Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Mesomorphic properties of symmetrical and asymmetrical triphenylene homologues possessing fluoroalkylated side chains

Naohiro Terasawa[a]; Hirosato Monobe[b]; Kenji Kiyohara[c]
[a] Research Institute for Ubiquitous Energy Devices, [b] Nanotechnology Research Institute, [c] Research Institute for Cell Engineering, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, 563-8577 Japan

To cite this Article Terasawa, Naohiro , Monobe, Hirosato and Kiyohara, Kenji(2007) 'Mesomorphic properties of symmetrical and asymmetrical triphenylene homologues possessing fluoroalkylated side chains', Liquid Crystals, 34: 3, 311 — 324
To link to this Article: DOI: 10.1080/02678290601104817
URL: http://dx.doi.org/10.1080/02678290601104817

Liquid Crystals, Vol. 34, No. 3, March 2007, 311–324

Taylor & Francis
Taylor & Francis Group

Mesomorphic properties of symmetrical and asymmetrical triphenylene homologues possessing fluoroalkylated side chains

NAOHIRO TERASAWA*†, HIROSATO MONOBE‡ and KENJI KIYOHARA§

†Research Institute for Ubiquitous Energy Devices
‡Nanotechnology Research Institute
§Research Institute for Cell Engineering, National Institute of Advanced Industrial Science and Technology (AIST), KANSAI, Midorigaoka 1-8-31, Ikeda, Osaka, 563-8577 Japan

(*Received 6 June 2006; accepted 21 August 2006*)

Two types of homologues (symmetrical and asymmetrical in rotational symmetry) of novel triphenylene compounds possessing fluoroalkyl and alkyl side chains were synthesized via an alternative method. X-ray diffraction and DSC measurements showed that these homologues are thermotropic liquid crystals with a hexagonal columnar (Col_h) mesophase. The phase transition temperatures (Col_h–Iso) for both symmetrical and asymmetrical fluoroalkyloxytriphenylenes increase to about 180°C, and are independent of fluoromethylene chain and the rotational symmetry of chemical structure. The Col_h phase of symmetrical and asymmetrical fluoroalkyloxytriphenylenes possessing three fluoroalkyl side chains are more stable than fluoroalkyloxytriphenylenes possessing six fluoroalkyl side chains and alkyloxytriphenylenes. The X-ray diffraction patterns for symmetrical and asymmetrical fluoroalkyloxytriphenylenes, fluoroalkyloxytriphenylenes and alkyloxytriphenylenes in the wide-angle region are compared.

1. Introduction

Fluorinated materials play a significant role in a variety of fields, e.g. polymers, plastics, coating materials, surfactants, pharmaceuticals and agrochemicals, due to their unique properties [1, 2]. The substitution of hydrogen atoms by fluorine atoms increases chemical and oxidative stability, weatherability and melting point, whereas it decreases flammability, adhesion, dielectric constant and refractive index [1], because of the properties of fluorine atoms and unique physical properties of the C–F bond. It is well known that the fluorinated alkanes are more rigid than the corresponding hydrogenated alkanes, and that the fluorophilic and fluorophobic interactions work around fluoroalkyl and alkyl chains [1–4]. The intermolecular interactions of fluoroalkyl chains are interesting not only for mesophase formation but also for its functionality.

As for rod-like liquid crystals, a large number of liquid-crystalline materials incorporating fluoroalkyl chains have been synthesized. It has been reported that fluorophilic and fluorophobic interactions around fluoroalkyl chains enhance the mesophase thermal stability and facilitates the formations of the smectic phase [5–20]. Furthermore, it has been reported that the combination of a suitable length of aliphatic chain and the ratio of the perfluorinated alkane segment to the perhydrogenated one in the chain relates to the microsegregation at the molecular level [21–28]. For example, (perfluorodecyl)decane shows smectic B liquid crystalline phase between 38°C and 61°C due to the amphiphilic character of the molecules [23] and the bilayer of glutamate-based amphiphiles having fluoroalkyl chains shows a lyotropic mesophase in water [27]. These strongly indicate that fluorophilic and fluorophobic interactions are responsible for the formation of thermotropic and lyotropic mesophase.

On the other hand, several reports have been published on columnar liquid crystals possessing fluoroalkyl side chains [29–40]. For example, it has been reported that all tapered building blocks, and the self-assembly polymers (perfluorinated methylenic groups of their alkyl tails) into tubular supermolecular architectures show an enantiotropic hexagonal columnar (Col_h) mesophase. Semifluorination of all model compounds and polymers decreases the melting temperature of the supramolecular assembly and enhances the thermal stability of the Col_h phase. A further increase of fluoromethylene chain number (from 4 to 8) increases both the isotropization temperature of the

*Corresponding author. Email: terasawa-naohiro@aist.go.jp

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601104817

Col_h phase and the melting temperature. A parallel increase of the diameter of the supramolecular columns with the increase of fluoromethylene chain number is observed. A mechanism for this dramatic increase in the self-assembly process *via* microsegregation of the perfluorinated and perhydrogenated parts of tapered groups due to the fluorophobic effect has been proposed [30].

Furthermore, two reports have been published on discotic liquid crystals possessing fluoroalkyl side chains, i.e. triphenylene and hexabenzocoronene liquid crystals, in which the effect of fluoroalkyl chain on the mesomorphic behaviour is discussed [39, 40]. In the report on triphenylene liquid crystals, it was shown that the temperature range of the mesophase is strongly affected by fluorinated side chains. Substitution of one aliphatic chain with a partially fluorinated side chain in triphenylene mesogens with six long chains decreases the clearing temperature, whereas substitution of all aliphatic chains broadens the mesophase range. However, systematic studies have not been presented so far for the effect of fluorination on discotic mesomorphism.

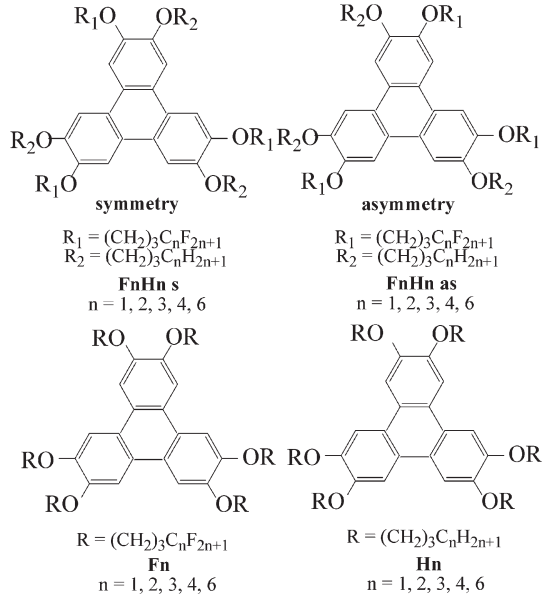
Since the discovery of fast electronic carrier transport in the columnar mesophase, liquid crystals have been recognized as a new class of organic semiconductor [41–45]. However, these liquid crystals usually have higher orientational order and, thus, tend to have higher viscosity than the lower ordered liquid crystals, such as nematic and smectic A phases. In the applications of these materials to electronic devices, the alignment control of liquid crystals is essential and therefore, it is required to find a useful method to obtain sufficient controllability of the molecular alignment for such highly ordered liquid crystals. On the other hand, recent studies on electronic properties of columnar mesophase have revealed fast one-dimensional transport of charged carriers [41, 46, 47] which exceeded the values by two to three orders of magnitude for amorphous polymers such as poly(*N*-vinylcarbazole), which has been applied in xerography and laser printing as a photoimaging material. Thus, the liquid crystals are recognized as a new class of organic semiconductor that exhibits self-organization and fluidity [48] and are expected to be used for electronic devices. This characteristic property of the mesophase is potentially applicable in the areas of EL devices, information storage, sensors and high-resolution xerography. The improvement of carrier mobility due to the stabilization of columnar structure could be expected if the triphenylene side chains are modified by fluoroalkyl chains.

Recently, several homologues of novel triphenylene derivatives possessing fluoroalkyl chains (**Fn**) were synthesized and they revealed a Col_h phase. These fluoroalkyloxytriphenylenes have a stabilized columnar mesophase and an increased melting point compared with the corresponding alkyloxytriphenylenes. In the case of fluoroalkyloxytriphenylenes possessing fluoromethylene side chains, an increase of fluoromethylene chain increases the thermal stability of columnar mesophase and the phase transition enthalpy (Col_h–Iso) and entropy (Col_h–Iso). The thermal stability of the columnar mesophase and the phase transition enthalpy (Col_h–Iso) and entropy (Col_h–Iso) for the fluromethylene side chains show the opposite tendency to the methylene side chains. The fluorophilic interaction around fluoromethylene chain plays a significant role in the thermal stability of columnar mesophase [49, 50].

In this work, two types of the homologues (**FnHn**) (symmetrical and asymmetrical in rotational symmetry, see scheme 1) as novel triphenylene compounds possessing fluoroalkyl and alkyl side chains were synthesized via an alternative method and their mesomorphism investigated in order to discuss the difference between the mesomorphism of the fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**).

2. Experimental section

To identify the compounds, ^1H NMR (500.0 MHz) and ^{19}F NMR (376.1 MHz) spectra were obtained on JEOL ALPHA-500, JEOL ECA-500 and JEOL JNM-AL400 FT-NMR spectrometers. MALDI-TOF mass spectra were also measured on a Applied Biosystems/Voyager



Scheme 1. Structure of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**), fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**).

