

Chemical Modulation of Charge Transport Perpendicular to the Molecular Plane

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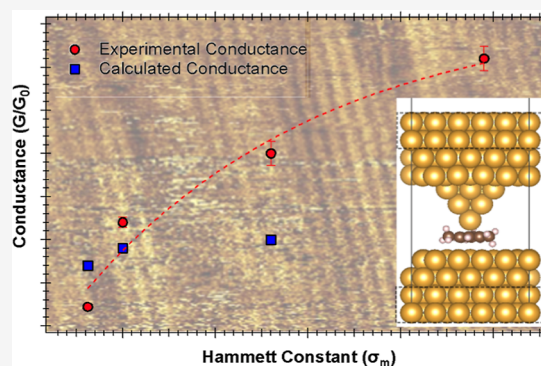
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ABSTRACT: The electronic structure of molecules can have a considerable effect on charge transport through molecular junctions. However, this is known only where molecular anchoring groups define the transport direction to be along the molecular plane. It is not clear how different chemical substituents can affect conductance perpendicular to the molecular plane. In this study, the conductance measurement perpendicular to the plane of mesitylene substituted with electron-withdrawing groups (e.g., NO₂, Br) and electron-donating groups (e.g., CH₃) showed that the conductance increases by introducing electron-withdrawing groups and decreases as electron-donating groups are added to the mesitylene molecule. These results are supported by density functional theory and nonequilibrium Green's function calculations. We demonstrated that the changes in the conductance perpendicular to the molecular plane correlate well with the Hammett constant of the corresponding functional groups, indicating the importance of the nature and strength of chemical substituents on the degree of conductance modulations, at least for mesitylene derivatives. The generalization of the Hammett parameters to the perpendicular charge transport through single molecules could serve as a predictive framework, motivating the design and fabrication of molecular devices with desired functionalities.



INTRODUCTION

Moving toward the practical utilization of single molecules and atoms as stable structures in miniaturized electric circuits requires a deep understanding of charge transport phenomena at the nanoscale. Over the past two decades, experimental and theoretical studies have shown that the overall charge transport mechanism through single-molecule junctions is a complex and cumulative function of properties of the molecular core,^{1–3} and the electrodes,^{4–6} as well as molecule-electrode coupling,^{7–13} the conformation and geometry of molecules in the junction,^{14–17} in addition to the junction's local environment.^{18–20} It is known that chemical substitution groups can modulate the electronic properties of molecules^{21–23} and induce changes in charge transport behavior, typically by altering the alignment of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with the Fermi level of the electrodes.^{24–28} Therefore, the application of substitution groups can be a feasible strategy to design molecules with tunable electrical charge transport properties.

While the significance of the chemistry of the molecular backbone in determining single-molecule conductance mechanism is well-recognized, only a handful of reports in the literature have addressed the effect of chemical substitution groups on charge transport through single molecules. For example, Venkataraman et al. showed that in small benzene derivatives, e.g., amine-terminated 1,4-diaminobenzene, the

HOMO energy increases (moves toward the Fermi level of the electrode) as H atoms are replaced with methoxy groups, due to the induced delocalization of the π -system of the benzene ring by the lone pairs of the oxygen atoms.²⁵ On the other hand, replacing H with electronegative Cl atoms removes electron density from the σ -system of the benzene, and lowers the HOMO energy level. Therefore, in a HOMO-mediated charge transport mechanism, the conductance of substituted molecules can be enhanced or reduced using electron-donating or electron-withdrawing groups, respectively.²⁵

The effect of substitution groups on the electronic structure and the dissociation reaction constant of benzoic acid relative to the substituted species was quantified for the first time by Hammett.²⁹ The observed shifts in the conductance of substituted benzene derivatives are correlated with the change in ionization potentials and the Hammett constant²⁹ (strength of electron-donating and withdrawing groups for meta and para substituents). In one of the first applications to single molecule electrical properties, Li et al. showed that the

