

От органической к молекулярной электронике

Конфигурации контакт/молекулы(а)/контакт

Органические полупроводники (проводящие полимеры)

Упорядочение молекулярной пришивкой

Переход к молекулам в макроскопических зазорах

Переход к единичным молекулам

Обзоры

Nature Nanotechnol. 1 (2006) 173-181

Isr. J. Chem. 54 (2014) 513 – 533

Chem. Soc. Rev. 46 (2017) 40—71

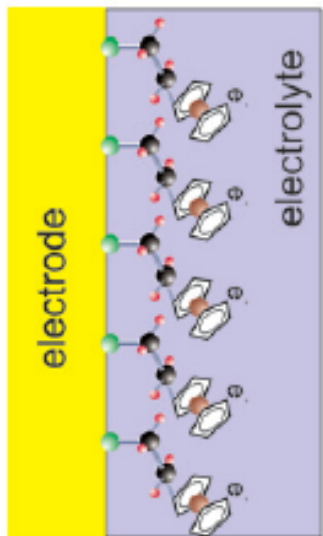
Chem. Rev. 117 (2017) 4248–4286

Rev. Modern Physics 92 (2020) 035001

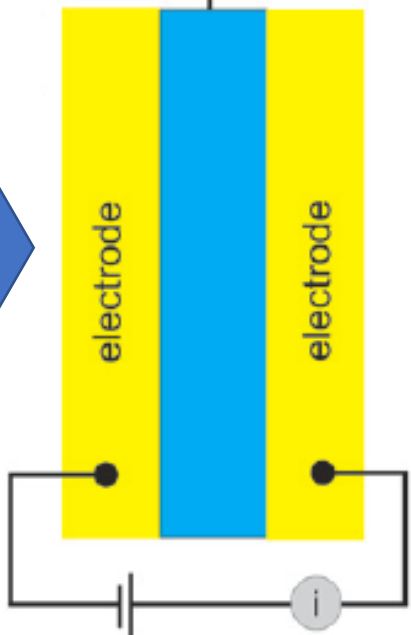
Chem. Soc. Rev. 49 (2020) 7505—7515

Adv. Mater. 32 (2020) 1905909

Электрохимия:



molecular film

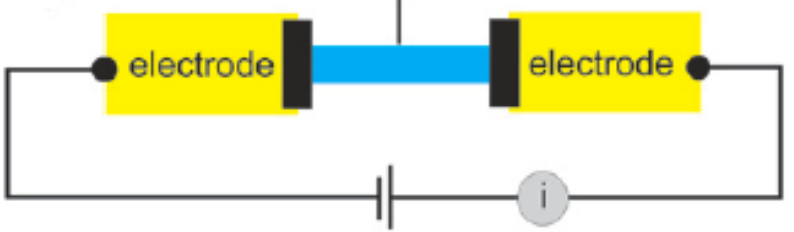


«органическая электроника»



Large-area молекулярная электроника

molecular wire

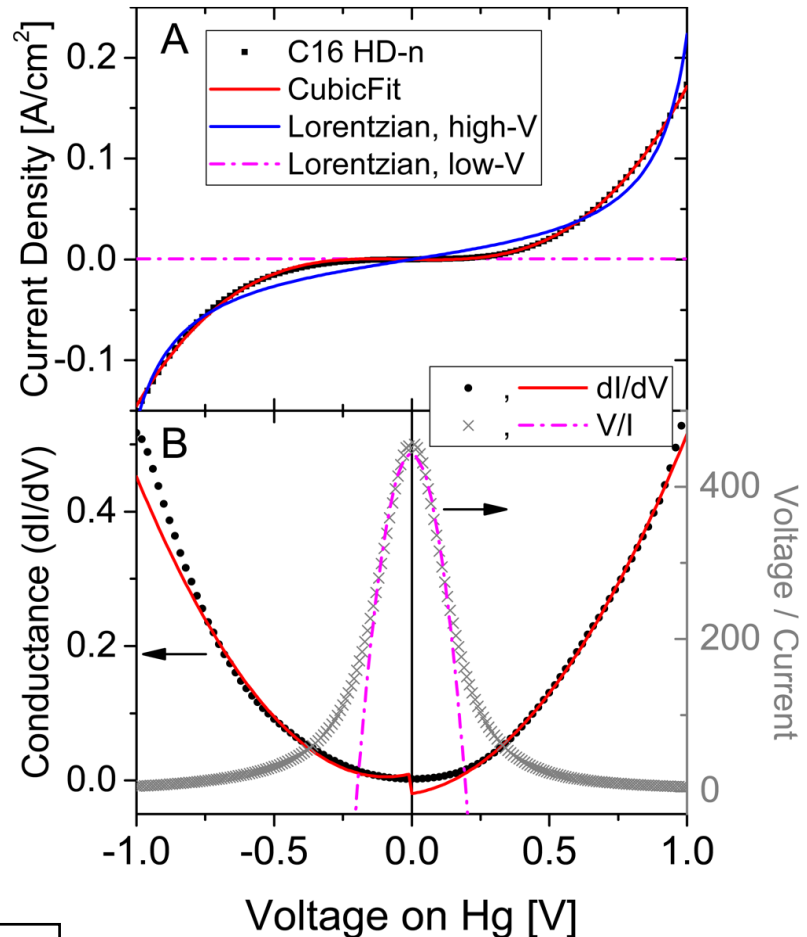


«одномолекулярная электроника»

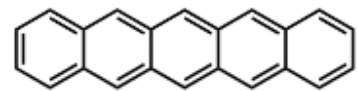
Проводящие полимеры



Во всех случаях есть проблемы с воспроизводимостью конфигураций молекул между контактами



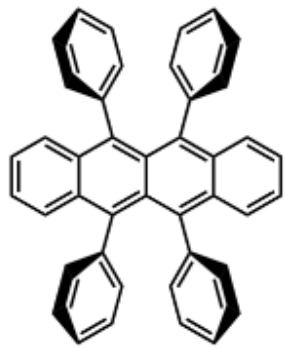
Si/C16 тиол/Hg



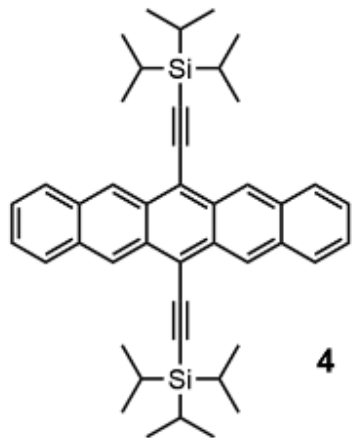
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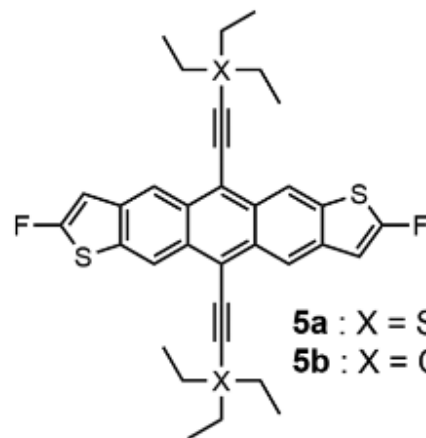
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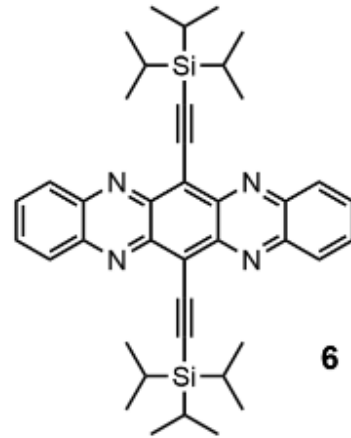


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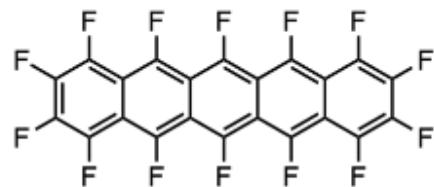


5a : X = Si

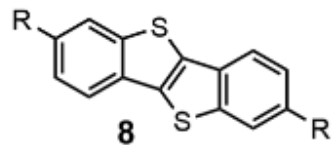
5b : X = Ge



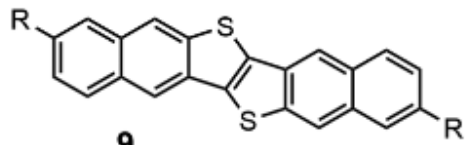
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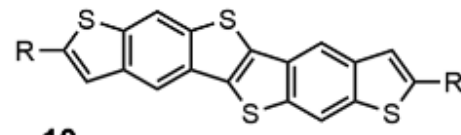
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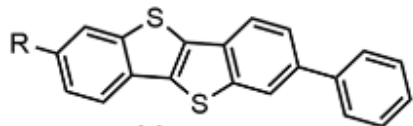
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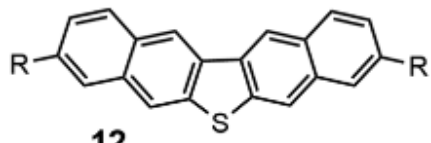
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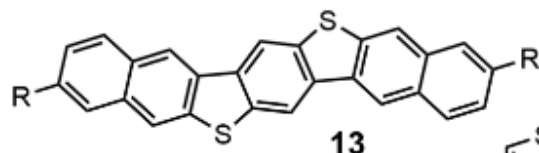
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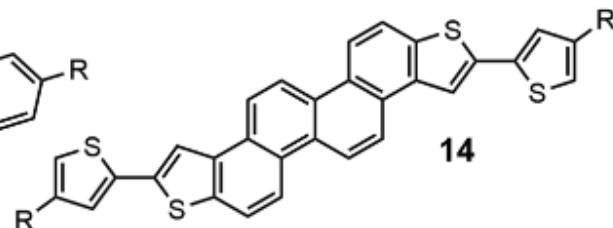
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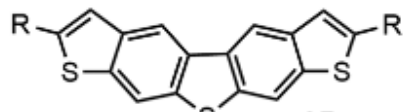
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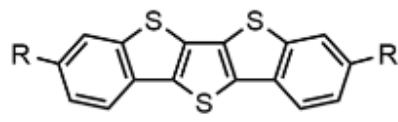
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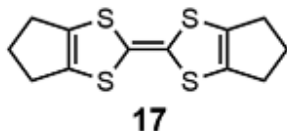
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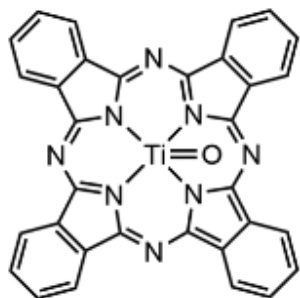
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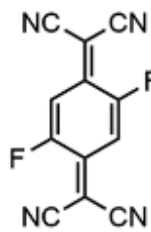
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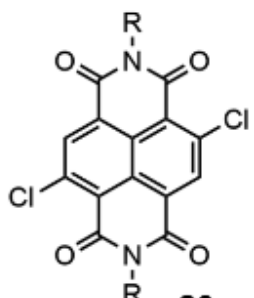
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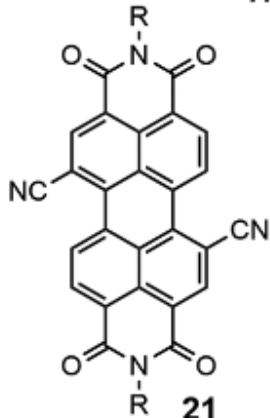
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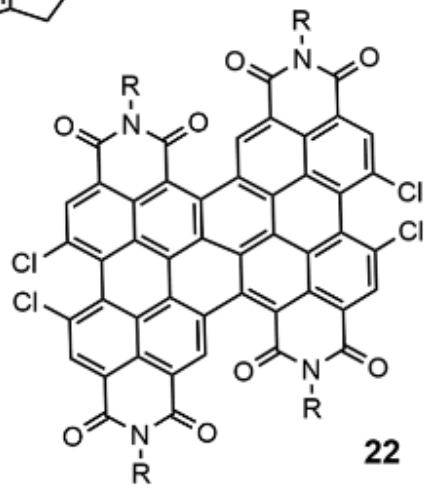
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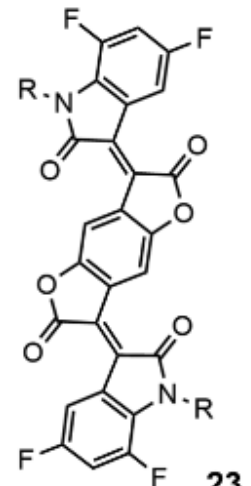
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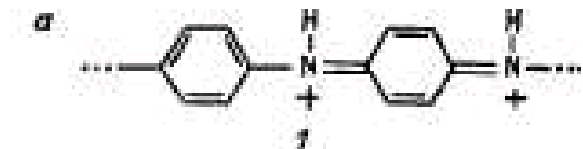
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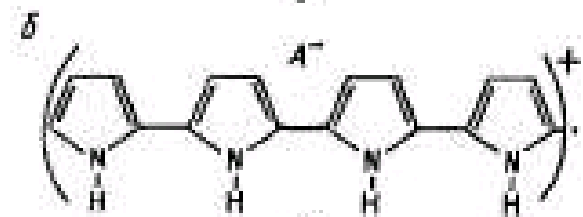
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Полупроводники
для органической
электроники

