

Supporting Information –

All-Optical Emission Control and Lasing in Plasmonic Lattices

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1. Photostationary state composition

The absorption spectra of a 53 μM indolinospiropyran solution in a 1 cm cuvette upon illumination with 365 and 550 nm are shown in Fig. S1. Upon illumination with 550 nm, the molecules are purely in the SPI form, whereas upon illumination with 365 nm, a photostationary state (PSS) with both SPI and MC forms is reached (see Fig. S1 (a)). Due to the spectral shape of the isomers, the PSS composition cannot be deduced from this data only.

However, the composition can be approximated by comparing the measured molar extinction coefficient of the MC absorption band with a literature value for the pure isomer. In polar protic solvents, ϵ_{MC} can be approximated to be $5.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.¹ From this value, the PSS composition can be estimated to contain 14% MC and 86% SPI. However, no specific value was available for benzyl alcohol and the approximation should thus be treated with caution. Similar spectra were acquired between a microscope slide and a cover glass (7.0 μl of 40 mM solution between the glass slides). The molar absorptivity cannot be measured as the precise optical length is not known, but based on the relative intensity of the peaks at *ca.* 350 and 550 nm, the PSS composition is very close to that observed in the more diluted solution.

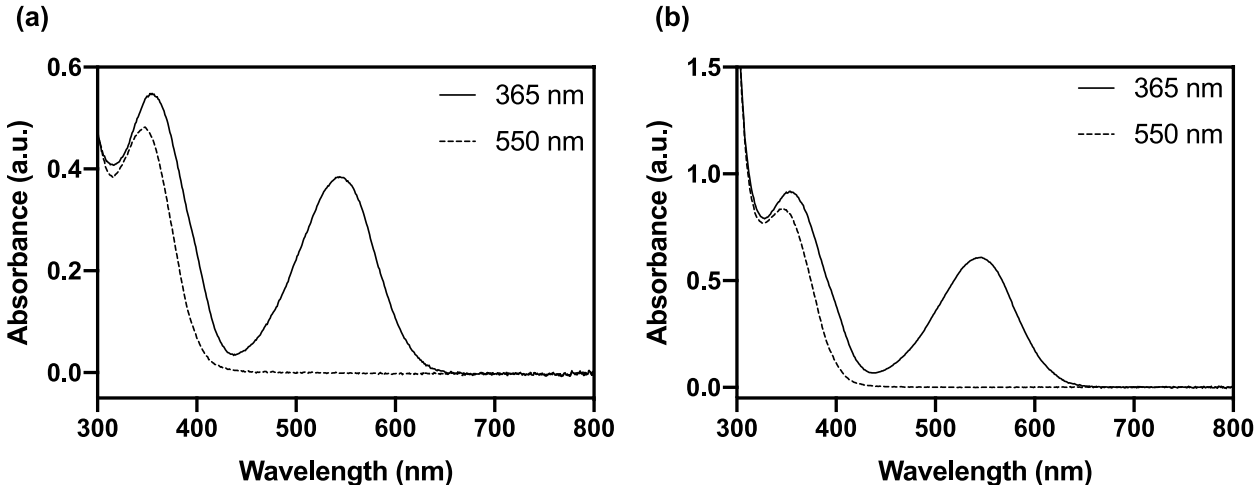


Figure S1: The absorption spectrum of the pure SPI isomer (dashed line) and the photostationary mixture of SPI and MC (solid line) in (a) 53 μM benzyl alcohol solution in a 1 cm quartz cuvette and (b) 40 mM benzyl alcohol solution between a microscope slide and a cover glass.

2. Thermal lifetime of the MC form

Thermal relaxation from the MC form back to the pure SPI was studied in both solutions at room temperature, yielding a good monoexponential fit in both cases. Interestingly, the lifetime of the relaxation was significantly longer for the more concentrated sample. It should

be noted that the relaxation seems to end up in a mixture of SPI and MC with *ca.* 3% MC with the earlier approximation, meaning that the isomerization is not fully reversed with heat. The monoexponential decay fits shown in Fig. S2 are of the form

$$A(t) = A_{\text{inf}} + (A_0 - A_{\text{inf}})e^{-t/\tau}, \quad (\text{S1})$$

where t is time, A_0 is the absorbance at $t = 0$, A_{inf} is the lowest absorbance reached *via* thermal relaxation and τ is the lifetime of the relaxation. Table S1 shows the thermal relaxation parameters for both solutions.

