Supplementary Information: A simple model to engineer single-molecule conductance of acenes by chemical disubstitution

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I. Transmissions and conductances obtained from our first-principles calculations

Figure S1 shows the transmission functions obtained from our first-principles calculations for the acene molecules considered in our work.



Figure S1. Transmission function of the acene molecules considered in our work. B: benzene. N: naphthalene. A: anthracene. T: tetracene. P: pentacene. Amino (-NH₂) anchoring groups in blue solid lines. Methylthio (-SMe) anchoring groups in red solid lines. 4-methylthio phenyl (-PhSMe) anchoring groups in green solid lines. Fermi level in vertical black dashed lines.

Table S1 shows the corresponding conductance values obtained from our first-principles calculations.

R	Conductance (10 ⁻³ G ₀)								
	B-R ₂	N-R ₂	A_1-R_2	A_2-R_2	T_1-R_2	T_2-R_2	P ₁ - R ₂	P_2-R_2	P ₃ - R ₂
NH ₂	6.29	9.80	12.47	17.33	14.64	22.47	15.61	24.98	28.28
SMe	7.69	7.66	8.58	8.36	9.38	9.92	8.50	9.38	10.85
PhSMe	0.37	0.13	0.14	0.01	-	-	-	-	-

Table S1. Values of the conductance in terms of G_0 for the acene molecules studied in this work.

II. Effect of the electrode-molecule-electrode geometry

As experimental conductance values are usually obtained from histograms involving many different electrode-molecule-electrode geometries, we have considered a few additional geometries to those shown in Fig. 2 of the main text, corresponding to local minima in the potential energy surface. Fig. S2 shows four of these geometries for the electrode/p-phenylenediamine/electrode system. The figure also includes the calculated values of the conductance. As can be seen, differences in conductance are roughly smaller than 30%, i.e., comparable or even smaller than the error bars of the experimental conductance values with which we compare in the main text. Therefore, one can expect that the observed trends will not be much affected by this effect. A similar conclusion concerning the comparison with experiment has been reached in our previous study of azaborines (Angew. Chem. 2021, 60, 6609–6616), where calculations were performed by using an even larger number of geometries.



Figure S2. (a-d) Four different geometries of the Au/p-phenylenediamine/Au system corresponding to four local minima of the corresponding potential energy surface and the resulting values of the conductance. The bottom panel shows the corresponding transmissions.

III. Conductance trends resulting from LUMO energies

We have compared the trends in the observed conductances with those resulting from the LUMO energies obtained from our extended-Hückel calculations. For consistency with Fig. 4 of the manuscript, the LUMO energies have been referred to the electron affinity of the smallest disubstituted molecule, i.e., disubstituted benzene. The results are shown in Fig. S3. As can be seen, the LUMO energies do not follow the trends observed experimentally, neither within a given family of compounds (i.e., with the same linker) nor when comparing the same molecules with different linkers.



Figure S3. Top and central panels: same as Fig. 4 in the main text. Bottom panel: LUMO energies resulting from our extended-Hückel calculations referred to the electron affinity of the smallest disubstituted molecule, i.e., disubstituted benzene.

IV. Effect of the linker from calculated HOMO orbitals

The analysis presented in the last paragraph of section 3 in terms of the electrostatic potential remains unchanged when considering the shapes of the HOMO orbitals resulting from our extended-Hückel calculations (see Fig. S4). This suggests that the differences in conductance between different systems are only sensitive to differences in the electronic density in the HOMO, at least when comparing systems in which the conduction path length is the same.



Figure S4. HOMO orbitals resulting from our extended-Hückel calculations. Notations as in Fig. 5 of the manuscript.

V. HOMO energies

Table S2 shows the HOMO energies resulting from our extended-Hückel and DFT calculations.

Table S2. HOMO energies resulting from our extended-Hückel and DFT-PBE calculations in eV. As in the main text, the Hückel energies have been referred to the experimental ionization potential of the smallest system by introducing the quantity $\delta_{HOMO} = HOMO+IP$, where IP stands for ionization potential of the smallest disubstituted molecule in each series. Notations as in Fig. 1 of the main text.

R	ΗΟΜΟ _{ΗÜCKEL} - δ _{ΗΟΜΟ} (eV)								
	B-R ₂	N-R ₂	A ₁ -R ₂	A ₂ -R ₂	T ₁ - R ₂	T ₂ -R ₂	P ₁ -R ₂	P ₂ -R ₂	P ₃ -R ₂
$\rm NH_2^*$	-7.61	-7.35	-7.19	-6.99	-7.08	-6.84	-7.00	-6.78	-6.71
SMe ^{**}	-7.74	-7.72	-7.71	-7.69	-7.71	-7.69	-7.72	-7.67	-7.67
PhSMe**	-7.99	-7.97	-7.95	-7.93	-	-	-	-	-

R	HOMO _{PBE} (eV)								
	B-R ₂	N-R ₂	A ₁ -R ₂	A_2 - R_2	T ₁ -R ₂	T ₂ -R ₂	P_1 - R_2	P ₂ -R ₂	P ₃ -R ₂
NH ₂	-3.93	-3.88	-3.81	-3.68	-3.75	-3.58	-3.73	-3.56	-3.51
SMe	-4.67	-4.78	-4.64	-4.56	-4.44	-4.34	-4.26	-4.19	-4.15
PhSMe	-4.63	-4.67	-4.50	-4.56	-	-	-	-	-

 $^*\delta_{HOMO}$ = -4.16 eV $^{**}\delta_{HOMO}$ = -2.59 eV

VI. Eigenchannels at frontier peaks

Fig. S5 shows the overlap between the molecule-electrode orbitals at Fermi energy, HOMO transmission energy and LUMO transmission energy for some representative molecules.



Figure S5. Eigenchannels of the B-R₂, A_1 -R₂ and A_2 -R₂ systems with $R = NH_2$ and SMe at the Fermi energy (left columns), the position of the HOMO transmission band (closest peak on the left of the Fermi energy in Fig. 2, middle columns) and the position of the LUMO transmission band (closest peak on the right of the Fermi energy in Fig. 2, right columns).