Supplementary Information

Environmental Control of Single-Molecule Junction Transport

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In Figure S1, we shown conductance histograms for BDA measurements in all 13 solvents used in this work. In addition to the most probable junction conductance, determined from the peak positions in these conductance histograms, we can extract experimental information such as the conductance peak width, junction-formation probability and molecular conductance plateau length distribution (see Table 1). We find that the junction formation probability is about 30-60% for all solvents except for measurements in iodobenzene, where it varies from 0% to 30% within one experiments when analyzing sets of 1000 conductance traces. Molecular plateau lengths are very similar for all solvents except for measurements in iodobenzene, as shown in Figure S2. Conductance peak widths vary from solvent to solvent. We find, comparing halogenated solvents, that broader histogram peaks are seen in solvents with higher binding probability, which induce more trace-to-trace variation in the conductance of the Au-BDA-Au junction, in agreement with the theoretical model. Measurements in iodobenzene are at the extreme end of the binding spectrum where BDA is now much less likely to be bound in the vicinity of the junction. This leads to a slight narrowing of the peak.

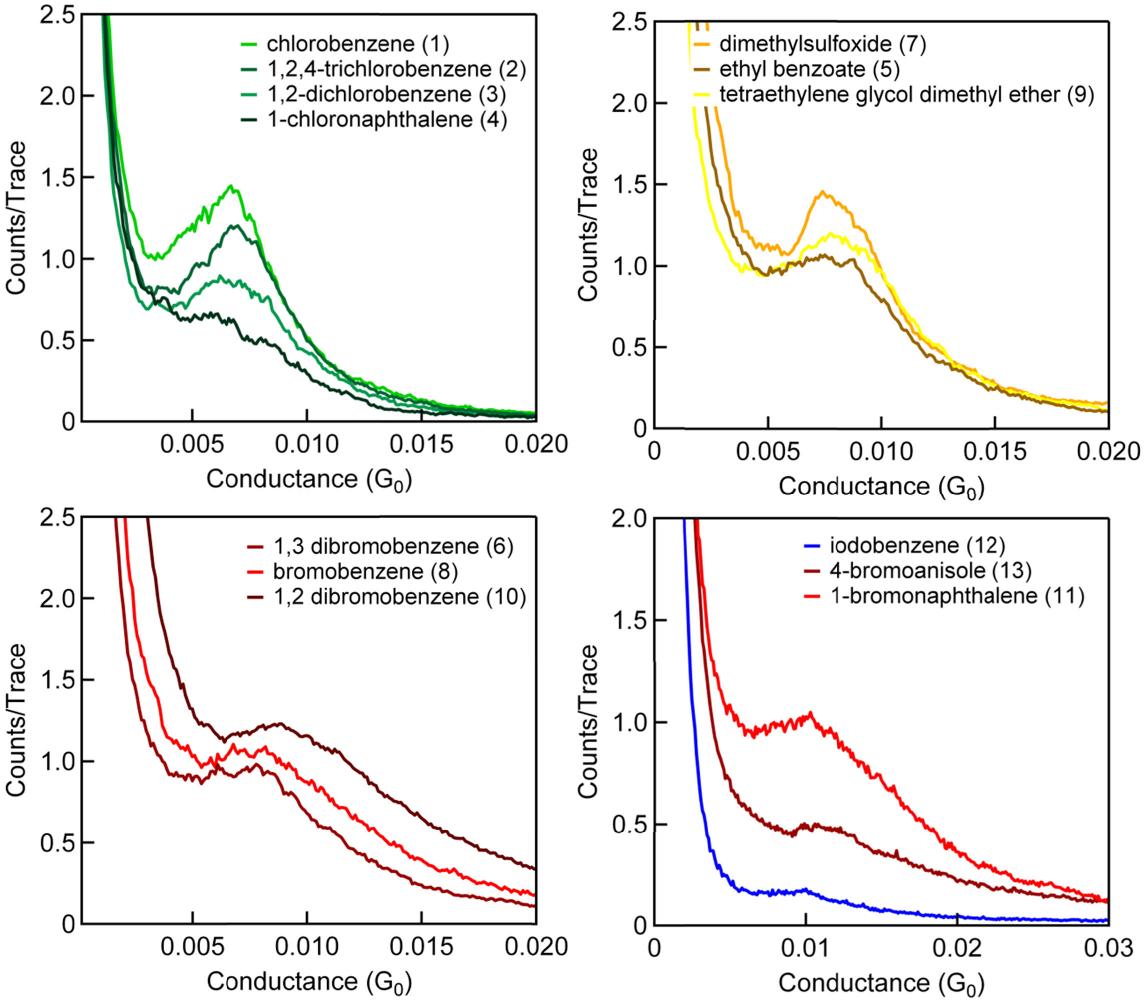

Figure S1: Conductance histograms for measurements of BDA in all solvents used. Linear bin size is 0.0001 G_0. The color trends used here for the solvents will be continued in the document: green for chlorinated solvents, red for brominated solvents, blue for iodized solvents, and yellow for the non-halogenated solvents.

Number	Solvent	G_{BDA} / G_0	Conductance Peak Width	Junction Formation Probability
