Supporting Information

Estimation of π-π Electronic Couplings from Current Measurements

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Figure S1 (a) Electrochemical cell with a sample. (b) Setup during the operation.
Figure S2 Gold nanodot electrode fabrication Coloured TEM images of an Au nanodot (adapted from Ref.1). Scale bar is 5 nm.
Figure S3 (a) Typical “oversimplified” schematic representation for Coulomb interactions between redox moieties and the related value of $G$. (b) Schematic representation of the dot to dot dispersion in the energy position for the HOMO level. We write $\delta \varepsilon$ instead of $\delta E_{\text{HOMO}}$ for simplicity and for consistency with conductance statistics analysis. (c) Graphs showing the impact of $G$ and $\delta \varepsilon$ parameters on cyclic voltammograms line shape. FWHM represents the full width at half maximum. (d) Graph showing the correlation between $G$ and $\delta \varepsilon$ parameters as there is always a couple $(G, \delta \varepsilon)$ of solutions to fit data. We see that $G \approx 0$ implies an upper value for $\delta \varepsilon = 45$ meV.
Figure S4 Raw CV measurements at 0.01, 0.1 and 1 V/s and different dots diameters (a) for 15 nm diameter dots. (b) for 22 nm diameter dots. c for 40 nm diameter dots.
Figure S5 CV after baseline removal at 1 V/s for different dots diameters (oxidation and reduction peak) (a) for 15 nm diameter dots. (b) for 22 nm diameter dots. (c) for 40 nm diameter dots.
Figure S6 CV after baseline removal for 22nm-diameter dots at different sweep rates (oxidation and reduction peak) (a) at 1 V/s (b) at 0.1 V/s (c) at 0.01 V/s. (d) Summary of the number of molecules per dot obtained for each peak and the three different sweep rates.
Figure S7 Estimation of the tilt angle from the STM image (a) Example of intercycle extraction from the STM image shown in Fig.1d. In this example, the intercycle distance is 0.27 nm. (b) Histogram of the estimated Inter-cycles distance from Fig.1d. (c) Schematic representation of the molecule tilt angle formed by the Fc and the normal axis (z), based on b. For this estimation, we considered an iron-cycle distance of 1.66 Å based on $^{2,3}$.
Figure S8 Additional DFT calculations (a) DFT calculation of parameter \( t_a \) between molecules 1 and 3. The position of the molecule 3 is translated along the Y axis to mimic disorder. At the maximum for \(|t_a|\), the related molecular configuration is shown in inset. The shape of the HOMO molecular orbital for the Fc moiety is also shown in inset. (b) Evolution of the transfer integral as a function of the intermolecular separation \( d \) modulated from the initial geometry (normal displacement = zero Å). The decay ratios \( \beta_a \) related to \( t_a \) is indicated in the figure. This value is close to the tunnel decay ratio considered in molecular electronics.
Figure S9 (a) 2D current experimental histogram obtained with FeC_{11}SH molecules on 45 nm dots. The dashed curve indicates +0.6 V. (b) Current histogram obtained at tip voltage of +0.6 V for 45 nm dots. Plain curve is the asymmetric log-normal fit and dashed curve is the related symmetric log-normal curve. Inset: Schematic view of the setup.
Figure S10 Optimization of the various parameters for 3x3 molecules and a Gaussian distribution of $t$. (a) Graph showing the impact of $\delta \varepsilon$ parameter on the extracted value of $t$ from fits. $\delta \varepsilon$ has a weak impact on $t$. (b) Graph showing the impact of $V_t$ and $V_b$ parameters on the extracted value of $t$ from fits. The error to fits are shown in (c),(d). Values corresponding to minimum fitting error are indicated by dashed lines (zone in between both lines) and by a blue area. The minimum in (c) is used to choose the value of $V_t$. There is no clear minimum for $V_b$, but value giving good results for all the study, including the current level, is 0.144. It corresponds to a parameter $\alpha = 0.9$. (e),(f) Effect of coupling asymmetry in histograms line shape. Only a large value of $\alpha$ provides reasonable fits.
Figure S11 Impact of the number of molecules considered in the model in the extracted distributions of $t$. (a) Histogram generated from the model with 9 molecules and with consideration of a Gaussian distribution of $t$. It corresponds to $\langle t \rangle = 0.21$ eV and $\delta t = 0.14$ eV. The red line indicates the experimental reference data. (b) Histogram generated from the model with 9 molecules and with consideration of a Gaussian distribution of $d$. It corresponds to $t_0 = 0.34$ eV and $\delta d = 0.29$ Å. The red line indicates the experimental reference data. (c) Distribution of $t$ extracted from the best fits with a Gaussian distribution of $t$, and for 9 and 81 molecules in the model. (d) Distribution of $t$ extracted from the best fits with a Gaussian distribution of $d$, and for 9 and 81 molecules in the model. (e) Graph showing the impact of the number of molecules considered in the model on the extracted value of $t$ from the 2 distributions of $t$ investigated in a-d. In
