

A Blue-Luminescent Dendritic Rod: Poly(phenyleneethynylene) within a Light-Harvesting Dendritic Envelope

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Dendrimers are nanosized hyperbranched macromolecules with well-predictable three-dimensional shapes,¹ and have attracted great attention as synthetic light-harvesting antennae,² in relation to biological energy transduction events in natural photosynthesis.³ We have recently found that a large, spherical azodendrimer traps infrared photons, and can channel the excitation energy to the focal azo unit to cause its cis/trans isomerization.⁴ In relation to this finding, a poly(benzyl ether) dendrimer porphyrin family displays a morphology-dependent intramolecular singlet energy transfer from the dendron subunits to the focal porphyrin unit.⁵ Herein we report the first light-emitting dendritic macromolecular rod having a rigid poly(phenyleneethynylene) backbone appended with flexible poly(benzyl ether) dendritic wedges of different generation numbers ($\mathbf{2}_{L_n}$, n [number of aromatic layers] = 2–4)⁶ and wish to highlight “shielding” and “antenna” effects of the dendritic envelope on the luminescence activity of the backbone.

Poly(phenyleneethynylene) has attracted special attention as an organic light-emitting diode that fluoresces a blue light, since blue-luminescent organic materials are very limited.⁷ However, because of its high conformational rigidity, poly(phenyleneethynylene) has a limited solubility and is difficult to process.^{8,9} On the other hand, from a photochemical point of view, such a strong aggregation tendency of poly(phenyleneethynylene) also results

in collisional quenching of the excited state and spoils its potential utility as a light emitter.

Dendritic macromolecular rods $\mathbf{2}_{L_n}$ ($n = 2-4$; Scheme 1) were synthesized by a Pd(0)/Cu(I)-catalyzed polycondensation of the corresponding dendritic diethynylbenzenes ($\mathbf{1}_{L_n}$; $n = 2-4$) with 1,4-diiodobenzene at 50 °C in THF/*i*-Pr₂NH.¹⁰ $\mathbf{1}_{L_n}$ ($n = 2-4$) were prepared by an alkaline-mediated coupling of poly(benzyl ether) dendron bromides ($\mathbf{L}_n\text{Br}$; $n = 2-4$)¹¹ with 2,5-diethynylhydroquinone¹² in DMF at 60 °C, and unambiguously characterized by ¹H NMR, UV–visible, and MALDI-TOF-MS spectroscopies.¹³ The polycondensation of $\mathbf{1}_{L_3}$ with 1,4-diiodobenzene took place smoothly and homogeneously to give in 48 h high molecular weight $\mathbf{2}_{L_3}$ with an M_w of 280000 ($M_w/M_n = 6.5$), as estimated by SEC using polystyrene standards. On the other hand, the polycondensation with $\mathbf{1}_{L_2}$ was accompanied by the formation of a large amount of precipitates even at the initial stage, where M_w of a THF-soluble fraction was only 11000 ($M_w/M_n = 1.5$). In contrast with these two cases, the polycondensation with the highest-generation $\mathbf{1}_{L_4}$ proceeded rather sluggishly but homogeneously to give after 2 weeks a polymer ($\mathbf{2}_{L_4}$) with an M_w of 34000 ($M_w/M_n = 1.5$).

