addition to data shown in Table S2, the Au-S bond length is indicated here. See the caption of Table S1 and Fig. 3 for notations. Lengths in angstrom, angles in degrees.

Method, BPMT	φ	$d^{(1)}$	$d^{(2)}$	$d^{(3)}$	$L=SC$	z	Z	θ
0.02	36.615	2.6695	2.6768	2.9802	8.9634	2.1981	10.2616	32.727
0.005	36.410	2.6901	2.6939	3.0816	8.9899	2.2410	10.2506	32.521
DZP-TZP	35.888	2.6729	2.6806	3.0414	8.9797	2.2167	10.2616	32.632

Method, BPDT	φ	$d^{(1)}$	$d^{(2)}$	$d^{(3)}$	$L=SS$	z	Z	θ
0.02	33.866	2.6459	2.7968	2.8011	10.7372	2.1810	12.6341	13.867
0.01	33.311	2.6469	2.7967	2.7990	10.7382	2.1806	12.6347	13.873
DZP-TZP	34.356	2.6452	2.7535	2.7755	10.7395	2.1537	12.7068	13.498
	36.946	2.7358	2.9308	2.9523	10.7645	2.3316	12.8097	13.987

Table S5 Results for SAMs consisting of BPMT and BPDT molecules arranged in a (6×6) adsorbate unit cell on the fcc Au (111) surface (*cf.* Fig. 2a). $d^{(1,2,3)}$ represent the distances of the sulfur atom to the closest gold atoms from the top layer. L is the length of the molecular backbone measured between the S and C$'$ (or S$'$) atoms of the opposite ends of the BPMT (or BPDT) molecule. φ is the twisting angle and z is the distance of the S atom to the top layer of the gold slab. The SAM height Z is defined as the distance between the top layer and the most distant H atom of the molecule. The tilt angle θ is the angle between the molecular axis (line through the S and C$'_1$ atoms for BPMT and through the S and S$'$ atoms) and the gold surface. Lengths in angstrom, angles in degrees.

Method, BPMT	φ_1	θ_1	$d_1^{(1)}$	$d_2^{(1)}$	$d_3^{(1)}$	L_1	z_1	Z_1
0.02	75.976	5.697	2.6564	2.6852	2.7880	8.9714	2.1430	12.1772
DZP-TZP	76.024	5.699	2.6701	2.6842	2.7916	8.9708	2.1420	12.1739
VDW-DRSLL	74.077	5.720	2.7552	2.7774	2.8779	9.0038	2.2526	12.3167
CABCAB	73.856	5.745	2.6632	2.6903	2.7833	8.9700	2.1385	12.1703
CAB-R	74.626	6.725	—	—	—	8.9559	—	—
CABCAB-R	74.936	7.933	—	—	—	8.9080	—	—

Method, BPMT	φ_2	θ_2	$d_1^{(2)}$	$d_2^{(2)}$	$d_3^{(2)}$	L_2	z_2	Z_2
0.02	75.935	5.670	2.6698	2.6860	2.7928	8.9721	2.1348	12.1700
DZP-TZP	75.987	5.676	2.6570	2.6845	2.7872	8.9710	2.1345	12.1670
VDW-DRSLL	77.179	5.745	2.7645	2.7700	2.8767	9.0011	2.2531	12.3141
CABCAB	77.992	5.765	2.6757	2.6902	2.7882	8.9698	2.1459	12.1768
CAB-R	78.294	6.945	—	—	—	8.9494	—	—
CABCAB-R	78.422	8.213	—	—	—	8.9162	—	—

Method, BPMT	α_u	α_l	CC_u	SS_l	HH_{uu}	HH_{ul}	HH_{lu}	HH_{ll}
0.02	74.994	76.422	4.9670	4.9574	2.9802	2.9891	2.9943	2.9951
DZP-TZP	75.060	76.456	4.9673	4.9603	2.9814	2.9907	2.9946	2.9958
VDW-DRSLL	74.681	74.681	4.9700	4.9672	2.9770	2.9871	3.0206	3.0301
CABCAB	75.042	75.042	4.9680	4.9607	2.9795	2.9899	2.9916	2.9941
CAB-R	75.356	75.356	4.7935	4.9692	2.9653	2.9867	3.0204	2.9978
CABCAB-R	75.205	75.205	4.2600	4.9714	2.9677	3.0044	3.0106	2.8924