both cases, $t$ depends exponentially on $N^2$ (with a decay factor of 0.045). The saturation is observed near $N=9$ (81 molecules). The plateau is at about 35 meV in both cases. This result does not mean that $t$ depends on $N$, but that the appropriate number of molecules has to be considered in the model to quantitatively extract $t$. The error to the fit is shown in the right axis. We see that the Gaussian distribution of $t$ gives the largest error, in particular at large $N$. (f) Dependence of estimated $t$ for different values of $V_t$ in the case of 9x9 molecules. This result indicate a weaker dependence of $t$ on molecules/electrode coupling (here $V_t$) when compared to a small number of molecules (see supplementary Fig.10). Also, the minimum error to fits corresponds to $V_t=0.4$eV (the error to fits is doubled when increasing $V_t$ to 0.45eV). Therefore, we can reasonably say that the extracted $t$ is $35 \pm 20$ meV.
Figure S12 Description of cooperative effects on the Transmission coefficient for 1,2,2x2 molecules and $t=0$. (a) Transmission as a function of the electrodes energy for a single molecule site at energy $\varepsilon = 1, 1.5$eV, and an electrode-molecule coupling $V = 0.2, 0.6$eV. For a single molecule, the conductance looks quite like a Lorentzian as a function of the energy of the electrodes. For a small electrode-molecule coupling, the transmission peak is narrow and centered around the molecule energy. When the electrode-molecule coupling is increased, the peak gets wider and it is also slightly shifted as the self-energy acquired because this coupling is larger. Finally, the transmission peak is drifted when the molecule energy is changed. (b-d) Average transmission per molecule as a function of the electrodes energy for $n = 1, 2, 2x2$ sites at energy $\varepsilon = 1, 1.5$eV, and an electrode-molecule coupling $V = 0.2, 0.6$eV. No direct charge transfer between molecules is allowed. When several molecules arranged in a wire couple the electrodes, a multiple path interference is observed, even when direct charge transfer between the molecules is forbidden. This effect does not depend much on the number of sites: the average transmissions per molecule $T(E)/n$ are almost the same for $n = 2$ and $n = 2x2$. 
Figure S13 Description of cooperative effects on the Transmission coefficient for 2, 2x2 molecules and $t \neq 0$. (a) Transmission as a function of the electrodes energy for $n = 2$ molecule sites arranged in a line at energy $\varepsilon = 1, 1.5$eV, and an electrode-molecule coupling $V = 0.2, 0.6$eV. When coupling between molecules is switched on, the transmission peak splits into 2 peaks. The peaks get more and more separated as transfer integral between molecules is increased. In fact, as many peaks as the number $n$ of molecules appear. This can be seen when diagonalizing $H_{mol}$ (see supplementary Methods): the peaks observed in the transmission are centered around its eigenvalues. This diagonal basis for $H_{mol}$ is called the conduction channels basis. For example, at $n = 2$, the eigenvalues of the molecular Hamiltonian are $\varepsilon \pm t$, which explains why the peaks are drifted away when $t$ is increased. (b) Transmission as a function of the electrodes energy for $n = 2x2$ molecule sites arranged in a square at energy $\varepsilon = 1, 1.5$eV, and an electrode-molecule coupling $V = 0.2, 0.6$eV. When charge transfer between molecules is switched on, the transmission peak splits into 4 peaks. The peaks get more and more separated as the transfer integral is increased.
Figure S14 Transmission function and evaluation of the approximation error in current estimation from eq 18 (a) Transmission as a function of electrode energy for 9×9 molecules (with parameters used to fit histograms). (b) Ratio of the current estimated from eq 18 and 13 considering the T(E) shown in (a).
**Table S1** Fitting parameters for CV. \(E_{p1}, E_{p2}\) are the peak position (oxidation state, 1V/s) for peak 1 and peak 2, respectively. FWHM\(_1\) and FWHM\(_2\) correspond to the FWHM of peak 1 and peak 2, respectively, and \(G_1, G_2\) Laviron interaction parameters (see supplementary Methods) used to obtain \(\phi_1\) and \(\phi_2\).

