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A pH responsive electrochemical switch sensor based on Fe(notpH$_3$) [notpH$_6$ = 1,4,7-triazacyclononane-1,4,7-triyl-tris(methylene-phosphonic acid)]

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ABSTRACT

The electrochemistry of a macrocyclic metal complex Fe(notpH$_3$) [notpH$_6$ = 1,4,7-triazacyclononane-1,4,7-triyl-tris(methylene-phosphonic acid)] reveals that the protonation/deprotonation of the non-coordinated P–OH groups in Fe(notpH$_3$) affects its formal potential value ($E^{0\prime}$) considerably. Plotting $E^{0\prime}$ as function of solution pH gives a straight line with a slope of $-585\,\mathrm{mV\,pH^{-1}}$ in the pH range of 3.4–4.0, which is about ten times larger than the theoretical value of $-58\,\mathrm{mV\,pH^{-1}}$ for a reversible proton-coupled single-electron transfer at 20 °C. A sensitive pH responsive electrochemical switch sensor is thus developed based on Fe(notpH$_3$) which shows an “on/off” switching at pH ∼ 4.0.

1. Introduction

Systems that have a switchable functionality are particularly important as the development of robust and configurable systems will open up new avenues and possibilities including molecular information processing, storage and sensor [1–5]. Among these systems, molecules that show reversible changes against external stimuli such as pH [6,7], temperature [8], light [9], redox potential [10,11], metal ions [12], and ion strength [12], have received increasing attentions. Such molecules, the properties of which can be modulated between two different stable states in a controlled and reversible manner, have emerged as promising materials for the construction of chemical and biological sensors as well as molecular memories and devices [13–15]. The switchable molecules can be the redox active macrocyclic complexes, fluorescent organic molecules showing ring on/ring off reaction, polymers capable of conformation change between an expanded and a collapsed form.

It is well known that polyazamacrocycles with phosphonate pendant arms exhibit strong coordination capabilities and high selectivities towards metal ions, and thus are of great interest in applications such as magnetic resonance imaging contrast agents, luminescence probes [16–19]. Although many efforts have been made in preparing the corresponding metal complexes and studying their structures and properties, the knowledge about their electrochemistry is not yet understood. In this paper, we investigate the pH dependence of the formal potential value of complex Fe(notpH$_3$) [notpH$_6$ = 1,4,7-triazacyclononane-1,4,7-triyl-tris(methylenephosphonic acid)] which posses three non-coordinated P–OH groups (Scheme 1A). Based on this property, a pH sensitive electrochemical sensor is constructed.

2. Experimental

2.1. Reagents and apparatus

1,4,7-Triazacyclononane-1,4,7-triyl-tris(methylenephosphonic acid) (notpH$_6$, Scheme 1B) was prepared according to literature methods [20,21]. All the other chemicals were of analytical grade and used without further purification. The infrared spectrum was recorded on a VECTOR 22 spectrometer with KBr pellet. The powder XRD pattern was recorded on a Shimadzu XD-3A X-ray diffractometer. The cell parameters of Fe(notpH$_3$) were

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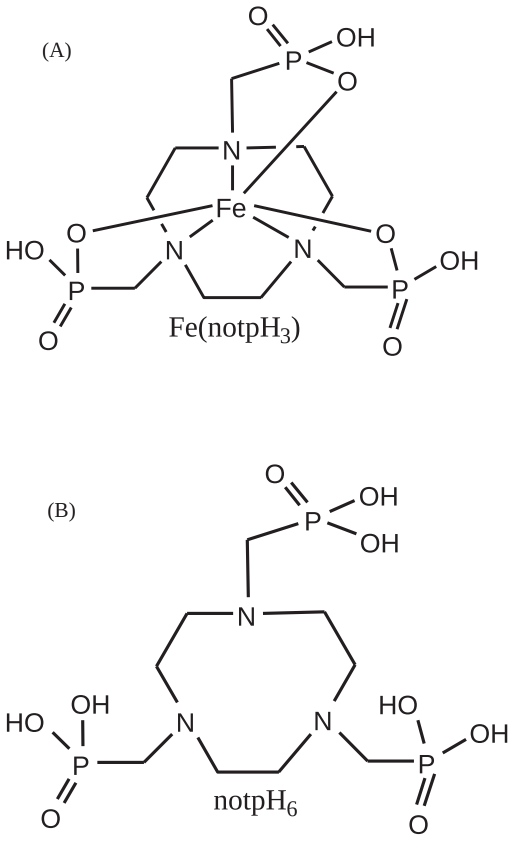