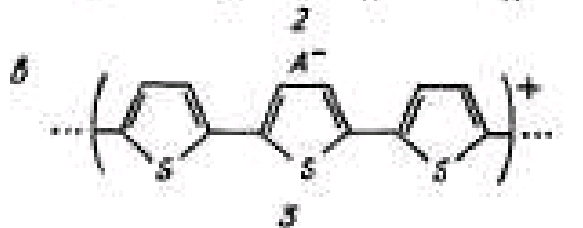
Осаждение полимеров (анодное)



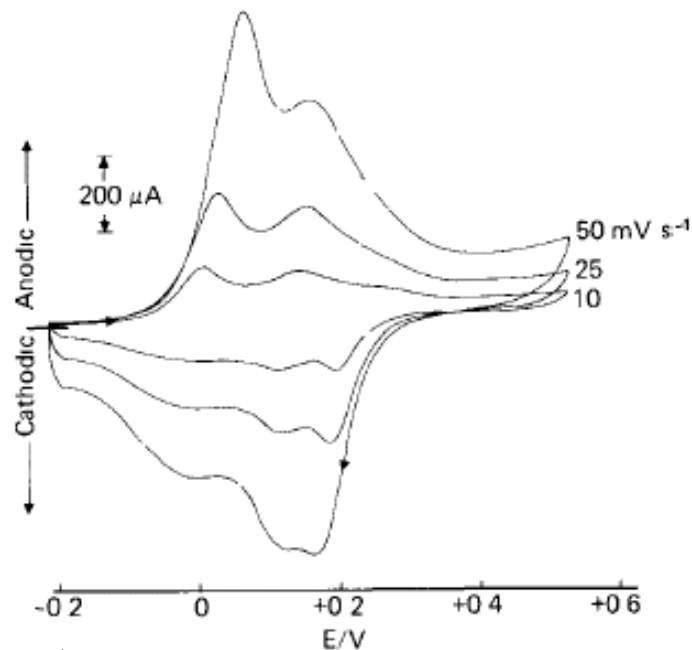
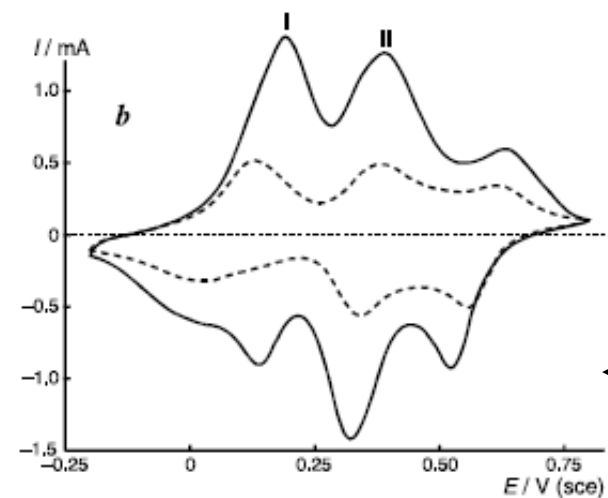
полианилин



полипиррол

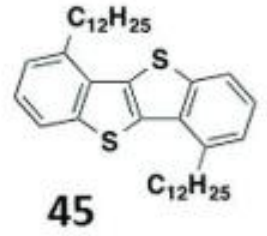
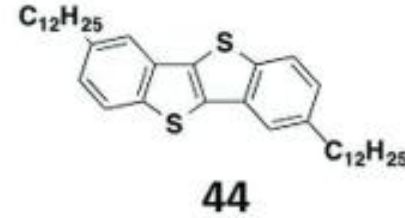
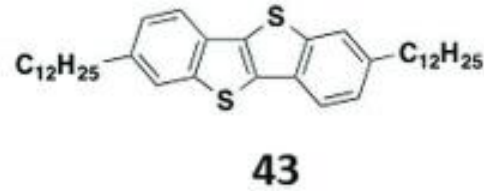
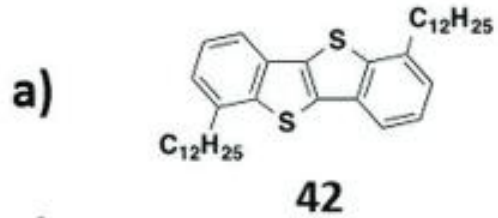
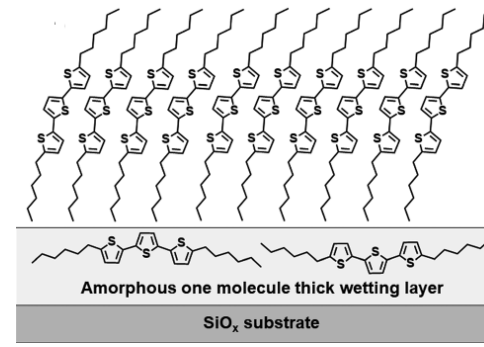


политиофен



перезарядка
полимеров и олигомеров

Проблема:
взаимное расположение молекул в
кристаллах и кристаллов на подложке

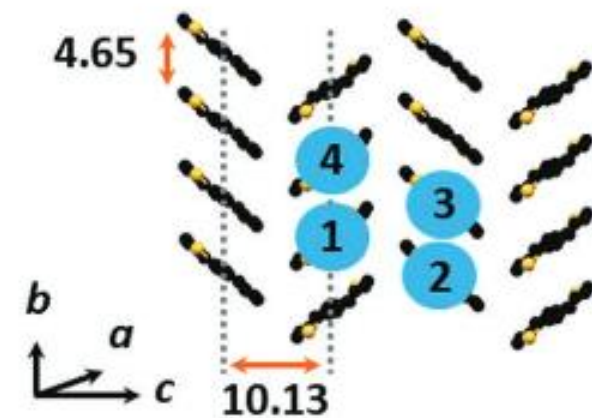
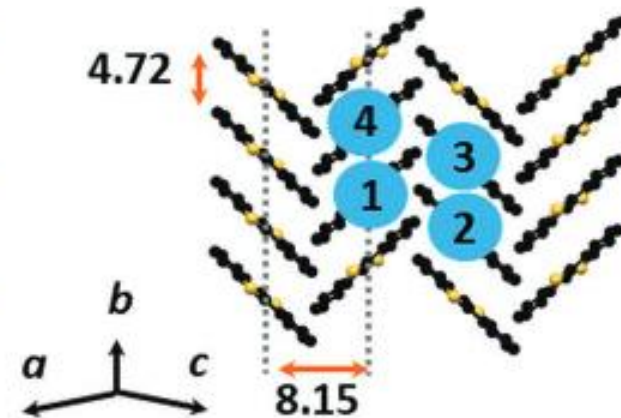
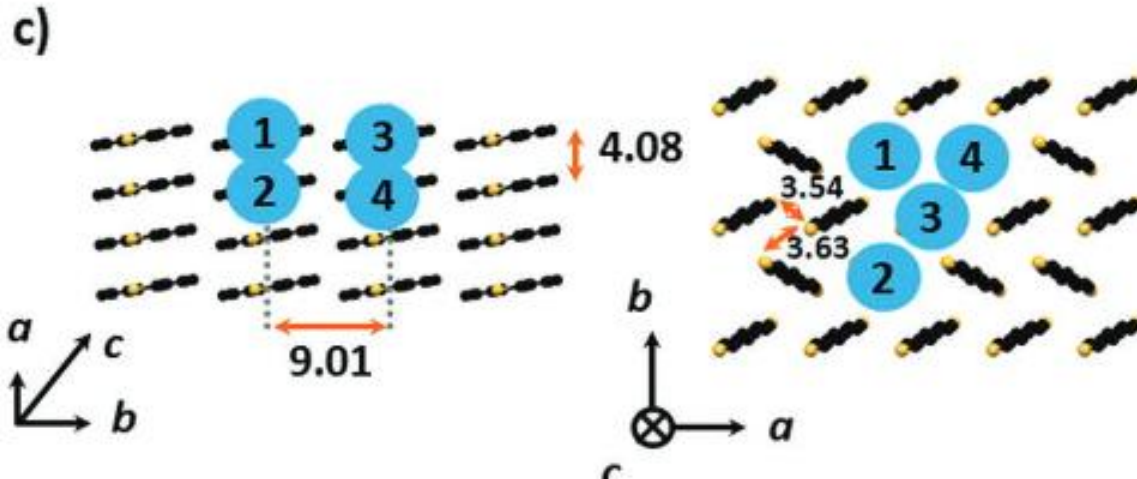


b) $a = 4.08 \text{ \AA}$ $\alpha = 90^\circ$
 $b = 9.01 \text{ \AA}$ $\beta = 90.80^\circ$
 $c = 44.32 \text{ \AA}$ $\gamma = 90^\circ$

