

Pyrrolo[3,2-*b*]pyrroles – Electron-Rich Functional Heterocycles

Daniel T. Gryko

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

E-mail: dtgryko@icho.edu.pl

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.¹ 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 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. 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.

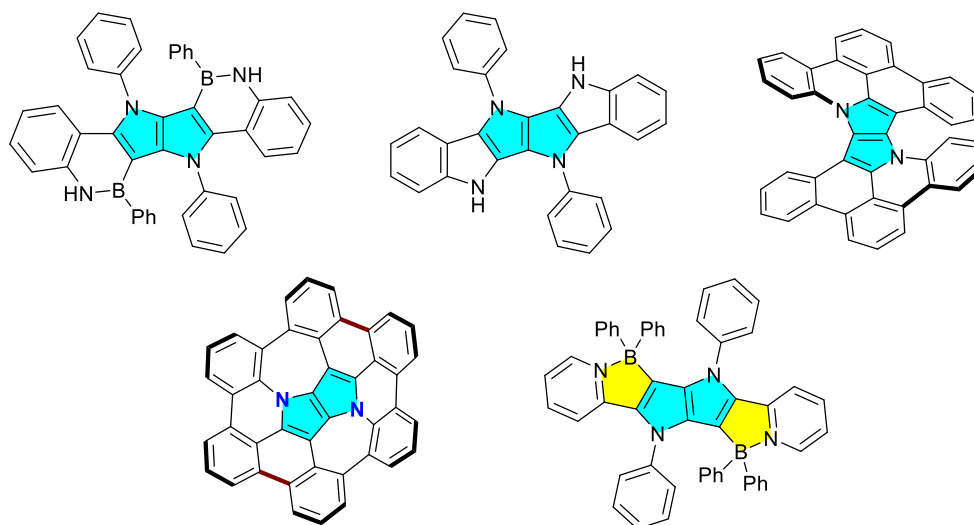


Figure 1. Exemplary architectures based on pyrrolo[3,2-*b*]pyrrole core.

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.