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Tailoring the Fermi level of the leads in molecular-electronic devices

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The dependence of the transport properties on the specific location of the Fermi level in molecular electronics devices is studied by using electrodes of different materials. The zero-bias transport properties are shown to depend dramatically on the elemental composition of the electrodes even though the shape of the transmission coefficients is very similar. By using alkaline materials it is possible to move the Fermi level from the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap to the LUMO resonance and change dramatically the length dependence of the conductance of molecular wires, which opens the possibility of using molecules with different lengths and very similar conductances in nanoscale circuits. This method shows how to dramatically increase the conductance of molecular devices and alter qualitatively and quantitatively their electronic and transport properties.

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I. INTRODUCTION

During recent years, the race to develop a viable technology for sub-10-nm electronic wires led a number of groups to study electron transport through single molecules bridging two metallic electrodes. Examples include both experimental[1–4] and theoretical[5–9] works. In all of these experiments one or more of the metallic electrodes are formed either from break junctions[2,4] or from the tip of a scanning tunnel microscope (STM).[1,3] None of these contacting methods is capable of being scaled to billions of devices on a single chip. One route to develop a scalable technology is to first deposit electrodes with a predefined gap and then deposit molecules whose length is matched to the electrode gap. Since reproducible electrode gaps significantly below 10 nm do not currently exist, whereas most studies of single molecules involve molecules of length $\lesssim 3$ nm, there is a need for systematic studies of families of molecules of varying lengths which bridge those length scales. Current examples include alkanedithiols and alkanemonothiols,[10] diaminoacenes,[11] and oligothiophenes.[12]

When a low-enough voltage is applied to a single molecule bridging two metallic electrodes, the measured electrical conductance G is governed by the spatial extent of the molecular orbitals, their level broadening Γ due to the contacts and the position of the highest occupied molecular orbital (HOMO) (E_H) and lowest unoccupied molecular orbital (LUMO) (E_L) levels relative to the Fermi energy (E_F) of the electrodes.[13–15] This dependence is captured by the Landauer formula, $G(E_F)=\frac{2e^2}{h}\int_{-\infty}^{\infty}dET(E)(-\frac{\partial f(E-E_F)}{\partial E})$, where $f(E)$ is the zero-bias Fermi distribution in the electrodes and $T(E)$ is the transmission coefficient for electrons of energy E passing from one electrode to the other. For synthetic molecules such as oligothiophenes[12] $\Gamma \ll E_L - E_H$ and therefore $T(E)$ exhibits the Breit-Wigner[16] or Fano resonances[17] in the vicinity of E_L and E_H. For conjugated symmetric molecules with extended wave functions along the backbones, resonant values of $T(E)$ can be of order of unity and therefore at low-enough temperatures $G(E_F) \sim 2e^2/h$ whenever E_F aligns with a resonance. In principle, this high-conductance channel could be observable in conjugated single-molecule wires of arbitrary length provided that inelastic scattering is negligible. In practice, for most recently studied families of molecules the measured conductance is much less than $2e^2/h$ because E_F lies in the HOMO-LUMO (HL) gap. This means a serious handicap from the point of view of molecular circuitry because the conductance will decrease exponentially as a function of length and from the point of view of molecular sensing because the movement of resonances produced by other molecules or environmental changes will have less effect on the middle of the gap. One approach to overcoming this problem is to introduce a third gate electrode, which shifts E_L and E_H relative to E_F. In what follows we explore an alternative approach based on varying the electrode composition to yield a E_F close to E_H or E_L and consequently high-conductance molecular wires without the need for a gate electrode.

The idea of using alkaline electrodes to tune the work function of electronic contacts is well known in the organic light-emitting diodes (OLEDs) community.[18–20] In this paper we examine the effect of using alkaline electrodes for single-molecule electronics. We present a series of *ab initio* calculations based on density-functional theory (DFT) (Ref. 21) and the nonequilibrium Green's functions (NEGFs) (Ref. 22) which determine the effect of tuning E_F. We examine two molecules: the archetypal benzene-1,4-dithiol (BDT) molecule that has been the subject of many experiments and theoretical works[2,23] and a longer molecule, namely, 1,4-bis[4–24 (acetylsulphanyl)phenylethynyl]-2,6-dimethoxybenzene (molecule R3), as shown in Fig. 1 (Ref. 24) made of three aromatic rings, with the middle ring slightly twisted by the effect of oxygen-related side groups. We also examine molecules $R5$, $R7$, and $R9$ with five, seven, and nine aromatic rings obtained by doubling, tripling, and quadrupling the number of phenyl rings in molecule R3, respectively.

