

Photosensitized Hydrogen Evolution from Water Using Conjugated Polymers Wrapped in Dendrimeric Electrolytes

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Abstract: High-efficiency light-driven hydrogen evolution from water was demonstrated by using poly(phenyleneethynylene) bearing negatively charged, [G3] poly(benzyl ether) dendrimeric side groups 3_{L4} as photosensitizer. Three-dimensional wrapping of the conjugated backbone suppressed self-quenching of the photoexcited state, while methyl viologen (MV^{2+}), a positively charged electron acceptor, was trapped on its negatively charged surface, to form a spatially separated donor–acceptor supramolecular complex. Studies with time-resolved fluorescence spectroscopy showed that the quenching rate constant ($k_q = 1.2 \times 10^{15} \text{ M}^{-1} \text{ s}^{-1}$) is much greater than diffusion control rate constants. Upon excitation of 3_{L4} in the presence of a mixture of MV^{2+} , triethanolamine (TEOA; sacrificial electron donor), and a colloidal PVA-Pt, hydrogen evolution took place with an overall efficiency of 13%, 1 order of magnitude better than precedent examples. Comparative studies with several reference sensitizers showed that spatial isolation of the conjugated backbone and its long-range π -electronic conjugation, along with electrostatic interactions on the exterior surface, play important roles in achieving the efficient photosensitized water reduction.

Introduction

Hydrogen (H_2) evolution from water is yet a challenging subject in relation to solar energy conversion, for which organic dye molecules have been used as sensitizers because of their tunable light-absorbing properties.¹ Examples of such dye molecules include ruthenium bipyridyl complexes, zinc porphyrin derivatives, and methyl acridine orange, all of which comprise of discrete π -conjugated systems.² On the other hand, unsaturated polymers with extended π -conjugated systems are interesting candidates, since they have large absorption cross sections for a wide range of the visible spectrum and have been reported to allow exciton and hole migration along the chain.³ Despite their intensive application to devices such as solar cells,⁴ organic LEDs,⁵ microactuators,⁶ and sensors,⁷ conjugated polymers have not yet been explored as an active component in sensitizing the H_2 evolution from water. Their photosensitization

activity is still unknown owing to their insolubility in water and strong tendency to cause self-quenching of the photoexcited states because of interchain interactions.⁸ Recently, we and other groups have reported the synthesis of conjugated polymers with dendrimer frameworks,^{9,10} where we highlight that a large dendrimeric envelope not only allows for a high solubility of the conjugated backbone in common organic solvents but also significantly enhances its photoluminescence activity.¹¹ Here, we report the synthesis of a series of water-soluble conjugated polymers wrapped with poly(benzyl ether) dendrimer frameworks bearing charged exterior surfaces (Scheme 1A and 1B) and highlight their high activities for the photosensitized H_2 evolution from water.

Our approach makes use of a negatively or positively charged large dendrimeric shell¹² that encapsulates and segregates a poly-

