

Cite this: *Nanoscale*, 2018, 10, 964

Work function and temperature dependence of electron tunneling through an N-type perylene diimide molecular junction with isocyanide surface linkers†

Christopher E. Smith,^{a,b} Zuoti Xie,^b Ioan Bâldea^b and C. Daniel Frisbie^{*b}

Conducting probe atomic force microscopy (CP-AFM) was employed to examine electron tunneling in self-assembled monolayer (SAM) junctions. A 2.3 nm long perylene tetracarboxylic acid diimide (PDI) acceptor molecule equipped with isocyanide linker groups was synthesized, adsorbed onto Ag, Au and Pt substrates, and the current–voltage (I – V) properties were measured by CP-AFM. The dependence of the low-bias resistance (R) on contact work function indicates that transport is LUMO-assisted ('n-type behavior'). A single-level tunneling model combined with transition voltage spectroscopy (TVS) was employed to analyze the experimental I – V curves and to extract the effective LUMO position $\epsilon_l = E_{\text{LUMO}} - E_F$ and the effective electronic coupling (Γ) between the PDI redox core and the contacts. This analysis revealed a strong Fermi level (E_F) pinning effect in all the junctions, likely due to interface dipoles that significantly increased with increasing contact work function, as revealed by scanning Kelvin probe microscopy (SKPM). Furthermore, the temperature (T) dependence of R was found to be substantial. For Pt/Pt junctions, R varied more than two orders of magnitude in the range 248 K < T < 338 K. Importantly, the $R(T)$ data are consistent with a single step electron tunneling mechanism and allow independent determination of ϵ_l , giving values compatible with estimates of ϵ_l based on analysis of the full I – V data. Theoretical analysis revealed a general criterion to unambiguously rule out a two-step transport mechanism: namely, if measured resistance data exhibit a pronounced Arrhenius-type temperature dependence, a two-step electron transfer scenario should be excluded in cases where the activation energy depends on contact metallurgy. Overall, our results indicate (1) the generality of the Fermi level pinning phenomenon in molecular junctions, (2) the utility of employing the single level tunneling model for determining essential electronic structure parameters (ϵ_l and Γ), and (3) the importance of changing the nature of the contacts to verify transport mechanisms.

Received 30th August 2017,
Accepted 24th November 2017

DOI: 10.1039/c7nr06461f

rsc.li/nanoscale

Introduction

One of the central goals of molecular electronics is to relate measured current–voltage (I – V) characteristics of metal–mole-

cule–metal tunnel junctions to electronic structure parameters, in particular $\epsilon_{\text{H/L}}$, the offset of the dominant molecular orbital (HOMO/LUMO) from the Fermi level, and Γ , the electronic coupling or broadening of the molecular orbital, Fig. 1.^{1–3} For simple tunnel junctions in which electron tunneling is assisted primarily by one molecular orbital, recent work has shown that ϵ and Γ can be extracted easily from an analytical expression for the I – V curve (e.g., the so-called single level model).^{4–9} Because of its simplicity, this compact analytical model – when it holds – greatly facilitates efforts by experimentalists to relate junction electronic structure to I – V behavior and *vice versa*.

In previous experiments on oligophenylene dithiol (OPD) junctions, for example, we demonstrated that the electronic coupling Γ is highly sensitive to the work function of the metal contacts, varying by orders of magnitude when the contacts were switched from Ag to Pt.¹⁰ In addition, we found that the

^aDepartment of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, USA

^bDepartment of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA. E-mail: zxie@umn.edu, frisbie@umn.edu

^cTheoretische Chemie, Universität Heidelberg, INF 229, D-69120 Heidelberg, Germany

^dNational Institute of Lasers, Plasmas and Radiation Physics, Institute of Space Science, POB MG-23 RO 077125 Bucharest, Romania.

E-mail: ioan.baldea@pci.uni-heidelberg.de

†Electronic supplementary information (ESI) available: Additional figures, experimental methods, synthesis of CN2PDI, and theoretical details. See DOI: 10.1039/c7nr06461f

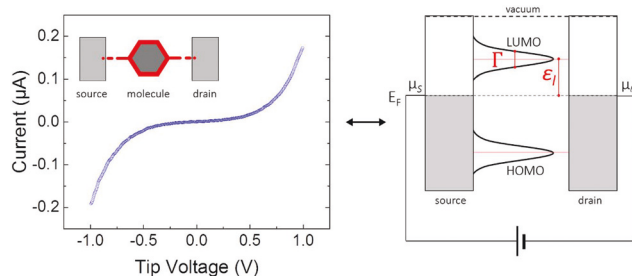


Fig. 1 (Left) Typical experimental I - V curve obtained from a metal-molecule-metal junction. Inset graphic represents a molecule sandwiched between metal contacts. (Right) Molecular junction energy level diagram depicting the E_F -molecular orbital offset (ϵ_l) for LUMO-mediated tunneling, and broadening (Γ) due to the molecule-metal electronic coupling. μ_S and μ_D are the chemical potentials of the source and drain, respectively.

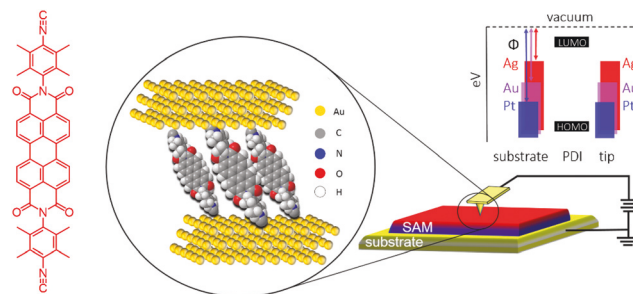


Fig. 2 (Left) Molecular structure of the isocyanide terminated perylene diimide (CN_2PDI) used in this study. (Right) Schematic representation of the CP-AFM formed nanoscopic junction. The tip is biased relative to the substrate and I - V curves are collected. The top right shows a simple energy level diagram of the contact work functions relative to the molecular orbitals. The CP-AFM measurement procedures have been described previously.

trend in low-bias junction resistance with contact work function (Φ) established that the Fermi level, E_F , lies closer to the HOMO than the LUMO of the OPD molecules, a conclusion that is hard to make from I - V measurements alone on junctions with one type of metal contact (generally density functional theory calculations – particularly with scissor corrections applied,^{11–18} or in rare cases thermopower measurements,^{19–22} are employed to determine the E_F alignment). Further, using the single level model and assuming that electron transport is a single-step, coherent tunneling process (see “Single-step versus two-step electron transfer” below), we were able to determine quantitatively the energy offset ϵ_h (*i.e.*, Fermi level relative to the HOMO) for each molecule-contact combination. This established that ϵ_h varied only weakly with contact work function, *i.e.*, the junctions exhibited moderate Fermi level pinning, which suppressed the junction conductance for high work function contacts.¹⁰

Our goal here is to examine work function effects on transport for a junction in which the LUMO, not the HOMO, is the closest frontier orbital to E_F . We are also interested in the specific effects of temperature on transport. We focus on a substituted perylene diimide with terminal isocyanide groups, Fig. 2. Perylene diimides are well known to be good electron acceptors, meaning that they have a relatively low lying LUMO. Furthermore, it has been shown previously that $-\text{N}\equiv\text{C}$ linkers facilitate n-type (LUMO-assisted) conduction.^{23–28} Conducting probe atomic force microscopy (CP-AFM) is employed to measure the I - V characteristics of junctions having different contact metals over the temperature range 250–340 K. We show that the I - V characteristics can be very well simulated by the single level model (*i.e.*, single-step tunneling) and that the work function dependence is indeed consistent with LUMO-assisted transport. As with the previously studied OPDs, we find strong evidence for Fermi level pinning in perylene diimide (PDI) junctions, *i.e.*, ϵ_l depends weakly on the contact work function, which appears to be the result of the formation of interface dipoles,^{29–31} as determined by scanning Kelvin probe microscopy (SKPM).³² Additionally, we find the elec-

tronic coupling Γ is very sensitive to both metal work function (Φ) and temperature (T), and that the variation in overall junction resistance with Φ and T mainly reflects the dependence of Γ (and not ϵ_l) on these variables. The similarity of the current results on n-type PDI with p-type OPD molecules suggests that Fermi level pinning is an important general phenomenon in molecular junctions with metal coordinating surface linking groups. Additionally, our results highlight the utility of the analytical single level model for extracting quantitative values of Γ and ϵ , thus adding to the growing body of literature demonstrating that this model is a highly effective theoretical tool for the analysis of simple molecular junctions.^{4,9,10,31,33–36}

From a theoretical perspective, an important result of our analysis is the development of a criterion for distinguishing between single-step and two-step tunneling. Specifically, we find that while activated transport can be consistent with both single-step and two-step tunneling, two-step electron transfer should be excluded in cases where the activation energy depends on the contact metallurgy.

