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Uncovering a law of corresponding states for electron tunneling in molecular junctions†

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Laws of corresponding states known so far demonstrate that certain macroscopic systems can be described in a universal manner in terms of reduced quantities, which eliminate specific substance properties. To quantitatively describe real systems, all these laws of corresponding states contain numerical factors adjusted empirically. Here, we report a law of corresponding states deduced analytically for charge transport *via* tunneling in molecular junctions, which we validate against current–voltage measurements for conducting probe atomic force microscope junctions based on benchmark molecular series (oligophenylenedithiols and alkanedithiols) and electrodes (silver, gold, and platinum), as well as against transport data for scanning tunneling microscope junctions. Two salient features distinguish the present law of corresponding states from all those known previously. First, it is expressed by a universal curve free of empirical parameters. Second, it demonstrates that a universal behavior is not necessarily affected by strong stochastic fluctuations often observed in molecular electronics. An important and encouraging message of this finding is that transport behavior across different molecular platforms can be similar and extraordinarily reproducible.

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1. Introduction

The idea of universality and the related law of corresponding states (LCS) trace back to van der Waals,¹ who predicted that all fluids at equilibrium behave similarly; if appropriately renormalized, their parameters of state (pressure p , volume V and temperature T) obey the same equation

$$\left(p_{\text{R}} + \frac{3}{V_{\text{R}}^2}\right) \left(V_{\text{R}} - \frac{1}{3}\right) = \frac{8}{3} T_{\text{R}} \quad (1)$$

In a fluid, the critical values (p_{c} , V_{c} , and T_{c}) at the liquid–gas transition represent the natural units to define the reduced (dimensionless) parameters entering eqn (1)

$$p_{\text{R}} \equiv p/p_{\text{c}}, V_{\text{R}} \equiv V/V_{\text{c}}, \text{ and } T_{\text{R}} \equiv T/T_{\text{c}} \quad (2)$$

Later on the notion of universality found its most fruitful realization in the renormalization group approach to phase

transitions and critical phenomena.² Laws of corresponding states were found for a series of equilibrium properties as well as transport coefficients (*e.g.*, thermal conductivity, viscosity and self-diffusion) describing macroscopic fluids in the linear response regime.^{3–6} More recently, laws of corresponding states^{7,8} and universal behaviors^{9,10} have also been discussed for charge transport *via* hopping in organic semiconducting materials.

It might seem obvious that experimental data could exhibit a universal behavior only in situations, wherein, like those mentioned above, the fabrication of the materials/devices under investigation is a well-controlled process, and their properties are highly reproducible. From this perspective, attempting to find laws of corresponding states for molecular electronic devices seems to be extremely out of place; it is hard to expect universality for molecular junctions that are fabricated with a broad spectrum of different architectures and wherein measurements often yield conductance histograms having widths comparable to or larger than the most probable values.^{11–15} Nevertheless, and this is one of the most striking aspects of the results reported below, we demonstrate that the current–voltage (I – V) curves measured for molecular junctions based on two prototypical, completely different molecular series (oligophenylenedithiols and alkanedithiols) and commonly employed electrodes (Ag, Au and Pt) obey a remarkably simple LCS.

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2. Results

2.1 Natural units for current and voltage

Similar to eqn (1), an LCS I_R vs. V_R relationship — expressing the I - V dependence in reduced, dimensionless quantities $I_R \equiv I/I_c$ and $V_R \equiv V/V_c$ —requires “critical” values for current I_c and voltage V_c to be used as natural units for these quantities. The challenge with respect to molecular junction measurements is to identify these natural units, given the fact that transport measurements on molecular junctions often yield featureless I - V curves (Fig. 1a). Our recipe is the following: recast the data as $|V^2/I|$ vs. V , and curves exhibiting maxima are obtained (Fig. 1b), which can be used to define the desired natural units V_c and I_c for voltage and current, respectively. The “critical” voltage V_c defined in this way represents an alternative to the so-called transition voltage introduced in recent molecular electronics studies;^{16–18} it characterizes the cross-over between a basically linear (ohmic) regime at (lower) biases $V < V_c$ and pronounced non-linear regime at (higher) biases $V > V_c$ ¹⁹ (cf. ESI†). Importantly for the present analysis, V_c and I_c represent properties of a given junction.

