



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



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### 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.

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Dendrimers are a class of highly branched, monodisperse, synthetic macromolecules with a well-defined chemical structure.<sup>1</sup> The unique structural and functional aspects of dendrimers have received immense scientific and technological applications in various research areas such as optoelectronics,<sup>2</sup> solar cells,<sup>3</sup> light-harvesting,<sup>4</sup> and sensor.<sup>5</sup> The  $\pi$ -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.<sup>6</sup> Dendrimers are extensively utilized for targeted drug delivery<sup>7</sup> 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.<sup>8</sup> Recently, the synthesis and stabilization of transition metal nanoparticles (NPs) inside dendrimers and their potential application in catalysis and nano science<sup>9</sup> 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)<sup>10</sup> and photovoltaic cells.<sup>11</sup> The stilbene skeleton could be an excellent choice as a central chromophore to construct new photoresponsive materials.<sup>12</sup> On the basis of their unique properties, monodisperse stilbenoid

dendritic materials have emerged as attractive candidates for photonic applications.<sup>13</sup>

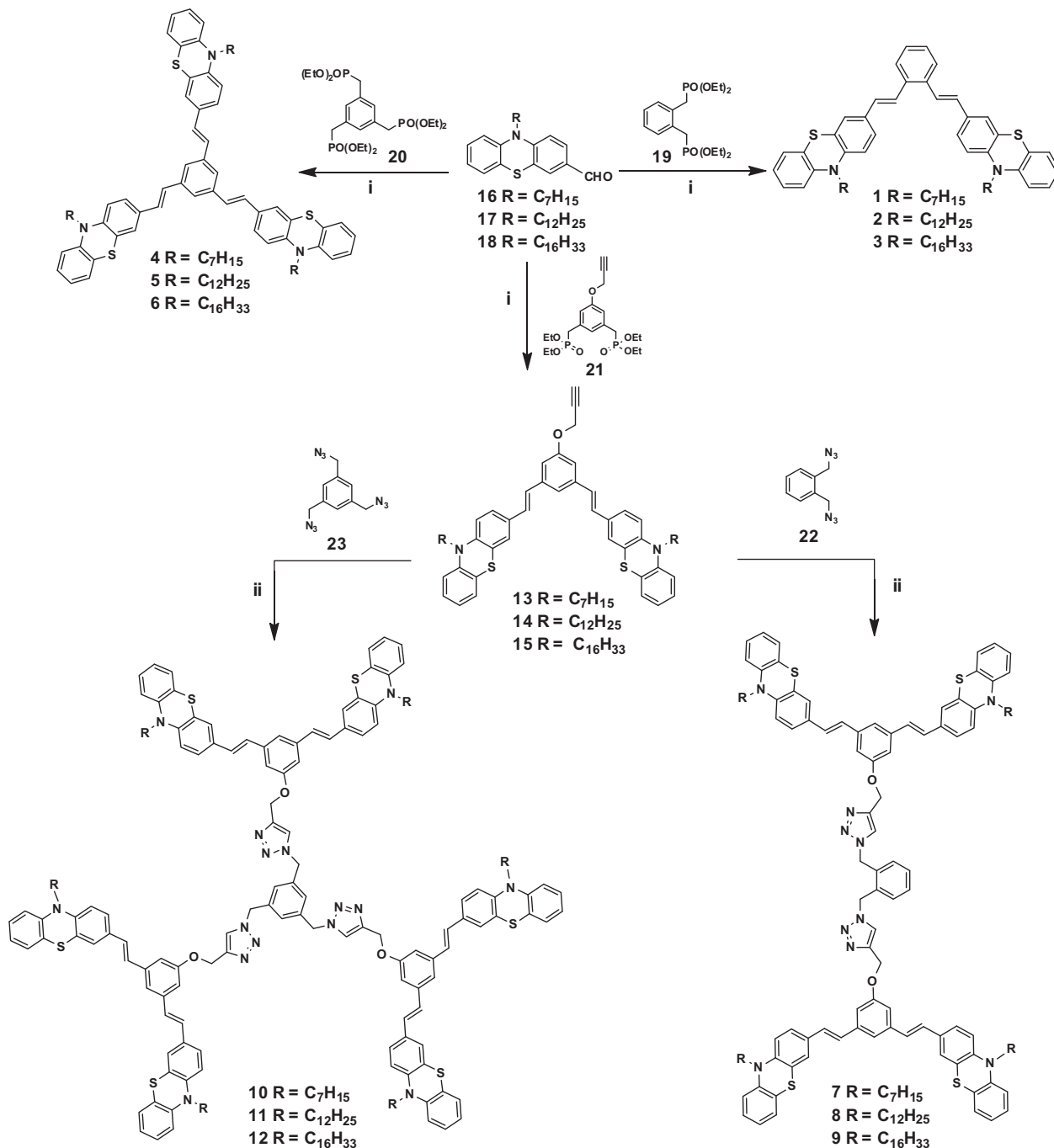
In dendrimer chemistry, chemoselective reactions are employed essentially to incorporate the large and various numbers of functional groups both at the branching and surface units. Recently, click chemistry methodology has been efficiently applied for the synthesis of various types of new functional dendrimers.<sup>14</sup> 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<sup>15</sup> and material field.<sup>16</sup>

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.<sup>17</sup> The strong electron donating property of phenothiazine finds applications in electroactive materials.<sup>18</sup> Phenothiazine containing systems show metallochromic cruciforms<sup>19</sup> and phenothiazine based stilbene dendrimers are promising materials in LED devices.<sup>20</sup>

Recently, chalcone dendrimer,<sup>21</sup> diphenylamine dendrimer,<sup>22</sup> benzothiazole–benzoxazole dendrimer,<sup>23</sup> ferrocenyl dendrimer,<sup>24</sup> phenothiazine dendrimer,<sup>25</sup> and photoresponsive stilbene

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**Scheme 1.** Reagents and conditions: (i) NaH, THF, room temperature, 8 h. (ii) CuSO<sub>4</sub>·5H<sub>2</sub>O (5 mol %), sodium ascorbate (10 mol %), THF/H<sub>2</sub>O (1:1, v/v), room temperature, 10 h.

dendrimer<sup>26</sup> have been reported from our laboratory through click chemistry and Wittig–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–Wadsworth–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 <sup>1</sup>H 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 <sup>1</sup>H NMR spectra of **1** showed a triplet at δ 3.84 (*J* = 6.9 Hz) for *N*-methylene protons along with the signals

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