

# Modulation of Charge Transport through Single Molecules Induced by Solvent-Stabilized Intramolecular Charge Transfer

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**ABSTRACT:** The modulation of charge transport through single molecules can be established by using the intrinsic characteristics of molecules and the physical properties of their environment. Therefore, the impact of the solvent on the electronic properties of molecules in the junction and their charge transport behavior are of great interest. Here, for the first time, we focused on charge transport through dimethylaminobenzonitrile (DMABN). This molecule shows unique behavior, specifically noticeable electronic structure modulations in bulk solvents, e.g., dual fluorescence in a polar environment. Using the scanning tunneling microscopy break junction (STM-BJ) technique, we find an order of magnitude increase in conductance along with a second conductance value in polar solvents over nonpolar solvents. Inspired by the twisted intramolecular charge transfer (TICT) explanation of the famous dual fluorescence of DMABN in polar solvents, we hypothesize stabilization of



twisted DMABN molecules in the junction in more polar solvents. Ab initio molecular dynamics (AIMD) simulations using density functional theory (DFT) show that DMABN can twist in the junction and have a larger dipole moment compared to planar DMABN junction geometries, supporting the hypothesis. The nonequilibrium Green's function with the DFT approach (NEGF-DFT) is used to calculate the conductance throughout the AIMD trajectory, finding a significant change in the frontier orbitals and transmission function at large internal twisting angles, which can explain the dual conductance in polar solvents in STM-BJ experiments.

# INTRODUCTION

The charge transport characteristics of molecular electronic components depend on the intrinsic properties of the constituent molecules, electrodes, and the environment. Control and modulation of the electronic properties of single molecules and the consequent charge transport using external physical and chemical parameters, e.g., light,<sup>1,2</sup> gate voltage,<sup>3-</sup> mechanical force,<sup>7,8</sup> molecule–electrode binding geome-try,<sup>9–12</sup> chemical reaction,<sup>13,14</sup> environmental pH,<sup>3,15</sup> have been extensively studied, leading to the emergence of a wide range of functionalities and applications. In addition, other extrinsic factors in the molecular junction architecture can impact the conductance. Many charge transport measurements are performed in a solvent environment, where the conducting molecules and electrodes directly interact with the solvent molecules. Despite the critical role of solvent molecules and their interaction with the molecular junction and electrodes, the impact of solvent on charge transport through single molecules has been addressed in only a few studies. On the other hand, due to the complexity and computational cost, the solvent effect on the conductance of single molecules has been overlooked in most theoretical studies, and the charge transport simulations are mainly performed in a vacuum, even though the solvent is an integral part of many experiments.

In a systematic study by Luka-Guth and Scheer et al., the electrical conductance of a series of typical pure solvents, e.g., mesitylene, 1,2,4-trichlorobenzene, toluene, ethanol, and the mixture of tetrahydrofuran (THF) and toluene or isopropanol, commonly used in single-molecule charge transport measurements, was investigated.<sup>16</sup> Interestingly, their results demonstrated that some of those molecules can form a junction and are therefore not suitable as solvents for single-molecule conductance measurements. The analysis of the I-V curves and modeling showed that mesitylene, toluene, and the mixture of toluene/THF are suitable for single-molecule conductance measurements as the majority of I-V curves did not fit well with tunneling models, and their charge transport characteristics can be distinguished from the functional molecule of interest.<sup>16</sup> In 2011, Fatemi et al. measured the conductance of benzenediamine (BDA) in 13 different solvents, revealing that the binding of solvent

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Figure 1. Structures of (a) planar dimethylaminobenzonitrile (DMABN), (b) twisted dimethylaminobenzonitrile (DMABN), and (c) tetramethylparaphenyldiamine (TMPD).

molecules to the gold electrode alters the probability of molecular junction formation as well as the work function of the gold electrodes.<sup>17</sup> Likewise, Kotiuga and Neaton et al. reported that the transport properties of the bipyridine junction can be modulated through the local potential induced by solvent molecules on the electrode surface.<sup>18</sup> The calculation results predicted that the highest occupied molecular orbital (HOMO)- and lowest unoccupied molecular orbital (LUMO)-mediated molecular junctions showed opposite responses to the solvent. Therefore, employing different solvents can be a feasible strategy to distinguish the charge transport mechanism.<sup>18</sup>