Results & discussion

Surface characterization

The molecular junctions studied here are based on a self-assembled monolayer (SAM) of a perylenediimide (PDI) acceptor molecule as an n-type transport material. By virtue of their low lying LUMO, PDIs are redox active, which makes molecular coverage determination relatively straightforward using cyclic voltammetry. Isocyanide linking groups are less utilized in molecular electronics,^{37–44} but are known to bond to coinage metals and appear to pin the LUMO of the molecule closer to E_F than thiols.^{45–48} Isocyanides also provide a reliable infrared tag with distinctly different stretching frequencies for metal-bound *versus* free $-\text{N}\equiv\text{C}$.

SAMs were formed by immersing gold surfaces in a 0.5 mM solution in toluene for 6 h (there was no noticeable difference in surface coverage of SAMs formed between 6–18 h). Specular-

reflectance IR spectroscopy of SAMs on Ag, Au and Pt surfaces (Fig. 3A, see also Fig. S1†) show the characteristic PDI vibrational modes corresponding to carbonyl (1710 cm^{-1}), amide $\text{C}=\text{O}$ (1673 cm^{-1}), $\text{C}-\text{N}$ (1594 cm^{-1}) and aromatic $\text{C}=\text{C}$ (1357 cm^{-1}) stretches. Importantly, both the terminal unbound isocyanide and the isocyanide bound to the gold surface are visible at 2117 cm^{-1} and 2172 cm^{-1} , respectively, suggesting that the molecules were not lying down on the surface as reported frequently in the literature for phenylenediisocyanide.^{49–52} To confirm this, angle resolved X-ray photoelectron spectroscopy (ARXPS) was performed, which revealed SAM thicknesses of $1.9 \pm 0.1\text{ nm}$ on Ag, Au and Pt substrates (see ESI†). The estimated length of the CN_2PDI molecule bonded to metal is 2.43 nm indicating there is a tilt angle of $\sim 40^\circ$ from normal, similar to findings in other studies of aryl isocyanides and perylenediimides adsorbed onto surfaces.^{41,53,54} XPS was also employed to verify the C, N, O chemical composition of PDI SAMs on Ag, Au, and Pt substrates (see Fig. S2 and Table S1†). On all three substrates the relative composition of C, N, and O was 80%, 10%, and 10%, in line with expectations. The UV-vis absorption (Fig. 3B) shows a 100 meV red-shift in the absorption edge to 575 nm, which corresponds to a renormalization of the optical band-gap from 2.25 eV to 2.15 eV upon SAM formation.

Cyclic voltammetry (CV) and cyclic square wave voltammetry (CSWV) were employed to investigate the redox properties of CN_2PDI . The PDI core exhibits the typical one-electron reversible reductions at approx. -0.8 V and -1.1 V relative to Fc/Fc^+ , Fig. S4.†⁵⁵ The SAM surface coverage was estimated from the cyclic voltammograms (see ESI†) to be 0.8 molecules per nm^2 , which is reasonable given the size of the PDI core and tilt angle of $\sim 40^\circ$ determined from ARXPS measurements. Surface coverages of thiol terminated PDI SAMs have been measured by voltammetry to be ~ 1 molecule per nm^2 in other studies.⁵⁶

Work function dependence of transport

The dependence of SAM junction transport properties on contact work function has been extensively studied in our group.^{10,31,57} In cases of LUMO-assisted electron transport the junction resistance is expected to increase with increasing contact work function (Φ) due to an increase in ϵ_1 . To investigate the n-type conduction of CN_2PDI , the SAMs were chemisorbed onto Ag^{TS} , Au^{TS} and Pt^{TS} (template stripped) substrates with an area of $\sim 1\text{ cm}^2$.

Conducting probe atomic force microscopy was employed to form nanoscopic junctions by touching a metal-coated tip (either Ag, Au or Pt) onto CN_2PDI SAMs, Fig. 2 (see Methods section). Contact areas are typically $\sim 50\text{ nm}^2$ corresponding to ~ 40 molecules in the junctions. Current *versus* voltage (I - V) curves were collected for junctions with the following metal contact combinations ($M_{\text{tip}}/M_{\text{substrate}}$; $M = \text{metal}$): Ag/Ag, Ag/Au, Ag/Pt, Au/Au, Au/Pt and Pt/Pt. As shown in Fig. 4A and S5,† the average current at all potentials steadily decreased as the average work function $M_{\text{tip}}/M_{\text{substrate}}$ increased, which indicates that transport is LUMO-assisted. Further, the low-bias resistance (R) was extracted from the slope of the I - V curves in the $\pm 0.2\text{ V}$ range and is plotted against the average work function of the junction in Fig. 4B. The fit changes by a factor of 100 over a 1.4 eV change in average Φ consistent with our previous studies that show changing the work function has a dramatic impact on junction transport properties.¹⁰

Analysis of I - V curves using the single level model; Fermi level pinning

Normally, when the frontier orbital (HOMO/LUMO) lies far from the contact E_F and the molecule in the junction is short ($< 4\text{ nm}$), the junction transport mechanism is direct (coherent) off-resonant tunneling mediated by a single orbital.⁵⁸ In this case the transport can be quantitatively simulated using a rela-

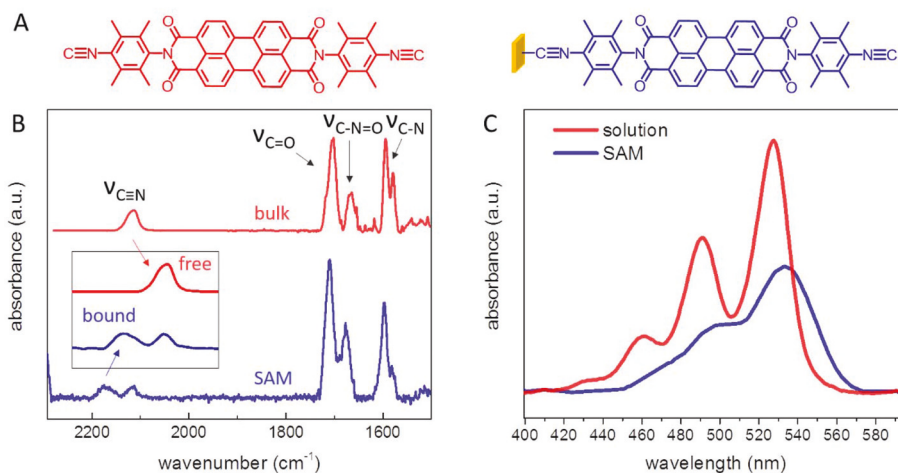


Fig. 3 (A) Molecular structure of CN_2PDI (red) and CN_2PDI SAM (blue). (B) Infrared spectra of CN_2PDI bulk solid (KBr) and specular-reflectance infrared spectra of CN_2PDI SAM on Au. (C) UV-vis of CN_2PDI in 1 mM DMSO and SAM assembled on a semi-transparent (20 nm) Au film that was thermally-evaporated onto a glass slide.

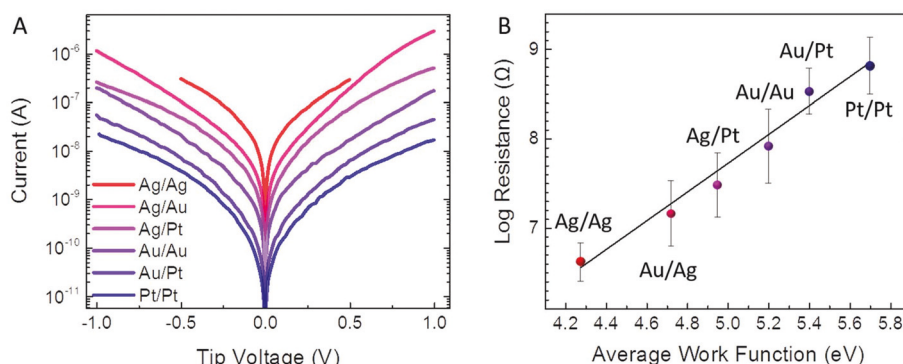


Fig. 4 (A) Semi-log plot of the average high-bias I - V curves. Each curve is an average of ~ 150 traces with no data selection (four locations sampled for each junction with ~ 40 curves collected at each location). (B) Average low-bias resistance versus average work function. Each data point represents resistances extracted as the inverse slope from the curves in (A) in the ± 0.2 V range. Error bars represent one standard deviation. There is no data selection in the resistance data.

tively simple single-level model derived from the Landauer formula.⁴ Assuming that ϵ_l is larger than $\Gamma_{t,s}$, the current over a bias range of $V < 1.5\epsilon_l/e$ can be expressed as,

$$I_1 = G_1 V \frac{\epsilon_l^2}{\epsilon_l^2 - (eV/2)^2} \quad (1)$$

where the zero-bias conductance of a single molecule is given by,

$$G_1 = G_0 \frac{\Gamma_s \Gamma_t}{\epsilon_l^2} \quad (2)$$

$G_0 = 2e^2/h = 77.48 \mu\text{S}$ being the conductance quantum.

