# Supporting Information

## for

## "Design of an efficient coherent multi-site single-molecule rectifier"

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#### I. ASYMMETRIC COUPLING TO THE ELECTRODES

To investigate the dependence of the rectification ratio on the coupling to the left ( $\Gamma_L$ ) and right ( $\Gamma_R$ ) electrode, both parameters were varied, as shown in Fig. S.1. In the main text,  $\Gamma_{L,R}$  were set to 100 meV. However, the plot shows that the rectification ratio can be significantly increased by having a weaker electronic coupling to the electrodes. More, introducing an asymmetry in the coupling can also slightly improve the diode performance.



FIG. S.1. **RR** versus  $\Gamma_L$  and  $\Gamma_R$  calculated using **DFT** + **NEGF** for the H-CCH-Cl-CN substituted molecule.

## II. FIT PROCEDURE

In the following, a detailed description of the fitting routines is provided.

#### A. Symmetric case

To obtain the parameters for  $\alpha_{1,2}$ ,  $\tau_{1,2}$  and  $\epsilon_{1,2}$ , the eigenvalues of the 4-site model were fitted to the values of the energy of the HOMO until HOMO-3 for different bias voltages. This was done using the following routine

• For a rough estimate of  $\epsilon_{1,2}$  and  $\tau_{1,2}$ , the mean-squared error (MSE) between the zerobias 4-site eigenvalues and the zero-bias DFT eigenvalues was calculated for a large range of  $\epsilon_{1,2}$  and  $\tau_{1,2}$  and the minimum MSE determined.

- To increase the resolution in  $\epsilon_{1,2}$  and  $\tau_{1,2}$ , the value obtained from the MSE minimum from the previous step was inserted in an unconstrained nonlinear optimization routine (fminsearch in Matlab).
- The values of  $\alpha_{1,2}$  were obtained by fitting the eigenvalues of the 4-site model to DFT calculations at finite bias, using the same unconstrained nonlinear optimization routine. The values of  $\epsilon_{1,2}$  and  $\tau_{1,2}$  are fixed at the values obtained in the previous step.

#### B. Asymmetric case

In the asymmetric case, the number of parameters increases from 6 to 11. As mentioned in the main text, for this reason, a different fit procedure was used.

- First, we create two symmetric molecules, one from the left side of the molecule, and one from the right side. These symmetric molecules are fitted as described in the section above.
- Based on the symmetric fits, an initial guesses for  $\alpha_{1,2,3,4}$ ,  $\tau_{1,2,3}$  and  $\epsilon_{1,2,3,4}$  is obtained.
- While keeping all parameters fixed, each parameters is fitted individually using an unconstrained nonlinear optimization routine, in the following order ε<sub>1</sub>, ε<sub>2</sub>, ε<sub>3</sub>, ε<sub>4</sub>, τ<sub>1</sub>, τ<sub>2</sub>, τ<sub>3</sub>, α<sub>1</sub>, α<sub>2</sub>, α<sub>3</sub>, α<sub>4</sub>.
- This fitting routine for the individual parameters is repeated 100 times resulting in 1100 individual routines in which every time only 1 parameter is fitted.

#### III. CONSTRUCTION OF LMO'S

Here, we would like to elaborate a bit further on the distinction between molecular orbitals (MOs) versus localized molecular orbitals (LMOs). Generally speaking, DFT calculations provide the energy and shape of the MOs, corresponding to the eigenvalues and eigenvectors of the Hamiltonian of the entire molecule, respectively. Moreover, the MOs ( $\Phi$ ) are linear combinations of all basis functions ( $\Psi$ ), in our case a set of atomic orbitals with dimension

M, of which the coefficients are given by the eigenvectors. Hence, the wave function of each MO with index m = 1, ..., M is given by

$$\Phi_m^{DFT} = \sum_{i=1}^M \Psi_i^{DFT} \cdot C_{m,i}^{DFT}, \qquad (1)$$

with  $C^{DFT}$  being the matrix containing all eigenvectors. The same holds for the N-site model, with as difference that the basis functions are now the individual sites with n = 1, ..., N, yielding

$$\Phi_n^{model} = \sum_{i=1}^N \Psi_i^{model} \cdot C_{n,i}^{model}.$$
 (2)

In our approach, the N MOs  $(\Phi_n^{model})$  resulting from the N-site model are equivalent to the N highest  $\pi$ -orbitals of the molecule  $(\Phi_p^{DFT}, \text{ with } p = \Pi[1, .., N], \Pi$  being the set of  $\pi$ -orbitals involved in transport). In these conditions,  $C_p^{DFT}$  is equal to  $C_n^{model}$  and one can therefore rewrite Eq. 1 as

$$\Phi_p^{DFT} = \sum_{i=1}^{N} \Psi_i^{DFT} \cdot C_{n,i}^{model}.$$
(3)

The wave functions  $\Phi_p^{DFT}$  are obtained from DFT, and using the fitted two-site model parameters, one can compute  $C^{model}$  and solve Eq. 3 to obtain the wave function of the LMOs ( $\Psi_i^{DFT}$ ).

