



## Synthesis of liquid crystalline materials based on 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-s-triazine

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### ABSTRACT

C<sub>3</sub>-symmetric alkyloxy/aryloxy polyether dendrimers have been synthesized from 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-s-triazine and their liquid crystalline properties have been studied. C<sub>3</sub>-symmetric derivatives with *n*-hexyl and *n*-dodecyl chains at the periphery show mesophase properties when they are complexed with trinitrofluorenone at different temperatures.

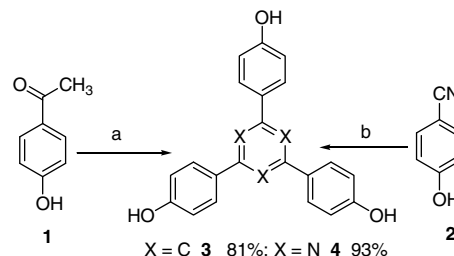
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Polyaromatic hydrocarbons have attracted considerable interest owing to their physical<sup>1</sup> and biological properties.<sup>2</sup> Among these, biphenyl-based polyaromatic compounds have gained significance due to their utility as building blocks in preparing hyper-branched polymers<sup>3</sup> and developing materials with photoelectric and luminescent properties.<sup>4</sup> In several cases, the 1,3,5-triphenylbenzene core has been used to develop organic light emitting diodes (OLEDs).<sup>5</sup> Triphenylbenzene has also been used in the synthesis of dendrimers<sup>6</sup> and fullerene fragments.<sup>7</sup> 1,3,5-*s*-Triazine and its derivatives are another class of interesting compounds which show various biological properties. Many triazine derivatives show antibacterial, antifungal, and antiviral<sup>8</sup> properties and the majority of triazine derivatives have been used in the cosmetic industry.<sup>9</sup> Along with these, much attention has been paid to these molecules for the preparation of liquid crystalline materials and for the development of OLEDs.<sup>10</sup>

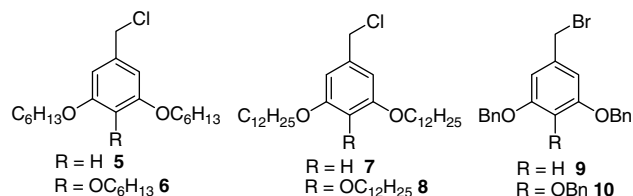
Though there are reports of utilizing 1,3,5-triphenylbenzene and the *s*-triazine moiety for the synthesis of materials science oriented molecules, very few reports are available, where 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-*s*-triazine units have been used for the development of OLEDs and liquid crystalline materials.<sup>11</sup> Thus, considering the importance of these molecules, and in continuation of our interest in C<sub>3</sub>-symmetric polyaromatic compounds<sup>12</sup> and liquid crystalline materials,<sup>13</sup> herein we report a simple and general method for the preparation of polyether dendrimers with triphenylbenzene and triphenyl-*s*-triazine units as

central units. Some of the dendrimers reported here show mesomorphic behavior when complexed with trinitrofluorenone (TNF).

Toward this goal, we prepared initially central cores **3** and **4** by an acid catalyzed cyclotrimerization reaction starting from *p*-hydroxyacetophenone **1** and *p*-hydroxybenzonitrile **2** (Scheme 1).<sup>14,15</sup> Thus, *p*-hydroxyacetophenone was treated with silicon

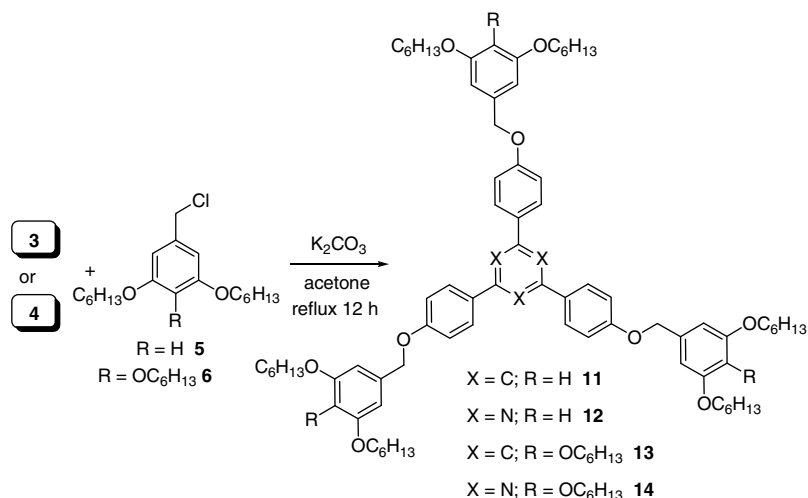


**Scheme 1.** Preparation of the central cores **3** and **4**. Reagents and conditions: (a) SiCl<sub>4</sub>, EtOH, rt, 12 h, 81%; (b) F<sub>3</sub>CSO<sub>3</sub>H, CHCl<sub>3</sub>, rt, 12 h, 93%.