So, we are led to define reduced, dimensionless voltage and current variables as

$$V_R \equiv V/V_c \text{ and } I_R \equiv I/I_c \quad (3)$$

Notice that, similar to eqn (2), where the critical parameters are specific properties of a given fluid, our natural units V_c and I_c are essential characteristics of a given molecular device.

2.2 CP-AFM experimental results as basis for the presently reported LCS

Experimental results confirming the basis of the LCS consist, initially, of our own I - V measurements done on conducting probe atomic force microscope (CP-AFM) molecular junctions fabricated using two prototype molecular series and three widely employed electrode materials ($M = \text{Ag, Au, Pt}$), Fig. 2. One series, alkanedithiols, $M/CnDT/M \equiv M-S-(CH_2)_n-S-M$ ($n = 8$ to 11) has a σ -saturated aliphatic backbone. The other

series, oligophenylenedithiols, $M/OPDn/M \equiv M-S-(C_6H_4)_n-S-M$ ($n = 1$ to 4) possesses π -electrons delocalized over aromatic rings.

Fig. 2 displays an ensemble comprising ~ 570 I - V curves measured up to biases (~ 1.5 V) with pronounced nonlinearity for the $24 = 3 \times (4 + 4)$ aforementioned classes of CP-AFM junctions, which we have recast in the reduced variables I_R and V_R defined in eqn (3). Despite the variability in the molecular species and electrodes of the CP-AFM junctions considered, despite the fact that the ohmic (low bias) conductances G across these 24 classes vary over more than five orders of magnitude (ohmic resistances $R \equiv 1/G$ are $R \approx 181$ M Ω for Ag/C11DT/Ag and $R \approx 900$ Ω for Pt/OPD1/Pt) and, to a lesser extent, within individual junctions of a given class (e.g., between the 28 individual I - V traces for Ag/OPD2/Ag, cf. Fig. S1a in the ESI†), all these reduced I_R - V_R curves are very close to each other: within statistical deviations (Fig. 2 and S1—S6 in the ESI†) and measurement errors (Fig. S8 and S9 in the ESI†), they collapse on a single universal I_R - V_R curve. This behavior exhibited by the reduced I_R - V_R curves (Fig. 2) clearly contrasts with the strong scattering in the raw I - V measurements depicted in Fig. 3.

2.3 Theoretical basis of the LCS

Most importantly, these experimental I_R - V_R curves excellently agree with a result that can be deduced theoretically. A preliminary comment is in order, however. It should be clear that a universal curve characterizing an experimental diversity of molecular junctions (and also applying to other experimental platforms, see below) can only follow if all these cases share a general common microscopic feature. It is implausible to expect universal transport behavior if demanding *ab initio* approaches or even sophisticated phenomenological models containing (many) system-specific parameters were needed to describe transport accurately for each of the cases considered here.²⁰ So, it is most natural to assume (or at least to start the analysis by assuming) that the charge transport is dominated by a single molecular orbital, the HOMO or the LUMO, as schematically depicted in Fig. 4.