Scheme 1. The structures of (A) Fe($notpH_3$) and (B) $notpH_6$.

determined on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The UV/vis spectra were recorded at room temperature on an UV3600 spectrophotometer. The electrochemical measurements were performed in a conventional three-electrode system by using a CHI 660C electrochemical analyzer. A gold disk electrode (2 mm in diameter) sealed in polymer shell was used as the working electrode. The gold disk electrode was pretreated by scanning in the potential region for the evolution of hydrogen and oxygen in 0.5 M H_2SO_4 solution. The potential scan was continued until a reproducible voltammogram was obtained. The real surface area of the gold disk electrodes was determined by integrating the cathodic peak for the reduction of surface gold oxide in 0.5 M H_2SO_4 solution [22–25]. Typically, the real surface area of the gold disk electrodes after the above pretreatment was 0.0736 cm^2. A Pt plate auxiliary electrode and a saturated calomel reference electrode (SCE) were used. All potentials refer to SCE. All electrochemical experiments were performed at room temperature (20 ± 2 °C).

2.2. Synthesis and characterization of Fe($notpH_3$)

To a stirring aqueous solution of $notpH_6$ (0.411 g, 1 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (0.60 g, 1.5 mmol) was added. The solution was heated to reflux, then the pH was adjusted over 10 by 1 M NaOH. The yellow filtrate, adjusted to pH 1 by using 2 M HCl, was allowed to stand in acetone atmosphere within a closed vessel. Yellow block-like crystals of Fe($notpH_3$) precipitated after several days, which were collected and washed with cool water. Yield: 77%. Elemental analysis calcd. (found) for $C_9H_{21}N_3P_3O_9Fe$: C 23.29 (23.20), H 4.53 (4.60), N 9.06 (9.01)%. IR (KBr, cm^{-1}): 3437(b), 1638(m), 1477(m), 1291(m), 1257(w), 1012(s), 1017(s), 778(m), 587(s), 523(s). IR (KBr, cm^{-1}) for $notpH_6$ (for comparison): 3386(b), 3002(m), 2902(m), 2287(w), 1638(w), 1503(m), 1461(w), 1408(m), 1337(m), 1305(w), 1269(w), 1218(m), 1159(s), 1069(s), 1015(s), 975(s), 940(s), 915(s), 779(m), 747(m), 726(m), 598(m), 549(s), 453(s), 418(w). The cell parameters of Fe($notpH_3$) are a = 14.315 Å, b = 14.313 Å, c = 13.583 Å, α = 89.96°, β = 90.02°, γ = 120.03°, which is almost consistent with reported values in the literature [26]. The powder X-ray diffraction pattern of the bulk sample fits well with that simulated from the single crystal data (Fig. 1), indicating that the as-synthesized sample is a pure phase of Fe($notpH_3$).

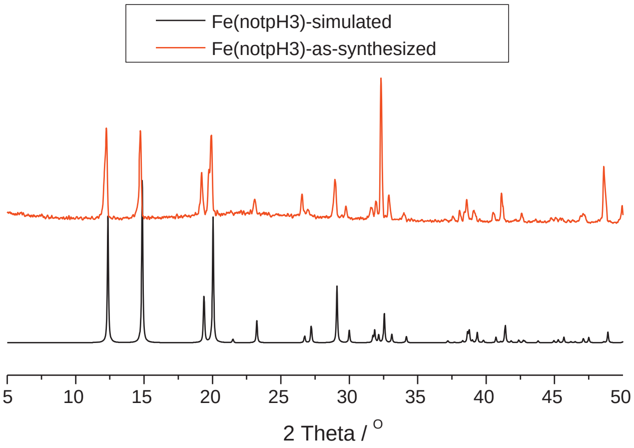

Fig. 1. Powder X-ray diffraction patterns for compound Fe($notpH_3$): as-synthesized (red) and simulated from single crystal data (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3. Results and discussion

Fig. 2 shows the pH dependence of the UV–visible absorption spectra of Fe($notpH_3$) aqueous solutions at 20 °C. Clearly, in the pH range of 0.7–4.1, the absorption peak at 250 nm ($O \rightarrow dx^2-y^2$ charge transfer band) decreases and the shoulder peak at 290 nm ($N_\sigma \rightarrow dx^2-y^2$ charge transfer band) increases with increasing pH [27], accompanying with a blue shift of the absorption peaks. In the pH range of 4.1–12.1, however, the absorption peak intensities remain almost constant. The spectrophotometric titration [28] indicates that the P–OH groups in Fe($notpH_3$) are gradually deprotonated with increasing pH, and form $Fe(notp)^{3-}$ above pH 4.1.

