

Investigation of Interfacial Consecutive Electron Transfer and Redox Behaviors of Zinc-tetraarylporphyrins



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ABSTRACT

This paper focused on study of the interfacial consecutive electron transfer (ET) kinetics and the redox behaviors of three 5,10,15,20-zinc-tetraarylporphyrins (ZnTArPs) with a systematic variation of meso- π -extension at a 2^n ($0 \leq n \leq 2$) pattern, where 2^n was the number of benzene ring in an aryl group. The two-step redox potentials of 5,10,15,20-zinc-tetraphenylporphyrin (ZnTPP) were more negative than that of 5,10,15,20-zinc-tetranaphthylporphyrin (ZnTNP) and 5,10,15,20-zinc-tetrapyrenylporphyrin (ZnTPyP), suggesting that ZnTPP was the most active reactant among three ZnTArPs. It was found that the consecutive two-step ET rate was insensitive to the change of the overall driving force in a wide potential region for ZnTArP-Fe(CN)₆⁴⁻ reaction systems. The solvation effect on consecutive ET rate constant is discussed in detail. The molecular structures of ZnTArP, [Zn(TArP*)]⁺ and [Zn(TArP*)]²⁺ were optimized by using density functional theory. The calculation results showed that ZnTPyP cation was the most active species among tree ZnTArP cations at a fixed valence state.

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1. Introduction

Porphyrins and derivatives are fundamental blocks in organisms and play varied key roles in physiological processes [1]. For instance, the core structure of chlorophyll is a magnesium porphyrin while that of hemoprotein is an iron complex. Because porphyrins possess a number of attractive electrochemical and photophysical properties [2–4], numerous studies have been carried out to examine the applications of porphyrins, including organic electronics [5–7], medicine and pharmacy [8,9]. Enlightened by their characters in nature and fascinating properties, a number of porphyrins and metal complexes have been synthesized to study biomimetic interfacial electron transfer, oxygen transport, metalloenzyme catalysis and photosynthesis antenna [10–16]. The structures of those porphyrins are designed and adjusted by variation of substituent groups, π -extension, and coordinated metal ions, which further have effects on their physical and chemical properties [17–20]. Investigation of the effects of these appendants on the properties of porphyrins and complexes is critical to understand the

biological activity and biosynthetic formation of natural compounds [21,22].

In nature, porphyrins participate in several fundamental reactions at membrane boundaries [14]. The interface between two immiscible electrolyte solutions (ITIES) is considered to be the simplest model to investigate the charge transfer processes of these reactions. The charge transfer consists of ion transport (IT) and electron transfer (ET), wherein, studies of the electron transfer process greatly facilitate our understanding of the fundamentals of chemical, biological and pharmaceutical sciences [23]. The interfacial ET includes single-step ET and multi-step ET. Of these, multi-step ET is much more important, significant and widespread in biological processes than single-step ET [24]. However, there have been only a few reports regarding multi-step ET at liquid-liquid (L-L) interfaces [25–30] mainly because of the difficulties in finding appropriate methods and breakthroughs of theory to study multi-step ET. Three electrochemical methods have been invented to investigate the ET at L-L interface: (1) four-electrode system invented by Samec et al [46] in the 1980s; (2) Scanning electrochemical microscopy (SECM) invented and developed by Bard and coworkers [35,37,39,47,48,50,51] in the 1990s; (3) Thin-layer cyclic voltammetry (TLCV) invented by Shi and Anson [31] in the late 1990s. Wherein, TLCV became popular in the last decade for investigation of interfacial ET [25,26,28–30] because of its simple operation and data analysis.

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Particularly, the requirement of very small amounts of reactants makes it applicable for our study. Recently, the TLCV theory is further improved for evaluation of consecutive multi-step ET at L-L interfaces by our group [29,30]. Thus, another attractive advantage of TLCV lies in that it can simultaneously evaluate more precise rate constants of multi-step ET reactions.

In this paper, we investigated the effects of systematic variation of meso- π -extension on the redox behaviors and the consecutive ET kinetics of 5,10,15,20-zinc-tetraarylporphyrins (ZnTArPs) at the L-L interface. The redox behaviors in bulk solution were examined by using cyclic voltammetry (CV) while the interfacial consecutive ET processes were evaluated by using TLCV measurement. The correlation between the driving force and the consecutive ET rate constants of the interfacial bimolecular reaction systems was discussed. The density functional theory was adopted to optimize the molecular structures of ZnTArPs and the corresponding ZnTArP cations with different valence state.

2. Experimental Section

2.1. Instrumentation

A CHI-900 electrochemical workstation (CH Instruments, Austin, TX) was employed to monitor the ET at L-L interfaces with a conventional three-electrode cell that consisted of a pyrolytic graphite working electrode (EPG, area 0.3 cm²), a platinum counter electrode and saturated calomel reference electrode (SCE). SCE was associated with a salt bridge in organic CV measurement. All the measurements were carried out at room temperature.

2.2. Chemicals

Sodium chloride (NaCl), sodium perchlorate (NaClO₄), potassium ferrocyanide (K₄Fe(CN)₆), tetrabutylammonium perchlorate (TBAClO₄) and nitrobenzene (NB) were used as received at AR or higher grade. All aqueous solutions were prepared by using ultrapure water with the resistivity of 1.825 × 10⁷ Ω cm. 5,10,15,20-tetraphenylporphyrin (ZnTPP), 5,10,15,20-tetranaphthalporphyrin (ZnTNP) and 5,10,15,20-tetrapyrenylporphyrin (ZnTPyP) were synthesized in our lab according to refs [41–44].

