Tetrahedron Letters 56 (2015) 321–326

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis, photophysical and electrochemical properties of stilbenoid dendrimers with phenothiazine surface group

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ARTICLE INFO

Article history:
Received 23 October 2014
Revised 18 November 2014
Accepted 18 November 2014
Available online 24 November 2014

Keywords:
Dendrimer
Phenothiazine
HWE reaction
Click chemistry
Photophysical and electrochemical

ABSTRACT

Synthesis of some novel stilbenoid dendrimers with the phenothiazine surface group has been achieved using Horner–Wadsworth–Emmons (HWE) and click reactions through convergent methodology. Alkyl chains have been incorporated at the periphery of phenothiazine moiety to enhance the solubility of the dendrimers. The photophysical properties indicate an increase in the molar extinction coefficient, fluorescence quantum yield, and lifetime as the generation of the dendrimer increases. The higher fluorescence quantum yield indicates the *trans* geometry for stilbene unit.

Dendrimers are a class of highly branched, monodisperse, synthetic macromolecules with a well-defined chemical structure.[1] The unique structural and functional aspects of dendrimers have received immense scientific and technological applications in various research areas such as optoelectronics,[2] solar cells,[3] light-harvesting,[4] and sensor.[5] The π-conjugated dendrimers which function as 'molecular photonic antenna' to harvest and transport energy are receiving significant attention due to their unique photochemical, photophysical, and electrochemical properties.[6] Dendrimers are extensively utilized for targeted drug delivery[7] due to their biocompatibility and the presence of a large number of functional group at the surface as well as in the bridging units and also find application as imaging agents.[8] Recently, the synthesis and stabilization of transition metal nanoparticles (NPs) inside dendrimers and their potential application in catalysis and nano science[9] have been also reported. However, conjugated dendrimers have attracted considerable attention because of their multifarious applications in photophysical and photoelectronic devices such as organic light-emitting diodes (OLEDs)[10] and photovoltaic cells.[11] The stilbene skeleton could be an excellent choice as a central chromophore to construct new photoresponsive materials.[12] On the basis of their unique properties, monodisperse stilbenoid dendritic materials have emerged as attractive candidates for photonic applications.[13]

In dendrimer chemistry, chemoselective reactions are employed essentially to incorporate the large and various numbers of functional groups both at the branching and surface units. Recently, click chemistry methodology has been efficiently applied for the synthesis of various types of new functional dendrimers.[14] Moreover, click chemistry is generally carried out under mild reaction conditions with excellent regioselectivity and high yields. 1,2,3-Triazole branching dendrimers find a wide range of applications in medical[15] and material field.[16]

Phenothiazine derivatives have received immense attention in recent years owing to their wide photophysical and redox properties. Hence, among the various types of dendrimers, phenothiazine-based dendrimers have emerged as new materials that possess several attractive applications. Dendrimer with phenothiazine nucleus could undergo facile electrochemical oxidation and can function as redox-active dendrimers.[17] The strong electron donating property of phenothiazine finds applications in electroactive materials.[18] Phenothiazine containing systems show metallochromic cruciforms[19] and phenothiazine based stilbene dendrimers are promising materials in LED devices.[20]

Recently, chalcone dendrimer,[21] diphenylamine dendrimer,[22] benzothiazole–benzoxazole dendrimer,[23] ferrocenyl dendrimer,[24] phenothiazine dendrimer,[25] and photoresponsive stilbene

