1,4-Dihydropyrrolo[3,2-b]pyrrole and Dipyrrolonaphthyridinedione – Novel Building Blocks for Optoelectronics

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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-2,3dione.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. Unparalleled simplicity and versatility of this one-pot reaction, non-chromatographic purification and superb optical properties (including strong violet, blue or green fluorescence both in solution as well as in the solid state), brought these molecules from virtual nonexistence to the intensively investigated area functional π -systems. The parent 1,4-dihydropyrrolo[3,2-b]pyrroles served as building block to construct various π -expanded analogs including nitrogen-embedded buckybowl with inverse Stone-Thrower-Wales topology^{2,3} 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. Recently, we have proved that the dipyrrolonaphthyridinedione (DPND) core constitutes an excellent scaffold for the design of strongly fluorescent dyes or guadrupolar-type materials with large two-photon absorption (TPA) cross-sections (up to 5,180 GM).³⁷ These properties result from an unusual arrangement of donor (pyrrole ring) and acceptor (carbonyl group) moieties within the DPND core.

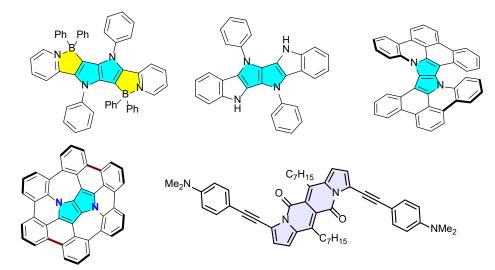


Figure 1. Exemplary architectures based on pyrrolo[3,2-*b*]pyrrole and DPND cores.

References

¹ M. Krzeszewski, D. Gryko and D. T. Gryko, Acc. Chem. Res., 2017, **50**, 2334-2345.

² S. Mishra, M. Krzeszewski, C. A. Pignedoli, P. Ruffieux, R. Fasel and D. T. Gryko, *Nat. Commun.*, 2018, 1714.

³ M. Krzeszewski, Ł. Dobrzycki, A. L. Sobolewski, M. K. Cyrański, D. T. Gryko, *Angew. Chem. Int. Ed.*, 2021, **60**, 14998-15005.