Electronic Supplementary Information

Polymorphism and microcrystal shape dependent luminescence, optical waveguiding and resonator properties of coumarin – 153

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Experimental Section:

1. Materials:

Coumarin-153 dye was purchased from Aldrich. For UV-Vis and Fluorescence measurements HPLC grade solvents were used. $CHCl_3$ and Acetonitrle (ACN) solvents were purchased from Merck chemicals, Hyderabad, India.

2. Instrumental Methods:

UV-Visible absorption spectra were recorded on a SHIMADZU-UV-3600 UV-VIS-NIR Spectrophotometer. Size and morphology of the self-assembled micro particles were examined by using a Zeiss field-emission scanning electron microscope (FESEM) operating at 3 kV.

3. Differential Scanning Calorimetry

DSC was performed on a Mettler Toledo DSC 822e module. Samples were placed in crimped but vented aluminum sample pans. The typical sample size is 3-5 mg; temperature range was 25–180 °C @ 10 °C/min. Samples were purged by a stream of nitrogen flowing at 60 mL/min.

4. Solid State Absorbance Studies:

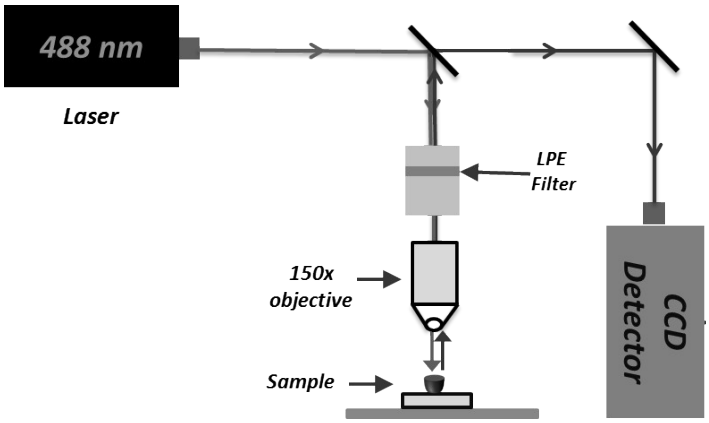
The solid state absorbance spectrum was recorded on a Shimadzu UV-3600 using diffuse reflectance UV-visible (DR-UV-vis) mode. The reflectance spectrum was converted to a absorbance spectrum using Kubelka-Munk function.

5. Electron Microscopy Studies:

Size and morphology of the self-assembled nanostructures were examined by using a Zeiss field-emission scanning electron microscope (FESEM) operating at 3 kV and a Tecnai G2 FEI F12 Transmission Electron Microscope (TEM) at an accelerating voltage of 200 kV. For FESEM analysis, the sample was predeposited with gold for 5 minutes using a sputter coater. FESEM images were captured at a working distance of 4-8 mm with a gun power of 3.0 kV. Carbon coated TEM grids (200 Mesh Type –B) were purchased from TED PELLA INC. USA.

6. Laser Confocal Optical Microscope Experimental Setup:

Single particle micro-spectroscopy experiment was carried out on a back scattering mode set up of the Wi-Tec alpha 300 AR laser confocal optical microscope (T-LCM) facility equipped with a Peltier cooled CCD detector. Using a 300 grooves/mm grating BLZ = 750 nm, the accumulation time was typically 10 s and integration time was typically 1.0 s. Ten accumulations was performed for acquiring a single spectrum. An argon ion 488 nm laser and 402 nm laser (i-beam smart-TOPTICA) were employed for the experiment. A 150x (0.95 NA) objective was used to excite a single micro-structure and images are processed by using WI-TEC 2.0 software. Laser lines, 402 nm, 488 nm and 633 nm (for Raman) were used for excitation.



7. Atomic Force Microscopy Studies:

AFM imaging was carried out on NT-MDT Model Solver Pro M microscope using a class 2R laser of 650 nm wavelength having maximum output of 1 mW. All calculations and image processing was carried out by a software NOVA 1.0.26.1443 provided by the manufacturer. The images were

recorded in a semicontact mode using a noncontact silicon cantilever (NSG10-DLC) tip purchased from NT-MDT, Moscow. The dimension of the tip is as follows: cantilever length = 100 (±5) μm, cantilever width 35 (±5) μm, and cantilever thickness = 1.7−2.3 μm, resonate frequency = 190−325 kHz, force constant = 5.5−22.5 N/m, chip size = 3.6 × 1.6 × 0.4 mm, reflective side = Au, tip height = 10−20 μm, tip curvature radius = 1−3 nm, and aspect ratio 3:1−5:1.

