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Extended Potential-Gradient Architecture of a Phenylazomethine Dendrimer

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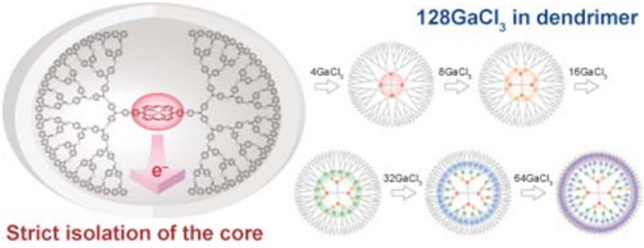
ABSTRACT



A dendritic nanoshell based on rigid phenylazomethine units was synthesized up to fifth generation around a zinc porphyrin core. Due to the finely organized sparse architecture, accessibility to the core can be discriminated by the size of the molecules and ionic species. By using this function, the lifetime of the photochemically produced radical ion pair can be extended over 200 times longer along with a good quantum yield.

Dendrimers have been extensively studied regarding their photochemical,[1] electrochemical,[2] and photoelectrochemical[3] properties that are quite different from those of small molecules or conventional macromolecules due to their uniform structure and large encapsulating effect.[4] The rigidity of these molecules plays a crucial role in characterizing their fundamental properties because the actual conformation strongly depends on this factor. A paradigm during the early stage of the dendrimer chemistry considered that they have a large hollow inside; however, recent studies revised the description as a "dense-core" model.[5−7] Actually, the hollow no longer exists because the peripheral dendritic monomers intrude into the interior until the dendrimer reaches its packing limit. In contrast, rigid dendrimers, such as the polyphenylene and phenylacetylene types, have a tendency to fit in a "sparse-core" model.[5,7,8] Therefore, the character of the dendritic encapsulation should be much different between the flexible and rigid shells. Phenylazomethine dendrimers composed of aromatic rings and imine bonds also belong to the rigid series.[10] The experimental results regarding the hydrodynamic property and metal ion coordination explained their rigidity as well as the CPK models produced

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by computer analysis.[10,11] Furthermore, the rigid architecture allows access to the "programmed" functions such as the stepwise metal-ion assembling[9−11] or control of electron transfer vector based on the unique electronic gradient of these dendrimers.[12,13]

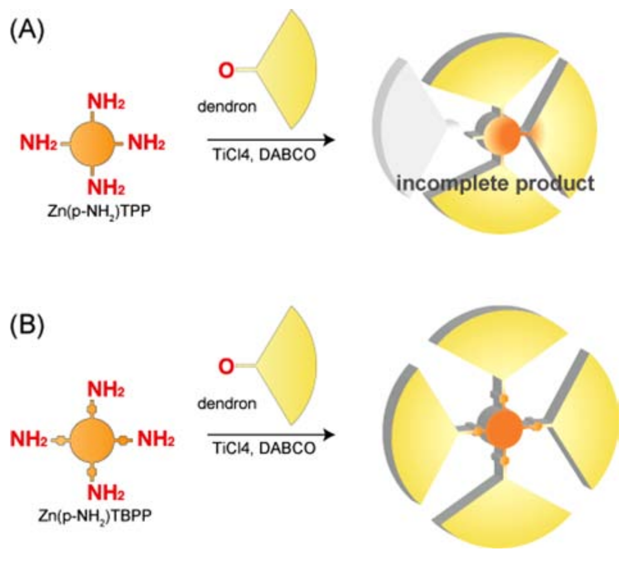

Figure 1. Schematic representaiton of the steric factor upon the synthesis of the largest phenylazomethine dendrimer. (A) One of the four dendrons cannot connected to the small core (TPP). (B) All dendron can be connected to the extended core (TBPP).

Another important factor of using a higher generation number is amplification of the effect by a dendritic structure, which is essential to access their intrinsic characteristics. For example, our previous examples demonstrated that the generation number increase provided an inversion of the charge separation/recombination kinetics[12,13] or production of the exceptionally high catalytic activity.[14] Although there are examples of the synthesis of extremely large dendrimers based on flexible backbones,[15] the growth of the ideal dendrimer structure based on the generation number increase potentially has the limit as predicted by the fractal dimension (d_f) higher than the dimension of Euclidean space ($d_e = 3$). The synthesis of large dendrimers based on a rigid architecture is quite limited, and it requires an ingenious approach.[16] Indeed, the generation number limit of phenylazomethine dendrimers (DPAs) was 4 when the tetraphenylporphyrin core was used. In this case, the coupling between the core and dendrons eventually stopped when 3 of 4 arms of the core were connected to the dendrons with 5 generations (Figure 1). In this study, we have succeeded in preparing a fifth-generation DPA with a porphyrin core ($M = 23243$) by an extension of the linker unit. Although this dendrimer seemingly exhibited the usual effect on the electrode reaction, intermolecular photochemical reactions involving this dendrimer were very unique. We now demonstrate that the "encapsulation" of the photoexcited core with a rigid shell results in the efficient production of a highly reactive radical ion pair, of which lifetime becomes much longer.