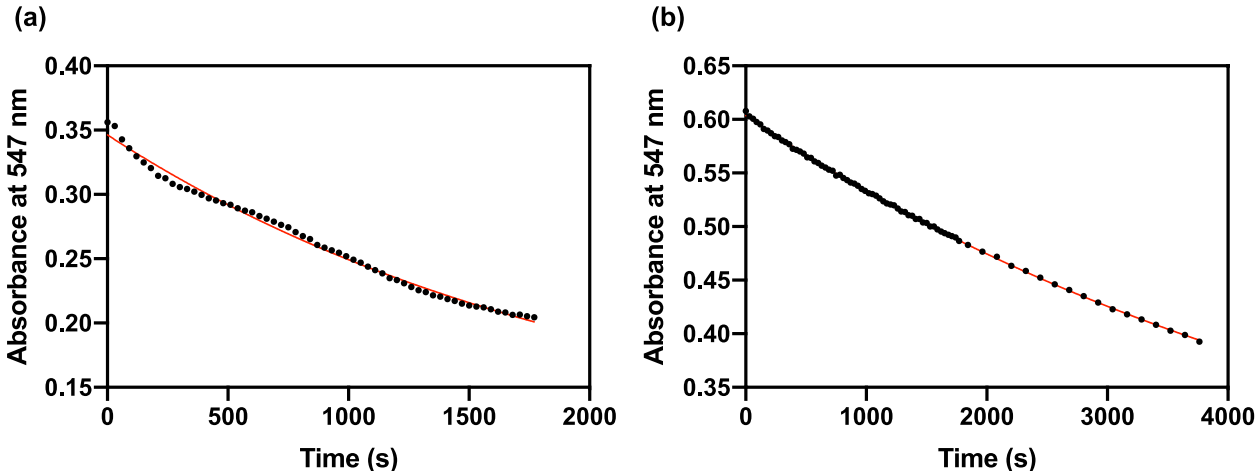


Figure S2: Measured absorbance of indolinospirpyran at 547 nm upon thermal relaxation from PSS to thermal equilibrium (black dots) and an exponential decay fit (red line) for (a) 53 μM and (b) 40 mM in benzyl alcohol solution.

Table S1: Parameters for the thermal relaxation (Eq. S1) from PSS after illumination with 365 nm. Here $\tau_{1/2}$ is the half-life of the fluorescence.

	$\tau_{1/2}(\text{s})$	$\tau(\text{s})$	A_0	A_{inf}	R^2
53 μM	1424	2055	0.3464	0.0945	0.9928
40 mM	3767	5435	0.6037	0.1840	0.9997

3. Fluorescence lifetimes

Fluorescence decay curves were measured for pure C6 as well as a mixture of C6 (30 mM) and indolinospiropyran (40 mM) after irradiation with 550 nm and 365 nm (SPI and MC forms). The fluorescence lifetime of pure C6 was measured in a more diluted solution (*ca.* 100 μ M). The fluorescence intensity decay curves are presented in Fig. S3. The decays of diluted C6, C6 + SPI and C6 + MC were fitted with bi- or triexponential functions (Table S2, Fig. S4).

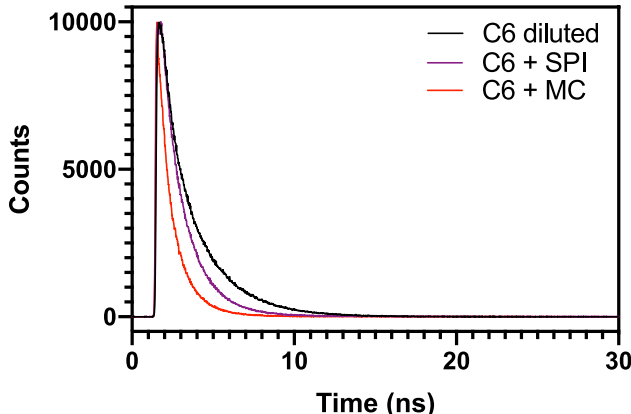


Figure S3: Fluorescence intensity decay of C6 at *ca.* 100 μ M concentration, and C6 (30 mM) + indolinospiropyran (40 mM) upon illumination with 550 nm (SPI) and 365 nm (MC).

Table S2: Lifetimes obtained by multiexponential fitting to the measured fluorescence lifetimes shown in Figs. S4 (a-c). Also shown are the pre-exponential factors (amplitudes) of each fitting in brackets.

