

Supporting Information

Towards the Rational Design of N-(1,3-dimethylbutyl)-N'-phenyl-1,4-benzenediamine (6PPD) Electrochemical Sensor

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1 Long-term stability test

Desorption kinetics were measured by first saturating a glassy carbon electrode with 6PPD and then, immersing the electrode in a solution of 100 mM phosphate buffer pH 6.9 that does not contain 6PPD. A cyclic voltammogram was recorded at regular time interval for 1 hour. The charge determined from integration of the anodic peak is plotted as a function of time in **Figure** . The red line is a least square regression of the equation:

$$Q = Q_{t=0} - \Delta Q e^{-k_{des}t} \quad \text{Eq S0}$$

where $Q_{t=0}$, ΔQ and k_{des} are the initial charge, the maximum charge lost during the desorption and the desorption rate constant, respectively. The satisfactory adjustment ($R^2 = 0.972$) is obtained with the following parameters $Q_{t=0} = 20.5 \pm 0.5$ nC, $\Delta Q = 9.6 \pm 0.7$ nC and $k_{des} = 0.09 \pm 0.02$ min⁻¹. The desorption kinetics were measured in a range of concentration that should lead to a monolayer formation (i.e. follow a Langmuir isotherm once equilibrium is reached). The ratio k_{ads}/k_{des} is expected to be equal to K_{ads} . From the values of the fitted kinetic parameters, we calculate a K_{ads} of 0.4×10^6 M, close from the value of $1.2 \mu\text{M}^{-1}$ determined previously. The difference may come from uncertainties on the kinetics parameters and contribution of the multilayers to the overall adjustment of the Langmuir portion of the isotherm.

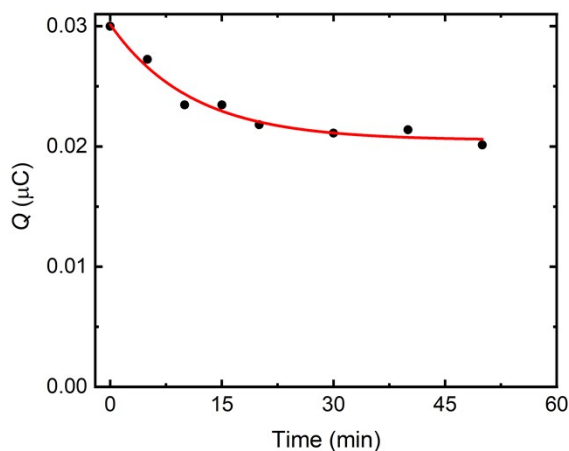


Figure S0. Anodic charge integrated from cyclic voltammograms recorded with a glassy carbon electrode initially immersed 2h in $0.3 \mu\text{M}$ 6PPD solution and then immersed in 100 mM phosphate buffer pH 6.9 while scanning at 0.100 V/s at regular time intervals. The red line is the adjustment of the Eq S0 with the following parameters $Q_{t=0} = 20.5 \pm 0.5$ nC, $\Delta Q = 9.6 \pm 0.7$ nC and $k_{des} = 0.09 \pm 0.02$ min⁻¹. A cyclic voltammogram was measured directly in the PB at regular time interval. The red line is a least square fit of Eq 5 on the experimental points with the parameters $Q_{t=0} = \mu\text{C}$, $1/k_{des} = 11 \pm 2$ min and $R^2 = 0.973$. All measurements were performed at room temperature ($T = 22$ °C) in the dark

2 Numerical Simulation of Cyclic Voltammetry

The numerical simulations were performed on a workstation equipped with an AMD Ryzen Thread ripper PRO 5975WX – 32 core 3.6 GHz GPU and 64 GB RAM. The workstation is running on Microsoft Windows 11 Pro 64-bit. Numerical simulations were performed using the Finite Element Modeling software COMSOL Multiphysics 6.2 with the modules “Transport of Diluted Species” and “Surface Reactions”. All simulation were performed in 1D. The first module allows to solve the diffusion equation (2nd Fick’s law):

$$\frac{d[6PPD]}{dt} = D \frac{d^2[6PPD]}{dx^2} \quad \text{Eq S1}$$

where [6PPD] is the concentration of 6PPD at a position “ x ” and time “ t ”. D is the diffusion coefficient of 6PPD. The second module allows simulation of adsorbed species by solving the equation:

$$\frac{d\Gamma}{dt} = R \quad \text{Eq S2}$$

where Γ is the surface concentration of 6PPD on the electrode and R is the rate of change of surface concentration. The boundary for the “bulk” solution is a concentration boundary set at the same value as the initial concentration of 6PPD.