1	**Chlorobenzene**	**6.6×10^{-3}**	**40%**	**50%**
2	1,2,4-trichlorobenzene	6.7×10^{-3}	40%	50%
3	1,2-dichlorobenzene	6.8×10^{-3}	50%	42%
4	1-chloronaphthalene	6.8×10^{-3}	50%	30%
5	Ethyl Benzoate	7.1×10^{-3}	52%	45%
6	1,3-dibromobenzene	7.8×10^{-3}	55%	40%
7	Dimethylsulfoxide	7.8×10^{-3}	45%	40%
8	**Bromobenzene**	**8.0×10^{-3}**	**60%**	**45%**
9	Tetra(ethylene glycol) dimethyl ether	8.1×10^{-3}	60%	50%
10	1,2-dibromobenzene	$9.5 \text{ x}10^{-3}$	70%	60%
11	1-bromonaphthalene	$1.0 \text{ x}10^{-2}$	70%	60%
12	**Iodobenzene**	**$1.0 \text{ x}10^{-3}$**	**55%**	**0-30%**
13	4-bromoanisole	$1.2 \text{ x}10^{-2}$	100%	45%

Table S1: *Conductance peak position, peak width and junction formation probability for Au-BDA-Au junctions. Junction formation probability gives the probability of determining a plateau in an individual trace that is longer than 0.02 nm, as determined from an automated algorithm as detailed in Quek et al, Nano Letters, vol. 7, pp. 3477-3482, 2007.*

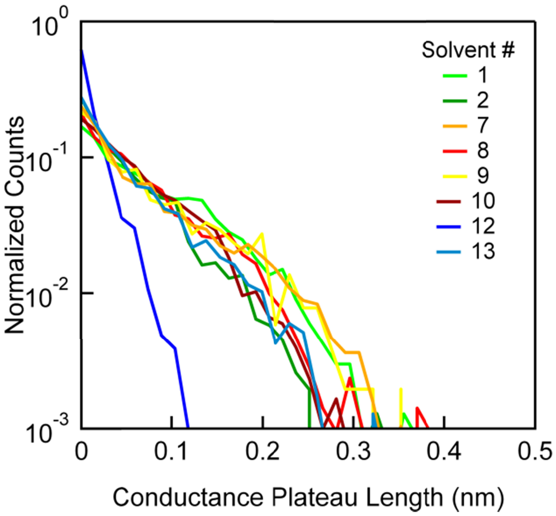

Figure S2: *Conductance plateau length distributions determined from an automated algorithm as detailed in Quek et al, Nano Letters, vol. 7, pp. 3477-3482, 2007 for Au-BDA-Au junctions measured in different solvents.*

Measurements in solvent alone for three sample solvents (no added BDA) are shown in SI Figure S3. We do not observe any peaks in the conductance histograms below G_0. However, the conductance histograms do show changes in the height and the width of the G_0 conductance peak. Specifically, in Iodobenzene, we see that the G_0 peak is clearly smaller. The height of the peak is strictly a result of shorter step lengths. We interpret this result as being an indication of strong solvent-gold interactions; however, we do not have an exact model for this result.

