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A Potential Gradient along the Layer-by-Layer Architecture for Electron Transfer Rectification

Takane Imaoka*, Hiroki Kobayashi, Makoto Katsurayama and Kimihisa Yamamoto*

Received ooth January 2012, Accepted ooth January 2012

Cite this: DOI: 10.1039/xoxxooooox

DOI: 10.1039/x0xx00000x

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Electrochemical and photochemical measurements demonstrated that dendritic phenylazomethines, which can make complexes with $SnCl_2$ by a stepwise process, only permit an outbound electron transfer. The unique dendrimer effect allows efficient production of photo-generated radical ion pairs by suppressing their charge recombination. In sharp contrast, the phenylenevinylene or benzylether dendrimers, which lacks a heteroatom or π -conjugation, did not exhibit such non-symmetric characters.

A potential cascade principle in nature is now recognized as the strategy for highly efficient artificial solar energy conversion.^{1,2} Looking at silicon-based or Grätzel-type photovoltaic devices, such potential gradients (smooth cascades) autonomously emerge at p/n junctions³ or Schottky barrier junctions.⁴ Thickness of this gradient layer (depletion layer) is typically nanometer order; therefore, backward electron tunneling leading to unfavorable carrier recombination is effectively repressed.⁵ However, utilizing these autonomous gradients with organic semiconducting materials is difficult because the steady-state electron (or hole) carrier density is very low. Another possible solution for the interfacial electron transfer optimization is the fabrication of an artificial cascade layers. The construction of self-assembling monolayers with large dipole moment is one of the possible ways between two organic or organometallic semiconducting interfaces. ⁶⁻⁸ In the case of electrode surface, redox potential cascades fabricated on an electrode surface were also the solutions.9-11 Alternatively, point charge can also provide such a cascade by the formation of imaginary induced dipoles on the electrode surface.¹² In any case, important thing is the sizes scale of the interfacial gradient. Too thick cascade cannot block backward electron tunneling (recombination). At least, potential gradient on a several-nanometer scale is required.

Dendritic architecture is one of the suitable molecular designs for the management of electron or energy transfer and their photochemical applications.¹³⁻¹⁵ We especially have studied heteroatom-containing π -conjugating dendrimers as the potential programming materials.¹⁶ By using dendritic phenylazomethine backbones for the donor-acceptor linkage, the charge separation efficiency and the lifetime was significantly increased.^{17,18} The sizes of dendrimers are about 3-5 nm, suitable for the interfacial charge rectification. However, the origin of such rectification property is yet ambiguous with respect to the relationship with the potential gradient and the topological factor.

We now report investigations employing various electron transfer (ET) systems. One is the parallel system, in which the direction of charge separation and potential gradient were identical. The other is antiparallel system, in which these directions are completely opposite. We also compare a phenylenevinylene backbone as a non-cascade type molecule. Previous study elucidated that this type of dendritic structure does not have any electron density gradient together with the significant dipole moment.¹⁷ Comparing these two backbones can provide information about the effect of potential gradient.

All dendrimers in this study were synthesized (Fig. 1). The phenylazomethine dendrimers with a zinc tetraphenylporphyrin core (DPAGX-ZnTPP: $X = 1 \sim 4$) were synthesized as previously reported.^{19,20} Phenylenevinylene dendrimers with a zinc porphyrin core (DPVGX-ZnTPP) were synthesized from the corresponding dendrons and the core. The dendrons were prepared utilizing the modified method from a previous report (see details in ESI).²¹ For the quantitative evaluation, the core and the dendron units were connected by the imine (C=N) bonds, which is identical to the phenylazomethine dendrimers (DPAGX-ZnTPP). This modification resulted in the same redox potential of the ZnP/ZnP⁺ redox couple between DPAG1-ZnTPP and DPVG1-ZnTPP. Dendrimers with a naphthalenediimide (**DPAGX-NDI**: $X = 1 \sim 4$) were also synthesized the convergent approach from the via corresponding phenylazomethine dendrons and the core precursors with amine groups (Details are shown in the Supplemental Information). Benzylether dendrimers with a zinc tetraphenylporphyrin core 1~4) were (BzEGX-ZnTPP: X = prepared as previously

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reported.²² These novel and reported materials were characterized using ¹H, ¹³C NMR, MALDI-TOF-Mass and HPLC (SEC) measurements.



