

Supplementary information for

One- and two-photon lasing from TCF-based AIE dye

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1. Materials and Methods

Samples preparation

Liquid samples were prepared by dissolution of 2,4,6-OMe-TCF in THF solvent. Next, every sample was placed in an Emmi-20HC ultrasonic bath for 1 hour at $\sim 70^{\circ}\text{C}$. All obtained concentrations were as follows: 0.10, 0.20, 0.35; 0.45; 0.50; 0.63; 0.71; 0.83; 0.90; 1.0; 1.1; 1.2; 1.4; 1.5; 2.0; 4.0 and 8.0 mg/mL.

For studying the influence of aggregation on laser emission, firstly 1ml of 0.90 mg/mL 2,4,6-OMe-TCF/THF was put into a quartz cuvette, and next, a 50 μL of H_2O was added repeatedly until the water amount reached the value of 58%.

A polymeric sample with polymethylmethacrylate (PMMA) was fabricated by adding 100 μl of 1.15 mg/mL 2,4,6-OMe-TCF in THF solution to 300 μl 2% PMMA/THF mixture. The 2,4,6-OMe-TCF was synthesized according to the procedure described in ref [1]. The PMMA was obtained from Sigma Aldrich, is characterized by the molecular weight of 120 *kDa*, and was used as received.

In order to fabricate thin polystyrene (PS) film, the 500 μL of 2 mg/mL 2,4,6-OMe-TCF were added to 630 μl 6% PS/THF solution. The PS of molecular weight equal to 280 *kDa* was purchased from Sigma Aldrich and used as received.

The concentrations of both samples with respect to the polymer mass were approximately equal to 1.92 % for PMMA and 2.53 % for PS.

The drop-casting technique was selected to obtain a layer for the PMMA sample mainly because the refractive index of this polymer is slightly lower than the refractive index of the glass substrate (1.49 at 633 nm for PMMA and 1.52 at 546 nm for glass). Therefore, a thicker layer was desired for our experiments, as the PMMA itself cannot support the waveguiding effect. The PMMA sample was dried in THF rich atmosphere to reduce the speed of the evaporation process and improve the quality of the resulting layer.

To fabricate the second sample, we have chosen PS, which has a refractive index higher than glass, approx. 1.59 at 633 nm. In such a case, the layer can be much thinner; thus, we decided to use a Polos SPIN150i spin-coater to fabricate the film.

The thicknesses of the samples were obtained using a DeKTAk3 profilometer by averaging five measurements for each sample.

Absorption and fluorescence measurements

Absorption measurements were carried out using the Jasco V-670 UV-VIS-NIR Spectrometer in the range between 385 and 700 nm. The fluorescence spectra were collected using the Hitachi F-4500 Fluorescence Spectrophotometer in a spectral range spanning between 500 and 700 nm.

One photon-excited lasing (1PEL)

a) Experimental setup

For one-photon excited lasing measurements, we have used the third harmonic ($\lambda = 355$ nm) of a nanosecond ($\tau = 5$ ns) Nd:YAG pulsed laser (Surleite II by Continuum), operating with the repetition frequency $f = 10$ Hz to pump the Optical Parametric Oscillator (Horizon, mid-band OPO by Continuum). The OPO was used to select the proper excitation wavelength, which was equal to $\lambda = 477$ nm in all of our measurements. The laser beam from the OPO was directed through a half-wave plate, a polarizer, and a system of lenses to excite samples containing the TCF derivative. The pair of a half-wave plate and polarizer was used to keep the vertical, linear polarization of the exciting beam and in order to provide control over its intensity by rotation of the half-wave plate azimuth. In each case, the sample was positioned behind a regulated slit, close to the cylindrical lens focal point. Such a design of an optical system was used to form an exciting area shape into a long and thin stripe. The laser emission from samples was collected via an optical fiber along the longer "excitation stripe" dimension and perpendicular both to the direction of the pumping beam propagation and polarization, followed by a Czerny-Turner Spectrometer (Andor Shamrock SR-303i) equipped with a CCD camera (Andor iDus).

b) Stimulated emission from liquid solutions in the function of dye concentration.

All measurements were carried out in a quartz cuvette with the dye solution and a magnetic stirrer. The cuvette was placed on a stirrer plate at the same distance from the cylindrical lens each time, and the stirring (1000 rpm, at room temperature) was enabled during all measurements. The excitation beam was focused on a sample in such a way that it formed a 6.5 mm long and 0.2 mm high "excitation stripe." In order to determine the threshold conditions, the energy of the pumping beam was changed during the experiment.

c) Stimulated emission from liquid solutions with water addition.

