

## Electronic supplementary information (ESI)

# Engineering Self-assembled fluorescent organic nanotapes and submicrotubes from $\pi$ -conjugated molecules†

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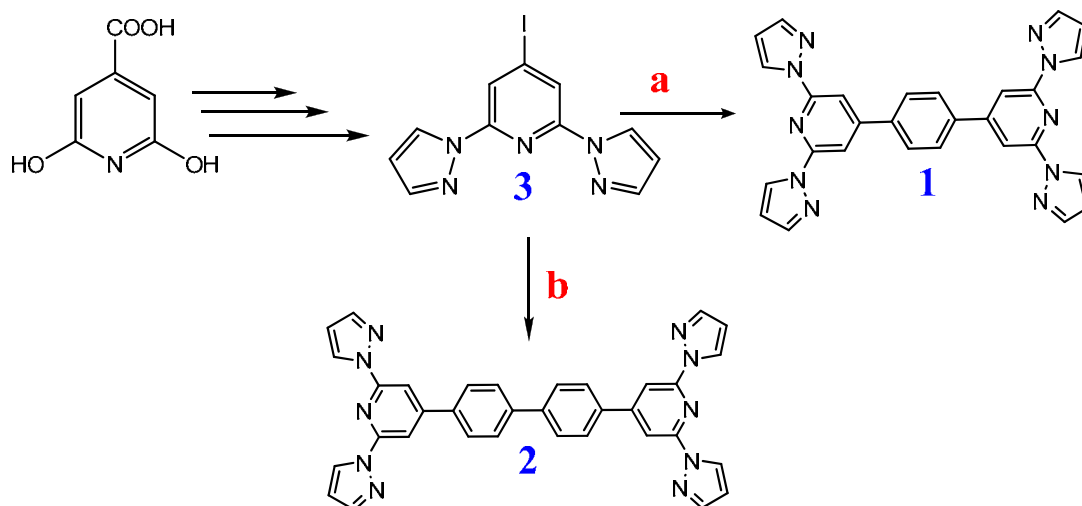
### Experimental section:

**Materials:** The materials cinnamic acid, 1,4-bisphenyleneboronic acid, 4,4'-biphenylenediboronic acid,  $[\text{Pd}(\text{PPh}_3)_4]$ , trifluoroacetic acid and pyrazole were purchased from Aldrich. Sodium azide, KI,  $\text{K}_2\text{CO}_3$ ,  $\text{NaNO}_2$ , sodium thiosulfate and diethylether were purchased from Merck chemicals. Oxalyl chloride,  $\text{POCl}_3$ , iodine and  $\text{NaHCO}_3$  were purchased from Avra Synthesis, Hyderabad. The solvents were distilled and dried before reactions and for extracting purposes. Column chromatography was performed using Merck silica gel (particle size 100-200 mesh). For UV-Vis and fluorescence measurements spectroscopic grade solvents were used.

**Instrumental methods:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data were recorded on a Bruker DPX 400 spectrometer with solvent proton as internal standard ( $\text{CDCl}_3$ - $d_1 = 7.26$  and  $\text{DMSO}-d_6 = 2.50$ ). Deuterated solvents  $\text{CDCl}_3$ - $d_1$ , and  $\text{DMSO}-d_6$  were obtained from Aldrich and Merck, respectively. LC mass spectrometry was performed on Shimadzu LCMS-2010A mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analysis was recorded on a Thermo Finnigan Flash EA 1112 analyzer. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light. Steady-state (UV-Visible absorption spectra) and fluorescence spectra were recorded on a spectrophotometer (Cary-100, Varian) and a spectrofluorimeter (FluoroLog-3, HoribaJobin

Yvon), respectively. For fluorescence quantum yield measurements, **1** and **2** solutions in DCM were matched optically at a absorbing wavelength (331 nm) and then the quantum yield of quinine-sulfate in 0.1M H<sub>2</sub>SO<sub>4</sub> ( $\Phi_f = 0.5$ , at 22°C) was used as reference.<sup>1</sup> Size and morphology of the nanotapes of **1** and semi-micro tubes of **2** were examined by using a Philips XL30 ESEM Scanning Electron Microscope (SEM) using a beam voltage of 20 kV and a Tecnai G<sup>2</sup>FEI F12 transmission electron microscope (TEM) at an accelerating voltage of 120 kV. Confocal fluorescence microscopic images of **1** and **2** were recorded from Leica Laser Scanning confocal microscope (TCS SP2 AOBS), Germany. UV-laser (280-360 nm) was used as excitation. XYλ mode used for graphs analysis.