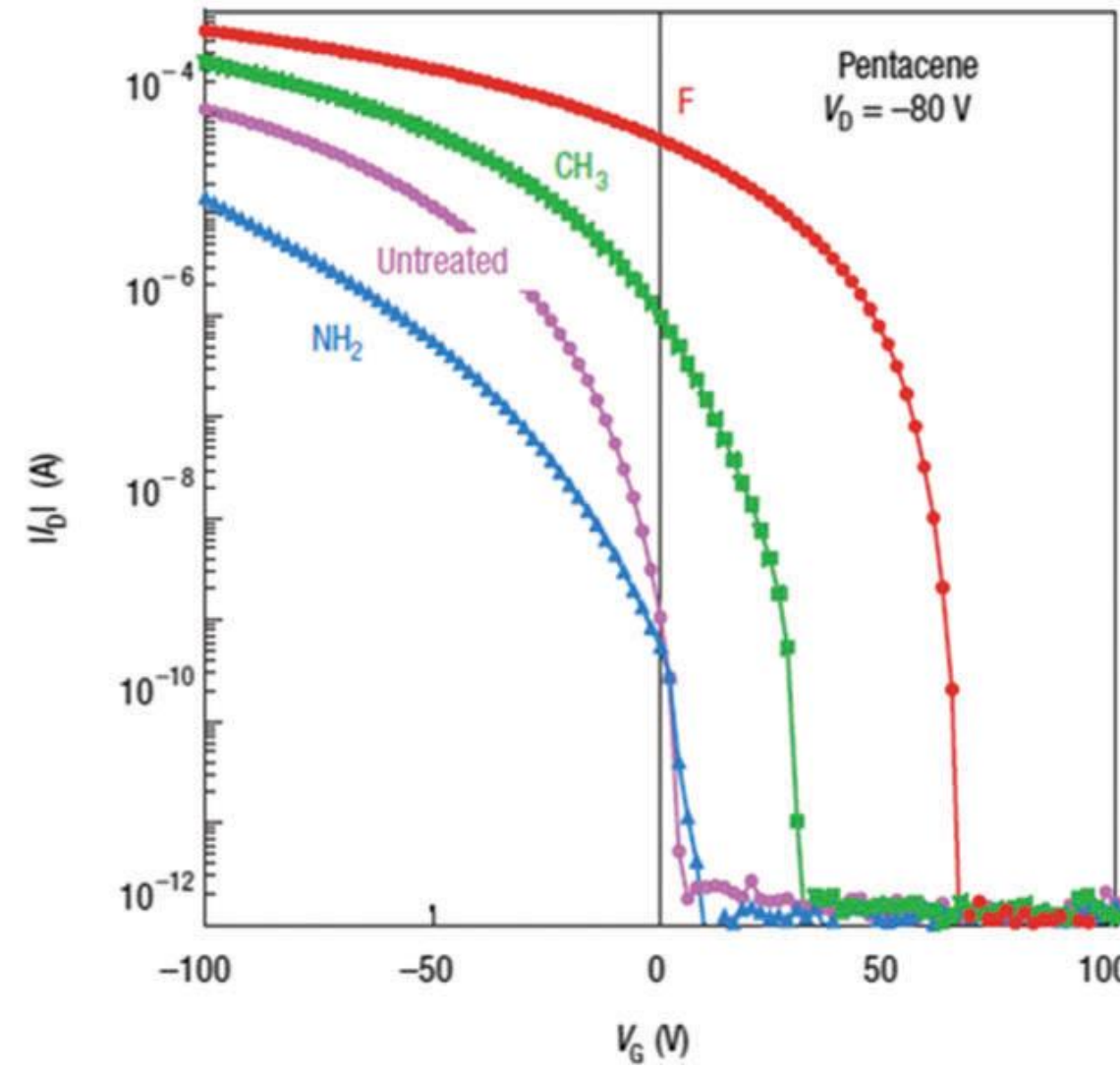
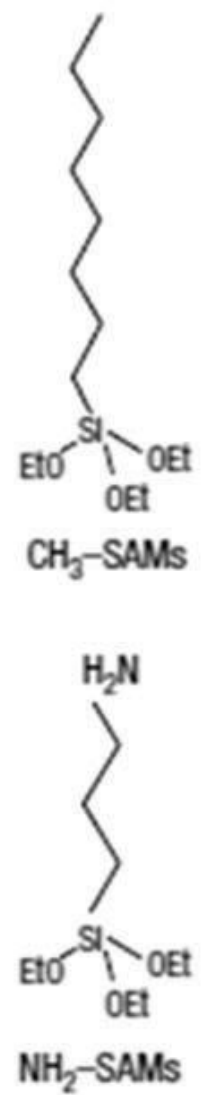
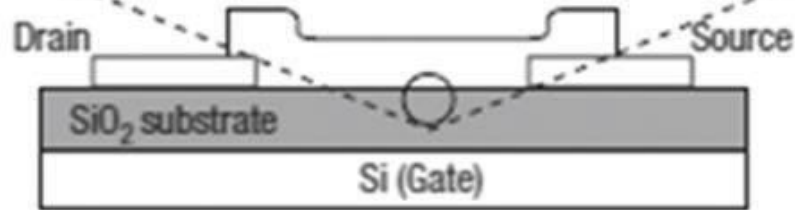
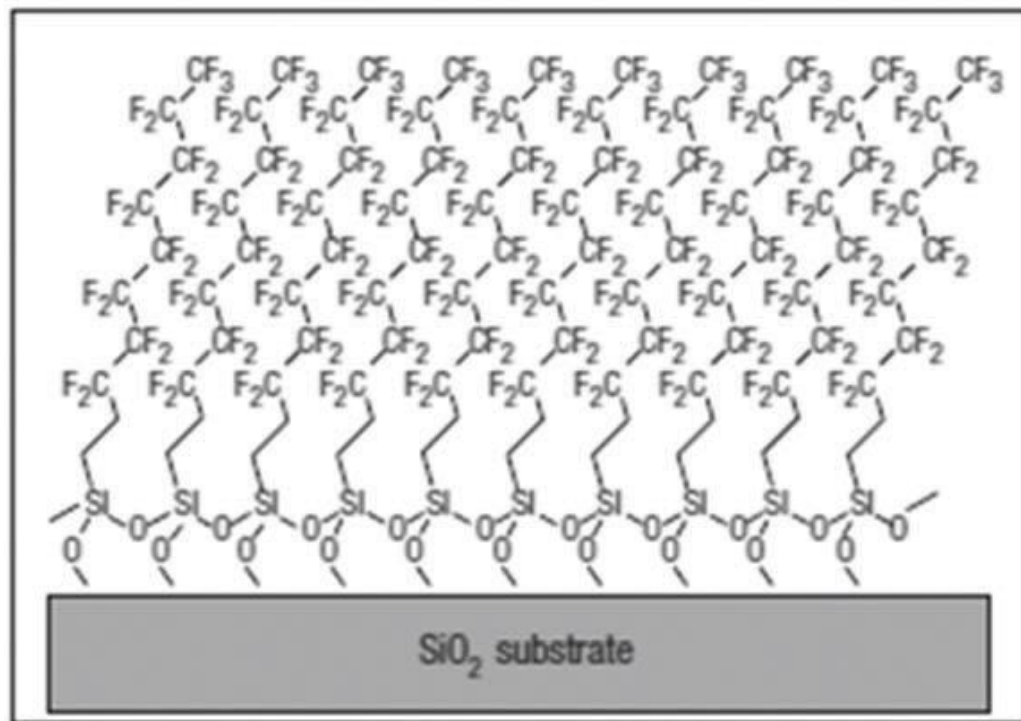
$a = 5.86 \text{ \AA}$ $\alpha = 90^\circ$
 $b = 7.74 \text{ \AA}$ $\beta = 90.59^\circ$
 $c = 37.91 \text{ \AA}$ $\gamma = 90^\circ$

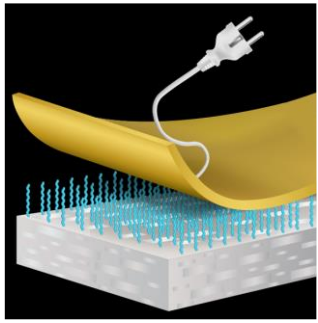
$a = 21.76 \text{ \AA}$ $\alpha = 90^\circ$
 $b = 4.72 \text{ \AA}$ $\beta = 99.34^\circ$
 $c = 16.30 \text{ \AA}$ $\gamma = 90^\circ$

$a = 17.51 \text{ \AA}$ $\alpha = 90^\circ$
 $b = 4.65 \text{ \AA}$ $\beta = 90.36^\circ$
 $c = 20.25 \text{ \AA}$ $\gamma = 90^\circ$



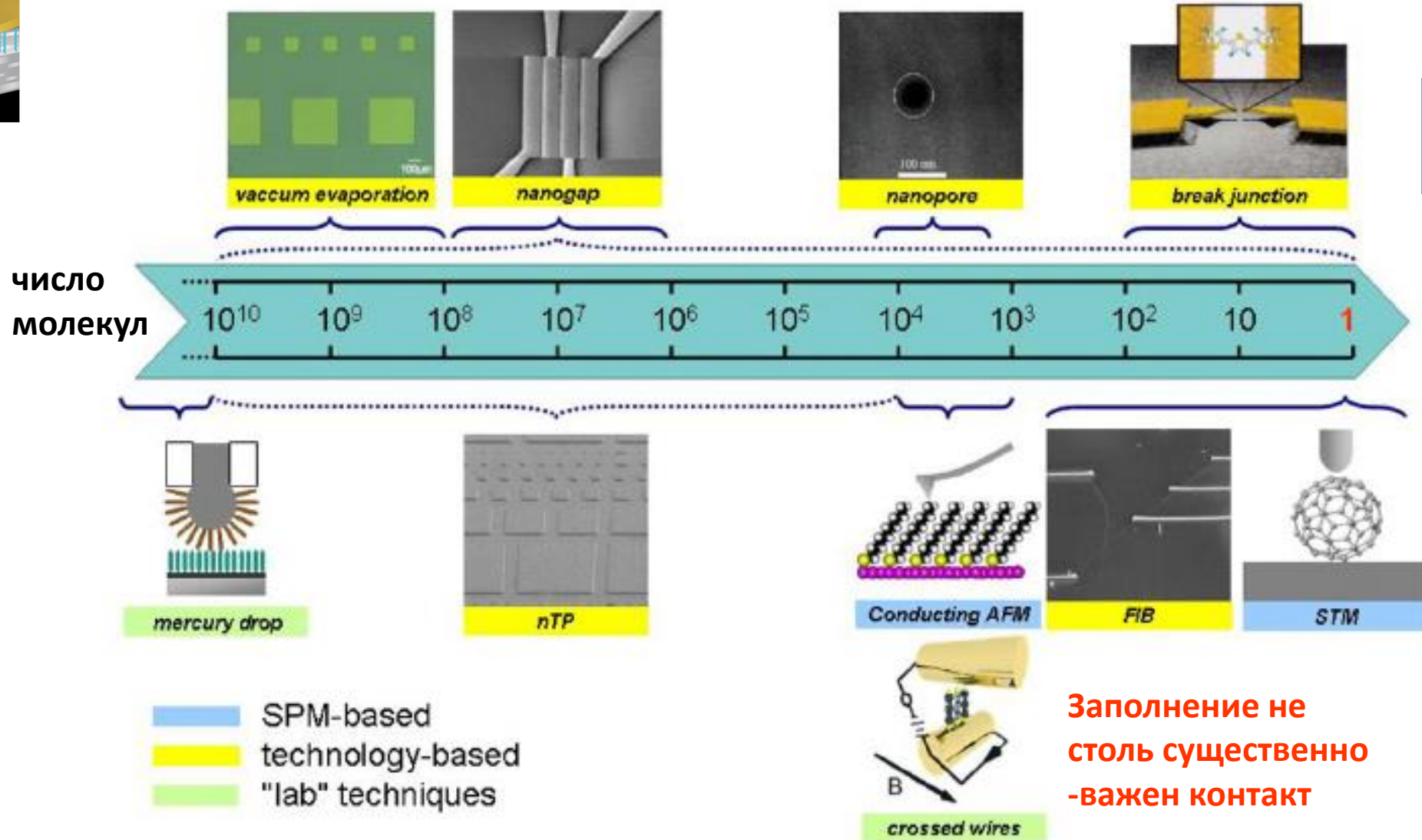
Молекулярная пришивка к подложке





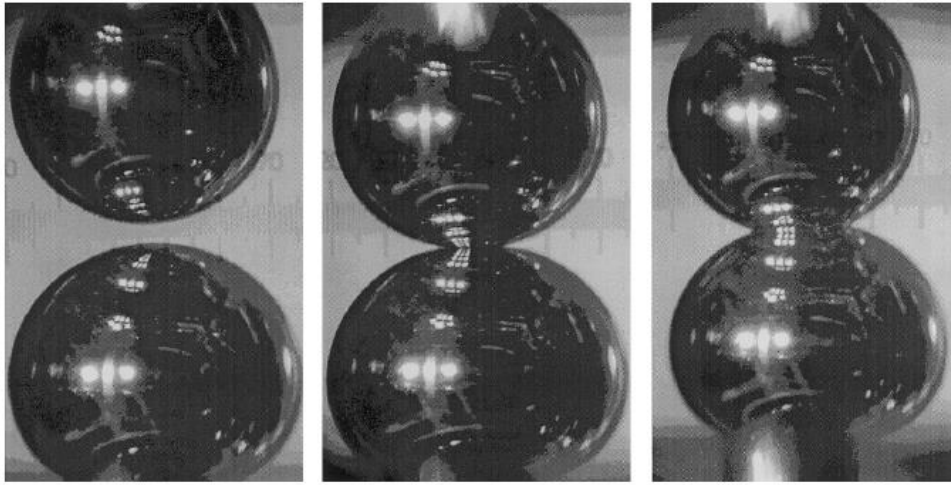
Large-area

Организация контактов MmM (металл-молекула-металл)

