

DESIGN AND PHOTOFUNCTIONS OF DENDRIMER-ENCAPSULATED POLY(PHENYLENEETHYNYLENE)S

Dong-lin Jiang*, Takafumi Sato and Takuzo Aida

*Department of Chemistry and Biotechnology, Graduate School of Engineering,
The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Abstract A series of dendrimer-encapsulated poly(phenyleneethynylene)s **4-6** were synthesized. The light-harvesting antenna functions of dendrimer frameworks together with the blue-light emitting activities of **4-6** were highlighted.

Keywords Dendrimer, Poly(phenyleneethynylene), Molecular wire, Light-harvesting antenna, Energy transfer

INTRODUCTION

To realize photosynthesis with a totally artificial system is a constant challenge in science and a dream of chemists. In nature, plants and photosynthetic bacteria thrive on photosynthesis utilizing elaborate chromophore arrays to trap solar energy, followed by an efficient energy transfer to the reaction center. Synthetic macromolecules have attracted attention as potential photosynthetic antennae, since multiple chromophoric functionalities can be incorporated and arranged. However, examples so far reported are mostly with linear-chain polymers which, unlike biological macromolecules, hardly adopt any defined morphologies, often leading to complicated photochemical events associated with intra- and inter-chain interactions. Moreover, distributions as to molecular weight and sequence, essential for linear-chain synthetic polymers, also make it difficult to provide a correlation between their structures and photochemical functions.

A recent development in the design of dendritic molecules has provided a new molecular architecture methodology for building up synthetically controllable macromolecules of globular-shaped, hyper-branched tree-like structures in nanoscopic scale. Recently, dendrimers have attracted great attention as artificial light-harvesting antennae, due to their morphological similarity to chromophore aggregates discovered in natural photosynthetic centers^[1-7]. Conjugated polymers have attracted special attention for their potential utility as molecular wire for the transfer of electron and excitation energy along the backbone, and also as organic photo/electro-luminescent devices. However, because of their high conformational rigidity, conjugated polymers usually have a limited solubility and are difficult to process. On the other hand, from a photochemical point of view, such a strong aggregation tendency of the conjugated macromolecular chain also results in a collisional quenching of the excited state, and therefore spoils its photofunctional properties. This paper presents details of the synthesis, structures, and photofunctions of dendrimer-encapsulated poly(phenyleneethynylene)s.

EXPERIMENTAL PROCEDURES

Materials

Tetrahydrofuran (THF) was refluxed over sodium benzophenone ketyl under Ar and distilled just before use. 18-

* Corresponding author: Dong-lin Jiang, E-mail: jiang@macro.t.u-tokyo.ac.jp

Invited lecture at the International Conference on New Trends in Functional Polymers, May 8th~13th, 2000, Huangshan, China

Received September 1, 2000

Crown-6 ether was recrystallized from acetonitrile, dried overnight under reduced pressure, and then stored under dry N₂. Potassium carbonate (K₂CO₃) was kept in an oven at 130 °C. *N,N*-Dimethylformamide (DMF) was purified by drying over magnesium sulfate (MgSO₄) and further distillation under nitrogen and under vacuum.

Dendritic Diethynylbenzenes 1–3

General procedure

A *N,N*-dimethylformamide (DMF) solution (3 mL) of a mixture of two-layered dendritic benzyl bromide (0.132 mmol) and 2,5-diethynylhydroquinone (0.06 mmol), containing K₂CO₃ (5.0 mmol), was stirred under Ar in the dark at 60 °C for 4 h and evaporated to dryness. The residue was poured into water (15 mL) and extracted with CHCl₃ (3 × 15 mL). The combined extracts were dried over anhydrous MgSO₄ and chromatographed on silica gel with CHCl₃ as an eluent. The first fraction was collected and evaporated to give **1** (0.021 mmol) as a white solid in 34.9% yield. In similar manners, **2** and **3** were synthesized from the corresponding dendritic benzyl bromides in yields of 50% and 38%, respectively.

