Efficient Energy Transfer Between Amphiphilic Dendrimers with Oligo(*p*-phenylenevinylene) Core Branches and Oligo(ethylene oxide) Termini in Micelles

Dong Wook Chang,[1] Seo-Yoon Bae,[2] Liming Dai,[3] Jong-Beom Baek[2]

[1]Department of Chemical Systematic Engineering, Catholic University of Daegu, 13-13, Hayang, Gyeongbuk 712-702, South Korea
[2]Interdisciplinary School of Green Energy/Low-Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology, 100, Banyeon, Ulsan 689-798, South Korea
[3]Department of Macromolecular Science and Engineering, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106
Correspondence to: Liming Dai (E-mail: liming.dai@case.edu) or Jong-BeomBaek (E-mail: jbbaek@unist.ac.kr)

ABSTRACT: The efficient fluorescence resonance energy transfer (FRET) between amphiphilic dendrimers with oligo(*p*-phenylenevinylene) core branches and oligo(ethylene oxide) termini have been observed in micelles. All dendrimers show the critical micelle concentration and lower critical solution temperature as well as fluorescent emission. Tailoring electronic structures of the conjugated amphiphiles for FRET have been conveniently achieved by varying the branch number and/or the conjugated core structure. The Stern-Volmer constants (K_{SV}) for FRET were found to be 4.51×10^{-5} and 8.78×10^{-5} M for Den 30–40 and Den 50–40, respectively. The effects external stimuli such as solvent and temperature on FRET have been also investigated. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: dendrimers; fluorescence; FRET; micelles; Stern-Volmer constants

INTRODUCTION Fluorescence resonance energy transfer (FRET) is a photophysical process, which involves the transfer of excited state energy from the initially excited donor (D) to an acceptor (A). A simultaneous quenching of donor fluorescence and enhancement of acceptor fluorescence can take place as a result of FRET.[1,2] The Coulomb interaction that leads to energy transfer is dipole-dipole interaction, which is strongly dependent on the distance between dipoles.[3] In addition to the distance between donor and acceptor, other factors also have significant contributions to the FRET process. The most important requirement for efficient energy transfer is resonance. The fluorescence spectrum of donor reveals the oscillation frequency of the exited donor dipoles, which should match the frequency of electronic transition of acceptor from ground state to excited state, that is, the absorption spectrum. If there is no resonance between donor in excited state and acceptor in ground state, the energy transfer is impossible.

FRET in various confined geometries, such as micelles, vesicles, clays, and zeolite, are specifically interesting.[4–7] This is because these systems can provide a high local concentration of chromophores and enhanced spatial proximity between donor and acceptor molecules associated with their well-organized structures to efficiently facilitate energy transfer.[8–12] In particular, FRET in micelles has been widely investigated due not only to their biological significance associated with the similarity between the micelles and biological membranes but also to the possible use of FRET as probes for micelle/membrane studies and biomedical imaging. Much effort has been focused on multicomponent micellar systems consisting of various host molecules such as surfactants, dendrimers, and guest molecules like dyes.[13–17] Although, π-conjugated molecules have several advantages for FRET,[18–20] only a few of studies have been reported on energy transfer between π-conjugated amphiphiles in aqueous medium as far as we are aware.[21,22] In most cases, totally different π-conjugated structures have often been used as donor and acceptor to realize FRET. In these approaches, multiple and complex synthetic steps are required and the FRET responses are somewhat complicated.[21,22]

Herein, we report efficient FRET between amphiphilic conjugated dendrimers in aqueous medium, **Den 30** (donor-1), **Den 50** (donor-2), and **Den 40** (acceptor), with oligo(*p*-phenylenevinylene) (OPV) cores and oligo(ethylene oxide) termini in micellar structure (Fig. 1). This strategy allows us to
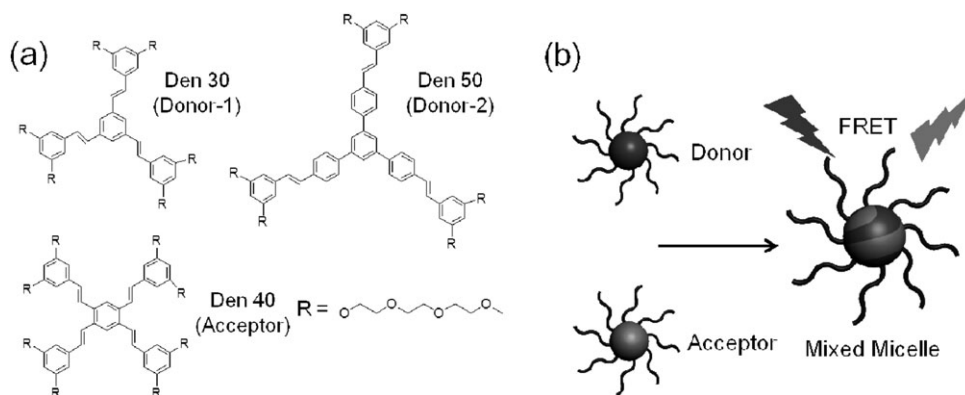
FIGURE 1 (a) Chemical structures of **Den 30, Den 50**, and **Den 40** and (b) schematic diagram of the formation of mixed micelle between donor and acceptor.

tailor electronic structures of the conjugated amphiphiles by using simple synthetic approaches like variation of the branch number and/or the conjugated core structure. The amphiphilic nature and structural similarity could easily promote the formation of a micelle-like confined geometry between donor and acceptor to further enhance FRET. As a result, efficient FRET has been achieved between these conjugated amphiphiles, although their spectral overlapping is not so significant. Furthermore, we have also investigated their unique FRET responses to external stimuli, such as solvents and temperature.

