Supporting Information

Sensing of molecules using quantum dynamics

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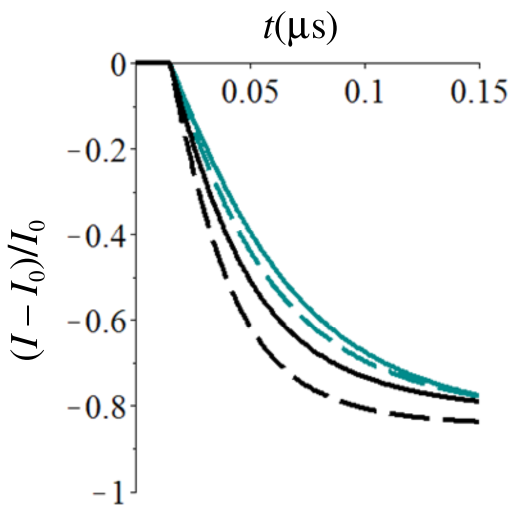


Fig. S1. Normalized current signal in a time scale of a fraction of μs, obtained by using the same model parameters as in Fig. 5b, except for $t_0 = 0.015\,\mu\mathrm{s}$ and $\Gamma_d/2 = 10^{-8}\,\mathrm{eV}$.

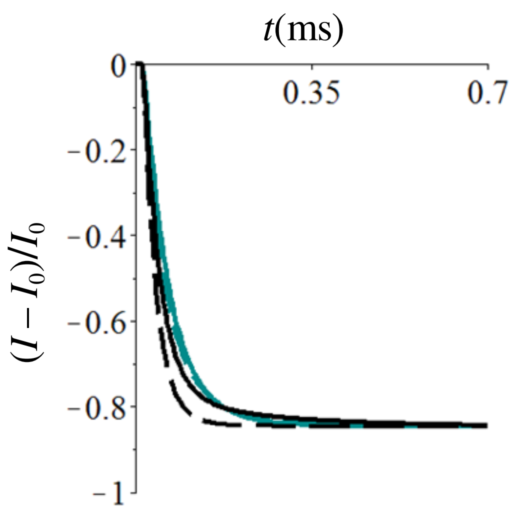


Fig. S2. Extension of Fig. 5b to a longer time scale.

S2. Explicit expression for the state vector in Eq. 5, under the initial conditions of Eqs. 6 and 13, and additional discussion of the model.

Before deriving expressions for the coefficients in Eq. **5**, we notice that the present one-electron model, especially in the interpretation *iii* of Eqs. **4** and **6**, extends the picture of the two-state model for coherent sensing to the more realistic situation in which a manifold of substrate electronic states are involved in the charge redistribution that follows the analyte binding. For small perturbation by the analyte, the onset of the system repolarization can be described by using the time-independent perturbation theory (1). Assume, for example, that $|d\rangle$ is the ground state of the one-electron system in the absence of the perturbation $\hat{V}$. To the first order in $\hat{V}$ the new ground state is

$$|d'\rangle = |d\rangle - \frac{V_{ad}}{\Delta E_{ad}}|a\rangle + \sum_{L} \frac{V_{ld}}{\Delta E_{dl}}|l\rangle \quad \textbf{[S1]}$$

(where $\Delta E_{ad} = E_a - E_d$) which, in the absence of the L manifold, reduces to

$$|d'\rangle = |d\rangle - \frac{V_{ad}}{\Delta E_{ad}}|a\rangle . \quad \textbf{[S2]}$$

Eq. **S2** is $|\psi\rangle = c_d|d\rangle + c_a|a\rangle$ with coefficients given by Eq. **3** to the first order in $\hat{V}$. The extension of Eq. **1** to this multistate model needs to be considered to obtain the equilibrium electronic charge distribution after analyte binding. Here we focus on a dynamical model for sensing in which charge is initially localized on the *d* site and the system state evolves so as to spread this charge over the *L* manifold of states.

Let us derive an analytical expression for the system state vector in Eq. **5**. The coefficients in the state expansion are obtained by solution of the time-dependent Schrödinger equation

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{H}|\psi(t)\rangle \quad \textbf{[S3]}$$

using Laplace transform and Green's function methods (2). Details on the methods can be found in ref. (2). First, for the initial condition in Eq. **6**, we determine the probability $P_d(t)$ that the system is found in state $\left|d\right\rangle$ at time *t*. Solution of Eq. **S3** by means of Laplace transforms leads to (2)

$$\left|\psi(t)\right\rangle = -\frac{1}{2\pi i}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty} dE\, e^{-iEt/\hbar}\,\frac{1}{E-\hat{H}+i\varepsilon}\left|\psi(0)\right\rangle \quad \textbf{[S4]}$$

Scalar multiplication of **[S4]** on the left by $\left\langle\psi(0)\right|$ and introduction of Eq. **6** and the Green operator

$$\hat{G}(E+i\varepsilon)\equiv\hat{G}(z)=\frac{1}{z-\hat{H}}=\frac{1}{z-\hat{H}_0-\hat{V}} \quad \textbf{[S5]}$$

give

$$c_d(t) = -\frac{1}{2\pi i}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty} e^{-iEt/\hbar}G_{dd}(E+i\varepsilon)\,dE \quad \textbf{[S6a]}$$

with

$$G_{dd}(z)=\left\langle d\right|\frac{1}{\hat{z}-\hat{H}}\left|d\right\rangle \quad \textbf{[S6b]}$$

namely, $c_d(t)$ is a Fourier transform of a diagonal (*dd*) matrix element of $\hat{G}(E+i\varepsilon)$. To find the expression of $G_{dd}(z)$, we introduce the simpler Green operator

$$\hat{G}_0(z)=\frac{1}{z-\hat{H}_0} \quad \textbf{[S7]}$$

consider that $\hat{G}(z)$ and $\hat{G}(z_0)$ satisfy the Dyson identities (2, 3)

$$\hat{G}(z)=\hat{G}_0(z)+\hat{G}_0(z)\hat{V}\,\hat{G}(z)=\hat{G}_0(z)+\hat{G}(z)\hat{V}\,\hat{G}_0(z) \quad \textbf{[S8]}$$

and use the resolution of the identity operator:

$$\left|d\right\rangle\left\langle d\right|+\left|a\right\rangle\left\langle a\right|+\sum_l\left|l\right\rangle\left\langle l\right|=\hat{1} \quad \textbf{[S9]}$$

The matrix elements of the operator in **[S7]** are

$$(G_0)_{jk}(z)=\frac{1}{z-E_j}\delta_{jk}, \qquad j,k=d,a,l \quad \textbf{[S10]}$$

Eqs. **S5** and **S7-9** produce the following relations between the matrix elements of $\hat{G}(z)$:

$$G_{dd}(z) = \langle d|G_0(z)|d\rangle + \langle d|\hat{G}_0(z)\hat{V}\hat{G}(z)|d\rangle = \frac{1}{z-E_d} + \langle d|\hat{G}_0(z)\hat{1}\hat{V}\hat{1}\hat{G}(z)|d\rangle$$

$$= \frac{1}{z-E_d}\left[1 + \langle d|\hat{V}\left(|d\rangle\langle d| + |a\rangle\langle a| + \sum_l |l\rangle\langle l|\right)\hat{G}(z)|d\rangle\right] \qquad \textbf{[S11]}$$

$$= \frac{1}{z-E_d}\left[1 + V_{da}G_{ad}(z) + \sum_l V_{dl}G_{ld}(z)\right]$$

$$G_{ad}(z) = \langle a|\hat{G}_0(z)\hat{1}\hat{V}\hat{1}\hat{G}(z)|d\rangle = \frac{1}{z-E_a}V_{ad}G_{dd}(z) \qquad \textbf{[S12]}$$

$$G_{ld}(z) = \langle l|\hat{G}_0(z)\hat{1}\hat{V}\hat{1}\hat{G}(z)|d\rangle = \frac{1}{z-E_l}V_{ld}G_{dd}(z) \qquad \textbf{[S13]}$$

Insertion of Eqs. **S12** and **S13** into Eq. **S11** gives

$$G_{dd}(z) = \frac{1}{z-E_d}\left[1 + \frac{V_{da}V_{ad}}{z-E_a}G_{dd}(z) + \sum_l \frac{V_{dl}V_{ld}}{z-E_l}G_{dd}(z)\right] \qquad \textbf{[S14]}$$

whence

$$G_{dd}(E+i\varepsilon) = \frac{1}{E+i\varepsilon-E_d-B_d(E+i\varepsilon)} \qquad \textbf{[S15]}$$

with

$$B_d(E+i\varepsilon) = \frac{|V_{ad}|^2}{E-E_a+i\varepsilon} + \sum_l \frac{|V_{dl}|^2}{E-E_l+i\varepsilon} \qquad \textbf{[S16]}$$

In **[S15]**, B_d appears as a change in (or correction to) E_d due to the coupling of $|d\rangle$ with the other electronic states. Thus, B_d has the meaning of a self-energy. To obtain an analytical expression for $B_d(E+i\varepsilon)$, we use the continuum approximation for the *L* manifold. Thus, Eq. **S16** becomes

$$\sum_l \frac{|V_{dl}|^2}{E-E_l+i\varepsilon} = \int_{-\infty}^{\infty} dE_l \frac{<|V_{dl}|^2>_{E_l}\ \rho_L(E_l)}{E-E_l+i\varepsilon} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dE_l \frac{\Gamma_d(E_l)}{E-E_l+i\varepsilon} \qquad \textbf{[S17]}$$

where $\rho_L(E_l)$ is the *L* density of states. $<|V_{dl}|^2>_{E_l}$ is the mean-square coupling for the states with energy E_l and

$$\Gamma_d(E) = 2\pi <|V_{dl}|^2>_E\ \rho_L(E) \qquad \textbf{[S18]}$$

Eq. **S18** reduces to the first Eq. **8** assuming that the density of L states (ρ_L) is independent of the state energy E and extends from $-\infty$ to ∞ [that is, the wide band approximation (2)], and that $<|V_{dl}|^2>_E$ is also independent of E (its value is denoted $<|V_{dl}|^2>_L$ in Eq. **8**). With these assumptions, $\Gamma_d(E) = \Gamma_d$ for any E and the integral in **[S17]** is solved as follows:

$$\begin{aligned}&\frac{\Gamma_d}{2\pi}\int_{-\infty}^{\infty} dE_l \frac{1}{E - E_l + i\varepsilon} = \frac{\Gamma_d}{2\pi}\int_{-\infty}^{\infty} dE_l \frac{E - E_l - i\varepsilon}{(E - E_l)^2 + \varepsilon^2} \\ &= -i\frac{\Gamma_d}{2\pi}\int_{-\infty}^{\infty} dx \frac{\varepsilon}{x^2 + \varepsilon^2} = -i\frac{\Gamma_d}{2\pi}\int_{-\infty}^{\infty} \frac{dx}{x^2 + 1} = -i\frac{\Gamma_d}{2\pi}[\arctan x]_{-\infty}^{+\infty} = -i\frac{\Gamma_d}{2}\end{aligned} \quad \textbf{[S19]}$$

Using Eq. **S19**, Eq. **S16** is written

$$B_d(E + i\varepsilon) = \frac{|V_{ad}|^2}{E - E_a + i\varepsilon} - i\frac{\Gamma_d}{2} = \frac{E - E_a}{(E - E_a)^2 + \varepsilon^2}|V_{ad}|^2 - i\left[\frac{\Gamma_d}{2} + \frac{\varepsilon}{(E - E_a)^2 + \varepsilon^2}|V_{ad}|^2\right]. \quad \textbf{[S20]}$$

Inserting Eq. **S20** into Eq. **S15** and the latter into Eq. **S6a**, we obtain

$$\begin{aligned}c_d(t) &= -\frac{1}{2\pi i}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty} \frac{e^{-iEt/\hbar} dE}{E - E_d - \frac{E - E_a}{(E - E_a)^2 + \varepsilon^2}|V_{ad}|^2 + i\left[\varepsilon + \frac{\varepsilon}{(E - E_a)^2 + \varepsilon^2}|V_{ad}|^2 + \frac{\Gamma_d}{2}\right]} \\ &= -\frac{e^{-iE_a t/\hbar}}{2\pi i}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x}\left(x^2 + \varepsilon^2\right) dx}{(x + \Delta E_{ad})(x^2 + \varepsilon^2) - |V_{ad}|^2 x + i\left[\left(\varepsilon + \frac{\Gamma_d}{2}\right)(x^2 + \varepsilon^2) + \varepsilon|V_{ad}|^2\right]} \\ &= -\frac{e^{-iE_a t/\hbar}}{2\pi i}\int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x} x dx}{(x + \Delta E_{ad})x - |V_{ad}|^2 + i\frac{\Gamma_d}{2}x} = -\frac{e^{-iE_a t/\hbar}}{2\pi i}\int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x} x dx}{x^2 + (\Delta E_{ad} + i\Gamma_d/2)x - |V_{ad}|^2}\end{aligned} \quad \textbf{[S21]}$$

where we used the integration variable $x = E - E_a$, Eq. **2**, and, in writing the last line, the dominated convergence theorem. Note that one can also obtain Eq. **S21** by using the identity (1)

$$\lim_{\varepsilon\to 0^+}\frac{1}{\pi}\frac{\varepsilon}{(E - E_l)^2 + \varepsilon^2} = \delta(E - E_l) \quad \textbf{[S22]}$$

or

$$\lim_{\varepsilon\to 0^+}\frac{1}{E-E_l+i\varepsilon}=\mathrm{PP}\frac{1}{E-E_l}-i\pi\,\delta(E-E_l) \qquad \textbf{[S23]}$$

where PP denotes the Cauchy principal part. In order to solve the integral in Eq. **S21** by means of the residue theorem, we first decompose the denominator of the integrand as follows:

$$c_d(t)=-\frac{e^{-iE_a t/\hbar}}{2\pi i}\int_{-\infty}^{\infty}\frac{e^{-i\frac{t}{\hbar}x}\,x\,dx}{(x-x_+)(x-x_-)}=\frac{e^{-iE_a t/\hbar}}{2\pi i\,(x_- -x_+)}\left[\int_{-\infty}^{\infty}\frac{x_+}{x-x_+}e^{-i\frac{t}{\hbar}x}dx-\int_{-\infty}^{\infty}\frac{x_-}{x-x_-}e^{-i\frac{t}{\hbar}x}dx\right] \qquad \textbf{[S24a]}$$

with

$$x_\pm=\frac{-\Delta E_{ad}-i\Gamma_d/2\pm\sqrt{(\Delta E_{ad}+i\Gamma_d/2)^2+4|V_{ad}|^2}}{2}. \qquad \textbf{[S24b]}$$

To recast $x_\pm$ in a more convenient form, we rewrite the radicand in **[S24b]** as

$$(\Delta E_{ad}+i\Gamma_d/2)^2+4|V_{ad}|^2=\Delta E_{ad}^2+4|V_{ad}|^2-\Gamma_d^2/4+i\Gamma_d\Delta E_{ad}=\xi^2e^{i\theta} \qquad \textbf{[S25]}$$

with ξ^2 given in Eq. **8** and

$$\theta=\arccos\left(\frac{\Delta E_{ad}^2+4|V_{ad}|^2-\Gamma_d^2/4}{\xi^2}\right). \qquad \textbf{[S26]}$$

Eq. **S26**, after a phase choice, yields

$$\cos\frac{\theta}{2}=\sqrt{\frac{1+\cos\theta}{2}}=\frac{1}{\xi}\sqrt{\frac{\xi^2+\Delta E_{ad}^2+4|V_{ad}|^2-\Gamma_d^2/4}{2}} \qquad \textbf{[S27a]}$$

and

$$\sin\frac{\theta}{2}=\mathrm{sgn}(\Delta E_{ad})\sqrt{\frac{1-\cos\theta}{2}}=\frac{\mathrm{sgn}(\Delta E_{ad})}{\xi}\sqrt{\frac{\xi^2-\Delta E_{ad}^2-4|V_{ad}|^2+\Gamma_d^2/4}{2}} \qquad \textbf{[S27b]}$$

