



Energetic Tuning in Spirocyclic Conjugated Polymers

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ABSTRACT

The key to enabling their use in optoelectronic devices is precision control of the energy levels in a conjugated polymer. Traditionally, the incorporation of spirocycles into conjugated polymers was used to improve their microstructure of the solid state. Here we present a highly novel method of energy tuning by the use of spirocyclic electronically active systems. By altering a heteroatom's size and oxidation state in an orthogonal spirocycle, we demonstrate energetic fine tuning in both the absorption and emission of a conjugated polymer. In addition, the synthesis of the highly novel spirocyclic conjugated triplet-decker polymers is presented. This new method of energetic manipulation in a conjugated polymer paves the way for selective synthesis of polymers with electronically active spirocycles for future use.

One of the most commonly used approaches to energetic tuning in conjugated polymers is the donor-acceptor approach, whereby orbital hybridization between an electron rich and an electron poor monomer allows the optical band gap to be accurately tuned. Control of thin film nanostructure in conjugated polymers is usually achieved by modulation of the planarity of the backbone and variation in the alkyl chains that are attached.

Multiple reports have been provided of conjugated polymers with spirocyclic ring systems. The use of a tetrahedral core in combination with a planar conjugated backbone was used to monitor thin film microstructure and increase system efficiencies in many cases. In particular, spirocyclic fluorine and sila-fluorine based conjugated polymers have demonstrated increased stability and decreased emission

relative to their comparable non-spirocyclic. Spirocycles are widely used as electron-acceptors in organic solar cells. Similarly, spirocyclic small molecules are the most common type of hole transport materials in hybrid solar cells. Interestingly, small molecule spirocyclic hole conveying materials were also used to produce high-efficiency solar cells even at low concentrations. Nevertheless, so far, the use of spirocycles in conjugated polymers has been primarily to regulate their solid state structure, and their ability in terms of the polymer backbone's electronic manipulation has largely been overlooked. In contrast, spiro conjugation has been used several times in small molecules to monitor the molecular frontier orbitals and their respective interactions. Here we present a series of spirocyclic conjugated polymers, where you can use the orthogonal ring method to control the polymer's electronic structure. Therefore we envisage a method by which both electronic and morphological properties can be simultaneously enhanced. Whereas the polymeric materials described in this study are more suitable for emissive applications, we assume that this novel energetic tuning approach extends to all fields of conjugated polymer electronics. To establish this new approach, we have chosen to research fluorine containing conjugated polymers in all fields of organic electronics because of its widespread use. In addition, due to its improved chemical stability, the use of spirocycles containing fluorene polymers has been extensively studied. We were therefore interested in further investigating related spiro-systems in which the anthracene unit's C-10 atom was changed to integrate both electron donation and electron withdrawal functions to investigate its effect on the band gap of

polymers.

Keywords: fluorene; spirocyclic; conjugated polymer; xanthene