Electronic Supplementary Material (ESI) for CrystEngComm.

Mechano-Photonic Aspects of a Room Temperature Phosphorescent Flexible Organic Microcrystal

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SUPPORTING INFORMATION

1. Experimental Procedures

Synthesis of PTX-CHO:

PTX-CHO was synthesized using the procedure reported by Hudson *et al.* For this, a mixture of phenothiazine (15 mmol), potassium phosphate tribasic (45 mmol) and DMF (25 mL) was added to a 100 ml two necked round bottom flask. The flask was sealed with a rubber septum and sparged with N_2 for 15 minutes. The mixture was heated to 135°C and stirred for 30 minutes. 4-Fluorobenzaldehyde (30 mml) dissolved in DMF (10 mL) was then added dropwise under nitrogen atmosphere, and the temperature was increased to 150 °C. The mixture was stirred under nitrogen atmosphere until judged complete by TLC. After cooling to room temperature, it was filtered to remove inorganic salts and the organic layer was diluted with dichloromethane (100 mL) and washed several times with water. The crude product was purified with column chromatography on silica (1:11 Ethyl acetate/hexane).

Synthesis of PTX-2CF_3:

A mixture of of 3,5-Bis(trifluoromethyl)phenylacetonitrile (0.54 mmol), sodium methoxide (0.6 mmol), methanol (30ml) was added to a round bottom flask. The mixture to 40 °C and stirred for 30 minutes. 4-(10H-phenothiazin-10-yl) benzaldehyde (0.54 mmol) was added and kept for 8 h. When the reaction was completed (monitored by TLC), the reaction mixture was cooled to rt. After filtration the residue was purified by recrystallization in DCM/Methanol. ^{1}HNMR (500 MHZ, chloroform-d): δ8.06(s, 1H CHPh), 7.90(d, J=40Hz, 2H, CHPh), 7.86(s, 1H CHPh), 7.57(s, 1H, C=CCN), 7.4-7.38 (dd, 2H, CHPTZ), 7.22-7.19(m,4H, CHPTZ)7.28-7.25(m, 2H, CHPTZ), 7.22-7.19(m, $H, CHPTZ), 7.17-7.14(m, 2H, CHPh).

2. Self-assembly of PTX-2CF_3:

For self-assembly studies 0.92 mM methanol solution of PTX-2CF_3, by dissolving 0.5 mg in 1ml, was taken to fabricate micro-rods by self-assembly approach. Sonication of PTX-2CF_3 solution was carried out for complete dissolution for 2 minutes and kept for 5 minutes without any disturbance. Later 2-3 drops of the same was drop casted on glass substrate and left undisturbed for slow evaporation of solvent. Then the PTX-2CF_3 molecules aggregate to form micro-rods after evaporation.

I. NMR Spectroscopy:

^{1}H NMR and ^{13}C spectra were recorded at room temperature on Bruker 500 (spectrometer with tetramethylsilane as the internal reference; chemical shifts (δ) are given in parts per million (ppm) ($CDCl_3$: ^{1}H: 7.26 ppm).

II. Single Crystal Analysis:

The planes of the crystal were determined using a Rigaku Oxford XtaLAB ProPilatus3 R 200K-A detector system equipped with a CuK_α (λ = 1.54184 Å) MicroMax-003 microfocus sealed tube operated at 50 kV and 0.6 mA. Data were collected at 293 K.

III. Solid-State Absorbance and Emission Studies:

The solid-state absorbance spectra were collected using a Shimadzu UV-3600 spectrometer in a diffuse reflectance UV−visible (DR−UV−vis) mode. The solid-state emission spectra were collected using FLUOROMAX spectrofluorimeter (HORIBA, Jobin Yvon). Spin-coating was performed on a quartz substrate using a spin coater (Laurell Technologies Corporation; model WS- 400B-6NPP/LITE/8K).

IV. Confocal Micro Spectroscopy Studies:

The experiments were carried out using a Wi-Tec alpha 200 laser confocal optical microscope facility equipped with a Peltier-cooled CCD detector. 355/405/488/785 nm lasers were used as anexcitation source. The excitation and collection of signals from the output of the microstructure were performed by an upright microscope (20×; NA: 0.6). The output signal collection was performed using 20× objective for every 0.3 ms and the signal was sent to a CCD detector through amultimode optical fibre of diameter 100 μm (core). The time taken to complete one set of experiment is dependent upon the solvent evaporation time. All measurements were performed atambient condition and images were processed by using WI-TEC 2.0 software.