II. THEORETICAL METHOD

We use the SMEAGOL code,[9] which interfaces NEGF to the SIESTA code[26] and obtains self-consistently the density matrix and the transmission coefficients. We employ a basis set that includes polarization orbitals (single-ζ polarized or

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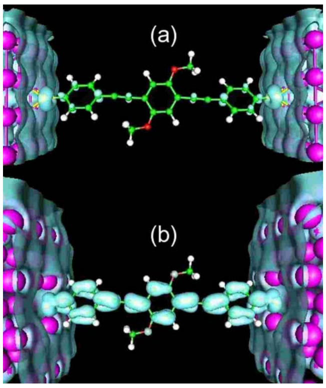

FIG. 1. (Color online) Real-space projection of the density of states on an interval of 0.2 eV around the Fermi level of the *R*3 molecule between (a) gold leads and (b) sodium leads.

SZP), which is good enough in this case.[27] To approximate the exchange and correlation we use the local-density approximation (LDA),[28] which works relatively well for organic molecules and noble or alkali metal. The real-space grid is defined by a plane-wave cutoff of 200 Ry. The leads are made of slices of fcc (gold) or bcc (alkali) lattices grown along the (001) direction with 16 atoms per slice and periodic boundary conditions along the directions perpendicular to the transport, corresponding to axes x and y. The system is also made periodic along z to avoid surface effects. The scattering region includes the molecule and five and six slices of the electrodes on the left and right parts of the unit cell, respectively. Each transport calculation has around 250 atoms.

III. PRELIMINARY CALCULATIONS

To evaluate how the Fermi level aligns relative to the molecular levels, we first calculate the energy states of the leads and each molecule separately. Since in SIESTA the energy origin is arbitrary[29] it is necessary to use a common reference to compare the levels of different calculations. For this purpose we use a hydrogen molecule 10 Å away from the slab or molecule, whose bonding orbital is taken as reference. The results are shown in Fig. 2. As can be seen, all Fermi levels of the slabs sit inside the *HL* gap of the BDT. The Fermi level is smallest for gold and increases through the alkali metals from Li to Cs. In the molecules, the *HL* gap is smaller in *R*3 than in BDT, as expected, and decreases as the number of rings increases toward *R*9. These results suggest that the conductance of molecular wires will change dramatically if gold is replaced by alkali leads. However, they describe only isolated molecules and do not include bonding to the surface and charge transfer. After coupling to the slabs the molecular states will broaden into transmission resonances and the LUMO will shift upward in energy toward E_F due to charge transfer onto the molecule.[15] To understand these effects we now perform complete transport calculations.

Since in most of these systems it is not exactly known where the molecule would attach on the surface, it is necessary first to determine the most stable bonding configuration.

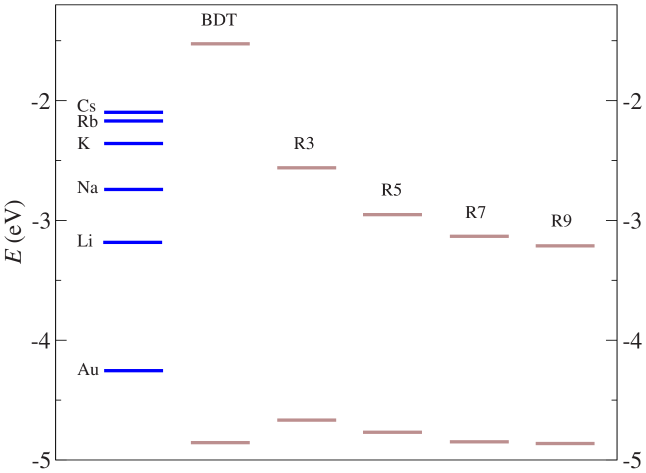

FIG. 2. (Color online) Relative position of the electrode Fermi energies and the molecular HOMO and LUMO states calculated with LDA and taking as reference the bonding orbital of a hydrogen molecule away from the system.