Eqn (1) and (2) refer to transport through a *single* molecule.⁴ Assuming all molecules in the CP-AFM junction (N) are characterized by the *same* LUMO energy offset ϵ_l , eqn (1) and (2) should be multiplied by N ($I = NI_1$, $G = NG_1$).^{4,59,60} The dependence of the contact-molecule coupling on the low-bias conductance G of the CP-AFM junction is then given by

$$G = G_0 \sum_{j=1}^N \frac{\Gamma_{sj} \Gamma_{tj}}{\epsilon_{lj}^2} \xrightarrow{\epsilon_{lj}=\epsilon_l} NG_0 \frac{\Gamma^2}{\epsilon_l^2}; \quad (3)$$

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

$$\Gamma^2 = \frac{1}{N} \sum_{j=1}^N \Gamma_{sj} \Gamma_{tj}$$

Here $\Gamma^2 = \Gamma_s \Gamma_t$ stands for an average width level *per* molecule and is calculated from eqn (4) assuming symmetric contacts ($\Gamma_s = \Gamma_t$). We note that the quantity ϵ_l refers to the renormalized LUMO energy in junction. This renormalization embodies the shift in the LUMO energy of the isolated molecule due to its interaction with the electrodes (*e.g.*, image charge effects and interface dipoles) as well as interactions with the neighboring molecules in the SAM.

In principle then, ϵ_l and Γ can be determined by fitting the I - V data to eqn (1) (multiplied by N) and treating ϵ_l and Γ as

freely adjustable fitting parameters. However, the procedure we follow is more prescriptive. We determine ϵ_l directly with an analysis method called transition voltage spectroscopy (TVS)^{61–64} in combination with eqn (5), derived from the single-level tunneling model at zero temperature. Within the single level model,^{4,13} ϵ_l can be obtained as

$$eV_t = 2\epsilon_l/\sqrt{3} \quad (5)$$

where V_t is the transition voltage identifying the point on the I - V curve where the differential conductance becomes twice the nominal (pseudo-ohmic) conductance.^{4,31}

$$\left. \frac{\partial I}{\partial V} \right|_{V=V_t} = 2 \left. \frac{I}{V} \right|_{V=V_t} \quad (6)$$

Note that $V_t = V_{t+} \approx |V_{t-}|$ in symmetric junctions. Many groups have utilized TVS to analyze experimental I - V curves in the non-linear bias regime to estimate the E_F -molecular orbital energy offset.^{65–69} In this approach, the high-bias I - V curves are re-casted to give V_t as the maximum in the $\text{abs}(V^2/I)$ versus V plot, Fig. S6† (Note: we choose this form over the former Fowler-Nordheim plot, $\ln(I/V^2)$ versus $1/V$, often used for TVS as it is simpler and the results are identical).

Fig. 5A shows that ϵ_l (determined from eqn (5)) increases with work function, consistent with n-type transport. The extracted ϵ_l values are 0.22 eV (Ag/Ag), 0.29 eV (Au/Au) and 0.34 eV (Pt/Pt). Note however, ϵ_l changes by less than 150 meV over a 1.4 eV range in electrode work function, indicating a strong pinning effect of E_F to the LUMO of the SAM.¹⁰

With ϵ_l and G in hand we can find Γ . We know from prior work that the number of molecules N in SAM junctions is 50–100.⁷⁰ We estimate N to be ~ 40 in the CN₂PDI junctions given the contact area of $\sim 50 \text{ nm}^2$ (ref. 70) and a surface coverage of ~ 0.8 molecules per nm^2 . Therefore, Γ was found straightforwardly from the low bias conductance G and energy offset ϵ_l using eqn (3) and is shown in Table 1. Fig. 5A also plots Γ versus Φ , and reveals that Γ decreases with increasing

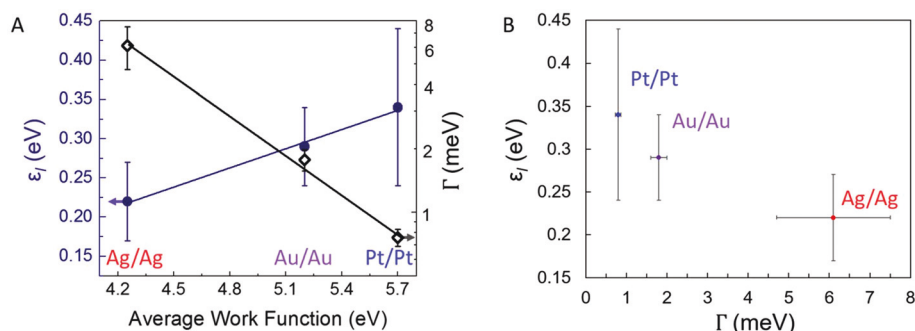


Fig. 5 (A) Extracted ϵ_l (circles) and Γ (diamonds) vs. contact work function (Φ) for symmetric Ag/Ag, Au/Au and Pt/Pt junctions. The weak dependence of ϵ_l on Φ is evidence of Fermi level pinning. Notice that Γ , the effective coupling defined via eqn (3), is shown on a semi log scale and varies by ~ 1 order. (B) Plot of ϵ_l versus Γ . Error bars represent one standard deviation.

Table 1 Summary of measured and theoretically extracted properties for the CN₂PDI junctions. The LUMO-offset values ϵ_l^{TVS} were obtained via eqn (5) and the values ϵ_l^{R} were deduced by fitting the R versus T data via eqn (7)

Parameters	Ag/Ag	Au/Au	Pt/Pt
$G/G_{0,\text{junction}}$	3.1×10^{-2}	1.5×10^{-3}	2.0×10^{-4}
V_t (eV)	0.26 ± 0.06	0.34 ± 0.06	0.39 ± 0.1
ϵ_l^{TVS} (eV)	0.22 ± 0.05	0.29 ± 0.05	0.34 ± 0.1
ϵ_l^{R} (eV)	0.15 ± 0.02 (Ag/Au)	0.22 ± 0.03	0.44 ± 0.03
Γ (meV)	6.1 ± 1.4	1.8 ± 0.2	0.8 ± 0.07
$\Delta\Phi$ (eV)	-0.1 ± 0.01 (Ag ^{TS})	-1.1 ± 0.01 (Au ^{TS})	-1.6 ± 0.01 (Pt ^{TS})

Φ , consistent with the qualitative expectation that higher work function electrodes should make poorer contacts with the LUMO of the CN₂PDI. The semilog plot of Γ versus Φ in Fig. 5A shows ~ 1 order decrease in the coupling, consistent with the relationship $R \propto 1/\Gamma^2$ shown in eqn (2) and the two orders of magnitude increase in R versus Φ shown in Fig. 4B.

Overall, Γ couplings on Ag, Au and Pt surfaces, which are on the order of 0.8–6 meV, are relatively small compared to those for OPDs (2–13 meV for the 2.1 nm long OPD4)¹⁰ and suggest that there is little electronic overlap with the contacts and the PDI core. This is not surprising when one considers that the redox-active core of the PDI is electronically isolated from the isocyanide linking groups in two ways. First, the conjugation through the molecule is broken by the imide groups between the PDI core and the phenyl units. Second, due to steric hindrance between the methyl groups of the phenyl ring and the carbonyls of the diimide groups it is expected that there is a large dihedral angle θ between the core and the phenyls, further isolating the frontier orbitals in the middle of the molecule. As is well known, the molecule–electrode couplings Γ depends on the matrix element t characterizing the effective electron transfer.⁷¹ In non-planar molecules t scales as the cosine of the characteristic dihedral angle θ ($t \sim \cos \theta$).⁷¹ The small Γ -values obtained for our CN₂PDI junctions can be therefore related to the large dihedral angle implying a small value of $\cos \theta$.

We used the extracted values of ϵ_l and G to simulate the I - V behavior via eqn (3). Fig. 6 shows the simulated I - V curves for Ag/Ag, Au/Au and Pt/Pt symmetric contacts to CN₂PDI, with both semilog and linear axes. The simulated curves (solid lines) fit the data very well over ± 0.4 V where the approximations inherent to the single level model can be expected to hold ($eV_t < 1.5\epsilon_l$). The good fit with no adjustment of ϵ_l and Γ indicates that the model applies well to this system.

