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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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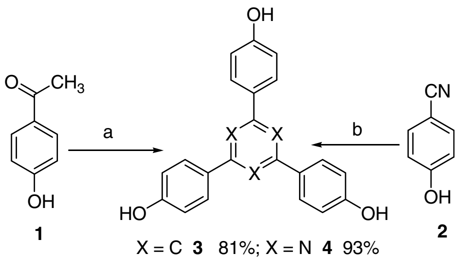
ABSTRACT

C_3-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_3-symmetric derivatives with *n*-hexyl and *n*-dodecyl chains at the periphery show mesophase properties when they are complexed with trinitrofluorenone at different temperatures.

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

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.[11] Thus, considering the importance of these molecules, and in continuation of our interest in C_3-symmetric polyaromatic compounds[12] and liquid crystalline materials,[13] 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).[14,15] Thus, *p*-hydroxyacetophenone was treated with silicon



Scheme 1. Preparation of the central cores **3** and **4**. Reagents and conditions: (a) $SiCl_4$, EtOH, rt, 12 h, 81%; (b) F_3CSO_3H, $CHCl_3$, rt, 12 h, 93%.

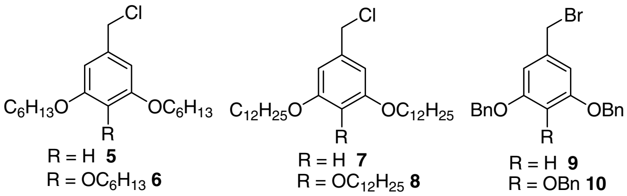


Figure 1. Structures of the dendritic wedges **5**–**10**.

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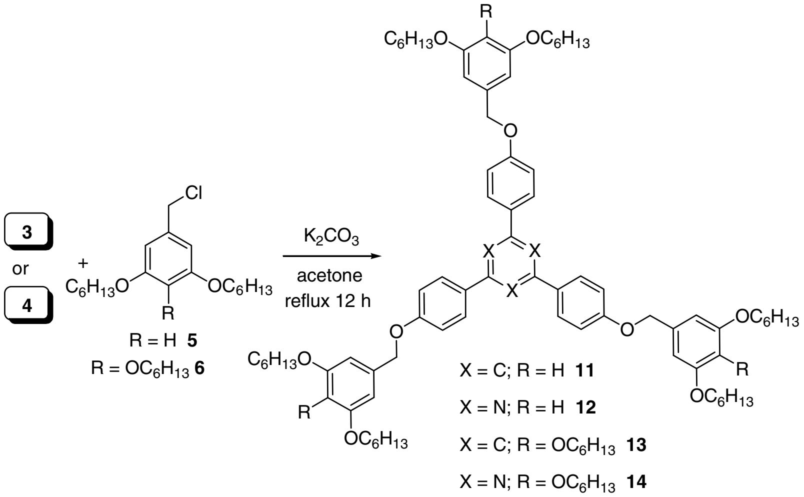
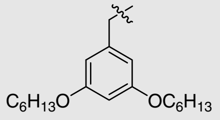
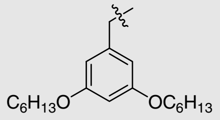
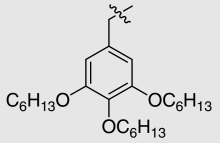
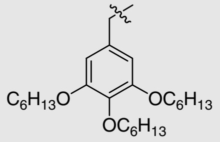
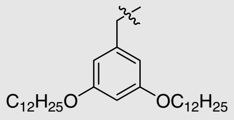
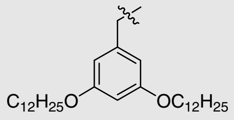
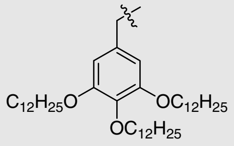
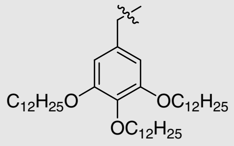
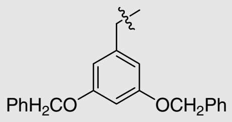
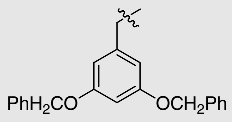
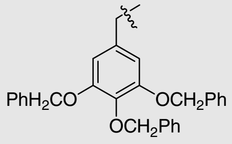
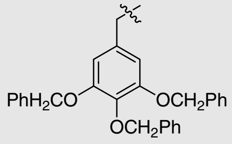


