## Spectroscopic ellipsometry of Self assembled Monolayers: interface effects. The case of phenyl selenide SAMs on gold.

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## Supplementary information



**Fig. 1** Absorption spectrum of DPhDSe in hexane (1 mM). Spectrum measured with a UV-530 (Jasco Corp.) spectrophotometer



**Fig. 2** The figure illustrates the effect of adding narrow-band absorptions to an otherwise transparent film (n=1.5;  $d_F$  = 1.0 nm). Symbols (red): SE data obtained on PhSe SAMs (65° angle of incidence). Grey Curve: TF model (n=1.5;  $d_F$  = 1.0 nm). Blue curve: Arrows indicate the positions of two Lorentzian oscillators (O1,O2) added to the otherwise transparent film. In this example, O1 and O2 have the same amplitude; the width of O2 is twice the one of O1, as suggested by the arrow thickness. Narrow dips in the  $\delta \Delta$ ,  $\delta \Psi$  curves, related to molecular absorptions (M. Prato et al. The Journal of Physical Chemistry C, 2009, 113, 20683; C. Toccafondi t al. Journal of Colloid and Interface Science, 2011, 364, 125) can be in principle reproduced by adjusting the parameters (line shape, position, amplitude and broadening ) of an adequate number of oscillators.

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Fig. 3 Dielectric functions related to model AFI1. (A) Substrate. The gold optical properties have been obtained by inversion of ellipsometric data. They are consistent with previous determinations (Aspnes, D. E.; Kinsbron, E.; Bacon, D. D. Phys. Rev. B 1980, 21, 3290; Prato, M. et al. The Journal of Physical Chemistry C 2008, 112, 3899.) (B) BEMA transition layer (note that the BEMA approximation does not warrant Kramers -Kronig consistency.) (C) Film layer. The film optical properties were modelled as  $\varepsilon(hv) = n^2 + G_1(A_1, E_1, \beta_1)$  where A<sub>1</sub>, E<sub>1</sub> and  $\beta_1$  are the amplitude, energy position, and broadening parameter of a Gaussian oscillator. n was set at 1.55, then looking for the best agreement with data by adjusting the thickness and oscillators parameters. A relatively intense absorption at about 245 nm (typical of aromatic ring, consistent with transmission measurements in hexane solution of DPhDSe) was indeed necessary to a good reproduction of the sharp dip in the highest energy portion of the  $\delta\Psi$  spectra (Fig. 6 of main text



**Fig. 4** Dielectric functions related to model AFI2. (A) Substrate. (B) BEMA layer. (C) Film layer. The film optical properties were modelled as  $\varepsilon(hv) = n^2 + G_1(A_1, E_1, \beta_1) + G_2(A_2, E_2, \beta_2)$  where  $A_i$ ,  $E_i$  and  $\beta_i$  i = 1, 2 are the amplitude, energy position, and broadening parameter of two Gaussian oscillators. *n* was set at 1.55, then looking for the best agreement with data by adjusting the thickness and oscillators parameters. Beyond a relatively intense absorption at about 245 nm, the best fit required a relatively broad and intense oscillator centred at 440 nm . The addition of this second oscillator improves the quality of fit in the 300-500 nm spectral range (Fig. 6 of main text). Under the BEMA scheme one is forced to add the oscillator to the film optical layer; however, from a comparison with Fig.1 one can also observe two evident effects on the  $\varepsilon_2$  function of the transition layer: (i) an increase of the MIR values.