Interface dipoles and Fermi level pinning

The change in the electrode work function ($\Delta\Phi$) due to the adsorbed PDI SAM was measured with scanning Kelvin probe microscopy (SKPM). As shown in Fig. 7, $\Delta\Phi$ depends strongly on the electrode type. Average Φ_{SAM} values are 4.2 ± 0.01 eV (Ag), 4.05 ± 0.01 eV (Au) and 4.1 ± 0.01 eV (Pt), compared to the intrinsic metal Φ values of 4.25 eV (Ag), 5.20 eV (Au) and 5.65 eV (Pt).⁵⁷ Importantly, the dependence of $\Delta\Phi$ on Φ represents the surface dipole induced from the metal–C $\equiv$ N–PDI bonds (or more rigorously, is proportional to the sum of the surface dipole and internal dipoles within the SAM) and is similar to thiol-bound SAMs.^{10,72} The surface dipole shifts the electrostatic potential in the molecular film with respect to the metal and thus determines the orbital alignment with respect to E_F . It is evident in Fig. 7 that the larger dipole for Pt contacts means that ϵ_l is not as large as might have been expected based only on a comparison of Φ for Pt and Ag, for example. The increase in $\Delta\Phi$ with increasing Φ is the cause of Fermi level pinning. Thus, while smaller electrode work functions indeed lead to higher coupling Γ and lower junction resistance in these n-type SAMs (Fig. 4B and 5B), ϵ_l is relatively weakly effected. We note that theoretical analysis of bond dipoles and their effect on the work function of SAM-covered metals has been reported in detail by Zojer and Heimel, *et al.*^{24,25,29}

Temperature dependence of transport parameters

Finally, variable-temperature CP-AFM measurements were performed, Fig. 8.⁷³ We examined the temperature dependence of resistance for Au/Ag, Au/Au and Pt/Pt junctions (Ag/Ag contacts yield current levels above the sensing capabilities of the instrument, see Methods section). All CP-AFM I - V curves were used

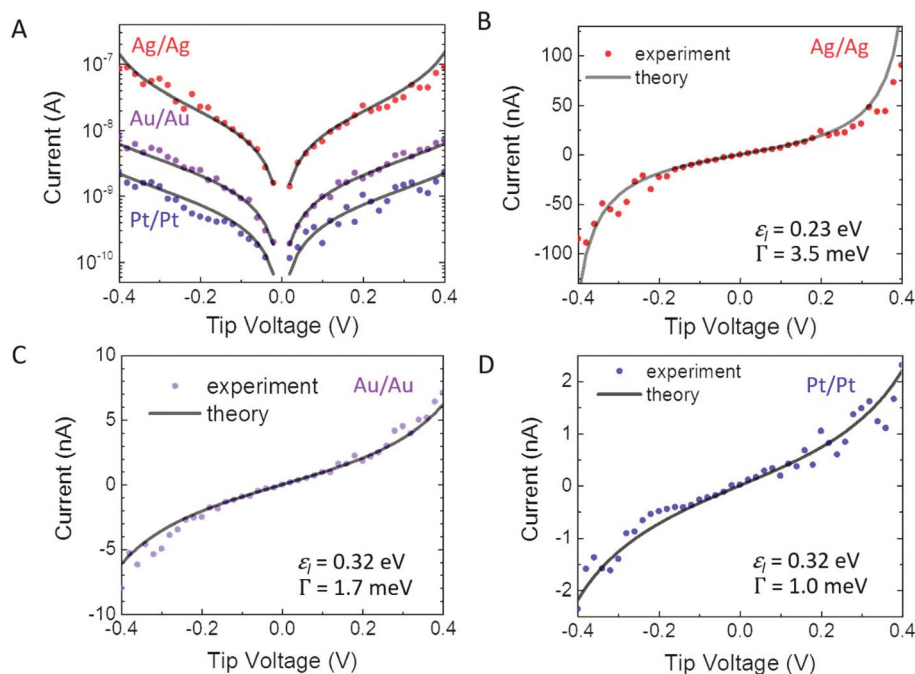


Fig. 6 (A) Semi-log plot of single experimental *I*-*V* curves (colored dots) collected with symmetric contacts and fit to eqn (1) (black lines). (B–D) Linear plots of the same curves. The parameters ϵ_l and Γ derived from these single curves are shown. Notice that the values of ϵ_l given in panels B–D are obtained by fitting the individual *I*-*V* traces shown in these panels, and therefore they differ from the values ϵ_l^{TVS} of Table 1, which represent statistical averages over all measured *I*-*V* traces.

without any data selection. Current decreased at all voltages with decreasing temperature, Fig. 8A and B, and both Au/Au and Pt/Pt junctions exhibited strongly temperature dependent transport, similar to the dithiol PDI break junctions studied by

Li *et al.*⁷⁴ *I*-*V* curves were collected as the sample stage was heated from 250 K to 338 K in 10 K increments, and Arrhenius plots $\log_{10}(R)$ versus $1000/T$ of the low-bias resistances are shown in Fig. 8C.

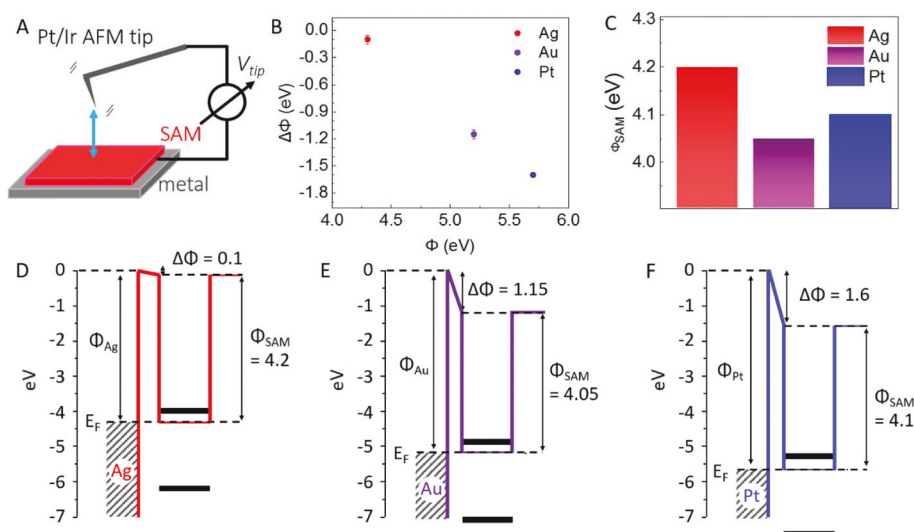


Fig. 7 (A) Schematic of the SKPM setup. The contact potential difference between the tip and substrate are measured, then differences between bare metal and SAM coated metal are calculated. (B) Change in work functions of the metal surfaces after SAM formation measured by SKPM. Values represent the average $\Delta\Phi$ measured from three locations on the sample and error bars are one standard deviation. (C) Φ_{SAM} values. Work functions were calibrated by referencing to the $\Delta\Phi$ measured on a nonane thiol SAM, an established value. (D–F) Energy level diagrams depicting the interfacial dipole formed by the metal–C≡N–PDI bonding. The HOMO and LUMO levels are shown in black and their positions are qualitatively assigned based of the SAM $E_{g,\text{opt}}$ (optical band gap defined by the absorption edge) and experimentally measured ϵ_l values.

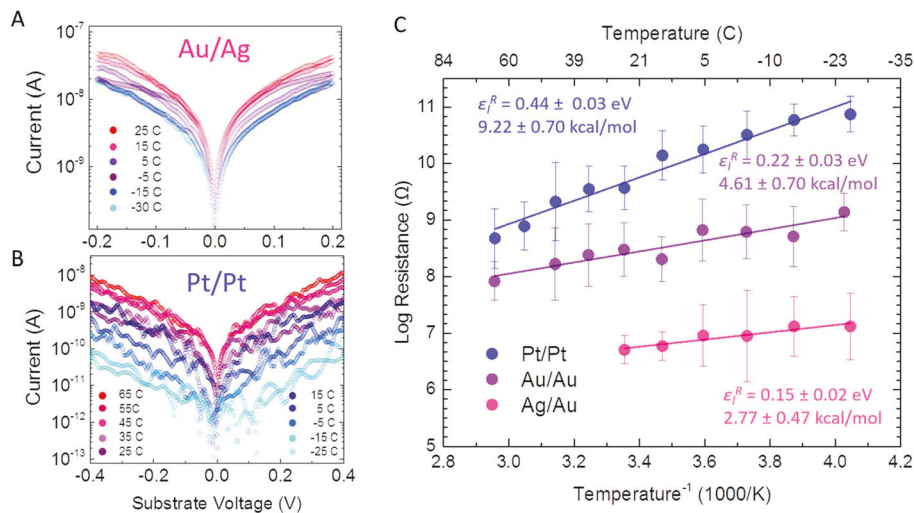


Fig. 8 (A and B) The temperature dependence of low-bias I - V curves for the Au/Ag and Pt/Pt junctions on a semi-log scale. (C) Arrhenius plots of low-bias resistance versus temperature for Ag/Au, Au/Au and Pt/Pt CN₂PDI junctions. Note that the fitting lines have been obtained via eqn (7) and are only qualitatively similar to the Arrhenius dependence expressed by eqn (S6) of the ESI.† Error bars represent one standard deviation.

