Supporting Information for:

Studies of Langmuir and Langmuir-Blodgett Films of NLO-Active Amphiphilic 1,3-Indandione Derivatives

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DERIVATION OF DICHROIC ANALYSIS OF POLARIZED UV-VISIBLE ABSOPRTION SPECTRUM

X-Y is the plane of the LB film, (Fig. Sup 1).

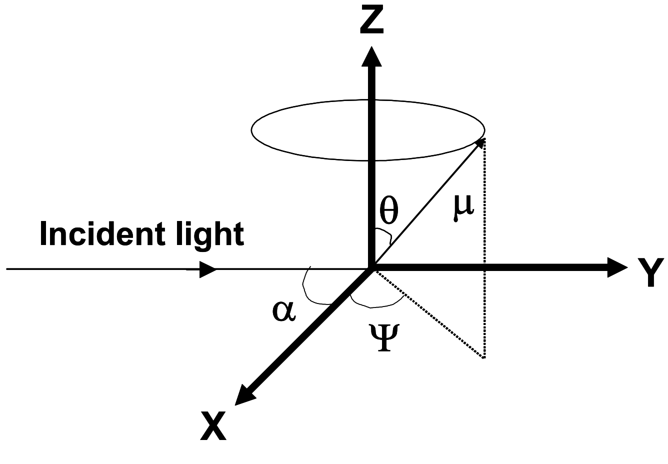

Fig. Sup. 1 – The definition of angles in the system

The molecular transition dipole $\mu = (\mu_0, \theta, \psi)$

$= \mu_0 (\sin\theta\cos\psi, \sin\theta\sin\psi, \cos\theta)$

The incident light propagates in the X-Z plane with angle α to the X-Y plane.

s-polarization is normal to the plane of incidence, p-polarization is parallel to it.

$$I_0 = |E_o|^2 = |E_{0s}|^2 + |E_{0p}|^2$$

Eos = (0, E_{0s}, 0)   and   Eop = (E_{op} sinα, 0, E_{op} cosα)

$$E_{os} = E_{op} = \frac{1}{\sqrt{2}}\sqrt{I_0}$$; For natural light

Absorption in s-polarization:

$$I_{abs,s} \propto |E_s \bullet \mu|^2 = k|E_{0s}\sin\theta\sin\psi|^2 = \mathrm{k}|E_{0s}|^2\sin^2\theta\sin^2\psi$$

Where k is a proportionality factor (equal for both polarizations).

Averaging over the azimuthal angle ψ

$$< I_{abs,s} > = \mathrm{k}\ |E_{0s}|^2\sin^2\theta.\frac{1}{2\pi}\int_0^{2\pi}\sin^2\psi d\psi = \frac{1}{2}\ \mathrm{k}|E_{0s}|^2\sin^2\theta \qquad (1)$$

Similarly for absorption in p-polarization:

$$I_{abs,p} \propto |E_p . \mu|^2 = k|E_{0p}(\sin\theta\sin\alpha\cos\psi + \cos\theta\cos\alpha)|^2$$

$$< I_{abs,p} > = \mathrm{k}|E_{0s}|^2\,[\frac{1}{2}\sin^2\theta\sin^2\alpha + \cos^2\theta\cos^2\alpha] \qquad (2)$$

The dichroic ratio (if the film would be suspended freely without a support) becomes

$$\frac{I_{abs,p}/|E_{op}|^2}{I_{abs,s}/|E_{os}|^2} = \left(\sin^2\alpha + 2\cot^2\theta\cos^2\alpha\right) = \frac{1-10^{-OD_p}}{1-10^{-ODs}} \qquad (3)$$

where OD is the optical density, and for an unsupported film $E_{os} = E_{op} = \frac{1}{\sqrt{2}}\sqrt{I_0}$.

However, the transmitted beam passes through the glass support so that E_s and E_p are modified by the reflectance at the air-glass interface and the multireflections within the slide (Figure Sup. 2). In Fig. 2 T_1 and T_2 are the (polarization dependent) Fresnel coefficients for transmittance at the air-glass and glass-air interfaces, and R_2 is the Fresnel coefficient of internal reflectivity at the glass-air interfaces. Therefore equation (1) needs to be modified. We will assume that the reflectivity and transmittance are determined by the glass (and air) alone, and are not affected by the presence of the film. We will bring evidence to corroborate the use of this assumption in a later section of this Supplementary material.

