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Hetero-aggregation between Gold Porphyrins and Zinc Porphyrins through Charge Transfer Interaction

Hiroshi SEGAWA, Hitoshi NISHINO, Taku KAMIKAWA, Kenichi HONDA,[†]
and Takeo SHIMIDZU[*]
Division of Molecular Engineering, Graduate School of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606

Hetero-aggregates composed of electron-attracting gold porphyrins and electron-releasing zinc porphyrins are investigated in aqueous solution. A charge transfer interaction is confirmed by the dependence of hetero-aggregation constants on charge transfer energy of the aggregates.

Studies on metalloporphyrin aggregates are important in relation to the function of chlorophyll dimer in natural photosynthesis, where effective photo-induced electron transfer reaction is accomplished.$^{1)}$ From this point of view, various aggregation systems have been investigated by many workers.$^{2-12)}$ Although many <u>self</u>-aggregation systems composed of water-soluble porphyrins have been reported so far,$^{2-8)}$ studies on <u>hetero</u>-aggregation systems are not so many in spite of the importance for understanding of the electron transfer in the porphyrin aggregate and development of an artificial photosynthetic system using the metalloporphyrins. In the previous papers,$^{9-12)}$ some hetero-aggregates composed of cationic and anionic porphyrins were reported. The main driving force of these hetero-aggregation was electrostatic attraction of peripheral substituent. In this paper we present new type of hetero-aggregate composed of anionic zinc and gold porphyrins by strong charge transfer interaction of the porphyrin moieties.

Gold and zinc complexes of anionic porphyrins (*meso*-tetrakis(4-sulfophenyl) porphin; TSPP and *meso*-tetrakis(4-carboxyphenyl)porphin; TCPP) were synthesized and purified according to the literatures.$^{13-15)}$ AuTSPP ($E_{1/2}(P/P^{\cdot -})$= -0.37±0.02 V vs.

[†]Present address: Tokyo Institute of Polytechnics, 2 Honcho, Nakano-ku, Tokyo 164.

NHE) and AuTCPP ($E_{1/2}(\mathrm{P}/\mathrm{P}^{\overline{\cdot}})=-0.41\pm0.02$ V vs. NHE) have relatively high oxidizing power among various anionic porphyrins and produce stable π-radical anions by the electrochemical reduction below the potentials.[15] ZnTSPP and ZnTCPP produce stable π-radical cations by the electrochemical oxidation above the potentials of 0.87 and 0.80 V vs. NHE, respectively.[14]

Many of metal complexes of TSPP and TCPP without axial ligands are known to show the tendency to self-aggregate in aqueous solution, which were recognized from deviation of absorption spectra by concentration change and/or ionic strength change.[2,3,16] Figure 1 shows the absorption spectral changes of the 1:1 mixture solution of AuTSPP and ZnTSPP with increasing of the ionic strength. According to the addition of NaCl, drastic absorption changes were observed with isosbestic points at 566, 584, and 599 nm. Since the same spectral changes and the same isosbestic points were also observed according to the addition of other neutral salts and according to increasing of the porphyrin concentration of the mixture solution, it was suggested that the absorption spectral changes resulted from aggregation of the porphyins. In the mixture solution of AuTSPP and ZnTSPP, the hetero-aggregation (1) and self-aggregations (2) and (3) are considered to occur.

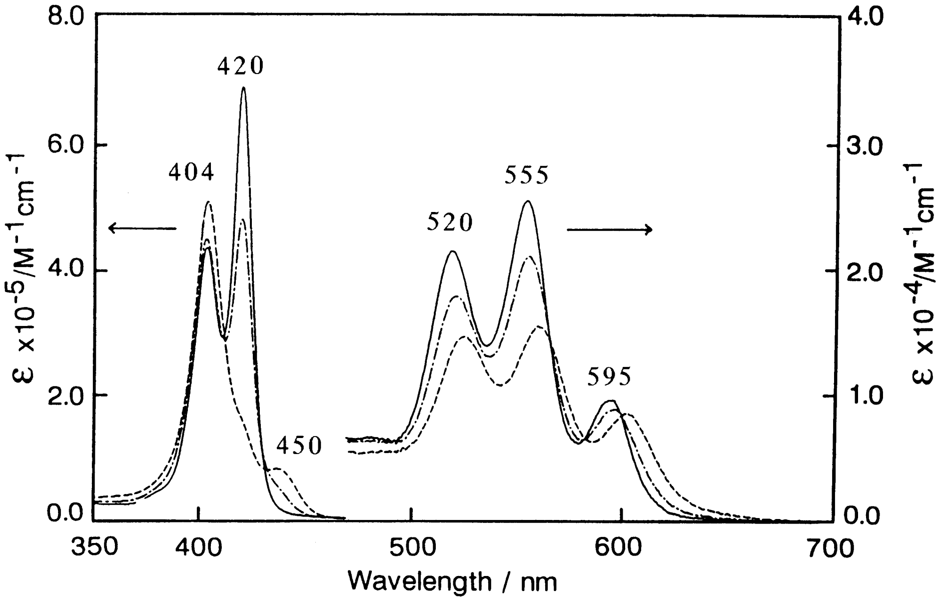

Fig. 1. Absorption spectral changes of the mixture solution of AuTSPP (2×10^{-6} mol dm^{-3}) and ZnTSPP (2×10^{-6} mol dm^{-3}) at pH 7 by the addition of NaCl. —— without NaCl, -·-·-NaCl 0.4 mol dm^{-3}, ---- NaCl 4.0 mol dm^{-3}.

