SUPPORTING INFORMATION

Mechanophotonics: Fabrication of a 2×2 hybrid directional coupler from flexible organic crystals

Avulu Vinod Kumar and Rajadurai Chandrasekar*

School of Chemistry, and Centre for Nanotechnology, University of Hyderabad, India.

Email: r.chandrasekar@uohyd.ac.in

1. Experimental Procedures

NMR Spectroscopy:

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

Single Crystal XRD Analysis:

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

Solid-State Optical 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). The FL quantum yield was measured using Horiba F1-3C.

Confocal Optical Micro PL 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. 405 nm laser was used as an excitation source. The excitation and collection of signals from the output of the microstructures were performed by an upright microscope (using 20x or 60x objectives). The output signal collection was performed using 20x objective for every 0.5 s and the signal was sent to a CCD detector through amultimode optical fiber of diameter 100 μm (core). Each spectrum was recorded with an acquisition period of 0.5 s and 10 accumulations. All measurements were performed under ambient conditions and the images were processed by using Wi-Tec Project 5.0 software.

Micromanipulation of Crystals: The micromanipulation experiments were performed using an atomic force microscopy cantilever-tip attached to the above-mentioned confocal microscope setup. The BPyIN crystal was transferred on to the coverslip (borosilicate; Borosil), containing selected CF_3OMe crystal, using AFM cantilever. An AFM cantilever (Tips Nano: NSG, with force constant

3.1 – 37.6 N/m) movable in the ±z directions was used to go closer/away from the selected crystal. The crystal mechanical micromanipulation was carried out by moving the sample stage (containing crystals) in the ±x and ±y directions.

Scanning Electron Microscopy

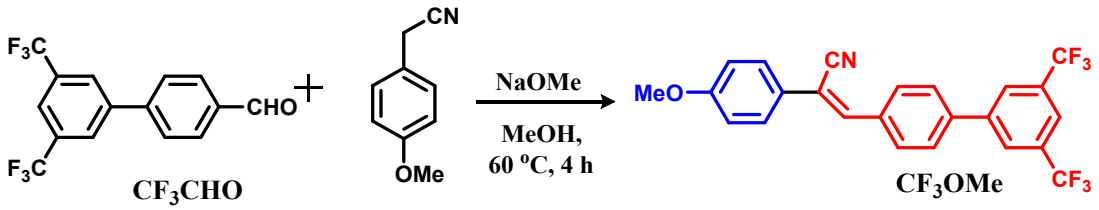
The size and morphology of microcrystals and circuit were examined by using a Zeiss field-emission scanning electron microscope (FESEM) operating typically at 6 kV. The samples were gold coated before imaging. The circuit was imaged after three months of fabrication.

Fluorescence Lifetime Imaging Microscopy

PL lifetime images were recorded on a time-resolved (Micro-Time 200, Pico Quant) confocal PLIM setup equipped with an inverted microscope (Olympus IX 71). The microcrystals were illuminated by a 405 nm ps diode pulse laser (power ≈5 μw) with a stable repetition rate of 20 MHz (FWHM: 176 ps) through a water immersion objective (Olympus UPlans Apo; 60 ×; NA 1.2). The 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-of-focus signal, recollimated, and directed onto a (50/50) beam splitter prior to entering two single-photon avalanche photodiodes. The data acquisition was carried out with a SymPhoTime software-controlled PicoHarp 300 time-correlated single-photon counting module in a time-tagged time-resolved mode. The overall resolution of the setup was 4 ps.

Transmission electron microscopy. The microstructures were probed for their detailed morphology and crystalline nature of molecular packing in nano/microcrystals using multipurpose electron microscope (JEOL JEM-F200) operating at an acceleration voltage of 200 kV. For the preparation of micro/nano structures, a dispersed solution containing sample was drop casted on a TEM grid under ambient conditions. The selected area electron diffraction dot pattern analysis was carried out using CrystBox software.

1. Synthesis:



Scheme S1. Scheme for the synthesis of CF_3OMe.

Synthesis of CF_3CHO:

Compound CF_3CHO was synthesized using the procedure reported by Jyothi *et al.*[1] A mixture of 1-bromo-3,5-bis(trifluoromethyl)benzene (5 mmol), (4-formylphenyl)boronic acid (5.5 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.05 g, 0.004 mmol) was dissolved in 45 mL of tetrahydrofuran. After addition of 12 mL of aqueous 2N potassium carbonate solution, the reaction mixture was stirred and heated to reflux overnight. The crude mixture was cooled to room temperature and poured into 200 mL of water. Later, the aqueous solution was extracted with ethyl acetate (150 mL), and dried over anhydrous sodium sulfate. Finally, silica gel column chromatography (n-hexane:EtOAc ,3:1) gave the product as a white powder in 80% yield.

