Supplementary Information for
Vibrational and electronic heating
in nanoscale junctions

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1 Correlated electrical conductance and Raman response data

Here are several examples of correlated electrical conductance and Raman response from nano-
junctions with OPV3 assembled on them. In the first three examples (Figures S1-3) the electrical
conductance is on the order of 0.01 $G_0$ with conductance fluctuations on the order of 0.001 $G_0$.
The conductance fluctuations are correlated with large changes in the Raman response mea-
sured at the nanojunction. This is consistent with a single molecule switching between different
conformations in the nanojunction. In all of these cases, we expect that the molecule is not
neatly bridging the gap, but does play a role in total electrical conduction. It has long been
establishedS2–S4 that conduction in such nanojunctions takes place via tunneling. Because of
the exponential dependence of tunneling on distance, the dominant volume for current flow is
of molecular scale. As argued previouslyS5, coincident conductance and Raman changes imply
(1) that at least some portion of a Raman-active molecule is influencing the tunneling electrons;
and (2) that Raman-active molecule is a significant (in many cases dominant) contributor to the
total Raman signal.

At higher nanojunction conductances ($0.5 \ G_0$, such as those observed in Figure S4), we observe similar correlations between conduction and Raman response, but the conductance fluctuation magnitude is much larger, as one might expect. At this conductance level, conduction is likely dominated by an atomic-scale metallic junction with transmission less than one. (One example of such a junction would be the beginnings of a tunneling contact, with two tip atoms slightly farther apart than their equilibrium lattice spacing.) Again, the conduction path is highly localized, with a transverse dimension of molecular or atomic dimensions. Still, given the correlation between Raman response and conductance, at least one Raman-active molecule must be significantly coupled to this current path. We note that it is very unlikely that the unusually high conductance of this particular junction results from many molecules in parallel. If this was the case, the observed, correlated conduction and Raman response would imply many molecules changing their configurations simultaneously, which is very unlikely. One would expect conductance fluctuations due to individual molecular motions to be much smaller such as those seen in nanojunctions with conductances of $0.01 \ G_0$; however this is not the case. Instead, high conductance nanojunctions are likely bridged by or strongly electronically coupled to just a part of a molecule, as the gaps are too small (based upon the conductance) to fit an entire molecule.

2 Junction configurations and contributions to the conductance

Figure S5 presents schematic examples of possible nanojunction configurations. Fig. S5a shows the idealized single-molecule junction that has been considered for more than fifteen years, with a single molecule neatly bridging and bound to both ends of a nanoscale interelectrode gap. In such a geometry, it is clear that interelectrode conduction would have a dominant contribution from current flow through the molecule.

However, as mentioned in the main text, this ideal configuration is unlikely in electromigrated junctions, since the electromigration process (unlike mechanical break junctions or scanning tunneling microscope junctions, for example) does not control interelectrode distance
with atomic precision. Rather, the closest interelectrode distance is determined by details of individual junctions and the breaking procedure.

Fig. S5b-d are examples of other nanojunction geometries, in which the closest interelectrode distance is not the length of a molecule of interest. In Fig. S5b and d, only a portion of the molecule of interest may be located at the point of closest interelectrode separation, while steric effects prevent the molecule from forming strong bonds with both electrodes. In Fig. S5c, the molecule is bound to both electrodes, but a closer point of interelectrode separation exists, and due to the exponential decay of tunneling with distance, the total conductance would have a dominant contribution from direct metal-metal tunneling. These configurations, while only schematic, show clearly that many reasonable junction arrangements are possible that can have total conductances higher than the idealized situation in Fig. S5a, but nonetheless involve contributions from current flow through a molecule. An example from the literature of such a situation is thought to be presented in Tal et al.\textsuperscript{56}. In that work, a benzene molecule is thought to lie down flat between two Pt electrodes in a mechanical break junction, leading to high conductance (comparable to 1 \( G_0 \)), but still with molecular influence on the current.