We have previously demonstrated that amphiphilic dendrons and dendrimers (**Den 30** and **Den 40**) with OPV core branches and oligo(ethylene oxide) termini have unique solvatochromic and stimuli responsive properties.[23,24] **Den 50** is newly synthesized and the detailed synthetic procedures were shown in Scheme 1. Above the critical micelle concentration (CMC) in aqueous solvent, these amphiphilic dendrons can form aggregated structures.[23,24] The CMC values

of **Den 30, Den 50**, and **Den 40** are 1.01×10^{-6}, 0.78×10^{-6}, and 2.14×10^{-6} M, respectively (Table 1). They also show typical lower critical solution temperature (LCST) behavior as the solubility of triethylene oxide end groups decreases with increasing temperature.[24]

EXPERIMENTAL

Materials and Equipments

The synthesis and characterization of **Den 30**, **Den 40**, and **3** have been previously reported.[24] The detailed synthetic procedures of **Den 50** are shown in Scheme 1. Hydrophobic dendritic core **1** and **2** were synthesized following the literature procedure.[26,27] All reagents and solvents were used as received from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VNMRS spectrometer at 600 and 150 MHz, respectively. UV–vis spectra were recorded on a Perkin-Elmer Lambda 900 UV–vis-NIR spectrometer, while photoluminescence (PL) emissions were measured on a Perkin-Elmer LS 55 spectrometer. An external circulation (Lauda RE 206) bath was used to control temperatures (± 0.02 °C) for PL spectrometers. Atomic force microscopy (AFM) analysis was conducted with a Veeco Multimode V using a silicone cantilever in a tapping mode. The samples of mixed micelles with **Den 30** and **Den 40** for AFM measurement were prepared by drop casting of aqueous solution on mica. The
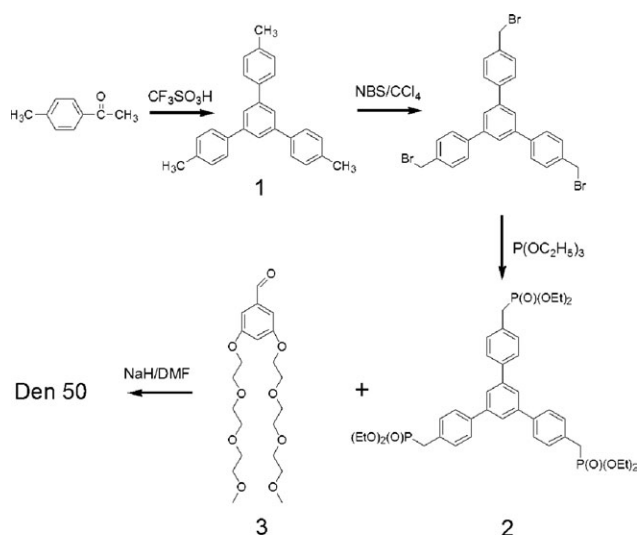
SCHEME 1 Procedures for synthesis of amphiphilic dendrimer (**Den 50**).

TABLE 1 Optical Properties and Critical Micelle Concentration (CMC) of **Den 30**, **Den 50**, and **Den 40** in Aqueous Medium

	UV–vis[a] (nm, ε:mol^{-1} cm^{-1})	PL[a,b] (nm)	Quantum Yield (%)[c]		CMC (10^{-6} M)
			Water	THF	
Den 30	310, 38650	400	0.05	0.35	1.01
Den 50	328, 40740	430	0.10	0.72	0.78
Den 40	330, 44450	460	0.20	0.27	2.14

[a] Obtained from aqueous solution.
[b] Excitation wavelength is 310 nm.
[c] Quinine sulfate was used as a standard reference with $\Phi = 0.51\%$ in 0.1 N sulfuric acid.[25]

energy transfer studies were done by taking the emission spectra of the solution at a series of acceptor concentration and comparing steady state PL intensities. The mixed micelles with various ratios of donor/acceptor were prepared via two step procedure. First, the concentrated stock solution of donor and acceptor are made in THF, which is good solvent for all amphiphiles. The stock solutions were protected from ambient light until use. The aliquots of donor and acceptor solutions were mixed to get homogenous phase of donor and acceptor in normal quartz cuvette with a 1 cm path length and 3.5 mL volume. Then predetermined large amount of water (95–99, v/v %) was injected into homogeneous THF solution with vigorous stirring for several minutes. The mixtures were directly used for UV–vis and PL measurement. The excitation wavelength for PL measurement was 310 nm. For temperature variation experiments, cuvettes were sealed with PTFE cover to minimized evaporation of solvents.

Synthesis

1,3,5-Tris(p-tolyl)benzene (1)

A mixture of 4-methylacetophenone (67.09 g, 0.50 mol) and trifluoromethanesulfonic acid (0.5 mL) in 350 mL anhydrous toluene was refluxed with Dean-Stark trap for the removal of water as a byproduct.[26] After 20 h, an additional 0.5 mL of trifluoromethanesulfonic acid added and then reflux continued for 60 h. The solvent was concentrated and subsequent cooling to room temperature led to products 1. (24.44 g, 42% yield) ^{1}H NMR (300 MHz, CDCl$_3$, ppm) δ: 2.42 (s, 9H), 7.28 (d, $J = 7.9$ Hz, 6H), 7.60 (d, $J = 7.9$ Hz, 6H), and 7.73 (s, 3H). ^{13}C NMR (300 MHz, CDCl$_3$, ppm) δ: 142.3, 138.5, 137.4, 129.7, 127.3, 124.7, and 21.3.