V. Scanning Electron Microscopy Studies:

The size and morphology of micro-crystals were examined by using a Zeiss field-emission scanning electron microscope (FESEM) operating at 3 kV. The samples were prepared freshly by self-assembly method and after solvent evaporation, the gold coating was carried out for imaging.

VI. Phosphorescence Spectra and Lifetime measurements:

The phosphorescence of **PTX-2CF$_3$** was measured with a chopping period of 400 msec with delay time of 20 msec and integration time

was set to be 20 msec. For all measurements excitation and emission band widths of 5 nm was kept constant. The sensitivity of measurement was observed to be 'very low'. In case of lifetime measurement, the shutter closing time of the instrument (108 msec) was chosen as delay time. The system generated (from instrument's software) lifetime was presented.

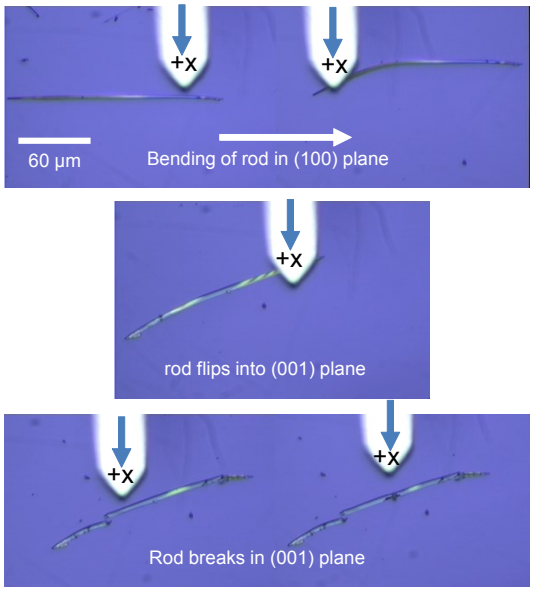

Figure S1. Flexibility of crystal in various planes when force is applied in perpendicular direction.

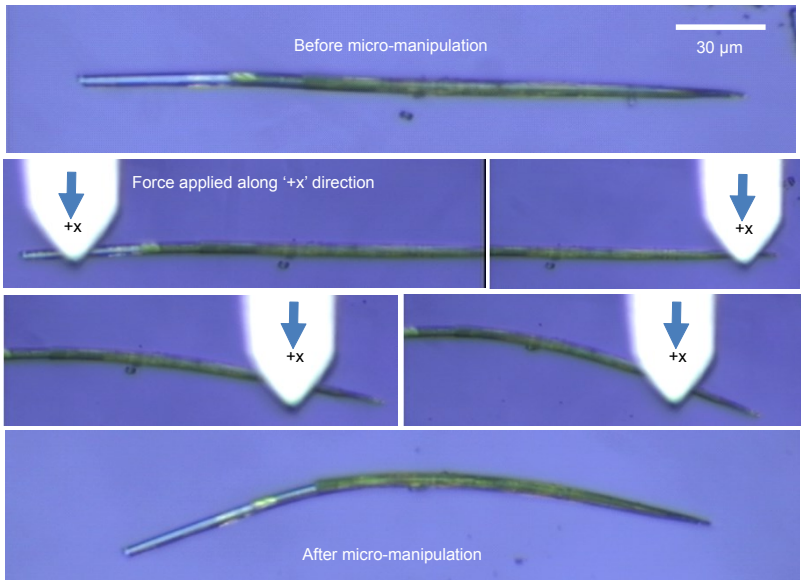

Figure S2. Micromanipulation of **PTX-2CF$_3$**.

3. Optical loss coefficient:

The optical loss coefficient, quantity which explains the quality of the obtained waveguide, was calculated using the following equation

$$I_{out} = I_{in}\, e^{-\alpha d}$$

where I_{out} and I_{in} are the FL intensities at the output and input, respectively, d is the propagation distance and α, is the optical loss coefficient in dB mm^{-1}. α can be converted to α', which bears the unit dB μm^{-1} by multiplying with 4.34.

