Supplementary Information

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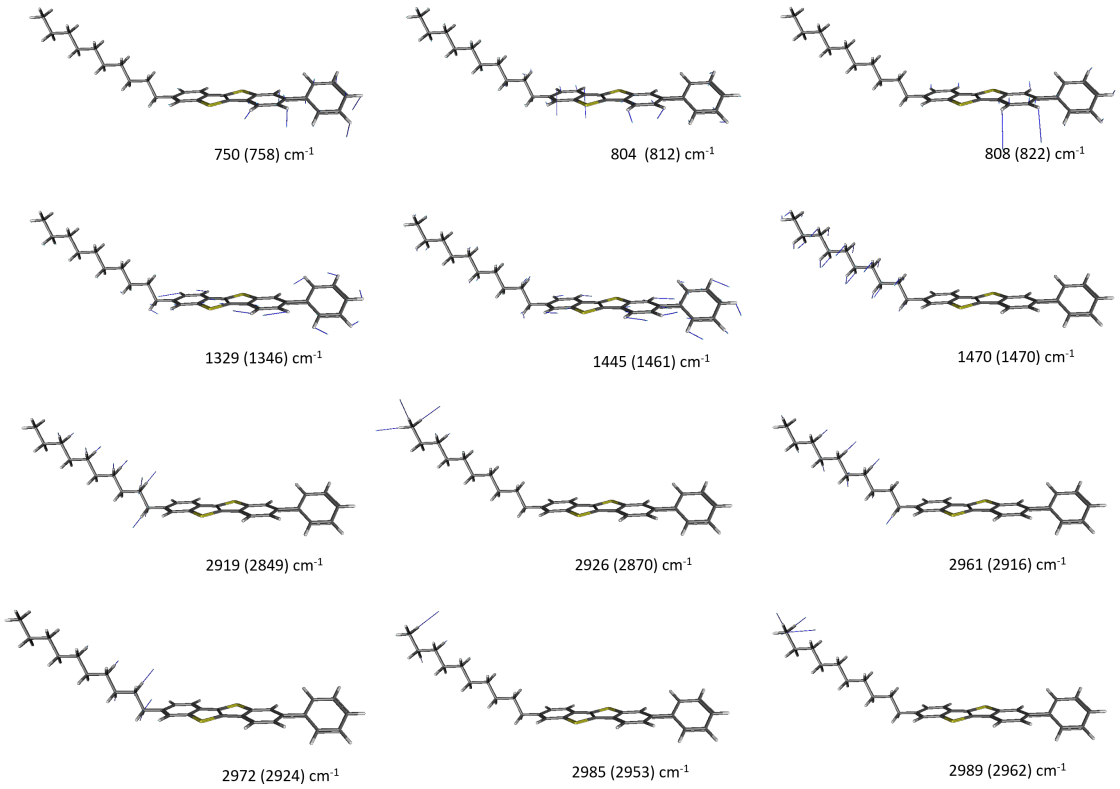

Figure S1: *Calculated eigenvectors of selected vibrational modes of the Ph-BTBT-10 isolated molecule. The calculated frequencies have been scaled by 0.97. The experimental ones, in parentheses, are averaged in the case of Davydov splitting.*

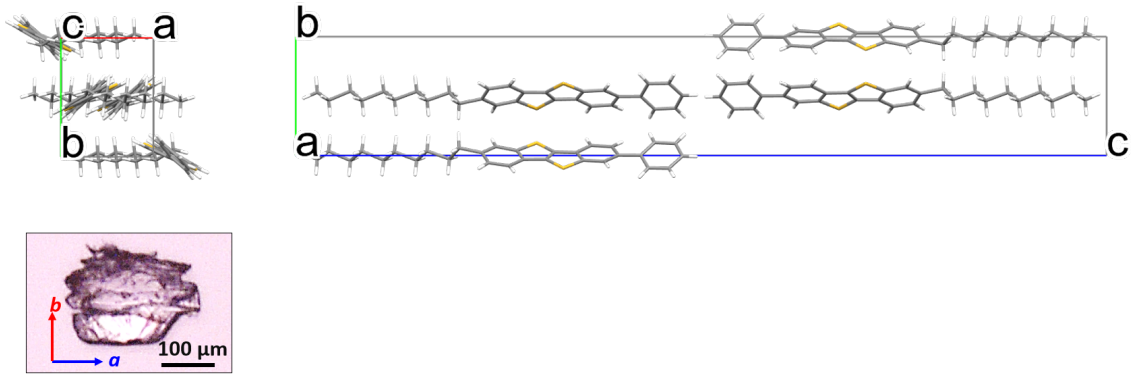

Figure S2: *Upper panel: Ph-BTBT-10 unit cell (CCDC refcode ROQSAT) viewed perpendicular to the ab (left) and bc planes (right). Lower panel: microscopic image of a crystal.*