Synthesis of CF_3OMe:

For the synthesis of CF_3OMe, 3,5-bis(trifluoromethyl)phenylacetonitrile (1.1 mmol) was taken in 20 mL methanol and added with sodium methoxide (2 mmol). To this solution, CF_3CHO (1 mmol in 5 mL methanol) was slowly added at rt. The reaction mixture was heated at 60 °C for 4 h. Then the white fibre-like compound was filtered and purified by recrystallization in (1:1) dichloromethane:hexane solution to obtain CF_3OMe in 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 2H), 8.00 (d, 2H, J = 4 Hz), 7.89 (s, 1H), 7.72 (d, 2H, J = 4 Hz), 7.63 (d, 2H, J = 4 Hz), 7.48 (s, 1H), 6.98 (d, 2H, 4 Hz), 3.91 (s, 3H).

Synthesis of BPyIN:

2-Hydroxy-1-naphthaldehyde (5 mmol, 1 eq) and 2-amino-5-bromo pyridine (5 mmol, 1 eq) were taken in ethanol in a 100 mL round bottomed flask. The reaction mixture was heated at 70 °C for 4 h. The formed precipitate was cooled to room temperature and purified by recrystallization in chloroform

solvent to obtain green needle-like crystals of BPyIN. Yield 70%.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 15.36 (s, ^{1}H), 9.95 (d, 1H, J = 1.8 Hz), 8.52 (d, 1H, J = 2.5 Hz), 8.15 (d, 1H, J = 8.5 Hz), 7.85 (dd, 1H, J_1 = 8.5, Hz J_2 = 2.4 Hz), 7.78 (d, 1H, J = 10 Hz), 7.64 (d, 1H, J = 8 Hz), 7.52 (dt, 1H, J_1 = 7.6 Hz, J_2 = 3.5 Hz), 7.33 (dt, 1H, J_1 = 7.6 Hz, J_2 = 1 Hz), 7.09 (d, 1H, J = 8.5 Hz), 6.94 (d, 1H, J = 9.5 Hz).

2. Self-assembly of CF_3OMe and BPyIN:

Self-assembly of CF_3OMe: For preparation of CF_3OMe microcrystals, 1 mg of compound was dissolved in methanol and left undisturbed for 12 h. Later a 20 µL solution was drop-casted on to a clean borosilicate coverslip. Complete evaporation of solvent under ambient conditions yielded in rod-like microstructures.

Self-assembly of BPyIN: The microcrystals of BPyIN required for circuit fabrication were obtained by drop-casting 20 µL of 2 mM hexane solution of BPyIN onto a coverslip and allowing the solvent to evaporate slowly at room temperature. After complete evaporation of the solvent, the confocal microscopy studies revealed the formation of rod-like microstructures.

