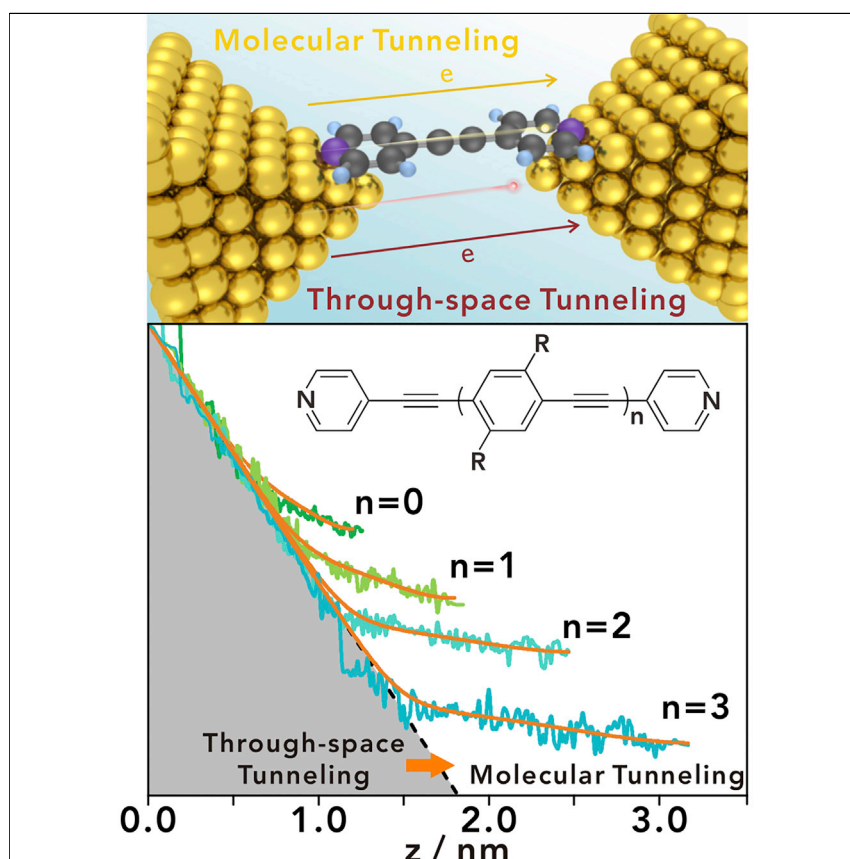


## Article

# Transition from Tunneling Leakage Current to Molecular Tunneling in Single-Molecule Junctions



Tunneling leakage is a major inevitable quantum obstacle that hinders further miniaturization of electronic devices. To explore the miniaturization limits of molecular electronics, the oligo(aryleneethynylene) (OAE) molecules were employed to investigate the transition distance between through-space tunneling and molecular tunneling. For the shortest OAE molecule, the intrinsic single-molecule charge transport can be outstripped from tunneling leakage down to 0.66 nm, suggesting the potential to push the miniaturization limit of molecular electronic devices to the angstrom scale.

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## HIGHLIGHTS

Single-molecule conductance evolutions varying electrode gap distance

Transition from molecular tunneling to tunneling leakage through single molecules

Miniaturization of single-molecule electronic devices to the angstrom scale

Determination of gap distance range where single-molecule device functions

Article

# Transition from Tunneling Leakage Current to Molecular Tunneling in Single-Molecule Junctions

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## SUMMARY

The tunneling leakage current will be a major quantum obstacle during miniaturization in the semiconductor industry down to the scale of several nanometers. At this scale, to promote charge transport and overcome the tunneling leakage current between the source and drain terminals, molecular electronic junctions offer opportunities by inserting molecules between these two electrodes. Employing a series of oligo(aryleneethynylene) (OAE) molecules, here we investigate the transition from tunneling leakage current to molecular tunneling in the single-molecule devices using a mechanically controllable break-junction technique, and the transition distances of the OAE molecular junctions were determined and even down to 0.66 nm for OAE2 molecular junction, which demonstrates that the intrinsic charge-transport properties of a single-molecule device can be outstripped from the tunneling leakage current. Consequently, molecular electronic devices show the potential to push the ultimate limit of miniaturization to the scale of several angstroms.

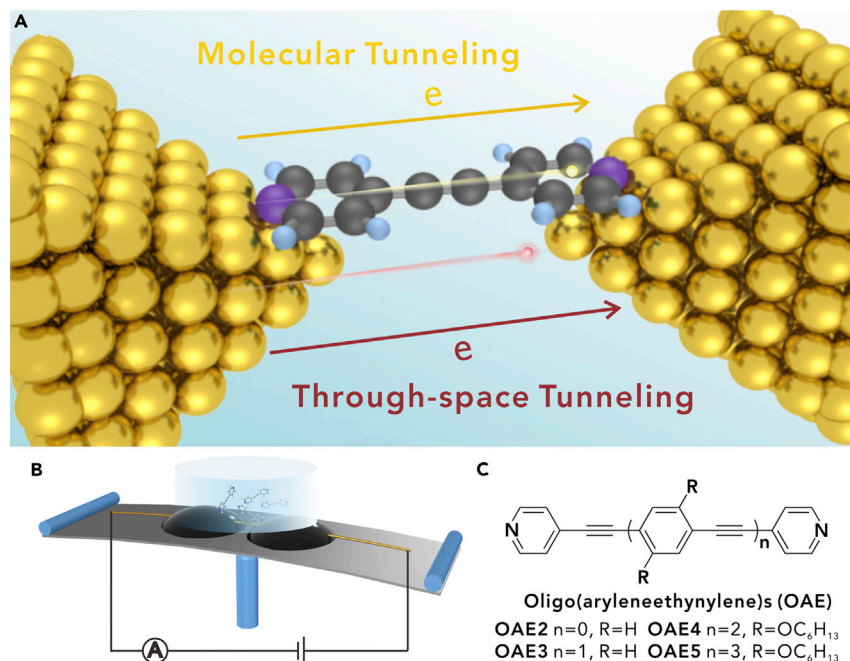
## The Bigger Picture

Advances of miniaturization in electronics have created dramatic impacts on the industrial innovations and our lives. Nowadays, the semiconductor industry is being devoted to scaling down the electronic devices to the scale of sub-5 nm. However, the inevitable quantum obstacles, especially the tunneling leakage, restrict the further miniaturization of electronic devices. Molecular electronics provides a unique opportunity to use molecules as primary elements in electronic circuitry, where the molecules possess intrinsic charge-transport properties to overcome the tunneling leakage.

In this work, we investigated the transition distance between through-space tunneling and molecular tunneling using the oligo(aryleneethynylene) molecules. We demonstrate that molecular tunneling can be distinguished and outstripped from the tunneling leakage down to the size of 0.66 nm, suggesting the potential to push the miniaturization limit of molecular electronic devices to the angstrom scale.

## INTRODUCTION

The semiconductor industry is committed to scaling down the silicon-based state-of-the-art CMOS (complementary metal-oxide-semiconductor) transistors to sub-5-nm nodes in the near future.<sup>1–3</sup> Moore's law, however, has not been the only priority in the semiconductor industry because of some inevitable quantum obstacles that hinder further miniaturization and integration, such as tunneling leakage current and thermal dissipation.<sup>4,5</sup> Meanwhile, various "More-than-Moore" and "Beyond CMOS" strategies have been considered. Among them, molecular electronics provides an alternative opportunity to use molecules as primary elements for building single-molecule electronic components in electronic circuitry,<sup>6–12</sup> where the molecules possess the intrinsic charge-transport properties to overcome the tunneling leakage between the same scale of nanogap distance. Hence, molecular electronics offers a chance to fabricate two-terminal functional molecular devices for new designs of key switching elements in electronic circuits,<sup>13–16</sup> such as the functions of signal processing and data storage. Nevertheless, during the shrinking of the nanogap between two-terminal devices, tunneling leakage current is dominated by the through-space tunneling between the source and drain terminals, which increases exponentially with the terminal distance and becomes non-negligible, as described in Figure 1A.<sup>17,18</sup> Therefore, the determination of transition distance between the intrinsic molecular tunneling and the tunneling leakage current through single-molecule devices is of fundamental significance and will enhance



**Figure 1. Schematic, Technique, and Molecules Used in This Work**

(A) Competition between the molecular conductance (molecular tunneling) and the tunneling leakage current (through-space tunneling) through the two-terminal system during charge transport in a single-molecular junction.

(B) The MCBJ method with gold electrodes immersed in a solution of targeted molecules.

(C) The oligo(aryleneethynylene) (OAE) series of molecules adopted in this study. The numbers 2–5 refer to the number of ethynylphenylene units in OAE molecules, and OAE2 is used as example in (A) and (B).

the understanding of the technical limitations and boundaries for using single-molecule components as electronic devices.

To explore the critical transition distance, the molecular ruler, which represents a family of molecules with a different number of repeating units, offers the chance to investigate charge transport through single-molecule devices at varying distances between the source and drain terminals. By employing a molecular ruler, previous studies revealed that the mechanism of charge transport through single-molecule devices evolved from tunneling to hopping,<sup>19–21</sup> which can be considered as the upper size limit of tunneling-based molecular electronics. Additionally, recent studies exploring conformational effects in single-molecule junctions demonstrated that there is also a significant dependence of conductance on distance, because the molecular conformations vary as the nanogap size changes.<sup>22–25</sup> Thus the entire junction configurations are mechanically controlled using break-junction techniques, which offer further fine-tuning in charge transport through the extended molecular rulers. With the ability to accurately tune nanogap distance between the two-terminal devices, break-junction techniques facilitate the extraction of intrinsic molecular tunneling properties from tunneling leakage current.

In this paper, we investigate the dominant size ranges of through-space tunneling and molecular tunneling through single-molecule junctions (Figure 1A) using a mechanically controllable break-junction (MCBJ) technique (Figure 1B).<sup>26–30</sup> A family of oligo(aryleneethynylene) (OAE) derivatives with a different number of repeating

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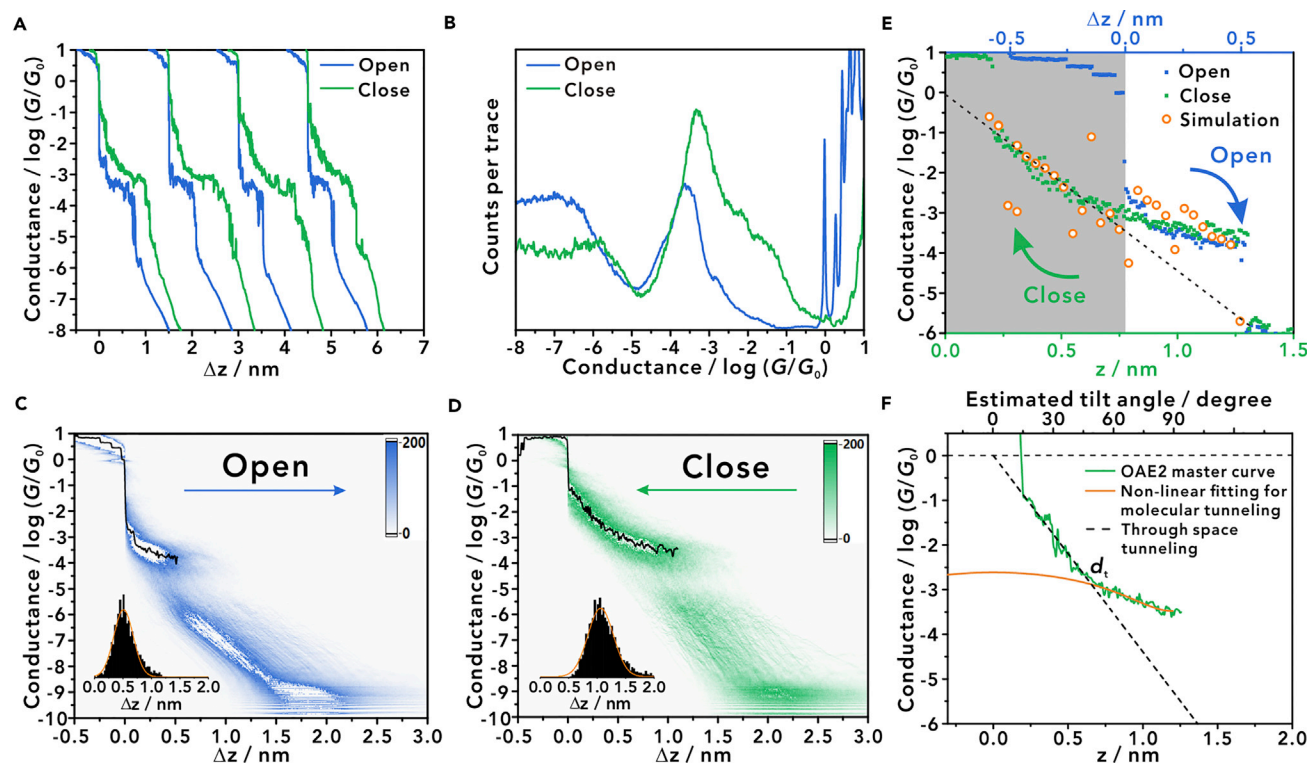
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**Figure 2. Conductance Measurements, Master Curve Extraction, and Fitting of OAE2 Molecule**

(A) Typical conductance-distance curves of OAE2 recorded during the opening (blue) and closing (green) processes. (B–D) 1D conductance histograms constructed from the opening and closing processes (B). 2D conductance-distance histograms with master curves of the (C) opening and (D) closing processes. Lower left insets: the distance distribution determined from  $10^{-1.0} G_0$  to  $10^{-4.8} G_0$ . (E) Superimposition of the opening (blue) and closing (green) master curves with the simulated dots (orange). The opening and simulated data are aligned to the conductance drop after the molecular plateau. The black dashed line labels the fitting of the through-space tunneling. The simulated data are from our previous report, reprinted with permission from Hong et al.<sup>24</sup> Copyright 2012, American Chemical Society. (F) Non-linear fitting (orange curve) of the through-molecule tunneling regime of the master curve in closing process. Top  $z$  axis shows the corresponding estimated tilt angle of molecular junction; the part of molecular junction break into background is omitted.

units (Figure 1C)<sup>21</sup> are used as molecular rulers to investigate the transition from through-space tunneling to molecular tunneling. The OAEs with repeating units of phenylethynyl are highly conjugated, rigid molecular systems that have been widely studied as benchmark molecular wires for single-molecule electronics.<sup>27,30,31</sup> For longer OAEs such as OAE4 and OAE5, the alkoxy side chains are used to enhance their solubilities in the solvent for single-molecule conductance investigation, which shows no significant variation in the charge transport through OAE backbones.<sup>21,32,33</sup> The closing process from the break-junction experiment is extracted to provide precise determination of the electrode-electrode distance for the conductance-nanogap size correlation. By screening this series of OAE molecules, a correlation of the characterized conductance of the molecules with different lengths and configurations is investigated, and the transition between through-space tunneling and molecular tunneling is quantitatively determined.

