## Electronic Supplementary Information for **Transition voltage spectroscopy reveals significant solvent effects on molecular transport and settles an important issue in bipyridine-based junctions**

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# 1 Quantum-chemical calculations of the solvent-driven change in LUMO energy

The theoretical results reported in the present study have been obtained by quantum-chemical calculations performed with the Gaussian 09 package<sup>1</sup> at density functional theory (DFT) level by using the B3LYP hybrid exchange functional. Basis sets of double-zeta quality augmented with diffuse functions (Dunning aug-cc-pVDZ) for the light atoms (C, N, H) and with relativistic core potential for gold (cc-pVDZ-PP<sup>2</sup>) have been employed.

Geometry optimizations and single-point calculations for electron affinities (*A*'s) can be straightforwardly performed in standard DFT Gaussian 09 runs. Bond metric data and total energies for the relevant optimized geometries of the (4, 4')-bipyridine molecule are collected in Table S1.

The quantity  $\delta E_0 = E_0^{sol} - E_0^0$  can be obtained via standard quantum chemical methods because it requires the knowledge of the LUMO energies  $E_0^{0,sol}$  of an *isolated* molecule, that is, a molecule uncoupled to electrodes. Still, as is well known, the Kohn-Sham "orbitals" do not represent true molecular orbitals, and this particularly applies to the LUMO. Therefore, the LUMO energies have been estimated within  $\Delta$ -DFT calculations from the lowest electron affinity levels,  $E_0^{0,sol} = -A_{0,sol}$  ("Koopmans theorem"), and thence  $\delta E_0 = -\delta A$ .

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$$\delta E_0 = -1.764 \,\mathrm{eV}.\tag{S1}$$

The values given above include zero-point motion corrections. Without zero-point motion corrections, the values are  $A_0 = 0.442 \text{ eV}$ ,  $A_{sol} = 2.207 \text{ eV}$ , and  $\delta E_0 = -1.759 \text{ eV}$ ; so, the comparison with eq. (S1) indicates that zero-point motion corrections to  $\delta E_0$  only amounts to a few meV.<sup>3</sup> The values presented above are for a 44bpy molecule. By attaching a gold atom at each of the two nitrogen atoms, one gets  $\delta E_0 = 1.765/1.767 \text{ eV}$  with/without zero-point motion corrections. This indicates that, by using a larger (Au<sub>n</sub>-44bpy-Au<sub>n</sub>) extended molecule,<sup>4</sup> as currently done in molecular transport studies, one cannot expect a notable modification of the value of eq. (S1).

The solvent-driven change in the affinity energy is related to the change in the solvation energies  $\Delta \mathcal{G}_{A,N}$  as follows

$$-\delta E_0 = \delta A = \Delta \mathscr{G}_N - \Delta \mathscr{G}_A + \lambda_A^0 - \lambda_A^{sol} \simeq \Delta \mathscr{G}_N - \Delta \mathscr{G}_A \equiv -\Delta \Delta G.$$
(S2)

The solvation energies  $\Delta \mathscr{G}_j$  of the various charge species *j* (anion *A* and neutral *N*) are defined by

$$\Delta \mathscr{G}_j = \mathscr{E}_j^{sol}(\mathbf{Q}_j^{sol}) - \mathscr{E}_j^0(\mathbf{Q}_j^0), \tag{S3}$$

where  $\mathbf{Q}_{j}^{m}$  denotes the equilibrium geometry of the charge species *j* in environment m(=0, sol). Above,  $\lambda_{j}^{m}$  are reorganization energies, which are defined by

$$\lambda_A^m = \mathscr{E}_A^m(\mathbf{Q}_N^m) - \mathscr{E}_A^m(\mathbf{Q}_A^m). \tag{S4}$$

The approximate expression of eq. (S2) is justified by the small difference between the reorganization energies found in actual calculations ( $\lambda_A^{sol} - \lambda_A^0 \sim 1 \text{ meV}$ ).

