Electronic supplementary information for

Electrochemical setup — a unique chance to simultaneously control orbital energies and vibrational properties of single-molecule junctions with unprecedented efficiency

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S1 Method to Compute the Raman Spectra

The quantum chemical computations done to obtain the results obtained in this work will be briefly described below. In the experiments of Ref. 1 considered here, the viologen core is not directly contacted to (gold) electrodes in the molecular junctions used in experiment, but rather via alkyl linkers. Therefore, we did not include metal atoms in our quantum chemical calculations, but merely considered the isolated charged species of interest, namely dication (44BPY+++) and radical cation (44BPY++). These charge species turned out to be essential for interpreting the transport experiments. 1 Focusing on these species allowed us to perform high-level quantum chemical calculations employing very good basis sets, namely, basis sets of triple-zeta quality augmented with diffuse functions (Dunning aug-cc-pVTZ).

Calculations for geometry optimizations and Raman spectra have been carried out at the DFT level by using the B3LYP hybrid exchange functional by means of GAUSSIAN 09. 2 The vibrational frequencies and the Raman intensities (activities in the language of GAUSSIAN 09) computed for the two charge species (44BPY+++ and 44BPY++*) in acetonitrile are collected in Table S1, and Fig. 1, Fig. 2, Fig. S1, Fig. S2, Fig. S3, and Fig. S4. We specifically refer to acetonitrile as solvent because studies on bipyridine employed this solvent in experiments 3 and because calculations using non-pure solvents 4 cannot be directly done with available program packages. 2 The data of Table S2 and S3 (computed for molecular species in benzene and vacuum, respectively) show no quantitative differences from those of Table S1 and emphasize that, for the effects considered in this paper, the nature of the environment is not critical; the essential role of the environment is to enable an efficient molecular orbital gating.

S2 Method to Estimate the Charge of a Molecule in EC-STM Junctions from Transport Data

As a central point of the present analysis, we have used the transport data of Ref. 1 to show that the EC-STM transport setup does enable the switching between nearly perfect oxidized and reduced states.

The charge of a molecule embedded in a junction cannot be directly deduced from transport measurements. To determine the molecular charge (=LUMO occupancy n_l) and to demonstrate that, under electrochemical control, a continuous switching between an almost fully oxidized state (n_l ≃ 0, 44BPY+++) and an almost fully reduced state (n_l ≃ 1, 44BPY++*), we have resorted to a model (namely, the Newns-Anderson model), which we have validated beforehand.

Originally proposed for chemisorption, 4 the Newns-Anderson model was generalized to account for reorganization effects 5 and further extended 6 to studies on the adiabatic
Table S1 Vibrational frequencies (ω) and Raman activities (A) of the 44BPY dication (D) and cation (C) computed in acetonitrile at DFT/B3LYP/aug-cc-pVTZ level.
<table>
<thead>
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<th>No.</th>
<th>( \omega_0 ) (cm(^{-1} ))</th>
<th>( \omega_c ) (cm(^{-1} ))</th>
<th>( \Delta \omega ) (cm(^{-1} ))</th>
<th>( A_D ) (( \text{\AA}^4/\text{a.m.u.} ))</th>
<th>( A_c ) (( \text{\AA}^4/\text{a.m.u.} ))</th>
<th>( A_D - A_c ) (( \text{\AA}^4/\text{a.m.u.} ))</th>
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Table S2 Vibrational frequencies (\( \omega \)) and Raman activities (\( A \)) of the 44BPY dication (\( D \)) and cation (\( C \)) computed in benzene at DFT/B3LYP/aug-cc-pVTZ level.
Table S3 Vibrational frequencies ($\omega$) and Raman activities ($A$) of the 44BPY dication ($D$) and cation ($C$) computed in vacuum at DFT/B3LYP/aug-cc-pVTZ level.
transport through redox molecules. Recently, it was emphasized that this model is able to provide a robust description of the three-terminal transport through redox units.

The basic idea underlying the Newns-Anderson model is that the molecular transport is dominated by a single energy level. The experimental transport data unambiguously indicated that the charge carriers are negative (n-type conduction). So, if there is a dominant molecular orbital (MO), it should be the lowest unoccupied molecular orbital (LUMO) of the dication 44BPY$^{++}$ ($n_D = 0$). The cation 44BPY$^+$ is described as a fully reduced LUMO ($n_C = 1$).

To microscopically validate the idea that the LUMO should be the dominant MO, we have calculated the lowest electron affinities at the EOM-CCSD (equation-of-motion coupled cluster singles and doubles) level, which represents the quantum chemistry state-of-the-art for molecules of this size. These calculations, performed with CFOUR, showed that the difference between the first and second and higher electron affinities (basically, the energies of LUMO and LUMO+1, LUMO+2, etc with reversed sign) are substantially larger than the LUMO offset relative to the metallic Fermi energy (as expressed by the small overpotential values of Fig. 4). This validates the transport description relying upon a single energy level, which is the basic idea of the Newns-Anderson model, within the realm of theory: the contribution coming from LUMO+1 (and higher unoccupied molecular orbitals) can be neglected.