Scheme 2. Preparation of polyether dendrimers **11**–**14**.

tetrachloride ($SiCl_4$) in absolute ethanol at room temperature to give the cyclotrimerized product **3** in 81% yield. Similarly, treatment of *p*-hydroxybenzonitrile **2** with trifluoromethanesulfonic acid (F_3CSO_3H) 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 = **3** Ar=	Yield (%)		Central core = **4** Ar=	Yield (%)
11		72	**12**		81
13		86	**14**		78
15		88	**16**		91
17		70	**18**		73
19		63	**20**		76
21		40	**22**		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).[16] 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 K_2CO_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.[17] 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.[18]

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
13	SS 59.4 (18.8) I	No transition
13:**TNF**	Viscous oil	
14	SS 66.0 (23.0) I	No transition
14:**TNF**	SS 56.2 (5.5) Col 77.6 (6.5) I	No transition
17	S 42.7 (48.8) I	No transition
17:**TNF**	SS 54–70 (0.8) I	I 61.7 (0.7) Col 54.5 (0.4) Col
18	Cr 57.1 (49.8) I	I 31.8 (36.9) Cr
18:**TNF**	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.

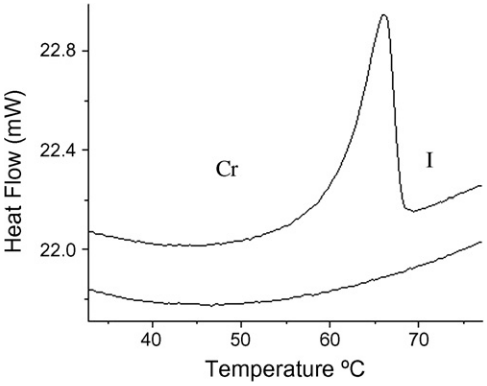


Figure 2a. DSC traces for compound **14** on heating and cooling (scan rate 5 °C min^{-1}).

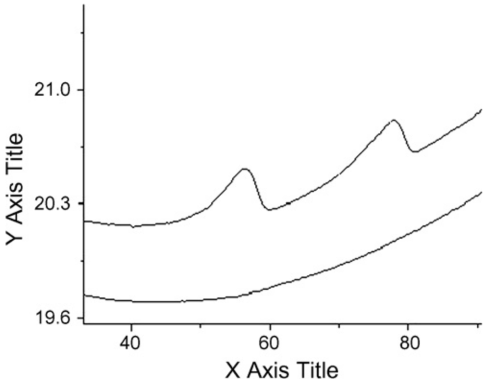


Figure 2b. DSC traces for compound **14**:TNF complex on heating and cooling (scan rate 5 °C min^{-1}).

cycle confirmed this observation, which did not show any transition down to room temperature. Upon doping with TNF (about 1:1 molar ratio), it changed to a red viscous oil which was not liquid crystalline. Compound **14** was also semi-solid at ambient temperature and on heating displayed a broad melting transition at about 66 °C (Fig. 2a). As with **13**, this material did not show any transition up to room temperature. The yellow-orange semi-solid TNF complex of **14** melted at about 56 °C to a mesophase, which cleared at about 78 °C (Fig. 2b). Upon cooling, columnar phase appeared at about 55 °C under POM (Fig. 5) but, surprisingly, the DSC did not display any transition in the cooling run indicating the second order nature of this transition. This could also be because of the small amount (about 2 mg) loaded in the DSC cup. Probably a weak transition would be noticed by loading a sufficient amount; say 5–7 mg of the sample.

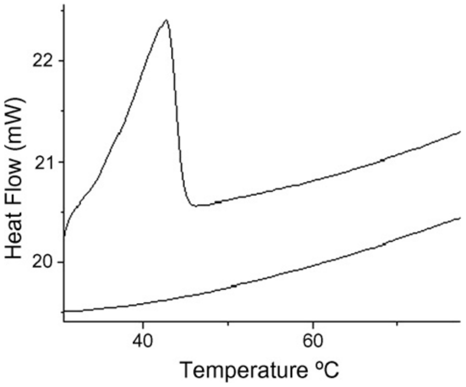


Figure 3a. DSC traces for compound **17** on heating and cooling (scan rate 5 °C min^{-1}).