TM DE STR-D1 spectrometer. IR spectra were obtained for KBr pellets by a Perkin Elmer Paragon 1000 FT-IR spectrometer.

The phase transitions and enthalpies were detected by a differential scanning calorimeter (TA Instrument, 2920 MDSC) and the textures of mesophase were observed by a polarizing microscope (Olympus, BH-2) equipped with a hot stage (Mettler, FP82HT). X-ray diffraction studies were carried out by a Rigaku Geigerflex X-ray diffractometer (CuKα) with a hand-made hot stage.

3. Synthesis

All materials used are commercially available and were used without further purification. The syntheses of compounds **FnHn** were carried out by methods in the literature [51–53].

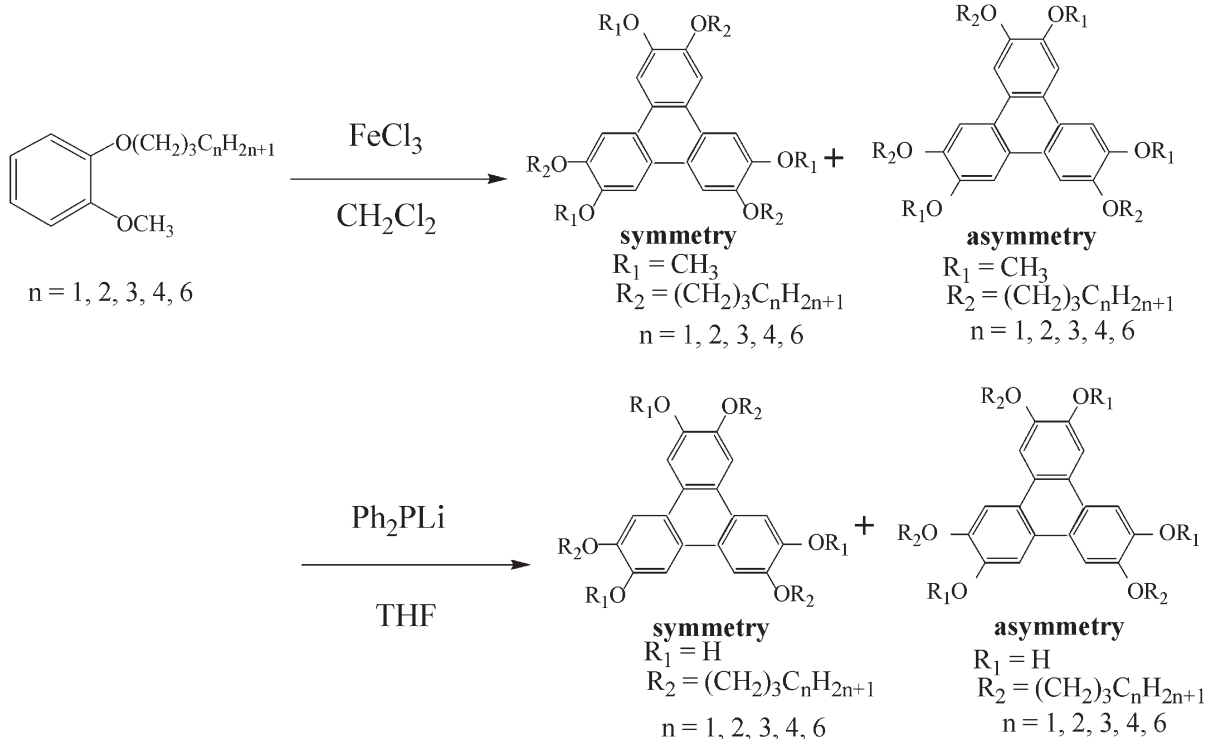
3.1. *Symmetrical and asymmetrical triphenylenes*

The synthesis of symmetrical and asymmetrical triphenylenes was carried out according to scheme 2.

3.1.1. 2,6,10-triheptyloxy-3,7,11-trimethoxytriphenylene and 2,6,11-triheptyloxy-3,7,10-trimethoxytriphenylene. 2-heptyoxyanisole (22.2 g, 0.1 mol), $FeCl_3$ (48.6 g, 0.3 mol) and conc. H_2SO_4 (3 drops) were added to Et_2O (100 ml). The reaction was monitored by TLC. When the reaction had finished, the mixture was carefully poured into methanol (300 ml) and cooled at 0°C. The crude product was filtered off, purified by column chromatography (silica gel, *n*-hexane:CH_3COOEt=9:1 and 85:15).

3.1.2. 2,6,10-triheptyloxy-3,7,11-trimethoxytriphenylene. (1.80 g, 8.2%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 0.91 (t, J=7.3 Hz, 9H), 1.30–1.48 (m, 18H), 1.52–1.62 (m, 6H), 1.97 (m, 6H), 4.10 (s, 9H), 4.25 (t, J=6.8 Hz, 6H), 7.79 (s, 3H) , 7.87 (s, 3H); MS m/z=660.2 (calcd. 660.4 for $C_{42}H_{60}O_6$) ; FTIR (KBr, cm^{-1}) 2960, 2938, 2873, 1619, 1516, 1439, 1386, 1336, 1261, 1231, 1173, 1152, 1064, 1031, 835; Anal Calcd. for $C_{42}H_{60}O_6$: C,76.33; H, 9.15; Found : C, 76.44; H, 9.44.

3.1.3. 2,6,11-triheptyloxy-3,7,10-trimethoxytriphenylene. (8.60 g, 39.1%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 0.91 (t, J=7.0 Hz, 3H), 1.30–1.48 (m, 6H), 1.54–1.62 (m, 6H), 1.97 (m, 6H), 4.09 (s, 9H), 4.25 (t, J=7.0 Hz, 2H), 7.78 (s, 1H), 7.80 (s, 2H), 7.80 (s, 2H) , 7.81 (s, 1H); MS m/z=660.4 (calcd. 660.4 for $C_{42}H_{60}O_6$); FTIR (KBr, cm^{-1}) 2950, 2929, 2857, 1619, 1516, 1468, 1422, 1390, 1260, 1203, 1162, 1049, 835, 793; Anal Calcd. for $C_{42}H_{60}O_6$: C,76.33; H, 9.15; Found : C, 76.33; H, 9.40.



Scheme 2. Synthesis of symmetrical and asymmetrical triphenylenes.

3.1.4. 2,6,10-tributyloxy-3,7,11-trimethoxytriphenylene. (1.06 g, 5.9%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 1.05 (t, J=7.5 Hz, 3H), 1.60 (m, 2H), 1.96 (m, 2H), 4.10 (s, 3H), 4.26 (t, J=6.8 Hz, 2H), 7.80 (s, 1H), 7.81 (s, 2H), 7.81 (s, 2H), 7.83 (s, 1H); MS m/z=534.2 (calcd. 534.1 for $C_{33}H_{42}O_6$); FTIR (KBr, cm^{-1}) 2957, 2934, 2870, 1619, 1519, 1466, 1451, 1425, 1389, 1262, 1203, 1163, 1047, 837, 790, 579; Anal Calcd. for $C_{33}H_{42}O_6$: C,74.13; H, 7.92; Found : C, 73.97; H, 7.97.

3.1.5. 2,6,11-tributyloxy-3,7,10-trimethoxytriphenylene. (1.42 g, 7.8%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 1.05 (t, J=7.3 Hz, 3H), 1.61 (m, 2H), 1.96 (m, 2H), 4.10 (s, 3H), 4.26 (t, J=6.8 Hz, 2H), 7.80 (s, 3H), 7.83 (s, 3H); MS m/z=534.1 (calcd. 534.1 for $C_{33}H_{42}O_6$); FTIR (KBr, cm^{-1}) 2959, 2935, 2871, 1618, 1518, 1466, 1422, 1390, 1262, 1204, 1163, 1050, 831, 790; Anal Calcd. for $C_{33}H_{42}O_6$: C,74.13; H, 7.92; Found : C, 73.97; H, 7.90.

3.1.6. 2,6,10-trinonyloxy-3,7,11-trimethoxytriphenylene. (0.66 g, 2.7%) ^{1}H NMR ($CDCl_3$, TMS, 399.7 MHz) 0.89 (t, J=6.8 Hz, 3H), 1.22–1.48 (m, 10H), 1.50–1.62 (m, 6H), 1.97 (m, 6H), 4.10 (s, 9H), 4.25 (t, J=6.8 Hz, 2H), 7.80 (s, 3H), 7.83 (s, 3H); MS m/z=744.4 (calcd. 744.5 for $C_{48}H_{72}O_6$); FTIR (KBr, cm^{-1}) 2922, 2853, 1617, 1516, 1463, 1450, 1424, 1263, 1194, 1163, 1048, 834; Anal Calcd. for $C_{48}H_{72}O_6$: C,77.38; H, 9.74; Found : C, 77.42; H, 9.68.

3.1.7. 2,6,11-trinonyloxy-3,7,10-trimethoxytriphenylene. (2.90 g, 11.8%) ^{1}H NMR ($CDCl_3$, TMS, 399.7 MHz) 0.89 (t, J=6.8 Hz, 3H), 1.22–1.48 (m, 10H), 1.52–1.62 (m, 6H), 1.98 (m, 6H), 4.10 (s, 9H), 4.26 (t, J=6.8 Hz, 2H), 7.81 (s, 1H), 7.82 (s, 4H), 7.84 (s, 1H); MS m/z=744.1 (calcd. 744.5 for $C_{48}H_{72}O_6$); FTIR (KBr, cm^{-1}) 2924, 2855, 1620, 1518, 1466, 1422, 1392, 1262, 1201, 1172, 1050, 831, 795, 722, 567; Anal Calcd. for $C_{48}H_{72}O_6$: C,77.38; H, 9.74; Found : C, 77.38; H, 9.80.

