Luminescent amphiphilic dendrimers with oligo(*p*-phenylene vinylene) core branches and oligo(ethylene oxide) terminal chains: syntheses and stimuli-responsive properties†

Dong Wook Chang and Liming Dai*

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A class of new dendrimers consisting of hydrophobic oligo(*p*-phenylene vinylene) core branches and hydrophilic oligo(ethylene oxide) terminal chains was synthesized. These amphiphilic dendritic molecules are highly luminescent and exhibit critical micellization behaviors. They also show a lower critical solution temperature (LCST) in an aqueous medium. Both the critical micelle concentration (CMC) and LCST increased with increasing branch number and the ratio of the hydrophilic oligo(ethylene oxide) to hydrophobic oligo(*p*-phenylene vinylene) moieties. Besides, a temperature-dependent phase transition from a clear to cloudy aqueous solution was observed. The temperature-induced phase transition was also reflected by fluorescence quenching, ^{1}H NMR resonance peak broadening, and UV–vis absorption shift arising from the hydrophobic conjugated core. These changes in the phase structure and photophysical properties were demonstrated to be highly reversible, indicating some interesting stimuli-responsive behaviors.

Introduction

A stimuli-responsive molecule is one that changes its physical structure and/or property in a controllable, reproducible, and reversible manner in response to an external stimulus (*e.g.* temperature, pH).[1] These stimuli-responsive changes can be utilized to create a large variety of smart devices, including sensors, actuators, and controlled release systems, for various practical applications.[1] As illustrated by the temperature-induced helix–coil transition of polypeptides,[2] biomacromolecules can respond to small alterations in an external variable with very dramatic conformational/property changes. Although stimuli-responsive biomacromolecules have attracted a great deal of interest for many years, it is the recent effort to exploit synthetic stimuli-responsive (macro)molecules.[1] Among them, amphiphilic diblock copolymers, such as poly(*N*-isopropylacrylamide)-*block*-poly(ethylene oxide), PNIPAM-*b*-PEO, can self-assemble into shell–core architectures by changing temperature, solvent composition, ionic strength, and/or pH.[1] While both PNIPAM and PEO blocks are hydrophilic and dissolve in water at room temperature, PNIPAM becomes hydrophobic and undergoes a "coil-to-globule" transition at temperatures higher than 32 °C, leading to the formation of self-assembled shell–core polymer nanoparticles consisting of a PNIPAM core and a PEO shell.[3] Apart from the temperature-induced inter- or intra-molecular structure/phase changes, similar changes can also occur in response to other stimuli. For instance, a micellization–dissociation transition can be induced by concentration changes around the critical micelle concentration (CMC).[4,5]

Dendrimers with a tree-like, monodispersed, three-dimensional globular architecture[5,6] would provide additional advantages for constructing stimuli-responsive molecular architectures.[6–10] Just like certain stimuli-responsive amphiphilic diblock copolymers, the amphiphilic dendritic molecules with hydrophobic oligo(*p*-phenylene vinylene), OPV, core branches and hydrophilic oligo(ethylene oxide), OEO, terminal chains synthesized in the present study (Fig. 1) are potential responsive materials in response to concentration and/or temperature changes. Indeed, we found these amphiphilic dendrimers showed a lower critical solution temperature (LCST) and critical micellization behavior. As a consequence, temperature- and concentration-responsive photophysical property changes (*e.g.* UV–vis, PL) were observed for these conjugated dendritic molecules. In this paper, we report the synthesis and stimuli-responsive properties of these new amphiphilic dendritic molecules (designated as: **Den 20**, **Den 30** and **Den 40** in Fig. 1).

Experimental

Materials and characterization

3,5-Dihydroxy benzaldehyde was used as received from Alfa Aesar. Tetrahydrofuran (THF) and dimethylformamide (DMF) from Aldrich were purified, according to the standard procedure.[11] Mesitylene, 1,2,4,5-tetramethyl benzene, *N*-bromosuccinimide, azobisisobutyronitrile (AIBN), diethyl azodicarboxylate (DEAD), tri(ethylene glycol) monomethyl ether, triethyl phosphite, tetrachloromethane, and analytical grade *p*-xylene were all used as received from Aldrich.

Departments of Chemical and Materials Engineering and Chemistry, School of Engineering and UDRI, University of Dayton, 300 College Park, Dayton, OH 45469, USA. E-mail: ldai@udayton.edu