## RESULTS AND DISCUSSION

### Conductance-Distance Measurement of Single-Molecule OAE2 Junctions

Typical conductance-distance curves of the OAE2 molecule from MCBJ experiments in solution<sup>24,34,35</sup> are shown in Figure 2A (see Figure 1B and Experimental Procedures for details). Both opening and closing curves<sup>36–38</sup> display clear plateaus at

around  $10^{-3} G_0$  (where  $G_0$  is the conductance quantum, which equals  $2 \times 10^2/h$ ). A sudden conductance drop to the molecular plateau followed by discrete  $G_0$  steps was observed in the opening process (blue curves in Figure 2A), which suggests the pulling of a gold atomic contact and formation of an initial nanogap from the inevitable snap-back after final rupture of the gold-gold atomic chain.<sup>24,39–41</sup> However, the closing curves exhibit longer plateaus than the opening ones, along with a conductance jump from  $10^{-1} G_0$  to tens of  $G_0$  when electrodes approach back (green curves in Figure 2A). This may suggest a “jump-to-contact” process in the distance scale less than one gold atom,<sup>42–44</sup> where the strong electrical field inside the nanogap induced a rapid joining of the gold terminals.

For quantitative comparison, conductance histograms of both opening and closing processes were established from 2,000 continuous cycles without data selection, as shown in Figure 2B. Compared with the histogram from the opening process, the discrete  $G_0$  steps disappear in the closing process, indicating the absence of the formation of a gold atomic chain. In both histograms, the conductance peaks dissipate at around  $10^{-4.8} G_0$ . Similar to our previous work,<sup>24</sup> this feature of single-conductance state originated from the configuration with stretched and rigid OAEs backbone and the face-to-face gold electrodes with a single atom atop. However, it is noticeable that there is a minor, yet significant, peak shift ( $10^{-3.6} G_0$  for opening and  $10^{-3.2} G_0$  for closing curves). Moreover, the conductance peak in the closing process also exhibited higher intensity on the higher conductance side. These findings suggest significantly different evolutions of molecular junctions in the opening/closing process of the two terminals.

To investigate the evolution of molecule tunneling versus distance, we extracted the master curves<sup>24</sup> of both opening and closing processes from their corresponding 2D histograms,<sup>45</sup> as superimposed as black curves on the 2D conductance-distance histograms in Figures 2C and 2D. To describe the statistical behavior for the conductance-distance trace, the master curve helps to find the most probable conductance value for every relative distance. Compared with that of the opening process, there is a more extended molecular conductance cloud in the conductance-distance histogram of the closing process. Besides, a more tilted conductance feature appears at around  $10^{-1.5} G_0$ , which can be attributed to the contribution of the through-space tunneling.<sup>17,18</sup> The relative distance distribution determined from the conductance range from  $10^{-0.3} G_0$  to  $10^{-4.8} G_0$  indicates a 0.5-nm difference in length between the opening curves (peak position at 0.5 nm, inset in Figure 2C) and the closing curves (peak position at 1.0 nm, inset in Figure 2D). This difference suggests the snap-back distance, which is close to previous reports.<sup>39,40,46</sup> It should be noted that the distance determined from the closing process is relatively smaller than the length of the OAE2 molecule.<sup>21,24</sup> This suggests that at the end of the opening process, the molecular junction will break and snap back into adsorption on a more energetically favorable metal tip,<sup>6</sup> while at the start of the consequent closing process the attached molecule will form contact with the opposite electrode to form an extended molecular junction.

### Measurement of Nanogap Size via Through-Space Tunneling

Because of the inevitable snap-back in opening process, the extraction of the absolute distance between two electrodes remains a challenge. Therefore, the key information to determine molecular configurations will be masked. The closing process, alternatively, provides characterization of the through-space tunneling regime, offering a unique opportunity to determine the absolute distance between the two gold terminals via the through-space tunneling regime. Since there is still a

jump-to-contact behavior of gold atoms that occurs at  $10^{-1} G_0$  during the closing process,<sup>42,43</sup> we fitted the through-space tunneling regime of the master curve in Figure 2D in the range of  $10^{-1}$  to  $10^{-3} G_0$ . The fitting of the slope provided a tunneling decay constant  $\beta_T$  value of about  $10 \text{ nm}^{-1}$  (for more details see Supplemental Information 4 and Figure S6), although from the pure solvent calibration under the same conditions of molecular conductance measurement we obtained a  $\beta_T$  of about  $12 \text{ nm}^{-1}$  (compared with a previous result of  $\log[\Delta G/G_0]/\Delta z = 5.5 \text{ nm}^{-1}$ ;<sup>34</sup> for more details see Supplemental Information 2 and Figure S2). This difference of  $\beta_T$  originates from the surface energy and barrier height differences between clean gold and molecule assembled gold surfaces.<sup>47</sup> The intercept was determined to be  $\sim 0.18 \text{ nm}$  when extending the fitting curve, owing to the occurrence of the jump-to-contact process at  $10^{-0.78} G_0$  (Supplemental Information 4 and Figure S6). This distance is quite close to the size of a single gold atom, suggesting a rapid joining of the gold terminals in the presence of a strong electrical field on the scale of atomic length.<sup>48</sup> Since the intercept represents an absolute distance between the two gold terminals, the master curves of the closing process can be calibrated, as shown in the green curve in Figure 2E. Thus, the bottom z axis is a representation of the absolute distance (size of the nanogap) between the two gold terminals, which is calibrated to a zero original point along with the through-space tunneling fitting labeled by a black dashed line (Supplemental Information 4).

Subsequently, the master curve of the opening process (blue curve) was aligned together with that of the closing process (green curve) at the point where the molecular junction began to rupture (Figure 2E). Obviously, the master curve of the closing process exhibits two significantly different regimes. The conductance evolution exhibits the through-space tunneling, which is shown by a light-gray background in Figure 2E, with a slope fitted to be  $-4.393 (\log(G/G_0) \text{ nm}^{-1})$ . Moreover, the conductance plateau with white background shows the molecular tunneling regime, which evolves a completely different behavior than the through-space tunneling regime according to the electrode distance. Since the adopted molecular system has a relatively rigid delocalized  $\pi$ -conjugated backbone, the conductance will strongly correlate to the adsorption angle  $\theta$  (see Figure S8) between the conjugated backbone and the electrode surface, resulting from the coupling and interaction between the lateral  $\pi$ -conjugated orbital with the gold electrode.<sup>23,25,49–51</sup> Quek et al. suggested the transmission peak of a 4,4'-bipyridine junction increase with  $\cos(\theta)$ ,<sup>23</sup> and other reports suggest a  $\cos^4(\theta)$  correlation.<sup>49–51</sup> To accurately describe the correlation, we use the equation  $\log(G/G_0) = \log(A \times \cos^n(\theta) + B)$  for the non-linear fitting, where  $A$ ,  $B$ , and  $n$  are the constants, and  $\theta$  can be calculated by  $\arcsin(z/d_m)$ , for which  $d_m$  is the molecular length (see Figure S8). The non-linear fitting to correlate molecular conductance of OAE2 and the absolute electrode distance can then be obtained (see Supplemental Information 4 and Figure S9 for more details). Therefore, for OAE2,  $A$ ,  $B$ , and  $n$  are equal to  $2.1 \times 10^{-3}$ ,  $3.3288 \times 10^{-4}$ , and 4.3304, respectively, as plotted in Figure 2F, where the top z axis represents the calculated junction angle  $\theta$ .

These findings suggest that two different tunneling-dominated conductance regimes are present during the closing process. Consequently, the through-space tunneling regime and the non-linear evolution of molecular tunneling regime will cross at the transition distance  $d_t$  of  $0.66 \text{ nm}$  (Supplemental Information 4 and Figure S9). This can be identified as the transition between through-space tunneling and molecular tunneling. As indicated by the black dashed line of through-space tunneling in Figure 2F, for OAE2 junctions the molecular tunneling conductance prominently outstrips the tunneling leakage current and dominates the charge transport in the range from  $0.66$  to  $1.20 \text{ nm}$ , demonstrating the potential for future

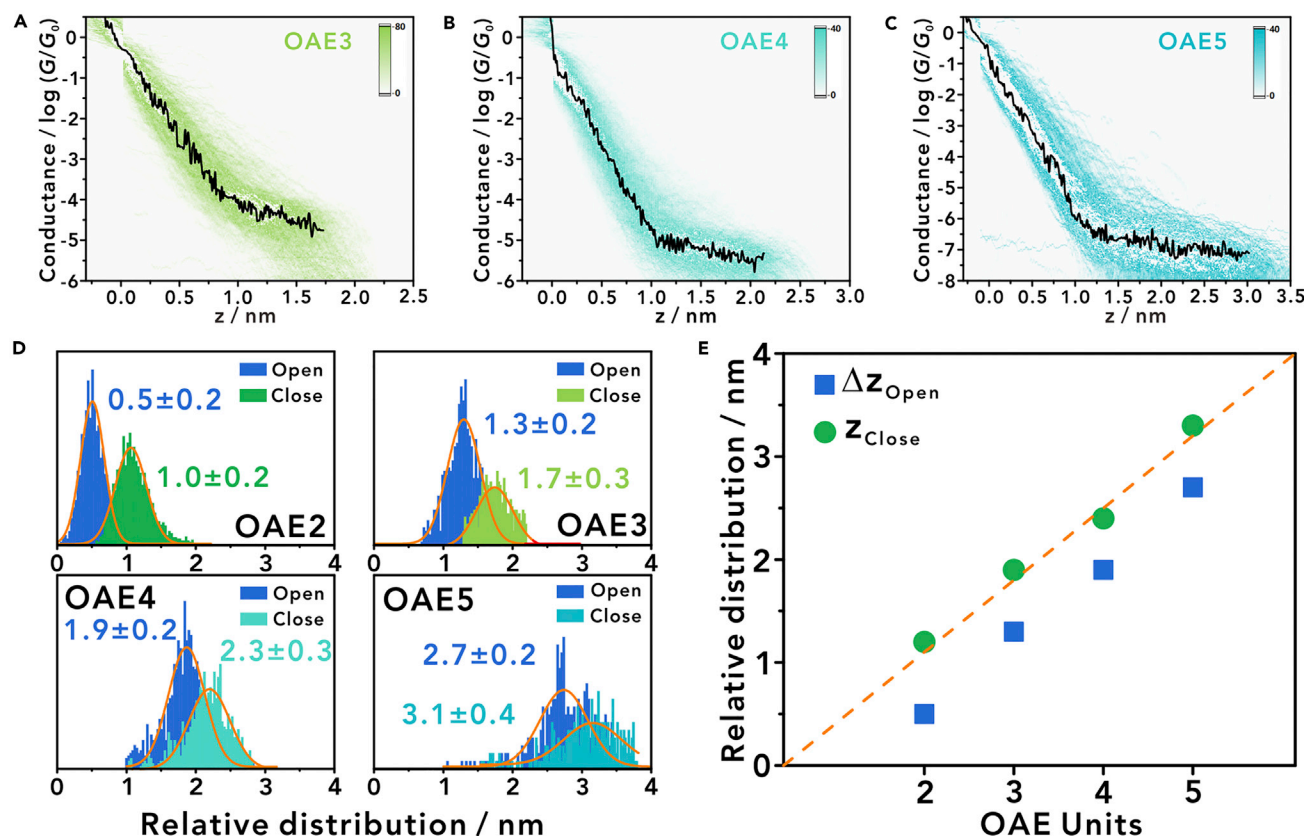
miniaturization and integration using a molecule as the functional unit in an electronic device.

Since the Au–N bond (0.8 nN) is weaker than the Au–Au bond (1.4 nN),<sup>52</sup> no significant deformation of the electrodes during the stretching process is expected for OAE2 molecules. Thus, the master curve from the opening process and the simulated junction evolution from DFT (density functional theory) calculations<sup>24</sup> could be aligned with the closing master curve using the last data point before the rupture of the molecular junction. Both opening and closing curves represent a similar trend to a previous study on the manipulation of atomic gold chains at low temperature,<sup>39</sup> which indicated the presence of gold atomic chains at room temperature, benefiting from the mechanical stability of the MCBJ process. Besides, the lengths of the closing curves are longer than the opening ones, suggesting that the closing process may offer some additional opportunity to probe missing configurations masked by the snap-back effect in the opening process. Furthermore, on comparing the closing curve with previous DFT simulation work in Hong et al.<sup>24</sup> labeled by orange dots in Figure 2E, the through-space tunneling regime from the closing process agrees with that of the simulation throughout the distance range from 0.18 nm to 0.66 nm. Starting from 0.66 nm until the rupture of the molecular junction, the calculations reveal that the conductance variations on the molecular conductance plateau come from the evolution of molecular configurations as the nanogap is extended.<sup>24</sup>

### The Transition from Through-Space Tunneling to Molecular Tunneling

Furthermore, by the same process we explored the transition from through-space tunneling to molecular tunneling for the extended OAE series. Figures 3A–3C show the original 2D conductance-distance histograms of the closing process with their corresponding master curves superimposed for OAE3, OAE4, and OAE5, respectively (see Supplemental Information 3 and Figures S3–S5 for the original 2D histograms and the analyses of opening and closing processes of OAE3 to OAE5). Moreover, the relative displacement distributions of all the OAE series extracted from both opening and closing processes are shown in Figure 3D. The distinct difference in plateau length between both processes unambiguously indicates the snap-back effect. Starting from the intercept of the fitting of the through-space tunneling regime, the lengths of the closing processes of molecules OAE2, OAE3, OAE4, and OAE5 are determined to be 1.2, 1.9, 2.5, and 3.3 nm, respectively, when adding the calibrated distance (0.18 nm) to their statistical lengths of the closing process in Figure 3D. These data indicate that the most probable closing distances are consistent with the corresponding molecular lengths. Table 1 summarizes the key results of the OAE series, along with Figure 3E. It is seen that the length distribution of the closing process falls precisely into the diagonal line to fit the corresponding molecular length.

From all master curves of the closing process of the OAE series, the molecular conductance plateau is witnessed at the early stage, after which all the curves approach the through-space tunneling regime with almost the same slope. The abrupt jump-to-contact process, however, does not always exist in all the OAE molecules, which might result from the stabilization of the configuration of the gold atoms by assembling of the surface molecule.<sup>53</sup> The same calibration method used for OAE2 was applied to the other three OAE molecules, by adding the intercept and fitting those three master curves, as shown in Supplemental Information 5 and Figure S10. Figure 4A shows the superimposed master curves of the closing processes extracted from 2D conductance-distance histograms of all the OAE molecules. Control experiments varying stretching rates and bias voltages demonstrated that the transition still existed, suggesting the



**Figure 3. Conductance Measurements and Relative Displacement Distributions of the OAE Series**

(A–C) The 2D conductance–distance histograms of the closing process with master curves extracted for (A) OAE3, (B) OAE4, and (C) OAE5.

(D) Relative displacement distributions of the OAE series in opening and closing processes. The conductance ranges to determine the distances were from  $10^{-1.0}$  to  $10^{-4.8}$   $G_0$ ,  $10^{-1.0}$  to  $10^{-6.0}$   $G_0$ ,  $10^{-1.0}$  to  $10^{-6.8}$   $G_0$ , and  $10^{-1.0}$  to  $10^{-8.0}$   $G_0$  for OAE2, OAE3, OAE4, and OAE5, respectively.