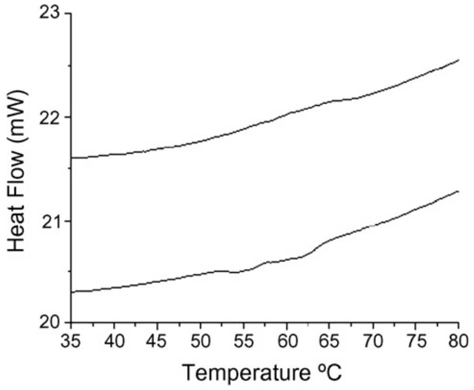


Figure 3b. DSC traces for compound **17**:TNF complex on heating and cooling (scan rate 5 °C min^{-1}).

The glassy-solid **17** displayed a melting transition at about 43 °C. On cooling, its behavior was similar to **13** and **14**, that is, no transition up to room temperature (Fig. 3a). The DSC of its CT complex with TNF showed a very broad and weak transition consisting of two or three peaks in the 55 °C to 70 °C temperature range (Fig. 3b). Upon cooling, the POM showed the appearance of columnar phase texture (Figs. 6a and 6b) at about 55 °C, which remained stable up to room temperature. The DSC cooling run exhibited two transitions; one centered at 61.7 °C and the other at 54 °C. The second transition could be due to a columnar phase to

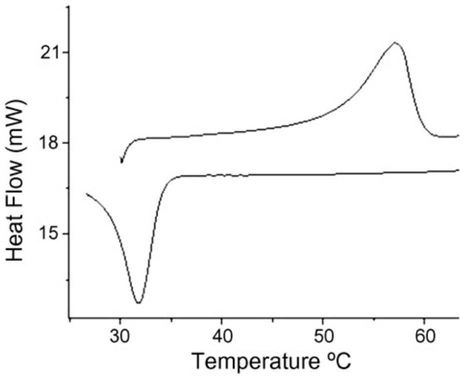


Figure 4a. DSC traces for compound **18** on heating and cooling (scan rate 5 °C min^{-1}).

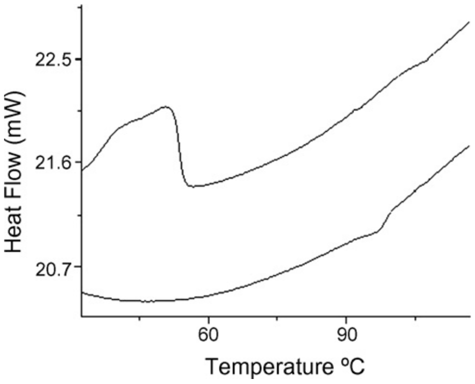


Figure 4b. DSC traces for compound **18**:TNF complex on heating and cooling (scan rate 5 °C min^{-1}).

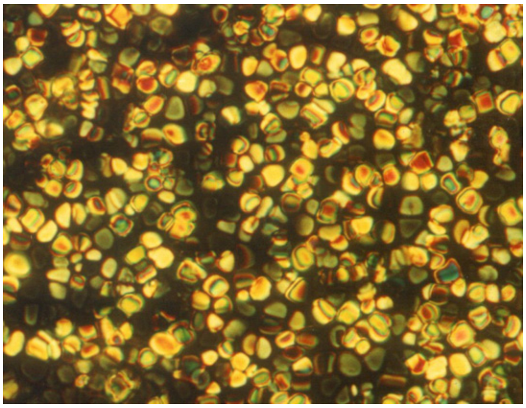


Figure 5. POM image of compound **14**:TNF at 55 °C (crossed polarizers, magnification 500).

columnar phase transition, but no change in optical texture was observed at this transition. The exact nature of the two columnar phases could only be deduced from detailed XRD studies.

