

Electronic Supplementary Information for

## Charge Percolation in Redox-Active Thin Membrane Hybrids of Mesoporous Silica and Poly(viologens)

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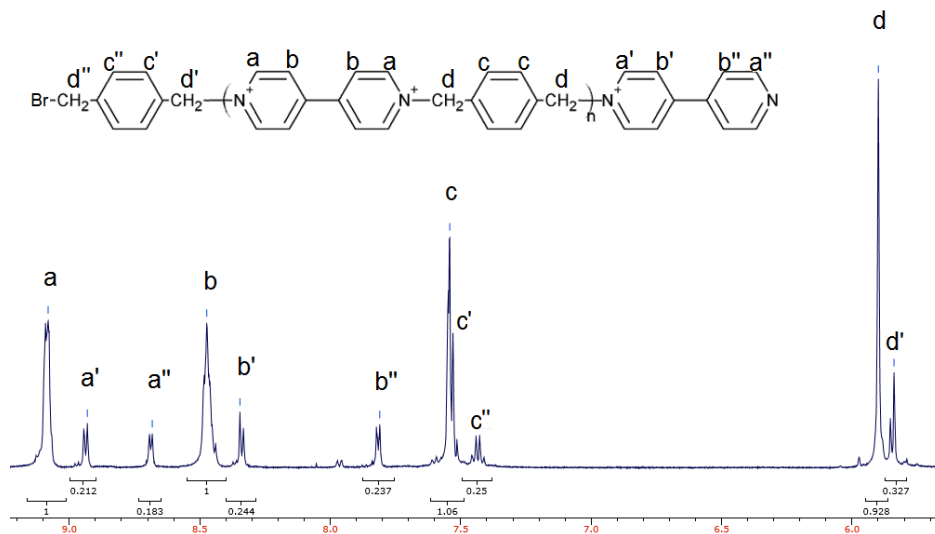
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## 1) NMRs of poly(viologens)



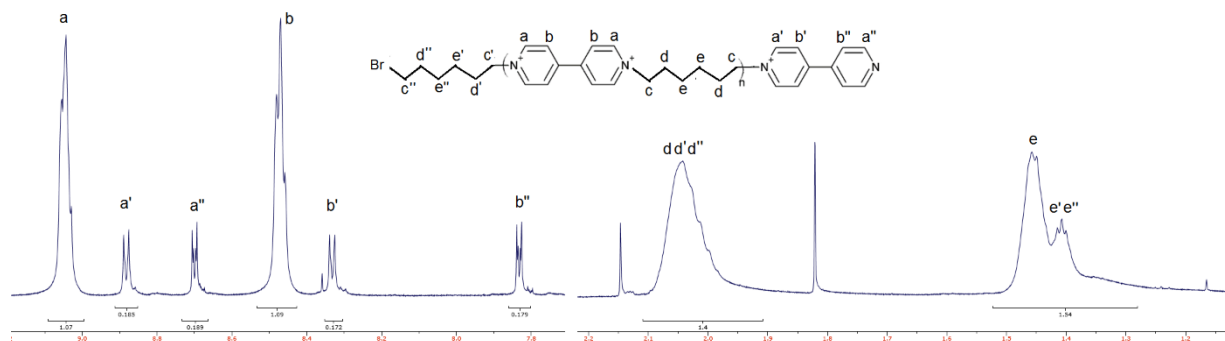
**Figure S1.**  $^1\text{H}$  NMR spectrum of PXV in  $\text{D}_2\text{O}$ .

Figure S1 shows the  $^1\text{H}$  NMR spectrum of PXV and the assignment of the peaks for the polymer, including those originating from the terminal segments. Assignment of pyridine/pyridinium peaks (a, b, a', b', a'', b'') and benzyl peaks c and d follows previous literature reports.<sup>1</sup> Peaks c' and c'' are assigned based on the NMR spectra of benzylviologen,<sup>2</sup>  $\alpha,\alpha'$ -Dibromo-p-xylene,<sup>3</sup> 4-methylbenzyl bromide,<sup>4</sup> and p-xylene-bis-pyridinium bromide (DPX).<sup>5</sup> The peak due to d'' protons is expected around 4.5 ppm, which is too close to the solvent ( $\text{D}_2\text{O}$ ) peak at 4.8 ppm.