Characterization of 1

MALDI-TOF-MS for C₆₀H₅₈O₁₄ *m/z*: calcd: 1025 [M + Na⁺]; found: 1025. ¹H-NMR (CDCl₃, δ): 3.34 (s, 2H, C≡CH), 3.78 (s, 24H, Ar(OCH₃)₂), 4.96 (s, 8H, Ar(OMe)₂-CH₂-OAr), 5.03 (s, 4H, inner Ar-CH₂-OAr'), 6.38 (t, 4H, *p*-H in C₆H₃(OMe)₂), 6.53 (d, 4H, *o*-H in inner C₆H₃), 6.55 (d, 8H, *o*-H in C₆H₃(OMe)₂), 6.68 (d, 2H, *p*-H in inner C₆H₃), 6.96 (s, 2H, *o*-H in C₆H₄(C≡CH)₂). UV/vis (THF): λ_{max} = 277.8, 335.5 nm.

Characterization of 2

MALDI-TOF-MS for C₁₂₄H₁₂₂O₃₀ *m/z*: calcd: 2114 [M + Na⁺]; found: 2116. ¹H-NMR (CDCl₃): δ = 3.32 (s, 2H, C≡CH), 3.75 (s, 48H, Ar(OCH₃)₂), 4.93 (s, 24H, mid and outer Ar-CH₂-OAr'), 5.00 (s, 4H, inner Ar-CH₂-OAr'), 6.38 (t, 8H, *p*-H in C₆H₃(OMe)₂), 6.52 (t, 6H, *p*-H in inner and mid C₆H₃), 6.54 (d, 16H, *o*-H in C₆H₃(OMe)₂), 6.64 (d, 8H, *o*-H in mid C₆H₃), 6.66 (d, 4H, *o*-H in inner C₆H₃), 6.95 (s, 2H, *o*-H in C₆H₂(C≡CH)₂). UV/vis (THF): λ_{max} = 278.2, 335.5 nm.

Characterization of 3

MALDI-TOF-MS C₂₅₂H₂₅₀O₆₂ *m/z*: calcd: 4292 [M + Na⁺]; found: 4292. ¹H-NMR (CDCl₃, δ): 3.30 (s, 2H, C≡CH), 3.72 (s, 96H, Ar(OCH₃)₂), 4.90 (s, 60H, dendron-Ar-CH₂-OAr'), 6.35 (t, 16H, *p*-H in C₆H₃(OMe)₂), 6.51 (br, 42H, *o*- and *p*-H in dendron-C₆H₃), 6.62 (br, 32H, *o*-H in C₆H₃(OMe)₂), 6.90 (s, 2H, *o*-H in C₆H₂(C≡CH)₂). UV/vis (THF): λ_{max} = 278.4, 335.5 nm.

Dendritic Poly(phenyleneethynylene)s 4–6

General procedure

A tetrahydrofuran (THF) solution (6 mL) of a mixture of **1** (0.03 mmol) and 1,4-diiodobenzene (0.03 mmol), containing (Ph₃P)₄Pd (0.15 μmol), CuI (0.15 μmol), and diisopropylamine (0.010 mmol), was stirred under Ar in the dark at 50 °C for 2 days. To the mixture was then added ethynylbenzene (0.60 mmol) for end-capping. After stirring at 50 °C overnight, the reaction mixture was evaporated to dryness, and the residue was dissolved in CHCl₃ and filtered to remove insoluble fractions. The resulting solution was subjected to preparative size exclusion chromatography (SEC) with CHCl₃ as eluent in order to remove catalyst residues, 1,4-diiodobenzene, ethynylbenzene, and **1** if any remained, to give **2** as a yellow solid in 30% yield. In similar manners, **5** and **6** were synthesized from the corresponding dendritic monomers **2** and **3** in yields of 85% and 90%, respectively.

Characterization of 4

¹H-NMR (CDCl₃, δ): 3.68 (br, Ar(OCH₃)₂), 4.87 (br, Ar-CH₂-OAr'), 6.31 (br, *p*-H in C₆H₃(OMe)₂), 6.46 (br, *o*-H in C₆H₃(OMe)₂), 6.51 (br, *o*-H in inner C₆H₃), 6.72 (br, *o*-H in C₆H₄(C≡C)₂), 7.01 (br, *o*-H in dendron-substituted C₆H₂(C≡C)₂). UV/vis (THF): λ_{max} = 278.4, 425.0 nm. SEC analysis (THF, polystyrene standards): M_w = 11,000 (M_w/M_n = 1.5).