We achieve this by calculating the energy as a function of the distance between a S-C_6H_4-SH molecule and a slab made of four layers of fcc Au or bcc Li, Na, K, R, or Cs grown along the 001 direction, as a function of the distance between the free sulfur atom and the surface. The results can be seen in Fig. 3. The same calculation was repeated for various positions, which include top, bridge, and a four-atom hollow configuration. In the hollow configuration, steric interactions between some of the atoms of the molecule and the surface atoms on the corners of the square can give different energies. We also computed then the case where the molecule was rotated 45° along the axis perpendicular to the surface, but the results were practically the same.

We found that in all cases the most stable configuration corresponds to the hollow position. For short distances, how-

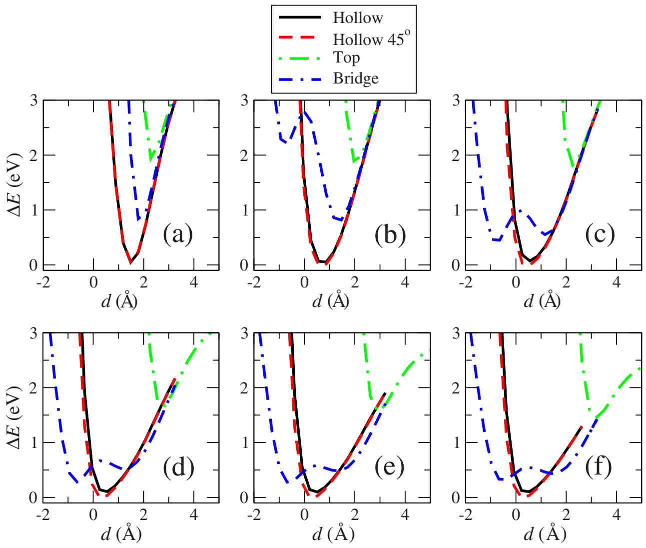

FIG. 3. (Color online) Energy of a S-C_6H_4-SH molecule on top of the surface of (a) fcc gold, (b) bcc lithium, (c) sodium, (d) potassium, (e) rubidium, and (f) cesium as a function of the distance between the free sulfur and the surface for various configurations.

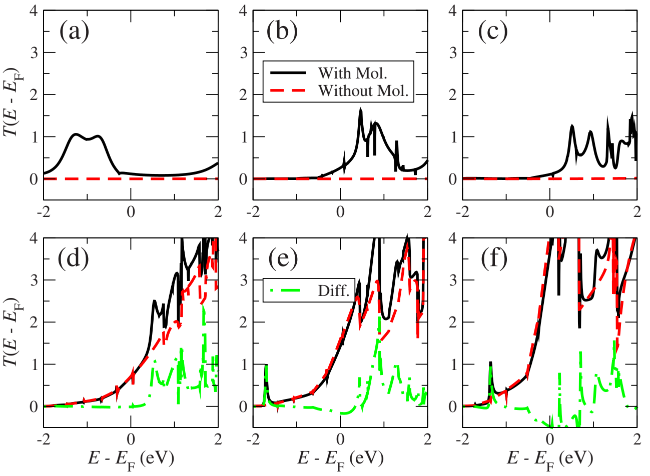

FIG. 4. (Color online) Transmission coefficients of the BDT molecule between (a) fcc gold and (b) bcc lithium, (c)sodium, (d) potassium, (e) rubidium, and (f) cesium. The dash-dotted line shows the difference between the transmission curves with and without molecule.

ever, the bridge can become the most favorable bonding configuration in the case of alkali leads. Its cohesive curve shows also two minima as opposed to the one-minimum curves of other configurations. The second minimum appears when the sulfur atom crosses the line between both surface atoms and goes deep into the surface. We expect then that the bonding configuration undergoes a transition between the hollow and bridge states when the molecule is compressed. That would also affect the transport properties and could be detected in the experiments as a small peak in the conductance histograms. A general trend is that, as the alkali atomic number increases, the molecule can approach closer to the surface due to the larger lattice constant of the surface atoms. This, in turn, slightly increases the bonding distance between the sulfur and the surface atoms, something which is manifested by the broadening of the parabola in the cohesion curve from Li to Cs, and decreases the interaction between the molecule and the surface.

