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Bromine-bromine interactions enhanced plasticity for the bending of a single crystal without affecting fluorescent properties[†]

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Ethyl 3-(3-bromo-4-methoxy-phenyl)-2-cyano-acrylate crystals exhibited very superior plasticity and shape persistent, selfstanding properties compared to their non-bromo analogue. The crystal plasticity, controlled by a bromine-bromine interaction, has been found to play a crucial role in generating a slip plane and thus, under mechanical force, the crystals undergo bending without affecting their fluorescent properties.

crystals of small organic molecules Flexible with optoelectronic properties are highly important for device fabrication and engineering.¹ Previously, it was reported that molecular crystals can bend,² twist,³ curl,⁴ or change their shape⁵⁻⁸ under external stimuli like heat, light, mechanical force, etc.⁶⁻⁸ Previously, most of the reported bending crystals were obtained by serendipity until a proper explanation was given by Reddy et al. on the strategy for the design and synthesis of bendable crystals.9 Both plastically (irreversible)¹⁰⁻¹² and elastically (reversible) bendable organic crystals13-16 have been well-studied in recent years. Plastic crystals are the type of crystal in which molecular rotation is enabled under sheer pressure without the loss of crystallinity. They are useful in the field of electrolytes,¹⁷⁻¹⁹ ferroelectrics,20,21 and molecular rotors.22 Recently, Reddy and his group reported various mechanically flexible organic crystals by introducing active slip planes within molecules and showed that some noninterfering supramolecular weak interactions like hydrogen bonding, π - π stacking and van der Waals interactions are the key elements to introducing the slip plane within a crystal.²³

Solid-state packing-induced photoluminescence is extremely important in the area of crystal engineering,²⁴ and it has potential applications in the field of lasers, OLEDs, optical data storage,²⁵ two-photon photoluminescence (PL) microscopy,²⁶ optical switching²⁷ and limiting.²⁸ It is well known in the literature that various synthetic organic dyes show different fluorescent colours due to their different solid state packing.^{29,30} It was also reported that solid-state molecular packing can enhance a luminescent phenomenon through aggregation-induced emission (AIE).³¹ Presently, non-dopant emitters with an enhanced emission property in the solid state are highly desirable to avoid the complicated doping process during the fabrication in OLEDs.^{32,33} So, the discovery of a novel solid-state red-emissive chromophore is in high demand as well as challenging,³⁴ as they are very rare in the literature.³⁵ It has also been reported that a compound having Br...Br interactions can control the luminescence property of the compound.³⁶ T. Koizumi and his group reported a fluorescent organic crystal which shows elastic bending.³⁷ Recently, we have reported a halogen bond induced self-assembly and solid state phosphorescence of a bromo-substituted capped γ -amino acid foldamer.³⁸ We have also reported the effect of packing on the solid state fluorescent properties of peptidic luminophores and their thermochromic behavior.39



Scheme 1 The schematic structures of compounds 1 and 2.

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[†] Electronic supplementary information (ESI) available: Synthesis and characterization of compounds 1 and 2, ¹H NMR, ¹³C NMR, solid state FTIR spectra, ESI Fig. 1–6, Fig. S1–S6. Crystallographic data: Compound 2: C₁₃H₁₂BrNO₃, MW = 310.15, monoclinic, space group *P*2₁/*n*, *a* = 11.5570(4), *b* = 4.03422(16), *c* = 27.4354(15) Å, *α* = 90, *β* = 95.906(4), *γ* = 90, *V* = 1272.35(10) Å3, *Z* = 4, dm = 1.619 g cm⁻³, *T* = 100 K, *R*₁ 0.0393 and *wR*₂ 0.0866 for 2241 data with *I* > 2*σ*(*I*). Intensity data of 2 were collected with MoKα radiation using a Bruker APEX-2 CCD diffractometer. Data were processed using the Bruker SAINT package and the structure solution and refinement procedures were performed using SHELX-2014/7.⁴² A Hirshfeld surface (HS) analysis⁴³ was carried out by using Crystal Explorer 17.5.⁴⁴ CCDC 1877329 contain the crystallographic data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ce02086h

Inspired by previous reports, here we aim to investigate the effect of a bromine atom on molecular packing, optical and mechanical properties of a small organic molecule (Scheme 1). For that purpose, we have designed and synthesized compound 1, (E)-ethyl 2-cyano-3-(4-methoxyphenyl) acrylate, and its meta substituted bromo derivative, compound 2. Surprisingly, we have observed plastic bending (Scheme 1) of compound 2 due to a unique Br...Br interaction which generates a slip plane between the two stacks of molecules in a higher order assembly. As that kind of Br…Br interaction is absent in compound 1, it has failed to exhibit a bending property. Rather, the compound 1 crystals broke under mechanical stress. Furthermore, due to this unique Br...Br interaction, compound 2 exhibits green and red fluorescence in the solid state upon excitation at 490 nm and 540 nm, respectively. So, herein, we attempt to explore both the crystalline solid-state properties that deal with the bromine-induced plastic bending of crystals, as well as the packing-induced solid state green and red emissions of the crystal of compound 2. This proves that the Br...Br interactions have an explicit effect on the unique combination of crystal packing of the compound 2 molecules.

