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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 $P\overline{1}$. Particular contacts between the two monomeric units (hydrogen bonds, $O \cdots H-C$ 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 (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%)].

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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 (S₁ and S₂) of the latter, considerably differ. The lifetime of the S₁ state, for example, is of the order of about 2 ns while that for the S₂ 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 (κ O-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 spectros-copy 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 CHCl₃ was kept over PbO₂ 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 (CH₃COO)₂Zn·2H₂O, 50 mL of chloroform and 250 mL of glacial acetic acid was boiled for 1 h (using of 7-fold excess of (CH₃COO)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 ≤ 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.

Table 1

Crystallographic parameters and details of the structure refinements of ZnTPP-IQNO complex.

| Compound | (κO-isoquinoline-N-oxide)-(α,β,γ,δ- tetraphenylporphinato)zinc(II) |
|---|---|
| Formula | C ₅₃ H ₃₅ N ₅ OZn |
| FW | 823.23 |
| Radiation (Å) | 0.71073 |
| (graph. monochromated) | |
| T (K) | 100(1) |
| Crystal system | triclinic |
| Space group | ΡĪ |
| a (Å) | 10.192(4) |
| b (Å) | 13.569(5) |
| <i>c</i> (Å) | 16.345(6) |
| α (°) | 67.06(3) |
| β(°) | 82.11(3) |
| γ(°) | 70.51(3) |
| V (Å ³) | 1962.3(13) |
| Z | 2 |
| D _{calc} (g cm ⁻³) | 1.393 |
| μ (mm ⁻¹) | 0.68 |
| n measd | 2418 |
| n ind | 8960 |
| n obs $(I \ge 2\sigma(I))$ | 7529 |
| $R(I \ge 2\sigma(I))$ | 0.036 |
| $R_w (I \ge 2\sigma(I))$ | 0.096 |
| GOF | 1.04 |

provided by nF900 nitrogen filled nanosecond flashlamp under computer control, with typical pulses width 1 ns, Pulse Repetition Rate typical 40 kHz and possibility of measuring decays from 100 ps to 50 µs. Data acquisition ensured Plug-in PC Card Model TCC900 with Maximum Count Rate 3 MHz, Time Channels per Curve up to 4096, and Minimum Time per Channel 610 fs. A Hamamatsu (R928-Hamamatsu) in Peltier Cooled Housing was used as detector.

2.2.5. Theoretical calculations

The calculations of electronic spectra of complex ZnTPP–IQNO and its components were performed at the TDDFT B3LYP and CAM-B3LYP/6-31G(d,p) level with GAUSSIAN09 [29] package of programs. Different geometric structures optimised by DFT B3LYP/6-31G(d,p) method and experimentally obtained the X-ray structure have been taken into consideration.

3. Results and discussion

3.1. Crystal structure of ZnTPP-IQNO complex

Mixing of acetone solutions of Zn-TPP and isoquinoline N-oxide produced the red-violet crystals of 1:1 ZnTPP–IQNO complex, depicted in Fig. 1. A single-crystal X-ray studies revealed that they are characterized by a centrosymmetric triclinic unit cell containing two molecules of ZnTPP–IQNO, space group $P\bar{1}$ (see Table 1 for details).

The X-ray study of the complex showed that the bond lengths and angles in Zn-TPP moiety are essentially the same as in other complexes of Zn-TPP. The same situation can be viewed in the case of isoquinoline fragment; some geometric parameters are described in Table 2. The X-ray structure of isoquinoline N-oxide has not yet been determined, but according to the literature data for isoquinoline analogs [30] one can assume that the structure of the isoquinoline N-oxide fragment is essentially the same as for the free base.

Elongation of the N–O distance in comparison to free N-oxide is caused by the oxygen coordination to the zinc atom and its sp^2-sp^3 rehybridization leading to contribution increase of the canonical [31] form I, presented in Fig. 2.