All measurements were carried out with stirring (1000 rpm, at room temperature) and light focused into a 6.5 mm long "excitation stripe." During the whole experiment duration, the

cuvette was placed in the same position with respect to the cylindrical lens. The pumping energy was kept at the same level and was above the threshold condition of a pristine sample ($\sim 285 \mu\text{J}$). The cuvette was filled with 1 mL of 0.9 mg/mL dye solution, and then 50 μL of water was added consecutively, dose by dose. After each dose of water was injected into the solution, we monitored 600 spectra to record the kinetic behavior of the laser emission upon water addition.

d) Stimulated emission from polymeric films.

In order to perform 1PEL experiments for thin films, we have removed the stirring plate from the experimental setup. Samples in the form of thin films deposited on glass slides were placed into a microscopy slide holder and were excited from the side of the layer. For this purpose, we used the same excitation source as in the previous case; however, the threshold comparison was carried out for "excitation stripes" of 3 mm in length and 0.25 mm in height for PS and 3 mm in length, and 0.5 mm in height for PMMA. Measurements concerning lasing threshold determination were carried out for spectra averaged over 15 pulses.

e) Stimulated emission from the powder.

The dye powder was placed between two microscopic glass slides, stuck together with transparent duct tape, and investigated in a similar way as polymeric layers. The "stripe" of excitation was 5 mm long and 0.78 mm high and had a wavelength equal to 477 nm. Measurements concerning lasing threshold determination were carried out for spectra averaged over 15 pulses.

Two-photon excited lasing (2PEL) measurements

Samples in the form of films deposited on glass slides were excited with a beam of femtosecond pulses generated by an amplified femtosecond system (Coherent Legend Elite Duo) at a 5 kHz repetition rate and Opera Solo optical parametric amplifier (OPA) providing femtosecond pulses (pulse width 110 fs) at the wavelength used in the current study (840 nm).

The output beam of the parametric amplifier was first expanded with a telescope formed by a pair of spherical lenses with focal lengths of -50 mm and 125 mm and then focused at the sample position with a cylindrical lens with a focal length of 75 mm. The energy of the pulses was controlled with a half-wave plate mounted in front of a reflective wire-grid polarizer (Meadowlark Versalight VLR-100-NIR), and the average beam power was measured with the Ophir Vega power meter with the 3A-SH head. Samples were mounted on a rotating mount with the rotation axis perpendicular to the film plane in order to reduce the photobleaching. The

emitted light was collected in the plane of the films, along the direction of the elongated linear focus of the cylindrical lens, and delivered to the Ocean Optics USB 2000 spectrometer with the help of an optical fiber.

Transmission and scattering measurements

The light from the He-Ne laser (Spectra-Physics Model 127, $\lambda = 633 \text{ nm}$, $P = 22.4 \text{ mW}$) was directed to a half-wave plate in order to change the light polarization from linear horizontal to linear vertical. Next, a PM120D photodiode coupled with PM100D digital console (Thorlabs) was used to measure the light transmission through the 1 cm long quartz cuvette (filled with THF only and studied solutions). During the transmission measurements, another PM120D photodiode coupled with PM100D digital console (Thorlabs) measured the He-Ne laser light scattered at the right angle with respect to the light direction propagation. In order to increase the intensity of scattered light, a spherical lens (1 inch in diameter and 10 cm of focal length) was used to focus the light on a detector.

Dynamic light scattering measurements

DLS analysis of the solutions/dispersions was performed using a Zetasizer Nano-ZS ZEN3600 system equipped with a red laser (633 nm, 4 mW) (Malvern Instruments Ltd., England). The incident laser power was adjusted to specific levels as needed by using a built-in attenuator. The detection angle was set at 173° . The temperature of the measurement was set as 25°C (equilibrated for the 60s). Refractive indexes and viscosities at 25°C for measured solvents were interpolated according to the data from reference [2]. Two or three DLS measurements were performed for each sample with an automatically set run time. The Zetasizer Software Version 7.13 was applied to process and analyze the data.

X-ray diffraction measurements

X-ray diffraction measurements were performed using a PANalytical Empyrean X-ray diffractometer equipped in PIXcel^{3D} detector. The powder was measured in continuous mode, in the range of angles spanning between 5.009 and 99.987 degrees, with size step equal to 0.0013 degrees and scan step time equal to 198.645s. The used wavelength was $\lambda = 1.39225 \text{ nm}$.