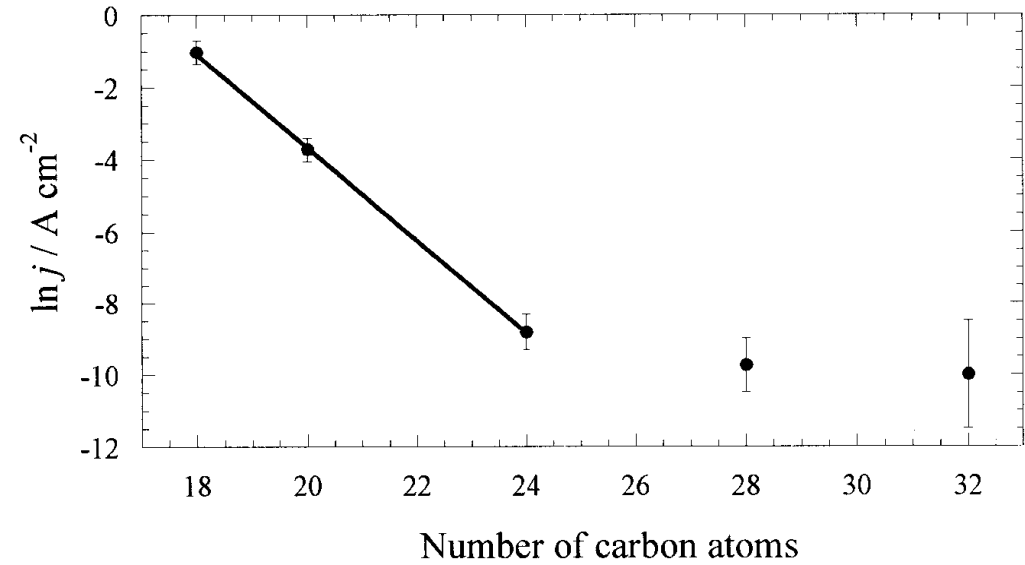
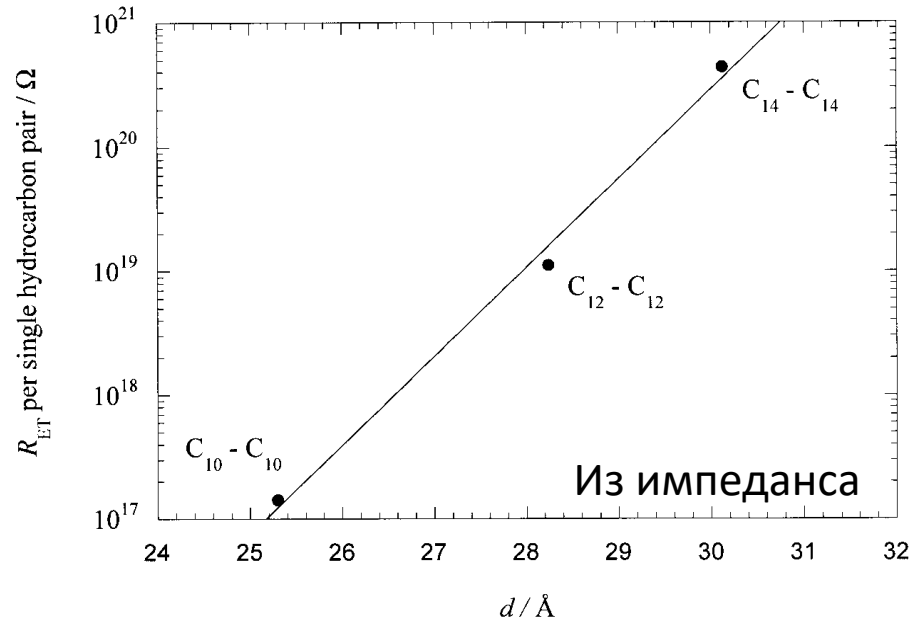
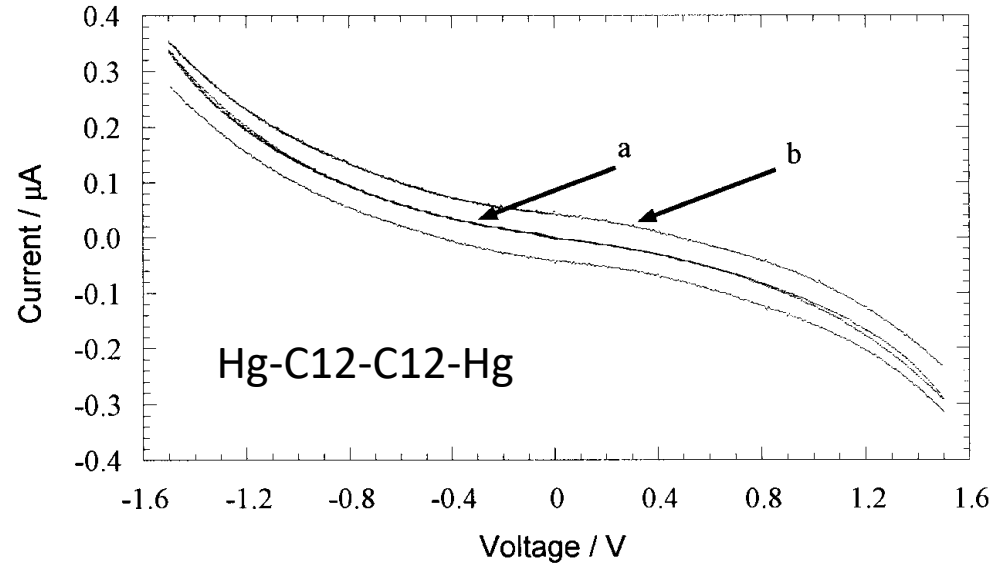


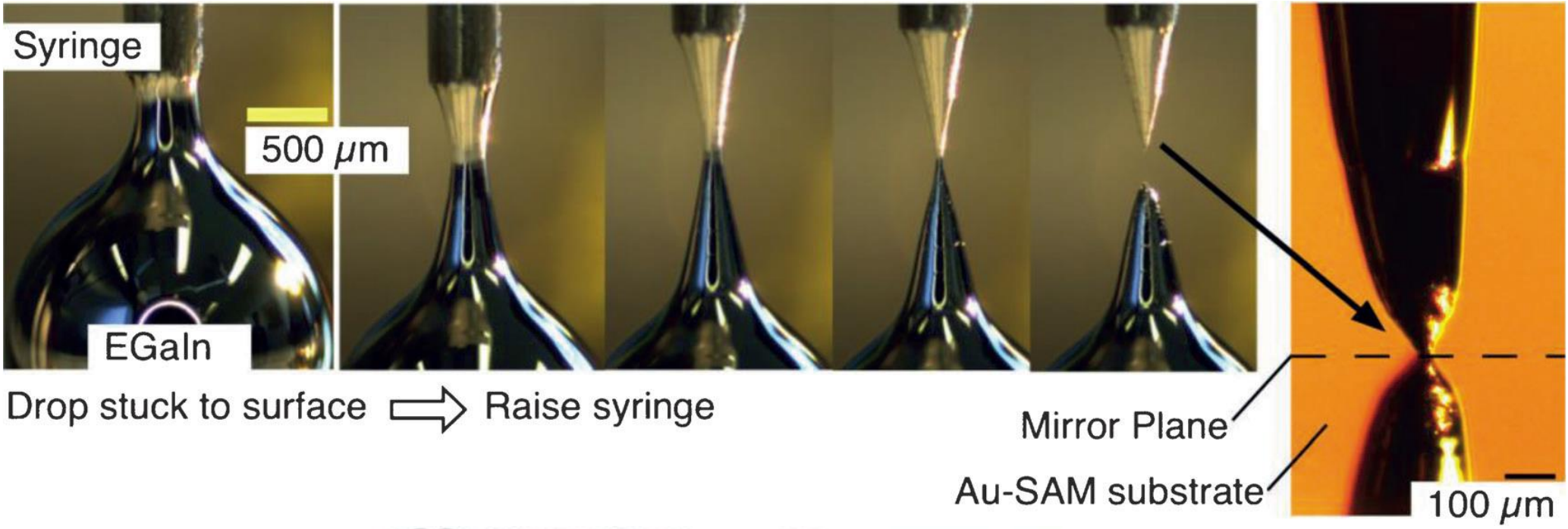
Single molecule

Важны предельное заполнение и бездефектный монослой

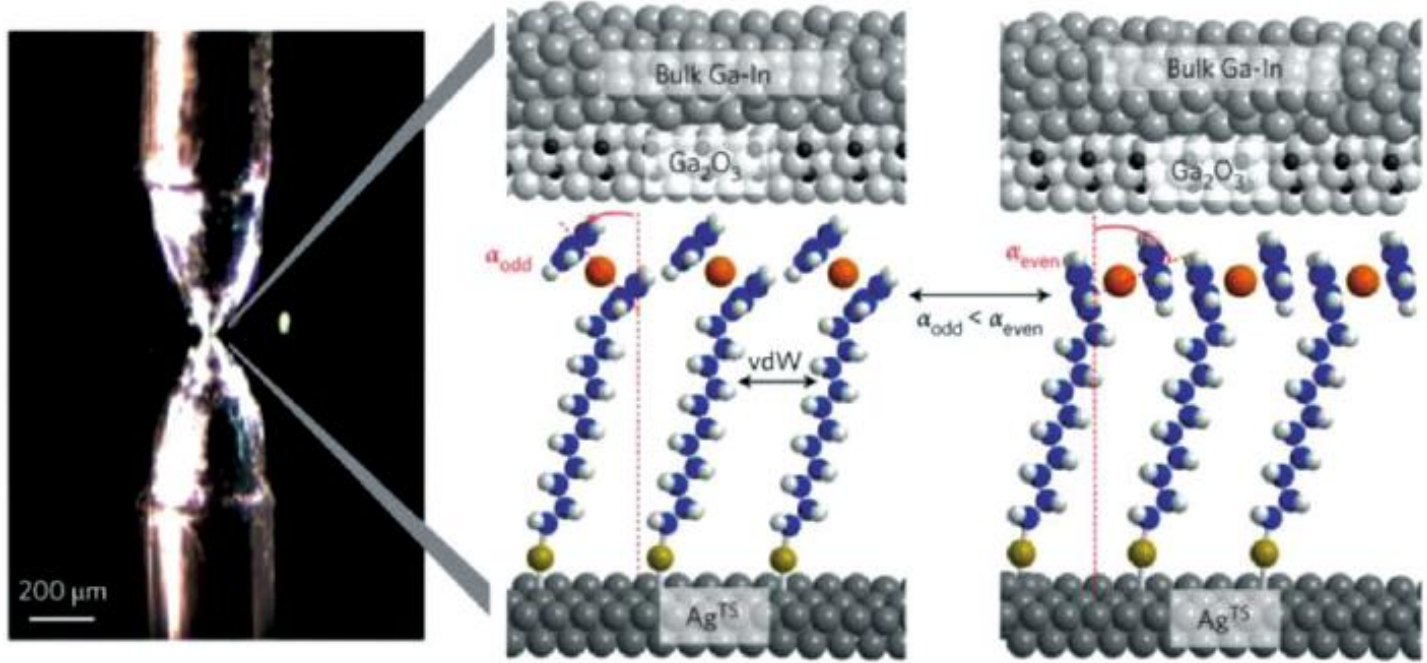


1 mm

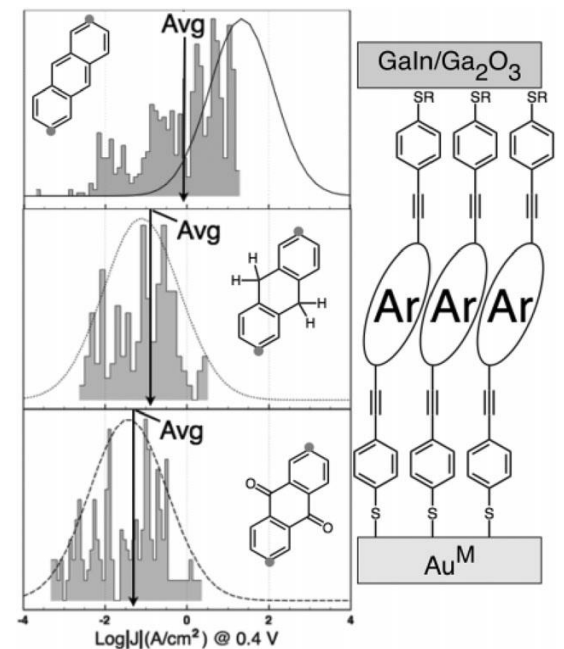




Второй контакт из жидкого металла (ртуть или In-Ga)