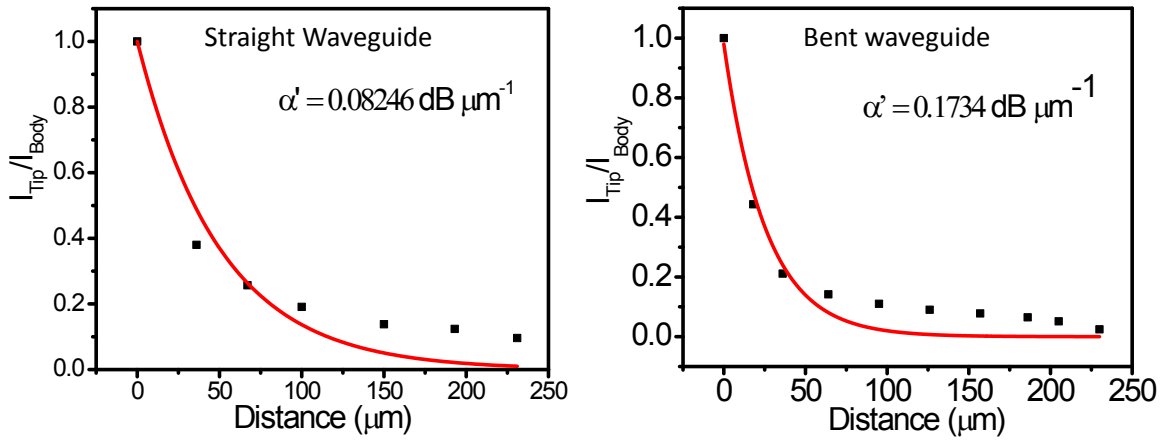

Figure S3. Optical loss fitting curves for straight and bent waveguides of **PTX-2CF$_3$**.

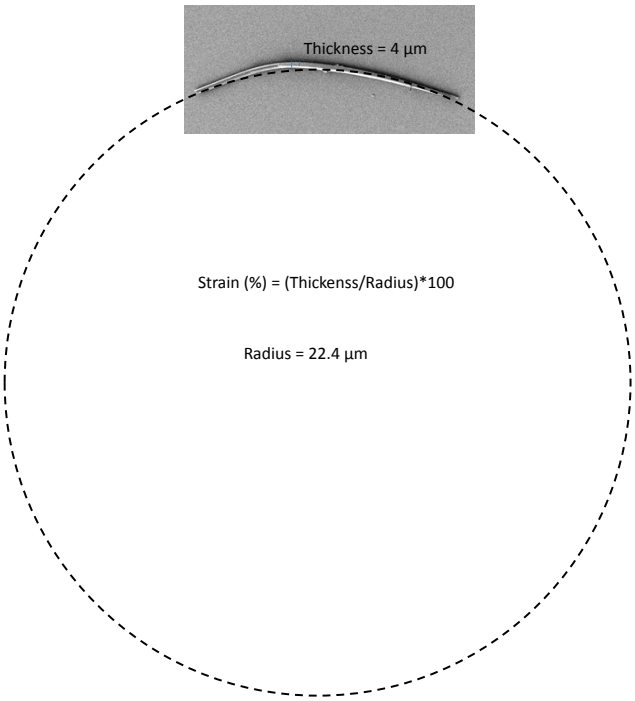

Figure S4. Strain caused due to bending of **PTX-2CF$_3$** straight crystal with AFM tip.