To process the measured $R = R(T)$ data, we employed the equation (see ref. 75 and ESI† for derivation)

$$R = \text{const} \times k_B T \cosh^2 \left(\frac{\epsilon_1}{2k_B T} \right) \quad (7)$$

which reduces to the standard Arrhenius relationship for $\epsilon_1 \gg 2k_B T$ (where k_B is the Boltzmann constant). Importantly, eqn (7) allows us to independently determine the LUMO energy offset ϵ_1 from the T -dependent data. The ϵ_1 -values (denoted by ϵ_1^R) thus obtained are presented in Table 1. These values are comparable to the TVS-based ϵ_1 -values (denoted by ϵ_1^{TVS}) deduced via eqn (5). As noted below, although relatively small, the differences between the two estimates (ϵ_1^{TVS} and ϵ_1^R) may be significant.

To address the differences in ϵ_1 , one can first of all mention that the expression of V_t in eqn (5) was deduced in ref. 4 in the zero-temperature limit while the present estimate ϵ_1^{TVS} is based on I - V curves measured at room temperature. The fact that, although non-negligible, the difference between ϵ_1^{TVS} (deduced from eqn (5), valid at zero temperature) and ϵ_1^R (deduced via eqn (7), valid in the temperature range sampled in our experiments) is not substantial demonstrates once more that V_t is a robust junction property. It may still be useful to mention at this point that recent calculations⁷⁶ indicated that, albeit not dramatic, some temperature-dependent corrections should be applied to eqn (5). These corrections – which were found to be significant in situations where Γ is substantially smaller than the thermal energy $k_B T$, that is, exactly our case (*cf.* Table 1) – yield smaller values of ϵ_1^{TVS} than the estimates of Table 1, improving thereby the agreement with the values of ϵ_1^R shown there. Second, we should note that, although the hypothesis of a single dominant level (LUMO in the present

case) underlies both eqn (5) and (7), eqn (5) assumes a Lorentzian transmission,⁴ while eqn (7) holds for an *arbitrary* form of the transmission function. So, a non-Lorentzian transmission may be another possible source of these differences. Third, one should also note that, in order to diminish measurement errors in the current, we determined the (low bias) conductance $G = I/V$ at $V = \pm 0.2$ V. This bias is *not* small with respect to the characteristic energies of the problem (Γ , $k_B T$, ϵ_1), a fact assumed in the derivation of eqn (5), (7), and (S3)–(S5).† Importantly, ϵ_1^{TVS} and ϵ_1^R exhibit a similar trend: like ϵ_1^{TVS} , ϵ_1^R is found to increase with Φ , Table 1.

To fit the variable temperature I - V curves (Fig. S7†) we used eqn (3). We thus extracted a LUMO energy value ϵ_1 that turned out to be independent of temperature (consistent with the $R(T)$ analysis above). The “bare” molecule–electrode coupling, as it enters eqn (3) is temperature independent. However, in order to present the temperature-dependent results $R = R(T)$ for resistance more intuitively, we define an *effective* molecule–electrode coupling $\Gamma(T)$ via the formula

$$R(T) = R_0 [\epsilon_1 / \Gamma(T)]^2 / N \quad (8)$$

in the spirit of eqn (3). Here, $R_0 = 1/G_0 = 12.9$ k Ω is the resistance quantum. Because $R = R(T)$ (strongly) depends on temperature while ϵ_1 in does not, the above formula implies that the effective coupling $\Gamma(T)$ is (strongly) temperature dependent. The temperature dependent $\Gamma(T)$ obtained in this way for Pt/Pt junctions is plotted in Fig. 9A. Within the presently utilized framework (eqn (7)), the strong increase of the effective coupling $\Gamma(T)$ with temperature shown in Fig. 9A is due to thermal broadening of the electron energy distributions in the contacts⁷⁷ (*cf.* eqn (S1)†) and not to the coupling to vibrational

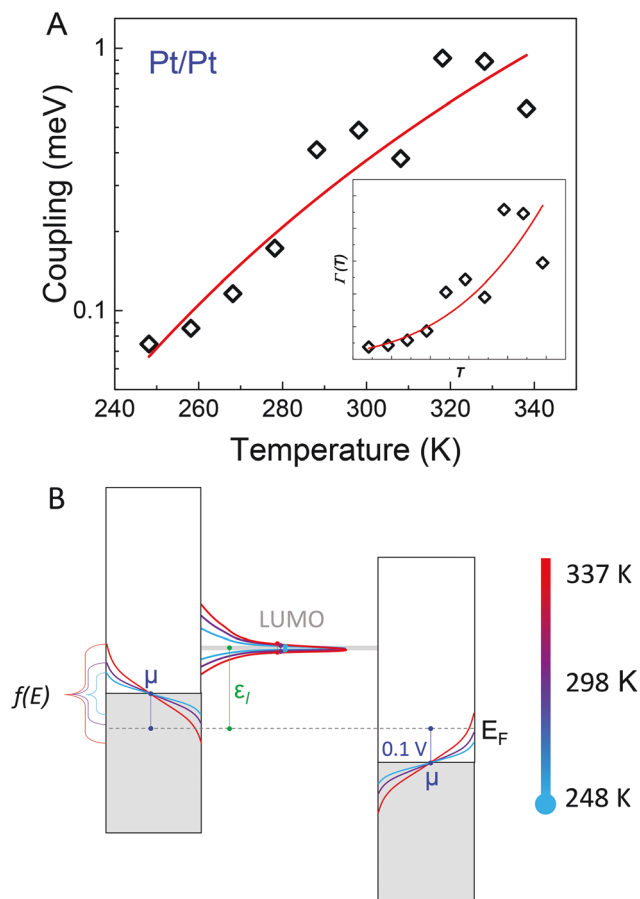


Fig. 9 (A) Semi-log plot of the extracted effective coupling $\Gamma(T)$ (in meV) from the average variable temperature I - V measurements on the Pt/Pt junction. To obtain the points (diamonds) shown here we analyzed I - V curves as a function of temperature T (in Kelvin) and used eqn (3) and the ϵ_l -values deduced *via* eqn (5). The inset shows the same data on a linear scale, and the red lines are the fits to the data using eqn (9). (B) A qualitative energy level diagram of a Pt/Pt junction showing the Fermi distribution $f(E)$ at the chemical potential of the contacts and the effective broadening $\Gamma(T)$ of the LUMO at 0.2 V bias (bias at which resistance is measured). The $f(E)$ and effective broadenings $\Gamma(T)$ are not drawn to scale for clarity.

modes (phonons) in the contacts.⁷⁸ $\Gamma(T)$ follows eqn (9) which has been used to fit the Fig. 9A data.

$$\Gamma(T) \propto T^{-1/2} \text{sech}\left(\frac{\epsilon_l}{2k_B T}\right) \quad (9)$$

(To avoid misunderstandings, we note that eqn (9) only applies to cases similar to the present one, *i.e.*, at sufficiently high temperatures where the second term in the RHS of eqn (S4)[†] dominates over the first term in the same equation.) The broadening of both the Fermi distribution $f(E)$ of electronic states in the contacts and the LUMO conduction band Γ with temperature are shown qualitatively in Fig. 9B. Under 0.2 V bias (*i.e.*, the bias at which G is measured) the overlap between $f(E)$ and the LUMO is shown at 248 K (lowest temperature), 298 K and 338 K (highest temperature).

While agreeing with the fact discussed earlier in the literature^{9,74,77} that the current *via* single step (coherent) tunneling may be strongly temperature dependent, our results do not *quantitatively* support an Arrhenius temperature dependence of the resistance. As discussed in the ESI (cf. eqn (S6)[†]), an *exponential* dependence of the resistance on ϵ_l/T , and thence an activation energy in the strict sense of this word,^{9,74,77} is quantitatively justified only for $\epsilon_l \gg 2k_B T$. Table 1 shows that this is a reasonable approximation for Pt/Pt junctions but not for Ag/Au junctions. Specifically, fitting with the Arrhenius formula (eqn (S6)[†]) yields an underestimated LUMO energy offset with respect to eqn (7): by 15% for Ag/Au junctions, by 11% for Au/Au junctions, and by 6% for Pt/Pt junctions.

To end this section, it is important to emphasize that, according to the present theoretical analysis (see ESI[†]), a significant temperature dependence of the transport *via* tunneling can only be observed for bare molecule-electrode couplings Γ substantially smaller than the thermal energy $k_B T$. The inspection of the values collected in Table 1 reveals that this condition (which is the condition under which eqn (7), (S4), and (S5)[†] were derived) is satisfied.

Single-step or two-step electron transfer?