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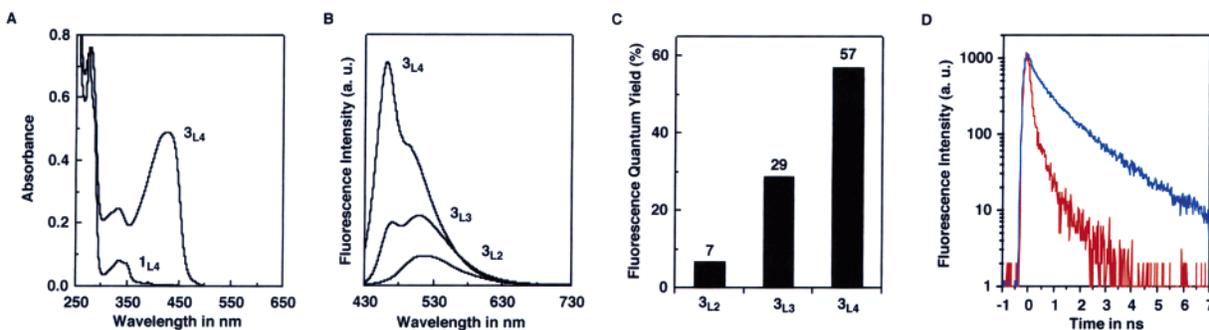
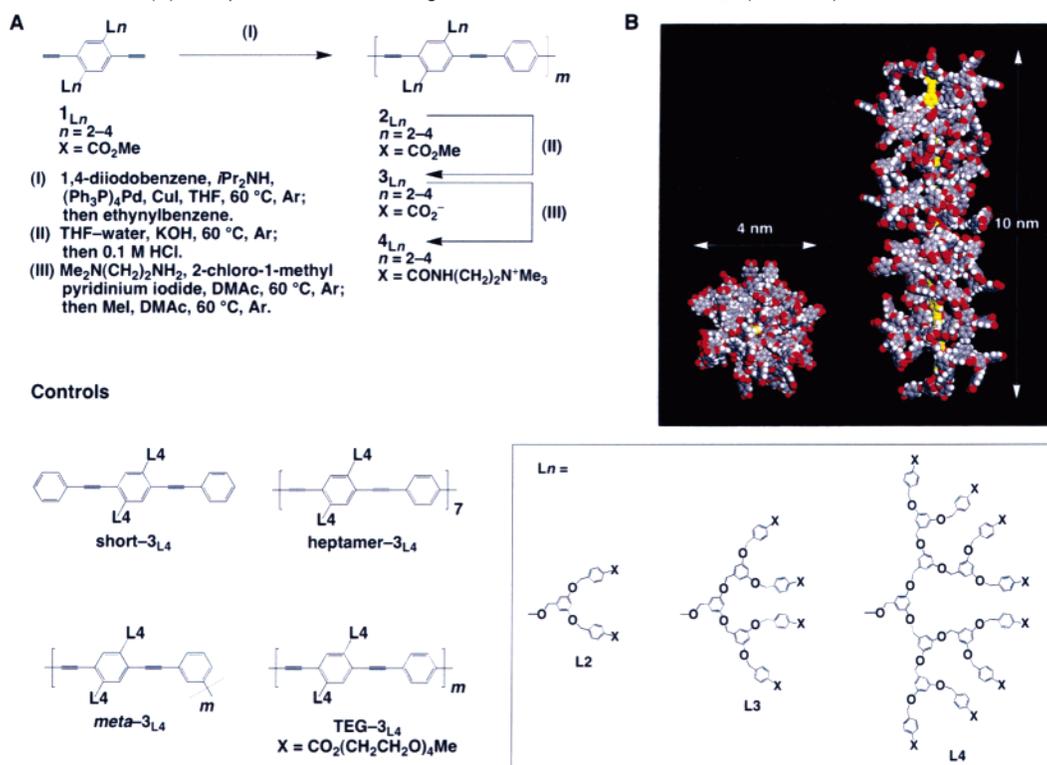


Figure 1. (A) Electronic absorption spectra of dendritic monomer 1_{L4} in THF and 3_{L4} in an aqueous Tris-HCl buffer (pH = 7.4, 5.0 mM) at 20 °C. (B) Fluorescence spectra and (C) quantum yields of 3_{Ln} ($n = 2-4$) in an aqueous Tris-HCl buffer (pH = 7.4, 5.0 mM) at 20 °C, upon excitation of the conjugated backbone (abs = 0.01) under Ar. (D) Fluorescence decay curves of 3_{L4} in the absence (blue) and presence (red) of MV^{2+} (7.8×10^{-6} M) in an aqueous Tris-HCl buffer (pH = 7.4, 5.0 mM), upon excitation at 420 nm (abs = 0.015) under Ar.

Scheme 1. (A) Schematic Representations of Dendritic Diethynylbenzenes 1_{Ln} (Monomers), Dendritic Poly(phenyleneethynylene)s 2_{Ln} , 3_{Ln} , 4_{Ln} ($n = 2-4$), and Controls. (B) Computer-Generated Images of Molecular Structure of 3_{L4} (Octamer)



(phenyleneethynylene) conjugated backbone because of an electrostatic repulsion, thereby suppressing self-quenching of its photoexcited state.¹³ On the other hand, such a spatially isolated conjugated backbone in the dendrimeric envelope may allow rapid migration of exciton and hole along the chain.³ We expected that such unique structural features could function cooperatively in controlling the photoinduced electron-transfer process, thus making the overall kinetics much different from those with conventional organic dyes.²