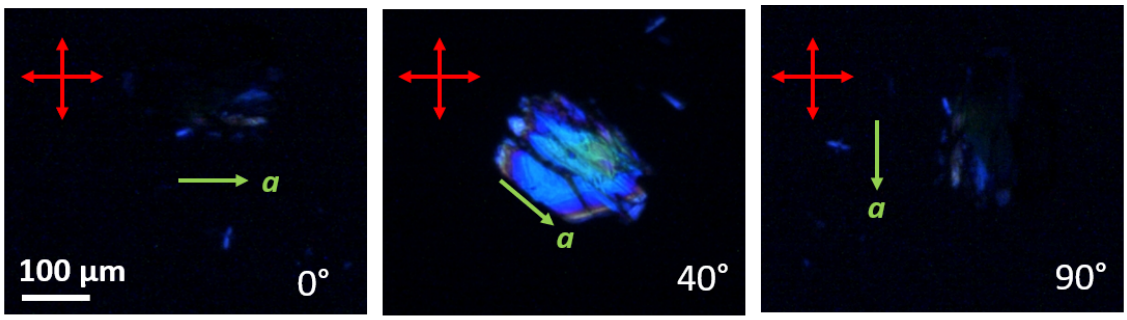

Figure S3: *Microscopic images of an oriented Ph-BTBT-10 crystal, in transmission mode between two crossed polarizers, whose polarization axes correspond to the red arrows. The rotation angle is indicated in each image: if the crystal is rotated of any angle between 0° and 90°, extinction does not occur.*

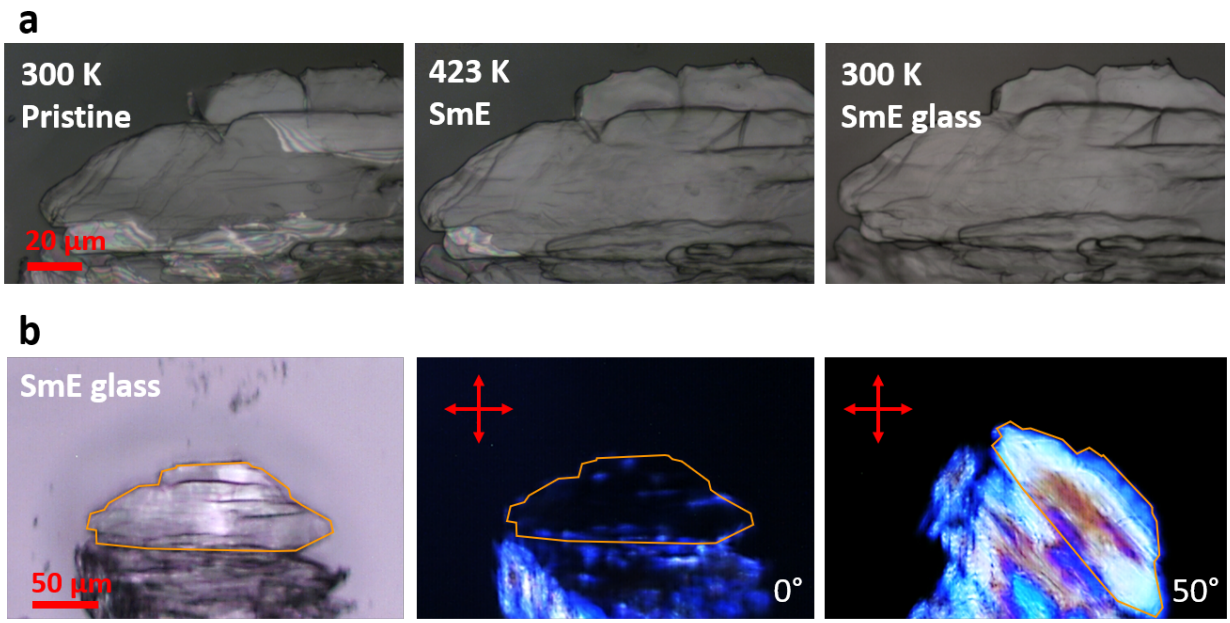

Figure S4: *a) Microscopic images of an oriented Ph-BTBT-10 sample, before heating (left); at 430 K (middle) and after cooling at 90 K/min (right). b) Frozen SmE phase, observed in reflection mode (left) and in transmission mode between two crossed polarizers (middle and right) to show the occurence of extinction directions. The reference single crystal domain is delimited with orange line.*