8. Fluorescence Lifetime Imaging Microscopy (FLIM) Studies:

PL decays and PL lifetime images were recorded on a time–resolved (Micro-Time 200, PicoQuant) confocal fluorescence lifetime imaging microscopy (FLIM) setup, which was equipped with an inverted microscope (Olympus IX 71). Measurements were performed at room temperature, on a micro particles deposited cover-slip. The samples were excited by a 405 nm ps diode pulse laser (power ~ 5μw) with a stable repetition rate of 20 MHz (FWHM: 176 ps) through a water immersion objective (Olympus UPlansApo; 60×; NA 1.2). Signal from the samples was collected by the same objective and passed through the dichroic mirror, filtered by using a 430 nm long-pass filter to cut off any exciting light. The signal was then focused onto a 50 μm diameter pinhole to remove the out-offocus signal, recollimated, and directed onto a (50/50) beam splitter prior to entering two singlephoton avalanche photodiodes (SPADs). The data acquisition was carriedouted with a SymPhoTime software controlled PicoHarp 300 time-correlated single-photon counting (TCSPC) module in a time tagged time-resolved mode. The overall resolution of the setup was 4 ps.

9. AFM, FESEM and TEM- Samples Preparation:

The sample solution was drop-casted (2-3 drops) on a clean cover-slip for AFM and FESEM studies. Two drops of the sample solution was drop casted on a carbon coated copper grid (200 Mesh) at different time intervals for TEM studies of rods, sheets and tubes. For Japan twin tubes the sample was scratched from the sample plate and transferred to a TEM grid.

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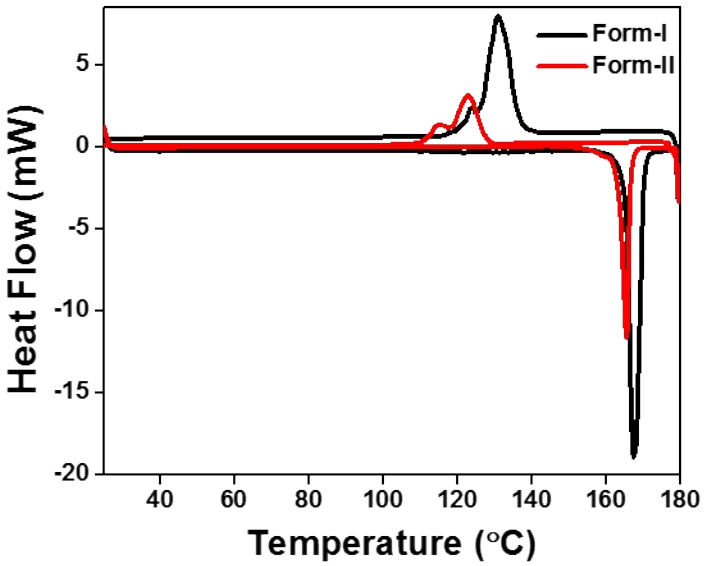


Fig. S1 DSC data of C-153 polymorphs I and II.

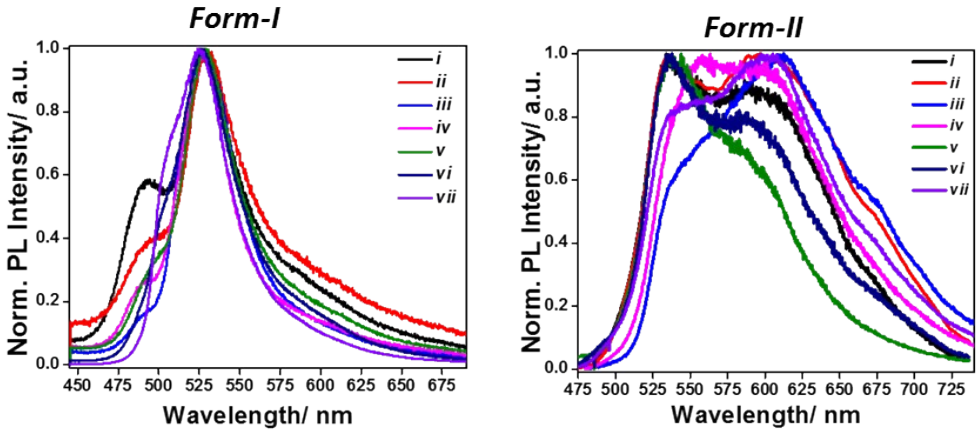


Fig. S2 Laser excitation position-dependent emissions from form I and II single crystals.