In THF at 20 °C, dendritic monomers $\mathbf{1}_{L_n}$ ($n = 2-4$) showed absorption bands at 335 and 278 nm due to the focal diethynylbenzene unit and the dendritic wedges, respectively (Figure 1; $\mathbf{1}_{L_4}$). On the other hand, dendritic macromolecular rods $\mathbf{2}_{L_n}$ ($n = 2-4$) displayed a strong absorption band in the visible region (400–460 nm), characteristic of an extended electronic conjugation in the backbone (Figure 1; $\mathbf{2}_{L_4}$).⁷ Upon excitation of the conjugated backbone at 425 nm in THF ($\text{abs}_{425\text{nm}} = 0.01$), $\mathbf{2}_{L_4}$ at 20 °C showed a strong blue fluorescence at 454 nm (Figure 2B), where the quantum yield (Φ_{FL}) was evaluated to be virtually 100%.¹⁴ Of much interest is the fact that the Φ_{FL} value of $\mathbf{2}_{L_4}$ stayed at nearly 100% even when the solution was concentrated until the absorbance at 425 nm ($\text{abs}_{425\text{nm}}$) was increased to 0.1 (Figure 3C). Such a high Φ_{FL} value over a rather wide concentration range has never been realized with other soluble poly(phenyleneethynylene) derivatives reported to date (35–40%).⁷ We also found that the luminescence activity of $\mathbf{2}_{L_n}$ is considerably dependent on the size of the dendritic wedges: Although the Φ_{FL} value of one-generation smaller $\mathbf{2}_{L_3}$ was also very high under dilute conditions (~100% at $\text{abs}_{431\text{nm}} = 0.01$), it showed a significant drop to 67% when the absorbance of the solution was increased to 0.1 (Figure 3B).¹⁵ Such a trend was more explicit in the case of the lowest-generation $\mathbf{2}_{L_2}$, where the Φ_{FL} value was only 56% even under dilute conditions ($\text{abs}_{425\text{nm}} = 0.01$), and further dropped upon concentration of the solution (Figure 3A). From these observations, the large dendrimer framework in $\mathbf{2}_{L_4}$ is likely to encapsulate the conjugated backbone as an “envelope” and prevent the photoexcited state from collisional quenching.

Since poly(benzyl ether) dendrimers of certain morphologies have been found to serve as excellent antennae for harvesting ultraviolet photons,⁵ we investigated intramolecular singlet energy transfer (ENT) from the dendrimer framework to the focal

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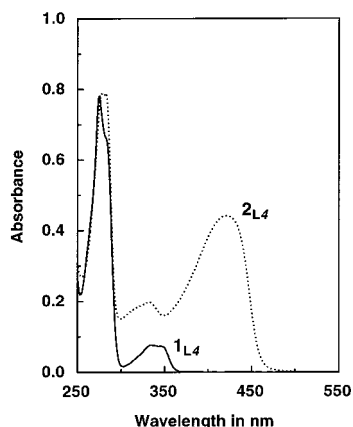
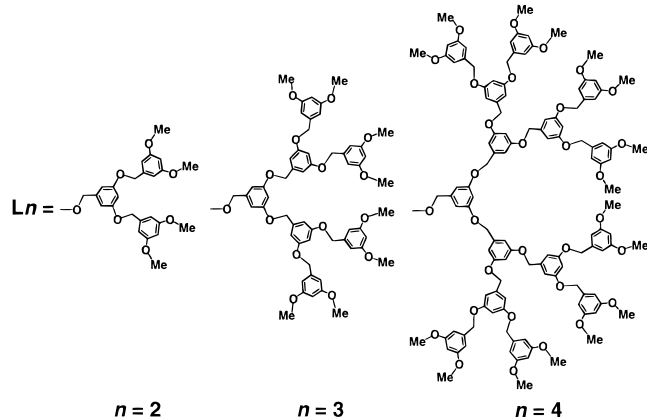
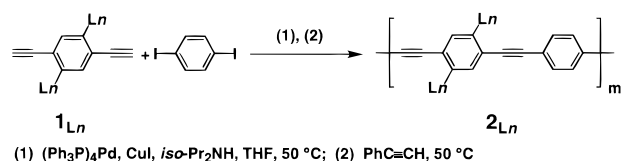
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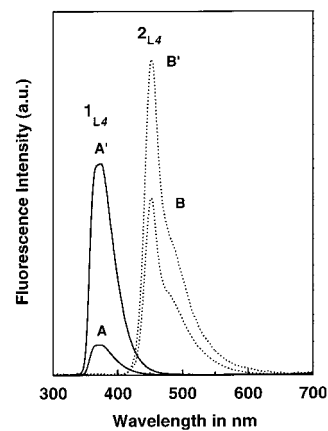
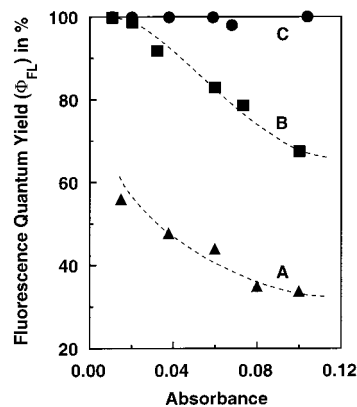
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(15) For investigating the effect of chain length on luminescence properties, a low molecular weight fraction ($M_w = 45000$, $M_w/M_n = 2.7$) was separated from $\mathbf{2}_{L_3}$ ($M_w = 280000$) by means of preparative SEC. In THF at 20 °C, the absorption ($\lambda_{\text{max}} = 431$ and 278 nm) and emission ($\lambda_{\text{em}} = 454$ nm) profiles and the concentration-dependency of the fluorescence quantum yield ($\Phi_{\text{FL}} = 97.3$ [$\text{abs}_{431} = 0.0150$], 89.3 [0.033], 80.4 [0.049], 77.2 [0.072], and 73.1% [0.122]) were virtually identical with those of parent $\mathbf{2}_{L_3}$ ($M_w = 280000$).