Once a positive sign is assigned to $\cos(\theta/2)$, $\sin(\theta/2)$ and $\sin\theta=2\sin(\theta/2)\cos(\theta/2)$ have the same sign. From the imaginary part of the quantity in **[S25]** it is seen that this sign is dictated by ΔE_{ad}, because Γ_d is a positive-definite quantity. Taking the square root of Eq. **S25**, one obtains

$$\sqrt{(\Delta E_{ad}+i\Gamma_d/2)^2+4|V_{ad}|^2}=\xi e^{i\theta/2}=u+iv \qquad \textbf{[S28]}$$

(see u and v in Eq. **8**). Inserting **[S28]** into **[S24b]**, the poles of the integrand in Eq. **S24a** are written

$$x_+ = \frac{-\Delta E_{ad} + u + i\left(v - \Gamma_d/2\right)}{2}, \qquad x_- = \frac{-\Delta E_{ad} - u - i\left(v + \Gamma_d/2\right)}{2} \qquad \textbf{[S29]}$$

(the other root of the quantity in **[S25]** with phase $\theta/2-\pi$ is disregarded, because it produces the same solutions for x). Any choice of the physical parameters leads to negative $\mathrm{Im}(x_\pm)$. In fact,

$$\begin{aligned} &\frac{\Gamma_d}{2} \geq |v| \;\Leftrightarrow\; \frac{\Gamma_d^2}{2} \geq \xi^2 - \Delta E_{ad}^2 - 4|V_{ad}|^2 + \frac{\Gamma_d^2}{4} \\ &\Leftrightarrow \left(\Delta E_{ad}^2 + 4|V_{ad}|^2 + \frac{\Gamma_d^2}{4}\right)^2 \geq \left(\Delta E_{ad}^2 + 4|V_{ad}|^2 - \frac{\Gamma_d^2}{4}\right)^2 + \Gamma_d^2 \Delta E_{ad}^2 \;\Leftrightarrow\; |V_{ad}|^2 \geq 0 \end{aligned} \qquad \textbf{[S30]}$$

which is always satisfied. Since the integrand in **[S24a]** tends to zero with increasing modulus of x in the lower half complex plane, we transform the integration path in the complex plane, by closing a clock-wise contour in this half plane, and taking the limit for infinite radius of the circular portion of the integration path. Both x_- and x_+ are enclosed by this contour. Thus, insertion of Eq. **S29** into Eq. **S24a** and application of the residue theorem produce

$$\begin{aligned} c_d(t) &= \frac{e^{-iE_a t/\hbar}}{x_+ - x_-}\left(x_+ e^{-ix_+ t/\hbar} - x_- e^{-ix_- t/\hbar}\right) = \exp\left(-i\frac{E_d + E_a}{2\hbar}t\right)\exp\left(-\frac{\Gamma_d}{4\hbar}t\right) \\ &\times \frac{\left[-\Delta E_{ad} + u + i\left(v - \frac{\Gamma_d}{2}\right)\right]\exp\left(\frac{v - iu}{2\hbar}t\right) - \left[-\Delta E_{ad} - u - i\left(v + \frac{\Gamma_d}{2}\right)\right]\exp\left(-\frac{v - iu}{2\hbar}t\right)}{2(u + iv)} \\ &= \exp\left(-i\frac{E_d + E_a}{2\hbar}t\right)\exp\left(-\frac{\Gamma_d}{4\hbar}t\right) \\ &\times \frac{(u + iv)\left[\exp\left(\frac{iu - v}{2\hbar}t\right) + \exp\left(\frac{v - iu}{2\hbar}t\right)\right] + \left(\Delta E_{ad} + i\frac{\Gamma_d}{2}\right)\left[\exp\left(\frac{iu - v}{2\hbar}t\right) - \exp\left(\frac{v - iu}{2\hbar}t\right)\right]}{2(u + iv)} \\ &= \frac{1}{2}\exp\left(-i\frac{E_a + E_d - u}{2\hbar}t\right)\exp\left(-\frac{v + \Gamma_d/2}{2\hbar}t\right) \\ &\times \left\{1 + \exp\left(\frac{v - iu}{\hbar}t\right) + \frac{\Delta E_{ad} + i\Gamma_d/2}{u + iv}\left[1 - \exp\left(\frac{v - iu}{\hbar}t\right)\right]\right\}. \end{aligned} \qquad \textbf{[S31]}$$

Introducing the abbreviated notation

$$\frac{\Delta E_{ad} + i\Gamma_d/2}{u+iv} = \chi e^{i\vartheta} \qquad \textbf{[S32]}$$

with χ and ϑ defined in Eq. **8**, we have

$$c_d(t) = \zeta_d(t)\exp\left(-\frac{\overline{\Gamma}_d}{2\hbar}t\right) \qquad \textbf{[S33a]}$$

with

$$\zeta_d(t) = \frac{1}{2}\exp\left(-i\frac{E_a+E_d-u}{2\hbar}t\right)\left[1+\chi e^{i\vartheta} + \left(1-\chi e^{i\vartheta}\right)e^{-i\frac{u}{\hbar}t}e^{\frac{v}{\hbar}t}\right] \qquad \textbf{[S33b]}$$

and $\overline{\Gamma}_d$ given in Eq. **8**. The squared modulus of $\zeta(t)$ is obtained from the equation

$$\begin{aligned}
4\left|\zeta_d(t)\right|^2 &= \left[1+\chi e^{i\vartheta} + \left(1-\chi e^{i\vartheta}\right)e^{-i\frac{u}{\hbar}t}e^{\frac{v}{\hbar}t}\right]\left[1+\chi e^{-i\vartheta} + \left(1-\chi e^{-i\vartheta}\right)e^{i\frac{u}{\hbar}t}e^{\frac{v}{\hbar}t}\right] \\
&= 1+\chi e^{-i\vartheta} + \left(1-\chi e^{-i\vartheta}\right)e^{i\frac{u}{\hbar}t}e^{\frac{v}{\hbar}t} + \chi e^{i\vartheta} + \chi^2 + \left(\chi e^{i\vartheta} - \chi^2\right)e^{i\frac{u}{\hbar}t}e^{\frac{v}{\hbar}t} + \left(1-\chi e^{i\vartheta}\right)e^{-i\frac{u}{\hbar}t}e^{\frac{v}{\hbar}t} \\
&+ \left(\chi e^{-i\vartheta} - \chi^2\right)e^{-i\frac{u}{\hbar}t}e^{\frac{v}{\hbar}t} + \left(1+\chi^2-\chi e^{i\vartheta}-\chi e^{-i\vartheta}\right)e^{2\frac{v}{\hbar}t} = 1+\chi^2+2\chi\cos\vartheta \\
&+ 2\left[\left(1-\chi^2\right)\cos(ut/\hbar) + \chi\cos(\vartheta+ut/\hbar) - \chi\cos(\vartheta-ut/\hbar)\right]e^{\frac{v}{\hbar}t} + \left(1+\chi^2-2\chi\cos\vartheta\right)e^{2\frac{v}{\hbar}t} \\
&= 1+\chi^2+2\chi\cos\vartheta + 2\left[\left(1-\chi^2\right)\cos(ut/\hbar) - 2\chi\sin\vartheta\sin(ut/\hbar)\right]e^{\frac{v}{\hbar}t} + \left(1+\chi^2-2\chi\cos\vartheta\right)e^{2\frac{v}{\hbar}t}
\end{aligned} \qquad \textbf{[S34]}$$

Thus, from Eq. **33** one obtains

$$\begin{aligned}
P_d(t) &\equiv \left|c_d(t)\right|^2 \\
&= e^{-\frac{\overline{\Gamma}_d}{\hbar}t}\left\{\frac{1+\chi^2+2\chi\cos\vartheta}{4} + \left[\frac{1-\chi^2}{2}\cos\left(\frac{u}{\hbar}t\right) - \chi\sin\vartheta\sin\left(\frac{u}{\hbar}t\right)\right]e^{\frac{v}{\hbar}t} + \frac{1+\chi^2-2\chi\cos\vartheta}{4}e^{2\frac{v}{\hbar}t}\right\}.
\end{aligned} \qquad \textbf{[S35]}$$

The expression for $\overline{\Gamma}_d$ in **[8]** and **[S30]** imply that $\overline{\Gamma}_d > 2v$ for $\left|V_{ad}\right|^2 > 0$. Hence, according to Eq. **S35**, $P_d(t) \to 0$ for $t \to \infty$. This limit also holds for the special case in which $\left|V_{ad}\right|^2 = 0$, because in this case $\xi^2 = \Delta E_{ad}^2 + \Gamma_d^2/4$, $u = \Delta E_{ad}$, $v = \Gamma_d/2$, and Eq. **S35** reduces to (2)

$$P_d(t) \cong \exp\left(-\frac{\Gamma_d}{\hbar}t\right) \qquad \textbf{[S36]}$$

Eq **S36** is also valid when, as in Fig. S3a, $\Delta E_{ad} >> V_{ad}, \Gamma_d$. In this regime of large ΔE_{ad}, the Rabi oscillation has an accordingly small amplitude, which makes the population of the high-energy state localized on a negligible throughout the relaxation process. Eq. **S35** (as well as Eq. **S36**) describes the irreversible process of quantum relaxation of the d population to the manifold L of substrate states. With the model parameters used in Fig. S3, the decay time $\tau_d = \hbar / (\overline{\Gamma}_d - 2|v|)$ of P_d is on the order of a picosecond. For $\Delta E_{ad} = 0$ and $\Delta E_{ad} = 2V_{ad}$ (Figs. S3b-c) one can see damped d-a Rabi oscillations during P_d decay, because the respective Rabi frequencies, $2V_{ad}/h$ and $2^{3/2}V_{ad}/h$, are similar to $1/\tau_d$. The amplitude of the Rabi oscillation is negligible in Fig. S3a where $\Delta E_{ad} >> 2V_{ad}$.

Eq. **S36** is also obtained for $\Gamma_d >> \Delta E_{ad}, V_{ad}$. In this case, the relaxation to the L manifold occurs before any appreciable effect arising from the d-a coupling because the coupling between d and L is much stronger than V_{ad}. Therefore, the relaxation rate is again $\Gamma_d/\hbar$, as in the absence of a. Indeed, the condition $\Gamma_d >> V_{ad}$ is sufficient to establish the regime described by Eq. **S36**, irrespective of the ΔE_{ad} value. This analysis extends the applicability of Eq. **S36** beyond its common use for the $\{d, L\}$ model.

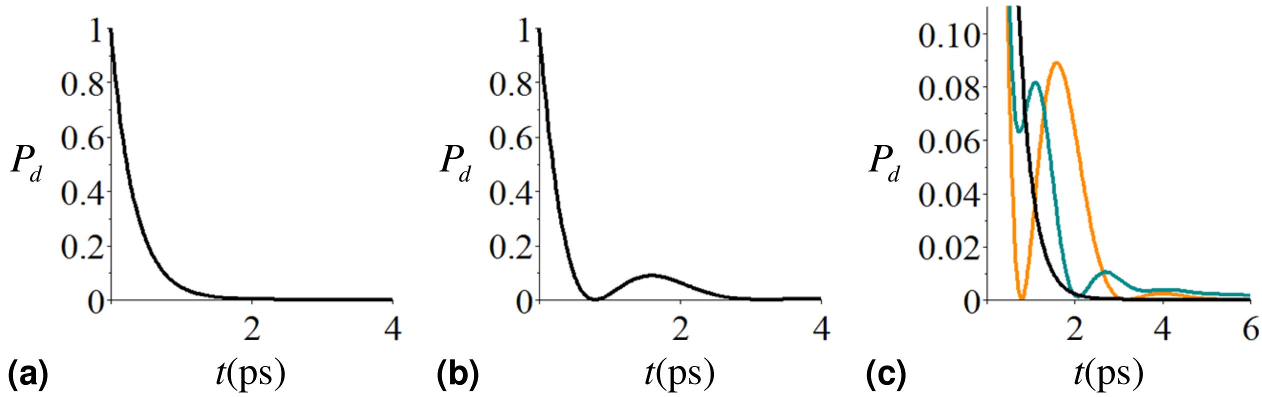


Fig. S3. $P_d = |c_d|^2$ vs. t, for $V_{ad} = \Gamma_d/2 = 1\,\text{meV}$ and (a) $\Delta E_{ad} = 1\,\text{eV}$; (b) $\Delta E_{ad} = 0$; (c) $\Delta E_{ad} = 1\,\text{eV}$ (black), $\Delta E_{ad} = 2V_{ad} = \Gamma_d$ (cyan), and $\Delta E_{ad} = 0$ (orange). Eq. **S35** is plotted.

In the opposite regime of large d-a coupling ($V_{ad} >> \Delta E_{ad}, \Gamma_d$), the Rabi oscillation is a dominant feature of the electronic dynamics and Γ_d causes a slow convolution (more specifically, a damping) of the oscillatory amplitude. In this regime, Eq. **S35** reduces to

$$P_d(t) \cong \exp\left(-\frac{\Gamma_d}{2\hbar}t\right)\left[1-\sin^2\left(\frac{V_{ad}}{\hbar}t\right)\right] \qquad \textbf{[S37]}$$

and $\hbar/V_{ad} << \tau_d$. $\Gamma_d/2$ and not Γ_d is the relaxation rate, because the system oscillates between $|d\rangle$ and $|a\rangle$ and there is no direct communication (zero electronic coupling) between the receptor layer and the substrate when $|a\rangle$ is the state of the system.

More generally, when $\Gamma_d/V_{ad} \to 0$ and/or $\Gamma_d/\Delta E_{ad} \to 0$ (considering, however, that $\Gamma_d t/\hbar$ is not negligible for large enough *t*, Eq. **S35** reduces to

$$P_d(t) \cong \exp\left(-\frac{\Gamma_d}{2\hbar}t\right) \times\left[\frac{1}{2}\left(1+\frac{\Delta E_{ad}^2}{\Delta E_v^2}\right)\sinh^2\left(\frac{\Gamma_d \Delta E_{ad}}{4\Delta E_v \hbar}t\right)-\frac{\Delta E_{ad}}{\Delta E_v}\sinh\left(\frac{\Gamma_d \Delta E_{ad}}{2\Delta E_v \hbar}t\right)+1-\frac{4V_{ad}^2}{\Delta E_v^2}\sin^2\left(\frac{\Delta E_v}{2\hbar}t\right)\right] \qquad \textbf{[S38]}$$

Eq. **S38** connects the limits $\Delta E_{ad} >> V_{ad}, \Gamma_d$ and $V_{ad} >> \Delta E_{ad}, \Gamma_d$, and holds for intermediate cases in which V_{ad} and ΔE_{ad} are comparable. Eqs. **S35** and **S38** show excellent agreement in Figs. S4-5.

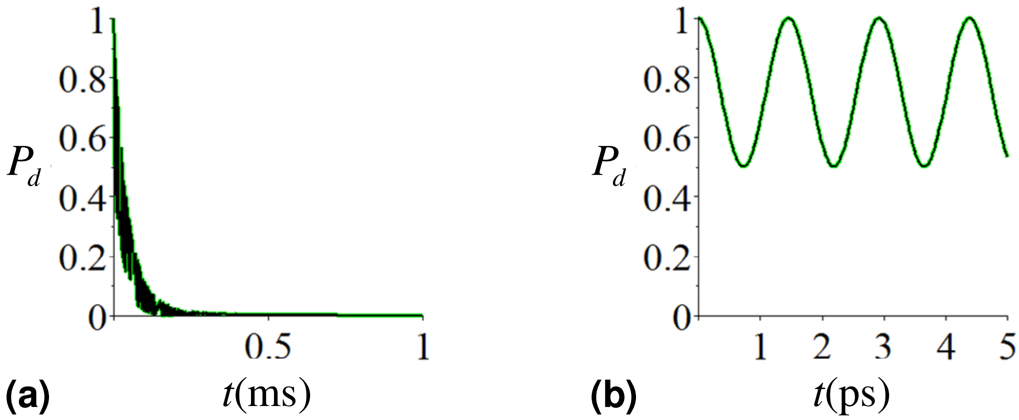


Fig. S4. (a) Time evolution of P_d (*d* site occupation probability) for $V_{ad} = 10^{-3}$ eV, $\Delta E_{ad} = 2V_{ad}$, and $\Gamma_d/2 = 10^{-11}$ eV. (b) Time evolution of P_d in a ps time scale that allows to appreciate only the Rabi oscillation between *d* and *a*. Eqs. **S35** and **S38** are plotted in black and green, respectively.