1,3,5-Tris(p-(diethoxyphosphonylmethyl)phenyl)benzene (2)

A mixture of 1 (5.00 g, 14.35 mmol), N-bromosuccinimide (7.66 g, 43.04 mmol) and catalytic amount of AIBN (10 mg) in dry tetrachloromethane (200 mL) was refluxed for overnight.[27] After cooling, succinimide was removed by filtration and the organic phase was washed with water. Then, the organic solvent was removed by rotary evaporation. Subsequent recrystallization in methanol with small amount of chloroform led to crystalline tribromo-compound (3.61 g, 6.16 mmol), which was heated, together with an excess quantity of triethyl phosphite (8.19 g, 49.28 mmol), for 5 h at 160 °C. Finally, the excess triethyl phosphite was removed by distillation to yield 2 as yellowish viscous oil. (4.67 g, 43% yield). ^{1}H NMR (300 MHz, CDCl$_3$, ppm) δ: 1.28 (t, $J = 7.0$ Hz, 18 H), 3.22 (d, $J = 21.9$ Hz, 6H), 4.06 (m, 12H), 7.42 (dd, $J = 8.2, 2.4$ Hz, 6H), 7.66 (d, $J = 7.7$ Hz, 6H), 7.76 (s, 3H) ^{13}C NMR (300 MHz, CDCl$_3$, ppm) δ:141.8, 139.6, 139.5, 131.0, 130.3, 127.4, 124.8, 62.2, 62.1, 34.3, 32.5, and 16.4.

1,3,5-Tris(4-{3,5-bis{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}styryl}phenyl)benzene (Den 50)

The compound 2 (0.40 g, 0.53 mmol) was dissolved in 5 mL of dry DMF under high purity argon. Two equivalent of NaH (60% dispersion in mineral oil; 0.13 g, 3.17 mmol) and 3,5-di(methyltriglycoloxy)benzaldehyde 3 (0.68 g, 1.59 mmol) were added consecutively. The reaction mixture was then refluxed for 1 h. After cooling to room temperature, it was neutralized by 1N HCl and extracted with CHCl$_3$. The organic layer was then washed with brine and dried over MgSO$_4$. After solvent evaporation, the residue was subjected to column chromatography using ethyl acetate/methanol (80/20) to produce Den 50 as yellow viscous oil (0.45 g, 54% yield). ^{1}H NMR (300 MHz, CDCl$_3$, ppm) δ: 3.39 (s, 18H), 3.56 (m, 12H), 3.66–3.78 (m, 36H), 3.88 (t, $J = 4.8$ Hz, 12H), 4.17 (t, $J = 4.8$ Hz, 12H), 6.45 (t, $J = 2.1$ Hz, 3H), 6.73 (d, $J = 1.9$ Hz, 6H), 7.11 (d, $J = 5.5$ Hz, 6H), 7.62 (d, $J = 8.4$ Hz, 6 H), 7.73 (d, $J = 8.4$ Hz, 6H), and 7.83 (s, 3H). ^{13}C NMR (300 MHz, CDCl$_3$, ppm) δ: 160.1, 141.9, 140.2, 139.2, 136.6, 128.9, 128.6, 127.6, 127.1, 105.6, 101.4, 71.9, 70.9, 70.7, 70.6, 69.7, 67.5, and 59.0. MALDI-TOF MS 1607.89 m/z [M + Na]$^+$ (calcd: 1584.82 m/z [M]$^+$). Elem. Anal.: calcd for C$_{90}$H$_{120}$O$_{24}$, C 68.2, H 7.6, O 24.2; found, C 68.2 H 7.6 O 24.3.

RESULTS AND DISCUSSION

Synthesis

As can be seen in Scheme 1, Wohl-Ziegler bromination of hydrocarbons and Arbusov rearrangement reactions were performed for the synthesis of the dendritic core 2. The spectroscopic results were well matched with literature reports.[26,27] Finally, the Honer-Wadsworth-Emmons coupling reaction was used to attach the aldehyde-functionalized periphery 3 onto the core 2, resulting in the formation of Den 50 (Scheme 1). These newly synthesized Den 50 also showed strong fluorescent emission which originated from the OPV core branches whilst their oligo(ethylene oxide) terminal chains impart a good solubility for the whole dendritic molecules in water and other common organic solvents (e.g. ethanol, chloroform, and THF).