From the NMR spectra, we calculated the chain length as:

$$N = \frac{s_{\text{end}}^v + s_{\text{end}}^b + s_{\text{chain}}^v + s_{\text{chain}}^b}{s_{\text{end}}^v + s_{\text{end}}^b} \quad (\text{S1})$$

where  $s_{\text{end}}^v$  and  $s_{\text{end}}^b$  are the number of viologen and benzyl terminal segments, respectively, and  $s_{\text{chain}}^v$  and  $s_{\text{chain}}^b$  are the viologen and benzyl segments in the chain (non-terminal segments). Using the integrations of the NMR signals, we obtain  $N = 3.2$ .



**Figure S2.**  $^1\text{H}$  NMR spectrum of PHV in  $\text{D}_2\text{O}$ .

Figure S2 shows the  $^1\text{H}$  NMR spectra of PHV. Assignment of pyridine/pyridinium peaks (a, b, a', b', a'', b'') follows the same criteria as for PXV. We assign the NMR peaks from the hexyl block (d, d' and d'' and e, e', e'') using the NMR spectra of 1,6 dibromohexane<sup>6</sup> and 1,1'-diheptyl-4,4'-bipyridinium dibromide.<sup>7</sup> The peaks c, c' and c'' are expected in the 4.5-4.7 ppm range,<sup>7</sup> which is close to the solvent peak. Equation (S1) yields a chain length of  $N = 3.7$ .

## 2) Estimation of porosity from SEM data

In order to estimate the porosity using pore diameter ( $d$ ) and separation between pores ( $l$ ) using SEM, we will assume cylindrical pores. The volume of a pore is:

$$V_{\text{pore}} = \pi \left( \frac{d}{2} \right)^2 \delta \quad (\text{S2})$$

where  $\delta$  is the thickness of the film. The volume of the film occupied by the pore corresponds to a hexagonal prism of apothem  $l/2$ , whose volume is:

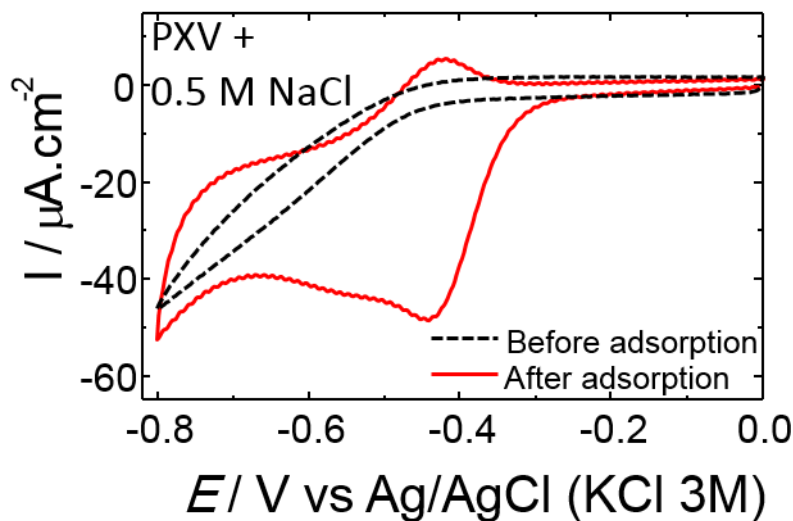
$$V_{\text{hex}} = \frac{pa}{2} \delta = \frac{\sqrt{3}}{2} l^2 \delta \quad (\text{S3})$$

The porosity is thus given by:

$$p = \frac{V_{\text{pore}}}{V_{\text{hex}}} = \frac{\pi}{2\sqrt{3}} \left( \frac{d}{l} \right)^2 \quad (\text{S4})$$

For  $d = 9$  nm and  $l = 19$  nm, eq. (S4) results in  $p = 20.3$  %.