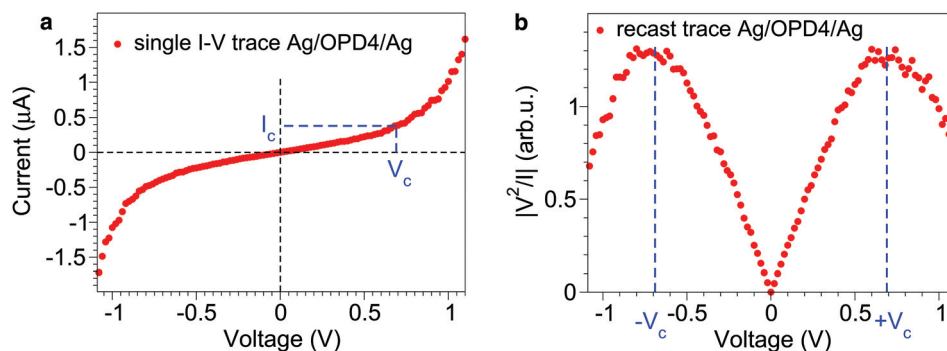


Fig. 1 Natural units for voltage V and current I in molecular junctions. (a) Example of a typical featureless I - V curve measured in transport experiments. (b) By recasting it as $|V^2/I|$ vs. V , a maximum is obtained that can be used to define natural units V_c and I_c for voltage and current, respectively. These units are employed to define reduced biases ($V_R \equiv V/V_c$) and currents ($I_R \equiv I/I_c$), which satisfy an appealingly simple law of corresponding states, eqn (6), for the charge transport via tunneling in molecular junctions.



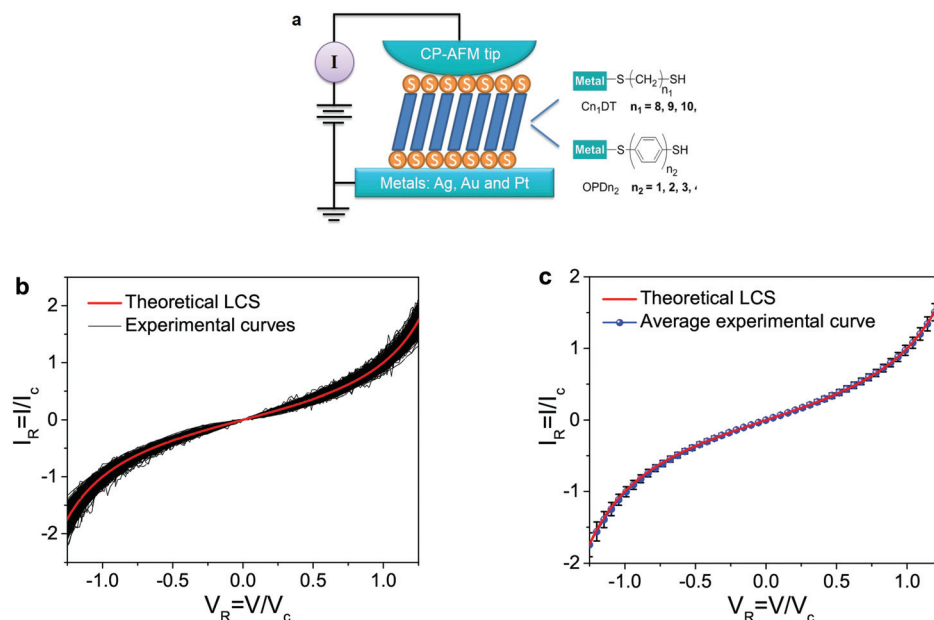


Fig. 2 Experimental and theoretical results for oligophenylene- and alkane-dithiol-based CP-AFM junctions. (a) Schematic representation of a metal-molecule-metal junction made by contacting a self-assembled monolayer (SAM) of oligophenylene- (M/OPDn/M, $n = 1$ to 4) and alkane- (M/CnDT/M, $n = 8$ to 11) dithiol species with a conducting atomic force microscope tip. (b) The theoretical universal (red) curve of eqn (6) plotted along with ~ 570 experimental I_R - V_R curves (black) measured for 24 different types of molecular junctions consisting of OPDn and CnDT molecules linked to metallic electrodes (M = Ag, Au, and Pt). (c) Comparison of the theoretical (red) curve, eqn (6), and the statistical average (blue line) of a statistical ensemble comprising ~ 570 experimental curves analyzed. Error bars (black) represent standard statistical deviations.