2. Dynamic behavior of RL emission

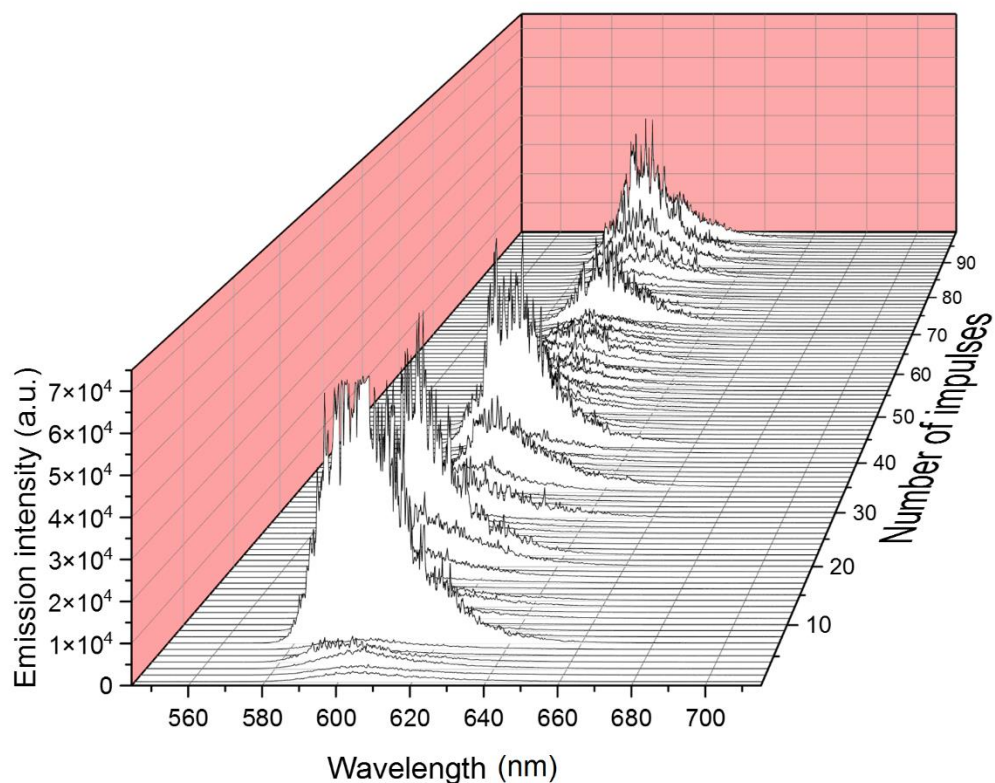


Fig. S1. The waterfall graph shows the chaotic character of RL in 0.9 mg/mL 2,4,6-OMe-TCF/THF solution over 100 pulses.

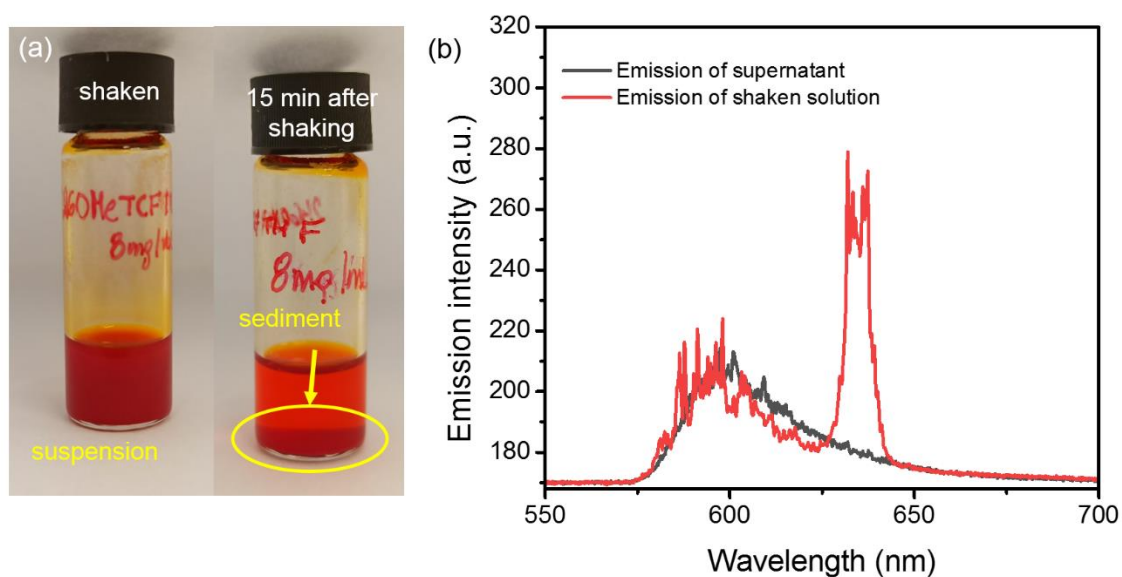


Fig. S2. Photographs of a shaken solution containing 8 mg/mL of TCF dye forming a suspension and the same solution after 15 min with clearly visible sediment (a). A comparison of a single RL spectrum recorded for a suspension formed just after shaking (red line) and clarified solution – a supernatant above the sediment (black line) (b).

