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Photoinduced electron transfer in pentacoordinated complex of zinc tetraphenylporphyrin and isoquinoline N-oxide. Crystal structure, spectroscopy and DFT studies

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ABSTRACT

A novel, pentacoordinated complex of (1:1) zinc tetraphenylporphyrin and isoquinoline N-oxide (ZnTPP–IQNO) was synthesized and its crystal structure along with photophysical properties by experimental methods (absorption, steady state and time-resolved emission) in conjunction with DFT and TD DFT calculations were investigated. In ZnTPP–IQNO complex, the isoquinoline N-oxide ligand (IQNO) is directly coordinated to the central zinc atom of the ZnTPP unit through the oxygen atom of the NO group and crystallizes in centrosymmetric triclinic unit, in the space group $P\bar{1}$. Particular contacts between the two monomeric units (hydrogen bonds, O···H–C interactions, …etc.) lead to a supramolecular dimer which forms the layers propagating both along the *a* and the *b*-axis. The electronic locally excited and the charge-transfer states of the complex were calculated by TDDFT CAM-B3LYP/6-31G(d,p) method. A surprising presence of the charge transfer states between the Soret and the Q bands leads to excitation energy dissipation processes involving the opening of the radiationless channels of excited ZnTPP–IQNO complex. Emission from the S_1 state (Q band) in ethyl acetate decays accordingly to monoexponential function (1.92 ns) while a bi-exponential decay is found in *n*-propanol [(2.5 ns (87%); 14.4 ns (13%)] and in the solid state [1.36 ns (67.5%), 7.31 ns (32.5%)].

1. Introduction

Much work has been done in the recent years on the structure and properties of porphyrins, metalloporphyrins and their complexes [1]. Metalloporphyrins, for example, are very useful and play an important role in the active site of many proteins. They also seem to be potential candidates both for artificial solar energy conversion systems and for electronic storage devices [2]. Besides that, metalloporphyrins find application in photodynamic therapy [3], in optoelectronics – as appropriate materials for molecular logic circuits [4], and as switchers in which by using different energies of light, the electron transfer between particular components may be controlled [5]. Many articles have been devoted, to a model and symmetric (D_{4h}) zinc tetraphenyl porphyrin (ZnTPP) [6–10] and to complementary investigations of photophysical properties of its unsymmetrical supramolecular arrays in the form of donor–acceptor dyads, triads, and other multicomponent molecular systems which are the subject of a deep ongoing interest [5]. The relaxation dynamics and assignment of excited states of porphyrins and metalloporphyrins became a "hot" subject of recent photophysical studies devoted to these macrocycles.

Despite that metalloporphyrins are relatively simple and photostable on excitation in the near-UV of the very allowed Soret band region (oscillator strength close to unity), nevertheless identification of their electronic states, as for example in derivatives of ZnTPP is still an open question. The literature data concerned with photophysical parameters like the quantum yield and the decay constants of the lowest two π–π^* excited states (S_1 and S_2) of the latter, considerably differ. The lifetime of the S_1 state, for example, is of the order of about 2 ns while that for the S_2 state is in the broad ps–fs range [11–15].

On the other hand, the literature, in a fact, contains only few structural as well as spectral data describing the interaction of metalloporphyrins with Lewis bases. The latter may be for example, heteroaromatic N-oxides [16–18] that represent a prominent biological activity [19–21]. Their combination with metalloporphyrins may result in a new type of materials with unique photophysical and electronic properties.

Zinc(II) tetraphenylporphyrin is particularly well suited for studying such combined molecular systems. It does not undergo neither changes in oxidation nor in the spin state, usually accepts

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only one axial ligand, does not have empty d-orbitals that might participate in bonding, providing in this way a very convenient model for tuning the effects of axial ligation upon its electronic structure.

The main goal of this work, is to get a deeper insight into electronic structure of the target (κO-isoquinoline-N-oxide)-(α,β,γ,δ-tetraphenylporphinato) zinc(II), [ZnTPP–IQNO] complex, where the isoquinoline N-oxide ligand is axially coordinated to ZnTPP unit. Specifically, by means of absorption and emission spectroscopy as well as TD DFT calculations, we identify the nature of its electronic states and in particular we check whether photoinduced electron transfer (PET) takes place on excitation.

The X-ray crystal structure and DFT optimized molecular structure along with absorption and preliminary emissive properties of ZnTPP–IQNO complex are also presented.

2. Materials and methods

2.1. Materials

2.1.1. Preparation of isoquinoline N-oxide

Isoquinoline N-oxide was synthesized by the method of Ochiai from isoquinoline by peroxide oxidation in acetic acid.

2.1.2. Synthesis of tetraphenylporphine

Tetraphenylporphine (TPP) was prepared from pyrrole and benzaldehyde in boiling propionic acid [22]. Pyrrole was obtained by the known method [23] using the thermal decomposition of diammonium salt of mucic acid which was prepared from mucic acid and NH_4OH. Mucic acid was synthesized by galactose oxidation with HNO_3 upon heating [24].