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conductance of substituted oligo phenylene ethynylene decreases as the corresponding Hammett constant moves toward higher values (stronger electron withdrawing effect).²⁴ The same trend was observed for disubstituted diaminobenzene,²⁵ and benzene dithiol-based thermoelectric devices,³⁰ where the hole transport-mediated conductance was increased by electron-donating groups, while electron-withdrawing groups lowered the conductance. Later, Yu et al. showed that a pyridine moiety connected perpendicular to a backbone pentaphenylene molecule can be functionalized with different chemical groups, and act as a gate (simulating gating voltage).³¹ These results demonstrated that, by changing the substitution groups in the para position of pyridine from electron acceptors to electron donors, the molecular orbital energy levels, and the tunneling barrier are tuned.³¹ The observed change in the conductance correlated with the Hammett parameters of the functional groups.³¹ In a theoretical study, DiLabio et al. demonstrated that the changes in the zero-bias transmission function of disubstituted benzene dithiol in a junction are consistent with the strength of electron donating and withdrawing groups, i.e., the Hammett parameter.³² Therefore, it is well established that different chemical functional groups can regulate charge transport through single-molecule junctions in a manner that is correlated with their Hammett parameter. However, this is known only for cases where molecular anchoring groups define the transport direction to be along the molecular plane. Interestingly, our previous experimental and theoretical studies showed that the fluorination of molecules does not affect the charge transport perpendicular to the molecular plane.^{9,33} To the best of our knowledge, there is no systematic study on whether the changes induced by chemical substitutions depend on the charge transport measurement axis, e.g., perpendicular vs parallel, nor on the correlation of these effects with Hammett parameter.

Recently, we showed that the orientation of molecules in the junction can be controlled through the stabilization provided by the formation of long-range ordered networks of molecules on the electrified substrate,^{9,15,33} or under open circuit potential conditions.³⁴ This strategy enabled us to measure charge transport perpendicular to the molecular plane, where the molecular orientation is stabilized through the interaction between the metal substrate and the π -system of the benzene derivatives. In this study, we build on our previous investigation of charge transport through single mesitylene molecules and explore how chemical substitution groups affect charge transport through junctions formed without the involvement of anchoring groups. Using the scanning tunneling microscope-break junction method (STM-BJ), we fabricated single-molecule junctions of trinitromesitylene (TNM), tribromomesitylene (TBM), and hexamethylbenzene (HMB) to determine the effect of electron-withdrawing ($-\text{Br}$ and $-\text{NO}_2$) and donating groups ($-\text{CH}_3$) on charge transport perpendicular to the mesitylene plane (Figure 1). The results provide a predictive framework for fabricating practical molecular electronic devices with desired conductivity and functionalities.

RESULTS AND DISCUSSION

STM of Target Molecules on Au(111) in 0.05 M H₂SO₄. STM imaging of the surface covered with the molecules of interest before the charge transport measurements is advantageous, as it can provide information about the orientation of

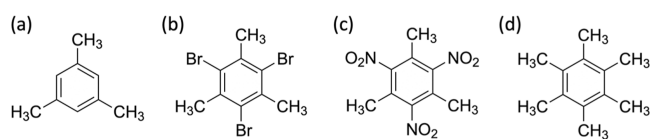


Figure 1. Molecular targets to probe the effect of chemical substituents on charge transport: (a) mesitylene, (b) tribromomesitylene (TBM), (c) trinitromesitylene (TNM), (d) hexamethylbenzene (HMB). From this perspective, the surface of the electrode is parallel to the page (and the molecule), while electron transport occurs perpendicular to the surface, which is out of the page.

molecules on the surface. Our previous study showed that mesitylene molecules form a long-range order structure on the Au(111) surface under open-circuit potential conditions, presumably as a result of strong molecule–substrate interactions.³⁴ Wan et al. reported that trinitrotoluene molecules adsorb on the Au(111) with the benzene ring parallel to the surface at electrode potentials below the zero charge potential of Au(111) ($0.3 V_{\text{SCE}}$).³⁵ In this study, TNM and TBM did not form any ordered structure on the Au(111) without electrode potential control.