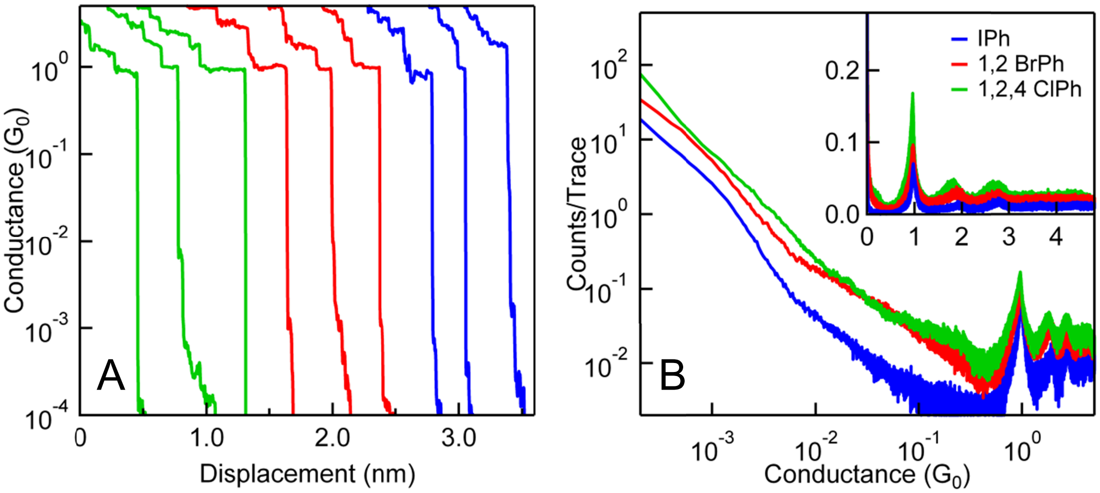

Figure S3 *A: Sample conductance traces measured in solvent alone (green – 1,2,4 trichlorobenzene, red – 1,2-dibromobenzene, blue – iodobenzene). B: Normalized conductance histograms shown on a log-log scale for measurements in solvent alone showing no peak below* G_0*. Linear bin size is 0.0001* G_0*. Inset: Same histograms shown on a linear scale, where changes in the height of the* G_0 *peak is clearly visible.*

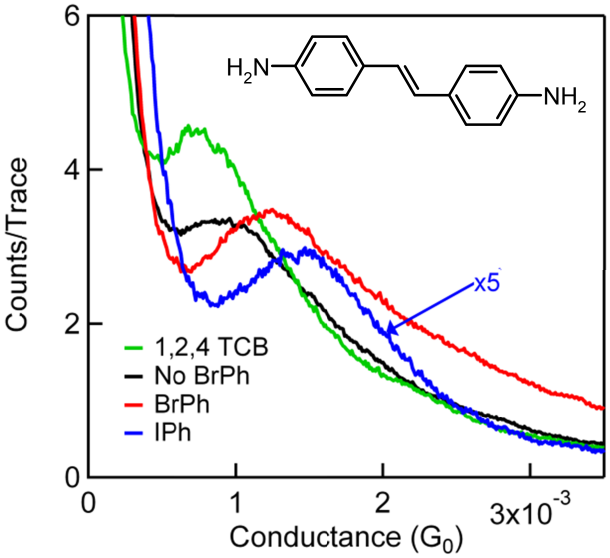

Figure S4: *Normalized conductance histograms for 4,4'diaminostilbene measured in 1,2,4 trichlorobenzene (green), bromobenzene (red), and iodobenzene (blue) shown on a linear scale. The histogram in iodobenzene has been multiplied by 5 for image clarity. Conductance histogram after bromobenzene evaporated from the substrate is shown in black. Linear Bin size is* $1\times10^{-5}G_0$*. Inset: Structure of 4,4'diaminostilbene.*

