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Novel Glass-Forming Liquid Crystals. 6. High-Temperature Glassy Nematics

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To furnish new insight into structure−property relationships governing glassy nematic liquid crystals, novel material systems were synthesized and characterized. Highly ordered, solid films were also prepared via spin-coating for the determination of optical birefringence. It was found that a linear nematogen, such as the cyanoterphenyl group, contributes to an elevated glass transition temperature and a wide nematic fluid temperature range with a mixed or an extended core structure. However, an angular nematogen, such as the cyanophenylnaphthyl group, is more versatile in inducing glass formation with a broader range of core structures. Morphologically stable, glassy nematics with a T_g close to 130 °C, a T_c close to 350 °C, a nematic fluid temperature range of 265 °C, and an optical birefringence of 0.44 accomplished in this study represent significant improvements over existing materials. A stereochemical modification of the bicyclooctene ring from an exo-, exo- to an endo-, and exo-configuration, fluorination of the cyanophenylnaphthyl group, and a longer spacer to nematic pendants were found to depress T_c to a much greater extent than T_g. An extension in the core structure accompanied by an increased number of nematic pendants per core was found to elevate T_g, but no consistent effect on T_c was observed.

I. Introduction

Most organic compounds, including liquid crystals, tend to crystallize upon cooling from the liquid state. Crystallization normally leads to grain boundaries that scatter light or limit charge transport, thus rendering materials unsuitable for use in electronic, optical, and photonic devices. As an effective way to surmount this problem, materials that freeze into amorphous glass, in which molecules are randomly oriented with respect to each other, have been successfully developed.[1−7] Glassy liquid crystals represent a higher degree of sophistication than amorphous glasses in that orientational order characteristic of liquid crystal fluids is frozen in the solid state. In essence, glass-forming liquid crystals are discrete molecular entities with a low molar mass in comparison to liquid crystalline polymers for which glass formation is a rule rather than an exception. An unusual feature of glass-forming liquid crystals is their ability to undergo reversible phase transitions upon thermal cycling between ordered glass and isotropic liquid without encountering crystallization. Since the first reports in the early 1970s,[8,9] numerous molecular design strategies[10−15] have been explored to improve morphological stability, i.e., resistance to recrystallize from anisotropic glass or mesomorphic melt. Our recent effort has generated a definitive set of morphologically stable glassy liquid crystals following a systematic approach in which *mesogenic pendants* are chemically bonded to a *central core*, including cyclohexane, bicy-

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clooctene, adamantane, and cubane.[16−23] These two structural elements readily crystallize as separate entities. However, “volume exclusion”, which originates in structural disparity between the two, prevents crystallization of the chemical hybrid. This study was motivated by three objectives: (i) to explore approaches to elevating glass transition temperature, T_g, and clearing point, T_c; (ii) to widen the mesomorphic fluid temperature range (i.e. $T_c - T_g$); and (iii) to characterize orientational order and optical birefringence of spin-coated thin films relevant to optical device application.

II. Experimental Section

Reagents and Chemicals. All chemicals, reagents, and solvents were used as received from Aldrich Chemical Co. or VWR Scientific with the following exceptions. Tetrahydrofuran (99%) was dried by refluxing over sodium in the presence of benzophenone until blue and then distilled for use. Silica gel 60 (EM Science, 230−400 mesh) was used for liquid chromatography.

Material Synthesis. Glass-forming liquid crystals, depicted as **I**−**XIX** in Figure 1, were prepared following Schemes 1−4 except **I**, **II**, **VI**, **VII**, **VIII**, **XI**, and **XII**, which have been reported elsewhere.[23] Synthesis and purification procedures, together with structural elucidation of intermediates and target compounds, are described in what follows.

2-(2-Hydroxyethoxy)-6-bromonaphthalene (**a**). To a solution of 6-bromo-2-naphthol (15.1 g, 67.7 mmol), 2-bromoethanol (10.11 g, 80.9 mmol) in *N*,*N*-dimethylformamide (60 mL) was added a solution of potassium hydroxide (5.41 g, 81.9 mmol) and potassium iodide (0.37 g, 2.20 mmol) in water (10 mL). Upon stirring at 85 °C for 4 h, the reaction mixture was filtered. The filtrate was shaken with diethyl ether (400 mL) and water (400 mL). The organic portion was washed with a 2% potassium hydroxide solution (100 mL). The solvent was evaporated off to obtain crude product. Recrystallization from a mixed solvent of methanol (20 mL) and water (200 mL) yielded **a** in 10.0 g (55%). ^{1}H NMR (CDCl$_3$, ppm): δ 2.16 (t, 1 H, HOCH$_2$), 4.10 (m, 2 H, HOCH_2CH$_2$), 4.22 (t, 2 H, ArOCH_2CH$_2$), 7.10−7.95 (m, 6 H, aromatic H).

2-[6′-(4′′-Cyanophenyl)-2′-naphthyl]-1-ethanol (**b**). A biphasic mixture of benzene (52 mL), ethanol (7 mL), and a 2 M sodium carbonate solution (59 mL) was sparged with argon before adding 4-cyanobenzeneboronic acid (3.85 g, 26.2 mmol), intermediate (**a**) (6.62 g, 24.8 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.65 g, 0.55 mmol). The reaction mixture was refluxed under argon overnight. Evaporation to dryness resulted in a crude product, which was purified by recrystallization from ethyl acetate to obtain **b** in 5.32 g (74%). ^{1}H NMR (CDCl$_3$, ppm): δ 4.08 (t, 2 H, HOCH_2CH$_2$), 4.26 (t, 2 H, ArOCH_2CH$_2$), 7.21−8.00 (m, 10 H, aromatic H).

1-(tert-Butyldimethylsilyloxy)-3,5-benzenedicarboxylic acid (**c**). 5-Hydroxyisophthalic acid (9.11 g, 50.0 mmol) and *tert*-butyldimethylsilyl chloride (25.2 g, 167 mmol) were dissolved in anhydrous *N*,*N*-dimethylformamide (55 mL). Upon adding imidazole (20.4 g, 300 mmol), the solution was stirred overnight before shaking with diethyl ether (200 mL) and water (600 mL). The organic portion was reduced in volume by evaporation to a clear oil, which was mixed with tetrahydrofuran (45 mL), water (30 mL), glacial acetic acid (30 mL), and acidified with 37% HCl solution. The reaction mixture was stirred for 2 h before shaking with methylene chloride (200 mL) and water (200 mL). The organic portion was washed with water (200 mL × 2), and the insoluble product was collected by filtration. Additional product was collected by washing with water the solid residue from evaporating off the solvent. A total of 10.1 g (68%) of **c** was obtained. ^{1}H NMR (acetone-d_6, ppm): δ 8.33−7.74 (m, 3 H, aromatic H), 1.05 (s, 9 H, SiC(CH_3)$_3$), 0.30 (s, 6 H, Si(CH_3)$_2$).

1-tert-Butyldimethylsilyloxy-3,5-benzenedicarboxylic acid, bis{2-[6′-(4′′-cyanophenyl)-2′-naphthyl-oxy]-1-ethyl ester} (**d**). Intermediate **b** (4.29 g, 14.8 mmol), **c** (2.18 g, 7.85 mmol), and triphenylphosphine, PPh$_3$ (4.10 g, 15.63 mmol), were dissolved in anhydrous tetrahydrofuran (60 mL) under argon. The reaction mixture was then chilled in an ice/water bath. Diethyl azodicarboxylate, DEAD (2.6 mL, 16.5 mmol), was slowly added to the solution, which was then stirred overnight at room temperature. The reaction mixture was evaporated to dryness, and the solid residue was dissolved in methylene chloride for silica gel column chromatography with methylene chloride as the eluent to yield **d** (4.68 g, 76%). ^{1}H NMR (CDCl$_3$, ppm): δ −0.04 (s, 6 H, Si(CH_3)$_2$), 0.83 (s, 9 H, Si(C(CH_3)$_3$), 4.44 (t, 4 H, ArOCH_2CH$_2$), 4.69 (t, 4 H, COOCH_2CH$_2$), 7.18−8.26 (m, 23 H, aromatic H).

1-Hydroxy-3,5-benzenedicarboxylic acid, bis{2-[6′-(4′′-cyanophenyl)-2′-naphthyloxy]-1-ethyl ester} (**e**). Intermediate **d** (5.8 g, 6.9 mmol) was dissolved in a mixed solvent of tetrahydrofuran (50 mL) and acetone (10 mL). The solution was chilled in an ice/water bath before tetrabutylammonium fluoride, TBAF (1 M tetrahydrofuran, 8.5 mL), was slowly added. The reaction was quenched after 45 min by adding a solution of ammonium chloride (0.65 g, 12 mmol) in water (6.5 mL). The solution was then shaken with methylene chloride (200 mL) and water (100 mL). The organic portion was washed with water (100 mL × 2) and saturated brine (50 mL) before drying over anhydrous MgSO$_4$. The crude product resulting from evaporating off the solvent was purified by recrystallization from acetone and then from methylene chloride to yield **e** (4.15 g, 83%). ^{1}H NMR (DMSO-d_6, ppm): δ 4.26 (t, 4 H, ArOCH_2CH$_2$), 4.67 (t, 4 H, COOCH_2CH$_2$), 7.15−8.23 (m, 23 H, aromatic H), 10.31 (s, 1 H, HOAr).

cis,cis-1,3,5-Cyclohexanetricarboxylic acid, tris{3,5-bis{2′-[6′′-4′′′-cyanophenyl)-2′′-naphthyloxy]-1′-ethyloxycarbonyl}-phenyl ester} (**III**). A reaction mixture was prepared by dissolving intermediate **e** (1.00 g, 1.39 mmol), *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid (0.10 g, 0.46 mmol), and *p*-toluenesulfonic acid/4-(dimethylamino)pyridine complex (0.054 g, 0.18 mmol) in anhydrous tetrahydrofuran (10 mL). Upon adding *N*,*N*′-dicyclohexylcarbodiimide, DCC (0.40 g, 1.94 mmol), the reaction mixture was refluxed for 36 h. A crude product was collected by precipitation of a methylene chloride solution into ethanol. Purification was accomplished by silica gel column chromatography via a gradient elution from methylene chloride to methylene chloride:acetone (30:1). The product was further purified by precipitation from a methylene chloride solution into ethanol to obtain **III** (0.49 g, 46%). ^{1}H NMR (CDCl$_3$, ppm): δ 1.85−2.05 (m, 3 H, cyclohexane ring), 2.60−2.90 (m, 6 H, cyclohexane ring), 4.43 (t, 12 H, ArOCH_2CH$_2$), 4.79 (t, 12 H, COOCH_2CH$_2$), 7.15−8.65 (m, 69 H, aromatic H). Anal. Calcd for C$_{147}$H$_{102}$N$_6$O$_{24}$: C, 75.57; H, 4.40; N, 3.60. Found: C, 75.18; H, 4.42; N, 3.63.