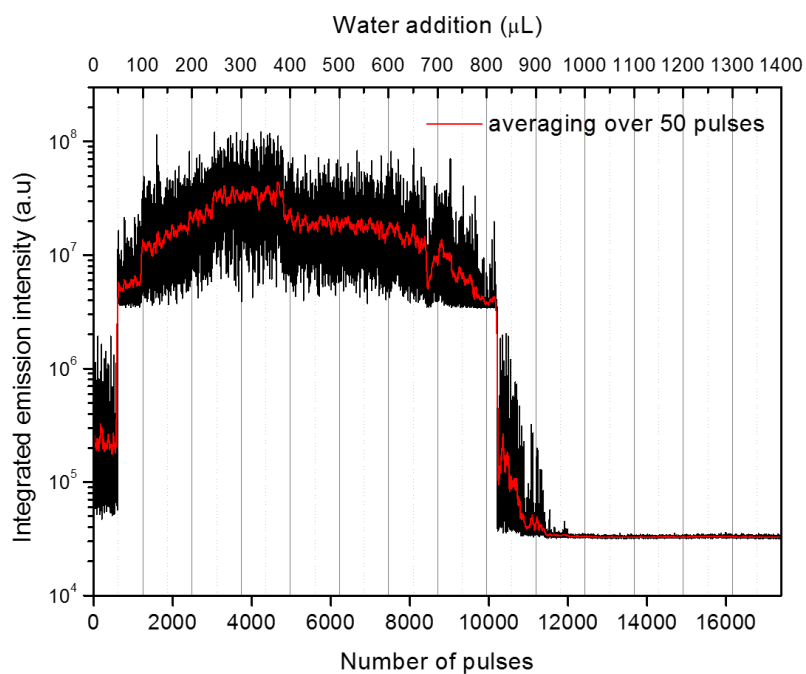


Fig. S3. Dynamics of the integrated emission intensity upon consecutive water addition. The red curve represents the averaged value of the intensity integrated over 50 spectra.

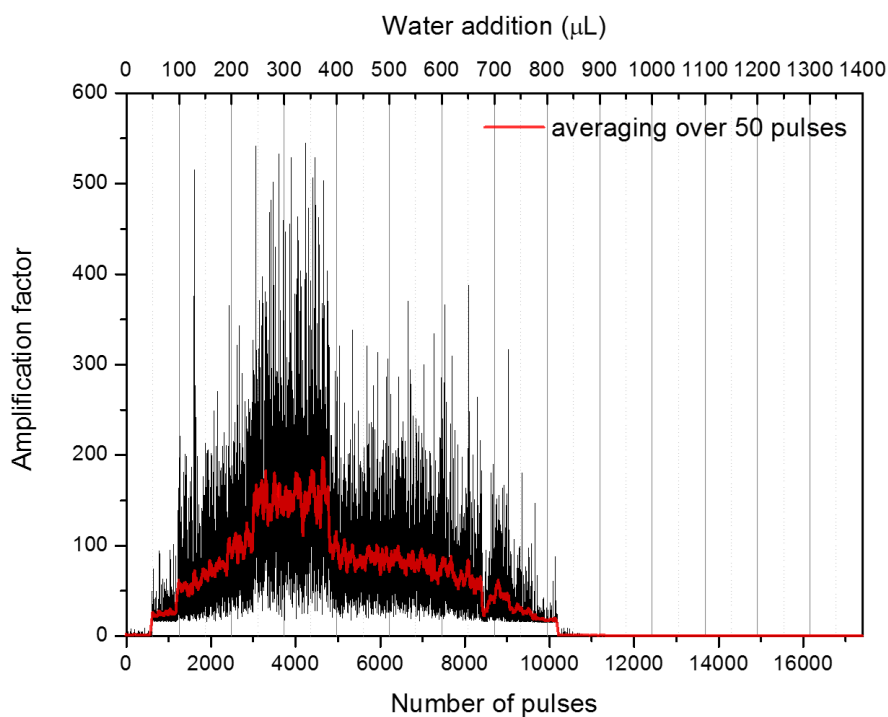


Fig. S4. Dynamics of the amplification factor upon consecutive water addition. The red curve represents the averaged value of the amplification factor over 50 spectra.