## 3) CV measurements of mesoporous silica film infiltrated with PXV adsorbed from a 0.5 M NaCl solution.



**Figure S3.** Cyclic voltamperograms under Ar atmosphere of mesoporous silica film on ITO-coated glass before and after adsorption of PXV with added NaCl 0.5 M. Scan rate: 100 mV/s.

#### 4) Random Sequential Adsorption/Charge Percolation (RSA/CP) Model

We describe below the RSA/CP model used to estimate the fraction of electrochemically active viologens adsorbed on the inner surface of the pore. Our model involves two steps: i) randomly placing the molecules on the inner surface of the pore, ii) running a percolation analysis on those molecules. These two steps are repeated 200 times for each condition in order to calculate an average fraction of electrochemically addressable molecules,  $f$ .

##### Random Sequential adsorption algorithm

We first define the number of molecules to be placed on the inner surface of the pore. Then we add one molecule at a time by first calculating a random position on the inner surface of the pore and then adding the molecule there, providing it does not overlap with previously adsorbed molecules or with the electrode. The process finishes when all molecules are placed.

##### Charge Percolation algorithm

For each molecule in the system, we first determine which other molecules are within hopping distance (*i.e.* we make a neighbor list). We “reduce” all molecules and then we “oxidize” only those molecules within hopping distance from the electrode. Subsequently, we loop over all molecules and “oxidize” them if they have at least one neighbor in the “oxidized” state. When no changes in the state of the molecules occur in an entire loop over all molecules, the calculation is stopped and  $f$  is calculated as the fraction of “oxidized” molecules.

Code for percolation program (Fortran 90):

```

1 program percolation
2 implicit none
3
4 real*4, parameter :: pi = acos(-1.0)
5 real*4, parameter :: sigmaini = 0.03, sigmabin = 0.5, signastep = 0.005 ! Surface coverage scan: initial, final and step
6 integer, parameter :: rep = 200 ! Number of repetitions of the RSA/Percolation algorithm
7 real*4, parameter :: lpore = 140 ! pore length in nm
8 real*4, parameter :: rpore = 4.5 ! pore radius in nm
9 real*4, parameter :: rr = 1.5 ! molecule size in nm
10 real*4, parameter :: dhop = 0.5 ! maximum hopping range in nm
11 real*4, parameter :: tdist = rr + dhop ! maximum center-to-center hopping distance in nm
12 integer, parameter :: NNmax = int(sigmabin*pi*2.0*rpore*lpore)+1 ! maximum number of molecules in system
13 integer, parameter :: maxneighbors = 10 ! maximum number of neighbors
14
15 integer neighbors(NNmax, maxneighbors), Nu(NNmax), Sneighbors(NNmax)
16 integer check, NN
17 real*4 rr2, tdist2
18 real*4 x, y, z, theta
19 real*4 pos(NNmax,3)
20 real*4 dist
21 integer Ns
22 integer ox(NNmax)
23 integer charge, change
24 real*4 counter, fporo(rep), fporomean, fporostd
25 real*4 sigma
26 integer j, i, ii
27
28 ! Auxiliary calculations
29
30 rr2 = rr**2
31 tdist2 = tdist**2
32 sigma = sigmaini
33