4-(tert-Butyldimethylsilyloxy)benzoic acid (**f**). 4-Hydroxybenzoic acid (4.01 g, 29.0 mmol) and *tert*-butyldimethylsilyl chloride (9.98 g, 66.2 mmol) were dissolved in dry *N*,*N*-dimethylformamide (21 mL) containing imidazole (8.65 g, 127 mmol). Upon stirring for 10 h under argon, the reaction mixture was shaken with diethyl ether (130 mL) and water (130 mL). The organic portion was washed with water (60 mL × 2). The crude product resulting from evaporating to dryness was dissolved in tetrahydrofuran (32 mL). Methanol (96 mL) and a solution of potassium carbonate (6.40 g, 46.3 mmol) in water (50 mL) were added. The mixture was then stirred for

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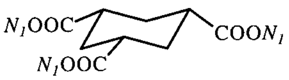

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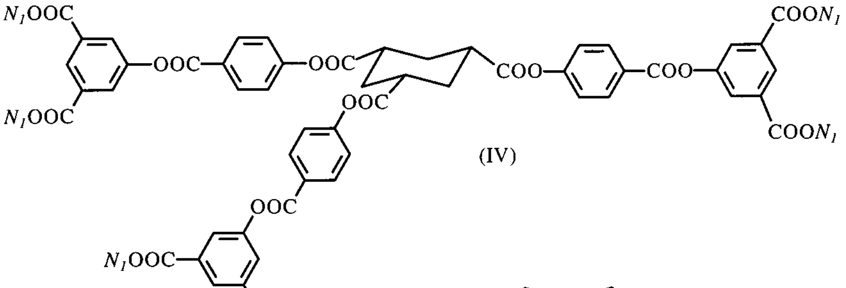

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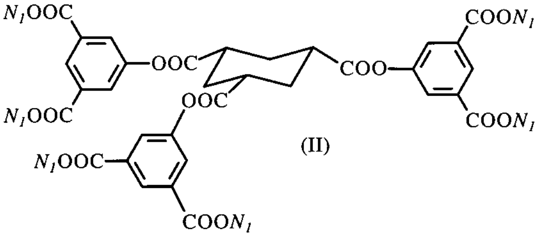

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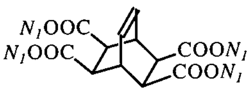

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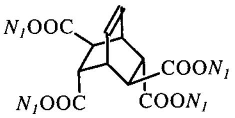

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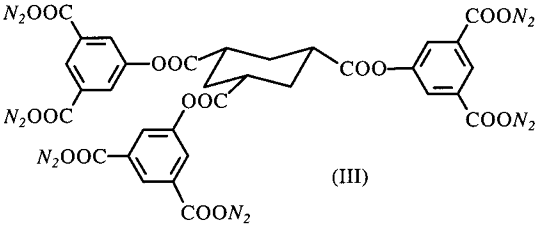

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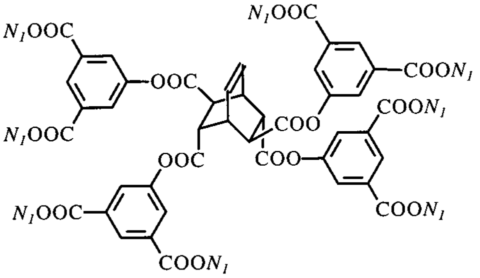

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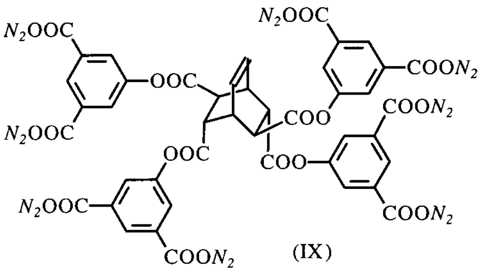

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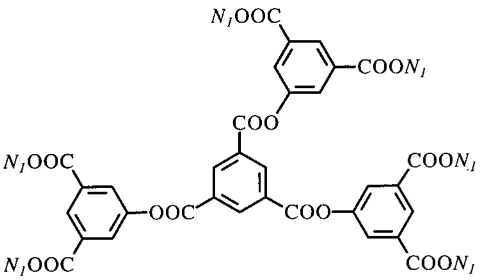

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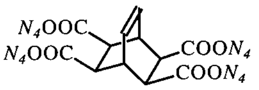

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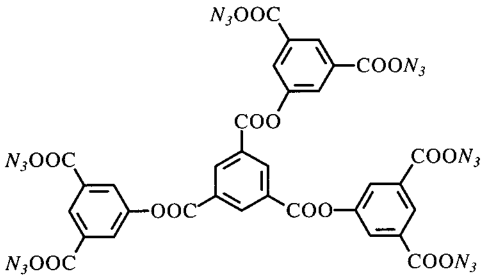

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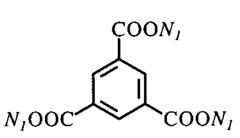

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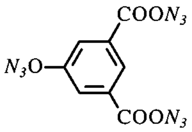

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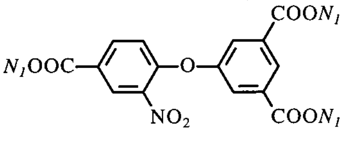

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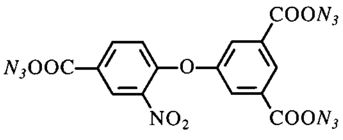

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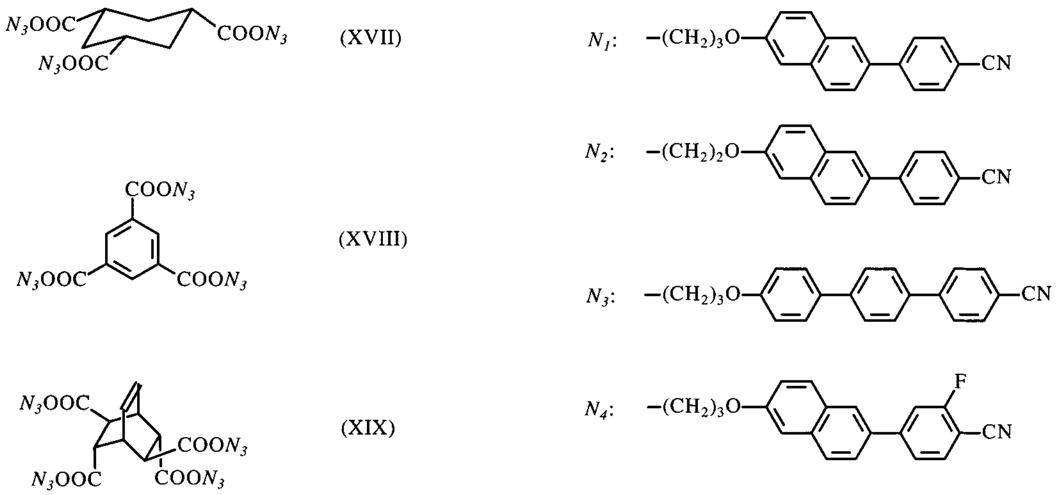
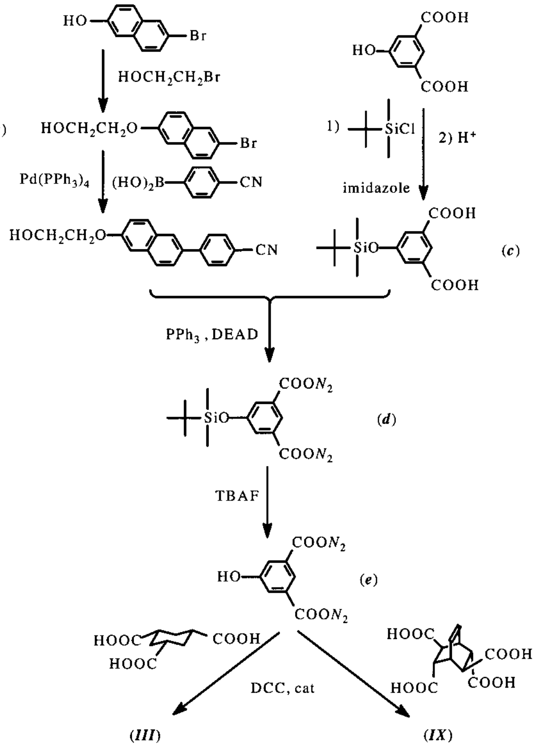


Figure 1. Structures of glass-forming liquid crystals, including morphologically unstable ones, designed and synthesized with an aim to unraveling structure−property relationships.

