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Doped Polymer Organic Semiconductor Films with Ultra Workfunctions

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Content:

Electrically-conductive films with extreme workfunctions (WFs) are required for ohmic charge-injection into and –collection from organic and other advanced semiconductors, including quantum dots, nanotubes and 2D materials. Commercially available heavily-doped polymer organic semiconductors (OSCs), such as poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid)(PEDT: PSSH) and sulfonated poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl): poly(4-hydroxystyrene) (S-P3MEET: PHOST), are largely restricted to the p-type with WF of ca. 5.2 eV. p- and n-Doped polymer OSCs together can in principle span the desired ultrahigh to ultralow} WF range, but need to be stabilized against de-doping and dopant migration whilst retaining solution processability. Here we show that these conflicting requirements can be met in self-compensated doped polymers, where mobile carriers on the polymer backbone are charge-compensated by suitable tethered counter-ions. This provides access to conductive films over an unprecedented ultrawide WF range (3.0 eV to 5.8 eV), overcoming key limitations of self-doped polymers,and undoped conjugated polyelectrolytes. We demonstrate ohmic injection of both carrier types into a variety of organic semiconductors in a number of device protocols (light-emitting diodes, transistors and solar cells), achieving new device performance and operation regimes, and the self-aligned assembly of ultra WF layers on regular metal electrodes, differentiating them into excellent hole and electron contacts. We anticipate that this approach will open up not only new device architectures for technology, but also new platforms to probe advanced semiconductors without being limited by contacts.