Characterization of **5**

$^1\text{H-NMR}$ (CDCl_3 , δ): 3.67 (*br*, $\text{Ar}(\text{OCH}_3)_2$), 4.81 (*br*, $\text{Ar-CH}_2\text{-OAr'}$), 6.25 (*br*, *p*-H in $\text{C}_6\text{H}_3(\text{OMe})_2$), 6.43 (*br*, *o*-H in $\text{C}_6\text{H}_3(\text{OMe})_2$ and mid C_6H_3), 6.54 (*br*, *o*-H in inner C_6H_3), 6.69 (*br*, *o*-H in $\text{C}_6\text{H}_4(\text{C}\equiv\text{C})_2$), 6.95 (*br*, *o*-H in dendron-substituted $\text{C}_6\text{H}_2(\text{C}\equiv\text{C})_2$). UV/vis (THF): $\lambda_{\text{max}} = 278.4, 431.0$ nm. SEC analysis (THF, polystyrene standards): $M_w = 280,000$ ($M_w/M_n = 6.5$).

Characterization of **6**

$^1\text{H-NMR}$ (CDCl_3 , δ): 3.54 (*br*, $\text{Ar}(\text{OCH}_3)_2$), 4.70 (*br*, $\text{ArCH}_2\text{-OAr'}$), 6.27 (*br*, *p*-H in $\text{C}_6\text{H}_3(\text{OMe})_2$), 6.37 (*br*, *o*-H in $\text{C}_6\text{H}_3(\text{OMe})_2$ and mid C_6H_3), 6.48 (*br*, *o*-H in inner C_6H_3), 6.50 (*br*, *o*-H in $\text{C}_6\text{H}_4(\text{C}\equiv\text{C})_2$), 6.80 (*br*, *o*-H in dendron-substituted $\text{C}_6\text{H}_2(\text{C}\equiv\text{C})_2$). UV/vis (THF): $\lambda_{\text{max}} = 278.6, 425.2$ nm. SEC analysis (THF, polystyrene standards): $M_w = 34,000$ ($M_w/M_n = 1.5$).

Measurements

The electronic absorption spectrum was recorded on a JASCO model V-560 spectrophotometer using a quartz cell of 1 cm path length.

Fluorescence and excitation spectra were recorded at designated temperatures, using a quartz cell of 1 cm path length, on a JASCO FP-777W spectrophotometer equipped with a temperature controller, and corrected for wavelength-dependent detector sensitivity and excitation light source output. All samples were degassed by five freeze-pump-thaw cycles and purged with Ar just before the measurements. The spectra were normalized to a constant absorbance at the excitation wavelength.

