

SUMMARY OF THE WORK

In the world of porphyrin chemistry, even after extensive reports on various expanded porphyrins, most of the tetrapphyrin[2.1.1.1]/homoporphyrins reported are those in which the complete conjugation is interrupted due to the sp^3 hybridized centre. Till date there are not much reports on the synthesis of stable completely conjugated free-base homoporphyrin/tetrapphyrin[2.1.1.1] systems. Although, Callot and coworkers were successful in synthesizing a complete conjugated homoporphyrin, it was reported to be unstable and decomposed even at 0°C in the solid state and thus leaving its study totally unexplored. However, even in the systems reported, one of the substituent at the vinylene bridge is limited only to the ester group. Hence, even after four decades of the discovery of tetrapphyrin[2.1.1.1]/homoporphyrins, a complete conjugated stable tetrapphyrin[2.1.1.1]/ homoporphyrin system has not been realized till now.

We have successfully demonstrated the synthesis of hitherto unknown para-fluoro substituted dipyrroethane starting from 4,4'-difluorobenzil. The reduction of 4,4'-difluorobenzil resulted in the formation of corresponding 1,2-para-difluoro-diphenylethane-1,2-diol. The diol upon mesylation and then treatment with pyrrole resulted in the synthesis of novel meso-5,6-para-difluorodiphenyldipyrroethane. We have successfully separated the meso isomer from other stereo isomers by column chromatography and thoroughly characterized newly synthesized meso-5,6-para-difluorodiphenyldipyrroethane by various spectroscopic techniques. We have also synthesized and thoroughly characterized meso-diphenyldipyrroethane, by same procedure starting from benzoin. The other starting materials like 5-aryldipyrromethanes, 1,9-bis(toluoyl)-5-(aryl)-dipyrromethanes, 1,9-bis(tolyhydroxymethyl)-5-(aryl)-dipyrromethanes were synthesized according to the literature procedure.

With the synthesized precursors, we have also successfully isolated and thoroughly characterized two novel 20π meso-pentaaryl free-base tetraphyrin[2.1.1.1] system which was earlier reported to be unstable. The stable tetraphyrin[2.1.1.1] system is the most contracted expanded porphyrin, a missing link in the rich area of expanded porphyrinoids ever since forty years after the synthesis of first expanded porphyrin. The tetraphyrin was synthesized by [2 + 2] MacDonald type condensation between meso- 5,6- para-difluoro -diphenyldipyrroethane/ meso- 5,6-diphenyldipyrroethane and 1,9-bis (tolylhydroxymethyl) -5-(aryl)-dipyrromethanes in the presence of p-TSA as an acid-catalyst followed by oxidation with DDQ as an oxidizing agent. The macrocycles were purified by column chromatography and analyzed by various spectroscopic techniques. The newly synthesized macrocycles are highly stable, 20π meso-pentaaryl free-base tetraphyrin[2.1.1.1] featuring four pyrrole rings and five meso carbons. We have introduced an additional meso carbon into the meso-aryldipyrromethane to generate meso-diaryldipyrroethane, to synthesise tetraphyrin[2.1.1.1] system.. In general, newly synthesized homoporphyrins are reported for the first time. The reported macrocycle represents the most contracted member in the area of expanded porphyrin, as further reduction of one meso carbon results in meso-tetraaryl porphyrin.

The key feature of the work is the incorporation of vinylene and/or ethylene unit in the porphyrin frame work and can be exploited to open a new area of various unexplored expanded porphyrinoids.. We have also studied the aromatic and coordination properties of the synthesized macrocycles. In general, Fluoro substituted dipyrroethane and two newly synthesized homoporphyrins are reported for the first time. More over that fluorine can influence the various spatial array of molecules. The crystallisation property of the above dipyrroethanes and tetraphyrins will be studied in future.

Publication

Meso-Aryl [20] π Homoporphyrin: The Simplest Expanded Porphyrin with the Smallest Mobius Topology: **K. S. Anju**, Mainak Das , B. Adinarayana, Cherumuttathu H. Suresh, and A. Srinivasan. *Angew. Chem. Int. Ed.* **2017**, *56*, 15667 – 15671.