Table 2

| Selected | experimental | values | of | bond | length | (Å) | and | angles | (°) | of | ZnTPP-IQNC |
|----------|--------------|--------|----|------|--------|-----|-----|--------|-----|----|------------|
| complex. | | | | | | | | | | | |

| Type of distance | Bond length (Å) | Type of angle | Value of the valence or dihedral angle (°) |
|---|--|---|---|
| N5-O5 Zn1-O5 Zn1-N1 Zn1-N2 Zn1-N3 Zn1-N4 | 1.325(2) 2.097(2) 2.066(2) 2.066(2) 2.080(2) 2.080(2) 2.089(2) | Zn1-05-N5 C51-N5-05-Zn5 C9-C10-C27-C28 C16-C15-C33-C34 N1-Zn1-05-N5 N2-Zn1-N1-C1 | 115.67(10) -77.96(16) 61.47 -69.16 131.33(11) 171.83(13) |

The Zn–O (2.097 Å) distance is quite small in comparison to complexes of Zn-TPP with other N- or O-donors (Table 1-S, Supporting materials) where the average value ranges between 2.1 and 2.4 Å. One may assume that steric availability of the N-oxide oxygen might be responsible for that phenomenon.

On the other hand, according to literature data (see Table 1-S, in Supporting materials), an average distance between the zinc atom and the porphyrin plane in complexes with N- and O-donors is almost the same (0.32 Å) as in the target complex (0.337 Å).

The oxygen atom is sp^3 -hybridized in the ZnTPP–IQNO complex and the dihedral angle between the least square planes drawn on the isoquinoline system and the Zn, O, and N atoms is 77.33°. Obviously, that in the case of sp^2 -oxygen hybridization, the angle would likely to be around 0° (see Fig. 3, Structure B).

The ZnTPP–IQNO complex resembles the structure of Zn-TPP complexes with anilines; indeed the nitrogen in anilines is sp²-hybridized (Fig. 3, Structure D) but in complexes with acceptors it is in sp³-hybridization state (Fig. 3, Structure C). For example, in the complex of 3-nitroaniline with Zn-TPP, the angle between porphyrin plane and the Zn–N–C_(phenyl)–C_{phenyl} plane is 86.96° (CSD refcode: HAMLAI-Table 1-S, Supporting materials) clearly indicating the Structure C.

The dihedral angle formed with the porphyrin and isoquinoline rings is 24.45°, and it is too big for any π - π -interactions between porphyrin ring and isoquinoline system, but the hydrogen atom of adjacent phenyl group of Zn-TPP can form a quite strong C-H··· π interaction [30]. The corresponding distance between H34A and the isoquinoline is 2.607 Å.

3.2. Supramolecular interactions in ZnTPP-IQNO complex

Two molecules of adduct form a supramolecular dimer (Fig. 4) in which the oxygen atoms (from the >NO group) form the weak $O \cdots H-C$ hydrogen bonds with the hydrogen of the phenyl ring of the neighboring molecule (2.675 Å, O5–H40A) and the short



Fig. 2. Equilibrium of two canonical forms of isoquinoline N-oxide molecule.

Fig. 3. Electronic structures of N-oxide and aniline in different hybrid conditions of donor centers.

contacts with two carbon atoms of the phenyl ring (3.130 Å O5–C40; 3.215 Å O5–C41). Also the same hydrogens from the phenyl rings, are involved in the C–H··· π contact (2.831 Å C4–H40A, 2.821 Å porphyrine plane–H40A) with the porphyrin system.

The interplanar distance in the dimer (4.373 Å) is much larger than the sum of van der Waals radii and, consequently, shows the impossibility of a strong direct interaction of the two porphyrin moieties. Such dimers form the infinite chains propagating along the *a*-axis.

Different types of van der Waals interactions may occur in these dimers: C-H··· π interactions formed by the hydrogen of isoquinoline ring and the π -system of the adjacent porphyrin molecule as well as possible the π - π interactions (distances between the least square plane drawn through the porphyrin moiety and atoms H55A, H56A, C55, C66 are: 2.786, 2.572, 3.066, 2.932 Å consequently). On the other hand, the dimers of ZnTPP–IQNO may propagate along the *b*-axis (Fig. 1-S-Supporting materials) forming between each other the infinite quasi two-dimensional layers with C-H··· π contacts. It is interesting to view the projections of such layers (Figs. 1-S and 2-S in supporting materials). These layers in turn, forming a 3D crystal structure are tightly connected through the above mentioned types of interaction, as for example: $05\cdots H40A = 2.676$ Å; $Zn1A\cdots C56 = 2.273$ Å or $C35\cdots H30A = 2.679$ Å. (Other appropriate interatomic distances are displayed in Table 2-S of Supporting materials).