3.1.8. 2,6,10-triheptyloxy-3,7,11-trihydroxytriphenylene. Diphenyphosphine (1.84 g, 9.9 mmol) was added to dried THF (30 ml) under argon at 0°C; butyllithium solution in hexane (10 ml, 1.6M, 16 mmol) was then added dropwise over 15 min, 2,6,10-triheptyloxy-3,7,11-trimethoxy-triphenylene (1.45g, 2.19 mmol) was added and the mixture was stirred at room temperature for 17 h. The mixture was poured into water, and organic matter extracted with Et_2O. The organic layer was washed with 2N HCl aq. and brine, dried and the solvents removed *in vacuo*. The crude product was filtered off, purified by column chromatography (silica gel, *n*-hexane:CH_3COOEt=85:15) (1.14 g, 83.8%). ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 0.92 (m, 9H), 1.32–1.48 (m, 6H), 1.54 (m, 6H), 1.93 (m, 6H), 4.25 (m, 6H), 7.78 (s, 3H), 7.91 (s, 3H); MS m/z=618.2 (calcd. 618.4 for $C_{39}H_{54}O_6$); FTIR (KBr, cm^{-1}) 3548, 3427, 2928, 2856, 1630, 1596, 1514, 1452, 1390, 1357, 1301, 1269, 1162, 1030, 854, 808, 572; Anal Calcd. for $C_{39}H_{54}O_6$: C,75.69; H, 8.79; Found : C, 75.92; H, 8.70.

3.1.9. 2,6,11-triheptyloxy-3,7,10-trihydroxytriphenylene. (0.80 g, 30.3%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 0.92 (m, 9H), 1.30–1.48 (m, 18H), 1.50–1.60 (m, 6H), 1.88–1.98 (m, 6H), 4.24 (m, 6H), 7.68 (s, 1H) , 7.69 (s, 1H), 7.76 (s, 1H) , 7.91 (s, 2H), 7.92 (s, 1H); MS m/z=617.9 (calcd. 618.4 for $C_{39}H_{54}O_6$); FTIR (KBr, cm^{-1}) 3559, 3533, 3378, 2929, 2857, 1631, 1597, 1514, 1466, 1433, 1394, 1348, 1307, 1267, 1162, 1036, 858, 808; Anal Calcd. for $C_{39}H_{54}O_6$: C,75.69; H, 8.79; Found : C, 75.89; H, 8.73.

3.1.10. 2,6,10-trbutyloxy-3,7,11-trihydroxytriphenylene. (0.40 g, 23.3%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 1.05 (t, J=7.5 Hz, 9H), 1.50–1.64 (m, 6H), 1.92 (m, 6H), 4.26 (t, J=6.5 Hz, 6H), 7.78 (s, 3H) , 7.91 (s, 3H); MS m/z=492.2 (calcd. 492.3 for $C_{30}H_{36}O_6$); FTIR (KBr, cm^{-1}) 3532, 3380, 2961, 2930, 2870, 1632, 1593, 1515, 1452, 1392, 1360, 1304, 1273, 1162, 1030, 860, 802; Anal Calcd. for $C_{30}H_{36}O_6$: C,73.15; H, 7.37; Found : C, 73.21; H, 7.30.

3.1.11. 2,6,11-tributyloxy-3,7,10-trihydroxytriphenylene. (0.43 g, 32.1%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 1.05 (m, 9H), 1.56–1.68 (m, 6H), 1.93 (m, 6H), 4.28 (m, 6H), 7.71 (s, 1H) , 7.73 (s, 1H) , 7.78 (s, 1H) , 7.92 (s, 1H) , 7.93 (s, 1H) , 7.93 (s, 1H); MS m/z=491.9 (calcd. 492.3 for $C_{30}H_{36}O_6$); FTIR (KBr, cm^{-1}) 3533, 3386, 2962, 2930, 2870, 1632, 1594, 1515, 1452, 1392, 1360, 1304, 1273, 1226, 1163, 1029, 860, 802; Anal Calcd. for $C_{30}H_{36}O_6$: C,73.15; H, 7.37; Found : C, 73.44; H, 7.42.

3.1.12. 2,6,11-trinonyloxy-3,7,10-trihydroxytriphenylene. (0.58 g, 41.1%) ^{1}H NMR ($CDCl_3$, TMS, 399.7 MHz) 0.89 (t, J=6.8 Hz, 9H), 1.26–1.44 (m, 30H), 1.46–1.60 (m, 6H), 1.93 (m, 6H), 4.25 (m, 6H), 7.70 (s, 1H) , 7.71 (s, 1H) , 7.77 (s, 1H) , 7.91 (s, 1H) , 7.92 (s, 1H) , 7.93 (s, 1H); MS m/z=702.6 (calcd. 702.5 for $C_{45}H_{66}O_6$); FTIR (KBr, cm^{-1}) 3541, 3446, 3354, 2925, 2855, 1632, 1595, 1513, 1455, 1360, 1304, 1269, 1227, 1165, 1034, 1012, 849, 808; Anal Calcd. for $C_{45}H_{66}O_6$: C,76.88; H, 9.46; Found : C, 76.87; H, 9.25.

3.1.13. 2,6,10-trinonyloxy-3,7,11-trihydroxytriphenylene. (0.84 g, 84.5%) ^{1}H NMR ($CDCl_3$, TMS, 399.7 MHz) 0.90 (t, J=7.0 Hz, 9H), 1.25–1.45 (m, 30H), 1.45–1.60 (m, 6H), 1.92 (m, 6H), 4.24 (t, J=6.8 Hz, 6H), 7.78 (s, 3H) , 7.91 (s, 3H); MS m/z=702.7 (calcd. 702.5 for $C_{45}H_{66}O_6$); FTIR (KBr, cm^{-1}) 3559, 3532, 3362, 2926, 2854, 1633, 1594,

1514, 1466, 1434, 1394, 1348, 1307, 1267, 1162, 1036, 1012, 858, 806; Anal Calcd. for $C_{45}H_{66}O_6$: C,76.88; H, 9.46; Found : C, 76.90; H, 9.38.

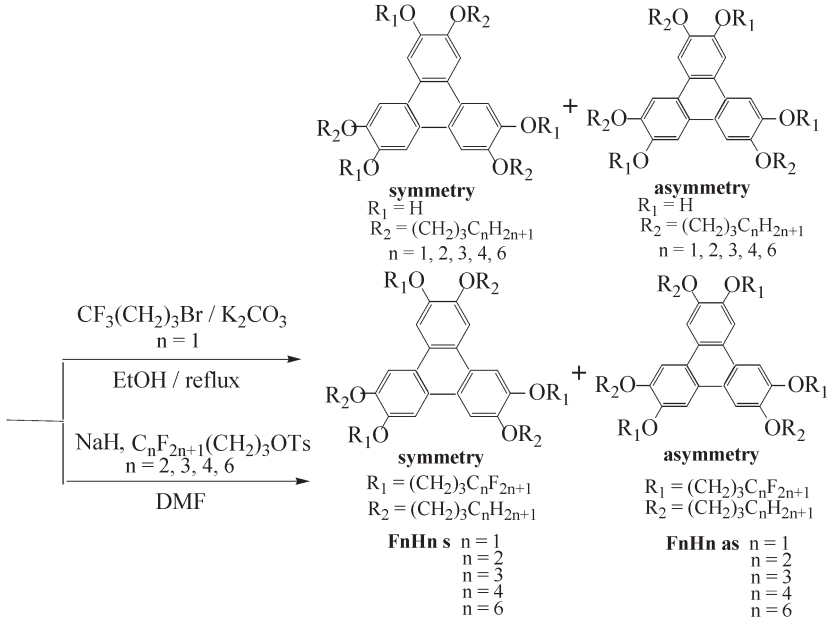
3.2. *Symmetrical and asymmetrical fluoroalkyloxytriphenylenes*

The synthesis of symmetrical and asymmetrical fluoroalkyloxytriphenylenes was carried out according to scheme 3.

3.2.1. 2,6,10-triheptyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)-triphenylene (F4H4s). 2,6,10-triheptyloxy-3,7,11-trihydroxytriphenylene (0.93 g, 1.5 mmol) was added to a suspension of sodium hydride (0.36 g, 15.0 mmol) in dry DMF (30 ml) at room temperature. After stirring for 1.5 h, 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoropentyl-*p*-toluenesulphonate [54] (2.59 g, 6 mmol) was added. The mixture was then heated to 130°C and stirred for 17 h. After cooling to room temperature, water was added into the reaction mixture. The product was extracted by ether and the organic layer was washed by 0.5N HCl aq. and brine. The crude product was purified by column chromatography (silica gel, *n*-hexane:ethyl acetate=96:4). Recrystallization from EtOH gave the product (0.30 g, 14.3%). ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 0.90 (t, J=7.0 Hz, 9H), 1.30–1.48 (m, 18H), 1.52–1.60 (m, 6H), 1.93 (m, 6H), 2.23 (m, 6H), 2.47 (m, 6H), 4.22 (t, J=6.5 Hz, 6H), 4.31 (t, J=5.8 Hz, 6H), 7.81 (s, 3H) , 7.85 (s, 3H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.1 MHz) −81.5 (t, J=9.8 Hz, 9F), −115.0 (m, 6F), −124.9 (m, 6F), −126.5 (t, J=12.2 Hz, 6F); MS m/z=1397.9 (calcd. 1398.5 for $C_{60}H_{69}F_{27}O_6$); FTIR (KBr, cm^{-1}) 2934, 2862, 1618, 1518, 1472, 1441, 1386, 1358, 1265, 1221, 1174, 1132, 1067, 1032, 836, 721; Anal Calcd. for $C_{60}H_{69}F_{27}O_6$: C,51.51; H, 4.97; F, 36.66; Found : C, 51.51; H, 4.93; F, 36.50.

