Pyrrolo[3,2-*b*]pyrroles and Diketopyrrolopyrroles - Functional Heterocycles for Optoelectronic Applications

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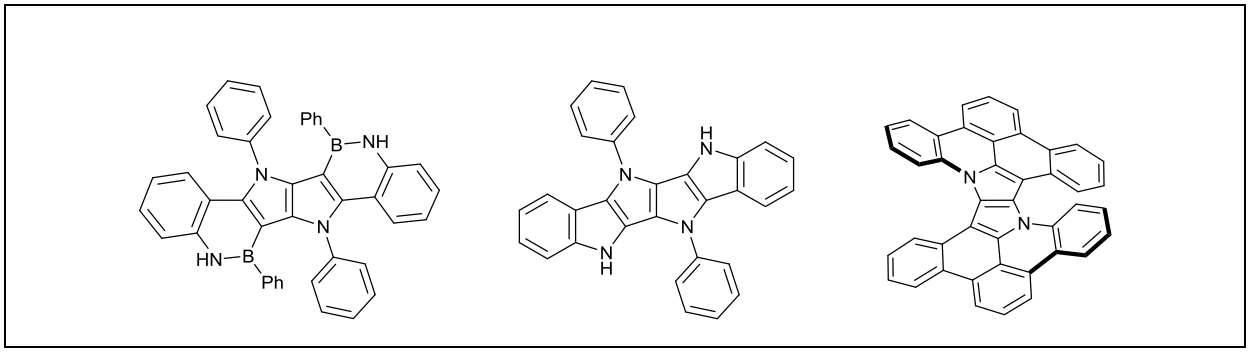
Recently we have discovered and optimized the first practical synthesis of non-fused pyrrole[3,2-*b*]pyrroles *via* domino reaction of aldehydes, primary amines, and butane-2,3-dione.[1] Six bonds are formed in heretofore unknown tandem process, which gives rise to substituted pyrrole[3,2-*b*]pyrroles – the 'missing link' on the map of aromatic heterocycles. The parent 1,4-dihydro-pyrrolo[3,2-*b*]pyrroles served as building block to construct various π-expanded analogs including nitrogen-embedded buckybowl with inverse Stone–Thrower–Wales topology[2] and diindolo[2,3-*b*:2′,3′-*f*]pyrrolo[3,2-*b*]pyrroles. These compounds constitute the most electron-rich ladder-type heteroacenes known to date - E_{HOMO} was located at ca. −4.6 eV. Strongly fluorescent diindolo[2,3-*b*:2′,3′-*f*]pyrrolo[3,2-*b*]pyrroles represent the only existing compounds bearing the pyrrolo[3,2-*b*]pyrrolo[2',3':4,5]pyrrolo[2,3-*d*]pyrrole core. In this presentation, I also would like to report three major discoveries related to chemistry of diketopyrrolopyrroles made during the last few months. Namely: (1) the entirely new method to synthesize unsymmetrical diketopyrrolopyrroles possessing three different substituents; (2) breakthrough methodology leading to novel type of π-expanded diketopyrrolopyrroles; and (3) boron-complexes of diketopyrrolopyrroles with superb emission properties. These three discoveries taken together ensure that diketopyrrolopyrroles will continue to attract attention for years to come.



1. Krzeszewski, M.; Gryko, D.; Gryko, D. T. *Acc. Chem. Res.*, **2017**, *50*, 2334.
2. Mishra, S.; Krzeszewski, M.; Pignedoli, C. A.; Ruffieux, P.; Fasel, R.; Gryko, D. T. ', *Nature Commun*. **2018**, 1714.