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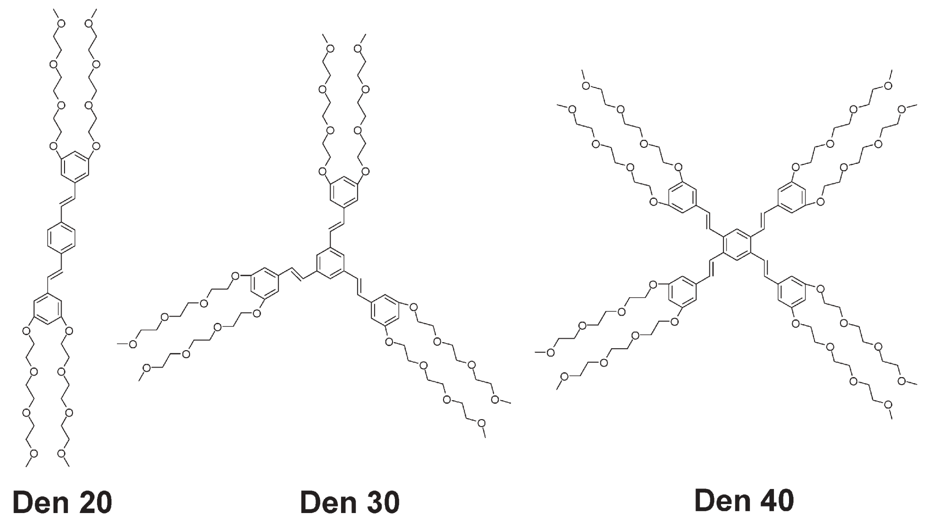


Fig. 1 Molecular structures for amphiphilic dendrimers with oligo(*p*-phenylene vinylene) core branches and oligo(ethylene oxide) terminal chains.

Deuterium oxide containing 0.05 wt% 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as reference for NMR studies was obtained from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz. UV–vis spectra were recorded on a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer, while photoluminescence emissions were measured on a Perkin-Elmer LS 55 spectrometer. An external circulation (Lauda RE 206) bath was used to control temperatures ($\pm$0.02 °C) for both the UV/VIS/NIR and PL spectrometers. All the optical measurements were carried out with the samples under argon and protected from light as much as possible to avoid unnecessary photo-oxidation. Surface tensions and the critical micelle concentration (CMC) were measured using a dataphysics DCAT 11 tensiometer at 25 °C with a Du-Noüy-ring. Atomic force microscopic (AFM) images were recorded by a silicon cantilever in a tapping-mode on a Dimension 3100 AFM with a Nanoscope 5 controller. Elemental analyses were conducted by Atlantic Microlab Inc.

Syntheses

1,4-Bis(diethoxyphosphinylmethyl)benzene (1)[12]. A mixture of *p*-xylene (3.00 g, 28.26 mmol), *N*-bromosuccinimide (10.17 g, 56.50 mmol) and a catalytic amount of AIBN (10 mg) in dry tetrachloromethane (200 ml) was refluxed overnight. 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 led to a white crystalline dibromo-compound (4.33 g, 16.39 mmol), which was heated, together with an excess quantity of triethyl phosphite (15.36 g, 92.54 mmol), for 5 h at 160 °C. Finally, the excess triethyl phosphite was removed by distillation to yield **1** as a white crystalline solid (5.24 g, 49%). Mp: 74–75 °C,[12] ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 1.22–1.27 (t, J = 7.1 Hz, 12H), 3.10–3.17 (d, J = 20.2 Hz, 4H), 3.99–4.04 (m, 8H), 7.26 (s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) δ: 130.0, 129.8, 62.0, 34.1, 32.3, 16.2. FT-IR (KBr, cm^{-1}): 2983, 2909, 1514, 1479, 1444, 1393, 1368, 1246, 1163, 1097, 1027, 965, 864.

1,3,5-Tris(diethoxyphosphinylmethyl)benzene (2)[12,13]. A mixture of mesitylene (6.00 g, 49.92 mmol), *N*-bromosuccinimide (26.95 g, 149.75 mmol) and a catalytic amount of AIBN (20 mg) in dry tetrachloromethane (300 ml) was refluxed overnight. 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 petroleum ether led to a white crystalline tribromo-compound (8.91 g, 24.96 mmol), which was heated, together with an excess quantity of triethyl phosphite (29.88 g, 240 mmol), for 5 h at 160 °C. Finally, the excess triethyl phosphite was removed by distillation to yield **2** as a yellowish viscous oil. (11.87 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 1.23–1.28 (t, J = 7.1 Hz, 18H), 3.08–3.15 (d, J = 22.0 Hz, 6H), 3.97–4.05 (m, 12H), 7.14 (d, J = 2.5 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 132.0, 129.6, 61.9, 34.0, 32.2, 16.1. FT-IR (KBr, cm^{-1}): 2983, 2910, 1603, 1479, 1458, 1369, 1248, 1164, 1098, 1027, 963, 887, 783.

1,2,4,5-Tetrakis(diethoxyphosphinylmethyl)benzene (3)[14]. A mixture of 1,2,4,5-tetrabromomethane (5.00 g, 37.25 mmol), *N*-bromosuccinimide (26.82 g, 149 mmol) and a catalytic amount of AIBN (15 mg) in dry tetrachloromethane (300 ml) was refluxed overnight. 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 led to white crystalline tetrabromo-compound (7.54 g, 16.76 mmol), which was heated, together with an excess quantity of triethyl phosphate (38.21 g, 230 mmol), for 5 h at 160 °C. Finally, the excess triethyl phosphite was removed by distillation to yield **3** as a colorless oil (9.35 g, 37%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 1.22–1.27 (t, J = 7.2 Hz, 24H), 3.36–3.40 (d, J = 20.0 Hz, 8H), 3.96–4.04 (m, 16H), 7.17 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 134.4, 129.6, 62.0, 31.5, 29.7, 16.3.

