1. Langmuirian extension of the diffusion-front model

As discussed in the main text, a way to effectively account for desorption in the diffusion-front model that we describe is to assume that C_{site} depends on the bulk dye solution concentration as predicted by the Langmuir model (here we keep the same equation numbers as in the main text):

$$C_{\mathrm{site}} = \frac{C_{\max} K c_0}{1 + K c_0}. \tag{8}$$

Using (8) for the mass-balance equation (5) finally results in

$$t_p = \frac{C_{\mathrm{site}} \cdot L^2}{2 D c_0} = \frac{C_{\max} K \cdot L^2}{2 D_*} \frac{1}{1 + K c_0}. \tag{9}$$

$C_{\max}$ is the maximum reachable concentration of the adsorbed dye during the rapid adsorption phase, *i.e.*, 79 mM. To validate the use of the latter equation, we notice that Eq. (5) was derived assuming that the concentration profile $c(x)$ is linear and that the dye coverage throughout the film is homogeneous once the front has reached the interface. This corresponds to the situation when the adsorption occurs at given time primarily near the front. For irreversible adsorption, this is exactly the case because the adsorbed overlayer is close to saturation behind the reaction front. For reversible adsorption, this is also a good approximation because the adsorbed overlayer is close to local equilibrium behind the reaction front and the adsorption at given time anyway occurs primarily near the front.

We can now fit the concentration dependence of the percolation time using equation (9). Fig. S1 compares the best least-square fits for the experimental data using (i) constant $C_{\mathrm{site}} = C_{\max}$ and equation (7) (produces the same fit as in Fig. 4B in the main text) and (ii) C_{site} varying as a Langmuir adsorption isotherm as in equation (9). The latter analysis results in a better fit (Fig. S1), and the extracted diffusion coefficient corresponds to 13.0 $\mu m^2/s$. Notably this value is now very close to the one obtained from the TiO_2 film thickness dependence (14.6 $\mu m^2/s$) at a constant (high) dye concentration. Although this analysis does not prove that we should use a dependence of C_{site} on bulk concentration, it points to one way to improve the theoretical and experimental agreement that is physically reasonable. Additional experiments on the exact adsorption kinetics are needed to further refine this analysis, *e.g.* experiments exploring the presence of adsorption sites with different binding energies, which could lead to desorption of a fraction of the adsorbed dye molecules, *i.e.* a mixture of irreversible and reversible adsorption.

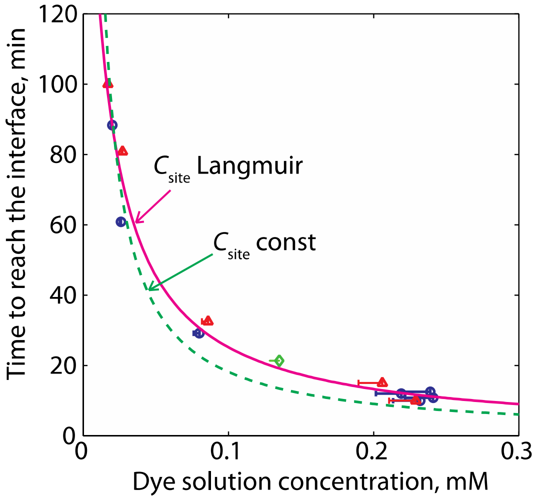

Figure S1. Percolation time as a function of the dye solution concentration, fitted in two ways; with a constant (independent of bulk concentration) surface coverage C_{site}=C_{max} and with one depending on bulk concentration, assuming reversible Langmuir-type adsorption C_{site} = f(c_0). Clearly the agreement can be improved by assuming a concentration dependence of C_{site} on the dye bulk concentration.

2. Solvent exchange in porous TiO_2

In order to know the time it takes for small molecules that do not stick to TiO_2 to diffuse through the porous film, we studied the kinetics of a solvent exchange. Using the same type of HI-INPS measurement and sample as in Fig. 2 in the main text, we studied diffusion of solvent mixtures made of acetonitrile and *tert*-butanol at different ratios. The plasmon peak position shift upon injection of the different mixtures is shown in Fig. S2. The peak shift is due to the difference in dielectric constant between the liquids. The typical time for the onset of the plasmon shift is about 10 s, and saturation is reached in 15 to 50 s. This is much shorter than the times observed for diffusion of the dyes in any of the systems studied (the corresponding values and discussion are in the main text). Since two different solvent mixtures mix in the flow cell before they arrive to the measurement point, the injection profile is not sharp, which is likely to lead to some overestimation of the solvent exchange times.