Milan et al. showed that the conductance of oligoyne-based molecular wires strongly depends on the solvent medium.<sup>19</sup> In mesitylene, the conductance of the whole series (n = 2-5) was the lowest, having the highest decay constant. However, 1,2,4-trichlorobenzene and propylene carbonate resulted in higher oligoyne-based molecular wire conductance values, with a lower length decay constant.<sup>19</sup> Tang et al. explored the solvent gating effect (up to 800%) on the conductance measurement of a series of oligophenylethynylene-sulfurmethyl (OPE-SMe) and its derivatives with different anchoring groups.<sup>20</sup> The efficiency of solvent-induced gating depends on the choice of anchoring groups and the resulting molecule–solvent interactions. Their findings were supported by density functional theory (DFT) calculations, showing a shift in relative energy alignment of molecular orbitals given the coupling strength of the anchoring group and electrodes.<sup>20</sup>

These experimental observations combined with theoretical calculations suggest that solvent-molecule and solventelectrode interactions are the main factors influencing the conductance of single molecules. However, there appears to be no study that distinguishes these effects and investigates the electronic and conformational changes within a molecule in the junction induced by the molecule-solvent interactions. Particularly, no single-molecule charge transport study has exploited the twisted intramolecular charge transfer (TICT) effect and its associated noticeable bulk electronic modulations as a function of the environment. Therefore, it is important to understand how and to what extent the modulation of the bulk electronic structure, e.g., TICT, affects the charge transport at the single-molecule level. The key contribution of this study is to comprehensively examine how the TICT effect, which affects the bulk electronic structure, influences charge transport at the single-molecule level. Detailed theoretical calculations in this study offer fresh insights into the intricate relationship between TICT properties and conductance behavior in DMABN molecules and also introduce the concept of accessing a second conductance state in polar solvents.

TICT Effect: Bulk Solvent Modulation of the Electronic Properties of Molecules. Herein, we focused on dimethylaminobenzonitrile (DMABN) (Figure 1a), which belongs to the specific class of donor (dimethylamine)—acceptor (nitrile) molecules. The bulk electronic properties of these molecules significantly depend on the solvent polarity

and viscosity.<sup>21-25</sup> The unique behavior of DMABN in different solvents can be explained by the well-studied and accepted mechanism of twisted intramolecular charge transfer (TICT).<sup>26</sup> According to the TICT model, excitation from the ground state to the excited state leads to an initially promoted locally excited state (LE), where the molecule is planar. Another excited state is accessible by internal motion, where the dimethylamino group twists  $90^{\circ}$  relative to the phenyl ring (Figure 1b), accompanied by an intramolecular charge transfer (CT) from the donor to the acceptor. The CT state is more polar than the LE state and can be stabilized through interactions with a polar solvent. This behavior is evident in the fluorescence spectra of DMABN in polar solvents, showing two bands. The first fluorescence band arises from the emission through the less polar LE state, and the emergence of the second longer wavelength band is due to the stabilized CT state.

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We hypothesized that because the electronic structure of DMABN is affected by its local environment (solvent polarity), the induced changes would impact the DMABN electrical conductance. We need to emphasize that although the original TICT theory involves an electron/hole photoexcitation process, in this study, no electron excitation occurs during the electrical conductance measurement. According to previous studies, the change in electronic properties of small molecules, e.g., excitation, electron loss/addition, and charge transfer, can cause a similar change in the structure and the consequent electronic properties of the molecules.<sup>27</sup> This behavior comes from the fact that the same orbital is usually occupied regardless of the mode of excitation (electrons/holes move from one electrode to another through molecular orbitals, typically HOMO or LUMO). Therefore, the excitation can be compared and contrasted with the changes induced by charge gain and loss (electron transport from one electrode through the molecule in the ground state to another).