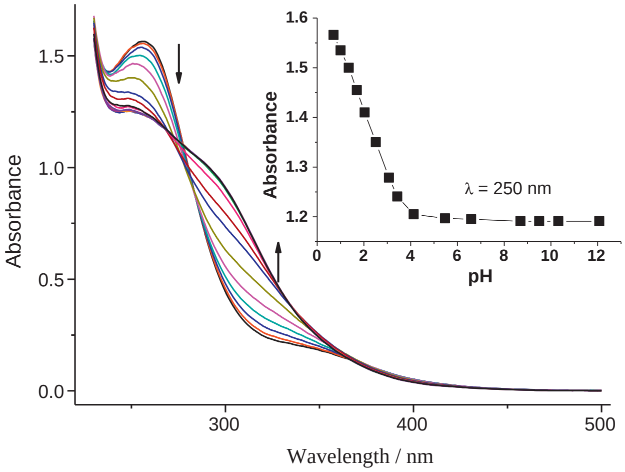

Fig. 2. UV–vis absorption spectra of 5×10^{-5} M Fe($notpH_3$) at pH range 0.7–12.1. Inset: plot of absorption peak intensity at 250 nm as a function of solution pH.

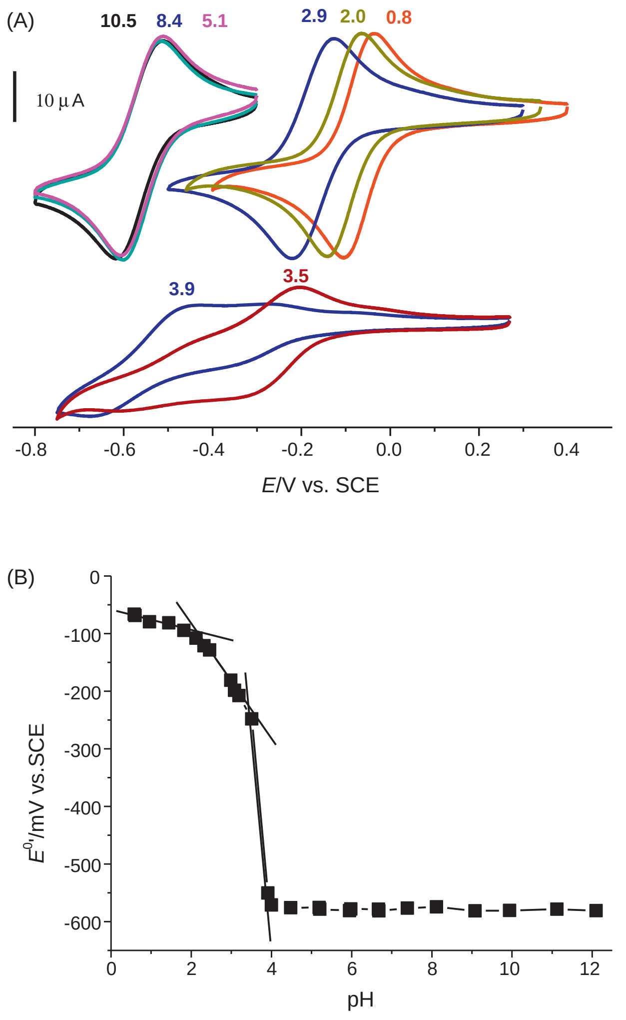

Fig. 3. (A) Cyclic voltammograms of a bare Au electrode in solutions of 5 mM Fe(notpH$_3$) in 1.0 M KCl with different pH value at a scan rate of 100 mV s^{-1}; (B) plot of $E^{0\prime}$ of Fe(notpH$_3$) as a function of solution pH.

The pH value at which fully deprotonation occurs for Fe(notpH$_3$) is very close to that for Ga(notpH$_3$) [29]. The results indicate that the protonation/deprotonation of non-coordinated –P–OH groups in Fe(notpH$_3$) results in the change of ligand-to-metal charge transfer transition, attributed to the change of electron-donating properties of the ligand.

