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Nanostructured columnar and cubic liquid-crystalline assemblies consisting of unconventional rigid mesogens based on triphenylmethanes

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ABSTRACT

Liquid-crystalline (LC) molecules of unconventional shapes that form columnar and micellar cubic structures have been synthesized using triarylmethyl moieties as building blocks. The molecules have bowl- and dumbbell-shape. Despite the rigidity and bulkiness of the triarylmethyl moieties, the molecules form columnar and micellar cubic LC phases. The bowl-shaped molecules containing one triarylmethyl moiety show LC phases. The LC temperature ranges of the dumbbell-shaped molecules containing two triarylmethyl moieties connected by rigid rods are wider than those of bowl-shaped molecules containing one triarylmethyl moiety. The UV–vis spectroscopy of the dumbbell-shaped molecules having a terphenyl moiety reveals that the terphenyl moieties aggregate in the mesophase.

1. Introduction

Soft materials such as liquid crystals, gels, and polymers have attracted a great deal of attention because of their structures and dynamic properties.[1] Liquid crystals are unique in soft materials because they combine molecular order and dynamic properties.[2] Liquid-crystalline (LC) molecular assemblies have great potential for dynamically functional materials.[3–12] For example, nematic liquid crystals have been widely used in display devices because of their anisotropic nature and dynamic behavior responsive to electric fields.[2] Recently, intensive studies have focused on nanostructured liquid crystals that exhibit smectic, columnar, and cubic phases.[2–12] They have been developed as new nanostructured functional materials in a variety of fields such as electrooptics, photonics, transportation of electron, ion, or molecules, sensory, catalysis, and bio-activity.[2–12] For the design of smectic and columnar liquid crystals, rod-like and disk-like molecular shapes are standard, respectively (Fig. 1). A number of new mesogens forming columnar and micellar cubic phases have been developed.[3–12] For example, fan-shaped,[13] bowl-shaped,[14] and polycatenar[11,15] mesogens have been reported to form 1D functional columnar liquid crystals. Furthermore, new aggregated structures of micellar cubic phases have received attention recently.[5,8,9,16–20]

Herein, we report on the synthesis and LC properties of bowl-shaped and dumbbell-shaped mesogens based on triarylmethyl moieties (Figs. 1 and 2). Molecules composed of triarylmethyl moieties designed as new mesogens in the present study are shown in Figures 3 and 4. Compounds **1**–**4** having bowl-shaped structures have triarylmethyl moieties with various groups (Fig. 3). Until now, a number of molecules such as metallomesogens,[14a] calixarenes,[14b] cyclotriveratrylenes,[14c] dendrons,[14d] C_{60} derivatives,[14e,f] and triphenylphosphine oxides[21a] have been used as structural parts of bowl-shaped mesogens. The linking of two triarylmethyl moieties via rigid spacers gives dumbbell-shaped compounds **5**–**8** (Figs. 2 and 4), which leads to the formation of a new mesogen.

2. Results and discussion

2.1. Synthesis of 1–8

Compounds **1** and **2** were synthesized by the nucleophilic substitution of the hydroxy groups of tris(4-hydroxyphenyl)-methane (**9**) and tris(4-hydroxyphenyl)ethane (**10**) with benzyl chloride derivatives, respectively (Scheme 1).[21] The reaction of 4-methoxyphenylmagnesium bromide with aromatic esters **11** and **12** yielded triphenylmethanol derivatives **13** and **14**, respectively. The tetraphenylmethane derivatives **15** and **16** were synthesized by acid-catalyzed reaction of the triphenylmethanol derivatives **13** and **14** with phenol. After the BBr_3 demethylation of the methoxy groups in **15** and **16**, nucleophilic substitution of the phenol groups with 3,4,5-tridodecyloxybenzyl chloride afforded compounds **3**

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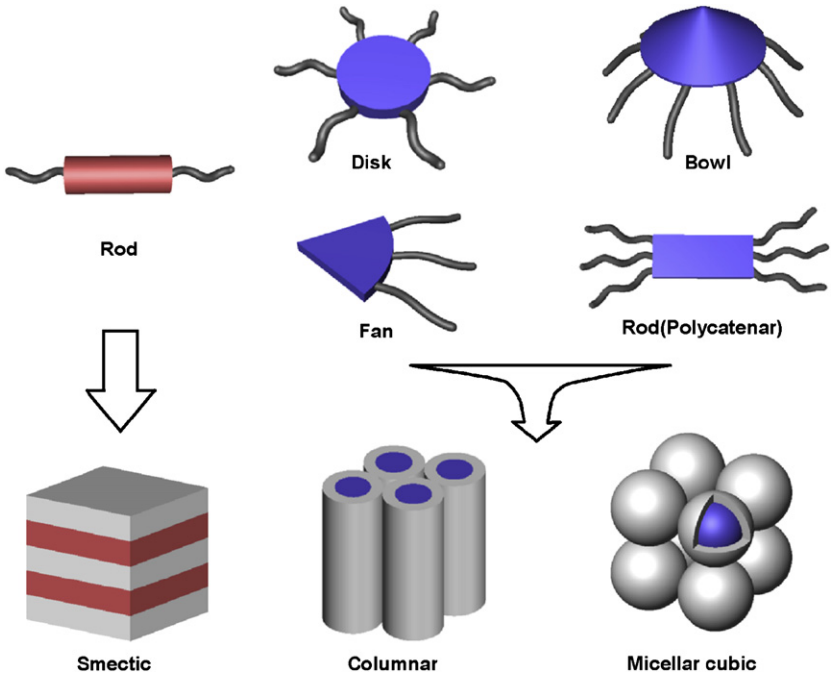


Figure 1. Schematic illustration of several representative mesogens forming nanostructured liquid-crystalline structures.

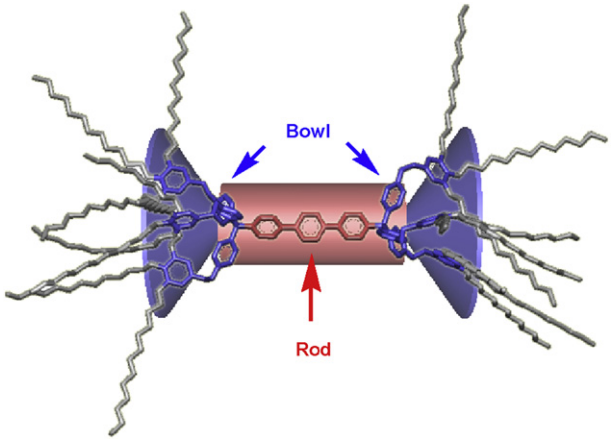


Figure 2. Molecular structure of the dumbbell-shaped liquid crystal composed of rigid rod (red part) and bowls (blue parts).

and **4** (Scheme 1). Compounds **5**–**7** were prepared as outlined in Scheme 2. Rod-shaped aromatic compounds with diester moieties **19**, **20**, and **27** were reacted with 4-methoxyphenylmagnesium bromide. The hydroxy groups in the generated alchols, **21**, **22**, and **28** were substituted for phenol groups with acid catalysis. Demethylation of the methoxy goups for **23**, **24**, and **29** with BBr_3 and the following reaction with 3,4,5-tridodecyloxybenzyl chloride gave compounds **5**–**7**. Compound **8** has a terphenyl moiety substituted at the 4- and 4″-position for the triarylmethyl groups. The terphenyl moieties were synthesized by cross-coupling reaction of 4-bromophenyltriarylmethane (**34**) and 1,4-phenyldiboronic acid. Following the demethylation reaction with BBr_3 and the nucleophilic substitution gave compound **8** (Scheme 3).