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http://dx.doi.org/10.1016/j.tetlet.2014.11.088
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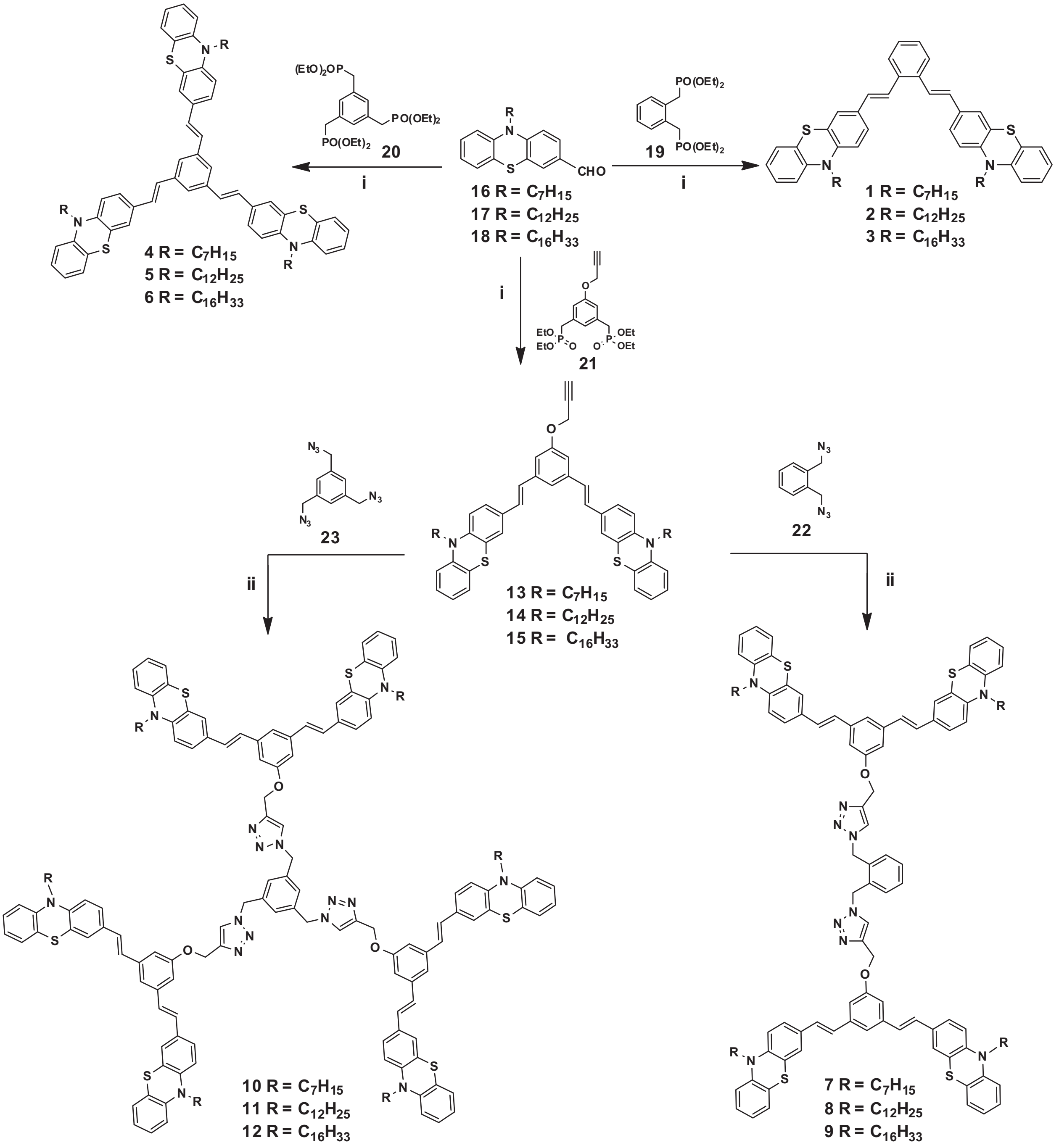

Scheme 1. Reagents and conditions: (i) NaH, THF, room temperature, 8 h. (ii) $CuSO_4 \cdot 5H_2O$ (5 mol %), sodium ascorbate (10 mol %), THF/H_2O (1:1, v/v), room temperature, 10 h.

dendrimer[26] have been reported from our laboratory through click chemistry and Witting–Horner reaction. Hence, it would be of great interest to synthesize conjugated dendrimers with phenothiazine surface units. The present investigation mainly focuses on the synthesis, photophysical and electrochemical properties of stilbenoid dendrimers **1**–**12** having the phenothiazine surface group by convergent approach using Horner–Wadwarth–Emmons and click reactions.