### IV. TWO-SITE MODEL

Figure S.3 shows DFT + NEGF calculations on the two-site counterpart of the C4-tetraene molecule, with in panel (a) the chemical structure. The splitting between the two molecular orbitals is given by

$$\Delta = \sqrt{(\alpha eV)^2 + 2\alpha eV(\epsilon_1 - \epsilon_2) + (\epsilon_1 - \epsilon_2)^2 + (2\tau)^2}.$$
(4)

Figure S.3b shows  $\Delta$  for a H-CN substituted molecule, including a fit to Eq. 4. From the fit, the energies of the sites and the induced level shift for a particular substituent can be obtained. The obtained shifts for all 11 substituents are shown in Fig. S.3c, ordered by electronegativity. By combining the different side groups, 121 molecules are obtained, for which the rectification ratios are displayed in Fig. S.3d. For small energies differences between the sites, the rectification is small, as in the reverse bias mode the current suppression is not



FIG. S.2. Two-site molecule. (a) Chemical struture of the two-site analogue of the C4-tetraene from the main text. (b) Energy splitting  $\Delta$  for the H - CN substituted molecule under application of a bias voltage. (c) Shift of the on-site energy of the sites under substitution of the sidegroups. (d) Rectification ratio versus energy splitting between the sites for all combinations of substituents.

effective. For increasing energies splitting, the suppression becomes more effective, yielding improved rectification ratios. The maximum ratio is about 200 and requires a splitting of 0.4-0.6 eV. For even higher splitting, when the sites align, other orbitals start to contribute as well, lead to an increase in reverse current and hence a deterioration of the rectification ratios.

### V. H - CCH - CL - CN

#### A. xyz coordinates

Au -14.338433 0.000000 0.000000 Au 14.338433 0.000000 0.000000 C -12.746692 0.902673 1.401020 C -11.462113 0.232521 1.261570 C -10.383004 0.704072 0.594170 C -9.068619 -0.003586 0.475010 C -7.865757 0.828699 0.955300 C -6.528260 0.117971 0.735100 C -5.319241 0.966813 1.165760 C -4.002352 0.252820 0.946230 C -3.694429 -0.789826 1.859810 C -3.659246 2.475302 -1.818480 C -3.488257 -1.660693 2.684480 C -3.458690 1.597468 -0.999790 C -3.152791 0.551461 -0.089140 C -1.852159 -0.183939 -0.333710 C -0.608146 0.656210 0.000640 C 0.693364 -0.076933 -0.333910 C 1.939530 0.750919 0.026750 C 3.230490 0.053129 -0.273140 Cl 3.589097 -1.284823 0.833830 Cl 3.777791 1.652423 -2.359180 C 4.113614 0.306180 -1.257270 C 5.409240 -0.394141 -1.536980 C 6.635149 0.364386 -0.996130 C 7.942124 -0.393366 -1.241980 C 9.160861 0.346650 -0.661390 C 10.448493 -0.433010 -0.768660

C 10.518014 -1.665674 -0.069530 C 11.524732 1.233610 -2.146300 C 11.576728 -0.026078 -1.459250 C 12.827769 -0.762389 -1.561410 H -13.255624 0.728244 2.355270 H-12.753398 1.961388 1.117400 H -11.365374 -0.742683 1.757140 H -10.464619 1.672305 0.082200 H -9.107598 -0.955584 1.031070 Н -8.891070 -0.271437 -0.585490 H -7.994110 1.067780 2.024600 H -7.860474 1.795501 0.421940 H -6.517357 -0.836411 1.287640 H -6.418176 -0.137518 -0.332460 H -5.415131 1.218766 2.234850 H -5.309685 1.910587 0.600830 H -3.845120 3.255253 -2.528680 H -3.298283 -2.435112 3.399590 H -1.848777 -1.107426 0.263480 H -1.810494 -0.476009 -1.396730 H -0.652410 1.609294 -0.552080 H -0.627847 0.912433 1.073550 H 0.721311 -0.313726 -1.410680 H 0.728900 -1.039007 0.202380 H 1.915958 0.994462 1.102180 H 1.925498 1.701966 -0.524120 H 5.366636 -1.393970 -1.081310 H 5.509043 -0.532088 -2.625400 H 6.501020 0.525296 0.086320 H 6.682258 1.362105 -1.462160 H 7.876215 -1.396118 -0.787640 H 8.094466 -0.547631 -2.323100