2.2. Liquid-crystalline properties of bowl-shaped molecules 1–4

Compounds **1**–**4** have one triarylmethyl group and the hydrogen, methyl, phenyl, and pyridyl groups as a head group. We

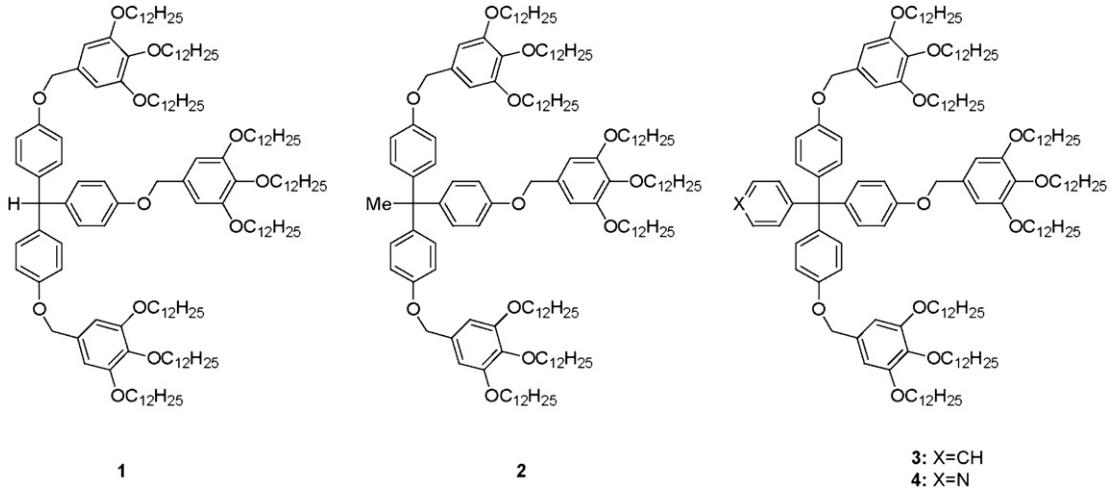
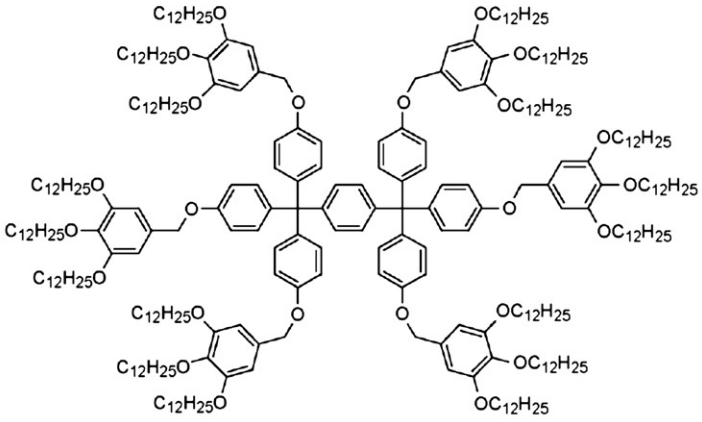


Figure 3. Structures of the bowl-shaped liquid crystals containing one triarylmethane moiety.



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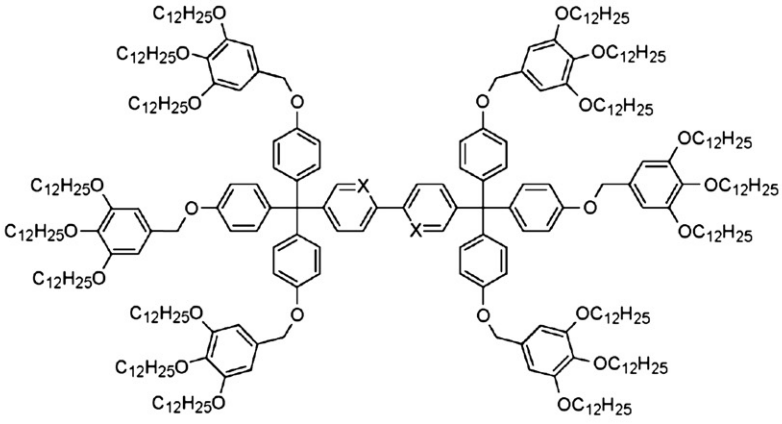
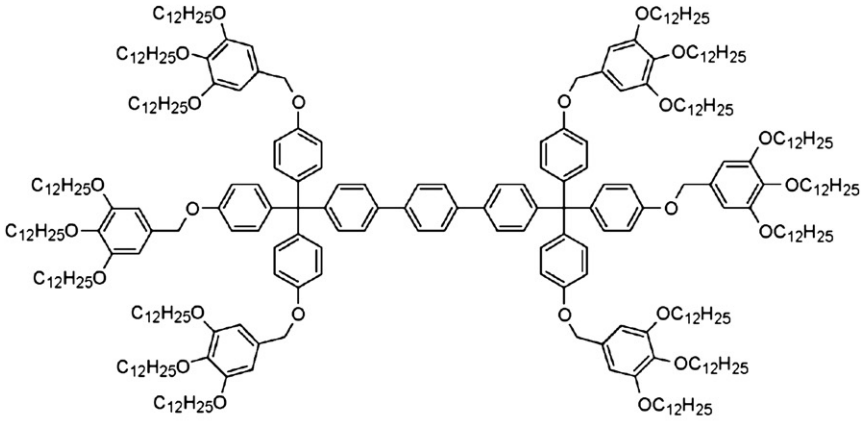


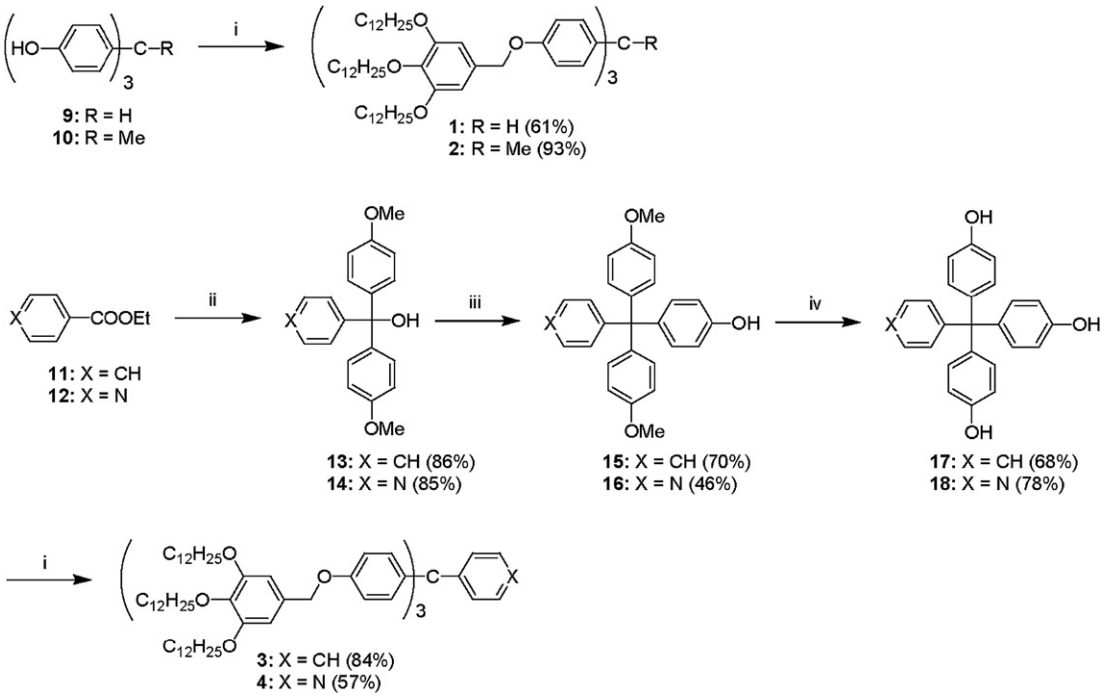
6: X=CH
7: X=N



8

Figure 4. Structures of the dumbbel-shaped liquid crystals containing two triarylmethane moieties.

examined the effects of the structural bulkiness of the head groups on the LC properties. Compounds **1**, **2**, and **4** show polarizing micrographs typical for columnar phases, while **3** shows a polydomain texture (Fig. 5). The DSC thermogram of **1** is shown in Figure 6. The exothermic peaks observed at 28 and 0 °C on cooling are ascribed to the isotropic–LC transition and the crystallization, respectively. The transition peaks due to the crystalline–LC transition and the isotropization are also seen on heating. The phase sequence, transition temperatures, and transition enthalpies are presented in Table 1. The crystalline–LC transition temperatures of the compounds become lower as the structural bulkiness of the head group increases. For example, the crystalline–LC transition temperature of **1** is 12 °C, while that of **3** is 7 °C. The structural bulkiness of **3** and **4** may disturb the close molecular packing in the crystalline states. The isotropization temperatures also decrease with the increase of the structural bulkiness except for **4** having the pyridyl moiety. The intermolecular dipole–dipole interactions of the pyridyl group may stabilize the LC state. The X-ray diffraction pattern of **1** shows reflection peaks at 34.2, 19.4, and 16.9 Å, which can be indexed as [100], [110], and [200], respectively (Fig. 7). The broad peak at 8 Å can be ascribed to the distance of the molecular stacking of **1**, since the value is similar to those obtained for the single crystals of triphenylmethane derivatives.[22] Compounds **2** and **4** give XRD patterns similar to that of **1**. The reflections for **1**, **2** and **4** are listed in



Scheme 1. Synthesis of liquid crystals **1**–**4**: (i) 3,4,5-tridodecyloxybenzyl chloride, K_2CO_3, DMF; (ii) 4-bromoanisole, Mg, THF; (iii) phenol, methanesulfonic acid; (iv) BBr_3, CH_2Cl_2.