We emphasized that our interpretation of the transport mechanism as single-step coherent off-resonant tunneling differs from previously proposed mechanisms for nanojunctions based on PDI-related molecules. Specifically, it has been suggested that the transport in single molecule junctions based on molecular species similar to that considered in the present work can be a two-step mechanism.⁷⁴ More precisely, this sequential process assumes that (i) an electron hops from one electrode onto the molecule to reduce the molecule, (ii) the molecule (and possibly also its surrounding environment) reorganizes upon charge transfer, and (iii) then the electron hops off to the second electrode to re-oxidize the molecule. With reference to that interpretation we note the following. Ref. 74 focused on low bias conductance and found that the measured temperature dependence approximately obeys an Arrhenius-type dependence. It is merely due to this Arrhenius-type dependence that the authors of ref. 74 have proposed the two-step scenario. An analysis based on a specific expression of the current (or conductance) as a function of bias has not been carried out in ref. 74. Notably, the authors were aware of the limitation of that description; they explicitly stated that neither the gate effect (which is very important for the context of ref. 74 but has no relevance in the present context) nor the temperature dependence of the low bias conductance satisfactorily fit with the equations for the two-step model.

The single molecule junctions in ref. 74, which involved an electrochemical environment, clearly are different from the CN₂PDI SAM based junctions reported here. We have shown above that all our experimental data for CN₂PDI junctions can indeed be quantitatively well described within a tunneling transport model assuming a single-step coherent charge transfer process. However, this is not the main or the only reason why we reject the two-step scenario.

By extending the recent analysis of ref. 75, we demonstrate below that the predictions of the two-step model are *qualitatively and quantitatively* incorrect. For the two-step model in the parameter range of interest, the following relationship between I and V can be deduced (see ESI† for derivation)^{78–80}

$$I = GV \exp[(e|V|)/(4k_B T)] \quad (10)$$

where the low bias conductance G can be expressed by

$$G = A \exp[-\lambda/(4k_B T)] = A \exp[-E_a/(k_B T)] \quad (11)$$

Here, A is a constant and λ is the energy associated with the reorganization of the active molecule and, possibly, of the surrounding molecules upon charge transfer. Eqn (11) expresses an Arrhenius dependence of the zero-bias conductance with the activation energy

$$E_a = \lambda/4. \quad (12)$$

Starting from the definition of V_t (eqn (6)), eqn (10) enables us to get the analytic expression of V_t

$$eV_t = 4k_B T. \quad (13)$$

Based on eqn (12) and (13) one can now see why the two-step model is inadequate to describe our transport data in CN₂PDI. Eqn (12) predicts an activation energy E_a merely dependent on the reorganization energy λ . However, λ is a molecular parameter, it does not depend on the nature of the electrode, while the experimental activation energy obtained from the Arrhenius plots of Fig. 8C exhibits a clear metal dependence: $E_a = 0.12$; 0.20 ; 0.40 eV for Ag/Au; Au/Au; Pt/Pt junctions. Thus, the predictions of the two-step model are at odds with our data. An illustration of the failure of the two-step model to correctly describe the measured I - V dependence in general and the transition voltage in particular is presented in Fig. S8.† Likewise, eqn (13) predicts that the transition voltage V_t is the same for all metal electrodes, which contradicts our experimental finding (see Table 1).

Conclusion

In summary, we have shown that the Fermi level pinning phenomenon, now well established for molecular junctions exhibiting HOMO-assisted tunneling, also pertains to PDI molecular junctions where electron tunneling is LUMO-assisted. A previously described single level model for the tunneling transport provided good fits to the experimental I - V data and allowed extraction of the key parameters ϵ_1 and Γ as a function of metal work function. Both ϵ_1 and Γ depend on electrode type and are roughly inversely correlated; the dependence of ϵ_1 on work function is generally understood but the dependence of Γ on metal work function will require further theoretical work.

Importantly, temperature dependent transport measurements revealed significantly activated behavior for CN₂-PDI junctions where the apparent activation energy increased with metal work function. Theoretical extension of the single level

model showed that such activated and contact metal-dependent behavior can be expected when the coupling Γ is small compared to the thermal energy $k_B T$. Fitting the temperature dependent data to the precise equation yielded values for ϵ_1 that agreed reasonably well with values obtained from fitting the full I - V characteristics. Thus, the analysis appears internally consistent. Furthermore, working with several electrodes, we were able to unambiguously rule out a two-step description of transport in our CN₂PDI junctions; all of the data are fully consistent with single step, LUMO-assisted tunneling. Our analysis led us to formulate a general, easy-to-apply criterion: if measured resistance data exhibit a pronounced Arrhenius-type temperature dependence, a two-step electron transfer scenario should be excluded in cases where the activation energy is dependent on contact metallurgy.

Overall, our findings clarify important aspects of single-step tunneling in molecular junctions and indicate criteria to discriminate between this mechanism and a two-step scenario. Our findings also provide further confirmation of the utility of the single level model for extracting quantitative electronic structure information for molecular junctions, in this case n-type junctions exhibiting LUMO-assisted transport.

Experimental

Materials

Au nuggets (99.999% pure) were purchased from Mowrey, Inc. (St Paul, MN). Ag pellets and evaporation boats and Cr evaporation rods were obtained from R. D. Matthis (Long Beach, CA). Platinum and chromium was e-beam evaporated in the Minnesota Nanofabrication Center and were purchased from Kamis, Inc. (San Jose, CA). Silicon (100) wafers were purchased from WaferNet (San Jose, CA). Contact mode AFM tips (DNP or NP silicon nitride probes) were purchased from Bruker AFM Probes (Camarillo, CA). Absolute ethanol was obtained from Fisher Scientific and used as received. The chemicals perylene-3,4,9,10-tetracarboxylic dianhydride and 2,3,5,6-tetramethyl-*p*-phenylenediamine were ordered from Sigma-Aldrich and used as received.

Reflection absorption infrared spectroscopy (RAIRS) and UV-vis methods

Preparation of FTIR samples were as follows. Au: 50 nm of Au was e-beam evaporated onto a Si wafer with 5 nm of Cr as an adhesion layer. Ag: 50 nm of Ag was thermally evaporated onto a Si wafer with 5 nm Cr as an adhesion layer. Pt: 50 nm of Pt was e-beam evaporated onto a Si wafer with 5 nm of Cr as the adhesion layer. The substrates were cut into 2×4 cm rectangles, then cleaned by sonication in acetone, methanol and isopropanol for 15 min each. The CN₂PDI was dissolved in toluene at 0.5–1 mM with sonication. Substrates were then immersed in the solution in 50 mL polypropylene centrifuge tubes for 6 h. Afterward, the samples were rinsed with 100 mL toluene, soaked in toluene for 30 min, then immediately measured with a Harrick-Seagull FTIR accessory set with the

IR beam at 84° from the surface normal. The analysis chamber was purged with dry N₂ for 15–30 min, depending on humidity, before spectra were collected. Both the bare metal background and the SAM sample were scanned 400 times at resolution 2 cm⁻¹.

Optical absorption spectra of the wires were measured on a Spectronic GENESYS-5 UV-visible spectrophotometer from 250–1000 nm at 1.0 nm resolution. SAMs were adsorbed onto semi-transparent 15 nm Au films thermally deposited onto the side of a polystyrene cuvette. Au-coated cuvettes were immersed in 1 mM CN₂PDI in DMSO for 6 h.

XPS methods

XPS was employed to analyze atomic composition of the SAMs. Each high-resolution spectrum was background-corrected using the Shirley method⁸¹ (black dots) and the peaks were fit with 80% Gaussian-20% Lorentzian line shapes (red lines). XPS spectra were taken on a SSX-100 XPS (Surface Science) (<10⁻⁹ Torr) with a Al K α X-ray monochromatic source (1486.3 eV) and a hemispherical analyzer. The X-ray anode was operated at 200 W, and the analyzer was set to a pass energy of 150 eV for survey scans and 50 eV for high-resolution scans. The binding energy scales were referenced to the Au 4f_{7/2} peak (84.0 eV).

Angle-resolved XPS (ARXPS) was employed to measure SAM thicknesses on Ag, Au, and Pt substrates using similar instrument settings with take-off angles of 20°, 30°, 40°, 50°, 60°, 70°, 80°, and 90°.