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**Table S2** Fittings of conductance histograms using asymmetric peaks (the function is given in Supplementary Methods). Full coverage by FcC\(_{11}\)SH on 45 nm diameter at +600mV and -600mV, full FcC\(_{11}\)SH coverage and diluted with C\(_{12}\)SH (1:1) on 15 nm dots. From plots in Fig.4.
Supplementary Note 1: History of conductance histograms in molecular electronics

Recognizing that experimental transport through molecules is usually a tunneling process in which the conductance $G$ is defined as $G = A \exp(-\beta d)$ where $A$ is a contact conductance, $\beta$ a tunnel decay constant and $d$ the molecule length, the shape of this peak is often well-described by a log-normal distribution\(^4\)\(^-\)\(^7\) (Fig. 1b). Peak width (its variance) has been mainly attributed to the adsorption chemistry of the molecule with the electrode, but not discussed quantitatively\(^5\)\(^,\)\(^7\)\(^-\)\(^2\)\(^1\). For micrometer-size devices, the log-normal distribution is related to the averaging over various molecular phases and to grain boundaries.
Supplementary Methods:

UHV-STM

The high resolution image was performed at room temperature with a substrate biased at 2V and at a constant current of 1 pA. We are not aware of such clear image at molecular (even sub-molecular: see supplementary Fig.7) level on a dense monolayer FcC_nSH monolayer (see ref.22 for an image obtained with a low density of molecules and ref.23 for the supramolecular structure obtained when n<5). A rectangular crystal-like structure distorted from the (√3x√3) R30° lattice of Au was previously observed in refs.22, 23. It is rather unexpected for the present monolayer to observe a similar trend as it is believed that Fc-Fc interactions dominate for the short SAMs (n<5) and when n>5, C_n-C_n interactions dominate. We believe that this discrepancy can be attributed to the gentle ultrasonication step in the process. As mentioned in the previous section, this step was required to avoid pollution of the tip from adsorbed molecules on silica. It may bring enough energy to release strain in the monolayer leading to a configuration where the Fc-Fc interactions dominate as for shorter alkyl chains. Interestingly, we find the same tilt angle of Fc (to the normal of the surface) as FcC_{11}SH monolayers with stronger van der Waals interactions. The present crystal-like structure is perfectly adapted to the present study.

Gold nanodot electrode fabrication

The fabrication of the gold nanocrystal arrays have been described elsewhere.²⁴ To perform this study, we have developed an high-speed e-beam lithography technique to get large areas covered with Au nanocrystals arrays.²⁴ For e-beam lithography, an EBPG 5000 Plus from Vistec Lithography was used. The (100) Si substrate (resistivity
= 10³ Ω.cm) was cleaned with UV-ozone and the native oxide etched before resist deposition. The e-beam lithography is optimized by using a 45 nm-thick diluted (3:5 with anisole) PMMA (950 K). For the writing, an acceleration voltage of 100 keV was used, which reduces proximity effects around the dots, compared to lower voltages. The dose per dot corresponds to 3-4 fC. The conventional resist development / e-beam Au evaporation (8 nm) / lift-off processes were used. Immediately before evaporation, native oxide is removed with dilute HF solution to allow good electrical contact with the substrate. Single crystal Au nanodots can be obtained after thermal annealing at 260°C during 2 h under N₂ atmosphere. During this process, a thin layer of SiO₂ covers the dots. This layer is removed by HF at 1% for 1 mn prior to SAM deposition. Minimum spacing between Au nanodots is 50 nm, which is the configuration used for cyclic voltammetry measurements.

**Self-assembled monolayers**

For the SAM deposition, we exposed the freshly evaporated gold surfaces and gold nanocrystals to 1 mM solution of 11-ferrocenyl-1-undecanethiol (95% pure from Aldrich) in 80% ethanol (VLSI grade from Carlo Erba) 20% dichloromethane during 24 h in a glovebox in the darkness. Then, we rinsed the treated substrates with ethanol followed by a cleaning with gentle ultrasonication (20% power, 80 kHz) in a bath of chloroform (99% from Carlo Erba) during 1 min. The gentle ultrasonication was required to avoid pollution of the tip from adsorbed molecules on silica. It may play a role in the present molecular organization. In the future, ultrasonication may not be necessary if a monolayer of silane molecules is grafted between dots to prevent non-specific adsorption. For the diluted monolayer of FeC₁₁SH with C₁₂SH molecules (95% pure from Aldrich), both molecules (1:1) were inserted simultaneously, and the
grafting/rinsing procedure remained identical. For the gold substrate electrode used for the STM image, 5 nm of Ti and 100 nm of Au were evaporated at 3 Å/s at 10⁻⁸ Torr, the self-assembly process remaining identical to the one for the gold nanodot electrodes.