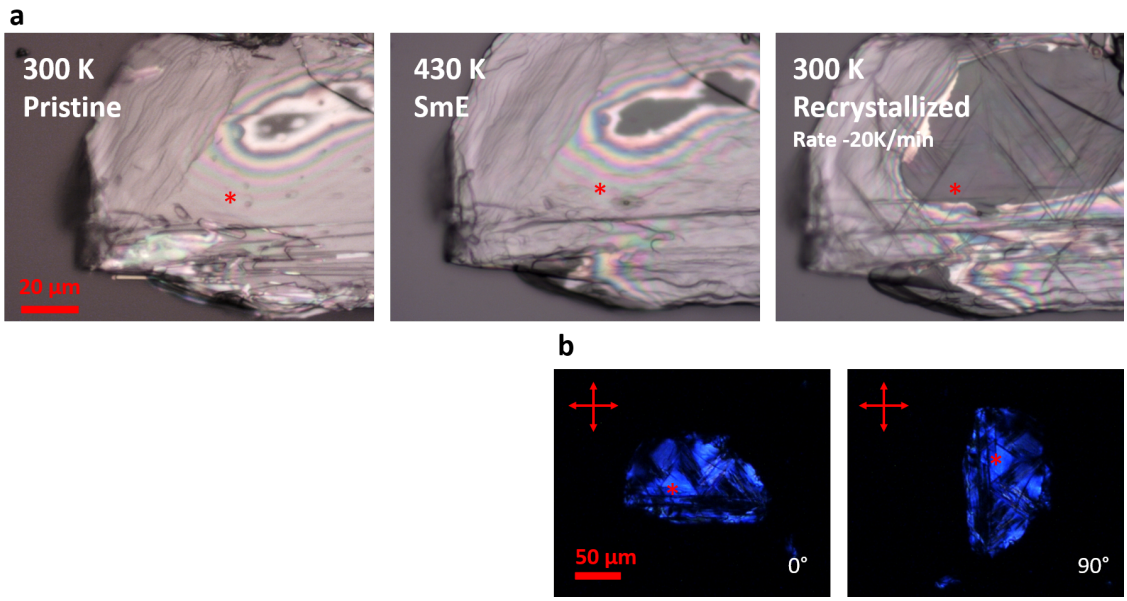

Figure S5: *a) Microscopic images of an oriented Ph-BTBT-10 sample: pristine crystal (left); SmE at 430 K (middle) and after fast cooling at 20 K/min (right). b) Same recrystallized sample observed in transmission mode between two crossed polarizers to show the presence of many different crystalline domains. The red asterisk marks the same point in the images. The rotation angle is indicated in each image.*

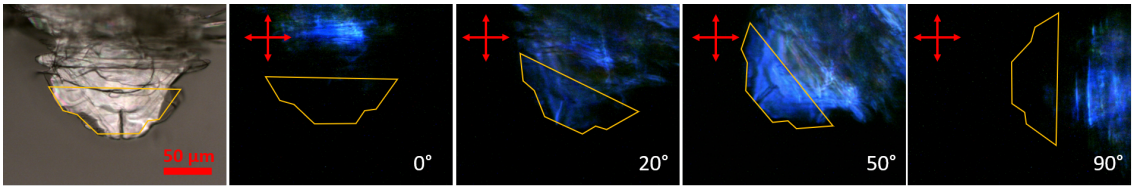

Figure S6: *Microscopic images of a Ph-BTBT-10 sample obtained by annealing the frozen SmE phase at 393 K. The left image was acquired in reflection mode. The remaining ones were obtained in transmission mode between two crossed polarizers, whose polarization axes correspond to the red arrows. The rotation angle is indicated in each image. The crystal shape is highlighted by the orange line.*

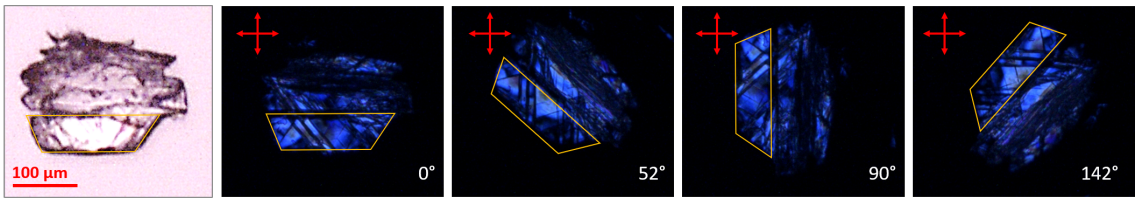

Figure S7: *Microscopic images of a Ph-BTBT-10 sample obtained by cooling the SmE phase with a rate of 1 K/min. The left image was acquired in reflection mode. The remaining ones were obtained in transmission mode between two crossed polarizers, whose polarization axes correspond to the red arrows. The rotation angle is indicated in each image. The crystal shape is highlighted by the orange line.*