Synthesis of a π-Extended Perylene Dication Featuring Negatively Curved Seven-Membered Rings

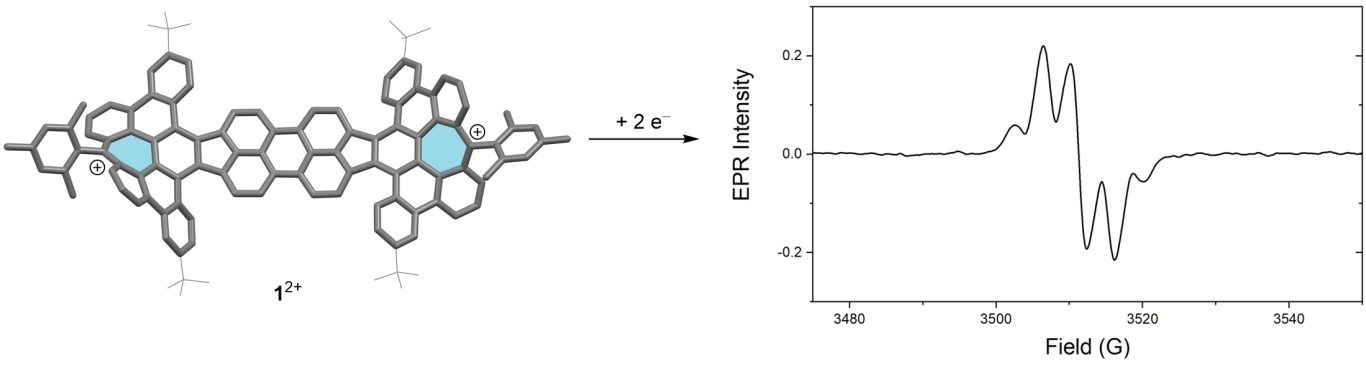
Georg Berger,[1,2] Dr. Jan Borstelmann,[1] Dr. Frank Rominger,[1] Prof. Dr. Milan Kivala[1]

[1] Institute of Organic Chemistry, University of Heidelberg, Im Neuenheimer Feld 271, 69120 Heidelberg, Germany

[2] Department of Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

georg.berger@chem.uzh.ch

π-Extended perylene derivatives comprising tropylium and tropyl moieties have been synthesized and characterized. The 7-membered rings introduce negative curvature to the π-system and stabilize positive charges due to the aromatic nature of the tropylium ring.[1] The dication $\mathbf{1}^{2+}$, obtained by treatment of an appropriate diol precursor with strong acids, was persistent under anhydrous conditions and could be characterized by common analytic techniques, including NMR spectroscopy and single crystal X-ray diffraction.



Cyclic voltammetry indicated facile reduction of $\mathbf{1}^{2+}$ to its corresponding biradical (E = −0.34 V *vs.* Fc/Fc^+ in CH_2Cl_2), which was also achieved chemically using decamethylferrocene as single electron reductant. The electronic structure of the biradical was analyzed computationally and by EPR spectroscopy, which indicated an open-shell structure with only negligible interaction of the unpaired electrons.

[1] J. Borstelmann, J. Bergner, F. Rominger, M. Kivala, *Angew. Chem. Int. Ed.* **2023**, *62*, e202312740.