# Nano-patterned layers of a grafted Coumarinic chromophore

## Electronic supplementary information

**Nadia Frederich,[a,b] Bernard Nysten,[a] Benoît Muls,[b] Johan Hofkens,[c] Jean-Louis Habib Jiwan*[b] and Alain M. Jonas *[a]**

### Homogeneously grafted coumarin layers

*XPS and XRR supplementary information.*

The success of the quaternization of C343D in the presence of the silanized surface is demonstrated by the appearance of a N 1s peak and a shift in the position of the Cl 2p peak (figure 1a and 1b)).

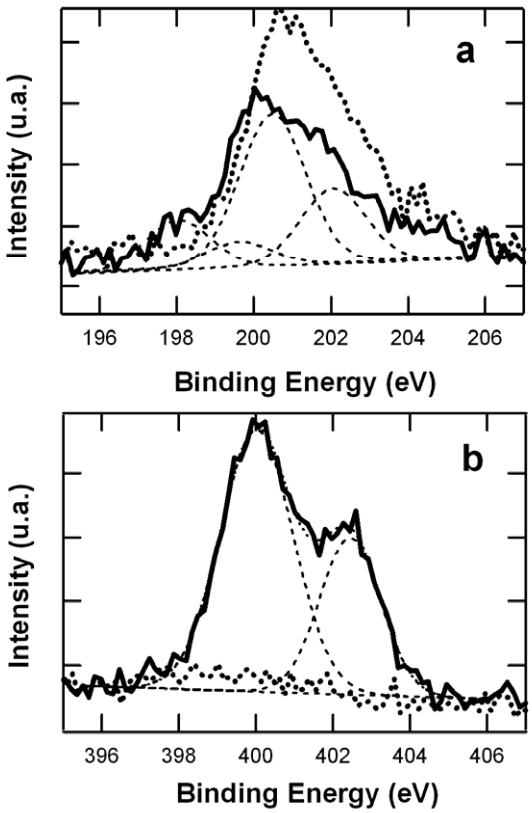


**Figure 1:** Cl 2p region (a) and N 1s region (b) of the XPS spectra of the CMPDCS silane layer before (dotted line) and after (continuous line) grafting of the C343D chromophore.

The yield of the reaction of quaternization of C343D, η(t) is defined as the relative proportion of CMPDCS molecules in the silane monolayers having reacted with the coumarin C343D. This parameter cannot be directly obtained from the Cl peak, because $Cl^-$ ions can exchange with other ions, subsequently to the quaternization. Therefore, η was obtained by the following equation:

$$\eta = \frac{[N]/3}{([Cl]+[N]/3)}$$

where [Cl] is the atomic content in unreacted benzylic chlorine obtained by decomposition of the Cl peak and [N] is the atomic content in nitrogen. The division by 3 results from the C343D possessing three N atoms per molecule. The variation with reaction

time of the N atomic fraction and of η are displayed in figure 2a and b. Figure 2b shows that after 64 h reaction time, ~ 50 % of the benzylic chlorine atoms remain unreacted.

Figure 2c presents the variation of the thickness of the total chromophore and silane layer with reaction time.

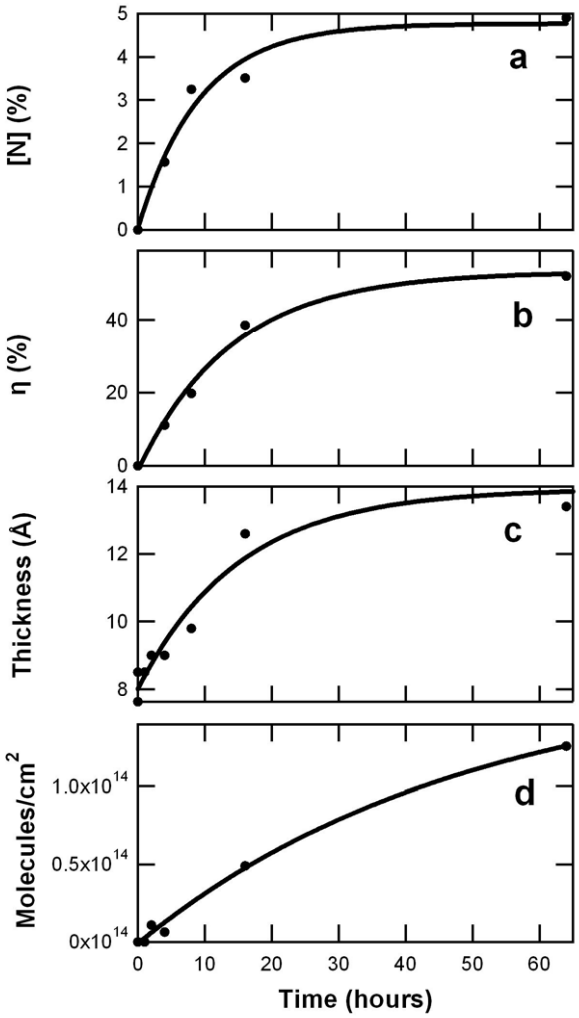


**Figure 2:** (a) Variation of the nitrogen atomic fraction of the grafted coumarin layer quantity as a function of the reaction time. (b) Variation with reaction time of the reaction yield η(relative amount of benzylic chlorine moieties of the silane layer which reacted with C343D). (c) Variation of the total thickness of the layer of coumarin and silane as a function of reaction time. The origin of time coincides with the thickness of the starting CMPDCS silane monolayer. (d) Variation of the surface density in coumarin as a function of reaction time

Figure 2c presents the variation of the thickness of the total chromophore and silane layer with reaction time.

The XRR data were then fitted by standard methods,[1] to obtain electron density profiles of the layers (figure 3b). Grafted coumarin layers present an electron density close to 0.4 $Å^{-3}$. This is in agreement with the value expected for dense organic conjugated layers.From the electron densities profiles, we determined the surface density of coumarin molecules:

$$\text{coumarin surface density} = \int_{-\infty}^{+\infty} (\rho(z)_{\text{coumarin}} - \rho(z)_{\text{silane}})dz \cdot \frac{1}{198}$$

where z is the vertical coordinate, $\rho(z)_{coumarin}$ is the electron density profile of the silane plus the grafted coumarin, $\rho(z)_{silane}$ is electron density profile of the silane only, and 198 is the known electron content of the coumarin molecule. Taking the 64 hours film as an example, the integrated electron content of the film is $2.5*10^{16}$ electron/$cm^2$ which, once divided by 198, gives

[1] A. Pallandre, K. Glinel, A. M. Jonas and B. Nysten, Binary Nanopatterned Surfaces Prepared from Silane Monolayers, *Nano Lett.,* 2004, **4**, 365-371

 

$1.26*10^{14}$ coumarin molecules/$cm^2$ or about one molecule per 0.81 $nm^2$. Taking the thickness of the chromophore layer (~0.6 nm) into account, we can deduce that one molecule occupies roughly 0.5 $nm^3$, corresponding to a density close to 1.2 $g/cm^3$. The estimated uncertainty on these numbers is about 10 %, the typical uncertainty on electron densities obtained from XRR. The results are shown in figure 2d as a function of reaction time, and confirm the progressive densification of the grafted coumarin layer.