As established previously, applying an external voltage to the electrodes can modulate the molecule–electrode interactions, leading to changes in the orientation of molecules.^{36–39} We took advantage of the electrochemical-STM and applied external potentials to the electrodes to control the orientation of molecules. For the first time, STM images of TNM and TBM in 0.05 M H₂SO₄ showed the formation of ordered molecular networks on the negatively charged Au(111) surface ($V_s = 0 V_{\text{SCE}}$ for TNM and $V_s = 250 \text{ mV}_{\text{SCE}}$ for TBM) (Figure 2). The cross-section analysis of STM images (Figure 2b,d,

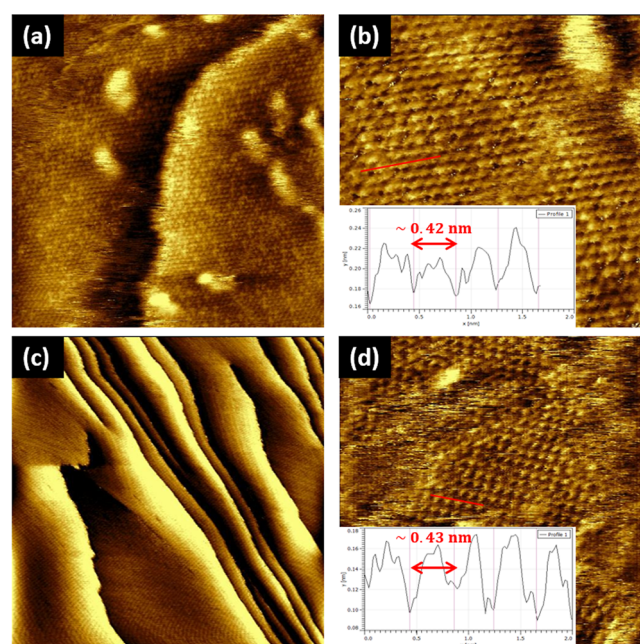


Figure 2. STM images of saturated solutions of trinitromesitylene (TNM) and tribromomesitylene (TBM) in 0.05 M H₂SO₄: TNM, $V_s = 0 V_{\text{SCE}}$ imaged over (a) $25 \times 25 \text{ nm}^2$, (b) $10 \times 10 \text{ nm}^2$. TBM, $V_s = 250 \text{ mV}_{\text{SCE}}$ imaged over (c) $200 \times 200 \text{ nm}^2$, (d) $15 \times 15 \text{ nm}^2$, insets: cross section analysis of STM images, size of feature consistent with molecular dimensions. All images are acquired at $I_t = 0.1 \text{ nA}$ and $V_{\text{tip}} = 50 \text{ mV}_{\text{SCE}}$.