2.1 Adsorbed species

For the simulation of cyclic voltammetry of surface adsorbed species only (that is no 6PPD in solution) the initial conditions were set as $\Gamma_{t=0} = 10 \text{ pmol.cm}^{-2}$ and $[6PPD] = 0 \text{ mol.L}^{-1} \forall x$. The rate of oxidation of 6PPD is defined using a Butler-Volmer kinetics:

$$R = k^0 \left\{ \Gamma e^{\frac{(1-\alpha)nF}{RT}(E_{WE} - E^0)} - (\Gamma_{t=0} - \Gamma) e^{-\frac{\alpha nF}{RT}(E_{WE} - E^0)} \right\} \quad \text{Eq S3}$$

where k^0 , α , n , F , R , T , E_{WE} and E^0 are the standard rate constant of electron transfer, the symmetry coefficient, the number of electrons exchanged, the Faraday’s constant, the gas constant, the temperature, the potential applied at the working electrode and the standard potential, respectively. A parametric sweep across the scan rate was used to compute the cyclic voltammograms from 0.01 V.s^{-1} up to 1 V.s^{-1} with increments of 0.01 V.s^{-1} . The procedure was repeated with various values of k^0 until we could reproduce the experimental peak splitting. The value of α is set at 0.5. **Figure S1** shows the simulated cyclic voltammograms used to plot the continuous lines in Figure 1D.

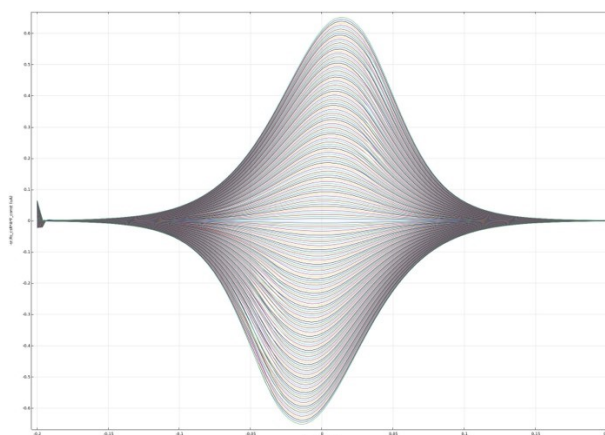


Figure S1. Cyclic voltammograms simulated for 10 pmol.cm^{-2} of 6PPD adsorbed onto a 0.0707 cm^2 electrode and scan rates comprised between 0.01 and 1 V.s^{-1} with increments of 0.01 V.s^{-1} . The standard rate constant for electron transfer and transfer coefficient are 50 s^{-1} and 0.5 , respectively.

2.2 Diffusing & adsorbed species

For the simulation of cyclic voltammetry of both surface adsorbed species and 6PPD in solution, the initial conditions were set as $\Gamma_{t=0} = 1 - 10 \text{ pmol.cm}^{-2}$ and $[6PPD] = 10^{-7} \text{ mol.L}^{-1} \forall x$. The rate of oxidation of adsorbed 6PPD is defined using Eq. S3 with $k^0 = 50 \text{ s}^{-1}$ and $\alpha = 0.5$. In the "Transport of Diluted Species" we used a concentration boundary to simulate the diffusional current and the Nernst equation:

$$[6PPD]_{ox} = \frac{C^0}{1 + e^{\frac{nF}{RT}(E_{WE} - E^0)}} \quad \text{Eq. S4}$$

where $[6PPD]_{ox}$ is the concentration of the oxidized form of 6PPD at the surface of the electrode. The value of the diffusion coefficient of 6PPD was assumed to be close from an analogue molecule n,n'-diphenyl-p-phenylenediamine, $D = 5.24 \times 10^{-6} \text{ cm.s}^{-2}$.^{1,2} In this numerical model the molecules of 6PPD in solution and adsorbed on the surface are treated independently, that is there is no redox reaction between those two. This assumption is reasonable for low coverage of as the case in the experimental kinetics of adsorption (about 10 % of a monolayer).