Results and Discussion

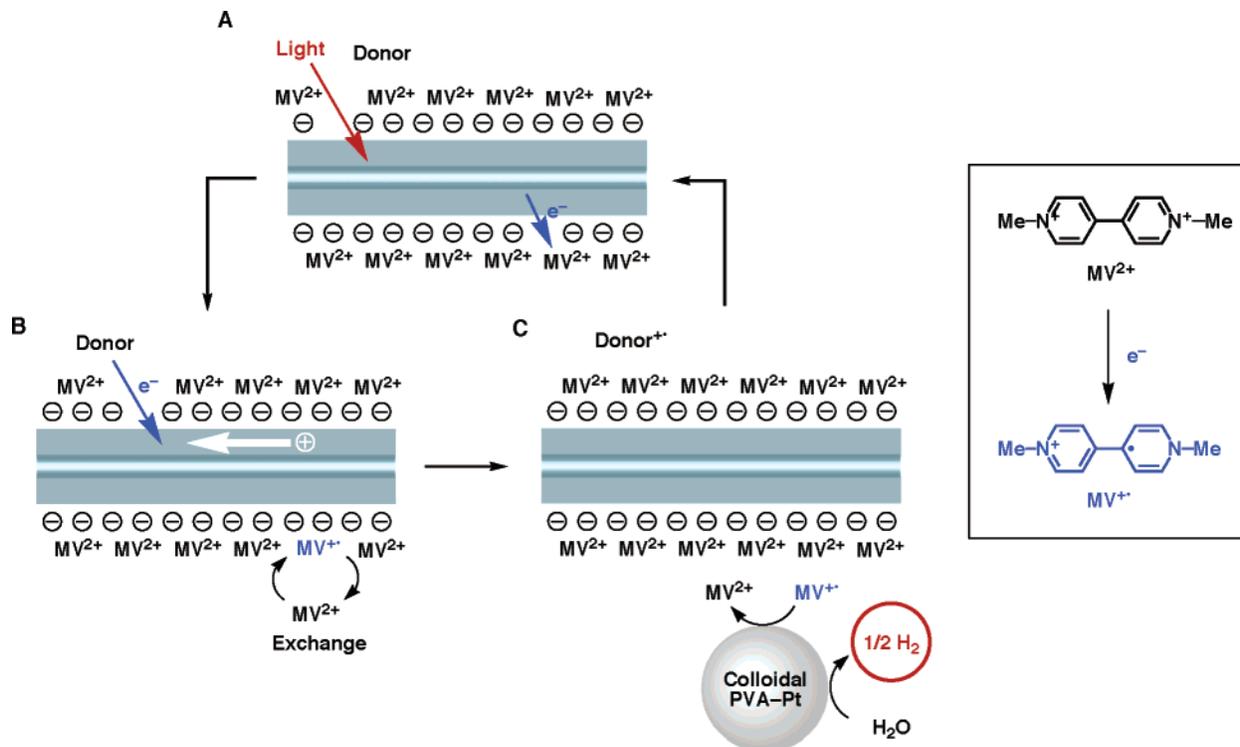
Dendritic poly(phenyleneethynylene)s 3_{Ln} ($n = 2-4$; Scheme 1A) were synthesized by alkaline hydrolysis of their ester precursors 2_{Ln} , obtained by a Pd(0)/Cu(I)-catalyzed coupling

of the corresponding dendritic monomers 1_{Ln} ($n = 2-4$) with 1,4-diiodobenzene in the presence of iPr_2NH . Positively charged 4_{L4} was synthesized by amidation of the carboxylic acid functionalities of 3_{L4} , followed by quarternization of the dimethylamino groups with MeI (III, Scheme 1A). Molecular modeling (Scheme 1B) suggested that the conjugated chain in the largest 3_{L4} (average number of repeating units (m_{SEC}) = 10, as estimated by SEC) is encapsulated in a cylindrical dendrimeric shell with a thickness of approximately 2 nm, which is yet a little smaller than the distance limit for electron transfer. 3_{L4} (aqueous Tris-HCl buffer [pH 7.4, 5 mM]; Figure 1A) and its ester precursor 2_{L4} (THF) both displayed electronic absorption spectra with an intense and broad absorption band in the visible region (400–490 nm) centered at 420 nm. An obvious red shift from the corresponding absorption band of monomer 1_{L4} (335 nm in THF; Figure 1A) clearly indicates an extended π -electronic conjugation along the backbones of 2_{L4} and 3_{L4} .