3 Additional optical vibrational pumping data

An example of optical vibrational pumping in OPV3 is shown in Figure S6. We observe several discrete spectral configurations. Each configuration has varying levels of optical pumping, with the most noticeable change occurring at 150 s, when several lower energy vibrations appear in the antiStokes signal.

4 Additional electrical vibrational pumping data

An additional example of electrical vibration pumping in OPV3 is shown in Figure S7. The two modes observed 880 cm\(^{-1}\) and 410 cm\(^{-1}\) have temperature differences of almost 150 K at \( V = 0.4 \) V. This device also exhibited optical pumping of both modes resulting in zero bias temperatures of 220 K and 120 K respectively. As expected both modes to not show
any electrical pumping until $V$ exceeds the vibrational energy. At 280 mV a sharp change in conductance is observed and no pumping is observed. The conductance changes again at 320 mV and pumping is observed but with less AS intensity than previously. This is strong evidence the importance of the local environment to pumping cross-sections.

5 **Additional electron heating data**

An additional example of electrical heating is shown in Figure S8. This sample had more symmetric $I - V$ curves and power dissipation than other samples presented. The effective temperature is observed to be more symmetric as well when considering the size of the error bars.

6 **Raman Stark effect**

Figure S9 provides a closer look at the Raman Stark effect seen in Figure 3B of the main text. A clear shift of 13 cm$^{-1}$ can be observed between zero bias and 0.5 V. All vibrational modes present experience similar shifts. These shifts are reproducible on subsequent voltage sweeps of this junction.

7 **OPV3 Synthesis**

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Triethylamine (TEA) was distilled from CaH$_2$ under N$_2$. Triethylphosphite (98%, Aldrich), 4-aminostyrene (90%, Aldrich), and palladium(II) acetate (98% Aldrich) were used as received. Silica gel plates were 250 mm thick, 40 F254 grade obtained from EM Science. Silica gel was grade 60 (230 - 400 mesh) from EM Science.

Anhydrous DMF (120 mL) was placed in a 250 mL round bottom flask and two freeze-pump-thaw cycles were performed to ensure the removal of oxygen. A large screw-cap tube was charged with 2,5-didecoxy-1,4-diiodobenzene (10.4 g, 16.2 mmol),$^{51}$ tetrabutylammonium bromide (15.7 g, 48.6 mmol), Pd(OAc)$_2$ (0.40 g, 1.62 mmol), and K$_2$CO$_3$ (4.48 g, 32.4 mmol). 4-Aminostyrene (5.00 g, 32.4 mmol) was added to the DMF and the resulting solution was can-
nulated into the screw-cap tube. The tube was sealed with the Teflon cap and the tube was heated to 100 °C for 1 d. After cooling, the crude reaction mixture was poured into water, extracted with Et₂O, dried over MgSO₄, and then the solvent was removed under reduced pressure. The crude product was then purified by silica gel chromatography using 1:1 CH₂Cl₂ : hexanes as eluent. The solid was then recrystallized from CH₂Cl₂ : hexanes to yield 1.57 g (16%) of an orange solid. IR: 3729, 3470, 3375, 3 207, 3025, 2925, 2851, 2648, 2321, 1976, 1622, 1599, 1516, 1466, 1413, 1254, 1172, 962, 895, 812 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.26 (d, J = 8.3 Hz, 4H), 7.18 (d, J = 16.5 Hz, 2 H), 7.01 (2 H), 6.96 (d, J = 16.5 Hz, 2 H), 3.95 (t, J = 6.5 Hz, 4 H), 3.73 (br s, 4 H), 1.78 (m, 4 H), 1.45 (m, 4 H), 1.34 (br m, 24 H), 0.80 (m, 6 H); ¹³C (100 MHz, CD₂Cl₂) δ 151.35, 147.02, 128.95, 128.91, 128.18, 127.21, 120.02, 115.51, 110.58, 70.10, 32.51, 30.26, 30.19, 30.14, 30.06, 29.96, 26.88, 23.29, 14.48. HRMS calcd for C₄₂H₆₀N₂O₂: 624.4655, found: 624.4662.