Compound 1 was synthesized with a 79.4% yield by a microwave-assisted Knoevenagel reaction between p-anisaldehyde and ethylcyanoacetate in the presence of ammonium formate. Further, compound 2 was obtained from a NaIO₄- and LiBr-mediated meta position bromination of compound 1 in AcOH (ESI† Scheme S1). Both the compounds were characterized by ¹H-NMR (nuclear magnetic resonance), ¹³C-NMR, FT-IR (Fourier-transform infrared) and mass spectrometry (MS) analysis.

Colourless crystals of compounds 1 and 2 were obtained from a methanol-water solution by slow evaporation. Using a needle and forceps, crystals of the compounds 1 and 2 were subjected to bend manually in a three-point geometry (Fig. 1a), under an optical microscope. Surprisingly, the crystals of compound 2 are flexible and bend under mechanical stress (Fig. 1b). However the non-bromo derivative, *i.e.* compound 1, crystals break into multiple parts under the same mechanical stress. Thus, we are able to tune the mechanical behaviour, as well as the supramolecular assembly, of compound 2 by introducing a heavy atom effect. As seen in Fig. 1c and d, the crystals of compound 2 bend upon application of local pressure at the end of the crystal and the bending is highly plastic in nature, *i.e.* the deformation is irreversible.

To investigate the nature of the surface of the crystals of compounds 1 and 2 under mechanical stress, we have used field emission scanning electron microscopy (FE-SEM). The FE-SEM image (Fig. 2a) shows that the compound 1 crystals are broken under the mechanical stress. However, under the same condition, the crystals of compound 2 depict a striped surface with rims along the length of the crystal (Fig. 2b). Fig. 2b shows that various macroscopic layers are stacked along the longitudinal axis of the crystal surface which are not clearly noticeable in the straight section of the crystal (Fig. 2c). Thus, we understood that layers have generated as a result of the shear stress by the mechanical force during the bending. The SEM images of the poked crystal clearly showed the slices of separated macroscopic layers. This type of macroscopic layer formation in a plastically bendable crystal was previously reported by Reddy and co-workers.⁴⁰

To examine the topographic features, as well as the roughness of the surface of the bent crystals, we have performed atomic force microscopy (AFM). From the AFM, we have also observed distinct stacking layers at a bent section of the crystals (ESI† Fig. S1a). From the 3D view, it is very clear that the layers are very rough in nature (ESI† Fig. S1b) and the roughness of the surface was *ca.* 0.67 μ m, as calculated from the AFM.

The effect of bending on the molecular arrangement and intermolecular interactions were investigated by micro-Raman spectroscopy (Fig. 2d). The symmetry-equivalent compound 2 molecular arrangement became dissimilar by the



Fig. 1 (a) Crystal of compound 2 bent on the 010 face. The arrows show the point of the applied forces. (b), (c) and (d) step-by-step pictures of 360° crystal bending.



Fig. 2 (a) FE-SEM image of a sharply broken compound 1 crystal under mechanical stress. (b) FE-SEM image of a compound 2 bent crystal showing various macroscopic layers stacked along the longitudinal axis of the crystal surface. (c) FE-SEM image of the straight section of a compound 2 crystal. (d) The micro-Raman spectra of bent (red) and straight (black) crystals of 2.

formation of layers on the crystal surface (Fig. 2d). Moreover, the symmetry lowering was reflected as significant intensity changes in the respective Raman spectra of the bent and straight crystals.

Colourless needle-shape crystals of compound 1 were suitable for X-ray diffraction, as was previously reported by S. Sreenivasa *et al.*⁴¹ Compound 1 crystallizes in the monoclinic space group *P*21/*n* with one molecule in the asymmetric unit. As expected, compound 1 adopts a planar conformation (Fig. 3a, red). In the crystal, molecules are interlinked into anti-parallel dimers through two C—H···O interactions (Fig. 3b). Further, the compound 1 molecules are stabilized by weak C—H··· π interactions, and weak π ··· π interactions (centroid-centroid separation = 4 Å) along the *c* axis.⁴¹ Thus, the compound 1 molecules are arranged in a herringbone-like pattern in a higher order assembly, but there is a lack of a slip plane.