H 8.966986 0.560672 0.405170 H 9.288645 1.316926 -1.164050 H 12.745117 -1.824459 -1.310990 H 13.384279 -0.573859 -2.483930 N 10.564021 -2.676458 0.519170 N 11.523227 2.252822 -2.714730

B. Orbital energies



FIG. S.3. Orbital structure for three bias voltages.

## VI. MOLECULAR ORBITALS

In the main text, only the LMOs are shown in combination with the HOMO under bias. Figure S.4 shows the four HOMO-3 till HOMO of the H-CCH-Cl-CN substituted molecule



FIG. S.4. Four highest occupied molecular orbitals for different bias voltages.

for various bias voltages. At zero bias, the four HOMOs are highly localized, and transport through the molecule is significantly suppressed. At -1.12 V (reverse bias mode), the HOMOs are localized on the left side of the molecule, and conductance is poor. At 1.12 V (forward bias mode) the four sites meet, and the figure shows that all HOMOs are delocalized across the molecule. They now constitute well conducting transmission channels. At 2 V, the electric field localizes the HOMOs on the right side of the molecule, and conduction is poor again.

## VII. ADDITIONAL DIODES

Table I show the rectification ratio (RR), operating voltage and maximum current ( $I_{max}$ ) for combinations of substituents yielding a current larger than 1e-2 a.u., and a rectification ratio larger than 300'000.

Substituent	RR	I <sub>max</sub> (a.u.)	Operating voltage
H - CCH - Cl - CN	$1.33e{+}06$	7.53e-02	1.12V
H - F - H - CN	$1.29\mathrm{e}{+06}$	2.42e-02	1.01V
H-CCH-Br-CN	$1.07e{+}06$	3.62e-02	1.14V
CCH-Br-H-NO2	$8.53\mathrm{e}{+05}$	1.18e-02	1.51V
I-H-H-CN	$7.98\mathrm{e}{+05}$	4.02e-02	0.78V
H-CCH-I-CN	$6.70\mathrm{e}{+}05$	3.58e-02	1.10V
CCH-Cl-H-NO2	$6.06\mathrm{e}{+05}$	2.36e-02	1.61V
I-Br-Br-CN	$5.96\mathrm{e}{+05}$	1.94e-02	0.79V
H-F-Cl-CN	$5.47\mathrm{e}{+05}$	5.44e-02	1.10V
F-F-H-CN	$5.09\mathrm{e}{+}05$	2.40e-02	$0.94\mathrm{V}$
H-CCH-H-CN	$5.07\mathrm{e}{+}05$	1.09e-02	1.06V
H-I-H-NO2	$5.05\mathrm{e}{+}05$	2.20e-02	1.72V
H-CCH-Br-NO2	$4.56e{+}05$	3.69e-02	1.03V
I-Br-H-CN	$4.24 e{+}05$	2.21e-02	$0.79\mathrm{V}$
CCH-I-H-NO2	$4.16e{+}05$	1.23e-02	$1.74\mathrm{V}$
CCH-F-H-CN	$3.92\mathrm{e}{+05}$	1.99e-02	$1.07\mathrm{V}$
F-CCH-Br-CN	$3.88e{+}05$	3.76e-02	0.98V
F-CCH-Cl-CN	$3.87\mathrm{e}{+05}$	5.57 e-02	$0.97\mathrm{V}$
H-F-Br-CN	$3.63\mathrm{e}{+05}$	2.35e-02	$1.07\mathrm{V}$
Cl-I-H-CN	$3.18\mathrm{e}{+05}$	3.42e-02	0.78V
CCH-CCH-Cl-CN	$3.15\mathrm{e}{+05}$	6.70e-02	1.08V

TABLE I. Properties of diodes with different chemical substituents using  $\Gamma_{L,R}$ =0.1 eV.