Scheme 1. Synthesis of Compounds III and IX



1 h. The volume was reduced by half via evaporation before adding a saturated brine (96 mL) followed by acidification with a 1 M solution of potassium hydrogensulfate. The aqueous portion was washed with diethyl ether (100 mL × 3), and the organic portion was evaporated to dryness. Recrystallization from a mixed solvent of water (200 mL), ethanol (75 mL), and acetone (20 mL) yielded **f** (4.61 g, 63%). ^{1}H NMR (acetone-d_6, ppm): δ 0.10 (s, 6 H, $Si(CH_3)_2$), 1.02 (s, 9 H, $Si(C(CH_3)_3)$, 6.99 (d, 2 H, aromatic *H*), 7.95 (d, 2 H, aromatic *H*).

3-[6′-(4-Cyanophenyl)-2′-naphthyloxy]-1-propanol (**g**) was synthesized following the procedures reported previously.[24] ^{1}H NMR (DMSO-d_6, ppm): δ 2.16 (p, 2 H, $CH_2CH_2CH_2$), 3.95 (t, 2 H, $HOCH_2CH_2CH_2$), 4.30 (t, 2 H, $CH_2CH_2CH_2OAr$), 7.21−8.00 (m, 10 H, aromatic H). Anal. Calcd for $C_{20}H_{17}N_1O_2$: C, 79.18; H, 5.65; N, 4.62. Found: C, 78.93; H, 5.67; N, 4.49.

1-tert-Butyldimethylsilyloxy-3,5-benzenedicarboxylic acid, bis{3-[6′-(4″-cyanophenyl)-2′-naphthyloxy]-1-propyl ester} (**h**). Intermediates **c** (1.80 g, 6.07 mmol) and **g** (3.63 g, 12.0 mmol) and PPh_3 (3.29 g, 12.6 mmol) were dissolved in anhydrous tetrahydrofuran (80 mL). Upon addition of DEAD (2.1 mL, 13.3 mmol), the solution was stirred at room temperature overnight. The solid residue resulting from evaporation to dryness was mixed with methylene chloride, and the insolubles were filtered off. The crude product in the filtrate was purified by silica gel column chromatography with methylene chloride as the eluent to obtain **h** in 3.49 g (67%). ^{1}H NMR (CD_3Cl, ppm): δ 7.17−8.32 (m, 23 H, aromatic *H*), 4.62 (t, 4 H, $COOCH_2CH_2$), 4.28 (t, 4 H, CH_2CH_2O), 2.38 (q, 4 H, $CH_2CH_2CH_2$), 1.02 (s, 9 H, $SiC(CH_3)_3$), 0.25 (s, 6 H, $Si(CH_3)_2$).

1-Hydroxy-3,5-benzenedicarboxylic acid, bis{3-[6′-(4″-cyanophenyl)-2′-naphthyloxy]-1-propyl ester} (**i**). Intermediate **h** (3.48 g, 4.0 mmol) was dissolved in tetrahydrofuran (30 mL) and acetone (5 mL) at room temperature. The solution was then chilled in an ice/water bath. A 1 M tetrabutylammonium fluoride, TBAF, solution (5 mL, 5.0 mmol) was added over $^1/_4$ h with subsequent stirring for $^1/_2$ h. The reaction was quenched with ammonium chloride (0.78 g, 14.5 mmol) in water (10 mL). After stirring for 10 min, the solution was shaken with methylene chloride (200 mL) and water (200 mL). The volume of the organic portion was reduced to 40 mL via evaporation. The solid product **i** was collected by filtration in 2.08 g (66%). ^{1}H NMR (DMSO-d_6, ppm): δ 10.32 (s, 1 H, phenol *H*), 7.18−8.22 (m, 23 H, aromatic *H*), 4.45 (t, 4 H, $COOCH_2CH_2$), 4.22 (t, 4 H, CH_2CH_2O), 2.21(q, 4 H, $CH_2CH_2CH_2$).

4-(tert-Butyldimethylsilyloxy)benzoic acid, 3,5-bis{3′-[6″-(4‴-cyanophenyl)-2″-naphthalyoxy]-1′-propyloxycarbonyl}phenyl Ester (**j**). A reaction mixture consisting of intermediates **f** (0.382 g, 1.51 mmol) and **i** (0.998 g, 1.33 mmol), DCC (0.399 g, 1.93 mmol), and *p*-toluenesulfonic acid/4-(dimethylamino)pyridine complex (0.11 g, 0.37 mmol) in anhydrous tetrahydrofuran (20 mL) was refluxed overnight. Solid residues were filtered off, and the filtrate was evaporated to dryness. The crude product was purified by silica gel column chromatography with methylene chloride:acetone (50:1) as the eluent to obtain **j** (0.85 g, 65%). ^{1}H NMR ($CDCl_3$, ppm): δ 0.25 (s, 6 H, $Si(CH_3)_2$), 1.02 (s, 9 H, $Si(C(CH_3)_3)$, 2.38 (p, 4 H, $CH_2CH_2CH_2$), 4.25 (t, 4 H, $ArOCH_2$), 4.62 (t, 4 H, $COOCH_2CH_2$), 6.90−8.85 (m, 27 H, aromatic *H*).

4-Hydroxybenzoic acid, 3,5-bis{3′-[6″-(4‴-cyanophenyl)-2″-naphthalyoxy]-1′-propyloxycarbonyl}phenyl ester (**k**). Intermediate **j** (0.80 g, 0.81 mmol) was dissolved in tetrahydrofuran (10 mL) and chilled in an ice/water/salt bath before adding a 1 M solution of TBAF in tetrahydrofuran (1 mL) dropwise. Upon stirring for $^3/_4$ h, the reaction was quenched with ammonium chloride (0.22 g, 4.11 mmol) in water (1 mL). Stirring was continued for additional $^1/_4$ h before shaking with methylene chloride (50 mL) and water (25 mL). The organic portion was washed with water (25 mL × 2) and then dried over anhydrous $MgSO_4$. Upon evaporating off the solvent, the

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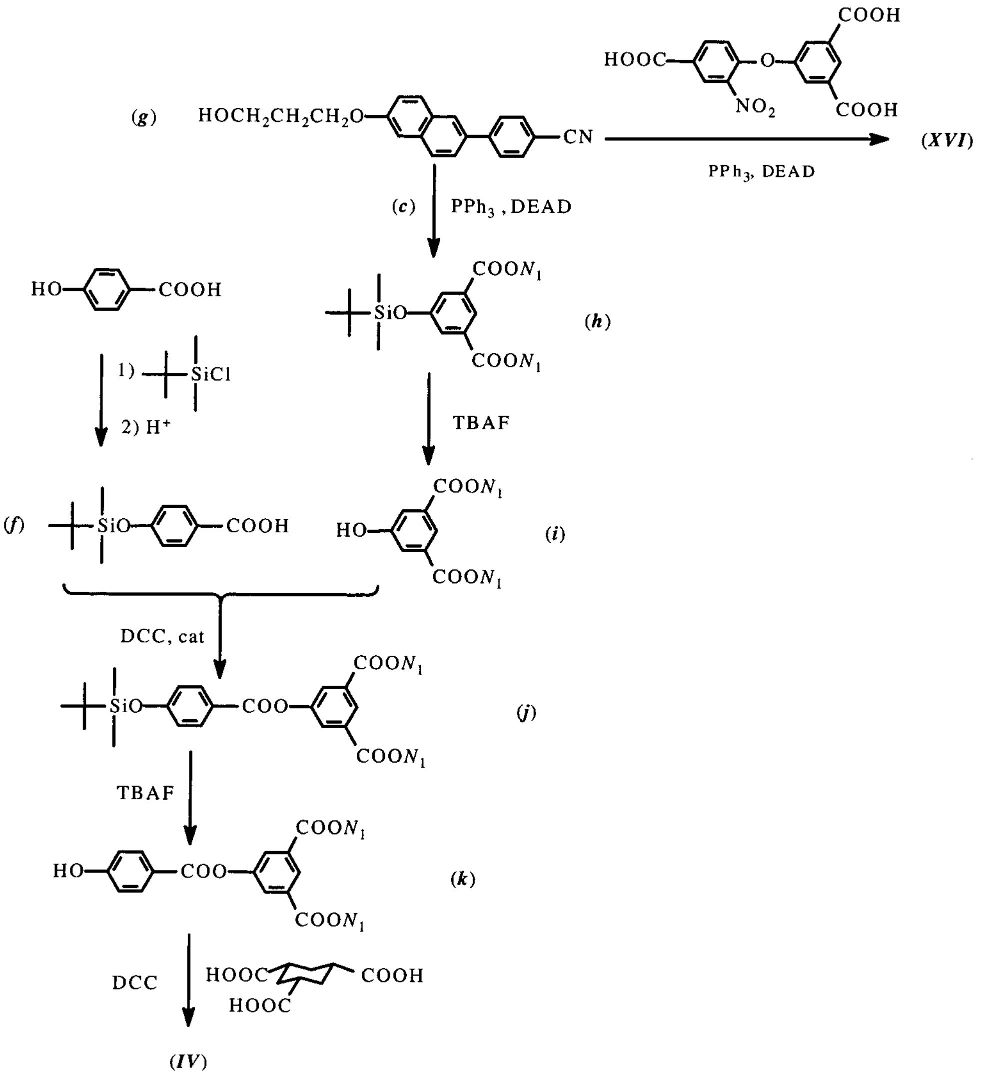
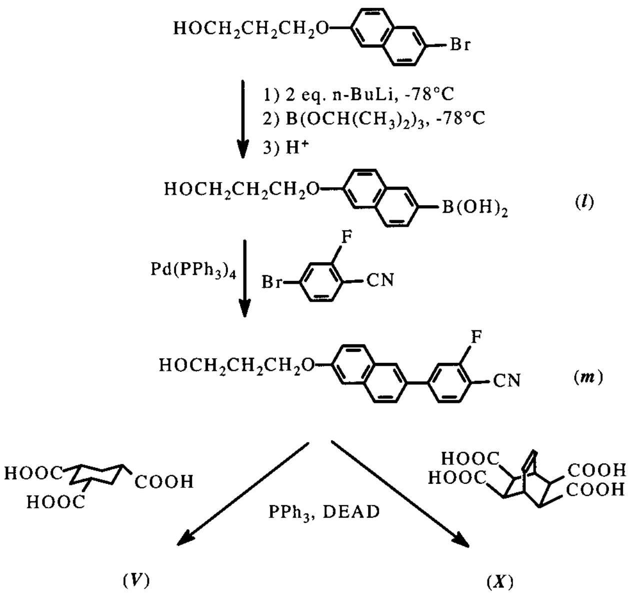
Scheme 2. Synthesis of Compounds IV and XVI



