*Electronic Supplementary Information for*

# Circularly polarized laser emission in optically active organic dye solutions

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**Supplementary experimental section:**

*Photophysical measurements:* The photophysical properties were registered using quartz cuvettes with optical pathway of 1 cm in diluted solutions (around $2\times10^{-6}$ M), prepared by adding the corresponding solvent to the residue from the adequate amount of a concentrated stock solution in acetone, after vacuum evaporation of this solvent. UV-Vis absorption and fluorescence spectra were recorded on a Varian model CARY 4E spectrophotometer and a SPEX Fluorolog 3-22 spectrofluorimeter, respectively. Fluorescence quantum yield ($\phi$) was obtained by using the commercial PM567 dye in ethanol as reference ($\phi^{r} = 0.84$). Radiative decay curves were registered with the time correlated single-photon counting technique (Edinburgh Instruments, model FL920), equipped with a microchannel plate detector (Hamamatsu C4878) of picosecond time-resolution (20 ps). Fluorescence emission was monitored at the maximum emission wavelength after excitation at 470 nm by means of a diode laser (PicoQuant, model LDH470) with 150 ps FWHM pulses. The fluorescence lifetime ($\tau$) was obtained after the deconvolution of the instrumental response signal from the recorded decay curves by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square) and the analysis of the residuals. Radiative ($k_{fl}$) and non-radiative ($k_{nr}$) rate constants were calculated as follows; $k_{fl} = \phi/\tau$ and $k_{nr} = (1-\phi)/\tau$.

*Circular Dicroism (CD) and Circularly Polarized Luminescence (CPL) measurements:* CD spectra were recorded in a Jasco (model J-715) spectropolarimeter using standard quartz cells of 1 cm optical path length. The circularly polarized luminescence (CPL) and total luminescence spectra were recorded on an instrument described previously [S1], operating in a differential photon-counting mode. The light source for excitation was a continuous wave 1000 W xenon arc lamp from a Spex Fluorolog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersion of 4 nm/mm (SPEX, 1681B). To prevent artifacts associated with the presence of linear polarization in the emission, a high quality linear polarizer was placed in the sample compartment, and aligned so that the excitation beam was linearly polarized in the direction of emission detection (z-axis). The key feature of this geometry is that it ensures that the molecules that have been excited and that are subsequently emitting are isotropically distributed in the plane (x,y) perpendicular to the direction of emission detection. The optical system detection consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emitted light was detected by a cooled EMI-9558B photomultiplier tube operating in photo-counting mode.

*Laser measurements experimental set-up:* A sketch of the experimental set-up used in this work is depicted in Figure S2. The dyes dissolved in organic solvents were placed in 1 cm optical path quartz and optically pumped at 532 nm with a frequency-doubled Q-switched Nd:YAG laser (Lotis TII SL-2132) emitting 20 ns full width at half maximum (FWHM) and operated at 15 Hz repetition rate. Pump energy was measured with a calibrated pyroelectric energy meter (ED200, GenTec). The pump laser radiation was horizontally polarized, which allows controlling the pulse energy incident on the sample by insertion into the pump beam path of a half-wave plate (HWP) and a linear polarized (LP) set with its polarization axis horizontal or vertical, depending on the desired final pump polarization. By rotating the HWP, the linear polarization of the input beam is rotated out of the horizontal, and the pump beam is blocked more or less by the LP, depending on the rotation angle introduced by the HWP. In the transversal pumping configuration measurements, the light incident on the sample was perpendicularly to the surface of the cuvette and focused onto that surface in a stripe shape of ~ 300 μm width by a combination of negative (NCL) and positive (PCL) cylindrical quartz lens (f=-15 and +15 cm, respectively) perpendicularly arranged. The oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminium back mirror and the end face of the cuvette as output coupler. A beam splitter was used to send a reflection of the pump beam into a photo-diode acting as the trigger. The trigger signal was fed to a boxcar (Standford Research, model 250) to convert it to a delayed TTL pulse to trigger the digital oscilloscope (Yokogawa, model DL1620). The photo-diode signal was also sent to the oscilloscope and used as reference signal to monitor and control the pump energy along the experiments. To analyze the polarization degree and state of the dye laser emission we tailored a polarimeter based on a Fresnel rhomb, acting as a quarter-wave plate, combined to a linear polarized (Thorlabs LPVISB100-MP) and a pyroelectric energy meter, which signal was registered with the oscilloscope.