3.2.2. 2,6,11-triheptyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)-triphenylene (F4H4as). (0.26 g, 18.6%) ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 0.90 (t, J=6.5 Hz, 9H), 1.28–1.46 (m, 18H), 1.50–1.62 (m, 6H), 1.93 (m, 6H), 2.23 (m, 6H), 2.47 (m, 6H), 4.22 (m, 6H), 4.30 (m, 6H), 7.81 (s, 1H) , 7.82 (s, 2H) , 7.83 (s, 2H) , 7.85 (s, 1H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.1 MHz) −81.5 (m, 9F), −115.0 (t, J=14.7 Hz, 6F), −124.9 (s, 6F), −126.5 (t, J=10.9 Hz, 6F); MS m/z=1398.2 (calcd. 1398.5 for $C_{60}H_{69}F_{27}O_6$); FTIR (KBr, cm^{-1}) 2934, 2862, 1618, 1518, 1471, 1440, 1386, 1358, 1265, 1221, 1174, 1132, 1066, 1032, 836, 721; Anal Calcd. for $C_{60}H_{69}F_{27}O_6$: C,51.51; H, 4.97; F, 36.66; Found : C, 51.78; H, 4.97; F, 36.40.

3.2.3. 2,6,10-tripentyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoropentyloxy)-triphenylene (F2H2s). (0.23 g, 36.5%) ^{1}H NMR ($CDCl_3$, TMS, 500.2 MHz) 0.97 (t, J=7.5 Hz, 9H), 1.40–1.60 (m, 12H), 1.94 (m, 6H), 2.22 (m, 6H), 2.43 (m, 6H), 4.22 (t, J=6.8 Hz, 6H), 4.30 (t, J=6.0 Hz, 6H), 7.81 (s, 3H), 7.85 (s, 3H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 470.6 MHz) −85.9 (s, 9F), −118.7 (t, J=19.1 Hz, 6F); MS m/z=1014.4 (calcd. 1014.4 for $C_{48}H_{57}F_{15}O_6$); FTIR (KBr, cm^{-1}) 2960, 2940, 2868, 1619, 1519, 1391, 1336, 1264, 1192, 1028, 837, 719, 596; Anal Calcd. for $C_{48}H_{57}F_{15}O_6$: C,56.80; H, 5.77; F, 28.08; Found : C, 56.64; H, 5.62; F, 28.18.



Scheme 3. Synthesis of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**).

3.2.4. 2,6,11-tripentyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorononyloxy)-triphenylene (F2H2as). (0.58 g, 32.6%) ^{1}H NMR ($CDCl_3$, TMS, 500.2 MHz) 0.97 (t, J=7.0 Hz, 9H), 1.45 (m, 6H), 1.57 (m, 6H), 1.94 (m, 6H), 2.22 (m, 6H), 2.42 (m, 6H), 4.22 (t, J=6.5 Hz, 6H), 4.31 (t, J=6.0 Hz, 6H), 7.81 (s, 3H), 7.85 (s, 3H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 470.6 MHz) −85.9 (s, 9F), −118.7 (t, J=19.1 Hz, 6F); MS m/z=1014.5 (calcd. 1014.5 for $C_{48}H_{57}F_{15}O_6$); FTIR (KBr, cm^{-1}) 2962, 2938, 2866, 1619, 1518, 1441, 1390, 1192, 1174, 1028, 837, 719; Anal Calcd. for $C_{48}H_{57}F_{15}O_6$: C,56.80; H, 5.77; F, 28.08; Found : C, 56.89; H, 5.66; F, 27.93.

3.2.5. 2,6,10-trihexyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorononyloxy)-triphenylene (F3H3s). (0.60 g, 34.5%) ^{1}H NMR ($CDCl_3$, TMS, 500.2 MHz) 0.93 (t, J=7.3 Hz, 9H), 1.39 (m, 12H), 1.57 (m, 6H), 1.93 (m, 6H), 2.24 (m, 6H), 2.46 (m, 6H), 4.22 (m, 6H), 4.30 (m, 6H), 7.81 (s, 1H), 7.82 (s, 2H), 7.83 (s, 2H), 7.85 (s, 1H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 470.6 MHz) −81.1 (t, J=10.8 Hz, 9F), −115.8 (t, J=10.8 Hz, 6F), −128.2 (s, 6F); MS m/z=1207.0 (calcd. 1206.4 for $C_{54}H_{63}F_{21}O_6$); FTIR (KBr, cm^{-1}) 2935, 2866, 1618, 1517, 1386, 1357, 1264, 1233, 1174, 1115, 1064, 1030, 957, 881, 837, 719; Anal Calcd. for $C_{54}H_{63}F_{21}O_6$: C,53.73; H, 5.26; F, 33.05; Found : C, 53.59; H, 5.21; F, 33.12.

3.2.6. 2,6,11-trihexyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorononyloxy)-triphenylene (F3H3as). (0.30 g, 19.9%) ^{1}H NMR ($CDCl_3$, TMS, 500.2MHz) 0.93 (t, J=7.0 Hz, 9H), 1.39 (m, 12H), 1.58 (m, 6H), 1.93 (m, 6H), 2.23 (m, 6H), 2.46 (m, 6H), 4.22 (m, 6H), 4.31 (m, 6H), 7.81 (s, 1H), 7.83 (s, 2H), 7.83 (s, 2H), 7.85 (s, 1H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 470.6 MHz) −81.0 (m, 9F), −115.8 (m, 6F), −128.2 (s, 6F); MS m/z=1206.9 (calcd. 1206.4 for $C_{54}H_{63}F_{21}O_6$); FTIR (KBr, cm^{-1}) 2936, 2866, 1618, 1517, 1441, 1386, 1357, 1264, 1233, 1219, 1174, 1115, 1065, 1030, 957, 838, 729; Anal Calcd. for $C_{54}H_{63}F_{21}O_6$: C,53.73; H, 5.26; F, 33.05; Found : C, 53.73; H, 5.26; F, 33.17.

3.2.7. 2,6,10-trinonyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorononyloxy)-triphenylene (F6H6s). (1.37 g, 83.5%) ^{1}H NMR ($CDCl_3$, TMS, 399.7 MHz) 0.88 (t, J=6.6 Hz, 9H), 1.26–1.46 (m, 30H), 1.50–1.62 (m, 6H), 1.93 (m, 6H), 2.23 (m, 6H), 2.48 (m, 6H), 4.22 (t, J=6.4 Hz, 6H), 4.31 (t, J=5.8 Hz, 6H), 7.81 (s, 3H), 7.85 (s, 3H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.1 MHz) −81.3 (t, J=9.8 Hz, 9F), −114.8 (t, J=15.8 Hz, 6F), −122.3 (s, 6F), −123.3 (s, 6F), −123.9 (s, 6F), −126.5 (m, 6F); MS m/z=1782.1 (calcd. 1782.5 for $C_{72}H_{81}F_{39}O_6$); FTIR (KBr, cm^{-1}) 2931, 2858, 1619, 1518, 1470, 1440, 1387, 1265, 1233, 1175, 1144, 1031, 838, 697; Anal Calcd. for $C_{72}H_{81}F_{39}O_6$: C,48.49; H, 4.58; F, 41.55; Found : C, 48.49; H, 4.58; F, 41.80.