The Newns-Anderson model allows one to compute the current $I = I(V_b, \eta)$ through an EC-STM junction as a function of the source-drain voltage $V_b = V_t - V_s$ and of the overpotential $\eta = V_{eq} - V_s$. All necessary formulas can be found in earlier work. Here we only briefly mention that the LUMO energy

$$\varepsilon_l = \lambda (1 - 2Q) - \xi e \eta - \gamma e V_b,$$

(S1)

fluctuates due to reorganization effects described by an effective mode coordinate $Q$ and the reorganization energy $\lambda$. The LUMO energy shift caused by the overpotential $\eta$ and the source-drain bias $V_b$ is characterized by the solvent gating efficiency ($0 < \xi < 1$) and the bias division factor ($0 < \gamma < 1$). In an EC-STM junction, finite level broadenings $\Gamma_{l,s}$ arise due to

**Fig. S2** Raman scattering activities (in Å$^4$/a.m.u.) of the dicationic and cationic species in acetonitrile.

**Fig. S3** Differences between the vibrational frequencies of the dicationic and cationic species in acetonitrile $\omega_D - \omega_C$ plotted against the average frequencies $(\omega_D + \omega_C)/2$.

**Fig. S4** Differences between the Raman scattering activities (in Å$^4$/a.m.u.) of the dicationic and cationic species in acetonitrile plotted against the average frequencies $(\omega_D + \omega_C)/2$. 
couplings of the LUMO to the STM tip and substrate. The asymmetry of the molecule-electrode couplings \( \delta \equiv \Gamma_t/\Gamma_s \) where \( \Gamma \equiv (\Gamma_t + \Gamma_s)/2 \), of the viologen-based EC-STM junctions is substantial albeit not so pronounced as recently found for azurin-based EC-STM junctions.\(^7\)

We have used the Newns-Anderson model to fit the experimental currents measured in experiment\(^1\) both in variable bias mode and constant bias modes. As visible in Fig. 3 and Fig. 4, the theoretical curves obtained within the Newns-Anderson model successfully reproduce the experimental currents\(^1\) measured both in constant bias and variable bias modes.

Once the model has been validated against experiment\(^1\) and the parameter values determined (they are indicated in the legends), the \( \eta \)- and \( V_b \)-dependent LUMO occupancy \( n_l \) (also shown in Fig. 3 and Fig. 4) has been determined using formulas reported earlier.\(^6,7\)

S3 Vibrational Frequencies and Raman Scattering Intensities of a Redox Molecule in a Biased Nanojunction

We have adopted a simple interpolation method to estimate the \( \eta \)- and \( V_b \)-dependent vibrational frequencies \( \omega \) and Raman scattering intensities \( A \) of the various modes \( \nu \). Namely, we have computed weighted averages of the dicationic (label \( D \)) and anionic (label \( C \)) species with appropriate weights \( n_l \) and \( 1 - n_l \), respectively expressed in terms of the LUMO occupancy \( n_l \)

\[
\omega_{\nu}(\eta, V_b) = n_l(\eta, V_b)\omega_{\nu,D} + [1 - n_l(\eta, V_b)]\omega_{\nu,C},
\]

\[
A_{\nu}(\eta, V_b) = n_l(\eta, V_b)A_{\nu,D} + [1 - n_l(\eta, V_b)]A_{\nu,C}.
\]

The results expressing the dependencies of the vibrational frequencies and Raman scattering intensities on \( \eta \) and \( V_b \) are depicted in Fig. 5 and Fig. 6, respectively.

Besides modes 10 and 49 mentioned in the main text, we show in Fig. 5 and Fig. 6 the modes identified in Raman spectra of the radical anion 44BPY\(^{•-}\) measured in acetonitrile:\(^3,4\) (ring in-plane deformation; 6a\(^{3,9,10}\), 16 (ring breath; 1\(^{3,9,10}\)); 23 (ring in-plane deformation; 12\(^{3,9,10}\), 27 (ring in-plane deformation; 18a\(^{3,9,10}\), 36 (CH in-plane bending; 9a\(^{3,9,10}\) and 46 (ring stretch; 8a\(^{3,9,10}\)). Along with the present numbering in order of increasing frequencies (cf. S1), above we have given in parentheses the mode notation in use\(^3,10\) derived from benzene.\(^9\) The last mode (64 or 8a\(^9\)) is related to the so-called quinoidal distortion, corresponding to a shortening of the inter-ring C-C bond and of the C-C bond parallel to it, and a lengthening of the C-C bond between them as well as of the C-N bond.\(^3,11\)

Fig. S5 presents the dependencies of the integrated Raman spectrum \( A_{tot}(\eta, V_b) \equiv \sum_{\nu} A(\eta, V_b) \). (Notice that signs of \( V_b \rightarrow E_b \) and \( \eta \) of Ref.\(^1\) are opposite to those employed here.)
Notes and references