The Spectroscopic Study

The basic photophysical properties of amphiphilic dendrimers were studied in aqueous medium by using UV–vis and PL spectroscopy [Fig. 2(a)] and their numerical values were summarized in Table 1. As observed in Figure 2(a), the increase in the number of branches from Den 30 to Den 40 leads to bathochromic shifts for both absorption and fluorescence peaks. Photoexcitation of pure solutions of Den 30 and Den 40 at $\lambda_{ex} = 310$ nm revealed the intense fluorescence peak maxima at $\lambda_{em} = 400$ and 460 nm, respectively. The spectral overlap between fluorescence of Den 30 (donor-1) and absorption of Den 40 (acceptor), which is indispensable for FRET, was also observed [Fig. 2(a)]. As shown in Figure 2(b), donor and acceptor in a mixture solution (designated as: Den 30–40) in aqueous medium showed no detectable change in their respective spectroscopic features. Thus, the electronic absorption spectra of donor in aqueous solution were not affected by the presence of acceptor or vice versa. However, fluorescence spectra of the mixed micelles of Den 30–40 excited at 310 nm in an aqueous medium showed a significant decrease in donor luminescence at 400 nm with a concomitant increase in the emission of acceptor [Fig. 2(c)]. This result is an indication of FRET from donors to acceptor. On the contrary, in case of THF solution in which both donor and acceptor are well
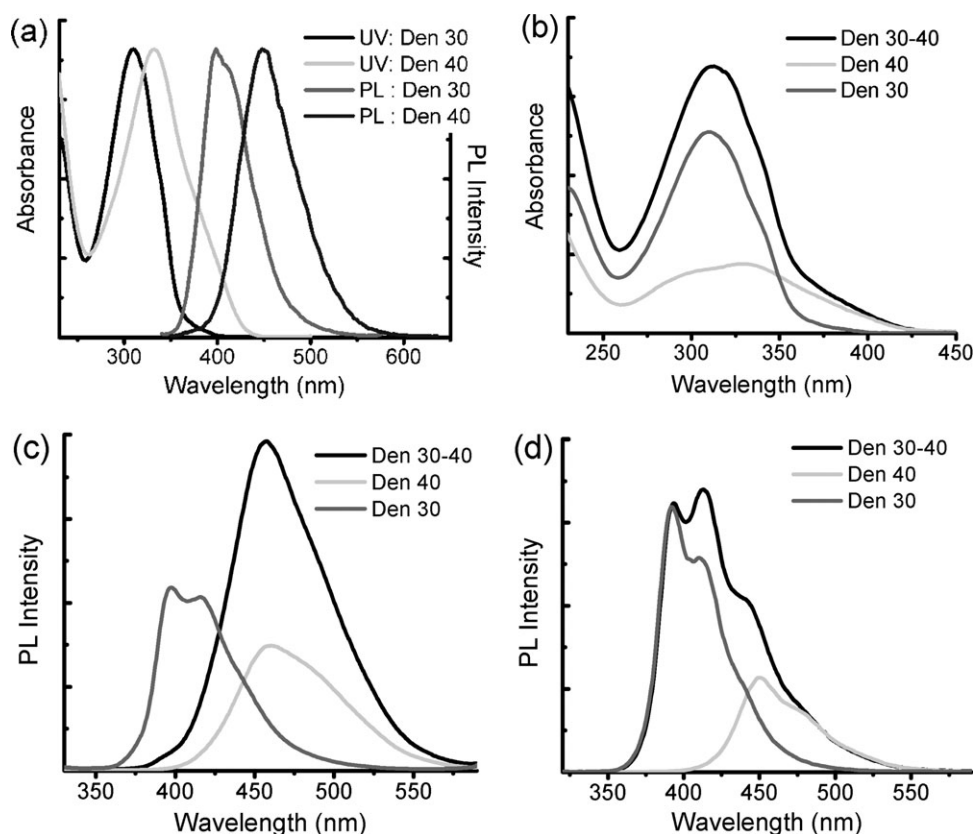
FIGURE 2 (a) Normalized UV–vis and PL spectra of **Den 30** and **Den 40** in water, (b) UV–vis spectra of **Den 30**, **Den 40**, and **Den 30-40** in water. PL spectra of **Den 30**, **Den 40**, and **Den 30-40** in (c) water and (d) THF. The concentration of **Den 30** and **Den 40** are 6.65×10^{-6} and 5.13×10^{-6} M, respectively.

soluble into molecular level, the emission of donor was not altered by the presence of acceptor, revealing that no energy transfer from donor to acceptor occurred in THF [Fig. 2(d)]. These results indicate that the formation of aggregated (e.g., in water) structures between donor and acceptor is the key factor for efficient FRET, which depends strongly on the distance between donor and acceptor. Similar results were obtained between **Den 50** (donor-2) and **Den 40** (acceptor) except absorption and emission of **Den 50** is more red-shifted than that of **Den 30** (Fig. 3). In **Den 50**, the core of amphiphilic dendrimer has been changed into a more rigid structure (Scheme 1).

Effect of Concentration on FRET

The efficiency of energy transfer is also dependent on molar ratio of donor and acceptor. Mixed micelles with various donor/acceptor ratios were prepared. As can be seen in Figure 4(a), the fluorescence of **Den 30** (donor-1) was gradually decreased with increasing **Den 40** (acceptor) concentrations, showing an isobestic point near 420 nm [Fig. 4(a)]. As shown in Figure 3(b), similar results were also observed in **Den 50** (donor-2) and **Den 40** (acceptor). Typically, the concentration of acceptor was increased from 0 to 3.41×10^{-6} M with the fixed concentration of donors at 8.60×10^{-6} M. Stern-Volmer analysis was a useful method of presenting data for the energy transfer according to following equation,