3.3. Electronic absorption and emission spectra

3.3.1. Experimental absorption spectra

Absorption spectrum of ZnTPP consists of a double set of clearly separated Q_x , and Q_y bands (540–600 nm) and the higher energetic Soret band located around 420 nm. The former ones, origin from the transition to S_1 state while the latter corresponds to $S_0 \rightarrow S_2$ transition. The longest wavelength Q band is broad and structured while the Soret band shows a strong intensity although is relatively narrow. In the absorption spectrum, the Q band is significantly weaker as compared to a totally allowed the Soret band.

Upon adding the excess of iso-quinoline N-oxide ligand to the chloroform solution of ZnTPP (see Fig. 5), a bathochromic shift of the Soret, Q_x and Q_y bands was found in the UV–Vis spectrum ($\Delta\lambda$, nm: 9.6, 12.5, 14.5, respectively) what is common for axial coordination of metalloporphyrines in solutions [32–35].

A more detailed absorption spectrum of ZnTPP-IQNO in a larger spectral range (250–650 nm) is presented in Fig. 6.

In this figure a third absorption band of ZnTPP–IQNO complex is shown in 250–400 nm region. It is higher in energy scale than both, the Q and the Soret band and its intensity is comparable to that of the Q band although is slightly larger than absorption of parent ZnTPP in the same spectral region.



Fig. 5. Changes in the electronic absorption spectrum of Zn-TPP in chloroform upon addition of isoquinoline *N*-oxide; Q-band intensity shown in the 12.5-fold enlargement compared to the intensity of the Soret band.



Fig. 4. A supramolecular dimer formed by two molecules of ZnTPP-IQNO complex. The ligand moieties are drawn as a ball and stick models.





Fig. 6. Absorption spectrum of ZnTPP-IQNO in ethyl acetate. Over the fragments of the spectrum shown in the magnification, the value of the expanding factor for their intensity is presented.

More detailed analysis of absorption spectrum in this region requires relevant quantum chemical calculations performed in the next chapter.

3.3.2. The calculated electronic transitions

Since the literature data confirm applicability of the DFT B3LYP and TD DFT B3LYP method for ZnTPP and its supramolecular systems [33,36–40], hence the same methods have been applied for

the complex under investigation. However, taking into considerations the fact that the accuracy of TD DFT B3LYP method with respect to the energy gaps between the LE and the CT states should be treated with caution [41–44], we carried out additional calculations by using the CAM-B3LYP functional, which provides the best description of the overall excitation energy.

The results obtained from the calculations showed that the geometric structure of the ZnTPP–IQNO complex, optimized by B3LYP/ 6-31G(d,p) method, is in good agreement with the above described crystal structure (Table 2).

It is worthwhile to note, that accordingly to calculation results, the N–O bond length in the iso-quinoline N-oxide molecule, optimized as a free, unbounded species, is 1.28 Å, while that found in the calculations for the complex (1.309 Å) is only a little bit smaller than the experimental (1.325 Å) value. Hence, the N–O bond elongated about 0.03 Å in the ZnTPP–IQNO complex supports the iso-quinoline N-oxide binding to the parent ZnTPP moiety.

The calculations show also that a significant fraction of charge ($\delta q = 0.146$) separated in the electronic ground state between the two components of the studied complex results in a relatively large value of the dipole moment [7.1D – as calculated by B3LYP/ 6-31G(d,p), and 7.5D – obtained by HF/6-31G(d,p) method]. Its direction is presented in Fig. 7.

The calculated vertical energies and oscillator strength values of electronic transitions for ZnTPP–IQNO complex both with the use of TDDFT B3LYP/6-31G(d,p) and TDDFT CAM-B3LYP/6-31G(d,p) methods are presented in Table 3.

The latter calculations are performed for the same geometry of the complex that was used for the B3LYP/6-31G(d,p) optimization. The character of electronic transitions is revealed in terms of



Fig. 7. The DFT B3LYP/6-31G(d,p) calculated direction of the ground state dipole moment in ZnTPP-IQNO complex.