3. AIE of 0.1mg/mL TCF solution

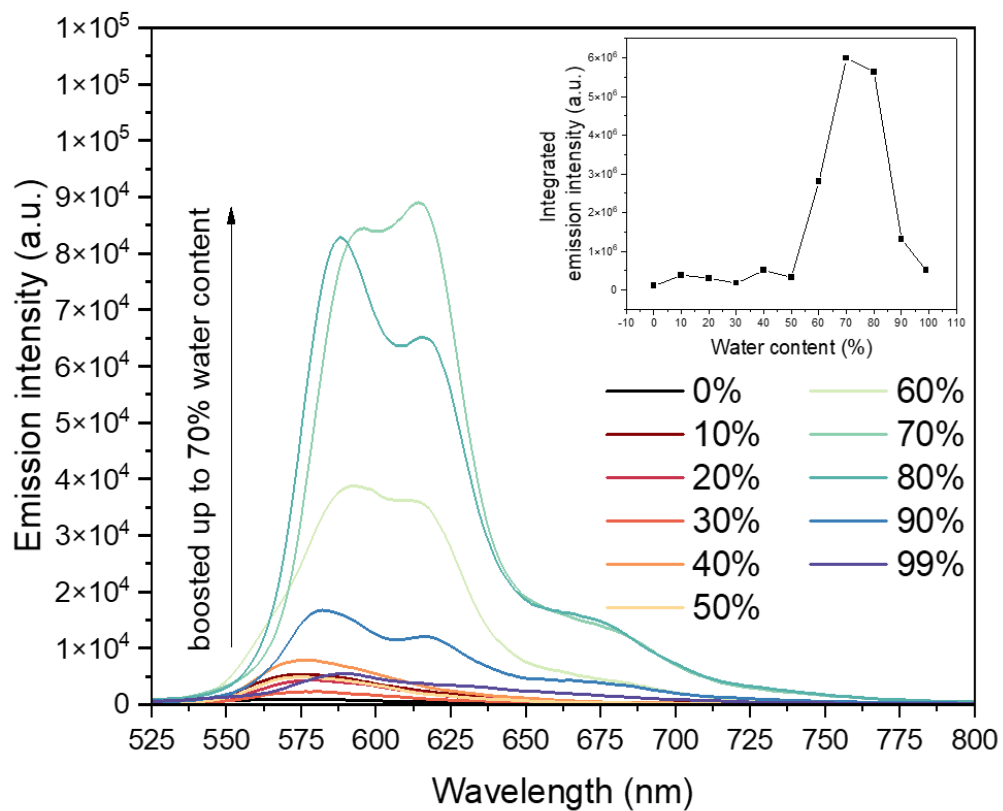


Fig. S5. Evolution of fluorescence spectra for 2,4,6-OMe-TCF in THF solution (0.1 mg/mL) after adding water. The inset presents the emission intensity boosted up to 55 times for 70% water content.

4. RL in polymeric layers

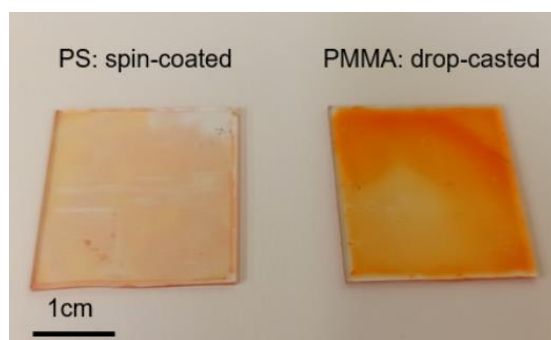


Fig. S6. A photograph of spin-coated and drop-casted polymeric samples made of PS and PMMA doped with 2,4,6-OMe-TCF at the concentration of ~2% with respect to the polymer mass.