3.2.8. 2,6,11-trinonyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorononyloxy)-triphenylene (F6H6as). (0.89 g, 66.7%) ^{1}H NMR ($CDCl_3$, TMS, 399.7 MHz) 0.88 (t, J=6.6 Hz, 9H), 1.24–1.46 (m, 30H), 1.48–1.64 (m, 6H), 1.93 (m, 6H), 2.23 (m, 6H), 2.45 (m, 6H), 4.22 (m, 6H), 4.30 (m, 6H), 7.80 (s, 1H), 7.82 (s, 2H) , 7.83 (s, 2H), 7.85 (s, 1H); ^{19}F NMR

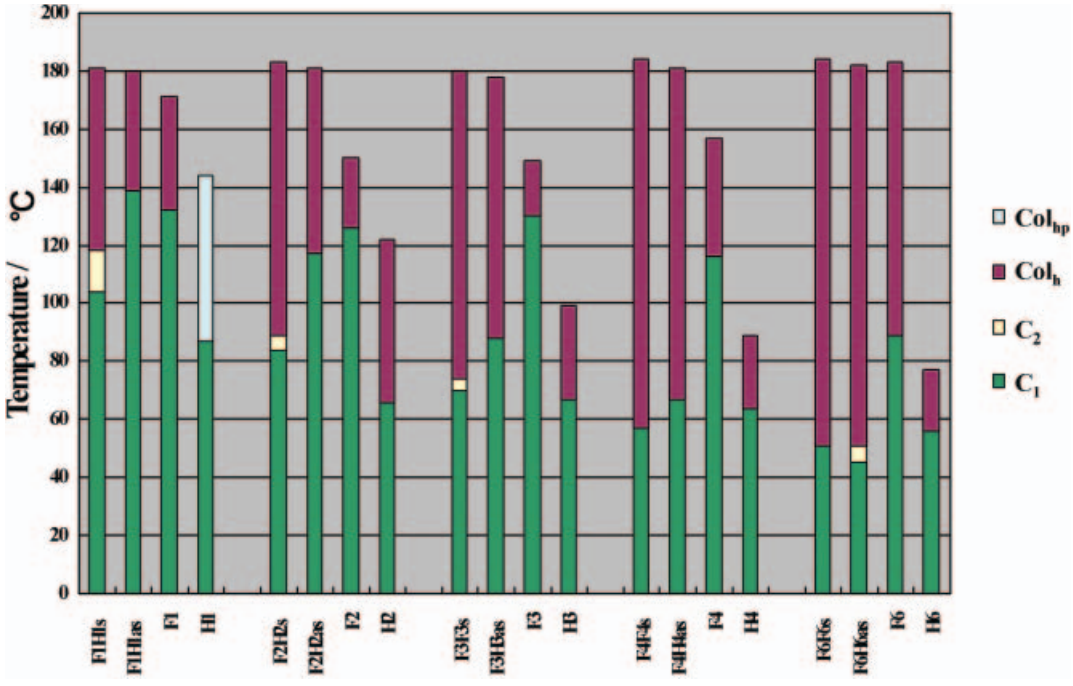


Figure 1. Phase transition behaviour of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**), fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**).

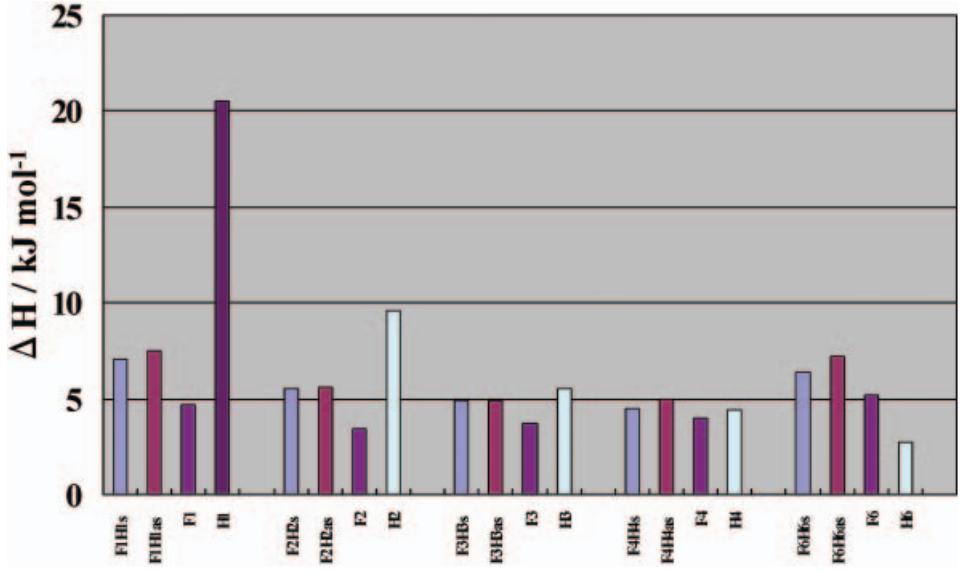


Figure 2. Phase transition enthalpies (Col_h–Iso) of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**), fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**).

($CDCl_3$, $CFCl_3$, 376.1 MHz) −81.3 (m, 9F), −114.8 (t, J=15.8 Hz, 6F), −122.4 (s, 6F), −123.4 (s, 6F), −123.9 (s, 6F), −126.6 (m, 6F); MS m/z=1782.6 (calcd. 1782.5 for $C_{72}H_{81}F_{39}O_6$); FTIR (KBr, cm^{-1}) 2931, 2858, 1618, 1518, 1471, 1441, 1386, 1263, 1233, 1176, 1146, 1029, 838, 697; Anal Calcd. for $C_{72}H_{81}F_{39}O_6$: C,48.49; H, 4.58; F, 41.55; Found : C, 48.57; H, 4.56; F, 41.55.

3.2.9. 2,6,10-tributyloxy-3,7,11-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorobutyloxy)-triphenylene (F1H1s). A mixture of 2,6,10-trbutyloxy-3,7,11-trihydroxytriphenylene (0.37 g, 0.75 mmol), 1-bromo-4,4,4-trifluorobutane (0.72 g, 3.75 mmol), K_2CO_3 (0.52 g, 3.75 mmol) and EtOH (100 ml) was refluxed for 85 h. The solvent was evaporated *in vacuo* and the residue was resolved with CH_2Cl_2. The organic layer was separated and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, *n*-hexane:ethyl acetate=94:6) and recrystallization from MeOH gave the product (0.25 g, 40.3%). ^1H NMR ($CDCl_3$, TMS, 500.0 MHz) δ1.05 (t,

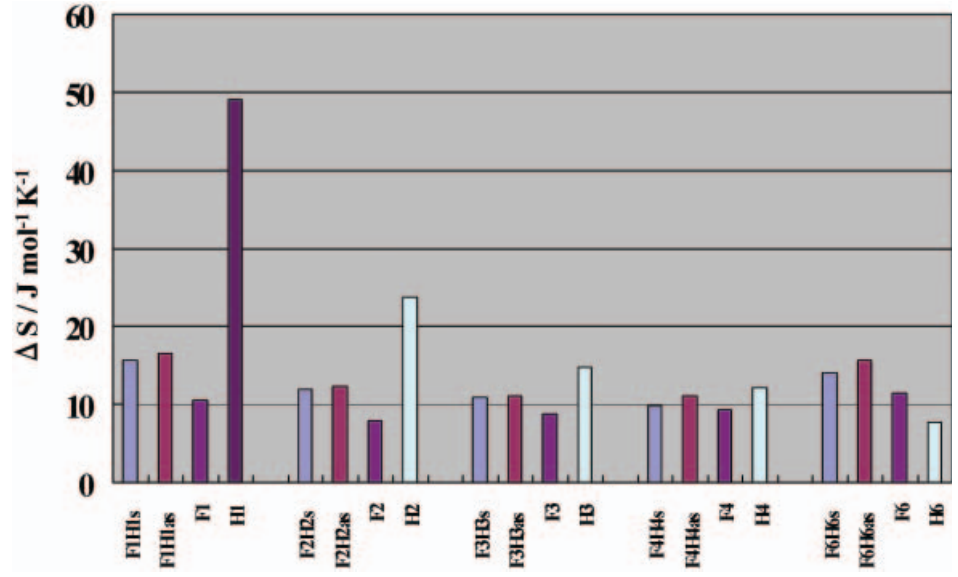


Figure 3. Phase transition entropies (Col_h–Iso) of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**), fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**).

Table 1. Phase transition parameters of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**), fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**).

Compound	Transition	Temperature/ °C	ΔH/ kJ mol^{-1}	ΔS/ J mol^{-1} K^{-1}
F1H1s	$C_1 \rightarrow C_2$	104	20.4	54.2
	$C_2 \rightarrow Col_h$	118	9.5	24.3
	$Col_h \rightarrow Iso$	181	7.1	15.7
F1H1as	$C \rightarrow Col_h$	139	43.3	105.0
	$Col_h \rightarrow Iso$	180	7.5	16.5
F1	$C \rightarrow Col_h$	132	22.1	54.5
	$Col_h \rightarrow Iso$	171	4.7	10.6
H1[a]	$C \rightarrow Col_{hp}$	87	24.7	68.6
	$Col_{hp} \rightarrow Iso$	144	20.5	49.1
F2H2s	$C_1 \rightarrow C_2$	84	27.6	77.2
	$C_2 \rightarrow Col_h$	89	4.1	11.3
	$Col_h \rightarrow Iso$	183	5.5	12.0
F2H2as	$C \rightarrow Col_h$	117	44.1	113.2
	$Col_h \rightarrow Iso$	181	5.6	12.3
F2	$C \rightarrow Col_h$	126	44.4	111.2
	$Col_h \rightarrow Iso$	150	3.4	8.0
H2	$C \rightarrow Col_h$	66	35.4	104.4
	$Col_h \rightarrow Iso$	122	9.6	23.7
F3H3s	$C_1 \rightarrow C_2$	70	21.7	63.2
	$C_2 \rightarrow Col_h$	74	20.2	58.1
	$Col_h \rightarrow Iso$	180	4.9	10.9
F3H3as	$C \rightarrow Col_h$	88	44.8	123.8
	$Col_h \rightarrow Iso$	178	4.9	11.0
F3	$C \rightarrow Col_h$	130	48.0	119.2
	$Col_h \rightarrow Iso$	149	3.7	8.8
H3	$C \rightarrow Col_h$	67	39.2	115.3
	$Col_h \rightarrow Iso$	99	5.5	14.8
F4H4s	$C \rightarrow Col_h$	57	50.6	153.1
	$Col_h \rightarrow Iso$	184	4.5	9.8
F4H4as	$C \rightarrow Col_h$	67	45.3	133.0
	$Col_h \rightarrow Iso$	181	5.0	11.0
F4	$C \rightarrow Col_h$	116	55.1	141.5
	$Col_h \rightarrow Iso$	157	4.0	9.4
H4	$C \rightarrow Col_h$	64	56.5	167.6
	$Col_h \rightarrow Iso$	89	4.4	12.1
F6H6s	$C \rightarrow Col_h$	51	46.0	142.2
	$Col_h \rightarrow Iso$	184	6.4	14.0
F6H6as	$C_1 \rightarrow C_2$	45	12.1	38.1
	$C_2 \rightarrow Col_h$	51	46.9	144.6
	$Col_h \rightarrow Iso$	182	7.2	15.7
F6	$C \rightarrow Col_h$	89	55.2	152.6
	$Col_h \rightarrow Iso$	183	5.2	11.4
H6	$C \rightarrow Col_h$	56	72.9	221.5
	$Col_h \rightarrow Iso$	77	2.7	7.7

[a]Col_{hp}: plastic hexagonal columnar phase.