IV. ALKALI VS GOLD ELECTRODES

First we simulated the benzene molecule between gold electrodes and obtained the well-known result that the Fermi level is close to the HOMO resonance.[30,31] When gold was replaced by Li, however, the LUMO resonance moved toward the Fermi level and the conductance increased, as can be seen in Fig. 4. This was expected from the results of Fig. 2 due to the change in position of the Fermi level relative to the molecular orbitals. The same trend was also found for the other alkali metals. However, for the heavier alkali elements, K, Rb, and Cs, there was direct transport between the electrodes even in the absence of the molecule. This effect was produced by the reduction in the distance between the leads due to the penetration of the molecule in the surface for large lattice constants and the increasing electronic delocalization of the outer electrons as the atomic number increases in these elements. This can be clearly seen in the lower panels of Fig. 4 where the direct transmission increases for high energies, which correspond to less-bounded electrons. In some cases the molecule acted also as an impurity reducing the total transmission between the leads. As a consequence, it was not easy to clearly distinguish the molecular contribution from the electrode contribution. For that reason, our attention moved to the $R3$ molecule for which the electrodes are far enough.

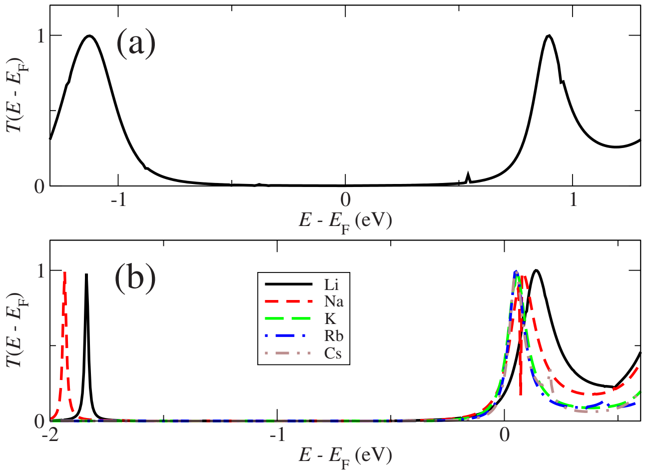

FIG. 5. (Color online) Transmission coefficients of $R3$ between (a) gold electrodes and (b) alkali electrodes.

Figure 5 shows the transport properties of the $R3$ molecule between gold and alkali leads. As can be seen, the transmission coefficients are very similar in all cases and are characterized by the presence of two main resonances, corresponding to the HOMO and LUMO orbitals, and a large HL gap. In the case of gold, the Fermi level sits in the middle of the HL gap, which produces a very small zero-bias conductance. However, for the alkali elements the Fermi level moves to the LUMO resonance and dramatically increases the value of the conductance.[32] An increase in the conductance can also be seen by plotting on real space the density of states (DOS) on an energy interval of 0.2 eV around the Fermi level, as shown in Fig. 1. In the gold case the DOS of the leads does not penetrate into the molecule and electrons have to tunnel between both surfaces. When E_F moves toward the LUMO, DOS appears also in the molecule and makes it metallic.

We found that the conductance increases from Li to K, but after that it decreases toward Cs. Such nontrivial behavior can be explained by taking into account the movement of the Fermi level, charging effects, and changes arising from bonding to different surfaces. As the alkali atomic number increases, the LUMO resonance moves downward (see Fig. 5); but as it starts to cross the Fermi energy, the charge on the molecule increases and the intralevel repulsion moves the states upward again.[15] The total amount of charge transferred to the molecule increases with the atomic number of the alkali elements, as can be seen in Table I, which is expected due to the increasing electropositivity and delocalization. At the same time, the lattice constant of the contact increases with the atomic number, and therefore the space in the hollow position becomes larger, which reduces the coupling be-

TABLE I. Total charge gained by the molecule after connecting it to the electrodes obtained from the Mulliken populations.

	Au	Li	Na	K	Rb	Cs
ΔQ (e)	0.45	0.63	0.88	1.15	1.24	1.34

tween the contact sulfur atom and the surface and decreases the width of the LUMO resonance. The first effect increases the conductance from Li to K, whereas the second decreases it toward Cs.

We therefore expect a dramatic increase in the conductance if gold electrodes were replaced by alkali leads. Based on our calculations we predict that gold is one of the worst possible choices for high-conductance molecular nanowires since the conductance decreases exponentially as the length of the nanowire increases.