Table 3

Comparison of electronic transition energies, oscillator strengths, and the character of transition for ZnTPP-IQNO complex calculated by TDDFT B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p). (For electronic configurations see Fig. 8). In the last three entries are the results of TDDFT CAM-B3LYP/6-31G(d,p) calculations for the crystal structure.

| TDDFT B3LYP/6-31G(d,p)//DFT B3LYP/6-31G(d,p) | | | TDDFT CAM-B3LYF 31G(d,p) | P/6-31G(d,p)//D | FT B3LYP/6- | TDDFT CAM-B3LYP/6-31G(d,p)//crystal structure | | | |
|--|------------------------|-------------------------|--|------------------------|-------------------------|---|------------------------|-------------------------|--|
| Transition energy [cm ⁻¹] | Oscillator strength | Character of transition | Transition energy [cm ⁻¹] | Oscillator strength | Character of transition | Transition energy [cm ⁻¹] | Oscillator strength | Character of transition | |
| 15492 | 0.0099 | CT1 | | | | | | | |
| 17579 | 0.0004 | CT2 | | | | | | | |
| 18064 | 0.0234 | LE1 | 17843 | 0.0129 | LE1 | 17679 | 0.0208 | LE1 | |
| 18109 | 0.0222 | LE2 | 17893 | 0.0132 | LE2 | 17738 | 0.0121 | LE2 | |
| 21180 | 0.0037 | CT3 | 22625 | 0.0111 | CT1 | 22489 | 0.0038 | CT1 | |
| 23354 | 0.0067 | CT4 | 24625 | 0.0029 | CT2 | 24675 | 0.0136 | CT2 | |
| 25480 | 0.8613 | LE3 | 26862 | 1.1955 | LE3 | 26694 | 1.1304 | LE3 | |
| 25669 | 0.8408 | LE4 | 27034 | 1.3247 | LE4 | 26879 | 1.1980 | LE4 | |



Fig. 8. The frontiers HOMO and the LUMO orbitals of ZnTPP-IQNO complex presented in two projections to facilitate their proper localization. It is seen that HOMO-a, HOMO-b, LUMO-a and LUMO-b are localized on ZnTPP component while LUMO-c and LUMO-d are localized on IQNO fragment. The electronic configurations of HOMO-b \rightarrow LUMO-c and HOMO-a \rightarrow LUMO-c contribute to the electronic states CT1 and CT2, respectively (see Tab.3). The CT3 and CT4 states are described by the configurations HOMO-b \rightarrow LUMO-d and HOMO-a \rightarrow LUMO-d. The locally excited states LE1 and LE3 are described by symmetric and anti-symmetric combinations of HOMO-a \rightarrow LUMO-a and HOMO-b \rightarrow LUMO-b configurations while LE2 and LE4 by the combinations of HOMO-a \rightarrow LUMO-b and HOMO-b \rightarrow LUMO-b.

electronic configurations described by the frontier molecular orbitals, shaped as shown in Fig. 8.

As you can see, there are two HOMO orbitals localized on ZnTPP and four LUMO orbitals, two of which are located on the ZnTPP and two on NOIQ moiety. Due to the fact that the energy ordering of LUMO orbitals calculated in the two methods are not identical, in presentation in Fig. 8, literal marks were used to characterize them appropriately (HOMO – a, b and LUMO – a, b, c, d). It is worthwhile to note that in TDDFT B3LYP method, the LUMO – c orbital is the lowest of LUMO orbitals whereas in TDDFT CAM-B3LYP method, the lowest is the LUMO – a.

A reflection of differences in the orbital energy ordering is also manifested in different arrangement of the excited states calculated in the two ways. As shown in Table 3, in the description of the lowest excited state of the complex calculated by TDFFT B3LYP method, the CT1 configuration dominates, whereas in the CAM-B3LYP method, the dominating is the LE1 configuration. The excited state which has a dominant CT1 configuration lies above. Hence, this result is yet another example of a more confirmatory data and arguments given in reference [44].

Table 3, moreover, shows that the above-mentioned similarity between the experimental crystal structure and B3LYP optimized molecular structure is reflected in the similarity of their corresponding electronic spectra.

In Fig. 9, the simulated absorption spectrum of ZnTPP–IQNO complex and its components, as based on the data of Table 2S of Supplementary data, are presented.Comparison of theoretical (Table 3 and Fig. 9) and experimental (Figs. 5 and 6) results allows us to note a fairly good agreement between them, although all the calculated vertical energies for the complex are slightly larger (~800 cm⁻¹ in the case of the Q band and ~3000 cm⁻¹ in the case of the Soret band) with respect to experiment. The ratio of the Q band relative to the Soret band, resulting from the calculations, is smaller than the measured one (0.016 versus 0.045).

