



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 [6-31G(d,p)] calculations



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ABSTRACT

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 $P\bar{1}$. Zinc atom in the studied complex is pulled out 0.365 Å 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 Q_x and Q_y 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 S₁ 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 (0.6 ns) was revealed for the solid complex, while in toluene (1.5 ns) and in *n*-propanol (2.7 ns), they shown to be several times longer.

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1. Introduction

Porphyrins and metalloporphyrins are specific building blocks for synthesis of donor–acceptor systems, in which photoinduced electron transfer process and the charge transport mechanisms can be studied [1]. The latter is important in understanding reaction mechanisms both in natural and artificial systems and is crucial in development of technologies connected to molecule-based devices [2–6]. One way of obtaining such type of constructs is the ligand coordination to metalloporphyrin moiety. It is known, in fact, that interaction of organic ligands with Lewis acids may strongly affect the energy and electron transfer processes in the systems of interest [7]. Hence, coordination of ligand, for example, to zinc tetraphenylporphyrin (ZnTPP), as

the most extensively studied among metalloporphyrins [8–12], often leads on irradiation to photoinduced electron transfer and appearance of excited states of the charge transfer (CT) nature [13].

Also investigations of covalently linked porphyrin–fulleren dyads have shown that ligation provides a practical tool to control the charge separation (CS) and the charge recombination (CR) reactions [14].

In these systems, the quantitative analysis of both intramolecular exciplex formation and electron transfer reactions have been investigated by means of time-resolved transient absorption and emission decay measurements in a range of solvents with different polarities [15,16].

In turn, systems consisting of multiple porphyrin units may be explored as models for practical charge-separation devices, as for example, in organic photovoltaics solar cells [17–20] or photo sensors [21].

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An interesting sources of the results on electron and energy transfer are the molecular complexes of ZnTPP with axially coordinated ligands. In recent years a variety of such systems have been designed [8–11]. Their photophysical properties and specifically, the excited electronic states, have been the subject of considerable interest and study. Many of them involve heteroaromatic N-oxides [22–24], which show a push–pull behavior and are the components of great amount of natural products with specific biological properties [25]. Hence, their constructs with ZnTPP moiety forms a new sub-group of D-A systems of unique photophysical properties and promising future applications.

Recently, we also used the *iso*-quinoline N-oxide (IQNO) and 1,4-dioxane as ligands to obtain ZnTPP–IQNO [26] and ZnTPP–(dioxane)₂ [27] complexes, respectively, where they are axially coordinated to the ZnTPP unit. It should be clarified in this place, however, that the ZnTPP in the excited state may become an electron donor, despite that in the ground state it is a Lewis acid. This is the case for the ZnTPP–IQNO complex [26]. From TD DFT CAM-B3LYP/6-31G(d,p) calculations and specifically from analysis of electronic configurations, we found that upon photoexcitation, the internal transfer of charge occurs between the ZnTPP moiety acting here as an electron donor, and the *iso*-quinoline N-oxide as electron acceptor. In consequence, the S₁ excited state shows the CT nature.

On the other hand, in a unique structure of ZnTPP–(dioxane)₂ complex [27], where two dioxane molecules are connected to one ZnTPP unit in equatorial and in axial position, the ZnTPP demonstrates a state rarely observed in the excited state the role of electron acceptor. Analysis of TD DFT B3LYP/6-31G(d,p) electronic wave functions of this complex, also identifies new CT bands, absent in its components. These bands correspond to the excited state transitions from the HOMO (Highest Occupied Molecular Orbital) localized on dioxane molecule into direction of two LUMO (Lowest Unoccupied Molecular Orbitals) orbitals placed on the ZnTPP unit.

In the present work a continuation of the two previously published papers, the ZnTPP moiety is covalently linked to 2-(4-methoxy-*trans*-styryl)quinoline-1-oxide (MSQNO) molecule to form the ZnTPP–MSQNO complex.

The choice of this ligand, however, was not accidental. Recently, we studied the excited state processes in the N-oxide of another styryl derivative, i.e. *trans*-(dimethylamino-styryl) pyridine N-oxide (DPO) [28] where in a wide range of various solvents, an adiabatic, ultra-fast photoinduced electron-transfer and an ultra-fast solvent relaxation leading to the S₁ emissive state of the CT character have been confirmed. Our results on DPO are in line with previously extensively discussed in the literature data on the *trans*-4-(dimethylamino)-4'-cyanostilbene (DCS) [29].