FT-IR (KBr, cm^{-1}): 2983, 2923, 1509, 1476, 1443, 1393, 1237, 1163, 1024, 964, 848, 792.

3,5-Di(methyltriglycoloxy)benzaldehyde (4)^{15}**.** Diethyl azodicarboxylate (DEAD) (1.27 g, 7.06 mmol) in 5 ml dry THF was added dropwise to the mixture of 3,5-dihydroxybenzaldehyde (0.498 g, 3.53 mmol), tri(ethylene glycol) monomethyl ether (1.22 g, 7.06 mmol) and triphenyl phosphine (1.76 g, 7.06 mmol) in 30 ml dry THF. The solution was stirred in the dark at room temperature for 24 hours. After evaporation of the solvent, the reaction mixture was purified by silica gel column chromatography using ether–acetone (80 : 20) to yield **4** as a colorless oil (0.90 g, 59%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 3.38 (s, 6H), 3.56 (m, 4H), 3.67–3.75 (m, 12H), 3.87 (m, 4H), 4.16 (m, 4H), 6.76 (t, J = 2.4 Hz, 1H), 7.02 (d, J = 2.3 Hz, 2H), 9.88 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 191.2, 160.2, 138.3, 107.9, 71.7, 70.6, 70.3, 70.1, 69.3, 67.6, 58.7. FT-IR (KBr, cm^{-1}): 2877, 1698, 1594, 1449, 1350, 1298, 1249, 1108, 947, 850.

1,4-Bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}styryl)-benzene (Den 20). **1** (0.14 g, 0.38 mmol) was dissolved in 5 ml of dry DMF under high purity argon. Two equivalents of NaH (60% dispersion in mineral oil) (30.00 mg, 0.76 mmol) and 3,5-di(methyltriglycoloxy)benzaldehyde **4** (0.33 g, 0.76 mmol) were added consecutively. The reaction mixture was then refluxed for 1 hour. After cooling to room temperature, it was neutralized by 1 N 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 20** as a yellow viscous oil (0.19 g, 55%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 3.38 (s, 12H), 3.56 (m, 8H), 3.64–3.78 (m, 24H), 3.87 (t, J = 4.8 Hz, 8H), 4.16 (t, J = 4.8 Hz, 8H), 6.43 (t, J = 2.1 Hz, 2H), 6.69 (d, J = 2.1 Hz, 4H), 7.05 (d, J = 2.8 Hz, 4H), 7.49 (s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) δ: 160.0, 139.2, 136.5, 128.7, 128.5, 126.9, 105.5, 101.2, 71.9, 70.8, 70.5, 70.4, 69.7, 67.4, 59.0. FT-IR (KBr, cm^{-1}): 2874, 1588, 1448, 1350, 1297, 1246, 1108, 960, 845. MALDI-TOF MS 953.60 m/z [M + Na]$^+$ (theory: 930.50 m/z [M]$^+$). Elemental analysis: calcd for $C_{50}H_{74}O_{16}$, C 64.5, H 8.01, O 27.49; found, C 64.21 H 8.02 O 27.88%.

1,3,5-Tris(3,5-bis{2[2-(2-methoxyethoxy)ethoxy]ethoxy}styryl)benzene (Den 30). **2** (0.20 g, 0.40 mmol) was dissolved in 5 ml of dry DMF under high purity argon. Three equivalents of NaH (60% dispersion in mineral oil) (45.40 mg, 1.14 mmol) and the aldehyde **4** (0.50 g, 1.10 mmol) were added consecutively. The reaction mixture was refluxed for 1 hour. After cooling to room temperature, it was neutralized by 1 N 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 30** as a yellow viscous oil (0.23 g, 44%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.39 (s, 18H), 3.56 (m, 12H), 3.64–3.79 (m, 36H), 3.88 (t, J = 4.8 Hz, 12H), 4.17 (t, J = 4.8 Hz, 12H), 6.45 (t, J = 2.2 Hz, 3H), 6.73 (d, J = 2.1 Hz, 6H), 7.10 (s, 6H), 7.53 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) δ: 160.1, 139.1, 137.8, 129.3, 128.7, 124.1, 105.5, 101.4, 71.9, 70.8, 70.6, 70.5, 70.0, 67.5, 59.0. FT-IR (KBr, cm^{-1}): 2874, 1591, 1449, 1350, 1292, 1246, 1108, 968, 850. MALDI-TOF MS 1379.80 m/z [M + Na]$^+$ (theory: 1356.72 m/z [M]$^+$). Elemental analysis: calcd for $C_{72}H_{108}O_{24}$, C 63.7, H 8.02, O 28.28; found, C 63.4, H 8.17, O 28.33%.