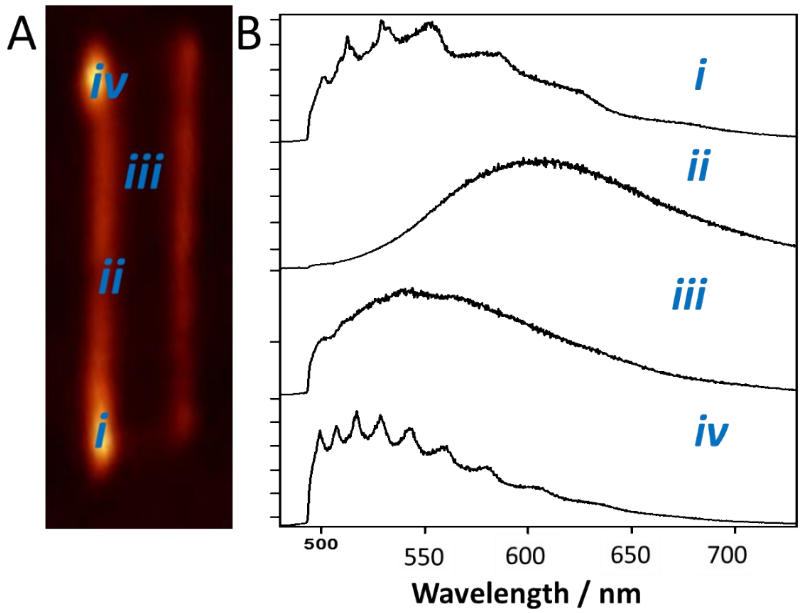


Fig. S3 A) FL map of a rod excited with a 488 nm Ar^+ laser. B) The corresponding FL spectra supporting FP modes.

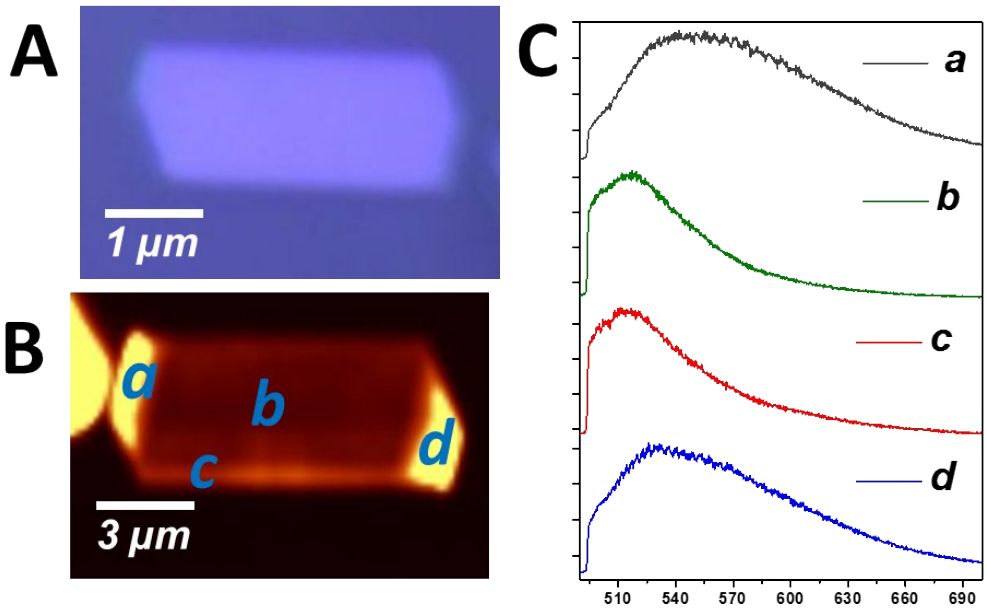


Fig. S4 A) Confocal micrograph of a C-153 sheet. B) FL map of a sheet excited with a 488 nm Ar^+ laser. C) The corresponding FL spectra supporting FP modes.