*Polarimetry formalism:* The global polarization state of a given arbitrary beam can be described in terms of the Stokes parameters $S_i$ (i = 0, 1, 2, 3) [S1], which are related to the beam energy ($E_{out}$), the degree of polarization ($DOP$), the degree of circular polarization ($DOCP$), and the orientation ($\psi$) and ellipticity ($\chi$) of the polarization ellipse (Fig. 2a) as:

$$\begin{aligned} &E_{out} = S_0 \\ &DOP = \frac{\sqrt{S_1^2 + S_2^2 + S_3^2}}{S_0};\ DOCP = \frac{S_3}{S_0} \\ &2\psi = \arctan\frac{S_2}{S_1} \\ &2\chi = \arcsin\frac{S_3}{DOP\cdot E_{out}} = \arctan\frac{S_3}{\sqrt{S_1^2 + S_2^2}} \end{aligned} \qquad \text{(S1)}$$

To measure the Stokes vector, we used a home-made polarimeter with a rotating polarizer (or analyzer) and a static λ/4 retarder, a Fresnel rhomb in our case (Figure S2), and applying the Mueller matrix formalism [S2] (see ref. S3 for full details). To retrieve $S_0$ to $S_3$ two sets of measurements must be performed. The first set corresponds to the energy of the beam after it has crossed the polarizer as a function of the polarizer transmission axis angel $\theta$, which follows the expression:

$$E_{out}^{p}(\theta)=\frac{T^{p}}{2}\left[S_0+S_1\cos 2\theta+S_2\sin 2\theta\right] \tag{S2}$$

where $T^p$ is the polarizer transmission. The second set corresponds to the energy of the beam after it has crossed first the λ/4 retarder with its fast axis at a given angle $\beta$ (~π/2) and then the polarizer as a function of $\theta$. In this case, the output energy will depend on $\theta$ as:

$$\begin{aligned}E_{out}^{p,\lambda/4}(\theta)=\frac{T^{p,\lambda/4}}{2}&\Big[S_0+\left(S_1\cos^2 2\beta+S_2\sin 2\beta\cos 2\beta-S_3\sin 2\beta\right)\cos 2\theta\\&+\left(S_1\sin 2\beta\cos 2\beta+S_2\sin^2 2\beta+S_3\cos 2\beta\right)\sin 2\theta\Big]\end{aligned} \tag{S3}$$

where $T^{p,\lambda/4}$ is the polarizer/rhomb combined transmission. A simultaneous fit of equations (S2) and (S2) to the first and second sets of data, respectively, will provide $S_0$ to $S_3$ as fitting parameters. Once the Stokes parameters are known, the polarization state in terms of $E_{out}$, *DOP*, *DOCP*, $\psi$ and $\chi$, can be calculated using equations (S1). There are alternative parameters to account for the degree of circularization or ellipticity of a given light beam. For example, the works dealing with Circularly Polarized Luminescence (CPL) make use of the so-called dissymmetry factor $g_{lum}$, which is minus twice the degree of circular polarization (*DOCP*) as defined in equations (S1). $g_{lum}$ will be as well evaluated in our work.