$PL_0/PL = 1 + K_{SV}[Q]$,[21,22,28] where PL_0 and PL represent the fluorescence intensity of the donor in the absence of acceptor and in the presence of acceptor, respectively, and [Q] is the acceptor concentration. The quenching rate constant, K_{SV}, could be calculated from the Stern-Volmer relation, showing that linear dependence was observed at lower acceptor concentration and it was saturated at higher concentration [Fig. 4(c)]. A linear region in Stern-Volmer plots indicated that only one type of quenching could occur in mixtures.[2] From the slope of the linear region in Stern-Volmer plots, the quenching rate constant K_{SV} values of 4.51 and 8.78×10^5 M^{-1} were calculated for **Den 30–40** and **Den 50–40**, respectively. The higher K_{SV} value in FRET observed for **Den 50** can be attributed to higher quantum efficiencies and more hydrophobic conjugated core lowering CMC. The efficiency of energy transfer can be also determined from the following relationship, $\Phi = 1 - PL/PL_0$,[13] where PL_0 and PL represent the fluorescence intensity of the donor in the absence and presence of acceptor, respectively. As shown in Figure 4(d), the efficiencies of energy transfer for **Den 30-40** and Den **50-40**, can be reached up to 59 and 75%, respectively. This high energy-transfer efficiency of **Den 50-40** is comparable with that of diblock conjugated polymer in film containing donor and acceptor in one molecule.[19] In addition, Förster's radius (R_o) can be calculated from a few experimental parameters.[29]
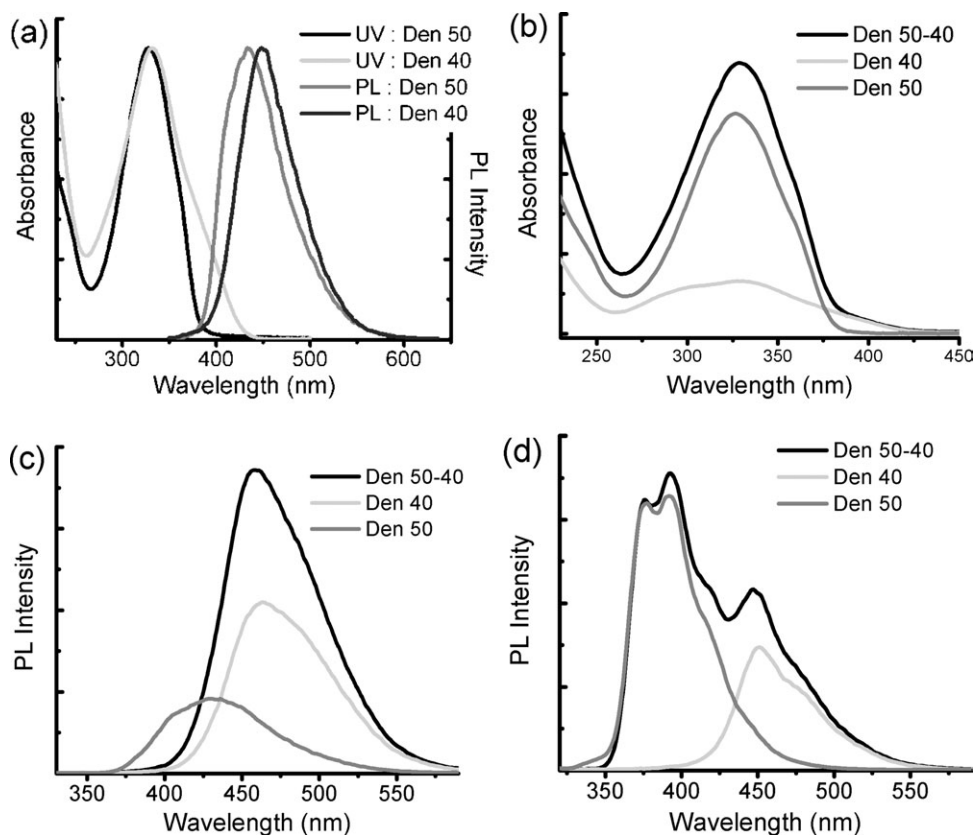
FIGURE 3 (a) Normalized UV–vis and PL spectra of **Den 50** and **Den 40** in water, (b) UV–vis spectra of **Den 50**, **Den 40**, and **Den 50-40** in water. PL spectra of **Den 50**, **Den 40**, and **Den 50-40** in (c) water and (d) THF. The concentration of **Den 50** and **Den 40** are 6.67 and 5.13 × 10^{-6} M, respectively.
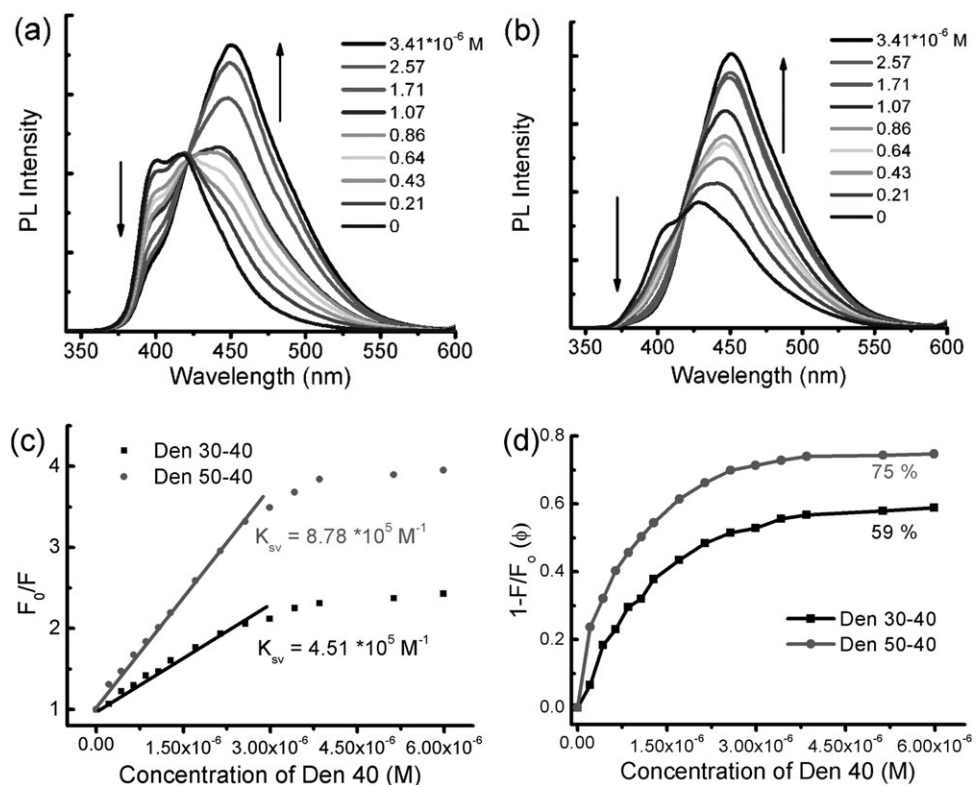