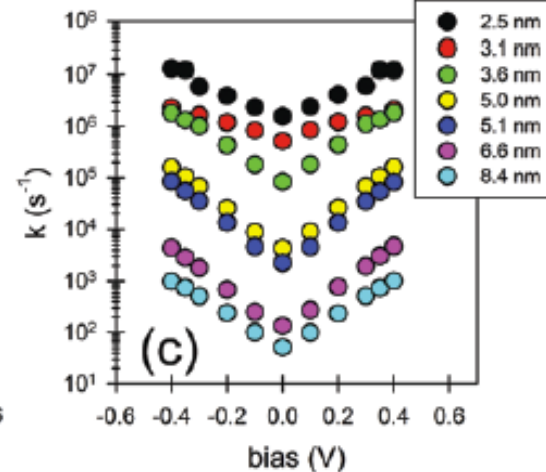
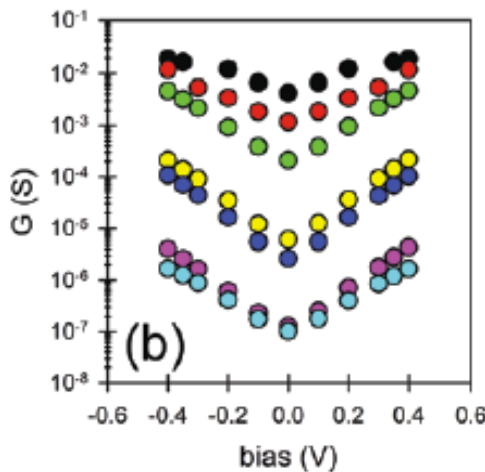
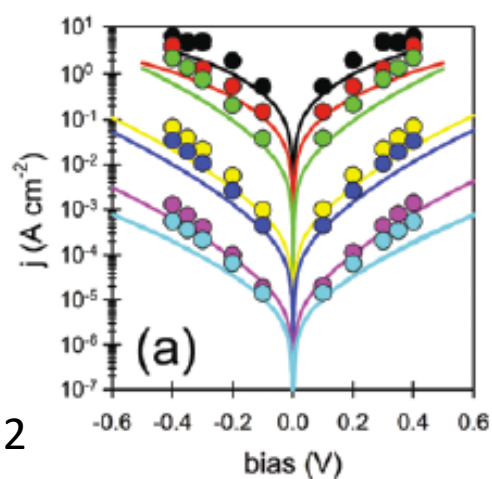
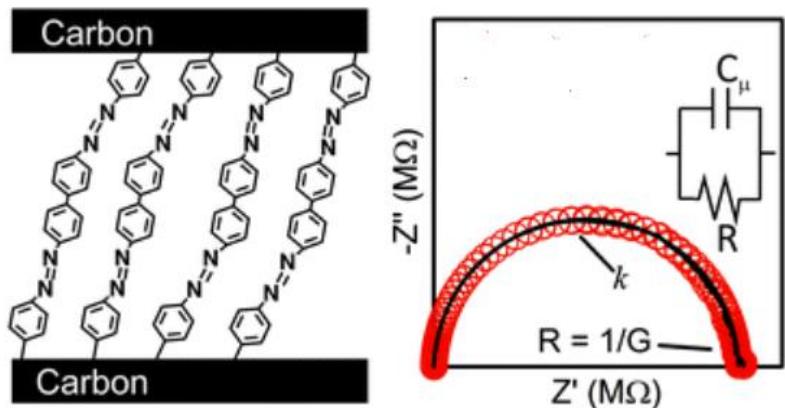


Образуются слой оксида галлия

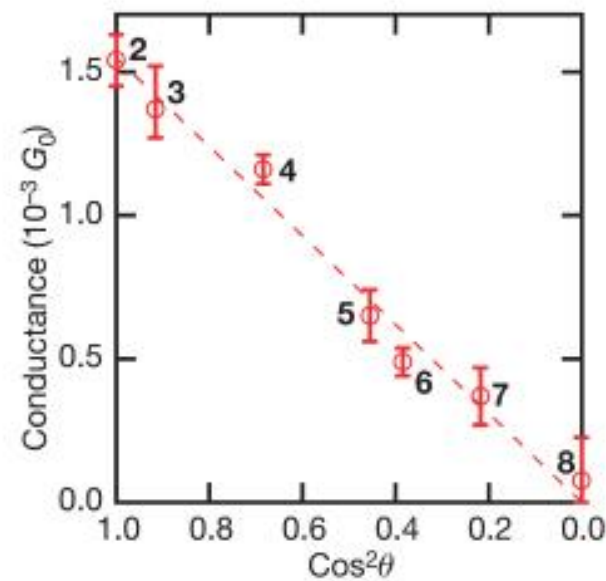
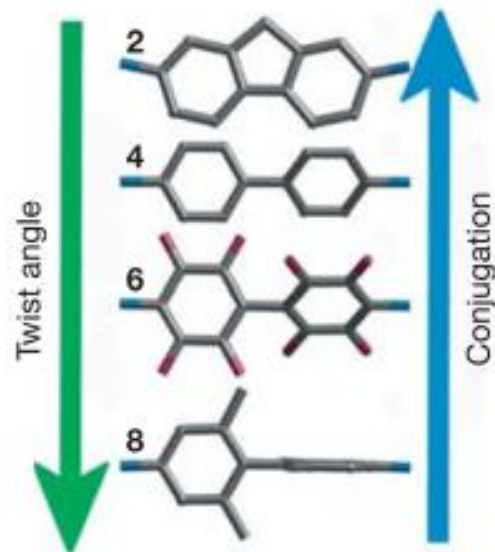
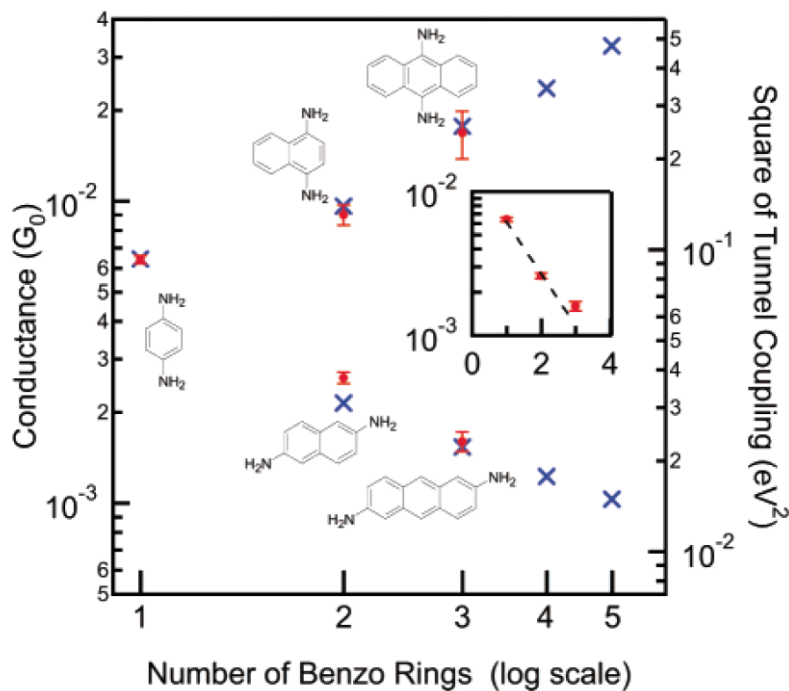


200 μm

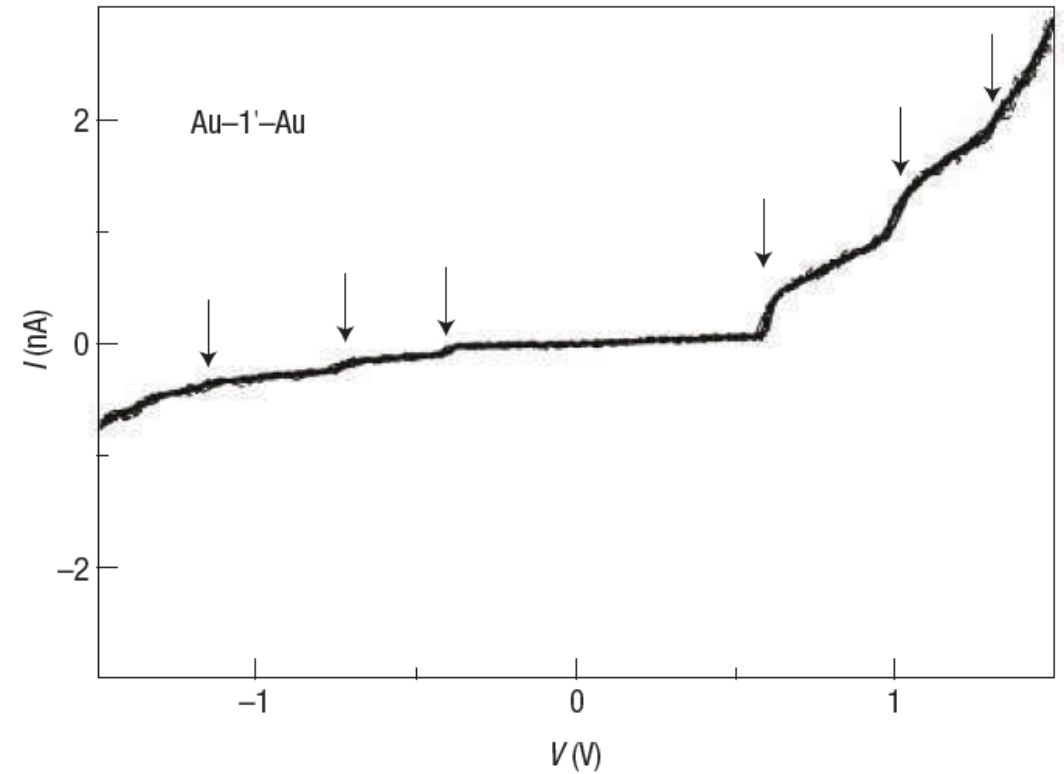
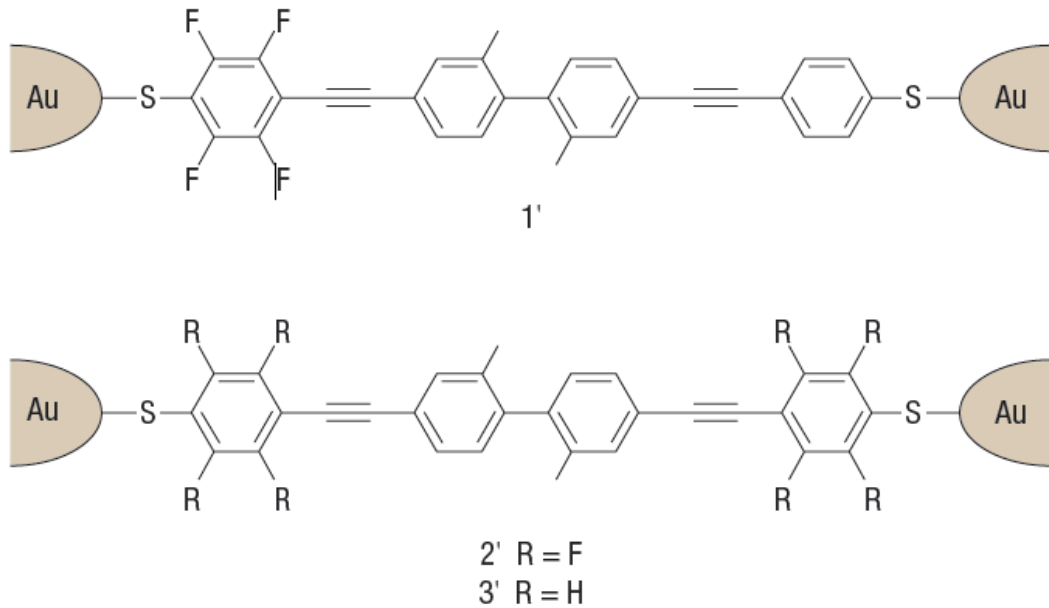
“Сухие» молекулярные контакты – Large-area



Phys. Chem. Chem. Phys. 22 (2020) 10828-10832

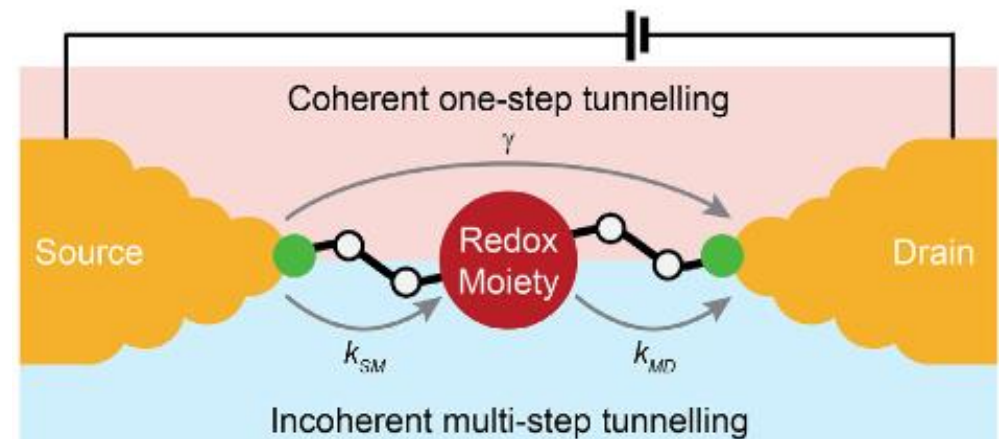


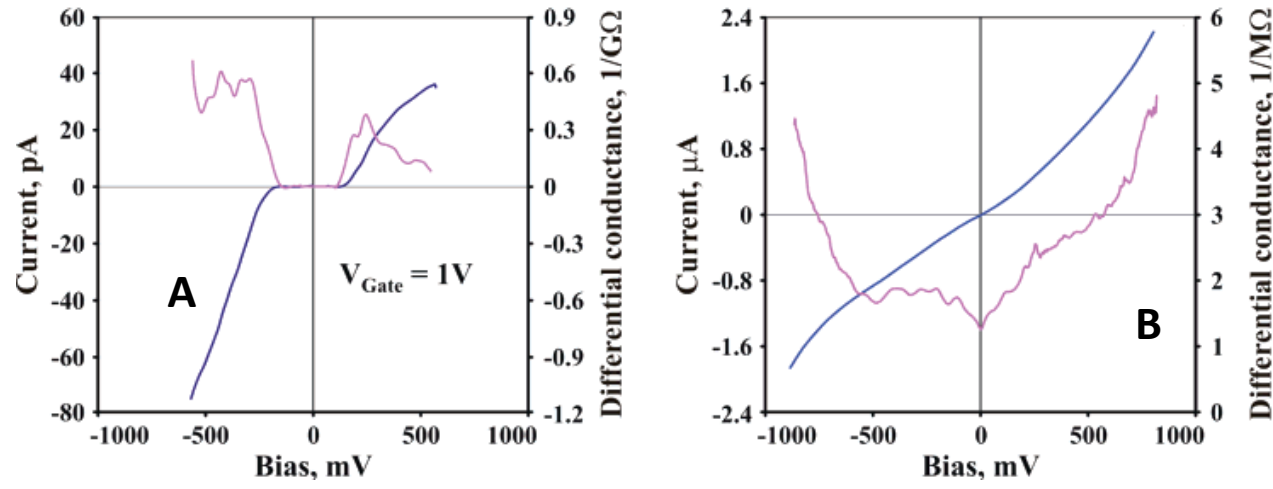
“Сухие» молекулярные контакты – single



Недостаточно стабильны даже при низких температурах.