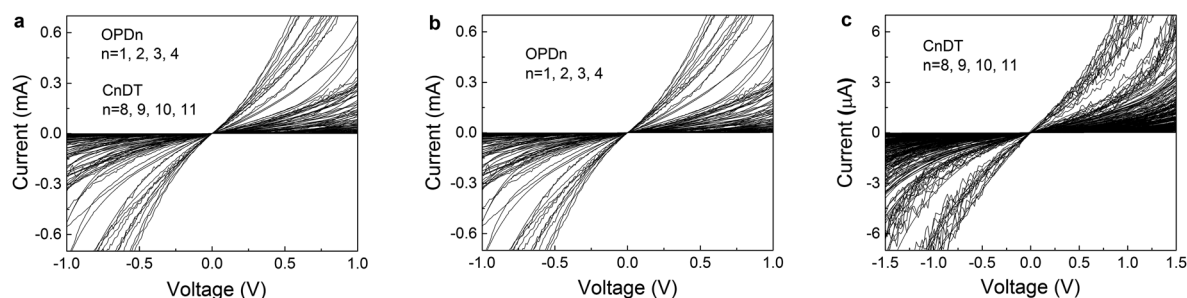


Fig. 3 Unlike the normalized I_R - V_R curves of Fig. 2, the raw current-voltage I - V curves of the CP-AFM junctions analyzed in the present work exhibit a strong scattering. In panel a, all (~ 570) I - V curves measured on the oligophenylene- (OPDn-) and alkane- (CnDT-)dithiol-based junctions are overlaid. Because of the different orders of magnitudes of the currents – similar to the low-bias conductance G ($G_{\min} < G < G_{\max}$ range given in the left panels of Fig. S1–S6 in the ESI† for each type of molecule and electrode) –, the curves for the two molecular series OPDn and CnDT are also presented separately (panels b and c, respectively).

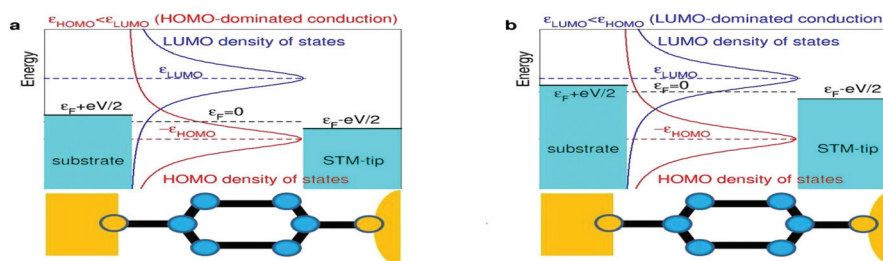


Fig. 4 In most cases one expects that the charge transport through a molecular junction is dominated by the frontier molecular orbital, i.e. HOMO (panel a) or LUMO (panel b), whichever is the closest to the Fermi level.

For biases of interest, not much larger than V_c (the curves analyzed are almost unchanged upon reversing the bias polarity, so we choose $V_c > 0$ here), the current through a junction due to the tunneling mediated by a single level characterized by an energy offset ε_0 relative to the electrodes' Fermi energy can be expressed in closed analytical form (e is the elementary charge)²¹

$$I = GV \frac{\varepsilon_0^2}{\varepsilon_0^2 - (eV/2)^2} \quad (4)$$

The values of the bias V_c and the current I_c at the maximum of the quantity $|V^2/I|$ can be immediately obtained by using eqn (4) as

$$eV_c = 2|\varepsilon_0|/\sqrt{3} \text{ and } I_c \equiv I(V = V_c) = G|\varepsilon_0|\sqrt{3}/e \quad (5)$$

Eqn (5) expresses in mathematical form the physical fact that the cross-over values V_c and I_c represent properties of a given junction. It is noteworthy that, in particular, the peak bias V_c in Fig. 1b is directly related to the energy alignment ε_0 relative to the Fermi energy of the dominant molecular orbital. Using the reduced quantities of eqn (3), we can recast eqn (4) in the form

$$I_R = \frac{2V_R}{3 - V_R^2} \quad (6)$$

Eqn (6) is our “law of corresponding states” for the charge transport *via* tunneling through molecular junctions. The agreement between the theoretical result of eqn (6) and experiments, based on statistics performed over an ensemble comprising ~570 I - V curves measured on a large variety of CP-AFM junctions (Fig. 2 and S1–S6 in the ESI†) is remarkable, particularly in view of the appealing simplicity of eqn (6).