Fig. 3A shows the cyclic voltammograms of Fe(notpH$_3$) at different pH. The dependence of the formal potential value ($E^{0\prime}$) of Fe(notpH$_3$) on solution pH is given in Fig. 3B, where $E^{0\prime} = (E_a + E_c)/2$ (E_a represents the anodic peak potential, E_c is the cathodic peak potential). At pH 0.6, the $E^{0\prime}$ value for the redox couple of Fe(notpH$_3$) is −68 mV. With increasing pH, the $E^{0\prime}$ value increases gradually in the pH range 0.6–2.0, faster in the pH range 2.1–3.3, and then sharply in the pH range 3.4–4.0, reaching −571 mV at pH 4.0. The results suggest that the proton must participate in the electron transfer process [30,31]. The shift of the $E^{0\prime}$ value with increasing pH is attributed to the deprotonation of the P–OH groups in Fe(notpH$_3$). After fully deprotonation at pH 4.0, the $E^{0\prime}$ value of Fe(notp)$^{3-}$ remains almost constant in the pH range 4.0–12.0. It has to be mentioned that both cyclic voltammograms of Fe(notpH$_3$) at pH 3.5 and 3.9 possess two pairs of redox peaks (Fig. 3A), which could be attributed to the coexistence of Fe^{III}(notpH)$^{2-}$ and Fe^{III}(notp)$^{3-}$ species. Thus the $E^{0\prime}$ values of Fe(notpH$_3$) at these pH are calculated by choosing one obvious pair of voltampere peak in each cyclic voltammograms, respectively.

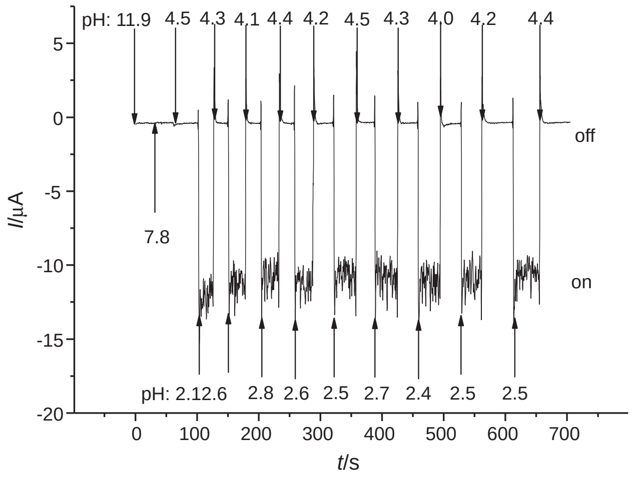

Fig. 4. Dependence of reduction currents of 5 mM Fe(notpH$_3$) on solution pH at a bare Au electrode. Conditions: the electrode potential was controlled at −300 mV vs. SCE and the solution was continuously stirred. The pH of Fe(notpH$_3$) solution containing 1.0 M KCl was adjusted with 2 M HCl or 2 M KOH solution.

It is very interesting to note that the change of the $E^{0\prime}$ value becomes steep when the solution pH is close to the fully deprotonation point. In the pH range 3.4–4.0, the $E^{0\prime}$ value shifts from −220 mV to −571 mV (Fig. 3B). The abrupt shift of $E^{0\prime}$ value, i.e. [(−220) to (−571)]/(3.4–4.0) = −585 mV per pH, indicates that the change of electron-donating properties of ligand can also drastically alter the $E^{0\prime}$ value of metal complex besides effect of proton-coupled single electron transfer reaction (theoretical value: −58 mV per pH [32]). It is clear that full deprotonation of three non-coordinated –P–OH groups result in generation of the negative charge –P–O$^-$ species. Obviously, the fully deprotonated negatively charged phosphonate groups stabilize the ferric state over the ferrous state, which leads to the abrupt change of the formal potential [33,34].

The unique electrochemical property of Fe(notpH$_3$) can be utilized to construct a pH sensitive electrochemical switching device based on the formal potential abrupt change mechanism. Fig. 4 shows the pH dependent reduction currents of Fe(notpH$_3$) at a bare Au electrode. At high pH of 11.9–4.5, no amperometric response is observed at an applied potential of −300 mV because the formal potential of Fe(notp)$^{3-}$ locates at −581 mV. Upon decreasing pH to 2.1, however, the reduction current increases quickly to *ca.* 10 μA. About 95% of its maximum steady-state-current is achieved in less than 2 s. Such a quick response originates from the rapid generation of Fe(notpH$_n$) (n = 1–3) due to the fast protonation process of Fe(notp)$^{3-}$. The “on/off” switching of the amperometric currents is reversible and stable upon repeatedly changing the solution pH between 4.2 ± 0.2 and 2.6 ± 0.2.

4. Conclusion

In conclusion, we present that the formal potential value of the electro-active complex Fe(notpH$_3$) is highly dependent on the proton dissociation degree of the non-coordinated P–OH groups. Thus protonation/deprotonation of non-coordinated –P–OH groups in Fe(notpH$_3$) results in the abrupt change of electron-donating properties of ligand. This property can be utilized to construct a pH sensitive electrochemical switching device.

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