Определение проводимости требует набора большой статистики



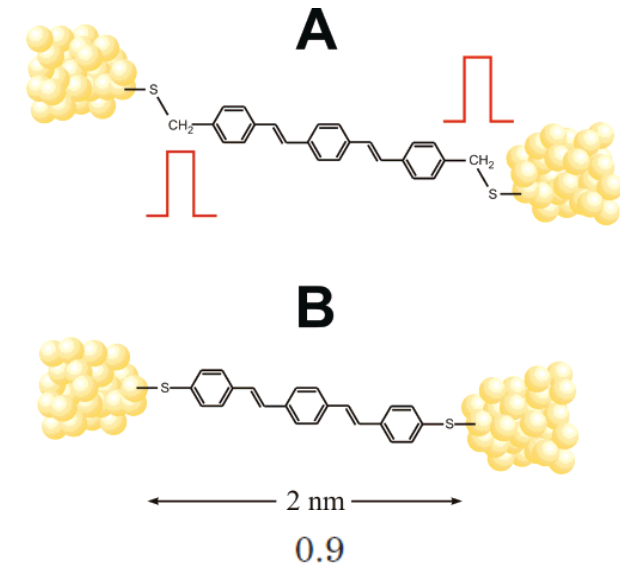


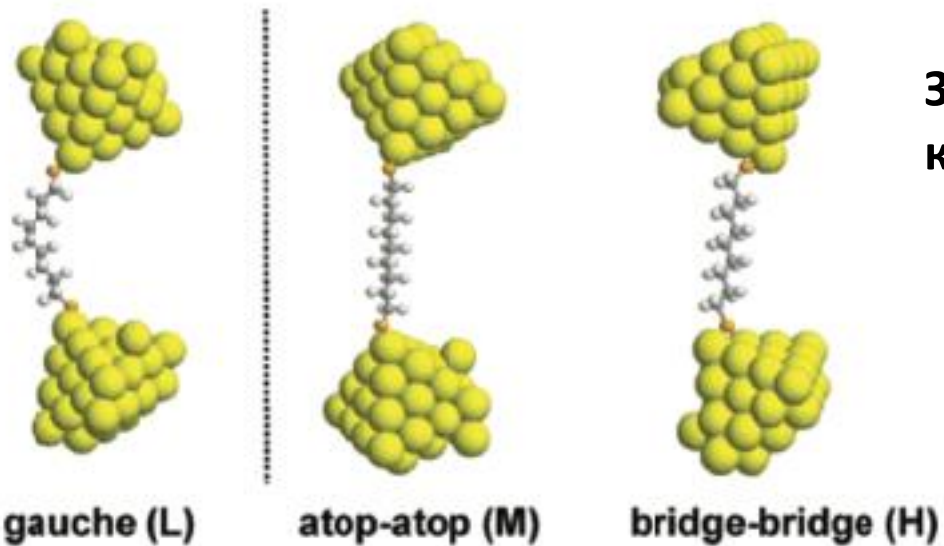
^a Device 4 had lead electrodes, and all other devices had gold electrodes. Two complete Coulomb diamonds were traced for device 4, and their parameters are presented separately in lines 4 and 4'. For devices with molecule **B** the symbol * marks the ones where a weak gate modulation was observed (see Figure 2c for example); all other devices had no measurable gate effect. Some devices changed their conductivity after moderate annealing (up to 20 K) or were switching between different conductance states, as explained in ref 15. For switching devices both upper and lower resistance limits are presented. The indicated dV/dI are for the transport bias 50 meV. We recorded $I-V$ curves at higher biases until the device was burned. Only device 16 (Figure 2d) was measured at high enough bias to estimate the transport gap of ~ 1 eV which is comparable to break junction measurements.

Measured

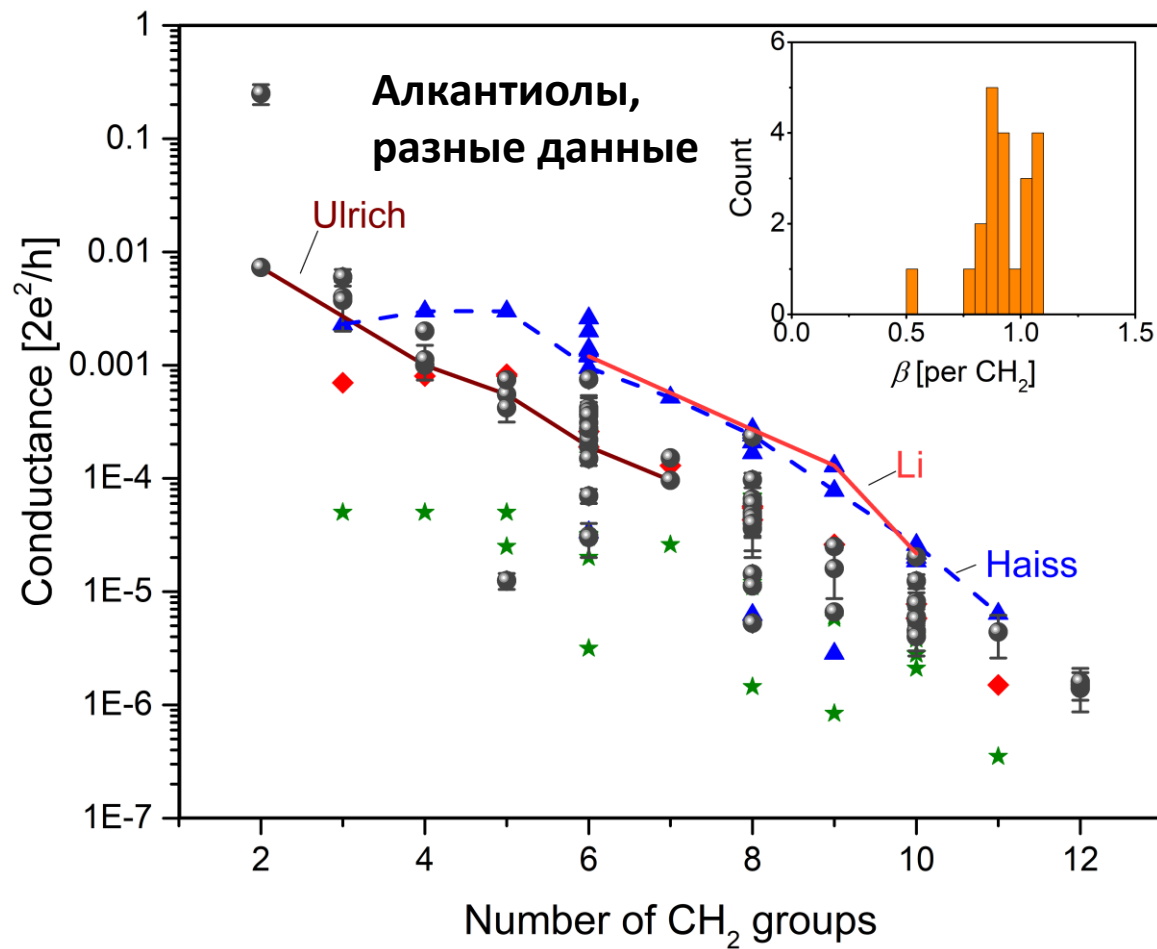
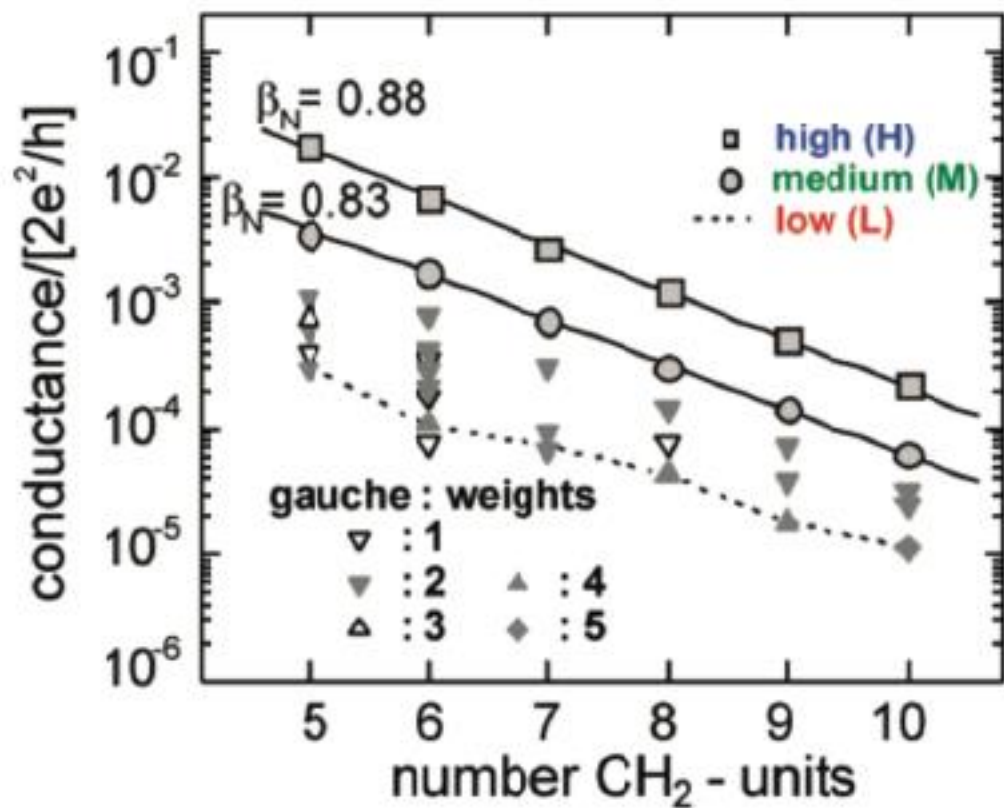
| Molecule A | | |
|------------|--|------------------------------|
| device | $R_{\text{open state}} (\text{M}\Omega)$ | $E_{\text{add}} (\text{eV})$ |
| 1 | 3500 | 0.722 |
| 2 | 3000 | 0.766 |
| 3 | 400 | 0.760 |
| 4 | 230 | 0.686 |
| 4' | 230 | 0.928 |