Scheme 3. Synthesis of Compounds V and X

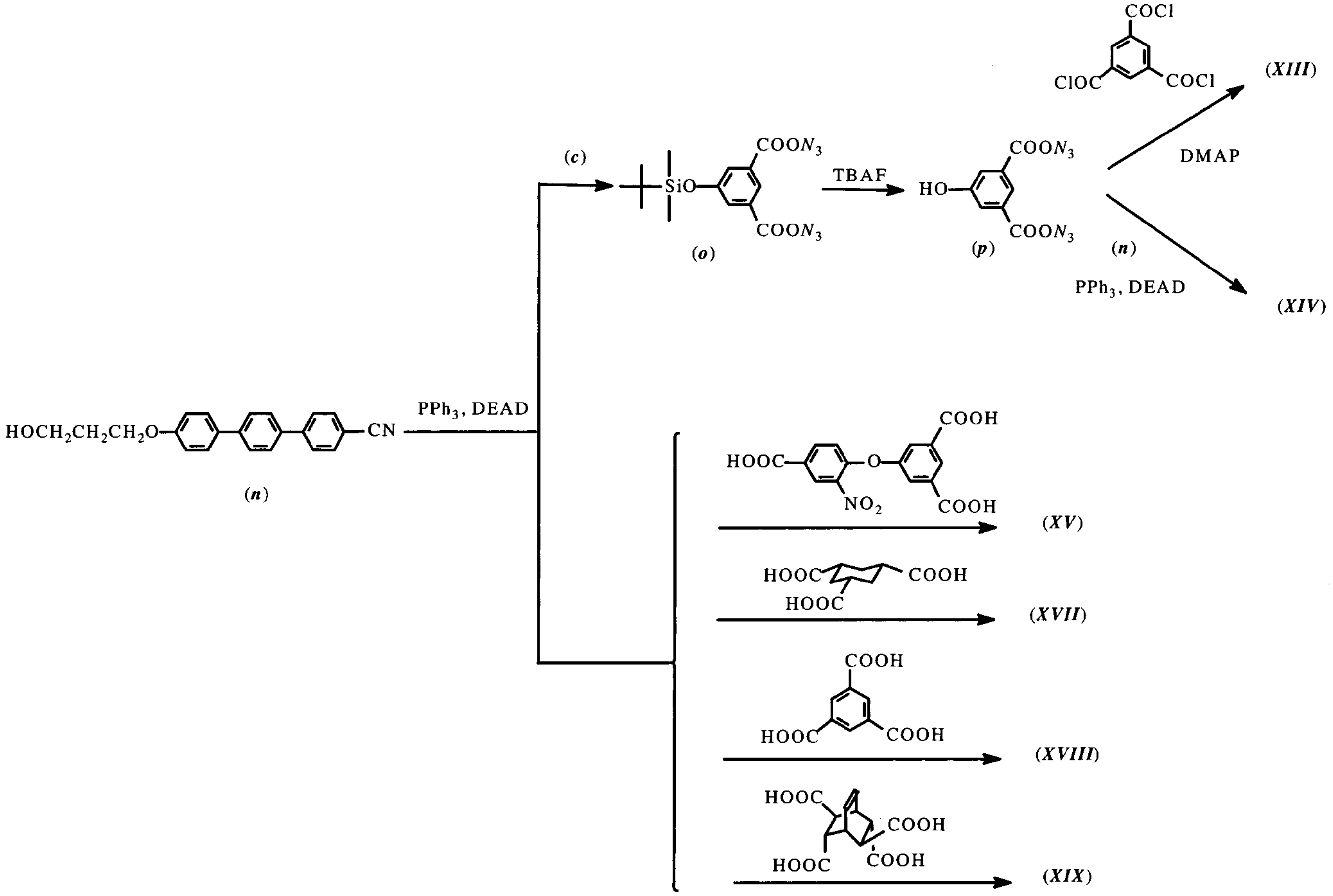


crude product was recrystallized from tetrahydrofuran and then from acetone to obtain **k** (0.70 g, 78%). ^{1}H NMR (DMSO-d_6, ppm): δ 2.22 (p, 4 H, $CH_2CH_2CH_2$), 4.25 (t, 4 H, $ArOCH_2$), 4.50 (t, 4 H, $COOCH_2CH_2$), 6.85−8.42 (m, 27 H, aromatic *H*).

cis,cis-1,3,5-Cyclohexanetricaroxylic acid, tris{4-{3′,5′-bis{3″-[6‴-(4‴-cyanophenyl)-2‴-naphthyloxy]-1″-propyl-oxycarbonyl}-phenyloxycarbonyl}phenyl ester} (**IV**). Intermediate **k** (0.65 g, 0.75 mmol), *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (0.053 g, 0.25 mmol), and DCC (0.20 g, 0.97 mmol) were dissolved in dry tetrahydrofuran (10 mL) under argon. Upon adding 4-pyrrolidinopyridine (0.12 g, 0.08 mmol), the reaction mixture was stirred overnight at room temperature. Solid residues were removed, and the filtrate was evaporated to dryness. The crude product was dissolved in methylene chloride (50 mL) and then shaken with dilute acetic acid (25 mL). The organic portion was washed with water (25 mL × 2) and then dried over anhydrous $MgSO_4$. Further purification was accomplished by silica gel column chromatography, via a gradient elution from methylene chloride to methylene chloride:acetone (30:1), followed by precipitation from a methylene chloride solution into methanol to obtain **IV** (0.15 g, 40%). ^{1}H NMR ($CDCl_3$, ppm): δ 1.85−2.05 (m, 3 H, cyclohexane), 2.38 (p, 12 H, $CH_2CH_2CH_2$), 2.65−3.00 (m, 6 H, cyclohexane), 4.26 (t, 12 H, $ArOCH_2CH_2$), 4.70 (t, 12 H, $COOCH_2CH_2$), 7.10−8.74 (m, 81 H, aromatic *H*). Anal. Calcd for $C_{174}H_{126}N_6O_{30}$: C, 75.15; H, 4.57; N, 3.02. Found: C, 74.95; H, 4.70; N, 3.13.

2-(3-Hydroxypropyl)-6-naphthaleneboronic acid (**l**). Under anhydrous conditions, 3-(3-hydroxypropyloxy)-6-bromonaphthalene (15.0 g, 0.0534 mol) was dissolved in dry tetrahydrofuran (125 mL) and chilled in a dry ice/acetone bath (−78 °C). After slowly adding a 2.5 M solution of *n*-butyllithium in tetrahydrofuran (43 mL, 0.108 mol), the resultant solution was stirred for 1 h before adding a chilled (−78 °C) solution of triisopropyl borate (31 mL, 0.13 mol) in dry tetrahydrofuran

Scheme 4. Synthesis of Compounds XIII–XIX Except XVI



(45 mL). After stirring at room temperature overnight, the reaction mixture was chilled in an ice/water bath. A dilute solution of HCl (25 mL of 37% HCl in 225 mL of water) was then added dropwise, followed by vigorous stirring for 1 h at room temperature. The reaction mixture was extracted with diethyl ether (80 mL × 3). The organic portion was washed with water (50 mL × 3) before drying over anyhydrous $\mathrm{MgSO_4}$. The volume of the solution was significantly reduced, by evaporating off the solvent, for precipitation into hexane (150 mL), yielding **l** (5.1 g 39%). ^{1}H NMR (DMSO-d_6, ppm): δ 1.90 (p, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$,), 3.60 (t, 2 H, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2}$), 4.10 (m, 4 H, overlap of $\mathrm{B(O}\mathit{H}\mathrm{)_2}$ and $\mathrm{COOC}\mathit{H}_2\mathrm{CH_2}$), 7.10–8.05 (m, 6 H, aromatic *H*).

