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## Dithienothiophene based quinoidal solution-processible n-type organic semiconductors

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The conjugated organic materials have attracted much attention for the potential applications of organic field effect transistors (OFETs) in memory devices, smart cards, radio frequency identification tags, electronic papers, flexible displays and sensors due to their low cost process ability and high flexibility. Currently solution processible small molecular organic semiconductors are of great interest to develop high performance and ambient stable organic materials for OFETs. A versatile building blocks with efficient solubility is important in developing solution processible organic semiconductors in which alkyl chains are a fundamental units. The alkyl chain modifications such as changing in length, installing branched alkyl side chains and position of branching are important features in achieving better device performances, molecular packing, and intermolecular interactions. Dithieno[3,2-b:2', 3'-d]thiophene (DTT) unit has shown as one of promising building block of conjugated materials with p and n channel charge carrier nobilities. We have designed and synthesized a series of dialkyldithieno [3, 2-b:2', 3'-d]- thiophene based dicyanomethylene end capped quinoidal n-channel organic semiconductors with various alkyl chains (DTTQ-3, DTTQ-6, DTTQ-11 DTTQ-15). We have applied one pot synthetic route for the preparation of dialkyldithieno [3, 2-b:2', 3'-d]- thiophene. Among the synthesized quinoidal compounds DTTQ-11 has exhibited the electron mobility of 0.45 cm² V-¹ s-¹. The single crystal x-ray diffraction of DTTQ-6 was determined and the charge transport in this packing structures can be achieved either through face-to-face parallel molecules in the same stack or through the well zip-zap connected neighboring molecules.

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## Controlled 3d nano-sculpturing and nano-sintering of silk proteins using electron beam lithography

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Cilk protein fibers produced by silkworms and spiders are renowned for their unparalleled mechanical strength and Dextensibility arising from their high- $\beta$ -sheet crystal contents as natural materials. Recently, exciting opportunities for silks in photonics, implantable bioelectronics and nanostructured scaffolds have been reported, revealing the need for innovative approaches to multi-scale fabrication with precision and manufacturing scalability. Silk was reported to be used either as a positive or negative EBL resist through interactions with electron beams given its polymorphic crystalline structure. The water-soluble film can be rendered insoluble by inducing crystallization (that is, beta sheet formation) of the silk protein. The inelastic collision of electrons with crystalline silk results in the formation of short polypeptides which are water-soluble. While in negative EBL using silk proteins where water radiolysis dominates, high electron beam doses are usually needed to form the intermolecular crosslinks to make the proteins water-insoluble. Either amorphous or crystalline silk can be used in both positive and negative tones by tuning the applied electron dosage. Furthermore, we report here for the first time, for crystalline silk exposed to the electron beam, scission of the crosslinked β-sheets tends to occur from top to bottom, resulting in the removal of materials after a water-based development, which is referred to as electron-nano-sculpturing (subtractive manufacturing). In contrast, for the amorphous silk exposed to the electron beam, crosslinking of unordered random coils (either intrinsic or deformed from crystalline proteins upon electron irradiations) proceeds from bottom to top, which is referred to as electron-nanosintering (additive manufacturing). Spider silk protein synthesized through genetic engineering with well-defined molecular structure (i.e., average molecular weight and molecular weight distribution) shows better performances (e.g., resolution, contrast and mechanical property) than silk fibroin extracted from natural silk cocoons. These new findings offer new rules to design protein-based architectures of unprecedented resolution and flexibility.

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