(E) Distance distributions in each process versus molecular length, which is plotted against the number of aryl rings in the OAE series (for the molecular length values, see Table 1). The orange dashed line represents the equality between molecular lengths of the OAE series and calibrated distance of the closing process.

transition is intrinsic in the charge transport through single molecules (for more details see Supplemental Information 6 and 7, and Figures S12 and S13). We chose the OAE series extended to OAE5, thus all the adopted OAEs are considered to be dominated by super-exchange tunneling<sup>21</sup> (for more details, see Supplemental Information 8 and Figures S14 and S15). For better comparison, their conductance histograms from closing processes are shown in the right panel of Figure 4A. It is noteworthy that there are small conductance differences comparing them with those from the opening processes. For OAE2 to OAE4, the conductance derived from closing was consistently higher than that from opening. Specifically, for OAE2 the peak shifts from  $10^{-3.6}$   $G_0$  to  $10^{-3.2}$   $G_0$ , for OAE3 from  $10^{-4.6}$   $G_0$  to  $10^{-4.3}$   $G_0$ , and for OAE4 from  $10^{-5.8}$   $G_0$  to  $10^{-5.3}$   $G_0$  (Figures S3–S5). Considering that the conductance peaks are composed of all the possible molecular configurations during the opening/closing processes, these differences suggest that, because of the snap-back effect, some configurations are unable to be determined in the break-junction experiments where only the opening process was taken into consideration. Especially for OAE2, as shown in Figure 2E, the initial stage of molecular tunneling plateau located in the shadowed area suggested that the molecular configurations with relatively small nanogap<sup>24</sup> are missing during the opening process (see Supplemental Information 4 and Figure S7 for the junction evolution through the opening and closing processes). In the case of longer molecules, such as OAE5, because all the missing configurations behaved as



**Table 1. Measured Charge-Transport Results and Calculated Transition Distance of OAE Series**

Molecule	Conductance (Log(G/G <sub>0</sub> ))		Molecular Length (nm)	$\Delta z_{\text{Open}}$ (nm)	$\Delta z_{\text{Closed}}, d_m$ (nm)	Transition Distance, $d_t$ (nm)	Tilted Angle, $\theta$ (°)
	Open	Closed					
OAE2	$-3.6 \pm 0.3$	$-3.2 \pm 0.3$	1.1	$0.5 \pm 0.2$	$1.2 \pm 0.2$	0.66	35.1
OAE3	$-4.6 \pm 0.3$	$-4.3 \pm 0.4$	1.8	$1.3 \pm 0.3$	$1.9 \pm 0.3$	0.91	31.4
OAE4	$-5.8 \pm 0.3$	$-5.3 \pm 0.4$	2.5	$1.9 \pm 0.3$	$2.5 \pm 0.3$	1.2	28.7
OAE5	$-7.0 \pm 0.3$	$-7.0 \pm 0.5$	3.2	$2.7 \pm 0.4$	$3.3 \pm 0.4$	1.5	27.0

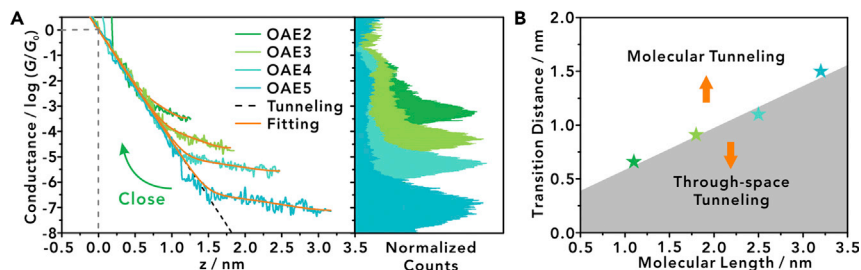
The conductance histograms of OAE3, OAE4, and OAE5 for the opening processes are shown in Figures S3–S5. The calibration in pure solvent and the absolute distance, and calculation of the transition distance are discussed in Supplemental Information 2, 4, and 5, respectively. Error bars are determined from the SD in Gaussian fitting of conductance and length distribution.

This table displays the measured conductance and length of different processes for the OAE series, compared with molecular length by calibration; the calculation of the transition distance from through-space tunneling regime to molecular tunneling regime; and the calculated tilted angle of the molecular junction at the transition distance.

through-space tunneling, no significant peak shift can be observed between the opening and closing histograms, and both conductance values are the same ( $10^{-7.0} G_0$ ).

Hence, all the master curves in the through-space tunneling regime are closely overlapped, as labeled by the black dashed line in Figure 4A, suggesting that the adsorption of homolog molecules does not significantly influence the tunneling barrier height. Thus the overall closing process of all the studied OAE molecules can be calculated by summing the total conductance of the through-space tunneling  $G_t$  and molecular tunneling  $G_m$ , for  $\log(G/G_0) = \log((G_t + G_m)/G_0) = \log(10^{-4.393}z + A \times \cos^n(\arcsin(z/d_m) + B)$  (Supplemental Information 4 and 5; Figures S9 and S10). Therefore, the plotted orange curves for all the closing processes of OAE molecules are shown in Figure 4A, which fits their corresponding master curves of the closing processes.

The transition distance  $d_t$  from through-space tunneling to molecular tunneling was found to be increased with molecules having larger repeating units. For OAE3, OAE4, and OAE5, the distances  $d_t$  therein were 0.91 nm, 1.2 nm, and 1.5 nm, respectively, as summarized in Figure 4B and Table 1 (for more details see Supplemental Information 5 and Figures S10 and S11). This length-dependent transition originates from the competition between the exponentially decreased through-space tunneling and the nonlinearly but more mildly decreased molecular tunneling in these homologous serial molecules. Figure 4B further indicates a guideline through those four dots to act as a boundary, where the white area above the line suggests molecular tunneling-dominated transport while the gray area below the line suggests through-space tunneling-dominated transport. The transition from through-space tunneling to molecular tunneling is a crucial issue for future single-molecule devices. Within the through-space tunneling-dominated regime, the measured properties of the device appeared solely as a tunneling diode and the contribution from molecular behavior could hardly be extracted (for more details see Supplemental Information 9 and Figure S16). In addition, the transition distance  $d_t$  varies from molecule to molecule, e.g., 0.66 nm for OAE2 and 1.5 nm for OAE5. As summarized in Table 1, we found that the transition distance of OAE2 is larger than  $\Delta z_{\text{Open}}$  while it is smaller for longer molecules of OAE3, OAE4, and OAE5. For a short molecule in which the snap-back distance is as considerable as the molecular length, some configurations of the initial period of molecular tunneling are missing because of the fast snap-back effect of electrode pair during the opening process, with as a consequence the transition point located in the shadowed area of Figure 2E. Although for longer molecules the molecular length is significantly longer than snap-back distance, the snap-back effect would not affect the



**Figure 4. Transition between Through-Space Tunneling and Molecular Tunneling**

(A) Left plot: the master curves of the OAE series are superimposed for comparison. The direct tunneling regime as tunneling background is fitted through the black dashed line and the molecular tunneling regime is fitted by non-linear fitting through the orange solid line. Right plot: 1D conductance histograms constructed from 1,000 curves for each molecule, where all the peak heights are normalized.

(B) The transition distance describes the transition from molecular tunneling to through-space tunneling process for each OAE molecule, which is plotted against the molecular lengths of the OAE series (for the transition distance values, see Table 1).

acquisition of the initial configurations of molecular tunneling during the opening process. When the electrode pair was further pulled open, the through-space tunneling still outstripped the molecular tunneling conductance so that the overall logarithmic conductance evolution showed linear behavior at the logarithmic scale before the transition.

These findings suggest that in future single-molecule electronics, in order to use the intrinsic properties of the target molecules, nanogaps within two terminals must reach a certain range of size according to the target molecules to outstrip the tunneling leakage current. The effective nanogap distance range whereby the single-molecule devices properly function for each OAE molecule is 0.66–1.2 nm for OAE2, 0.91–1.9 nm for OAE3, 1.2–2.5 nm for OAE4, and 1.5–3.3 nm for OAE5. The transition distance from molecular tunneling to tunneling leakage varied according to the structure of the molecules employed in the junctions (see Supplemental Information 10 and Figure S17 for another two examples). Indeed, in some extreme cases the molecular conductance cannot be accurately determined if the conductance of fully elongated molecular junction is still lower than the tunneling leakage current conductance.<sup>18,29</sup> Recently, quantum interference effects in single-molecule junctions were reported to significantly change the charge-transport properties through minor chemical structural and environmental variations within almost the same molecular length.<sup>8,29,54,55</sup> The conductance enhancement through constructive quantum interference inside the nanogap offers the potential to significantly surpass the tunneling leakage current and push the limit to an even smaller length scale.<sup>56</sup>

## Conclusion

To conclude, the transition distance from molecular tunneling to tunneling leakage current within a series of conjugated OAE molecules from 1.2 to 3.3 nm has been investigated using MCBJ techniques. We reveal that through-space tunneling and molecular tunneling dominate the charge transport of a molecular junction within different nanogap sizes, and it can be as small as 0.66 nm before the tunneling leakage current dominates the charge transport for the most conductive OAE2 molecules. Meanwhile, the charge transport dominated by molecular tunneling also exhibits a different dependence on nanogap size for molecules with different lengths, resulting from the tuning of molecule-electrode interactions by changing the tilt angle of the molecular junction.

Furthermore, the semiconductor industry has proposed the tunneling FET (Field Effect Transistor) blueprint for a future sub-2-nm node using quantum-mechanical band-to-band tunneling by ultrathin semiconducting films or nanowires.<sup>3,57</sup> As the linewidth will be very close to the radius of a single germanium atom, which is one of the largest elements adopted in the semiconductor industry, this suggests the atomic limit for miniaturization. Using the “bottom-up” strategy and the tunneling mechanism, molecular electronics offers a probability to bridge the gap of the “top-down” shrinking limit, which demonstrates that the leakage current will dominate until even below 0.66 nm in the OAE2 molecule. These conclusions suggest that conjugated molecules are highly promising materials for future miniaturization of electronic devices.

## EXPERIMENTAL PROCEDURES

### MCBJ Experiments

For MCBJ experiments, nanogaps were fabricated between a notched, suspended gold wire (0.1 mm diameter, 99.99%, Jiaming, Beijing) fixed onto a spring steel sheet (10 mm × 30 mm, thickness 0.25 mm) by a two-component epoxy glue (Stycast 2850 FT with catalyst 9). A Kel-F liquid cell assisted by a perfluoroelastomer O-ring was mounted onto the sheet. During the measurements, the sample sheet is bent with a pushing rod, which is driven by a combination of a stepping motor (Zaber NA14B16 linear actuator) and a piezo stack (Thorlab AE0505D18F). The setup is shown in Figure S1. By applying a DC voltage of 100 mV, the current passing through electrode pairs was measured by a lab-built I-V converter with a sensitivity of ~10 fA. The single-molecule conductance measurements were carried at room temperature in solution containing 0.1 mM of target molecule in a mixture of tetrahydrofuran (p.a., Aldrich) and 1,3,5-trimethylbenzene (p.a., Aldrich), 1:4 (v/v). Further technical details of the MCBJ experiments are given in our previous reports.<sup>24,34</sup>

### Data Analysis

Data analyses were conducted by a lab-developed program (WA-BJ code). The program enables the separate analysis of the opening or the closing process for break-junction experiments. The construction of 1D histograms and 2D conductance-distance histograms, and the extraction of master curves were thoroughly reported by Hong et al.<sup>24</sup> The fittings of master curves were conducted by MATLAB.

### Data Availability

Supplemental Information gives the description of the experimental setup of the MCBJ technique, calibration of the stretching rate and calculation of the snap-back distance by pure solvent, the original conductance measurement results of OAE3, OAE4, and OAE5, the molecular junction angle geometry and the fitting for the master curve from the closing process of OAE2, the conductance-distance evolution for OAE2, OAE3, OAE4, and OAE5, the evaluation of bias voltage and stretching rate, the super-exchange and hopping contribution calculation for the OAE series, and the calculation of the through-molecule tunneling contributions in the OAE series. The data that support the findings of this study are available from the corresponding author upon reasonable request.

## SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures and 17 figures and can be found with this article online at <https://doi.org/10.1016/j.chempr.2018.11.002>.

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## AUTHOR CONTRIBUTIONS

W.H. originally conceived the concept and designed the experiments. W.H., M.R.B., and Y.Y. co-supervised the project. J.L., Y.Y., M.R.B., and W.H. prepared the manuscript using feedback from other authors. Break-junction measurements were carried out in the laboratory of W.H. by J.L., J.Z., F.W., X.H., and L.W. MCBJ setup was designed and realized by W.H., J.S., R.L., and J.L. in the laboratory of W.H. Data analyses were carried out by J.L. with the assistance of Y.T., C.H., and W.H. Synthetic works of the OAE molecules were carried out in the laboratory of M.R.B. by X.Z. All authors have given approval to the final version of the manuscript.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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## REFERENCES AND NOTES

1. Wu, B., and Kumar, A. (2014). Extreme ultraviolet lithography and three dimensional integrated circuit—a review. *Appl. Phys. Rev.* **1**, 011104.
2. DeBenedictis, E.P. (2017). It's time to redefine Moore's law again. *Computer* **50**, 72–75.
3. Walter, M.W., and Thomas, M. (2017). Silicon and germanium nanowire electronics: physics of conventional and unconventional transistors. *Rep. Prog. Phys.* **80**, 066502.
4. Mitchell, W.M. (2016). The chips are down for Moore's law. *Nature* **530**, 145–147.
5. Khan, H.N., Hounshell, D.A., and Fuchs, E.R.H. (2018). Science and research policy at the end of Moore's law. *Nat. Electron.* **1**, 14–21.
6. Huang, C., Rudnev, A.V., Hong, W., and Wandlowski, T. (2015). Break junction under electrochemical gating: testbed for single-molecule electronics. *Chem. Soc. Rev.* **44**, 889–901.
7. Perrin, M.L., Burzuri, E., and van der Zant, H.S.J. (2015). Single-molecule transistors. *Chem. Soc. Rev.* **44**, 902–919.
8. Su, T.A., Neupane, M., Steigerwald, M.L., Venkataraman, L., and Nuckolls, C. (2016). Chemical principles of single-molecule electronics. *Nat. Rev. Mater.* **1**, <https://doi.org/10.1038/natrevmats.2016.2>.
9. Xiang, D., Wang, X., Jia, C., Lee, T., and Guo, X. (2016). Molecular-scale electronics: from concept to function. *Chem. Rev.* **116**, 4318–4440.
10. Xin, N., and Guo, X. (2017). Catalyst: the renaissance of molecular electronics. *Chem* **3**, 373–376.
11. Lörtscher, E. (2017). Reaction: technological aspects of molecular electronics. *Chem* **3**, 376–377.
12. Puebla-Hellmann, G., Venkatesan, K., Mayor, M., and Lörtscher, E. (2018). Metallic nanoparticle contacts for high-yield, ambient-stable molecular-monolayer devices. *Nature* **559**, 232–235.
13. Schwarz, F., Kastlunger, G., Lissel, F., Egler-Lucas, C., Semenov, S.N., Venkatesan, K., Berke, H., Stadler, R., and Lörtscher, E. (2016). Field-induced conductance switching by charge-state alternation in organometallic single-molecule junctions. *Nat. Nanotechnol.* **11**, 170–176.
14. Jia, C., Migliore, A., Xin, N., Huang, S., Wang, J., Yang, Q., Wang, S., Chen, H., Wang, D., Feng, B., et al. (2016). Covalently bonded single-molecule junctions with stable and reversible photoswitched conductivity. *Science* **352**, 1443–1445.
15. Chen, X., Roemer, M., Yuan, L., Du, W., Thompson, D., del Barco, E., and Nijhuis, C.A. (2017). Molecular diodes with rectification ratios exceeding 105 driven by electrostatic interactions. *Nat. Nanotechnol.* **12**, 797–803.
16. Atesci, H., Kaliginedi, V., Celis Gil, J.A., Ozawa, H., Thijssen, J.M., Broekmann, P., Haga, M.-A., and van der Molen, S.J. (2018). Humidity-controlled rectification switching in ruthenium-complex molecular junctions. *Nat. Nanotechnol.* **13**, 117–121.
17. Gotsmann, B., Riel, H., and Lörtscher, E. (2011). Direct electrode-electrode tunneling in break-junction measurements of molecular conductance. *Phys. Rev. B* **84**, 205408.
18. Quan, R., Pitler, C.S., Ratner, M.A., and Reuter, M.G. (2015). Quantitative interpretations of break junction conductance histograms in molecular electron transport. *ACS Nano* **9**, 7704–7713.
19. Choi, S., Kim, B., and Frisbie, C.D. (2008). Electrical resistance of long conjugated molecular wires. *Science* **320**, 1482–1486.
20. Hines, T., Diez-Perez, I., Hihath, J., Liu, H., Wang, Z.-S., Zhao, J., Zhou, G., Müllen, K., and Tao, N. (2010). Transition from tunneling to hopping in single molecular junctions by measuring length and temperature dependence. *J. Am. Chem. Soc.* **132**, 11658–11664.
21. Zhao, X., Huang, C., Gulcur, M., Batsanov, A.S., Baghernejad, M., Hong, W., Bryce, M.R., and Wandlowski, T. (2013). Oligo(aryleneethynylene)s with terminal pyridyl groups: synthesis and length dependence of the tunneling-to-hopping transition of single-molecule conductances. *Chem. Mater.* **25**, 4340–4347.
22. Haiss, W., Wang, C., Grace, I., Batsanov, A.S., Schiffrin, D.J., Higgins, S.J., Bryce, M.R., Lambert, C.J., and Nichols, R.J. (2006).