3-[6′-(3-Fluoro-4-cyanophenyl)-2′-naphthyloxy]-1-propanol (**m**). A biphasic mixture comprising benzene (60 mL) and a 2 M solution of sodium carbonate (60 mL) was sparged with argon before adding intermediate **l** (3.90 g, 15.8 mmol), 4-bromo-2-flourobenzonitrile (3.06 g, 15.3 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.71 g, 0.6 mmol). After refluxing with vigorous stirring for 16 h, the organic portion was separated, and the aqueous portion was extracted with methylene chloride (50 mL). The combined organic portion was washed with water (50 mL × 3) before drying over anyhydrous $\mathrm{MgSO_4}$. Further purification was accomplished by silica gel column chromatography via a gradient elution from methylene chloride to methylene chloride:acetone (5:1), yielding **m** (4.0 g, 81%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 2.18 (p, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 3.95 (t, 2 H, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2}$), 4.30 (t, 2 H, $\mathrm{COOC}\mathit{H}_2\mathrm{CH_2}$), 7.00–8.50 (m, 9 H, aromatic *H*).

cis,cis-1,3,5-Cyclohexanetricarboxylic acid, tris{3-[6′-(3″-fluoro-4″-cyanophenyl)-2′-naphthyloxy]-1-propyl ester} (**V**). DEAD (1.05 mL, 6.70 mmol) was added dropwise to a solution containing intermediate **m** (1.20 g, 3.70 mmol), *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (0.268 g, 1.20 mmol) and triphenylphosphine (1.03 g, 3.90 mmol) in anhydrous tetrahydrofuran (10 mL). Upon stirring overnight at room temperature, the solvent was evaporated off, and the mixture was redissolved in methylene chloride. Silica gel column chromatography with methylene chloride acetone (40:1) as the eluent yielded **V** (0.85 g, 61%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 1.60 (m, 3 H, cyclohexane), 2.20 (p, 6 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.23–2.40 (m, 6 H, cyclohexane), 4.09 (t, 6 H, $\mathrm{ArOC}\mathit{H}_2\mathrm{CH_2}$), 4.45 (t, 6 H, $\mathrm{COOC}\mathit{H}_2\mathrm{CH_2}$), 7.00–7.90 (m, 27 H, aromatic *H*). Anal. Calcd for $\mathrm{C_{69}H_{54}F_3N_3O_9}$: C, 73.59; H, 4.83; N, 3.73; F, 5.06. Found: C, 73.61; H, 4.78; N, 3.77; F, 4.91.

Bicyclo[2.2.2.]oct-7-ene-(2,5)-*exo*-(3,6)-*endo*-tetracarboxylic acid was prepared from bicyclo[2.2.2.]oct-7-ene-(2,5)-*exo*-(3,6)-*exo*-tetracarboxylic acid following the procedures described elsewhere.[23]

Bicyclo[2.2.2.]oct-7-ene-(2,5)-exo-(3,6)-endo-tetracarboxylic Acid, Tetrakis{3,5-bis{2′-[6″-(4‴-cyanophenyl)-2″-naphthyloxy]-1′-ethyloxycarbonyl}phenyl ester} (**IX**). Intermediate **e** (0.85 g, 1.17 mmol), bicyclo[2.2.2.]oct-7-ene-(2,5)-*exo*-(3,6)-*endo*-tetracarboxylic acid (0.084 g, 0.29 mmol), DCC (0.29 g, 1.42 mmol), and *p*-toluenesulfonic acid/4-(dimethylamino)pyridine complex (0.072 g, 0.24 mmol) were dissolved in anhydrous tetrahydrofuran (10 mL) and anhydrous *N*,*N*-dimethylformamide (4 mL). The reaction mixture was stirred overnight under argon at room temperature, followed by shaking with methylene chloride (50 mL) and dilute acetic acid (50 mL). The organic portion was washed with water (25 mL) and a saturated sodium bicarbonate solution (25 mL) before drying over anhydrous $\mathrm{MgSO_4}$. The crude product resulting from evaporating off the solvent was purified by silica gel column chromatography via a gradient elution from methylene chloride:hexanes (24:1) to methylene chloride:acetone (30:1). The product was further purified by precipitation from a methylene chloride solution into ethanol to obtain **IX** (0.46 g, 50%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 3.50–4.05 (m, 8 H, bicyclooctene *endo*–*exo*), 4.25–4.85 (m, 32 H, $\mathrm{COOC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{OAr}$), 7.05–8.70 (m, 92 H, aromatic *H*). Anal. Calcd for $\mathrm{C_{196}H_{132}N_8O_{32}}$: C, 75.67; H, 4.28; N, 3.60. Found C, 75.19; H, 4.41; N, 3.75.

Bicyclo[2.2.2.]oct-7-ene-(2,5)-exo-(3,6)-exo-tetracarboxylic acid, tetrakis{3-[6′-(3″-fluoro-4″-cyanophenyl)-2′-naphthyloxy]-1-propyl ester} (**X**). DEAD (0.68 mL, 4.30 mmol) was added dropwise to a solution containing intermediate **m** (2.00 g, 6.20 mmol), bicyclo[2.2.2.]oct-7-ene-(2,5)-*exo*-(3,6)-*exo*-tetracarboxylic acid (0.442 g, 1.56 mmol), and PPh_3 (1.70 g, 6.49 mmol) in anhydrous tetrahydrofuran (40 mL) and *N*,*N*-dimethylformamide (5 mL). Upon stirring overnight at room temperature, the solvent was evaporated off, and the solid residue was redissolved in methylene chloride. Column chromatography on activated basic alumina via a gradient elution from methylene chloride to methylene chloride: acetone (20:1) yielded **X** (1.29 g, 56%). ^1H NMR ($CDCl_3$, ppm): δ 2.10 (p, 8 H, $CH_2CH_2CH_2$), 3.10 (m, 4 H, tertiary C*H*), 3.35 (m, 2 H, bridgehead 2*H*), 3.90−4.30 (m, 16 H, OCH_2), 6.40 (m, 2 H, alkene *H*), 7.00−8.00 (m, 36 H, aromatic *H*). Anal. Calcd for $C_{92}H_{68}F_4N_4O_{12}$: C, 73.79; H, 4.58; F, 5.07; N, 3.74. Found: C, 73.27; H, 4.59; F, 4.32; N, 3.32.

3-(4′-Cyano-p-terphenyloxy)-1-propanol (**n**) was synthesized following the procedures reported previously.[24] ^1H NMR (DMSO-d_6, ppm): δ 2.10 (p, 2 H, $CH_2CH_2CH_2$), 3.92 (t, 2 H, $HOCH_2CH_2CH_2$), 4.21 (t, 2 H, $CH_2CH_2CH_2OAr$), 7.01−7.76 (m, 10 H, aromatic *H*). Anal. Calcd for $C_{22}H_{19}N_1O_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.15; H, 5.66; N, 4.31.

1-(tert-Butyldimethylsilyloxy)-3,5-benzenedicarboxylic acid, bis[3-(4′-cyano-p-terphenyloxy)-1-propyl ester] (**o**). DEAD (1.20 mL, 7.38 mmol) was added dropwise to a solution containing intermediate **c** (0.85 g, 2.87 mmol), intermediate **n** (2.00 g, 6.06 mmol), and PPh_3 (2.00 g, 7.63 mmol) in anhydrous tetrahydrofuran (250 mL). Upon stirring overnight at room temperature, the reaction mixture was poured into methanol (400 mL) after reducing the volume to 50 mL. The precipitated crude product collected by filtration was dissolved in chloroform (200 mL). The resulting solution was washed with a 10% solution of sodium bicarbonate (300 mL × 2) and water (300 mL × 2) consecutively before drying over anhydrous $MgSO_4$. Further purification was accomplished by silica gel column chromatography with methylene chloride as the eluent, yielding **o** (2.3 g, 87%). ^1H NMR (CD_3Cl, ppm): δ 7.00−8.32 (m, 27 H, aromatic *H*), 4.59 (t, 4 H, $COOCH_2CH_2$), 4.20 (t, 4 H, CH_2CH_2O), 2.32 (q, 4 H, $CH_2CH_2CH_2$), 1.02 (s, 9 H, $SiC(CH_3)_3$), 0.25 (s, 6 H, $Si(CH_3)_2$).

1-Hydroxy-3,5-benzenedicarboxylic acid, bis[3-(4′-cyano-p-terphenyloxy)-1-propyl ester] (**p**). To a solution of intermediate **o** (1.00 g, 1.09 mmol) in chloroform (50 mL) was added dropwise a 1 M solution of TBAF in tetrahydrofuran (4 mL). After stirring for 4 h at room temperature, a 1 M HCl solution (2 mL) and tetrahydrofuran (8 mL) were added. The reaction mixture was then washed with water (50 mL × 2). The organic portion was reduced in volume to 10 mL, from which the white solid precipitated, yielding **p** (0.74 g, 94%). ^1H NMR (DMSO-d_6, ppm): δ 10.32 (s, 1 H, phenol *H*), 7.03−8.00 (m, 27 H, aromatic H), 4.47 (t, 4 H, $COOCH_2CH_2$), 4.17 (t, 4 H, CH_2CH_2O), 2.20(q, 4 H, $CH_2CH_2CH_2$).

1,3,5-Benzenetricarboxylic Acid, Tris{3,5-benzenedicarboxylic acid, bis[3-(4′-cyano-p-terphenyloxy)-1-propyl]ester}phenyl Ester} (**XIII**). A solution of 1,3,5-benzenetricarbonyl trichloride (0.052 g, 0.20 mmol), intermediate **p** (0.50 g, 0.62 mmol), and (dimethylamino)pyridine (0.10 mg, 0.82 mmol) in 30 mL of anhydrous *N*,*N*-dimethylformamide (30 mL) and anhydrous tetrahydrofuran (30 mL) was heated at 80 °C for 3 h. The reaction mixture was then poured into ethanol (200 mL). The precipitate was dissolved in methylene chloride (50 mL) and then washed with a 10% solution of sodium bicarbonate (50 mL × 2) and then water (50 mL × 2) before drying over anhydrous $MgSO_4$. Further purification was accomplished by silica gel column chromatography, with methylene chloride: acetone (100:1) as the eluent, to yield **XIII** (0.040 g, 8%). ^1H NMR ($CDCl_3$, ppm): δ 6.99−9.25 (m, 84 H, aromatic *H*), 4.62 (t, 12 H, $COOCH_2CH_2$), 4.19 (t, 12 H, CH_2CH_2O), 2.32 (q, 12 H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{165}H_{120}N_6O_{24}$: C, 77.09; H, 4.71; N, 3.27. Found: C, 76.50; H, 4.64; N, 3.26.

