A negligible CT character of the lowest excited state of a novel complex of zinc tetraphenylporphyrin with axially bonded 2-(4-methoxy-*trans*-styryl)quinoline-1-oxide ligand : experimental studies and TD DFT/CAM B3LYP [6-31 G(d,p)] calculations.

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The crystal structure and photophysical behavior of the novel (1:1) ZnTPP–MSQNO complex composed of ZnTPP unit with axially bonded 2-(4-methoxy-trans-styryl)quinoline-1-oxide ligand (MSQNO) has been extensively investigated both in solution and in the solid state. The single-crystal X-ray measurements, stationary absorption and emission spectra and the time-resolved fluorescence spectroscopy combined with TD DFT/CAM B3LYP [6-31G(d,p)] calculations were employed. The crystal structure is characterized by the centrosymmetric triclinic unit cell, space group $P1^{-}$. Zinc atom in the studied complex is pulled out 0.365Å from the porphyrin macrocycle and the MSQNO ligand occurs in the anti-rotameric form of the trans-isomer. The complex formation in the solution is confirmed by the appropriate red shift of the Qx and Qy band in the absorption spectrum in toluene, which is in a good agreement with the results obtained by theoretical calculations. We have found that effective mixing of electronic configurations of the locally excited states with those of the charge transfer type leads to a negligible CT nature of the S_1 state of ZnTPP–MSQNO complex. We also hypothesized, that due to an overlap of the absorption spectrum of MSQNO and ZnTPP in the Soret band region, the electronic coupling becomes possible and the nonradiative energy transfer process as an additional deactivation channel may take place. An unusually short lifetime (0.6ns) was revealed for the solid complex, while in toluene (1.5ns) and in n-propanol (2.7ns), they shown to be several times longer.

Słowa kluczowe

crystal structure, Zinc tetraphenylporphyrin, 2-(4-Methoxy-trans-styryl)quinoline-1-oxide, lifetimes, CAM B3LYP calculations