FIGURE 4 PL spectra of (a) **Den 30-40**, (b) **Den 50-40**, and (c) Stern-Volmer plot of **Den 30-40** and **Den 50-40** with different concentration of **Den 40** (acceptor). (d) Plots of energy transfer efficiency (φ) of Den 30-40 and Den 50-40. The concentrations of **Den 30** and **Den 50** were fixed at 8.60 × 10^{-6} M and the concentration of **Den 40** was varied from 0 to 6.00 × 10^{-6} M.
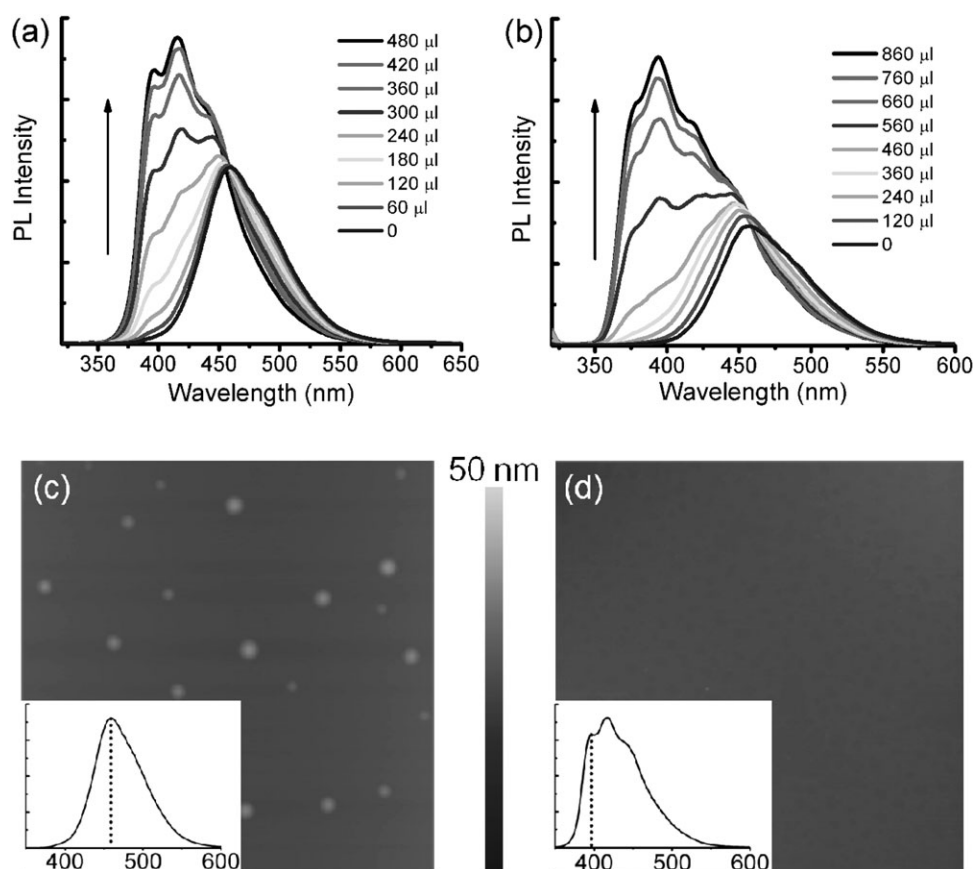
FIGURE 5 PL spectra of (a) **Den 30-40** and (b) **Den 50-40** in water with a consecutive adding of THF. The concentration of **Den 30**, **Den 50**, and **Den 40** were 8.60×10^{-6}, 8.60×10^{-6}, and 5.26×10^{-6} M, respectively. AFM images of mixed micelles, **Den 30-40**, (c) before and (d) after addition of THF. The scanning areas of both are 10×10 μm. Insets in Figure (c, d) represent the related PL emission spectra. The concentration of **Den 30** and **Den 40** for AFM images are 0.53 and 0.22 mM, respectively.

$$R_o^6 = \frac{(8.8 \times 10^{-25})\kappa^2\Phi_D}{n^4} \int_0^\infty f_D(v)\varepsilon_A(v)\frac{dv}{v^4}$$

The integral, known as the overlap integral, is a measure of the spectral overlap of the fluorescence of donor and the absorption spectrum of acceptor. The v represents units of frequency in wavenumber (cm^{-1}). The $\varepsilon_A(v)$ is the molar decadic extinction coefficient and the n is the refractive index of solvent. The K^2 is a constant that reflects the relative orientation of the electronic dipole. A value of 2/3 is normally taken for molecules that are rotating much faster than the energy transfer rate. From above equation, the critical radius of Den **30-40** and Den **50-40** mixtures are 2.64 and 2.83 nm, respectively.