Michaelis–Arbuzov reaction of 1,2-bis(bromomethyl)benzene and triethyl phosphite at 160 °C afforded the phosphonate esters **19** in 88% yield. Horner–Wadsworth–Emmons reaction of 1.0 equiv of phosphonate diester **19** with 2.1 equiv of 10-*n*-heptylphenothiazine-3-carbaldehyde, **16**/10-*n*-dodecylphenothiazine-3-carbaldehyde **17**/10-*n*-hexadecylphenothiazine-3-carbaldehyde **18** in the presence of NaH in THF gave the desired phenothiazinostilbenoid dendrimers **1**, **2**, and **3** in 73%, 70%, and 68% yields, respectively, (Scheme 1). The disappearance of aldehyde peak and increased integration values of aromatic protons in the ^1H NMR spectra of the conjugated phenothiazinostilbenoid dendrimers **1**, **2**, and **3** proves the successful coupling reaction between the respective aldehyde and the phosphonate diester. However, the aliphatic peaks in all cases can be clearly assigned and they confirm the purity of each dendrimer. The ^1H NMR spectra of **1** showed a triplet at δ 3.84 (J = 6.9 Hz) for *N*-methylene protons along with the signals for aliphatic and aromatic protons. The ^{13}C NMR spectrum of **1** showed signal for *N*-methylene carbon at δ 66.6 in addition to the aliphatic and aromatic carbon signals. The ^{1}H NMR spectrum could not be unequivocally used to locate the *trans* olefinic protons as it was mixed with the other aromatic protons.[27] Moreover, in IR spectrum of stilbenoid dendrimer **1** displayed the characteristic absorption band of *trans* double bond at 958 cm^{-1} indicating that HWE reaction has afforded the *trans* isomer. The mass spectrum (ESI) of **1** showed a peak at m/z 721.4 (M+H)$^{+}$ for molecular ion. The structure of **1** was further confirmed from elemental analysis. Similarly, the structure of dendrimers **2** and **3** was also confirmed from spectral and analytical data.

Similarly, Michaelis–Arbuzov reaction of 1,3,5-tris(bromomethyl) benzene with triethyl phosphite at 160 °C afforded the phosphonate esters **20** in 89% yield. HWE reaction of 1.0 equiv of phosphonate diester **20** with 3.1 equiv of 10-*n*-heptylphenothiazine-3-carbaldehyde, **16**/10-*n*-dodecylphenothiazine-3-carbaldehyde **17**/10-*n*-hexadecylphenothiazine-3-carbaldehyde **18** using NaH in THF afforded the phenothiazinostilbenoid dendrimers **4**, **5**, and **6** in 77%, 66%, and 63% yields, respectively (Scheme 1). The ^{1}H NMR spectra of **6** showed a triplet at δ 3.72 (J = 6.9 Hz) for *N*-methylene protons in addition to the signals for the aliphatic and aromatic protons. The ^{13}C NMR spectrum of **6** showed signal for *N*-methylene carbon at δ 47.4 in addition to the signals for aliphatic and aromatic carbons. The IR spectra of stilbenoid dendrimer **6** displayed the absorption band of *trans* double bonds at 958 cm^{-1}. The mass spectrum (MALDI-TOF) of **6** showed the molecular ion peak at m/z 1419.8. The structure of **6** was further confirmed from elemental analysis. Similarly, the structure of dendrimers **4** and **5** was also confirmed from spectral and analytical data.

The attention was then focused on the synthesis of dendrons **13**–**15** with phenothiazine units using HWE reaction. Michaelis–Arbuzov reaction of 1,3-bis(bromomethyl)-5-(prop-2-ynyloxy)benzene with triethyl phosphite at 160 °C gave the phosphonate esters **21** in good yields. Further, HWE reaction of 1.0 equiv of phosphonate diester **21** with 2.1 equiv of 10-*n*-heptylphenothiazine-3-carbaldehyde **16**/10-*n*-dodecylphenothiazine-3-carbaldehyde **17**/10-*n*-hexadecylphenothiazine-3-carbaldehyde **18** using NaH in THF gave alkyne dendrons **13**, **14**, and **15** in 66%, 57%, and 50% yields, respectively. The ^{1}H NMR spectrum of propargyl dendron **14** displayed a triplet at δ 2.55 (J = 2.1 Hz) for acetylenic proton and doublet at δ 4.75 (J = 2.1 Hz) for *O*-methylene protons, respectively, in addition to the signals for aliphatic and aromatic protons. The ^{13}C NMR spectrum of **14** showed *O*-methylene and acetylenic carbons at δ 55.9, 75.7, and 78.6 respectively, in addition to the signals for aliphatic and aromatic carbons. The IR spectra of stilbenoid dendrimer **14** displayed the absorption bands at 959 cm^{-1}, 2118 cm^{-1}, and 3268 cm^{-1} for *trans* double bond, $-C{\equiv}C-$ and $\equiv C{-}H$ units, respectively. The mass spectrum (ESI) of **14** showed the molecular ion at m/z 916.3 (M+H)$^{+}$. Similarly, the structure of the dendron **13** and **15** was also confirmed from spectral and analytical data.