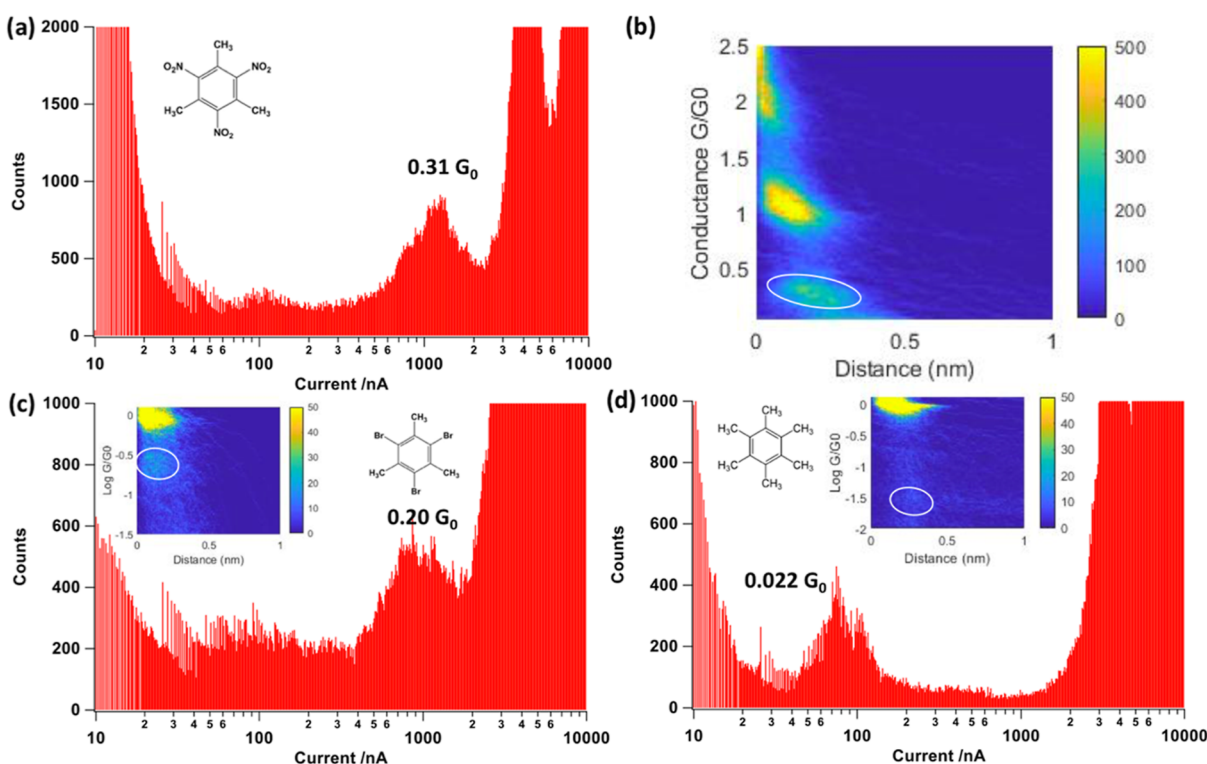


Figure 3. Single molecule conductance of benzene derivatives in 0.05 M H_2SO_4 : (a) trinitromesitylene (TNM), $V_s = -50 \text{ mV}_{\text{SCE}}$, $V_b = 50 \text{ mV}$, 2790 curves, (b) 2D histogram of TNM, circled area shows conductance at $0.31 G_0$. (c) Tribromomesitylene (TBM), $V_s = 150 \text{ mV}_{\text{SCE}}$, $V_b = 50 \text{ mV}$, 3079 curves, (d) hexamethylbenzene (HMB), no potential control, $V_b = 45 \text{ mV}$, 2753 curves. Insets in (c,d) are 2D histograms, length of the junction consistent with the flat oriented molecules.

insets) showed features ($\sim 0.4 \text{ nm}$ wide) consistent with planar benzene molecules,^{35,40} demonstrating that TNM and TBM molecules are oriented parallel to the surface of Au(111). Therefore, the electrode potential can be used to control the orientation of molecules in the junction regardless of the presence or lack of anchoring groups (TNM and TBM, respectively).

The lifting of the herringbone reconstruction of Au(111) often indicates molecule–substrate interactions.⁴¹ The STM image of TNM showed no underlying reconstruction pattern (Figure 2a) while it is preserved under the TBM molecular network (Figure 2c). This suggests stronger interactions between TNM molecules and Au(111) compared to TBM.⁴² The stronger interaction of TNM with the Au(111) electrode could stem from stronger impact of the $-\text{NO}_2$ functional group through sigma and pi bonds on the central benzene ring,^{43,44} resulting in stronger interaction between TNM molecules and the Au(111) surface. In addition, the STM images as a function of the electrode potential showed that the order to disorder transition is a reversible process for TNM and TBM, indicating that the electrode potential can be used to control the orientation of small molecules on the surface (Figures S1 and S2). The STM imaging of HMB on Au(111) under potential control was not successful due to the high noise level. Also, the imaging under open circuit potential conditions did not show any detectable ordered self-assembly, and the orientation of molecules cannot be determined from the images. According to the above results, we postulated that the attractive intermolecular interactions including weak hydrogen bonding between CH_3 and NO_2 groups in TNM^{43,46} and halogen–halogen interactions^{47,48} in TBM play critical roles in the formation of ordered structures.

