**One-Pot Synthesis of Thiepin-Fused Heteroacenes**

**Significance:** Polycyclic aromatic hydrocarbons with heteroatom substitution are attractive materials for semiconductor applications. The authors present the efficient installation of a thiepin unit onto easily accessible DIDT (C.-H. Chen, Y.-J. Cheng, M. Dubosc, C.-H. Hsieh, C.-C. Chu, C.-S. Hsu Chem. Asian J. 2010, 5, 2483). In this one-pot synthesis, DIDT was deprotonated with potassium tert-butoxide, reacted with carbon disulfide, and quenched with methyl iodide or hexyl bromide. The fused thiepins were obtained in 90% and 80% yield.

**Comment:** HOMO and LUMO energies were determined by cyclic voltammetry (~5.35 eV and ~3.26 eV, respectively, regardless of the alkyl chain). Both compounds exhibited typical p-type semiconducting behavior with hole mobilities up to $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Thin films were further characterized by AFM and XRD. Crystal structures were obtained for both compounds and showed multiple S=S contacts.