

This document is the Accepted Manuscript version of a Published Work that appeared in final form in The Journal of Physical Chemistry C, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <http://pubs.acs.org/doi/abs/10.1021/jp5084955>.

Impact of Collective Electrostatic Effects on Charge Transport through Molecular Monolayers

Veronika Obersteiner[†], David A. Egger^{†‡}, Georg Heimel[§], and Egbert Zojer^{*†}*

[†] Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

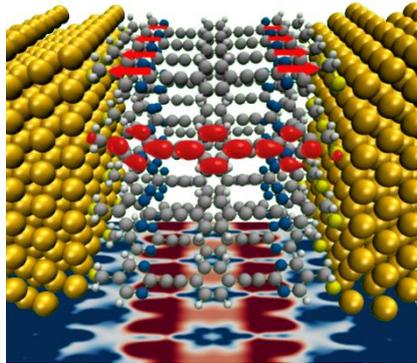
[‡] Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

[§] Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, 12489 Berlin, Germany

Corresponding Authors

* david.egger@tugraz.at; egbert.zojer@tugraz.at

TOC GRAPHIC



Abstract

A microscopic understanding of charge transport through molecule-based systems is essential for advancing the field of molecular electronics. In the present contribution we highlight fundamental differences between devices with an individual molecule or a homogeneous monolayer as the active element. These differences arise from collective electrostatic effects that govern the electronic level-alignment in monolayer-based devices, but are absent in the case of individual molecules. Employing density functional theory in conjunction with a Green's function approach, we show that depending on the chemical nature of the employed molecules collective electrostatic effects can result in either a significant increase or decrease of the current per molecule as a function of packing density, in certain cases even resulting in a change in the transport polarity. Understanding the underlying principles also allows for designing molecules in which dipolar effects cancel and, thus, the transport characteristics of individual molecules and monolayers remain similar.

KEYWORDS Molecular Electronics, Electronic Transport, Collective Effects

1. Introduction

The ultimate miniaturization of electrical components triggered paramount scientific interest in understanding charge transport on an atomistic length scale and lead to what is known today as ‘molecular electronics’.^{1,2,3} The collective (or cooperative) behavior of individual molecules condensed into a molecular assembly is particularly important, as it determines the ‘scaling’ of charge-transport properties with the size of a molecular junction⁴.

Experimentally, these scaling properties have been examined in several previous studies⁵. For example, Kushmerick et al. observed the conductance to scale directly with the number of molecules present in a self-assembled monolayer (SAM) junction⁶. Selzer et al., however, found that the scaling of conductance strongly depends on the applied bias, and that the per-molecule current can strongly decrease due to environment effects⁷. Similarly, also in theoretical studies^{8,9,10,11,12,13,14,15,16,17} it was reported that going from one molecule to a few and further to many molecules, collective effects can “help or hamper¹⁵” electronic transport. For example, direct molecular (π - π) and substrate-mediated coupling^{13,15}, or quantum-interference phenomena¹⁸ were shown to generally increase the conductance per molecule. On the other hand, incoherent scattering can strongly decrease the per-molecule conductance in a SAM¹⁶, and equally so can differences in the broadening of spectral properties when going from single molecules to monolayers^{12,13}. These previous findings clearly suggest that the evolution of charge-transport properties with the number of molecules is strongly system dependent.

While the above-mentioned effects originate mostly from quantum-mechanical interactions, in this Letter, the impact of collective *electrostatic* effects on charge-transport properties of molecular assemblies is systematically investigated. These arise from the peculiar way in which assemblies of dipoles influence the electrostatic potential-energy landscape (for recent reviews see refs 19,20,21,22). Such dipoles are present in the vast majority of molecular and monolayer

junctions due to polar docking groups and/or interfacial charge-rearrangements arising from the molecule-electrode bond formation. Previously, some of us have shown that the collective electrostatic interaction of dipolar units allows for switching the transport polarity in monolayer junctions²³. Here, we will exploit such intramolecular polar groups primarily to clearly illustrate the impact of collective electrostatic effects on charge-transport properties.

We find that the detailed chemical structure of the molecules forming the junction determines whether the per-molecule current increases or decreases, when the molecular packing density changes. We also show that by designing molecules such that internal dipoles compensate bonding-related dipoles, it becomes possible to realize systems in which the current per molecule becomes largely packing independent. This could, for example, be exploited for reducing fluctuations arising from structural imperfections in monolayer devices that cause lateral variations of the local packing density. Based on well-established concepts of electrostatics and molecule-metal interfaces, our study reveals that transport measurements may or may not depend on the number of molecules present in the junction.