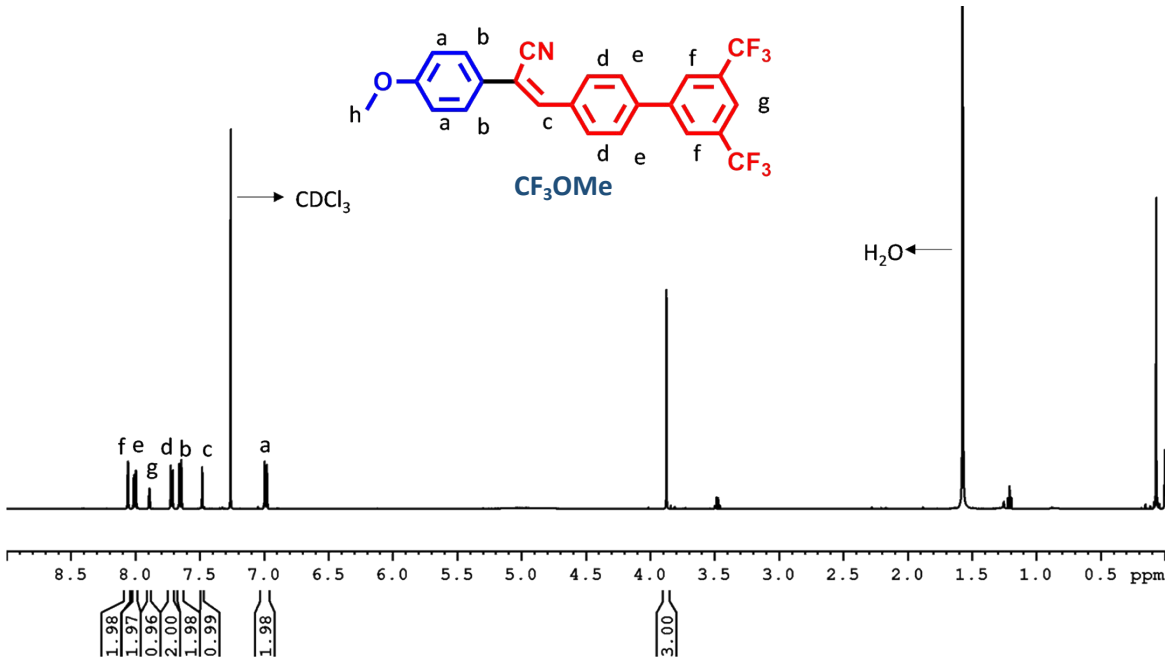


Figure S1. ^{1}H NMR (500 MHz) of CF_3OMe.

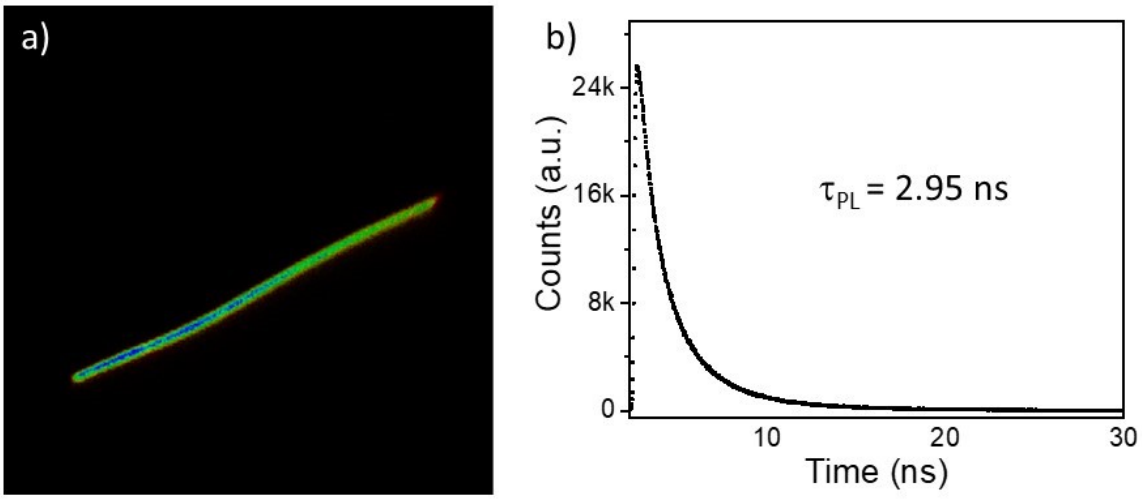


Figure S2. a) Photoluminescence (PL) lifetime mapping image of CF_3OMe crystal. b) PL lifetime decay for the crystal shown in a.

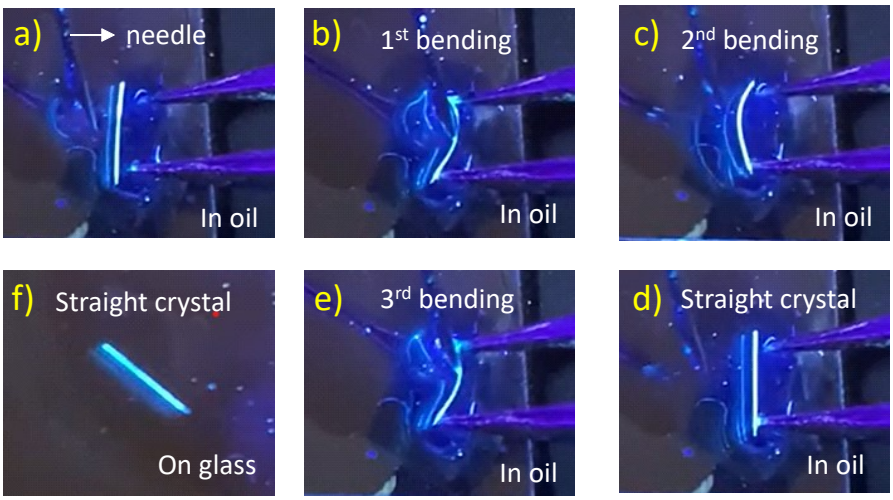


Figure S3. a-f) Three-point bending performed on a CF_3OMe milli-meter sized crystal using tweezers and needle in oil under UV torch illumination.

