Supporting information

Probing the High Performance of Photoinduced Birefringence in V-Shaped Azoaromatic/PMMA Guest-Host Films

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SI-1 Determination of absorption cross-section

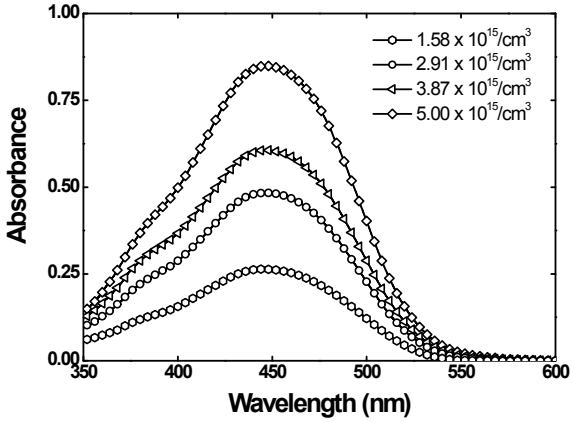

Figure SI.1 – Absorption spectrum for V-shaped azo-chromophores/PMMA in guest-host film for different dye concentration.

SI-1 Temporal evolution of the optical birefringence mechanism

We have employed the bi-exponential model is widely used to obtain the formation and relaxation times for the optical birefringence. Such a model can be described by:

$$\Delta n_f(t) = \alpha_1\left(1 - e^{-t/\tau_1}\right) + \alpha_2\left(1 - e^{-t/\tau_2}\right) \quad (1)$$

$$\Delta n_r(t) = \alpha_3 e^{-t/\tau_3} + \alpha_4 e^{-t/\tau_4} \quad (2)$$

in which $\Delta n_f(t)$ and $\Delta n_r(t)$ are, respectively, the temporal evolution of the formation and relaxation of birefringence; α_1, α_2, α_3, and α_4 are pre-exponential factors; τ_1 and τ_2 are the time constants for growth; τ_3 and τ_4 the constants of time for relaxation of birefringence. Such a model considers that both the growth and relaxation of photoinduced birefringence have slow and fast components determining its temporal dynamics. [1-4] For the growth process, the fast component is associated with photoisomerization *trans→cis* (AHB), and the subsequent molecular reorientation that is initially very efficient given the high the free volume in guest-host films. With the decrease of the free volume available to accommodate the chromophores reorienting, as a consequence of the orientation process itself, a slow component takes place due to a lower free volume available for reorientation which results in a slower increase in the photoinduced birefringence. In the relaxation of birefringence, the fast process is associated with *cis→trans* thermal isomerization and the one slow associated with thermal angular diffusion of azo-aromatic groups with the movement of the polymeric chains.[5] Figure SI.2 shows the slow (τ_1 and τ_3) and fast (τ_2 and τ_4) characteristic times for the formation and relaxation optical birefringence a function of the laser power. As observed, all time constants decrease as a function of the increase of laser power. Such behavior is characteristic of optical storage in guest-host films. [6] Table SI.2 shows the slow and fast time constants after the saturation. As can be noted, all the times are higher for the Film 1 due to the higher chromophores density, which decreases the free volume to occur *trans→cis→trans* photoisomerization cycle.