Table 2. The reciprocal d-spacing of $1:3^{1/2}:4^{1/2}$ for these materials is characteristic of hexagonal columnar structures. The intercolumnar distances of **1**, **2**, and **4** are 39.5, 40.8, and 40.5 Å, respectively. Despite the large difference in the structural bulkiness of the head groups, the intercolumnar distances of **1**, **2**, and **4** show almost the same value. Triarylmethane derivatives can be assembled into one-dimensional columnar structure in the single crystal by the simple stacking of molecules.[22] The columnar structures of **1**–**4** may be formed upon the stacking of the bowl-shaped molecules.

2.3. Liquid-crystalline properties of dumbbell-shaped molecules 5–8

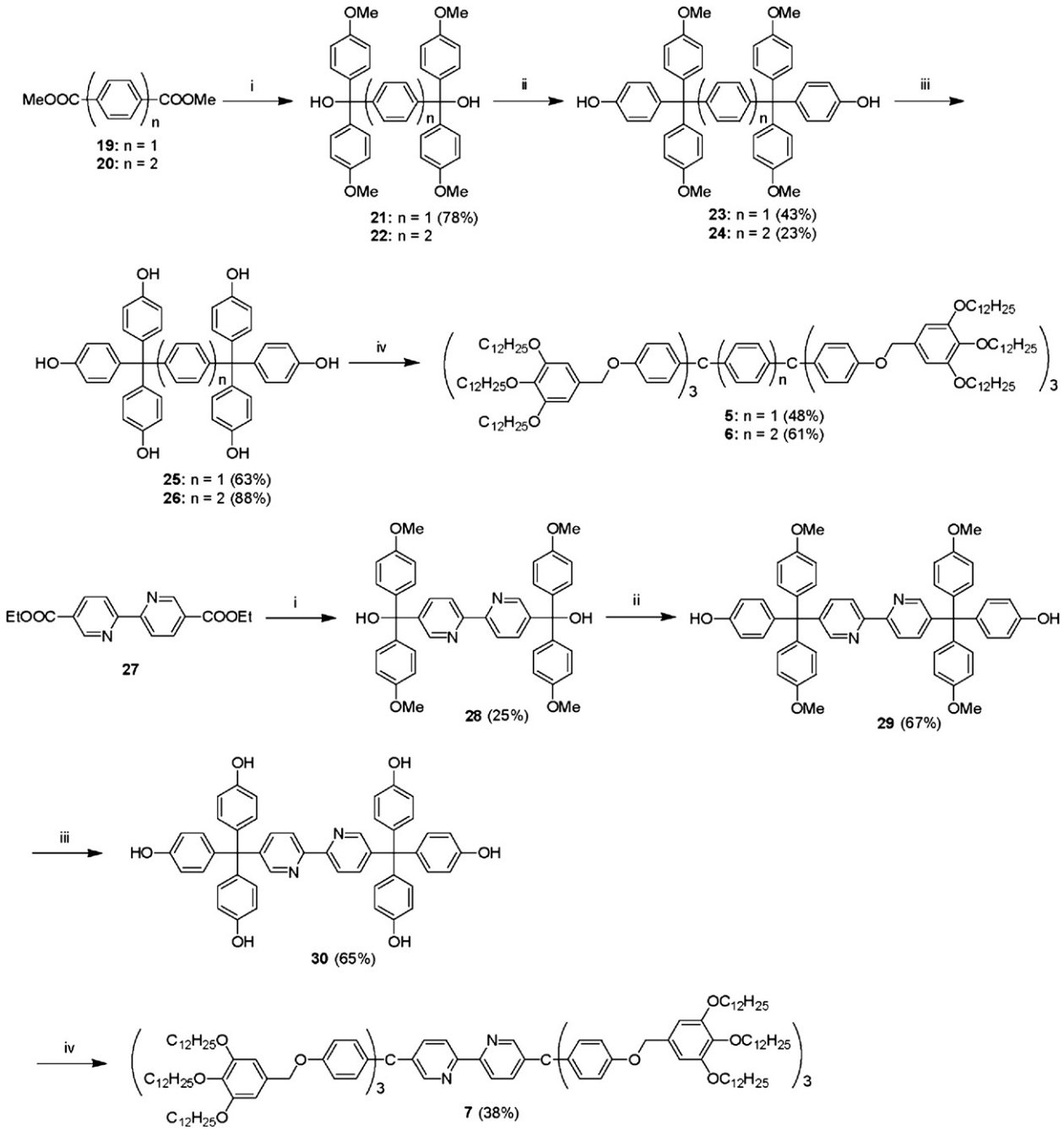
Compounds **5**–**8** have dumbbell-shaped structures composed of two bowl-shaped triphenylmethane moieties connected by *p*-phenylenes that function as rod-shaped rigid spacers. The DSC thermograms of **5**–**8** are shown in Figure 8 and the thermal properties are listed in Table 3. The linkage of two tirarylmethane derivatives by the rigid spacers induces transition temperatures that are higher than those of **1**–**4**. Figure 9 shows polarized optical microscopic images of the LC phases of **5**. A typical texture for columnar liquid crystals is observed for **5** (Fig. 9). It is of interest that compounds **6**–**8** show no birefringence in their mesophases, suggesting the formation of cubic phases. Compounds **6**–**8** having longer phenylene spacers show cubic phases for wider temperature ranges. The isotropization temperature of **6** containing the biphenyl spacer is the highest among the dumbbell-shaped liquid crystals prepared in the present study. The replacement of the biphenyl group by the bipyridyl group induces a slight decrease of the isotropization temperature. The calculated molecular structures of **5** and **8** are shown in Figure 10. The wider space around the rod-shaped part of **8** may promote the aggregation of the terphenyl core, which results in the formation the micellar cubic phase. The SAXD pattern of **5** at 68 °C shows only the (100) reflection at 32.6 Å. For compound **6**, the SAXD profile for the cubic phase at 80 °C presents the reflections of 31.3, 22.1, 18.1, and 15.6 Å. The reciprocal d-spacing of $1:2^{1/2}:3^{1/2}:4^{1/2}$ for **6** can be ascribed to a primitive cubic lattice structure. The SAXD pattern of **7** suggests that the replacement by the pyridyl moiety does not affect the phase structure. The SAXD profile for the cubic phase of **8** is rather complicated, which prevents the determination of the lattice parameter.

2.4. Emission properties of dumbbell-shaped molecule 8

The aggregated structures of **8** having the terphenyl group have been examined by spectroscopic methods. Figure 11a shows the UV–vis absorption spectra of **8** in the cubic phase and in hexane solution (4 μmol dm^{-3}). The absorption peaks due to the terphenyl group are observed at 292 and 288 nm in the cubic phase and in hexane solution, respectively. The absorption maximum for the cubic phase is red-shifted from that for the hexane solution, which suggests the formation of an aggregated structure of the terphenyl group in the cubic phase. The emission spectrum of **8** in the cubic phase shows two peaks at 341 and 362 nm and a shoulder around 390 nm, while the spectrum obtained for the hexane solution represents two peaks at 332 and 353 nm and a shoulder around 380 nm (Fig. 11b). This observation also supports the aggregation of the terphenyl groups in the cubic phase.[23] Terphenyl derivatives show excimer emission at around 400 nm upon the parallel stacking of their long axis of the molecules.[24] As no excimer emission peak is seen in the spectrum of **8** in the cubic phase, the terphenyl groups should aggregate with random orientations in the cubic phase. Recently, luminescent liquid crystals have been prepared as new functional liquid crystals.[25–27] These dumbbell-shaped mesogens based on the terphenyl moiety may be used as new photo-functional molecular assemblies.

3. Conclusion

Bowl- and dumbbell-shaped LC molecules have been synthesized by using triarylmethyl moieties as building blocks. The thermal stability of the LC phases for the bowl-shaped molecules is dependent on the structural bulkiness and the polarity of the molecules. The LC properties of the dumbbell-shaped molecules are



Scheme 2. Synthesis of liquid crystals **5**–**7**: (i) 4-bromoanisole, Mg, THF; (ii) phenol, methanesulfonic acid; (iii) BBr_3, CH_2Cl_2; (iv) 3,4,5-tridodecyloxybenzyl chloride, K_2CO_3, DMF.

greatly dependent on the length of the rigid spacers. Recently, a variety of LC molecular objects, such as dendrons,[10,28] rotaxanes,[29,30] catenanes,[31] and nanoclusters[32] have been prepared. The mesogens reported in the present paper represent new building blocks for these LC objects.

