Electronic Supplementary information

Molecular photo-oscillators based on highly accelerated heterocyclic azo dyes in nematic liquid crystals

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Synthesis of azo dyes 1-4:

Azo dyes **1-4** have been prepared as reported elsewhere.[1]

Physical data for mesogens I52 and ZLI-1695:

Mesogen	ε	d g·cm^{-3}	μ cm^2·s^{-1}	γ_1 g·cm^{-1}·s^{-1}	K_{11} pN
I52	2.9[2]	1.003[1]	0.18[3]	0.180	9.4[1]
ZLI-1695	8.7[1]	0.937[4]	0.61[2]	0. 575	7.0[5]

Table S1. Dielectric permittivity, ε, density, d, kinematic and rotational viscosities (μ and γ_1, respectively, where $\gamma_1 = \mu \times d$) and elastic constant for the director deformation, K_{11}, for the nematic mesogens **I52** and **ZLI-1695**.

Preparation and analysis of the samples used for the kinetic studies:

For the experiments in isotropic solvents, 20 μM solutions of the azo dye in the corresponding solvent were measured in 1 cm optical path quartz cells. For the nematic solutions, the concentration was *ca.* 4 mM and 10 μm quartz cells were used instead. Such samples were prepared by mixing the desired amounts of the mesogen and the corresponding azo dye followed by homogenization by magnetic stirring for 10 minutes in the isotropic state. Monodomain (macroscopically oriented) samples were prepared in 10 μm optical path quartz cells, its surface being rubbed with a piece of cloth in a single direction. Homogeneity of the samples was checked by local probe microscopy. POM experiments were run by rotation of the analyzer of the microscope with respect to the rubbing direction. On reaching 45º, the expected change from darkness to brightness was observed, which together with the absence of any characteristic texture was indicative of a successful macroscopic orientation of the nematic director. Polarized optical microscopy (POM) was performed in a Nikon Eclipse polarizing microscope at room temperature.

Kinetic measurements:

Nanosecond laser flash-photolysis setup: A population of *cis* isomers was created by pulsed-laser irradiation of the *trans* isomer at 532 nm employing a Continuum Surelite I-10 Q-switched Nd-YAG laser (5 ns pulse width, *ca.* 10 mJ per pulse). The concomitant absorbance changes were monitored at 90º by a white-light analysing beam produced by a Xe lamp (PTI, 75 W) in combination with a dual-grating monochromator (PTI 101) coupled to a Hamamatsu R928 photomultiplier for detection.[6] All transient absorptions were analysed at λ_{obs} = 500 nm.

UV-vis spectra:

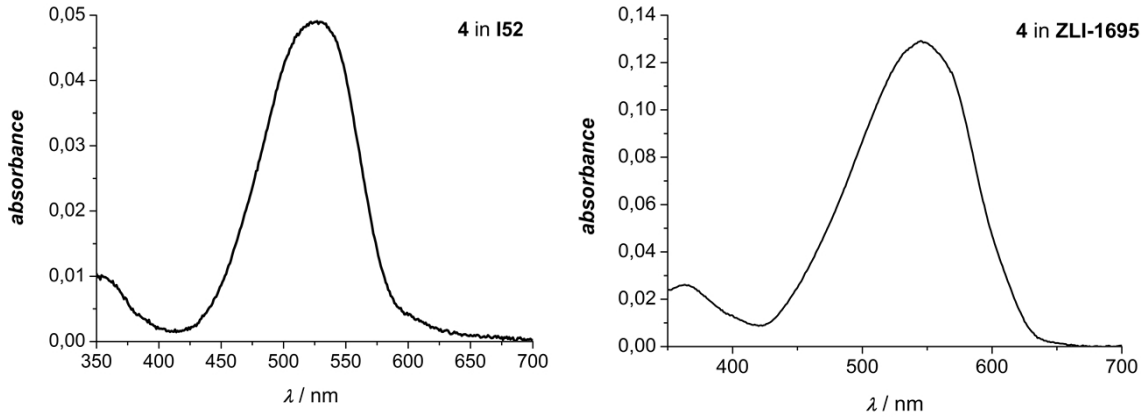

Figure S1. Absorption spectra for azo derivative 4 in the nematic mesogens **I52** (left) and **ZLI-1695** (right).

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[1] J. Garcia-Amorós, M. Cidália R. Castro, P. Coelho, M. Manuela M. Raposo and D. Velasco, *Chem. Commun.*, 2013, **49**, 11427.

[2] D. A. Dunmur, D. A. Hitchen and H. Xi-Jun, *Mol. Cryst. Liq. Cryst.*, 1986, **140**, 303.

[3] Data provided by Nematel Co.

[4] H. S. A Golicha, M. L. Mukhebi and H. S. Subramahanyam, *Chem. Proc. Eng. Res.*, 2013, **14**, 32.

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[6] N. Rubio, A. Jiménez-Banzo, T. Torres and S. Nonell, *J. Photochem. Photobiol. A*, 2007, **185**, 214.