**Cyclic Voltammetry**

Supplementary Fig. 3 shows the electrochemical cell used in this study. The 0.5 mL container is filled with NaClO₄ (0.1M in water) as the electrolyte. The cell is connected with the Solartron ModuLab potentiostat by the three typical electrodes. The nanocrystals operate as the working electrode, a platinum wire as the counter electrode, and a typical Ag/AgCl electrode is used as the reference electrode. Before the experiment, the electrochemical cell is cleaned with ethanol and DI water. “Test” sweeps between -0.1 and 0.6 V with a highly doped silicon substrate (without dots) are measured to confirm that there is no peak due to contamination. Cyclic voltammetry (stable under several voltage cycles) proves the presence of ferrocene-thiol electroactive molecules and allows their quantification. The electrochemical characterization of a sample with few molecules per dot is challenging, in particular in the gold nanoarray structure. Indeed, in Cyclic Voltammetry, the ratio of capacitive current (background noise) to faradic current (signal) is magnified due to the presence of areas (capacitors) between dots without molecules. The Square Wave Voltammetry is the technique of choice to reduce the capacitive contribution. It is based on the fact that the capacitive current decays faster than the Faradic current. The wave has to be optimized to measure the current when the charging current can be considered negligible, but not too low for getting enough signal. Also, due to the increased complexity of the waveform, a calibration procedure has to be done for the SwV (based on cyclic voltammetry) in order to estimate the density of molecules assembled on the dots. A linear regression
has been obtained between the CyV at 1V/s and the SwV with the effective scan speed of 0.1 V/s (step: 1 mV, pulse: 20 mV, frequency: 100 Hz, integration period: 100%), the experimental condition selected in this study. CyV and SwV were performed on the same samples with 15 nm diameter dot and at three different dilution ratios (1:0, 1:1 and 1:10).

**Voltammograms fits with consideration of Coulomb interactions**

The extended Laviron model based on Coulomb interactions between redox molecules, leads to the following equations. It enables a direct comparison with experimental data:

\[
i(\theta_O) = \frac{n^2 F^2 A v \Gamma_{\text{max}}}{RT} \frac{\theta_O (\theta - \theta_O) \theta}{\theta^2 - 2G\theta_O \phi(\theta)(\theta - \theta_O)}
\]  

(Eq.S1)

where \(i\) is the measured voltammetry current, \(A\) is the cell area, \(\Gamma_{\text{max}}\) is the total surface coverage (mol.cm\(^{-2}\)) of the redox-active species; \(n\) is the number of electrons exchange per molecule during a redox process; \(v\) is the potential scan rate (V.s\(^{-1}\)); \(F, R\) and \(T\) are the Faraday constant, the universal gas constant and the absolute temperature, respectively. \(\theta_O\) and \(\theta_R\) are the oxidized and reduced normalized surface coverage values with \(\theta_O + \theta_R = 1\), \(G\) a global constant of interaction, \(\Theta\) represents the total fraction of molecules and \(\phi(\theta)\) the segregation factor. A versatile function was recently introduced to fit symmetric voltammograms (\(I\) vs \(E\)) with intermolecular interactions as in the present paper.26
**Estimation of Coulomb interaction energy $\phi$ from Laviron model and Frumkin isotherm**

Cooperative effects can be discussed quantitatively based on $G$ parameter (a Coulomb energy normalized by the thermal energy). $G>0$ corresponds to global attractive interactions (voltammogram FWHM below 90 mV) and $G<0$ to global repulsive interactions (voltammogram FWHM above 90 mV). The link between $G$ and $\phi$ can be obtained based on the Frumkin isotherm,\(^{27}\) in the special case of oxidized species interactions:

$$\phi = -\frac{2{kT}G}{N_a}$$  \hspace{1cm} (Eq.S2)

where $k$ is the Boltzmann constant, $T$ the temperature, and $N_a$ the number of nearest neighbors on the completely covered surface (4 in the present configuration based on the STM image). Values obtained from Eq.S2 correspond to the Coulomb energy interactions between punctual neighboring sites. From fits of Figs.2e-h, we get $G_1\approx -0.356$ ($G_2\approx +0.959$) for all dot diameters. This parameter is in the range of previous reports with Fe SAMs\(^{28}\), although values as large as -1.4 have been reported. Based on Eq.5 with $N_a=4$, it corresponds to $\phi=4.5$ meV.

