Systematic tuning of optical bandgaps in organic molecules can be achieved by homologation (oligomerization) of linear π-conjugated motifs, by ring expansion of π-conjugated macrocycles, and by extension of fused ring systems in two dimensions. A complementary approach relies on combining donor and acceptor (D–A) moieties, with diverse recent applications in small-molecule and polymer chemistry. The D–A paradigm is particularly suitable for the development of tunable building blocks, which can be constructed by judicious merging of existing electron-deficient and electron-rich motifs. A simple and potentially productive design of such a hybrid structure is achieved by combining naphthalenemonoimide (NMI, red) and pyrrole (blue), as shown below [1,2]. We will discuss the application of such pyrroles as building blocks for the synthesis of diverse polycyclic aromatics, including macrocycles [2], nanographenoids [3,4], and bipyroles [5,6], some of which are characterized by persistent helicene-like chirality. These systems reveal rich redox chemistry, spanning multiple oxidation levels, as well as tunable optical signatures extending into the near infrared.