The theory agrees with experiments even better than Fig. 2b (with ~570 individual I - V traces) and Fig. 2c (statistically averaged measurements) may indicate. The theory stands the test of trace-by-trace analysis. For each class out of the 24 classes of junctions considered, we depict in Fig. S8 and S9 in the ESI†

the individual I_R - V_R trace with the largest deviation from the theoretical curve, along with its vertical and horizontal error bars, which we refer to as “measurement errors”; they are related to uncertainties in identifying the bias $V = V_c$ at the minimum location (Fig. S7 in the ESI†).

2.4 LCS beyond the CP-AFM platforms

Above, we have validated the LCS for the CP-AFM junctions fabricated and measured by us. To demonstrate that the class of universality is even broader, we present results in Fig. 5 for the reduced current-voltage curves reported for scanning tunneling microscope (STM) junctions by other groups.^{11,22–24} These data, spanning a spectrum of different molecules, also agree very well with the theoretical curve (*cf.* Fig. 5).

2.5 How universal is the present LCS?

Section 2.3 made it clear that the physics underlying eqn (6) is the single-level picture. The examples presented above demonstrated that the present LCS applies to sufficiently broad classes of systems. Nevertheless, one cannot expect that, as general as it might be, an LCS like that presently discussed holds in all cases. Renormalization group theory speaks of some systems that belong to a certain universality class and other systems belonging to a different class of universality. Universal laws governing Fermi liquids do not apply to Luttinger liquids and *vice versa*; they belong to different classes of universality.

We do not claim that the present LCS holds in all molecular junctions and do not rule out that cases to which it does not apply may exist. Still, as a last result reported in this paper, we want to show that this LCS also holds in situations where there is no straightforward reason why it should survive: namely, junctions wherein quantum interference effects^{26–29} occur. For illustration (Fig. 6), we will consider a schematic molecular junction consisting of a bridge comprising a donor moiety (D, onsite energy ε_D) and an acceptor moiety (A, onsite energy ε_A) connected to side group (S, onsite energy ε_S).

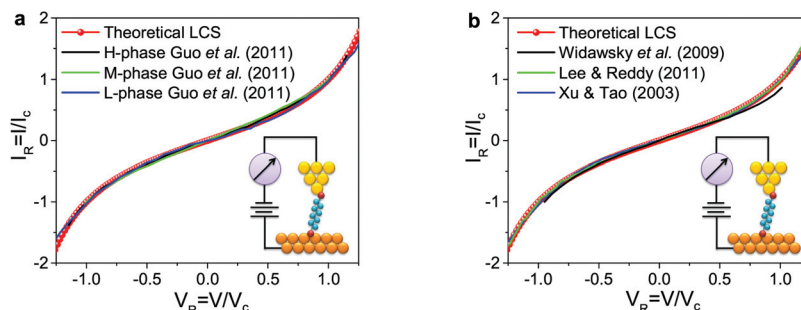


Fig. 5 Reduced current-voltage I_R - V_R curves for STM junctions. The theoretical curve of eqn (6) is plotted along with: (a) averages of 2151; 1661; 1661 I - V traces for the high- (H); medium- (M); low- (L) conductance phases of octanedithiol (C8DT) junctions with gold electrodes (*cf.* ref. 24) and (b) individual I - V traces measured for 4,4'-diaminostilbene,²² C8DT,²³ and 44bpy \equiv 4,4'-bipyridine¹¹ linked to gold electrodes. For these STM junctions, the ohmic resistance R varies over three orders of magnitudes [$R \approx 1.3$ M Ω (ref. 11) to $R \approx 1.2$ G Ω (L-phase, ref. 24)]. Notice that the 44bpy-based junction exhibits n-type conduction and was measured in solvent,^{11,25} in contrast to all the other junctions considered in this work, which are characterized by p-type conduction and measured in ambient conditions.



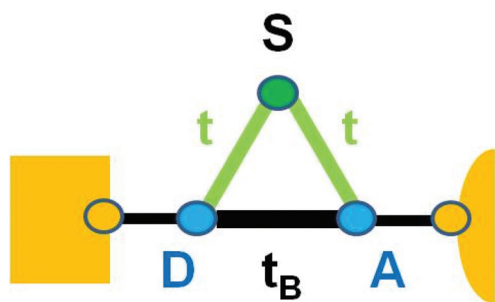


Fig. 6 To model quantum interference effects, we consider a schematic molecular junction consisting of donor (D) and acceptor (A) units coupled to a side group (S), each described as single level having energy offsets ε_D , ε_A , and ε_S relative to electrodes' Fermi level. Their coupling is characterized by the hopping integrals t and t_B , as indicated in the figure.