Fig. 1 Structures of dendrimers with a zinc porphyrin (photosensitizing electron donor) or naphthalenediimine (electron acceptor) as the core. The molecular CPK model represents **DPAG4-ZnTPP**.

The hydrodynamic radii of two different dendrimers with a zinc porphyrin core (DPAGX-ZnTPP, DPVGX-ZnTPP) were identical. This result suggests the similarity in their conformational structure between these dendrimers reducing their back-foldings.²³⁻²⁵ In addition, each dendrimer exhibited optical absorptions around 350 nm attributed to the π - π * transition of the dendrons, together with the Soret band (430 nm) and Q bands (600 nm) of the porphyrin core. The dendron-based absorption exhibited a red-shift in the UV-vis absorption with the generation number increases up to 3 (Fig. S1 in ESI). This result indicates an extension of the π -conjugation within the three generations of monomers. The limited electron delocalization on the dendrimers is important to retain their inherent dipole moments due to the electron polarizations. Previous molecular orbital (MO) calculations¹⁷ of each dendrimer model compound provided results showed that the lowest unoccupied molecular orbital (LUMO) of DPAG3-H is mainly distributed on the terminus monomer whereas the highest occupied molecular orbital (HOMO) is on the core-side one. The other unoccupied MOs of DPAG3-H above the LUMO displayed potential steps. In contrast, there were no significant potential steps in DPVG3-H.

The newly synthesized phenylazomethine dendrimer (**DPAGX-NDI**) exhibited stepwise complexation of SnCl₂ from the innermost layer. Four independent isosbestic points in the UV-vis absorption spectra (Fig. 2), which appeared in turn upon the stepwise additions, were the evidence. Our previous studies²⁶ have revealed that this stepwise complexation is based on the dendron-specific property, which does not affected by replacements of the core. This present result also supports an idea that the potential gradient within the dendritic phenylazomethine structure is also available in **DPAGX-NDI**.



Fig. 2 UV-vis absorption spectra of DPAGX-NDI (2.5 μ M) on the addition of SnCl₂ in benzene/acetonitrile (1/1) solvent. The isosbestic points (inset) were shifted stepwise according to the equimolar amount of SnCl₂. (a) *X* = 1, (b) *X* = 2, (c) *X* = 3, (d) *X* = 4. (e) Schematic representation of the stepwise complexation to the dendrimer (*X* = 4).

These two types of dendrimers have different trends in their electrochemical properties. In our previous study,¹⁹ the phenylazomethine dendrimers with a zinc porphyrin core (DPAGX-ZnTPP) exhibited a cathodic-shift of the redox potentials corresponding to the ZnP/ZnP⁺ redox couple with the generation number increase.¹⁹ However, no significant shift was observed for the open-shell dendrimers of which the cores (porphyrin) are not fully encapsulated.²⁷ These results suggest that the shift is not due to the direct substitution effect based on the electronic induction through the covalent bonds, but a result of the dendritic encapsulation.²⁸ We also examined the trend in redox potentials of DPVGX-ZnTPP under the same experimental conditions. Interestingly, any shift due to the encapsulation was not determined at all for DPVGX-ZnTPP. Because all the redox potentials of the core units in the phenylazomethine dendrimers (DPAGX-ZnTPP, DPAGX-NDI) exhibited a cathodic shift due to the encapsulation, a unique electron transporting property of the phenylazomethine dendrimer is expected. In other words, the oxidation of the core units has become easier with the generation number increases of the phenylazomethine shells probably due to asymmetric feature of the ET through this type shell.

