

Supporting Information:

Laser Emission from Self-assembled Colloidal Crystals of Conjugated Polymer Particles in a Metal-halide Perovskite Matrix

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Experimental Section

Materials

The CPPs were synthesized using a method established before²² and explained in more detail in the supporting information section. All reagents and solvents were purchased from Sigma-Aldrich and used without further purification. They were opened and stored in a nitrogen glove-box. The purities of the materials were as follows: Dimethylsulfoxide $\geq 99.7\%$, acetonitrile anhydrous 99.8%, Pb(II)Cl₂ 99.999%, Pb(II)Br₂ 99.999%, NH₃CH₃Cl, NH₃CH₃Br anhydrous $\geq 99.7\%$.

Fabrication of Films

The CPP stock solution is diluted to 3 wt% of solid loading. 1 ml of the dispersion is centrifuged at 9000 rpm for 5 min to sediment the colloids. The supernatant solution is discarded and the colloids are left to dry over night. The perovskite precursor solutions are prepared in a concentration of 1.5 mol/L. The Cl-perovskite and Br-perovskite precursor solutions are prepared separately. MACl (0.051g, 0.75 mmol) and Pb(II)Cl₂ (0.208 g, 0.75 mmol) are dissolved in DMSO (0.8 ml) and acetonitrile (0.2 ml) at 75°C over night in a nitrogen glove-box. MABr (0.085 g, 0.75 mmol) and Pb(II)Br₂ (0.275 g, 0.75 mmol) are dissolved as described above. The precursor solutions are left to cool before adding to the immersion solution consisting of DMSO (3.6 ml) and acetonitrile (0.9 ml) in the following volumes.

Br fraction	V (Br- solution) [ml]	V (Cl -solution) [ml]
x = 0.4	0.24	0.36
x = 0.1	0.06	0.54

The dried CPPs are redispersed in 0.05 ml of the immersion solution and then added to the remaining immersion solution. Cover glasses are cleaned with acetone and then in an Ar-plasma cleaner for 10 min at 0.1 atm. The cover glasses are then immersed vertically in the immersion solution at 75 °C on a ceramic hot plate in the nitrogen glove-box. Evaporation of the solvents takes place over a week at least. The dried co-assemblies are sealed to protect them against air during measurements by gluing another cover glass on top with a UV curable and UV-transparent glue.

Field-emission scanning electron microscopy

The co-assemblies are sputter-coated with gold (layer thickness 4 nm) before measuring with a FE-SEM S-4800 from Hitachi operating between 2.0 and 5.0 kV. The cross-sections are prepared by cutting the co-assemblies in the glove-box before sputter-coating. The images are analyzed using ImageJ image analysis software.

Wide-angle x-ray scattering

WAXS was conducted on an Empyrean setup from PANalytical. A Cu X-ray tube (line source of $12 \times 0.04 \text{ mm}^2$) provided CuK_α radiation with $\lambda = 0.1542 \text{ nm}$. The K_β line was removed by a Ni filter. Source and detector moved in the vertical direction around a fixed horizontal sample. After passing a divergence slit of $1/8^\circ$ and an anti-scatter slit of $1/4^\circ$, the beam reached the sample at the center of a phi-chi-z stage. In the Bragg-Bretano geometry used, the beam was refocused at a secondary divergence slit of $1/4^\circ$. Finally, the signal was recorded by a pixel detector (256×256 pixels of $55 \mu\text{m}$) as a function of the scattering angle 2θ . Subsequently, the peak positions were calculated from $q = 2\pi/d = (4\pi/\lambda)\sin\theta$, in which q is the scattering vector. The detector was used in a scanning geometry that allowed all rows to be used simultaneously. To reduce the background, the divergent beam perpendicular to the scattering plane was controlled by a mask of 4 mm restricting the width of the beam at the sample position to about 10 mm . In addition, the perpendicular divergence was restricted by soller slits to angles $\leq 2.3^\circ$. Scans were made with $2q$, the detector axis, moving at twice the rate of the q -axis of the incident beam. The calibration was checked using a Si reference sample.

Laser spectroscopy

The co-assemblies were characterized on an AIQTEC microscopic imaging spectrometer (MIS1000) at a magnification of $40\times$. The spectrometer is equipped with a white light source as well as a frequency-tripled Nd:YAG laser source with an optical parametric oscillator to tune the excitation wavelength for laser spectroscopic measurements. The pulse duration was 10 ns at a repetition rate of 10 or 20 Hz . For detection, the MIS 1000 is equipped with a spectrometer/monochromator with gratings of 300 , 600 , and 1200 lines and a cooled charge-coupled device detector. Spectra were obtained by accumulating $20 - 100$ pulses. The samples were measured at ambient conditions (room temperature and air). However, they were encapsulated prior to measurements. The excitation density was varied by neutral density filters and measured simultaneously with a thermoelectric detector. The photoluminescence was collected perpendicular to the substrate with the deposit in between two glass slides and focused onto the entrance slit of the spectrometer.

