Electronic supplementary information to:

Revealing tunnelling details by normalized differential conductance analysis of transport across molecular junctions

1. Derivation of Eqs. 7,8

Here is a short derivation of the relation between the $V_{t,q}$ values at an arbitrary NDC=q and V_0 and *S* parameters:

Inserting Eqs. 1 and 2 into Eq. 4 of main text yields:

$$NDC = G\frac{V}{I} = \frac{1 + 2S\left(\frac{V}{V_0}\right) + 3\left(\frac{V}{V_0}\right)^2}{1 + S\left(\frac{V}{V_0}\right) + \left(\frac{V}{V_0}\right)^2} \qquad \text{(S.1)}$$

Rearranging S.1 and setting NDC = *q* and V = V_q, yields:

$$\left(\frac{V_q}{V_0}\right)^2 + \left(\frac{V_q}{V_0}\right) \cdot S\frac{2-q}{3-q} - \frac{q-1}{3-q} = 0 \qquad \text{(S.2)}$$

Eq. S.2 is a quadratic equation, with:

$$x^2 + x \cdot SA - B = 0 \qquad \text{(S.3)}$$

$$x = V_q/V_0; \qquad \text{(S.3a)}$$

$$A = (2-q)/(3-q); \qquad \text{(S.3b)}$$

$$B = (q-1)/(3-q); \qquad \text{(S.3c)}$$

Notice that both A and B are positive for 1<q<2, which is the normal definition range of q.

Solving Eq. S.3 for x, and setting $V_q = V_0 \cdot x$, yields:

$$V_{q\pm} = V_0 \cdot \frac{-SA \pm \sqrt{S^2A^2 + 4B}}{2} \qquad \text{(S.4)}$$

To extract V_0 the SA term should be eliminated; this can be done using $(-a+b)(-a-b) = -(b^2-a^2)$:

$$-V_{q-} \cdot V_{q+} = \frac{V_0^2}{4} \cdot \left[S^2A^2 + 4B - S^2A^2\right] = V_0^2 \cdot B \qquad \text{(S.5)}$$

And therefore:

$$V_0^2 = \frac{-V_{q-} \cdot V_{q+}}{B} \overset{S.3c}{\Rightarrow} V_0 = \sqrt{-V_{q-} \cdot V_{q+} \frac{3-q}{q-1}} \tag{S.6}$$

The simplest way to extract S, is by relaying on the above-extracted V_0 and using the sum of $V_{q\pm}$ values to eliminate the square-root term:

$$V_{q+} + V_{q-} = -V_0 SA \rightarrow S = -\frac{V_{q+} + V_{q-}}{V_0 A} \overset{S.3b}{\Rightarrow} S = -\frac{V_{q+} + V_{q-}}{V_0} \cdot \frac{3-q}{2-q} \tag{S.7}$$

2. Statistic over full data sets

The next two figures show that the reproducibility in NDC-V traces is as good as or even better than the reproducibility of the raw data (see heat maps). The smooth Ag gave narrower distribution of NDC (Fig. S1c) and V_0 (Fig. S1d) than the rough Ag (Figs. S2c,d); the poorer reproducibility of the latter is in line with the explanation of ill-controlled defects.

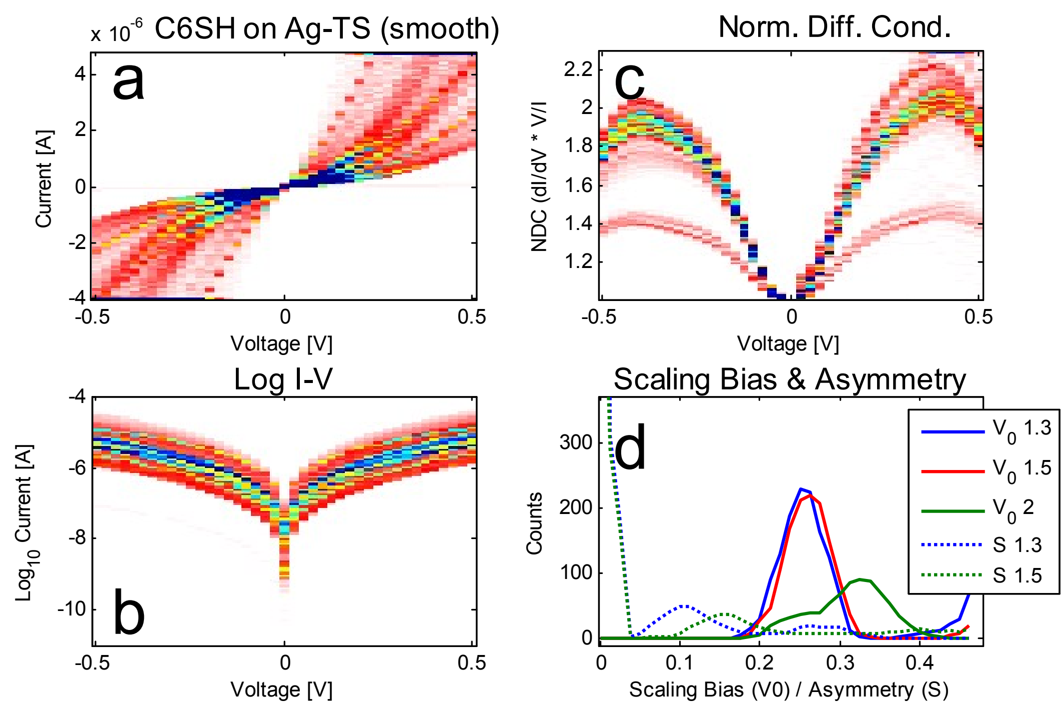

Figure S1: Statistical summary for smooth Ag^{TS}-SC/EGaIn, showing a) heat-maps for linear I-V traces; b) heat-maps for $\log_{10}$(I)-V; c) heat-maps for NDC-V plots; d) histograms of the extracted V_0 and S values (solid and dotted lines respectively), extracted using three values of q = 1.3, 1.5

or 2. There is no *S* value for q=2 because *S* is ill-defined within the parabolic approximation at q=2.