2. System Setup and Theoretical Methods

In our calculations, we considered metal-molecule-metal junctions with varying lateral molecular packing densities, Θ (see Fig. 1a). Employing periodic boundary conditions, we represented the leads present on each ‘side’ of the junction by three layers of Au(111) (i.e., there are 6 layers of Au between periodic replicas of the organic monolayers). For the molecular part of the junction, we started from a densely-packed ($\Theta=1$) self-assembled monolayer (SAM) with one molecule per (2x2) Au(111) surface unit cell. The lateral molecular packing density

was then gradually reduced by replicating the unit cell in the x and y -directions removing all but one molecule. In this way, we generated molecular packing

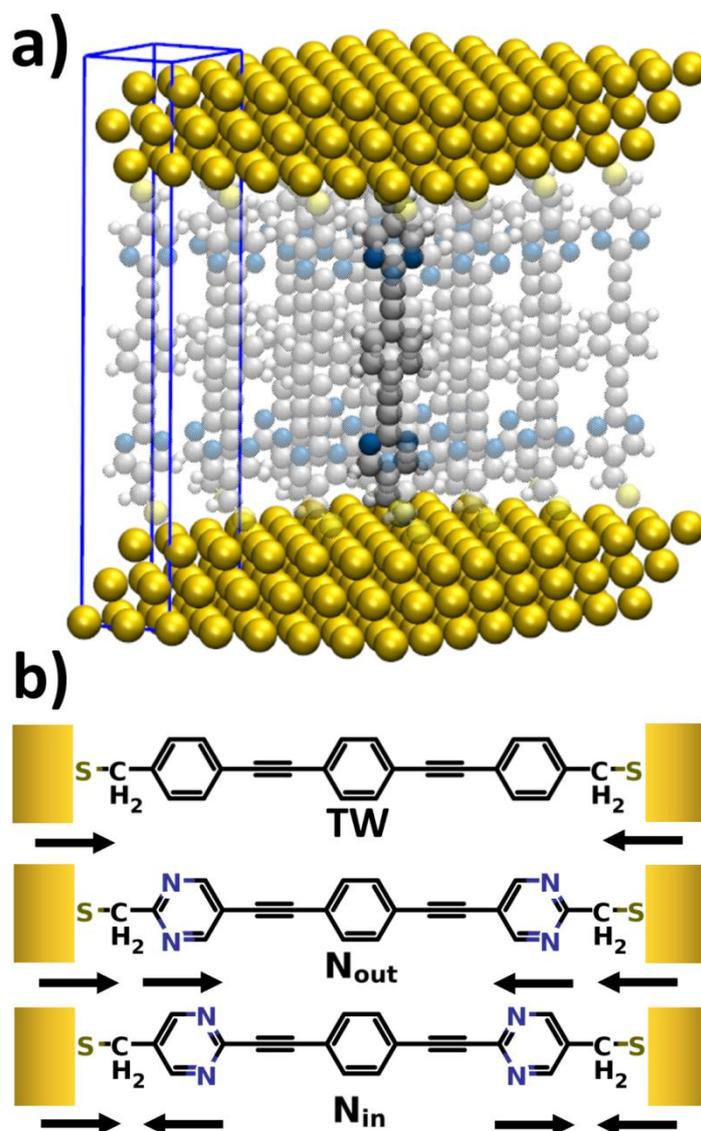


Figure 1. (a) Structure of the densely packed ($\Theta=1$; all molecules) junction and the model system for the single-molecule situation ($\Theta=1/16$; dark molecule only). The unit-cell for $\Theta=1$ is indicated by the blue box, while for $\Theta=1/16$ the whole displayed structure (excluding the shaded molecules) represents the unit cell used in the calculations. (b) Chemical structures of the investigated molecules TW, N_{out} and N_{in} , including arrows indicating the relevant local dipoles present in the systems.

densities of $\Theta=1/2$, $\Theta=1/4$, $\Theta=1/8$, and $\Theta=1/16$. The latter, which corresponds to one molecule per (8x8) surface unit-cell, strictly speaking is a very sparse monolayer, which we here consider as a model for a single molecule junction. This is justified by the far-reaching electrostatic interactions between neighboring molecules becoming very small in the case of $\Theta=1/16$, as will be shown below. The procedure of varying the molecular packing density is schematically indicated in Fig. 1a; a more detailed description including depictions of all unit cells is contained in the supporting information (SI).

As a prototypical example for molecular and monolayer junctions, we studied ‘Tour-wire’²⁴ based systems, *i.e.*, 1,2-bis(2-phenylethynyl)benzene bonded two the Au electrodes with methylthiolate groups (TW molecule; see Fig. 1b). The methylene (-CH₂-) spacers are used to electronically decouple the π -conjugated backbone from the metal to avoid substrate-induced effects that are not the focus of our present study. To investigate the impact of polar groups built into the molecular backbone²⁵, we followed the strategy from ref 23 and symmetrically replaced the two outermost phenyl rings with pyrimidine units, resulting in the N_{out} and the isomeric N_{in} molecules (see Fig. 1b). Importantly, this procedure hardly affects molecular quantities, *i.e.*, the frontier orbitals of N_{out} and N_{in} are delocalized π -states (see SI) and their ionization potential and electron affinity are essentially equal. However, the differently oriented C-N bonds lead to differently oriented ‘local’ dipoles in the peripheries of the N_{out} and N_{in} molecules, indicated by black arrows in Fig. 1b. Furthermore, all systems exhibit an additional local dipole, namely through the polar C-S-Au bonds (see Fig. 1b), comprising also the polarization response in the substrate.²⁶ The collective effects due to these dipoles are the main focus of our study and will be explored in detail below. Note that the term ‘local dipole’ is not used in a rigorous sense (which would require local charge neutrality), but rather to specify a local charge distribution that affects the electrostatic potential in a way similar to a

(point) dipole. Overall, all three considered molecules exhibit inversion symmetry along the long molecular axis and, thus, do not possess a net dipole moment in this direction.