The absolute and relative values of V_{ad} and ΔE_{ad} influence the electronic relaxation time τ_d via the parameter v in Eq. **8**, but they also control the shape of the current signal and its sensitivity to the perturbation to be sensed. We now discuss how the sensitiveness of the quantum relaxation process to a change in ΔE_{ad} caused by the external perturbation may increase with decreasing V_{ad}.

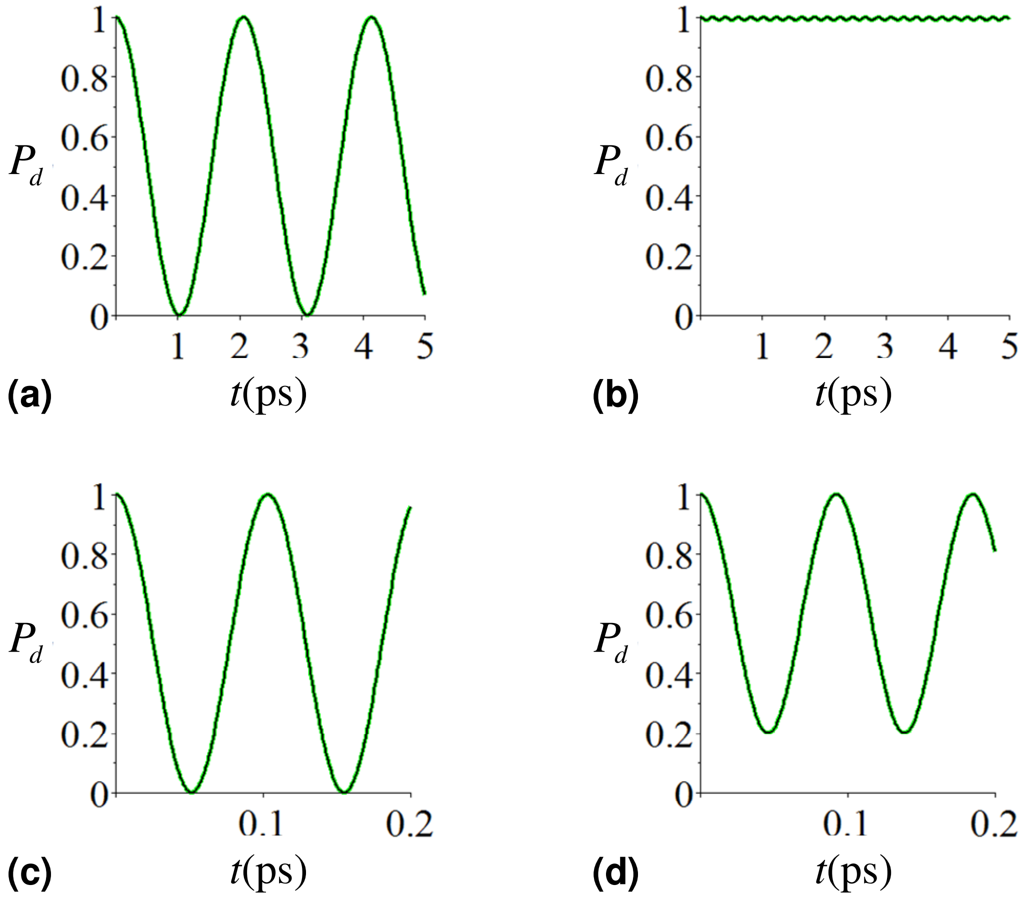


Fig. S5. (a) P_d vs. time, for $\Gamma_d/2 = 10^{-11}$ eV and (a) $V_{ad} = 10^{-3}$ eV, $\Delta E_{ad} = 0$; (b) $V_{ad} = 10^{-3}$ eV, $\Delta E_{ad} = 10 \cdot (2V_{ad}) = 0.02$ eV; (c) $V_{ad} = 0.02$ eV, $\Delta E_{ad} = 0$; and (d) $V_{ad} = 0.02$ eV, $\Delta E_{ad} = 0.02$ eV. The color code is used as in Fig. S4.

In Figs. S4-5, the *d*-*a* Rabi oscillation occurs on the ps time scale (with a frequency depending on ΔE_{ad}), while the relaxation to L occurs in a fraction of a ms because $\Gamma_d/2 = 10^{-11}$ eV (coherence in this time scale is an ideal limit, as discussed in the article). In Fig. S4 the oscillation of $P_d(t)$ has an amplitude of ½ because $\Delta E_{ad} = 2V_{ad}$. In Figs. S5a and S5c, $P_d(t)$ oscillates between zero and unity because $\Delta E_{ad} = 0$, while the state relaxation to the L manifold is negligible on the represented time scale. For $V_{ad} = 10^{-3}$ eV, changing ΔE_{ad} from zero to $10 \cdot (2V_{ad}) = 0.02$eV (note that such a change may also arise from thermal motion, which would break the coherence, at room temperature) causes a drastic change in the oscillation amplitude of P_d (cf. Figs. S5a-b). For $V_{ad} = 0.02$eV, a change of ΔE_{ad} in the same range produces a much smaller change in the oscillation amplitude of P_d (cf. Fig. S5c-d). Thus, with the parameters used in Figs. S4-5, the relaxation dynamics on the ps time scale is more sensitive to ΔE_{ad} perturbations for smaller coupling between receptor and anchoring sites.

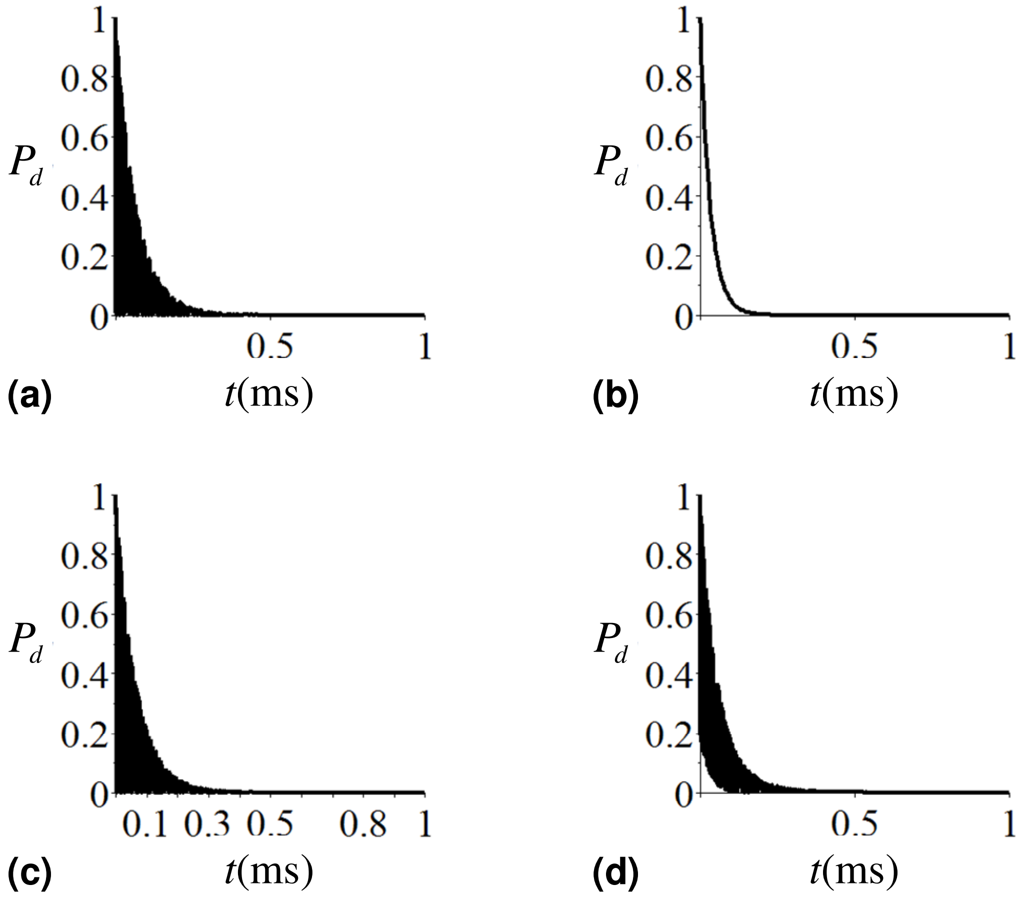


Fig. S6. Extension of the diagrams in Fig. S5 to the ms time scale, using only Eq. **S35**. The small-amplitude Rabi oscillations in Fig. S5b are not visible on the much longer time scale of Fig. S6b.

Fig. S6 extends Fig. S5 to the ms time scale. The increasing sensitivity of the *d* site depopulation to ΔE_{ad} changes with decreasing V_{ad} is a feature of the electronic relaxation dynamics that persists on the time scale of Fig. S6. Since *d* depopulation implies substrate population, hence change in the gate voltage, in this case the sensitivity of the detector is higher for larger thickness of the receptor.

The oscillations in Figs. S5-6 may well be averaged out by the influence on the current signal of simultaneous events at the receptor surface and by the data acquisition procedure. Thereby, smooth signals may be found in experiments. Averaging over the Rabi oscillations produces the smooth P_d time evolutions in Fig. S7, which correspond to the four cases of Fig. S6. Smoothed time evolutions were used to relate the electronic relaxation dynamics in the analyte-receptor-substrate subsystem to the current, which flows through the metal-substrate-metal junction of the FET. Anyway, P_L has a smooth evolution (see Fig. S8), as the Rabi oscillations occur between the *d* and *a* states.

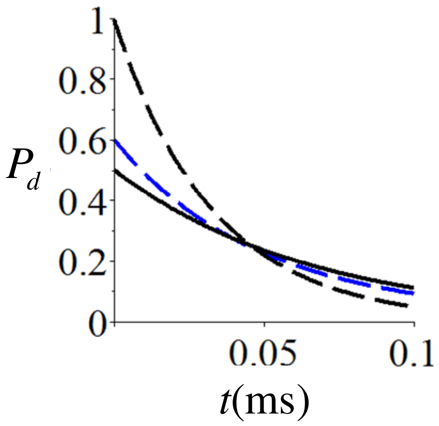


Fig. S7. Time decay of P_d, after averaging out the Rabi oscillation, for the cases in Figs. S6a (black solid curve), S6b (black dashed line), S6c (blue solid line, which is indistinguishable from the black solid line) and S6d (blue dashed line). A shorter time range of 0.1 ms is shown compared to Fig. S6. The larger difference between the black lines compared to the blue ones expresses the larger change in the charge relaxation dynamics, when ΔE_{ad} is varied, for smaller electronic coupling.

Next, consider the coefficient $c_a(t)$ in Eq. **5**, hence the probability $P_a(t) = |c_a(t)|^2$ that the system is in the *a* state at time *t*. Multiplying Eq. **S4** on the left by $\langle a|$ and inserting **[6]** and **[S12]**, we find

$$c_a(t) = -\frac{1}{2\pi i} \lim_{\varepsilon \to 0^+} \int_{-\infty}^{\infty} \frac{e^{-iEt/\hbar}}{E - E_a + i\varepsilon} V_{ad} G_{dd}(E + i\varepsilon) dE \quad \textbf{[S39]}$$

By exploiting the algebra in Eq. **S24**, Eq. **S39** is recast in the form

$$
\begin{aligned}
c_a(t) &= -\frac{e^{-iE_a t/\hbar}}{2\pi i} V_{ad} \lim_{\varepsilon\to 0^+} \int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x} x\,dx}{(x+i\varepsilon)(x-x_+)(x-x_-)} \\
&= -\frac{V_{ad}\, e^{-iE_a t/\hbar}}{2\pi i} \lim_{\varepsilon\to 0^+} \left[\int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x} x^2\,dx}{(x^2+\varepsilon^2)(x-x_+)(x-x_-)} - i\varepsilon \int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x} x\,dx}{(x^2+\varepsilon^2)(x-x_+)(x-x_-)} \right] \\
&= -\frac{e^{-iE_a t/\hbar}}{2\pi i} V_{ad} \int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x}\,dx}{(x-x_+)(x-x_-)}
\end{aligned}
\quad \textbf{[S40]}
$$

As an alternative, one may use Eq. **S23** and consider that x_+ and x_- have negative imaginary parts:

$$
\begin{aligned}
c_a(t) &= -\frac{e^{-iE_a t/\hbar}}{2\pi i} V_{ad}\, \mathrm{PP} \int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x} x\,dx}{x(x-x_+)(x-x_-)} + \frac{e^{-iE_a t/\hbar}}{2} V_{ad} \int_{-\infty}^{\infty} \delta(x) \frac{e^{-i\frac{t}{\hbar}x} x\,dx}{(x-x_+)(x-x_-)} \\
&= -\frac{e^{-iE_a t/\hbar}}{2\pi i} V_{ad} \int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x}\,dx}{(x-x_+)(x-x_-)}.
\end{aligned}
\quad \textbf{[S41]}
$$

At this point, the residue theorem yields

$$
\begin{aligned}
c_a(t) &= \frac{V_{ad}\, e^{-iE_a t/\hbar}}{2\pi i (x_- - x_+)} \left[\int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x}}{x-x_+} dx - \int_{-\infty}^{\infty} \frac{e^{-i\frac{t}{\hbar}x}}{x-x_-} dx \right] = \frac{V_{ad}\, e^{-iE_a t/\hbar}}{x_+ - x_-} \left(e^{-ix_+ t/\hbar} - e^{-ix_- t/\hbar} \right) \\
&= \frac{V_{ad}}{u+iv} \exp\left(-i\frac{E_a+E_d}{2\hbar}t\right) \exp\left(-\frac{\Gamma_d}{4\hbar}t\right) \left[\exp\left(\frac{v-iu}{2\hbar}t\right) - \exp\left(-\frac{v-iu}{2\hbar}t\right) \right] \\
&= \frac{V_{ad}}{\xi^2} \exp\left(-i\frac{E_a+E_d-u}{2\hbar}t\right) \exp\left(-\frac{\overline{\Gamma}_d}{2\hbar}t\right) (u-iv) \left[\exp\left(\frac{v-iu}{\hbar}t\right) - 1 \right]
\end{aligned}
\quad \textbf{[S42]}
$$

or, in more compact notation,

$$
c_a(t) = \frac{V_{ad}}{\xi} \zeta_a(t) \exp\left(-\frac{\overline{\Gamma}_d}{2\hbar}t\right) \quad \textbf{[S43a]}
$$

with

$$
\zeta_a(t) = \frac{u-iv}{\xi} \exp\left(-i\frac{E_a+E_d-u}{2\hbar}t\right) \left[\exp\left(\frac{v-iu}{\hbar}t\right) - 1 \right] \quad \textbf{[S43b]}
$$

Being

$$\frac{1}{4\xi^2}(u-iv)\left[\exp\left(\frac{v-iu}{\hbar}t\right)-1\right](u+iv)\left[\exp\left(\frac{v+iu}{\hbar}t\right)-1\right]=\frac{1}{4}\left[e^{2\frac{v}{\hbar}t}-e^{\frac{v}{\hbar}t}\left(e^{i\frac{u}{\hbar}t}+e^{-i\frac{u}{\hbar}t}\right)+1\right]$$
$$=e^{\frac{v}{\hbar}t}\left[\frac{1}{4}\left(e^{\frac{v}{\hbar}t}+e^{-\frac{v}{\hbar}t}\right)-\frac{1}{2}\cos\left(\frac{u}{\hbar}t\right)\right]=e^{\frac{v}{\hbar}t}\left[\sin^2\left(\frac{u}{2\hbar}t\right)+\sinh^2\left(\frac{v}{2\hbar}t\right)\right] \quad \textbf{[S44]}$$

and using Eq. **8**, one obtains the following time-dependent occupation probability for site a:

$$P_a(t)\equiv|c_a(t)|^2=\frac{|V_{ad}\zeta_a(t)|^2}{\xi^2}\exp\left(-\frac{\overline{\Gamma}_d}{\hbar}t\right)=\frac{4|V_{ad}|^2}{\xi^2}e^{-\frac{\Gamma_d}{2\hbar}t}\left[\sin^2\left(\frac{u}{2\hbar}t\right)+\sinh^2\left(\frac{v}{2\hbar}t\right)\right] \quad \textbf{[S45]}$$

Finally, the population of the L manifold in Eq. **7** results from the normalization condition $\sum_l |c_l(t)|^2 = 1-|c_d(t)|^2-|c_a(t)|^2$.