$$\mathrm{AuTSPP} + \mathrm{ZnTSPP} \rightleftharpoons (\mathrm{AuTSPP\text{-}ZnTSPP}) \qquad (1)$$

$$2\ \mathrm{AuTSPP} \rightleftharpoons (\mathrm{AuTSPP})_2 \qquad (2)$$

$$2\ \mathrm{ZnTSPP} \rightleftharpoons (\mathrm{ZnTSPP})_2 \qquad (3)$$

However, the absorption spectral changes of the mixture solution with increasing of the ionic strength seem rather simple and have isosbestic points as shown in Fig. 1. While the red-shift in the Q-band was the similar feature as the ordinary self-aggregation systems,[2-8] the strong hypochromicity at 520 nm and 555 nm with the weak hypochromicity at 595 nm was not interpreted as the self-aggregations (2) and (3).[17] Moreover, the absorption at 420 nm (originated from ZnTSPP) completely disappeared and new peak at 450 nm appeared according to the aggregation, which was not explained by the self-aggregations (2) and (3). Therefore, it is suggested that the absorption spectral changes in Fig. 1 reflect mainly hetero-aggregation (1). In fact, the maximum absorbance deviation from Beer's law was found at 1:1 ratio of AuTSPP and ZnTSPP. The presence of isosbestic points reveals that the 1:1 hetero-aggregate of AuTSPP and ZnTSPP is formed in preference to the both self-aggregations and that the amounts of the self-aggregates are negligibly small.[18)]

In other combinations of gold and zinc porphyrins (AuTSPP-ZnTCPP, AuTCPP-ZnTSPP and AuTCPP-ZnTCPP), the absorption spectral changes due to the hetero-aggregation were similar to that of AuTSPP and ZnTSPP. However, the extent of the hetero-aggregations was strongly influenced by the reduction potentials of the gold porphyrins and the oxidation potentials of the zinc porphyrins. The hetero-aggregation constants (K)[18] became greater according to decrease of charge transfer energy (E(CT)),[19] estimated by the oxidation potentials of zinc porphyrins and the reduction potentials of gold porphyrins, as shown in Fig. 2. The relationship between log K and E(CT) implies that the main driving force of the hetero-aggregation is charge transfer interaction.

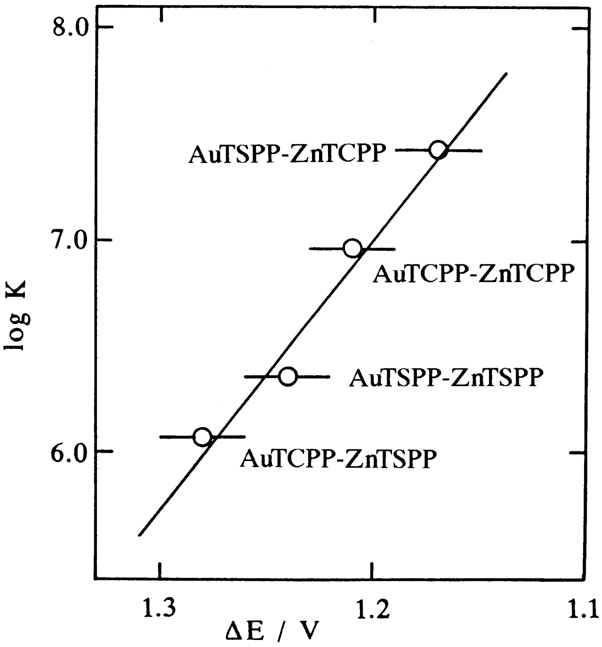

Fig. 2. The relationship between the aggregation constant (K / dm^3 mol^{-1}) in NaCl (1 mol dm^{-3}) solution and charge transfer energy (E(CT) / eV) estimated by the oxidation potentials of the zinc porphyrins and the reduction potentials of the gold porphyrins.

The charge transfer complex composed of donor metalloporphyrin and acceptor metalloporphyrin is presented for the first time with this study. An existence of such charge transfer complex is to be useful for designing of photo-induced electron transfer material. Further investigation is in progress.

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16) It was suggested that the increase of ionic strength reduced electrostatic repulsion and induced the dimerization (reference 2).
17) The hypochromicity due to the self-aggregation of ZnTSPP is same degree at 555 nm and 595 nm. The absorption at 555 nm and 595 nm are scarcely changed by the self-aggregation of AuTSPP.
18) Aggregation constants of the hetero-aggregate (1) and the self-aggregates (2) and (3) were determined by multi-equilibrium treatment. The preferential formation of the hetero-aggregate is also confirmed by comparison of the aggregation constants where $K_{hetero} >> K_{self}$. Details of such calculations and obtained aggregation constants will be published separately.
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