

Abstract

Thiophene-based materials are characterized by a wide range of interesting properties, including ease of synthetic modification, controllable tuning of the absorption and emission spectra, charge conduction in the oxidized/reduced states, and biocompatibility. These characteristics have enabled their application in several fields particularly in optoelectronics, as active materials in organic light-emitting diodes, organic field-effect transistors, photovoltaic cells, and in biology, as biosensors, bioimaging agents, and photosensitizers. Of particular interest in the design of thiophene-based materials is the development of push-pull systems, in which electron donor (D) and electron acceptor (A) units are covalently linked and alternated along the conjugated backbone. The different nature of the D and A fragments allows for modulating the shift of electron density from the D to the A moiety, achieving a fine control of the optoelectronic properties. Herein, we report two families of push-pull oligothiophenes and show how modifying the strength of the acceptor units (*i.e.*, benzo[*c*][1,2,5]thiadiazole < thieno[3,4-*b*]pyrazine < thieno[1,2,5]thiadiazole) allows modulating π -electron delocalization and photoinduced charge transfer processes. These structural changes determine the electrochromic color modulation of materials reaching the NIR region, their bifunctional behavior in bulk heterojunction solar cells, and their ability to convert light into singlet oxygen or heat making them suitable candidates as photosensitizers in photodynamic therapy and photothermal.