Work function measurements

Scanning Kelvin probe microscopy (SKPM) measurements were used to determine the work function without (Φ) and with a SAM adsorbed on the metal surface ($\Phi_{\text{SAM}} = \Phi + \Delta\Phi$). SKPM measurements to acquire the surface potential of the samples were carried out using the same instrument that was employed for *I*-*V* characterization. The AFM instrument was placed in an Ar-filled glovebox (H₂O, O₂ < 0.1 ppm). The work functions of the samples were referenced to the UPS value of benzene-1,4-dithiol on an Au substrate (5.2 eV for bare Au).⁵⁷

CP-AFM methods

Metal-molecule-metal junctions were formed by touching a metal-coated AFM tip onto the molecular arrays in contact mode. The tips were prepared by the same evaporation methods as described above for the preparation of the RAIRS substrates. The substrates for AFM measurements were prepared with a template-stripping method (^{TS}) described previously.^{82,83} All electrical measurements were performed with a 2 nN load on the AFM tip to ensure a consistent top contact. Current-voltage curves were obtained by biasing the tip relative to the substrate. The junctions were formed and high bias curves were collected on a Multimode AFM (Veeco Instruments) in a glovebox (<1 ppm O₂, H₂O) using a Keithley 6517A electrometer and 236 source meter controlled by LabView code. Variable-temperature measurements were performed with an environmentally controlled Molecular Imaging

PicoScan/PicoSPM equipped with a current sensing scanner and temperature control from 248–338 K with a Lake Shore controller. The PicoSPM chamber was purged with N₂ and humidity was kept <1%. Picoview software was used to simultaneously operate the AFM and perform *I*-*V* measurements. Instead of electrometers, the PicoSPM utilizes an accessory current sensing nose cone (Keysight CS-AFM model N9541A) with 0.1 nA V⁻¹ sensitivity. With this accessory, currents can be measured in the range of ± 10 nA. For each junction, *I*-*V* curves were sampled from 4–6 different locations, with 25–50 curves taken at each location.

SAMs form very stable junctions with CP-AFM and all reported *I*-*V* curves are reproducible and are an average of all traces taken with no data selection. The low bias resistance was calculated from the linear portion of the curves within ± 0.2 V. Before transport measurements the quality of the tips was tested to ensure they gave a tunneling resistance on the order to 10⁸ Ω through a nonanethiol SAM standard on Au^{TS} and that the trend in the resistance *versus* work function was as expected (higher Φ = lower resistance).

For the variable-temperature measurements, the PicoSPM could measure Pt/Pt junction currents up to a ± 0.4 V bias. The Au/Au and Au/Ag junctions however, are more conductive and the ± 10 nA limit only allowed current measurements up to a ± 0.2 V bias. Therefore, we were not able to find V_b , ϵ_1 , and Γ for these systems.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

We thank NSF (CHE-1708173) for financial support. Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from NSF through the MRSEC program. Mass spectra were obtained at the University of Massachusetts Mass Spectrometry Center. Z. X. thanks Liwei Wu of the National Synchrotron Radiation Laboratory, University of Science and Technology of China, for advice concerning Angle-Resolved X-Ray Photoelectron Spectroscopy. I. B. acknowledges financial support from the Deutsche Forschungsgemeinschaft (grant BA 1799/3-1) and computational support by the State of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/467-1 FUGG.

References

- 1 J. A. Malen, P. Doak, K. Baheti, T. D. Tilley, R. A. Segalman and A. Majumdar, *Nano Lett.*, 2009, **9**, 1164–1169.
- 2 S. Datta, *Quantum Transport: Atom to Transistor*, Cambridge University Press, Cambridge, U.K., and New York, 2005.

- 3 T. Kim, P. Darancet, J. R. Widawsky, M. Kotiuga, S. Y. Quek, J. B. Neaton and L. Venkataraman, *Nano Lett.*, 2014, **14**, 789–794.
- 4 I. Bâldea, *Phys. Rev. B: Condens. Matter*, 2012, **85**, 035442.
- 5 C. Guo, X. Yu, S. Refaely-Abramson, L. Sepunaru, T. Bendikov, I. Pecht, L. Kronik, A. Vilan, M. Sheves and D. Cahen, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 10785–10790.
- 6 C. Jia, A. Migliore, N. Xin, S. Huang, J. Wang, Q. Yang, S. Wang, H. Chen, D. Wang, B. Feng, Z. Liu, G. Zhang, D.-H. Qu, H. Tian, M. A. Ratner, H. Q. Xu, A. Nitzan and X. Guo, *Science*, 2016, **352**, 1443–1445.
- 7 I. Bâldea, *Phys. Chem. Chem. Phys.*, 2015, **17**, 20217–20230.
- 8 A. R. Garrigues, L. Wang, E. del Barco and C. A. Nijhuis, *Nat. Commun.*, 2016, **7**, 11595.
- 9 A. R. Garrigues, L. Yuan, L. Wang, E. R. Mucciolo, D. Thompon, E. del Barco and C. A. Nijhuis, *Sci. Rep.*, 2016, **6**, 26517.
- 10 Z. Xie, I. Bâldea, C. E. Smith, Y. Wu and C. D. Frisbie, *ACS Nano*, 2015, **9**, 8022–8036.
- 11 Z. Crljen, A. Grigoriev, G. Wendin and K. Stokbro, *Phys. Rev. B: Condens. Matter*, 2005, **71**, 165316.
- 12 Y. Q. Xue and M. A. Ratner, *Phys. Rev. B: Condens. Matter*, 2003, **68**, 115406.
- 13 C. Jin, M. Strange, T. Markussen, G. C. Solomon and K. S. Thygesen, *J. Chem. Phys.*, 2013, **139**, 184307.
- 14 D. J. Mowbray, G. Jones and K. S. J. Thygesen, *Chem. Phys.*, 2008, **128**, 111103.
- 15 S. Y. Quek, L. Venkataraman, H. J. Choi, S. G. Louie, M. S. Hybertsen and J. B. Neaton, *Nano Lett.*, 2007, **7**, 3477–3482.
- 16 S. Y. Quek, H. J. Choi, S. G. Louie and J. B. Neaton, *Nano Lett.*, 2009, **9**, 3949–3953.
- 17 S. Y. Quek, H. J. Choi, S. G. Louie and J. B. Neaton, *ACS Nano*, 2011, **5**, 551–557.
- 18 M. Kondratenko, S. R. Stoyanov, S. Gusarov, A. Kovalenko and R. L. McCreery, *J. Phys. Chem. C*, 2015, **119**, 11286–11295.
- 19 K. Baheti, J. A. Malen, P. Doak, P. Reddy, S. Y. Jang, T. D. Tilley, A. Majumdar and R. A. Segalman, *Nano Lett.*, 2008, **8**, 715–719.
- 20 M. Paulsson and S. Datta, *Phys. Rev. B: Condens. Matter*, 2003, **67**, 241403.
- 21 P. Reddy, S. Jang, R. A. Segalman and A. Majumdar, *Science*, 2007, **315**, 1568–1571.
- 22 E. J. Dell, B. Capozzi, J. Xia, L. Venkataraman and L. M. Campos, *Nat. Chem.*, 2015, **7**, 209–214.
- 23 C. D. Zangmeister, S. W. Robey, R. D. van Zee, J. G. Kushmerick, J. Naciri, Y. Yao, J. Tour, B. Varughese, B. Xu and J. E. Reutt-Robey, *J. Phys. Chem. B*, 2006, **110**, 17138–17144.
- 24 G. Heimel, L. Romaner, E. Zojer and J. Brédas, *Nano Lett.*, 2007, **7**, 932–940.
- 25 G. Heimel, L. Romaner, J. Brédas and E. Zojer, *Phys. Rev. Lett.*, 2006, **96**, 196806.
- 26 J. Balachandran, P. Reddy, B. D. Dunietz and V. Gavini, *J. Phys. Chem. Lett.*, 2013, **4**, 3825–3833.
- 27 A. Mishchenko, L. A. Zotti, D. Vonlanthen, M. Bürkle, F. Pauly, J. C. Cuevas, M. Mayor and T. Wandlowski, *J. Am. Chem. Soc.*, 2010, **133**, 184–187.
- 28 C. B. Zangmeister, J. M. Beebe, J. Naciri, J. G. Kushmerick and R. D. van Zee, *Small*, 2008, **4**, 1143–1147.
- 29 D. A. Egger and E. J. Zojer, *Phys. Chem. Lett.*, 2013, **4**, 3521–3526.
- 30 D. Cahen, R. Naaman and Z. Vager, *Adv. Funct. Mater.*, 2005, **15**, 1571–1578.
- 31 I. Bâldea, Z. Xie and C. D. Frisbie, *Nanoscale*, 2015, **7**, 10465–10471.
- 32 J. Lü, E. Delamarche, L. Eng, R. Bennewitz, E. Meyer and H. J. Güntherodt, *Langmuir*, 1999, **15**, 8184–8188.
- 33 C. Jia, A. Migliore, N. Xin, S. Huang, J. Wang, J. Yang, S. Wang, H. Chen, D. Wang, B. Feng, Z. Lui, D. Qu, H. Tian, M. A. Ratner, H. Q. Xu, A. Nitzan and X. Guo, *Science*, 2016, **352**, 1443–1445.
- 34 R. Hayakawa, M. A. Karimi, J. Wolf, T. Huhn, M. S. Zöllner, C. Herrmann and E. Scheer, *Nano Lett.*, 2016, **16**, 4960–4957.
- 35 M. A. Karimi, S. G. Bahoosh, M. Herz, R. Hayakawa, F. Pauly and E. Scheer, *Nano Lett.*, 2016, **16**, 1803–1807.
- 36 Z. Xie, I. Bâldea, S. Oram, C. E. Smith and C. D. Frisbie, *ACS Nano*, 2017, **11**, 569–578.
- 37 J. J. Stapleton, T. A. Daniel, S. Uppili, O. M. Cabarcos, J. Naciri, R. Shashidhar and D. L. Allara, *Langmuir*, 2005, **21**, 11061–11070.
- 38 S. A. Swanson, R. McClain, K. S. Lovejoy, N. B. Alamdari, J. S. Hamilton and J. C. Scott, *Langmuir*, 2005, **21**, 5034–5039.
- 39 J. C. Applegate, M. K. Okeowo, N. R. Erickson, B. M. Neal, C. L. Berrie, N. N. Gerasimchuk and M. V. Barybin, *Chem. Sci.*, 2016, **7**, 1422–1429.
- 40 T. R. Maher, A. D. Spaeth, B. M. Neal, C. L. Berrie, W. H. Thompson, V. W. Day and M. V. Barybin, *J. Am. Chem. Soc.*, 2010, **132**, 15924–15926.
- 41 B. Shong, T. E. Sandoval, A. M. Crow and S. F. Bent, *J. Phys. Chem. Lett.*, 2015, **6**, 1037–1041.
- 42 J. Zhou, Y. Li, P. Zahl, P. Sutter, D. J. Stacchiola and M. G. White, *J. Chem. Phys.*, 2015, **142**, 101901.
- 43 J. J. Stapleton, T. A. Daniel, S. Uppili, O. M. Cabarcos, J. Naciri, R. Shashidhar and D. L. Allara, *Langmuir*, 2005, **21**, 11061–11070.
- 44 R. J. Angelici and M. Lazar, *Inorg. Chem.*, 2008, **47**, 9155–9165.
- 45 J. Balachandran, P. Reddy, B. D. Dunietz and V. J. Gavini, *J. Phys. Chem. Lett.*, 2013, **4**, 3825–3833.
- 46 J. A. Malen, S. K. Yee, A. Majumdar and R. A. Segalman, *Chem. Phys. Lett.*, 2010, **491**, 109–122.
- 47 A. Mishchenko, L. A. Zotti, D. Vonlanthen, M. Bürkle, F. Pauly, J. C. Cuevas, M. Mayor and T. Wandlowski, *J. Am. Chem. Soc.*, 2011, **133**, 184–187.
- 48 C. D. Zangmeister, S. W. Robey, R. D. van Zee, J. G. Kushmerick, J. Naciri, Y. Yao, J. M. Tour,