Because our goal was to isolate the impact of collective electrostatics on charge transport, we chose to suppress several other effects usually superimposed in an actual junction. Therefore, we deliberately did not account for specifics in the junction geometry²⁷, disorder, or molecular orientation (varying tilt²⁸ and azimuthal angles). Also the gap reduction due to polarization effects in the films is not considered^{29,30,31}. To nevertheless allow for a realistic structural setup of the studied systems, we fully optimized the SAM structures including the innermost gold layers and the length of the junction in z-direction (see SI for further details).

To determine the electronic structure of the systems and optimize their geometry, we performed band-structure calculations within the framework of density-functional theory (DFT), using the VASP³² code and the Perdew-Burke-Enzerhof PBE³³ exchange-correlation functional. For computing the charge-transport properties of the metal-molecule-metal junctions, we followed a three step procedure: First, we used a locally modified version of the periodic electronic-structure code SIESTA³⁴ for extracting the Hamilton and overlap matrix of the central region (comprising the above-described unit cells; i.e., six layers of gold and the molecules at different packing densities). We applied a double-zeta polarized basis set. To achieve compatibility of the packing-dependent trends with the VASP results, we reduced the ‘PAO energy shift’ to 0.001Ry (see SI for more information). Then, we computed the self-energies of the leads in the recursive Green’s function formalism³⁵, using a $(2 \times 2 \times \sqrt{6})$ unit cell for bulk gold, which was suitably increased at lower packing densities. Finally, the zero-bias transmission function, $T(E)$, was calculated to obtain current-voltage (I-V) characteristics, employing the Landauer-Büttiker^{36,37} approach as

$$I(V) = \frac{2e}{h} \int T(E) [f(E - \mu_{\text{left}}) - f(E - \mu_{\text{right}})] dE. \quad (1)$$

Here, $f(x)$ is the Fermi-Dirac occupation function at 300K, and $\mu_{\text{left/right}} = E_{\text{F}} \pm \frac{eV}{2}$ with e the elementary charge, E_{F} the Fermi energy and V the voltage. Because we rely on zero-bias transmission functions, polarization effects due to an applied voltage are not included in our treatment. Nevertheless, qualitatively reliable results can be expected for current-voltage characteristics plotted in voltage regions far from resonances³⁸. OVITO,³⁹ XCrySDen⁴⁰ and Mayavi⁴¹ were used for graphical visualization. For full details on the applied computational methodology and numerical parameters used in our calculations, see SI.

3. Results and Discussion

3.1. Charge-Transport Properties of Monolayers with Different Packing Densities

The resulting current-voltage (I-V) curves for TW, N_{out} and N_{in} molecules at highest ($\Theta=1$) and lowest ($\Theta=1/16$) considered packing density are shown in Fig. 2a (thick, solid lines). At $\Theta=1$, the transport characteristics of the three systems display certain differences: For example, for a per-molecule current of $0.5 \mu\text{A}$ to flow, voltages of 1.4 V, 1.0 V, and 1.2 V have to be applied for TW, N_{out} and N_{in} , respectively. What is more surprising, however, are the distinctly different shifts of the charge-transport characteristics that are observed when approaching the single molecule (i.e., low packing density) limit: Reducing the molecular packing density in the junctions significantly increases the current per molecule for TW, whereas for N_{out} a marked decrease is observed. For N_{in} , where the orientation of the polar C-N bonds is reversed, the current per molecule is almost independent of the molecular packing density.