However, the lack of strong intermolecular interactions between methyl groups in HMB prevents the development of the molecular network. It is worth mentioning that while we cannot entirely exclude the possibility of molecular interactions with H^+ , the combined effect of electrode potential control, reversible transitions, and the strong correlation between experimental and theoretical results provides confidence that the primary factors influencing the state of the molecules are the applied potentials and the intrinsic electronic properties of the substituents under the conditions of these experiments.

Single Molecule Conductance of TNM, TBM and HMB on Au(111) in 0.05 M H_2SO_4 . Following the STM imaging, we performed single-molecule conductance measurements of TNM and TBM at the electrode potentials where the molecules adsorbed on Au(111) with the central ring parallel to the surface [below the zero charge potential of bare Au(111)]. The current histograms generated using ~ 2500 current–distance traces collected on the negatively charged Au(111) showed conductance peaks at $\sim G_0$ (assigned to the quantum of conductance) and $0.31 G_0$ and $0.20 G_0$ for TNM and TBM, respectively (Figure 3a,b). The conductance measurements for HMB with no electrode potential control showed a peak at $0.022 G_0$, almost ten times smaller than the values observed for TNM and TBM (Figure 3c).

Previous studies have shown that when there are no anchoring groups, a single molecule junction can be formed through the interaction of the π -system of the benzene ring with the metal electrodes, and the charge transport can be measured perpendicular to the molecular plane.^{49–53} For example, mesitylene, which has no appropriate anchoring groups, showed a conductance of $0.13 G_0$, assigned to the flat oriented molecule in the junction.³⁴ Our past research

extensively illustrated the propensity of these benzene derivatives to align horizontally on the electrode surfaces within well-defined, long-range structures, a behavior attributed to the interplay between π -stacking interactions and surface-molecule interactions that promote this orientation. Accordingly, as HMB and TBM do not have suitable anchoring groups to form a junction along the molecular plane, the observed conductance peak likely arises from a charge transport pathway perpendicular to the benzene ring. In addition, we need to point out that any ohmic contact between the STM tip and surface implies one or more bridging atoms. Yet the fact that the multiple G_0 peaks are typically much smaller suggests that multiple atom/junction contacts are rare. The lack of damage in the postjunction formation STM images in our original mesitylene paper³⁴ are consistent with a soft-landing experiment.

The conductance values observed for TNM and TBM are consistent with the relatively high values identified for other flat-oriented benzene derivatives in the literature.^{9,15,33,34,49,51–53} In the case of TNM, it is possible for nitro groups to bind to the surface and form a junction along the molecular plane. However, according to the previous studies and the STM images obtained in this study (Figure 2b), benzene derivatives tend to lie flat on negatively charged electrodes.^{15,33,36} Therefore, we concluded that the conductance peak observed for TNM stems from the charge transport measurement perpendicular to the molecule's π -system.

Previous experimental and theoretical studies showed that the conductance of flat-oriented mesitylene is around 0.13 G_0 .^{34,54,55} The findings of this study suggest that bromine and nitro substitution of mesitylene increases the conductance to 0.20 G_0 and 0.31 G_0 , respectively. However, for HMB the conductance value decreases to 0.022 G_0 , five times smaller than for mesitylene. Therefore, it is evident that the charge transport perpendicular to the π -system of mesitylene depends on the nature of functional groups attached to the benzene. It is worth mentioning that a small peak was observed around 100 nA for TNM and TBM. This peak may indeed indicate the formation of a single molecule junction via the anchoring group. Such occurrences are not uncommon in molecular electronics, where the creation of such junctions with weak anchoring groups can be transient and less enduring compared to alternative conduction pathways. While we acknowledge that the anchoring group may offer a secondary conduction route, albeit less stable for these molecules, it may account for the observed peak. Nonetheless, the primary and most enduring conduction mechanism stems from the π structure of the benzene ring. This assertion is supported by the more pronounced conductance peaks and the stability of these junctions, indicating that the charge transport is predominantly facilitated by the π -electron system of the benzene ring. This pathway benefits from delocalized electrons that enable effective overlap and electron transfer between the molecule and the electrodes.