Compound 2 crystallizes in the monoclinic space group P21/n with one molecule in the asymmetric unit (ESI† Fig. S2). As seen in Fig. 3a, compound 2 also adopts a planar conformation and there is no significant difference from the backbone conformation of compound 1. In the packing of compound 2, individual subunits are also interlinked into anti-parallel dimers, through two C—H…O interactions (ESI† Fig. S3). However, the 2D fingerprint plot (a visual summary of the frequency of each combination of d_e and d_i across compound 2's surface) shows Br…Br interactions present in

compound 2 (highlighted in colour in Fig. 3c). It is evident from the crystal structure of compound 2 that there is an intermolecular Br···Br interaction which generates the slip plane between the two stacks of molecules (Fig. 3d and ESI† Fig. S4). Due to this Br···Br interaction, the two molecules of compound 2 come closer compared to 1, and for this reason the π ··· π interaction is also stronger in the case of compound 2 (centroid-centroid distance = 3.56 Å).

Then, we studied a concentration-dependent emission for both the compounds to understand their self-assembly propensities. The emission spectra ($\lambda_{ex} = 340 \text{ nm}$) show that with an increasing concentration the emission intensity decreases gradually (ESI† Fig. S5) for both the compounds. This is due to an aggregated form that causes the molecules to return to their ground state in a non-radiative pathway. This phenomenon is known as aggregation-induced fluorescence quenching. This result clearly indicates that both compounds have a similar type of aggregation in the solution state as they both possess a similar chromophore.

Next, to understand the effect of the Br…Br interaction, here we have studied and compared the solid state fluorescence behaviour of brominated and non-brominated compounds. In solution, both the compounds exhibit a similar type of aggregation pattern, however, they differ in the solid state. Crystals of compound 2 show emission peaks at 590





Fig. 3 (a) The overlay of the molecular conformations of compounds 1 (red) and 2 (green) in the solid state showing the structural similarity. (b) The packing diagram of compound 1 in crystal (carbon: grey; oxygen: red; nitrogen: blue). C-H···O and C-H···N interactions are shown as black dotted lines. (c) 2D fingerprint plot with Br···Br interactions highlighted in colour for compound 2. (d) Br···Br interactions in the crystal of compound 2 with a slip plane (green box). π ··· π interactions between aromatic rings oriented along different directions (red and blue arrows).

Fig. 4 (a) and (b) Green and red fluorescence of the straight section of the crystal of compound 2 under a fluorescence microscope. (c) and (d) Green and red fluorescence of the bent section of the crystal of compound 2 under a fluorescence microscope showing the striped surface with stacked layers along the length of the crystal. (e) Effect of bending on the Br…Br interaction. (f) The origin of fluorescence.

nm and 610 nm upon excitation at 490 nm and 540 nm, respectively (ESI[†] Fig. S6). But crystals of compound 1 failed to emit in that particular wavelength (ESI[†] Fig. S6). We have also done fluorescence microscopy imaging of the crystals of compound 2 and they show intense green and red emissions on excitation at 490 nm and 540 nm, respectively (Fig. 4a and b). Due to the conjugate effect of a Br...Br interaction and strong π - π stacking, the compound 2 crystals show a solid state packing-induced emission. Fig. 4c and d show the green and red fluorescence of the bent section of the crystal of compound 2 on excitation at 490 nm and 540 nm under fluorescence microscope. Moreover, Fig. 4c and d show the striped surface with stacked layers (marked with a white arrow) along the length of the crystal. However, these kind of stacked layers are absent in the straight section of the crystal. Thus, under mechanical force, the bending of the compound 2 crystals does not affect their fluorescent properties due to heavy atom effect (Fig. 4e and f).

In conclusion, we have reported that a Br…Br interaction significantly enhanced the plasticity of the crystal and helped with bending of the crystal. The studies showed that stacked layers slid on top of one another, but ultimately bound to each other due to a restorative effect of the Br…Br interaction. Raman spectra of bent and straight crystals showed significant intensity changes on bending, but amorphous material did not appear. Furthermore, due to a heavy atom effect compound 2 also showed green and red fluorescence under suitable conditions which did not change under mechanical stress. This crystal with plasticity and optoelectronic properties has potential for device fabrication.

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Conflicts of interest

There are no conflicts to declare.

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