From Fig. 5 it is possible to deduce some general properties which can help to understand the influence of various factors. For example, it is noticeable that while the LUMO resonances in all cases have a similar width, the HOMO resonance is very sharp when the molecule is coupled to the alkali leads, as compared to the gold case, and its width decreases with the atomic number of the alkali element. This arises because the LUMO is delocalized along the molecule (see Fig. 1) and it is better coupled to the contacts, whereas the HOMO is localized in the middle of the molecule and is sensitive to any change in the coupling. Since the coupling to the alkali leads is smaller than the coupling to gold and decreases from Li to Cs, the width of the HOMO resonance is much smaller in the former and becomes sharper as the atomic number increases.[35]

Additional information on the electronic structure and its influence on the transport properties can be obtained by analyzing the projected density of states (PDOS), which we show in Figs. 6 and 7 for the Au and Na configurations corresponding to Fig. 5. In both cases the transmission resonances associated with the HOMO and LUMO orbitals coincide with features in the PDOS of the C and S atoms related to the p_{-1} orbitals, which are perpendicular to the transport direction and make on the molecular backbone the delocalized states near the Fermi level. Such orbitals penetrate into the molecule and generate the channels associated with the resonances. In the case of gold there is an additional p_1 contribution on the S near the HOMO due to the strong interaction with the surface atoms that move these orbitals up in energy, but it does not go inside the molecule because it almost disappears in the C atom. The small transmission in the *HL* gap is produced by the absence of C states in this region even though there are S states generated by hybridization with the surface states. The density of states of gold and sodium is finite in all the energy windows and is mainly due to the *s* orbitals. Notice that we plot the density of states per atom; so even in regions where it looks relatively small it has a finite contribution which allows the formation of a conductance channel, such as, for example, in Fig. 6 between 0.5 and 1 eV.

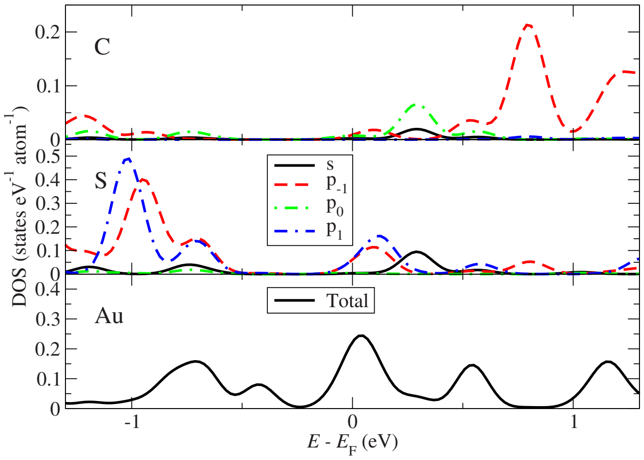

FIG. 6. (Color online) Projected densities of states on the first C atom, the S atom, and the Au electrodes for a *R*3 molecule in the same configuration as in Fig. 5(a).

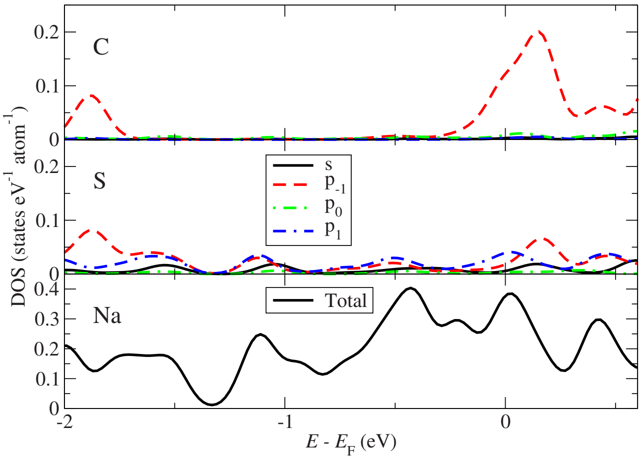

FIG. 7. (Color online) Projected densities of states on the first C atom, the S atom and the Na electrodes for a *R*3 molecule in the same configuration as in Fig. 5(b).

V. LENGTH DEPENDENCE

The fact that the Fermi energy is close to the LUMO resonance opens the possibility of having nonexponential dependence of the conductance as a function of the molecular length provided that the Fermi level for longer molecules is still close enough. Such a possibility would allow the use of molecular wires with various lengths to connect different parts of a nanoscale circuit with almost no change in the conductance. We checked this possibility by using longer molecules with the same central unit and more benzene rings. To ensure that only the length was varied and no additional effects were introduced, the rings were made coplanar with the outer ones and the same number was added on both sides. The lengths of such molecules—which we call *R*5, *R*7, and *R*9—were 3.4, 4.7, and 6.1 nm, respectively.