	τ_1	τ_2	τ_3
C6 <i>ca.</i> 100 μ M	2.36 ns (0.0816)	-	0.41 ns (0.0541)
C6 + SPI	1.42 ns (0.1072)	5.51 ns (0.0016)	0.26 ns (0.0231)
C6 + MC	1.06 ns (0.0796)	5.17 ns (0.0006)	0.14 ns (0.0977)

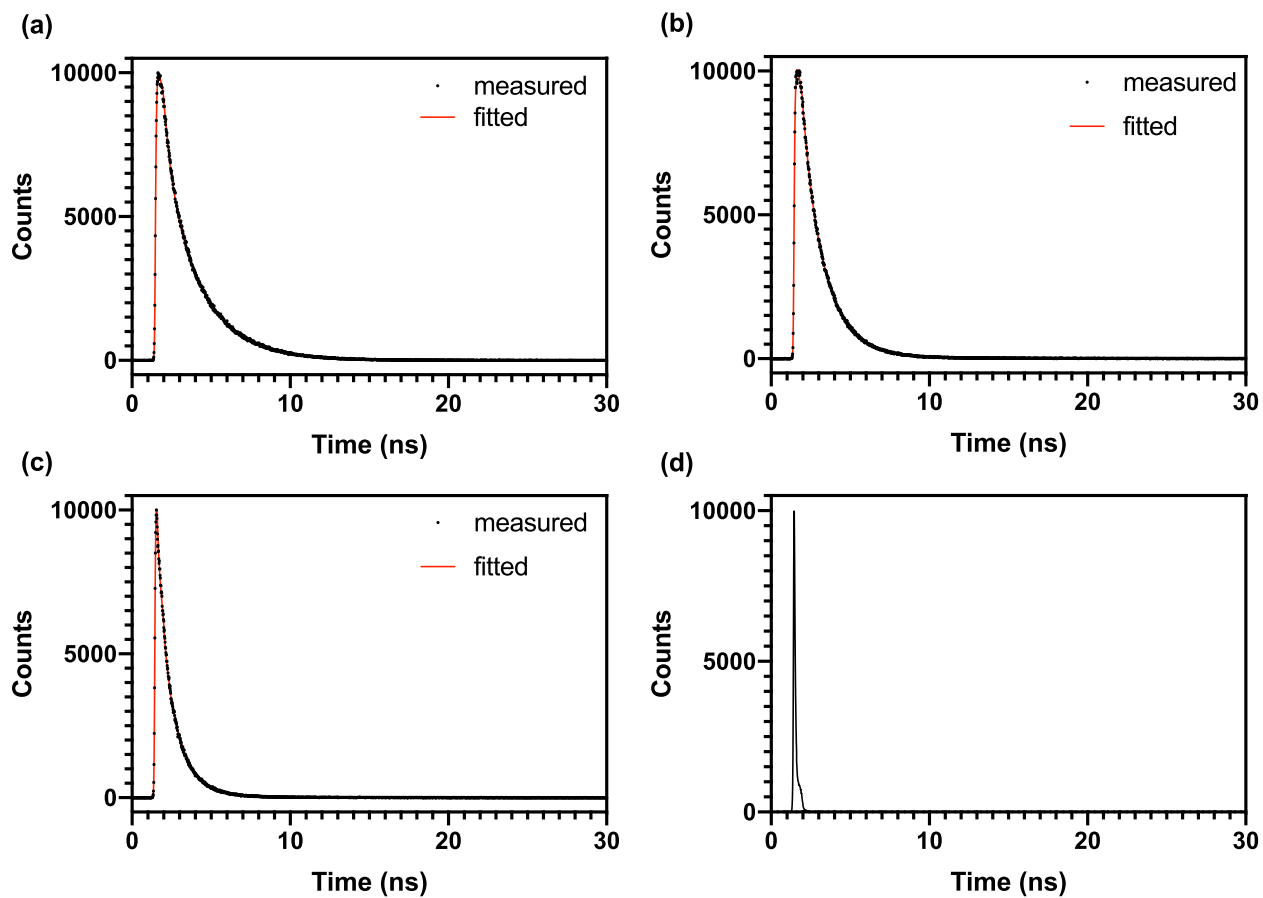


Figure S4: Measured and fitted fluorescence decay curves for (a) *ca.* 100 μ M C6, (b) C6 + SPI and (c) C6 + MC, and (d) instrument response function.