Having successfully synthesized the zero-generation dendrimers **1**–**6**, we focused our attention on the convergent synthesis of first-generation dendrimers **7**–**12** through click chemistry as shown in Scheme 1. The reaction of 1.0 equiv of azide **22** with 2.1 equiv of propargyloxy conjugated dendrons **13**, **14**, and **15** in the presence of Cu-(I) catalyzed click reaction conditions afforded the first-generation dendrimers **7**, **8**, and **9** in 87%, 86%, and 83% yields, respectively. The ^{1}H NMR spectrum of dendrimer **7** displayed two singlets at δ 5.16 and 5.21 corresponding to the *N*-methylene and *O*-methylene protons, in addition to the signals for aliphatic and aromatic protons. In the ^{13}C NMR spectrum, first-generation dendrimer **7** showed the *N*-methylene and *O*-methylene carbons at δ 49.4 and 61.9 along with signals for aliphatic and aromatic carbons. Similarly, structure of the dendrimers **8** and **9** was also confirmed from spectral and analytical data.

Further, in order to increase the number of stilbene and phenothiazine units in the first-generation dendrimers 1.0 equiv of 1,3,5-tris(azidomethyl)benzene **23** was reacted with 3.1 equiv of propargyloxy conjugated dendrons **13**, **14**, and **15** under click reaction conditions to give the first generation dendrimers **10**, **11**, and **12** in 82%, 81%, and 81% yields, respectively, (Scheme 1). The ^{1}H NMR spectrum of stilbenoid dendrimer **12** displayed the *N*-methylene protons at δ 5.14, the *O*-methylene protons at δ 5.32, in addition to the other signals for the aliphatic and aromatic protons. In the ^{13}C NMR spectrum, dendrimer **12** showed *N*-methylene and *O*-methylene carbons at δ 53.3 and 62.1 in addition to the signals for the aliphatic and aromatic carbons. The mass spectrum (MALDI-TOF) of **12** showed the molecular ion peak at m/z 3323.5. Similarly, the structure of dendrimers **10** and **11** was also confirmed from spectral and analytical data.

The UV–visible absorption and fluorescence data of dendrimers **1**–**12** are summarized in Table 1. Two prominent absorption bands were observed around 300 and 382 nm corresponding to the π–π^* transition of stilbene and phenothiazine units, respectively, (Fig. 1a). Similar absorption spectral behavior is exhibited by all the dendrimers, which shows the absence of aggregates and charge transfer complexes even with increasing the number of stilbene group. Further, the butterfly conformation of phenothiazine unit also prevents the inter- and intra-molecular aggregations.[28] No shift in λ_{max} or broadening of the absorption band was observed in the UV–vis spectrum even with increasing the concentration of dendrimer indicating that there is no aggregation of dendrimers even at higher concentrations which may be due to butterfly conformation of phenothiazine that prevents the flat structure for the dendrimers. Such nonaggregating nature of bulky molecules with electron rich moieties is important for solar cell application. The absorption maximum of dendrimers **1**–**3**, **4**–**6**, **7**–**9**, and **10**–**12** does not vary much with increasing alkyl chain length attached to the phenothiazine unit which indicates that increasing the chain length of the alkyl group on phenothiazine does not alter the UV–visible absorption properties.

For dendrimers **1**, **2**, and **3** the shorter wavelength band and the longer wavelength band centered around 291 and 377 nm where as for dendrimers **4**–**12**, the shorter wavelength band and the longer wavelength band centered around 306 and 384 nm, respectively.

