DOI: 10.1002/anie.201101643

Counterion Pinning in Conjugated Polyelectrolytes for Applications in Organic Electronics

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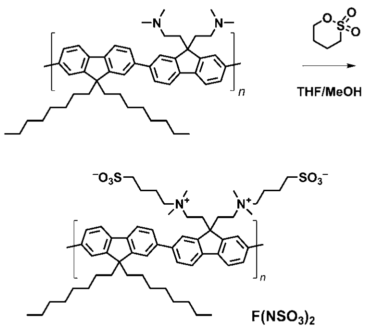
conjugation · light-emitting diodes ·
organic electronics · polymers · zwitterions

Cationic conjugated polyelectrolytes (cationic CPEs)[1,2] as components of electronic devices came in the focus of interest since the first demonstration of their potential as effective electron-injecting layers in organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). A further application in "bulk heterojunction"-type organic solar cells (OSCs) has also been reported.[3–6] The improved charge-injection ability of these compounds may result from a combination of two or more effects, including 1) charge accumulation at interfaces and 2) formation of permanent dipoles at the organic/metal interface towards the low-work-function metal electrode, thus facilitating efficient electron injection into the organic layer.

These cationic conjugated polyelectrolytes offer a couple of advantages: They often show quite excellent electron-injection abilities, leading to significant improvement of the device performance. Moreover, their solubility in polar solvents (such as methanol) and insolubility in nonpolar solvents (aromatic solvents) allow for a so-called orthogonal processing of multilayer devices by "wet-processing" techniques. After the active semiconducting layer is spin-coated from organic solvents such as toluene, chlorobenzene, or 1,2-dichlorobenzene, the electron-injection layer can be processed from a polar solvent without redissolution of the already deposited layer. Alternatively, in devices with an inverted sequence of the layers the semiconductive layer can be deposited on top of the CPE-based injection layer.

One main feature but also possible disadvantage in the application of such cationic CPE layers in electronic devices the presence of mobile counterions (here anions). On the one hand, the motion of fluoride counterions can be used to create p-n junctions in combination with fluoride-accepting functions in double-layer (heterojunction) devices, was as impressively demonstrated by Bazan and co-workers.[7] However, the motion of the counterions often causes problems, especially in OLED and OFET devices, because of the creation of unwanted space charges. To circumvent this problem, the replacement of small and mobile anions of the cationic CPE (such as fluoride, chloride, or bromide) by bulky, immobile, and weakly coordinating anions (such as tetrakis(imidazolyl)borate[5]) has been successful in many examples.

Recently, Huck, Friend, and co-workers reported another, very elegant solution to this problem. They directly "attached" the counter anions to the immobile, cationic CPE main chain and created a zwitterionic CPE.[8] This was accomplished in a very simple, straightforward way. Starting from a well-described, neutral 9,9-bis(*N*,*N*-dimethylaminoethyl)-substituted poly(2,7-fluorene) precursor a one-step reaction with cyclic 1,4-butane sultone directly yields the zwitterionic target polymer. The polymer-analogous derivatization is carried out under relatively mild reaction conditions (3 days at 70 °C) and leads to nearly complete conversion of the tertiary amino functions into zwitterionic sulfobetaine side groups (Scheme 1). Purification of the methanol- and DMSO-soluble CPE was achieved by simple solvent extraction.



Scheme 1. Generation of zwitterionic polyfluorenes by Huck, Friend, and co-workers through the polymer-analogous derivatization of neutral *N*,*N*-dimethylaminoethyl-substituted precursors.[8]

The application of these zwitterionic polyfluorenes as an electron-injection layer in polymer-based OLED devices with F8BT as the polymeric emitter in the device configuration ITO/PEDOT:PSS/F8BT, ca. 100 nm/F$(NSO_3)_2$, ca. 5 nm/Al led to impressive improvements of the device performance [Al: aluminum, F8BT: poly(9,9-dioctylfluorene-*alt*-benzothiadiazole, ITO: indium tin oxide, PEDOT: poly(3,4-ethylenedioxy)thiophene, PSS: polystyrene sulfonate]. First, the emitting F8BT layer was spin-coated from toluene solution onto PEDOT:PSS-coated ITO plates. The next, thin electron-

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injection layer of the zwitterionic, conjugated polyelectrolyte $F(NSO_3)_2$ was deposited on top of the F8BT layer from methanolic solution. Remarkably, this strategy makes it possible to replace the very sensitive low-work-function calcium cathodes by less-reactive aluminum. The replacement is accompanied by a slight (twofold) improvement (!) of the OLED performance. Moreover, the OLED devices showed short response times of $< 10\,\mu s$, thus indicating that the pinned counter anions are fully immobilized.

A very similar approach was reported independently two months later by Huang and co-workers.[9] They used a structurally related 9,9-bis(*N*,*N*-diethylaminohexyl)-substituted poly(2,7-fluorene) precursor in a polymer-analogous derivatization with 1,3-propane sultone. Again, the resulting zwitterionic CPE derivatives (here called CZPE) showed excellent electron-injection properties in OLED devices with P-PPV, a phenyl-substituted poly(*para*-phenylene vinylene) derivative, as the polymeric emitter. The authors reported an impressive maximum luminance efficiency of up to $23.8\,\mathrm{Cd\,A^{-1}}$ for P-PPV as a green emitter.

Besides the zwitterionic polyfluorenes and related copolymers discussed here, zwitterionic polythiophenes were also reported by Ingenäs and co-workers already 20 years ago.[10] However, they were used for sensor applications and have not been applied in electronic devices.

In conclusion, zwitterionic CPE derivatives are very promising polymeric materials for highly efficient charge-injection layers in solution-processed organic multilayer devices.

Received: March 7, 2011

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