As we mentioned in the previous section, we were not able to detect any ordered layer structure for HMB. However, this does not necessarily mean that flat orientation is impossible. The lack of long-range stable ordered layers might result from weaker interactions, leading to less stable and less probable junction formation under the experimental conditions used. In addition, the conductance measurements for HMB showed a significant decrease compared to TNM and TBM. This

observation aligns with the hypothesis that electron-donating groups like CH_3 raise the LUMO level, resulting in lower conductance, consistent with theoretical predictions.

Now, the question is how do different functional groups influence the charge transport perpendicular to the molecular plane? The change in the conductance of TNM, TBM, and HMB relative to mesitylene could stem from modulations of the physical and electronic properties induced by the addition of electron-donating/withdrawing groups. Our experimental and theoretical studies showed that tunneling perpendicular to the π -system of benzene rings is mediated through LUMO orbitals (closest orbital to the Fermi level of the gold electrode).^{9,33} This is also supported in this work from theoretical analysis of the transport mechanism (*vide infra*). It is known that electron-donating groups raise the energy of LUMO orbitals, and electron-withdrawing groups have the opposite effects.⁵⁶ Therefore, we can hypothesize that upon the addition of methyl groups to mesitylene (in HMB), the LUMO orbital moves away from the Fermi level, resulting in a lower conductance of HMB. However, upon the addition of bromine and nitro groups, the energy of LUMO decreases and moves closer to the Fermi level of the gold electrode, leading to the increased conductivity in TNM and TBM relative to mesitylene.

Interestingly, our previous experiments combined with the theoretical calculations showed that the conductance perpendicular to the plane of flat oriented terephthalic acid (TPA) and tetracyanoquinodimethanefluorination (TCNQ) did not change upon addition of fluorine atoms.^{9,33} This is somewhat surprising as it is well-established that charge transport along the molecular plane (when molecules are linked to the electrodes via anchoring groups) can be modulated using chemical substitution.^{24,25,30–32} One possible explanation is that the varying interactions between molecules within the monolayer influence energy alignment, given that TCNQ exhibits intermolecular hydrogen bonding while F_4TCNQ does not. Additionally, differential interactions with the solvent could further impact the energy alignment, as one molecule might interact more readily with the solvent than the other. However, the nonequilibrium Green's function (NEGF)-density functional theory (DFT)-based calculation results predicted that the conductance parallel to the molecular plane of TPA is ~ 2 times higher than its fluorinated analogue.³³ It is established that molecules interact differently with electrodes when they form a junction via anchoring groups compared to the case where there is no anchoring group involved (i.e., metal- π interactions vs chemical bonding).^{15,56} Also, different orientations of molecules in the junction could lead to different electronic structures and molecular orbital alignment relative to the Fermi level of electrodes.^{9,15} Therefore, first, we hypothesized that the effect of chemical substitutions on the electronic properties and the conductance of molecules in the junction could depend on the axis along which the charge transport is being measured (parallel vs perpendicular to the molecular plane). In the current study, we observed noticeable variations in the conductance perpendicular to the central ring of trisubstituted molecules relative to the mesitylene conductance. So, it appears that for TNM, TBM and HMB, as opposed to TPA and TCNQ, the chemical substitution can affect the perpendicular charge transport in a similar manner as it affects parallel charge transport. The magnitude of the conductance change could arise from the strength and reactivity of corresponding functional groups.²⁹

Following prior analysis of chemical substitution, we investigated the correlation of the Hammett parameter with the induced changes by different substituent groups in charge transport perpendicular to single molecules. The conductance of mesitylene, TNM, TBM, and HMB perpendicular to the π -system of benzene derivatives increases as the Hammett parameter moves to more positive values (Figure 4). This