```

```

34 do while(sigma.le.signafin) ! scan surface coverages
35
36 do ii = 1, rep ! loop over repetitions
37 NN = int(sigma*2.0*pi*rpore*lpore)+1 ! number of molecules
38
39 ! RSA
40 do j = 1, NN ! loop over all molecules
41 check = 0
42 do while (check.eq.0) ! check = 1 if molecule fits, check = 0 if it does not
43 check = 1
44 ! random position:
45 theta = 2.0*pi*rand()
46 z = lpore*rand()
47 x = cos(theta)*rpore
48 y = sin(theta)*rpore
49
50 if ((z - rr/2).lt.0.0) then
51 check = 0 ! collision with electrode
52 endif
53
54 do i = 1, j-1
55 dist = (x-pos(i,1))**2 + (y-pos(i,2))**2 + (z-pos(i,3))**2;
56 if(dist.lt.rr2) then
57 check = 0 ! overlap with previous molecule
58 exit
59 endif
60 enddo
61 enddo
62 ! store position
63 pos(j,1) = x
64 pos(j,2) = y
65 pos(j,3) = z
66 enddo ! j
67
68 ! Generate neighbor lists
69 neighbors = 0
70 do j = 1, NN
71 Nu(j) = 0 ! number of neighbors of molecule j
72 do i = 1, NN
73 if(i.ne.j) then
74 dist = (pos(j,1)-pos(i,1))**2 + (pos(j,2)-pos(i,2))**2 + (pos(j,3)-pos(i,3))**2
75 if(dist.le.tdist2) then ! it is a neighbor
76 Nu(j) = Nu(j) + 1
77 if(Nu(j).gt.maxneighbors)stop('Increase maxneighbors')
78 neighbors(j,Nu(j)) = i ! i is neighbor of j
79 endif
80 enddo
81 enddo ! i
82 enddo ! j
83
84 ! Molecules next to electrode
85 Ns = 0
86 Sneighbors = 0 ! number of molecules next to electrode
87 do i = 1, NN
88 if(pos(i,3).lt.tdist) then
89 Ns = Ns + 1
90 Sneighbors(Ns) = i ! i is neighbor of the electrode
91 endif
92 enddo
93
94
95
96 ! Percolation algorithm
97
98 ox = 0 ! ox has the oxidated molecules
99 if(Ns.eq.0) then ! there are not molecules next to electrode
100 fporo(ii) = 0 ! contains fraction of addressable molecules for repetition ii
101 endif
102
103 ! oxidize all molecules next to electrode
104 do i = 1, Ns
105 ox(Sneighbors(i)) = 1
106 enddo
107
108 ! particle-particle loop
109 change = 1
110 do while(change.eq.1) ! stop when there is no change after a full loop over all molecules
111 change = 0
112 do j = 1, NN ! loop over all molecules
113 if(ox(j).eq.1) then ! molecule j is oxidized
114 do i = 1, Nu(j) ! loop over neighbors of molecule j
115 if(ox(neighbors(j,i)).eq.0) then ! molecule is a neighbor but is not oxidized
116 ox(neighbors(j,i)) = 1 ! oxidize neighbor
117 change = 1 ! there is a change
118 endif
119 enddo ! i
120 endif
121 enddo ! j
122 enddo ! change = 1
123
124
125 ! Calculation of number of oxidized molecules
126
127 counter = 0.0
128 do j = 1, NN
129 if(ox(j).eq.1)counter = counter + 1.0
130 enddo
131 fporo(ii) = counter/float(NN)
132 enddo ! repetition
133
134 ! calculate average number and print to screen
135 fporomean = 0.0
136 fporostd = 0.0
137 do ii = 1, rep
138 fporomean = fporomean + fporo(ii)
139 enddo
140 fporomean = fporomean/float(rep)
141 do ii = 1, rep
142 fporostd = fporostd + (fporomean-fporo(ii))**2
143 fporostd = sqrt(fporostd / float(rep-1))
144 enddo
145 print*, sigma, fporomean, fporostd
146
147 sigma = sigma + signastep ! increase sigma
148
149 enddo ! loop sigma
150 end
151

```

## 5) Simulation of 'Split Wave' voltammograms

In order to assess the influence of oxygen reduction on the estimation of the viologen surface coverage from the anodic peak in the cyclic voltammograms in Figure 5, we simulated the electrochemical response of the system following the model of Compton and coworkers for the catalytic reduction of oxygen by the viologen radical.<sup>8</sup> The only difference of our model and that of Compton and coworkers is that we consider a thin film of viologens rather than viologens in solution.