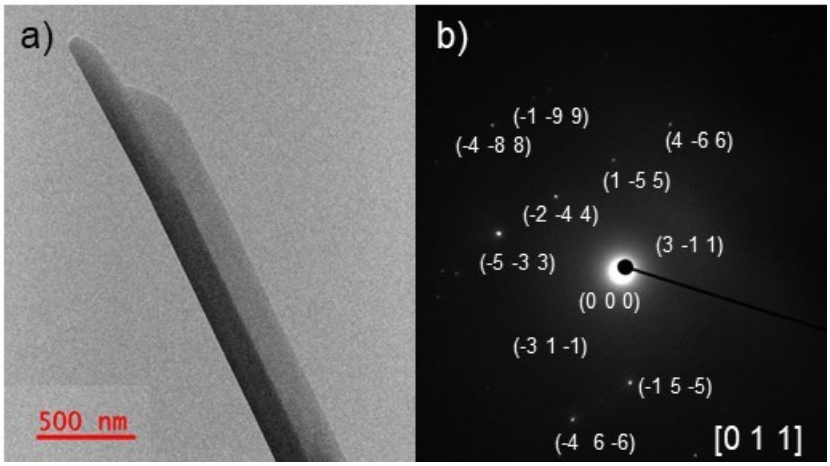


Figure S4. a) Transmission electron microscope image and b) selected area electron diffraction from the corresponding microcrystal shown in a.

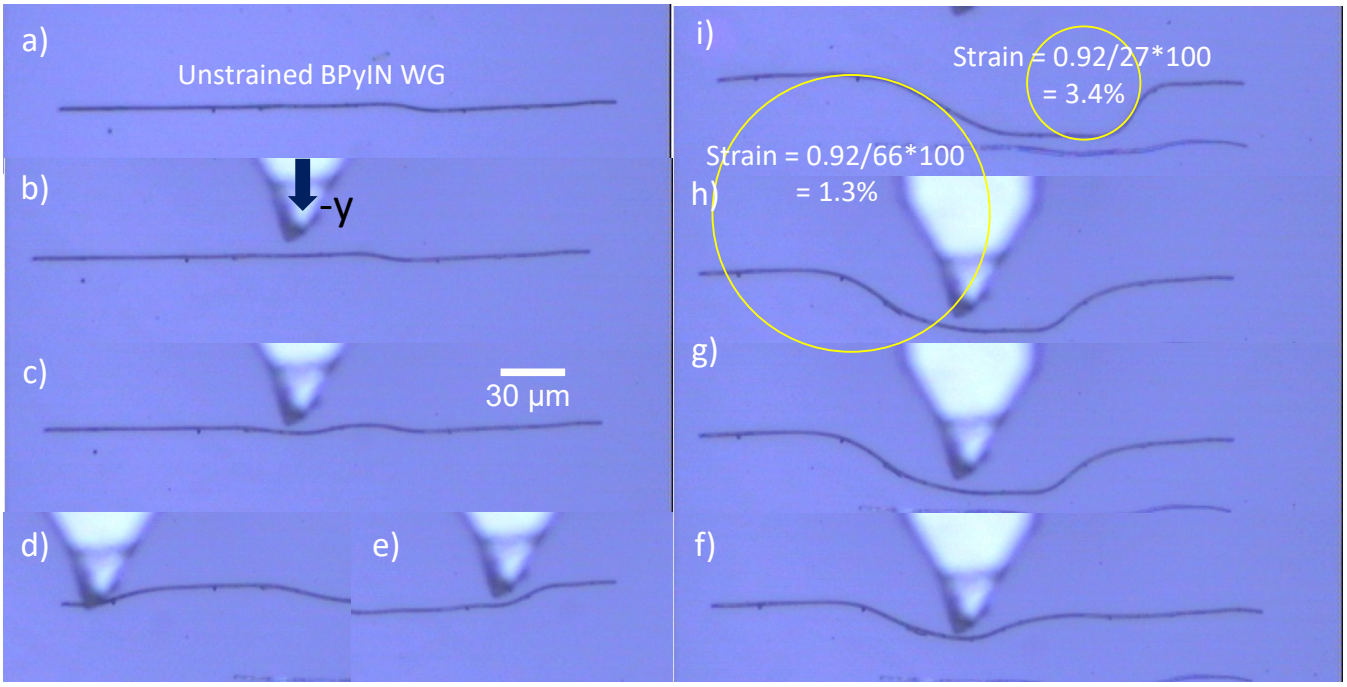


Figure S5. a-h) Micromechanical bending of unstrained BPyIN waveguide into a doubly bent waveguide. Insets in 'i' present the bending induced strain on the bent regions of the waveguide. The scale is provided in c.