The relationship between the changes in electron affinity and solvation energies [cf. eq. (S2)] suggests to determine  $\delta E_0$  by going beyond the PCM solvent's description and using the universal solvation model (SMD).<sup>5</sup> The latter was particularly developed to accurately estimate solvation energies by

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	44bpy in vacuo	44bpy in water	Au-44bpy-Au in vacuo	Au-44bpy-Au in water				
$C_1C_3$	1.397	1.396	1.393	1.392				
$C_3C_5$	1.404	1.404	1.404	1.404				
$C_5C_6$	1.484	1.485	1.484	1.484				
$C_1 N_1$	1.340	1.343	1.341	1.344				
$C_1H_1$	1.093	1.092	1.090	1.089				
$C_3H_3$	1.090	1.089	1.089	1.088				
$N_1N_2$	7.150	7.149	7.104	7.097				
$Au_1Au_2$	- 1	_	11.776	11.655				
N <sub>1</sub> Au <sub>1</sub>	_	_	2.336	2.279				
$C_3C_5C_6$	121.6	121.5	121.4	121.3				
$C_1C_3C_5$	119.3	119.3	119.6	119.6				
$N_1C_1C_3$	123.9	123.8	122.6	122.4				
$C_1 N_1 C_9$	116.8	116.8	118.5	118.7				
$H_3C_3C_5$	120.9	121.2	121.1	121.4				
$H_1C_1C_3$	120.0	119.8	121.1	121.0				
$H_1C_1N_1$	116.2	116.4	116.3	116.6				
$C_1 \dot{C}_2 \dot{C}_3 \dot{C}_4$	37.3	35.4	37.5	35.6				
total energy & (a.u.)	-495.434936776	-495.444272357	-766.957254649	-766.969011619				

**Table S1** The optimized geometry of the neutral 44BPY molecule in vacuo and in water computed at the DFT/B3LYP level of theory using aug-cc-pVDZ basis sets for the light atoms (C, H, N), and relativistic core potential (cc-pVDZ-PP<sup>2</sup>) for calculations including two gold atoms (Au-44bpy-Au) at the two ends. Interatomic distances are expressed in angstrom and angles in degrees. The atom numbering is given in Figure 4a of the main text.

including not only electrostatic interactions (as done within the PCM model<sup>6</sup>), but also nonelectrostatic effects. Within SMD, nonelectrostatic interactions are included in terms of empirical atomic and molecular surface tensions. Besides the macroscopic surface tension of the solvent, they depend on the optical (high-frequency) dielectric constant  $\kappa_r^{\infty}$  (related to the solvent's refractive index  $n^2 = \kappa_r^{\infty}$ ), Abraham's hydrogen bond acidity and basicity parameters, and the fractions of aromatic carbon (carbon aromaticity) and halogens (electronegative halogenicity) atoms in the solvent.

The results of the calculations within the PCM and SMD models for a series of solvents are collected in Table S2. They underline Figure 5 of the main text. These results indicate that, in the case of 44bpy, nonelectrostatic interactions only have a small effect: for water,  $\delta A^{PCM} \simeq 1.76 \text{ eV}$  and  $\delta A^{SMD} \simeq 1.71 \text{ eV}$ . The difference between the above values is less relevant, since it is comparable with typical experimental errors  $\sim 0.06 \text{ eV}$  in  $\Delta \Delta G$ .<sup>7</sup>

The results of Table S2 are represented graphically in Figure 5 of the main text. This table demonstrates that, by including (SMD) or not (PCM) solvent's nonelectrostatic interactions,  $\kappa_r$  is the solvent property with the strongest impact on the LUMO energy shift and thence the Born-type behavior  $\delta E_0 \propto (1 - 1/\kappa_r)^8$  mentioned in the main text.

### 2 Computation of the LUMO density

As expressed by eqs. (11) and (12) of the main text, a realistic estimate of the LUMO shift  $\Phi$  due to image charges requires the ab initio determination of the LUMO spatial distribution

 $\rho_{1D}^{LUMO}(z).$ 

As is well known, the Kohn-Sham "orbitals" do not represent true molecular orbitals, and this particularly applies to the LUMO. Therefore, the LUMO wave function needed to compute the density  $\rho_1^{LUMO}(z)$  needed in eq. (12) of the main text has been obtained from separate SCF runs. As is also well known, individual virtual or unoccupied Hartree-Fock (HF) orbitals (in particular, the LUMO) have physical significance, e. g., in the description of anionic bound or resonance states, provided that the size of the atomic orbital (AO) basis used is not too large. For large AO basis sets, the virtual HF orbitals have mathematical rather than physical meaning, namely, in providing an expansion manifold for the physical states of interest.

