

SUPPLEMENTARY MATERIAL TO Unimolecular amplifier: principles of a three-terminal device with power gain

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Table A: Molecular orbital energies (in eV) for molecules UA1 through UA4, from DFTB calculations (here P,H,T,B = significant wavefunction amplitude P: on pyrene donor, T: on TTF donor, B: on bridge, A: on acceptor), and experimental gas-phase ionization potentials (I_D) for TTF and pyrene, and experimental electron affinities A_A for TCNQ, and benzoquinone. The empirical formulae are $C_{43}H_{24}O_2N_2S_6$ for UA1, $C_{43}H_{28}O_2N_2S_6$ for UA2, $C_{41}H_{24}O_4S_6$ for UA3, and $C_{41}H_{28}O_4S_6$ for UA4.

Energies (eV)	UA1	UA2	UA3	UA4
HOMO-1	-4.854 ^T	-4.850 ^T	-5.525	-5.388 ^{P,B,T}
HOMO	-4.523 ^A	-4.688 ^A	-5.129 ^A	-4.973 ^{B,T}
LUMO	-3.423 ^{P,A}	-3.362 ^{P,B}	-3.963 ^{T,B}	-4.250 ^A
LUMO+1	-3.029 ^A	-2.672 ^{P,B}	-3.288 ^{P,B,T,A}	-3.317 ^{P,B,T}
HOMO-LUMO	1.100	1.326	1.166	0.724
I_D (T=TTF)	6.83 [22]	6.83 [22]	6.83 [22]	6.83 [22]
I_D (P=pyrene)	7.41 [23]	7.41 [23]	7.41 [23]	7.41 [23]
A_A (TCNQ or benzoquinone)	3.3 [24]	3.3 [24]	1.9 [25]	1.9 [25]
I_D (T) - A_A (A)	3.53	3.53	4.93	4.93
I_D (P) - A_A (A)	4.11	4.11	5.51	5.51

The LUMO wavefunction amplitudes, were naively expected to be largest for the A part of the molecule, and were indeed so for UA1 and UA4, but not for UA2 or UA3. Similarly, it was expected that the largest HOMO and HOMO-1 wavefunction amplitudes would be largest on the donor atoms of T and P, respectively, but this is not seen in **Table A**. Linking these donors and acceptors covalently (in particular with an ethynyl bridge) made considerable changes in the intramolecular electron distribution, despite a saturated alkyl bond in the A part of the molecule: clearly a longer saturated bridge should have been assumed.

To show how the central voltage V_C affects the current for this case, the currents through each molecule-electrode junction, I_L , I_C , and I_R , as well as the corresponding energy of each of the molecular levels on each part of the molecule, are plotted in **Figure A** for $V_C = 1.0$ V. Increasing the central voltage V_C charges the central component of the molecule, and also exerts an electric field on it, causing the

molecular levels in this part of the molecule to increase in energy. Therefore, the HOMO of the central moiety enters into the bias window at a lower voltage, resulting in an earlier switching on of the current.