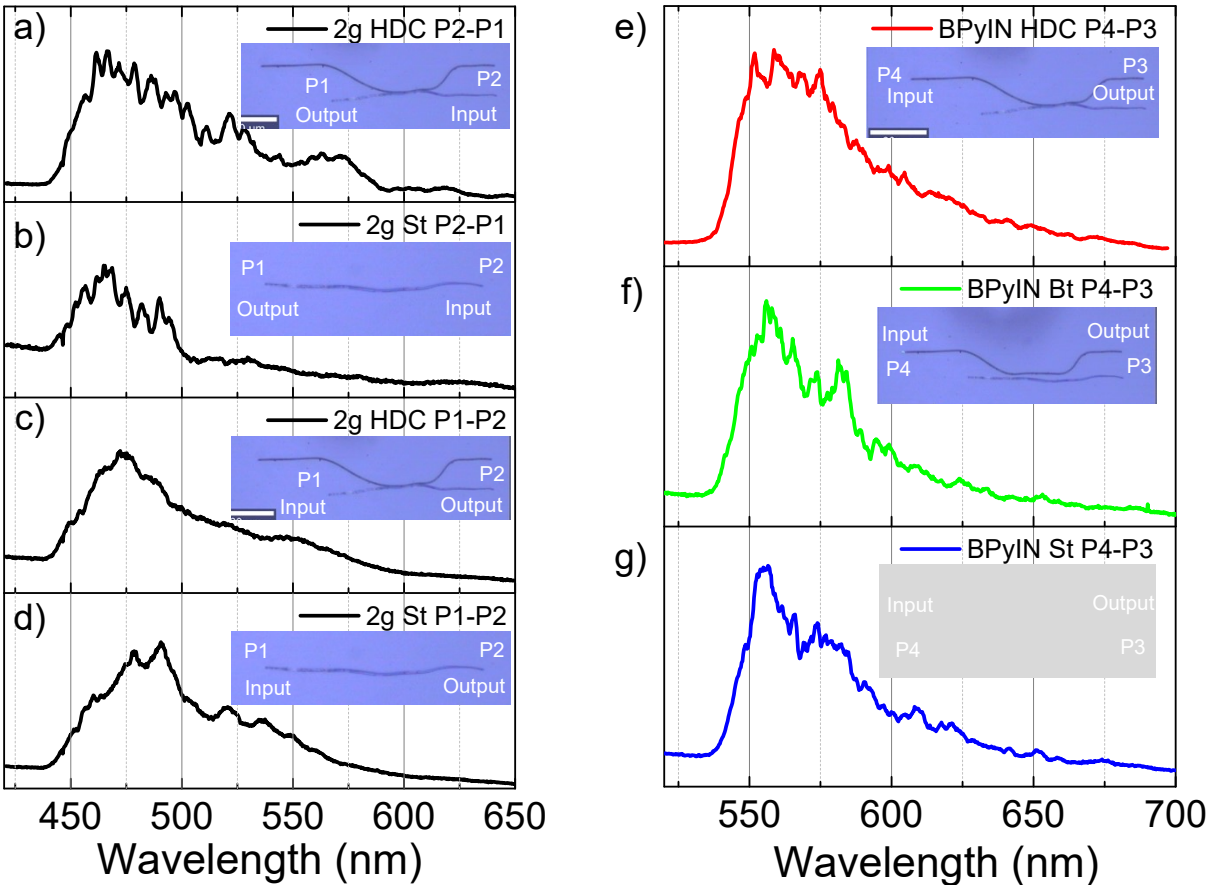


Figure S6. a-d) Comparative FL spectra consisting optical modes in straight CF_3OMe microcrystal with hybrid directional coupler (HDC). e-g) Comparative changes in optical modes for HDC, bent and straight BPyIN microcrystal.

References:

1. M. Jyothi, M. Annadhasan, V. V. Pradeep, R. Chandrasekar. *Soft Matter,* 2020, ***16,*** 2664-2668.
2. A. V. Kumar and R. Chandrasekar. *Adv. Opt. Mater*. 2022, 2201009. DOI:10.1002/adom.202201009.