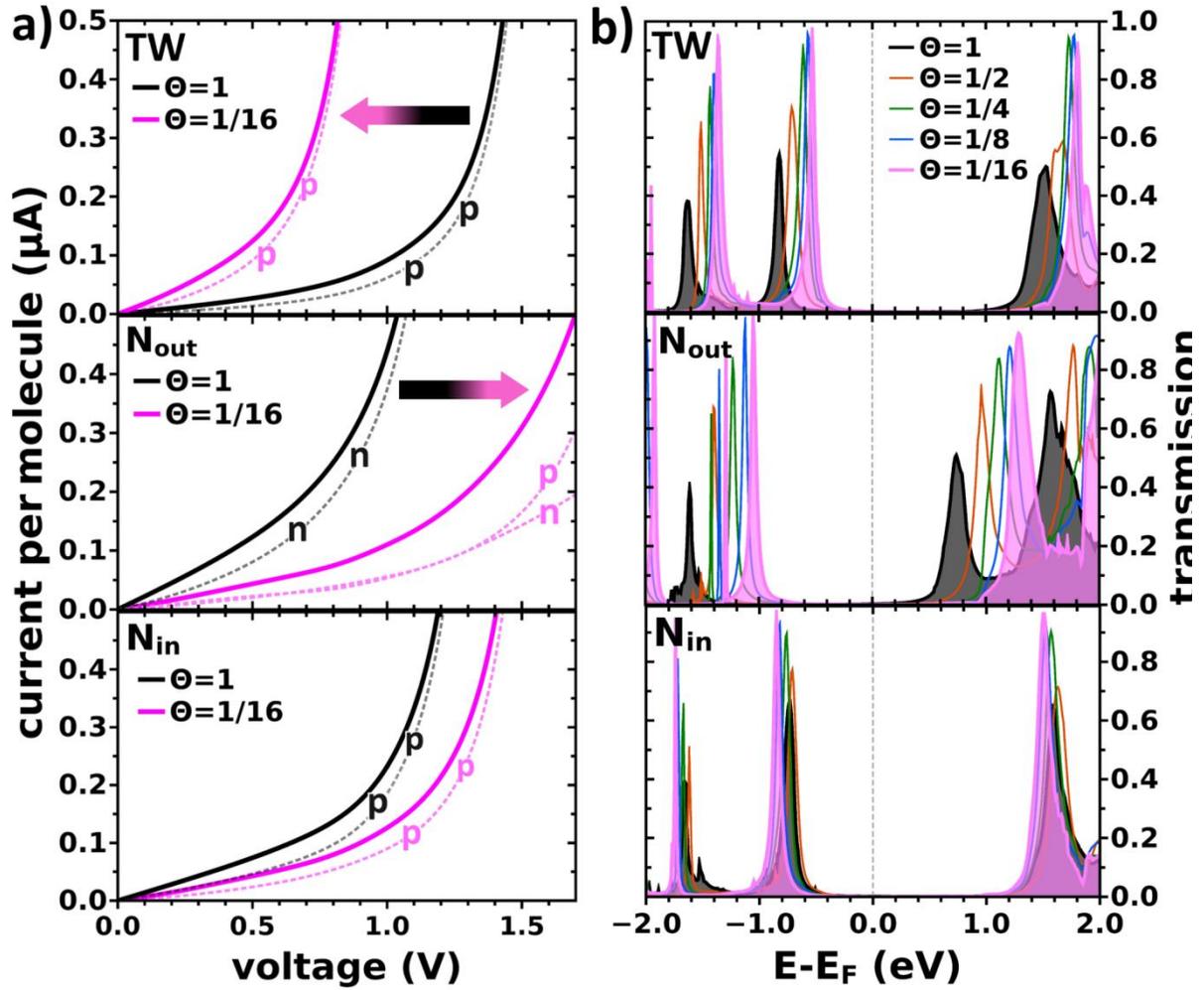


Figure 2. (a) Calculated current-voltage characteristics of the TW, N_{out} and N_{in} systems for full monolayer with a packing density $\Theta = 1$, and the model for a single molecule junction with $\Theta=1/16$. Thick-solid lines denote full currents, whereas thin-dashed lines denote the dominant types of current arising from electron (n-type) or hole (p-type) transport; see text for details. (b) Calculated transmission functions of the TW, N_{out} and N_{in} systems for different packing densities Θ . The Fermi level E_F is used as the energy reference. The area below the curves for the highest and lowest considered packing densities is shaded.

We have previously shown for densely-packed N_{in} and N_{out} layers²³ that local intramolecular dipoles can influence the polarity of charge transport through molecular monolayers. This determines, for example, the sign of the Seebeck coefficient^{42,43,44} and, thus, the thermoelectric properties of molecular or monolayer junctions. Therefore, it is interesting to investigate the charge-transport polarity for the different junctions also as a function of the packing density. To achieve this, we calculated the current through occupied and unoccupied states separately (by setting the remainder of $T(E)$ to zero and re-evaluating Eq. 1) with the results shown as dashed lines in Fig. 2a. At highest-packing density, the transport through TW and N_{in} SAMs is essentially p-type, while for the N_{out} SAM we find a more pronounced n-type current. When reducing the packing density, again an intriguing system-dependent effect occurs: For TW and N_{in} , the charge-transport polarity observed at highest packing density (p-type) prevails; for N_{out} , however, the polarity changes such that for the isolated molecule in the chosen configuration p-type and n-type conduction become very similar.

3.2. Evolution of the Transmission Functions with Molecular Packing Density

As current-voltage characteristics are directly affected by the energetic alignment of molecular transport channels relative to the Fermi level, E_F , the above-discussed trends can be directly traced back to the transmission functions shown in Fig. 2b. For TW and N_{out} , a reduction in the packing density results in a continuous shift of the transmission functions to more positive energies with respect to E_F . Thus, in both cases the occupied channels approach E_F , while the unoccupied channels retreat from it, with the effect significantly more pronounced in the N_{out} case (+0.3 eV vs. +0.6 eV). As TW conducts via occupied channels, reducing the packing density reduces the tunnel barrier, and, consequently leads to an increase in the per-molecule current (see Fig. 2a). For N_{out} , however, the current at $\Theta=1$ is dominated by electrons flowing

through unoccupied states (see Fig. 2a). Therefore, the energy shift of the transmission function causes a decrease in the current per molecule when reducing the packing density. This eventually leads to the above-described change in transport-polarity at $\Theta=1/16$ (where for N_{out} the energetic distances of the occupied and unoccupied transport channels from E_F become very similar). In the case of N_{in} , changes of the transmission function are comparably small, which is why current and polarity are essentially independent of the molecular packing density.