1,2,4,5-Tetrakis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]-ethoxy}styryl)benzene (Den 40). **3** (0.40 g, 0.59 mmol) was dissolved in 5 ml of dry DMF under high purity argon. Four equivalents of NaH (60% dispersion in mineral oil) (93.80 mg, 2.35 mmol) and the aldehyde **4** (1.00 g, 2.35 mmol) were added consecutively. The reaction mixture was refluxed for 1 hour. After cooling to room temperature, it was neutralized by 1 N HCl and extracted with $CHCl_3$. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed by evaporation, and the residue was subjected to column chromatography using ethyl acetate–methanol (80 : 20) to produce **Den 40** as a yellow viscous oil (0.39 g, 37%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 3.37 (s, 24H), 3.54 (m, 16H), 3.36–3.76 (m, 48H), 3.86 (t, J = 4.8 Hz, 16H), 4.15 (t, J = 4.8 Hz, 16H), 6.46 (t, J = 2.2 Hz, 4H), 6.71 (d, J = 2.1 Hz, 8H), 7.00 (d, J = 16.0 Hz, 4H), 7.39 (d, J = 16.0 Hz, 4H), 7.72 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) δ: 160.1, 139.3, 135.6, 131.7, 126.8, 105.8, 101.4, 71.9, 70.8, 70.6, 70.5, 69.7, 67.5, 59.0. FT-IR (KBr, cm^{-1}): 2875, 1589, 1447, 1350, 1295, 1248, 1108, 960, 848. MALDI-TOF MS 1806.03 m/z [M + Na]$^+$ (theory: 1783.95 m/z [M]$^+$). Elemental analysis: calcd for $C_{94}H_{142}O_{32}$, C 63.28, H 8.02, O 28.70; found, C 62.95, H 8.01, O 29.06%.

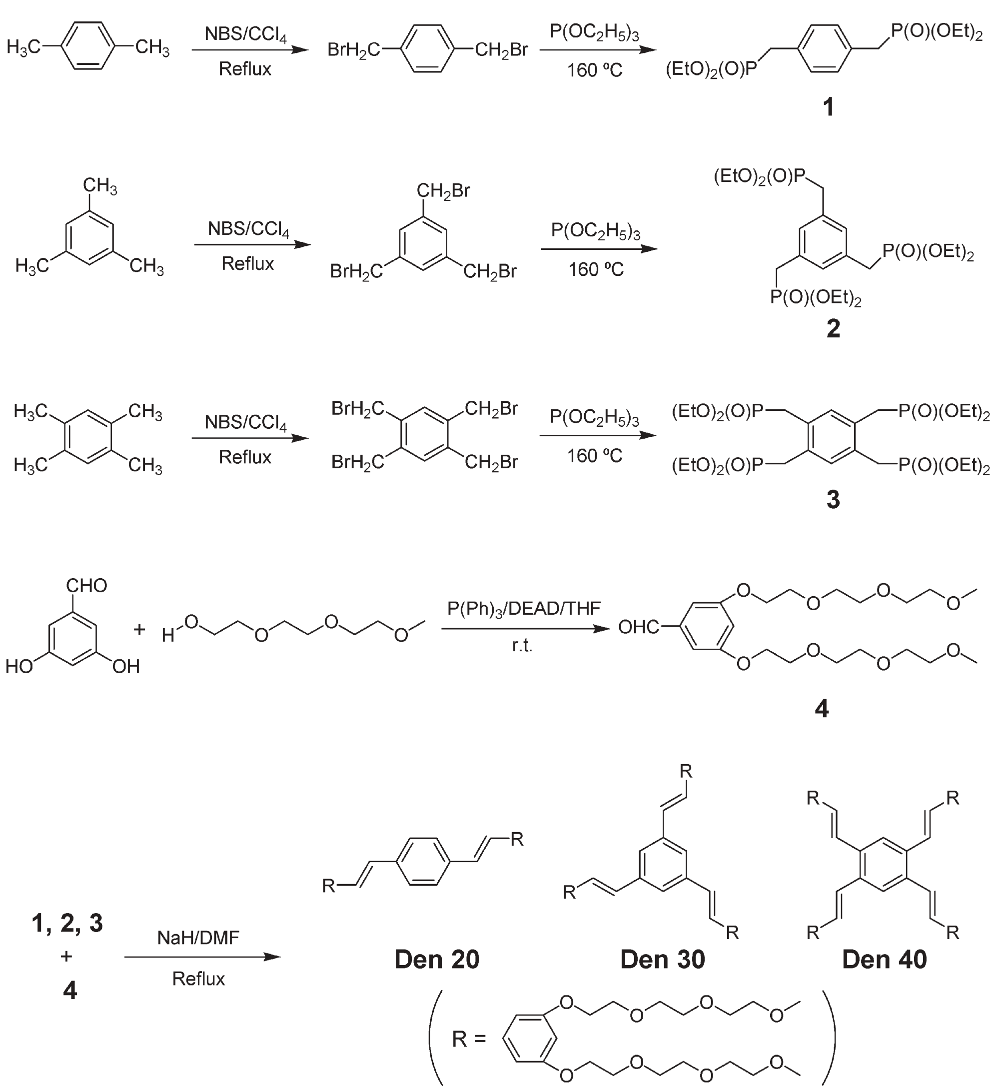
Results and discussion

Syntheses

As can be seen in Scheme 1, hydrophilic tri(ethylene oxide) chains were introduced onto the benzaldehyde unit *via* the Mitsunobu reaction using DEAD and triphenyl phospine. For the syntheses of the dendritic cores (**1–3**, Scheme 1), Wohl–Ziegler bromination of hydrocarbons and Arbusov rearrangement reactions were performed (Scheme 1). Finally, the Horner–Wadsworth–Emmons coupling reaction was used to attach the aldehyde-functionalized pheriphery **4** onto the core structures (**1**, **2**, and **3**), resulting in the formation of **Den 20**, **Den 30** and **Den 40** (Scheme 1). These newly-synthesized dendritic molecules 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, THF).