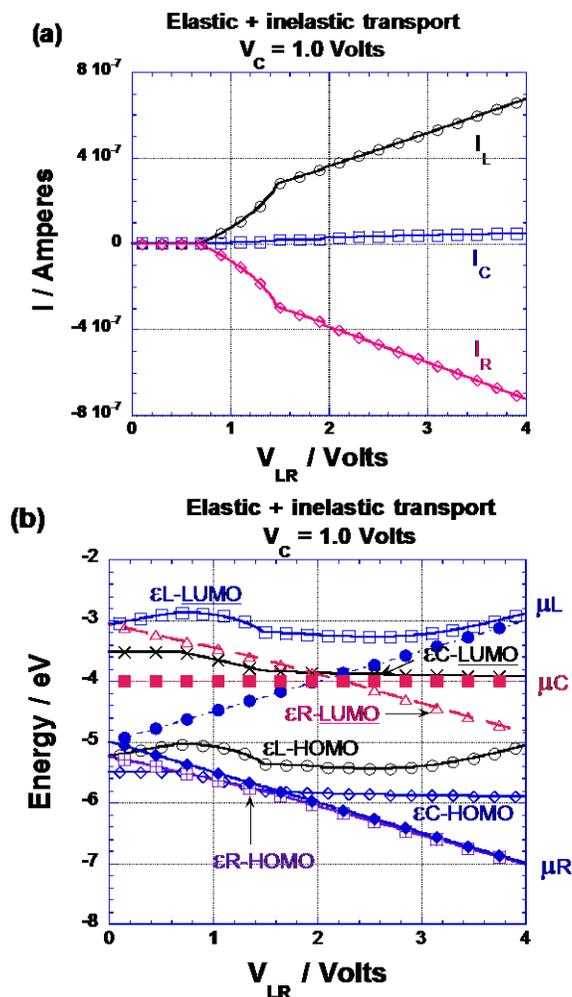


Figure A: (a) Currents through each molecule-electrode junction, I_L , I_C , and I_R , for $V_C = 1.0$ V for UA6, for the case where there is both elastic and inelastic transport through the molecule. (b) Energies of molecular levels ϵ_L HOMO, ϵ_C HOMO, ϵ_R HOMO, ϵ_L LUMO, ϵ_C LUMO, and ϵ_R LUMO for the same bias range. At zero V_{LR} , the chemical potential of the electrodes is at -5.0 eV, and V_{LR} is the bias between the left and right electrodes. The central voltage V_C charges the central part of the molecule and also exerts an electric field on it, causing the molecular levels in this part of the molecule to increase in energy. This causes the HOMO of the central moiety to enter into the bias window at a lower voltage, resulting in an earlier switching on of the current.

There are two components to the mechanism shifting the orbitals in the central moiety: the electric field due to the bias applied to the electrodes and the net

charge on the molecule itself. To demonstrate that this device is not simply a field-effect transistor, we switched off the effect of the electric field by setting $U_{ja}^{ee} = 0.0$ eV. The results for the case of elastic-only transport are shown in **Figure B(a)**, and those for the case of both elastic and inelastic transport are shown in **Figure B(b)**. These results show that the device produces current amplification **even in the absence of electric field effects on the molecular orbitals**, demonstrating that it is not simply a field-effect transistor.

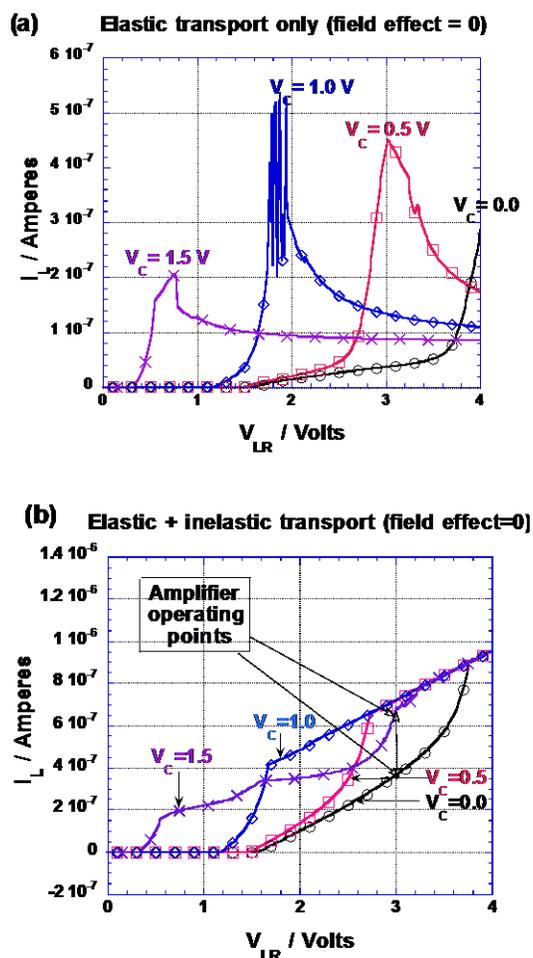


Figure B: Current I_L for UA6 for different values of V_C with $U_{ja}^{ee} = 0.0$ eV for (a) elastic-only transport (b) both inelastic and elastic transport. The voltage on the x-axis V_{LR} is the bias between the left and right electrodes. The device produces current amplification even in the absence of electric field effects on the molecular orbitals, demonstrating that it is not simply a field-effect transistor.

Again, the gradual displacement of the I_L currents with increasing control electrode voltage V_C seen in **Figure B(b)** is exactly what is needed to discuss molecule UA6 as a unimolecular amplifier; the separated I_L curves still merge at higher currents in **Figure B(b)**.

As in **Figure 8(a)**, the open two-sided vertical arrow in **Figure B(b)** shows two points (“amplifier operating points”) which could be used to discuss power gain, one on the $V_C = 0$ curve ($V_{LR} = 3.0$ Volts, $I_L = 3.63 \times 10^{-7}$ A) and the other at the $V_C = 1.5$ Volt curve ($V_{LR} = 3.0$ Volts, $I_L = 6.72 \times 10^{-7}$ A). If a load resistor of $1.0 \times 10^7 \Omega$ is placed between the L and R electrodes, then the voltage drop across them changes from $3.63 \times 10^{-7} \times 10^7 = 3.63$ Volts to $6.72 \times 10^{-7} \times 10^7 = 6.72$: this is a change of 3.09 Volts for a control potential change of 1.5 Volts: the amplification factor is now $3.09/1.5 = 2.06$.