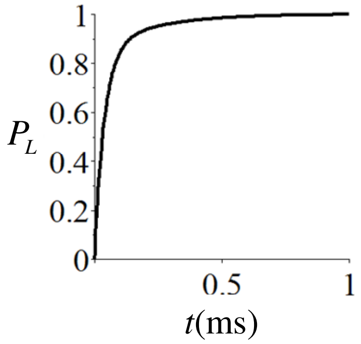


Fig. S8.

Fig. S8. $P_L(t)\equiv\sum_l |c_l(t)|^2$ vs. time, for $\Gamma_d/2=10^{-11}$ eV, $V_{ad}=10^{-3}$ eV, and $\Delta E_{ad}=2V_{ad}$.

$P_a(t)$ is related to $P_d(t)$ by Rabi oscillations that initially increase the average a population. Then $P_a(t)$ vanishes for $t\to\infty$, while $P_L(t)\to 1$ for $t\to\infty$ (see Fig. S8, where P_L increases to unity on a millisecond time scale for a coupling strength to the L manifold as small as $\Gamma_d/2=10^{-11}$ eV). The oscillation is damped as $|d\rangle$ relaxes to $\{|l\rangle\}$ in a time of the order of $\hbar/\Gamma_d$. This relaxation also causes loss of coherence (dephasing) in the evolution of the d-a subsystem. The departure from coherent d-a Rabi oscillations is quantified by the parameters Γ_d , v and ϑ in the state probabilities of Eqs. **S35** and **S45**, with $v = \vartheta = 0$ for $\Gamma_d = 0$. Residual electronic charge on the *a* site (or, in general (4), residual occupancy of $|a\rangle$) near $t = \hbar/\Gamma_d$ is finally released to *L* by mediation of site *d*. The complete decay of $P_a(t)$ to zero occurs over the τ_a time scale described in the upper inset of Fig. 3. Both approximations to τ_a in this inset hold for the parameters used in Figs. S9-10. The first approximation shows that τ_a increases with decreasing V_{ad} and/or increasing ΔE_{ad}. In fact, the parameter choice in Fig. S10 implies complete decay of $P_a(t)$ to zero on a second time scale, even if $\Gamma_d/2 = 10^{-11}$ eV as in Fig. S9 (again, coherence can be maintained on these time scales depending on the nature of the electronic states and possible special conditions, such as $T \to 0$). However, the residual population of the *a* site is of the order of $10^{-4} e$ for the model parameters of Fig. S10 (cf. Figs. S9a and S10b-c), which demands high sensitivity of the FET current to the electronic relaxation dynamics in order toexploit the long-time evolution of P_a for sensing purposes, provided that the P_a tail is not erased by system fluctuations. The cumulative effect of tails of this sort needs to survive to fluctuations in a detector that is subject to simultaneous perturbing events (5).

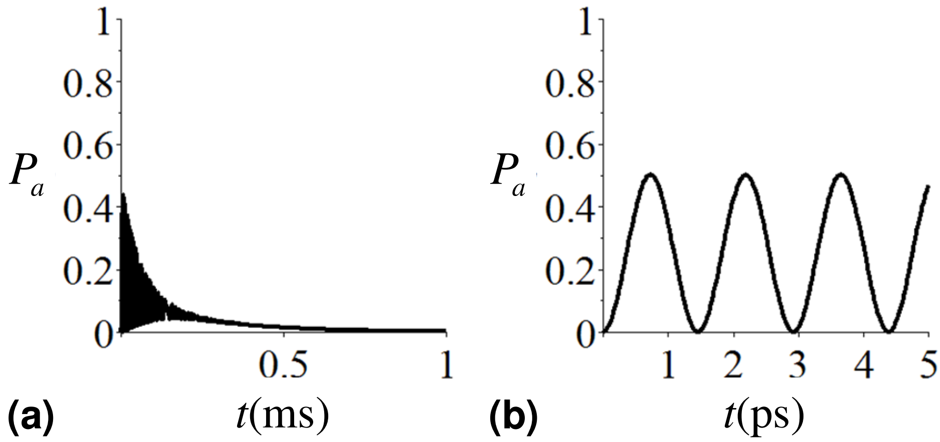


Fig. S9. (a) P_a vs. time with the initial condition of Eq. **6**, for $\Gamma_d/2 = 10^{-11}$ eV, $V_{ad} = 10^{-3}$ eV and $\Delta E_{ad} = 2V_{ad}$. (b) Same graph, limited to a picosecond time scale. Eq. **S45** is plotted.

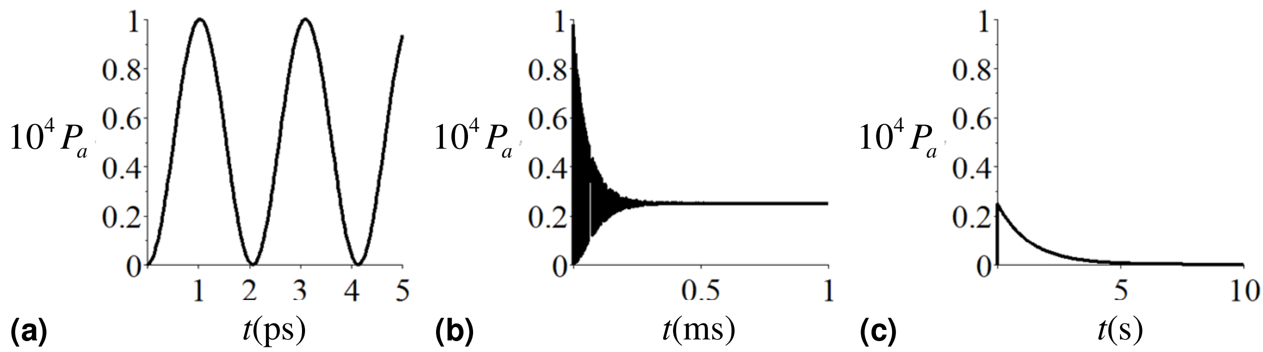


Fig. S10. (a) $10^4 P_a$ vs. time for $\Gamma_d/2 = 10^{-11}$ eV, $V_{ad} = 10^{-5}$ eV and $\Delta E_{ad} = 2 \cdot 10^{-3}$ eV. (b) Time evolution of $10^4 P_a$ over a millisecond scale. (c) Evolution of $10^4 P_a$ over a second time scale.

Next, we derive the state occupation probabilities at time t starting from the initial condition in Eq. **13**. In terms of Green's functions, we have now (6)

$$C_a(t) = -\frac{1}{2\pi i} \lim_{\varepsilon \to 0^+} \int_{-\infty}^{\infty} e^{-iEt/\hbar} G_{aa}(E + i\varepsilon)\, dE \quad \textbf{[S46]}$$

$$C_d(t) = -\frac{1}{2\pi i} \lim_{\varepsilon \to 0^+} \int_{-\infty}^{\infty} e^{-iEt/\hbar} G_{da}(E + i\varepsilon)\, dE \quad \textbf{[S47]}$$

$$C_l(t) = -\frac{1}{2\pi i} \lim_{\varepsilon \to 0^+} \int_{-\infty}^{\infty} e^{-iEt/\hbar} G_{la}(E + i\varepsilon)\, dE \quad \textbf{[S48]}$$

with

$$\begin{aligned} G_{aa}(z) &= \langle a | G_0(z) | a \rangle + \langle a | \hat{G}_0(z) \hat{1} \hat{V} \hat{1} \hat{G}(z) | a \rangle \\ &= \frac{1}{z - E_a} \left[1 + \langle a | \hat{V} \left(|d\rangle\langle d| + |a\rangle\langle a| + \sum_l |l\rangle\langle l| \right) \hat{G}(z) | a \rangle \right] = \frac{1}{z - E_a} \left(1 + V_{ad} G_{da} \right) \end{aligned} \quad \textbf{[S49]}$$

$$G_{da}(z) = \langle d | \hat{G}_0(z) \hat{1} \hat{V} \hat{1} \hat{G}(z) | a \rangle = \frac{1}{z - E_d} \left(V_{da} G_{aa} + \sum_l V_{dl} G_{la} \right) \quad \textbf{[S50]}$$

$$G_{la}(z) = \langle l | \hat{G}_0(z) \hat{1} \hat{V} \hat{1} \hat{G}(z) | a \rangle = \frac{1}{z - E_l} V_{ld} G_{da} \quad \textbf{[S51]}$$

Insertion of Eq. **S51** into Eq. **S50** leads to

$$G_{da}(z) = \frac{V_{da} G_{aa}}{z - E_d - \sum_l \frac{|V_{dl}|^2}{z - E_l}} \qquad \textbf{[S52]}$$

Then, substitution of Eq. **S52** into Eq. **S49** and use of Eqs. **S17**-**19** gives

$$\begin{aligned} G_{aa}(z) \equiv G_{aa}(E + i\varepsilon) &= \frac{1}{z - E_a - \frac{|V_{da}|^2}{z - E_d - \sum_l \frac{|V_{dl}|^2}{z - E_l}}} = \frac{1}{z - E_a - \frac{|V_{da}|^2}{z - E_d + i\Gamma_d/2}} \\ &= \frac{z - E_d + i\Gamma_d/2}{(z - E_a)(z - E_d + i\Gamma_d/2) - |V_{da}|^2} = \frac{E - E_d + i(\varepsilon + \Gamma_d/2)}{(E - E_a + i\varepsilon)[E - E_d + i(\varepsilon + \Gamma_d/2)] - |V_{da}|^2} \end{aligned} \qquad \textbf{[S53]}$$

from which

$$G_{da}(z) = \frac{V_{da}}{(z - E_a)(z - E_d + i\Gamma_d/2) - |V_{da}|^2} \qquad \textbf{[S54]}$$

and

$$G_{la}(z) = \frac{1}{z - E_l} \frac{V_{ld} V_{da}}{(z - E_a)(z - E_d + i\Gamma_d/2) - |V_{da}|^2} . \qquad \textbf{[S55]}$$

Moreover,

$$G_{aa}(E) = \lim_{\varepsilon \to 0} G_{aa}(E + i\varepsilon) = \frac{E - E_d + i\Gamma_d/2}{(E - E_a)(E - E_d + i\Gamma_d/2) - |V_{da}|^2} , \qquad \textbf{[S56]}$$

$$G_{da}(E) = \lim_{\varepsilon \to 0} G_{da}(E + i\varepsilon) = \frac{V_{da}}{(E - E_a)(E - E_d + i\Gamma_d/2) - |V_{da}|^2} . \qquad \textbf{[S57]}$$

Inserting Eq. **S56** into Eq. **S46**, one obtains

$$C_a(t) = -\frac{e^{-iE_a t/\hbar}}{2\pi i} \int_{-\infty}^{\infty} e^{-i\frac{t}{\hbar}x} \frac{x + \Delta E_{ad} + i\Gamma_d/2}{x^2 + (\Delta E_{ad} + i\Gamma_d/2)x - |V_{da}|^2} dx \qquad \textbf{[S58]}$$

where, as above, $x = E - E_a$. The denominator of the integrand in Eq. **S58** can be decomposed as in Eq. **S24a**. Then, comparison with Eqs. **S21** and **S40**, and use of Eqs. **S33** and **S43**, gives

$$C_a(t) = c_d(t) + \frac{\Delta E_{ad} + i\Gamma_d/2}{V_{ad}} c_a(t) = \left[\zeta_d(t) + \frac{\Delta E_{ad} + i\Gamma_d/2}{\xi}\zeta_a(t)\right]\exp\left(-\frac{\overline{\Gamma}_d}{2\hbar}t\right) \qquad \textbf{[S59]}$$

hence

$$\begin{aligned} |C_a(t)|^2 &= |c_d(t)|^2 + \frac{\Delta E_{ad}^2 + \Gamma_d^2/4}{|V_{ad}|^2}|c_a(t)|^2 + 2\,\mathrm{Re}\left[\bar{c}_d(t)\,c_a(t)\frac{\Delta E_{ad} + i\Gamma_d/2}{V_{ad}}\right] \\ &= \left\{|\zeta_d(t)|^2 + \frac{\Delta E_{ad}^2 + \Gamma_d^2/4}{\xi^2}|\zeta_a(t)|^2 + 2\,\mathrm{Re}\left[\overline{\zeta}_d(t)\,\zeta_a(t)\frac{\Delta E_{ad} + i\Gamma_d/2}{V_{ad}}\right]\right\}\exp\left(-\frac{\overline{\Gamma}_d}{\hbar}t\right) \end{aligned} \qquad \textbf{[S60]}$$

For the last term in Eq. **S60**, Eqs. **S31** and **S42** yield

$$\begin{aligned} &2\exp\left(\frac{\overline{\Gamma}_d}{\hbar}t\right)\mathrm{Re}\left[\bar{c}_d(t)\,c_a(t)\frac{\Delta E_{ad} + i\Gamma_d/2}{V_{ad}}\right] = \frac{1}{\xi^2} \\ &\times \mathrm{Re}\left\{\left[1 + \frac{\Delta E_{ad} - i\Gamma_d/2}{u - iv} + \left(1 - \frac{\Delta E_{ad} - i\Gamma_d/2}{u - iv}\right)e^{\frac{v}{\hbar}t}e^{i\frac{u}{\hbar}t}\right](\Delta E_{ad} + i\Gamma_d/2)(u - iv)(e^{\frac{v}{\hbar}t}e^{-i\frac{u}{\hbar}t} - 1)\right\} \\ &= \frac{1}{\xi^2}\mathrm{Re}\left\{(\Delta E_{ad} + i\Gamma_d/2)(u - iv)(e^{\frac{v}{\hbar}t}e^{-i\frac{u}{\hbar}t} - 1) + (\Delta E_{ad}^2 + \Gamma_d^2/4)(e^{\frac{v}{\hbar}t}e^{-i\frac{u}{\hbar}t} - 1)\right. \\ &\left. + (\Delta E_{ad} + i\Gamma_d/2)(u - iv)(e^{2\frac{v}{\hbar}t} - e^{\frac{v}{\hbar}t}e^{i\frac{u}{\hbar}t}) - (\Delta E_{ad}^2 + \Gamma_d^2/4)(e^{2\frac{v}{\hbar}t} - e^{\frac{v}{\hbar}t}e^{i\frac{u}{\hbar}t})\right\} \end{aligned}$$

$$\begin{aligned} &= \frac{1}{\xi^2}\mathrm{Re}\left\{\left[u\Delta E_{ad} + v\frac{\Gamma_d}{2} + i\left(u\frac{\Gamma_d}{2} - v\Delta E_{ad}\right)\right]\left[e^{2\frac{v}{\hbar}t} - (e^{i\frac{u}{\hbar}t} - e^{-i\frac{u}{\hbar}t})e^{\frac{v}{\hbar}t} - 1\right]\right. \\ &\left. - \left(\Delta E_{ad}^2 + \frac{\Gamma_d^2}{4}\right)\left[e^{2\frac{v}{\hbar}t} - (e^{i\frac{u}{\hbar}t} + e^{-i\frac{u}{\hbar}t})e^{\frac{v}{\hbar}t} + 1\right]\right\} \\ &= \frac{1}{\xi^2}\mathrm{Re}\left\{\left[u\Delta E_{ad} + v\frac{\Gamma_d}{2} + i\left(u\frac{\Gamma_d}{2} - v\Delta E_{ad}\right)\right]\left[e^{2\frac{v}{\hbar}t} - 1 - 2i\sin\left(\frac{u}{\hbar}t\right)e^{\frac{v}{\hbar}t}\right]\right\} \\ &- \frac{1}{\xi^2}\left(\Delta E_{ad}^2 + \frac{\Gamma_d^2}{4}\right)\left[e^{2\frac{v}{\hbar}t} - 2\cos\left(\frac{u}{\hbar}t\right)e^{\frac{v}{\hbar}t} + 1\right] \\ &= \frac{1}{\xi^2}\left\{\left(u\Delta E_{ad} + v\frac{\Gamma_d}{2}\right)\left(e^{2\frac{v}{\hbar}t} - 1\right) + 2\left(u\frac{\Gamma_d}{2} - v\Delta E_{ad}\right)\sin\left(\frac{u}{\hbar}t\right)e^{\frac{v}{\hbar}t}\right. \\ &\left. - \left(\Delta E_{ad}^2 + \frac{\Gamma_d^2}{4}\right)\left[e^{2\frac{v}{\hbar}t} - 2\cos\left(\frac{u}{\hbar}t\right)e^{\frac{v}{\hbar}t} + 1\right]\right\} \\ &= 2\left[\frac{u\Delta E_{ad} + v\Gamma_d/2}{\xi^2}\sinh\left(\frac{v}{\hbar}t\right) - \chi^2\cosh\left(\frac{v}{\hbar}t\right) + \frac{-v\Delta E_{ad} + u\Gamma_d/2}{\xi^2}\sin\left(\frac{u}{\hbar}t\right) + \chi^2\cos\left(\frac{u}{\hbar}t\right)\right]e^{\frac{v}{\hbar}t} \end{aligned} \qquad \textbf{[S61]}$$