J=7.5 Hz, 9H), 1.52–1.60 (m, 6H), 1.93 (m, 6H), 2.18 (m, 6H), 2.47 (m, 6H), 4.23 (t, J=6.3 Hz, 6H), 4.28 (t, J=6.3 Hz, 6H), 7.81 (s, 3H), 7.84 (s, 3H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.1 MHz) −66.8 (t, J=11.1 Hz, 9F); MS m/z=822.4 (calcd. 822.4 for $C_{42}H_{51}F_9O_6$); FTIR (KBr, cm^{-1}) 2961, 2940, 2873, 1616, 1517, 1385, 1336, 1261, 1232, 1174, 1152, 1136, 1067, 1031, 836; Anal Calcd. for $C_{42}H_{51}F_9O_6$: C,61.31; H, 6.25; F, 20.78; Found : C, 61.29; H, 6.02; F, 20.78.

3.2.10. 2,6,11-tributyloxy-3,7,10-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluorobutylloxy)-triphenylene (F1H1as). (0.09 g, 21.9%). ^{1}H NMR ($CDCl_3$, TMS, 500.0 MHz) 1.03 (t, J=7.5 Hz, 9H), 1.58 (m, 6H), 1.91 (m, 6H), 2.16 (m, 6H), 2.43 (m, 6H), 4.22 (m, 6H), 4.27 (m, 6H), 7.80 (s, 1H), 7.81 (s, 2H), 7.82 (s, 2H) , 7.83 (s, 2H); ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376.1 MHz) −66.8 (t, J=11.1 Hz, 9F); MS m/z=822.6 (calcd. 822.4 for $C_{42}H_{51}F_9O_6$); FTIR (KBr, cm^{-1}); 2960, 2938, 2873, 1619, 1518, 1439, 1386, 1336, 1263, 1231, 1173, 1152, 1136, 1066, 1031, 835; Anal Calcd. for $C_{42}H_{51}F_9O_6$: C,61.31; H, 6.25; F, 20.78; Found : C, 61.06; H, 5.99; F, 20.52.

4. Results and discussion

Figure 1 shows the phase transition temperature of symmetrical and asymmetrical fluoroalkyloxytriphenylenes possessing three fluoroalkyl side chains (**FnHn**), fluoroalkyloxytriphenylenes possessing six fluoroalkyl side chains (**Fn**) and alkyloxytriphenylenes (**Hn**). The phase transition temperature (Col_h–Iso) for all **FnHn** increased to about 180°C and formed a stabilized columnar mesophase, compared with **Fn** and **Hn**. The phase transition temperature (Col_h–Iso) of **FnHn** was independent of fluoromethylene chain or the rotational symmetry of chemical structure. It is suggested that the balance of the fluoroalkyl side chains and alkyl side chains plays a significant role in the thermal stability of columnar mesophase.

The phase transition enthalpies (Col_h–Iso) of **FnHn**, **Fn** and **Hn** are indicated in figure 2. The phase transition enthalpies (Col_h–Iso) of asymmetrical fluoroalkyloxytriphenylenes (**FnHn as**) are a little larger than those of symmetrical fluoroalkyloxytriphenylenes (**FnHn s**), and the phase transition enthalpies (Col_h–Iso) of **FnHn** are larger than those of **Fn**. In the case of compounds **F1H1**–**F4H4,** the increase of the fluoromethylene chain length made the phase transition enthalpy (Col_h–Iso) decrease. However, in the case of compounds **F4H4**–**F6H6,** the increase of the fluoromethylene chain length made the phase transition enthalpies (Col_h–Iso) increase. It is suggested that the fluorophilic interaction around the fluoroalkyl chain can be strongly influenced by the introduction of appropriate fluoromethylene group in the peripheral chain of triphenylene mesogen. Furthermore, in earlier studies [49, 50], in the case of fluoroalkyloxytriphenylenes possessing fluoromethylene side chains (**F2**–**F6**), the increase of fluoromethylene chain increased the thermal stability of the columnar mesophase, the phase transition enthalpies (Col_h–Iso) and entropies (Col_h–Iso). The phase transition enthalpies (Col_h–Iso) for the fluoromethylene side chains showed the opposite tendency for the methylene side chains.

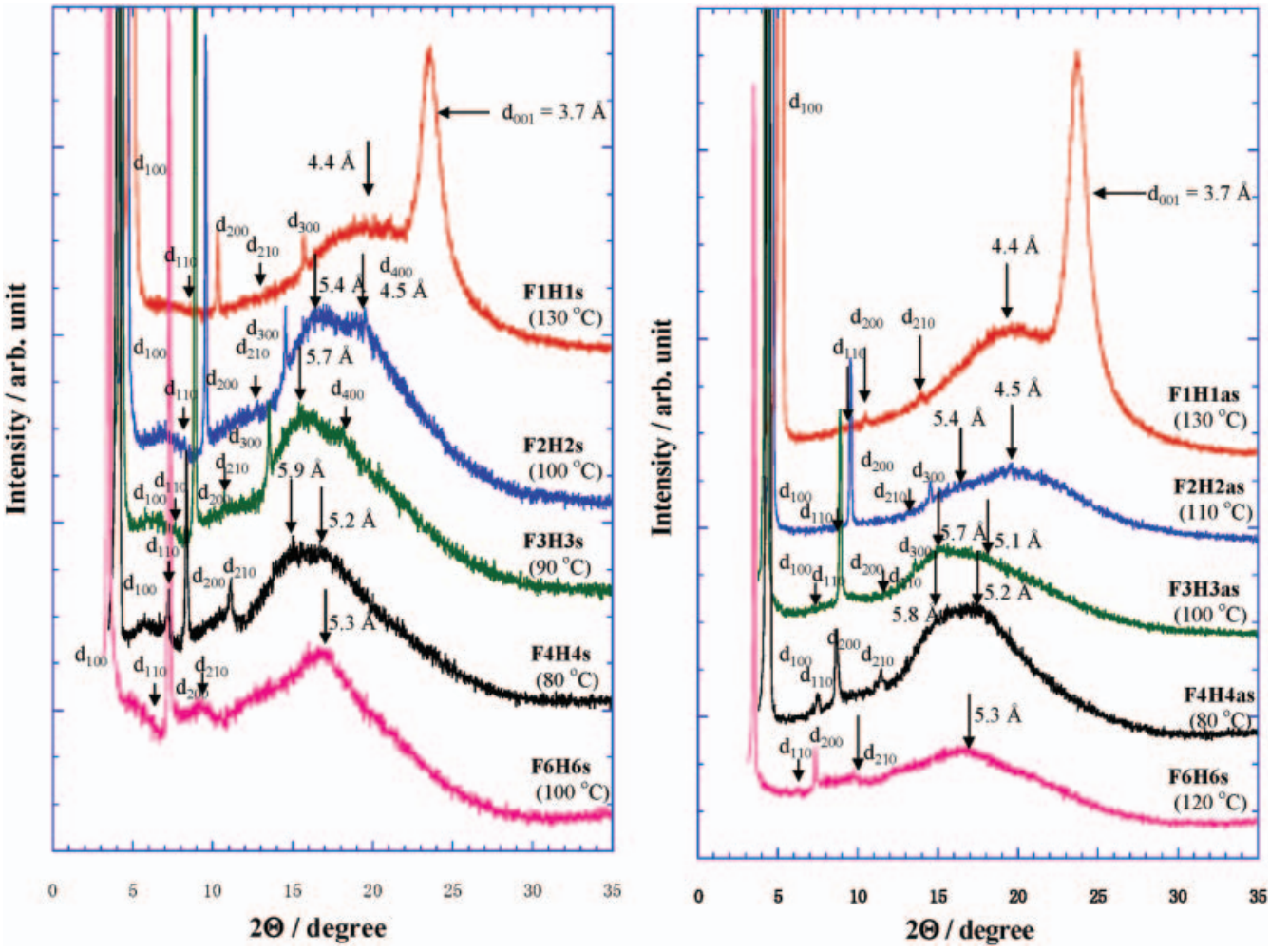


Figure 4. X-Ray diffraction patterns of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**).

As shown in figure 3, the phase transition entropies (Col_h–Iso) of **FnHn**, **Fn** and **Hn** show same trend as for the phase transition enthalpy. These results of the phase transition enthalpies (Col_h–Iso) and entropies (Col_h–Iso) support the idea that the balance of the fluoroalkyl and alkyl side chains plays a significant role in the thermal stability of the columnar mesophase.