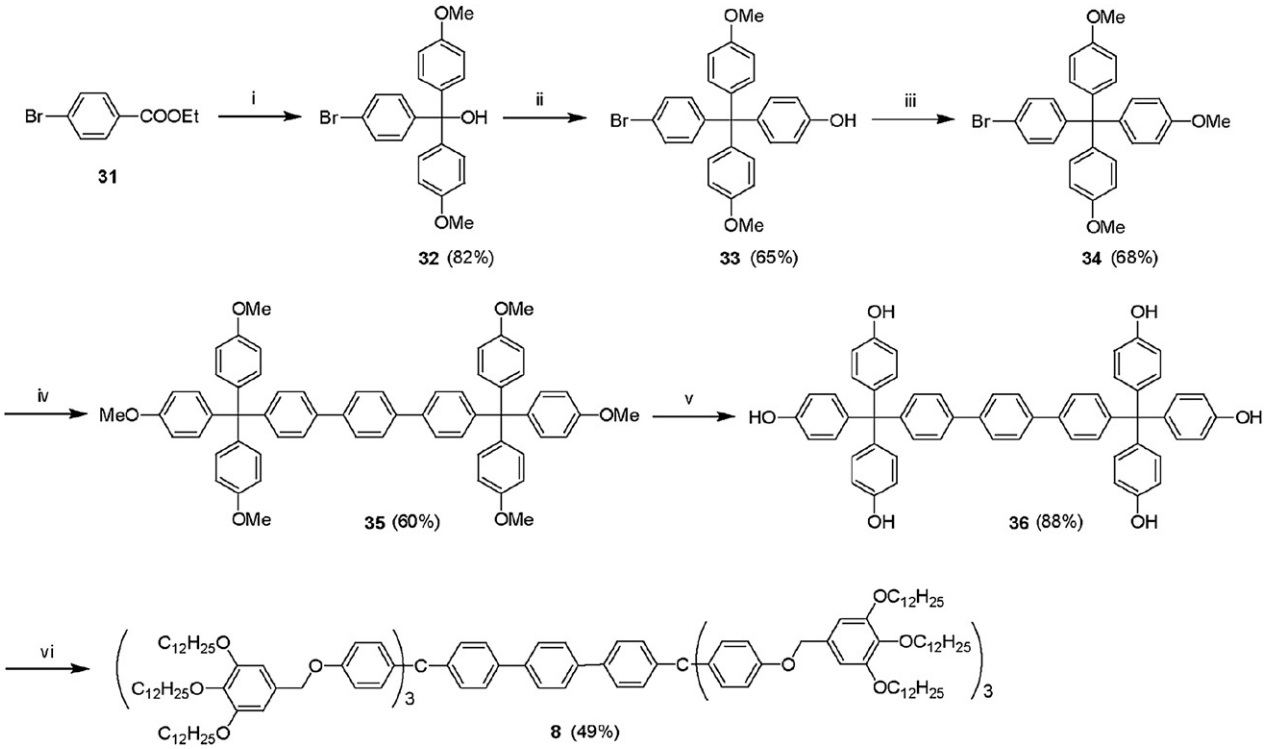
4. Experimental section

4.1. Materials

All reagents and solvents were purchased from Aldrich, Tokyo Kasei, and Wako, and were used as-received. Analytical thin layer chromatography (TLC) was performed on silica gel plates from E. Merck (silica gel F_{254}). Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (silica gel 60, spherical 40–50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-908 chromatograph. 3,4,5-Tridodecyloxybenzylchloride[21] and diethyl-2,2′-bipyridyl-5,5′-dicarboxylate[33] were prepared by similar procedures reported in the literature.

4.2. Instrumentation

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer. Mass spectra were obtained with a PerSeptive Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out with a Yanaco MT-6 CHN autocorder. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 30 at a scanning rate of 5 °C min^{-1}. Transition temperatures were taken at the maximum of transition peaks. A polarizing optical



Scheme 3. Synthesis of the liquid crystal **8**: (i) 4-bromoanisole, Mg, THF; (ii) phenol, methanesulfonic acid; (iii) CH_3I, K_2CO_3, DMF; (iv) 1,4-phenyldiboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, THF, H_2O; (v) BBr_3, CH_2Cl_2; (vi) 3,4,5-tridodecyloxybenzyl chloride, K_2CO_3, DMF.

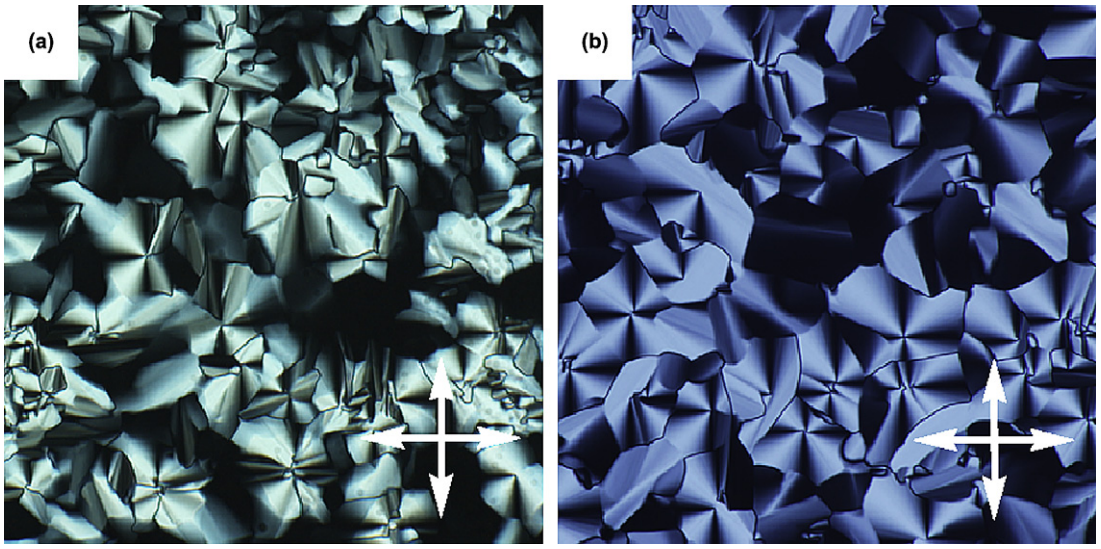


Figure 5. Polarized optical microscopic images of (a) **1** at 25 °C and (b) **4** at 20 °C.

microscope Olympus BH-51 equipped with Mettler FP82 HT hot stage was used for visual observation. X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT-2500 diffractometer with a heating stage using Ni-filtered Cu Kα radiation. UV–vis absorption and photoluminescence (PL) spectra were measured with a Agilent 8453 and a JASCO FP-777 W spectrometers, respectively.

4.3. Synthesis

All target liquid-crystalline compounds were fully characterized by all available techniques. Intermediate compounds were characterized by ^1H and ^{13}C NMR to provide basic proof of identity and were then fully used in the ongoing synthetic pathway.

*4.3.1. Tris[4-(3,4,5-tridodecyloxybenzyloxy)phenyl]methane (**1**)*

To a 10 ml of DMF solution of tris(4-hydroxyphenyl)methane **9** (28 mg, 96 μmol) and 3,4,5-tridodecyloxybenzyl chloride (200 mg, 0.29 mmol) was added K_2CO_3 (138 mg, 1.0 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture water was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under

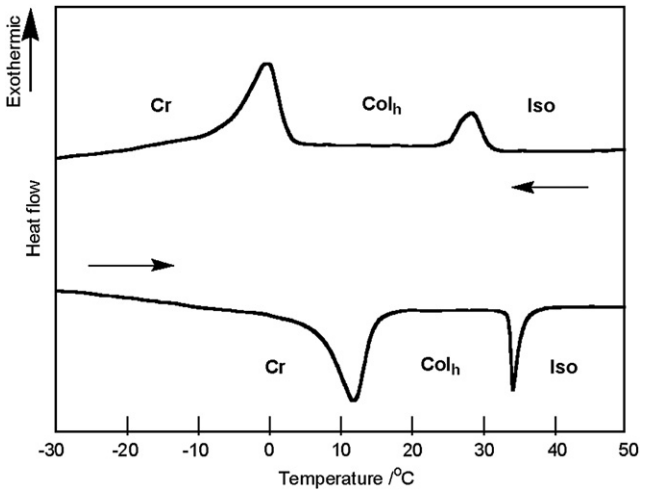


Figure 6. DSC heating and cooling trace of **1** (5 °C min^{-1}).