Substitution of Eqs. **S35**, **S45,** and **S61** into Eq. **S60** produces

$$
\begin{aligned}
\mathcal{P}_a(t) &\equiv \left|C_a(t)\right|^2 \\
&= \left\{ \frac{1+\chi^2+2\chi\cos\vartheta}{4} e^{-\frac{v}{\hbar}t} + \left[\frac{1-\chi^2}{2}\cos\left(\frac{u}{\hbar}t\right) - \chi\sin\vartheta\sin\left(\frac{u}{\hbar}t\right) \right] + \frac{1+\chi^2-2\chi\cos\vartheta}{4} e^{\frac{v}{\hbar}t} \right. \\
&+ 4\chi^2\left[\sin^2\left(\frac{u}{2\hbar}t\right) + \sinh^2\left(\frac{v}{2\hbar}t\right) \right] + 2\left[\frac{u\Delta E_{ad}+v\Gamma_d/2}{\xi^2}\sinh\left(\frac{v}{\hbar}t\right) - \chi^2\cosh\left(\frac{v}{\hbar}t\right) \right. \\
&\left.\left. + \frac{-v\Delta E_{ad}+u\Gamma_d/2}{\xi^2}\sin\left(\frac{u}{\hbar}t\right) + \chi^2\cos\left(\frac{u}{\hbar}t\right) \right] \right\} e^{-\frac{\Gamma_d}{2\hbar}t}.
\end{aligned}
\quad \textbf{[S62]}
$$

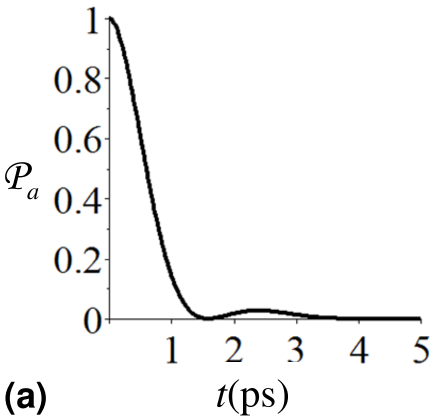
For $C_d(t)$, the comparison of Eqs. **S47** and **S57** with Eq. **S40** shows that

$$C_d(t) = \frac{V_{da}}{V_{ad}} c_a(t) = \frac{V_{da}}{\xi}\zeta_a(t)\exp\left(-\frac{\overline{\Gamma}_d}{2\hbar}t\right) \quad \textbf{[S63]}$$

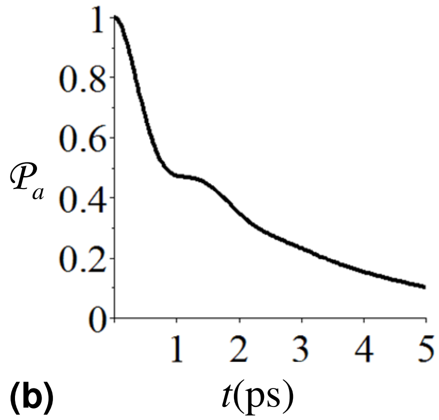
$$\mathcal{P}_d(t) \equiv \left|C_d(t)\right|^2 = P_a(t) = \frac{4\left|V_{da}\right|^2}{\xi^2} e^{-\frac{\Gamma_d}{2\hbar}t}\left[\sin^2\left(\frac{u}{2\hbar}t\right) + \sinh^2\left(\frac{v}{2\hbar}t\right)\right]. \quad \textbf{[S64]}$$

Finally, Eq. **14** results from the normalization condition on the expansion coefficients of Eq. **7**.

Examples of the time evolution of $\mathcal{P}_a$ are illustrated in Fig. S11. If ΔE_{ad} is zero or comparable to V_{ad}, wide Rabi oscillations between $|a\rangle$ and $|d\rangle$ assure efficient state relaxation to the *L* manifold, compatibly with the value of Γ_d (Figs. S11a-b). In contrast, in Fig. S11c or Fig. S11d, the condition $\Delta E_{ad} >> V_{ad}, \Gamma_d$ implies small-amplitude Rabi oscillations, hence slow (*d*-mediated) relaxation to *L*, with a dramatically reduced decay factor of the *a* population compared to the cases of Figs. S11a-b. This difference is relevant to possible implementations of the pertinent sensing mechanism.



(a)



(b)

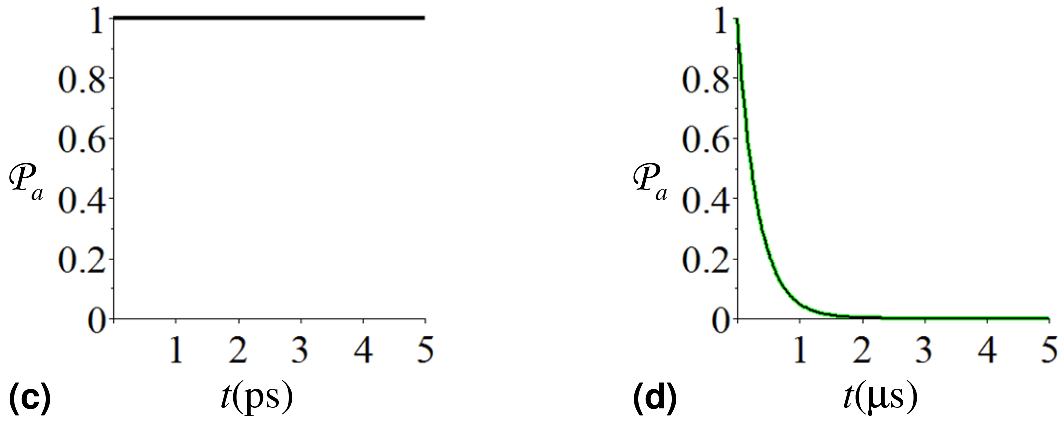


Fig. S11. $\mathcal{P}_a(t)$, as obtained using Eq. **S62** for $V_{ad} = \Gamma_d/2 = 10^{-3}$ eV and (a) $\Delta E_{ad} = 0$ (cf. Fig. S3b, where $|d\rangle$ is the initial state of the receptor-substrate system); (b) $\Delta E_{ad} = 2V_{ad}$ (cf. cyan line in Fig. S3c); (c) $\Delta E_{ad} = 1\text{eV}$ (cf. Fig. S3a); (d) $\Delta E_{ad} = 1\text{eV}$ (longer time scale than in panel c). The green line was obtained using the approximation in Eq. **S65**.

The short-time behavior of $\mathcal{P}_a(t)$ in Fig. S11c is obtained as follows. Since ΔE_{ad} is much larger than V_{ad} and Γ_d, we expand ξ^2 up to the second order in $V_{ad}/\Delta E_{ad}$ and $\Gamma_d/\Delta E_{ad}$, thus obtaining $\xi^2 \cong \Delta E_{ad}^2 + 4|V_{ad}|^2 + \Gamma_d^2/4$, hence $u \cong \sqrt{\Delta E_{ad}^2 + 4|V_{ad}|^2}$, $v \cong \Gamma_d/2$, $\vartheta \cong 0$, $\chi \cong 1 - 2|V_{ad}|^2/\Delta E_{ad}^2$ in Eq. **8**. In the time scale of Fig. S11c, inserting such approximations in **[S62]**, applying the cosine and hyperbolic cosine sum formulas and expressing the hyperbolic sine in terms of exponentials, we obtain $\mathcal{P}_a(t) \cong 1$. To describe the decay of $\mathcal{P}_a(t)$ over the large time range represented in Fig. S11d, ξ^2 has to be expanded up to the fourth order: $\xi^2 \cong \Delta E_{ad}^2 + 4|V_{ad}|^2 + (\Gamma_d^2/4) - 2\Gamma_d^2|V_{ad}|^2/\Delta E_{ad}^2$; then, $v \cong (\Gamma_d/2)(1 - 2|V_{ad}|^2/\Delta E_{ad}^2)$ and thus

$$\mathcal{P}_a(t) \approx \exp\left(\frac{v - \Gamma_d/2}{\hbar}t\right) = \exp\left(-\frac{\Gamma_d|V_{ad}|^2}{\hbar\Delta E_{ad}^2}t\right). \quad \textbf{[S65]}$$

Note that the integrands in the expressions of the above coefficients have larger numbers of poles in the presence of bridge states localized between *a* and *d*. For example, with one additional state of energy E_b, the denominator of the integrand in $c_d(t)$ is the third-order polynomial

$$x^3+2\left(E_b-\frac{E_d+E_a}{2}+i\frac{\Gamma_d}{4}\right)x^2+\left[(E_b-E_d)(E_b-E_a)-|V_{bd}|^2-|V_{ba}|^2+i(E_b-E_a)\frac{\Gamma_d}{2}\right]x$$
$$-|V_{ba}|^2(E_b-E_d)-|V_{bd}|^2(E_b-E_a)-i|V_{ba}|^2\frac{\Gamma_d}{2} \qquad \textbf{[S66]}$$

S3. Analytical expressions for the ET rates constants in Eq. 12.

The ET rates for the junction model of Fig. S12 and the pertinent Eq. **12** for the current are written using the zero-order Hale's approximation (7) to the sums [see Methods section in ref. (8)]

$$k_{OR}^J=\frac{\gamma}{4}S(\lambda,T,\alpha_J)\exp\left[-\frac{(\alpha_J-\lambda)^2}{4\lambda k_BT}\right], \qquad k_{RO}^J=\frac{\gamma}{4}S(\lambda,T,\alpha_J)\exp\left[-\frac{(\alpha_J+\lambda)^2}{4\lambda k_BT}\right] \qquad \textbf{[S67]}$$

with

$$\alpha_J(t;V)\equiv\varepsilon_F-\varepsilon_1(t)-eV_J \qquad \textbf{[S68a]}$$

$$S(\lambda,T,\alpha)=\sum_{n=0}^{N}\frac{1}{2^n}\sum_{j=0}^{n}(-1)^j\binom{n}{j}[\chi_j(\lambda,T,\alpha)+\chi_j(\lambda,T,-\alpha)] \qquad \textbf{[S68b]}$$

$$\chi_j(\lambda,T,\alpha)=\exp\left\{\frac{[(2j+1)\lambda+\alpha]^2}{4\lambda k_BT}\right\}\operatorname{erfc}\left[\frac{(2j+1)\lambda+\alpha}{2\sqrt{\lambda k_BT}}\right] \qquad \textbf{[S68c]}$$

In Eq. **S67**, *J* = *S*, *D*; the upper limit *N* truncates (9) the series expansions of the ET rates; λ denotes the reorganization energy for ET to or from the bridge; and the bridge-source and bridge-drain potential differences are $V_S=-V/2$ and $V_D=V/2$, respectively. γ is again the coupling strength to the leads and will assume smaller values in the regime of applicability of the hopping model, compared to the coherent tunneling model.

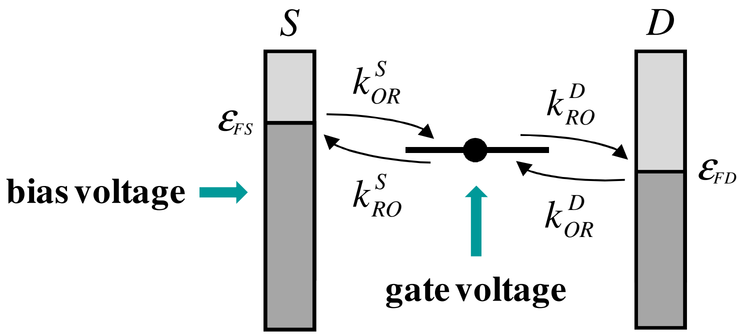


Fig. S12. One-channel hopping model for charge transport through a redox junction in a transistor configuration. *O* and *R* denote the oxidized and reduced states of the bridge, respectively. Assuming symmetric contacts to the source (S) and drain (D) metal electrodes, the *S* and *F* chemical potentials at nonzero *V* are $\varepsilon_{FS} = \varepsilon_F + eV/2$ and $\varepsilon_{FD} = \varepsilon_F - eV/2$. The ET rates are described in the main text.

S4. Expression for the state vector in Eq. 16, under the initial conditions of Eqs. 6 and 13.

In this section, we derive the state occupation probabilities in section 4, using the same approach as in Section S2. Considering the initial condition of Eq. **13**, in the presence of the *R* manifold the set of Eqs. **S46-48** needs to be complemented with

$$C_r(t) = -\frac{1}{2\pi i}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty} e^{-iEt/\hbar} G_{ra}(E+i\varepsilon)\,dE\,. \qquad \textbf{[S69]}$$

Moreover, the Green's operator matrix elements in Eqs. **S46-48** and **S6** need to be evaluated for the present model, where the resolution of the identity operator is

$$\hat{1} = |d\rangle\langle d| + |a\rangle\langle a| + \sum_l |l\rangle\langle l| + \sum_r |r\rangle\langle r|\,. \qquad \textbf{[S70]}$$