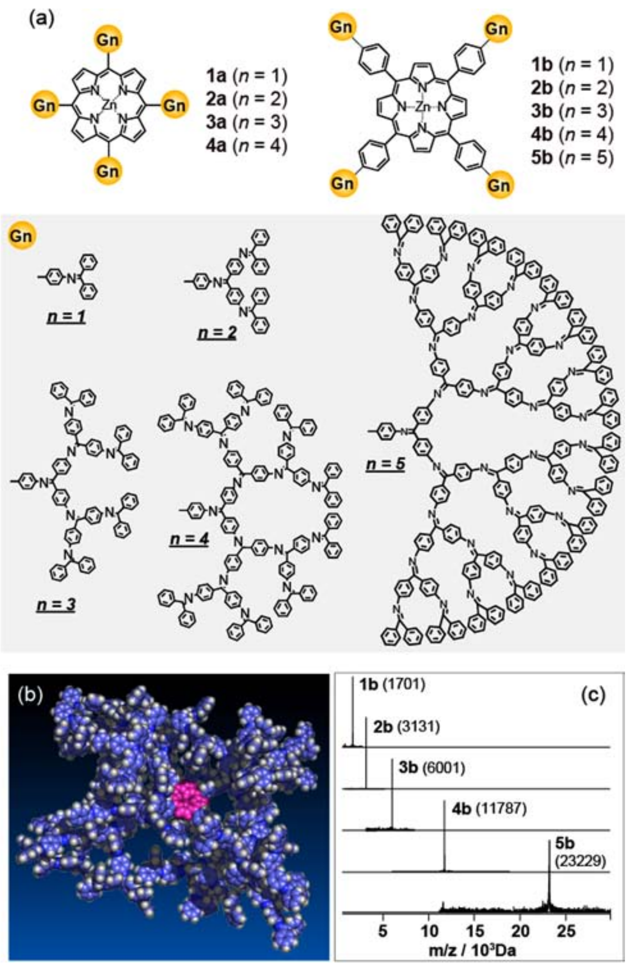

Figure 2. (a) Chemical structures of dendrimers **1a**−**4a** and **1b**−**5b**. (b) An optimized structure of the dendrimer **5b** drawn as a CPK model. The porphyrin core is colored in magenta. (c) MALDI-TOF-Mass spectra of dendrimers **1b**−**5b** using dithranol as the matrix.

These dendrimers could be prepared by coupling between dendritic ketones[17] and an aminophenyporphyrin[18] via dehydration to produce the imine (C=N) bonds.

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This convergent synthesis was applicable to the dendrimers **1a**−**4a** (Figure 2) as already reported.[11] However, the reaction to produce a larger one ($n = 5$) was abruptly stopped when three dendrons were connected to the core. The fourth dendron did not react with the tris-dendronized precursor for 48 h even in the presence of a large excess amount of the dendritic ketone and dehydrating reagent ($TiCl_4$ and DABCO). However, the aminobiphenylporphyrin[19] core successfully produced the dendrimers **1b**−**5b** (Figure 2) up to the fifth generation. This result suggested that the aminophenylporphyrin system reached a steric limit at $n = 4$ which prevents formation of a giant round-shaped structure. These materials were characterized by ^1H, ^{13}C NMR, MALDI-TOF-mass, and size-exclusion chromatography (SEC) using an HPLC instrument.

The intrinsic viscosity $[\eta]$ measurements of the dendrimers (**1b**−**5b**) were carried out by SEC experiments using an online detector and provided information about the solution-phase structure. As demonstrated elsewhere,[10,20] the relationship between the molecular weight and $[\eta]$ provides the morphology of the macromolecules in the solution. The present result showed that $[\eta]$ does not significantly change as the generation number increases suggesting a sphere-like morphology. The hydrodynamic radii (R_h) calculated from $[\eta]$ and the molecular weights are shown in Table 1. For example, the diameter of the largest dendrimer **5b** is larger than 5 nm (Figure 3).