- Precision control of single-molecule electrical junctions. *Nat. Mater.* 5, 995–1002.
23. Quek, S.Y., Kamenetska, M., Steigerwald, M.L., Choi, H.J., Louie, S.G., Hybertsen, M.S., Neaton, J.B., and Venkataraman, L. (2009). Mechanically controlled binary conductance switching of a single-molecule junction. *Nat. Nanotechnol.* 4, 230–234.
24. Hong, W., Manrique, D.Z., Moreno-García, P., Gulcur, M., Mishchenko, A., Lambert, C.J., Bryce, M.R., and Wandlowski, T. (2012). Single molecular conductance of tolanes: experimental and theoretical study on the junction evolution dependent on the anchoring group. *J. Am. Chem. Soc.* 134, 2292–2304.
25. Aradhya, S.V., Frei, M., Hybertsen, M.S., and Venkataraman, L. (2012). Van der Waals interactions at metal/organic interfaces at the single-molecule level. *Nat. Mater.* 11, 872–876.
26. Reed, M.A., Zhou, C., Muller, C.J., Burgin, T.P., and Tour, J.M. (1997). Conductance of a molecular junction. *Science* 278, 252–254.
27. Wu, S., Gonzalez, M.T., Huber, R., Grunder, S., Mayor, M., Schonberger, C., and Calame, M. (2008). Molecular junctions based on aromatic coupling. *Nat. Nanotechnol.* 3, 569–574.
28. Kim, Y., Song, H., Strigl, F., Pernau, H.-F., Lee, T., and Scheer, E. (2011). Conductance and vibrational states of single-molecule junctions controlled by mechanical stretching and material variation. *Phys. Rev. Lett.* 106, 196804.
29. Manrique, D.Z., Huang, C., Baghernejad, M., Zhao, X., Al-Owaidi, O.A., Sadeghi, H., Kaliginedi, V., Hong, W., Gulcur, M., Wandlowski, T., et al. (2015). A quantum circuit rule for interference effects in single-molecule electrical junctions. *Nat. Commun.* 6, 6389.
30. Frisenda, R., Janssen, V.A.E.C., Grozema, F.C., van der Zant, H.S.J., and Renaud, N. (2016). Mechanically controlled quantum interference in individual  $\pi$ -stacked dimers. *Nat. Chem.* 8, 1099–1104.
31. Tour, J.M. (2000). Molecular electronics. Synthesis and testing of components. *Acc. Chem. Res.* 33, 791–804.
32. Huber, R., González, M.T., Wu, S., Langer, M., Grunder, S., Horhoiu, V., Mayor, M., Bryce, M.R., Wang, C., Jitchati, R., et al. (2008). Electrical conductance of conjugated oligomers at the single molecule level. *J. Am. Chem. Soc.* 130, 1080–1084.
33. González, M.T., Zhao, X., Manrique, D.Z., Miguel, D., Leary, E., Gulcur, M., Batsanov, A.S., Rubio-Bollinger, G., Lambert, C.J., Bryce, M.R., et al. (2014). Structural versus electrical functionalization of oligo(phenylene ethynylene) diamine molecular junctions. *J. Phys. Chem. C* 118, 21655–21662.
34. Hong, W., Valkenier, H., Mészáros, G., Manrique, D.Z., Mishchenko, A., Putz, A., García, P.M., Lambert, C.J., Hummelen, J.C., and Wandlowski, T. (2011). An MCBJ case study: the influence of  $\pi$ -conjugation on the single-molecule conductance at a solid/liquid interface. *Beilstein J. Nanotechnol.* 2, 699–713.
35. Liu, J., Zhao, X., Al-Galiby, Q., Huang, X., Zheng, J., Li, R., Huang, C., Yang, Y., Shi, J., Manrique, D.Z., et al. (2017). Radical enhanced charge transport in single-molecule phenothiazine electrical junctions. *Angew. Chem. Int. Ed.* 56, 13061–13065.
36. Balogh, Z., Visontai, D., Makk, P., Gillemot, K., Oroszlány, L., Pósa, L., Lambert, C., and Halbritter, A. (2014). Precursor configurations and post-rupture evolution of Ag-CO-Ag single-molecule junctions. *Nanoscale* 6, 14784–14791.
37. Moreno-García, P., La Rosa, A., Kolivoška, V., Bermejo, D., Hong, W., Yoshida, K., Baghernejad, M., Filippone, S., Broekmann, P., Wandlowski, T., et al. (2015). Charge transport in c60-based dumbbell-type molecules: mechanically induced switching between two distinct conductance states. *J. Am. Chem. Soc.* 137, 2318–2327.
38. Yelin, T., Korytar, R., Sukenik, N., Vardimon, R., Kumar, B., Nuckolls, C., Evers, F., and Tal, O. (2016). Conductance saturation in a series of highly transmitting molecular junctions. *Nat. Mater.* 15, 444–449.
39. Yanson, A.I., Bollinger, G.R., van den Brom, H.E., Agrait, N., and van Ruitenbeek, J.M. (1998). Formation and manipulation of a metallic wire of single gold atoms. *Nature* 395, 783–785.
40. Kamenetska, M., Quek, S.Y., Whalley, A.C., Steigerwald, M.L., Choi, H.J., Louie, S.G., Nuckolls, C., Hybertsen, M.S., Neaton, J.B., and Venkataraman, L. (2010). Conductance and geometry of pyridine-linked single-molecule junctions. *J. Am. Chem. Soc.* 132, 6817–6821.
41. González, M.T., Díaz, A., Leary, E., García, R., Herranz, M.Á., Rubio-Bollinger, G., Martín, N., and Agrait, N. (2013). Stability of single- and few-molecule junctions of conjugated diamines. *J. Am. Chem. Soc.* 135, 5420–5426.
42. Kolb, D.M., Ullmann, R., and Will, T. (1997). Nanofabrication of small copper clusters on gold(111) electrodes by a scanning tunneling microscope. *Science* 275, 1097–1099.
43. Untiedt, C., Caturla, M.J., Calvo, M.R., Palacios, J.J., Segers, R.C., and van Ruitenbeek, J.M. (2007). Formation of a metallic contact: jump to contact revisited. *Phys. Rev. Lett.* 98, 206801.
44. Yang, Y., Liu, J., Feng, S., Wen, H., Tian, J., Zheng, J., Schöllhorn, B., Amatore, C., Chen, Z., and Tian, Z. (2016). Unexpected current-voltage characteristics of mechanically modulated atomic contacts with the presence of molecular junctions in an electrochemically assisted MCBJ. *Nano Res.* 9, 560–570.
45. Martin, C.A., Ding, D., Sørensen, J.K., Bjørnholm, T., van Ruitenbeek, J.M., and van der Zant, H.S.J. (2008). Fullerene-based anchoring groups for molecular electronics. *J. Am. Chem. Soc.* 130, 13198–13199.
46. Untiedt, C., Yanson, A., Grande, R., Rubio-Bollinger, G., Agrait, N., Vieira, S., and van Ruitenbeek, J.M. (2002). Calibration of the length of a chain of single gold atoms. *Phys. Rev. B* 66, 085418.
47. Huisman, E.H., Guédon, C.M., van Wees, B.J., and van der Molen, S.J. (2009). Interpretation of transition voltage spectroscopy. *Nano Lett.* 9, 3909–3913.
48. Ittah, N., Yutsis, I., and Selzer, Y. (2008). Fabrication of highly stable configurable metal quantum point contacts. *Nano Lett.* 8, 3922–3927.
49. Diez-Perez, I., Hihath, J., Hines, T., Wang, Z.-S., Zhou, G., Mullen, K., and Tao, N. (2011). Controlling single-molecule conductance through lateral coupling of [pi] orbitals. *Nat. Nanotechnol.* 6, 226–231.
50. Kornilovitch, P.E., and Bratkovsky, A.M. (2001). Orientational dependence of current through molecular films. *Phys. Rev. B* 64, 195413.
51. Toyoda, K., Morimoto, K., and Morita, K. (2006). First-principles study on current through a single  $\pi$  conjugate molecule for analysis of Carrier injection through an organic/metal interface. *Surf. Sci.* 600, 5080–5083.
52. Frei, M., Aradhya, S.V., Koentopp, M., Hybertsen, M.S., and Venkataraman, L. (2011). Mechanics and chemistry: single molecule bond rupture forces correlate with molecular backbone structure. *Nano Lett.* 11, 1518–1523.
53. Huisman, E.H., Trouwborst, M.L., Bakker, F.L., de Boer, B., van Wees, B.J., and van der Molen, S.J. (2008). Stabilizing single atom contacts by molecular bridge formation. *Nano Lett.* 8, 3381–3385.
54. Huang, C., Jevric, M., Borges, A., Olsen, S.T., Hamill, J.M., Zheng, J.-T., Yang, Y., Rudnev, A., Baghernejad, M., Broekmann, P., et al. (2017). Single-molecule detection of dihydroazulene photo-thermal reaction using break junction technique. *Nat. Commun.* 8, 15436.
55. Garner, M.H., Li, H., Chen, Y., Su, T.A., Shangguan, Z., Paley, D.W., Liu, T., Ng, F., Li, H., Xiao, S., et al. (2018). Comprehensive suppression of single-molecule conductance using destructive  $\sigma$ -interference. *Nature* 558, 415–419.
56. Vazquez, H., Skouta, R., Schneebeli, S., Kamenetska, M., Breslow, R., Venkataraman, L., and Hybertsen, M.S. (2012). Probing the conductance superposition law in single-molecule circuits with parallel paths. *Nat. Nanotechnol.* 7, 663–667.
57. Ionescu, A.M., and Riel, H. (2011). Tunnel field-effect transistors as energy-efficient electronic switches. *Nature* 479, 329–337.

**Chem, Volume 5**

## **Supplemental Information**

**Transition from Tunneling Leakage**

**Current to Molecular Tunneling**

**in Single-Molecule Junctions**

**Junyang Liu, Xiaotao Zhao, Jueting Zheng, Xiaoyan Huang, Yongxiang Tang, Fei Wang, Ruihao Li, Jiuchan Pi, Cancan Huang, Lin Wang, Yang Yang, Jia Shi, Bing-Wei Mao, Zhong-Qun Tian, Martin R. Bryce, and Wenjing Hong**

## Table of Content:

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7. The conductance measurements of OAE2 under different bias voltages.
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9. Calculation of the through-molecule tunneling contributions of the OAE series.
10. The transition in other conjugated system.

1. The experimental setup of the MCBJ technique

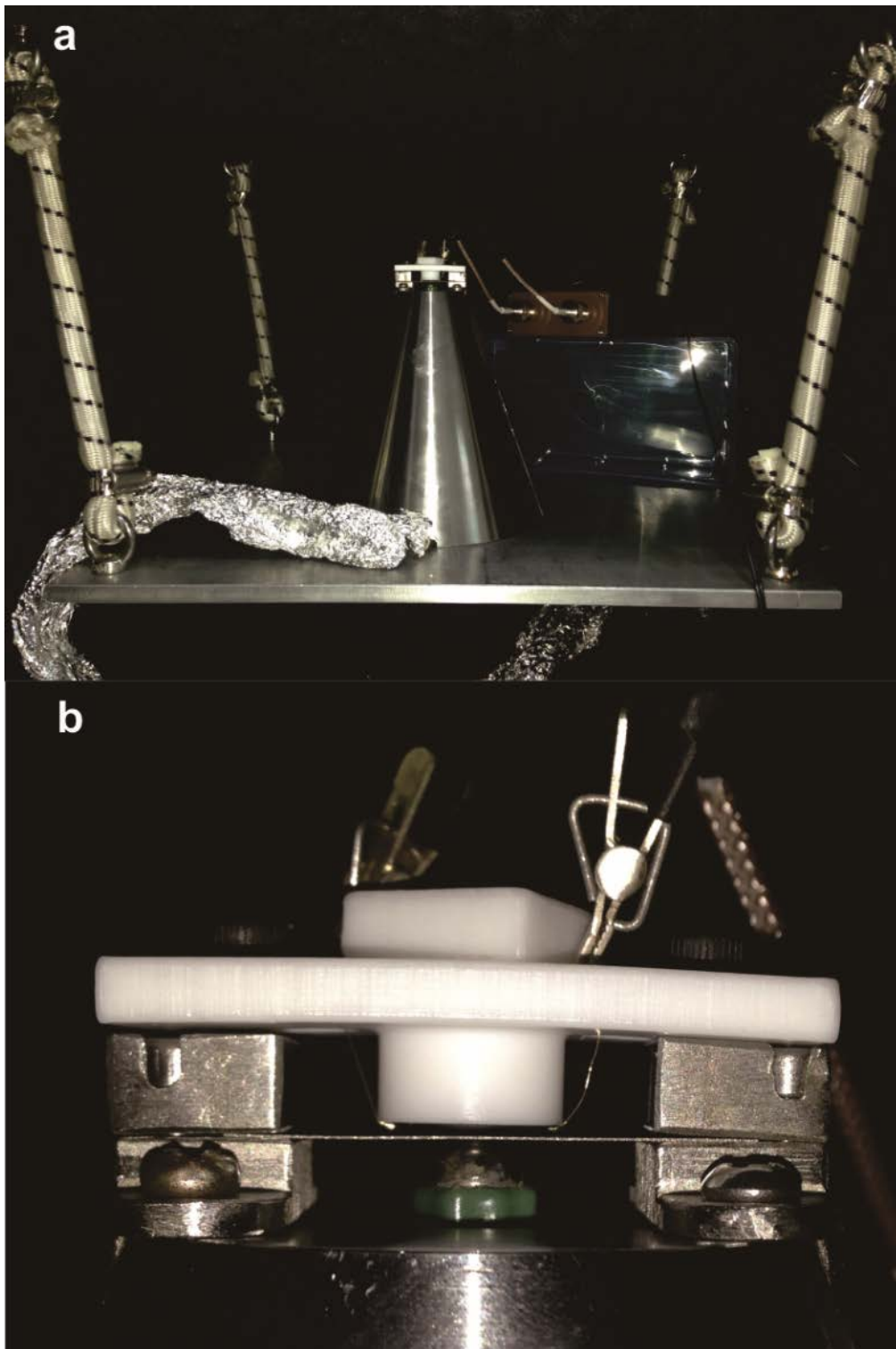


Figure S1. Schematic of (a) MCBJ setup and (b) the zoom-in image of the chip position.