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A zinc tetraphenylporphyrin is known as a photosensitizer affording a radical ion pair in the presence of electron acceptor molecules.²⁹ First, the singlet excited (¹ZnP*) species was produced upon photoexcitation at 532 nm. The ¹ZnP* state was readily converted (within 2~3 ns) to the triplet excited (³ZnP*) state through an intersystem crossing. As preciously reported,¹⁸ intermolecular ETs from the dendrimer to external acceptors such as 3,5-di-tert-buthylphenyl-naphtalenediimide (^tBuPh-NDI) are starting from the ³ZnP* state. Radical ion pairs (RIPs) were produced in these systems as the result of this ET and ion pair dissociations. The RIPs then return to the ground state through intermolecular ET to the opposite direction. All (forward and backward) ETs are exergonic for typical electron acceptors.

The transient species characterized as RIPs (ZnP⁺ - ^tBuPh-NDI⁻) have identical absorption spectra based on the summation of the electrochemically generated ZnP⁺ (broad absorption peak at 690 nm) and the acceptor (the absorbance is much weaker). Similar spectral changes were also observed in other polar solvents (DMF, benzonitrile, benzene/acetonitrile). In any case, the generation number ($N = 0 \sim 4$) significantly affects the lifetime of the FRIs produced with each dendrimer. The trend that the lifetime increased with the generation number was observed in the measurements of all the pairs using DPVGX-ZnTPP and BzEGX-ZnTPP as the electron donors, and ^tBuPh-NDI, DPAGX-NDI as the acceptors (see spectroscopic data in ESI). The quantum yield of ${}^{3}ZnP*$ (Φ_{T}) could be experimentally calculated from the transient absorption spectrum, which was obtained without the electron acceptors. Similarly, we could also calculate the yields of RIP (Φ_{RIP}) from the transient spectra obtained with the excess electron acceptors. Accordingly, the guantum yield of the charge-separating step (Φ_{CS}) could be estimated as the division of Φ_{RIP} by Φ_{T} .¹⁸

The intermolecular ET rate constants could be calculated by the curve fitting of the transient absorption decays corresponding to the two transitions observed upon excitation. The forward ET from the porphyrin core to the electron acceptor was observed as the decay of ³ZnP*. As previously reported, ¹⁸ the presence of ^tBuPh-NDI (3 mM) provided an initial monoexponential decay of the transient absorption (DPAG4-ZnTPP) at 500 nm within a few µs with a residual absorption of the RIP. The apparent rate constant (k_{obs}) of the decay was proportional to the concentration of ^tBuPh-NDI (acceptor), suggesting that the quenching of ³ZnP* is a pseudo-first-order reaction. The plot between the concentration of acceptors and k_{obs} gave the second-order constant (k_f) as the slope. The same treatments were successfully applied to the present pairs of the zinc porphyrins and the electron acceptors with different dendrimer structures. The backward ET from the acceptor (radical anion) to the porphyrin core (radical cation) was purely observed as a second-order reaction, which displayed an inverse functional decay. This kinetics is due to the equivalent amount of each reactive species (radical anion and cation). In this case, the second-order rate constant $(k_{\rm b})$ was calculated as the slope of the plot between the time and an inverse of the RIP concentration (C_{RIP}). Accordingly, each rate constant of the forward (k_f: RIP formation) and backward ET (k_b: charge recombination) was obtained. The calculated ratio of $k_{\rm b}$ between X = 1and 4 (k_{bG_4}/k_{bG_1}) was 16 for **DPAGX-ZnTPP** / ^t**BuPh-NDI** system, which is almost equivalent to that of the interfacial ET rate constant for the

ZnP/ZnP⁺ redox couple observed in the electrochemical analysis of **DPAGX-ZnTPP** ($X = 1 \sim 4$).¹⁹

The most significant feature in our study is that each attenuation factor for the forward (k_f) and backward (k_b) ET was not equivalent. The trend in the less attenuated forward reaction (k_f) was observed with each electron acceptor. The observed rate constants of the forward (k_f) and backward (k_b) intermolecular reactions are much slower than the diffusion limited rate constant calculated by Smoluchowski's theory to be $k_s = 7.1 \times 10^{10} \text{ mol}^{-1} \text{ L s}^{-1,29,30}$ which is also applicable for the reactions of dendrimers.³¹ This fact strongly suggests that the ET as the rate-determining step is not equivalent for each direction of the ET.