- B. Varughese, B. Xu and J. E. Reutt-Robey, *J. Phys. Chem. B*, 2006, **110**, 17138–17144.
- 49 J. Kestell, R. Abuflaha, J. A. Boscoboinik, M. Garvey, D. W. Bennet and W. T. Tysoe, *J. Phys. Chem. Lett.*, 2014, **5**, 3577–3581.
- 50 J. A. Boscoboinik, F. C. Calaza, Z. Habeeb, D. W. Bennett, D. J. Stacchiola, M. A. Purino and W. T. Tysoe, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11624–11629.
- 51 J. Boscoboinik, J. Kestell, M. Garvey, M. Weinert and W. Tysoe, *Top. Catal.*, 2011, **54**, 20–25.
- 52 J. Zhou, D. Acharya, N. Camillone, P. Sutter and M. G. White, *J. Phys. Chem. C*, 2011, **115**, 21151–21160.
- 53 Y. Zeng, F. M. Jradi, T. C. Parker, S. Barlow, S. Marder and S. S. Saavedra, *ACS Appl. Mater. Interfaces*, 2016, **8**, 34089–34097.
- 54 Y. Zheng, A. J. Giordano, R. C. Shallcross, S. R. Fleming, S. Barlow, N. R. Armstrong, S. R. Marder and S. S. Saavedra, *J. Phys. Chem. C*, 2016, **120**, 20040–20048.
- 55 G. Battagliarin, Y. Zhao, C. Li and K. Mullen, *Org. Lett.*, 2011, **13**, 3399–3401.
- 56 S. Bkhach, Y. Le Duc, O. Aleveque, C. Gautier, P. Hudhomme and E. Levillain, *ChemElectroChem*, 2016, **3**, 887–891.
- 57 B. Kim, C. Seong Ho, X.-Y. Zhu and C. D. Frisbie, *J. Am. Chem. Soc.*, 2011, **133**, 19864–19877.
- 58 C. Joachim and M. A. Ratner, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 8801–8808.
- 59 M. G. Reuter, M. C. Hersam, T. Seidemen and M. A. Ratner, *Nano Lett.*, 2011, **12**, 2243–2248.
- 60 M. Magoga and C. Joachim, *Phys. Rev. B: Condens. Matter*, 1999, **59**, 16011–16015.
- 61 J. M. Beebe, B. Kim, C. D. Frisbie and J. G. Kushmerick, *ACS Nano*, 2008, **2**, 827–832.
- 62 H. Song, Y. Kim, Y. H. Jang, H. Jeong, M. A. Reed and T. Lee, *Nature*, 2009, **462**, 1039–1043.
- 63 J. M. Beebe, B. Kim, J. W. Gadzuk, C. D. Frisbie and J. G. Kushmerick, *Phys. Rev. Lett.*, 2006, **97**, 026801.
- 64 E. H. Huisman, C. M. Guedon, B. J. van Wees and S. J. van der Molen, *Nano Lett.*, 2009, **9**, 3909–3913.
- 65 D. Nose, K. Dote, T. Sato, M. Yamamoto, H. Ishii and Y. Noguchi, *J. Phys. Chem. C*, 2015, **119**, 12765–12771.
- 66 L. Xiang, T. Hines, J. L. Palma, X. Lu, V. Mujica, M. A. Ratner, G. Zhuo and N. J. Tao, *J. Am. Chem. Soc.*, 2016, **138**, 679–687.
- 67 N. Bennet, G. Xu, L. J. Esdaile, H. L. Anderson, J. E. Macdonald and M. Elliot, *Small*, 2010, **6**, 2604–2611.
- 68 S. Guo, J. Hihath, I. Diez-Perez and N. J. Tao, *J. Am. Chem. Soc.*, 2011, **133**, 19189–19197.
- 69 G. Ricoeur, S. Lenfant, D. Guerin and D. Vuillaume, *J. Phys. Chem. C*, 2012, **116**, 20722–20730.
- 70 Z. Xie, I. Bâldea, A. T. Demissie, C. E. Smith, Y. Wu, G. Haugstad and C. D. Frisbie, *J. Am. Chem. Soc.*, 2017, **139**, 5696–5699.
- 71 J. C. Cuevas and E. Scheer, *Molecular Electronics: An Introduction to Theory and Experiment*, World Scientific Publishers, 2010.
- 72 Z. Xie, S. Shi, F. Liu, D. L. Smith, P. P. Ruden and C. D. Frisbie, *ACS Nano*, 2016, **10**, 8571–8577.
- 73 C. E. Smith, S. O. Odoh, S. Ghosh, L. Gagliardi, C. J. Cramer and C. D. Frisbie, *J. Am. Chem. Soc.*, 2015, **137**, 15732–15741.
- 74 X. Li, J. Hihath, F. Chen, T. Masuda, L. Zang and N. J. Tao, *J. Am. Chem. Soc.*, 2007, **129**, 11535–11542.
- 75 I. Bâldea, *Phys. Chem. Chem. Phys.*, 2017, **19**, 11759–11770.
- 76 I. Bâldea, *Org. Electron.*, 2017, **49**, 19–23.
- 77 M. Poot, E. Osorio, K. O'Neill, J. M. Thijssen, D. Vanmaekelbergh, C. A. van Walree, L. W. Jenneskens and H. S. J. van der Zant, *Nano Lett.*, 2006, **6**, 1031–1035.
- 78 I. G. Medvedev, *Phys. Rev. B: Condens. Matter*, 2007, **76**, 125312.
- 79 I. V. Pobelov, Z. Li and T. Wandlowski, *J. Am. Chem. Soc.*, 2008, **130**, 16045–16054.
- 80 I. Bâldea, *J. Phys. Chem. C*, 2013, **117**, 25798–25804.
- 81 D. A. Shirley, *Phys. Rev. B: Solid State*, 1972, **5**, 4709–4714.
- 82 S. A. DiBenedetto, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2009, **131**, 7158–7168.
- 83 Q. Lu, K. Liu, H. M. Zhang, Z. B. Du, X. H. Wang and F. S. Wang, *ACS Nano*, 2009, **3**, 3861–3868.