2. Calibration of the stretching rate and calculation of the snap-back distance in pure solvent of THF/TMB.

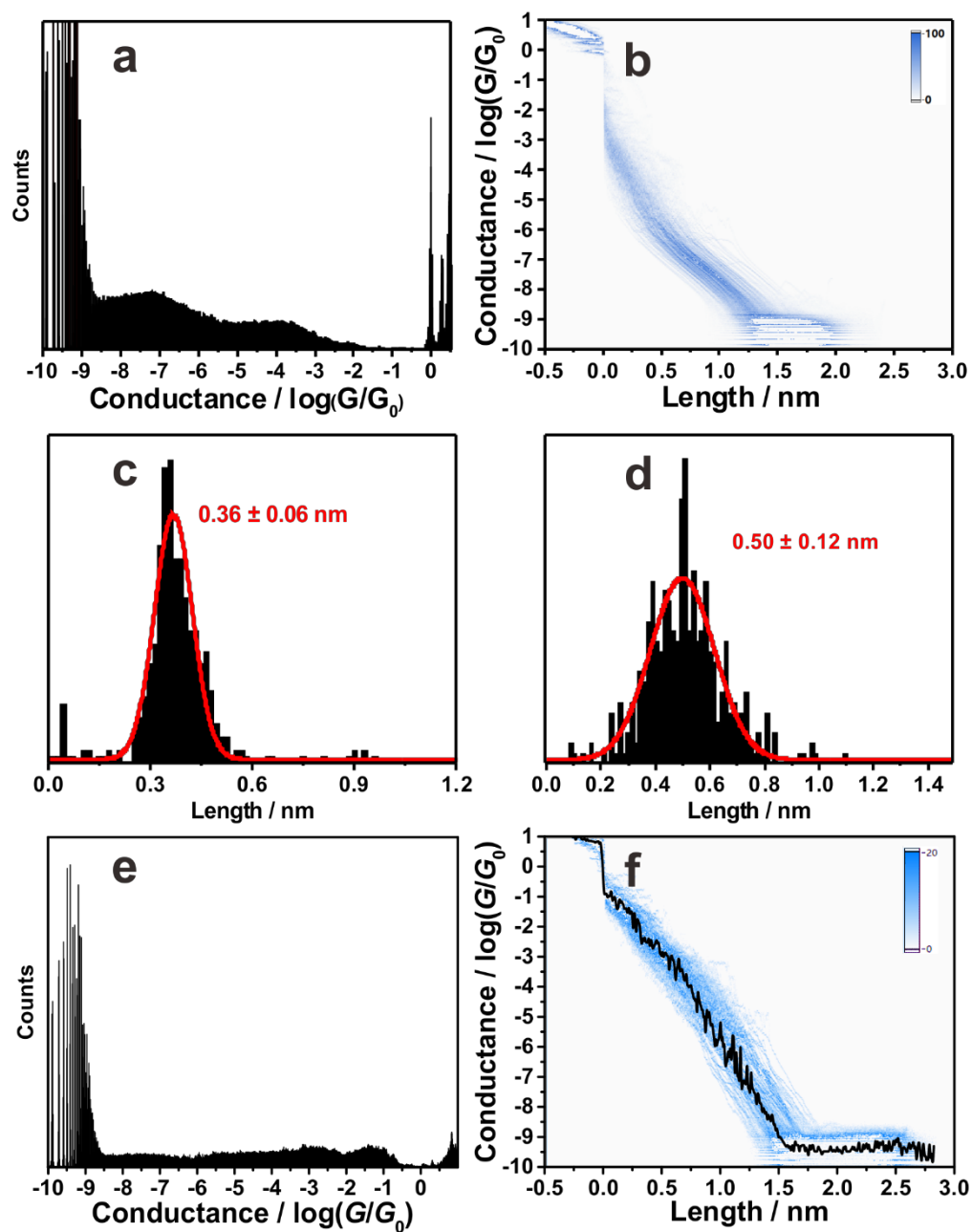


Figure S2. (a) 1D conductance histogram of the opening process in pure solvent (1:4 v/v THF:TMB). (b) 2D conductance-distance histogram of pure solvent. Characteristic length distribution (c) from  $10^{-4.0} G_0$  to  $10^{-6.0} G_0$  and (d) from  $10^{-0.3} G_0$  to  $10^{-6.0} G_0$  in a blank experiment. (e) 1D conductance histogram of the closing process in pure solvent. (f) 2D conductance-distance histogram of pure solvent with the extracted master curve.

We used the same method described elsewhere previously to calibrate the stretching rate of the electrode pair in pure solvent.<sup>1,2</sup> Without the target molecule, the 1D conductance histogram and 2D conductance-distance histogram in Figure S2(a) and S2(b) show direct tunneling and clear non-plateau features, suggesting a pure and clean environment inside the gap. In order to calculate the snap-back distance, firstly we needed to calibrate the stretching rate of the pulled electrodes pair.

Since the tunneling equation can be written as follows,

$$(1) \quad G = G_0 e^{-\beta_T \Delta z}$$

Where  $\beta_T$  is the tunneling decay constant in the solution environment,  $\Delta z$  is the absolute distance, herein  $\Delta z = z - z_{\text{corr}}$ , where  $z_{\text{corr}}$  is the snap-back distance. Equation (1) can be transferred as follows when taking the logarithm of each side,

$$(2) \quad \log\left(\frac{G}{G_0}\right) = -0.434\beta_T(z - z_{\text{corr}})$$

Then a plot of  $\log(G/G_0)$  versus  $z$  has a slope of  $-0.434\beta_T$  and an intercept of  $0.434\beta_T z_{\text{corr}}$ , therefore, we can use the plot to get  $\beta_T$  and  $z_{\text{corr}}$ . As we had calibrated the tunneling decay constant under the liquid atmosphere of THF:TMB (v/v 1:4) and already obtained the slope as  $\log[\Delta G/G_0]/\Delta z = -5.5 \text{ nm}^{-1}$ ,<sup>2</sup> for the tunneling conductance range from  $10^{-4.0}$  to  $10^{-6.0} G_0$ ,  $\Delta z$  should be 0.36 nm.

Hence, we calibrated the length histogram between  $10^{-4.0}$  to  $10^{-6.0} G_0$  to fit the  $\Delta z$  for 0.36 nm, as shown in Figure S2(c). As a consequence, the plot will extend to an intercept of 2.75, the  $z_{\text{corr}}$  will be  $2.75/5.5 = 0.5 \text{ nm}$ . Therefore, when the plateau length statistical range extends to between  $10^{-0.3}$  (extend to the intercept) to  $10^{-6.0} G_0$ , it will be 0.5 nm, as shown in Figure S2(d), which is the snap-back distance close to the previous report. The stretching and approaching rate of electrodes pair was calculated to be  $\sim 8.4 \text{ nm/s}$ .

Moreover, we extracted the conductance evolution of the closing process in the pure solvent. Figure S2(e) and S2(f) shows the corresponding 1D and 2D conductance histograms with the extracted master curve. The through-space tunneling regime ranges from  $10^{-1} G_0$  to even down to the scale of  $10^{-8} G_0$ , which demonstrated that the electron can tunnel between the face-to-face electrodes through a very long range. The small peak at around  $10^{-1} G_0$  is in Figure S2(e) originated from the "jump-to-contact" process when the electrodes gap was too small that the electrodes will easily form contact. The fitted slope of the range from  $10^{-1}$  to  $10^{-8} G_0$  is  $5.33 \text{ nm}^{-1}$ , which is very close to the slope of the opening process ( $5.5 \text{ nm}^{-1}$ ), suggesting that the closing process is able to obtain the whole range of the conductance evolution. Besides, this pure tunneling character demonstrates a clean gold surface without contaminations adsorbed in the closing process, which enables further investigation with solution of target molecule.

3. The original conductance measurement results of OAE3, OAE4 and OAE5.

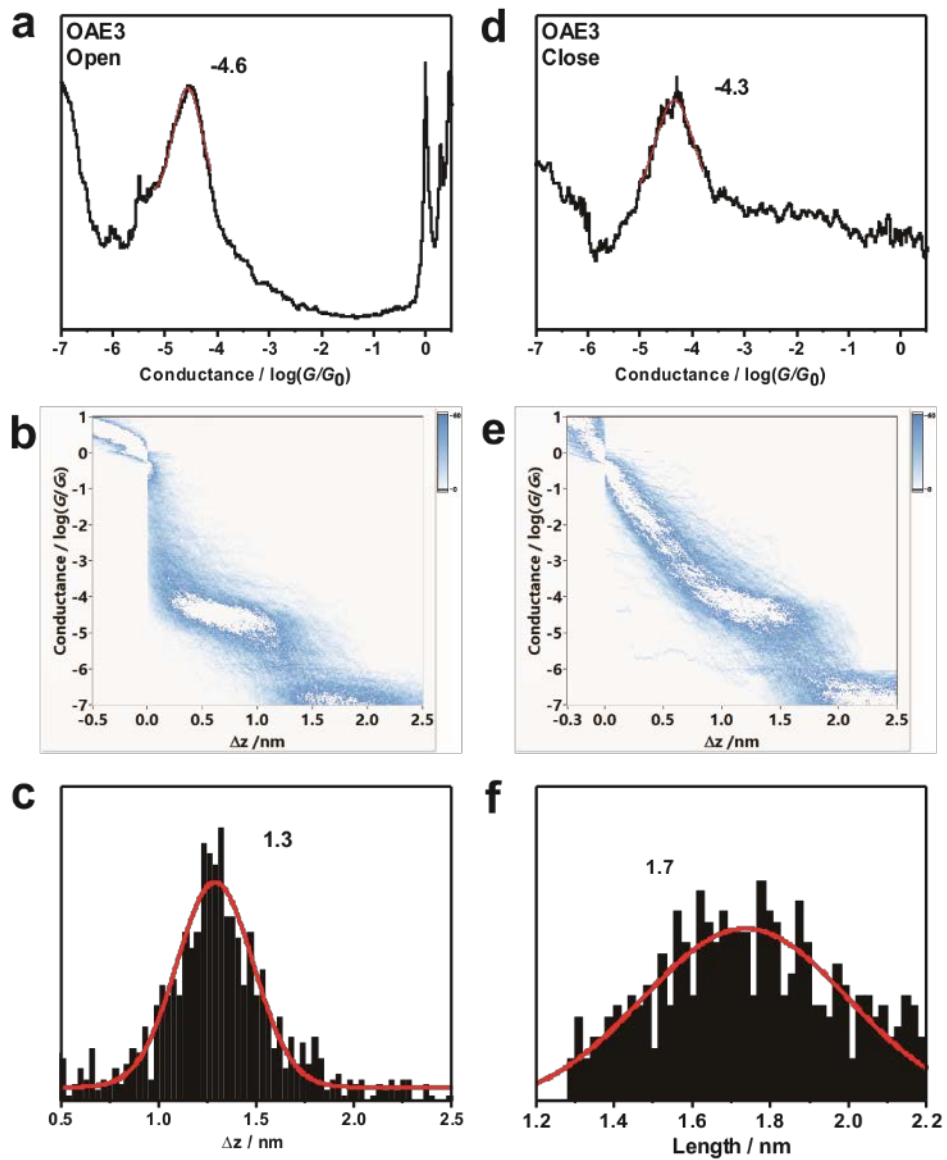


Figure S3. 1D conductance histogram of opening (a) and closing (d) processes, 2D conductance-distance histogram of opening (b) and closing (e) processes of OAE3. Plateau length histograms of stretch (c) and relax (f) processes, for both the analysis range is from  $10^{-0.3}$  to  $10^{-6.0} G_0$ .

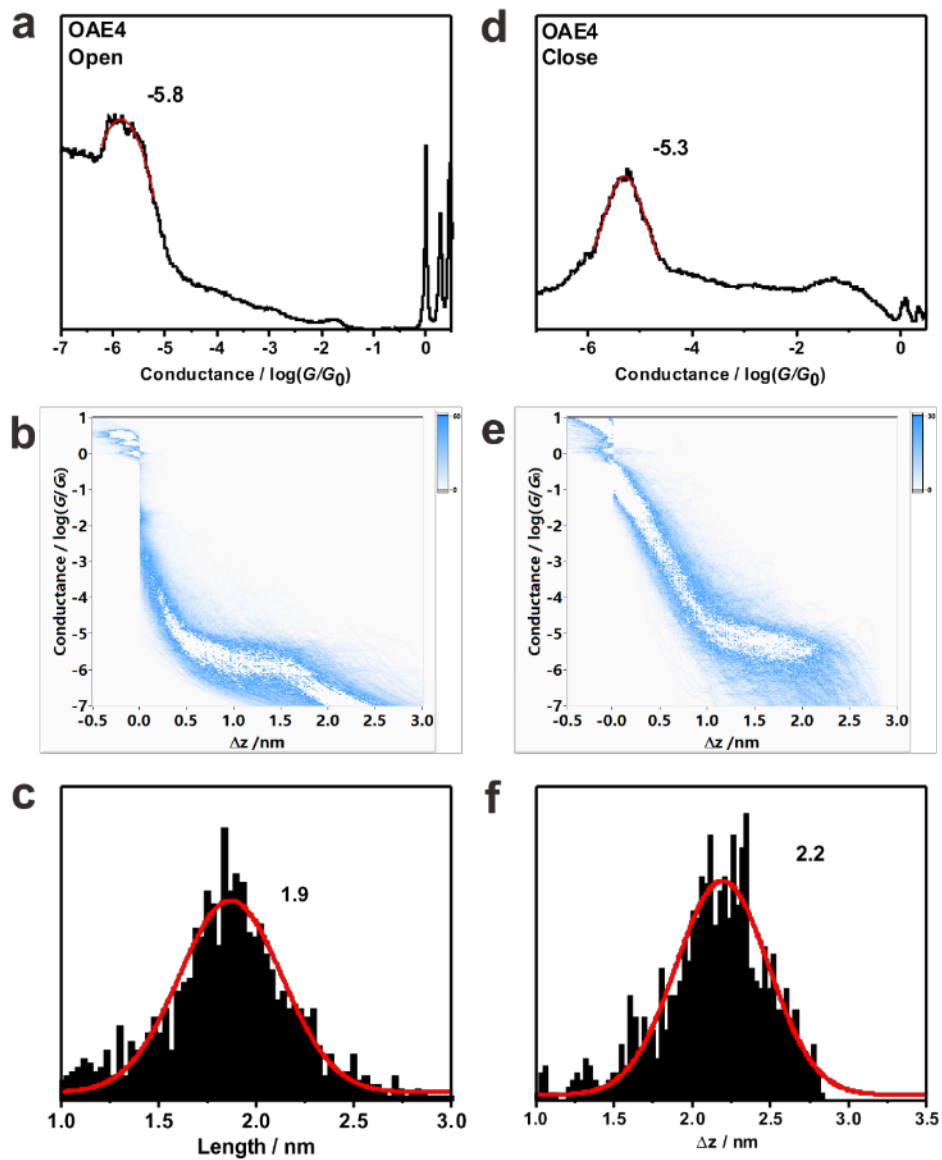


Figure S4. 1D conductance histogram of opening (a) and closing (d) processes, 2D conductance-distance histograms of opening (b) and closing (e) processes of OAE4. Plateau length histograms of stretch (c) and relax (f) processes, for both the analysis range is from  $10^{-0.3}$  to  $10^{-6.8} G_0$ .