Use of **[S5]**, **[S7]** and **[S8]** yields

$$\begin{aligned} G_{aa}(z) &= \langle a|G_0(z)|a\rangle + \langle a|\hat{G}_0(z)\hat{1}\hat{V}\hat{1}\hat{G}(z)|a\rangle \\ &= \frac{1}{z-E_a}\left[1+\langle a|\,\hat{V}\left(|d\rangle\langle d|+|a\rangle\langle a|+\sum_l |l\rangle\langle l|+\sum_r |r\rangle\langle r|\right)\hat{G}(z)|a\rangle\right] \\ &= \frac{1}{z-E_a}\left(1+V_{ad}G_{da}+\sum_r V_{ar}G_{ra}\right) \end{aligned} \qquad \textbf{[S71]}$$

$$G_{ra}(z) = \langle r | \hat{G}_0(z) \hat{1} \hat{V} \hat{1} \hat{G}(z) | a \rangle = \frac{1}{z - E_r} V_{ra} G_{aa} \qquad \textbf{[S72]}$$

while $G_{da}(z)$ and $G_{la}(z)$ preserve the formal expression in **[S50]** and **[S51]**; thus, Eq. **S52** is again obtained. Substituting Eqs. **S52** and **S72** into Eq. **S71**, one obtains

$$\begin{aligned} G_{aa}(z) \equiv G_{aa}(E + i\varepsilon) &= \frac{1}{z - E_a - \dfrac{|V_{da}|^2}{z - E_d - \sum_l |V_{dl}|^2 / (z - E_l)} - \sum_r \dfrac{|V_{ra}|^2}{z - E_r}} \\ &= \frac{1}{z - E_a + i\dfrac{\Gamma_a}{2} - \dfrac{|V_{da}|^2}{z - E_d + i\Gamma_d/2}} = \frac{E - E_d + i(\varepsilon + \Gamma_d/2)}{[E - E_a + i(\varepsilon + \Gamma_a/2)][E - E_d + i(\varepsilon + \Gamma_d/2)] - |V_{da}|^2} \end{aligned} \qquad \textbf{[S73]}$$

where Γ_a is defined similarly to Γ_d with reference to the *R* manifold of states:

$$\Gamma_a(E) = 2\pi < |V_{ar}|^2 >_E \ \rho_R(E) \qquad \textbf{[S74a]}$$

which reduces to

$$\Gamma_a(E) = 2\pi < |V_{ar}|^2 >_R \ \rho_R(E) \qquad \textbf{[S74b]}$$

under the assumptions that the density of states in *R* (ρ_R), similarly to ρ_L, can be treated according to the wide band approximation (2) and is independent of the state energy *E*, and that $< |V_{ar}|^2 >_E$ (that is, the average of the squared *a*-*r* electronic coupling for all *R* states with energy *E*) does not depend on *E*. Equations similar to Eqs. **S17** and **S19** are written with the assumptions leading to Eq. **S74b** and the continuum approximation for the *R* manifold. Clearly, it is

$$G_{aa}(E) = \lim_{\varepsilon \to 0^+} G_{aa}(E + i\varepsilon) = \frac{E - E_d + i\Gamma_d/2}{(E - E_a + i\Gamma_a/2)(E - E_d + i\Gamma_d/2) - |V_{da}|^2} \qquad \textbf{[S75]}$$

for any *E*, because Γ_a and Γ_d are nonzero and thus the imaginary quantities in the denominator are never zero. Inserting Eq. **S73** into **[S72]**, we have

$$\lim_{\varepsilon\to 0^+} G_{ra}(E+i\varepsilon) = \frac{V_{ra}}{(E-E_a+i\Gamma_a/2)(E-E_d+i\Gamma_d/2)-|V_{da}|^2}\lim_{\varepsilon\to 0^+}\frac{E-E_d+i\Gamma_d/2}{E-E_r+i\varepsilon}$$
$$= \frac{V_{ra}}{(E-E_a+i\Gamma_a/2)(E-E_d+i\Gamma_d/2)-|V_{da}|^2}\left(1+\lim_{\varepsilon\to 0^+}\frac{E_r-E_d-i\varepsilon+i\Gamma_d/2}{E-E_r+i\varepsilon}\right) \quad \textbf{[S76]}$$
$$= \frac{V_{ra}}{(E-E_a+i\Gamma_a/2)(E-E_d+i\Gamma_d/2)-|V_{da}|^2}\left(1+\lim_{\varepsilon\to 0^+}\frac{E_r-E_d+i\Gamma_d/2}{E-E_r+i\varepsilon}\right)$$

Substitution of Eqs. **S17**, **S18**, and **S75** into Eq. **S52** gives

$$G_{da}(E) = \lim_{\varepsilon\to 0^+} G_{da}(E+i\varepsilon) = \frac{V_{da}}{(E-E_a+i\Gamma_a/2)(E-E_d+i\Gamma_d/2)-|V_{da}|^2} \quad \textbf{[S77]}$$

and use of Eq. **S51** leads to

$$\lim_{\varepsilon\to 0^+} G_{la}(E+i\varepsilon) = \frac{V_{ld}V_{da}}{(E-E_a+i\Gamma_a/2)(E-E_d+i\Gamma_d/2)-|V_{da}|^2}\lim_{\varepsilon\to 0^+}\frac{1}{E-E_l+i\varepsilon}. \quad \textbf{[S78]}$$

These limits are used together with the dominated convergence theorem to obtain the expressions of the state vector coefficients. By inserting Eq. **S75** into Eq. **S46**, we obtain

$$C_a(t) = -\frac{e^{-iE_a t/\hbar}}{2\pi i}\int_{-\infty}^{\infty} e^{-i\frac{t}{\hbar}x}\frac{x+\Delta E_{ad}+i\Gamma_d/2}{x^2+(\Delta E_{ad}+i\Gamma/2)x-|V_{da}|^2-\Gamma_a\Gamma_d/4}dx \quad \textbf{[S79]}$$

where, again, $x = E - E_a$ and $\Gamma = \Gamma_d + \Gamma_a$. The poles of the integrand are

$$X_\pm = \frac{-\Delta E_{ad} - i\Gamma/2 \pm \sqrt{(\Delta E_{ad}+i\Gamma/2)^2 + 4|V_{ad}|^2 + \Gamma_a\Gamma_d}}{2} \quad \textbf{[S80]}$$

We rewrite the radicand of Eq. **80** in the form

$$(\Delta E_{ad}+i\Gamma/2)^2 + 4|V_{ad}|^2 + \Gamma_a\Gamma_d = \Delta E_{ad}^2 + 4|V_{ad}|^2 + \Gamma_a\Gamma_d - (\Gamma_d+\Gamma_a)^2/4 + i\Gamma\Delta E_{ad}$$
$$= \Delta E_{ad}^2 + 4|V_{ad}|^2 - (\Gamma_d-\Gamma_a)^2/4 + i\Gamma\Delta E_{ad} = \varsigma^2 e^{i\phi} \quad \textbf{[S81]}$$

where

$$\varsigma^2 = \sqrt{[\Delta E_v^2 - (\Gamma_d-\Gamma_a)^2/4]^2 + \Gamma^2\Delta E_{ad}^2} \quad \textbf{[S82a]}$$

$$\phi = \arctan\left[\frac{\Gamma\Delta E_{ad}}{\Delta E_{ad}^2 + 4|V_{ad}|^2 - (\Gamma_d - \Gamma_a)^2/4}\right] \quad \textbf{[S82b]}$$

A root of Eq. **S81** (the other root is disregarded using the same arguments as for Eq. **S25**) is

$$\sqrt{(\Delta E_{ad} + i\,\Gamma/2)^2 + 4|V_{ad}|^2 + \Gamma_a\Gamma_d} = \varsigma\, e^{i\phi/2} = \mu + i\,\upsilon \quad \textbf{[S83a]}$$

with

$$\mu = \sqrt{\frac{\varsigma^2 + \Delta E_v^2 - (\Gamma_d - \Gamma_a)^2/4}{2}}\,, \quad \textbf{[S83b]}$$

$$\upsilon = \mathrm{sgn}(\Delta E_{ad})\sqrt{\frac{\varsigma^2 - \Delta E_v^2 + (\Gamma_d - \Gamma_a)^2/4}{2}}\,. \quad \textbf{[S83c]}$$

Insertion of Eq. **S83** into Eq. **S80** gives

$$X_+ = \frac{-\Delta E_{ad} + \mu + i(\upsilon - \Gamma/2)}{2}, \qquad X_- = \frac{-\Delta E_{ad} - \mu - i(\upsilon + \Gamma/2)}{2}. \quad \textbf{[S84]}$$

It is $\mathrm{Im}(X_\pm) < 0$ for choice of the physical parameters, as

$$\begin{aligned}
&\frac{\Gamma}{2} \ge |\upsilon| \;\Leftrightarrow\; \frac{\Gamma^2}{2} \ge \varsigma^2 - \Delta E_{ad}^2 - 4|V_{ad}|^2 + \frac{(\Gamma_d - \Gamma_a)^2}{4} \\
&\Leftrightarrow\; \Delta E_{ad}^2 + 4|V_{ad}|^2 + \frac{2(\Gamma_d + \Gamma_a)^2 - (\Gamma_d - \Gamma_a)^2}{4} = \Delta E_{ad}^2 + 4|V_{ad}|^2 + \Gamma_d\Gamma_a + \frac{\Gamma^2}{4} \ge \varsigma^2 \\
&\Leftrightarrow\; \left(\Delta E_{ad}^2 + 4|V_{ad}|^2 + \Gamma_d\Gamma_a + \frac{\Gamma^2}{4}\right)^2 \ge \left[\Delta E_{ad}^2 + 4|V_{ad}|^2 + \Gamma_d\Gamma_a - \frac{\Gamma^2}{4}\right]^2 + \Gamma^2\Delta E_{ad}^2 \\
&\Leftrightarrow\; \Gamma^2\left(\Delta E_{ad}^2 + 4|V_{ad}|^2 + \Gamma_d\Gamma_a\right) \ge \Gamma^2\Delta E_{ad}^2 \;\Leftrightarrow\; 4|V_{ad}|^2 + \Gamma_d\Gamma_a \ge 0
\end{aligned} \quad \textbf{[S85]}$$

At this point, we recast Eq. **S79** in the form

$$\begin{aligned}
C_a(t) &= -\frac{e^{-iE_a t/\hbar}}{2\pi i}\int_{-\infty}^{\infty} e^{-i\frac{t}{\hbar}x}\,\frac{x + \Delta E_{ad} + i\Gamma_d/2}{(x - X_+)(x - X_-)}\,dx \\
&= -\frac{e^{-iE_a t/\hbar}}{2\pi i}\left[\int_{-\infty}^{\infty}\frac{x\,e^{-i\frac{t}{\hbar}x}}{(x - X_+)(x - X_-)}\,dx + \left(\Delta E_{ad} + i\frac{\Gamma_d}{2}\right)\int_{-\infty}^{\infty}\frac{e^{-i\frac{t}{\hbar}x}}{(x - X_+)(x - X_-)}\,dx\right] \\
&\equiv I_1(t) + \left(\Delta E_{ad} + i\frac{\Gamma_d}{2}\right) I_2(t)
\end{aligned} \quad \textbf{[S86]}$$

where the integrals $I_1(t)$ and $I_2(t)$ are clearly identified from Eq. **S86**. $I_1(t)$ is written as

$$\begin{aligned} I_1(t) &= \frac{e^{-iE_a t/\hbar}}{X_+ - X_-}\left(X_+ e^{-iX_+ t/\hbar} - X_- e^{-iX_- t/\hbar}\right) \\ &= \frac{1}{2}\exp\left(-i\frac{E_a + E_d - \mu}{2\hbar}t\right)\exp\left(-\frac{\upsilon + \Gamma/2}{2\hbar}t\right) \\ &\times\left[1 + \frac{\Delta E_{ad} + i\Gamma/2}{\mu + i\upsilon} + \exp\left(\frac{\upsilon - i\mu}{\hbar}t\right)\left(1 - \frac{\Delta E_{ad} + i\Gamma/2}{\mu + i\upsilon}\right)\right] \end{aligned} \qquad \textbf{[S87]}$$

(see the similar procedure to go from **[S24]** to **[S31]**). Defining

$$\kappa = \frac{\sqrt{\Delta E_{ad}^2 + \Gamma^2/4}}{\varsigma} \qquad \textbf{[S88a]}$$

$$\varphi = \arctan\frac{-\upsilon\Delta E_{ad} + \mu\Gamma/2}{\mu\Delta E_{ad} + \upsilon\Gamma/2} \qquad \textbf{[S88b]}$$

we can write

$$\frac{\Delta E_{ad} + i\Gamma/2}{\mu + i\upsilon} = \kappa e^{i\varphi} \qquad \textbf{[S88c]}$$

hence

$$I_1(t) = \frac{1}{2}\exp\left(-i\frac{E_a + E_d - \mu}{2\hbar}t\right)\exp\left(-\frac{\overline{\Gamma}}{2\hbar}t\right)\left[1 + \kappa e^{i\varphi} + \exp\left(\frac{\upsilon - i\mu}{\hbar}t\right)\left(1 - \kappa e^{i\varphi}\right)\right] \qquad \textbf{[S89]}$$

with

$$\overline{\Gamma} = \upsilon + \frac{\Gamma}{2} = \mathrm{sgn}(\Delta E_{ad})\sqrt{\frac{\varsigma^2 - \Delta E_{ad}^2 - 4|V_{ad}|^2 + (\Gamma_d - \Gamma_a)^2/4}{2}} + \frac{\Gamma}{2}. \qquad \textbf{[S90]}$$

The other integral in Eq. **S86** is obtained along the same lines as Eq. **S42**:

$$I_2(t) = \frac{1}{\varsigma^2}\exp\left(-i\frac{E_a + E_d - \mu}{2\hbar}t\right)\exp\left(-\frac{\overline{\Gamma}}{2\hbar}t\right)(\mu - i\upsilon)\left[\exp\left(\frac{\upsilon - i\mu}{\hbar}t\right) - 1\right]. \qquad \textbf{[S91]}$$

Eqs. **S88**-**91** lead to

$$
\begin{aligned}
&2\varsigma^2 \exp\left(\frac{\bar{\Gamma}}{\hbar}t\right)\mathrm{Re}\left[I_1(t)\left(\Delta E_{ad} - i\frac{\Gamma_d}{2}\right)\bar{I}_2(t)\right] \\
&= \mathrm{Re}\left\{[1+\kappa e^{i\varphi} + (1-\kappa e^{i\varphi})e^{\frac{\upsilon}{\hbar}t}e^{-i\frac{\mu}{\hbar}t}]\left(\Delta E_{ad} - i\frac{\Gamma_d}{2}\right)(\mu + i\upsilon)(e^{\frac{\upsilon}{\hbar}t}e^{i\frac{\mu}{\hbar}t} - 1)\right\} \\
&= \mathrm{Re}\left\{\left[\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2} + i\left(\upsilon\Delta E_{ad} - \mu\frac{\Gamma_d}{2}\right)\right]\right. \\
&\left.\times[e^{2\frac{\upsilon}{\hbar}t} - 1 - \kappa e^{i\varphi}e^{2\frac{\upsilon}{\hbar}t} - \kappa e^{i\varphi} + (e^{i\frac{\mu}{\hbar}t} - e^{-i\frac{\mu}{\hbar}t})e^{\frac{\upsilon}{\hbar}t} + \kappa e^{i\varphi}(e^{i\frac{\mu}{\hbar}t} + e^{-i\frac{\mu}{\hbar}t})e^{\frac{\upsilon}{\hbar}t}]\right\} \\
&= 2e^{\frac{\upsilon}{\hbar}t}\mathrm{Re}\left\{\left[\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2} + i\left(\upsilon\Delta E_{ad} - \mu\frac{\Gamma_d}{2}\right)\right]\right. \\
&\left.\times\left[\frac{e^{\frac{\upsilon}{\hbar}t} - e^{-\frac{\upsilon}{\hbar}t}}{2} + \frac{e^{i\frac{\mu}{\hbar}t} - e^{-i\frac{\mu}{\hbar}t}}{2} + \kappa(\cos\varphi + i\sin\varphi)\left(\frac{e^{i\frac{\mu}{\hbar}t} + e^{-i\frac{\mu}{\hbar}t}}{2} - \frac{e^{\frac{\upsilon}{\hbar}t} + e^{-\frac{\upsilon}{\hbar}t}}{2}\right)\right]\right\} \\
&= 2\mathrm{Re}\left\{\left[\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2} + i\left(\upsilon\Delta E_{ad} - \mu\frac{\Gamma_d}{2}\right)\right]\left[\sinh\left(\frac{\upsilon}{\hbar}t\right) + \kappa\cos\varphi\cos\left(\frac{\mu}{\hbar}t\right) - \kappa\cos\varphi\cosh\left(\frac{\upsilon}{\hbar}t\right)\right.\right. \\
&\left.\left.+ i\sin\left(\frac{\mu}{\hbar}t\right) + i\kappa\sin\varphi\cos\left(\frac{\mu}{\hbar}t\right) - i\kappa\sin\varphi\cosh\left(\frac{\upsilon}{\hbar}t\right)\right]\right\}e^{\frac{\upsilon}{\hbar}t} \\
&= 2e^{\frac{\upsilon}{\hbar}t}\left\{\left(\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2}\right)\left[\sinh\left(\frac{\upsilon}{\hbar}t\right) + \kappa\cos\varphi\cos\left(\frac{\mu}{\hbar}t\right) - \kappa\cos\varphi\cosh\left(\frac{\upsilon}{\hbar}t\right)\right]\right. \\
&\left.-\left(\upsilon\Delta E_{ad} - \mu\frac{\Gamma_d}{2}\right)\left[\sin\left(\frac{\mu}{\hbar}t\right) + \kappa\sin\varphi\cos\left(\frac{\mu}{\hbar}t\right) - \kappa\sin\varphi\cosh\left(\frac{\upsilon}{\hbar}t\right)\right]\right\} \\
&= 2e^{\frac{\upsilon}{\hbar}t}\left\{\left(\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2}\right)\sinh\left(\frac{\upsilon}{\hbar}t\right) + \left(\mu\frac{\Gamma_d}{2} - \upsilon\Delta E_{ad}\right)\sin\left(\frac{\mu}{\hbar}t\right)\right. \\
&\left.+ \kappa\left[\cos\varphi\left(\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2}\right) + \sin\varphi\left(\mu\frac{\Gamma_d}{2} - \upsilon\Delta E_{ad}\right)\right]\left[\cos\left(\frac{\mu}{\hbar}t\right) - \cosh\left(\frac{\upsilon}{\hbar}t\right)\right]\right\}
\end{aligned}
\quad \textbf{[S92]}
$$