Table 1. Fundamental Properties and Photochemical Reaction Data of the dendrimers **1a**−**4a** and **1b**−**5b** with **NDI**

	$R_h{}^a$ (Å)	τ_T (μs) (Φ_T)^b	$k_{rec} \times 10^{-8}$ (M^{-1} s^{-1}) ($-\Delta G°$ (eV))^c	$\Phi_{ET}{}^d$
1a	9.6	2.1 ± 0.08 (0.82)	7.9 ± 0.14 (1.23)	0.88
2a	13.4	11 ± 0.1 (0.71)	4.1 ± 0.08 (1.22)	0.75
3a	17.5	11 ± 0.1 (0.60)	1.5 ± 0.04 (1.20)	0.60
4a	22.0	12 ± 0.1 (0.50)	0.50 ± 0.03 (1.17)	0.57
1b	^{e}	^{e}	^{e}	^{e}
2b	15.0	5.4 ± 0.10 (0.48)	3.8 ± 0.10 (1.31)	0.62
3b	18.5	5.6 ± 0.03 (0.43)	1.0 ± 0.04 (1.28)	0.81
4b	22.1	5.4 ± 0.02 (0.53)	0.52 ± 0.03 (1.27)	0.53
5b	27.6	10 ± 0.1 (0.45)	0.032 ± 0.012 (1.26)	0.45

[a] Hydrodynamic radius of the dendrimers measured by TriSEC analysis. [b] Lifetime of the triplet excited state. Values in parentheses are quantum yields of the T_1 production. [c] Second-order rate constant of the charge-recombination between the radical ion pairs in THF (23 °C) containing 0.05 M tetra-*n*-butylammonium bromide (TBABr) as the supporting electrolyte. Values in parentheses are driving force energy of the reaction calculated from the redox potentials. [d] Quantum yields of the radical ion pair formation from the triplet-excited state (T_1). **NDI** (3 mM) was used as the electron acceptor. [e] Data were not available due to the low solubility in THF.

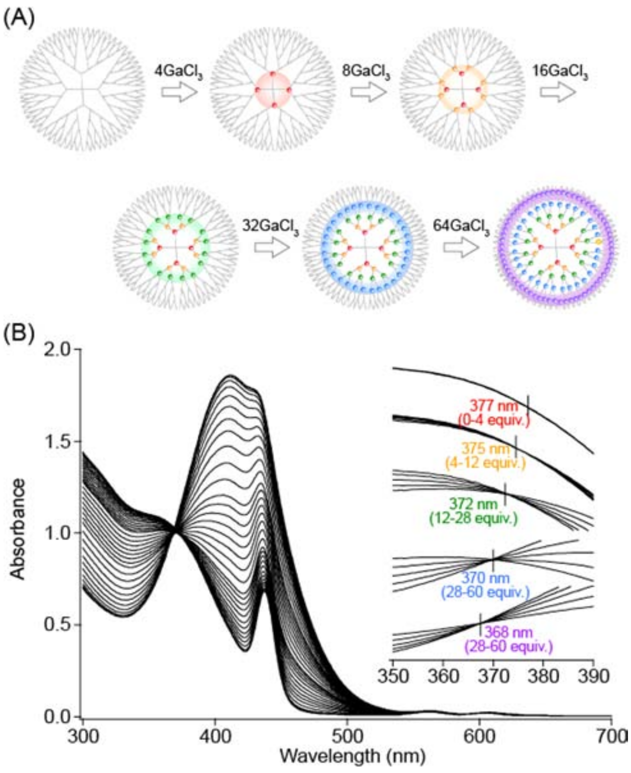

Figure 3. (A) Schematic representation of the stepwise complexation of $GaCl_3$ to the dendrimer **5b**. (B) UV−vis absorption spectra of **5b** upon the repetitive addition of aliquots of $GaCl_3$. Inset shows the enlargements of the isosbestic points that appeared in turn.

Similar to the previously reported DPAs,[9,11] the present series also exhibited a stepwise complexation behavior upon the UV−vis titration experiments using $GaCl_3$. The smaller dendrimer showed several distinguishable isosbestic points, of which the number is identical to the number of generations. All the isosbestic points appeared in turn moving to shorter wavelength. The equimolar amount of $GaCl_3$ required a shift in isosbestic point equal to the number of vacant coordination sites (free imines) in the dendrimers. All these behaviors were the same as the previously reported DPAs with a zinc porphyrin core.[11] Although the complexation behavior of the generation 5 dendrimer (**5b**) was similar, the shift in the isosbestic points per one generation was smaller. The first one appeared at 377.0 nm up to the addition of 4 equimolar $GaCl_3$. Although, the second, third and forth isosbestic points appeared at 375.0 nm (12 equiv), 372.0 (28 equiv) and 370.0 nm (60 equiv), respectively, the width of the shift was small. The further addition from 60 eq. again exhibited a distinguishable isosbestic point at 368.0 nm. These observations indicate that the overall complexation started from the innermost layer, followed by complexation to the outer layers as a step-by-step process. This idea is consistent with the previous result showing that the binding constants between the innermost and outermost layers are almost the same for the dendrimers with 3 generations and 4 generations.[10] It could be explained that the generation number increase causes an increase in the number of potential steps, but not the height of the steps.