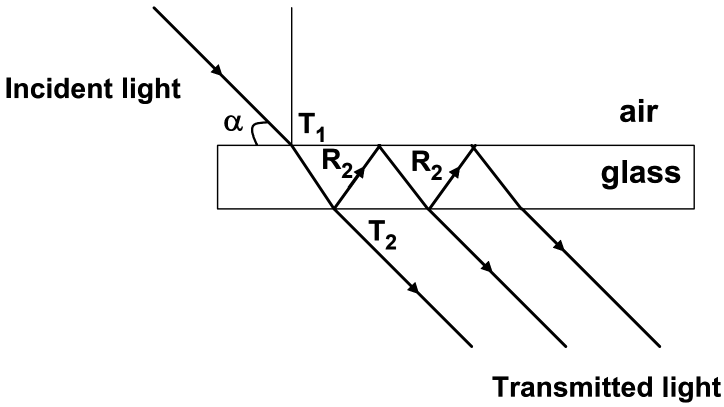

Fig. Sup. 2 – Cartoon of transmission and multireflection of light beams in a glass slide.

Light with an electric field $E_{p(s)}$ incident from air on a glass slide is transmitted through it directly and after multiple internal reflections in the glass (Fig. Sup. 2), so that

$$E^{trans}_{p(s)} = E^{inc}_{p(s)} T_{1,p(s)} (1 + R^2_{2,p(s)} + R^4_{2,p(s)} + R^6_{2,p(s)} + \dots\dots\dots\dots) T_{2,s(p)} = E^{inc}_{p(s)} T_{1,p(s)} \frac{1}{1 - R^2_{2,p(s)}} T_{2,p(s)} =$$

$$= E^{inc}_{p(s)} T_{1,p(s)} \frac{1}{1 - (1 - T^2_{2,p(s)})} T_{2,p(s)} = E^{inc}_{p(s)} \frac{T_{1,p(s)}}{T_{2,p(s)}}$$

Giving

$$\mathrm{I}_{p(s)}^{trans} = \mathrm{I}_{p(s)}^{inc} \left| \frac{T_{1,s(p)}}{T_{2,s(p)}} \right|^2$$

$\mathrm{I}_{p(s)}^{inc}$ is the intensity of the beam after absorption in the film, as calculated from equations (1) and (2)

$$I_{p(s)}^{inc} = I_{o,p(s)} - I_{abs,p(s)}$$

So that the transmitted light, accounting for both absorption in the film and the reflection and transmission of the air-glass interface, is given by

$$\mathrm{I}_{p(s)}^{trans} = (I_{o,p(s)} - I_{abs,p(s)}) \left| \frac{T_{1,s(p)}}{T_{2,s(p)}} \right|^2$$

We used in our measurements a clean glass slide as the blank ($\alpha' = \pi/2 - \alpha = 0$) so that

$$\mathrm{I}_{p(s)}^{trans}(blank) = I_{o,p(s)} \left| \frac{T_{1,s(p)}(\alpha'=0)}{T_{2,s(p)}(\alpha'=0)} \right|^2$$

The apparent (measurable) OD is now given by

$$10^{-\mathrm{OD}_{p(s)}} = \frac{\mathrm{I}_{p(s)}^{trans}}{\mathrm{I}_{p(s)}^{trans}(blank)} = \frac{(I_{o,p(s)} - I_{abs,p(s)}) \left| \frac{T_{1,s(p)}}{T_{2,s(p)}} \right|^2}{I_{o,p(s)} \left| \frac{T_{1,s(p)}(\alpha'=0)}{T_{2,s(p)}(\alpha'=0)} \right|^2} =$$

$$= (1 - \frac{I_{abs,p(s)}}{I_{o,p(s)}}) \frac{\left| \frac{T_{1,s(p)}}{T_{2,s(p)}} \right|^2}{\left| \frac{T_{1,s(p)}(\alpha'=0)}{T_{2,s(p)}(\alpha'=0)} \right|^2} \tag{4}$$