Our model comprises a planar electrode modified by surface-bound viologens and a solution containing dissolved oxygen. The oxygen can diffuse in the solution, while the viologen is constrained to the electrode. For simplicity, we assumed fast charge transport and transport in the viologen film. Therefore, the concentration of the oxidized viologen ( $c_{V,ox}$ ) and the reduced viologen radical cation ( $c_{V,red}$ ) on the surface of the electrode at any given time follows Nernst's equation:

$$c_{V,ox} = c_{V,total} \frac{\exp\left(\frac{F}{RT}(E - E_V^{0'})\right)}{1 + \exp\left(\frac{F}{RT}(E - E_V^{0'})\right)} \quad (S5)$$

and,

$$c_{V,red} = c_{V,total} \frac{\exp\left(-\frac{F}{RT}(E - E_V^{0'})\right)}{1 + \exp\left(-\frac{F}{RT}(E - E_V^{0'})\right)} \quad (S6)$$

where  $E_V^{0'}$  is the formal redox potential of the  $V^{2+}/V^{\bullet+}$  redox couple ( $V$  = viologen),  $E$  is the electrode potential and  $c_{V,total}$  is the total viologen concentration in the film ( $c_{V,total} = \Gamma/\delta$ , where  $\Gamma$  is the surface coverage of viologens and  $\delta$  is the thickness of the film).

Following Compton and coworkers,<sup>8</sup> we consider the following reactions in the system:

- i)  $V^{2+}(ox) + e^- \rightleftharpoons V^{\bullet+}(red)$
- ii)  $V^{\bullet+}(red) + O_2 \rightarrow V^{2+}(ox) + O_2^{\bullet-}$
- iii)  $V^{\bullet+}(red) + O_2^{\bullet-} + 2H^+ \rightarrow V^{2+}(ox) + H_2O_2$
- iv)  $2O_2^{\bullet-} + 2H^+ \rightarrow O_2 + H_2O_2$

Table S1 summarizes the different parameters used in the calculations. We obtained them from the work of Compton of workers, with the exception of  $E_V^{0'}$  (which we set to -0.6 V),  $c_{O_2,ini}$  (initial oxygen

concentration in solution, we set this parameter to obtain catalytic peak currents of the same order of magnitude as in the experiments) and  $c_{V,\text{total}}$ , which we calculated as  $c_{V,\text{total}} = \Gamma/\delta$ , using  $\Gamma = 0.1 \text{ nmol}\cdot\text{cm}^{-2}$  (see Table 2 in the main text) and  $\delta = 140 \text{ nm}$ . We also explored different values for the rate constant for reaction ii in addition to that reported by Compton and coworkers for methylviologen ( $6\cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ ), because different types of viologen will exhibit different reaction rates with oxygen (the rate constant of reaction iii should change as well, but it has an almost negligible effect on the simulated CV).

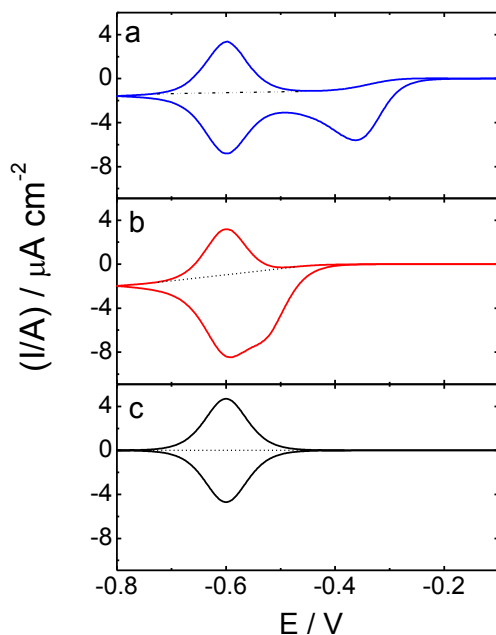
**Table S1:** Parameters used in the simulation of ‘split-wave’ cyclic voltammograms.

Parameter	Description	Value
$c_{V,\text{total}}$	Total concentration of viologens in the film	$7.1\cdot 10^{-3} \text{ M}$
$E^0_V$	Viologen formal redox potential	-0.6 V
$c_{\text{O}_2,\text{ini}}$	Initial oxygen concentration	$1\cdot 10^{-5} \text{ M}$
$D_{\text{O}_2} = D_{\text{O}_2\bullet}$	Oxygen and superoxide diffusion coefficients in solution	$1.96\cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
$k_{\text{ii}}$	Rate constant of reaction ii.	varies
$k_{\text{iii}}$	Rate constant of reaction iii.	$6.5\cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$
$k_{\text{iv}}$	Rate constant of reaction iv.	$1.3\cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$
$v$	Scan rate	50 mV/s
T	Temperature	298 K