**DFT calculations**

The transfer integral has been calculated within the dimer fragment approach, as implemented in the Amsterdam Density Functional package.\(^{29}\) Dimer orbitals are expressed as a linear combination of molecular orbitals of the fragments, which are obtained by solving Kohn Sham equations. Transfer integrals $t_{ij}$ are obtained by computing:

$$t_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$$  \hspace{1cm} (Eq.S3)

where $\phi_i$ and $\phi_j$ correspond to HOMO orbitals of the isolated molecules (i.e., fragments). The HOMO is localized over the $\pi$ orbitals of the cyclopentadienyl rings without a
significant weight over the Fe atom. Transfer integral $t_{12}$ has been evaluated at the DFT level\textsuperscript{30} by using the B3LYP (Becke, three-parameter, Lee Yang Parr) hybrid functional\textsuperscript{31} with a Triple Zeta Polarized basis set. Due to non-orthogonality of the basis set, the transfer integral value is not uniquely defined and depends on the definition of the energy origin\textsuperscript{32}. This problem is solved by applying a Löwdin transformation to the initial electronic Hamiltonian, resulting in the following expression of the transfer integral between orthogonal functions used in charge transport models:

$$\tilde{t}_{12} = \frac{t_{12} - (\varepsilon_1 + \varepsilon_2)S_{12}}{1 - S_{12}} \quad \text{(Eq. S4)}$$

where $S_{12}$ represents orbital overlap.

The transfer integral has been calculated for two neighboring Fc units (fragments). Initial position parameters for the neighboring fragments have been deduced from the experimental STM images (base $a = 6.778\text{Å}$, $b = 4.675\text{Å}$, $\gamma = 75.78^\circ$). The tilt angle formed by Fc and the normal axis is $\theta = 60^\circ$, in agreement with previous works and the STM image. The external electric field barely affects parameter $t^{33}$.

**Image treatment**

Images are treated on Origin C program. The 1st function (Threshold) applies a threshold to put 0 in the matrix below the threshold, it removes the background noise. Then, 2nd function (maxi) obtains the maximum per dot by checking the nearest neighbors. The functions are available in Supplementary Methods.
Origin C functions for Histogram generation from CAFM images

```c
void Threshold(string strName, double thmin, double thmax, int ibegin, int iend, int jbegin, int jend)
{
    Matrix mm(strName);
    for (int i=ibegin; i<iend; i++)
    {
        for (int j=jbegin; j<jend; j++)
        {
            if ((mm[i][j]<thmin)||(mm[i][j]>thmax)) {mm[i][j]=0};
        }
    }
}

void maxi(string strName, int neighbors, int ibegin, int iend, int jbegin, int jend)
{
    Matrix mm(strName);
    for (int i=ibegin; i<iend; i++)
    {
        for (int j=jbegin; j<jend; j++)
        {
            if(mm[i][j]!=0)
            {
                for (int k=-1*neighbors; k<=neighbors; k++)
                {
                    for (int l=-1*neighbors; l<=neighbors; l++)
                    {
                        if ((i+k)>=0&&((j+l)>=0)&&(i+k)<iend)&&(j+l)<jend))
                        if(mm[i+k][j+l]>mm[i][j])
                            {mm[i][j]=0};
                    }
                }
            }
        }
    }
}
```
int a=0;

Worksheet wks;
wks.Create("histogram.otw");
WorksheetPage wksp=wks.GetPage();
wksp.Rename("histogram");

string str;

for (int m=ibegin; m<iend; m++)
{
    for (int n=jbegin; n<jend; n++)
    {
        if (mm[m][n]!=0)
        {
            str.Format("%f",mm[m][n]);
            wks.SetCell(a, 0, str); // set the value to a cell of worksheet
            a++;
        }
    }
}

**Theoretical histogram generation (Landauer-Buttiker-Imry formalism)**

Electron transport between two normal electrodes through an array of molecules at temperature $T = 0$ is considered. Each electrode is modeled as a semi-infinite cubic lattice of single-state sites and any site on its surface can be connected to one molecule modeled as a single-level quantum dot (QD).

Two electrodes modeled as semi-infinite 3D tight-binding metals connected via an array of molecules. Each electrode site (black ball) can be connected to one molecule (green ellipse).