Fig. 9 shows also two spectra calculated for the isolated ZnTPP unit. One of them corresponds to ZnTPP in the same geometry, which it has in the ZnTPP–IQNO complex, and the second one refers to ZnTPP geometry of CI symmetry which it adopted in its own crystal [45]. A similar procedure was applied also to IQNO molecule.

As seen in both cases, adoption by the isolated molecule of such geometry which it keeps in the complex, is associated with the band redshift, the effect that is strengthened by the complex interaction. For example, the calculated maximum of the Soret band for the isolated ZnTPP in its own geometry is 28 300 cm⁻¹, for isolated ZnTPP but with geometry which it has in the complex is 27 600 cm⁻¹ and finally in the complex it is 26 800 cm⁻¹. Indeed, such a red shift is observed in reality, what illustrate the spectra shown in Fig. 5.

Comparing the two spectra of isolated ZnTPP one can also see the effect of lowering the symmetry of ZnTPP unit in combined ZnTPP–IQNO complex.

The fact, that coordination of the axial ligand to ZnTPP unit leads to a loss of its symmetry in the complex has been established by the X-ray experiment and manifested by differentiation of geometrical parameters in the complex relative to those in parent ZnTPP unit. As can be seen from Fig. 9, the symmetry reduction of ZnTPP in its complex is linked to appearance in its absorption spectrum, the bands that are absent in the spectrum of symmetric ZnTPP moiety (e.g. ~32 070 and ~32 770 cm⁻¹). A detailed spectral analysis shows that in spectrum of the complex, there are also the CT bands characteristic only of the complex as a whole, not present in the spectra of its components separately.

Apparently, you can see it among the calculated transitions for the ZnTPP–IQNO complex: \sim 22 500 and \sim 24 700 cm⁻¹, located in the region between the Q and the Soret band.

Unfortunately, these are weak bands with a small oscillator strength, which in experiment are additionally covered by the



Fig. 9. Simulated absorption spectrum of ZnTPP-IQNO complex and its components, based on the data of Table 3 (in the full form in Table 3S-of Supplementary Data). Each of the calculated line was convoluted with a Gaussian distribution of 250 cm⁻¹ width [such operation allowed the experimental width of the Soret band (see Fig. 6) in the simulated spectrum to be reproduced]. Spectra of each component are calculated for two geometries: the same, which a component has in the complex and their own geometries: For ZnTPP-in its crystal and for IQNO-in DFT B3LYP;6-31G(d,p) optimized geometry. All the calculations were performed by TD CAM-B3LYP/6-31G(d,p) method. In the main scale the Soret band is shown. Intensity of the remaining bands are presented in enlargement described by the appropriate numbers (*50 in the case of the long wavelength bands and *12 in the case of the short wavelength bands. See text for discussion).

components of a rich vibrational structure of the band Q [40-44,46].

Hence, at the present time, from all the above mentioned reasons we are unable to demonstrate a direct experimental confirmation of predicted CT states. In a fact, for this kind of experiment, a low temperature spectroscopy with a higher spectral resolution is required. Nevertheless, such CT transitions were found in transient absorption experiments of other porphyrin complexes [33–35,37, 46-48] where they were used for explanation and modeling of the results related to electron transfer process. Difficulties with interpretation and assignment of the calculated transitions to those experimentally observed in ZnTPP-IQNO complex, are also connected with the higher (in the energetic scale) energy region than the Soret band. In this region, as Fig. 9 shows, many electronic transitions of different type [LE_{ZnTPP}, LE_{IONO} and CT_{complex}) contribute to particular absorption bands of the complex. It is evident that only the measurements with a high spectral resolution can help to resolve this problem.

3.3.3. Preliminary fluorescence spectra

The fluorescence spectra of ZnTPP–IQNO performed at different excitation wavelength are presented in Fig. 10.

The findings related to fluorescence in \sim 400–700 nm region of the complex are similar to those for unbounded ZnTPP [6,11,12]

although the excitation at the Q band [S₁ state of ZnTPP, but S₃ (and S₄) state of the complex] leads, accordingly to Fig. 9, to the LE fluorescence from the S₃ state of the complex. On the other hand, excitation at the Soret band of the complex [S₂ state of ZnTPP but S₇ (and S₈) state of the complex], leads to a dual fluorescence from both LE states of the complex.