Our single-molecule conductance measurements of DMABN in different solvents show that the conductance of DMABN (the dominant peak) in acidified water and dimethylformamide (polar solvents) is ten times higher than the conductance in toluene and trichlorobenzene (nonpolar solvents). In contrast, the single-molecule conductance of tetramethylphenylenediamine (TMPD; no TICT effect) in polar and nonpolar solvents exhibited no polarity-dependent conductivity, suggesting that the TICT state (or twisted geometry) is the main reason for the enhanced conductance of DMABN. Ab initio molecular dynamics (AIMD) calculations show that DMABN can twist to large internal angles in the junction. The transmission function is calculated using the nonequilibrium Green's functions with density functional theory method (NEGF-DFT) and shows a drastic change in the transmission function compared to the planar molecule. Therefore, molecules that exhibit the TICT effect can be considered as promising candidates to design molecular devices with switching and sensing functionality.

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**Figure 2.** Bulk electronic properties dimethylaminobenzonitrile (DMABN) in different solvents: (a) UV–vis spectra of 10  $\mu$ M DMABN in water (blue) and toluene (red) and (b) fluorescence of 10  $\mu$ M DMABN in toluene (red) and water (blue) showing single and dual fluorescence emission, respectively. Excitation was at 290 nm. The observed peaks at 580 nm in both water and toluene spectra (as indicated by arrows) are due to second-order diffraction of the excitation photons (290 nm). The peak at 325 nm is the Raman scattering of water molecules.



**Figure 3.** Single-molecule conductance of dimethylaminobenzonitrile (DMABN) in different solvents: (a) Current histogram for (DMABN) at  $V_{\text{bias}}$ = 0.05 V recorded in acidified water generated from 4687 curves, (b) two-dimensional (2D) conductance histogram of curves recorded in water, showing three conductance regions, (c) current histogram for DMABN at  $V_{\text{bias}}$ = 0.05 V recorded in toluene generated from 6126 curves, and (d) 2D conductance histogram of curves recorded in toluene, showing a single conductance region. The high-intensity regions observed at log( $G/G_0$ ) = -4.5, present in both histograms, are background noise due to the preamplifier. The lower count for the DMABN conductance peak in water compared to toluene could be a result of the lower number of curves recorded in water than the curves recorded in toluene.

### EXPERIMENTAL RESULTS AND DISCUSSION

**Bulk Electronic Properties Investigation by Fluorescence Spectroscopy.** It is known that the electronic structure of molecules showing the TICT effect depends on the properties of the bulk solvents. Previous studies have investigated the electronic spectra of DMABN and showed that the absorption peak shifts by as much as 10 nm due to the changes in the solvent polarity.<sup>23,28</sup> To illustrate the electronic structure changes in DMABN induced by bulk solvents, we measured the UV–vis absorption of DMABN in polar and nonpolar solvents (water and toluene, respectively), confirming that the absorption band red shifts as the polarity of the solvent increases (Figure 2a), which is indicative of electronic structure modulation due to the interaction of the solvent with the target molecules. The electron transfer from the ground state (HOMO) to the excited state (LUMO) upon photoexcitation results in a polar biradical state.<sup>21,27</sup> We concluded that the polar solvents stabilize the CT state more than the LE state, resulting in a decreased gap between the excited state and the ground state.

The dual fluorescence of DMABN in polar solvents and the emergence of two excited states are best explained by the TICT model and have been previously investigated. Hubisz et al. and Redi-Abshiro et al. showed that, except for the polar solvent cyclohexane, DMABN in dioxane, tetrahydrofuran, chloroform, dichloromethane, ethanol, acetonitrile, and glyc-



Figure 4. Current histograms for DMABN at  $V_{\text{bias}}$ = 0.05 V recorded in (a) trichlorobenzene generated from 3244 curves and (b) dimethylformamide generated from 517 curves out of 2764.