The crystalline compound **18** melted at about 50 °C and crystallized at about 31 °C on cooling (Fig. 4a). Its 1:1 molar CT complex with TNF was an orange-red semi-solid at room temperature. The DSC showed two endothermic transitions in the first heating cycle (Fig. 4b). The first one centered at about 50 °C was due to the melting of the solid to a columnar phase and the second, centered at 101 °C was a columnar phase to isotropic phase transition. Upon cooling, the columnar phase appeared at 97 °C (Figs. 7a and 7b). This phase remained stable down to room temperature and no crystallization peak was observed on cooling. As the compound did not crystallize, the second heating run of the DSC was devoid of the melting transition and only a mesophase to isotropic transition at 100.4 °C was observed. The isotropic phase to columnar phase transition appeared at the same temperature on second cooling.

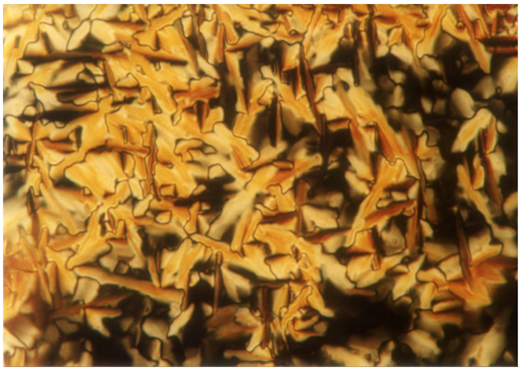


Figure 6a. POM image of compound **17**:TNF at 55 °C (crossed polarizers, magnification 200).

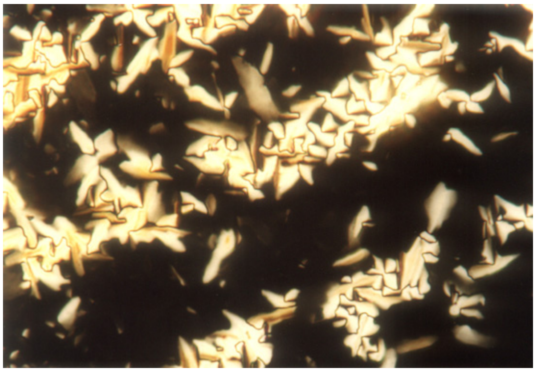


Figure 6b. POM image of compound **17**:TNF at 55 °C (crossed polarizers, magnification 500).

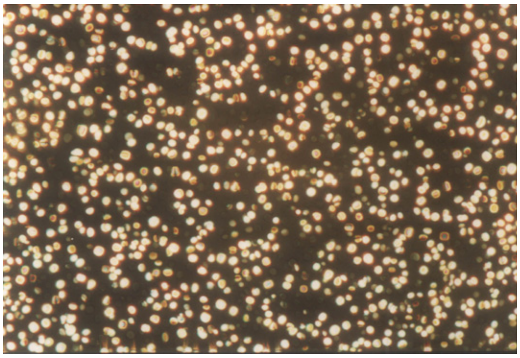


Figure 7a. POM image of compound **18**:TNF at 97 °C (crossed polarizers, magnification 200).

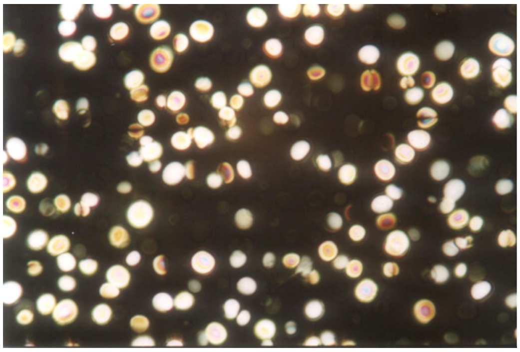


Figure 7b. POM image of compound **18**:TNF at 97 °C (crossed polarizers, magnification 500).

In conclusion, we have demonstrated a simple synthesis of polyether dendrimers with 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-*s*-triazine central cores with long alkyl chains at the peripheries and their utility for the development of liquid crystalline materials.