**Supplementary figures**

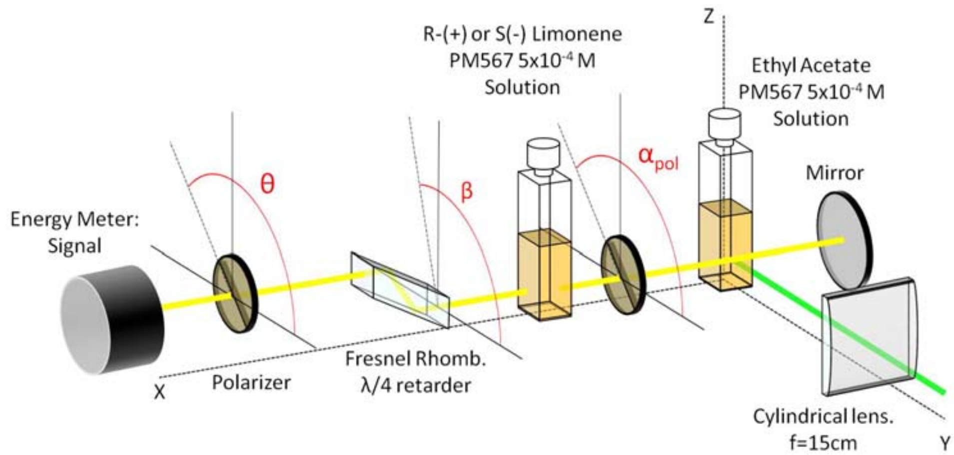


**Figure S1:** Sketch of experimental set-up used to measure the OA specific rotation.

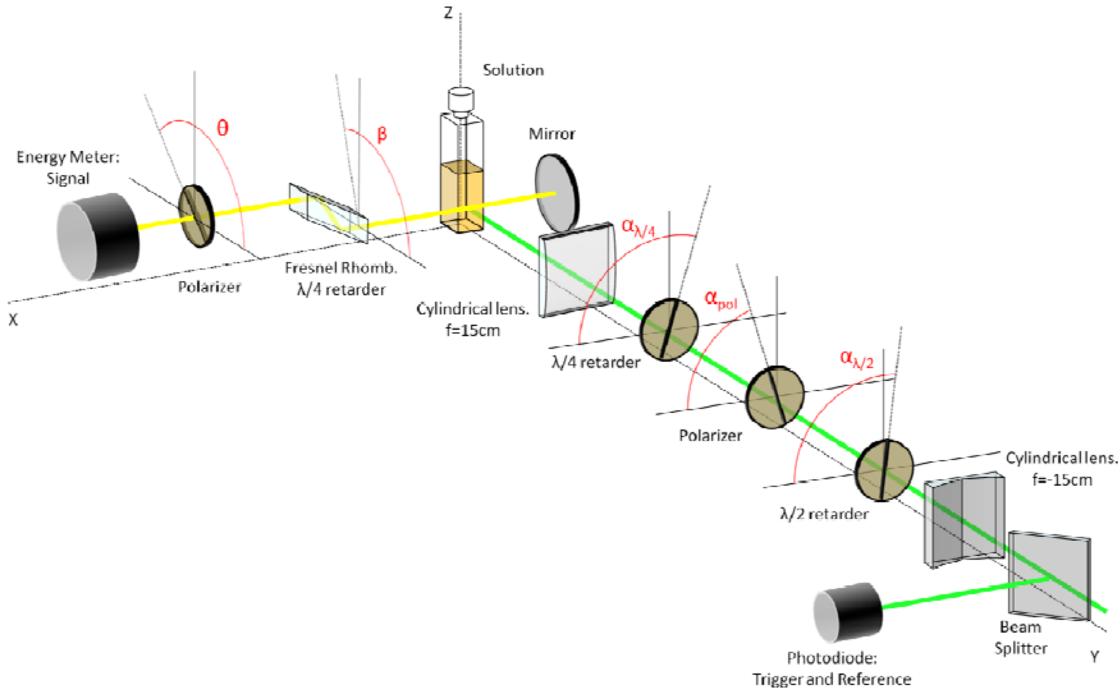


**Figure S2**: Sketch of experimental set-up used to determine the polarization state of a dye laser as a function of the pump polarization state. The optical elements axis angles and ellipticity direction of the different beams are determined looking towards the source of light.

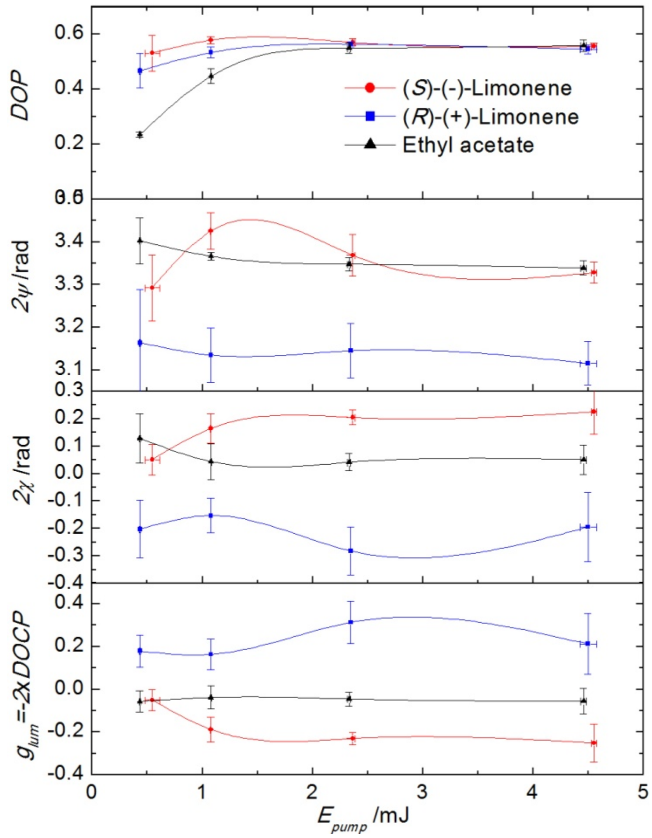


**Figure S3:** Laser emission polarization state parameters as a function of pump energy for a linear 45º pump polarization. Each point and error bar represents the average and standard deviation, respectively, of the fitting parameters obtained over 4 sets of measurements. Lines are guides to the eye.

**References:**.

[S1] E. Brunet, L. Jiménez, M. de Victoria-Rodríguez, V. Luu, G. Muller, O. Juanes, J. C. Rodríguez-Ubis, *Microporous and Mesoporous Mater.* **2013**, *169*, 222-234., and references therein.

[S2] M. Born and E. Wolf, *Principles of Optics*, 5$^{th}$ Ed. (Pergamon Press, 1975)

[S3] R. A. Chipman, "Polarimetry," chapter 22 in *Handbook of Optics II*, 2nd Ed, M. Bass, editor in chief (McGraw-Hill, New York, 1995).

[S4] L. Cerdán, S. García-Moreno, A. Costela, I. García-Moreno, S. de la Moya, *Sci. Rep.* **2016**, *6*, 28740.