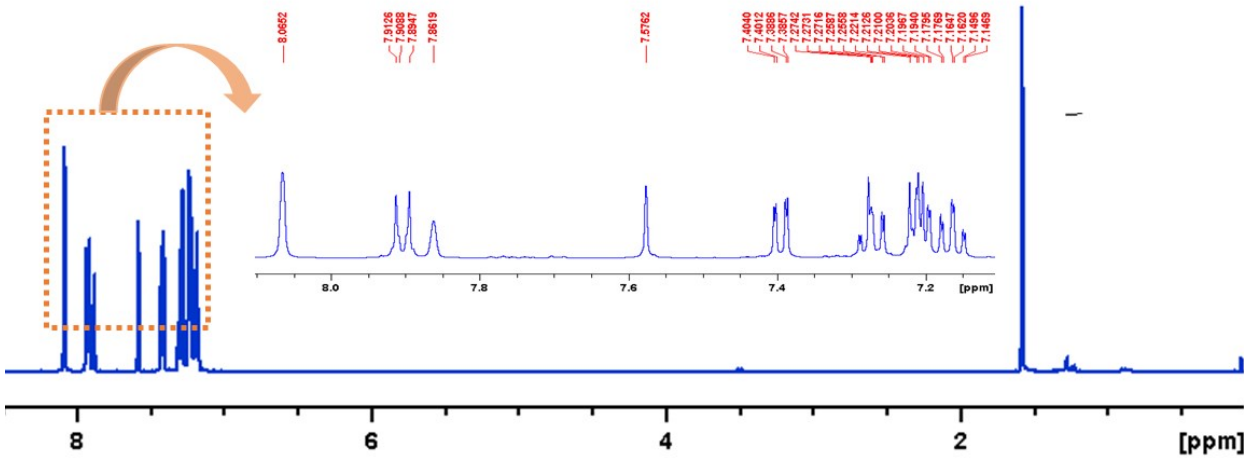

Figure S5. ^{1}H NMR spectra of molecule **1** in $CDCl_3$ (C = 0.01 M).

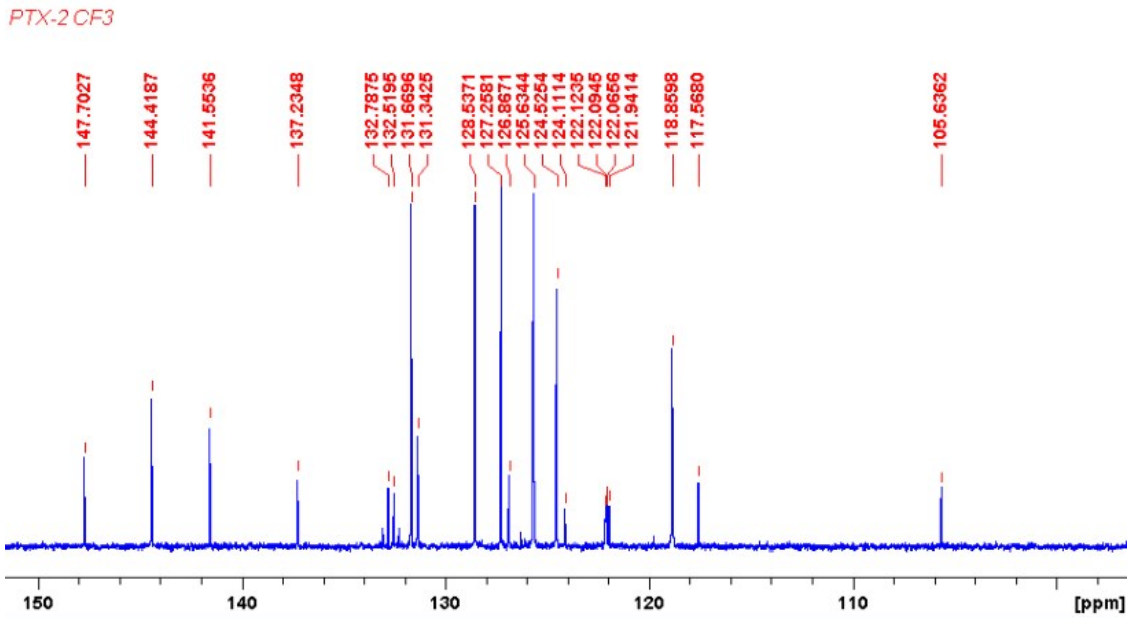

Figure S6. ^{13}C NMR spectra of molecule **1** in $CDCl_3$ (C = 0.1 M).