Such asymmetric character may also originate from the dendritic topology as the electron-transporting pathway.³² To confirm this, we also examined the opposite ET system in which the direction of the initial charge separation is inbound. The dendrimers with an electron-accepting core (**DPAGX-NDI**: X = 1 - 4) were used with a non-dendritic zinc tetraphenylporphyrin (ZnTPP) as the sensitizer and an electron donor. Upon the excitation of ZnTPP at 532 nm, similar transitions involving two decays were found, and each rate constant (k_f and k_b) was calculated from the decay curves. As the generation number increased, the rate constant of the forward ET (k_f) significantly decreased while the backward ET (k_b) showed a relatively smaller attenuation. Accordingly, the rate constants demonstrated a completely opposite trend to the pairs employing **DPAGX-ZnTPP**.

Further study using other dendrimer structure was carried out to confirm whether this non-symmetric ET is a unique feature of the phenylazomethine architecture. We tested the benzylether (BzEGX-**ZnTPP**: $X = 1 \sim 4$) and phenylenevinylene (PPVGX-ZnTPP: X = 1 ~ 4) series. As usual, BzEGX-ZnTPP and DPVGX-ZnTPP also exhibited two-step decays producing a transient RIP. Analysis of the decay curves gave each rate constant ($k_{\rm f}$ and $k_{\rm b}$) for the dendrimers with different generation numbers. BzEG4-ZnTPP exhibited an overall trend that the ET is slower than those of the others. One possible reason for the stronger attenuation is the difference in the π conjugation on these dendrimers. The partial conjugation of the benzylether structure may result in a weaker electronic coupling between the donor, bridge and acceptor. Again, DPVGX-ZnTPP exhibited a roughly similar lifetime of the RIPs to those of DPAGX-ZnTPP because their attenuation factors are similar. Both the phenylenevinylene and benzylether dendrimers showed the symmetric character of the ET rates in contrast to the phenylazomethine series. These results suggest that the nonsymmetric ET was not due to the effects, which accompany the common dendrimer architecture.

Results of the bimolecular rate constants suggest that the ET through the phenylazomethine dendritic shell has a non-symmetric property. We have also confirmed that the apparent redox potentials of the core of the phenylazomethine dendrimers shifted in the negative direction. This observation supports a more facile outbound ET than the opposite inbound transfer. This fact strongly suggests the domination of a electron hopping process although a partial contribution by super-exchange ET is not excluded.^{33,34} Theoretical representation of the non-symmetric ET is under consideration.

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Fig. 3 (a) An assumed scheme of the photoinduced ET reaction. (b) Bimolecular rate constants for the photoinduced ET reactions. Generation number dependences of the forward (k_f : red) and backward (k_b : blue) rate constants are shown in the bar charts. The **DPAGX-ZnTPP** data were reproduced from the previous study (ref. 16).

Conclusions

This simple strategy might be useful to define the ET vector at the molecular solid-solid interfaces in solar cells or other electronic devices. In a previous approach, direct modification of the HOMO/LUMO level was the only way to control the ET reactions at the interface. This present method allows us to modify the apparent redox equilibrium at a specific interface without changing the redox center.

Acknowledgement

This work was supported in part by the CREST program of the Japan Science and Technology (JST) Agency, and JSPS KAKENHI Grant Nos. 25410086 and 24350116.

Notes and references

Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, 226-8503, Japan. E-mail: yamamoto@res.titech.ac.jp and timaoka@res.titech.ac.jp

† Electronic Supplementary Information (ESI) available: Synthesis, characterizations, static and time-resolved UV-vis absorption spectra. See DOI: 10.1039/c000000x/

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Potential gradient along a phenylazomethine dendrimer structure can control favorable electron transfer direction.