Extracting $I_{abs,\, p(s)}$ from eq. (4), taking their ratio and using the two terms on the l.h.s. of eq. (3)

$$\frac{I_{abs,p}/I_{op}}{I_{abs,s}/I_{os}} = \frac{1-10^{-OD_p}}{1-10^{-OD_s}}\frac{f_p}{f_s} = 2\left(\frac{1}{2}\tan^2\alpha + \cot^2\theta\right)\cos^2\alpha$$

$$f_{p(s)} = \frac{\left|\dfrac{T_{1,s(p)}(\alpha'=0)}{T_{2,s(p)}(\alpha'=0)}\right|^2}{\left|\dfrac{T_{1,s(p)}}{T_{2,s(p)}}\right|^2} \tag{5}$$

f_p and f_s are factors correcting equation (3) for the reflectance and transmittance of the glass support. The Fresnel transmittance coefficients are measured with the refractive index of glass (1.52), and are given in any text book on optics.

For glass slide coated on both sides with the films the same analysis holds, except the experimental OD values will be larger accordingly.

Another possible correction that, in principle, needs to be considered is the incidence angle dependence of the optical path of the light within the films. This requires dividing the OD values by cos α', giving

$$\frac{I_{abs,p}/I_{op}}{I_{abs,s}/I_{os}} = \frac{1-10^{-OD_p/\cos\alpha'}}{1-10^{-OD_s/\cos\alpha'}}\frac{f_p}{f_s} = 2.\left(\frac{1}{2}\tan^2\alpha + \cot^2\theta\right)\cos^2\alpha \tag{6}$$

As noted above, this derivation is based on the assumption that the film itself does not affect these correction factors. We now show that this assumption holds in our measurements.

Our experimental s-polarized spectra at all angles of incidence converge to the same value (zero) away from the maximum of the absorbance. This indicates that the refractive index of the film (away from resonance) does not affect the reflectivity.

Furthermore, the s-polarized spectra at all angles are super-imposable (Fig. Sup 3), without any deformation of the spectrum. This holds also for the p-polarized spectra (though their relative intensity changes with angle, as expected on the basis of simple reflectivity considerations involving the glass-air interface). This indicates that the reflectance at all wavelengths is the same, i. e. the film itself does not have any effect, even on resonance.

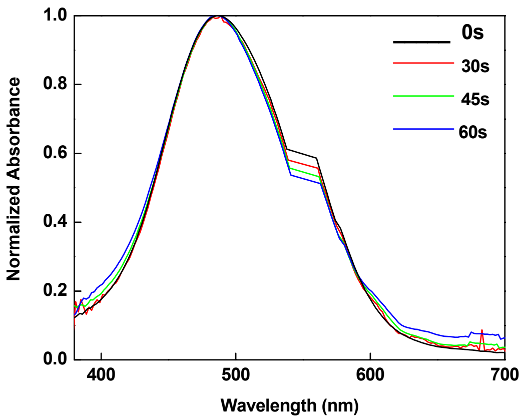

Fig. Sup. 3 – Intensity normalized s-polarized spectra of LB films of dye **2a** at various angles of incidence.

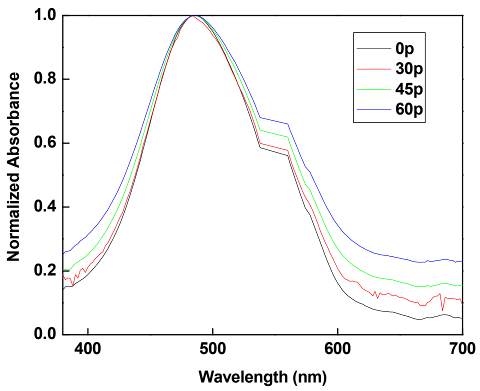

Fig. Sup. 4 – Intensity normalized p-polarized spectra of LB films of dye **2a** at various angles of incidence.

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Lastly, we show that (at least for our systems) the corrections to eq. (3) – the simple analysis – as summarized in eqs. (5) and (6), do not have any significant effect on the derived values of the tilt angle of the chromophore.

Fig. Sup. 5-7 show the results of the dichroic analysis for dye 2a using equations (3), (5) and (6), respectively. The tilt angles we evaluate from the respective intercepts are: 54.4, 55.4 and 55.3. This spread of values is well within the experimental uncertainty.

Also dye 2b exhibits similar behavior (see Fig. Sup. 8-10), with tilt angles of ~50^{o}.