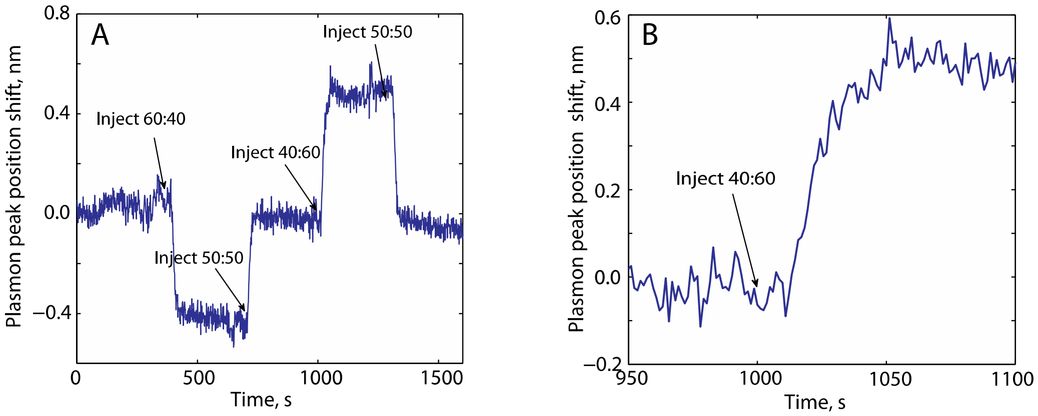

Figure S2. Kinetics of solvent exchange in the porous TiO_2 film 7.5 μm thick. The solvents used were mixtures of acetonitrile and tert-butanol in proportions indicated in the plots (the percentage of acetonitrile comes first). (B) is a zoomed-in part of (A), which resolves the exchange from a 50:50 mixture to a 40:60 one.

3. Blue shift in solvent

Porous TiO_2 HI-INPS samples used in this work exhibited a slow blue shift of the plasmon resonance when left in solvent. This blue shift has minor influence for the measurements of the percolation times like those in Fig.2D and Fig. 4, but is still a phenomenon that may be important for other types of studies, and therefore a comment is made here. A blue shift implies that the dielectric constant of the region close to the plasmonic nanoparticles decreases. The blue shift was usually close to saturation after about 15 h, as shown in Fig. S3. The origin of this is still unclear to us, and here we briefly discuss the possible reasons for it:

1) Some contaminations (of a higher dielectric constant compared to the solvent) are being washed away from the TiO_2 surface. This natural explanation seems to not be supported by the fact that the rate of the plasmon blue shift did not depend on whether the liquid in the cell was still or was pumped through.

2) Species with a lower dielectric constant than the solvent adsorb on the TiO_2 surface. A candidate for this could be water, which indeed has a lower refractive index than any of the solvents used in this work, and which is known to adsorb on TiO_2 surfaces. Small amounts of water might be present in the solvents used, since we did not ensure complete water-free environment during measurements.

3) Properties of the TiO_2 nanoparticles (either those that compose most of the film, or those produced by a $TiCl_4$ pre-treatment) change in the presence of solvent. Those could include slight re-shaping of the particles or possible nano-pores in them.

4) Some changes might be occurring in the Au sensing nanoparticles themselves. This is not very likely, since they are protected by a sputtered TiO_2 film.

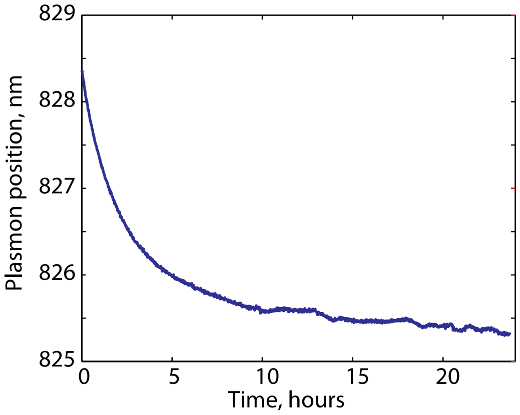

Figure S3. Plasmon peak position for an HI-INPS sample during incubation in static solvent.

4. Long impregnation runs on fresh and incubated TiO_2 samples

As seen in Fig. S4 A, samples that were exposed to the solvent only shortly (*ca.* 10 min) before dye injection exhibit a blue shift of the plasmon peak position. This shift stabilized after about 15 hours, similarly to incubation in pure solvent as in Fig. S3. The presence of the blue shift makes it difficult to resolve the impregnation kinetics over long times by following the plasmon peak position shift. However, the percolation time (*i.e.,* the time for the onset of the red shift) can be easily deduced from these measurements. As seen in Fig. S4 B, incubation in the solvent helps getting rid of the blue shift and then the plasmon peak position continues shifting over long impregnation times.