Table 1
Thermal properties of **1**–**4**[a]

Compounds	Transition temperature/°C (enthalpy/kJ mol^{-1})
1	Cr 12 (23.3) Col$_h$ 34 (6.1) Iso
2	Cr 12 (25.0) Col$_h$ 28 (5.5) Iso
3	Cr 7 (13.3) M 22 (4.8) Iso
4	Cr 3 (24.5) Col$_h$ 32 (4.4) Iso

[a] Determined by DSC on heating (5 °C min^{-1}), Cr=crystalline, Col$_h$=hexagonal columnar, M=mesophase, Iso=isotropic.

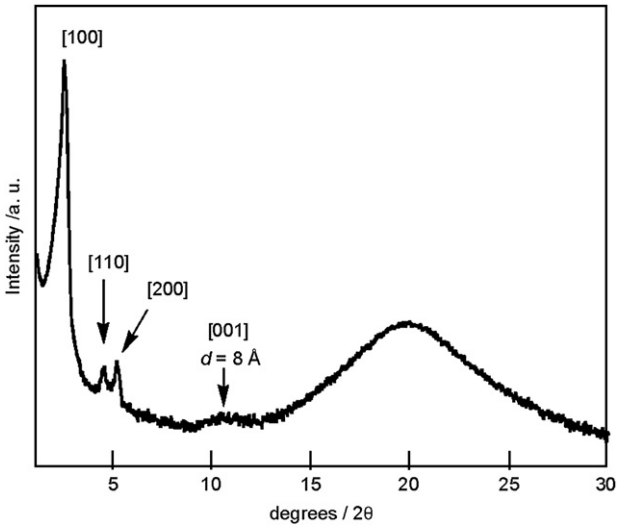


Figure 7. XRD pattern of **1** at 25 °C.

Table 2
X-ray diffraction data of **1**, **2**, and **4** obtained from XRD measurements

Compounds	Temperature/°C	d/Å		
		[100]	[110]	[200]
1	25	34.2	19.4	16.9
2	15	35.3	20.0	17.3
4	15	35.0	19.8	17.2

reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane–ethyl acetate=20:1) gave a white highly viscous oil (0.13 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, J=8.4 Hz, 6H, ArH), 6.90

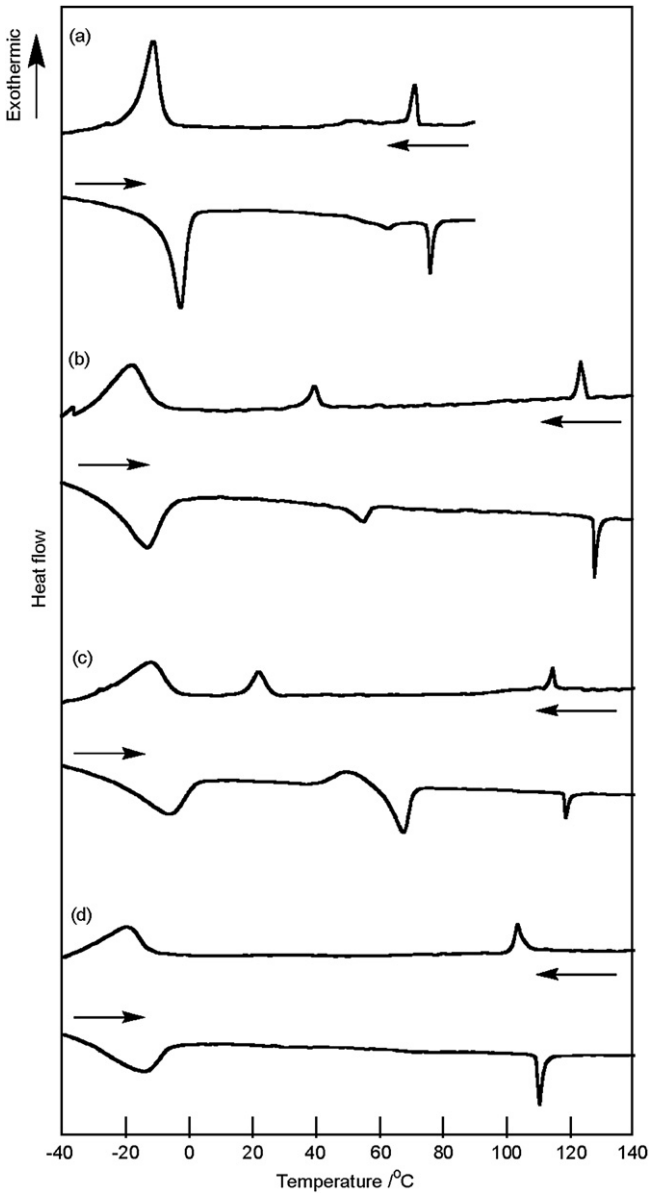


Figure 8. DSC thermograms of (a) **5**, (b) **6**, (c) **7**, and (d) **8** on heating and cooling (5 °C min^{-1}).

Table 3
Thermal properties of **5**–**8** determined by DSC on heating (5 °C min^{-1})[a]

Compounds	Transition temperature/°C (enthalpy/kJ mol^{-1})
5	Cr −3 (92.1) Col 63 (4.8) Col 76 (12.5) Iso
6	Cr −13 (86.3) M 55 (7.0) Cub 128 (8.4) Iso
7	Cr −6 (105.2) Cr 68 (51.3) Cub 119 (5.3) Iso
8	Cr −15 (79.1) Cub 110 (13.4) Iso

[a] Cr=crystalline, Col=columnar, M=mesophase, Cub=cubic, Iso=isotropic.

(d, J=8.8 Hz, 6H, ArH), 6.61 (s, 6H, ArH), 5.42 (s, 1H, Ar$_3$CH), 4.90 (s, 6H, OCH_2Ar), 3.98–3.92 (m, 18H, CH_2CH_2O), 1.82–1.72 (m, 18H, $CH_2CH_2CH_2O$), 1.49–1.41 (br d, 18H, $CH_2CH_2CH_2CH_2O$), 1.30–1.24 (br d, 144H,CH_2), 0.88 (t, J=7.2 Hz, 27H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.21, 153.26, 137.90, 136.99, 131.86, 130.21, 114.48, 106.19, 73.40, 70.44, 69.17, 31.94, 31.92, 30.32, 29.76, 29.73, 29.70, 29.66, 29.63, 29.62, 29.41, 29.40, 29.36, 26.13, 26.09, 22.69, 14.12;

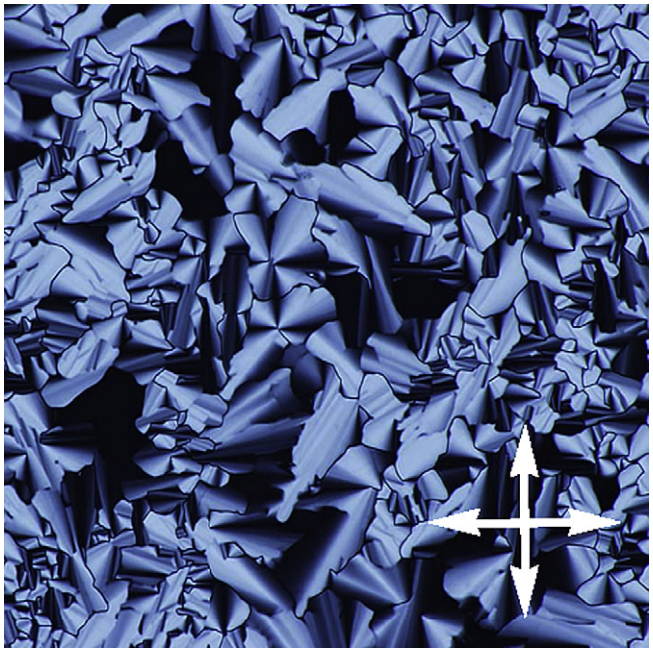


Figure 9. Polarized optical microscopic images of **5** at 70 °C.