Cosolvent Effect on FRET
FRET in micelle is quite sensitive to solvents, which can cause drastic changes in their aggregation state. Thus, we can expect that the change of solvent polarity can also make large differences in micelle structures of aggregates in solution. THF is a good solvent for all the amphiphiles studied in this work and can well separate donors from acceptors. We

investigated the effects of solvent on FRET by a consecutive addition of THF droplets to a pre-formed aqueous solution of mixed micelle. As the amount of THF increased, the suppressed fluorescence of donors by FRET at 400 nm was gradually restored to their original intensity with an isobestic points at 450 nm [Fig. 5(a, b)]. These results showed that the solvent polarity has a strong influence on the aggregated structure of amphiphilic dendrimers and the efficiency of energy transfer. AFM images shown in Figure 5(c, d) confirmed the changes in micellar structures of mixed micelles, **Den 30-40**, upon addition of THF. When the mixed micelles were generated, in which the emission from acceptor is prominent via efficient FRET, AFM image showed the globular micelles with bigger size [Fig. 5(c)]. However, the mixed micelles were completely disappeared, when THF was added until the emission of donor was almost restored [Fig. 5(d)].

Effects of Temperature on FRET
All amphiphilic dendrimers show unique LCST behavior in aqueous medium due to a polar–nonpolar transition of triethylene oxide periphery at elevated temperature, which results in the diminished solubility of it with increasing temperature.[24] Both solutions of individual and mixed micelles in aqueous solution become turbid above cloud point as a
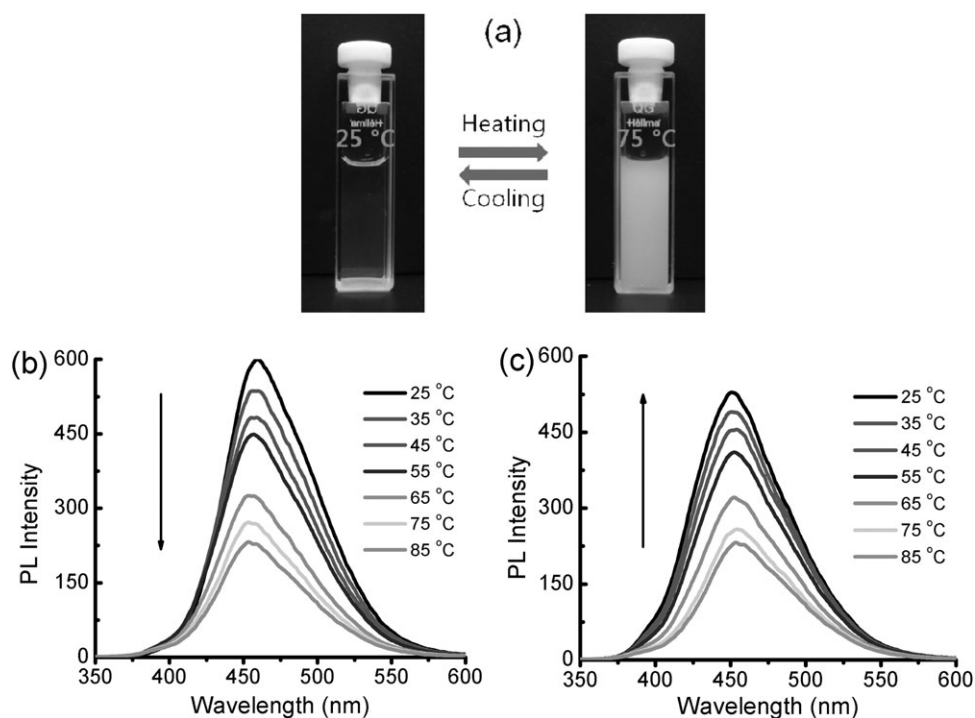
FIGURE 6 (a) Reversible LCST behavior of mixed micelles composed of **Den 30** and **Den 40**. The concentrations of **Den 30** and **Den 40** are 0.53 and 0.22 mM, respectively. Fluorescence spectra of **Den 30-40** in aqueous medium during (b) heating and (c) cooling. The concentrations of **Den 30** and **Den 40** were 8.60×10^{-6} and 6.00×10^{-6} M, respectively.

result of aggregation [Fig. 6(a)]. The fluorescence of amphiphilic dendrimers was quenched at elevated temperature, because nonradiative decays were developed by the formation of aggregates.[24] To study the stability of mixed micelles, repeated heat and cooling treatments in aqueous solution were performed, followed by fluorescence measurements. **Den 30-40** showed a sharp decrease in the fluorescence peak centered at 460 nm with increasing temperature; however, the PL intensity is almost recovered with decreasing temperature [Fig. 6(b, c)]. The similar trend has also been obtained from **Den 50-40** (data not shown). Thus, the mixed micelles composed of amphiphilic dendrimers, **Den 30**, **Den 50**, and **Den 40**, are relatively stable at repeated heating and cooling processes. The persistence of FRET during the repeated heating-cooling cycles indicates that the micellar structure remained unchanged with individual constituent chains changing their conformations in response to the temperature change.