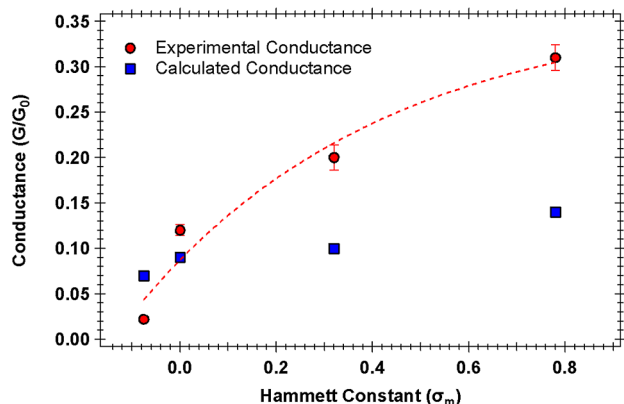


Figure 4. Experimental (red) and calculated (blue) single molecule conductance of trinitromesitylene (TNM), mesitylene, tribromomesitylene (TBM), and hexamethylbenzene (HMB) as a function of Hammett constant of the functional groups. The error bars are the standard deviations for conductance values measured in different experiments. The dotted line is a guide to the eye. The Hammett constants are adopted from ref 57.

trend is consistent with the expected LUMO-mediated tunneling described above. Accordingly, as the nitro groups pull electrons from the π -system of the ring,⁴⁴ we expect a decrease in the LUMO energy level which results in almost two times higher conductance value relative to the unsubstituted mesitylene ($0.31 \pm 0.01 G_0$). The smaller change in the conductance of TBM compared to mesitylene ($0.20 \pm 0.01 G_0$) is consistent with the weaker electron-withdrawing nature of bromine atoms. On the other hand, the

energy of the LUMO in the HMB is increased due the additional electron donating groups, resulting in a decrease in conductance compared to mesitylene ($0.02 G_0$). Overall, we can conclude that chemical substitution groups affect charge transport perpendicular to the molecular plane in the same way as they affect transport along the molecular axis. These experimental results are further supported by DFT-calculations.

CALCULATIONS

NEGF-DFT^{58,59} based calculations were employed to investigate the low bias conductance of mesitylene, TNM, TBM, and HMB. For our model, we used a flat Au surface and an atomically sharp tip as the other electrode, with a molecule bridging the two as shown in Figure 5a, to simulate the experimental arrangement consistent with an STM soft-landing approach. We note that the simulations used a single adsorbed molecule instead of a monolayer for computational efficiency, though we expect intermolecular interactions to play a minor role in the single molecule conductance properties. Structures are optimized with DFT at different electrode separations to determine the optimal distance. The right electrode in Figure 5a starts far from the molecule on the surface and is moved closer at 0.1 Å increments. The Au tip is initially centered on the benzene ring, but as the electrode is moved closer, the mesitylene molecule shifts such that the Au tip is located above a carbon atom, suggesting that the Au–C alignment is the preferred geometry (see Figure 5b).

The same approach is used for each mesitylene derivative and their transmission functions are plotted in Figure 5c,d. The large peaks ($\sim >1$ au) above the Fermi energy (0 eV) are a mix of LUMO and LUMO+1 channels, while features beginning at ~ -2 eV are HOMO and HOMO–1 channels. The exception to this is TNM, whose LUMO peak is located between zero and 1 eV. For a more detailed analysis of the transmission peaks and their associate molecular orbitals see the Supporting Information (Figures S3–S6).