Table S6 Results for SAMs of BPMT forming a regular herringbone superstructure on an fcc Au (111) surface (*cf.* Fig. 2b). Here, $d_1^{(1,2,3)}$ and $d_2^{(1,2,3)}$ represent the shortest three (superscripts $1, 2, 3$) S-Au bond lengths corresponding to the sulfur atoms of the two (subscripts $1, 2$) crystallographically nonequivalent BPMT molecules having twisting angles denoted by $\varphi_{1,2}$; $\theta_{1,2}$ are the angles to the metal surface of the lines passing through the S and C$'$ atoms at opposite molecular ends; $z_{1,2}$ are the distances to the electrode surface of the two S atoms, $Z_{1,2}$ are molecular heights, and $L_{1,2}$ are the lengths of the molecular backbones measured between the S and C$'$ atoms at opposite molecular ends. HH's, CC and SS denote distances between atoms belonging to the two molecules of the supercell as visible in Fig. 3, where the angles $\alpha_{u,l}$ between oppositely placed rings on of the two nonequivalent molecules are also depicted. The reason why some entries are missing in this table is given in the main text. Lengths in angstrom, angles in degrees.

Method, BPDT	φ_1	θ_1	$d_1^{(1)}$	$d_2^{(1)}$	$d_3^{(1)}$	L_1	z_1	Z_1
0.02	75.036	10.006	2.6287	2.7851	2.8833	10.7074	2.1973	12.8746
DZP-TZP	71.881	9.990	2.6248	2.7842	2.8824	10.7071	2.1947	12.8733
VDW-DRSLL	74.700	9.819	2.6976	2.8951	3.0177	10.7465	2.3192	13.0660
0.01	75.152	10.018	2.6313	2.78293	2.8719	10.7074	2.1939	12.8655
0.005	73.562	10.034	2.6276	2.7844	2.8706	10.7040	2.1922	12.8636
CABCAB	74.672	10.277	2.6240	2.7827	2.8882	10.7041	2.1956	12.7280
CAB-R	74.457	11.424	—	—	—	10.6903	—	—
CABCAB-R	74.541	11.695	—	—	—	10.6784	—	—

Method, BPDT	φ_2	θ_2	$d_1^{(2)}$	$d_2^{(2)}$	$d_3^{(2)}$	L_2	z_2	Z_2
0.02	75.561	10.244	2.6185	2.7865	2.8827	10.7056	2.1925	12.8523
DZP-TZP	71.891	10.236	2.6151	2.7838	2.8814	10.7059	2.1892	12.8517
VDW-DRSLL	71.583	9.933	2.7069	2.8957	2.9996	10.7472	2.3197	13.0580
0.01	75.322	10.227	2.6194	2.7784	2.8847	10.7093	2.1903	12.8472
0.005	73.779	10.270	2.6177	2.7900	2.8798	10.7105	2.1925	12.8508
CABCAB	74.535	10.050	2.6355	2.7828	2.8854	10.7063	2.2005	12.7426
CAB-R	74.769	11.382	—	—	—	10.6789	—	—
CABCAB-R	74.851	11.603	—	—	—	10.6698		

Method, BPDT	α_u	α_l	SS_u	SS_l	HH_{uu}	HH_{ul}	HH_{lu}	HH_{ll}
0.02	74.070	72.510	4.9710	5.7271	2.8833	2.9055	2.9227	3.3043
DZP-TZP	75.221	71.801	4.9706	5.7265	2.884	2.9082	2.9257	3.3054
VDW-DRSLL	76.439	72.953	5.0242	5.6716	2.9256	2.9084	2.9159	3.2629
0.01	74.418	71.066	4.9615	5.7349	2.8750	2.9170	2.9523	3.3215
0.005	74.335	72.760	4.9566	5.7366	2.8836	2.9326	2.9793	3.3506
CABCAB	73.972	72.420	4.9697	5.7236	2.8831	2.9076	2.9261	3.3044
CAB-R	74.580	70.779	4.9320	5.8431	2.8807	2.9444	3.0133	3.4369
CABCAB-R	74.371	70.764	4.9361	5.6901	2.8813	2.9315	2.9907	3.3956

Table S7 Results for SAMs of BPDT forming a regular herringbone superstructure on an fcc Au (111) surface (*cf.* Fig. 2b). See the caption of Table S6 and Fig. 3 for notations. The reason why some entries are missing is given in the main text. Lengths in angstrom, angles in degrees.