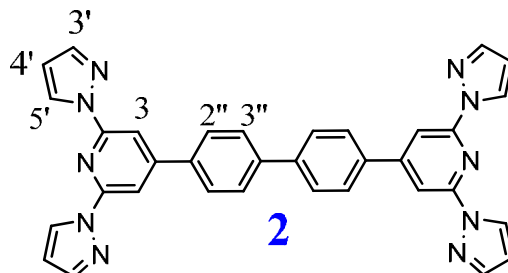
### Reaction Scheme:



**Reaction conditions:** (a) 1,4-bisphenyleneboronicacid, [Pd(PPh<sub>3</sub>)<sub>4</sub>] and 2 M Na<sub>2</sub>CO<sub>3</sub> (5 mL) / 1,4-Dioxane (30 mL) / 3 days / 70 °C, (b) 4,4'-biphenylenediboronicacid, [Pd(PPh<sub>3</sub>)<sub>4</sub>] and 2M Na<sub>2</sub>CO<sub>3</sub> / 1,4-Dioxane/ 3 days/ 70 °C.

**Synthesis of 1 and 3 were as per our reported procedure.<sup>2</sup>**

**Synthesis of 2 ( 4,4'-bis(2,6-di(1H-pyrazol-1-yl)pyridin-4-yl)biphenyl):**



A solution of 1,4-dioxane (30 ml) containing 2 M Na<sub>2</sub>CO<sub>3</sub> (5 ml) was taken in a clean 250 mL flask and N<sub>2</sub> gas was bubbled into the solution for 10 min. To this solution 4-iodo-2,6-di-pyrazol-1-ylpyridine (**3**) (0.145 g, 0.413 mmol), 4,4'-biphenyldiboronic acid (0.050 g, 0.206 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.035 g, 5 mol %) were added and heated in the dark at 70 °C for 3 days. The course of the reaction was monitored by TLC (1: 19 ratio of MeOH : CH<sub>2</sub>Cl<sub>2</sub>). The solvent was evaporated and the crude solid was extracted with a water-CH<sub>2</sub>Cl<sub>2</sub> mixture several times. The collected organic layers were combined and dried over MgSO<sub>4</sub>. Evaporation of the organic extract yielded crude light yellow solid product. The solid residue was washed with cold dichloromethane and methanol solvents to remove soluble impurities and to afford analytically pure white colour powder of **2**. Yield 0.118 mg (48%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.65 (d, 4H, <sup>3</sup>J<sub>H,H</sub> = 2.36 Hz), 8.20 (s, 4H), 7.97(d, 4H, <sup>3</sup>J<sub>H,H</sub> = 8.2 Hz), 7.83-7.81 (m, 8H, 3''), 6.6-6.5 (m, 4H)

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 150.7, 142.4, 141.5, 136.8, 127.8, 127.3, 108.1, 107.1.

**FT-IR** (KBr) ν in cm<sup>-1</sup>: 3439, 3148, 2932, 2856, 1613, 1572, 1539, 1510, 1460, 1394, 1207, 1157, 1119, 1067, 1036, 953, 936, 914, 872, 824, 787,768, 690, 627, 606, 507.