Our general simulation strategy involves comparing the surface coverage of viologens determined from the integrated anodic peak in the simulated cyclic voltammograms with that used as an input in the simulation. While we explored the effect of different variables on this comparison, we did not attempt to use the simulated cyclic voltammograms to fit the experimental results in Figure 5 because the experimental results are affected by other processes not considered in our model, including charge transport in the film, the capacitive current from charging the double layer and the direct reduction of oxygen on the ITO electrode. Simulations were performed using the Finite Element Method implemented into Comsol Multiphysics 4.3.

Figure S4 shows the cyclic voltammograms simulated with the parameters of Table S1. Panel a shows the results using  $k_{\text{ii}} = 6\cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$  (same value used by Compton and coworkers for methylviologen). This value results in two well-defined cathodic peaks, such as the CV observed in Figure 5c (PHV). We also performed a calculation using  $k_{\text{ii}} = 3\cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$  (Figure S4b). In this case, the catalytic reduction of oxygen is displaced to more negative potentials than the peak in Figure S4a and, therefore, there is an overlap of the viologen and catalytic reduction peaks, which results in a broad asymmetric peak, such as those observed in Figures 5a and 5b in the main text. Finally, in Figure S4c, we show a control calculation where the catalytic reduction of oxygen is disabled ( $k_{\text{ii}} = 0$ , the same result is obtained by setting a zero oxygen concentration in solution). Using the simulated cyclic voltammograms, we estimated the surface coverage of viologens in the film using the formula:  $\Gamma = (Q/A)/F$ , where  $(Q/A)$  is the integrated charge of the anodic peak and  $F$  is

Faraday's constant. We obtained  $\Gamma = 0.097 \text{ nmol}\cdot\text{cm}^{-2}$  for Figure S4a,  $0.080 \text{ nmol}\cdot\text{cm}^{-2}$  for Figure S4b and  $0.097 \text{ nmol}\cdot\text{cm}^{-2}$  for Figure S4c, which should be compared with the value of  $0.1 \text{ nmol}\cdot\text{cm}^{-2}$  used as an input in the simulations (Table S1). As a conclusion, the integrated charge of the anodic peak allows to estimate the surface coverage of viologens, with a maximum error of 20% for the case where the viologen and catalytic reduction peaks overlap.



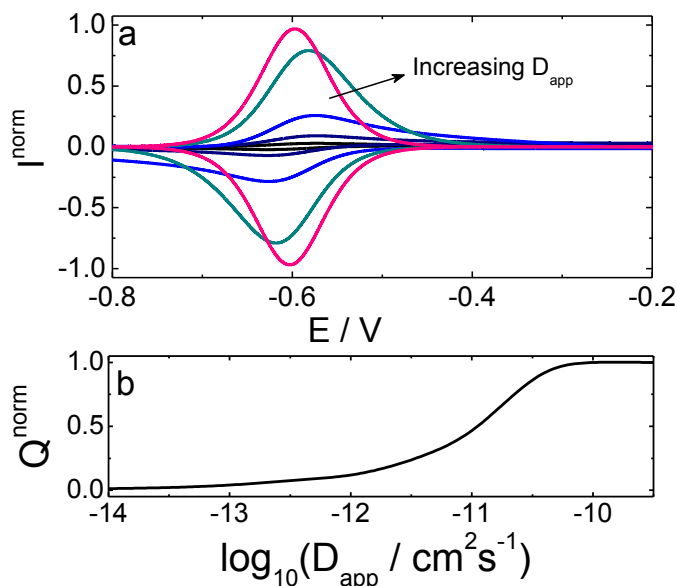
**Figure S4:** Simulated cyclic voltammograms showing the effect of oxygen reduction on the electrochemical response of a thin film of viologen sites. The panels show calculations produced with the parameters in Table S1 and  $k_{ii}$  (rate constant for reaction ii) of: a.  $6\cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ , b.  $3\cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$ , c.  $0 \text{ M}^{-1}\text{s}^{-1}$  (no reduction of oxygen by viologen). The dashed lines show the baseline used to integrate the area of the anodic peak (see text).