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Similar to the other dendrimers, the present dendrimers (**1b**–**5b**) also have a characteristic encapsulation property for the core unit. For example, the electron-transfer rates corresponding to the first voltammetric oxidation of the zinc porphyrin core decreased with an increase in the generation number. Unfortunately, the dendrimer (**1b**) could not be studied due to its low solubility in most of organic solvents. The cyclic voltammograms of the dendrimer (**2b**–**4b**) demonstrated decrease in the rate constant and diffusion coefficient with the increasing separation of the anodic/cathodic peaks and decreasing peak currents. The largest dendrimer (**5b**) hardly showed a clear redox because its encapsulation property is very high. This encapsulation effect also plays an important role in a photoinduced electron-transfer system involving the dendrimers as photosensitizers.

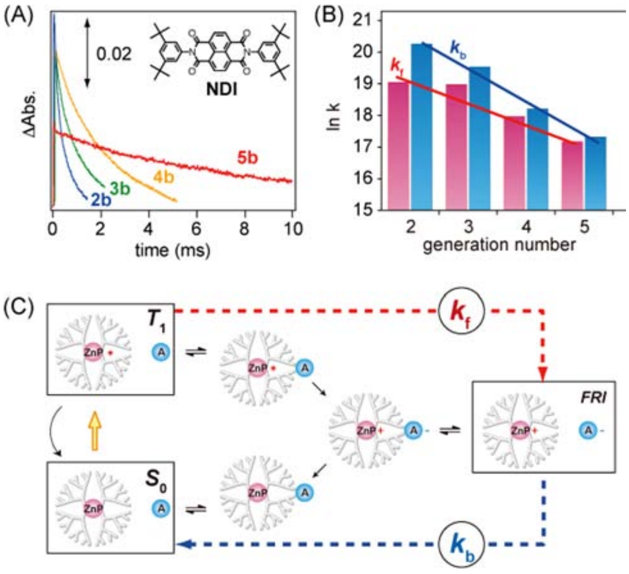

Figure 4. (A) Transient absorption decay at 680 nm upon excitation of the dendrimer **1b**–**5b** in the presence of **NDI**. (B) Dependence of the intermolecular electron transfer kinetics (k_f: charge separation, k_b: charge recombination) on the generation number of the dendrimer. (C) Proposed scheme showing the photoinduced electron-transfer reactions.

In the presence of electron acceptors (**NDI**: naphthalene diimide derivative shown in Figure 4A), photoinduced electron transfer from the dendrimer (**2b**–**5b**) was observed. Similar to the previous case,[12] cation radical species of the zinc porphyrin core could be detected by the transient absorption measurement. Upon photoexcitation at 532 nm in deaerated THF containing 0.05 M tetrabutylammonium bromide (TBABr) as the supporting electrolyte, a typical absorption of triplet excited state (T_1) was observed. This absorption was quickly decayed and produced a radical ion pair at the same time, which could be observed as a decay of the typical absorption at 500 nm. The radical ion pair also decayed to the ground state more slowly, which could be monitored at 680 nm. Each decay time of **2b**–**5b** was strongly dependent on the generation number similar to those of **1a**–**4a**, and the electron-transfer process controls the entire kinetics. Especially, the lifetime of the radical ion pair using **5b** with **NDI** was much longer than the others and it could survive over 10 ms (Figure 4A).

The intermolecular electron transfer rates of both the charge separation and recombination for all the dendrimers were determined by a curve fitting method (Figure 4B). The generation number dependence of **2b**–**5b** exhibited a trend similar to that for the series of **1a**–**4a**. It should be noted that the charge-separating reaction is less attenuated than the recombination reaction.

In summary, phenylazomethine dendrimers with a zinc porphyrin core were synthesized up to the fifth-generation by applying an extended core unit to reduce the steric constraint. The largest 5-generation dendrimer also exhibited the stepwise complexation of $GaCl_3$ as a typical characteristic of the phenylazomethine dendrimers of which the generation number is smaller. In addition, the largest dendrimer acted as a rectifier controlling the electron transfer direction. Based on this property, the dendrimer allows the production of a charge-separating radical ion pair living over 10 ms, which is significantly longer than those produced using conventional small molecules. Further investigation of the application to photosensitized catalysts using these dendrimers is underway.

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Supporting Information Available. Experimental methods, synthesis of the materials, characterizations, HPLC–SEC analysis data, cyclic voltammograms, and transient absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.