Measurements of 4,4' diaminostilbene in 1,2,4 trichlorobenzene, bromobenzene and iodobenzene are shown in SI Figure 2 along with the chemical structure of 4,4'diaminostilbene. We see that the conductance histogram peak for 4,4'diaminostilbene is at 0.7×10^{-3} G_0, 1.2×10^{-3} G_0, and 1.4×10^{-3} G_0 in 1,2,4-trichlorobenzene, bromobenzene and iodobenzene respectively. We also see, in the measurements with bromobenzene that the peak position shifts reversibly between 1.2×10^{-3} G_0 and 0.9×10^{-3} G_0 when the solvent evaporates. For this molecule, we see an increase of almost a factor of 2 going from a chlorinated solvent to iodobenzene, in comparison with the 50% increase seen for BDA. This larger increase is consistent with the fact that the HOMO of 4,4'diaminostilbene is closer to Au Fermi, however detailed calculations would be necessary to provide a complete understanding.

Solvent-BDA Interactions: Although it is possible that the solvent interacts with the molecule in a junction, we find these do not correlate with the data. Specifically, in Figure S2A, we show conductance of BDA in different solvents plotted against the solvent dipole moment. There are clear outliers highlighting the lack of correlation. For example, Chlorobenzene and 1,2-dichlorobenzene are similar in chemical structure but have very different dipole moments. However, both solvents result in the same junction conductance. Conversely, chlorobenzene and bromobenzene result in a quite different junction conductance even though they have very similar dipole moments. In Figure S2B, we show junction conductance against bulk solvent dielectric constant. Again, the lack of correlation is very clear. We thus rule out direct intermolecular electrostatic interactions as the mechanism for modulating conductance.

Since direct electrostatic interactions are unlikely to be the dominant mechanism, weaker forces such as intermolecular van der Waals are also expected not to be of significance. Hydrogen-bonding is possible in principle, but significant hydrogen bonding would not be expected for the bromine- and iodine-functionalized solvents and could not account for the large variation in the junction conductance between bromobenzene and iodobenzene, and especially for the difference between bromobenzene and bromonaphthalene, which is taken into account below.

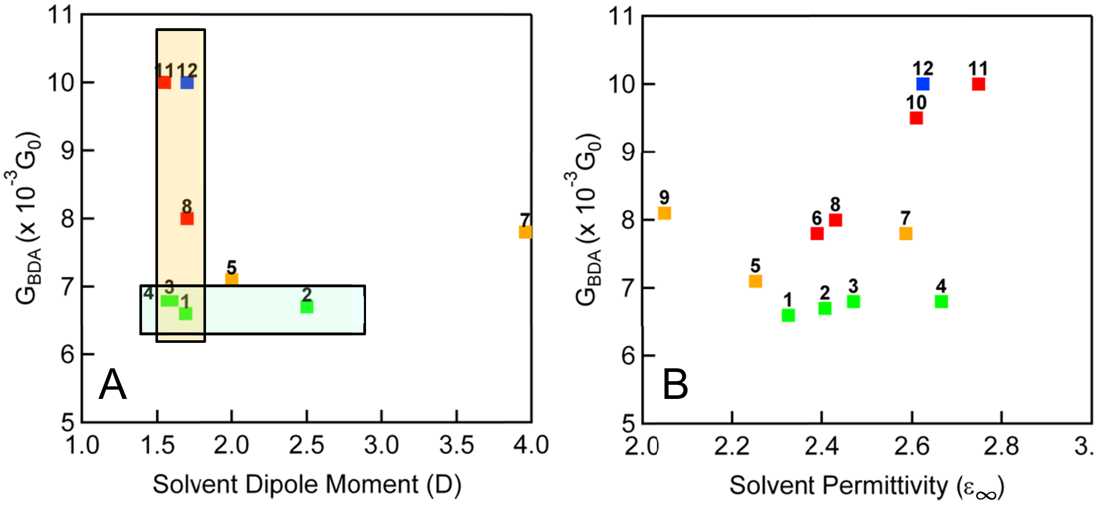

Figure S5: *Conductance of single BDA junctions versus A: solvent dipole moment and B: solvent permittivity*