Exact results for this model can be obtained *via* straightforward Landauer-based calculations.³⁰ Conductance G , energy-dependent transmission $T(E)$, and current-voltage curves are depicted in Fig. 7. As a result of destructive quantum interference, the transmission $T(E)$ and the conductance G are found to exactly vanish at $E - \varepsilon_S = t^2/t_B$ and $t^2 + t_B\varepsilon_S = 0$, respectively. In Fig. 7, the green, blue and magenta colors correspond to situations where the coupling ($t \neq 0$) to the side group S depresses *via* quantum interference the conductance G by factors of 10, 100, and 1000 with respect to the value without coupling ($t = 0$, coded as red color). For given values of ε_D , ε_A , ε_S , and t_B (see legend of Fig. 7b), each of these situations is defined by a given value of t . The substantial decrease in G demonstrates that quantum interference effects are pronounced in those cases. Nevertheless, deviations from the LCS of eqn (6) of the I_R - V_R curves calculated for all those t -values are insignificant (*cf.* Fig. 7c).

To conclude this analysis, nontrivial effects like quantum interference do not necessarily invalidate the present LCS.

3. Discussion

The starting point of eqn (1) was an equation (the van der Waals equation) proposed empirically and justified later microscopically based on certain assumptions.⁴ While its merit in bringing the notion of universality to the attention of scientific community is undeniable, we should remember that it represents a rather poor approximation of reality; empirical modifications of eqn (1) represent usual practice.⁶ Resorting to numerical coefficients determined *via* fitting is unavoidable to achieve a satisfactory description of the real systems (fluids) to which it refers.^{3,6} Later on, laws of corresponding states as expression of universal behaviors have been reported for a series of equilibrium^{2-4,6} and non-equilibrium^{5,7,8} properties, including full current-voltage curves for charge transport *via* hopping in semiconducting polymers.^{9,10} However interesting these findings are, like in all post-van-der-Waals developments for real fluids, the associated laws of corresponding states for charge transport *via* hopping contain empirical constants that can only be deduced by fitting experimental data.

The fact that the present LCS, eqn (6), deduced analytically for charge transport *via* tunneling, contains no free parameters needing adjustment to experimental data is an important distinction from all the aforementioned cases. Whether p- or n-type (HOMO- or LUMO-mediated) conduction, whether STM-junctions containing a single-molecule or CP-AFM junctions consisting of a larger number molecules, which may furthermore significantly differ from junction to junction, the experimental current-voltage curves in reduced units collapse within errors on a single line agreeing with the theoretically predicted I_R - V_R curve free from any adjustable parameters.

This LCS is robust; it is not affected by the fact that, across the classes of junctions considered here, the conductance varies over more than five orders of magnitude. Significant spreads in conductance values from junction to junction for a given class¹¹⁻¹⁵ do not affect this universal behavior either. So, the LCS is also robust against stochastic fluctuations related to, *e.g.*, the large variability of contact binding mode (*e.g.*,