3.3. Impact of Local Dipoles on the Electrostatic Potential Energy

Fig. 3 shows the plane-averaged electrostatic energy of an electron along the transport direction for all three systems at $\Theta=1$. Interestingly, the electrostatic energy in the region of the molecular backbone is quite different in all three systems, which is highly relevant for the charge-transport properties because it energetically shifts the delocalized orbitals (see SI)

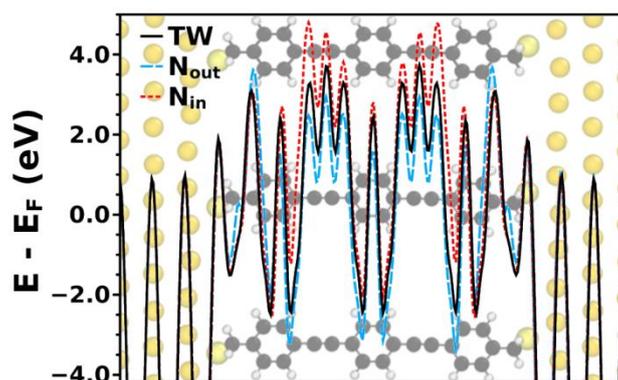


Figure 3. Calculated plane-averaged electron electrostatic energy for full packing density, $\Theta=1$, of TW (solid black line), N_{out} (dashed light-blue line), and N_{in} (dotted red line). The Fermi energy is set to zero.

that serve as transport channels. These distinct qualitative differences in the local electrostatics of the three considered systems can be understood considering the different orientations of the local dipoles, as schematically indicated by the black arrows in Fig. 1b. As has been discussed extensively in the literature^{19,20,21,22}, a 2D-periodic assembly of molecules with polar groups results in an energy shift left and right of the plane in which the dipoles are assembled. Interestingly, for point dipoles one can show that the decay length of the associated electric field is by nearly an order of magnitude shorter than the dipole-dipole distance¹⁹.

To visualize the resulting abrupt changes in the electrostatic potential for the studied systems and analyze the effect of the local dipoles, we also plotted the electron electrostatic energy in a plane parallel to the central benzene rings for the densely-packed SAMs, $\Theta=1$, see Fig. 4 a-c. In the TW monolayer, the most prominent energy shift occurs in the region of the bond between the Au surface and the methylthiolate bond (C-S-Au dipole). As the C-S-Au dipoles point towards the center of the junction, this effect shifts all transport channels in the monolayer to more negative energies with respect to E_F . Otherwise, only relatively weak variations in the energy are visible, especially further away from the nuclei.

In the N_{in} and N_{out} SAMs (see Figs. 4 b & c) the situation changes dramatically compared to the TW monolayer: An additional, rather steep potential energy gradient appears in the region of polar C-N bonds that strongly shifts the overall energy landscape for the molecules to more negative energies (N_{out} ; blue shading in the central region of Fig. 3b), respectively positive energies (N_{in} ; red shading in the central region of Fig. 3b) in energy. These are

‘global’ shifts, meaning that they affect the whole scattering region in-between the leads.