The total Hamiltonian of the system reads:

$$
\hat{H} = \begin{pmatrix}
\hat{H}_{el,R} & \hat{V}_R & 0 \\
\hat{V}_R & \hat{H}_{mol} & \hat{V}_L \\
0 & \hat{V}_L & \hat{H}_{el,L}
\end{pmatrix} \quad (Eq. \ S5)
$$

where $\hat{H}_{mol}$ is the Hamiltonian for the array of molecules and $\hat{H}_{el,R/L}$ the one of the right and left electrodes, while the couplings between electrodes and molecules read

$$
\hat{V}_{R/L} = \sum_{\alpha,\beta} V_{R/L} |\alpha, \beta\rangle \langle m_\alpha, n_\beta| \quad (Eq. \ S6)
$$
with electrode-molecule coupling constants \( V_R \) and \( V_L \) (assumed equal for all molecules). \( |\alpha, \beta\rangle \) is the state at site \((\alpha, \beta)\) on the electrode surface while \(|m_\alpha, n_\beta\rangle\) is the state of the molecule at position \((m_\alpha, n_\beta)\).

\( \hat{H}_{mol} \) can be written generally as:

\[
\hat{H}_{mol} = \varepsilon |m_\alpha, n_\beta\rangle \langle m_\alpha, n_\beta| - t \left[ |m_\alpha, n_\beta\rangle \langle m_\alpha, n_\beta + 1| + |\alpha, \beta\rangle \langle m_\alpha, n_\beta + 1| \right] + \text{h.c.}
\]

where \( \varepsilon \) is each molecule energy level and \( t \) is a nearest neighbor transfer integral between molecules, which can be switched on and off. Note that molecules are not only coupled each other, but also via the electrodes: this is a substrate-mediated coupling. These two couplings are collectively termed cooperative effects. Focusing on electronic transport through the molecules, the leads degrees of freedom are integrated out leaving us with the following effective Hamiltonian:

\[
\hat{H}_{eff} = \hat{H}_{mol} + \hat{\Sigma}_R(E) + \hat{\Sigma}_L(E) \quad \text{(Eq. S7)}
\]

\[
\hat{\Sigma}_{R/L}(E) = V_{R/L} \hat{g}_{el}(E) V_{R/L}^\dagger = |V_{R/L}|^2 \hat{g}_{el}(E) \quad \text{(Eq. S8)}
\]

The isolated electrode Green’s function \( \hat{g}_{el}(E) \) is obtained through Haydock recursion \(^{34}\), leading to the matrix components

\[
g_{|m-m'|,|n-n'|}(E) = \langle m', n'| \hat{g}_{el}(E) |m, n\rangle = \frac{1}{2|V_{el}|^2} \int_0^\pi d\theta_1 \cos(|m - m'| \theta_1) \int_0^\pi d\theta_2 \cos(|n - n'| \theta_2) 
\times \Xi \left( \frac{E}{2|V_{el}|} + \cos \theta_1 + \cos \theta_2 \right) \quad \text{(Eq. S9)}
\]

\[
\Xi(x) = 2x - 2 \text{sign}(x + 1) \sqrt{x^2 - 1} \quad \text{(Eq. S10)}
\]

where the nearest-neighbor coupling within the electrodes is set to \( V_e = 0.82 \ eV \). \(^4\)

It follows that the full Green’s function of the molecules dressed by the coupling to the electrodes can be defined as:

\[
\hat{G}(E) = \left[ E \hat{1} - \hat{H}_{eff}(E) \right]^{-1} \quad \text{(Eq. S11)}
\]

The transmission through the molecular QDs finally reads:
\[ T(E) = Tr \left( \hat{\Gamma}_R(E) \hat{G}(E) \hat{\Gamma}_L(E) \hat{G}^\dagger(E) \right) \]  
(Eq. S12)

where we introduced the scattering rate between molecules and electrode \( \mu \) as \( \hat{\Gamma}_\mu(E) = -2 \left| V_\mu \right|^2 \text{Im} \{ \hat{g}_{el}(E) \} \).

The zero-temperature current through the molecules biased at voltage \( V \) is then given by

\[ I(V) = \frac{2e}{h} \int_{E_F}^{E_F+eV} dE \ T(E, V) \]  
(Eq. S13)

where \( E_F \) is the Fermi energy of the electrodes and \( T(E, V) \) corresponds to the energy-dependent transmission \( T(E) \) where we accounted for a bias-related shift in the dot level energy \( \epsilon \to \epsilon(V) = \epsilon + eV \frac{|V_R|^2}{|V_R|^2 + |V_L|^2} \).