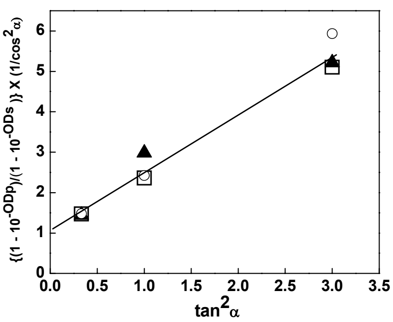

Fig. Sup. 5 Analysis of polarized absorption spectra of the LB films of 2a deposited at different surface pressures: 40 mN/m (open squares), 25 mN/m (solid triangles) and 10 mN/m (open circles).

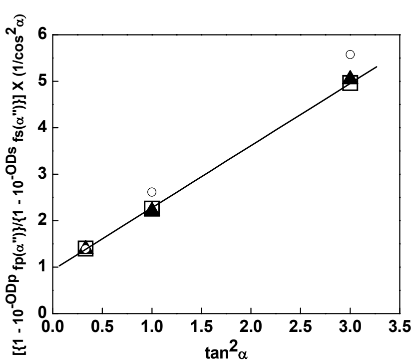

Fig. Sup. 6 Analysis of polarized absorption spectra of the LB films of 2a deposited at different surface pressures: 40 mN/m (open squares), 25 mN/m (solid triangles) and 10 mN/m (open circles) including transmittance correction.

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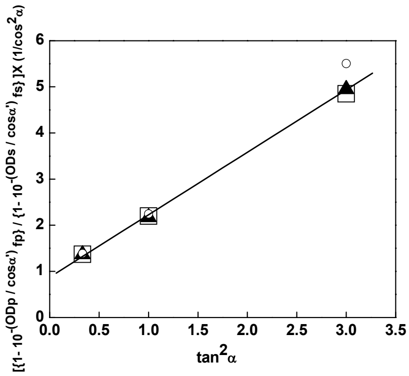

Fig. Sup. 7 Analysis of polarized absorption spectra of the LB films of 2a deposited at different surface pressures: 40 mN/m (open squares), 25 mN/m (solid triangles) and 10 mN/m (open circles) including corrections for transmittance and optical path.

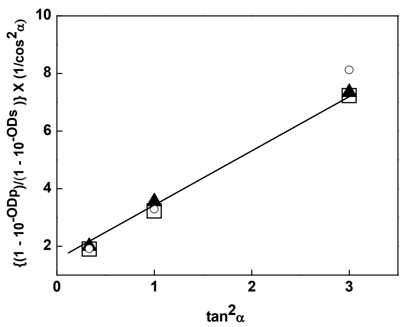

Fig. Sup. 8 Analysis of polarized absorption spectra of the LB films of 2b deposited at different surface pressures: 40 mN/m (open squares), 25 mN/m (solid triangles) and 10 mN/m (open circles).

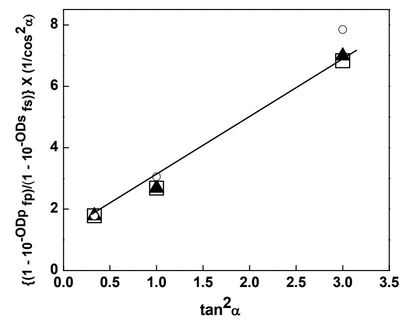

Fig. Sup. 9 Analysis of polarized absorption spectra of the LB films of 2b deposited at different surface pressures: 40 mN/m (open squares), 25 mN/m (solid triangles) and 10 mN/m (open circles) including transmittance correction

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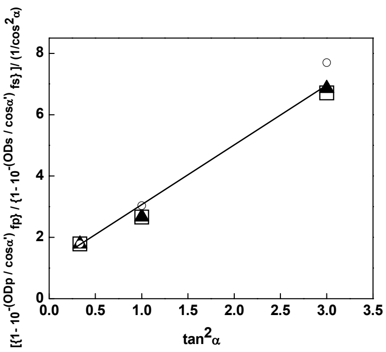

Fig. Sup. 10 Analysis of polarized absorption spectra of the LB films of **2b** deposited at different surface pressures: 40 mN/m (open squares), 25 mN/m (solid triangles) and 10 mN/m (open circles) including corrections for transmittance and optical path.