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References and notes

1. (a) Romagnoli, B.; van Baal, I.; Price, D. W.; Harwood, L. M.; Hayes, W. *Eur. J. Org. Chem.* **2004**, 4148; (b) Romagnoli, B.; Harwood, L. M.; Hayes, W. *Tetrahedron Lett.* **2003**, *44*, 37; (c) Engel, G. D.; Gade, L. H. *Chem. Eur. J.* **2002**, *8*, 4319; (d) Stone, L.; Smith, D. K.; McGrail, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 856; (e) Zhang, W.; Cao, X.-Y.; Zi, H.; Pei, J. *Org. Lett.* **2005**, *7*, 959; (f) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1 and references cited therein.
2. (a) Covell, D. G.; Huang, R.; Wallqvist, A. *Mol. Cancer Ther.* **2007**, *6*, 2261; (b) Basnet, A.; Thapa, P.; Karki, R.; Na, Y.; Jahng, Y.; Jeong, B.-S.; Jeong, T. C.; Lee, C. S.; Lee, E.-S. *Bioorg. Med. Chem.* **2007**, *15*, 435; (c) Tabacco, A.; Bardelli, F.; Meiattini, F.; Tarli, P. *Clin. Chim. Acta* **1980**, *104*, 405.
3. Zeng, S.; Zimmerman, S. C.; Kolotuchin, S. V.; Reichert, E. C. E.; Ma, Y. *Tetrahedron* **2002**, *58*, 825.
4. Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.
5. Pang, J.; Marcotte, E. J.-P.; Seward, C.; Brown, R. S.; Wang, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4042.