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Scheme 2. Schematic Diagram for Photoinduced H₂ Evolution from Water, Sensitized by Dendritic Poly(phenyleneethynylene) **3**_{L4}, in Conjunction with Methyl Viologen (MV²⁺) as Electron Acceptor, Triethanolamine (TEOA) as Sacrificial Donor, and a Colloidal PVA-Pt as Catalyst. Inset: Scheme for One-Electron Reduction of MV²⁺ to MV^{•+}



The extent of aggregation of the conjugated polymers depended critically on the size (generation number) of the dendrimer framework. Upon excitation at 420 nm ($\text{abs} = 0.01$), **3**_{L4} emitted an intense blue fluorescence centered at 461 nm (Figure 1B) with a quantum yield (Φ_{FL}) of 57% (Figure 1C).¹⁴ The quantum yield remained unchanged with the concentration of **3**_{L4}, even when the solution was concentrated until the absorbance at 420 nm was increased up to 0.1.¹⁵ In contrast with **3**_{L4}, conjugated polymer **3**_{L2} (average $m_{\text{SEC}} = 47$) bearing the smallest dendritic wedges showed a red-shifted absorption band at 431 nm¹⁶ and emitted at a longer wavelength of 521 nm (Figure 1B) with a Φ_{FL} value of only 7% (Figure 1C). These spectral features indicate that **3**_{L2} self-aggregates at the ground state and loses most of the excitation energy because of the formation of an excimer.⁸ Similarly, one-generation higher **3**_{L3} (average $m_{\text{SEC}} = 20$), though hardly showed a red shift in the absorption band,¹⁶ displayed a sign of excimer formation (521 nm) in its luminescence spectrum (Figure 1B), where the quantum yield was evaluated as 29% (Figure 1C). Thus, it is evident that the large, 2-nm thick, dendrimeric shell of **3**_{L4} is the most effective in isolating the conjugated backbone and suppressing the loss of excitation energy resulting from the excimer formation.^{11a}

We investigated photoinduced electron transfer from the conjugated backbone of **3**_{L4} to methyl viologen (MV²⁺), a dicationic acceptor that is electrostatically attractive for the

dendrimer surface (Scheme 2A).^{17a} If electron transfer takes place from the conjugated backbone to MV²⁺, the fluorescence of **3**_{L4} should be quenched. In fact, addition of MV²⁺ resulted in a significant decrease in the fluorescence intensity of **3**_{L4} ($\text{abs}_{420 \text{ nm}} = 0.01$; $8.5 \times 10^{-8} \text{ M}$) even at a low [MV²⁺] of $2.6 \times 10^{-8} \text{ M}$ (Figure 2A).¹⁶ The Stern–Volmer constant K_{SV} was evaluated to be $1.8 \times 10^7 \text{ M}^{-1}$.^{16,18} Thus, the conjugated backbone of **3**_{L4}, though embedded in the dendrimeric shell, can transfer electrons quite efficiently to MV²⁺. The fluorescence titration profile clearly showed a saturation signature at [MV²⁺] = 0.5 mM (Figure 2B, ●), indicating that **3**_{L4} and MV²⁺ form a spatially separated donor–acceptor supramolecular complex (Scheme 2A).¹⁷ Time-resolved fluorescence spectroscopy of an aqueous Tris–HCl buffer solution (pH = 7.4, 5.0 mM) of **3**_{L4} upon excitation at 420 nm ($\text{abs} = 0.015$) displayed a decay profile (blue curve, Figure 1D) with an average lifetime

(14) By reference to a quinine sulfate solution (1.0 N, $\text{abs}_{350 \text{ nm}} = 0.06$; $\Phi_{\text{FL}} = 55\%$ upon excitation at 350 nm) with corrections for wavelength-dependent detector sensitivity and excitation light source output, according to a method reported in Haugland, R. P.; Yguerabide, J.; Stryer, L. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 23–30.

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(18) Defined as $I_0/I = 1 + K_{\text{SV}}[\text{MV}^{2+}]$ (I_0 and I represent fluorescence intensities in the absence and presence of MV²⁺, respectively).