**Figure 1.** Structures of the dendritic wedges **5–10**.

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**Scheme 2.** Preparation of polyether dendrimers **11–14**.

tetrachloride ( $\text{SiCl}_4$ ) in absolute ethanol at room temperature to give the cyclotrimerized product **3** in 81% yield. Similarly, treatment of *p*-hydroxybenzotrile **2** with trifluoromethanesulfonic acid ( $\text{F}_3\text{CSO}_3\text{H}$ ) in dry chloroform at room temperature generated the cyclotrimerized product **4** in 93% yield (Scheme 1).

**Table 1**  
Structures of the peripheral moieties of dendrimers **11–22**

Central core = <b>3</b> Ar=	Yield (%)	Central core = <b>4</b> Ar=	Yield (%)
	72		81
	86		78
	88		91
	70		73
	63		76
	40		85

In a separate route, the dendritic wedges (chlorides and bromides) **5–10** were synthesized starting from 3,5-dihydroxybenzoic acid, gallic acid, and alkyl/aryl halides (*n*-hexyl chloride, *n*-dodecyl chloride, and benzyl bromide) (Fig. 1).<sup>16</sup> We then focused our attention toward coupling these dendritic wedges with central cores **3** and **4** under phase-transfer catalysis (PTC) conditions.

Thus, the trihydroxyl compounds **3** and **4** were reacted with dendritic wedge **5** or **6** (derived from the 3,5-dihydroxy benzoic acid, gallic acid, and *n*-hexylchloride) in the presence of  $\text{K}_2\text{CO}_3$  in acetone for 12 h to give polyether dendrimers **11**, **12**, **13**, and **14** in 72%, 81%, 86%, and 78% yields, respectively (Scheme 2). Dendrimers with a dodecyl group at the periphery (**15–18**) were also synthesized using the same reaction conditions in good yields.<sup>17</sup> Polyether dendrimers with a benzyl group at the periphery (**19–22**) were prepared using the 18-crown-6 as a phase-transfer catalyst in DMF under refluxing conditions. All the final dendrimers (Table 1) were characterized from spectral data.<sup>18</sup>

Having demonstrated the synthesis of polyether dendrimers with *n*-hexyl, *n*-dodecyl, and benzyl groups at the periphery, we focused our attention toward the physical properties of these derivatives. The thermal behavior of all the materials and their charge transfer (CT) complexes with trinitrofluorenone (TNF) were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Thermal data obtained from the DSC heating and cooling cycles are collected in Table 2.

Compound **13** was semi-solid at room temperature. It showed a broad melting peak centered at about 59 °C in the first heating run of the DSC. On cooling from the isotropic phase, it stayed in optically transparent state up to room temperature. The DSC cooling

**Table 2**  
Phase transition temperatures (peak temperature/°C) and associated enthalpy changes (J/g in parentheses) of alkyloxy polyether dendrimers (**13**, **14**, **17** and **18**) and their 1:1 molar CT complexes with TNF

Compound Number	Heating scan	Cooling scan
<b>13</b>	SS 59.4 (18.8) I	No transition
<b>13:TNF</b>	Viscous oil	
<b>14</b>	SS 66.0 (23.0) I	No transition
<b>14:TNF</b>	SS 56.2 (5.5) Col 77.6 (6.5) I	No transition
<b>17</b>	S 42.7 (48.8) I	No transition
<b>17:TNF</b>	SS 54–70 (0.8) I	I 61.7 (0.7) Col 54.5 (0.4) Col
<b>18</b>	Cr 57.1 (49.8) I	I 31.8 (36.9) Cr
<b>18:TNF</b>	SS 50.6 (24.1) Col 101.5 (0.6) I	I 96.9 (1.2) Col

S = solid, SS = semi-solid, Cr = crystals, Col = columnar phase, I = isotropic.

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