erol exhibits short and long wavelength bands corresponding to the LE and CT states, respectively.<sup>23,28</sup> Towrie et al. reported the formation and coexistence of the two excited states of DMABN and 4-dimethylamino-3,5-dimethylbenzonitrile (TMABN) using time-resolved infrared absorption spectra of the CN band.<sup>22</sup> In this study, following the UV absorption measurements, the fluorescence emission spectra of DMABN were obtained in water and toluene solvents, and the effect of the polarity variation on the emission behavior of DMABN was examined. The emission spectra of DMABN in toluene show only one band at 350 nm assigned to the LE state emission. This spectrum is independent of the excitation wavelength. However, the fluorescence spectrum of DMABN in water consists of two bands at 360 and 520 nm, associated with the LE and the CT states, respectively (Figure 2b). Although the emission is independent of the excitation wavelength, the relative intensities of the two fluorescence bands are affected by the excitation wavelength, demonstrating that the emission originates from two different electronic states. It is worth mentioning that the single-molecule conductance measurement was performed in acidified water (0.05 M sulfuric acid). According to the  $pK_a$  for DMABN  $(\sim 2)$ , at pH 1, this molecule is likely protonated in 0.05 M sulfuric acid. A control experiment of fluorescence of DMABN in 0.05 M  $H_2SO_4$  (Figure S1) along with previous studies showed that the protonation of molecules and hydrogen bonding with solvent molecules only affects the CT/LE peak ratio and does not quench dual fluorescence and the TICT effect in DMABN.<sup>28,29</sup> These results establish that the electronic structure of DMABN in bulk solvents can undergo remarkable changes as the polarity of the environment changes.

# SINGLE-MOLECULE ELECTRICAL CONDUCTANCE MEASUREMENT

**SMC of DMABN in Toluene and Acidified Water.** The charge transport measurement through DMABN molecules in acidified water and toluene was performed by using the STM break junction (BJ) method in ambient conditions. In the BJ approach, the STM tip gradually approaches the Au(111) substrate to form a gentle contact with the surface and then is withdrawn to form a nanogap between the gold tip and the gold surface. Molecules on the substrate can be trapped in the nano junction between the STM tip and Au(111) to form the

metal-molecule-metal junctions. As the STM tip is retracted from the surface, the current response is monitored simultaneously as a function of the tip-substrate distance. The current histograms generated from ~5000 currentdistance traces recorded in two different solvents showed a single conductance peak at 0.25 m $G_0$  in toluene (Figure 3c,d) and three peaks at 0.25 m $G_0$ , 0.77 m $G_0$ , and 2.1 m $G_0$  in acidified water (Figure 3a,b).

It is essential to be aware of potential noise sources in singlemolecule conductance measurements using the STM break junction method. One of the primary sources of the noise is thermal fluctuations, which result in vibrations within the atomic-scale junctions at room temperature. These fluctuations can lead to variations in the contact geometry and affect the conductance measurements. Also, conductance measurements at the single-molecule level can inherently involve some level of variability due to the discrete nature of molecules and the varying quality and stability of the atomic-scale contact between the electrodes. In addition, the presence of contaminants on the electrodes, solvent, and the molecule itself can influence the conductance measurements. Nevertheless, the objective of the Gaussian fittings is to reveal the most probable conductance values.

Inspection of the 2D histogram in water shows that 2.1 m $G_0$ is the most pronounced peak in acidified water compared to the rest of the peaks. We hypothesized that acidified water solvent can tune the HOMO/LUMO level alignment relative to the Fermi level of the electrode and improve the low-bias conductance compared to toluene. In addition, a polar solvent allows the stabilization of a new state, the twisted geometry of DMABN, resulting in a lower conductance value (0.25  $mG_0$ ) compared to the planar conformation. While it is not an excited state effect, it is nonetheless an electronic stabilization that is only possible in polar solvents, resulting in two distinct conductance values under those conditions. At this moment, the origin of the peak observed at  $0.77 \text{ m}G_0$  is not definitive. This peak did not appear when we repeated the experiment two more times. Therefore, we believe that this peak did not arise from a defined and specific event, e.g., a distinct configuration or molecular structure, and determining its origin requires further investigation.

SMC of DMABN in Trichlorobenzene (TCB) and *N*,*N*-Dimethylformamide (DMF). In addition to toluene, the electrical measurements of DMABN were performed in trichlorobenzene (TCB) as a nonpolar solvent to confirm



**Figure 5.** Control single-molecule conductance measurements of tetramethyldiphenylene (TMDP): Conductance histograms at  $V_{\text{bias}}$  = 0.05 V recorded in toluene (data selection of 284 out of 3846 curves), acidified water (data selection of 260 out of 5162 curves), TCB (data selection of 326 out of 4680 curves), and DMF (data selection of 466 out of 4617 curves).