$$
\kappa\cos\varphi = (\mu\Delta E_{ad} + \upsilon\Gamma/2)/\varsigma^2, \qquad \kappa\sin\varphi = (-\upsilon\Delta E_{ad} + \mu\Gamma/2)/\varsigma^2 \quad \textbf{[S93]}
$$

$$
\begin{aligned}
&\kappa\left[\cos\varphi\left(\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2}\right) + \sin\varphi\left(\mu\frac{\Gamma_d}{2} - \upsilon\Delta E_{ad}\right)\right] \\
&= \frac{1}{\varsigma^2}\left[\left(\mu\Delta E_{ad} + \upsilon\frac{\Gamma}{2}\right)\left(\mu\Delta E_{ad} + \upsilon\frac{\Gamma_d}{2}\right) + \left(\mu\frac{\Gamma}{2} - \upsilon\Delta E_{ad}\right)\left(\mu\frac{\Gamma_d}{2} - \upsilon\Delta E_{ad}\right)\right] \\
&= \frac{1}{\varsigma^2}\left[\mu^2\Delta E_{ad}^2 + \upsilon^2\frac{\Gamma_d\Gamma}{4} + \mu\upsilon\Delta E_{ad}\frac{\Gamma + \Gamma_d}{2} + \mu^2\frac{\Gamma_d\Gamma}{4} + \upsilon^2\Delta E_{ad}^2 - \mu\upsilon\Delta E_{ad}\frac{\Gamma + \Gamma_d}{2}\right] \\
&= \Delta E_{ad}^2 + \frac{\Gamma_d\Gamma}{4}.
\end{aligned}
\quad \textbf{[S94]}
$$

By use of Eqs. **S90** and **S94**, we recast Eq. **S92** in the form

$$
\begin{aligned}
&2\,\mathrm{Re}\left[I_1(t)\left(\Delta E_{ad}-i\frac{\Gamma_d}{2}\right)\bar{I}_2(t)\right]=2\frac{e^{-\frac{\Gamma}{2\hbar}t}}{\varsigma^2}\left\{\left(\mu\,\Delta E_{ad}+\upsilon\frac{\Gamma_d}{2}\right)\sinh\left(\frac{\upsilon}{\hbar}t\right)\right.\\
&\left.+\left(\mu\frac{\Gamma_d}{2}-\upsilon\,\Delta E_{ad}\right)\sin\left(\frac{\mu}{\hbar}t\right)+\left(\Delta E_{ad}^2+\frac{\Gamma_d\Gamma}{4}\right)\left[\cos\left(\frac{\mu}{\hbar}t\right)-\cosh\left(\frac{\upsilon}{\hbar}t\right)\right]\right\}
\end{aligned}
\qquad \textbf{[S95]}
$$

Moreover,

$$
\begin{aligned}
&\left|I_1(t)\right|^2\\
&=e^{-\frac{\bar{\Gamma}}{\hbar}t}\left\{\frac{1+\kappa^2+2\kappa\cos\varphi}{4}+\left[\frac{1-\kappa^2}{2}\cos\left(\frac{\mu}{\hbar}t\right)-\kappa\sin\varphi\sin\left(\frac{\mu}{\hbar}t\right)\right]e^{\frac{\upsilon}{\hbar}t}+\frac{1+\kappa^2-2\kappa\cos\varphi}{4}e^{2\frac{\upsilon}{\hbar}t}\right\}\\
&=e^{-\frac{\Gamma}{2\hbar}t}\left\{\frac{1+\kappa^2+2\kappa\cos\varphi}{4}e^{-\frac{\upsilon}{\hbar}t}+\frac{1-\kappa^2}{2}\cos\left(\frac{\mu}{\hbar}t\right)-\kappa\sin\varphi\sin\left(\frac{\mu}{\hbar}t\right)+\frac{1+\kappa^2-2\kappa\cos\varphi}{4}e^{\frac{\upsilon}{\hbar}t}\right\}
\end{aligned}
\qquad \textbf{[S96]}
$$

and

$$
\left|I_2(t)\right|^2=4\frac{e^{-\frac{\Gamma}{2\hbar}t}}{\varsigma^2}\left[\sin^2\left(\frac{\mu}{2\hbar}t\right)+\sinh^2\left(\frac{\upsilon}{2\hbar}t\right)\right] \qquad \textbf{[S97]}
$$

(cf. **[S35]** and **[S45]**). Thus, the squared modulus of $C_a(t)$ produces:

$$
\begin{aligned}
\mathcal{P}_a(t)=&\left\{\frac{1+\kappa^2+2\kappa\cos\varphi}{4}e^{-\frac{\upsilon}{\hbar}t}+\frac{1-\kappa^2}{2}\cos\left(\frac{\mu}{\hbar}t\right)-\kappa\sin\varphi\sin\left(\frac{\mu}{\hbar}t\right)+\frac{1+\kappa^2-2\kappa\cos\varphi}{4}e^{\frac{\upsilon}{\hbar}t}\right.\\
&+4\frac{\Delta E_{ad}^2+\Gamma_d^2/4}{\varsigma^2}\left[\sin^2\left(\frac{\mu}{2\hbar}t\right)+\sinh^2\left(\frac{\upsilon}{2\hbar}t\right)\right]+2\frac{\mu\,\Delta E_{ad}+\upsilon\Gamma_d/2}{\varsigma^2}\sinh\left(\frac{\upsilon}{\hbar}t\right)\\
&\left.+2\frac{-\upsilon\,\Delta E_{ad}+\mu\Gamma_d/2}{\varsigma^2}\sin\left(\frac{\mu}{\hbar}t\right)+2\frac{\Delta E_{ad}^2+\Gamma_d\Gamma/4}{\varsigma^2}\left[\cos\left(\frac{\mu}{\hbar}t\right)-\cosh\left(\frac{\upsilon}{\hbar}t\right)\right]\right\}e^{-\frac{\Gamma}{2\hbar}t}
\end{aligned}
\qquad \textbf{[S98]}
$$

Next consider $C_d(t)$. Inserting Eq. **S77** into Eq. **S47** and comparing with the expression of $I_2(t)$ (see Eqs. **S86** and **S91**), we obtain

$$
\begin{aligned}
C_d(t)&=-\frac{V_{da}}{2\pi i}\int_{-\infty}^{\infty}\frac{e^{-iEt/\hbar}}{\left(E-E_a+i\Gamma_a/2\right)\left(E-E_d+i\Gamma_d/2\right)-\left|V_{da}\right|^2}dE\\
&=\frac{V_{da}}{\varsigma^2}\exp\left(-i\frac{E_a+E_d-\mu}{2\hbar}t\right)\exp\left(-\frac{\bar{\Gamma}}{2\hbar}t\right)\left(\mu-i\upsilon\right)\left[\exp\left(\frac{\upsilon-i\mu}{\hbar}t\right)-1\right]
\end{aligned}
\qquad \textbf{[S99]}
$$

from which

$$\mathcal{P}_d(t) = \frac{4|V_{da}|^2}{\varsigma^2}\left[\sin^2\left(\frac{\mu}{2\hbar}t\right) + \sinh^2\left(\frac{\upsilon}{2\hbar}t\right)\right] e^{-\frac{\Gamma}{2\hbar}t}. \qquad \textbf{[S100]}$$

For the L manifold of states, Eqs. **S48** and **S78** give

$$\begin{aligned} C_l(t) &= -\frac{V_{ld}V_{da}}{2\pi i}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty}\frac{1}{E - E_l + i\varepsilon}\,\frac{e^{-iEt/\hbar}}{(E - E_a + i\Gamma_a/2)(E - E_d + i\Gamma_d/2) - |V_{da}|^2}dE \\ &= -\frac{V_{ld}V_{da}\,e^{-iE_a t/\hbar}}{2\pi i}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty}\frac{e^{-i\frac{t}{\hbar}x}}{(x + \Delta E_{al} + i\varepsilon)(x - X_+)(x - X_-)}dx \end{aligned} \qquad \textbf{[S101]}$$

with $\Delta E_{al} \equiv E_a - E_l$. Using the partial-fraction decomposition technique and the residue theorem:

$$\begin{aligned} C_l(t) &= \frac{V_{ld}V_{da}\,e^{-iE_a t/\hbar}}{2\pi i}\lim_{\varepsilon\to 0^+}\frac{1}{(X_- - X_+)(X_- + \Delta E_{al} + i\varepsilon)(X_+ + \Delta E_{al} + i\varepsilon)} \\ &\times\int_{-\infty}^{\infty} e^{-i\frac{t}{\hbar}x}\left(\frac{X_+ - X_-}{x + \Delta E_{al} + i\varepsilon} + \frac{X_- + \Delta E_{al} + i\varepsilon}{x - X_+} - \frac{X_+ + \Delta E_{al} + i\varepsilon}{x - X_-}\right)dx \\ &= \frac{(X_+ - X_-)e^{i\Delta E_{al}t/\hbar} + (X_- + \Delta E_{al})e^{-iX_+t/\hbar} - (X_+ + \Delta E_{al})e^{-iX_-t/\hbar}}{(X_+ - X_-)(X_- + \Delta E_{al})(X_+ + \Delta E_{al})}V_{ld}V_{da}\,e^{-iE_a t/\hbar} \end{aligned} \qquad \textbf{[S102]}$$

where the limit $\varepsilon \to 0^+$ was taken after integrating. Only the first exponential in Eq. **S102** survives at sufficiently long times, because $\mathrm{Im}(X_\pm) < 0$. Thus,

$$C_l(t) = \frac{V_{ld}V_{da}}{(X_- + E_a - E_l)(X_+ + E_a - E_l)}\exp\left(-i\frac{E_l}{\hbar}t\right) \qquad (t >> \tau) \qquad \textbf{[S103]}$$

where

$$\tau = \frac{\hbar}{\Gamma/2 - |\upsilon|} \qquad \textbf{[S104]}$$

because $\mathrm{Im}(X_\pm) = -i(\Gamma/2 \mp \upsilon)$. Note that for $t >> \tau$ $|C_a|^2$ and $|C_d|^2$ are negligible. Eq. **S84** implies

$$\begin{aligned} X_- + E_a - E_l &= \frac{E_d + E_a - 2E_l - \mu - i(\upsilon + \Gamma/2)}{2} \\ &= \frac{E_d + E_a}{2} - E_l - i\frac{\Gamma}{4} - \frac{\mu + i\upsilon}{2} = \frac{E_d + E_a - \mu}{2} - E_l - i\frac{\upsilon + \Gamma/2}{2} \end{aligned} \qquad \textbf{[S105]}$$

from which

$$\left|X_{-}+\Delta E_{al}\right|^{2}=\left(\frac{E_d+E_a-\mu}{2}-E_l\right)^{2}+\frac{(\upsilon+\Gamma/2)^{2}}{4} \qquad \textbf{[S106]}$$

and

$$X_{+}+E_a-E_l=\frac{E_d+E_a}{2}-E_l-i\frac{\Gamma}{4}+\frac{\mu+i\upsilon}{2}=\frac{E_d+E_a+\mu}{2}-E_l+i\frac{\upsilon-\Gamma/2}{2} \qquad \textbf{[S107]}$$

from which

$$\left|X_{+}+\Delta E_{al}\right|^{2}=\left(\frac{E_d+E_a+\mu}{2}-E_l\right)^{2}+\frac{(\upsilon-\Gamma/2)^{2}}{4} \qquad \textbf{[S108]}$$

Substitution of Eqs. **S105** and **S107** into Eq. **S103** leads to

$$C_l(t)=\frac{V_{ld}V_{da}\,e^{-i\frac{E_l}{\hbar}t}}{\left[\frac{E_d+E_a-\mu-i(\upsilon+\Gamma/2)}{2}-E_l\right]\left[\frac{E_d+E_a+\mu+i(\upsilon-\Gamma/2)}{2}-E_l\right]} \quad (t>>\tau) \qquad \textbf{[S109]}$$

whence

$$\left|C_l(t)\right|^{2}=\frac{\left|V_{ld}\right|^{2}\left|V_{da}\right|^{2}}{\left[\left(\frac{E_d+E_a-\mu}{2}-E_l\right)^{2}+\frac{(\upsilon+\Gamma/2)^{2}}{4}\right]\left[\left(\frac{E_d+E_a+\mu}{2}-E_l\right)^{2}+\frac{(\upsilon-\Gamma/2)^{2}}{4}\right]} \quad (t>>\tau) \qquad \textbf{[S110]}$$

The probability $\mathcal{P}_L(t)$ that the system, starting from $\left|a\right\rangle$ for t = 0, is in any state of the L manifold for $t>>\tau$ is easily computed by using the continuum approximation, that is, writing $\mathcal{P}_L(t>>\tau)$ as

$$\begin{aligned}\mathcal{P}_L(t>>\tau)&=\int_{-\infty}^{\infty}\left|C_l(t)\right|^{2}\rho_L(E_l)dE_l\\&=\frac{\Gamma_d\left|V_{da}\right|^{2}}{2\pi}\int_{-\infty}^{\infty}\frac{dE_l}{(X_{-}+E_a-E_l)(\overline{X}_{-}+E_a-E_l)(X_{+}+E_a-E_l)(\overline{X}_{+}+E_a-E_l)}.\end{aligned} \qquad \textbf{[S111]}$$

Two poles of the integrand in Eq. **S111** fall within the lower half complex plane and two in the upper half complex plane. Clearly, the integrand vanishes over any arc with radius tending to infinity. We rewrite the integral as

$$\mathcal{P}_L(t>>\tau)=\frac{\Gamma_d|V_{da}|^2}{2\pi}\int_{-\infty}^{\infty}\frac{dE_l}{(X_-+E_a-E_l)(X_++E_a-E_l)}\frac{1}{(E_l-\overline{X}_--E_a)(E_l-\overline{X}_+-E_a)}$$
$$=\frac{\Gamma_d|V_{da}|^2}{2\pi(\overline{X}_--\overline{X}_+)}\int_{-\infty}^{\infty}\frac{dE_l}{(X_-+E_a-E_l)(X_++E_a-E_l)}\left(\frac{1}{E_l-\overline{X}_--E_a}-\frac{1}{E_l-\overline{X}_+-E_a}\right) \quad \textbf{[S112]}$$

and close the integration path through an anticlockwise contour in the upper half plane, so obtaining

$$\mathcal{P}_L(t>>\tau)=\frac{i\Gamma_d|V_{da}|^2}{\overline{X}_+-\overline{X}_-}\left[\frac{1}{(\overline{X}_+-X_-)(\overline{X}_+-X_+)}-\frac{1}{(X_--\overline{X}_-)(X_+-\overline{X}_-)}\right] \quad \textbf{[S113]}$$