**Isolated molecule**

The single-molecule Hamiltonian reduces to

\[ \hat{H}_{mol} = \epsilon |0, 0\rangle \langle 0, 0| \]  
(Eq. S14)

so that the transmission finally takes the Breit-Wigner-like form

\[ T(E, V) = \frac{\frac{4}{|V_R|^2} \frac{|V_L|^2}{|V_R|^2 + |V_L|^2} \text{Im}(\hat{g}_{00}(E))^2}{E - \epsilon - eV - \frac{V_R^2}{|V_R|^2 + |V_L|^2}} \]  
(Eq. S15)

Integrating it over the energy window set by the external voltage, this expression allows us to get the current value and check the reasonable choice of coupling parameters.

**Array of \( N \times N \) molecules**

We consider a square of \( N \times N \) molecules, the site basis being ordered as \( \{|1, 1\}, |1, 2\}, ..., |1, N\}, |2, 1\}, |2, 2\}, ..., |N, N\} \). The Hamiltonian of this system
describes the coupling of each molecule to both its horizontal and vertical nearest neighbors, and reads, in the case $N = 3$,

$$
\tilde{\mathcal{H}}_{mol} = \begin{pmatrix}
\epsilon & t & 0 & t & 0 & 0 \\
 t & \epsilon & t & 0 & t & 0 \\
 0 & t & \epsilon & 0 & 0 & t \\
 t & 0 & 0 & \epsilon & t & 0 \\
 0 & t & 0 & t & \epsilon & t \\
 0 & 0 & t & 0 & t & \epsilon
\end{pmatrix}
$$

(Eq. S16)

where $\epsilon$ is the molecular energy level and $t$ is the transfer integral, coupling nearest neighbors of the array in both directions.

The electrode Green’s function is then expressed in this site basis using Eq. S9 and the horizontal and vertical lengths $|m - m'|$ and $|n - n'|$ between the two considered molecules. In the case of, e.g. $N = 3$, one thus has in this basis

$$
\hat{g}_{el}(E) = \begin{pmatrix}
g_{00} & g_{01} & g_{02} & g_{10} & g_{11} & g_{12} & g_{20} & g_{21} & g_{22} \\
 g_{01} & g_{00} & g_{01} & g_{10} & g_{11} & g_{12} & g_{20} & g_{21} & g_{22} \\
 g_{02} & g_{01} & g_{00} & g_{12} & g_{11} & g_{10} & g_{22} & g_{21} & g_{20} \\
 g_{10} & g_{11} & g_{12} & g_{00} & g_{01} & g_{02} & g_{10} & g_{11} & g_{12} \\
 g_{11} & g_{10} & g_{12} & g_{01} & g_{00} & g_{01} & g_{11} & g_{10} & g_{11} \\
 g_{12} & g_{11} & g_{10} & g_{02} & g_{01} & g_{00} & g_{11} & g_{10} & g_{11} \\
 g_{20} & g_{21} & g_{22} & g_{10} & g_{11} & g_{12} & g_{00} & g_{01} & g_{02} \\
 g_{21} & g_{20} & g_{22} & g_{11} & g_{10} & g_{11} & g_{01} & g_{00} & g_{01} \\
 g_{22} & g_{21} & g_{20} & g_{12} & g_{11} & g_{10} & g_{02} & g_{01} & g_{00}
\end{pmatrix}
$$

(Eq. S17)

Using the symmetry $g_{|m-m'|,|n-n'|}(E) = g_{|n-n'|,|m-m'|}(E)$ one can reduce this $N^2 \times N^2$ matrix down to only $\frac{N(N+1)}{2}$ independent coefficients. Once $\hat{g}_{el}$ is known, the self-energy $\hat{\Sigma}$ entering the effective Hamiltonian can be computed, ultimately giving access to the full Green's function $\hat{G}(E)$ expressed in the same site basis, and finally to the energy-dependent transmission $T(E)$. 
Computing transport histograms

In order to compare to the experimental results, we would like to compute current histograms. Each histogram typically relies on $10^6$ realizations which requires a very large number of integrals (Eq.S13), making the computation untractable. This is particularly true for large values of $N$. In order to speed up the numerical computations, we need to significantly reduce the number of evaluations of the transmission. To do so, we approximate the current integral using a midpoint rule:

$$I(V) = \frac{2e}{h} eV T \left( E_F + \frac{eV}{2}, V \right).$$  \hspace{1cm} (Eq.S18)