**Figure 6.** AIMD trajectory of a DMABN molecular junction in water. (a) Three dihedral angles monitored throughout the AIMD trajectory whose plot colors correspond to the dihedral colors in panel (c) and line colors in panel (e). Green circles in panel (a) are the dipole moments of the DMABN molecule at a given time step calculated using DDEC6 net atomic charges and atomic positions. (b) Amino-Au tip (amino) bond length and various nitrile-Au surface bond lengths (nitrile) monitored throughout the trajectory. (c) Image of (left) the entire junction and (right) a close-up of the junction and dihedrals. Visualized using VESTA.<sup>38</sup> (d) NEGF-DFT calculated transmission function at specific time steps. Plot colors correspond to vertical bars in plots in parts (a) and (b). (e) Head-on view from the nitrile end of four different types of DMABN molecule geometries showing the rotation of the benzene ring (dotted brown line) relative to the two methyl groups (light orange and light blue lines) and the Au–N bond on the amino end (black line), which is fixed to vertical, since in the simulation, it is fixed by the location of the electrode.

the effect of solvent polarity. The current histogram measured in TCB shows a single conductance peak at  $0.26 \text{ m}G_0$ , similar to the peak observed in toluene (Figure 4a). Therefore, it is evident that the single-molecule conductance of DMABN does not undergo any changes in nonpolar solvents, presumably due to the lack of stabilization of the CT state in nonpolar solvents. Also, we performed conductance measurements in the polar but aprotic solvent *N*,*N*-dimethylformamide (DMF), where no protonation of molecules is expected (Figure 4b). The current histogram shows a well-defined peak at 2.5  $mG_0$ , consistent with the main conductance observed in acidified water. Another broad peak was observed at 0.31  $mG_0$ , consistent with the peak observed in water in a lower current value, assigned to the charge transport through the LE state. Therefore, we can conclude that (1) the conductance of DMABN can be modulated in a polar solvent and (2) the

protonation of molecules does not play a significant role in the effect of solvent polarity on the charge transport through DMABN. These observations indicate that the appearance of the new conductance state observed in acidified water and DMF could be due to the polar solvent-stabilized intra-molecular charge transfer state.

Control Experiments: SMC of TMPD in Toluene, Acidified water, TCB, and DMF. To support the fact that the appearance of the second conductance state in a polar solvent due to the TICT effect, i.e., the stabilized charge transfer state and induced internal rotation in DMABN, is the main reason for the second conductance peak in the polar solvents, we measured the conductance of a control molecule (N,N,N',N') tetramethyl-1,4-benzenediamine (TMPD)) with no known TICT effect in the bulk solvents. The conductance histogram (Figure 5), constructed from traces that contained plateaus longer than 100 pm (more details are provided in the Supporting Information), shows no polarity dependence, with a single conductance value in all of the solvents ( $\sim 0.13-0.15$  $mG_0$ , Figure 5). Therefore, the structural change associated with the charge transfer state (dihedral angle change) and the shift in HOMO/LUMO levels appears to play an essential role in the change observed in the DMABN dual conductance values.

**Computational Approach.** To elucidate upon the experimental findings, a combination of AIMD and NEGF-DFT<sup>30,31</sup> calculations was performed to investigate the DMABN junction-solvent system. At the level of PBE,<sup>32</sup> specific solvent-molecule interactions, including hydrogen bonds,<sup>33</sup> are treated well and the trajectory will provide a realistic evolution of the geometry given sufficient equilibration time. While this approach is costly, the benefit is that various effects are included, such as temperature, collisions, and bond breaking and/or formation, with the ability to track all parameters throughout the trajectory.