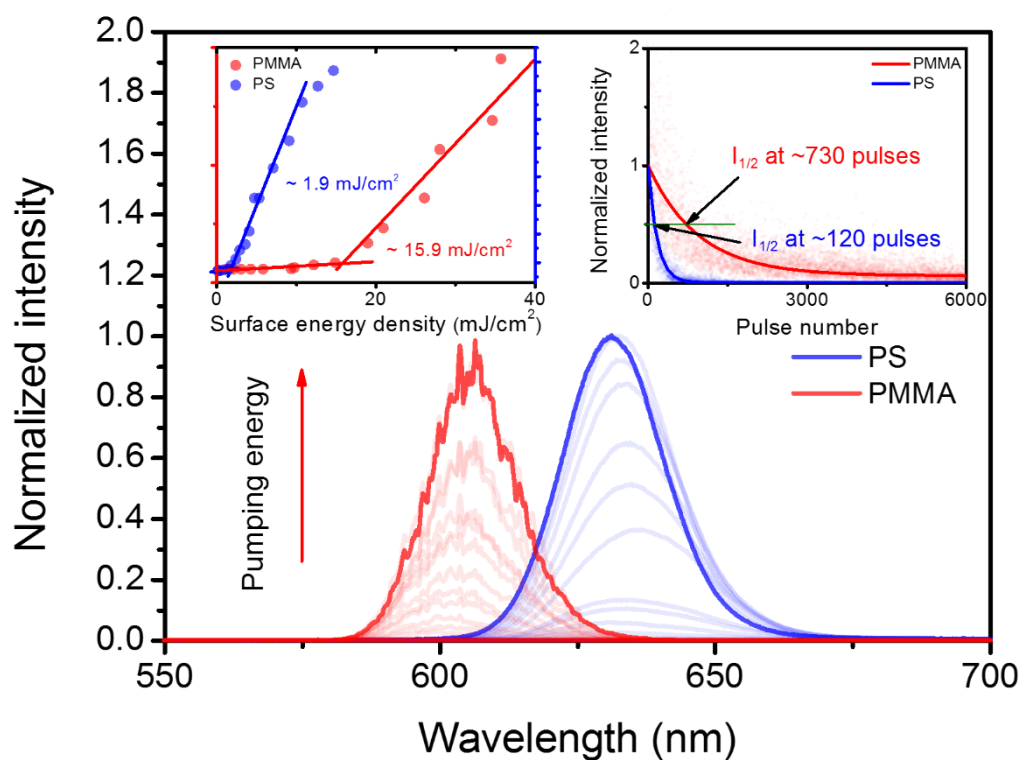


Fig. S7. An evolution of stimulated emission spectra with increasing pumping energy acquired from PS and PMMA samples. Insets show the energy thresholds and photodegradation curves recorded for the same excitation energy fluence equal to 306 μ J.

5. RL in the powder sample

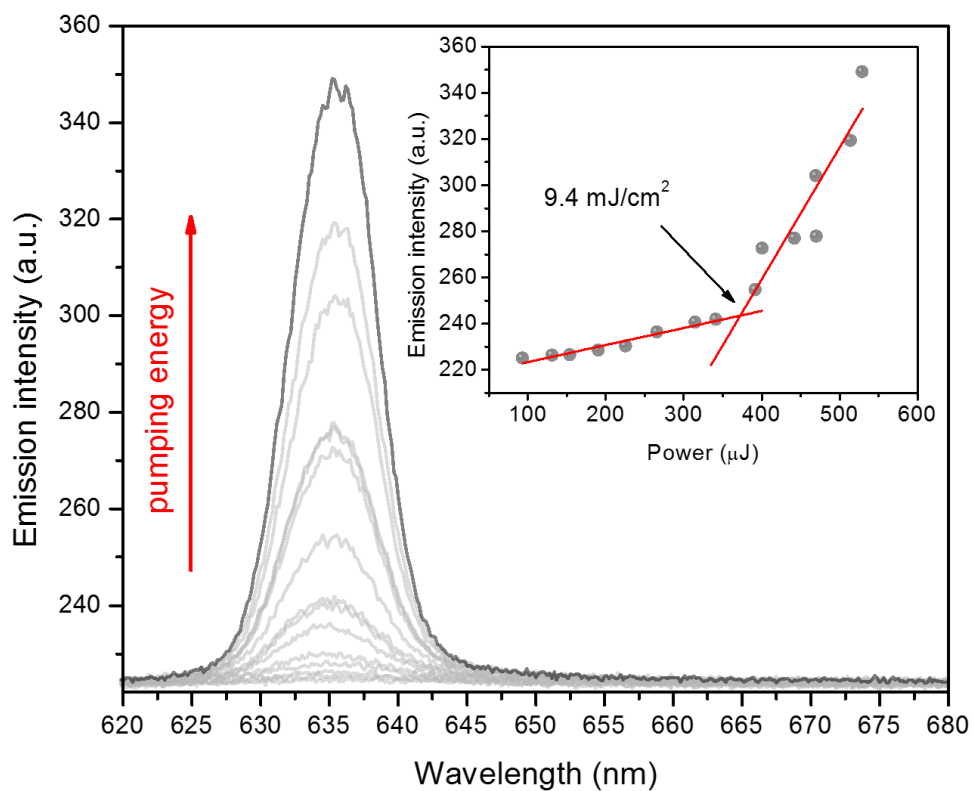


Fig. S8. Random lasing (RL) in TCF powder. Insert shows the plot used for the determination of the threshold of the laser action.

