Supporting Information

Bromine-Bromine interactions enhanced plasticity for bending of a single crystal without affecting fluorescent properties

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ESI Figure 1. Surface morphology of a bent crystal of 2 observed with AFM. (a) 2D image of the bent section of the crystal showing stacking layers within the molecule. (b) 3D AFM topography of bent section of the crystal showing roughness of the layers (c) Height profile diagram of the crystal.



ESI Figure 2. The displacement ellipsoid plot with atom numbering scheme of compound **2**. 50% probability.



ESI Figure 3. Higher order packing of compound **2**. Hydrogen and halogen bonds are shown as black dotted lines.



ESI Figure 4. Formation of slip plane through Br...Br interaction of crystal of compound **2**.



ESI Figure 5: Concentration dependent emission spectra of (a) compound 1 and (b) compound 2



ESI Figure 6: Solid state fluorescence of compound **2** shows green and red fluorescence upon excitation on 490 nm and 540 nm respectively but compound **1** does not.



Reagents and Conditions: (a) NH₄HCO₂, microwave (800w), 30sec, (b) LiBr, NaIO₄ in AcOH ESI Scheme 1: Reaction scheme for synthesis of compound 1 and compound 2.

Experimental

General

All reagents were purchased from Sigma chemicals and SRL.

Synthesis

The compound **1** was synthesized by microwave assisted Knoevenagel reaction between *p*-methoxy benzaldehyde and ethylcyanoacetate in presence of ammonium formate. Then bromination done to get compound **2**. The products were purified by column chromatography using silica (100–200 mesh size) gel as a stationary phase and an n-hexane-ethyl acetate mixture as an eluent. The intermediates and final compounds were fully characterized by 500 MHz and 400 MHz ¹H NMR spectroscopy, 125 MHz ¹³C NMR spectroscopy, FT-IR spectroscopy and mass spectrometry. The compound **1** and **2** were characterized by X-ray crystallography.

Compound (1). 2.359ml P-Anisaldehyde (19.39mmol), 2.132 ml Ethylcyanoacetate (18.06mmol) and 1.26g Ammonium formate taken in a 250ml conical flask and heated to microwave for 90sec. The mixture was cooled and poured into 100g crushed ice and stir by a glass rod till pale yellow precipitate appears. The product was filtered, washed several times by water and dried. Yield: 3.55g (15.4 mmol,79.4%)

¹**H** NMR (CDCl₃, 400 MHz, δ in ppm): 8.1665 [s, 1H, Double bond proton], 8.0081-7.9852 [d, 2H, Aro Hs, *J*=9.1MHz], 6.9986-6.9757 [d, 2H, Aro Hs, *J*=9.16 MHz], 4.3879- 4.3443 [q, 2H, -OCH₂], 3.8898 [s, 1H, OMe proton], 1.4012-1.3650 [t, 3H, CH₃ of OEt].

¹³C NMR (CDCl₃, 400 MHz, δ in ppm): 164.2075, 163.5496, 154.8350, 134.0782, 124.7725, 116.6681, 115.1902, 99.7346, 62.8644, 56.0567, 14.6290.

Compound (2). 2g (8.64mmol) of compound 1 was dissolved in 13ml of acetic acid and then LiBr (900.4mg, 10.368mmol) and NaIO₄ (462mg, 2.16mmol) was added portion wise in the reaction mixture. Reaction was monitored by TLC and after completion of reaction yellow precipitate comes out. Precipitate was filtered off and washed with hexane and then water. Then the ppt was dissolved in ethylacetate solution and washed with diluted NaHCO3 (3x50ml) and then brine solution (3x50ml). The pale yellow solid product was dried over anhy. Na₂SO₄ and then purified by column chromatography (3% ethyl acetate in hexane). Yield: 1.5g, (5.01mmol, 58%).

¹**H NMR** (CDCl₃, 400 MHz, δ in ppm): 8.1436-8.1372 [d, 1H, Double bond proton, J= 2.56MHz], 8.1035- 8.0672 [m, 2H, Aro Hs], 7.01-6.9871 [d, 2H, Aro Hs, J=9.16 MHz], 4.4012- 4.4345 [q, 2H, -OCH₂], 3.9903 [s, 1H, OMe proton], 1.4089-1.3745[t, 3H, CH₃ of OEt].

¹³C NMR (CDCl₃, 100 MHz, δ in ppm): 163.8626, 154.5283, 152.7834, 133.7429, 131.8360, 124.4562, 116.1516, 114.8549, 99.3326, 62.5386, 55.7214, 14.2937.

Mass spectra: m/z 310, $[M + Na]^+$; M_{calcd} 332.05.

NMR Experiments

All NMR studies were carried out on a Brüker AVANCE 500 MHz and Jeol 400 MHz spectrometer at 278 K. Compound concentrations were in the range 1-10 mM in CDCl₃ and (CD₃)₂SO.

FT-IR Spectroscopy

All reported solid-state FT-IR spectra were obtained with a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique.

Mass Spectrometry

Mass spectra were recorded on a Q-Tof Micro YA263 high-resolution (Waters Corporation) mass spectrometer by positive-mode electrospray ionization.

UV/Vis spectroscopy

Absorption spectra were recorded on a Perkin Elmer spectrophotometer.

Atomic force microscopy

The morphology of the reported compound was investigated by atomic force microscopy (AFM). A small amount of dry crystal was placed on a clean microscope cover glass and then dried under vaccum. The material was then allowed to dry under vacuum at 30°C for two days. Images were taken with an NTMDT instrument, model no. AP-0100 by semicontact-mode.

Field Emission Scanning Electron Microscopy

Morphologies of the reported solid compounds were investigated using field emissionscanning electron microscopy (FE-SEM). A small amount of dry crystal was placed on the top of the coated plated and it was gold-coated, and the micrographs were taken in an FE-SEM apparatus (Jeol Scanning Microscope-JSM-6700F).

Single crystal X-ray diffraction study

Intensity data of compounds **1** and **2** were collected with MoK α radiation using Bruker APEX-2 CCD diffractometer. Data were processed using the Bruker SAINT package and the structure solution and refinement procedures were performed using SHELXL-2014/7. CCDC 1877328 and 1877329, contain the supplementary crystallographic data for compound **1**, **2** respectively.



Fig. S1: ¹H NMR (CDCl₃, 400 MHz, δ in ppm) spectra of compound 1.



Fig. S2: ¹³C NMR (CDCl₃, 100 MHz, δ in ppm) spectra of compound 1.



Fig. S3: ¹H NMR (CDCl₃, 400 MHz, δ in ppm) spectra of compound 2.



Fig. S4: ¹³C NMR (CDCl₃, 100 MHz, δ in ppm) spectra of compound 2.



Fig. S5: Mass spectra of compound 2.



Fig. S6: FT-IR spectra of compound 1 and 2.