**LCMS** analysis *m/z*: experimental value: 572.86, calculated value: 572.62.

**Elemental analysis**: experimental value: C 71.25, H 4.38, N 24.65; calculated value: C 71.31, H 4.22, N 24.46.

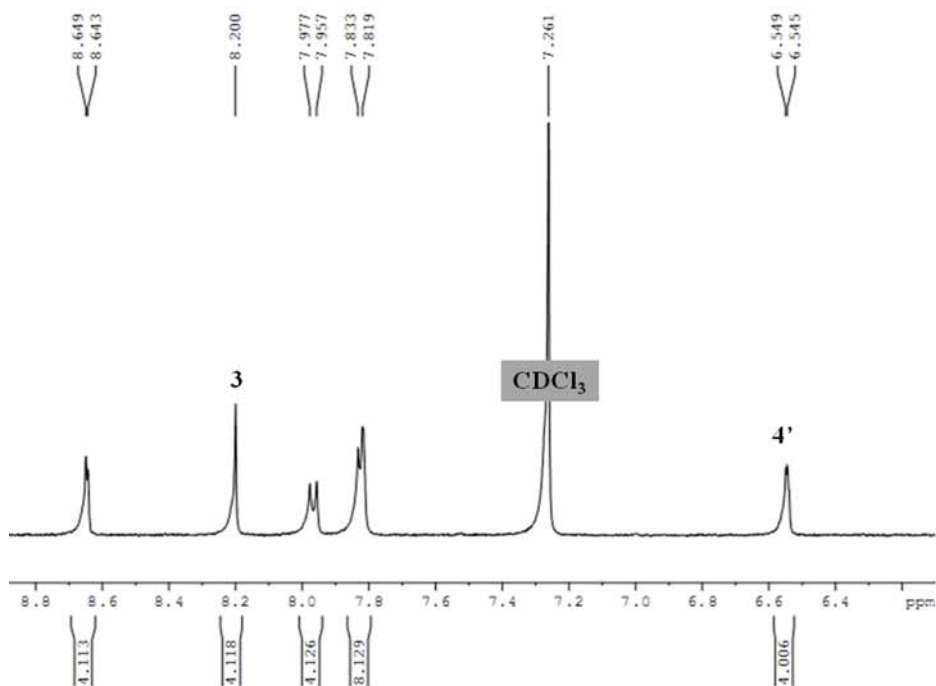
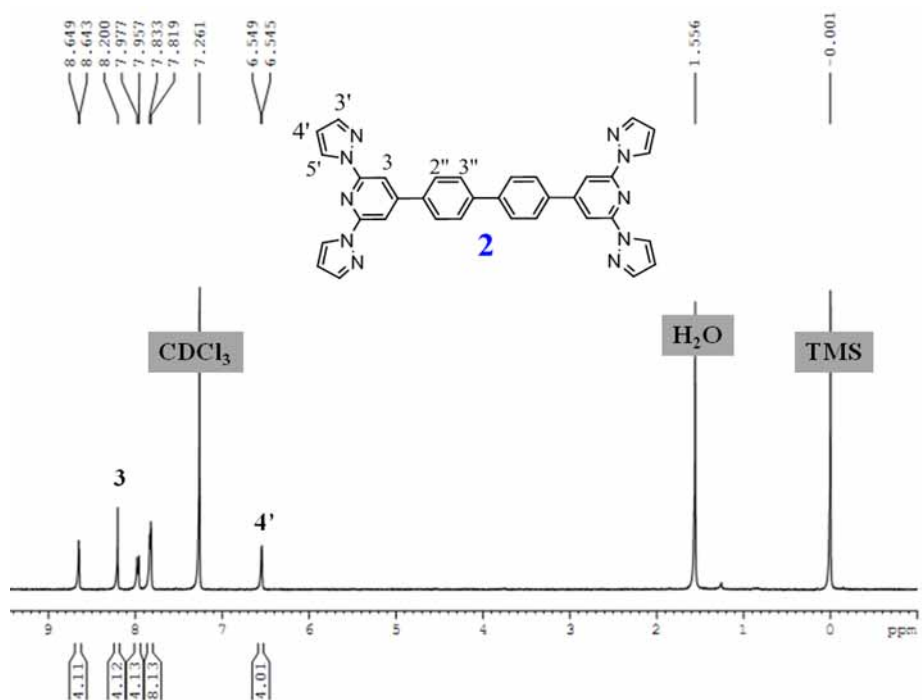


Figure S1:  $^1\text{H}$ -NMR spectra of Compound 2

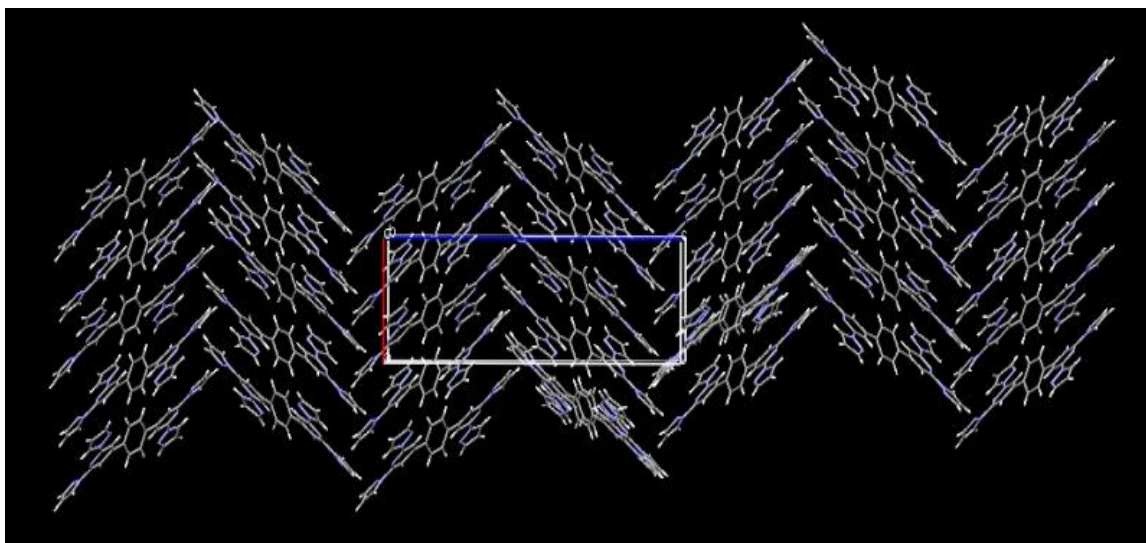
SEM- samples Preparation:

