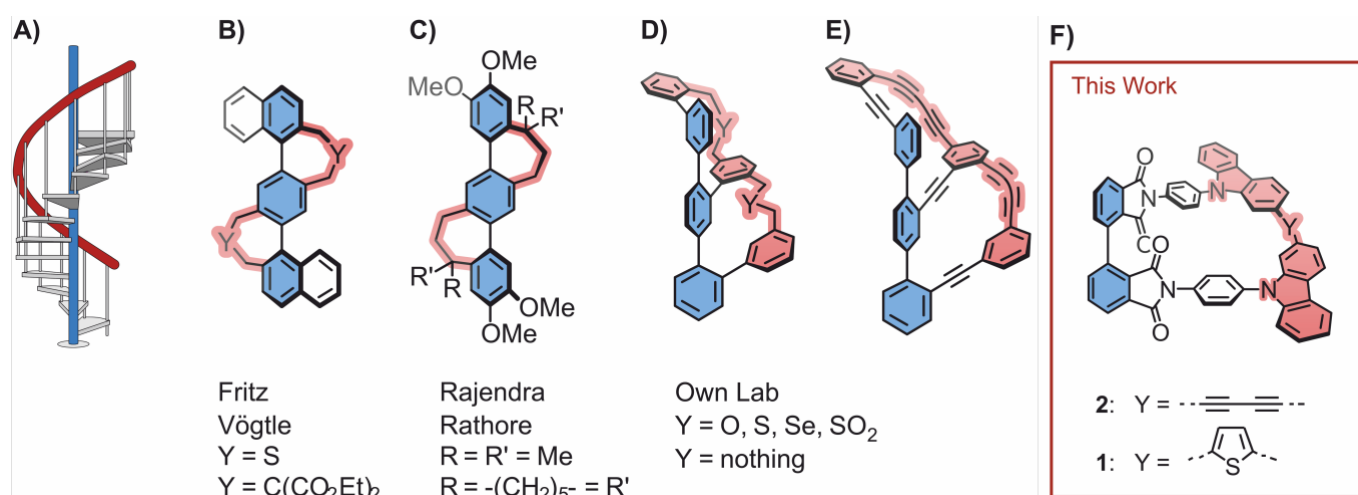


Geländer Molecules with orthogonal joints: Design and Synthesis of Macrocyclic Dimers

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Linking a molecular rod (backbone) with long linkers (banister) forces the latter to wrap around the former, inducing helical chirality (Scheme 1). The wrapping of the linker is reminiscent of the banister of a spiral staircase (Scheme 1A), thus prompting Vögtle and co-workers to coin the German term "Geländer"-oligomers for these architectures (Scheme 1B).[1] In their early investigation, they linked adjacent phenylenes in terphenylene with short linkers yielding beside the chiral (*M,M*) and (*P,P*) isomers the achiral (*M,P*) meso-form in a statistical distribution.[2] Our group introduced the concept of length mismatch in ladder-oligomers, reporting the first "Geländer"-oligomer with the banister wrapping continuously around the backbone in 2014 (Scheme 1D). If a single strand in a ladder-oligomer is elongated, the longer strand (banister) wraps around, the shorter strand (backbone).[3] These structures only contain one helical axis, and therefore, only chiral (*M*) and (*P*) isomers are found. Due to the asymmetry of the junction connecting backbone and banister, regioisomers are eventually formed in a late divergent step by the rotation of the junctions.[4] By symmetrizing the molecular design, the divergent step is circumvented. The helical structure can be formed in two subsequent robust homo-coupling steps and, together with the symmetrical design, eventually allows to synthesize longer oligomers efficiently.



Scheme 1: Figure 1: **A)** Sketch of a spiral staircase as inspiration of "Geländer" molecules with an axle (blue) and a helical banister (red). "Geländer" helices of **B)** Vögtle, **C)** Rathore, and **D)** and **E)** from our own lab. **F)** New "Geländer" macrocycles **1** and **2** with rectangular arrangements between axle and rung, as well as between rung and banister.

The macrocycles herein described are the first symmetric "Geländer" dimer (Scheme 1F). We report their synthesis, their chiral resolution, and their chiroptical activity.

References

- [1] B. Kiupel *et al.*, *Angew. Chem. Int. Ed.* **37** (1998) 3031.
- [2] M. Rickhaus *et al.*, *Chem. Soc. Rev.* **45** (2016) 1542.
- [3] M. Rickhaus *et al.*, *Angew. Chem. Int. Ed.* **53** (2014) 14587.
- [4] R. Mannancherry *et al.*, *Chem. Sci.* **9** (2018) 5758.