MS27-1-3 High-pressure structure and phase behaviour of naphthyl end-capped oligothiophene
#MS27-1-3

N. Giordano [1], S. Guha [2], B. Stewart [3], J. Kjelstrup-Hansen [4], M. Knaapila [5]
[1]DESY - Hamburg (Germany), [2]University of Missouri - Columbia (United States), [3]University of Bradford - Bradford (United Kingdom), [4]University of Southern Denmark - Sønderborg (Denmark), [5]Norwegian University of Science and Technology - Trondheim (Denmark)

Abstract
Pressure provides a clean tool to modify molecular packing without chemical interference, including intermolecular separation and relative displacements as shown for optically active materials like π-conjugated molecules.[1] Understanding macromolecular self-organisation is essential in the physics and materials science of π-conjugated molecules giving rise to their intriguing opto-electronic properties and applications.[2,3,4] Brédas and others studied thiophenes including sexithienyls and other π-conjugated molecules and established fundamental principles in how the charge transport and other properties depend on their intermolecular separation and the relative displacements between molecules.[5,6]
Here, we present high-pressure crystal structures of naphthyl end-capped oligothiophene, 5,5′-bis(naphth-2-yl)-2,2′-bithiophene (NaT2), derived from single-crystal X-ray diffraction synchrotron experiments supported by high pressure optical and Raman spectroscopy and molecular modelling. First, we report high pressure crystal structures to 0.8 Å resolution and show reversible unit cell modifications with increasing pressure ending up with a new high-pressure phase at 3 GPa. Second, we describe interaction directionalities and identify new sulfur-hydrogen contacts that demonstrate the fundamental difference between thiophenes and acenes and other fused-ring molecules. Our results complement both earlier ambient condition studies of NaT2 and other thiophenes as well as earlier high-pressure studies of small π-conjugated molecules, polymers and other materials.

References
(1) Schmidtke, J. P.; Friend, R. H.; Silva, C. Tuning Interfacial Charge-Transfer Excitons at Polymer-Polymer Heterojunctions under Hydrostatic Pressure. Phys. Rev. Lett. 2008, 100 (15), 157401. https://doi.org/10.1103/PhysRevLett.100.157401.
(2) Da Como, E.; von Hauff, E. The WSPC Reference on Organic Electronics: Organic Semiconductors. Materials and Energy Series. Volume 1: Basic Concepts, Volume 2: Fundamental Aspects of Materials and Applications. Edited by Jean-Luc Brédas and Seth R. Marder. Angew. Chem. Int. Ed. 2017, 56 (18), 4915–4916. https://doi.org/10.1002/anie.201701913.
(3) Mishra, A.; Ma, C.-Q.; Bäuerle, P. Functional Oligothiophenes: Molecular Design for Multidimensional Nanoarchitectures and Their Applications. Chem. Rev. 2009, 109 (3), 1141–1276. https://doi.org/10.1021/cr8004229.
(4) Zhang, L.; Colella, N. S.; Cherniawski, B. P.; Mannsfeld, S. C. B.; Briseno, A. L. Oligothiophene Semiconductors: Synthesis, Characterization, and Applications for Organic Devices. ACS Appl. Mater. Interfaces 2014, 6 (8), 5327–5343. https://doi.org/10.1021/am4060468.
(5) Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. Charge-Transfer and Energy-Transfer Processes in π-Conjugated Oligomers and Polymers: A Molecular Picture. Chem. Rev. 2004, 104 (11), 4971–5004. https://doi.org/10.1021/cr040084k.
(6) Mannebach, E. M.; Spalenka, J. W.; Johnson, P. S.; Cai, Z.; Himpsel, F. J.; Evans, P. G. High Hole Mobility and Thickness-Dependent Crystal Structure in α,ω-Dihexylsexithiophene Single-Monolayer Field-Effect Transistors. Adv. Funct. Mater. 2013, 23 (5), 554–564. https://doi.org/10.1002/adfm.201201548.

Reversible yellow to red colour change in NaT2