IX-L Development of New Nanomaterials as Components in Advanced Molecular Systems

Nanometer-sized materials exhibit unique electronic behavior. In the quest of advanced redox catalysis, we are currently interested in combining nanometer-sized materials into molecular redox systems. As a basic architecture, a new type of dendrimers were synthesized and their dynamic behavior was examined.

IX-L-1 Synthesis and Properties of New, Spatially Relaxed Dendrons Containing Internal Carboxyl Groups

KIKUZAWA, Yoshihiro; NAGATA, Toshi

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We synthesized a series of new dendrons with up to fourteen internal carboxyl groups. These dendrons are made from a branching unit and a spacer unit with a carboxyl group. The growth reactions (formation of the benzylic ether bonds) completed within a few hours, which suggests the high reactivity at the “focal” point of the dendritic framework. The final deprotection of the internal ester groups also proceeded smoothly. These high reactivities were attributed to the presence of the spacer units, which caused spatially relaxed conformations of these molecules. The carboxylate salt form of the dendron produced both normal and reverse micelles in a THF/water mixed solvent according to the fraction.

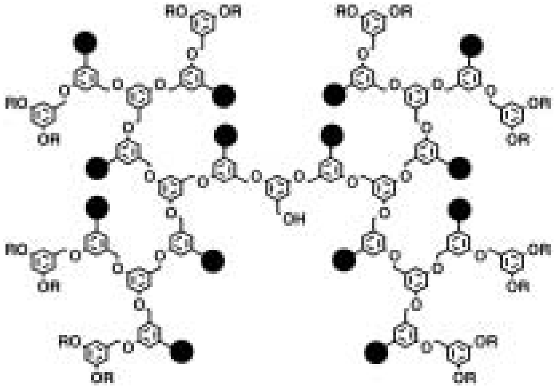


Figure 1. The chemical structure of the dendron (generation 3).

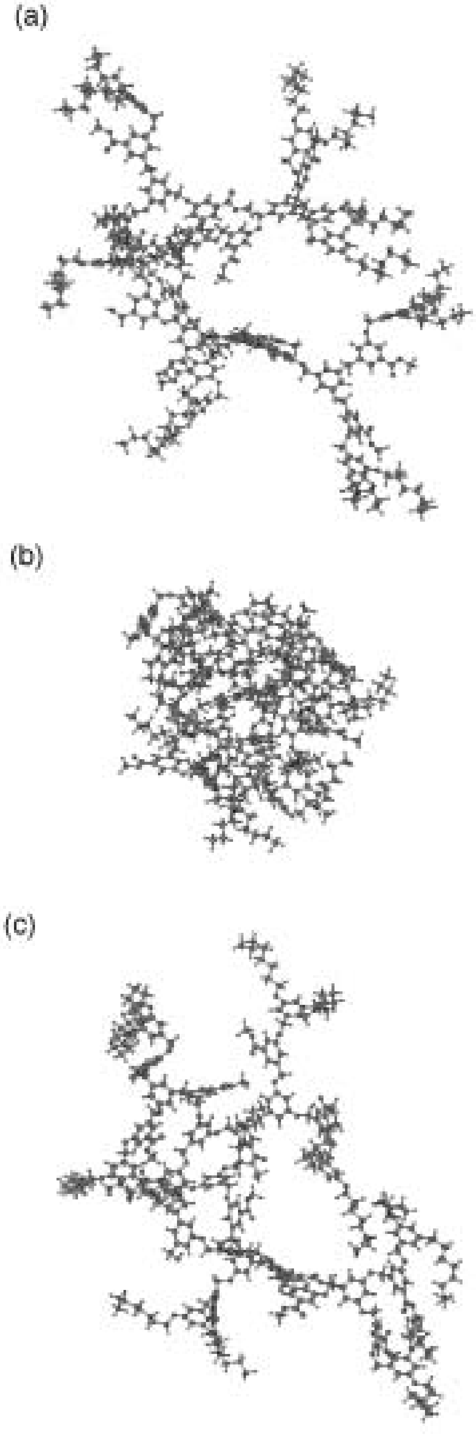


Figure 2. Ball-and-stick representations of the dendron, (a) before the molecular dynamics (MD) run, (b) after 100-ps MD without solvent, (c) after 100-ps MD with explicit solvent ($CHCl_3$).

IX-M Designing Artificial Photosynthesis at Molecular Dimensions

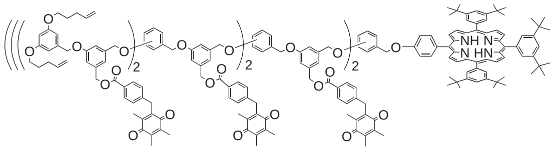
Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

IX-M-1 Synthesis of Dendrimer-Linked Porphyrins Bearing Multiple Quinone Moieties at Internal Positions

KIKUZAWA, Yoshihiro; ITO, Hajime; HINO, Takami; NAGATA, Toshi

By use of dendrons described above, we synthesized dendrimer-linked porphyrins bearing up to fourteen quinone moieties at internal positions of the dendrimer. The CV (cyclic voltammetry) and DPV (differential pulse voltammetry) measurements revealed that all the quinone moieties were simultaneously reduced at –1.18 V. The steady-state fluorescence spectra showed reduced emissions (10–15%), which recovered by chemical reduction of quinones by sodium dithionite.

The quinones in these compounds were quantitatively converted to hydroquinone disilyl ethers by irradiation of these compounds in the presence of $PhSSiMe_3$. This suggests that even the quinones at the third-generation positions may accept electrons from the photoexcited porphyrin.



P-G^3(Q)$_{14}$

Figure 1. The structure of the quinone-dendrimer-linked porphyrins.

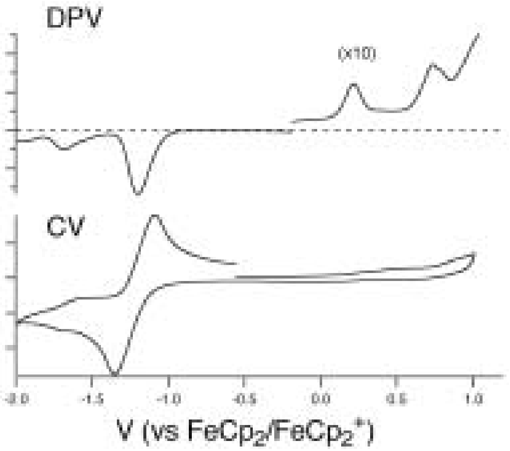


Figure 2. The CV and DPV voltammograms of the quinone-dendrimer-linked porphyrin zinc complex.