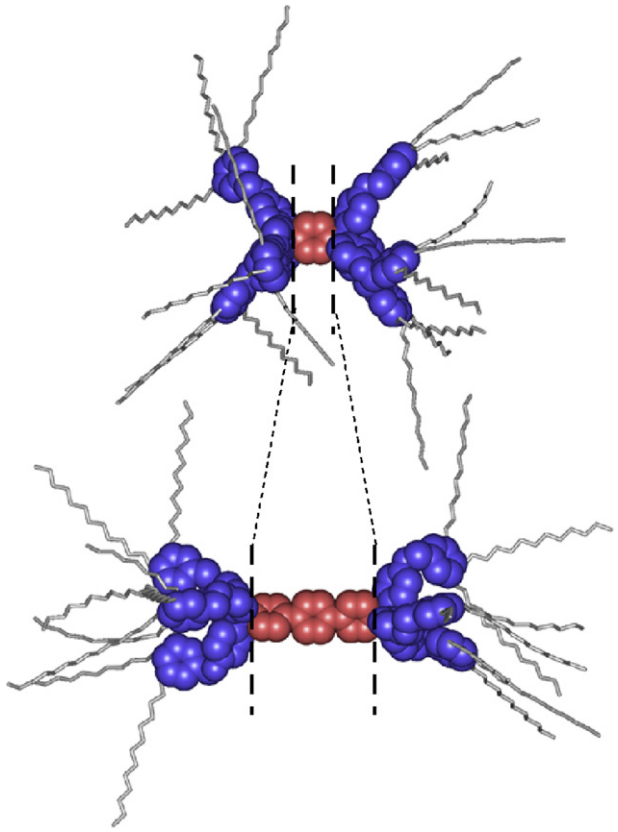


Figure 10. Molecular structures of **5** and **8** calculated by molecular mechanics; the red and blue parts show rod and bowl moieties, respectively.

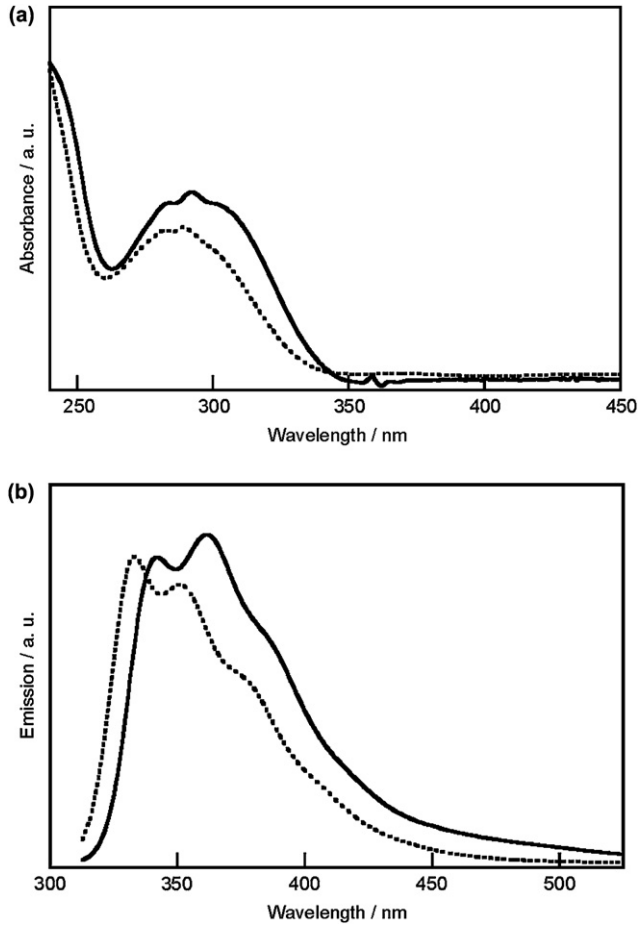


Figure 11. (a) UV–vis absorption spectra of **8** in the cubic phase (—) and on hexane solution (- - -) at 25 °C and (b) emission spectra of **8** in the cubic phase (—, excitation at 317 nm) and on hexane solution (- - -, excitation at 317 nm).

m/*z* (MALDI-TOF) 2222.4 (calcd $[M+H]^+$=2222.5); IR (neat): 2921, 2851, 1591, 1505, 1467, 1439, 1377, 1334, 1235, 1174, 1117, 1000, 848, 720, 579 cm^{-1}; Anal. Calcd for $C_{148}H_{250}O_{12}$: C, 80.02; H, 11.34. Found: C, 80.07; H, 11.56.

4.3.2. *Tris[4-(3,4,5-tridodecyloxybenzyloxy)phenyl]ethane (**2**)*

To a DMF (10 ml) solution of tris(4-hydroxyphenyl)ethane **10** (41 mg, 0.13 mmol) and 3,4,5-tridodecyloxybenzyl chloride (300 mg, 0.44 mmol) was added K_2CO_3 (138 mg, 1.0 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture, water (100 ml) was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane/ethyl acetate=20:1) gave a white highly viscous oil (0.27 g, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, *J*=8.4 Hz, 6H, Ar*H*), 6.90 (d, *J*=8.8 Hz, 6H, Ar*H*), 6.61 (s, 6H, Ar*H*), 4.90 (s, 6H, OCH_2Ar), 3.98–3.92 (m, 18H, CH_2CH_2O), 2.12 (s, 3H, Ar_3CCH_3), 1.82–1.72 (m, 18H, $CH_2CH_2CH_2O$), 1.49–1.41 (br d, 18H, $CH_2CH_2CH_2CH_2O$), 1.30–1.24 (br d, 144H, CH_2), 0.88 (t, *J*=7.2 Hz, 27H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.85, 153.26, 142.01, 137.91, 131.87, 129.60, 113.90, 106.21, 73.39, 70.41, 69.06, 50.63, 31.94, 31.91, 30.32, 29.75, 29.73, 29.69, 29.65, 29.63, 29.62, 29.41, 29.39, 29.36, 26.12, 26.09, 22.68, 14.10; *m*/*z* (MALDI-TOF) 2235.1 (calcd $[M]^+$=2235.6); IR (neat): 2924, 2852, 1591, 1505, 1463, 1435, 1378, 1334, 1291, 1235, 1180, 1116, 1010, 828, 721, 583 cm^{-1}; Anal. Calcd for $C_{149}H_{252}O_{12}$: C, 80.05; H, 11.36. Found: C, 79.89; H, 11.43.

4.3.3. *Bis(4-methoxyphenyl)phenylmethanol (**13**)*

In an oven-dried 50 ml three-necked flask equipped with a condenser, mechanical stirrer, and argon system were placed magnesium turnings (0.58 g, 24 mmol) with dry THF (20 ml).

4-Bromoanisole (3.0 g, 16 mmol) was added dropwise with gentle heating until the reaction was started. The reaction was allowed to go for 1 h. A brown color was observed. Ethyl benzoate **11** (1.2 g, 8.0 mmol) was added. The mixture was stirred overnight under argon. The reaction mixture was neutralized with 5 wt % HCl aq and extracted with $CHCl_3$. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The filtrate was concentrated and chromatographed on silica with 20% ethyl acetate in hexane to afford compound **13** as a reddish oil (2.2 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.24 (5H, m, Ph*H*), 7.17 (4H, d, *J*=8.8 Hz, Ar*H*), 6.82 (4H, d, *J*=8.8 Hz, Ar*H*), 3.76 (6H, s, OC*H*$_3$), 2.77 (1H, s, O*H*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.55, 147.27, 139.40, 129.09, 127.81, 127.72, 127.03, 113.11, 81.37, 55.20; IR (neat): 3501, 3002, 2954, 2835, 1606, 1505, 1446, 1413, 1296, 1247, 1176, 1115, 1032, 899, 826, 754, 702, 667, 634, 585 cm^{-1}.

4.3.4. 4-[Bis(4-methoxyphenyl)phenylmethyl]phenol (**15**)

In a 100 ml flask equipped with a condenser, mechanical stirrer, and argon system was placed bis(4-methoxyphenyl)phenylmethanol **13** (2.2 g, 6.9 mmol) with phenol (3.2 g, 34 mmol). A few drops of methanesulfonic acid were added with gentle heating. A deep-red solution was obtained. The reaction mixture was stirred for 36 h at 120 °C. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was dried with sodium sulfate and concentrated. The crude compound was chromatographed on silica with 25% ethyl acetate in hexane to afford compound **15** as a reddish oil (1.9 g, 70%). Mp 176.6–182.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.15 (5H, m, Ph*H*), 7.08 (4H, d, *J*=8.8 Hz, Ar*H*), 7.03 (2H, d, *J*=8.8 Hz, Ar*H*), 6.77 (4H, d, *J*=8.8 Hz, Ar*H*), 6.70 (2H, d, *J*=8.8 Hz, Ar*H*), 3.79 (6H, s, OC*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.32, 153.54, 147.45, 139.46, 132.22, 132.02, 130.94, 127.32, 125.73, 114.12, 112.59, 62.85, 55.15; *m*/*z* (MALDI-TOF) 396.29 (calcd [M]$^+$=396.17); IR (KBr): 3407, 3031, 2950, 2834, 1034, 1506, 1461, 1442, 1351, 1289, 1251, 1179, 1116, 1034, 825, 757, 727, 705, 600, 580, 533 cm^{-1}.