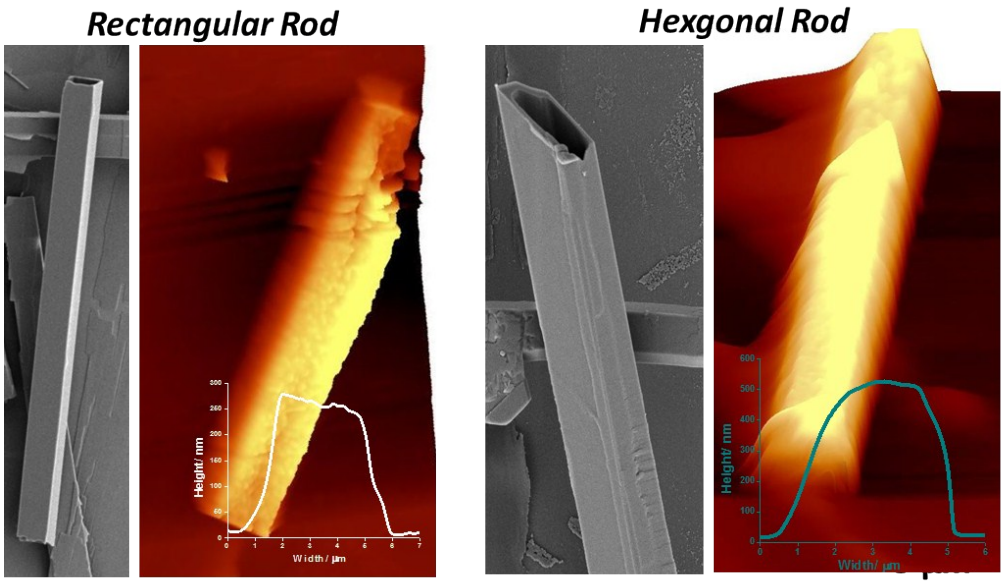


Fig. S5 FESEM and AFM of rectangular rods and hexagonal rods.

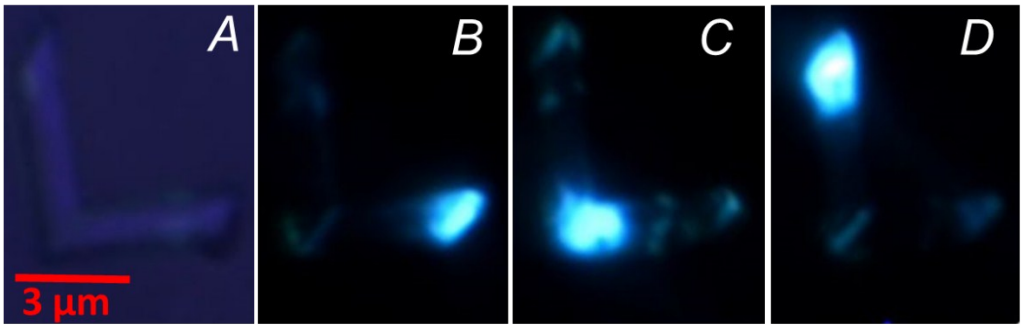


Fig. S6 A) Confocal micrograph of a C-153 Japanese- twines tubes. B) FL images at different excitation positions (488 nm Ar^+ laser).

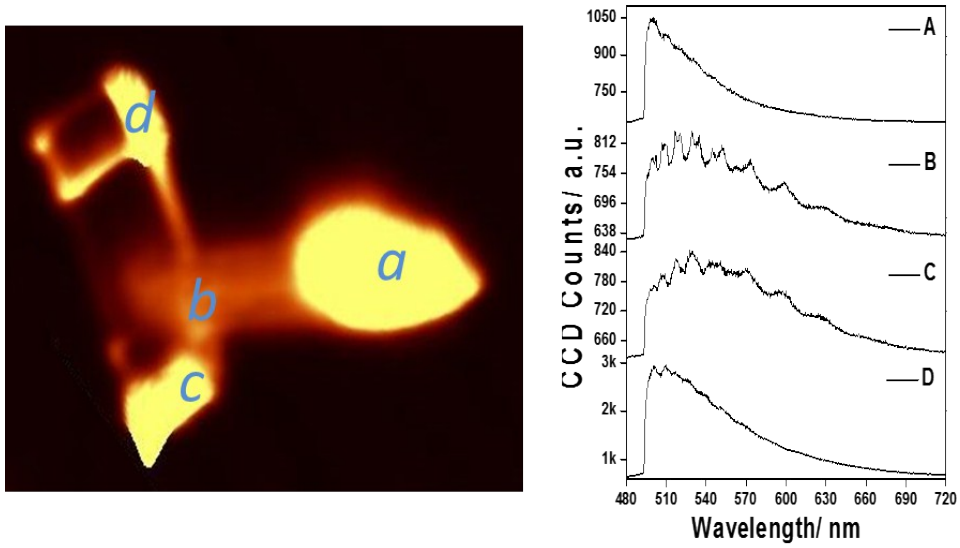
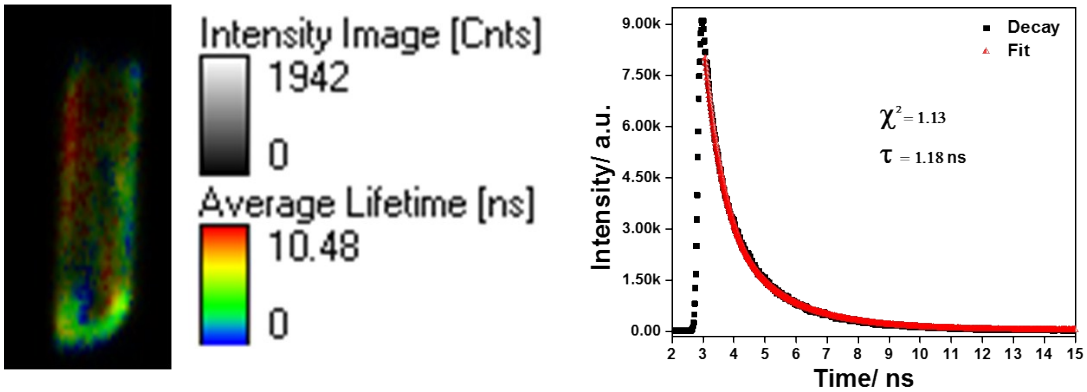