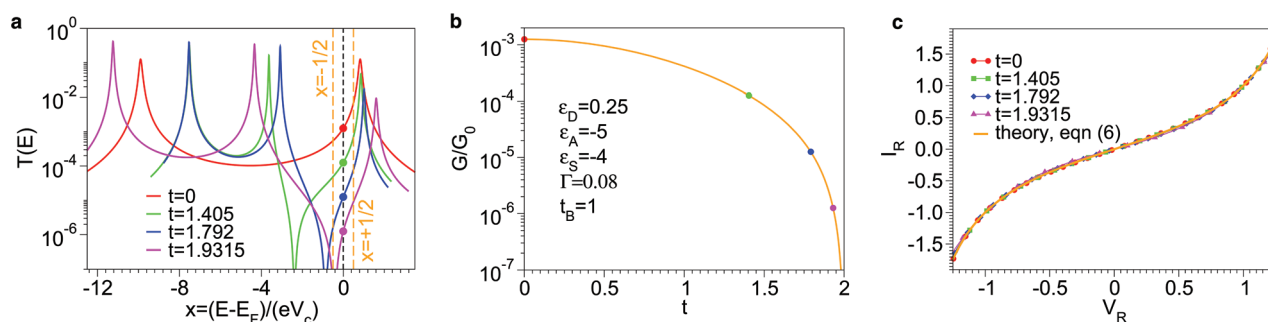


Fig. 7 Results for the junction of Fig. 6: (a) energy-dependent transmission T , (b) conductance G , and (c) current-voltage curves in reduced variables. Quantum interference effects manifest themselves as a vanishing transmission and decreased conductance (G exactly vanishes for $t^2 + t_B\varepsilon_S = 0$). The orange vertical lines in panel a delimitate the energy window $-eV_c/2 < E - E_F < eV_c/2$ that contributes to the current at the bias $V = V_c$. Parameter values as indicated in panel b.

chemi- or physisorption) or geometry (e.g., atop, bridge or hollow²⁴), which typically manifest themselves in very broad histograms.^{11–15} This is another striking contrast with the previously known laws of corresponding states that apply to systems or devices whose fabrication is highly reproducible. Thus, a bright side of the present LCS is that fundamental insight into the nanoscale charge transport of molecular junctions can be gained even with devices for which controllable fabrication still remains a desirable step for the future.

4. Conclusion

Universal laws extensively discussed in phase transitions and critical phenomena utilize physical properties at the critical point like those of eqn (2) as natural units to define relevant reduced dimensionless parameters. As expressed by eqn (3), in formulating the present LCS for tunneling transport, eqn (6), the cross-over voltage V_c (Fig. 1b) and the associated current value I_c at this bias ($V = V_c$) turned out to play an essential role in directly setting the natural units for bias and current. Similar to the critical parameters of eqn (1), it is possible to absorb all specific characteristics of molecular junctions in these natural units V_c and I_c , and the LCS is just the manifestation of this possibility. We believe that the present LCS is an important result for molecular electronics because it shows how straightforwardly results on charge transport can be compared across different platforms and how systems so extremely different at the molecular scale can obey a unique, parameter free, and simple equation.

5. Methods

The metal-molecule-metal junctions were made based on molecules of oligophenylene dithiols (OPDn) and alkane-dithiols (CnDT) bound to three types of electrodes (Ag, Au and Pt). Self-assembled monolayers (SAMs) of these molecules were formed by immersing clean template-stripped flat metal substrates³¹ in ethanol solution: OPDn ($n = 1$ to 4) at a concentration of ~ 0.05 mM and CnDT ($n = 8$ to 11) at a concentration of 1 mM for ~ 20 h. We measured about 570 current-voltage I - V characteristics for these (24 in total) types of CP-AFM junctions; details can be found elsewhere.³² The conductive AFM probes were made by coating the metals (Ag, Au and Pt) on contact mode AFM tips (DNP-10, Bruker Probes). The measurements were completed by mounting the substrates in the AFM and bringing the tip into contact with the SAM under ~ 1 nN of applied compressive load. Voltages were applied to the tip with a Keithley model 236 electrometer operated in “DC mode”. The bias was swept at the tip, the sample was grounded and current-voltage characteristics were recorded. The measurements were carried out in an Ar-filled glove-box (H_2O , $O_2 < 0.1$ ppm). The inverse of the slope of the linear portion of the I - V characteristic at low biases was used to extract the ohmic resistance $R = 1/G$. The cross-over voltage V_c was estimated

from the maximum of the quantity $|V^2/I|$ (Fig. 1 and S7 in the ESI†).

Acknowledgements

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of Charge Transport in Oligophenylene Dithiol Junctions as a Function of Molecular Length and Contact Work Function, preprint), we demonstrated that the HOMO energy offset ε_0 deduced via the present eqn (6) agrees very well both with *ab initio* calculations and with UPS estimates (where the latter are available).

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