NMR studies

The good solubility of the resultant amphiphilic dendrimers with oligo(*p*-phenylene vinylene) core branches and oligo(ethylene oxide) terminal chains facilitates their characterization by ^{1}H NMR and ^{13}C NMR measurements. As expected, **4** exhibited ^{1}H and ^{13}C peaks at 9.88 and 191.2 ppm, respectively, arising from proton and carbon atoms in the aldehyde group. These magnetic resonances disappeared upon successful coupling of the aldehyde focal point in **4** with the phosphonate core reagents (**1–3**).



Scheme 1 Procedures for the synthesis of amphiphilic dendrimers with oligo(*p*-phenylene vinylene) core units and oligo(ethylene oxide) terminal chains.

^{1}H-NMR spectra of **Den 30** in $CDCl_3$ and D_2O are shown in Fig. 2. Peaks corresponding to all protons in the molecular structure of **Den 30** are seen in Fig. 2a as $CDCl_3$ is a good solvent for both the oligo(*p*-phenylene vinylene) core and the oligo(ethylene oxide) terminal chains. In contrast, the corresponding ^{1}H-NMR spectrum in D_2O (Fig. 2b) shows broad and featureless magnetic resonances due to restricted chain mobilities caused by the poor solubility of the hydrophobic core in water. Similar NMR spectra were observed for **Den 20** and **Den 40**. These results indicate possible micellization of the amphiphilic dendrimers in water to minimize interactions between the hydrophobic core and a polar aqueous medium. Temperature dependent NMR measurements in D_2O (Fig. 3) added substance to the above conclusion. As can be seen in Fig. 3, the resonance intensities of aromatic core protons over 6–7 ppm gradually decreased with increasing temperature. At high temperatures, the OEO terminal chains became less soluble in water, causing the hydrophobic OPV core branches to be surrounded by a more rigid shell so that the relaxation time of the aromatic core protons decreased significantly to diminish the resonance signals from the core units.[16] This result is consistent with other thermo-responsive materials like poly-*N*-isopropylacrylamide (PNIPAM) that shows similar LCST behavior.[16,17] Similar results were observed for **Den 20** and **Den 40**.

Temperature-induced phase transition

Closely related to the NMR results, a temperature-induced transition from a clear solution to a turbid one was observed for all of the amphiphilic dendrimers in an aqueous medium at a concentration above the critical micelle concentration (CMC), as exemplified by Fig. 4 for an aqueous solution of **Den 30** upon changing the solution temperature from 25 to 75 °C. The CMC values for **Den 20**, **Den 30**, and **Den 40** were measured, by the surface tension method with a platinum ring, to be 0.56, 1.37, and 3.81 mg L^{-1}, respectively. These CMC values are consistent with those reported for some other amphiphilic dendritic macromolecules and copolymers,[18,19] though they are much lower than those of certain low

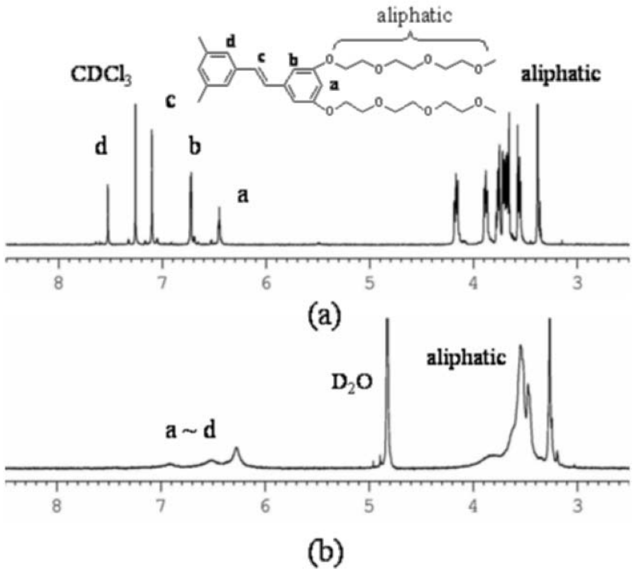


Fig. 2 ^{1}H NMR spectra of **Den 30** in (a) $CDCl_3$ and (b) D_2O at 298 K. Inset in (a) shows the chemical unit structure of **Den 30**. The concentration of **Den 30** is 2.7 g L^{-1}.