Compound **1** (0.5 mg/mL,  $1.06 \times 10^{-3}$  M) was dissolved in DCM solvent and the obtained clear solution was dispersed on silica substrate (glass slide) and the sample was dried at room temperature. Similarly, the same procedure was followed for compound **2** (0.2 mg/mL,  $0.35 \times 10^{-3}$ ).

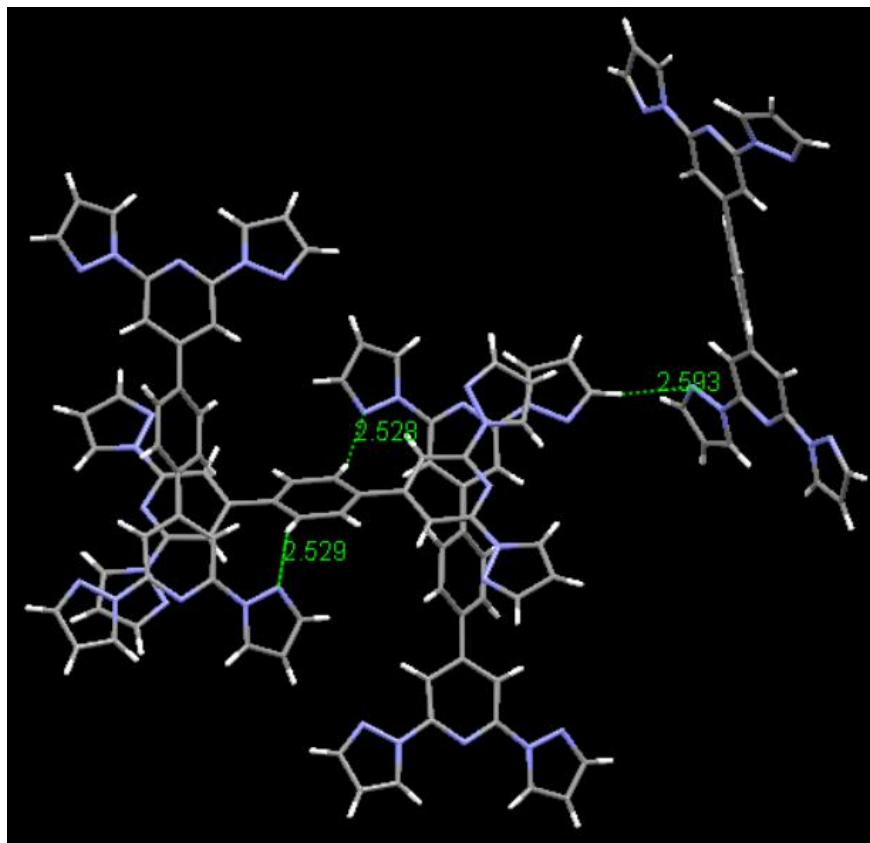
**TEM- samples Preparation:**

Two drops of DCM solution of compound **1** (0.5 mg/mL,  $1.06 \times 10^{-3}$  M) was dispersed on carbon coated copper grid.