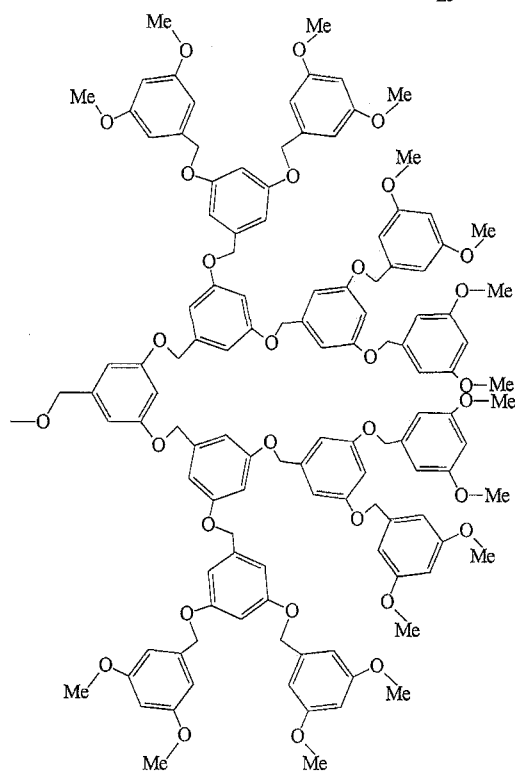
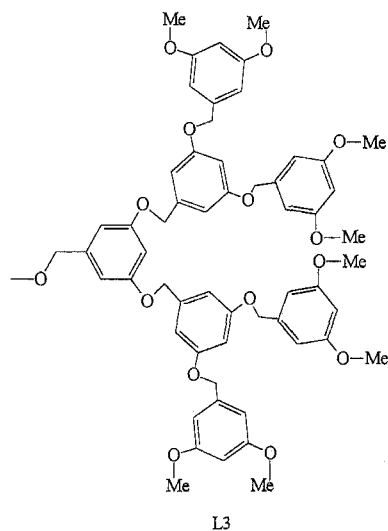
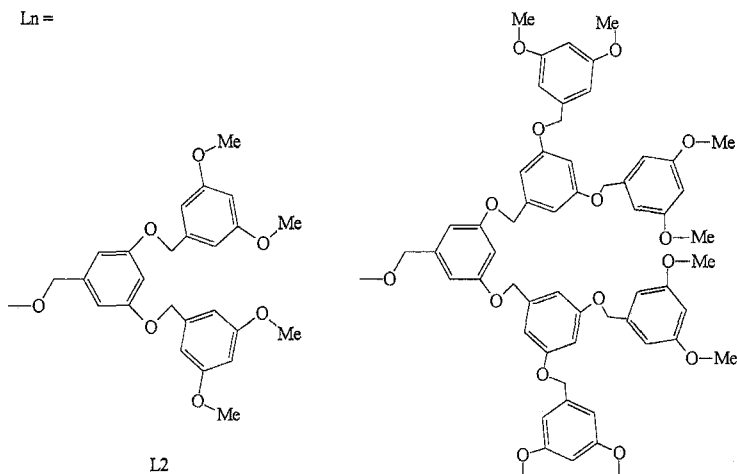
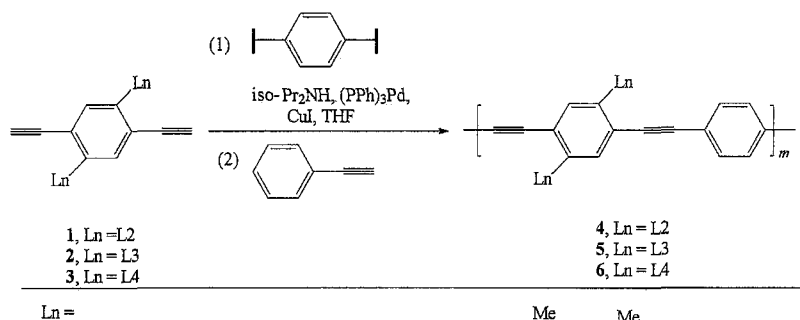
$^1\text{H-NMR}$ measurements were performed in CDCl_3 at 21°C on a JEOL GSX-270 spectrometer operating at 270 MHz, where the chemical shifts were determined with respect to CHCl_3 ($\delta = 7.28$).

Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Bruker model ProteinToF^{FTM} mass spectrometer using 9-nitroanthracene (9NA) as a matrix.

RESULTS AND DISCUSSIONS

As shown in Scheme 1, dendritic poly(phenyleneethynylene)s **4–6** were synthesized by a Pd(0)/Cu(I)-catalyzed polycondensation of dendritic monomers **1–3** with diiodobenzene in the presence of diisopropyl amine. As a matter of interest, the polycondensation was found to be highly dependent on the size of the dendrimer framework. In the cases of large dendritic monomers **2** and **3**, the polycondensations occur homogeneously and smoothly, whereas the smallest **1** afforded a large amount of yellow precipitate, even at an early stage of the polymerization for tens of minutes. SEC analyses of the polycondensation mixtures indicated that **4–6** thus prepared have quite different molecular weights. For example, **5** displayed a single peak in SEC, where the weight-average molecular weight (M_w) was evaluated to be 280,000 ($M_w/M_n = 6.5$) by SEC based on polystyrene standards. However, polymerization of the largest monomer **3** with diiodobenzene after even 4 weeks, affords a polymer with a much lower M_w of 3,4000 ($M_w/M_n = 1.5$), indicating that a large dendrimer framework resulted in a steric hindrance and thus prevent a smooth polymerization progress. In sharp contrast, a THF-soluble fraction of **4** is mainly oligomer with a M_w of 11,000 ($M_w/M_n = 1.5$).