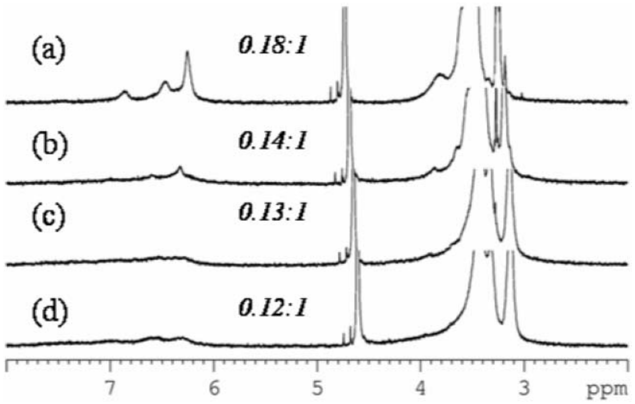


Fig. 3 ^{1}H NMR spectra of **Den 30** at (a) 300 K, (b) 303 K, (c) 306 K, and (d) 309 K, respectively, in D_2O at 2.7 g L^{-1}. Numbers in the figure represent the apparent integration ratios between the aromatic (6–7 ppm) and aliphatic (3–4 ppm) protons for each of the temperatures.

Fig. 4 Temperature-induced reversible micellization behavior of **Den 30** in water at 25 °C (left) and at 75 °C (right). The concentration is 2.7 g L^{-1}.

molecular weight surfactants (*e.g.* 2.30 g L^{-1} for sodium dodecyl sulfate, SDS).[18] All of the CMCs increased with increasing branch number and the ratio of the hydrophilic OEO/hydrophobic OPV moieties in the series from **Den 20** through **Den 30** to **Den 40**.

The temperature-induced phase transition seen in Fig. 4 is attributable to the fact that the oligo(ethylene oxide) terminal chains undergo a polar–nonpolar transition[20,21] at the lower critical solution temperature (LCST) of 32.2 °C (*vide infra*). The interaction between the polar oligo(ethylene oxide) terminal chains and water molecules is favorable below the LCST, whereas the oligo(ethylene oxide) terminal chains become non-polar above the LCST due to their conformational changes with temperature.[21] At high temperatures, therefore, water is a poor solvent for the oligo(ethylene oxide) terminal chains and micellization occurred to cause light scattering. **Den 20** and **Den 40** exhibited similar temperature-induced phase transition behaviors with a slightly varied LCST, depending on their chemical structure. In all cases, the transition is very fast (within seconds) and highly reversible.

The LCSTs (or cloud points) for all of the amphiphilic dendrimers were determined on the Lambda 900 UV/VIS/NIR spectrometer as the temperature at which optical transmittance of the dendrimer solution sharply reduced (below 1% of the original value). The optical transmittance at 600 nm was used for the cloud point measurements because the transmittance change at this wavelength was clearly noticeable. As can be seen in Fig. 5a, the cloud points of **Den 20**, **Den 30**, and **Den 40** at a constant molar concentration of 15.57 mM are 23.7 °C, 32.2 °C and 49.5 °C, respectively. The observed increase in the cloud points along the series **Den 20**, **Den 30**, and **Den 40** indicates, once again, a better solvency for the amphiphilic dendrimers with a higher ratio of hydrophilic OEO/hydrophobic OPV moieties. In comparison with poly(ethylene oxide)-poly (propylene oxide) block copolymers, these newly-synthesized amphiphilic dendrimers showed lower phase transition temperatures with a stronger temperature dependence due to the shorter oligo(ethylene oxide) terminal chains.[22,23] The concentration-dependence given in Fig. 5b shows that the solution concentration also affects the phase transition temperature of the amphiphilic dendrimers in an aqueous medium, which decreased with increasing solution concentration.

Photophysical properties

The above temperature-dependent phase behavior, together with interesting optoelectronic properties intrinsically associated with the oligo(*p*-phenylene vinylene)[1] cores in these amphiphilic dendrimers, prompted us to investigate the possible stimuli-responsive photophyscial properties of **Den 20**, **Den 30**, and **Den 40**. Fig. 6a shows optical absorption spectra for aqueous solutions of **Den 20**, **Den 30**, and **Den 40** above the