Statistical Model Details: As noted in the paper, we use a simple two-level Boltzmann model to elucidate the importance of the variation in binding energy. This is simple model, as it neglects possible variations in binding site numbers and assumes similar desorption rates for the different molecules, but it explains trends and provides good insight. We consider the two states, one with two BDA molecules bound in a unit cell and the other with one BDA and one solvent molecule bound in the unit cell. We approximate the energy to replace one BDA with one solvent molecule via the difference in maximum binding energy configurations of the BDA+BDA and BDA+Solvent systems (the solid circles in Fig. 4B). We also take a degeneracy g = 10,000 relating to the number ratio of solvent molecules to BDA molecules based on the solution concentrations used in the measurements. The equation for the probability of the higher-energy state (i.e. BDA replaced by solvent) of a classical two level system is

$$P = \frac{1}{1 + \frac{1}{g} e^{\frac{\Delta E}{kT}}}$$

From this equation, we obtain binding probabilities of 0.99, 0.27 and 0.01 for IPh, BrPh and ClPh respectively. This simple model correlates well with experimental data. The overwhelming binding probability for iodobenzene not only implies higher conductance, but also that fewer Au-BDA-Au junctions will be formed, as seen in the experiments (see below). Furthermore, the extremely low probability for chlorobenzene indicates that it is essentially non-interacting, so that BDA completely dominates the surface. This result also helps to validate previous theoretical work that does not incorporate solvent effects, since most experimental work is conducted in chlorinated or bare hydrocarbon solvents. Finally, the intermediate binding probability for bromobenzene puts it in a unique position: we would expect a reasonably large number of high-conducting junctions, but also a broad range of possible surface coverage distributions – i.e. it would be reasonable to see junctions with almost all BDA in the vicinity as well as junctions with many solvent molecules in the vicinity. Experimentally this would manifest as a broad histogram peak, which is what is observed (see below, and Fig. 1A in the text).

Van der Waals Interactions: van der Waals (vdW) interactions are likely significant, but unfortunately vdW contributions to the binding energy are not present in DFT within the standard approximations used here, as is well known. However, since only binding energy *differences* enter our explanation, we do not expect vdW interactions to complicate our interpretation of the data. All three model solvents and BDA are of similar molecular size and orbital character, and have similar molecular polarizabilities, and so they should have approximately equal vdW interactions with the substrate. However, if we were to change from halo-benzene solvents to halo-naphthalene solvents, the binding energy to the substrate could be stronger due to enhanced vdW interactions (ignoring possible complications due to steric effects). This should increase somewhat the BDA-replacement probability, and thereby (a) increase the conductance and (b) lower junction probability according to our model. Indeed, the data does qualitatively bear this out. Between iodobenzene and iodonaphthalene, junction formation probability goes from very low to statistically immeasurable. From bromobenzene to bromonaphthalene, we see the conductance increase by 22%, though the junction formation probability is 45% and 60% respectively. From chlorobenzene to chloronaphthalene we see no difference, indicating that the increase in binding energy in that case is simply not enough to affect the data. An alternative interpretation of the trend between the benzenes and naphthalenes is that the binding probabilities for halo-benzenes and halo-naphthalenes are similar, but that the larger size of the halo-naphthalenes can exclude BDA from occupying nearby sites, which would significantly affect the surface dipole density (much more than by simply replacing a single BDA). Strictly following this latter picture makes it difficult to explain the complete lack of junction formation in iodonaphthalene. Both vdW and steric effects are likely to play important roles, and future studies are needed to address their competition at a quantitative level.