

Abstract

A series of indeno[1,2-*b*]fluorene-6,12-dione-thiophene derivatives with hydrocarbon substituents at α,ω -positions as side groups have been designed and synthesized. The new compounds were fully characterized by $^1\text{H}/^{13}\text{C}$ NMR, mass spectrometry, cyclic voltammetry, UV-vis absorption spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and melting point measurements. The solid state structure of the indeno[1,2-*b*]fluorene-6,12-dione acceptor core has been identified based on single-crystal X-ray diffraction (XRD). The structural and electronic properties were also studied using density functional theory calculations, which were found to be in excellent agreement with the experimental findings and provided further insight. The detailed effects of alkyl chain size and orientation on the optoelectronic properties, intermolecular cohesive forces, thin-film microstructures, and charge transport performance of the new semiconductors were investigated. Two of the new solution-processable semiconductors, **2EH-TIFDKT** and **2OD-TIFDKT**, were deposited as thin-films *via* solution-shearing, drop-casting, and droplet-pinned crystallization methods, and their morphologies and microstructures were investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM). The solution-processed thin-film transistors based on **2EH-TIFDKT** and **2OD-TIFDKT** showed ambipolar device operations with electron and hole mobilities as high as $0.12\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and $0.02\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, respectively, with $I_{\text{on}}/I_{\text{off}}$ ratios of 10^5 to 10^6 . Here, we demonstrate that rational repositioning of the β -substituents to molecular termini greatly benefits the π -core planarity while maintaining a good solubility, and results in favorable structural and optoelectronic characteristics for more efficient charge-transport in the solid-state. The ambipolar charge carrier mobilities were increased by two–three orders of magnitude in the new indeno[1,2-*b*]fluorene-6,12-dione-thiophene core on account of the rational side-chain engineering