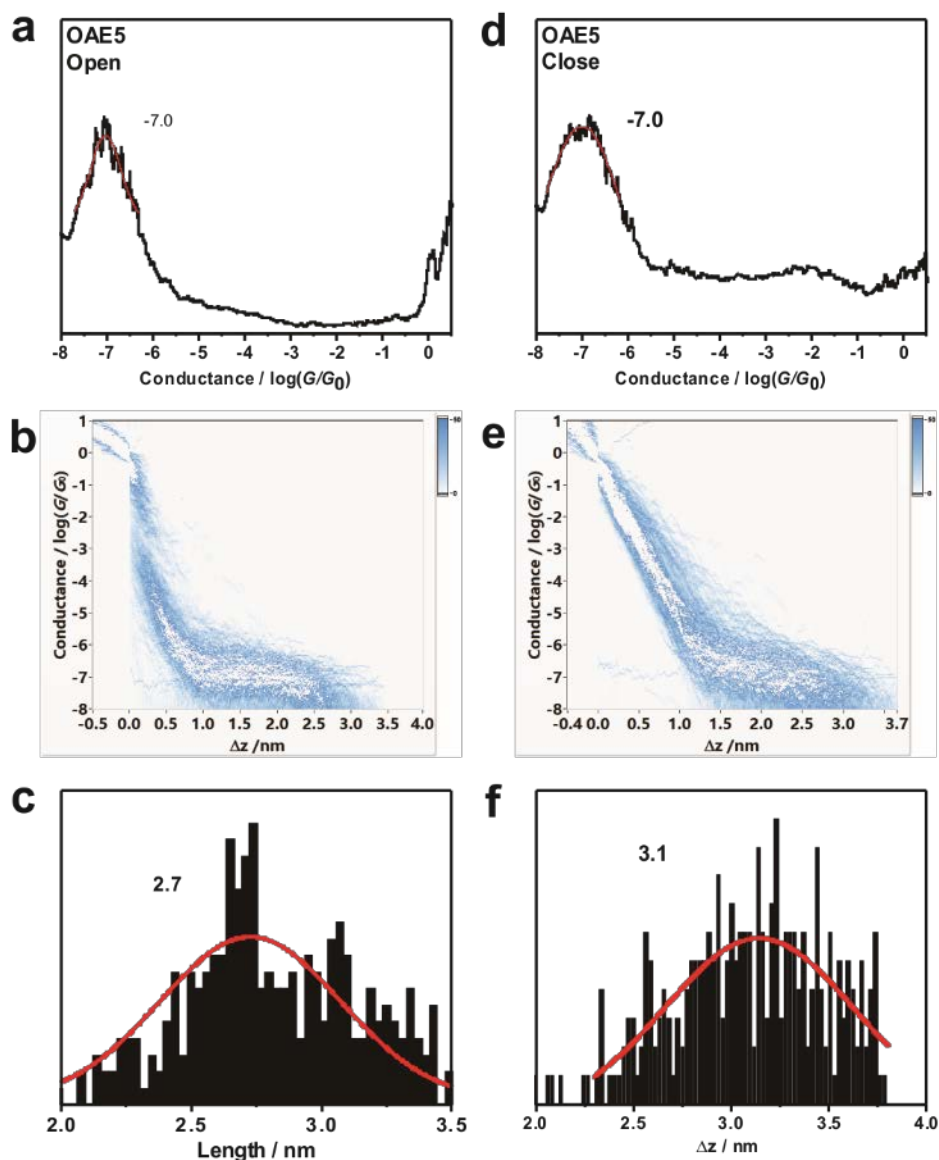


Figure S5. 1D conductance histograms of opening (a) and closing (d) processes, 2D conductance-distance histogram of opening (b) and closing (e) of OAE5 molecule. Plateau length histogram of stretch (c) and relax (f) processes, for both the analysis range is from  $10^{-0.3}$  to  $10^{-8.0} G_0$ .

#### 4. Molecular junction angle geometry and fitting for the master curve from the closing process of OAE2.

As we had calibrated the stretching rate to obtain the snap-back distance, we used the same system and operational parameters for molecular conductance measurements, by replacing the pure solvent with 0.1 mM target molecule solution in the same solvent. Figure S6 shows the master curve extracted from the 2D conductance-distance histogram of the closing process of

OAE2. The prominent different regime suggests the different major contribution between through-space tunneling and through molecule tunneling.

A jump-to-contact process is observed at the conductance of about  $10^{-0.78} G_0$ , which is similar to previous results.<sup>3</sup> Therefore, the logarithmic conductance evolved linearly with the electrode distance, we used the linear fitting over the range of -1.0 to -3.0  $\log(G/G_0)$ , and found the slope is -4.393. According to equation (2), the  $\beta_T$  in the molecular solution will be

$$(3) \quad \beta_T = -4.393 / -0.434 = 10 \text{ nm}^{-1}$$

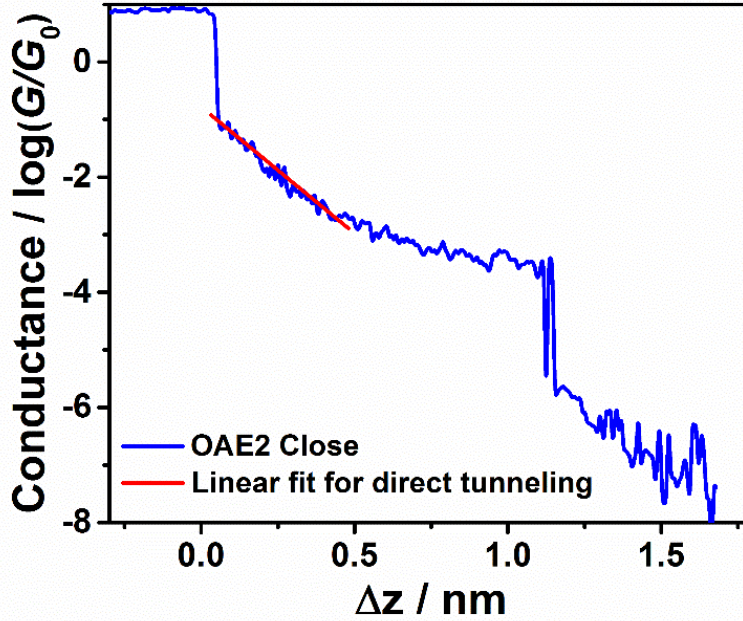


Figure S6. The master curve extracted from 2D conductance-distance histogram of closing process of OAE2, with red linear fitting for through-space tunneling regime.

Although there is a slight difference of the  $\beta_T$  between the pure solvent ( $-5.5/-0.434 = 12 \text{ nm}^{-1}$ ) and the OAE solution, which can be attributed to the change of tunneling barrier because of the molecular adsorption,<sup>4</sup> we considered that the  $\beta_T$  in the molecular solution was entirely reasonable.

Furthermore, through the fitting, as shown in Figure S6, the tunneling equation will be

$$(4) \quad \log\left(\frac{G}{G_0}\right) = -4.393\Delta z - 0.7801$$

Therefore, in order to calibrate the absolute distance, we set  $\Delta z$  equals to  $z + \Delta d$ .  $\Delta d$  is the calibrated distance between the  $z$  axis of the previous obtained master curve in Figure S6 and the calibrated  $z$  axis. It is known that when  $z$  equals to 0,  $G$  equals to  $G_0$ , which means the gold atomic contact forms. Therefore, we obtained

$$(5) \quad \log\left(\frac{G}{G_0}\right) = \log\left(\frac{G_0}{G_0}\right) = -4.393z + 4.393\Delta d - 0.7801 = 0$$

Then the  $\Delta d$  will be

$$(6) \quad \Delta d = 0.177 \text{ nm}$$

Hence, we calibrated all the closing master curves by adding  $\Delta d$  in the  $z$  axis, as shown in Figure 2E, 2F and Figure 4A in the main text. The tunneling  $G_t$ , the equation (5) ( $\log(G_t/G_0) = -4.393z$ ) was also plotted as a black dash line in Figure 2E, 2F and Figure 4A.

Therefore, the closing process and the corresponding opening process can be described as followed in Figure S7, which indicates the junction evolution during the opening/closing processes. The blue curve indicates the stretching of a molecular junction from the configuration  $a$  to  $f$ , while the closing process exhibited a reverse sequence. Among those configurations,  $a$  represents multiple gold atomic contact when the electrodes pair join together, while  $b$  represents a single-atom contact with the conductance of  $1 G_0$ . The configuration  $e$  and  $f$ , represents the most extended molecular junction and the molecular junction breakage, respectively. Therefore, configurations from  $c$  to  $d$  suggest the formed molecular junction with tilted configurations. Hence, as shown in the green curve of closing process, the molecule adsorbed on the end of one electrode starts to contact with the end of the other electrode from the configuration  $f$  to  $e$ , during which the conductance might exhibit a jump from background to a conductance plateau. As the two electrodes approach further, the distance becomes smaller than the molecular length, and the molecular junction starts to tilt from configuration  $e$  to  $c$ . During this process, the overall conductance becomes larger, the through-space tunneling becomes inevitable and starts to dominate at the configuration  $d$ . The further approaching causes the conductance jumps from  $10^{-1}$  to  $10^0 G_0$ , where a jump-to-contact process occurs to make two gold electrodes contact, and the conductance quickly changes to above  $G_0$ , as shown in configuration  $a$ . In the opening process, due to the fast snap-back of gold electrodes, the opening process evolves directly from single gold atomic contact of configuration  $b$  to configuration  $d$ , some parts even the whole series of configuration  $c$  might be missing. In the closing process, since the snap-back effect can be avoided, it enables the full detection of series configurations  $c$  but without the single gold atomic contact of configuration  $b$ .

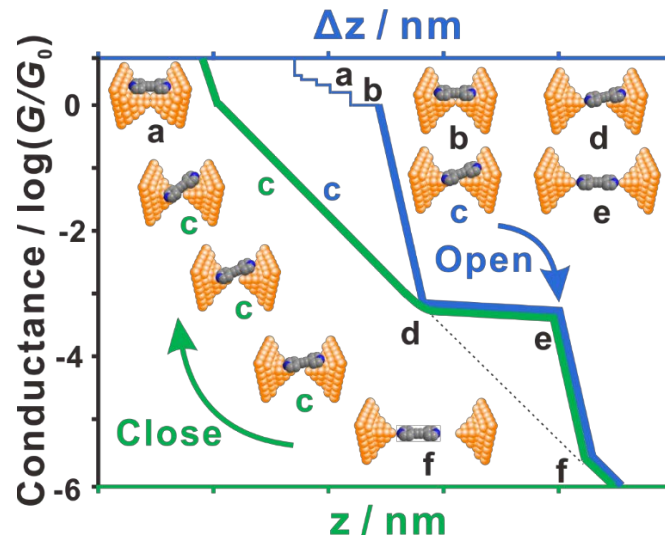


Figure S7. The hypothesized evolution of the molecular configuration during the opening and closing processes.

While in another part of the closing master curve of OAE2, the conductance plateau represents the through-molecule tunneling, according to the previous reports.<sup>5-7</sup> The conductance of  $\pi$ -conjugated molecular junctions in the non-resonant tunneling regime will significantly correlate with the adsorption angle  $\theta$  between the conjugated backbone and the electrode surface, especially for the large delocalized rigid conjugated molecular systems, where it is predicted that the conductance  $G \propto \cos^4\theta$ . Figure S8 shows the junction geometry changes of the short OAE2 and long OAE5 (the  $\text{OC}_6\text{H}_{13}$  side groups are omitted) as examples. Therefore,  $\theta$  can be estimated by the arcsine of  $z/d_m$ , where  $z$  is the absolute electrode distance calibrated as discussed above,  $d_m$  is the molecular length. For the Au-pyridyl contacts, the correlation between the conductance variation with the tilt angle mainly originates from the coupling between the lateral  $\pi$ -orbital and the gold electrode. Since the tilted angle correlates with the electrode distance, the distance changes will lead to the conductance change due to the tilted angle variation. As the possible sliding of Au-pyridyl contact didn't cause the changes of the angle, the molecular conductance change may be quite small since the target molecules we used are long, rigid backbones with lateral  $\pi$ -orbitals, therefore, the conductance changes were dominated by the changes of the tilt angles during the break junction process.

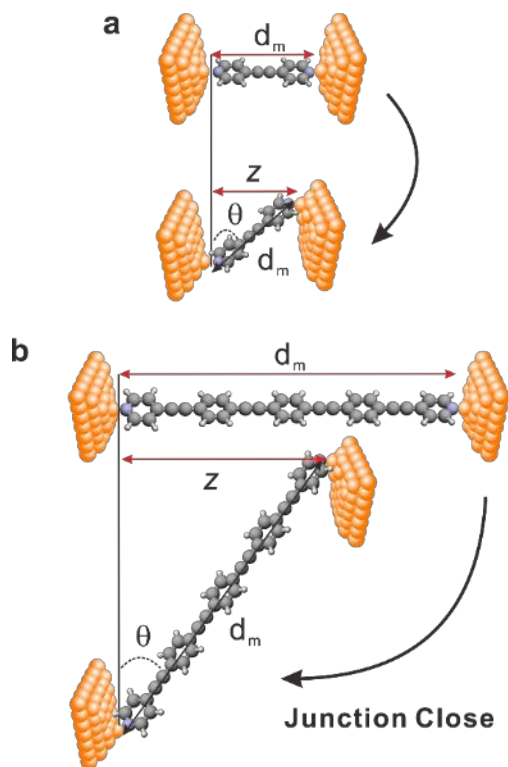


Figure S8. Schematics of junction geometries when the molecule is fully extended (upper panels) and tilted with an angle  $\theta$  (lower panels) for (a) OAE2 and (b) OAE5,  $d_m$  is the molecular length and  $z$  is the electrode distance.