Besides that, the excitation fluorescence spectra observed for both fluorescence maxima match agreeably with the absorption spectrum. Hence, it allows to conclude that there are no other pathways of excitation energy dissipation than just a return to the S₀ state. Of course, a question arises regarding a quantitative explanation of this finding. In a fact, many other questions are not cleared out yet, as for example, whether the presence of the two CT bands between the Soret and Q band, does affect radiationless rate constants of deactivation processes? In other words, a pertinent question appears whether additional radiationless channels in the complex are or can be opened? Such channels, like for example the S₅ (or S₆) \rightarrow S₃ (or S₄), and S₃ (or S₄) \rightarrow S₁ (or S₂), are in reality, the radiationless charge separated (CS) transitions and charge recombination (CR) processes, respectively.

With excitation in the higher energy region (280 nm), an additional band exhibiting maximum at 380 nm in the fluorescence spectrum of ZnTPP–IQNO (Fig. 10) is observed. Excitation spectrum observed for this band, however, does not overlap with absorption



Fig. 10. Fluorescence spectra of ZnTPP-IONO complex in ethyl acetate, excited at 300, 400 and 555 nm. All the spectra were normalized at 655 nm.

spectrum of the complex indicating a different source of this fluorescence, as for example, a photoproduct.

The emission decay curve of ZnTPP–IQNO complex in ethyl acetate solution, excited around the Soret band (385 nm) and observed at the Q band (656 nm), is monoexponential and the estimated lifetime (1.92 ns) agrees with the value of about 2 ns found in the literature for the parent ZnTPP system [11–15]. However, in the protic medium of n-propanol, a bi-exponential decay was observed. In this case, the shorter component connected with the lifetime of the S₁ state is a little bit elongated [2.5 ns (87%)] relative to unbounded ZnTPP in ethyl acetate, while the longer one [14.4 ns (13%)] seems to origin from the hydrogen bonded associates formed between the complex and the alcohol molecule. Somewhat peculiar seems to look the emission spectrum of the solid ZnTPP-IQNO complex, presented in Fig. 11.

The sample excited both at 420 and 553 nm, does not show the Soret band at all and the Q band is represented only in the form of a single band peaking at 670 nm (0-0 transition). As the result of ZnTPP coordination to isoquinoline N-oxide ligand, the Q band is shifted to the red by 20 nm with respect to fluorescence maximum in the solid (654 nm), free ZnTPP unit [49]. Likewise to *n*-propanol,



Fig. 11. Emission spectrum of ZnTPP-IQNO complex in the solid state excited at 420 nm (upper line), and 553 nm (lower line).

the emission decay of the solid complex, follows a bi-exponential function. The lifetime in the S₁ state relative to free ZnTPP [11–15] is considerably reduced [1.36 ns (67.5%)], indicating a quenching due to a dynamic process like, for example, photoin-duced electron transfer that may occur on the nanosecond time scale. The longer lived component [7.31 ns (32.5%)] of the crystalline complex may be attributed to dimeric structures of ZnTPP-IQNO that were found in the X-ray experiment.

4. Conclusions

On the basis of the results of TD DFT CAM-B3LYP/6-31G(d,p) calculations and analysis described in terms of both electronic configurations and frontiers of molecular orbitals, has been revealed that excited photoinduced electron transfer (ET) can takes place in ZnTPP–IQNO complex. The transfer of charge occurs from the HOMO orbitals of ZnTPP moiety, to the LUMO orbitals localized exclusively on axially coordinated isoquinoline N-oxide ligand.

Presence of the CT states between the Q-band and the Soret band can run additional deactivation channels in the form of radiationless charge separation and charge recombination transitions.

Excitation above the Soret band in the complex gives also the third emission band exhibiting the maximum around 380 nm. We suppose that the latter may origin from a photoproduct. The fluorescence of the complex decays bi-exponentially in alcohols and in the solid state and the longer time constant in the former may be referred to the hydrogen bonded associates (14.4 ns in n-propanol) and to dimeric structures in the latter (7.31 ns), what, in a fact, has been found in the X-ray experiment. On the other hand, the shortening of the second time constant in the solid complex [1.36 ns (67.5%)] may be due to photoinduced electron transfer as a dynamic, quenching process occurring on the nanosecond time scale.