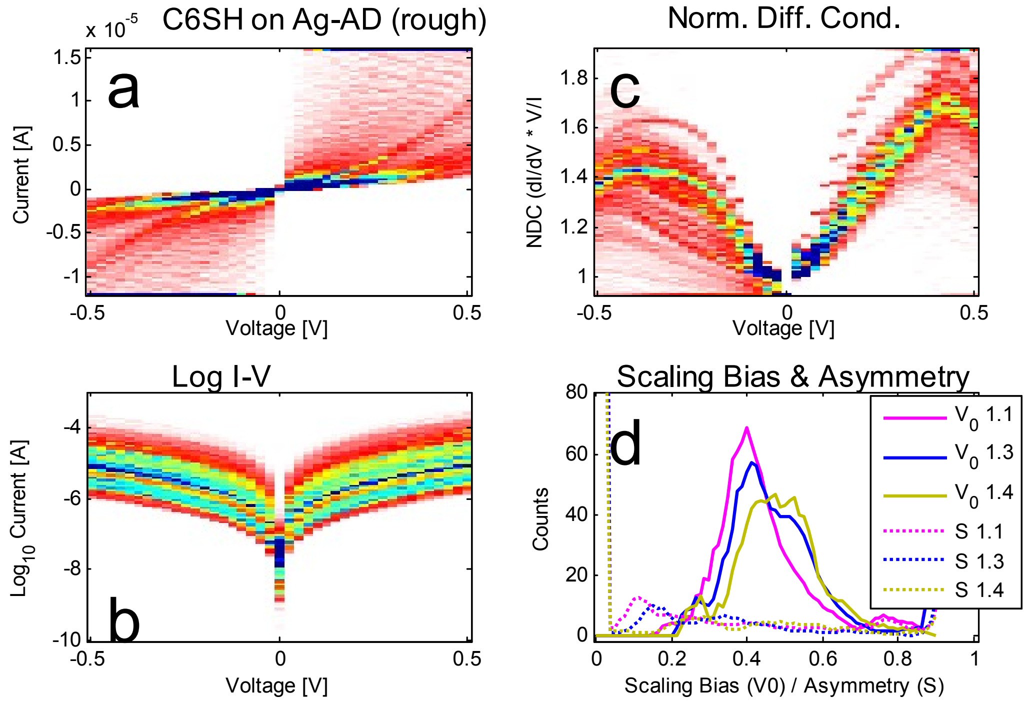

Figure S2: Statistical summary for rough Ag^{AD}-SC/EGaIn, showing a) heat-maps for linear I-V traces; b) heat-maps for $\log_{10}$(I)-V; c) heat-maps for NDC-V plots; d) histograms of the extracted V_0 and *S* values (solid and dotted lines respectively), extracted using three values of q = 1.1, 1.3, or 1.4. The chosen q values are lower than in Fig. S1, because NDC of Ag^{AD} reaches lower values.

3. Derivation the effective G_{eq} and V_0 in the presence of shunt conductance (Eq. 9)

Substituting the parabolic approximation (Eq. 2) into the tunnelling term (I_{Tnl}) of Eq. 9 yields:

$$I_{Total} = G_{eq}V\left[1+\left(\frac{V}{V_0}\right)^2\right] + G_{Shunt}\cdot V \qquad \text{(S.8)}$$

where the *S* term is ignored for shortness. Collecting terms:

$$I_{Total} = (G_{eq}+G_{Shunt})V + G_{eq}\frac{V^3}{V_0^2} \qquad \text{(S.9)}$$

The coefficient multiplying V is the effective equilibrium conductance:

$$G_{eq,eff} = G_{eq} + G_{Shunt} \tag{S.10}$$

Eq. S.9 can be re-written in the form of Eq. 2 by dividing and multiplying the V^3 term by $G_{eq,eff}$:

$$I_{Total} = G_{eq,eff}V + G_{eq,eff}V \cdot \frac{G_{eq} \quad V^2}{G_{eq,eff}V_0^2} \tag{S.11a}$$

Or:

$$I_{Total} = G_{eq,eff}V\left[1 + \left(\frac{V}{V_{0,eff}}\right)^2\right] \tag{S.11b}$$

It implies that the apparent $V_{0,\mathrm{eff}}$ contains an artificial factor:

$$\frac{1}{V_{0,eff}^{\ 2}} = \frac{G_{eq} \quad 1}{G_{eq,eff}V_0^2} \tag{S.12}$$

$$\left(\frac{V_{0,eff}}{V_0}\right)^2 = \frac{G_{eq,eff}}{G_{eq}} \tag{S.13}$$