The **Figure S2A** shows the cyclic voltammograms originating from the adsorbed 6PPD (red trace) and 6PPD in diffusion (black trace) for 10 pmol.cm^{-2} (surface concentration at the final time of the adsorption kinetics). The scan rate is $\nu = 0.1 \text{ V.s}^{-1}$. **Figure S2A** evidences the relatively low magnitude of the diffusional current versus the current coming from adsorbed species. Using these simulations, we estimated the upper bound of the contribution of diffusional current to the total current (used when determining the anodic charge). To do so we made a simulation for the lowest amount of adsorbed 6PPD (when the diffusional contribution is maximum) versus the current from adsorbed species. The simulated anodic current from adsorbed species and species in diffusion are plotted on **Figure S2B** in black and red, respectively. The combination of those two currents leads to the total current (continuous blue line). Then, we analyzed the simulated voltammograms following the procedure used for experimental data. As shown in **Figure S2B** we plot the anodic peak of the total current (continuous blue line) and create a baseline that is subtracted before integration of the area under the peak. When comparing the area integrated under the baseline-subtracted blue curve and the black curve (only adsorbed species) we obtained an area 4% higher for the blue curve than the black curve. We conclude that our experimental protocol and procedure of analysis leads to an overestimation of the total amount of 6PPD adsorbed on the surface by at most 4%.

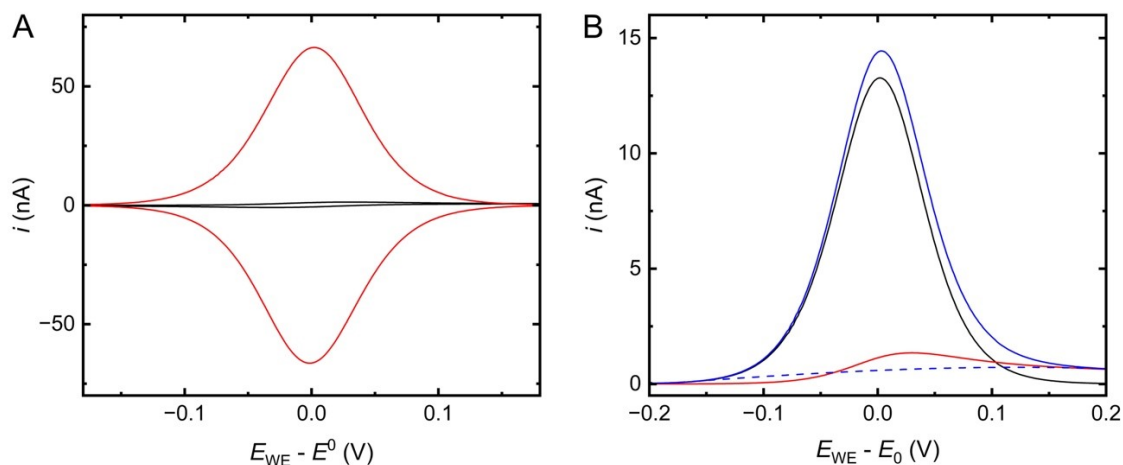


Figure S2. (A) The red and black lines correspond to the contribution of 6PPD adsorbed onto the electrode and diffusing to the electrode, respectively. $\nu = 0.1 \text{ V/s}$, $\Gamma_{t=0} = 10 \text{ pmol.cm}^{-2}$. (B) The black and red lines correspond to the contribution of 6PPD adsorbed onto the electrode and diffusing to the electrode, respectively. The continuous blue line is the summation of the red and black lines. The dashed blue line is a baseline subtracted from the continuous blue line before integration of the peak.

$\Gamma_{t=0} = 1 \text{ pmol.cm}^{-2}$. For both (A) and (B) [6PPD] = 0.1 μM . The concentration of 6PPD on the surface is lowered in (B) to reflect conditions where the diffusional current is highest versus current of adsorbed species.

3 Numerical simulation of mixed reaction-diffusion adsorption kinetics

The kinetics of adsorption is modeled with the Langmuir-Hinshelwood equation:

$$\frac{d\Gamma(t)}{dt} = k_{ads}c(0,t)\{\Gamma_{max} - \Gamma(t)\} - k_{des}\Gamma(t) \quad \text{Eq. S5}$$

where $\Gamma(t)$, k_{ads} , $c(0,t)$, Γ_{max} and k_{des} are the surface concentration, the adsorption rate constant, the concentration at the surface of the electrode, the maximum surface concentration and the desorption rate constant, respectively. To ensure conservation of matter the rate of change of surface concentration obeys first Fick's law:

$$\frac{d}{dt}\Gamma(t) = D \left. \frac{dc(x,t)}{dx} \right|_{x=0} \quad \text{Eq. S6}$$

where D is the diffusion coefficient. The transport of species in solution is governed by diffusion. Diffusion is described by the second Fick law (Eq. S1). The solution of this problem is given by the Ward-Tordai equation. Seki and coworkers proposed an elegant form of the problem by plugging the Ward-Tordai equation in the Eq. S5 and using dimensionless parameters:³

$$\frac{d\theta(\tau)}{d\tau} = \left\{ \kappa_{ads} - \frac{d}{d\tau} \int_0^\tau \frac{\theta(\tau_1)}{\sqrt{\pi(\tau - \tau_1)}} d\tau_1 \right\} \{1 - \theta(\tau)\} - \kappa_{des}\theta(\tau) \quad \text{Eq. S7}$$

