

A novel complex of zinc tetraphenylporphyrin with two dioxane molecules in a rare attachment. Crystal structure, spectroscopy and theoretical calculations.

Autorzy

Krzysztof Oberda

Irena Deperasińska

Yakov P. Nizhnik

Anna Szemik-Hojniak

Rok wydania

2013

Czasopismo

Polyhedron

Numer woluminu

51

Strony

61-69

DOI

10.1016/j.poly.2012.12.014

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

We have shown the X-ray crystal structure of a novel ZnTPP–(Dioxane)₂ complex and the results of solution studies by means of steady state absorption and fluorescence as well as time-resolved fluorescence techniques complemented by theoretical DFT and TD DFT B3LYP/6-31G(d,p) calculations. The ZnTPP–(Dioxane)₂ crystallizes in centrosymmetric monoclinic unit cell, space group *P*2₁/*c* and shows a unique structure, with two dioxane molecules in “chair” conformation, placed in equatorial and axial position relative to ZnTPP core. Analysis of TD DFT B3LYP/6-31G(d,p) wave functions of ZnTPP–(Dioxane)₂, allowed us to describe the nature of particular electronic transitions and to identify two bands (LE, CT) absent in its components. The former, results from the symmetry reduction of ZnTPP and the latter, from a mixed character of the HOMO (220) orbital of the complex. A red shift of the Soret and the Q band found in absorption and fluorescence spectra indicating the complex formation in solution is confirmed by the simulated absorption spectra of ZnTPP–(Dioxane)₂ relative to ZnTPP unit both in the gas phase and in dioxane solution by PCM model. The estimated lifetime of the complex (1.75 ns) is shorter than that of free ZnTPP unit (~2 ns).

Słowa kluczowe

crystal structure, Complex, dioxane, Zinc tetraphenylporphyrin, excited states, theoretical calculations

Adres publiczny

<http://dx.doi.org/10.1016/j.poly.2012.12.014>

Strona internetowa wydawcy

<http://www.elsevier.com>