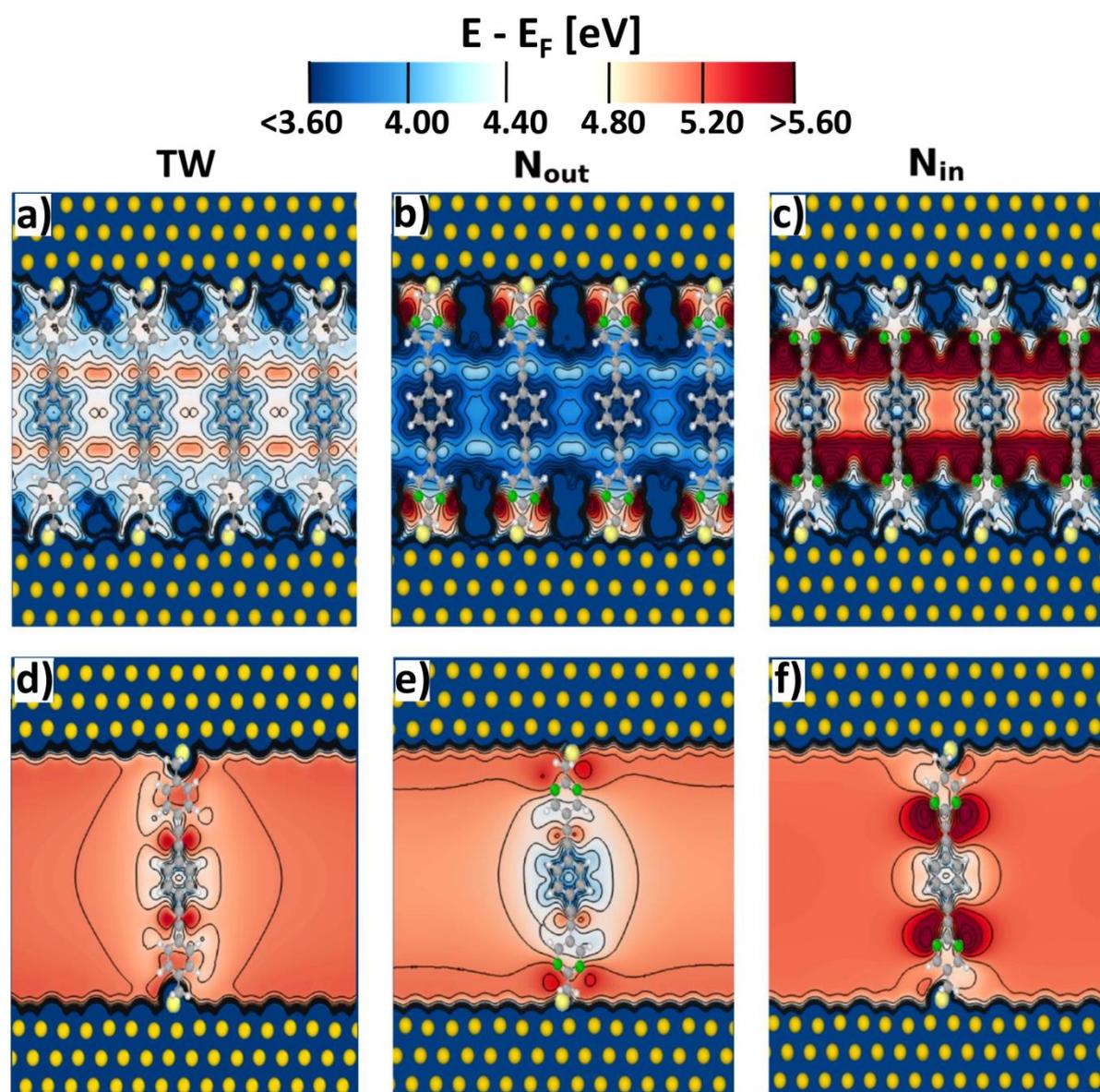


Figure 4. Contour plot of the electron electrostatic energy for full packing density $\Theta=1$ (a) - (c) and lowest packing density $\Theta=1/16$ (e) - (f) of TW, N_{in} and N_{out} in a plane parallel to the central benzene ring, approx. 1.6 Å away from that ring to (i) avoid extensive variations in the potential near the nuclei and (ii) to avoid artifacts caused by the bending of the molecules (see SI). The choice of the plane in which the potential is plotted is also the reason for the potential features between the molecular backbones. These originate from potential variations caused from the (bent) molecules in the neighboring unit cells. The potential energy is given relative to the respective Fermi level. Isolines are drawn every 0.2 eV; no isolines are drawn for electrostatic energies below 2.4 eV.

Naturally, as such they also shift the electronic states in the monolayer relative to the Fermi-level and, therefore, also the corresponding conducting channels in the transmission functions. We also find that these shifts are superimposed by ‘local’ (i.e., molecular) perturbations of the potential energy, especially close to the N atoms, and a weaker energy gradient along the carbon-carbon triple bonds that to some extent compensates the shift due to the pyrimidines. We attribute the latter, which is clearly a secondary effect, to a pyrimidine-induced polarization of that molecular region. The discussed ‘global’ energy variations are fully consistent with the plane-averaged potentials (cf. Fig. 3).

When reducing the molecular packing density, the potential energy shifts caused by the superposition of the fields of the dipoles arranged in parallel decrease continuously⁴⁵. This decrease depends sub-linearly on the packing density, owing to a smaller depolarization of C-N and C-S-Au dipoles at lower packing densities^{46,47,48}. Nevertheless, already for $\Theta=1/16$ (i.e., the lowest packing density considered here) only ‘local’ potential energy variations prevail, which reflect the different nature of the involved chemical elements. The ‘global’ gradients in the direction perpendicular to the electrode surfaces have disappeared (see Fig. 4 d-f). This clearly shows that at low packing density, i.e. close to the single-molecule junction regime, the properties of the individual molecules prevail. In systems with interacting molecules, however, the collective electrostatic effects of superimposed dipole fields can significantly shift the electronic states in energy. These effects then determine the packing-dependent charge transport: At $\Theta=1$, the energy shift due to the C-S-Au dipole that occurs for all studied systems in a similar way adds to the effect of the pyrimidine dipole in the case of N_{out} . At lower packing densities, these shifts disappear, which explains the strong packing-density dependence of the transmission functions of TW and N_{out} . For N_{in} , however, at $\Theta=1$, the impact of the reversed

pyrimidine dipole cancels that of the C-S-Au bond giving rise to its packing-independent charge-transport properties. This shows that collective electrostatic effects can be effectively ‘switched off’.

4. Conclusions

To summarize, we studied the impact of collective electrostatic effects on the charge-transport properties of molecular systems. Our results clearly demonstrate that these effects can change the transport characteristics of molecular ensembles even qualitatively, as they strongly affect the total current as well as its polarity. Most importantly, we have shown that collective effects emerge naturally from the bonding of the molecules to (metallic) leads (i.e., they occur in virtually all monolayer junctions) and that they are strongly affected by the presence of polar bonds. Depending on the magnitude, orientation, and location of the associated dipoles, collective electrostatic effects can significantly increase or decrease the current per molecule. They can be significant, shifting transmission maxima sometimes by more than 1 eV and are, thus, larger than many of the otherwise discussed collective effects in molecular junctions. By appropriate molecular design, these effects can also be avoided. As collective electrostatic effects are operational only in (densely) packed monolayers but absent in individual molecules, the aforementioned trends directly map onto packing-dependent molecular conductivities. Consequently, the phenomena discussed here can play an important role in many of the relevant charge-transport scenarios and might help explaining some of the seemingly conflicting observations of cooperative charge-transport behavior in molecular and monolayer systems.

ACKNOWLEDGMENTS

We thank Leor Kronik for stimulating discussions. Financial support by the Austrian Science Fund (FWF): P24666-N20 and I937-N19 as well as by the Deutsche Forschungsgemeinschaft (DFG) through SFB 951 'HIOS' is gratefully acknowledged. The work of D.A.E. has been partly supported by a DOC fellowship of the Austrian Academy of Sciences. The computational studies presented have been performed using the clusters of the division for high performance computing at the Graz University of Technology.

Supporting Information

Further details of the computational methodology, additional information regarding system setup and geometry optimization and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Corresponding Authors

*Email: david.egger@tugraz.at, egbert.zojer@tugraz.at

Notes

The authors declare no competing financial interests.