Table 1
Photophysical properties of the dendrimers **1**–**12**

Dendrimers	λ_{abs} (nm)	ε 10^5 M^{-1} cm^{-1}	λ_{em} (nm)	Φ_f	τ_f (ns)
1	292 377	2.11 0.92	537	0.632	5.27
2	291 378	1.60 0.66	537	0.605	5.24
3	291 377	3.18 1.56	537	0.685	5.30
4	303 384	2.90 1.85	531	0.876	5.15
5	303 383	5.08 3.31	531	0.922	5.16
6	303 383	3.69 2.33	531	0.923	5.15
7	305 382	5.57 3.46	528	0.888	5.24
8	305 382	4.37 2.66	527	0.937	5.31
9	306 382	5.38 3.35	526	0.956	5.34
10	306 382	10.90 6.90	527	0.927	5.30
11	306 382	8.87 5.67	527	0.947	5.31
12	304 382	8.73 5.49	527	0.953	5.32

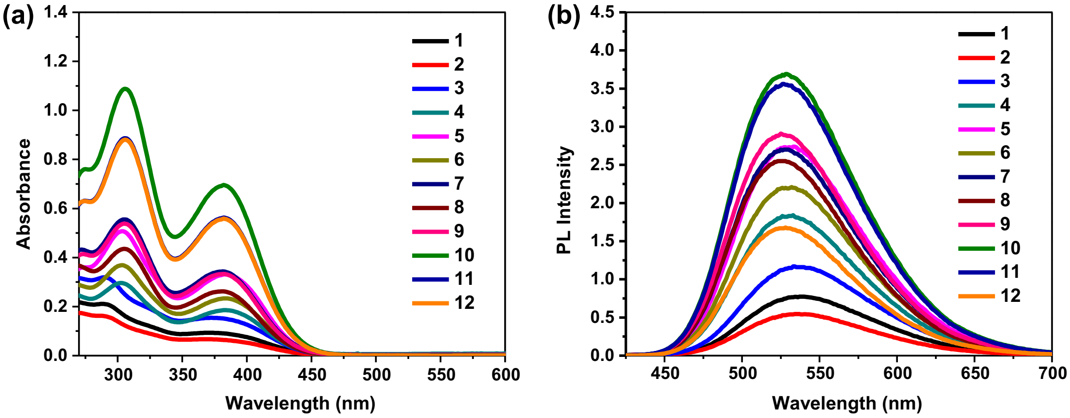

Figure 1. Absorption spectra (a) and Emission spectra (b) of dendrimers **1**–**12** in DMF (1 μM).

Thus an average red shift of 10 nm was observed for the shorter and longer wavelength band in dendrimers **4**–**12** when compared to dendrimers **1**–**3**. This is due to increase in conjugation with increasing the number of stilbene and phenothiazine units. Molar extinction coefficient of both shorter and longer wavelength bands of dendrimers have been found to increase significantly as the generation of the dendrimer increases. For all the dendrimers the high energy band possesses higher extinction coefficient than low energy band.

Figure 1b shows fluorescence spectra of dendrimers **1**–**12** in DMF, upon excitation at longer wavelength absorption maximum and the fluorescence parameters are shown in Table 1. All the dendrimers exhibit intense fluorescence emission in the region 527–537 nm, on excitation at 360 nm. Around 6 nm blue shift was observed for the dendrimers **4**–**6** when compared with dendrimers **1**–**3** and a 4 nm blue shift was observed for the dendrimers **7**–**12** when compared with the dendrimers **4**–**6**. This is due to increase in the number of phenothiazine units and the presence of triazole units which provides rigidity to the molecule to some extent. The fluorescence quantum yield (Φ_f) of dendrimers **1**–**12** has been measured in DMF using quinine sulfate in 0.1 N H_2SO_4 as the standard. The quantum yields of dendrimers **1**–**12** are listed in Table 1. As the generation of the dendrimer increases, the quantum yield also increases consistently due to increasing the number of phenothiazine and *trans*-stilbene unit. For *trans*-stilbene unit there is an increase in fluorescence efficiency and lifetime when