To simulate the STM-BJ system, a model was used in which one electrode is flat and the other has a four-Au-atom apex as shown in Figure 6c. The two lower Au layers (enclosed by thick solid black lines in Figure 6c) are fixed during geometry optimization for varying electrode distances. A reasonable electrode separation is used such that the molecule can remain anchored under thermal motion, and the electrodes are kept at a constant separation throughout the simulation. This is a reasonable assumption since the retraction rate of the STM tip during a single trace event is about 15 nm/s. This corresponds to a 0.1 Å tip displacement every 10<sup>9</sup> ps, whereas the time scale of torsional molecular motion is on the order of 1 ps.<sup>34</sup> Therefore, the molecule has ample time to explore the conformational space in the limit of static electrodes. The asymmetry of the DMABN molecule and electrodes leads to two unique junction arrangements, both of which were explored initially, but since they showed similar conductance character (see the SI), only one was used for the remainder of the investigation. It is worth mentioning that what the simulation shows is that the molecule has several switches in its dihedral angle, and therefore conductance, even in such a short time scale as that simulated (10 ps). This implies that many more of these switches occur in longer time scales, supporting the experimental observation that two conformations are sampled, resulting in the two measured conductance values.

It has been shown previously, both experimentally and theoretically, that the electrode structure has little influence on

how the amine-anchoring group (NH<sub>2</sub>) bonds to gold electrodes or on the conductance.<sup>35</sup> The nitrogen lone pair in the amine group bonds above an Au atom with the Au 6s orbital, and only small changes in conductance occur due to the Au coordination number. It is more likely to form a bond with an undercoordinated Au atom in a very specific way<sup>36</sup> and will tend to drift away from atop an Au site if the surface is flat.<sup>35</sup> The same is expected to happen for the dimethylamino group in DMABN, especially since the "bulkier" methyl groups are expected to hinder bonding to flat electrodes due to steric effects, more so than the hydrogen atoms in the amine group.

Given the gentle tip approach used in the STM-BJ setup and to ensure a well-connected junction is maintained throughout the finite temperature simulations, the dimethylamino group is chosen to be attached to the tip end of the simulation electrodes as shown in Figure 6c. Upon relaxation of the initial geometry, the Au–N bond length of 2.77 Å was larger than the computed optimal Au–N bond length for amine, 2.33–2.54 Å.<sup>36</sup> During the AIMD simulation, the Au–N bond length stays closer to 2.3 Å. The initial Au–N bond length on the nitrile side is 2.2 Å, which is also representative of other simulations that calculate an optimal length of ~2.1 Å.<sup>36</sup>

Based on previous STM-BJ experiments on nitrileterminated biphenyls,<sup>34</sup> the -CN anchor site with gold electrodes is preferential. In the same work, DFT calculations found that the nitrogen lone pair forms a stable bond only above a Au atom and the difference in Au–N bond strength with different coordinated Au atoms is minimal. Both results suggest that regardless of the electrode geometry, stable junctions will form when the nitrile groups form bonds above a Au atom. Therefore, it seems reasonable to claim that anchoring geometry and conductances in the present model electrode geometries would be similar for other electrode geometries. This may not be the case for how the AIMD trajectory evolves over time. A second trajectory is performed with a single Au atom in the nitrile side instead of a flat surface, which is explored in the SI.

AIMD and Transmission. A 9-ps AIMD trajectory was performed on a DMABN junction with a pure  $H_2O$  solvent.  $H_2SO_4$  was not included in the simulation for simplicity and since experiments suggest that pH is less important than the polarity of the water solvent. The DMABN junction was fixed for the first 0.5 ps while the solvent was free to move. The junction and solvent were then free to move for the remainder of the simulation. All systems involving the solvent were built with the aid of PACKMOL<sup>37</sup> and further simulation details are available in the SI.

Snapshots of the transmission function at specific times are shown in Figure 6d. The peaks in transmission near 0 and 2 eV display little change in character or energy, while the HOMO peak ( $\sim$ -1 eV) shifts in energy and broadens. To help characterize each junction geometry along the trajectory, the anchoring Au–N bond lengths and dihedral angles are plotted as a function of time in Figure 6a,b. On the amino side, the Au–N bond (with the Au apex) remains well connected and oscillates regularly around a bond length of 2.3 Å. The movement of solvent molecules around the DMABN molecule had a noticeable effect on the transmission function but was much less significant than the anchoring group bond distance. AIMD trajectories with fixed DMABN junctions in dynamic solvents were also performed to explore the solvent effect on transmission and are available in the SI.