Electron transfer properties of the above investigated donoracceptor photo-molecular system seem to be promising regarding studies related to solar energy harvesting processes.

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Appendix A. Supplementary data

CCDC <szem09n> contains the supplementary crystallographic data for (κ O-isoquinoline-N-oxide)-(α , β , γ , δ -tetraphenylporphina-to)zinc(II). These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.06.009.

References

- (a) D. Dolphin (Ed.), The Porphyrins, vol. I–VI, Academic, New York, 1978;
 (b) K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, Academic Press, San Diego, 2003;
 - (c) P.R. Ortiz deMontellano (Ed.), Cytochrome P450: Structure, Mechanisms and Biochemistry, second ed., Plenum Press, New York, 1995;
 - (d) H.B. Dunford, Heme Peroxidases, Wiley-VCH, New York, 1999;
- (e) H. Scheer (Ed.), Chlorophylls, CRC Press, Boca Raton, FL, 1991.
- [2] C.A. Mirkin, M.A. Ratner, Ann. Rev. Phys. Chem. 43 (1992) 719.

- [3] P.G. Van Patten, A.P. Shreve, J.S. Lindsey, R.J. Donohue, J. Phys. Chem. B 102 (1998) 4209.
- [4] F.S. Speiser, R.D. Levine, J. Phys. Chem. B 105 (2000) 5589.
- [5] (a) D.M. Guldi, M. Prato, Acc. Chem. Res. 33 (2000) 695;
- (b) D. Kim, A. Osuka, Acc. Chem. Res. 37 (2004) 735.
- [6] H.Z. Yu, J.S. Baskin, A.H. Zewail, J. Phys. Chem. A 106 (2002) 9845.
- [7] G.G. Gurzadyan, T.-H. Tran-Thi, T. Gustavsson, J. Chem. Phys. 108 (1998) 385.
 [8] H. Chosrowjan, S. Taniguchi, T. Okada, S. Takagi, T. Arai, K. Tokumaru, Chem.
- Phys. Lett. 242 (1995) 644.
 [9] B. Dietzek, R. Maksimenka, W. Kiefer, G. Hermann, J. Popp, M. Schmitt, Chem.
- Phys. Lett. 415 (2005) 94.
- [10] S. Sorgues, L. Poisson, K. Raffael, L. Krim, B. Soep, N. Shafizadeh, J. Chem. Phys. 124 (2006) 114302.
- [11] A. Lukaszewicz, J. Karolczak, D. Kowalska, A. Maciejewski, M. Ziolek, R.P. Steer, Chem. Phys. 331 (2007) 359.
- [12] J. Karolczak, D. Kowalska, A. Lukaszewicz, A. Maciejewski, R.P. Steer, J. Phys. Chem. A 108 (2004) 4570.
- [13] S.I. Yang, J. Seth, J.P. Strachan, S. Gentemann, D. Kim, D. Holten, J.S. Lindsey, D.F.J. Bocian, J. Porphyrins Phthalocyanines 3 (1999) 117.
- [14] O. Ohno, Y. Kaizu, H. Kobayashi, J. Chem. Phys. 82 (1985) 1779.
- [15] S.E.J. Bell, A.H.R. Ali-Obaidi, M. Hegarty, R.E. Hester, J.J. McGarvey, J. Phys. Chem. 97 (1993) 11599.
 [16] M.P. Bryn, C.J. Curtis, Y. Hsiou, S.I. Khan, P.A. Sawin, S.K. Tendick, A. Terzis, C.E.
- Strouse, J. Am. Chem. Soc. 115 (1993) 9480. [17] Y.-T. Mashiko, M.E. Kastner, K. Spartalian, W.R. Scheidt, C.A. Reed, J. Am. Chem.
- Soc. 100 (1978) 6354.
- [18] C.L. Hill, M.M. Wiliamson, Inorg. Chem. (1985) 323024.
- [19] S. Kondo, Br. J. Cancer 35 (1977) 595.
- [20] D. Kanojia, M.M. Vaidya, Oral Oncol. 42 (2006) 655.
 [21] Y. Nizhnik, J. Lu, R.V. Rosokha, J.K. Koichi, Cryst. Eng. Commun. 11 (2009) 2400.
- and references therein.
 [22] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, J. Org.
- [22] A.D. Adier, F.A. Edigo, J.D. Finareni, J. Goldmacher, J. Assour, L. Korsakon, J. Org. Chem. 32 (1967) 476.
- [23] A.F. Pozharskii, V.A.T. Anisomova, E.B. Cupak, Practical Works on Heterocycles Chemistry, Rostov-on-Don, 1985. pp. 54–57.
- [24] Y.A. Zhdanov, Practicum on Carbohydrates Chemistry, Moscow, 1973, p. 204 (in Russian).
- [25] P. Rothemund, A.R. Menotti, J. Am. Chem. Soc. 70 (1948) 1808.
- [26] E.A. Venedictov, V.V. Mozhzhukhin, N.G. Lipatov, Russ. J. Gen. Chem. 63 (1993) 1155.