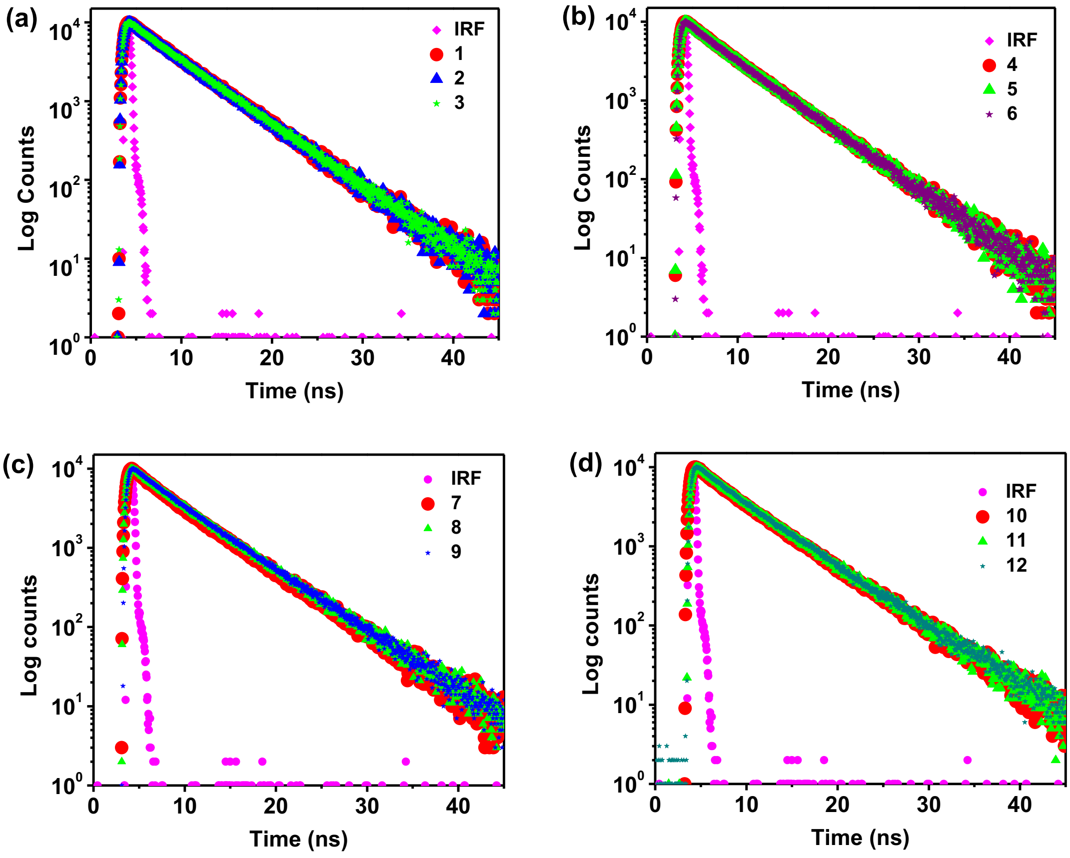

Figure 2. Fluorescence decay of dendrimers (a) **1**–**3**, (b) **4**–**6**, (c) **7**–**9**, and (d) **10**–**12**.

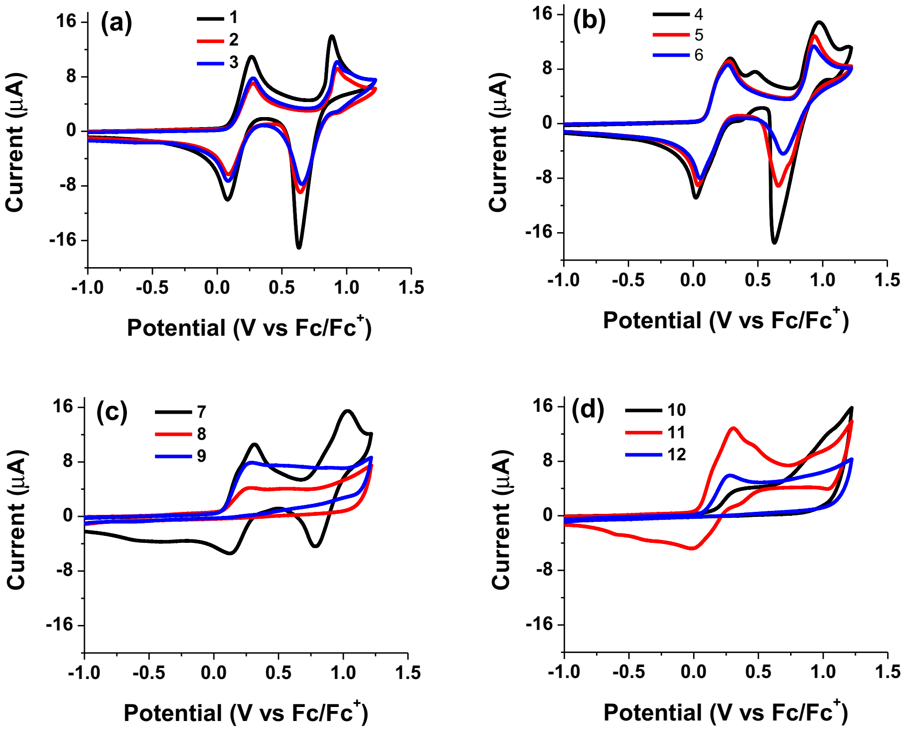

Figure 3. Cyclic voltammograms of dendrimers (a) **1**–**3**, (b) **4**–**6**, (c) **7**–**9**, and (d) **10**–**12** in dichloromethane (1 mM).