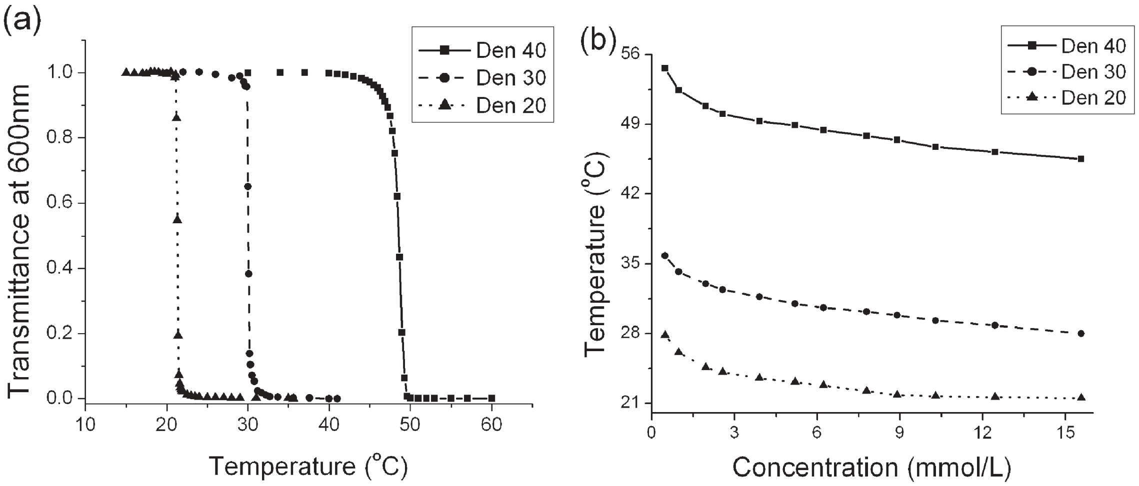


Fig. 5 (a). Temperature-dependence of light transmittance for aqueous solutions of **Den 20**, **Den 30**, and **Den 40** with a molar concentration of 15.57 mM. (b) Concentration-dependence of the LCSTs for aqueous solutions of **Den 20**, **Den 30**, and **Den 40**.

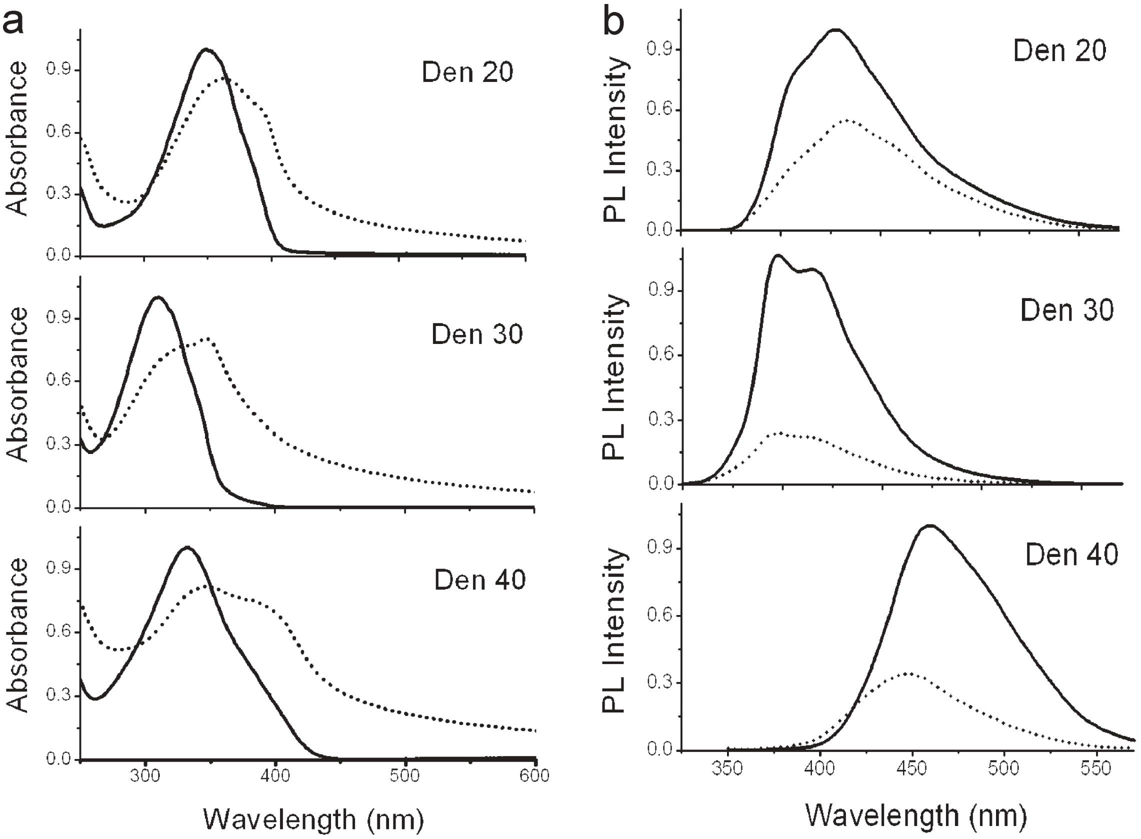


Fig. 6 Temperature-dependent (a) UV–vis and (b) PL spectra of: **Den 20**, **Den 30**, and **Den 40** in water at 20 °C (solid line) and 75 °C (dotted line). Excitation wavelength: 310 nm. The concentrations are 20 mM and 0.003 mM for UV–vis and PL, respectively—note that a higher concentration was used for the UV–vis measurements because of the much lower sensitivity for the UV–vis signal than for that of PL.

CMC at 20 and 75 °C. As can be seen in Fig. 6a, all of the dendrimer solutions showed a relatively well-defined optical absorption band over 300–400 nm below their respective phase transition temperature at 20 °C. Above the phase transition temperature, however, all the optical absorption bands red-shifted and became broad, most probably indicating a micellization-induced increase in the effective conjugation length through intermolecular overlapping of the oligo(*p*-phenylene vinylene) cores. This indication was supported by the corresponding intermolecular fluorescence quenching with increasing temperature, as shown in Fig. 6b, though the observed fluorescence quenching could also be partially caused by light scattering associated with the micellar structures.