6. (a) Mongin, O.; Brunel, J.; Porrés, L.; Blanchard-Desce, M. *Tetrahedron Lett.* **2003**, *44*, 2813; (b) Brunel, J.; Ledoux, I.; Zyss, J.; Blanchard-Desce, M. *Chem. Commun.* **2001**, 923; (c) He, Q.; Haung, H.; Yang, J.; Lin, H.; Bai, F. *J. Mater. Chem.* **2003**, *13*, 1085.
7. (a) Gómez-Lor, B.; Echavarren, A. M. *Org. Lett.* **2004**, *6*, 2993; (b) Gómez-Lor, B.; Gonzalez-Cantalapiedra, E.; Ruiz, M.; de Frutos, Ó.; Cárdenas, D. J.; Santos, A.; Echavarren, A. M. *Chem. Eur. J.* **2004**, *10*, 2601.
8. (a) Srinivas, K.; Srinivas, U.; Rao, V. J.; Bhanuprakash, K.; Kishore, K. H.; Murty, U. S. N. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1121. and references cited therein; (b) Srinivas, K.; Srinivas, U.; Bhanuprakash, K.; Kishore, K. H.; Murty, U. S. N.; Rao, V. J. *Eur. J. Med. Chem.* **2006**, *41*, 1240.
9. (a) Uli, O.; Lim, H. W. *Basic Clin. Dermat.* **2007**, *38*, 279; (b) Couteau, C.; Pommier, M.; Paparis, E.; Coiffard, L. J. M. *Pharmazie* **2007**, *62*, 449; (c) Uli, O.; Bernd, H. *Cosmet. Toiletries* **2004**, *119*, 61.
10. (a) Shirota, Y.; Kuwabara, H.; Inada, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807; (b) Bulovic, N.; Gu, G.; Burrows, P. E.; Forrest, S. R. *Nature* **1996**, *380*, 29; (c) Shen, Z.; Burrows, P. E.; Bulovic, N.; Forrest, S. R.; Thompson, M. E. *Science* **1997**, *276*, 2009; (d) Cammidge, A. N.; King, A. M. *Tetrahedron Lett.* **2006**, *47*, 5569.
11. (a) Lee, C.-H.; Yamamoto, T. *Tetrahedron Lett.* **2001**, *42*, 3993. and references cited therein; (b) Chérioux, F.; Mailotte, H.; Audebert, P.; Zyss, J. *Chem. Commun.* **1999**, 2083; (c) Shu, W.; Valiyaveettil, S. *Chem. Commun.* **2002**, 1350.
12. (a) Kotha, S.; Chakraborty, K.; Brahmachary, E. *Synlett* **1999**, 1621; (b) Kotha, S.; Kashinath, D.; Lahiri, K.; Sunoj, R. B. *Eur. J. Org. Chem.* **2004**, 4003.
13. (a) Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83; (b) Bisoyi, H. K.; Kumar, S. *Tetrahedron Lett.* **2007**, *48*, 4399; (c) Kumar, S.; Bisoyi, H. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 1501; (d) Kumar, S.; Pal, S. K.; Kumar, P. S.; Lakshminarayanan, V. *Soft. Mater.* **2007**, *2*, 896.
14. Elmorsy, S. S.; Khalil, A. G. M.; Girges, M. M.; Salama, T. A. *J. Chem. Res. (S)* **1997**, 232.
15. Iyoda, M.; Fukuda, M.; Yoshida, M.; Sasaki, S. *Chem. Lett.* **1994**, 2369.
16. (a) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539; (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
17. *Preparation of compound* **17**: A mixture of **5** (20 mg, 0.05 mmol), K_2CO_3 (100 mg, 0.73 mmol), 18-crown-6 (0.02 equiv), and 3,4,5-tris-*n*-dodecyloxybenzyl chloride (184 mg, 2.5 mmol) in dry acetone (10 mL) was refluxed for 24 h. At the conclusion of reaction (TLC monitoring), it was cooled to rt, diluted with water (10 mL), and extracted with EtOAc (3 × 10 mL). Organic layers were washed with brine, water, dried over $MgSO_4$, and concentrated under reduced pressure to give the crude product which was purified by silica gel column chromatography. Elution of the column with 2% EtOAc–petroleum ether mixture gave the desired 1st generation dendrimer **17** (96 mg, 70%) as a sticky solid. R_f 0.3 (2% EtOAc–petroleum ether).
18. *Spectral data for compound* **17**: ^{1}H NMR (300 MHz $CDCl_3$): δ 0.87 (t, $J = 6$ Hz, 27H, terminal CH_3), 1.25–1.29 (m, 144H, alkyl –CH_2–), 1.42-1.47 (br s, 18H, alkyl –CH_2–), 1.70–1.80 (heptet, $J = 6.9$ Hz, 18H, Ar-O–CH_2–CH_2–), 3.99 (m, 18 H, Ar-O–CH_2–CH_2–), 5.00 (s, 6H, Ar-O–CH_2-Ar), 6.65 (s, 6H, *ortho* Ar-H of dendritic wedge), 7.08 (d, $J = 9$ Hz, 6H, Ar-H of core), 7.63 (d, $J = 8.7$ Hz, 6 H, Ar-H of core) 7.66 (s, 3H, Ar-H of central benzene ring). ^{13}C NMR (75.4 MHz $CDCl_3$): δ 14.21 (terminal CH_3), 22.77, 26.19, 29.49, 29.73, 29.78, 29.85, 30.42, 32.01, 69.21 (*meta* Ar-O–CH_2–CH_2–), 70.64 (*para* Ar-O–CH_2–CH_2–), 73.51 (Ar-O–CH_2-Ar), 106.23, 115.24, 129.98, 128.41, 131.95, 134.13, 138.04, 141.86, 153.41, 158.63. Mass (MALDI-TOF): 2284.; *Spectral data for compound* **18**:^{1}H NMR (300 MHz $CDCl_3$): δ 0.88 (t, $J = 5.4$ Hz, 27H, terminal CH_3), 1.26 (br s, 144H), 1.42–1.47 (br s, 18H), 1.70–1.80 (heptet, $J = 6.8$ Hz, 18H, Ar-O–CH_2–CH_2–), 3.93–4.01 (m, 18H, Ar-O–CH_2–CH_2–), 5.06 (br s, 6H, Ar-O–CH_2-Ar), 6.66 (s, 6H, *ortho* Ar-H of dendritic wedge), 7.13 (br s, 6H, Ar-H of core), 8.72 (br s, 6H, Ar-H of core). ^{13}C NMR (75.4 MHz $CDCl_3$): δ 14.19 (terminal CH_3), 22.76, 26.18, 26.21, 29.44, 29.47, 29.50, 29.73, 29.78, 29.84, 30.42, 32.00, 69.22 (*meta* Ar-O–CH_2–CH_2–), 73.51 (*para* Ar-O–CH_2–CH_2–), 106.26, 114.85, 129.29, 130.95, 131.40, 138.11, 153.43, 162.43, 170.72. Mass (MALDI-TOF): 2288.