References

- ¹ Cuevas, J.C.; Scheer, E. *Molecular electronics an introduction to theory and experiment*. World Scientific, Singapore; Hackensack, NJ, 2010.
- ² Song, H.; Reed, M. A.; Lee, T. Single molecule electronic devices. *Advanced Materials*, 2011, 23(14), 1583-1608.
- ³ McCreery, R. L.; Yan, H.; Bergren, A. J. A critical perspective on molecular electronic junctions: there is plenty of room in the middle. *Physical Chemistry Chemical Physics*, 2013, 15(4), 1065-1081.
- ⁴ Akkerman, H. B.; Blom, P. W.; De Leeuw, D. M.; De Boer, B. Towards molecular electronics with large-area molecular junctions. *Nature*, 2006, 441(7089), 69-72.
- ⁵ Salomon, A.; Cahen, D.; Lindsay, S.; Tomfohr, J.; Engelkes, V. B.; Frisbie, C. D. Comparison of electronic transport measurements on organic molecules. *Advanced Materials*, 2003, 15(22), 1881-1890.
- ⁶ Kushmerick, J. G.; Naciri, J.; Yang, J. C.; Shashidhar, R. Conductance scaling of molecular wires in parallel. *Nano Letters*, 2003, 3(7), 897-900.
- ⁷ Selzer, Y.; Cai, L.; Cabassi, M. A.; Yao, Y.; Tour, J. M.; Mayer, T. S.; Allara, D. L. Effect of local environment on molecular conduction: Isolated molecule versus self-assembled monolayer. *Nano letters*, 2005, 5(1), 61-65.
- ⁸ Yaliraki, S. N.; Ratner, M. A. Molecule-interface coupling effects on electronic transport in molecular wires. *The Journal of chemical physics*, 1998, 109(12), 5036-5043.
- ⁹ Magoga, M.; Joachim, C. Conductance of molecular wires connected or bonded in parallel. *Physical Review B*, 1999, 59(24), 16011.
- ¹⁰ Lang, N. D.; Avouris, P. Electrical conductance of parallel atomic wires. *Physical Review B*, 2000, 62(11), 7325.
- ¹¹ Liu, R. U. I.; Ke, S. H.; Baranger, H. U.; Yang, W. Intermolecular effect in molecular electronics. *The Journal of chemical physics*, 2005, 122(4), 044703.
- ¹² Landau, A.; Kronik, L.; Nitzan, A. Cooperative effects in molecular conduction. *Journal of Computational and Theoretical Nanoscience*, 2008, 5(4), 535-544.
- ¹³ Landau, A.; Nitzan, A.; Kronik, L. Cooperative Effects in Molecular Conduction II: The Semiconductor–Metal Molecular Junction. *J. Phys. Chem. A* 2009, 113, 7451–7460.
- ¹⁴ Reuter, M. G.; Solomon, G. C.; Hansen, T.; Seideman, T.; Ratner, M. A. Understanding and Controlling Crosstalk between Parallel Molecular Wires. *The Journal of Physical Chemistry Letters*, 2011, 2(14), 1667-1671.
- ¹⁵ Reuter, M. G.; Seideman, T.; Ratner, M. A. Molecular conduction through adlayers: Cooperative effects can help or hamper electron transport. *Nano letters*, 2011, 11(11), 4693-4696.
- ¹⁶ Galperin, M.; Nitzan, A. Cooperative Effects in Inelastic Tunneling. *J. Phys. Chem. B* 2013, 117, 4449–4453.
- ¹⁷ Dubi, Y. Transport Through Self-Assembled Monolayer Molecular Junctions: Role of In-Plane Dephasing. *The Journal of Physical Chemistry C*, 2014, DOI: 10.1021/jp503887p
- ¹⁸ Vazquez, H.; Skouta, R.; Schneebeli, S.; Kamenetska, M.; Breslow, R.; Venkataraman, L.; Hybertsen, M. S. Probing the conductance superposition law in single-molecule circuits with parallel paths. *Nature nanotechnology*, 2012, 7(10), 663-667.