2.3. Thin-layer cyclic voltammetry

2.3.1. Procedure

The detailed procedure of TLCV was adopted from references [29,31], except that the NB phase (2 μL) contained the different ZnTArPs.

2.3.2. Theoretical analysis

The quantitative theory of TLCV is described in Eq. (1)–(4) [29,32], where i_{obs} stands for observed plateau current, i_D is the steady-state diffusion limit current, i_{ET} is a characteristic current of cross-phase electron transfer at the NB-H₂O interface, n is the number of electrons transferred, F is the Faraday's constant, A is the geometrical area of EPG, c_{NB}^* is the concentration of zinc-porphyrins dissolved in the NB layer, D_{NB} is the diffusion coefficient of zinc-porphyrins in NB, and d is the thickness of the organic layer. k_{et} is the bimolecular reaction rate constant (cm s⁻¹ M⁻¹) between the two reactants at the L-L interface with the concentration of c_{NB}^* in NB and $c_{H_2O}^*$ in the aqueous solution, respectively. Based on Eq. (4), the plot of $(i_{obs})^{-1}$ vs. $(c_{H_2O}^*)^{-1}$ is expected to exhibit a linear profile with the slope of $(nFAc_{NB}^*k_{et})^{-1}$ and intercept of $(i_D)^{-1}$, from which we can calculate k_{et} and i_D .

$$(i_{obs})^{-1} = (i_D)^{-1} + (i_{ET})^{-1} \quad (1)$$

$$i_D = nFAc_{NB}^*D_{NB}/d \quad (2)$$

$$i_{ET} = nFAk_{et}c_{NB}^*c_{H_2O}^* \quad (3)$$

$$(i_{obs})^{-1} = d/(nFAc_{NB}^*D_{NB}) + (nFAc_{NB}^*)^{-1}(c_{H_2O}^*)^{-1}k_{et}^{-1} \quad (4)$$

According to our previous work [29,30], for a multi-step ET process, i_{D_n} is the steady-state diffusion limit current of the n th step ET, which can be calculated by Eq. (4) for consecutive ET processes at the interface. $c_{NB_n}^*$ stands for the initial concentration of the reactant in NB for the n th ET and can be obtained by Eq. (5) [29]. Furthermore, Eq. (5) could be revised to Eq. (6) based on plenty of experimental data and Faraday's law of electrolysis [30]. Thus, k_{et} for each step ET can be obtained more precisely.

$$c_{NB_n}^* = (i_{D_n}/i_{D_1}) \times c_{NB_1}^* (n > 1) \quad (5)$$

$$0.5c_{NB_n}^* = (i_{D_n}/i_{D_1}) \times 0.6c_{NB_1}^* (n > 1) \quad (6)$$

2.4. Theoretical calculations

The molecular structures of three ZnTArPs, [Zn(TArP*)]⁺ and [Zn(TArP*)]²⁺ are optimized by using density functional theory at the B3LYP/6-31G(d) level. All calculations are performed with a Gaussian 03 software suite [45].

3. Results and discussion

3.1. Redox behaviors of ZnTArPs in conventional cyclic voltammetric measurement

The structures of ZnTArPs are shown in Fig. 1, where 2ⁿ is the number of benzene ring in an aryl group and Ar stands for phenyl, naphthyl and pyrenyl group. The three types of zinc porphyrins are abbreviated as ZnTPP ($n = 0$), ZnTNP ($n = 1$), and ZnTPyP ($n = 2$) (see structures 1–3). The redox behaviors of ZnTArPs were first examined in bulk NB solution containing 0.01 M TBAClO₄ by using conventional CV. Fig. 2 depicted the cyclic voltammograms of ZnTPP, ZnTNP and ZnTPyP at EPG with a potential scan rate of 5 mV s⁻¹. It could be seen that (i) the three kinds of zinc porphyrins exhibited similar electrochemical behaviors with two reversible one-electron redox processes within the potential range from 0.1 V to 1.5 V, as summarized in Eq. (7); (ii) the formal potentials of two redox couples for each ZnTArP followed the order of ZnTPP

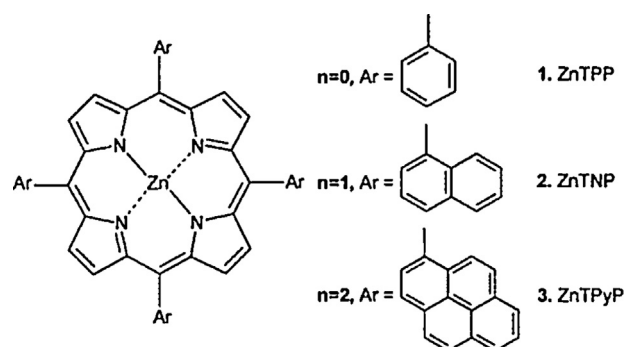


Fig. 1. Molecular structures of ZnTArPs with a systematic variation of meso- π -extension at a 2ⁿ pattern ($n = 0, 1, 2$).

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