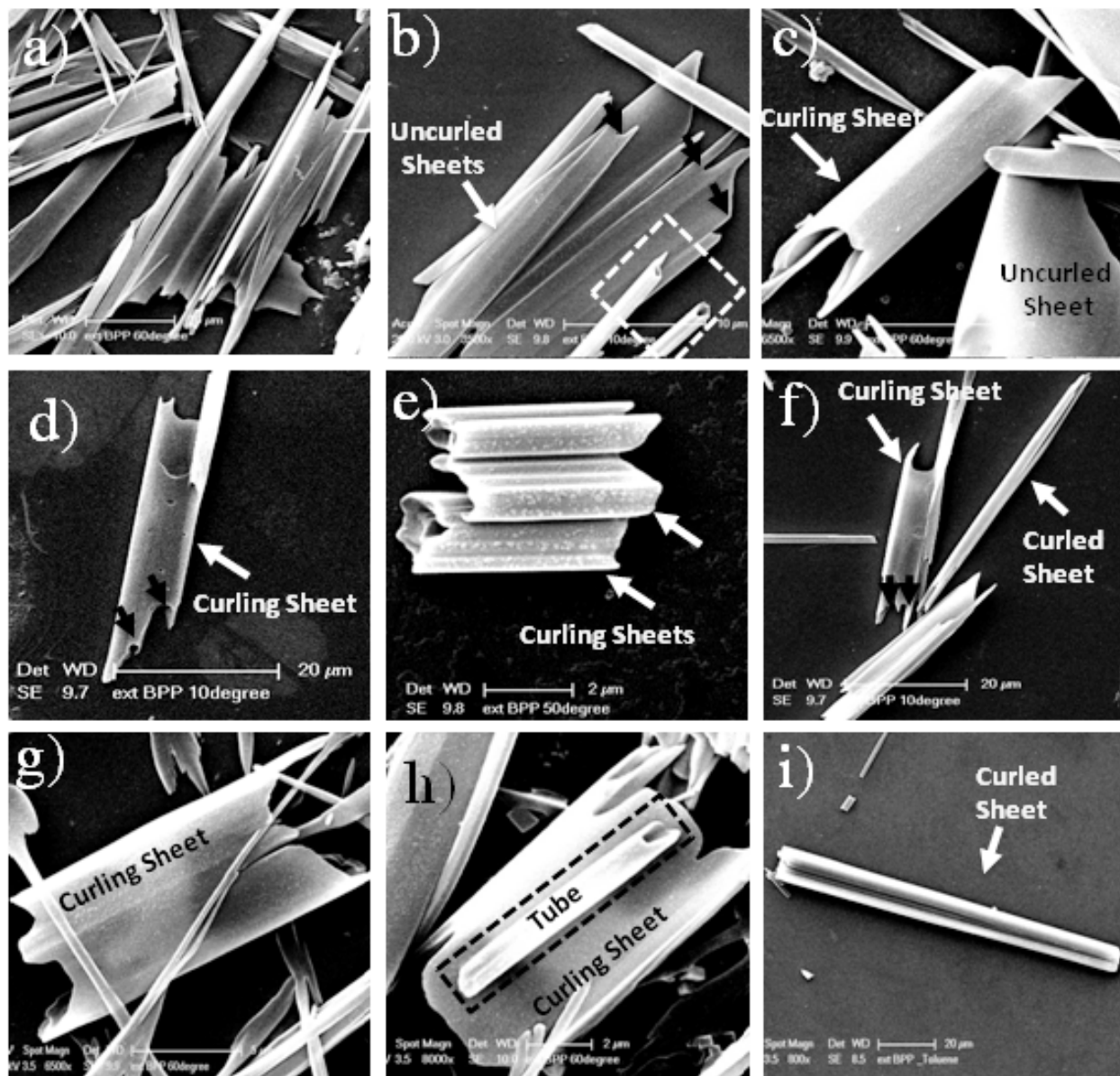
**Single crystal X-ray analysis:**



**Figure S2:** Packing diagram of **1** along the crystallographic *b*-axis



**Figure S3:** Solid state hydrogen bonding [ $\text{N}_{\text{pyrazole}} \cdots \text{H}_{\text{pyrazole}}$  (2.593 Å) and  $\text{H}_{\text{pyridine}} \cdots \text{N}_{\text{pyrazole}}$  (2.529 Å)] interactions responsible for the formation of nanotapes of **1**.



**Figure S4:** SEM micrographs of **2** showing tubular growth mechanism a) Growth of sheet-like structures, b) White arrows: Fully grown uncurled sheets. Black Arrows: Variation in lengths along the sheet axis. White dotted rectangle: fully grown tubes with open ended feature. (scale bar is 10  $\mu\text{m}$ ), c) Rolling of a sheet in the tubular growth process (from a precursor sheet to tubular morphology). d) White arrows: Curling of a sheet. Black Arrows: Variation in lengths along the sheet axis. e) Curling of independent three sheets involved in the tubular growth. f, g) Curling of a sheet. Black Arrows: Variation in lengths along the sheet axis. h) Curling of a sheet, black dotted rectangle: a fully grown tube on a sheet i) a completely curled sheet.

**References:**

1. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2<sup>nd</sup> ed.; Kluwer/Plenum Publishers; New York, **1999**.
2. Rajadurai, C. ; Fuhr O.; Kruk, R.; Ghafari, M.; Hahn, H.; Ruben, M.; *Chem. Commun.*, **2007**, 45, 2636-2648.