CONCLUSIONS

We have studied the micellar formation of amphiphilic dendrimers of OPV cores and oligo(ethylene oxide) termini and demonstrated efficient FRETs between these amphiphilic dendrimers with different core and terminal structures in micelles. The confined micellar geometries, coupled with the tailor-made amphiphilic dendrimers, allow us to regulate their optoelectronic properties with and without external stimuli, such as solvent nature and temperature. Thus, this study provides important insights into the design of new conjugated macromolecules with controllable molecular and micellar structures, and hence tunable FRET for potential for biomedical applications (e.g., as optical probes for membrane studies and biomedical imaging).

REFERENCES AND NOTES

1 Förster, T. *Ann. Phys.* **1948,** *2*, 55–75.

2 Lakowicz, R. Principles of Fluorescence Spectroscopy, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, **1999.**

3 Atkins, P. W. Physical Chemistry, 4th ed; Oxford University Press, Oxford, **1990.**

4 Leong, K.; Scales, P. J.; Healy, T. W.; Boger D. V.; Buscall, R. *J. Chem. Soc. Faraday Trans.* **1993,** *89*, 2473–2478.

5 Kalyansundaram, K. *Chem. Soc. Rev.* **1978,** *7*, 453–472.

6 Thomas, J. J. *J. Phys. Chem.* **1987,** *91*, 267–276.

7 Berleram-Santos, M. N.; Prieto, M. J. E. *J. Chem. Soc. Faraday Trans.* **1987,** *83*, 1391–1410.

8 Koglin, P. K. F.; Miller, D. J.; Steinwandel, J.; Hauser, M. *J. Phys. Chem.* **1981,** *85*, 2363–2366.

9 Kaschke, M.; Kittlemann, O.; Vogler, K.; Graness, A. *J. Phys. Chem.* **1988,** *92*, 5998–6003.

10 Nakashima, K.; Liu, Y. S.; Zhang, P.; Duhamel, J.; Peng, J.; Winnik, M. A. *Langmuir* **1993,** *9*, 2825–2831.

11 Ballet, P.; Auweraer, M.; De Schryver, F. C.; Lemmetyien, H.; Vuorimaa, E. *J. Phys. Chem.* **1996,** *100*, 13701–13715.

12 Yekta, A.; Winnik, M. A.; Farinha, J. P. S.; Martinho, J. M. G. *J. Phys. Chem. A* **1997,** *101*, 1787–1792.

13 Chatterjee, S.; Nandi, S.; Bhattacharya, S. C. *J. Photochem. Photobiol. A* **2005,** *173*, 221–227.

14 Oliveira, H. P. M.; Gehlen, M. H. *Chem. Phys.* **2003,** *290*, 85–91.

15 Cramb, D. T.; Beck, S. C. *J. Photochem. Photobiol. A* **2000,** *134*, 87–95.

16 Frauchiger, L.; Shirota, H.; Uhrich, K. E.; Castner, E. W. *J. Phys. Chem. B* **2002,** *106*, 7463–7468.

17 Schenning, A. P. J.; Peeters, E.; Meijer, E. W.; *J. Am. Chem. Soc.* **2000,** *122*, 4489–4495.

18 Hohloch, M.; Mössmer, C. M.; Hanack, M. *Chem. Mater.* **1998,** *10*, 1327–1332.

19 Grey, J. K.; Kim, D. Y.; Lee, Y. J.; Gutierrez, J. J.; Luong, N.; Ferraris, J. P.; Barbara, P. F. Angew. Chem. Int. Ed. **2005,** *44*, 6207–6210.

20 Hoeben, F. J. M.; Herz, L. M.; Daniel, C.; Jonkheijim, P.; Schenning, A. P. H. J.; Silva, C.; Meskers, S. C. J.; Beljonne, D.; Phillips, R. T.; Friend, R. H.; Meijer, E. W. Angew. Chem. Int. Ed. **2004,** *43*, 1976–1979.

21 Stork, M.; Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *Adv. Mater.* **2002,** *14*, 361–366.

22 Liu, B.; Gaylord, B. S.; Wang, S.; Bazan, G. C. *J. Am. Chem Soc.* **2003,** *125*, 6705–6714.

23 Ding, L.; Chang, D. W;. Dai, L.; Ji, T.; Li, S.; Lu, J.; Tao, Y.; Delozier, D.; Connell, J. *Macromolecules* **2005,** *38*, 9389–9392.

24 Chang, D. W.; Dai, L. *J. Mater. Chem.* **2007,** *17*, 364–371.

25 Demas, N.; Crosby, G. A. *J. Phys. Chem.* **1971,** *75*, 991–1024.

26 Kim, Y. H.; Beckerbauer, R. *Macromolecules* **1994,** *27*, 1968–1971.

27 Brunel, J.; Mongin, O.; Jutand, A.; Ledoux, I.; Zyss, J.; Desce, M. B. *Chem. Mater.* **2003,** *15*, 4139–4148.

28 Stern, O.; Volmer, M. Z. *Phys.* **1919,** *20*, 183–188.

29 Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W.E. *J. Phys. Chem. B* **2004,** *108*, 1537–1543.