- [27] Oxford Diffraction Ltd. CrysAlis CCD and CrysAlisRED Version 1.171; Oxford Diffraction Ltd: Abingdon, Oxfordshire, England, 2003.
- [28] G.M. Sheldrick, SHELXTL, Version 5.1, Brucker AXS Inc., Madison, Wisconsin, USA, 1998.
- [29] M.J. Frisch, et al., Gaussian 09, Revision B.01; Gaussian, Inc., Wallingford CT, 2010.
- [30] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885-3896.
- [31] V.P. Andreev, V.V. Vapirov, Y.P. Nizhnik, L.A. Aleshina, T.A. Semenova, Russ. J. Gen. Chem. 78 (2008) 973.
- [32] V.P. Andreev, Y.P. Nizhnik, D.G. Bezruchko, A.K. Morozom, Russ. J. Gen. Chem. 75 (2005) 1309.
- [33] K. Harada, M. Fujitsuka, A. Sugimoto, T. Majima, J. Phys. Chem. A 111 (2007) 11430.
- [34] M. Fujitsuka, H. Shimakoshi, S. Tojo, L. Cheng, D. Maeda, Y. Hisaeda, T. Majima, J. Phys. Chem. A 113 (2009) 3330.
- [35] M. Fujitsuka, H. Shimakoshi, S. Tojo, L. Cheng, D. Maeda, Y. Hisaeda, T. Majima, J. Phys. Chem. A 114 (2010) 4156.
- [36] K.A. Nguyen, P.N. Day, R. Pachter, S. Tretiak, V. Chernyak, S. Mukamel, J. Phys. Chem. A 106 (2002) 10285.
- [37] M.P. Balanay, D.H. Kim, Phys. Chem. Chem. Phys. 10 (2008) 5121.
- [38] P.J. Walsh, K.C. Gordon, D.L. Officer, W.M. Campbell, j. Mol. Struct. THEOCHEM 759 (2006) 17.
- [39] M.-S. Liao, P. Bonifassi, J. Leszczynski, M. Huang, J. Mol. Phys. 106 (2008) 147.
 [40] B. Minaev, Y.-H. Wang, C.K. Wang, Y. Luo, H. Agren, Spectrochim. Acta A 65
- (2006) 308. [41] A. Szemik-Hojniak, W. Rettig, I. Deperasińska, Chem. Phys. Lett. 343 (2001) 404.
- [42] M. Parac, S. Grimme, Chem. Phys. 292 (2003) 11.
- [43] L.D. Betowski, M. Enlow, L. Lee Riddick, Comput. Chem. 26 (2002) 371.
- [44] (a) L. Serrano-Andres, M. Merchan, J. Mol. Struct. THEOCHEM 729 (2005) 99;
 (b) Michael J.G. Peach, Peter Benfield, Trygve Helgaker, David J. Tozer, J. Chem. Phys. 128 (2008) 044118.
- [45] E.B. Fleischer, C.K. Miller, L.E. Webb, J. Am. Chem. Soc. 86 (1964) 2342.
- [46] O. Schalk, H. Brands, T.S. Balahan, A.-N. Unterreainer, J. Phys. Chem. A 112 (2008) 1719.
- [47] S. Wallin, C. Monnereau, E. Blart, J.-R. Gankou, F. Odobel, L. Hammarstrom, J. Phys. Chem. A 114 (2010) 1709.
- [48] A. Morandeira, A. Engeli, E. Vauthey, J. Phys. Chem. A 106 (2002) 4833.
- [49] Y. Li, W.W. Han, M.X. Liao, Acta. Phys. Chim. Sin. 25 (2009) 2493.