To avoid issues related to this fact, which implies in particular that too large basis sets yield an unphysical LUMO, basis sets smaller than those for the DFT geometry optimizations (see above) have been used for these SCF calculations. The basis sets 6-31+g(d), 6-31++g(d, p), and 6-311++g(d,p) employed in these single-point SCF calculations at geometries optimized within DFT as described above yield a physically relevant LUMO spatial distribution. The differences in the one-dimensional LUMO densities  $\rho_{1D}^{LUMO}(z)$  computed with these basis sets are insignificant; they would be hardly visible within the drawing accuracy of Figure 4b of the main text.

Results for  $\rho_{1D}^{LUMO}$  obtained as described above are presented in Figure 4b of the main text. They show that the assumption of a point-like LUMO placed at the center of the 44bpy molecule<sup>9,10</sup> is completely unrealistic. As also the case for  $\delta E_0$ ,  $\rho_{1D}^{LUMO}(z)$  does not notably change when gold atoms are attached to 44bpy;<sup>4</sup> compare the red and green curves in

Solvent	K <sub>r</sub>	$-\delta E_0^{PCM} = \delta A^{SMD}$	$-\delta E_0^{SMD} = \delta A^{PCM}$
water	78.36	1.71	1.76
dimethylformamide	36.71	1.70	1.74
acetonitrile	35.69	1.70	1.74
ethanol	24.85	1.67	1.71
methanol	32.59	1.69	1.73
acetone	20.49	1.66	1.70
dichloromethane	8.93	1.55	1.58
tetrahydrofuran	7.43	1.50	1.53
1,2,4-trichlorobenzene	6.75	1.48	1.51
chloroform	4.71	1.36	1.39
ether	4.24	1.32	1.35
toluene	2.37	0.99	1.01
benzene	2.27	0.96	0.98

**Table S2** Change in the electron affinity ( $\delta A$ ) and LUMO ( $\delta E_0$ ) energies in various solvents relative to vacuum calculated by describing the solvents within the PCM and SMD models.

Figure 4b of the main text.

Essentially, the LUMO distributions of Figure 4b are also little affected by the solvent. Therefore eq. (11) of the main text yields

$$\delta \Phi = \Phi^{sol} - \Phi^0 \simeq -\Phi^0 (1 - 1/\kappa_r). \tag{S5}$$

#### **3** LUMO shift due to image charges

The interaction energy  $\phi_i(z)$  between a point charge *e* located on the *z*-axis between two infinite metallic planes at  $z = z_s - z_0$ and  $z = z_t + z_0$  (see Figure 3 in the main text) can be computed by considering the infinite series of image charges and expressed in closed analytical form<sup>11</sup>

$$\phi_{i,0}(z;\kappa_r) = \frac{e^2}{4d\kappa_r} \left[ -2\psi(1) + \psi\left(\frac{z-z_s}{d}\right) + \psi\left(\frac{z_t-z}{d}\right) \right].$$
(S6)

Here  $d \equiv z_t - z_s$ ,  $\psi(z) \equiv d \log \Gamma(z)/dz$  is the digamma function, and  $\kappa_r$  is the permittivity of the medium. For, e. g.,  $z \gtrsim z_s$ , eq. (S6) recovers the classical expression

$$\phi_{i,0}(z;\kappa_r) \stackrel{z \gtrsim z_s}{\approx} \phi_{i,cl}(z;\kappa_r) = -\frac{e^2}{4\kappa_r(z-z_s)}$$
(S7)

for a single image plane.

As illustrated in Figure 3 of the main text, the positions  $z_{s,t}$  of the image planes are outwardly displaced by  $z_0$  from the electrode surfaces  $z'_{s,t} = z_{s,t} \mp z_0$ <sup>12,13</sup>. The nonvanishing value  $z_0$  represents a quantum correction to the result obtained within classical electrostatics; in order to asymptotically recover the classical expression of eq. (S7) within quantum mechanical calculations, a fictitious image plane at  $z = z_s$  shifted from the real metallic surface located at  $z = z'_s = z_s - z_0$  should be considered.<sup>12</sup>