-
- ¹⁹ Natan, A.; Kronik, L.; Haick, H.; Tung, R. T. Electrostatic Properties of Ideal and Non-ideal Polar Organic Monolayers: Implications for Electronic Devices. *Advanced Materials*, 2007, 19(23), 4103-4117.
- ²⁰ Heimel, G.; Salzmann, I.; Duhm, S.; Koch, N. Design of Organic Semiconductors from Molecular Electrostatics†. *Chemistry of Materials*, 2010, 23(3), 359-377.
- ²¹ Blumenfeld, M. L.; Steele, M. P.; Monti, O. L. Near-and far-field effects on molecular energy level alignment at an organic/electrode interface. *The Journal of Physical Chemistry Letters* 2009, 1(1), 145-148.
- ²² Heimel, G.; Rissner, F.; Zojer, E. Modeling the Electronic Properties of π -Conjugated Self-Assembled Monolayers. *Advanced Materials*, 2010, 22(23), 2494-2513.
- ²³ Egger, D. A.; Rissner, F.; Zojer, E.; Heimel, G. Polarity Switching of Charge Transport and Thermoelectricity in Self-Assembled Monolayer Devices. *Advanced Materials*, 2012, 24(32), 4403-4407.
- ²⁴ Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D.L.; Tour, J.M.; Weiss, P. S. Are single molecular wires conducting?. *Science*, 1996, 271(5256), 1705-1707.
- ²⁵ Egger, D. A.; Rissner, F.; Rangger, G. M.; Hofmann, O. T.; Wittwer, L.; Heimel, G.; Zojer, E. Self-assembled monolayers of polar molecules on Au (111) surfaces: distributing the dipoles. *Physical Chemistry Chemical Physics*, 2010, 12(17), 4291-4294.
- ²⁶ Deutsch, D.; Natan, A.; Shapira, Y.; Kronik, L. Electrostatic Properties of Adsorbed Polar Molecules: Opposite Behavior of a Single Molecule and a Molecular Monolayer. *J. Am. Chem. Soc.* 2007, 129, 2989–2997.
- ²⁷ Otálvaro, D.; Veening, T.; Brocks, G. Self-Assembled Monolayer Induced Au (111) and Ag (111) Reconstructions: Work Functions and Interface Dipole Formation. *The Journal of Physical Chemistry C*, 2012, 116.14, 7826-7837.
- ²⁸ Diez-Perez, I.; Hihath, J.; Hines, T.; Wang, Z. S.; Zhou, G.; Müllen, K.; Tao, N. Controlling single-molecule conductance through lateral coupling of π orbitals. *Nature nanotechnology*, 2011, 6(4), 226-231.
- ²⁹ Sato, N.; Seki, K.; Inokuchi, H. Polarization Energies of Organic Solids Determined by Ultraviolet Photoelectron Spectroscopy. *J. Chem. Soc. Faraday Trans. 2* 1981, 77, 1621.
- ³⁰ Neaton, J.; Hybertsen, M.; Louie, S. Renormalization of Molecular Electronic Levels at Metal-Molecule Interfaces. *Phys. Rev. Lett.* 2006, 97, 216405.
- ³¹ Refaely-Abramson, S.; Sharifzadeh, S.; Jain, M.; Baer, R.; Neaton, J. B.; Kronik, L. Gap renormalization of molecular crystals from density-functional theory. *Physical Review B*, 2013, 88(8), 081204.
- ³² Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, 1996, 54.16, 11169.
- ³³ Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Physical review letters*, 1996, 77(18), 3865.
- ³⁴ Soler, J. M. ; Artacho, E.; Gale, J. D. ; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. J. *Phys.: Condens. Matter*, 2002, 14, 2745.
- ³⁵ Sancho, M. P. L.; Sancho, J. M.; Sancho, J. M. L.; Rubio, J. Highly convergent schemes for the calculation of bulk and surface greens functions. *J. Phys. F: Met. Phys.* 1985, 15, 851.
- ³⁶ Büttiker, M.; Imry, Y.; Landauer, R.; Pinhas, S. Generalized many-channel conductance formula with application to small rings. *Physical Review B*, 1985, 31(10), 6207.

-
- ³⁷ Xue, Y.; Datta, S.; Ratner, M. A. First-principles based matrix Green's function approach to molecular electronic devices: general formalism. *Chemical Physics*, 2002, 281(2), 151-170.
- ³⁸ Darancet, P.; Widawsky, J. R.; Choi, H. J.; Venkataraman, L.; Neaton, J. B. Quantitative Current–Voltage Characteristics in Molecular Junctions from First Principles. *Nano letters*, 2012, 12(12), 6250-6254.
- ³⁹ Stukowski, A.; *Modelling Simul. Mater. Sci. Eng.*, 2010, 18, 015012.
- ⁴⁰ Kokalj, A. XCrySDen—a New Program for Displaying Crystalline Structures and Electron Densities. *J. Mol. Graph. Model.* 1999, 17, 176–179.
- ⁴¹ Ramachandran, P. and Varoquaux, G., *IEEE Computing in Science & Engineering*, 2011, 13 (2), 40-51.
- ⁴² Paulsson, M.; Datta, S. Thermoelectric effect in molecular electronics. *Physical Review B*, 2003 67.24, 241403.
- ⁴³ Reddy, P.; Jang, S. Y.; Segalman, R. A.; Majumdar, A. Thermoelectricity in molecular junctions. *Science*, 2007, 315, 1568-1571.
- ⁴⁴ Widawsky, J. R.; Darancet, P.; Neaton, J. B.; Venkataraman, L. Simultaneous determination of conductance and thermopower of single molecule junctions. *Nano letters*, 2011, 12(1), 354-358.
- ⁴⁵ Romaner, L.; Heimel, G.; Zojer, E. Electronic structure of thiol-bonded self-assembled monolayers: Impact of coverage. *Physical Review B*, 2008, 77, 045113.
- ⁴⁶ Natan, A.; Zidon, Y.; Shapira, Y.; Kronik, L. Cooperative Effects and Dipole Formation at Semiconductor and Self-Assembled-Monolayer Interfaces. *Phys. Rev. B* 2006, 73, 193310.
- ⁴⁷ Cornil, D.; Olivier, Y.; Geskin, V.; Cornil, J. Depolarization Effects in Self-Assembled Monolayers: A Quantum-Chemical Insight. *Adv. Funct. Mater.* 2007, 17, 1143.
- ⁴⁸ Monti, O. L. A. Understanding Interfacial Electronic Structure and Charge Transfer: An Electrostatic Perspective. *J. Phys. Chem. Lett.* 2012, 3, 2342–2351.