The dimensionless parameters are defined in Table S1 below:

Table S1. Dimensionless parameters used in the adsorption kinetics equation

Dimensionless Parameter	bounds
$\tau = \frac{t}{D}(k_{ads}\Gamma_{max})^2$	0 to infinity
$\theta(\tau) = \frac{\Gamma(t)}{\Gamma_{max}}$	0 (no adsorption) to 1 (saturated monolayer)
$\kappa_{ads} = \frac{DC_0}{k_{ads}\Gamma_{max}^2}$	$\kappa_{ads} \gg 1$ reaction limited $\kappa_{ads} \ll 1$ diffusion limited
$\kappa_{des} = \frac{Dk_{des}}{(k_{ads}\Gamma_{max})^2}$	$\kappa_{des} \gg 1$ diffusion limited $\kappa_{des} \ll 1$ reaction limited

Seki and coworkers compute the integro-differential part of Eq. S3 (term in the large parenthesis) using the Grunwald-Letnikov formula:

$$\frac{d}{d\tau} \int_0^\tau \frac{\theta(\tau_1)}{\sqrt{\pi(\tau - \tau_1)}} d\tau_1 = \frac{1}{\sqrt{h}} \sum_{n=0}^{\tau/h} \omega_j \theta(\tau - nh) \quad \text{Eq. S8}$$

where τ/h corresponds to the number of steps of duration "h" used to discretize time and ω_j is given by

$$\omega_0 = 1 \text{ and } \omega_n = \left(1 - \frac{3}{2n}\right) \omega_{n-1} \quad \text{Eq. S9}$$

The Eq S3 was numerically integrated using a forward Euler method implemented on MATLAB R2023b:

$$\theta(\{n + 1\}h) = \theta(nh) + h \times \frac{d\theta(nh)}{d\tau} \quad \text{Eq. S10}$$

Our code was tested against the curves provided by Seki and coworkers. With our set of parameters, a stable numerical solution was obtained with a value of $h = 0.001$ of the total dimensionless time. Numerical solutions were computed for various values of k_{ads} until a satisfactory adjustment was obtained. The quality of the adjustment was estimated by computing the R^2 defined as

$$R^2 = \frac{\sum (\theta_{sim} - \theta_{exp})^2}{\sum \theta_{sim} - \bar{\theta}_{exp}} \quad \text{Eq. S11}$$

where θ_{sim} , θ_{exp} and $\bar{\theta}_{exp}$ are the simulated values, experimental values and the average of the experimental values, respectively. The summation in **Eq. 11** is performed over the entire set of experimental points. The value of k_{ads} was adjusted until the third significant digit of R^2 could not be maximized. The value of k_{des} is fixed using the adsorption constant obtained from the independent measurement of the adsorption isotherm and the relation $K_{ads} = k_{ads}/k_{des}$. The value of the diffusion coefficient of 6PPD was assumed to be close from an analogue molecule n,n'-diphenyl-p-phenylenediamine.^{1,2} The value of the different parameters of the simulation are gathered in **Table S2**.

Table S2. Parameters used for the numerical simulation of the adsorption kinetics.

Parameter/variable name	Symbol	Value
diffusion coefficient	D	$5.24 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
bulk concentration	C_0	$1 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-3}$
adsorption rate constant	k_{ads}	$8.5 \times 10^5 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
desorption rate constant	$k_{des} = k_{ads}/K_{ads}$	$k_a/K_a = 7.08 \times 10^{-4} \text{ s}^{-1}$
adsorption equilibrium constant	K_{ads}	$1.2 \times 10^9 \text{ cm}^3 \cdot \text{mol}^{-1}$
initial surface concentration	$\Gamma(t = 0)$	$0 \text{ mol} \cdot \text{cm}^{-2}$
total time of the kinetics	t_{tot}	6600 s
maximum surface concentration	Γ_{max}	$98 \times 10^{-12} \text{ mol} \cdot \text{cm}^{-2}$

1. C. L. Yaws and C. Gabbula, *Yaws" Handbook of thermodynamic and physical properties of chemical compounds*, Knovel, 2003.
2. F. Gharagheizi, *Industrial & Engineering Chemistry Research*, 2012, **51**, 2797-2803.
3. T. Miura and K. Seki, *The Journal of Physical Chemistry B*, 2015, **119**, 10954-10961.