Absorption and Fluorescence Spectra of Bis(porphyrinato)zinc(II) Complexes with a Flexible Polyatomic Chain

Yuzo Nishida*, Masaya Okamoto, and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812, Japan
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Relationship between the steric conformation and the efficiency of energy transfer in binuclear zinc(II) porphyrin complexes was interpreted in terms of the absorption and fluorescence spectra.

1. Introduction

It is well known that the spectral and magnetic properties, and the reactivities of dimeric metal complexes differ from those of the corresponding mononuclear ones. For example, NMR and the absorption spectra of metal porphyrins and phthalocyanins are frequently dependent on the concentration, which has been elucidated in terms of the presence of aggregated species in the solution [1].

Much attention has been focused upon these changes in absorption and fluorescence spectra of dimeric metal porphyrins (or phthalocyanins) in relation to the property of chlorophyll in the active center [2–4]. Although several authors have investigated the spectral properties of bis(porphyrinato)zinc(II) complexes [5–8], little information is available at present on the relationship between the steric conformation of two porphyrin rings and the decrease of the fluorescence intensity. In this study we have prepared several bis(porphyrinato)zinc(II) complexes (cf. Fig. 1) in which two porphyrins are linked by a flexible polyatomic chain, and measured the absorption and fluorescence spectra of these compounds.

2. Materials and Methods

The bis(porphyrin) ligands used in this study (exemplified by H_4(p-2-6-4-p) in Fig. 1) were prepared according to the literature methods [9, 10]. The zinc(II) complexes were obtained by the general procedure, and purified by the column chromatography (silica-gel, CHCl_3 eluent) in the dark. Absorption spectra in water (containing Triton X-100 and acetone) [11] were measured with a Shimadzu Spectrophotometer model UV-240 with a graphic display at 288 K, and the fluorescence spectra on the same solutions were obtained with a Hitachi Fluorescence Spectrometer model 220 at 288 K. In the latter experiment, the highest fluorescence intensity in 603–606 nm by the light irradiation in the Soret band region (390–410 nm) was recorded.

3. Results

In Fig. 2, several absorption spectra are illustrated, and the results are summarized in Table I. As shown in Fig. 2, the spectral properties of bis(porphyrinato)zinc(II) in water are different from that of the corresponding monomeric complex, Zn(TTP).

Abbreviations: H_4(TTP); tetra(p-tolyl)porphyrin. Bch-b; bacteriochlorophyll b.
* Reprint requests to Dr. Y. Nishida.
These zinc(II) compounds studied here can be divided into two groups according to their spectral properties; i.e., A-group, in which the Soret band is shifted to higher energy region from that of Zn(TTP), such as Zn₂(p-2-3-2-p) and Zn₂(p-2-4-4-p). In the B-group, the band position of Soret are similar to that of Zn(TTP), however, the peak height of the Soret band decreases and the half-width of the absorption band increases, as shown in Table I and Fig. 2.

The relative fluorescence intensity of these compounds (compared with the peak height) are given in Table I. It is known that Zn(TTP) shows strong fluorescence peak at 605 nm by the irradiation of the light in the Soret band region under the same conditions [11]. It should be noted that the fluorescence intensities of B-group compounds are much smaller than those of A-group compounds and Zn(TTP).

4. Discussion

The spectral changes due to the dimerization (or aggregation) in porphyrins can be interpreted in terms of the molecular exciton theory [5, 12], the results being shown in Fig. 3. The interaction energy, J (cf. Fig. 3) may be calculated as

\[ J = R^{-2} \left[ (m_1 \cdot m_2)R^2 - 3(m_1 \cdot R)(m_2 \cdot R) \right], \]

where \( m_1 \) and \( m_2 \) are the transition dipole moments at the chromophore 1 and 2, respectively, and \( R \) denotes the distance between the two chromophores. According to this theory, the shifts of higher-energy or lower-energy region is expected for the case (a) or (b), respectively (cf. Fig. 3). In the case of (c), the splitting or the broadening of the absorption band is anticipated. The splitting of the Soret band was already reported for the “Gable Porphyrin” [7], which should correspond to the case (c). On the basis of the above discussion, we can conclude that the steric conformation of B-group is similar to that of “Gable Porphyrin”, and is different from those in A-group compounds, for the latter group the conformer (a) is assumed.

The notable decrease of the fluorescence intensities observed for B-group compounds (similar decrease of fluorescence intensity was also observed for the “Gable Porphyrin” [7]), is suggesting that the energy transfer occurs more efficiently in the conformer (c). Very recently, the crystal structure of photosynthetic reaction center from \textit{Rhodopseudomonas viridis} has been determined at 3 Å resolution [13]. According to the result, the angle between the two ring planes in “special pair” is 15°, and the angle between the BCh-b and the tetrapyrrole plane of one of the special pair is 70°. These orientations observed in the biological system may correspond to the case (c) in Fig. 3. Thus, the present results seem to be consistent with the structural properties in biological system.
Fig. 3. Exciton levels and selection rules in electronic transitions for molecular dimers (E and G represent excited and ground state, respectively. The --- and ---- denote forbidden and allowed transitions, respectively.)