

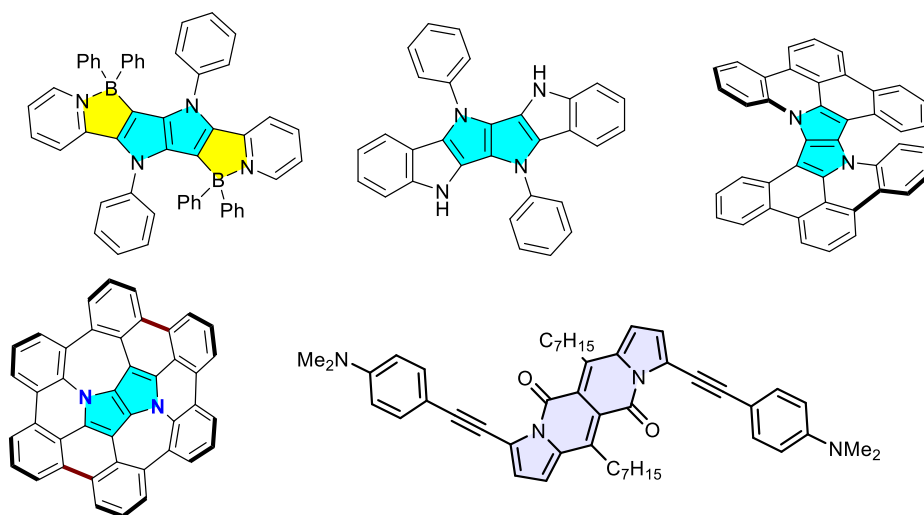
# 1,4-Dihydropyrrolo[3,2-*b*]pyrrole and Dipyrrolonaphthyridinedione – Novel Building Blocks for Optoelectronics

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Recently we have discovered and optimized the first practical synthesis of non-fused pyrrolo[3,2-*b*]pyrroles *via* domino reaction of aldehydes, primary amines, and butane-2,3-dione.<sup>1</sup> Six bonds are formed in heretofore unknown tandem process, which gives rise to substituted pyrrolo[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 non-existence to the intensively investigated area functional  $\pi$ -systems. The parent 1,4-dihydropyrrolo[3,2-*b*]pyrroles served as building block to construct various  $\pi$ -expanded analogs including nitrogen-embedded buckyball with inverse Stone–Thrower–Wales topology<sup>2,3</sup> 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 -  $E_{\text{HOMO}}$  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 quadrupolar-type materials with large two-photon absorption (TPA) cross-sections (up to 5,180 GM).<sup>37</sup> 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

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