Since $\overline{X}_+-\overline{X}_-=\mu-i\upsilon$, $\overline{X}_+-X_-=\mu+i\Gamma/2$, $\overline{X}_+-X_+=-i(\upsilon-\Gamma/2)$, $X_--\overline{X}_-=-i(\upsilon+\Gamma/2)$ and $X_+-\overline{X}_-=\mu-i\Gamma/2$, we finally obtain

$$\mathcal{P}_L(t>>\tau)=\frac{\Gamma_d|V_{da}|^2}{\mu-i\upsilon}\left[\frac{1}{(\upsilon+\Gamma/2)(\mu-i\Gamma/2)}-\frac{1}{(\upsilon-\Gamma/2)(\mu+i\Gamma/2)}\right]$$
$$=\frac{\Gamma_d|V_{da}|^2}{\mu-i\upsilon}\frac{(\upsilon-\Gamma/2)(\mu+i\Gamma/2)-(\upsilon+\Gamma/2)(\mu-i\Gamma/2)}{(\upsilon^2-\Gamma^2/4)(\mu^2+\Gamma^2/4)}$$
$$=\frac{\Gamma_d|V_{da}|^2}{\mu-i\upsilon}\frac{(\upsilon-\Gamma/2-\upsilon-\Gamma/2)\mu+i(\upsilon-\Gamma/2+\upsilon+\Gamma/2)\Gamma/2}{(\upsilon^2-\Gamma^2/4)(\mu^2+\Gamma^2/4)}$$
$$=\frac{\Gamma_d|V_{da}|^2}{\mu-i\upsilon}\frac{-\Gamma(\mu-i\upsilon)}{(\upsilon^2-\Gamma^2/4)(\mu^2+\Gamma^2/4)}=\frac{|V_{da}|^2\Gamma_d\Gamma}{(-\upsilon^2+\Gamma^2/4)(\mu^2+\Gamma^2/4)}$$
$$=\frac{4|V_{da}|^2\Gamma_d\Gamma}{(\Delta E_{ad}^2+4|V_{ad}|^2-\varsigma^2+\Gamma_d\Gamma_a+\Gamma^2/4)(\Delta E_{ad}^2+4|V_{ad}|^2+\varsigma^2+\Gamma_d\Gamma_a+\Gamma^2/4)}$$
$$=\frac{4|V_{da}|^2\Gamma_d\Gamma}{(\Delta E_{ad}^2+4|V_{ad}|^2+\Gamma_d\Gamma_a+\Gamma^2/4)^2-\varsigma^4}$$
$$=\frac{4|V_{da}|^2\Gamma_d\Gamma}{\left[\Delta E_{ad}^2+4|V_{ad}|^2-\frac{(\Gamma_d-\Gamma_a)^2}{4}+\frac{\Gamma^2}{2}\right]^2-\left[\Delta E_{ad}^2+4|V_{ad}|^2-\frac{(\Gamma_d-\Gamma_a)^2}{4}\right]^2-\Gamma^2\Delta E_{ad}^2}$$
$$=\frac{4|V_{da}|^2\Gamma_d\Gamma}{\frac{\Gamma^4}{4}+\left[4|V_{da}|^2-\frac{(\Gamma_d-\Gamma_a)^2}{4}\right]\Gamma^2}=\frac{4|V_{da}|^2\Gamma_d/\Gamma}{4|V_{da}|^2+\Gamma_d\Gamma_a}=\frac{\Gamma_d}{\Gamma}\frac{1}{1+\frac{\Gamma_d\Gamma_a}{4|V_{da}|^2}} \quad \textbf{[S114]}$$

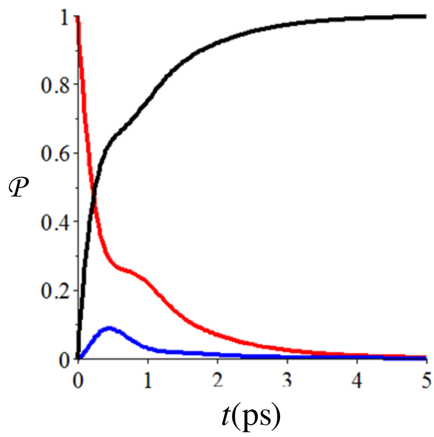


Fig. S13. $\mathcal{P}_a(t)=|C_a(t)|^2$ (Eq. **S93**, red line), $\mathcal{P}_d(t)=|C_d(t)|^2$ (Eq. **S95**, blue), and total population $1-[\mathcal{P}_a(t)+\mathcal{P}_d(t)]$ of the L and R manifolds (in black), for $\Delta E_{ad}/2=V_{ad}=\Gamma_d/2=\Gamma_a/2=10^{-3}\ \text{eV}$. With these model parameters, Eq. **S99** gives $\tau\approx 1\,\text{ps}$.

that is the first Eq. **17**. Then, since $|C_a|^2$ and $|C_d|^2$ are negligible for $t>>\tau$ (*e.g.*, see Fig. S13), the normalization condition yields

$$\mathcal{P}_R(t>>\tau)=1-\mathcal{P}_L(t>>\tau)=\frac{\Gamma_a}{\Gamma}\frac{1+\dfrac{\Gamma_d\Gamma}{4|V_{da}|^2}}{1+\dfrac{\Gamma_d\Gamma_a}{4|V_{da}|^2}}. \qquad \textbf{[S115]}$$

To obtain the long-time expression of C_r we compare Eq. **S76** with Eqs. **S77** and **S78**, consider that C_d is vanishingly small for $t>>\tau$, and exploit Eq. **S109**, thus obtaining

$$C_r(t>>\tau)=\frac{\left(E_r-E_d+i\dfrac{\Gamma_d}{2}\right)V_{ra}\,e^{-i\frac{E_r}{\hbar}t}}{\left[\dfrac{E_d+E_a-\mu-i(\upsilon+\Gamma/2)}{2}-E_r\right]\left[\dfrac{E_d+E_a+\mu+i(\upsilon-\Gamma/2)}{2}-E_r\right]} \qquad \textbf{[S116]}$$

from which

$$|C_r(t>>\tau)|^2=\frac{\left[(E_r-E_d)^2+\dfrac{\Gamma_d^2}{4}\right]|V_{ra}|^2}{\left[\left(\dfrac{E_d+E_a-\mu}{2}-E_r\right)^2+\dfrac{(\upsilon+\Gamma/2)^2}{4}\right]\left[\left(\dfrac{E_d+E_a+\mu}{2}-E_r\right)^2+\dfrac{(\upsilon-\Gamma/2)^2}{4}\right]}. \qquad \textbf{[S117]}$$

The total occupation of the R manifold can easily obtained from the normalization condition:

$$\mathcal{P}_R(t) = 1 - \mathcal{P}_a(t) - \mathcal{P}_d(t) - \mathcal{P}_L(t)\,. \qquad \textbf{[S118]}$$

With the initial condition in Eq. **6**, by considering the symmetry of the Hamiltonian with respect to $\{d,l\}$ and $\{a,r\}$, the occupation probability of the *L* manifold after the electronic relaxation is given by Eq. **18** and that of the *R* manifold is obtained from the normalization condition.

The above analysis describes the charge relaxation leading to the equilibrium charge distributions in Eq. **17** starting from non-equilibrium initial conditions. This relaxation may be used for a sensing mechanism similar to the ones described in the third section of the article. The sensing mechanism modeled in the fourth section of the article only uses the charge distributions achieved at the end of the electronic relaxation, given by Eq. **17** or **18** depending on the initial condition.

Note that in the model of the third section we consider only one manifold of (substrate) electronic states that is occupied with unit probability at sufficiently long times. Thus, if we apply the sensing mechanism of the fourth section to that model, $\varepsilon_1(t)$, hence the shape of the output signal, is strictly determined by the diffusion equation (Eq. **19**), irrespective of the V_{da} and Γ_d values (Fig. S14).

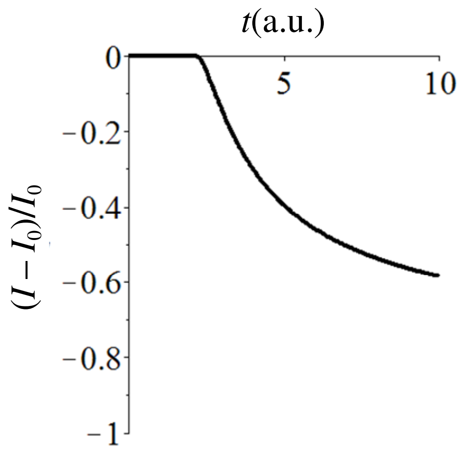


Fig. S14. Current signal, normalized to the current in the absence of analyte, using Eqs. **12**, **19**, and (with the same result) **10** or **20**, in combination with the system model of section 3. The parameters are the same as in Fig. 8.

S5. Solution of Eq. 21 using a simple ET model.

In Eq. **21**, the rate constant for ET from r to l is written using the Marcus theory (10) as

$$k_{rl} = \sqrt{\frac{\pi}{\lambda k_B T}} \frac{V^2}{\hbar} \exp\left[-\frac{(E_l - E_r + \lambda)^2}{4\lambda k_B T} \right] \quad \textbf{[S119]}$$

In Eq. **S119**, for simplicity, we assume that the coupling has the same value, $V_{lr} = V$, for all L and R states responsible for CT through the SAM over the $\tau_{\text{incoherent}}$ time scale defined in the article. In Eq. **S119** λ is the reorganization (free) energy associated with ET through the SAM. The expression for k_{lr} is obtained exchanging r and l.

To solve Eq. **21**, we need to find expressions for $\sum_r k_{lr}$ and $\sum_r k_{rl}$ To obtain the overall rate of ET from a given state in R to any state in L, we sum Eq. **S119** over $\{|l\rangle\}$. Simply summing the transition probabilities per unit time, we are neglecting the correlation between the occurrence probabilities of the different events, which are mutually exclusive. This is allowed by the small values of all k_{lr} and of the overall probability (per unit time) of ET. In addition, in evaluating the $r \to L$ rate constant, we approximate the L manifold as a continuum of states, thus reducing the sum to an integral:

$$\begin{aligned}\sum_l k_{rl} &= \int_{-\infty}^{\infty} dE_l\, \rho_L \sqrt{\frac{\pi}{\lambda k_B T}} \frac{V^2}{\hbar} \exp\left[-\frac{(E_l - E_r + \lambda)^2}{4\lambda k_B T} \right] \\ &= \frac{2\pi}{\hbar} V^2 \rho_L \frac{1}{2\sqrt{\pi \lambda k_B T}} \int_{-\infty}^{\infty} dE_l \exp\left[-\frac{(E_l - E_r + \lambda)^2}{4\lambda k_B T} \right] \\ &= \frac{\gamma_L}{2\sqrt{\pi \lambda k_B T}} \int_{-\infty}^{\infty} dE_l \exp\left[-\frac{(E_l - E_r + \lambda)^2}{4\lambda k_B T} \right] = \frac{\gamma_L}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-x^2/2} dx = \gamma_L\end{aligned} \quad \textbf{[S120a]}$$

where the coupling strength constant γ_L is expressed according to the golden rule as

$$\gamma_L = \frac{2\pi}{\hbar} V^2 \rho_L \quad \textbf{[S120b]}$$

and gives the order of magnitude of the inverse relaxation time to equilibrium. The quantity $\sum_r k_{lr}$

is similarly obtained and is needed, together with Eq. **S120**, to solve the dynamical problem of Eq. **21**. Once the equilibrium is achieved for $t > 1/\gamma_L$, the L and R populations are easily obtained by using the detailed balance principle, which implies that

$$\frac{\left|C_r\right|_{\text{eq}}^2}{\left|C_l\right|_{\text{eq}}^2} = \frac{k_{lr}}{k_{rl}} = \exp\left(-\frac{E_r - E_l}{k_B T}\right) \quad \forall\, l \in \{l\},\, r \in \{r\}. \qquad \textbf{[S121]}$$

Writing Eq. **S121** for two states in *L* or *R*, one obtains Boltzmann relations for the states inside each manifold. Eq. **S121** shows that for $t \sim 1/\gamma_L \sim \tau_{\text{incoherent}} >> \tau$ the quantum information (coherently) built into the system state coefficients is lost. Using Eq. **S121** one obtains

$$\mathsf{P}_R\left(t >> \tau_{\text{incoherent}}\right) \equiv \sum_r \left|C_r\right|_{\text{eq}}^2 = \left|C_l\right|_{\text{eq}}^2 \exp\left(\frac{E_l}{k_B T}\right) \sum_r \exp\left(-\frac{E_r}{k_B T}\right) \qquad \textbf{[S122]}$$

from which

$$\left|C_l\right|_{\text{eq}}^2 = \frac{\mathsf{P}_R\left(t >> \tau_{\text{incoherent}}\right) \exp\left(-\frac{E_l}{k_B T}\right)}{\sum_r \exp\left(-\frac{E_r}{k_B T}\right)}. \qquad \textbf{[S123]}$$

Summing both sides of Eq. **S123** over $\{l\}$, rearranging, and using the continuum approximation for the two manifolds of states, we find

$$\frac{\mathsf{P}_L\left(t >> \tau_{\text{incoherent}}\right)}{\mathsf{P}_R\left(t >> \tau_{\text{incoherent}}\right)} = \frac{\sum_l \exp\left(-\frac{E_l}{k_B T}\right)}{\sum_r \exp\left(-\frac{E_r}{k_B T}\right)} = \frac{\int_{-\infty}^{\infty} dE_l\, \rho_L \exp\left(-\frac{E_l}{k_B T}\right)}{\int_{-\infty}^{\infty} dE_R\, \rho_R \exp\left(-\frac{E_r}{k_B T}\right)} = \frac{\rho_L}{\rho_R} \qquad \textbf{[S124]}$$

Note that the last equality in Eq. **S124** results from the assumption that the densities of states in the two state manifolds are independent of the state energy, but the penultimate equality is also valid by dropping this assumption. For example, assume that *L* is uniformly distributed with density of states ρ_0 over the energy range $[E_1; E_2]$ and zero elsewhere, and that the *R* density of states is similarly spread over the interval $[E_1 + \Delta E; E_2 + \Delta E]$. In this manner, the model does not use the wide band approximation; yet, width and location of the two energy ranges with respect to the *a* and *d* on-site energies may allow this approximation, as used in the previous sections. With such ρ_L and ρ_R, it is

$$\int_{-\infty}^{\infty} dE_l\, \rho_L(E_l)\exp\left(-\frac{E_l}{k_BT}\right) = \rho_0 \int_{E_1}^{E_2} dE \exp\left(-\frac{E}{k_BT}\right) = k_BT\rho_0\left[\exp\left(-\frac{E_1}{k_BT}\right) - \exp\left(-\frac{E_2}{k_BT}\right)\right]$$

$$= 2k_BT\rho_0 \exp\left(-\frac{E_1+E_2}{2k_BT}\right)\sinh\left(\frac{E_2-E_1}{2k_BT}\right) \qquad \textbf{[S125]}$$

$$\int_{-\infty}^{\infty} dE_r\, \rho_R(E_r)\exp\left(-\frac{E_r}{k_BT}\right) = 2k_BT\rho_0 \exp\left(-\frac{E_1+E_2+2\Delta E}{2k_BT}\right)\sinh\left(\frac{E_2-E_1}{2k_BT}\right). \qquad \textbf{[S126]}$$

Then, Eq. **S124** becomes

$$\frac{\mathsf{P}_L(t >> \tau_{\text{incoherent}})}{\mathsf{P}_R(t >> \tau_{\text{incoherent}})} = \exp\left(\frac{\Delta E}{k_BT}\right) \qquad \textbf{[S127]}$$

and use of the normalization condition leads to

$$\mathsf{P}_L(t >> \tau_{\text{incoherent}}) = \frac{1}{1+\exp\left(-\frac{\Delta E}{k_BT}\right)}, \qquad \mathsf{P}_R(t >> \tau_{\text{incoherent}}) = \frac{\exp\left(-\frac{\Delta E}{k_BT}\right)}{1+\exp\left(-\frac{\Delta E}{k_BT}\right)} \qquad \textbf{[S128]}$$

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4. This terminology is more appropriate for interpretations of the model where no net charge is injected in the system by analyte binding, as discussed after eq 6.
5. Note that P_d and P_a substantially decay in the same time scale, which is given by the first τ_d and τ_a expressions in the insets of Fig. 3. However, physical conditions produced by the sensed event, such as a large increase in ΔE_{ad}, can lead to the small-amplitude tail of P_a that survives at longer times.
6. Capital letters are used to distinguish these coefficients from those describing the evolution of the system state under the initial condition of Eq. **6**.

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