6. Scattering in liquid samples

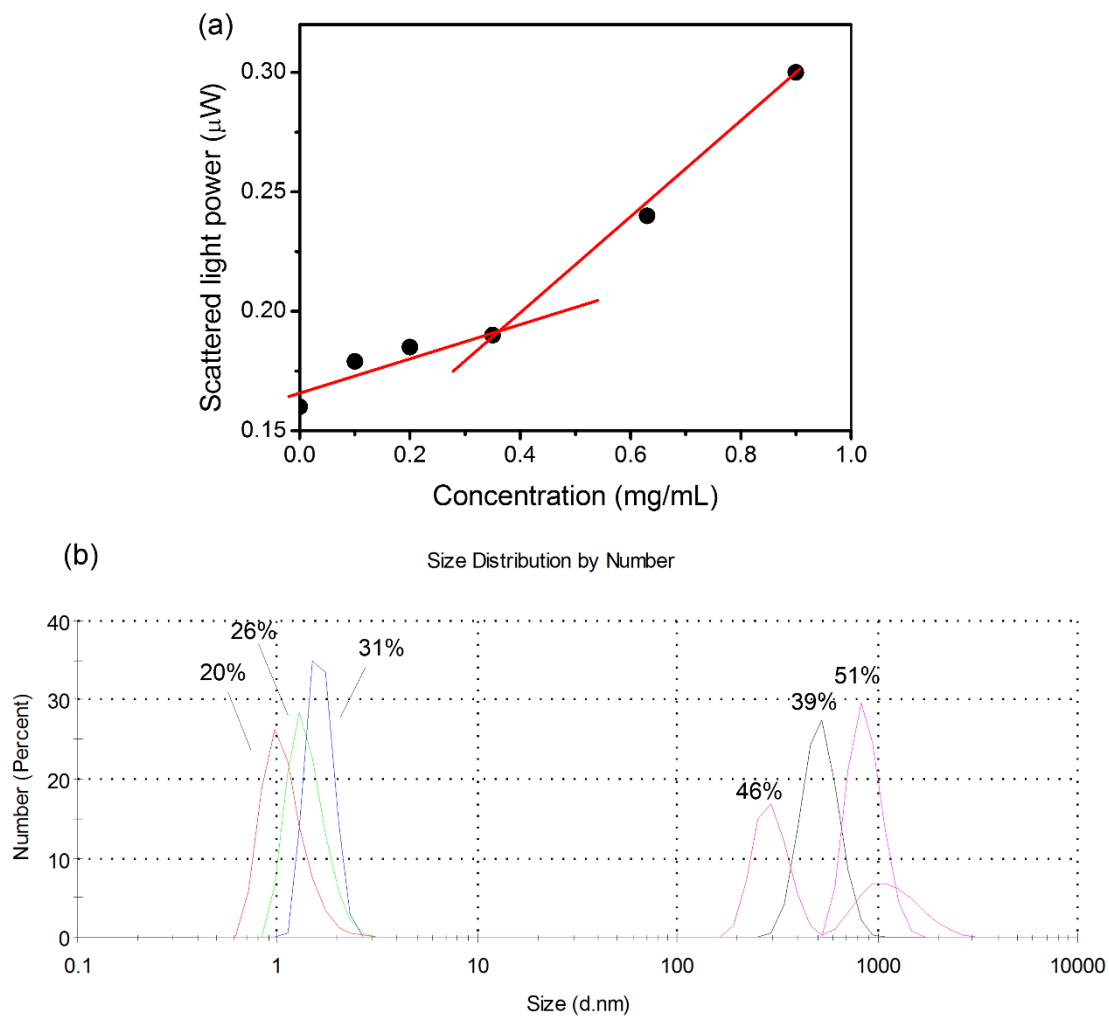


Fig. S9. An inflection point in scattered light power for concentration 0.35 mg/mL (a). Size distributions, measured by number in DLS experiment for different water contents.

