

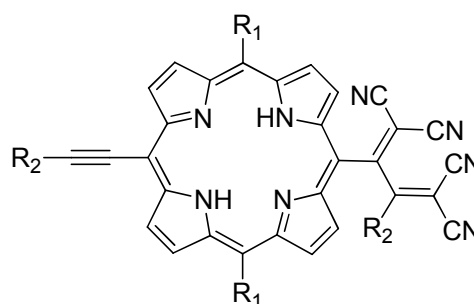
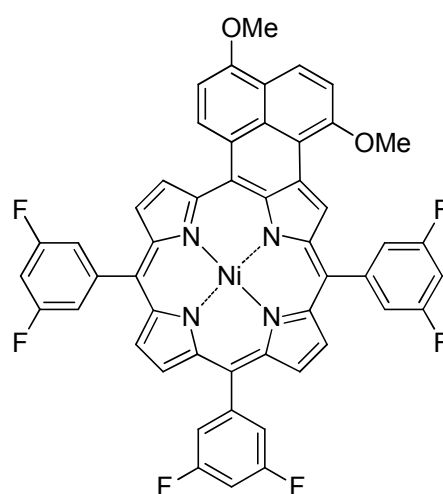
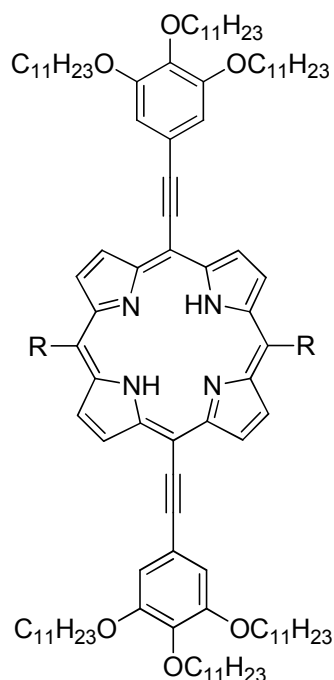
π -Extended porphyrins - synthesis and optical properties
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Modification of porphyrin chromophore clearly has many potential applications, particularly when this results in the presence of strong absorption bands in the red and NIR regions [1]. Furthermore these modifications provide insight into the nature of conjugation and aromaticity in porphyrinoid system. To this end the synthesis of porphyrin isomers, expanded porphyrins and modified porphyrins has been widely investigated. Optical limiting is a nonlinear effect consisting of a decrease in the transmittance of the NLO material under high-intensity illumination. Among different functions optical limiting devices can perform, the most useful one is the protection of optical elements, sensors and human eye against damage by exposure to a sudden high-intensity light. Dipolar or quadrupolar aromatic molecules have been shown to be of particular interest since they allow combining very fast (femtoseconds) intrinsic two-photon absorption (2PA) with somewhat slower excited state absorption (ESA) We have developed the general principle to design porphyrins possessing low melting-point and we synthesized first liquid porphyrins: 5,10,15,20-tetrakis[3,4,5-tris(decyloxy)phenyl]porphyrin and 5,10,15,20-tetrakis[3,4,5-tris(undecyloxy)phenyl]porphyrin. We also discovered the superior reagent for carrying out intramolecular oxidative coupling of porphyrins which avoids formation of troublesome side-products. All these developments combined with liquid porphyrin principle allowed us to produce first liquid porphyrin possessing large two-photon absorption cross-section – suitable for optical limiting. The synthesis of various types of π -expanded porphyrins and their two-photon absorption properties will be presented.



References:

1. Lash T. In *The Porphyrin Handbook*; Kadish, K. M.; Smith, K. M. Guillard, R., Eds.; Academic Press: New-York, 2000; Vol.2, pp 125-199.