The electronic absorption spectrum is informative of conjugation status in **4–6**. In THF at 21°C , dendritic monomer **1–3** showed a peak at 335 nm due to absorption of the diethynylbenzene unit, whereas the absorption maximum of the dendrimer framework was observed at 278 nm. The spectrum of monomer **3** is shown in Fig. 1. In comparison, a completely new absorption band appeared in the visible region (400–450 nm) for **4–6** families, while that of the dendrimer framework stayed at 278 nm. For example, the largest **6** (Fig. 1) displayed an absorption band due to the polymer backbone at 425 nm, which is 90 nm bathochromically shifted from that of **3**. A similar degree of red shift was also observed for one-generation smaller **5** (97 nm red shift) and the smallest **4** (90 nm red shift). These observations indicate that an extended conjugation chain in **4–6** is formed upon polycondensation of **1–3** with diiodobenzene.



Scheme 1 Schematic representations of dendritic monomers (1~3) and dendritic poly(phenyleneethynylene)s 4~6

Interestingly, the dendrimer frameworks in **4–6** function as a light-harvesting antenna, which transfers singlet excitation energy to the poly(phenyleneethynylene) backbone. As shown in Fig. 1, since the emission of dendrimer framework (L5OH, 310 nm) is partially overlapped with the absorption band of the dendritic poly(phenyleneethynylene) backbone functionality, the dendrimer frameworks in **4–6** have a chance to communicate photochemically with the poly(phenyleneethynylene) chain by energy transfer from the excited singlet state. As shown in Fig. 2, upon excitation of the dendrimer framework at 278 nm of **6**, no emission at 310 nm from dendrimer framework itself was observable; but only a fluorescence at 454 nm from poly(phenyleneethynylene) backbone was observed. Therefore, the strong poly(phenyleneethynylene) emission, observed for **6** upon 280 nm excitation, is obviously due to an intramolecular singlet energy transfer from the dendrimer framework to the poly(phenyleneethynylene) backbone (energy trap). The excitation spectrum of **6**, monitored at 454 nm, was very similar to the absorption spectrum, and the energy transfer quantum yield was evaluated to be approximately 100%. Similarly, upon 280 nm excitation of the dendrimer framework, **4** and **5** fluoresced only from the poly(phenyleneethynylene) backbones, again suggesting a high probability of intramolecular energy transduction from the dendrimer framework to the poly(phenyleneethynylene) backbone. In fact, the quantum yield of intramolecular energy transfer was also evaluated to be approximately 100% for **4** and **5**.

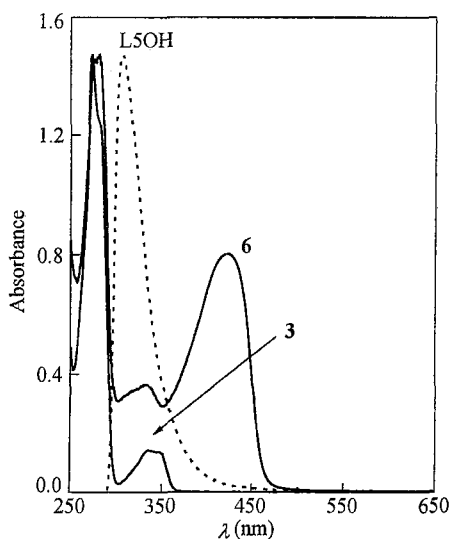


Fig. 1 Electronic absorption spectra of **3** and **6** in THF at 20°C

The dotted curve represents fluorescence of a five-layered benzylalcohol L5OH upon excitation at 278 nm in THF at 20°C.

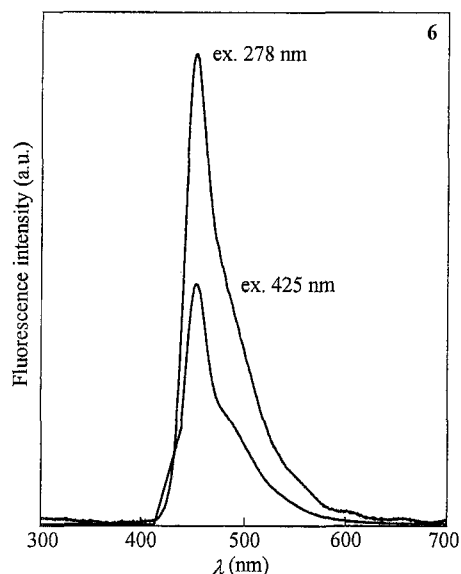


Fig. 2 Fluorescence spectra of **6** upon excitation of the dendrimer framework (278 nm) and the wire backbone (425 nm)