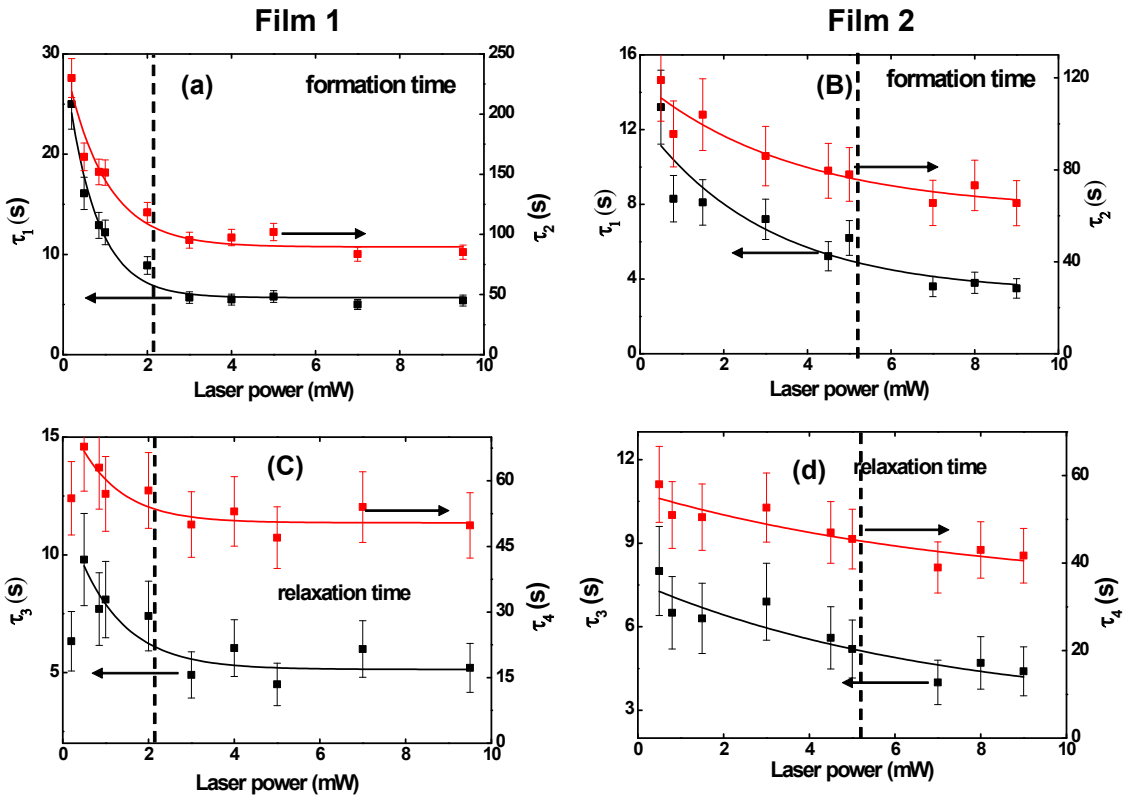

Figure SI.2 - Slow (τ_1 **and** τ_3) and fast (τ_2 **and** τ_4) time constants related to formation and relaxation optical birefringence. Vertical dashed lines show the saturation laser power.

Table SI.1 – Formation and relaxation time constants obtained for Film 1 and Film 2.

times	**Film 1**	**Film 2**
τ_1	5.7 ± 0.6	3.9 ± 0.5
τ_2	92.5 ± 6.6	69.3 ± 8.2
τ_3	5.2 ± 1.0	4.4 ± 0.9
τ_4	50.4 ± 7.5	41.3 ± 6.2

SI-2 - Long-term residual memory

We characterized the long-term residual memory (Figure SI.3) and for Film 1, its value was 4% after 10 hours. This value for the residual memory was still observed after months, indicating the V-shaped azo-chromophore as a potential material for application in optical switching devices.

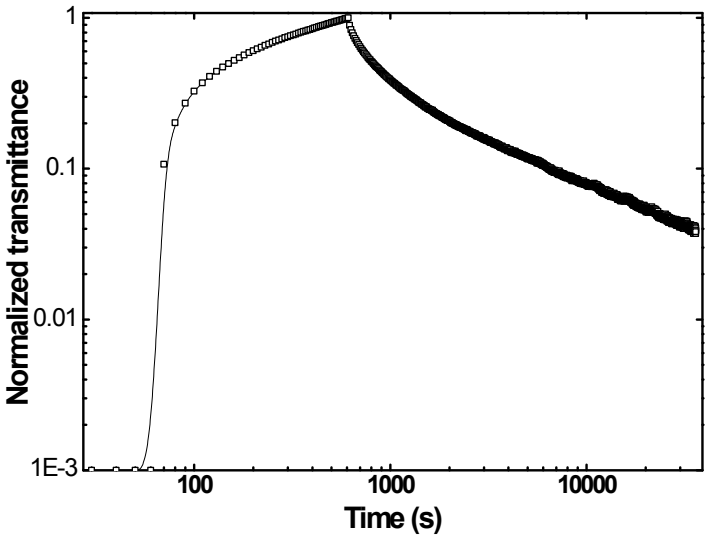

Figure SI.3 – Normalized transmittance as a function of the time (log-log scale).

References

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