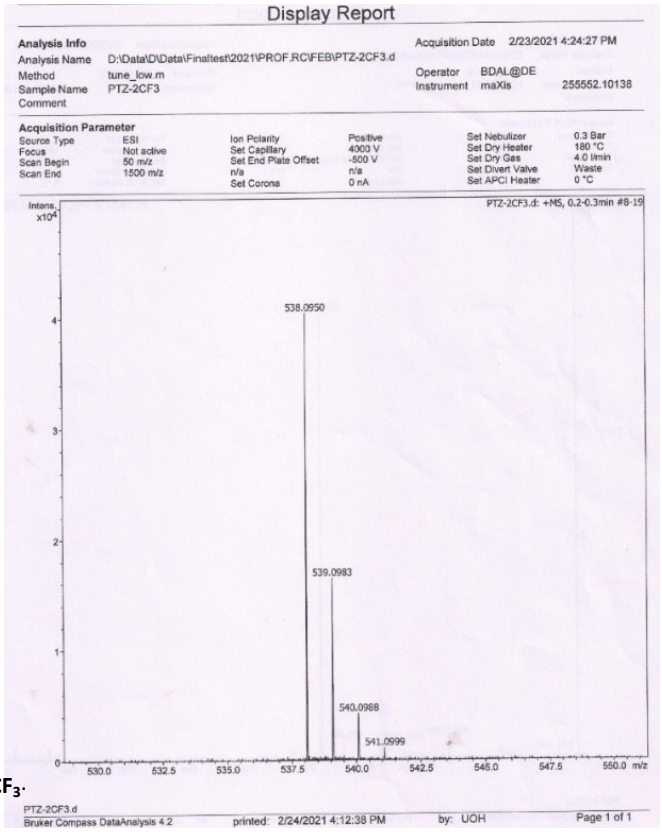

Figure S7. HRMS analysis of **PTX-2CF$_3$**.

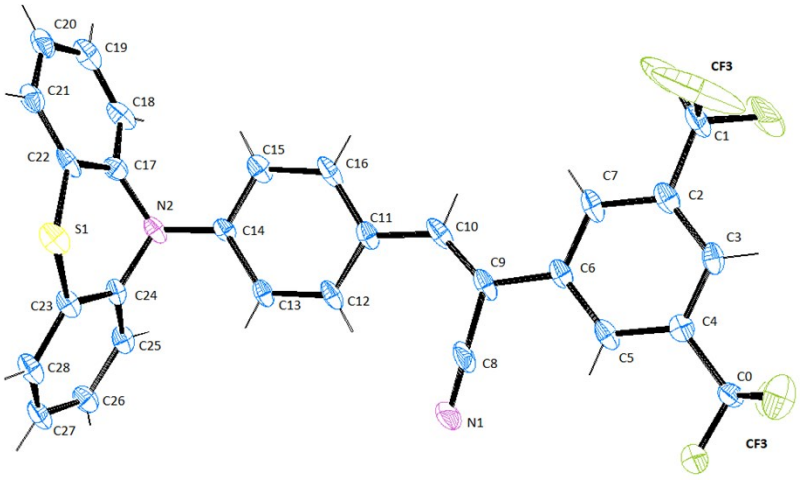

Figure S8. ORTEP view of **PTX-2CF$_3$** with thermal ellipsoids shown at 30% probability.

4. Solution state studies:

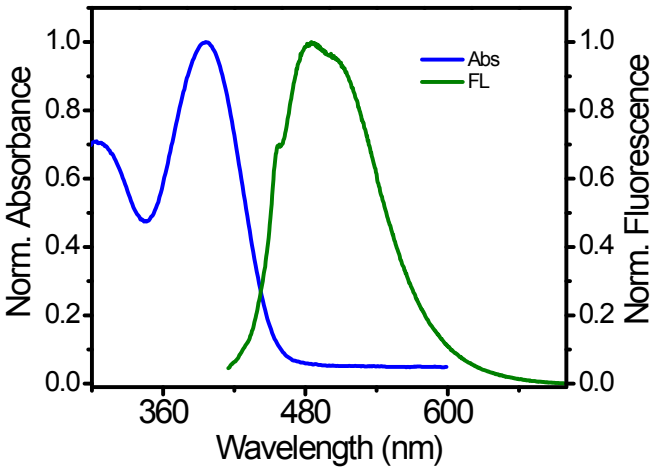

Figure S9. Normalized Absorbance and emission of **PTX-2CF$_3$** in THF solution (C = 1.2 x 10^{-5} mM).

5. References:

1. A. M. Polgar, J. Poisson, N. R. Paisley, C. J. Christopherson, A. C. Reyes, and Z. M. Hudson, *Macromolecules* 2020, ***53***, 2039-2050.