Quite interestingly, the dendrimer frameworks have a significant effect on the emission quantum yield of the poly(phenyleneethynylene) backbone. Upon 425 nm excitation at the conjugation backbone in a degassed THF ($\text{Abs}_{425\text{ nm}} = 0.06$) at 21°C, **6** emitted a brilliant blue light (Fig. 2) at 454 nm with a very high emission quantum yield of 0.97. On the contrary, under the same conditions, the smallest representative **4** also emitted at 454 nm, where the emission quantum yield was estimated to be only 0.44, typical of those of unshielded poly(phenyleneethynylene) derivatives (emission quantum yield: 0.35–0.40). Along this line, we excited a THF solution of one-generation larger **5**, and found that **5** fluoresced with an increased emission quantum yield of 0.83. Therefore, the exceptionally high emission quantum yield observed for **6** indicates that a large dendrimer framework could protect the conjugated backbone from collisional energy dissipation. As shown in Fig. 3, upon

excitation of the dendrimer framework at 278 nm in THF under the same conditions ($\text{Abs}_{425\text{ nm}} = 0.1$), the dendritic poly(phenylene-ethynylene)s 4~6 tended to display increasing fluorescence intensity with the size of the dendrimer framework, where the light-emitting activity of the largest 6 is about 11 times as high as that of the smallest 4. Therefore, the largest 6 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 blue emission.

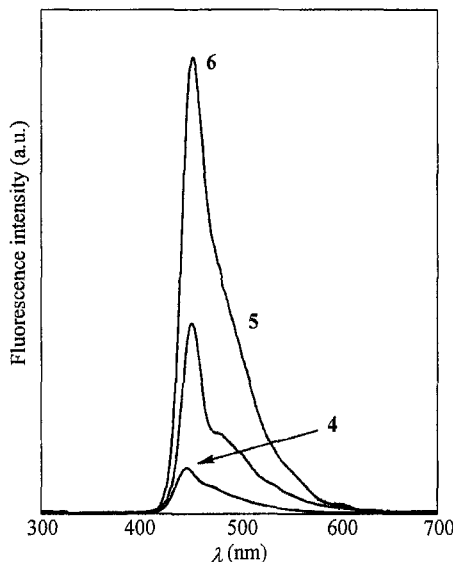


Fig. 3 Fluorescence spectra of 4~6, upon excitation at 278 nm in THF at 20°C, while the absorbance at 425 nm remains at 0.1 for all samples

CONCLUSION

We have synthesized a series of dendritic rods with poly(phenyleneethynylene) backbone, where the dendrimer framework serves as a light-harvesting antenna, which transfer excitation energy to the 4~6 backbones at a very high efficiency of unity. Dendritic poly(phenyleneethynylene) 6 with a large dendrimer framework displayed a strong resistance towards collisional energy dissipation, and showed very high fluorescence quantum yield ($\approx 100\%$) under certain conditions.

REFERENCES

- 1 Jiang, D.L. and Aida, T., *Chem. Commun.*, 1996, 1235
- 2 Tomoyose, Y., Jiang, D.L., Jin, R.H., Aida, T., Yamashita, T., Horie, K., Yashima, E. and Okamoto, Y., *Macromolecules*, 1996, 29: 5236
- 3 Jang, W.D., Jiang, D.L. and Aida, T., *J. Am. Chem. Soc.*, 2000, 122: 3232
- 4 Jiang, D.L. and Aida, T., *Nature*, 1997, 388: 454
- 5 Jiang, D.L. and Aida, T., *J. Am. Chem. Soc.*, 1998, 120: 10895
- 6 Wakabayashi, Y., Tokeshi, M., Jiang, D.L., Aida, T., Kitamori, T., *J. Luminescence*, 1999, 83: 313
- 7 Sato, T., Jiang, D.L. and Aida, T., *J. Am. Chem. Soc.*, 1999, 121: 10658