Another reason for undertaking this study is the biological activity of heterocyclic N-oxides related to their ligation to metalloporphyrins [30]. Our experimental results indicate that the most important process leading to apoptosis of the leukemic cell of the K562 type is coordination of these N-oxides to the cytochrome b, c1, and P450 [31,32].

Finally, all the above mentioned reasons and important roles of styryl quinolines both in pharmacology [33,34] and in material sciences [35–37], have focused our interest in studying the optical properties of the complex where MSQNO ligand, as styryl derivative, is linked to the ZnTPP unit. Our experimental results involve the X-ray crystal structure of this complex as well as the stationary absorption and emission spectra along with the time-resolved emission. The whole experimental data are complemented by the results of theoretical calculations on DFT and TD DFT/CAM level of theory.

2. Materials and methods

2.1. Materials

Zn-tetraphenylporphyrin, 2-methylquinoline-1-oxide, 4-methoxybenzaldehyde, and CH₃OK as well as methanol, ethanol and acetone for synthesis and recrystallizations were of analytical grade (POCH, Sigma Aldrich). Solvents for absorption, steady state and time-resolved fluorescence were of spectroscopic grade and used fresh as purchased (Merck, Uvasol).

2.1.1. Synthesis of 2-(4-methoxy-*trans*-styryl)quinoline-1-oxide

2-(4-Methoxy-*trans*-styryl)quinoline-1-oxide [MSQNO] was synthesized using the method described in literature [38] as follows: 1.6 g (0.01 mol) of 2-methylquinoline-1-oxide and 1.9 g (1.7 mL, 0.014 mol) of 4-methoxybenzaldehyde were placed into 5 mL of 10% CH₃OK in methanol. The mixture was refluxed 3 h under nitrogen and then the solvent was evaporated *in vacuo*. The substance was twice recrystallized from ethanol. Yield: 1.94 g (70%), Yellow powder; M.p. 142.5–143 °C (140 °C [38]).

2.1.2. Synthesis of ZnTPP–MSQNO complex

To 34 mg (0.05 mM) of Zn-TPP (obtained as described in [26]) dissolved in 15 mL of acetone, 1 mL of acetonic solution of 2-(4-methoxy-*trans*-styryl)quinoline-1-oxide (13.9 mg, 0.05 mM) was added. The red-violet crystals appeared thereafter and were washed with acetone (1 mL, 2 times) and dried in air. Yield: 70% (33.5 mg). *Anal. Calc.* for C₆₂H₄₃N₅O₂Zn: C, 77.94; H, 4.54; N, 7.33. *Found:* C, 77.96; H, 4.62; N, 7.24%. The substance was slowly recrystallized from acetone before picking up the crystal for X-ray analysis.

2.2. Methods

2.2.1. X-ray structure determination and refinement

Intensity data collection for X-ray structure determination 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 [39]. 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 [40]. The X-ray crystal structure of ZnTPP–MSQNO complex is presented in Fig. 1 whereas the corresponding experimental details are summarized in Table 1. The data of crystal structure of ZnTPP–MSQNO complex [(κO¹-2-{2-(4-methoxyphenyl)-*trans*-ethen-1-yl}quinolone-1-oxide)-(α,β,γ,δ,-tetraphenylporphyrinato) zinc (II)] have been deposited at the Cambridge Crystallographic Data Centre. The data have been assigned the following deposition numbers: CCDC (szem11) 983906.

2.2.2. Electronic absorption spectra

Electronic UV–Vis absorption spectra of ZnTPP–MSQNO complex in toluene (spectral grade) was recorded on Perkin Elmer Lambda 25 Spectrophotometer with concentration of 4 · 10^{−5} M.

2.2.3. Steady state emission spectra

Emission spectra both in toluene and in the solid state were recorded on FSL920 combined fluorescence lifetime and steady state spectrofluorimeter (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. Luminescence was detected using a red sensitive (185–850 nm) single photon counting photomultiplier tube (R928-Hamamatsu)

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