The phase transition parameters of **FnHn**, **Fn** and **Hn** are summarized in table 1.

X-ray diffraction measurements for symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**) were carried out; the patterns obtained are shown in figure 4. The assignments of the diffraction peaks of **FnHn**, fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**) are given in table 2. In the low-angle region, three or four sharp peaks are seen and the *d*-spacings are in the ratio of $d_{100}:d_{110}:d_{200}:d_{210}=1:1/\sqrt{3}/\sqrt{4}/\sqrt{7}$. This is a typical set of reflections for a hexagonal arrangement of molecules. In the wide-angle region of **FnHn**, **F1H1** showed broad and sharp reflections, one broad reflection centred at ca. 4.4 Å corresponding to the liquid-like order of the aliphatic hydrocarbon chains [55] and another sharp reflection centred at ca. 3.7° corresponding to the stacking periodicity of the core part [56]. There is no reflection of the trifluoromethyl group in spite of introducing trifluoromethyl group in triphenylene side chain. **F2H2** showed two diffuse reflections, they centred at ca. 4.5 Å which corresponds to the liquid-like order of the hydrocarbon aliphatic chains [55] and at ca. 5.4 Å which corresponds to the disordered perfluoroalkyl chains [21–23, 30]. In the case of **F3H3**–**F6H6**, they centred at ca. 5.1–5.9 Å which correspond to the disordered perfluoroalkyl chains [21–23, 30]. When a fluoromethylene chain (compounds **F2H2**–**F6H6**) is introduced in triphenylene side chains, the interaction of fluoroalkyl chains is shown. This indicates that fluoroalkyl groups of intracolumnar order exist close to each other. It is

Table 2. The assignment of X-ray diffraction peaks of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**), fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**).

Compound	a_{hex}/Å	hkl	d_{hkl}/Å	Compound	a_{hex}/Å	hkl	d_{hkl}/Å
F1H1s (130°C)	20.3	100	17.6	**F6H6as** (120°C)	29.0	100	25.1
		110	9.9			110	14.0
		200	8.6			200	12.0
		210	6.5			210	9.0
		300	5.6				5.3 (broad)
			4.4 (broad)	**F1** (125°C)	18.2	100	15.8
		001	3.7			110	9.1
F1H1as (130°C)	19.6	100	17.0			200	7.9
		110	9.7				4.1 (broad)
		200	8.4	**F2** (110°C)	20.1	100	17.4
		210	6.3			110	10.0
			4.4 (broad)			200	8.6
		001	3.7				5.3(broad)
F2H2s (110°C)	21.9	100	19.0				4.2(broad)
		110	10.7	**F3** (180°C)	21.5	100	18.6
		200	9.2			110	10.6
		210	7.0			200	9.3
		300	6.0				5.3(broad)
			5.4 (broad)				4.2(broad)
			4.5 (broad)	**F4** (140°C)	23.7	100	20.5
F2H2as (110°C)	22.0	100	19.1			110	11.8
		110	10.7			200	10.1
		200	9.2			210	7.6
		210	7.0				5.3(broad)
		300	6.1				4.2(broad)
			5.4 (broad)	**F6** (80°C)	26.1	100	22.6
			4.5 (broad)			110	13.0
F3H3s (90°C)	23.8	100	20.6			200	11.4
		110	11.5			210	8.5
		200	10.0				5.2(broad)
		210	7.4				4.1(broad)
		300	6.5	**H1** (115°C)	19.2	100	16.6
			5.7 (broad)			110	9.5
		400	4.9			200	8.2
F3H3as (100°C)	23.6	100	20.5			210	6.3
		110	11.5			220/211	4.7
		200	9.9				4.2(broad)
		210	7.5			002	3.5
		300	6.5			102	3.4
			5.7(broad)	**H2** (100°C)	20.6	100	17.8
			5.1(broad)			200	8.9

Table 2. (*Continued.*)

Compound	a_{hex}/Å	hkl	d_{hkl}/Å	Compound	a_{hex}/Å	hkl	d_{hkl}/Å
F4H4s (80°C)	24.8	100	21.5			210	6.7
		110	12.2				4.2(broad)
		200	10.6				3.6(broad)
		210	8.0	**H3** (80°C)	22.0	100	19.0
			5.9 (broad)			110	10.9
			5.2 (broad)			200	9.4
F4H4as (80°C)	23.3	100	20.2				4.2(broad)
		110	11.8	**H4** (75°C)	23.0	100	19.8
		200	10.2			110	11.5
		210	7.7			200	9.8
			5.8 (broad)				4.2(broad)
			5.2 (broad)	**H6** (45°C)	25.2	100	21.9
F6H6s (100°C)	29.0	100	25.1			110	12.6
		110	13.9			200	10.8
		200	12.1				4.2(broad)
		210	9.1				

considered that the fluoromethylene chain stabilizes the columnar mesophase via the fluorophilic interaction.

Figure 5 shows the dependence of the lattice constant for **FnHn**, **Fn** and **Hn** on the fluoromethylene chain length (n) and methylene chain length (n). The lattice constant, a_{hex}, of symmetrical fluoroalkyloxytriphenylenes (**FnHn s**) showed similar values corresponding to those of asymmetrical fluoroalkyloxytriphenylenes (**FnHn as**). In the instance of **FnHn**, it was found that the increase of lattice constant is proportional to the increase of chain length (n). However, this increase in column diameter is about 3.2 Å smaller than the increase of fluoromethylene chain length (n) (-CF_2CF_2- bond length: 1.58 Å). In contrast, the lattice constant a_{hex} of **FnHn** showed bigger values than those corresponding to **Fn** and **Hn**. It is found that the rate of cross penetration of symmetrical and asymmetrical **FnHn** is lager than that of **Fn** and **Hn**. It is suggested that interaction between fluoroalkyl chains and alkyl chains for symmetrical and asymmetrical **FnHn** is bigger than fluorophobic interaction of **Fn** and hydrophobic interaction of **Hn**.

A schematic of the Col_h phase of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**) is proposed in figure 6. As **F1H1** showed a sharp reflection at ca. 3.7 Å corresponding to the stacking periodicity of the core part [56], it is suggested that triphenylene core provided the stacking. As the **F2H2–F6H6** reflection was centred at ca. 5.1–5.9 Å which correspond to the disordered perfluoroalkyl chains [21–23, 30], it is suggested that that **F2H2-F6H6** is the packing of peripheral fluoroalkyl chain. Furthermore, the phase transition temperature (Col_h–Iso) for all **FnHn** increased to about 180°C and stabilized the columnar mesophase, compared with **Fn** and **Hn**. These results may reveal that the rotational fluctuation of the core part of **FnHn** is smaller than that of **Fn** and **Hn** for the interaction of fluoroalkyl and alkyl side chain.

5. Conclusions

Novel symmetrical and asymmetrical triphenylene compounds possessing fluoroalkyl side chains were synthesized. X-ray diffraction and DSC measurements revealed that these homologues show a hexagonal columnar (Col_h) mesophase with a different manner of the intracolumnar order from each other. The thermal stability of these Col_h phases is higher than that of the corresponding fluoroalkyloxytriphenylenes and alkyloxytriphenylenes. The balance of the fluoroalkyl side chains and alkyl side chains plays a significant role in the thermal stability of columnar mesophase. Furthermore, the fluorophilic and fluorophobic interaction around fluoromethylene chain may play a

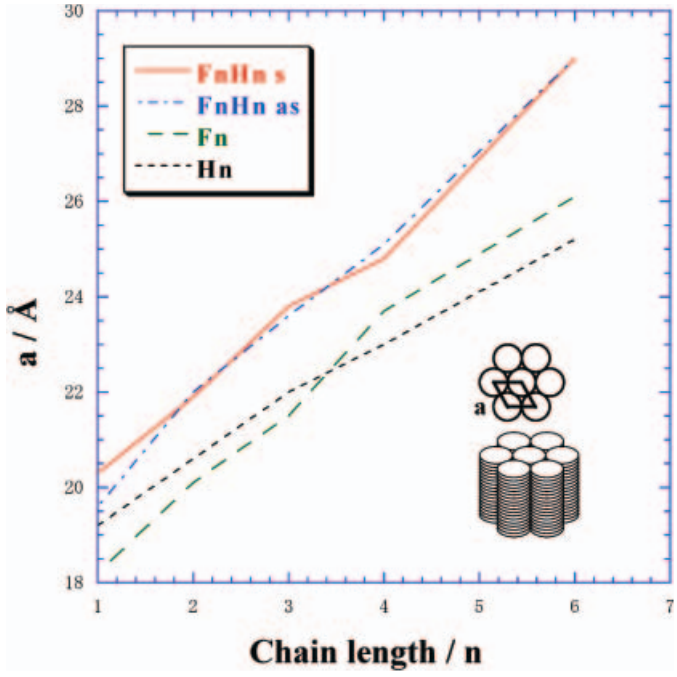


Figure 5. Dependence of the lattice constant for symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**), fluoroalkyloxytriphenylenes (**Fn**) and alkyloxytriphenylenes (**Hn**) on the fluoromethylene chain length (n) and methylene chain length (n).