As it is the case for any Newton-Cotes-like scheme, the error is related to the second derivative of the integrand. Focusing on an applied bias $V=-0.6$ V, one readily sees that the transmission, although not quite linear, is monotonous and only weakly convex over the domain of integration (Fig.S14a), therefore justifying our approximation. For this choice of external bias, the current is thus dominated by the transmission evaluated at the center of the voltage window. Fig.S14b shows the ratio of the approximated current (Eq.S18) over the current obtained from the integrated transmission (Eq.S13) as a function of the applied voltage. The error from the approximation made with Eq.S18 is acceptable at the studied bias given that the current distribution spreads over more than one decade. We stress that a larger error arises at positive bias. In any case, further studies would benefit from a refined evaluation of the current integral (using e.g. Simpson's rule) concomitantly with an overall optimization of the numerical computations.
At fixed voltage $V$, and for a given array of $N \times N$ molecules, transmission histograms are evaluated assuming a Gaussian distribution of all four relevant parameters of the effective Hamiltonian $\hat{H}_{\text{eff}}$, thus requiring a total of 8 parameters to be determined, namely

$\epsilon$: molecular energy
$
\delta\epsilon$: molecular energy standard deviation
$V_{e/b}$: electrode-molecule coupling constants
$
\delta V$ : standard deviation of the coupling constants
$t$: average inter-molecule coupling energy
$
\delta t$: standard deviation of the coupling energy between molecules

**Estimating the relevant parameters**

Focusing on the particular case of an external voltage bias $V = -0.6$ $eV$, we could determine the values of the coupling constants $V_{e/b}$ by computing the current in the isolated molecule case (numerically integrating Eq. S15 over energy) and matching it to the experimentally measured value.

Moreover, experimental data suggest that the molecular energy level $\epsilon$, measured from the Fermi energy of the electrodes is of the order of 0.2 $eV$. From electrochemistry results, we could infer that the standard deviation of the molecular energy is bounded, so that $\delta\epsilon < 0.045$ $eV$. In order to probe the effect of this distribution in molecular energy, we typically consider several possible values of $\delta\epsilon$ within this interval. However, when studying the influence of other parameters, we assume an average value of $\delta\epsilon = 40$ meV.
We now focus on the experimental situation of (1:1) dilution. This situation corresponds to weak cooperative effects and is more accurately described in our case by the isolated molecule approach. Assuming for simplicity that \( \delta V_t = \delta V_b \), this allows us to determine the value of \( \delta V \) upon generating the conductance histogram which best reproduces the experimentally measured log-normal shape.

We then move on to the (1:0) dilution ratio. There, the cooperative effects are expected to be strong and we use our model relying on an array of \( N \times N \) molecules. We thus need to determine the values of the two remaining parameters, namely the average inter-molecule coupling energy \( t \) and the corresponding standard deviation \( \delta t \). These are obtained from the current histogram that best approaches the asymmetric double sigmoidal function (Eq.4) where the values of the various parameters are presented in Table S2.

In order to perform a systematic determination of these parameters, we introduce a new quantity \( d_{fit} \) which measures the distance in the space of real-valued functions between the asymmetric function \( f(x) \) that fits the experimental data, and the transmission histogram generated from the present theoretical approach

\[
d_{fit} = \sum_{i=1}^{N_{bin}} \frac{|H_i - f(x_i)|}{N_{bin}}
\]

(Eq.519)

where \( i \) labels the \( N_{bin} \) bins of the histogram, of height \( H_i \) and centered on \( x_i \). We then determine the values of \( t \) and \( \delta t \) that minimize this distance \( d_{fit} \) to the fitting function.

**Normalizing histograms**

In order to compare experimental and theoretical results, we need to find a common normalization as different histograms can be constructed with different number of total counts. One possibility is to scale the experimental data so that the tallest bin
corresponds to a count of 1. This in turn leads to a fitting function equivalent to the one in Eq. S18, only with a new parameter $A'$ (in place of $A$), accounting for this rescaling.

It follows that the total area covered by the fitting function is now

$$S = \int_{-\infty}^{\infty} dx \ A' \ \frac{1}{1+e^{-(x-x_c+w_1/2)/w_2}} \left( 1 - \frac{1}{1+e^{-(x-x_c-w_1/2)/w_3}} \right) \approx 0.436 \ A' \quad \text{(Eq.S20)}$$

where we used the values of $w_1$, $w_2$ and $w_3$ from supplementary Table 3. We then apply a rescaling prefactor to the transmission histograms generated according to the formalism described above in order for their total area to precisely match the one in Eq. S20.
Supplementary References:

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