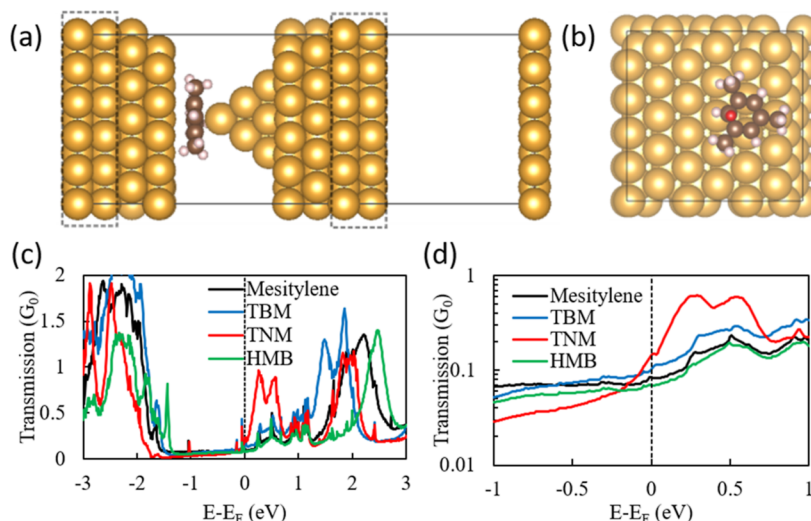


Figure 5. Simulation cell and calculated transmission functions of benzene derivatives. Mesitylene optimized geometry in the junction, (visualized with VESTA⁶⁰), (a) side view: black dotted lines enclose atoms which are fixed during geometry optimization, (b) top view: the small red circle is the Au-tip and was changed for clarity of the tip-mesitylene alignment. Wide energy range (c) and zoomed-in (d) transmission functions of mesitylene and substituted mesitylene molecules.

The calculated conductance values are consistent with experimental conductance measurements of mesitylene, TNM, TBM, and HMB (Table 1). The calculated conductance values increase as the respective Hammett constants increase, confirming the effect of different substitution groups observed in the experiment.

Table 1. Summary Experimental and Calculated Conductance of Mesitylene and Tri-substituted Derivatives

molecules	Hammett constant ⁵⁷	conductance (experiment/ G_0)	conductance (theory/ G_0)
HMB	−0.07	0.02	0.07
mesitylene	0	0.13	0.09
TBM	0.32	0.20	0.10
TNM	0.71	0.31	0.14

Upon analysis of the transmission spectra, one can see that the shifting in energy of the LUMO peak correlates well with the Hammett parameters. The order of the transmission height near the Fermi level (0 eV) is also in agreement with the experiment, at least qualitatively. We note that, even though computed conductance is often larger than the experimental value due to the underestimation of the HOMO–LUMO gap in DFT, other factors also play a role, such as the exact position of the tip over the molecule, the electrode–molecule distance, and Fermi level position relative to the frontier molecular orbitals. Better *quantitative* agreement may also be achieved were it not for the wide feature near 0.5 eV (Figure 5d) that remains at the same energy, in all but TNM, despite the shift of the LUMO feature. The source of this feature is not investigated here since it is thought to have less influence on the measured relative conductance than the energy position of the LUMO/LUMO+1 orbitals. In Figure 5d, a built-in broadening functionality^{59,61} is used to smooth out smaller features ($\eta = 0.01$) to get a clean, representative trend of the conductance in the vicinity of E_F , which is in agreement with the experimental results.

CONCLUSIONS

We investigated the effect of chemical substituent groups on charge transport perpendicular to the π -system of mesitylene to address whether the impact is the same as for charge transport along the molecular plane. Initially, we hypothesized that the different orientation and nature of interactions in the absence of anchoring groups might lead to distinct conductance modulation behaviors. However, our experimental results, along with theoretical calculations, showed that the perpendicular conductance of the parent molecule (mesitylene) increases upon the addition of electron-withdrawing groups (Br and NO_2), and decreases in hexamethyl benzene, where electron-donating groups (CH_3) are introduced. These results are consistent with the established trends observed in parallel charge transport through single molecule junctions.

The observed consistency reinforces the idea that the modulation of conductance by chemical substituents, whether in perpendicular or parallel transport, fundamentally relies on the change in energy of the conducting orbital (LUMO in this case). This conclusion highlights the robustness of the electronic effects of substituents on molecular conductance and suggests that the principles governing conductance modulation are broadly applicable across different transport geometries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c02372>.

Solution and materials (chemicals, STM cell preparation), electrochemical STM imaging, in situ-STM-BJ, ab initio calculations (DFT method, NEGF-DFT method, scattering states, transmission functions at different broadening) (PDF)

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Notes

The authors declare no competing financial interest.

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