

Supporting Information

Order, Viscoelastic and Dielectric Properties of Symmetric and Asymmetric Alkyl[1]benzothieno[3,2-b][1]benzothiophenes

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1. Synthetic pathway to C₈-BTBT and C₈-BTBT-C₈ and potential impurities

C₈-BTBT and C₈-BTBT-C₈ have been obtained by reduction with hydrazine in basic conditions from their corresponding mono- and di-ketones, respectively (Fig. S1). [Bedřich Košata, Václav Kozmík, Jiří Svoboda, *Collect. Czech. Commun.* **2002**, *67*, 645-664] [Bedřich Košata, Václav Kozmík, Jiří Svoboda, Vladimíra Novotná, Přemysl Vaněk, Milada Glogarová, *Liq. Cryst.* **2003**, *30*, 603-610] According to [Yun Li, Chuan Liu, Michael V. Lee, Yong Xu, Xu Wang, Yi Shi, Kazuhito Tsukagoshi, *J. Mater. Chem. C*, **2013**, *1*, 1352-1358], this reduction procedure generates some side products as traces that are depicted below and that, in principle, might contribute to dielectric response. However, we have not observed any impurities by ¹H-NMR spectroscopy and thin layer chromatography (Fig. S2).

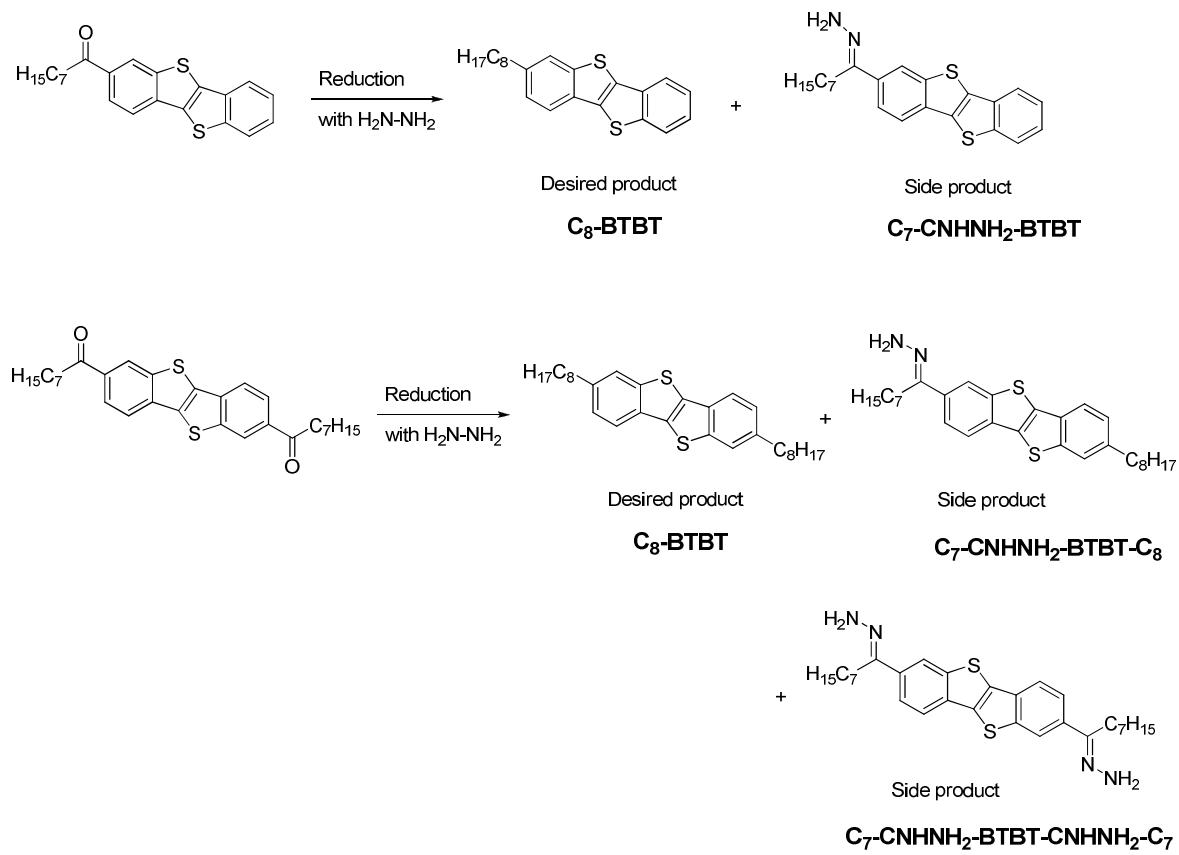


Fig. S1. Synthesis scheme and possible traces of side-products

2. ^1H -NMR spectra of C₈-BTBT and C₈-BTBT-C₈

