

XAFS Study of Zinc(II) Porphyrins Associated with PAMAM Dendrimers

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Introduction

Dendrimers are unique and nontraditional polymers with a well-defined macromolecular architecture consisting of a core, iterative branch units, and terminal groups [1]. Dendrimers have been demonstrated to be capable of encapsulating various organic molecules, and their application to drug delivery systems has been studied extensively. A full generation polyamidoamine (PAMAM) dendrimer is constructed based on an ethylenediamine core and terminated with amino groups, while a half generation PAMAM dendrimer is terminated with carboxy groups. The fourth (G4) or higher generation PAMAM dendrimers are approximately spherical molecules. The periphery region secludes the organic species captured in the interior from the solution phase, making higher generation PAMAM dendrimers very useful as molecular capsules (or containers). Indeed, an anionic porphyrin can be associated electrostatically with G4 PAMAM dendrimer in the aqueous solution [2]. The net charge on a dendrimer molecule is determined by the protonation of the terminal groups and tertiary amines of the branch unit. In this study, the electrostatic interaction between the anionic zinc(II) porphyrin and the PAMAM dendrimer in the aqueous solution was studied by XAFS technique.

Experimental

The aqueous solution of water-soluble anionic zinc(II) porphyrins, *meso*-tetrakis(4-carboxyphenyl)porphyrinato zinc(II) (ZnTPPC⁴⁻) and *meso*-tetrakis(4-sulfonato-phenyl)porphyrinato zinc(II) (ZnTPPS⁴⁻), in the presence of 7.0×10^{-5} mol dm⁻³ NH₂-terminated G4 or carboxy-terminated G3.5 PAMAM dendrimer were prepared in several pH conditions and molar ratios, i.e., [zinc(II) porphyrin]:[dendrimer]. The aqueous solution was examined by XAFS measurements in a fluorescent mode. The Zn K-edge XAFS spectra of zinc(II) porphyrins were obtained by using a 19-element Ge solid state detector.

Results and Discussion

XAFS spectra for zinc(II) porphyrins were dependent on the pH condition and the molar ratio. In the case of G4 PAMAM dendrimer, the near edge structure at the Zn K-edge in both ZnTPPC⁴⁻ and ZnTPPS⁴⁻ systems was significantly changed in the presence of the dendrimer at ca. pH 8, where the 64-terminal amino groups in the periphery moiety ($pK_a = 9.20$ [3]) are fully protonated. Typical XANES spectra for the ZnTPPC⁴⁻ system at various molar ratios are shown in Figure 1. It should be noted that the XANES spectrum of ZnTPPC⁴⁻ was hardly

affected by the pH condition ($5.5 < \text{pH} < 10$) in the absence of the dendrimer. In the aqueous solution, the coordination structure of the zinc(II) center is octahedral with four equatorial nitrogen atoms in the porphyrin plane and two axial hydrations. A white line peak at 9665 eV in Figure 1 significantly decreases in the presence of a 1:1 molar ratio of the dendrimer. The spectral changes could be related to the coordination structure of ZnTPPC⁴⁻ modified by the ion-association with the G4 PAMAM dendrimer with 64 positive charges, for instance, the substitution of the axial coordinations by amidoamine branch units. The relative intensity of the peak at 9665 eV is regrowth by the increase of ZnTPPC⁴⁻, molar ratio of 8:1, in which the bulky ZnTPPC⁴⁻ molecules would not be fully-captured by the dendrimer and free ZnTPPC⁴⁻ molecules exist in the bulk aqueous solution. The increase of relative concentration of the bulk species reproduces the XANES spectrum in the absence of the dendrimer. The XANES spectra at pH 10, where the terminal amino groups are deprotonated and the positive charge on the dendrimer is efficiently reduced, did not exhibit apparent spectral changes indicating rather weak electrostatic interaction between ZnTPPC⁴⁻ and the dendrimer in the alkaline condition.

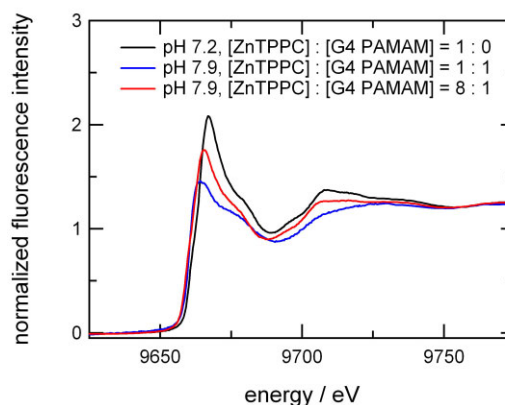


Figure 1. Typical XANES spectra at Zn K-edge for ZnTPPC⁴⁻ at various molar ratios with respect to the G4 PAMAM dendrimer.

References

- [1] D.A. Tomalia, *Prog. Polym. Sci.*, **30**, 294 (2005).
- [2] H. Nagatani et al., *Electrochim. Acta*, **53**, 6428 (2008).
- [3] D. Leisner et al., *J. Phys. Chem. B*, **107**, 13158 (2003).

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