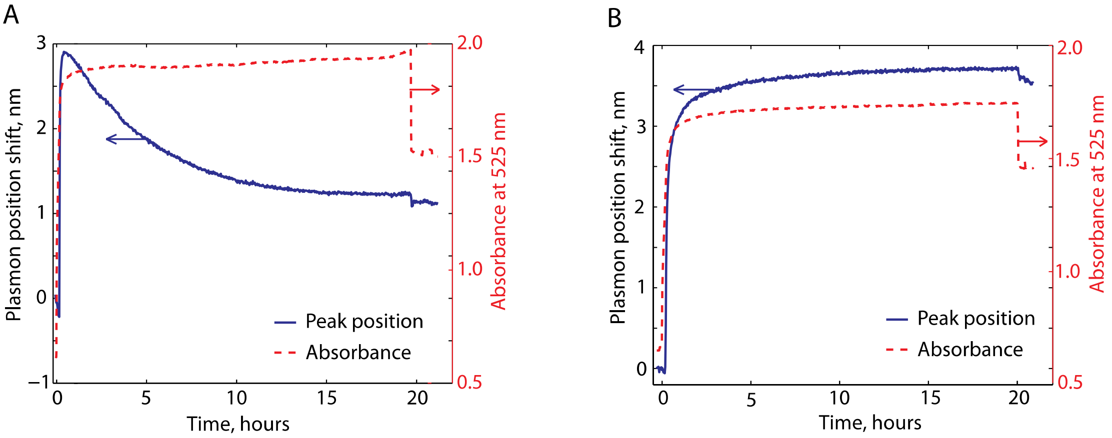

Figure S4. Impregnation runs for HI-INPS samples, where the dye solution was injected (A) after the sample spent about 10 min in the solvent, and (B) after a 24 hour long incubation in the solvent (as in Fig. S3). The dye concentration was about

0.23 mM in (A), and 0.13 mM in (B). The time to reach the bottom (i.e., the time for the onset of the red shift) was 0.15 h in (A) and 0.18 h in (B).

5. Preliminary HI-INPS impregnation data on dye Z105

In order to check the generality of our approach for different dyes, we have performed several impregnation measurements on dye Z105, which has one phosphonic acid instead of two carboxylic acid groups. For these measurements, Z105 was dissolved in a mixture of acetonitrile (45%), *tert*-butanol (45%) and DMSO (10%). The data are preliminary, since we discovered that the dye was not completely dissolved at the highest measured concentrations (and might have formed aggregates at the lower ones). Nevertheless, the percolation time, *i.e.* the delay in the onset of the plasmon peak shift, was clearly present in all measurements, and it scaled approximately as $1/c_0$, where c_0 is the bulk dye concentration (Fig. S5).

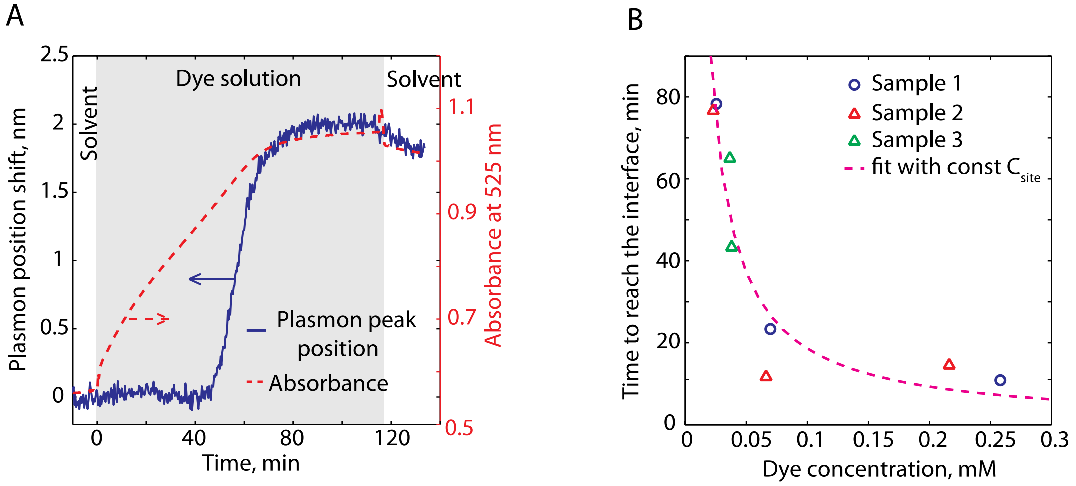

Figure S5. (A) An HI-INPS measurement of impregnation of a 7.5 μm thick, mesoporous TiO_2 film with dye Z105 at a concentration of 0.038 mM in an acetonitrile:tert-butanol:DMSO 0.45:0.45:0.1 mixture. The dye solution was injected at 0 min, and was rinsed by pure solvent at about 117 min. (B) A preliminary dependence of the dye percolation time on the bulk dye concentration.