1-[3-(4′-Cyano-p-terphenyloxy)-1-propyl]-3,5-benzenedicarboxylic acid, bis[3-(4′-cyano-p-terphenyloxy)-1-propyl Ester] (**XIV**). DEAD (0.14 mL, 0.90 mmol) was added dropwise to a solution of intermediate **p** (0. 50 g, 0.62 mmol), intermediate **n** (0.23 g, 0.70 mmol), and PPh_3 (0.24 g, 0.92 mmol) in anhydrous tetrahydrofuran (30 mL) and anhydrous *N*,*N*-dimethylformamide (30 mL). Upon stirring overnight at room temperature, the reaction mixture was poured into methanol (200 mL), affording a white precipitate, which was collected by filtration and then dissolved in methylene chloride (200 mL). The resulting solution was washed with a 10% solution of sodium bicarbonate (200 mL × 2) and then water (200 mL × 2) before drying over anhydrous $MgSO_4$. Further purification by silica gel column chromatography, with methylene chloride: acetone (50:1) as the eluent, yielded **XIV** (0.35 g, 51%). ^1H NMR ($CDCl_3$, ppm): δ 7.01−8.32 (m, 39 H, aromatic *H*), 4.60 (t, 4 H, $COOCH_2CH_2$), 4.25 (m, 8 H, $OCH_2CH_2CH_2O$, $COOCH_2$-CH_2CH_2O, overlap), 2.33 (m, 6 H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{74}H_{57}N_3O_8$: C, 79.62; H, 5.15; N, 3.77. Found: C, 79.12; H, 5.28; N, 3.64.

5-(4-Carboxy-2-nitrophenoxy)isophthalic acid, tris[3-(4′-cyano-p-terphenyloxy)-1-propyl ester] (**XV**). DEAD (0.31 mL, 1.97 mmol) was added dropwise to a solution containing intermediate **n** (0.500 g, 1.52 mmol), 5-(4-carboxy-2-nitrophenoxy)-isophthalic acid (0.158 g, 0.455 mmol), and PPh_3 (0.520 g, 1.98 mmol) in anhydrous tetrahydrofuran (60 mL). Upon stirring overnight at room temperature, the reaction mixture was poured into methanol (400 mL), affording a white precipitate collected by filtration and then dissolved in methylene chloride (200 mL). The resulting solution was washed with a 10% solution of sodium bicarbonate (200 mL × 2) and water (200 mL × 2) before drying over anhydrous $MgSO_4$. Further purification was accomplished by silica gel column chromatography methylene chloride:acetone (100:1) as the eluent, yielding **XV** (0.40 g, 69%). ^1H NMR (CD_3Cl, ppm): δ 6.99−8.67 (m, 42 H, aromatic *H*), 4.61 (t, 6 H, $COOCH_2CH_2$), 4.19 (t, 6 H, CH_2CH_2O), 2.32 (q, 6 H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{81}H_{60}N_4O_{12}$: C, 75.92; H, 4.72; N, 4.37. Found: C, 75.84; H, 4.82; N, 4.32.

5-(4-Carboxy-2-nitrophenoxy)isophthalic acid, tris{3-[6′-(4-cyanophenyl)-2′-naphthyloxy]-1-propyl ester} (**XVI**). The same procedure as that for compound **XV** was followed to produce **XVI** (69%) using intermediate **g** instead of **n**. ^1H NMR (CD_3Cl, ppm): δ 6.99−8.65 (m, 36 H, aromatic *H*), 4.63 (m, 6 H, $COOCH_2CH_2$), 4.27 (m, 6 H, CH_2CH_2O), 2.35 (m, 6 H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{75}H_{54}N_4O_{12}$: C, 74.86; H, 4.52; N, 4.66. Found: C, 75.04; H, 4.61; N, 4.63.

cis,cis-1,3,5-Cyclohexanetricarboxylic acid, tris[3-(4′-cyano-p-terphenyloxy)-1-propyl ester] (**XVII**). DEAD (0.60 mL, 3.82 mmol) was added dropwise to a solution containing *cis, cis*-1,3,5-cyclohexanetricarboxylic acid (0.20 g, 0.93 mmol), intermediate **n** (1.00 g, 3.03 mmol), and PPh_3 (1.00 g, 3.82 mmol) in anhydrous tetrahydrofuran (100 mL). Upon stirring overnight at room temperature, the reaction mixture was reduced to 20 mL then poured into methanol (100 mL), affording a white precipitate, which was collected by filtration and then dissolved in methylene chloride (200 mL). The resultant solution was washed with a 10% solution of sodium bicarbonate (200 mL × 2) and then water (200 mL × 2) before drying over anhydrous $MgSO_4$. Further purification by silica gel column chromatography, with methylene chloride:acetone (50:1) as the eluent, yielded **XVII** (0.78 g, 71%). ^1H NMR ($CDCl_3$, ppm): δ 6.97−7.76 (m, 36 H, aromatic *H*), 4.33 (t, 6 H, $COOCH_2CH_2$), 4.25 (t, 6 H, $COOCH_2CH_2CH_2O$), 2.30−2.44 (m, 6 H, cyclohexane ring), 2.16 (p, 6 H, $CH_2CH_2CH_2$), 1.54−1.64 (m, 3 H, cyclohexane ring). Anal. Calcd for $C_{75}H_{63}N_3O_9$: C, 78.31; H, 5.52; N, 3.65. Found: C, 78.35; H, 5.52; N, 3.66.

1,3,5-Benzenetricarboxylic acid, tris[3-(4′-cyano-p-terphenyloxy)-1-propyl ester] (**XVIII**). DEAD (0.30 mL, 1.98 mmol) was added dropwise to a solution containing 1,3,5-benzenetricarboxylic acid (0.096 g, 0.457 mmol), intermediate **n** (0.50 g, 1.52 mmol), and PPh_3 (0.518 g, 1.52 mmol) in anhydrous tetrahydrofuran (50 mL). Upon stirring overnight at room temperature, the reaction mixture was reduced to 10 mL and then poured into methanol (100 mL), affording a white precipitate, which was collected by filtration. Recrystallization from a mixed solvent of *N*,*N*-dimethylformamide and chloroform afforded **XVIII** (0.35 g, 67%). ^1H NMR ($CDCl_3$, ppm): δ 7.00−

8.90 (m, 39 H, aromatic *H*), 4.64 (t, 6 H, COOC*H*$_2$CH$_2$), 4.20 (t, 6 H, COOCH$_2$CH$_2$C*H*$_2$O), 2.34 (p, 6 H, CH$_2$C*H*$_2$CH$_2$). Anal. Calcd for $C_{75}H_{57}N_3O_9$: C, 78.72; H, 5.02; N, 3.67. Found: C, 79.10; H, 5.10; N, 3.78%.

Bicyclo[2,2,2]oct-7-ene-2,5-exo-3,6-endo-tetracarboxylic acid, tetrakis[3-(4′-cyano-p-terphenyloxy)-1-propyl ester] (**XIX**). DEAD (0.12 mL, 0.759 mmol) was added dropwise to a solution containing bicyclo[2.2.2.]oct-7-ene-(2,5)-*exo*-(3,6)-*endo*-tetracarboxylic acid (0.035 g, 0.13 mmol), intermediate **n** (0.18 g, 0.55 mmol), and PPh_3 (0.20 g, 0.76 mmol) in anhydrous tetrahydrofuran (20 mL). Upon stirring overnight at room temperature, the reaction mixture was poured into ethanol (200 mL), affording a white precipitate, which was collected by filtration and then dissolved in methylene chloride (50 mL). The resulting solution was washed with a 10% solution of sodium bicarbonate (50 mL × 2) and then water (50 mL × 2) before drying over anhydrous $MgSO_4$. The crude product was purified by column chromatography on silica gel via a gradient elution from methylene chloride:acetone (200:1) to (50:1), yielding **XIX** (0.050 g, 26%). ^1H NMR ($CDCl_3$ ppm): δ 6.93−7.74 (m, 48 H, aromatic *H*), 6.32 (m, 2 H, olefinic *H*), 4.38 (m, 4 H, COOC*H*$_2$-CH$_2$, *endo*), 4.26 (m, 4 H, COOC*H*$_2$CH$_2$, *exo*), 4.07 (t, 4 H, CH$_2$C*H*$_2$O, *endo*), 4.00 (t, 4 H, CH$_2$C*H*$_2$O, *exo*), 3.57 (m, 2 H, C*H*, bridgehead), 3.26 (m, 2 H, C*H*, tertiary, *endo*), 3.01 (m, 2 H, C*H*, tertiary, *exo*), 2.17 (m, 4 H, CH$_2$C*H*$_2$CH$_2$, *endo*), 2.08 (m, 4 H, CH$_2$C*H*$_2$CH$_2$, *exo*). Anal. Calcd for $C_{100}H_{80}N_4O_{12}$: C, 78.51; H, 5.27; N, 3.66. Found: C, 78.53; H, 5.39.

