5,10,15,20-tetraphenylsapphyrin - identification of a pentapyrrolic expanded porphyrin in the Rothemund synthesis.

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1995

Czasopismo

Chemistry-A European Journal

Numer woluminu

1

Strony

68-73

DOI

10.1002/chem.19950010111

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The Rothemund-type condensation of pyrrole and benzaldehyde yields, apart from 5,10,15,20-tetraphenylporphyrin ($TPPH_2$) and inverted tetraphenylporphyrin 2-aza-21-carba-5,10,15,20-tetraphenylporphyrin ($CTPPH_2$), a unique pentapyrrolic macrocyclic molecule with the aromatic nucleus of sapphyrin, namely, 5,10,15,20-tetraphenylsapphyrin ($TPSH_3$). Its unorthodox structural skeleton with an inverted pyrrole ring lying opposite to the bipyrrole unit accounts for the spectroscopic properties of the novel sapphyrin. The diprotonation of $TPSH_3$ acts as a trigger for a structural transformation involving a flip of the pyrrole units, which relocates the 27-NH pyrrolic nitrogen from the periphery into the center of the macrocycle. The formation of 5,10,15,20-tetraphenylsapphyrin proves that the pentapyrrolic product is accessible by the mechanism of the Rothemund synthesis.

Adres publiczny

https://doi.org/10.1002/chem.19950010111

Strona internetowa wydawcy

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