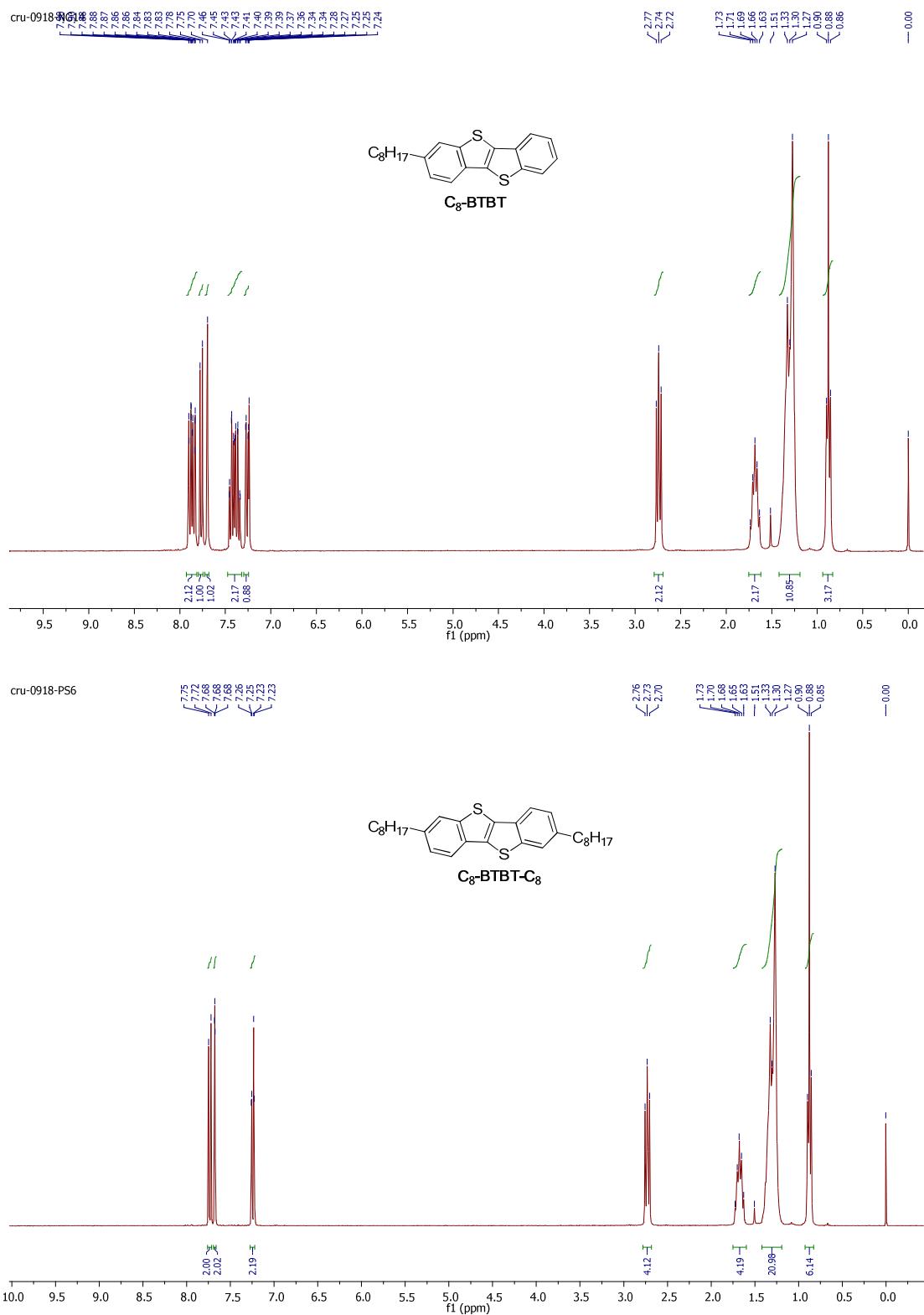


Fig. S2. ^1H -NMR spectra

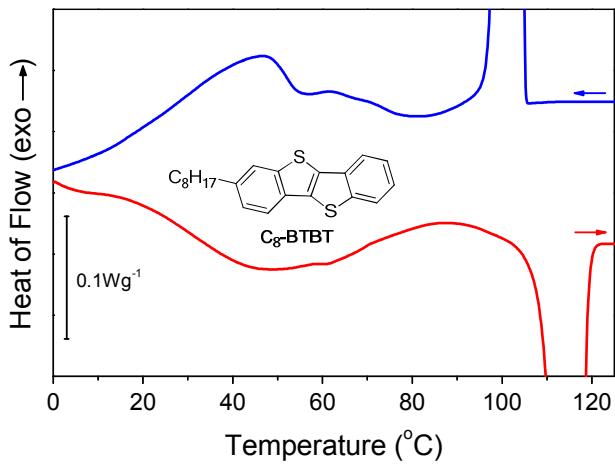


Fig. S3. Expanded DSC trace of C₈-BTBT obtained during cooling (blue) and subsequent heating (red) with 10 K/min. Arrows indicate the direction of temperature change.

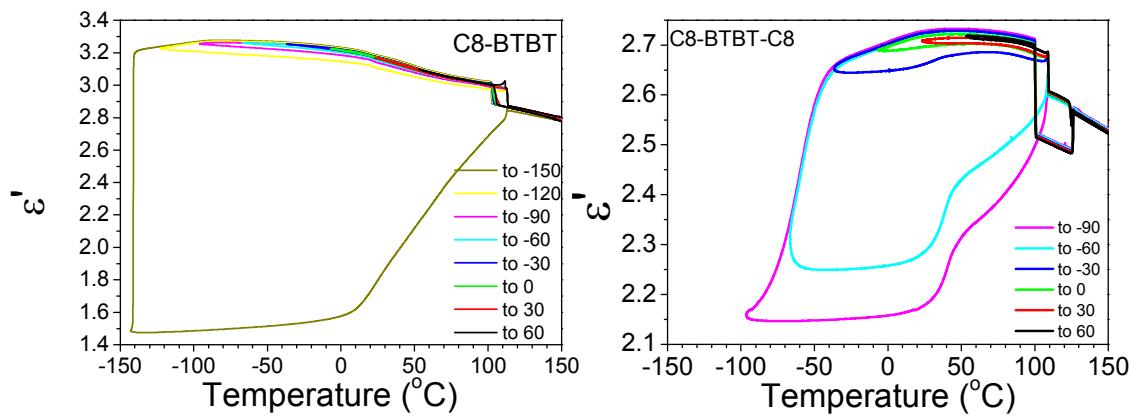


Fig. S4. Temperature dependence of the dielectric permittivity of C₈-BTBT (left) and C₈-BTBT-C₈ (right) obtained under isochronal conditions ($f=0.1$ MHz) on cooling/heating cycles to different final temperatures. All temperature ramps are made with the same rate (2 K/min).