Molecular Structures, Thermotropic Properties, and Morphology. Chemical structures were elucidated with elemental analysis (performed by Oneida Research Services, Whitesboro, NY), FTIR (Nicolet 20 SXC), and ^1H NMR (Avance-400, Bruker, and QE-300, GE) spectroscopic techniques. Thermal transition temperatures were determined by DSC (Perkin-Elmer DSC-7) with a continuous N_2 purge at 20 mL/min. Samples were preheated to the isotropic state followed by cooling at −20 °C/min to −30 °C before taking the reported heating scans at 20 °C/min. The reported values of T_g and T_c were reproducible to within ±1 °C. Liquid crystal mesomorphism was characterized with a polarizing optical microscope (DMLM, Leica, FP90 central processor and FP82 hot stage, Mettler Toledo). The morphology of pristine and thermally processed samples was further analyzed with X-ray diffractometry (XRD) across an extended temperature range. X-ray diffraction data were collected in reflection mode geometry using a Rigaku D-2000 Bragg−Brentano diffractometer equipped with a copper rotating anode and position sensitive detector. Samples were analyzed in powder form (as received), and as films (powders heated above T_c and then cooled to 25 °C at a rate of −40 °C/min). In situ high-temperature X-ray diffraction measurements were performed using a Rigaku hot stage with a continuous N_2 purge at 30 mL/min.

Preparation and Characterization of Glassy Nematic Films. Optical elements for orientational order parameter measurements were fabricated using optically flat, calcium fluoride substrates (1.00 in. diameter × 0.04 in. thickness, Almaz Optics) that are transparent in the infrared region. The substrates were cleaned, spin-coated with Nylon 66, and then buffed with a velvet roller. All films were prepared by spin-coating at 2500 rpm from solution in UV-grade chloroform or methylene chloride at a concentration ranging from 0.5 to 3.0 wt %. Films were subsequently annealed on a hot plate at a temperature from 10 to 20 °C above T_g for 1 h before cooling at −2 °C/min to room temperature. Film thickness, τ, was measured using a white light interferometer (Zygo New View 100). The orientational order parameter, S, was measured via linear dichroism associated with the stretching vibration of $-C{\equiv}N$ at 2224 cm^{-1} using a FTIR spectrometer (Nicolet 20 SXC). Two measurements were performed with the transmission axis parallel and perpendicular to the nematic director (i.e. the buffing direction) of the film. The procedures for determining the orientational order parameter in a glassy nematic film based on linear dichroism are as described previously.[23] Optical birefringence, Δn, was determined using a He−Ne laser ($\lambda = 632.8$ nm, 4 mW/cm^2, Uniphase). The beam was passed through a Glan-Thompson linear polarizer (Newport, with a polarization efficiency better than 99.9%), a calibrated Soleil-Babinet compensator (Special Optics), and a glassy nematic film, followed by an analyzer. The analyzer consisted of a second Glan-Thompson linear polarizer crossed with the first and an integrating sphere (UDT) coupled to a multimeter. By determining the amount of light detected with the analyzer, the retardance, δ_r, was measured. The value of Δn was then calculated using the formula $\Delta n = \delta_r/\tau$. A commercially available quarter waveplate centered at $\lambda = 632.8$ nm (OFR, Inc.) was employed to validate the experimental apparatus; the ratio δ_r/λ was found to be 0.250 ± 0.001. It should be remarked that an annealing time of $^1/_2$ h was sufficient for both S and Δn to reach their asymptotic values, although thermal annealing for 1 h was consistently performed for all films.

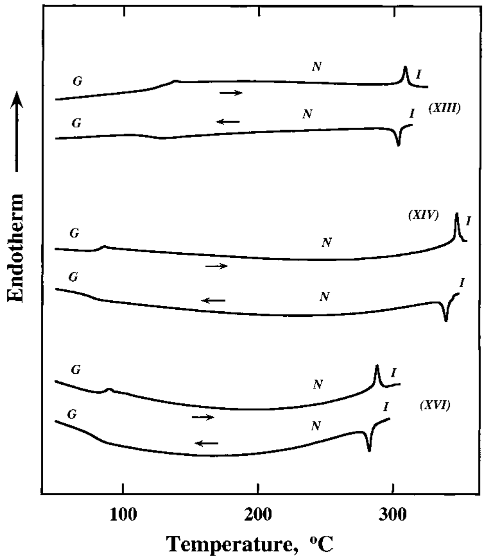


Figure 2. DSC heating and cooling scans at 20 °C/min of samples of **XIII**, **XIV**, and **XVI** preheated to the isotropic state followed by cooling at −20 °C/min to −30 °C. Symbols: *G*, glassy state; *N*, nematic fluid; *I*, isotropic fluid. Morphological stability of these three glassy liquid crystals is confirmed by the absence of crystallization and crystalline melting under hot-stage polarizing optical microscopy and high-temperature X-ray diffractometry.

III. Results and Discussion

The molecular structures of glassy nematic liquid crystals, including those from a previous study[23] for comparative purposes, are shown in Figure 1. In general, glass-forming liquid crystals (GLCs) consist of nematic pendants chemically bonded to a central core. On the basis of this set of material systems, the effects of structural parameters, including central core, nematic pendant, spacer length, and stereochemistry, on thermal properties have been evaluated. Presented in Figure 2 are the DSC heating scans of samples of compounds **XIII**, **XIV**, and **XVI** that have been preheated to isotropic liquid with subsequent cooling to −30 °C. The fact that no crystallization is evident in heating or cooling scans, as corroborated by hot-stage polarizing optical microscopy and high-temperature X-ray diffractometry, indicates morphological stability. Table 1 summarizes the phase transition temperatures of **I**−**XVI**, all of which are identified as morphologically stable GLCs. Morphological stability is further evidenced by the absence of crystallization from selected glassy nematic films left at room temperature more than 2 years. Note that **XIII** shows a T_g of 127 °C and that

Table 1. Thermotropic and Optical Properties of Glass-Forming Nematic Liquid Crystals[a]

material syst	phase transition temp,[b] °C	film thickness, nm	annealing temp, °C	order param (*S*)	opt birefringence (Δn) at 632.8 nm
I	*G* 68(0.29) *N* 195(1.80) *I*	110	80	0.63	0.31
II	*G* 108(0.18) *N* 197(2.14) *I*				
III	*G* 123(0.30) *N* 154(0.724) *I*	230	135	0.44	0.22
IV	*G* 111(0.19) *N* 184(0.869) *I*				
V	*G* 63(0.34) *N* 142(0.725) *I*	120	75	0.62	0.33
V	*G* 63(0.34) *N* 142(0.725) *I*	260	75	0.56	0.25
VI	*G* 84(0.28) *N* 222(2.51) *I*	120	90	0.71	0.30
VII	*G* 71(0.28) *N* 173(1.20) *I*	130	90	0.63	0.35
VIII	*G* 102(0.16) *N* 187(1.19) *I*	105	110	0.69	0.35
IX	*G* 120(0.33) *N* 143(−[c]) *I*				
X	*G* 79(0.26) *N* 141(1.07) *I*	260	90	0.54	0.24
XI	*G* 75(0.24) *N* 235(1.72) *I*				
XII	*G* 109(0.24) *N* 183(2.09) *I*				
XIII	*G* 127(0.25) *N* 308(4.04) *I*	55	135	0.71	0.44
XIV	*G* 82(0.31) *N* 347(7.09) *I*	40	95	0.73	0.35
XV	*G* 76(0.25) *N* 153(1.57) *I*				
XVI	*G* 86(0.29) *N* 288(3.32) *I*	90	95	0.76	0.37

[a] Based on different devices prepared with the same material following the same procedure, film thickness, order parameter, and optical birefringence measured generally to within ±5 nm, ±0.05, and ±0.05, respectively. [b] Thermal transition temperatures were determined from the DSC heating scans at 20 °C/min of samples preheated to isotropic state followed by cooling at −20 °C/min to −30 °C. Nematic mesophase was identified as threaded textures under polarizing optical microscopy. Symbols: *G*, glassy state; *N*, nematic fluid; and *I*, isotropic fluid. The numbers following *G* and *N* are glass and nematic-to-isotropic transition temperatures, respectively. The numbers in parentheses following *G* denote heat capacity change in J/(g·°C) accompanying glass transition, and those following *N* denote enthalpy of clearing in J/g. [c] The clearing temperature was identified under hot-stage polarizing optical microscopy, but the DSC heating scan revealed no visible clearing peak.

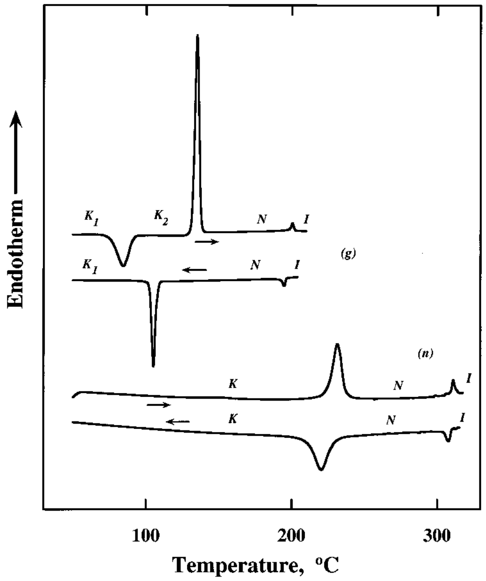


Figure 3. The DSC heating and cooling scans at 20 °C/min of samples of 3-[6′-(4-cyanophenyl)-2′-naphthyloxy]-1-propanol (**g**) and 3-(4′-cyano-*p*-terphenyloxy)-1-propanol (**n**) preheated to the isotropic state followed by cooling at −20 °C/min to −30 °C. Symbols: *K*, crystalline solid; *N*, nematic fluid; *I*, isotropic fluid. Note the much higher "crystalline melting" and "nematic clearing" points of linear **n** than those of angular **g** and the crystalline modification at 84 °C between K_1 and K_2.