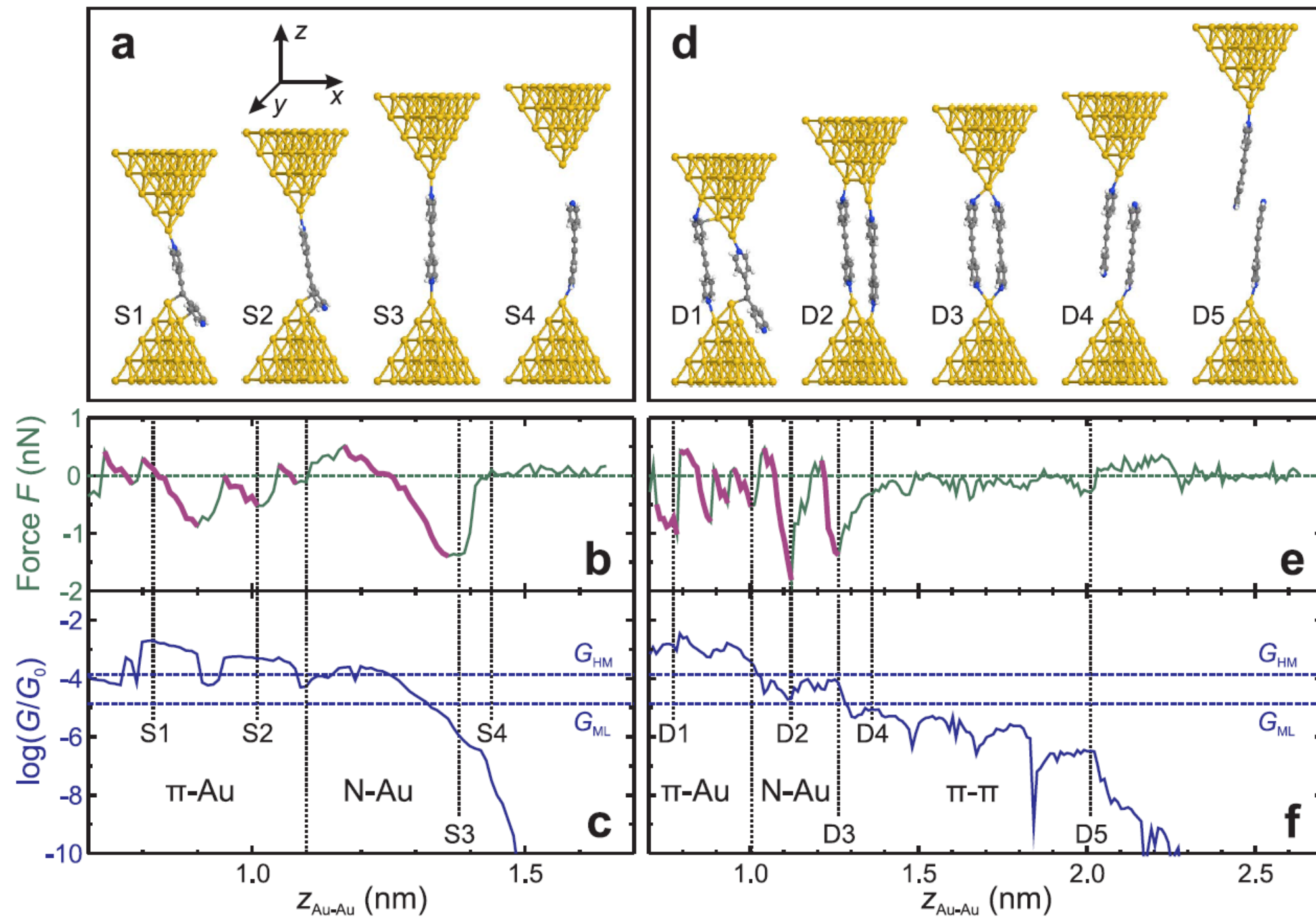
| Molecule B | | |
|------------|---|--------------------|
| device | $dV/dI (\text{M}\Omega) _{\text{at bias } 50 \text{ mV}}$ | transport gap (eV) |
| 5 | 5.6–6.4 | |
| 6 | 4.2–5.8 | |
| 7* | 3.7–3.8 | |
| 8 | 1.6 | |
| 9* | 2.3 | |
| 10* | 17–53 | |
| 11 | 23 | |
| 12 | 2.4 | |
| 13 | 0.34–0.38 | |
| 14 | 0.43–0.55 | |
| 15 | 0.33–0.51 | |
| 16 | 0.49 | 0.9 |



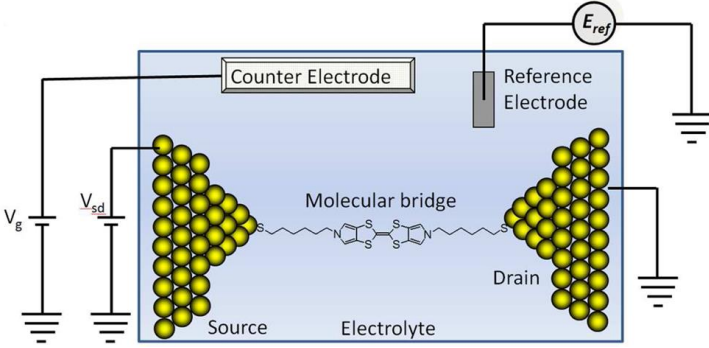
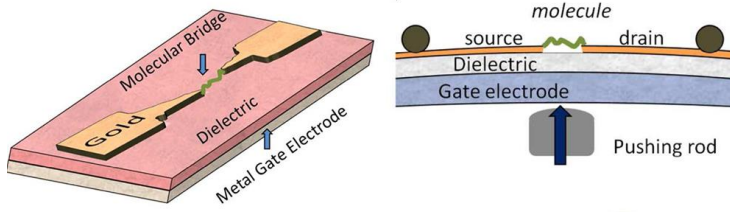


Зависимость молекулярной проводимости от конфигурации контакта и молекулы

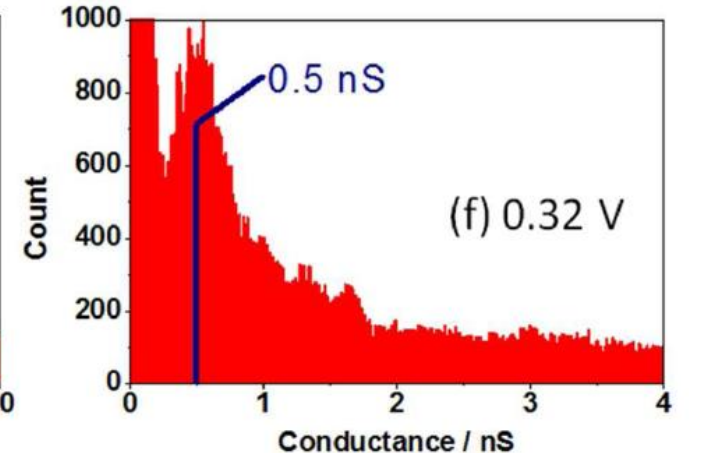
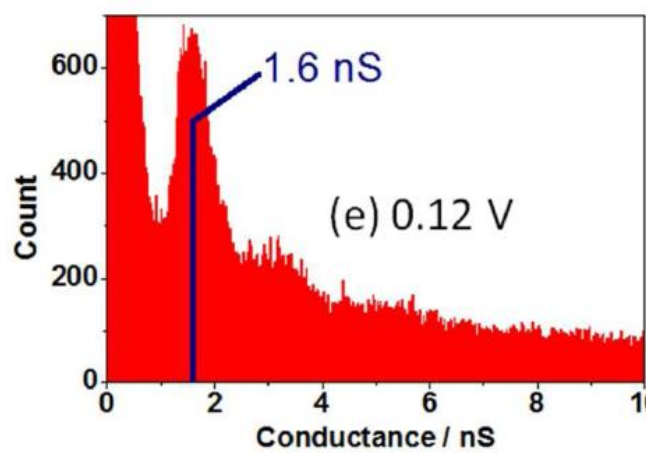
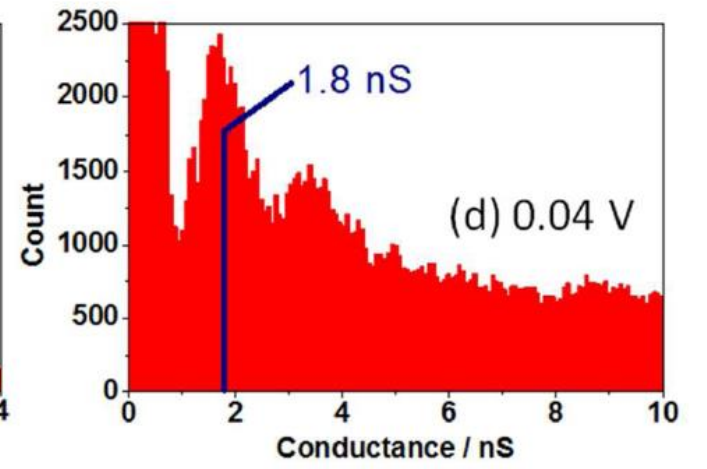
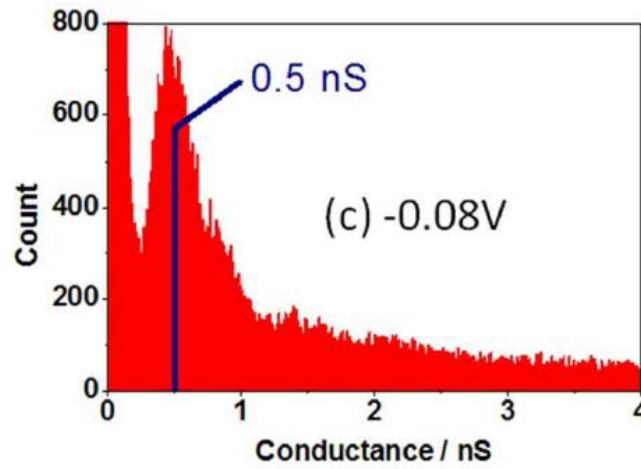
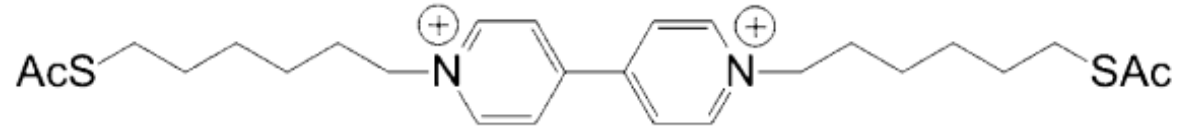
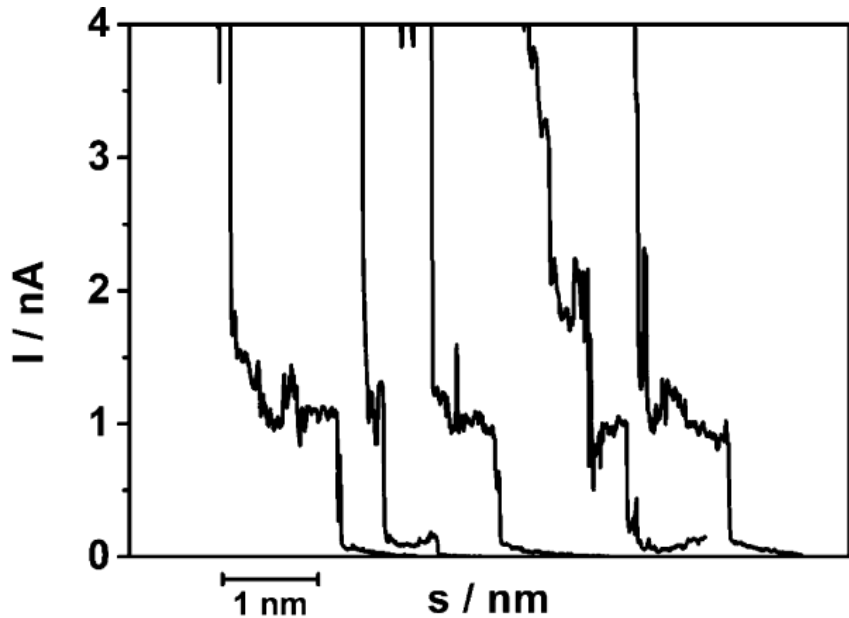