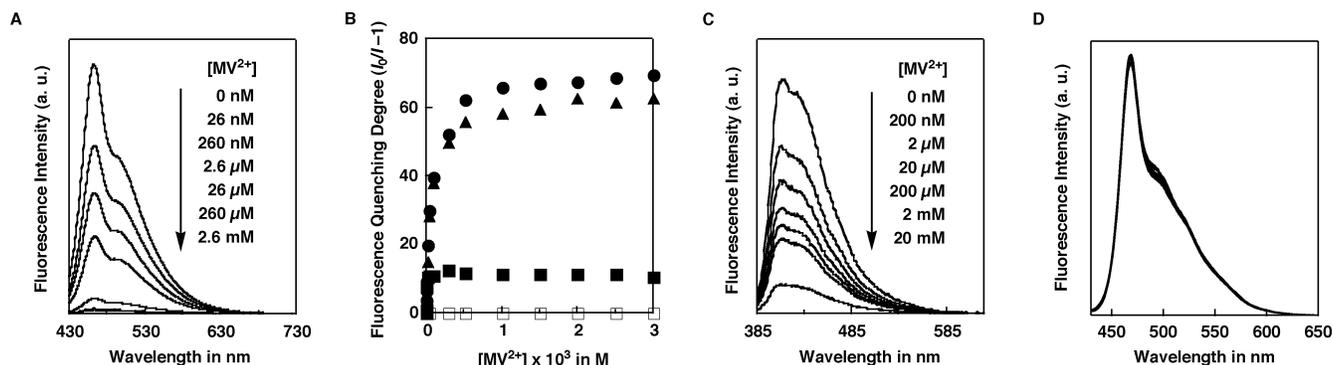


Figure 2. (A) Fluorescence spectral change of 3_{L4} . (B) Stern–Volmer plots for 3_{L2} (■), 3_{L3} (▲), 3_{L4} (●), and 4_{L4} (□), and fluorescence spectral changes of (C) *meta*- 3_{L4} and (D) $TEG-2_{L4}$, upon titration with MV^{2+} . Spectra were obtained upon excitation of the conjugated backbones ($abs = 0.01$) in an aqueous Tris–HCl buffer (pH = 7.4, 5.0 mM) at 20 °C under Ar. Conditions for (D): $[MV^{2+}] = 0, 1.0 \times 10^{-9}, 2.0 \times 10^{-9}, 5.0 \times 10^{-9}, 1.0 \times 10^{-8}, 1.5 \times 10^{-8}, 2.0 \times 10^{-8}, 2.5 \times 10^{-8}, 5.0 \times 10^{-8}, 2.6 \times 10^{-7}, 2.6 \times 10^{-6}, 2.5 \times 10^{-5}, 1.5 \times 10^{-4}, 6.5 \times 10^{-4},$ and 1.2×10^{-3} M.

τ_{ave} (none) = 880 ps. On the other hand, in the presence of MV^{2+} (7.8 μ M), the lifetime was considerably shortened (red curve, Figure 1D) to give τ_{ave} (acceptor) = 96 ps.¹⁶ From these lifetimes, the rate constant of the electron transfer (k_{ET}) from 3_{L4} to MV^{2+} was estimated by using an equation $k_{ET} = (\tau_{ave}(\text{acceptor}))^{-1} - (\tau_{ave}(\text{none}))^{-1}$ to be 9.3×10^9 s⁻¹. The quenching rate constant (k_q) of 1.2×10^{15} M⁻¹ s⁻¹, given by $((\tau_{ave}(\text{acceptor}))^{-1} - (\tau_{ave}(\text{none}))^{-1})/[MV^{2+}]$, is much greater than diffusion control rate constants (10^9 – 10^{10} M⁻¹ s⁻¹),¹⁹ again indicating that the electron transfer takes place within the supramolecular complex between 3_{L4} and MV^{2+} .

We synthesized *meta*- 3_{L4} as a short-conjugation reference for 3_{L4} . Although the molecular weight of *meta*- 3_{L4} is almost identical to that of 3_{L4} , the absorption band due to the backbone was obviously blue-shifted by 55 nm from that of 3_{L4} . Of interest, the K_{SV} value, upon titration of *meta*- 3_{L4} with MV^{2+} , was 2.0×10^6 M⁻¹ (Figure 2C), which is about 1 order of magnitude smaller than that of 3_{L4} .^{3b} These observations indicate the importance of a π -electronic conjugation along the backbone for the efficient electron transfer to MV^{2+} .

To illustrate the influences of dendrimer size and surface charge, several control experiments were carried out. One-generation smaller 3_{L3} (Figure 2B, ▲) showed a fluorescence quenching profile similar to 3_{L4} (●). In sharp contrast, the lowest-generation 3_{L2} (■) exhibited only a low degree of fluorescence quenching with a maximum quenching degree (I_0/I) – 1 close to 10, only one-seventh that of 3_{L4} . On the other hand, positively charged 4_{L4} did not exhibit any fluorescence quenching even at high $[MV^{2+}]$ (□; $\Phi_{FL} = 15\%$), indicating that MV^{2+} cannot attach to the dendrimer surface because of an electrostatic repulsion. We also synthesized $TEG-2_{L4}$, a nonionic version of 3_{L4} , having tetraethylene glycol chains on the dendrimer surface (Scheme 1). This water-soluble dendrimeric conjugated polymer in aqueous Tris–HCl buffer showed a visible absorption band at 425 nm, which is virtually identical in wavelength to that of 3_{L4} . However, in contrast with 3_{L4} , $TEG-2_{L4}$ did not exhibit fluorescence quenching even when MV^{2+} was added in large excess (1.23 mM) (Figure 2D). These control experiments indicate that in the $3_{L4}/MV^{2+}$ system, several structural factors play a cooperative role in achieving the efficient photoinduced electron transfer. First, the inherent photoactivity of the poly(phenyleneethynylene) backbone, because of a long-range π -electronic conjugation, is of primary

importance for the high photosensitivity of the system. Equally important is the large dendrimeric envelope with negative charges on its surface, which help the conjugated backbone to be isolated, to maintain the inherent high photoactivity even in water. The negative charges on the dendrimer surface are also essential for the acceptor to be trapped within an electron-transfer distance from the conjugated backbone.