As visible in eqs. (S6) and (S7), the image energy  $\phi_i(z)$  diverges as  $z \rightarrow z_{s,t}$ , which is unphysical: the potential at the surface should be finite at  $z = z_{s,t}$  and smoothly evolve into the constant potential of the bulk metal. These divergences can be removed by using appropriate multiplicative factors.<sup>14,15</sup> In our calculations, the interaction energy between electrodes and a point charge *e* located at *z* has been taken of the form

$$\phi_i(z;\kappa_r) = \frac{e^2}{4d\kappa_r} \left\{ -2\psi(1) + \psi\left(\frac{z-z_s}{d}\right) \left[1 - e^{-\mu(z-z_s)}\right] + \psi\left(\frac{z_t-z}{d}\right) \left[1 - e^{-\mu(z_t-z)}\right] \right\}.$$
(S8)

The square parentheses of eq. (S8) ensure that the limits  $\lim_{z\to z_{s,t}} \phi_i(z)$  remain finite and provide good fits of the microscopically calculated potential for the single-plane problem  $(z\gtrsim z_s, z\lesssim z_t)$ .<sup>14,15</sup>

A variety of methods, mostly based on the DFT, have been proposed to determine  $z_0$ .<sup>12,14–21</sup> Calculations based on the jellium model yield an image plane located at a distance  $z'_0$  measured outwards from a fictitious geometrical surface, which is defined to be one half  $[d_{111}^{Au}/2$  for Au(111)] of the interplanar separation  $d_{111}^{Au} = a^{Au}/\sqrt{3}$  outside the top layer of atomic nuclei, where  $a^{Au}$  is the bulk lattice constant of gold. So, the image plane is located at a distance  $z_0 = d_{111}^{Au}/2 + z'_0$ from the plane of the outermost nuclei.

In the absence of estimates for  $z_0$  and  $\mu$  for gold, we have used values for aluminum, because of their similar properties (bulk lattice constants  $a_{Au} = 4.079$  Å,  $a_{Al} = 4.050$  Å interplanar separations  $d_{111}^{Al} = 2.338$  Å,  $d_{111}^{Au} = 2.354$  Å, and effective free-electron density parameters  $r_s^{Al} = 2.42$ ,  $r_s^{Au} = 2.54^{22}$ ). So, we have used the value  $z_0 \simeq 1.58$  Å ( $z'_0 \simeq 0.4$  Å) obtained for Al(111) within a *GW* approach,<sup>23</sup> which is a genuine microscopic treatment. For  $\mu$  we could not find an estimate

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for Al(111), and used therefore the value  $\mu = 1.25$  a.u. for Al(001), <sup>15</sup> because the properties for the Al(001) face are usually thought to be close to those for the Al(111) face. <sup>15</sup>

Within this description, the coordinate of the left image plane is  $z_s = z_{Au_1} + z_0$ , where  $z_{Au_1}$  is the coordinate of the atom Au<sub>1</sub> (cf. Figures 3 and 4b in the main text).

As emphasized by the cartoon presented in Figure 3 of the main text, an important aspect to be taken into account in the calculations is the STM tip-substrate asymmetry. This is particularly relevant because the STM tips can be atomically sharp. To support this idea, we will refer to a recent STM study.<sup>24</sup> To be able to reproduce the experimental STM measurements in ref. 24, the authors of that experimental study used a model assuming a spherical STM tip of radius R = 5 Å. The main aspect related to image effects is that the STM-tip can not be considered as being an infinite plane bound to the molecule, unlike the case of the STM substrate, and that departures from infinite plates significantly diminish image effects. The fact that the image interaction energy  $\Phi$  is substantially reduced for non-planar electrodes with finite spatial extension has been extensively documented by the STM community especially in the 1980's and 1990's. Some relevant works are cited in ref. 52 of the main text. If departures from planar infinite electrodes were insignificant, they would have not been so amply considered in that literature.

To account for the STM tip-substrate asymmetry discussed in the main text (cf. Figure 3 there), we have considered locations of the right image plane  $z_t = z_{Au_2} - z_0 + n d_{111}^{Au}$ , which corresponds to modeling of a sharp (e. g., pyramidal) STM tip with a height  $n d_{111}^{Au}$  extending over a number of n Au(111) layers.