Scheme 1. Synthetic Approach to a Series of Dendritic Poly(phenyleneethynylene)s 2_{L_n} ($n = 2-4$)**Figure 1.** Electronic absorption spectra of 1_{L_4} (A) and 2_{L_4} (B) in THF at 20 °C.

chromophore units in dendritic monomers 1_{L_n} and polymers 2_{L_n} ($n = 2-4$): Upon excitation of the dendritic wedges at 278 nm ($\text{abs} = 0.06$) in THF at 20 °C, 1_{L_4} emitted a fluorescence at 373 nm from the focal diethynylbenzene unit, while no fluorescence was detected from the dendritic wedges at 308 nm (Figure 2A). The fluorescence at 373 nm was much more intense than that upon direct excitation of the focal diethynylbenzene unit at 355 nm (Figure 2A), indicating an efficient intramolecular singlet ENT from the dendritic wedges to the focal chromophore unit (quantum efficiency $\Phi_{\text{ENT}} \sim 100\%$).¹⁶ Similarly, dendritic macromolecular rod 2_{L_4} displayed highly efficient ENT characteristics: Upon excitation of the dendrimer framework at 278 nm ($\text{abs} = 0.06$), only a blue fluorescence at 454 nm from the conjugated backbone was observed without any luminescence from the dendrimer framework. Furthermore, the fluorescence intensity was much higher than that upon direct excitation of the conjugated backbone at 425 nm (Figure 2B). The excitation spectrum, monitored at 454 nm, was perfectly a superimposed image of the absorption spectrum, again indicating a 100% ENT quantum efficiency (Φ_{ENT}).¹⁶ Owing to the prominent light-harvesting function together with the efficient isolation effect of the large dendritic

(16) Similar high Φ_{ENT} values ($\sim 100\%$) were observed for lower-generation 1_{L_n} and 2_{L_n} ($n = 2, 3$).

**Figure 2.** Fluorescence spectra of 1_{L_4} upon excitation at 335 (A) and 278 (A') nm and of 2_{L_4} upon excitation at 425 (B) and 278 (B') nm in THF ($\text{abs}_{278\text{nm}} = 0.06$) under Ar at 20 °C.**Figure 3.** Fluorescence quantum yields (Φ_{FL}) of 2_{L_2} (A), 2_{L_3} (B), and 2_{L_4} (C) upon excitation of the conjugated backbone in THF with absorbances at the excitation wavelength of 0.01–0.1 under Ar at 20 °C.

envelope, 2_{L_4} is much superior to lower-generation 2_{L_n} ($n = 2, 3$) in terms of the luminescence activity. For example, upon 278-nm excitation of the dendritic wedges of 2_{L_4} in THF ($\text{abs}_{425\text{nm}} = 0.1$), the observed fluorescence was 11 times more intense than 2_{L_2} under identical conditions. Therefore, the highest-generation 2_{L_4} is an excellent candidate as an organic light emitter, which can efficiently collect photons of a rather wide wavelength range from ultraviolet to visible and convert them into the blue emission.

In conclusion, we have developed the first blue-luminescent dendritic rod (2_{L_4}) consisting of a rigid poly(phenyleneethynylene) conjugated backbone wrapped with the flexible poly(benzyl ether) dendritic envelope. Due to the steric effect and antenna function of the envelope, the luminescence activity of the conjugated backbone was significantly enhanced. Synthesis of end-functionalized 2_{L_n} with a photo- or redox-active functionality is our future concern.

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Supporting Information Available: Details for synthetic procedures and spectral data of 1_{L_n} and 2_{L_n} ($n = 2-4$) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.