2.1.3. Synthesis of Zn-tetraphenylporphine

Zn-tetraphenylporphine (Zn-TPP) was synthesized according to known procedure [25] with some changes. Tetraphenylporphine (TPP) in $CHCl_3$ was kept over PbO_2 during 2 days to remove admixture of tetraphenylchlorine (2–10% of which can be formed at TPP synthesis) and a radical of unknown structure [26]. A mixture of 0.5 g (0.813 mmol) TPP, 0.25 g (1.14 mmol, 1.4-fold excess) of $(CH_3COO)_2Zn{\cdot}2H_2O$, 50 mL of chloroform and 250 mL of glacial acetic acid was boiled for 1 h (using of 7-fold excess of $(CH_3COO)_2Zn$ leads to the final substance almost without the initial TPP). The resultant dark blue crystals of Zn-TPP were washed with acetic acid. Then the substance was chromatographed on an alumina column with chloroform. TLC was used (Silufol, chloroform–hexane 2:1) for Zn-TPP purity determination. Yield 0.43 g (77%).

2.1.4. Synthesis of ZnTPP–IQNO complex

To 34 mg (0.05 mM) of Zn-TPP dissolved in 15 mL of acetone, 1 mL of an acetone solution of isoquinoline N-oxide (7.3 mg, 0.05 mM) was added. The red-violet crystals appeared in 30 min, which were washed with acetone (1 mL, 2 times) and air dried. Yield 70% (29 mg).

Anal. Calc. for $C_{53}H_{35}N_5OZn$ (%): C, 77.32; H, 4.29; N, 8.51. Found (%): C, 77.29; H, 4.44; N, 8.33%. The substance was slowly recrystallized from acetone before picking up the crystal for X-ray analysis.

2.2. Methods

2.2.1. Electronic absorption spectra

Electronic absorption spectra in chloroform, ethyl acetate and *n*-propanol solutions were measured using UV–Vis Cary 50, Varian spectrophotometer. All solvents were of spectral grade.

2.2.2. Emission spectra

Luminescence spectra were recorded on FSL920 combined fluorescence lifetime and steady state spectrometer (Edinburgh Instruments Ltd.) using as excitation source Xe900, 450 W steady state xenon lamp (ozone free) with computer controlled excitation shutter and with spectral bandwidth of $\leqslant$5 nm for both excitation and emission spectra.

2.2.3. X-ray structure determination and refinement

A crystal suitable for X-ray diffraction determinations was grown from acetone as mentioned above. Intensity data collection was carried out on a KUMA KM4 κ-axis diffractometer equipped with a CCD camera and an Oxford Cryo-system. All data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the KUMA Diffraction programs [27]. The structure was solved by the direct methods and refined by the full-matrix least squares method on F^2 data using the SHELXTL (version 5.1) program [28]. The X-ray crystal structure of complex is presented in Fig. 1 and corresponding experimental details are summarized in Table 1.

2.2.4. Time-resolved emission

Luminescence decay curves were recorded using nanosecond Time-Correlated Single Photon Counting (TCSPC) option of FSL920 setup (Edinburgh Instruments Ltd.). Excitation was

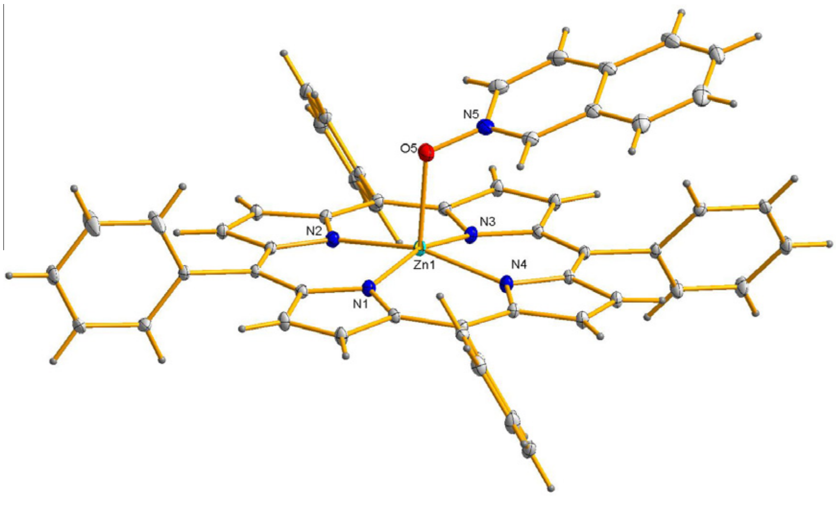

Fig. 1. X-ray crystal structure of ZnTPP-IQNO complex.