Therefore, in order to establish the relationship between the electrode distance and the molecular conductance  $G_m$ , the master curve was fitted with equation (7) below



$$(7) \quad \log(G_m/G_0) = \log\{A [\cos(\arcsin(z/d_m))]^n + B\}$$

where we used A, B, n as fitting parameters. A means the pre-factor where ref. 5 suggested  $A \cdot G_0$  equals  $e^2/h \cdot \Gamma^2/t_\pi^2$ ,  $\Gamma$  stands for the coupling between molecule and the gold electrode, and  $t_\pi$  correlates with the energy difference between HOMO-LUMO gap of molecule. While  $B \cdot G_0$  is the molecular conductance when the molecular junction is fully extended when the angle reaches 90 degree (configuration *e* in Figure S7). For n, it supposed to be 4 according to the ref. 5, however since the junction evolves under room temperature and solution phase, the molecular level broadening and the coupling between molecule and electrode will be different, causing the actual circumstance different from ideal theoretical assumption, it will be better to fit the n also. The  $d_m$  for OAE2 is 1.2 nm, and the fitting range of z is from 0.7 to 1.2 nm for the molecular conductance plateau, as shown in Figure S9 and equation (8), the regression coefficient  $r^2 = 0.9141$ .

$$(8) \quad \log(G_m/G_0) = \log\{2.1 \times 10^{-3} [\cos(\arcsin(z/1.2))]^{4.3304} + 3.3288 \times 10^{-4}\}$$

Then the overall conductance  $G$  originates from the through-space tunneling conductance  $G_t$  and molecular tunneling conductance  $G_m$  by combining equation (5) with equation (8),

$$(9) \quad \log(G/G_0) = \log((G_t + G_m)/G_0) \\ = \log\{10^{-4.393z} + 2.1 \times 10^{-3} [\cos(\arcsin(z/1.2))]^{4.3304} + 3.3288 \times 10^{-4}\}$$

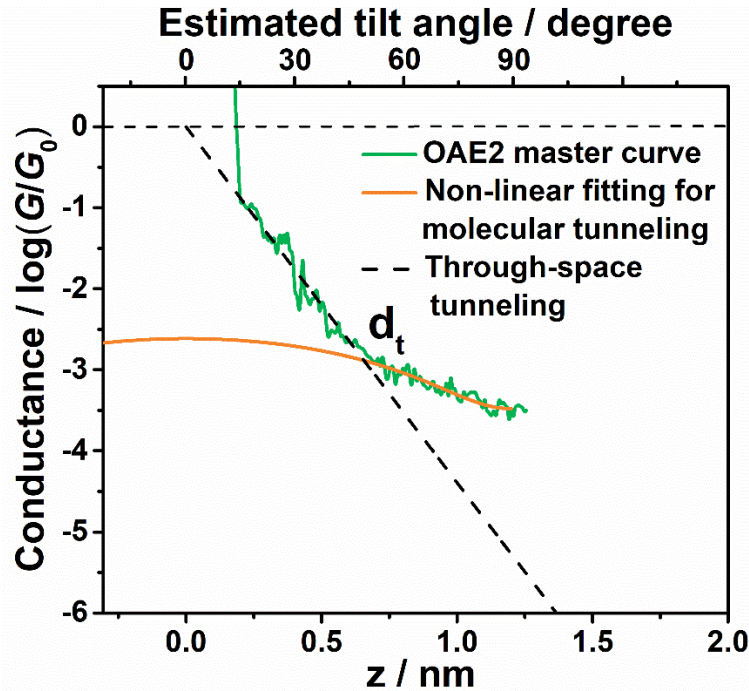


Figure S9. Non-linear fitting (orange curve) of the through-molecular tunneling regime of the master curve of the closing process. The top-z axis shows the corresponding estimated tilt angle of the molecular junction, the parts of the master curve where the molecular junction break into background are omitted.

Therefore, the intersection of the through-space tunneling and molecular tunneling will be obtained by setting the equation (5) equal to equation (8), and the transition distance  $\alpha_t$  will be about 0.66 nm, as shown in Figure S9.

5. The conductance-distance evolution for OAE2, 3, 4 and 5.

Furthermore, for other OAE molecules, the non-linear fitting of the molecular conductance plateau  $G_m$  was also conducted based on equation (7).

For OAE3, the molecular length is 1.9 nm, the fitting range of  $z$  is from 1.0 to 1.8 nm for the molecular conductance plateau, the  $r^2$  is 0.9086.

$$(10) \quad \log\left(\frac{G_m}{G_0}\right) = \log\left\{1.5099 \times 10^{-4} [\cos(\arcsin(z/1.9))]^{4.5403} + 2.2712 \times 10^{-5}\right\}$$

Then the whole close curve of OAE3 can be fitted as

$$(11) \quad \begin{aligned} \log\left(\frac{G}{G_0}\right) &= \log\left(\frac{G_t + G_m}{G_0}\right) \\ &= \log\left\{10^{-4.393z} + 1.5099 \times 10^{-4} [\cos(\arcsin(z/1.9))]^{4.5403} + 2.2712 \times 10^{-5}\right\} \end{aligned}$$

For OAE4, the molecular length is 2.5 nm, the fitting range of  $z$  is from 1.2 to 2.5 nm for the molecular conductance plateau, the  $r^2$  is 0.8078.

$$(12) \quad \log\left(\frac{G_m}{G_0}\right) = \log\left\{8.3686 \times 10^{-6} [\cos(\arcsin(z/2.5))]^{4.1514} + 2.7518 \times 10^{-6}\right\}$$

Then the whole close curve of OAE4 can be fitted as

$$(13) \quad \begin{aligned} \log\left(\frac{G}{G_0}\right) &= \log\left(\frac{G_t + G_m}{G_0}\right) \\ &= \log\left\{10^{-4.393z} + 8.3686 \times 10^{-6} [\cos(\arcsin(z/2.5))]^{4.1514} + 2.7518 \times 10^{-6}\right\} \end{aligned}$$

For OAE5, the molecular length is 3.3 nm, the fitting range of  $z$  is from 1.5 to 3.2 nm for the molecular conductance plateau, the  $r^2$  is 0.8309.

$$(14) \quad \log\left(\frac{G_m}{G_0}\right) = \log\left\{3.8405 \times 10^{-7} [\cos(\arcsin(z/3.3))]^{4.2380} + 7.8576 \times 10^{-8}\right\}$$

Then the whole closing curve of OAE5 can be fitted as

$$(15) \quad \begin{aligned} \log\left(\frac{G}{G_0}\right) &= \log\left(\frac{G_t + G_m}{G_0}\right) \\ &= \log\left\{10^{-4.393z} + 3.8405 \times 10^{-7} [\cos(\arcsin(z/3.3))]^{4.2380} + 7.8576 \times 10^{-8}\right\} \end{aligned}$$

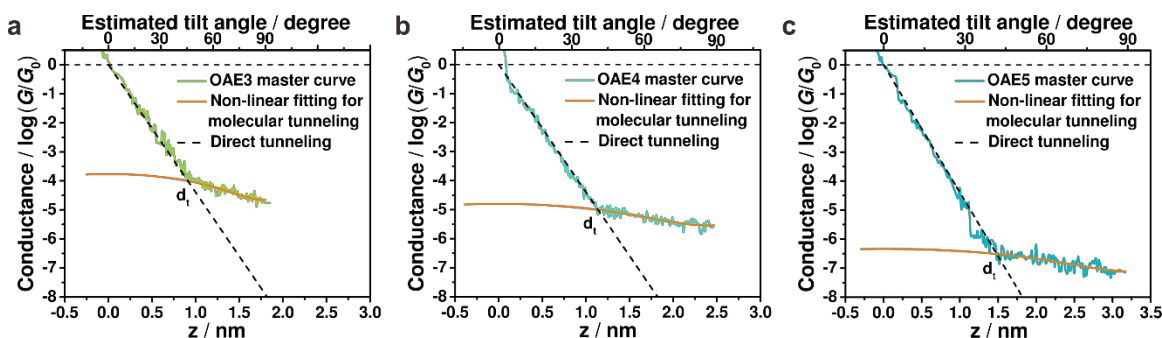


Figure S10. The master curves of the closing processes of (a) OAE3 (b) OAE4 and (c) OAE5, with orange lines for non-linear fittings of the through molecular tunneling regime, top- $z$  axes show the corresponded estimated tilt angles of the molecule junctions, the parts of the master curve where the molecular junctions break into background are omitted.

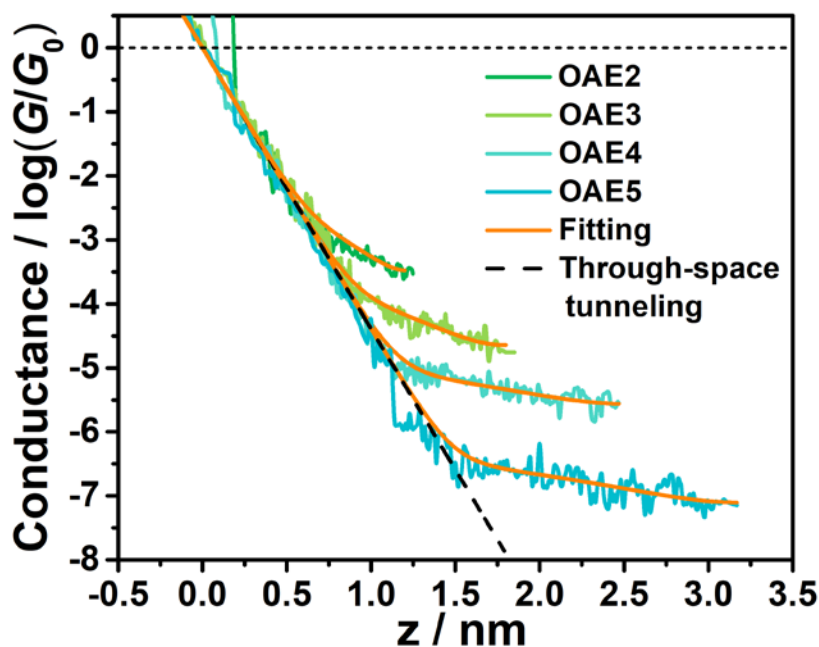


Figure S11. The superimposed master curves of the closing processes of OAE molecules, with orange lines for non-linear fittings of the through-molecular tunneling regime.

Therefore, we can also calibrate the absolute distance for the other three closing processes. The non-linear fitting, as mentioned above, was also conducted for the original extracted master curves of OAE3 to OAE5, along with OAE2, which are shown as orange lines in Figure S10. Hence, as discussed for OAE2, the fitted molecular tunneling curve of other three OAE molecules will also cross over the through-space tunneling, and the transition points from molecular tunneling regime to through-space tunneling regime can be obtained for setting equations (10), (12) and (14) equals to equation (5), respectively, which are 0.91, 1.2 and 1.5 nm. In summary, the transition distances for OAE2 to OAE5 will be 0.66, 0.91, 1.2 and 1.5 nm, respectively, as shown in Table 1 in the main text.

Besides, the correlation between the absolute electrode distance and the overall conductance evolution was obtained. As a consequence, all the master curves from the closing processes of OAE2 to OAE5 were aligned at the original point according to the above discussion, and the fitted overall conductance evolution can be plotted by equations (9), (11), (13) and (15) for OAE2 to OAE5, respectively, as shown in Figure S11 and Figure 4A in the main text. Interestingly, the slopes of the through-space tunneling regime of OAE3 – OAE5 molecules were almost the same as that of OAE2, suggesting that the  $\beta_T$  in the molecular solution was actually different from that in pure solvent, and moreover, the  $\beta_T$  is almost the same while using different OAEs self-assembled on gold surfaces.

## 6. The conductance measurements of OAE2 under different stretching rates

We have also tried different stretching rates of 6.9 nm/s and 14 nm/s using different samples, both of the 2D conductance-distance histograms exhibited the same scenarios with two regimes of through-space tunneling and molecular tunneling. The master curves under those two stretching rates also show a prominent transition feature, as shown and summarized in Figure S12 below, the dash line indicates the transition point before adding the calibration distance. Therefore, we consider that different stretching rates have no influence on the conductance measurements.

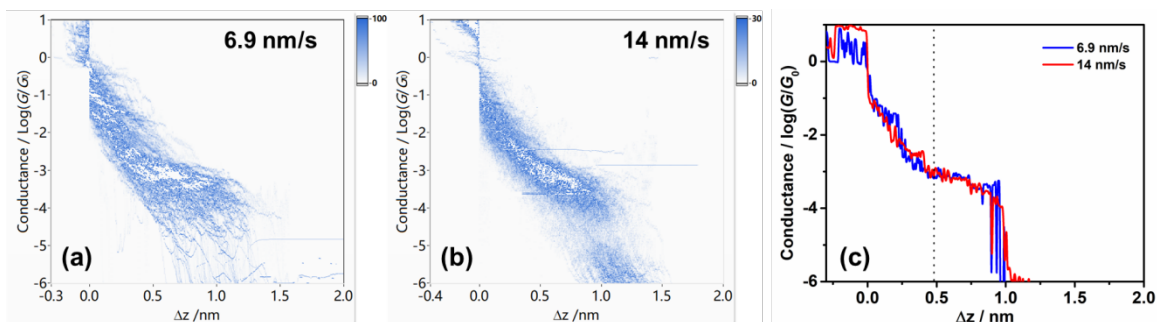


Figure S12. The conductance distance histograms of closing process under the electrodes approaching rate of (a) 6.9 nm/s and (b) 14 nm/s. The master curves extracted from both conditions were plotted together for comparison, the dash line indicates the transition between through-space tunneling and molecular tunneling.

## 7. The conductance measurements of OAE2 under different bias voltages.

The current of tunneling leakage will increase as the electric field increase, however in our measurement, we used conductance values to provide more intrinsic properties. Nevertheless, we still need to evaluate the voltage dependence of the transition distance.

Further experiments on OAE2 under different bias voltage are shown in Figure S13. The closing process under different bias also exhibited two regimes with through-space tunneling and molecular tunneling, same as the phenomenon observed under bias voltage of 100 mV. After the same calibration process described in section 4&5 in supplemental information, the fitting results are shown below:

For 50 mV, the molecular tunneling regime was fitted as plotted in orange line in Figure S13(a):

$$\log\left(G_m/G_0\right) = \log\left\{2.8 \times 10^{-3}[\cos(\arcsin(z/1.2))]^{4.0949} + 5.68 \times 10^{-4}\right\}$$

which the regression coefficient  $r^2 = 0.9403$ . The transition distance is 0.63 nm.

For 200 mV, the molecular tunneling regime was fitted as plotted in orange line in Figure S13(b):

$$\log\left(G_m/G_0\right) = \log\left\{3.2 \times 10^{-3}[\cos(\arcsin(z/1.2))]^{4.2267} + 5.94 \times 10^{-4}\right\}$$

which the regression coefficient  $r^2 = 0.9573$ . The transition distance is 0.62 nm.

For 300 mV, the molecular tunneling regime was fitted as plotted in orange line in Figure S13(c):

$$\log\left(G_m/G_0\right) = \log\left\{3.1 \times 10^{-3}[\cos(\arcsin(z/1.2))]^{4.1520} + 4.30 \times 10^{-4}\right\}$$

which the regression coefficient  $r^2 = 0.9296$ . The transition distance is 0.64 nm.

Since the transition distance obtained in our previous condition of 100 mV was 0.66 nm, the above calculated transition distance under other bias voltages were in accord with our prediction, which indicating that the transition between through-space tunneling and molecular tunneling is independent to the small bias voltage range.

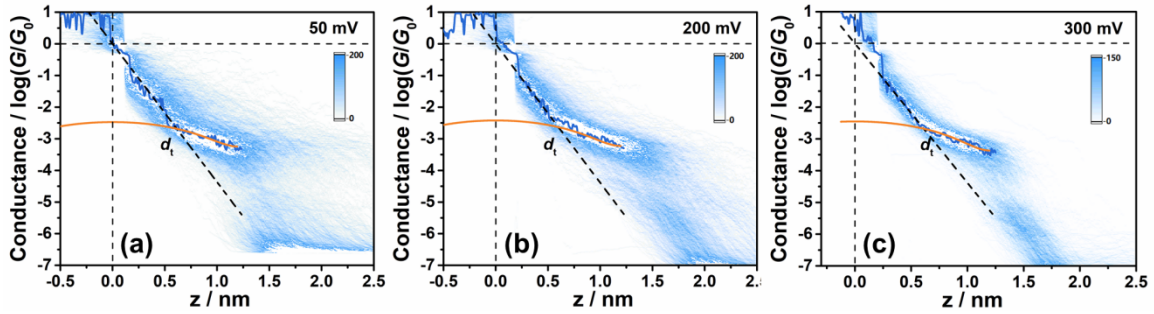


Figure S13. The calibrated closing processes with the corresponded 2D conductance-distance histograms under the bias voltage of (a) 50 mV, (b) 200 mV and (c) 300 mV. The orange line plotted on the master curve shows the fitting result of the molecular tunneling regime, while the tilt dash line shows through-space tunneling regime.