The results of the above fluorescence quenching experiments promoted us to use 3_{L4} as a sensitizer for catalytic MV^{2+} reduction in the presence of triethanolamine (TEOA) as a sacrificial electron donor. Thus, a quartz cell containing an aqueous Tris–HCl buffer solution (pH = 7.4, 5 mM) of a mixture of 3_{L4} ($abs_{420\text{ nm}} = 0.05$), MV^{2+} (1.67 mM), and TEOA (0.83 M) was exposed to a 150-W Xenon arc light through a band-pass filter at 410–430 nm. The light-yellow solution, when stirred vigorously, turned blue immediately, indicating a rapid response to light irradiation. Figure 3A shows the time-dependent absorption spectral change, where a new absorption band appeared at 605 nm, characteristic of one-electron reduced MV^{2+} (MV^+).²⁰ Over a period of 4 h, the absorption at 605 nm increased almost linearly in intensity with irradiation time, without showing any saturation tendency (Figure 3B, ●). Thus, this system is quite stable in photoreduction performance. The energy of visible photon harvested by the conjugated backbone flows steadily to MV^{2+} and is stored in the form of MV^+ . In sharp contrast, the systems with one-generation smaller 3_{L3} (Figure 3B, ▲) and the lowest-generation 3_{L2} (Figure 3B, ■) both exhibited poor performance for the accumulation of MV^+ . Consistent with the poor fluorescence quenching profile with MV^{2+} (Figure 2B, □), positively charged 4_{L4} did not show any response to light irradiation, with no reduction of MV^{2+} detectable.

Figure 3C shows the overall quantum efficiency ($\Phi = \text{number of } MV^+/\text{number of photons absorbed}$) of the reaction sensitized by 3_{L4} . A 60-s exposure to light of wavelength 410–430 nm ($abs = 0.2$) generated 1.2×10^{16} molecules of MV^+ . The solution absorbed 4.1×10^{16} photons (with light intensity of 0.33 mW cm⁻²). Thus, Φ was evaluated to be 29%. This result compares favorably with those of representative sensitizers, that is, Ru(bpy)₃Cl₂, 10-methyl acridine orange (MAO⁺), and zinc tetrakis(1-methylpyridinium-4-yl)porphyrin (ZnTMPyP⁴⁺).² Under conditions identical to those with 3_{L4} , Φ values with these sensitizers were only 1, 3, and 6%, respectively (Figure 3C).

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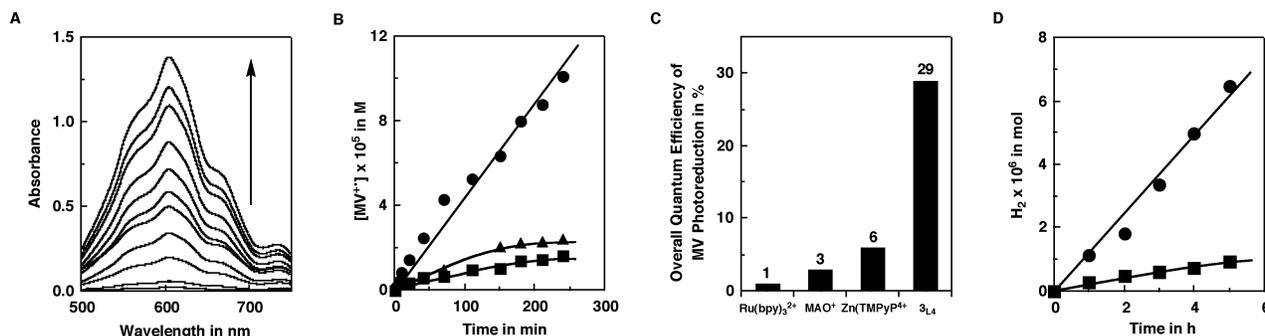