Fig. S7 FL map of a Japanese twined tube and the corresponding FL spectra collected at different positions.

Type of micro structure / Type of measurement	μ- rods	L- shaped crystals	Hexagonal or rectangular μ-tubes
Life time (ns)	**1.18**	**1.3- 1.37**	**0.7-0.77**



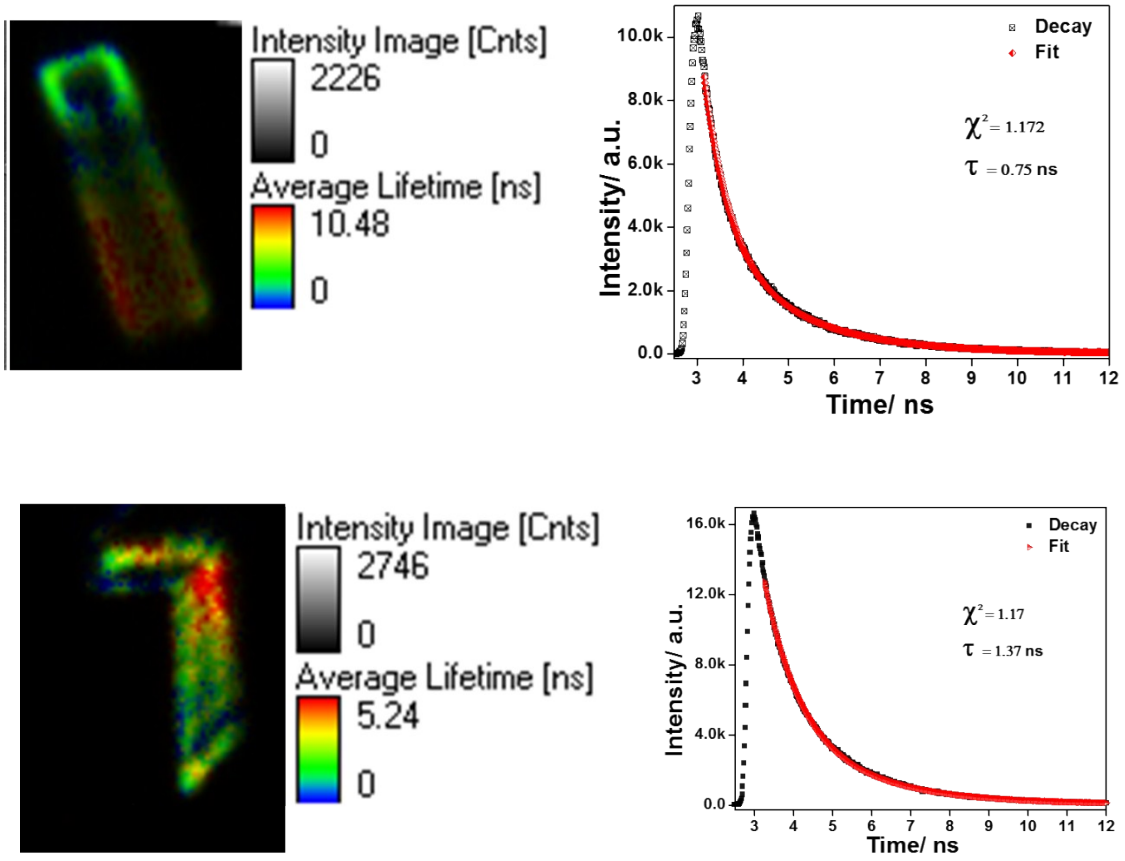


Fig. S8 FL life time decay (right) and FILM image (left) of a rod, tube and Japanese twined tube.