The structure of the OPV3 Molecule is shown in Figure S10.
References


**Figure 1** Waterfall plot of Raman spectrum (1 s integrations) and electrical conduction measurement for an OPV3 devices. The Raman response is observed to change whenever a change in conductance occurs. Colorbar indicates Raman intensity in CCD counts.

**Figure 2** Waterfall plot of Raman spectrum (1 s integrations) and electrical conduction measurement for an OPV3 devices. The Raman response is observed to change whenever a change in conductance occurs. The number of Raman vibrational modes observed also changes with conductance level. Colorbar indicates Raman intensity in CCD counts.

**Figure 3** Waterfall plot of Raman spectrum (5 s integrations) and electrical conduction measurement for an OPV3 devices. The Raman response is observed to change whenever a change in conductance occurs. Colorbar indicates Raman intensity in CCD counts.

**Figure 4** Waterfall plot of Raman spectrum (1 s integrations) and electrical conduction measurement for an OPV3 devices. The Raman response is observed to change whenever a change in conductance occurs. Colorbar indicates Raman intensity in CCD counts.

**Figure 5** Cartoon of possible junction configurations, using the OPV3 molecule as an example (saturated side chains omitted for clarity). (a) The idealized single-molecule junction, a configuration unlikely in these experiments since interelectrode separation is not precisely controlled. (b-d) Alternative junction configurations, in which interelectrode conduction would be expected to include a contribution from current interacting with the molecule, as well as direct metal-metal tunneling.

**Figure 6** Raman response of an OPV3 junction as a function of time under zero bias. Blue indicates 0 counts and red indicates 100 (8000) counts for antiStokes (Stokes)
sides. Integration time is 1 s. The junction switches stochastically between several stable configurations, each with characteristic spectra that exhibit strong optical pumping of different vibrational modes.

**Figure 7**  A) Effective vibrational temperature as a function of $V$ for two OPV3 modes: 880 cm$^{-1}$ (red) and 410 cm$^{-1}$ (blue). Error bars indicate the uncertainty in inferred effective temperature due to the statistical limitations of the antiStokes amplitude measurements. Inset) IV curve for this device. B) Raman response of this device as a function of $V$. Blue indicates 10 (2500) counts and red indicates 250 (10,000) counts for antiStokes (Stokes). The strong Stokes peak at 520 cm$^{-1}$ is from the Si substrate. C) Sample spectra for given voltage. All antiStokes (Stokes) spectra are plotted on the same scale. Full amplitude corresponds to 1200 (18,000) counts for antiStokes (Stokes).

**Figure 8**  A) Effective electronic temperature (blue) and dissipated electrical power (red) for a device with very little vibrational Raman activity. Error bars are described in text. Inset) $I - V$ curves for these devices. B) Raman response for these devices. Blue indicates 0 counts and red indicates 350 counts. C) Sample spectra (blue) and best fit given by Equation 2 in main text (green) for a given voltage.

**Figure 9**  A) Raman response of the same device shown in Figure 3a in main text. A shift of about 15 cm$^{-1}$ is present for many spectral lines. Blue indicates 2500 counts and red indicates 10000 counts. B) Zoom in of Raman response for the mode centered at 1523 cm$^{-1}$. Blue indicates 2500 counts and red indicates 7000 counts. C) Sample spectra for given voltage. All spectra are plotted on the same scale with a base line of 3000 counts subtracted. Full amplitude corresponds to 4000 counts. The peak at 1523 cm$^{-1}$ can clearly be seen systematically shifting to lower energy at higher voltages reaching 1510 cm$^{-1}$ at 500 mV.

**Figure 10**  OPV3 Molecule