Abstract

A range of pyrrole-based polycyclic heteroaromatic compounds was synthesized via α–α coupling and α–α bridging of pyrrole subunits. An efficient approach for the introduction of methylene bridges in sterically congested surroundings between two pyrrolic subunits of electron-deficient hexapyrrolylbenzenes was established. The acid-catalyzed aldehyde condensation reaction was employed for the preparation of a periphery-expanded azacoronene σ-dimer. When exposed to ultraviolet or visible light, this new σ-dimer azacoronene cleaves into two stable 139 π-electron radical monomers. The process of dissociation is fully reversible in oxygen- and water-free conditions. The dimer is split into monomers and subsequently oxidized to the ketone form after being exposed to light and atmospheric oxygen (air). The acid-catalyzed condensation reactions with paraformaldehyde were also used for the synthesis of doubly, triply, and quintuply bridges azacoronenes. The introduction of up to six bridges to the azacoronene core was possible by the application of the developed α–α bridging method. The approach was shown to succeed not only for electron-deficient compounds, and several differentially expanded hexapyrrolylbenzenes were examined for the synthesis of azacoronene analogues with six bridges.

An efficient method for the synthesis of α,α'-bipyrroles via palladium-catalyzed oxidation coupling reaction was also explored. The influence of the concentration of starting material and additives on the outcome of the reaction was investigated. Brightly fluorescent and, in some cases, chiral boomerangs were synthesized and thoroughly characterized. New thiophene-containing pyrroles were developed and their reactivity in palladium-mediated oxidative coupling reactions was tested.