4.3.5. Tris(4-hydroxyphenyl)phenylmethane (**17**)

4-[Bis(4-methoxyphenyl)phenylmethyl]phenol **15** (1.9 g, 4.8 mmol) was placed in a 100 ml two-neck flask equipped with mechanical stirrer and argon system. Dry CH_2Cl_2 (50 ml) was added and the mixture was kept at −78 °C. A 1.0 M solution of BBr_3 in methylene chloride (9.6 ml, 9.6 mmol) was slowly added. The temperature was slowly raised to 25 °C and the mixture was stirred for 12 h at 25 °C. The reaction was quenched with water at 0 °C and generated precipitate was filtered. Reddish brown solid was obtained by washing with water and chloroform (1.2 g, 68%). The compound was used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.34 (3H, s, O*H*), 7.24–7.12 (3H, m, Ph*H*), 7.04 (2H, d, *J*=7.6 Hz, Ph*H*), 6.83 (6H, d, *J*=8.8 Hz, Ar*H*), 6.62 (6H, d, *J*=8.8 Hz, Ar*H*); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.05, 147.82, 137.59, 131.51, 130.45, 127.33, 125.56, 114.14, 62.27; *m*/*z* (MALDI-TOF) 368.36 (calcd [M]$^+$=398.14); IR (KBr): 3676, 1595, 1507, 1437, 1363, 1176, 826, 703, 581 cm^{-1}.

4.3.6. Tris[4-(3,4,5-tridodecyloxybenzyloxy)phenyl]phenylmethane (**3**)

To a DMF (10 ml) solution of tris(4-hydroxyphenyl)phenylmethane **17** (50 mg, 0.14 mmol) and 3,4,5-tridodecyloxybenzyl chloride (305 mg, 0.45 mmol) was added K_2CO_3 (138 mg, 1.0 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture, water (100 ml) was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane–ethyl acetate=15:1) gave a colorless oil (0.27 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.15 (5H, m, Ph*H*), 7.10 (6H, d, *J*=8.8 Hz, Ar*H*), 6.86 (6H, d, *J*=9.2 Hz, Ar*H*), 6.61 (6H, s, Ar*H*), 4.90 (6H, s, ArC*H*$_2$O), 3.99–3.91 (18H, m, CH_2CH_2O), 1.87–1.70 (18H, m, $CH_2CH_2CH_2O$), 1.52–1.37 (18H, br, $CH_2CH_2CH_2CH_2O$), 1.37–1.19 (144H, br, C*H*$_2$), 0.88 (27H, t, *J*=6.8 Hz, C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.74, 153.25, 147.40, 139.66, 137.90, 132.05, 131.80, 130.97, 127.33, 125.77, 113.42, 106.22, 73.38, 70.36, 69.03, 62.94, 31.93, 31.91, 30.32, 29.75, 29.72, 29.69, 29.64, 29.63, 29.61, 29.40, 29.39, 29.36, 26.13, 26.08, 22.69, 22.67, 14.10; *m*/*z* (MALDI-TOF) 2296.1 (calcd [M]$^+$=2295.9); IR (neat): 2921, 1592, 1505, 1463, 1435, 1378, 1334, 1295, 1235, 1181, 1115, 1013, 897, 824, 756, 721, 704, 591 cm^{-1}; Anal. Calcd for $C_{154}H_{254}O_{12}$: C, 80.50; H, 11.14. Found: C, 80.46; H, 11.38.

4.3.7. Bis(4-methoxyphenyl)-4-pyridylmethanol (**14**)

In an oven-dried 50 ml three-necked flask equipped with a condenser, mechanical stirrer, and argon system were placed magnesium turnings (0.66 g, 27 mmol) with dry THF (30 ml). 4-Bromoanisole (3.4 g, 18 mmol) was added dropwise with gentle heating until the reaction was started. The reaction was allowed to go for 1 h. A brown color was observed. Methyl isonicotinate **12** (1.0 g, 7.3 mmol) was added. The mixture was stirred overnight under argon. The reaction mixture was neutralized with 5 wt % HCl aq and extracted with $CHCl_3$. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The filtrate was concentrated and chromatographed on silica with $CHCl_3$–methanol (10:1) to afford compound **14** as a white solid (2.0 g, 85%). Mp 152.6–157.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (2H, d, *J*=5.6 Hz, Py*H*), 7.27 (2H, d, *J*=4.4 Hz, Py*H*), 7.15 (4H, d, *J*=8.8 Hz, Ar*H*), 6.85 (4H, d, *J*=8.8 Hz, Ar*H*), 3.81 (6H, s, OC*H*$_3$), 2.97 (1H, s, O*H*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.93, 155.97, 149.29, 138.16, 129.04, 127.70, 122.55, 114.12, 113.40, 80.55, 55.26; IR (KBr): 3074, 2835, 1606, 1579, 1508, 1457, 1440, 1413, 1305, 1276, 1248, 1177, 1032, 1006, 924, 826, 782, 674, 639, 610, 591 cm^{-1}; Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.56; H, 6.10; N, 4.26.

4.3.8. 4-[Bis(4-methoxyphenyl)-4-pyridylmethyl]phenol (**16**)

In a 100 ml flask equipped with a condenser, mechanical stirrer, and argon system were placed bis(4-methoxyphenyl)phenylmethanol **14** (0.50 g, 1.6 mmol) with phenol (1.5 g, 16 mmol). A few drops of methanesulfonic acid were added with gentle heating. A dark-purple solution was obtained. The reaction mixture was stirred for 18 h at 120 °C. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was dried with sodium sulfate and concentrated. The crude compound was chromatographed on silica with ethyl acetate–$CHCl_3$ (1:2) to afford compound **16** as a white solid (0.28 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (2H, d, *J*=6.4 Hz, Py*H*), 7.19 (2H, d, *J*=5.6 Hz, Py*H*), 7.04 (4H, d, *J*=8.8 Hz, Ar*H*), 7.04 (4H, d, *J*=8.8 Hz, Ar*H*), 6.96 (2H, d, *J*=8.8 Hz, Ar*H*), 6.79 (4H, d, *J*=8.8 Hz, Ar*H*), 6.75 (2H, d, *J*=8.8 Hz, Ar*H*), 3.79 (6H, s, OC*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.47, 156.73, 155.34, 148.69, 137.89, 136.22, 131.65, 131.63, 125.80, 114.45, 112.67, 62.44, 55.00; *m*/*z* (MALDI-TOF) 398.53 (calcd [M+H]$^+$= 398.18); IR (KBr): 2998, 2834, 1601, 1507, 1463, 1414, 1252, 1177, 1117, 1070, 1032, 1011, 828, 813, 667, 590 cm^{-1}.

4.3.9. Tris(4-hydroxyphenyl)-4-pyridylmethane (**18**)

4-[Bis(4-methoxyphenyl)-4-pyridylmethyl]phenol **16** (0.25 g, 0.63 mmol) was placed in a 100 ml two-neck flask equipped with mechanical stirrer and argon system. Dry CH_2Cl_2 (15 ml) was added and the mixture was kept at −78 °C. A 1.0 M solution of BBr_3 in methylene chloride (2.5 ml, 2.5 mmol) was slowly added. The temperature was slowly raised to 25 °C and the mixture was stirred for 12 h at 25 °C. The reaction was quenched with water at 0 °C and extracted with ethyl acetate. The collected organic fraction was

washed with water, dried over Na_2SO_4, and filtered. Removal of the solvent gave a white solid (0.18 g, 78%). The compound was used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.40 (3H, s, O*H*), 8.45 (2H, d, *J*=6.4 Hz, Py*H*), 7.06 (2H, d, *J*=4.4 Hz, Py*H*), 6.84 (6H, d, *J*=8.8 Hz, Ph*H*), 6.67 (6H, d, *J*=8.8 Hz, Ar*H*); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 156.48, 155.51, 148.96, 136.11, 131.32, 125.41, 114.44, 62.00; *m*/*z* (MALDI-TOF) 370.26 (calcd $[M+H]^+$= 370.14); IR (KBr): 3421, 1601, 1508, 1453, 1381, 1255, 1177, 1070, 1010, 825, 601, 579 cm^{-1}.