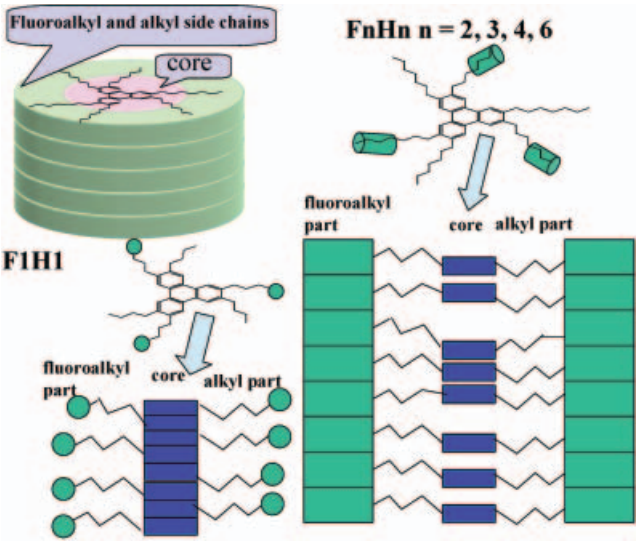


Figure 6. Schematic of Col_h phase of symmetrical and asymmetrical fluoroalkyloxytriphenylenes (**FnHn**).

significant role for the thermal stability of columnar mesophase.

Acknowledgements

We thank Dr T. Nakamura and Dr N. Yumoto for measuring MALDI-TOF mass spectra.

References

[1] R.E. Banks, B.E. Smart, J.C. Tatlow. *Organofluorine Chemistry. Principles and Commercial Applications*. Plenum, New York (1994).
[2] M. Hudlicky, A.E. Pavlath. *Chemistry of Organic Fluorine Compounds* ACS Monograph 187, ACS, Washington DC (1995).
[3] D.F. Eaton, B.E. Smart. *J. Am. chem. Soc.*, **112**, 2821 (1990).
[4] C.W. Burn, E.R. Howells. *Nature*, **174**, 549 (1954).
[5] A.C. Griffin, N.W. Buckley. *Mol. Cryst. liq. Cryst.*, **41**, 141 (1978).
[6] S. Misaki, S. Takamatsu, M. Suefuji. *Mol. Cryst. liq. Cryst.*, **66**, 123 (1981).
[7] N.A. Vaz, S.L. Arora, J.W. Doane, A. de Vries. *Mol. Cryst. liq., Cryst.*, **128**, 23 (1985).
[8] L.M. Wilson, A.C. Griffin. *Macromolecules*, **27**, 1928 (1994).
[9] B.Q. Chen, Y.G. Yang, J.X. Wen. *Liq. Cryst.*, **24**, 539 (1998).
[10] P. Kromm, M. Cotrait, J.C. Rouillon, P. Barois, H.T. Nguyen. *Liq. Cryst.*, **21**, 121 (1996).
[11] P. Kromm, M. Cotrait, H.T. Nguyen. *Liq. Cryst.*, **21**, 95 (1996).
[12] F.G. Tournilhac, L. Bosio, J. Simon, L.M. Blinov, S.V. Yablonsky. *Liq. Cryst.*, **14**, 405 (1993).
[13] H. Liu, H. Nohira. *Liq. Cryst.*, **22**, 217 (1997).
[14] F. Tournilhac, L.M. Blinov, J. Simon, S.V. Yablonsky. *Nature*, **359**, 621 (1992).
[15] H.T. Nguyen, G. Sigaud, M.F. Achard, F. Hardouin, R.J. Twieg, K. Betterton. *Liq. Cryst.*, **10**, 389 (1991).
[16] H. Okamoto, N. Yamada, S. Takenaka. *J. Fluorine Chem.*, **91**, 125 (1998).
[17] T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabayashi, Y. Nishihata, H. Terauchi. *J. Mater. Chem.*, **1**, 169 (1991).
[18] S. Takenaka. *J. chem. Soc., Chem. Commun.*, 1748 (1992).
[19] H. Okamoto, H. Murai, S. Takenaka. *Bull. chem. Soc. Japan*, **70**, 3163 (1997).
[20] M. Duam, H. Okamoto, V.F. Petrov, S. Takenaka. *Bull. chem. Soc. Japan*, **71**, 2735 (1997).
[21] J.F. Rabolt, T.P. Russel, R.J. Twieg. *Macromolecules*, **17**, 2786 (1984).
[22] W. Mahler, D. Guillon, A. Skoulios. *Mol. Cryst. liq. Cryst.*, **2**, 111 (1985).
[23] C. Viney, R.J. Twieg, B.R. Gordon, J.F. Rabolt. *Mol. Cryst. liq. Cryst.*, **198**, 285 (1991).
[24] J. Hopken, C. Pugh, W. Richtering, M. Moller. *Makromol. Chem.*, **189**, 911 (1988).
[25] J. Hopken, S. Faulstich, M. Moller. *Mol. Cryst. liq. Cryst.*, **210**, 59 (1992).
[26] M.P. Turberg, J.E. Brady. *J. Am. chem. Soc.*, **110**, 7797 (1988).
[27] H. Kawahara, M. Hamada, Y. Ishikawa, T. Kunitake. *J. Am. chem. Soc.*, **115**, 3002 (1993).
[28] F. Giulieri, M.P. Kraft, J.G. Riess. *Angew. Chem. Int. Ed.*, **33**, 1514 (1994).
[29] G. Johansson, V. Percec, G. Ungar, J.P. Zhou. *Macromolecules*, **29**, 646 (1996).
[30] G. Johansson, V. Percec, G. Ungar, K. Smith. *Chem. Mater.*, **9**, 164 (1997).
[31] V. Percec, G. Johansson, G. Ungar, J.P. Zhou. *J. Am. chem. Soc.*, **118**, 9855 (1996).
[32] V. Percec, T.K. Bera. *Tetrahedron*, **58**, 4031 (2002).
[33] V. Percec, M. Glodde, G. Johansson, V.S.K. Balagurusamy, P.A. Heiney. *Angew. Chem. Int. Ed.*, **42**, 4338 (2003).
[34] A. Pegenau, X.H. Cheng, C. Tschierske, P. Goring, S. Diele. *New J. Chem.*, **23**, 465 (1999).
[35] C. Tschierske. *J. Mater. Chem.*, **11**, 2647 (2001).
[36] X. Cheng, M.K. Das, S. Diele, C. Tschierske. *Langmuir*, **18**, 6521 (2002).
[37] X. Cheng, M. Prehm, M.K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume, C. Tschierske. *J. Am. chem. Soc.*, **125**, 10977 (2003).
[38] X. Cheng, M.K. Das, U. Baumeister, S. Diele, C. Tschierske. *J. Am. chem. Soc.*, **126**, 12930 (2004).
[39] U. Dahn, C. Erdelen, H. Ringsdorf, R. Festag, J.H. Wendorf, P.A. Heiney, N.C. Maliszewskyj. *Liq. Cryst.*, **19**, 759 (1995).
[40] B. Almandine, O.F. Ambusher, W. Am rein, B. Donnie, R. Desschenaux, D. Guillon, C. Savary, D. Scanu, O. Scheidegger, T.A. Jenny. *Chem. Mater.*, **17**, 4798 (2005).
[41] D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K.H. Etzbach, H. Ringsdorf, D. Haarer. *Nature*, **371**, 141 (1994).
[42] M. Funahashi, J. Hanna. *Appl. Phys.Lett.*, **73**, 3733 (1998).

[43] D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, K. Siemensmeyer. *Phys. Rev. Lett.*, **70**, 457 (1993).
[44] A.M. Van de Craats, J.M. Warman, A. Fechtenkötter, J.D. Brand, M.A. Harbison, K. Müllen. *Adv. Mater.*, **11**, 1469 (1999).
[45] K. Hatsusaka, K. Ohta, I. Yamamoto, H. Shirai. *J. Mater. Chem.*, **11**, 423 (2001).
[46] T. Christ, B. Glusen, A. Geriner, A. Kettner, R. Sander, V. Stumpflen, V. Tsukruk, J.H. Wendorff. *Adv. Mater.*, **9**, 48 (1997).
[47] I.H. Stapff, V. Stumpflen, J.H. Wendorff, D.B. Spoohn, D. Mobius. *Liq. Cryst.*, **23**, 613 (1997).
[48] K. Kogo, T. Goda, M. Funahashi, J. Hanna. *Appl. Phys. Lett.*, **73**, 1595 (1998).
[49] N. Terasawa, H. Monobe, K. Kiyohara, Y. Shimizu. *Chem. Lett.*, **32**, 214 (2003).
[50] N. Terasawa, H. Monobe, K. Kiyohara, *J. Fluorine Chem.* accepted.
[51] M.T. Allen, K.D.M. Harris, B.M. Kariyuki, N. Kumari, J.A. Preece, S. Diele, D. Lose, T. Hegmann, C. Tschierske. *Liq. Cryst.*, **27**, 689 (2000).
[52] N. Boden, R.J. Bushby, Z.B. Lu. *Liq. Cryst.*, **25**, 47 (1998).
[53] H. Liu, H. Nohira. *Liq. Cryst.*, **20**, 581 (1996).
[54] R. Asep, Y. Aoki, T. Hirose, H. Nohira. *Mol. Cryst. Liq. Cryst.*, **346**, 51 (2000).
[55] D. Markovitsi, I. Lecuyer, P. Lianos, J. Mathsts. *J. chem. Soc., Faraday Trans.*, **7**, 1785 (1991).
[56] A.M. Levelut. *J. Phys. Lett.*, **40**, L81 (1979).