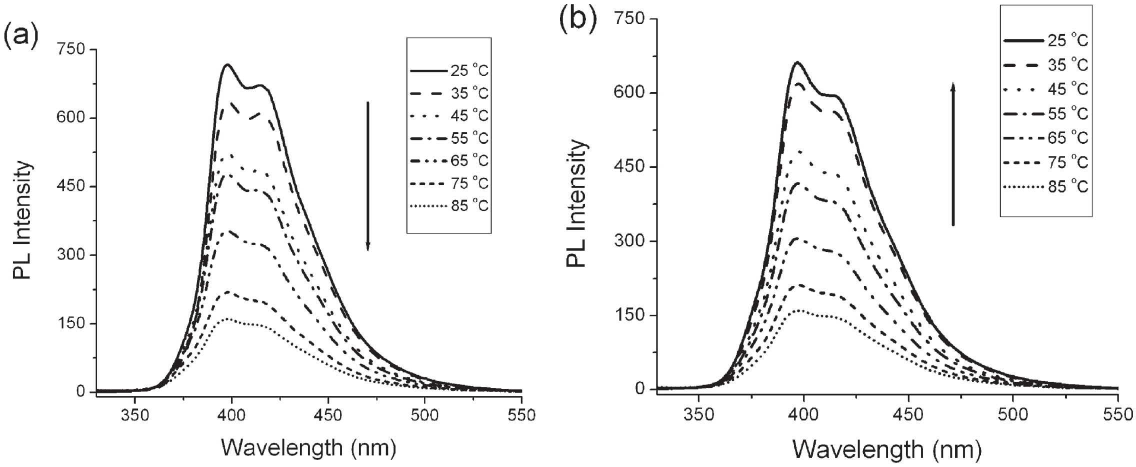


Fig. 7 Temperature-dependent PL spectra of **Den 30** in an aqueous medium: around CMC (1.8 mg L^{-1}): (a) heating, (b) cooling.

We have also investigated the reversibility of the temperature-induced changes in the photoluminescence emissions for **Den 20**, **Den 30**, and **Den 40**. As expected, there was a monotonic decrease in PL intensity by heating up an aqueous solution of **Den 30** above the CMC (Fig. 7a). The spectroscopic changes shown in Fig. 7a are fully reversible upon cooling the same **Den 30** solution (Fig. 7b). The changes seen in Fig. 7a and b can be reproduced with many heating–cooling cycles. **Den 20** and **Den 40** showed similar temperature-responsive PL intensity changes.

AFM studies

The concentration-dependent micellization of the amphiphilic dendrimers was further investigated by AFM imaging. As seen in Fig. 8a, spherical micelles about 80 nm in diameter with a well-defined structure formed from the aqueous solution of **Den 30** above the CMC after air-drying. In contrast, there is no detectable aggregated structure observable for the corresponding sample below the CMC (Fig. 8b).

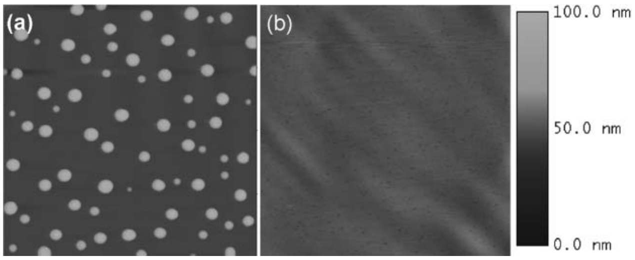


Fig. 8 AFM images for samples from aqueous solutions of **Den 30** with different concentrations (a) above CMC (1.88 g L^{-1}) and (b) below CMC (0.5 mg L^{-1}). Scanning area: 10 μm × 10 μm.

Conclusions

We have synthesized a class of new amphiphilic dendrimers consisting of oligo(*p*-phenylene vinylene) core branches and oligo(ethylene oxide) terminal chains. These dendrimers combine the hydrophobic conjugated core branches with the hydrophilic soluble oligo(ethylene oxide) terminal chains in one macromolecule. Due to the amphiphilic properties arising from the large difference in hydrophobicity/hydrophilicity between the two constituent components, unique temperature-/concentration-responsive phase transition and photophysical property changes were observed. These amphiphilic dendrimers exhibited a lower critical solution temperature (LCST) and the critical micellization (CMC) behavior, as evidenced by UV–vis, PL spectroscopic and ^{1}H NMR measurements. AFM images showed spherical aggregates and featureless surface for solution-cast thin films from aqueous solutions of the amphiphilic dendrimers with solution concentrations above and below CMC, respectively. These highly fluorescent, stimuli-responsive amphiphilic dendrimers possess unusual phase structures and photophysical properties which are attractive for a wide range of potential applications, including sensing, photoswitching, and controlled drug delivery systems.

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