μ -PL measurements

μ -PL measurement system consists of an optical microscope with a long-distance $100\times$ objective ($\text{NA} = 0.8$) to magnify the co-assemblies. For measurements, a WITec μ -PL system was used with a model Alpha 300S microscope combined with a Princeton Instruments model Action SP2300 monochromator (grating: $300 \text{ grooves mm}^{-1}$) and an Andor iDus model DU-401A BR-DD.352 CCD camera cooled to -60°C . The samples were excited with a 407 nm CW laser coupled into an optical fiber and emission was collected through the same fiber simultaneously.

Fluorescence lifetime measurements

The AIQTEC MIS1000 is equipped with two ps-pulsed laser diodes with emission wavelengths at 375 nm and 440 nm . Here, 375 nm are used at 80 MHz repetition rate to excite mainly the perovskite matrix. The samples are placed on top of the objective with $40\times$ magnification and focused onto the co-assembly. The signal is detected by a time correlated single photon counting (TCSPC) photodiode attached to the spectrometer. The grating is centered at the wanted detection wavelength and the slit of the spectrometer is set at $100 \mu\text{m}$. The pumping laser can be attenuated by inserting optical density filters.

Rate equation model

The differential model of a bimolecular decay mechanism:

$$\frac{dn_{\text{per}}(t)}{dt} = -k_{\text{nr}}n_{\text{per}}(t) - k_{\text{r}}n_{\text{per}}^2(t) \quad (2)$$

The intensity time dependent $I(t)$ scales with the population of the excited state over time $n(t)$: $I(t) \propto n(t)$. k_{nr} as the rate constant of the non-radiative decay, and k_{r} as the radiative decay constant. The solution of the rate equation is

$$I(t) = \frac{-A}{B - e^{Ct}} \quad (1).$$

The parameters in equation (1) contain the rate constants also used in equation (2):

$$A = k_{\text{nr}}e^{C_1 k_{\text{nr}}}; B = k_{\text{r}}e^{C_1 k_{\text{nr}}}; C = k_{\text{nr}}.$$

The rate constants k_{r} and k_{nr} are calculated from the parameters in equation (1). and the lifetimes τ determined using

$$\tau = 1/k.$$

The rate equations for the co-assemblies are extended with an additional term representing the energy transfer as an additional decay channel.

$$\frac{dn_{\text{co}}(t)}{dt} = -(k_{\text{nr}} + k_{\text{ET}}) n_{\text{co}}(t) - k_{\text{r}} n_{\text{co}}^2(t) \quad (5).$$

Sample	k_{r} [ns ⁻¹]	k_{nr} [ns ⁻¹]	k_{ET} [ns ⁻¹]	τ_{r} [ns]	τ_{nr} [ns]	τ_{ET} [ns]
MAPb(Br _{0.1} Cl _{0.9}) ₃ (per/o.1)	5.62 x 10 ⁻⁷	1.11		1.78 x 10 ⁶	0.90	
MAPb(Br _{0.1} Cl _{0.9}) ₃ /CPP (co/o.1)	2.06 x 10 ⁻²	1.70	0.59	4.86 x 10 ¹	0.59	1.69
MAPb(Br _{0.4} Cl _{0.6}) ₃ (per/o.4)	5.16 x 10 ⁻⁴	0.81		1.94 x 10 ³	1.24	
MAPb(Br _{0.4} Cl _{0.6}) ₃ /CPP (co/o.4)	3.83 x 10 ⁻³	2.07	1.26	2.61 x 10 ²	0.48	0.79

Average lifetime determined from the biexponential fit

The biexponential fit is given in the text above. We determine the average lifetime using: $\tau = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$

Förster resonance energy transfer model

The model used here to estimate the Förster Radius is formulated for two points for example a donor and an acceptor molecule in solution. For FRET in the bulk the Radius can be even longer because of the higher concentration of interacting molecules. The calculation was only made for a rough estimate because the main focus of this paper is the transfer facilitated laser activity. The two point model used here is provided by the software Decayfit from Fluorotools.

$$\sum_i a_i e^{\{(-t/\tau_i) \cdot [1 + (R_0/R_{\text{DA}})^6]\}}$$

The Förster Radius here is $R_0 = 11.9$ nm and the average distance of the donor-acceptor pairs $R_0 = 6.8 \pm 4.3$ nm.