It is well known that as the molecular length increases, the *HL* gap decreases due to the higher electronic delocalization along the molecule. The *HL* gap and the relative position of the HOMO and LUMO of all molecules can be seen in

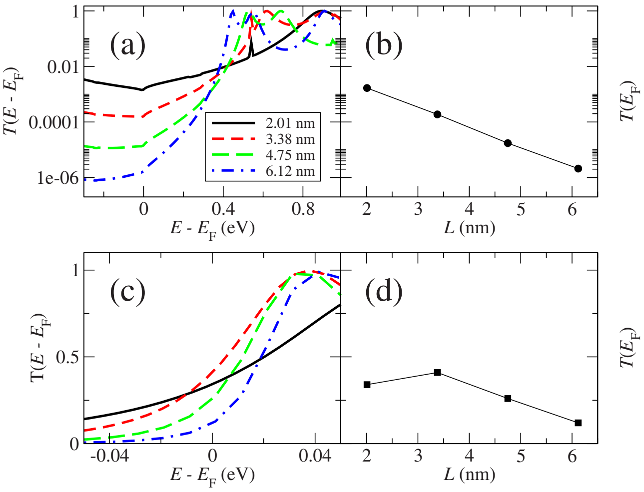

FIG. 8. (Color online) Length dependence of the transmission coefficients and low-bias conductance for molecules between gold electrodes [(a) and (b), respectively], and molecules between sodium electrodes [(c) and (d), respectively].

Fig. 2. However, as the *HL* gap decreases, the value of the transmission coefficients inside the gap is exponentially reduced due to the larger separation between the electrodes. This implies again that if the Fermi level sits inside the gap the conductance will decrease exponentially as a function of the molecular distance. In Fig. 8 we show the transmission coefficients around the Fermi energy as a function of the distance for (a) gold and (c) sodium electrodes. As can be seen in Figs. 8(a) and 8(b), which are plotted on a logarithmic scale, the transmission at the Fermi level decreases exponentially when the molecules are contacted to gold. Such exponential behavior has a beta of 0.16 Å^{-1} and indeed proves that the quantum transport is in the tunneling regime. As the molecular size increases, the LUMO resonance moves downward and the distance between levels decreases, but these effects are not enough to eliminate the exponential behavior.

However, in the case of sodium leads [shown in Fig. 8(c)], the Fermi level is located near the LUMO resonance for all molecules. This makes the length dependence nonexponential and almost linear, as can be seen in Fig. 8(d). Such evolution comes from interplay between the downward shift of the LUMO resonance, charge transfer, and changes in the coupling. The first molecule does not fit well into the linear trend due to the much bigger width of the LUMO resonance. Such an anomalous resonance is produced by a very large interaction between the leads and the molecular central part, where this orbital has the biggest weight. At the same time, in order to keep the same charge on the molecule, this orbital is also shifted upward. The LUMO resonances of longer molecules have a width which decreases and a position that increases slightly with the molecular length. The reduction in the width can be explained by taking into account that the weight of the LUMO decreases at the edges of the molecule, and therefore the coupling between this orbital and the contacts tends to decrease as the length increases (the same, but more pronounced, happens to the HOMO orbital). The upward movement of the LUMO resonance looks counterintuitive since as the molecular length grows the orbitals move downward, but it can be explained by the upward shift of the levels produced by the additional charge on the molecule.

VI. CONCLUSIONS

The long-term goal of using high-conductance molecular wires as interconnects in sub-10-nm electronics requires that HOMO or LUMO resonances coincide with the Fermi energy of metallic electrodes so that the conductance does not decrease exponentially and all nanoscale electronic elements are connected with almost the same conductance. The pinning of the Fermi level at the LUMO is also important from the point of view of sensing since the effect produced by other molecules or environmental changes, which is manifested mainly by movements of the resonances, will be much higher. In this paper we have shown that by analogy with current technology used in OLEDs, this can be achieved by using alkali metals[36] instead of the more commonly used gold.

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[27] Based on calculations with the BDT molecule, a SZP basis is enough to accurately describe the results of this work. We note that the inclusion of polarization orbitals is a key factor to correctly reproduce the states above the Fermi level, in particular the LUMO, whereas the inclusion of double zetas only produces a shift in the energy of the isolated systems which is corrected when they become coupled.

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[36] We would like to point out, however, that from an experimental point of view the use of alkali electrodes would be a difficult task due to the high reactivity of such materials.