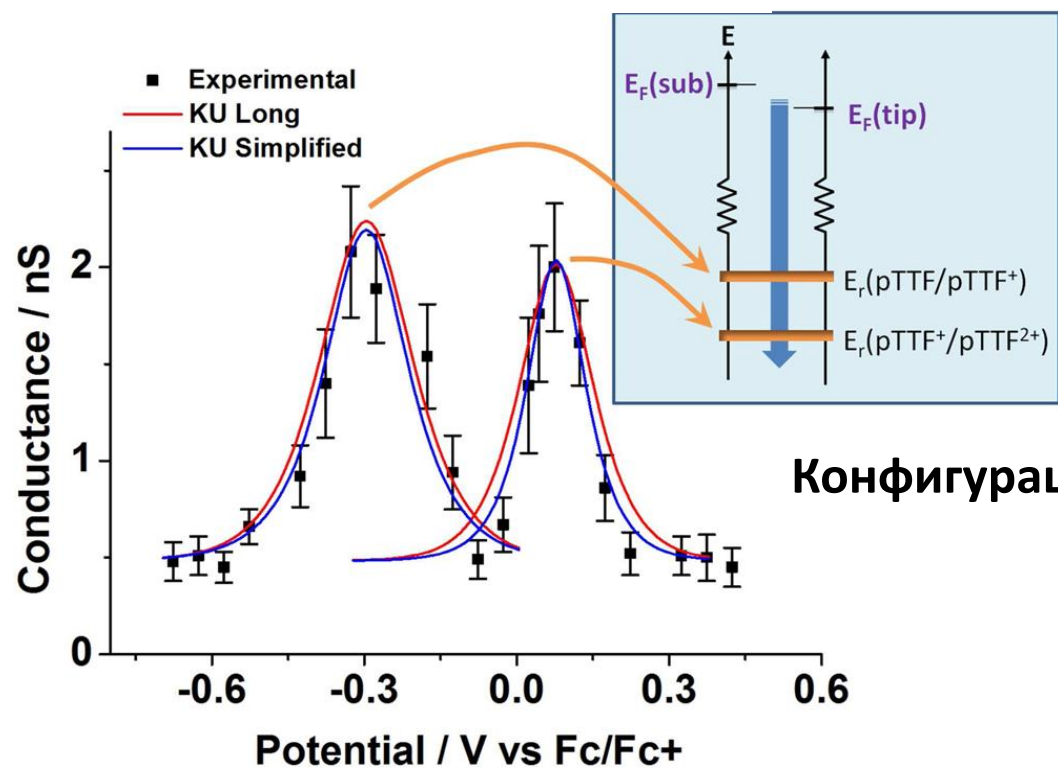
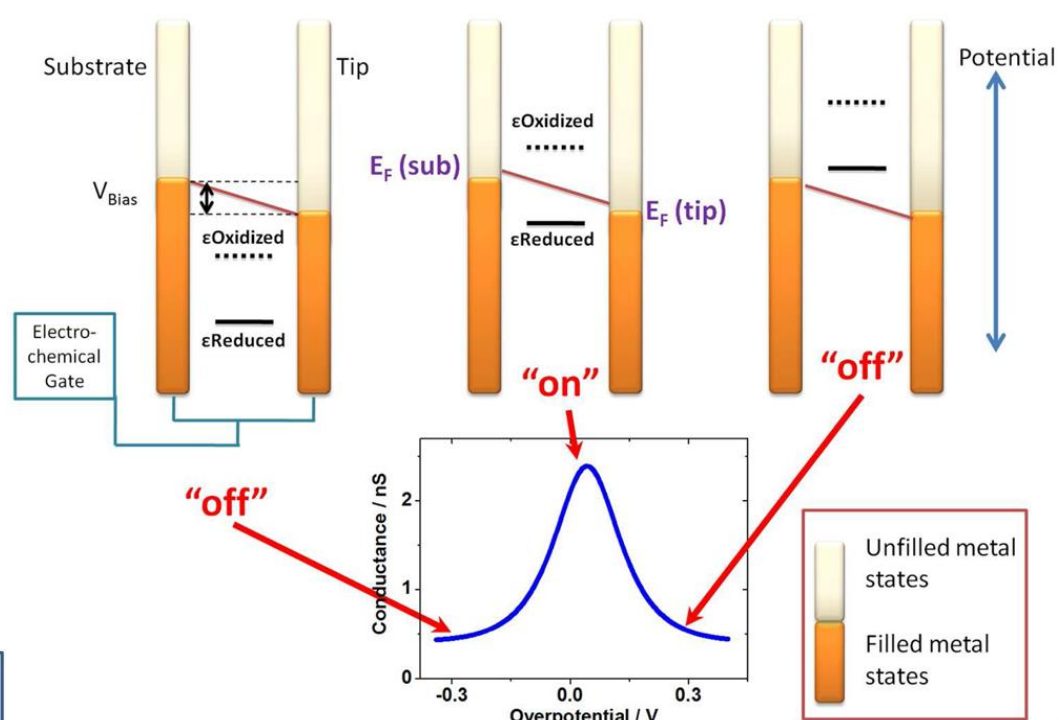
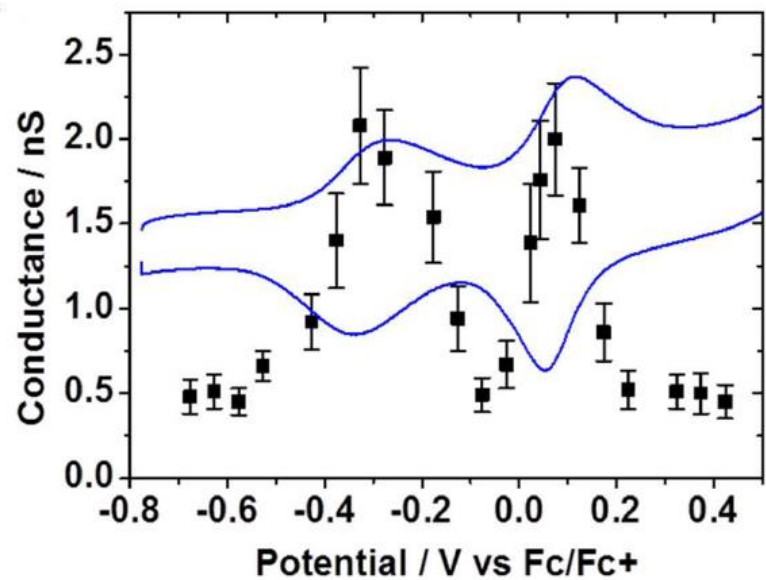


“Мокрые» молекулярные контакты – single

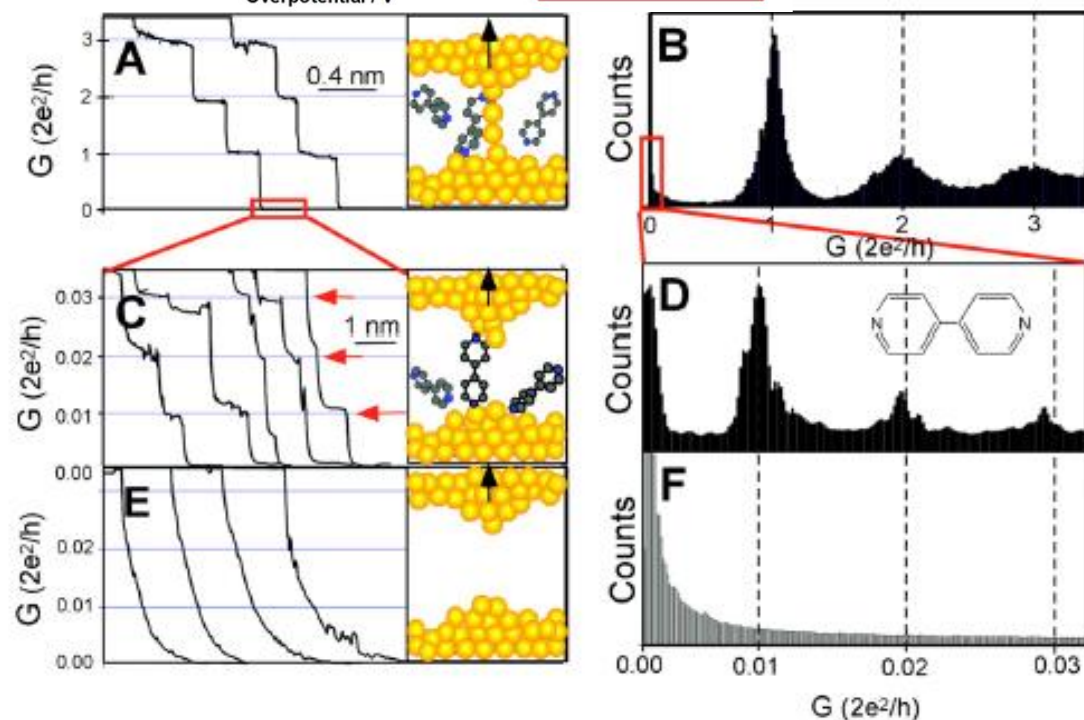


Или конфигурация СТМ

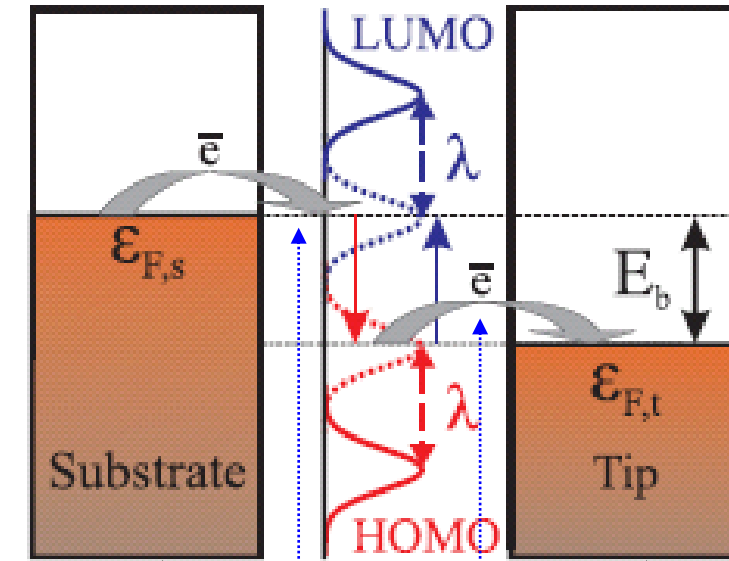
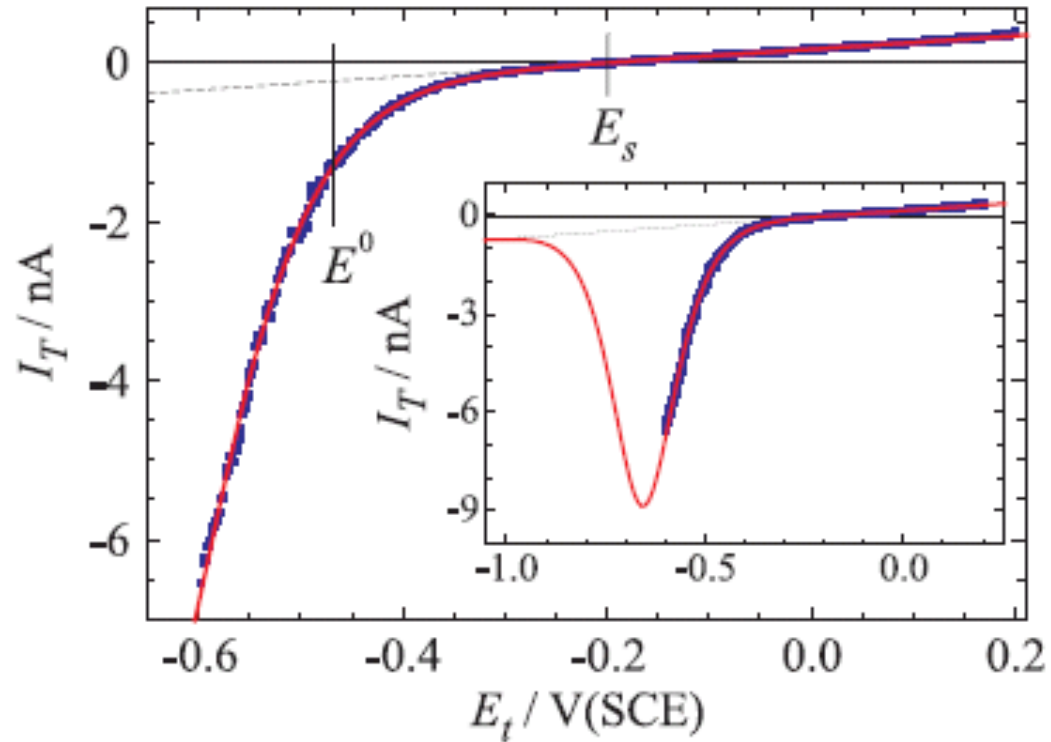




Конфигурация СТМ



Молекулярная проводимость в зазоре
электрохимического СТМ:
теория в Chem. Rev. 108 (2008) 2737



Контролируются потенциалами
поверхности подложки и зонда

Скорости (вероятности
переноса электрона)
могут быть рассчитаны
для разных потенциалов