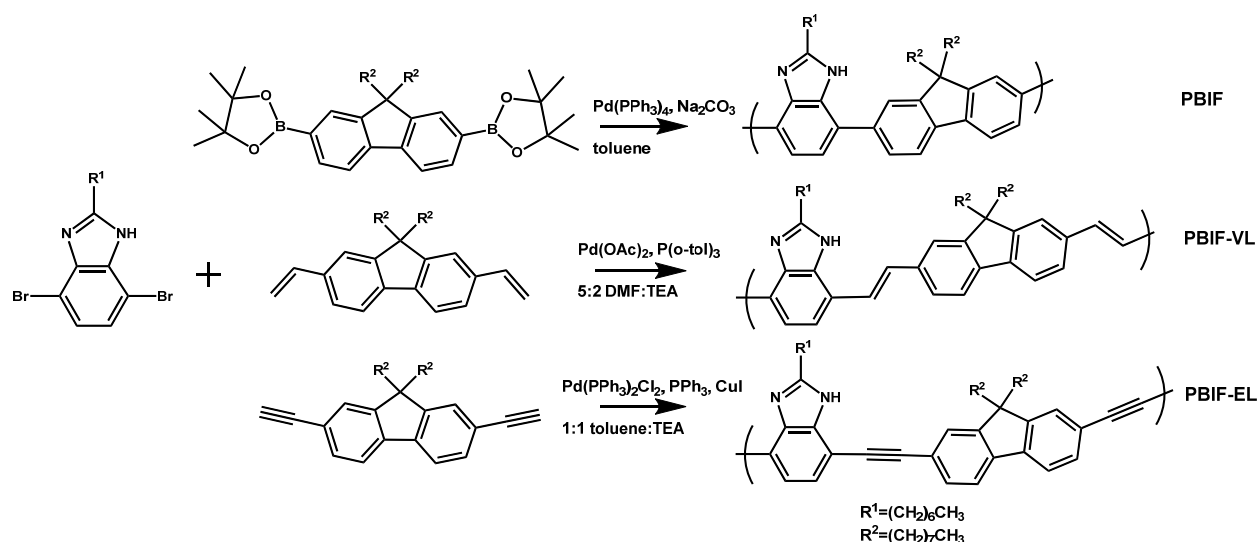


Synthesis of π -Bridged Dually-Dopable Conjugated Polymers from Benzimidazole and Fluorene: Separating Sterics from Electronics

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We have explored the synthesis and characterization of three new alternating copolymers containing fluorene and a dually-dopable benzimidazole moiety. Poly(2-*n*-heptyl-benzimidazole-*alt*-9,9-di-*n*-octylfluorene) (**PBIF**), poly(2-*n*-heptyl-benzimidazole-vinylene-9,9-di-*n*-octylfluorene) (**PBIF-VL**), and poly(2-*n*-heptyl-benzimidazole-ethynylene-9,9-di-*n*-octylfluorene) (**PBIF-EL**) were synthesized from Suzuki, Heck, and Sonogashira cross-coupling reactions in reasonable yield. The materials were characterized through ultraviolet-visible (UV-vis) spectroscopy, photoluminescence (PL), and cyclic voltammetry (CV). The vinyl and ethynyl bridges in **PBIF-VL** and **PBIF-EL** were incorporated to separate benzimidazole and fluorene units while retaining conjugation. This allowed us to differentiate between steric and electronic contributions to the band gap (E_g) changes that occur upon acid/base doping of these materials. We demonstrate that the blue shift arising from acid doping **PBIF** is due to steric torsion while the red shift found upon base doping **PBIF** is due to both sterics and possibly an electronic effect. These findings are supported through the use of molecular modeling. This work is supported by the National Science Foundation (CHE-1213072) as well as the National Science Foundation Graduate Research Fellowship Program (GRFP-451512). (*last edited June 6, 2015*)