4. Lifetimes in the rate-equation model

We obtain the radiative and non-radiative lifetimes from the fluorescence lifetime measurement shown in manuscript Fig. 2 (c). The decrease of the effective fluorescence lifetime from 1.42 ns to 1.06 ns upon SPI-MC isomerization is attributed to the increased non-radiative energy transfer between the compounds. We can write the following relations between the radiative (rad) and non-radiative (nrad) lifetimes of the dye in the SPI and MC forms:

$$\frac{1}{\tau_{\text{C6+SPI,rad}}} + \frac{1}{\tau_{\text{C6+SPI,nrad}}} = \frac{1}{1.42} \quad (\text{S2})$$

$$\frac{1}{\tau_{\text{C6+MC,rad}}} + \frac{1}{\tau_{\text{C6+MC,nrad}}} = \frac{1}{1.06}. \quad (\text{S3})$$

Assuming the SPI-MC isomerization does not directly affect the radiative spontaneous emission lifetime, we can write $\tau_{\text{C6+SPI,rad}} = \tau_{\text{C6+MC,rad}}$ and denote this lifetime as τ_{21} . Further, taking that the intermolecular non-radiative energy transfer is negligible in the case of non-absorbing form, $1/\tau_{\text{C6+SPI,nrad}} \approx 0$, we arrive to

$$\frac{1}{\tau_{21}} = \frac{1}{1.42} \quad (\text{S4})$$

$$\frac{1}{\tau_{21}} + \frac{1}{\tau_{20}} = \frac{1}{1.06}. \quad (\text{S5})$$

From here we obtain $\tau_{21} = 1.42$ ns and $\tau_{20} = 4.2$ ns. When modelling the photoswitching, τ_{20} is changed linearly from 4.2 ns (MC form) to a large value 10 ns (SPI form). The upper value 10 ns is chosen sufficiently long such that it has negligible effect on the system dynamics. We note that, overall, the values of τ_{20} are so large compared to other timescales of the system that the parameter has very little effect on the simulation results.

5. Schematic of the angle-resolved measurement setup

A schematic of the experimental setup used in the angle- and wavelength-resolved intensity measurements is shown in Fig. S5. A pump iris and a pump lens are used to image a flat pump spot to the sample. An infinity-corrected objective and a corresponding tube-lens form a magnified image of the sample at the real space iris, which spatially restricts the setup to only image the sample array. Finally, a k-space lens is used to form a Fourier image of the sample at the spectrometer slit. A halogen lamp is used to both illuminate the sample for the real space camera and function as a light source in transmission measurements.

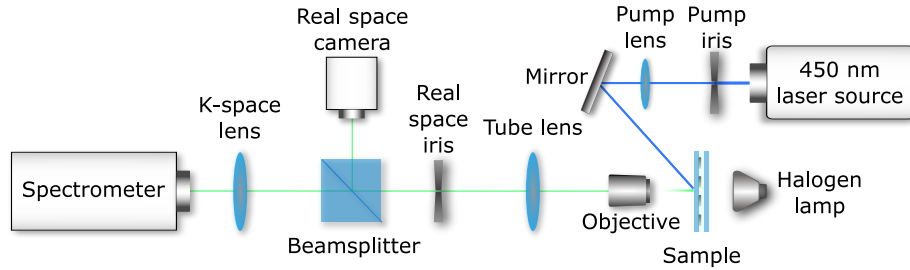


Figure S5: Schematic of the experimental setup used to obtain the angle- and wavelength-resolved intensity data.

6. Sample emission line width as a function of pump fluence

Fig. S6 shows the emission line width of the lasing sample as a function of pump fluence measured from the data set presented in Fig. 3 (a-b). The lower limit of the measured line widths was instrument-limited and shows slightly higher values compared to the data shown in Fig. 5 (d).

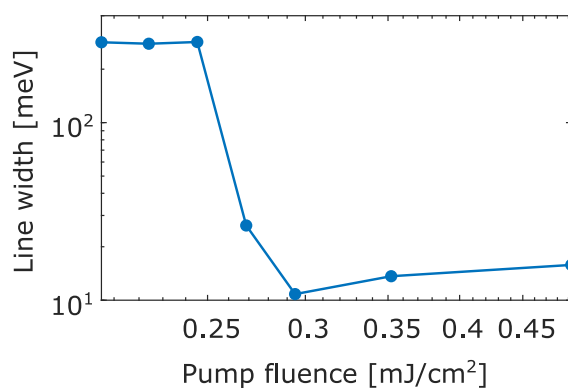


Figure S6: Emission line width (FWHM) of the lasing sample as a function of pump fluence.

Supplementary References

- (1) Görner, H. Photochromism of nitrospiropyrans: effects of structure, solvent and temperature. *Phys. Chem. Chem. Phys.* **2001**, *3*, 416–423.