To calculate  $\Phi$  via eq. (11), besides of using the exact expressions of the LUMO density  $\rho_{1D}^{LUMO}$  [eq. (12)] and the exact image potential  $\phi_i(z)$  [eq. (S8)], we have also considered two approximations ( $\Phi \approx \overline{\Phi}$  and  $\Phi \approx \widetilde{\Phi}$ ) expressed as

$$\begin{split} \Phi(\kappa_r) &\approx \overline{\Phi}(\kappa_r) \equiv \int_{z_{N_1}}^{z_{N_2}} \phi_{i,0}(z;\kappa_r) \rho_{1D,unif}^{LUMO} dz \\ &= \frac{e^2}{4\kappa_r} \left\{ -\frac{2}{d} \psi(1) \quad (S9) \right. \\ &+ \frac{1}{l_{N1N_2}} \log \left[ \frac{\Gamma\left(\frac{z_{N_2}-z_s}{d}\right)}{\Gamma\left(\frac{z_{N_1}-z_s}{d}\right)} \frac{\Gamma\left(\frac{z_t-z_{N_1}}{d}\right)}{\Gamma\left(\frac{z_t-z_{N_2}}{d}\right)} \right] \right\}, \\ \Phi(\kappa_r) &\approx \tilde{\Phi}(\kappa_r) \equiv \int_{z_{N_1}}^{z_{N_2}} \tilde{\phi}_{i,0}(z;\kappa_r) \rho_{1D,unif}^{LUMO} dz \\ &= \frac{e^2}{4\kappa_r} \left[ \frac{1.227}{d} \quad (S10) \\ &- \frac{1}{l_{N1N_2}} \log \left( \frac{z_{N_2}-z_s}{z_{N_1}-z_s} \frac{z_t-z_{N_1}}{z_t-z_{N_2}} \right) \right]. \end{split}$$

Both approximations are based on the assumption of a

nearly constant LUMO density inspired by Figure 4b of the main text

$$\rho_{1D}^{LUMO}(z) \approx \rho_{1D,unif}^{LUMO} = const = \frac{1}{l_{N_1N_2}} \text{ for } z_{N_1} < z < z_{N_2}.(S11)$$

Eq. (S10) is based on the following approximation of the image potential  $^{25,26}$ 

$$\begin{split} \phi_{i,0}(z;\kappa_r) &\approx \quad \tilde{\phi}_{i,0}(z;\kappa_r) \quad (S12) \\ &= \quad -\frac{e^2}{4\kappa_r} \left(4\frac{\log 2 - 1}{d} + \frac{1}{z - z_s} + \frac{1}{z_t - z}\right). \end{split}$$

To illustrate how accurate the above approximation is, in Figure S1 we present the image potentials in two cases, which correspond to a number n = 3 and n = 5 of Au(111) layers. The difference between the curves for  $\phi_{i,0}(z; \kappa_r = 1)$  (red circles) and  $\tilde{\phi}_{i,0}(z; \kappa_r = 1)$  (red solid lines) can not be seen within the drawing accuracy of Figure S1. For completeness, in the same figure we also present the curves for  $\phi_i(z; \kappa_r = 1)$  and  $\tilde{\phi}_i(z; \kappa_r = 1)$  (green triangles and green dashed lines, respectively), which are also indistinguishable within the drawing accuracy. The latter is obtained from eq. (S12) by applying the same renormalization procedure as in eq. (S8)

$$\tilde{\phi}_{i}(z;\kappa_{r}) \approx -\frac{e^{2}}{4\kappa_{r}} \left[ 4 \frac{\log 2 - 1}{d} + \frac{1 - e^{-\mu(z-z_{s})}}{z - z_{s}} + \frac{1 - e^{-\mu(z_{t}-z)}}{z_{t} - z} \right].$$
(S13)

The rationale of using  $\phi_{i,0}$  instead of  $\phi_i$  in eq. (S9) [or  $\phi_{i,0}$  instead of  $\tilde{\phi}_i$  in eq. (S10)] is that the points  $z = z_s(\langle z_{N_1} \rangle)$  and  $z = z_t(\langle z_{N_2} \rangle)$  where  $\phi_{i,0}(z)$  [or  $\tilde{\phi}_{i,0}(z)$ ] is divergent lie beyond the integration range  $z_{N_1} \langle z \langle z_{N_2} \rangle$ ; so, the square parentheses entering the RHS of eq. (S8) do not significantly differ from unity within the integration range.

Eqs. (S9) and (S10) are very convenient to apply, because the RHS can be integrated in closed analytical form. The corresponding results for the image-driven LUMO shift ( $\overline{\Phi}$  and  $\tilde{\Phi}$ ) are those expressed by eqs. (18) and (19) in the main text.