## 6) Estimation of the charge-transport diffusion coefficient within the film.

In the main text, we reported that slow-scan-rate (50 mV/s) cyclic voltammetry allows accessing between 3.8% and 15% of the total population of viologens in the film. Based on this information, we propose to estimate the effective diffusion coefficient of charge transport by using the model of Laviron<sup>9</sup> using the finite-element implementation described by Tagliazucchi *et al.*<sup>10</sup> This model considers charge diffusion within a redox-active film of thickness  $\delta$  (we refer the reader to ref. 10 for further details on the model), surface coverage  $\Gamma$  and heterogeneous rate constant for electron  $k_s$ . We simulated cyclic voltammograms using  $\delta = 140 \text{ nm}$ ,  $\Gamma = 0.1 \text{ nmol}\cdot\text{cm}^{-2}$ , a scan rate of  $\nu = 0.05 \text{ V/s}$  and different values of the charge-transport diffusion coefficient,  $D_{app}$ . We chose a large value for  $k_s$  in order



to guarantee equilibrium between the electrode and the adjacent redox sites (*i.e.* Nernst's equation holds for the viologens adjacent to the electrode). Figure S5a shows that as  $D_{app}$  decreases, there is a decrease in the areas of the anodic and cathodic peak and an increase in the separation of the peaks up to the maximum value of 58 mV for a diffusion-controlled CV response.<sup>11</sup> Figure S5b shows the integrated peak area of the anodic peak as a function of  $D_{app}$ . We observe that in order to obtain a 3.8-15 % of the maximum peak area (observed in the limit of large  $D_{app}$ ), we need  $D_{app}$  between  $8 \cdot 10^{-14}$  (for 3.8 % of the maximum peak area) and  $1.2 \cdot 10^{-12}$  cm<sup>2</sup>/s (for 15 % of the maximum peak area).



**Figure S5:** a. Simulated cyclic voltammograms for a film of redox sites with thickness  $\delta = 140$  nm and different values of the charge-transport diffusion coefficient,  $D_{app}$  (in the direction of the arrow,  $D_{app} = 1 \cdot 10^{-13}, 1 \cdot 10^{-12}, 1 \cdot 10^{-11}, 1 \cdot 10^{-10}, 1 \cdot 10^{-9}$  cm<sup>2</sup>/s). The scan rate in the simulation was set to 0.05 V/s and currents have been normalized to the maximum peak current. b. Normalized peak charge for the cyclic voltammograms in panel a as a function of  $D_{app}$ .

## 7) Derivation of the equation to estimate the real surface coverage of molecules, $\Gamma^{real}$ , from experiments.

We estimated the real surface coverage of viologens (viologen units per area of the inner surface of the pore,  $\Gamma^{real}$ ) from the experimentally measured surface coverages (molecules per geometric area of the electrode,  $\Gamma$ ), the film thickness and film porosity ( $\rho$ ). In the following calculation we will assume that the pores are cylinders with radius  $r_{pore}$  and length  $l_{pore}$  (this is, the thickness of the mesoporous film is equal to  $l_{pore}$ ).

For a given geometric area  $A$  of the electrode containing  $N_p$  pores, the volume occupied by the pores is:

$$V_{pores} = \pi \cdot r_{pore}^2 \cdot l_{pore} \cdot N_p \quad (S7)$$

and the total volume is:

$$V = A \cdot l_{pore} \quad (S8)$$

From the definition of porosity,  $p = V_{pores}/V$ , we isolate  $N_p/A$ :

$$\frac{N_p}{A} = \frac{p}{\pi \cdot r_{pore}^2} \quad (S9)$$

The total real area of the cylinders is

$$A^{real} = \pi \cdot r_{pore} \cdot l_{pore} \cdot N_p \quad (S10)$$

We now use the fact that  $\Gamma \cdot A = \Gamma^{real} \cdot A^{real}$  with eqs. (S9) and (S10) to finally get,

$$\Gamma^{real} = \frac{r_{pore} \cdot \Gamma}{l_{pore} \cdot p} \quad (S11)$$

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