Since our previous work had obtained the  $I$ - $V$  properties of OAE2 junction,<sup>1</sup> the bias voltage of 100 mV in this work is relatively small and still locates at the linear area in the current-voltage curves of OAE molecular junctions, we considered the conductance features obtained are bias independent within the small bias range. Therefore, when using a small measuring voltage, the charge transport mechanism through molecular junction is still coherent tunneling, the transition distance might not be changed.

While for a much higher voltage, the Fowler-Nordheim tunneling will happen with increased conductance.<sup>8</sup> Previous simulation suggested that as the electrodes gap becomes smaller, the transition voltage decreases,<sup>4</sup> which means that as the gap decreases, it needs smaller bias voltage to evolve to the Fowler-Nordheim tunneling, thus much higher tunneling leakage will outstrip the intrinsic molecular tunneling when the electrodes approaching together. As a consequence, it will be earlier to reach the transition point from molecular tunneling to through-space tunneling during the closing process, causing a longer transition distance. However, since it needs high bias voltage (such as OPE3-NH<sub>2</sub> the  $V_{\text{trans}}$  was reported to be 0.65 V)<sup>9</sup> to realize the

Fowler-Nordheim tunneling, the conductance measurement is difficult to be done because the molecular junction becomes rather unstable. Unfortunately, we cannot find obvious conductance features under such high bias voltage. Nevertheless, it is of vital importance to confirm our assumption and we try to make thorough investigations about the bias-dependent transition in another work in the future.

8. Super-exchange and hopping contribution calculations for the OAE series.

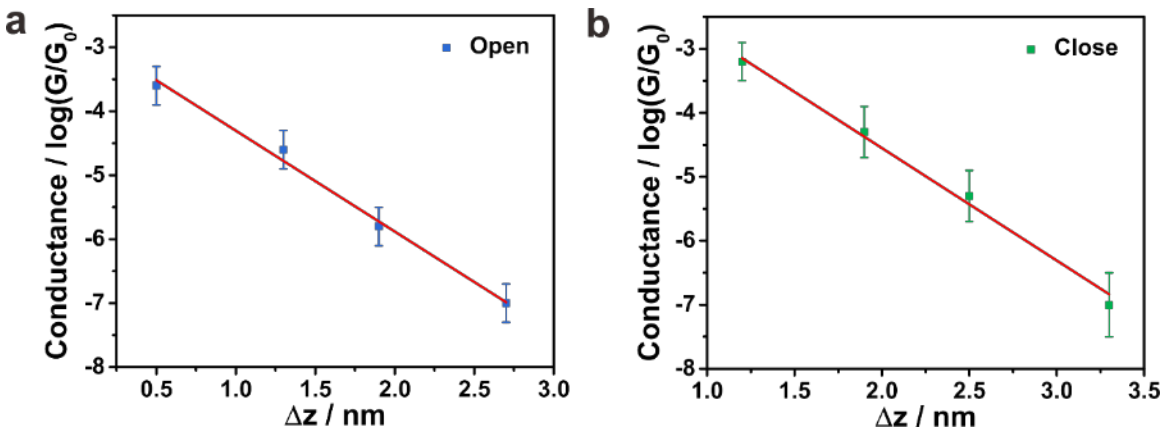


Figure S14. Tunneling decay constant fitting for the measured (a) opening and (b) closing processes of the OAE series.

Single molecule charge transport may originate from different mechanisms even in the same junction geometry. Therefore, we chose the OAE series extended only to OAE5, for which previous data established that the super-exchange mechanism still predominates.<sup>10</sup> Using the measured conductance data, we are able to obtain the tunneling decay constant  $\beta$  of the opening and closing processes, as shown in Figure S14(a) and Figure S14(b), respectively. The fitted  $\beta$  values of opening and closing processes are  $3.6 \pm 0.2 \text{ nm}^{-1}$  and  $4.0 \pm 0.2 \text{ nm}^{-1}$ , respectively. Both values are close to those calculated by Zhao et al.,<sup>10</sup> indicating that the super-exchange tunneling is indeed the major contribution from OAE2 to OAE5. Moreover, we also adopted the  $\beta$  value of the hopping mechanism obtained previously from OAE6 to OAE9 by Zhao et al.,<sup>10</sup> to extend to the short OAE series for calculating the hopping contribution. It was found that the hopping contributions from OAE2 to OAE4 are 0.093%, 0.851% and 12.3%, respectively, as shown in Figure S15. Therefore, the hopping contributions in OAE2 and OAE3 can be totally eliminated, while in OAE4 and OAE5 they cannot be neglected.

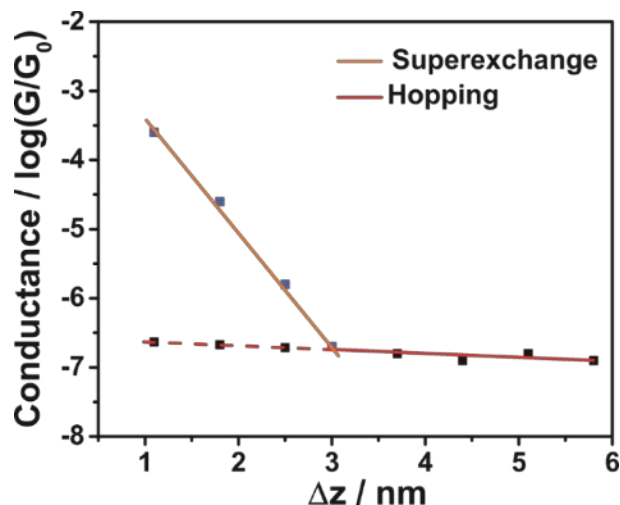


Figure S15. Hopping contribution fitted for shorter OAE series.

Nevertheless, although this work mainly focused on the through-space tunneling between the pair of electrodes and through-molecule tunneling, the ballistic and hopping tunneling both belong to the latter, which both originate from the molecular junction configuration.

9. Calculation of the through-molecule tunneling contributions of the OAE series.

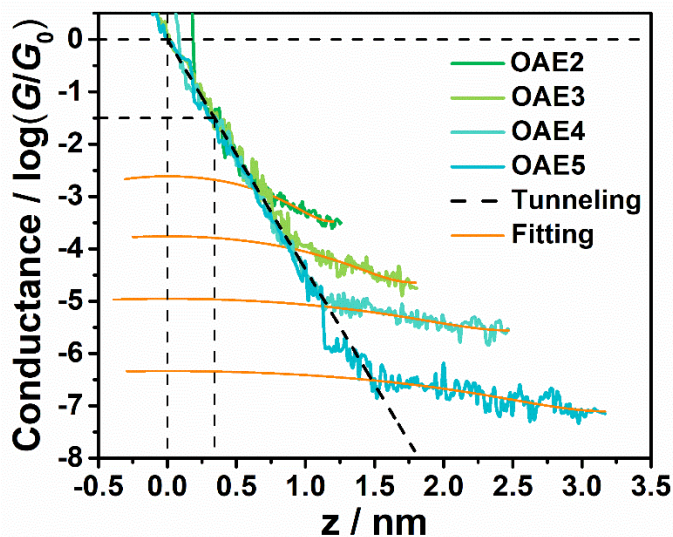


Figure S16. Calculation of through-molecule tunneling contribution of the OAE series.

We assumed that the molecular junction configurations in the lower panels of Figure S8(a) and S8(b) are typical configurations when the molecule has not been fully stretched in a relatively small gap between the pair of electrodes. Therefore, both the direct and molecular tunneling could contribute to the total conductance. Since we had calibrated the absolute distance scale, the

conductance evolution with an exact electrode gap size can be determined. Hence, here we discuss the shoulder feature around  $10^{-1.5} G_0$  in Figure 2B in the main text, and the specific electrode gap size can be deduced by equation (5), which  $z$  will be 0.341 nm.

As shown in Figure S16, the through-molecule tunneling contribution can be calculated according to equation (8) to (11) for such a gap, and we found that the molecular tunneling contributions around  $10^{-1.5} G_0$  of OAE2 to OAE5 are about  $10^{-2.68} G_0$ ,  $10^{-3.79} G_0$ ,  $10^{-4.96} G_0$  and  $10^{-6.34} G_0$ , respectively, which suggests that the through-molecule tunneling contributes 6.61% for OAE2, 0.513% for OAE3, 0.0347% for OAE4 and 0.00144% for OAE5. Therefore, the case of OAE2 confirmed the former theoretical prediction, suggesting that through-space tunneling predominates, while molecular tunneling cannot be neglected. However, in longer OAE molecules the through-space tunneling around  $10^{-1.5} G_0$  predominates, and their molecular tunneling can be neglected. That is probably the reason that there is no other shoulder feature around  $10^{-1.5} G_0$  for all other longer OAE molecules. In conclusion, the through-space tunneling contributes mostly in the smaller gap beyond the molecular junction is fully stretched.

#### 10. The transition in other conjugated system.

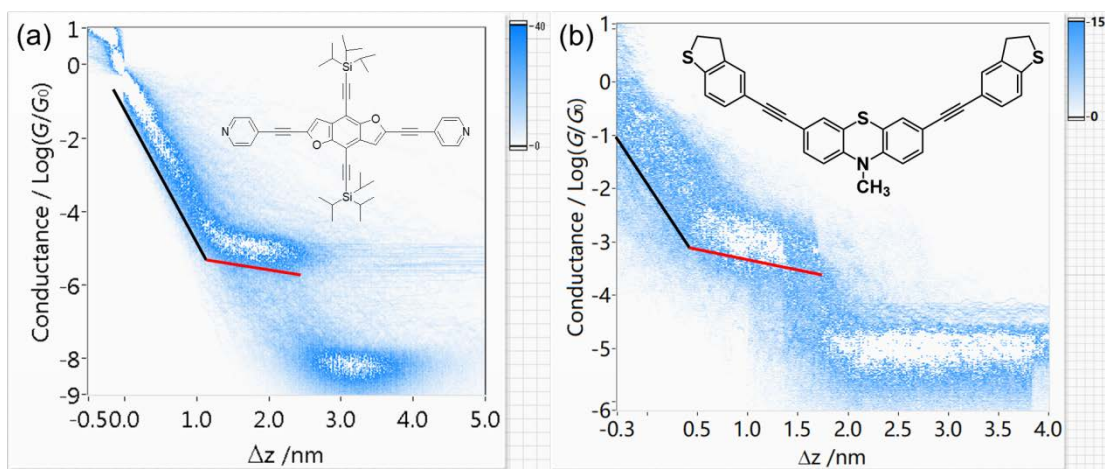


Figure S17. The conductance-distance histogram of the closing process of (a) the cruciform benzondifuran molecule and (b) phenothiazine derivative. Both of the histogram shows two distinct different regimes of firstly molecular tunneling (labelled by red line) then transitioning to through-space tunneling (labelled by black line) during the electrodes approaching.

There're other rigid conjugated examples exhibiting the same closing behaviour as the OAE series. The cruciform benzondifuran molecule<sup>11</sup> and the phenothiazine derivatives<sup>12</sup> which we had just published their conductance features in opening process, also showed prominent transition features in the closing process, as shown in Figure S17 (those data haven't been published). The transition distance from Figure S17(a) of the cruciform benzondifuran molecule is about 1 nm however the molecular length is 2.2 nm, and from Figure S17(b), the transition distance of the phenothiazine derivative is about 0.5 nm however the molecular length is 2.1 nm, suggesting that this physical phenomenon of transition is common in conjugated systems and highly depends the chemical structure of the molecular junctions.



## References

1. Hong, W., Manrique, D.Z., Moreno-García, P., Gulcur, M., Mishchenko, A., Lambert, C.J., Bryce, M.R., and Wandlowski, T. (2012). Single molecular conductance of tolans: Experimental and theoretical study on the junction evolution dependent on the anchoring group. *J. Am. Chem. Soc.* *134*, 2292-2304.
2. Hong, W., Valkenier, H., Mészáros, G., Manrique, D.Z., Mishchenko, A., Putz, A., García, P.M., Lambert, C.J., Hummelen, J.C., and Wandlowski, T. (2011). An MCBJ case study: The influence of  $\pi$ -conjugation on the single-molecule conductance at a solid/liquid interface. *Beilstein J. Nanotechnol.* *2*, 699-713.
3. Untiedt, C., Caturla, M.J., Calvo, M.R., Palacios, J.J., Segers, R.C., and van Ruitenbeek, J.M. (2007). Formation of a metallic contact: Jump to contact revisited. *Phys. Rev. Lett.* *98*, 206801.
4. Trouwborst, M.L., Martin, C.A., Smit, R.H.M., Guedon, C.M., Baart, T.A., van der Molen, S.J., and van Ruitenbeek, J.M. (2011). Transition voltage spectroscopy and the nature of vacuum tunneling. *Nano Lett.* *11*, 614-617.
5. Kornilovitch, P.E., and Bratkovsky, A.M. (2001). Orientational dependence of current through molecular films. *Phys. Rev. B* *64*, 195413.
6. Toyoda, K., Morimoto, K., and Morita, K. (2006). First-principles study on current through a single  $\pi$  conjugate molecule for analysis of carrier injection through an organic/metal interface. *Surf. Sci.* *600*, 5080-5083.
7. Diez-Perez, I., Hihath, J., Hines, T., Wang, Z.-S., Zhou, G., Mullen, K., and Tao, N. (2011). Controlling single-molecule conductance through lateral coupling of  $[p]$  orbitals. *Nat. Nanotechnol.* *6*, 226-231.
8. Beebe, J.M., Kim, B., Gadzuk, J.W., Daniel Frisbie, C., and Kushmerick, J.G. (2006). Transition from direct tunneling to field emission in metal-molecule-metal junctions. *Phys. Rev. Lett.* *97*, 026801.
9. Lu, Q., Liu, K., Zhang, H., Du, Z., Wang, X., and Wang, F. (2009). From tunneling to hopping: A comprehensive investigation of charge transport mechanism in molecular junctions based on oligo(*p*-phenylene ethynylene)s. *ACS Nano* *3*, 3861-3868.
10. Zhao, X., Huang, C., Gulcur, M., Batsanov, A.S., Baghernejad, M., Hong, W., Bryce, M.R., and Wandlowski, T. (2013). Oligo(aryleneethynylene)s with terminal pyridyl groups: Synthesis and length dependence of the tunneling-to-hopping transition of single-molecule conductances. *Chem. Mater.* *25*, 4340-4347.
11. Huang, C., Chen, S., Baruël Ørnsø, K., Reber, D., Baghernejad, M., Fu, Y., Wandlowski, T., Decurtins, S., Hong, W., Thygesen, K.S., *et al.* (2015). Controlling electrical conductance through a  $\pi$ -conjugated cruciform molecule by selective anchoring to gold electrodes. *Angew. Chem. Int. Ed.* *54*, 14304-14307.
12. Liu, J., Zhao, X., Al-Galiby, Q., Huang, X., Zheng, J., Li, R., Huang, C., Yang, Y., Shi, J., Manrique, D.Z., *et al.* (2017). Radical enhanced charge transport in single-molecule phenothiazine electrical junctions. *Angew. Chem. Int. Ed.* *56*, 13061-13065.