**Figure 7.** Scattering states of DMABN junction in water in a planar (0.0 ps) and twisted (5.3 ps) geometry visualized with VESTA.<sup>38</sup> (a) Transmission functions with two peaks of interest marked in each, labeled (1) and (2). (b) Scattering state wave functions for the DMABN junction at t = 0 ps (dotted black box) and t = 5.3 ps (solid black box). The gas-phase HOMO and LUMO are shown for reference.

Inspecting the dihedral angles in Figure 6a, there are two events in which the phenyl ring rotates to  $\sim 90^{\circ}$  with respect to the dimethylamino group, once at t = 3.25 ps (blue vertical line) and again at 5.3 ps (black vertical line). Simplified graphics in Figure 6e show the relative rotations of different parts of the molecule at those times (e2 and e3). After  $\sim$ 250 fs in the twisted geometry, the molecule returns to the planar geometry (e1), remaining well connected in the junction throughout the whole process. It should be noted that similar AIMD simulations of an out-of-junction DMABN molecule in explicit water solvent show that large twisting does not occur as readily or at all (see the SI). The e1 and e4 orientations lead to similar transmission functions, while the transmission functions at 3.25 and 5.30 ps (e2 and e3, respectively) show a significantly different character, including an overall reduction in transmission with a more pronounced peak near 0 eV.

Using the DDEC6<sup>39</sup> even-tempered net atomic charges (NAC) at the atomic positions, the dipole moment of the DMABN molecule is calculated roughly every 0.5 ps across the trajectory and at finer increments when a large twist angle occurs. The results are plotted in Figure 6a (green dots) and show a clear increase in the DMABN molecule dipole moment at a large twist angle compared to planar geometries. There is also a third, intermediate, twist orientation e4, which results in a similar increase in dipole moment. Calculations of gas-phase DMABN with varying twist angles in vacuum, water, and toluene, using a polarizable continuum solvent model (PCM)<sup>40,41</sup> all show a decrease in dipole moment with increasing twist angle (see the SI). This suggests that the interaction with the electrodes is vital to produce larger dipole moments in the ground-state electron density in twisted geometries. Further evidence of the effect of the electrodes is the much smaller dipole moment calculated at t = 1.5 ps (red vertical line), where the DMABN molecule is the most detached from the electrodes. The larger dipole moments in e2, e3, and e4 may lead to increased stabilization of these geometries in more polar solvents.

**Scattering States.** To better understand the change in the transmission function in different orientations, scattering states were calculated at t = 0 and 5.3 ps for two different features. The main features (1) and (2) in Figure 7a are associated with HOMO and LUMO, respectively. The molecular orbitals had to be calculated for the isolated molecule using the geometries of the molecule in the junction at the different time steps since the twisting causes such a drastic change in the electronic

structure. In the planar geometry (t = 0 ps), the HOMO is  $\pi$ conjugated and extends across the length of the molecule, while in the twisted geometry (t = 5.3 ps), the  $\pi$ -conjugation is destroyed. In the twisted molecule, the HOMO is predominantly localized to the amino side of the molecule. There are also small persistent features around E = -0.07 eV in the planar geometries (also see Figure 6d), but those are a result of mixing of the HOMO/LUMO with electrode states. This has been seen in calculations with thiol anchors<sup>42</sup> but not in molecules with similar anchoring groups to DMABN.<sup>43-45</sup> This is discussed further in the SI.

Calculations of the planar molecule in a vacuum and toluene show LUMO transport but a shift toward HOMO transport in water (see the SI). This shift is explained by the surface dipole induced by the polar water molecules in the vicinity of the Au surfaces. LUMO transport is expected in the DMABN molecule and it is known that DFT will not produce the correct placement of the Fermi energy.<sup>46–48</sup> If the direction of the shift is correct and LUMO transport is assumed, then transmission should decrease in the twisted geometry due to the worsened alignment of the LUMO with the Fermi energy. Our interpretation is that there is global shifting of the DMABN levels in water relative to toluene, leading to the higher conductance value measured in water, which corresponds to a flat geometry. It turns out, by coincidence, that the large reduction in transmission in the twisted geometry combined with the effect of the global shift results in the measured lower conductance value, which happens to be similar to the flat conductance value measured in toluene.