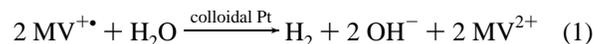
Figure 3. (A) Electronic absorption spectral change of a mixture of $\mathbf{3L}_4$ ($\text{abs}_{420 \text{ nm}} = 0.05$), methyl viologen (MV^{2+}), and triethanolamine (TEOA). (B) Time dependency of the accumulation of one-electron-reduced MV^{2+} ($\text{MV}^{+\bullet}$) with $\mathbf{3L}_2$ (■), $\mathbf{3L}_3$ (▲), and $\mathbf{3L}_4$ (●) as sensitizers ($\text{abs} = 0.05$). (C) Overall quantum efficiencies of MV^{2+} photoreduction with $\text{Ru}(\text{bpy})_3^{2+}$, MAO^+ , ZnTMPyP^{4+} , and $\mathbf{3L}_4$ as sensitizers ($\text{abs} = 0.2$). (D) Time dependencies of the H_2 productions from water in the systems of $\mathbf{3L}_4/\text{MV}^{2+}/\text{TEOA}$ (●) and $\mathbf{3L}_2/\text{MV}^{2+}/\text{TEOA}$ (■), catalyzed by a colloidal PVA-Pt. Conditions: $[\text{MV}^{2+}]_0 = 1.67 \text{ mM}$; $[\text{TEOA}]_0 = 0.83 \text{ M}$; stirring vigorously at 20°C under Ar, upon exposure to a 150-W Xenon arc light at $420 (\pm 10) \text{ nm}$ for $\mathbf{3L}_4$, $450 (\pm 10) \text{ nm}$ for $\text{Ru}(\text{bpy})_3^{2+}$, $490 (\pm 10) \text{ nm}$ for MAO^+ , and $560 (\pm 10) \text{ nm}$ for ZnTMPyP^{4+} .

The turnover number with $\mathbf{3L}_4$ was roughly 12 $\text{MV}^{+\bullet}$ molecules per $\mathbf{3L}_4$ molecule per min, which is much higher than that observed with, for example, MAO^+ (0.8). Thus, $\mathbf{3L}_4$ is superior to these nondendritic sensitizers in terms of efficiency.

We also investigated the photosensitization activity of $\mathbf{3L}_4$ by using simulated and natural sunlights, in place of the Xenon arc light, under conditions otherwise identical to the above. When the system was exposed to a solar simulator Air Mass 1.5G (500 W) for 150 s through a band-pass filter at $420 (\pm 10) \text{ nm}$, it turned blue as a result of the generation of 9.6×10^{16} molecules of $\text{MV}^{+\bullet}$. Since the system absorbed 3.5×10^{17} photons, the Φ value was evaluated to be 27%. A comparable Φ value (29%) was observed when the system was exposed to natural sunlight for 120 s, where 1.4×10^{17} molecules of $\text{MV}^{+\bullet}$ were generated per 4.8×10^{17} photons at $420 (\pm 10) \text{ nm}$. The results of these two experiments again indicate a high potential of spatially isolated conjugated wire $\mathbf{3L}_4$ as excellent photosensitizer for the evolution of H_2 from water.

A diagram for the above photochemical reduction is outlined in Scheme 2. Once an electron is transferred to MV^{2+} , a hole is left behind in the conjugated backbone, and thereby a one-electron reduced MV^{2+} ($\text{MV}^{+\bullet}$) molecule is generated (Scheme 2B). Since $\text{MV}^{+\bullet}$ should have a lower affinity than MV^{2+} toward the negatively charged dendrimer surface, it may rapidly exchange in position with MV^{2+} in the bulk solution (Scheme 2B→2C), resulting in a lower probability of back electron transfer. Furthermore, migration of the hole along the conjugated backbone (Scheme 2B),³ if any occurs, could help to further suppress the recombination of the charge-separated state. Consequently, the conjugated chain should have a high probability of recovering its original neutral state (Scheme 2A). To investigate possible effects of π -electronic conjugation on the photoreduction of MV^{2+} , three control experiments were carried out. In the first, **short- $\mathbf{3L}_4$** ($\text{abs}_{\text{max}} = 360 \text{ nm}$, Scheme 1A), a short-chain reference for $\mathbf{3L}_4$, was used in place of $\mathbf{3L}_4$, where the reduction of MV^{2+} took place much less efficiently with a Φ value of only 3%. Second, meta-linked poly(phenyleneethynylene) **meta- $\mathbf{3L}_4$** ($\text{abs}_{\text{max}} = 365 \text{ nm}$), having a comparable molecular weight to $\mathbf{3L}_4$ but a much shorter conjugation length, was employed, where the reduction also took place but with an efficiency of only 5%. Finally, when a heptamer (**heptamer- $\mathbf{3L}_4$**), separated from $\mathbf{2L}_4$, was hydrolyzed and utilized for the photoreduction, a high efficiency of 30%, similar to the case with $\mathbf{3L}_4$, was observed.