XIV shows a T_c of 347 °C, both the highest values ever reported for GLCs. Furthermore, **I**−**XVI** show nothing but a nematic fluid between T_g and T_c, thus facilitating the preparation of glassy nematic films without complications from other mesomorphism in the process of thermal annealing or subsequent cooling to room temperature.

Compounds **I**, **VI**, and **XI** represent a basic GLC molecular structure comprising a nematic pendant, 3-[6′-(4-cyanophenyl)-2′-naphthyloxy]-1-propyl group or N_1, to a *cis*,*cis*-cyclohexane, benzene, and *exo*,*exo*-bicyclooctene core, respectively. Note the differences between these three GLCs in T_g and T_c without a definite trend attributable to the core structure. With a stereochemical variation from an exo-, exo- to an exo-, endo-configuration on the bicyclooctene core, T_g and T_c are depressed by 13 and 51 °C, respectively, as **VII** is compared with **VI**. Fluorination of the nematic pendant was found to cause a 5 °C depression in T_g and a 50−80 °C depression in T_c, as **I** and **VI** are compared to **V** and **X**, respectively. Compounds **II**, **VIII**, and **XII** contain an extended core and an increased number of pendants per core in comparison to **I**, **VII**, and **XI**. Whereas T_g is consistently elevated by 30−40 °C with an extended core, the effect on T_c is dependent on the core structure. With a shorter spacer length, N_2 versus N_1, T_g is elevated by 15 °C but T_c depressed by 43 °C, the combination of which substantially reduces the nematic fluid temperature range of **III** below that of **II**. It is also noted that additional phenyl rings in the core with the same number of pendants, **IV** versus **II**, results in minor modifications to T_g and T_c. Of all the GLCs containing N_1, the widest nematic fluid temperature range is achieved with **XI**, 160 °C, but with a modest T_g, 75 °C.

A unique feature of GLCs is that cores and pendants, which are crystalline as separate entities, combine to form glassy hybrid systems. One strategy for elevating T_g and further widening the nematic fluid temperature range has been successfully implemented with the 3-(4′-cyano-*p*-terphenyloxy)-1-propyl group, or N_3. As shown in Figure 3, intermediate **n**, i.e., N_3OH, possesses a much higher T_m (crystalline melting point) and T_c than intermediate **g**, i.e., N_1OH. The two crystalline forms, K_1 and K_2, exhibited by **g** were identified by in situ X-ray diffraction patterns. As **XIII** is compared to **XII**, T_g and T_c are elevated by 18 and 125 °C, respectively. A simple core, 5-hydroxyisophthalic acid, was found to produce **XIV** with a T_g of 82 °C and a T_c of 347 °C, yielding the widest nematic fluid temperature range (265 °C) ever reported for any liquid crystals. Subsequent cooling and heating scans produced T_g and T_c to within ±1 °C of the values reported in Table 1, thereby validating

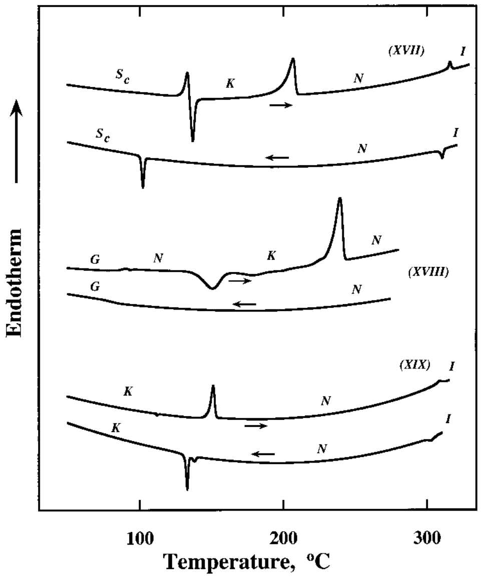


Figure 4. DSC heating and cooling scans at 20 °C/min of samples of **XVII** and **XIX** preheated to the isotropic state and that of **XVIII** to 280 °C followed by cooling at −20 °C/min to −30 °C. Symbols: *K*, crystalline solid; *G*, glassy state; S_C, smectic-C fluid; *N*, nematic fluid; *I*, isotropic fluid. The lack of morphological stability of these three glassy liquid crystals is indicated by crystallization on heating and/or cooling scans and confirmed by hot-stage polarizing optical microscopy and high-temperature X-ray diffractometry.

thermal stability up to 360 °C during the DSC experiment. In contrast to morphologically stable **XIV**, compounds **XVII**−**XIX** were found to undergo crystallization upon heating and/or cooling, as revealed by DSC, X-ray diffraction, and hot-stage polarizing optical microscopy (Figure 4). Moreover, **XVII** exhibits a nematic to smectic C transition at 105 °C on cooling, and further cooling to −30 °C resulted in no visible glass transition. The smectic C mesophase was identified an X-ray diffraction peak at small angles and the Schlieren texture. To avoid thermal decomposition, a sample of **XVIII** was heated to 280 °C in the DSC scan to show both crystallization at 150 °C and melting point at 239 °C. A comparison of the DSC scans of **XIV** with **XVIII** indicates that replacing one of the three ester linkages with an ether linkage is favorable to glass formation. As an alternative approach to stabilizing nematic GLCs, 5-(4-carboxy-2-nitrophenoxy)isophthalic acid was used to prepare **XVI**, showing a broad nematic fluid temperature range with a T_g of 86 °C and a T_c of 288 °C. Therefore, with the same number of ester linkages, a mixed core in **XVI** is superior to simple cores in **XVII**−**XIX** in terms of glass formation. With pendant N_1 to the same mixed core, 5-(4-carboxy-2-nitrophenoxy)isophthalic acid, **XV** possesses a reduced nematic fluid temperature range in comparison to **XVI**, 77 versus 202 °C. Thus, the linear nematogen, N_3, appears to be responsible for a higher T_g and T_c with a wider nematic fluid temperature range than the angular nematogen, N_1. Nevertheless, the angular nematogen is more favorable than the linear counterpart to glass formation with a broader range of core structures, **I**, **VII,** and **XI** versus **XVII**, **XVIII**, and **XIX**.

Consistent efforts have been made in the past to produce nematic liquid crystals with high values of optical birefringence, Δn, and dielectric anisotropy.[25] These two parameters govern the performance of various optical and electrooptic devices. A very successful approach is based on extended π-conjugation with a terminal cyano group. However, the inevitable high crystalline melting point is a major hurdle to practical application. Glass-forming nematic liquid crystals preclude spontaneous crystallization upon heating and cooling, thus permitting the desired uniaxial molecular alignment to be preserved in solid films. A wide nematic fluid temperature range, as indicated by the phase transition temperatures of numerous GLCs presented in Table 1, allows for thermal annealing at a high temperature to maximize molecular alignment at a much reduced viscosity. To assess the potential of the presently reported GLCs for practical application, thin films of selected materials were prepared via spin-coating from a dilute solution. As shown in Table 1, thermal annealing at a temperature from 10 to 20 °C above T_g followed by cooling to room temperature produced well-ordered solid films as characterized by the orientational order parameter, *S*. Note that in general the *S* value increases with a decreasing film thickness, as illustrated with **V**, and with an increasing nematic fluid temperature range. Moreover, thin films (up to 0.3 μm in thickness) on single substrates are consistently better ordered than 14 μm thick, sandwiched films reported previously.[23] Since the difference in the Δn values between the nematic pendants is insignificant,[25,26] the variation in the measured Δn values for GLCs (see Table 1) is largely due to the difference in orientation order between devices.

IV. Conclusions

A series of morphologically stable, glass-forming nematic liquid crystals have been synthesized and characterized as part of our systematic effort aimed at novel materials with a high T_g, a wide nematic fluid temperature range, and ease of material processing into well-ordered thin films with a high value of optical birefringence. Glassy nematics with a T_g close to 130 °C, a T_c close to 350 °C, a nematic fluid temperature range of 265 °C, and an optical birefringence of 0.44 accomplished in the present study represent significant improvements over existing materials. In addition, a definitive set of GLC materials serves to furnish new insight into structure−property relationships as recapitulated in what follows:

(1) An angular nematogen, such as the cyanobiphenylnaphthyl group, is more versatile than a linear nematogen, such as the cyanoterphenyl group, in inducing glass formation by a liquid crystalline molecular system with a broader range of central core structures.

(2) Extended or mixed core structures were found to enable a linear nematogen to form glassy nematics with a higher T_g and a wider nematic fluid temperature range than an angular counterpart.

(3) Modification from an exo-, exo- to an exo-, endo-configuration on a bicyclooctene core, fluorination of the cyanobiphenylnaphthyl group, and a longer spacer to

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(25) Hird, M.; Toyne, K. J.; Gray, G. W.; Day, S. E.; McDonnell, D. G. *Liq. Cryst.* **1993**, *15*, 123.

(26) Wu, S.-T.; Ramos, E.; Finkenzeller, U. *J. Appl. Phys.* **1990**, *68*, 78.

nematic pendants were all found to depress T_c to a much greater extent than T_g.

(4) An extension in core structure accompanied by an increased number of pendants per core was found to elevate T_g, but no consistent effect on T_c was observed.

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