7. Solid samples morphology

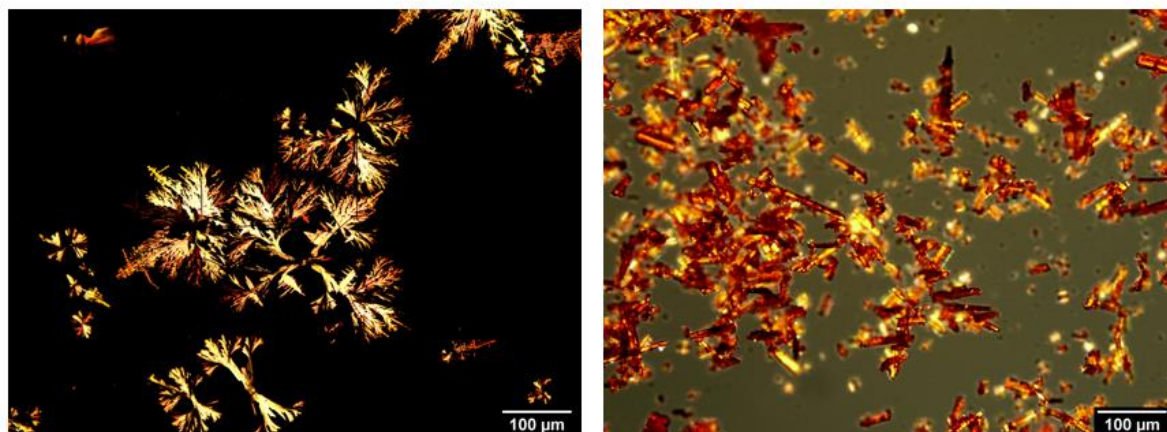


Fig. S10. Morphology micrographs of the 2,4,6-Ome-TCF in PMMA sample (left) and powder of the 2,4,6-Ome-TCF (right).

8. XRD of a powder

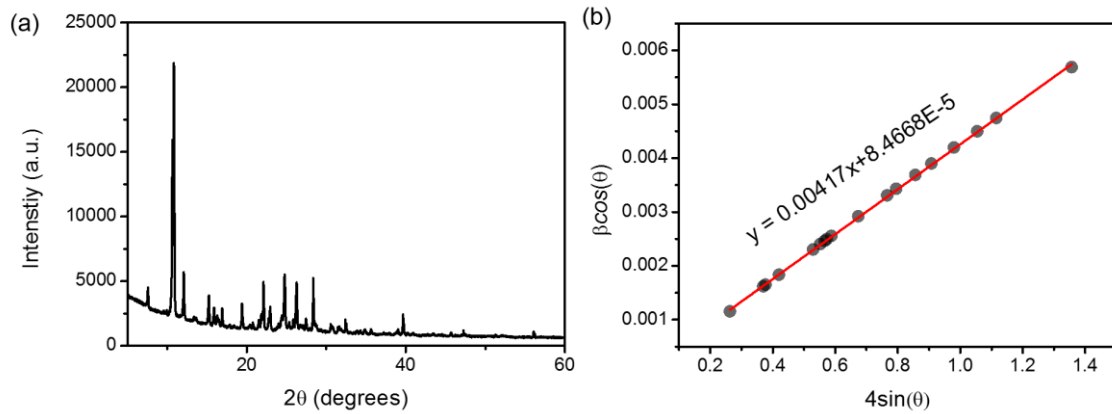


Fig. S11. Diffraction spectrum of a 2,4,6-OMe-TCF powder (a) and corresponding Williamson-Hall plot (b).

The Williamson-Hall plot was used to estimate the average grain sizes D according to the equation [3]:

$$\beta \cos(\theta) = \varepsilon(4 \sin(\theta)) + \frac{k\lambda}{D},$$

where: θ is a scattering angle of a particular peak, β is the FWHM of a particular peak, k is a shape factor (0.68-2.08), ε is strain, and $\lambda = 1.39225 \text{ nm}$. As can be seen, from the intercept of a Williamson-Hall plot, it is possible to determine the size of crystal grains. By taking limit values of shape factor (polycrystalline sample with crystals of different shapes), we obtain the sizes of crystals ranging from 11.1 to 34.2 μm , which is in quite good agreement with crystal sizes observed under the microscope.

9. References

- [1] M. Ipuay, Y.-Y. Liao, E. Jeanneau, P.L. Baldeck, Y. Bretonnière, and C. Andraud, *Solid state red biphotonic excited emission from small dipolar fluorophores*. Journal of Materials Chemistry C, 2016, **4**, 766-779.
- [2] T. M. Aminabhavi and B. Gopalakrishna, *Density, Viscosity, Refractive Index, and Speed of Sound in Aqueous Mixtures of N,N-Dimethylformamide, Dimethyl Sulfoxide, N,N-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1,4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K*. J. Chem. Eng. Data 1995, **40**, 856—861
- [3] D. Nath, F. Singh, and R. Das, *X-ray diffraction analysis by Williamson-Hall, Halder-Wagner and size-strain plot methods of CdSe nanoparticles- a comparative study*. Materials Chemistry and Physics, 2020, **239**, 122021