High efficiency in the accumulation of reduced MV^{2+} also offers the possibility of continuous H_2 evolution from water, since reduced MV^{2+} is known to drive, under certain conditions, the reduction of water to H_2 , according to eq 1.²¹



To demonstrate this, we further coupled the above photoreduction system with a colloidal PVA-Pt catalyst for H_2 production. In a typical experiment, a 3.5-mL Tris-HCl buffer solution (pH = 7.4, 5.0 mM) of a mixture of $\mathbf{3L}_4$ ($3.2 \times 10^{-6} \text{ M}$), MV^{2+} (1.67 mM), TEOA (0.83 M), and PVA-Pt ($4.3 \times 10^{-4} \text{ M}$), while stirred vigorously at 20°C , was exposed to a light of wavelength 410–430 nm with a 150-W Xenon arc lamp. After a designated period, the gas phase above the solution was analyzed by gas chromatography. Figure 3D (●) shows plots of total amount of H_2 produced *versus* time. A steady generation of H_2 ($1.3 \times 10^{-6} \text{ mol h}^{-1}$) was observed without an induction period or a decrease in activity during 5 h of irradiation. The absorbance of the solution at 400–490 nm because of the conjugated backbone remained unchanged during the photoirradiation, indicating that the system is quite stable against photobleaching. The overall quantum efficiency for the hydrogen evolution (number of H_2 generated/number of photons absorbed) was 13%, more than 1 order of magnitude better than reported examples. Considering the photoreduction efficiency of MV^{2+} (29%), the observed efficiency of the hydrogen evolution appears to be reasonable, since two molecules of reduced MV^{2+} ($\text{MV}^{+\bullet}$) are required for the production of one H_2 molecule from water (Scheme 2C).²² In contrast, the use of $\mathbf{3L}_2$ in place of $\mathbf{3L}_4$ for the above reaction (Figure 3D, ■) resulted in only a poor performance in H_2 evolution.

Conclusions

By using the built-in dendrimeric core-shell strategy, we have demonstrated the great potential of conjugated polymers as highly efficient photosensitizers for the hydrogen evolution from water. By virtue of the three-dimensional wrapping with a surface-charged large dendrimeric shell, self-quenching of the photoexcited conjugated backbone is suppressed in aqueous media, while methyl viologen (MV^{2+}), a positively charged electron acceptor, is trapped on the negatively charged dendrimer

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(22) No evolution of H_2 took place in the absence of MV^{2+} in the system.

surface, to form a spatially separated donor–acceptor supramolecular complex. Together with this unique donor–acceptor geometry, hole migration along the conjugated backbone,³ if possible, may also lower the relative rate of charge recombination. Consequently, one-electron reduced MV²⁺ is efficiently accumulated. Under irradiation in the presence of a colloidal PVA-Pt, hydrogen evolution takes place without any induction period. The system is tolerant to bleaching and exhibits a high overall efficiency of 13%, 1 order of magnitude better than precedent examples. Dendrimeric architectures are unique in that they possess a mechanical stability unlike micellar aggregates,²³ while maintaining appropriate conformational change dynamics, thereby casting a clear contrast to other nanoscopic architectures such as inorganic multilayers²⁴ and zeolite pores²⁵

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so far investigated as intervening media for electron-transfer reactions.

Acknowledgment. We thank Prof. A. Tsutsumi of the University of Tokyo for GC measurements.

Supporting Information Available: Experimental section consisting of materials and synthesis, measurements, photoreduction of MV²⁺ in the presence of triethanolamine, and hydrogen evolution from water. Electronic absorption spectra in an aqueous Tris–HCl buffer of **3_{L_n}** (*n* = 2, 3), **short-3_{L₄}**, **heptamer-3_{L₄}**, **TEG-2_{L₄}**, **meta-3_{L₄}**, **4_{L₄}**, **3_{L₄}**/MV²⁺, and photosensitizer/MV²⁺/TEOA mixtures before and after irradiation. Stern–Volmer plots for **3_{L_n}** (*n* = 2–4) and fluorescence decay curves of **3_{L₄}** in the absence and presence of MV²⁺ in an aqueous Tris–HCl buffer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA048912E