The results depicted in Figure S2 demonstrate two important facts:

(i) The LUMO-shift due to charge images  $\overline{\Phi}$  and  $\overline{\Phi}$  computed via eqs. (18) and (19) of the main text [or, alternatively, via eqs. (S9) and (S10)] represent accurate estimates of exact value  $\Phi$  obtained from eqs. (11)+(12); the differences  $\sim 0.1 \text{ eV}$  between them are even smaller than experimental uncertainties [cf. eqs. (7) and (14)];

(ii) Whether computed exactly  $(\Phi = \Phi_n)$  or within the approximations described above  $(\overline{\Phi} = \overline{\Phi}_n, \tilde{\Phi} = \tilde{\Phi}_n)$  the imagedriven LUMO shift rapidly saturates with increasing *n*. To reasonably model an STM tip one can consider n = 3 to 5

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**Fig. S1** Curves for the image potential obtained by using various analytical forms expressed by the equations given in the legend.

layers, and this yields (exact) values  $-\Phi_{n=3}^0 = 1.387 \text{ eV}$  to  $-\Phi_{n=5}^0 = 1.329 \text{ eV}$  (superscript 0 means vacuum/air,  $\kappa_r = 1$ ). These values are not substantially different from the (exact) asymptotic value  $-\Phi_{n\to\infty}^0 = 1.296 \text{ eV}$ . So, including a practically infinite number  $(n \to \infty)$  of Au(111) layers or only a few layers  $(n \sim 3 - 5)$  in the actual calculations of  $\Phi$  is of reduced importance.

Much more than mathematical convenience, this fact is an indication of physical *robustness*: Uncertainties in STM-tip



**Fig. S2** The LUMO energy shift due to image charges  $\Phi$  in vacuo/air ( $\kappa_r = 1$ ) as a function of *n* computed exactly by using eqs. (11)+(12), and approximately via eqs. (18), and (19) of the main text. The curves presented here clearly demonstrate both the the accuracy of the approximations underlying eqs. (18) and (19) [or, alternatively, eqs. (S9) and (S10)] as well as the rapid saturation of  $\Phi$  with *n*;  $\Phi$ -values computed for small *n*'s (say, n = 3 - 5) do not substantially differ from the asymptotic limit ( $n \rightarrow \infty$ ).

geometries (shape and size), which may differ from instrument to instrument and from one experimental group to another, have a rather small impact on the  $\Phi^0$ -values. This is expressed by the rather narrow range  $-\Phi^0 \simeq 1.3 - 1.4$  eV given by eq. (13) in the main text.

	<i>n</i> = 3	<i>n</i> = 5	$n = \infty$
$-\Phi^0/eV)$	1.387	1.329	1.296
$-\overline{\Phi}^0/eV)$	1.252	1.210	1.188
$-\tilde{\Phi}^0/\mathrm{eV})$	1.242	1.200	1.187

**Table S3** Values of the image potential in vacuo  $[\Phi^0 \equiv \Phi(\kappa_r = 1)]$  computed exactly via eqs. (11)+(12), and approximately via eqs. (18) and (19) of the main text by considering  $n = 3;5; \infty$  Au(111) layers, which reveal the accuracy of the approximations employed as well as the rapid saturation with *n*.

Several  $\Phi$ -values computed exactly and approximately for vacuum/air ( $\kappa_r = 1$ ) collected in Table S3 may convey a flavor on the accuracy of the approximations discussed above as well as on the rapid saturation with *n*.

At the same time, one should emphasize that these values *substantially* differ from  $\Phi^0 = \Phi_n^0|_{n=0} = -2.28 \text{ eV}$ , which is the value obtained with the ab initio computed LUMO density

 $\rho_{1D}^{LUMO}(z)$  and eq. (S8) by assuming electrodes (thence image planes) located *symmetrically*, i. e., by taking  $z_s = z_{Au_1} + z_0$  and  $z_t = z_{Au_2} - z_0$  (n = 0).

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- 3 This is the reason why we have given more digits in the values given in this paragraph.
- 4 Quantum chemical calculations to larger extended extended molecules  $Au_n$ -44bpy- $Au_n$  including more gold atoms (n > 1) are possible, but the comparison of those results with and without solvent is questionable. It makes little sense to perform solvent calculations considering clusters with several gold atoms treating the solvent as a continuum medium; in a molecular transport setup, it is unrealistic to assume that all gold atoms are embedded in the cavity used in calculations with solvents.
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