#### CONCLUSIONS

Electrical conductance through single molecules is a function of both the intrinsic characteristics of molecules and the physical properties of their environment. Particularly, charge transport through molecules that show unique effects, e.g., remarkable bulk electronic modulations in response to stimuli, is of great interest. In this study, we focused on DMABN, which belongs to a specific class of molecules, TICT, which shows dual fluorescence in polar solvents. We hypothesized that the bulk electronic structure modulations induced by different local environments (solvent polarity) can be detected in the electrical conductance of single molecules. Our results reveal that DMABN in water (polar solvent) shows two conductance values, which are attributed to the planar geometry and a solvent-stabilized twisted geometry. The latter is not measured in a nonpolar solvent. TMPD molecules, which do not show the TICT effect in bulk solvents, did not exhibit multiple conductance values, indicating that the observed dual conductance values in DMABN in polar solvents are not just the result of the interaction of solvent with the target molecules or with the electrode but represent the dynamic conformational changes within the molecule itself. The intrinsic properties of DMABN (TICT effect) lead to a stabilized charge transfer state and induced structural change in molecules upon charge transfer in the polar solvents.

AIMD calculations suggest that the DMABN molecule in a molecular junction can access geometries with large twisting of the benzonitrile side with respect to the dimethylamino group. The transmission undergoes a significant change at a large twisting angle due to the breaking of the  $\pi$ -conjugation in the HOMO orbital. Dipole moment calculations of the molecule in-junction show an increase in the dipole moment in small and largely twisted geometries compared to more planar ones. This supports the experimental findings, suggesting that polar solvents may further stabilize a twisted state with respect to planarity, leading to another conductance feature. Simulations show that in-junction, the DMABN molecule can access a larger twist angle than out-of-junction and the dipole moment as a function of twist angle differs as a result of interaction with the electrodes. This illustrates the important effects that both the solvent and electrodes have on the trajectory of molecular vibrations and on the ground-state electronic structure.

Experiments performed in the present work rule out multiple possibilities that could lead to two conductance features in polar solvents. Calculations confirm the hypothesis that twisting can occur and be stabilized by a polar solvent and that two different conductance values would arise. Further elucidation of the precise origin of the enhanced conductance feature in polar solvents is essential to identify other molecules, which may exhibit similar transport properties and offer avenues toward sensing and monitoring conformational changes in conducting molecules.

# ASSOCIATED CONTENT

#### **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.3c03576.

Solution and Materials: a. Chemicals: Listing the chemicals used in the study. b. Sample and Measurement Cell Preparation: Describing the process of preparing the samples and measurement cells. Fluorescence of DMABN in 0.05 M H<sub>2</sub>SO<sub>4</sub>: Investigating the fluorescence behavior of DMABN in an acidic solution. In situ-Scanning Tunneling Microscopy Break Junction (STM-BJ): c. Method: Explaining the methodology used for in situ STM-BJ measurements. d. Data Selection Criteria: Describing the criteria for selecting data from measurements. e. Data Correction for 2D Histograms: Detailing the correction process for creating 2D histograms. f. Current-distance curve examples: Providing examples of current-distance curves obtained from measurements. DFT calculations: g. DFT method: Explaining the density functional theory (DFT) approach used. h. NEGF-DFT method: Describing the nonequilibrium Green's function (NEGF) approach coupled with DFT. i. DMABN junctions: Discussing the study's focus on DMABN molecule junctions. j. More AIMD transmission function: Exploring additional

aspects of the ab initio molecular dynamics (AIMD) transmission function. k. Constrained trajectories: Describing the use of constrained trajectories in simulations. l. States near 0 eV in planar geometries: Investigating electronic states near 0 eV in flat geometries. m. Free DMABN molecules in explicit solvent: Exploring DMABN properties as free molecules in the solvent. n. DMABN properties in a PCM as a function of twist angle: Studying DMABN properties with a solvent continuum model and varying twist angles. o. DDEC6 calculated DMABN dipole moment: Discussing the calculated dipole moment using the DDEC6 method. p. Single Au apex on nitrile side with optB86b-vdW functional: Detailing the computational setup involving the Au apex and functional used in simulations (PDF)

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## Notes

The authors declare no competing financial interest.

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