compared to the *cis* stilbene unit and when *trans* to *cis* photoisomerization occurs the fluorescence efficiency and lifetime decreases.[29] Relatively high quantum yields of all the dendrimers indicate, that the *trans*-stilbene undergoes isomerization to a lesser extent or does not undergo isomerization to *cis* form.

Further, to study the fluorescence lifetime of dendrimers **1**–**12**, time-resolved fluorescence studies were carried out by selectively exciting the phenothiazine units at 375 nm by using DMF as solvent (Fig. 2). The fluorescence decay of all the samples was fitted in single exponential with a lifetime of around 5 ns which indicates that the excited state of dendrimers experience radiative decay alone (Table 1). The above findings and the higher fluorescence quantum yield values confirm the absence of charge transfer process or exciton formation between inter or intra-dendrimer phenothiazine units. The longer lifetime of 5 ns corresponds to the intramolecular charge transfer (ICT) character of phenothiazine. The longer fluorescence lifetime, nonaggregating nature and the presence of strong electron donating units make these dendrimers as ideal molecules for electron and energy transfer process and higher light harvesting capabilities.

Table 2
Electrochemical parameters for dendrimers **1**–**12** in DMF (1 mM)

Dendrimer	E_{ox}[a] (V)	E_{0-0}[b] (eV)	E_{red}[c] (V)
1	0.886	2.77	−1.88
2	0.926	2.77	−1.84
3	0.923	2.77	−1.84
4	0.973	2.79	−1.81
5	0.936	2.81	−1.87
6	0.927	2.80	−1.87
7	1.037	2.82	−1.78
8	0.982	2.83	−1.84
9	0.992	2.83	−1.83
10	0.926	2.83	−1.90
11	0.904	2.82	−1.91
12	0.978	2.83	−1.85

[a] Ground state oxidation potential.

[b] Values were estimated from the intersection of the absorption and fluorescence spectra.

[c] Excited state reduction potential.

The ground state oxidation potential of the dendrimers **1**–**12** was measured by using the cyclic voltammetry technique (Fig. 3). Accordingly, the optical band gap (E_{0-0} values) of the dendrimer **1**–**12** were estimated from the UV–vis absorption spectra is in the range of 2.77–2.83 eV (Table 2). The optical band gap of dendrimers **1**–**3** is slightly smaller than that of other dendrimers **4**–**12**. The overall band gap energy of each dendrimers was not affected significantly by an increase in dendrimer generation and length of the alkyl chain in the surface unit. The excited state reduction potential of the dendrimers is (~ -1.88 V) well below the conduction band of semiconductors such as TiO_2 (−0.5 eV) and ZnO (−0.5 eV).[30] The absorption spectral studies also reveal that there is no aggregation of dendrimers. From the above observations, we conclude that these dendrimers can be used as co-sensitizer or co-adsorber in dye sensitized solar cells in order to prevent the aggregation.

In conclusion, we have synthesized conjugated dendrimers using HWE and click reactions. Photophysical measurements show that with increasing the generation the extinction coefficient and quantum yield also increases. Further, the higher quantum yield of dendrimers, indicates the *trans* geometry of the stilbene unit. Aggregation was not observed even at higher concentration and higher generation dendrimers due to nonplanar, butterfly conformation of the phenothiazine unit. The nonaggregating nature even at higher concentrations and the absence of charge/energy transfer process and excimer formation are ideal characteristics for efficient light harvesting process in solar cells. Hence, the use of such electron rich, bulky nonaggregating dendrimers as co-sensitizer and co-adsorber in dye sensitized solar cell is under progress.

Acknowledgements

C.S.K. thanks Council of Scientific and Industrial Research (CSIR) and M.R. thanks University Grants Commission (UGC), New Delhi and University of Madras for financial support. The authors thank DST-FIST, New Delhi for providing NMR facility to the Department Organic Chemistry, University of Madras.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.11.088.

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