4.3.10. Tris[4-(3,4,5-tridodecyloxybenzyloxy)phenyl]-4-pyridylmethane (**4**)

To a DMF (10 ml) solution of tris(4-hydroxyphenyl)-4-pyridylmethane **18** (50 mg, 0.14 mmol) and 3,4,5-tridodecyloxybenzyl chloride (0.28 g, 0.41 mmol) was added K_2CO_3 (0.19 g, 1.4 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture, water (100 ml) was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane–ethyl acetate=6:1) gave a white highly viscous oil (0.18 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (2H, d, *J*=6.4 Hz, Py*H*), 7.13 (2H, d, *J*=6.4 Hz, Ar*H*), 7.06 (6H, d, *J*=8.8 Hz, Ar*H*), 6.88 (6H, d, *J*=8.8 Hz, Ar*H*), 6.61 (6H, s, Ar*H*), 4.91 (6H, s, ArCH_2O), 3.99–3.91 (18H, m, CH_2CH_2O), 1.84–1.70 (18H, m, $CH_2CH_2CH_2$O), 1.50–1.40 (18H, br, $CH_2CH_2CH_2CH_2$O), 1.40–1.20 (144H, br, CH_2), 0.88 (27H, t, *J*=6.8 Hz, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.04, 156.35, 153.24, 149.11, 138.16, 137.93, 131.81, 131.61, 125.82, 113.74, 106.17, 73.33, 70.36, 69.01, 62.66, 31.89, 31.88, 30.23, 29.71, 29.69, 29.65, 29.59, 29.57, 29.37, 29.36, 29.32, 26.09, 26.06, 22.66, 22.64, 14.06; *m*/*z* (MALDI-TOF) 2299.3 (calcd $[M+H]^+$=2299.6); IR (neat): 2922, 1590, 1505, 1463, 1435, 1378, 1334, 1236, 1182, 1115, 1012, 825, 721, 658, 634, 593 cm^{-1}; Anal. Calcd for $C_{153}H_{253}NO_{12}$: C, 79.94; H, 11.09; N, 0.61. Found: C, 79.78; H, 11.31; N, 0.69.

4.3.11. 1,4-Bis[bis(4-methoxyphenyl)hydroxymethyl]benzene (**21**)

In an oven-dried 50 ml three-necked flask equipped with a condenser, mechanical stirrer, and argon system were placed magnesium turnings (0.53 g, 22 mmol) with dry THF (30 ml). 4-Bromoanisole (3.0 g, 16 mmol) was added dropwise with gentle heating until the reaction was started. The reaction was allowed to go for 1 h. A brown color was observed. Dimethyl terephthalate **19** (0.73 g, 3.7 mmol) was added. The mixture was stirred overnight under argon. The reaction mixture was neutralized with 5 wt % HCl aq and extracted with $CHCl_3$. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The filtrate was concentrated and reprecipitated with ethyl acetate–hexane (1:2) to afford compound **21** as a white solid (2.1 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.14 (12H, m, Ar*H*), 6.82 (8H, d, *J*=8.8 Hz, Ar*H*), 3.80 (12H, s, OCH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.29, 142.97, 136.11, 130.05, 127.67, 112.93, 86.25, 55.16; IR (KBr): 3496, 2951, 2834, 1723, 1608, 1508, 1463, 1440, 1303, 1251, 1176, 1113, 1069, 1034, 826, 595 cm^{-1}.

4.3.12. 1,4-Bis[bis(4-methoxyphenyl)-4-hydroxyphenylmethyl]benzene (**23**)

In a 100 ml flask equipped with a condenser, mechanical stirrer, and argon system was placed 1,4-bis[bis(4-methoxyphenyl)-hydroxymethyl]benzene **21** (2.1 g, 2.9 mmol) with phenol (3.5 g, 38 mmol). A few drops of methanesulfonic acid were added with gentle heating. A deep-red solution was obtained. The reaction mixture was stirred for 18 h at 120 °C. Reprecipitation with methanol–H_2O (10:1) afforded compound **23** as a white solid (1.2 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06–7.00 (16H, m, Ar*H*), 6.76 (8H, d, *J*=9.2 Hz, Ar*H*), 6.69 (4H, d, *J*=8.8 Hz, Ar*H*), 4.69 (2H, s, O*H*), 3.78 (12H, s, OCH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.36, 153.45, 144.76, 139.56, 139.45, 132.26, 132.04, 129.96, 114.03, 112.51, 65.47, 55.17; IR (KBr): 3420, 3032, 2952, 2834, 1606, 1506, 1463, 1441, 1293, 1249, 1179, 1116, 1034, 824, 599, 581 cm^{-1}.

4.3.13. 1,4-Bis[tris(4-hydroxyphenyl)methyl]benzene (**25**)

1,4-Bis[bis(4-methoxyphenyl)-4-hydroxyphenylmethyl]-benzene **23** (0.60 g, 0.84 mmol) was placed in a 100 ml two-neck flask equipped with mechanical stirrer and argon system. Dry CH_2Cl_2 (50 ml) was added and the mixture was kept at −78 °C. A 1.0 M solution of BBr_3 in methylene chloride (6.4 ml, 6.4 mmol) was slowly added. The temperature was slowly raised to 25 °C and the mixture was stirred for 12 h at 25 °C. The reaction was quenched with water at 0 °C and generated precipitate was filtered. Reddish brown solid was obtained by washing with water and chloroform (0.35 g, 63%). The compound was used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.28 (6H, s, O*H*), 6.93 (4H, s, Ar*H*), 6.82 (12H, d, *J*=8.4 Hz, Ar*H*), 6.62 (12H, d, *J*=8.4 Hz, Ar*H*); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.03, 144.87, 137.55, 131.46, 129.37, 114.06, 61.86; IR (KBr): 3364, 1609, 1507, 1437, 1363, 1235, 1178, 1014, 826, 600, 577 cm^{-1}.

4.3.14. 1,4-Bis[tris(4-(3,4,5-tridodecyloxybenzyloxy)phenyl)-methyl]benzene (**5**)

To a DMF (10 ml) solution of 1,4-bis[tris(4-hydroxyphenyl)-methyl]benzene **25** (25 mg, 0.038 mmol) and 3,4,5-tridodecyloxybenzyl chloride (0.31 g, 0.45 mmol) was added K_2CO_3 (0.14 g, 1.0 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture, water (100 ml) was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane–ethyl acetate=20:1) gave a white highly viscous oil (83 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.04 (16H, m, Ar*H*), 6.86 (12H, d, *J*=9.2 Hz, Ar*H*), 6.61 (12H, s, Ar*H*), 4.89 (12H, s, ArCH_2O), 3.99–3.91 (36H, m, CH_2CH_2O), 1.87–1.70 (36H, m, $CH_2CH_2CH_2$O), 1.52–1.37 (36H, br, $CH_2CH_2CH_2CH_2$O), 1.37–1.19 (288H, br, CH_2), 0.89–0.85 (54H, m, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.79, 153.25, 144.74, 139.65, 137.95, 132.08, 131.74, 130.00, 113.31, 106.25, 73.36, 70.37, 69.04, 62.55, 31.92, 31.89, 30.32, 29.73, 29.72, 29.68, 29.63, 29.62, 29.40, 29.38, 29.35, 26.12, 26.09, 22.66, 14.08; IR (neat): 2922, 1589, 1505, 1435, 1377, 1334, 1239, 1181, 1115, 1012, 821, 721, 635, 599, 542 cm^{-1}; Anal. Calcd for $C_{302}H_{502}O_{24}$: C, 80.30; H, 11.20. Found: C, 80.12; H, 11.44.

4.3.15. 4,4′-Bis[bis(4-methoxyphenyl)-4-hydroxyphenylmethyl]-biphenyl (**24**)

In an oven-dried 50 ml three-necked flask equipped with a condenser, mechanical stirrer, and argon system were placed magnesium turnings (0.58 g, 24 mmol) with dry THF (30 ml). 4-Bromoanisole (3.0 g, 16 mmol) was added dropwise with gentle heating until the reaction was started. The reaction was allowed to go for 1 h. A brown color was observed. Dimethyl 4,4′-biphenyldicarboxylate **20** (1.1 g, 4.0 mmol) was added. The mixture was stirred overnight under argon. The reaction mixture was neutralized with 5 wt % HCl aq and extracted with $CHCl_3$. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent was removed in vacuo and crude compound of 4,4′-bis[bis(4-methoxyphenyl)hydroxymethyl]biphenyl **22** was obtained as a reddish oil. In a 100 ml flask equipped with a condenser, mechanical stirrer, and argon system were placed the crude **22** with phenol (3.8 g, 40 mmol). A few drops of methanesulfonic acid were added with gentle heating. A deep-red solution was

obtained. The reaction mixture was stirred for 36 h at 120 °C. Reprecipitation with methanol–H_2O (6:1) and following washing with $CHCl_3$ afforded compound **24** as a pale yellow solid (0.91 g, 23%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.40 (2H, s, O*H*), 7.55 (4H, d, *J*=8.4 Hz, Ar*H*), 7.13 (4H, d, *J*=8.4 Hz, Ar*H*), 7.00 (8H, d, *J*=8.8 Hz, Ar*H*), 6.88 (4H, d, *J*=8.8 Hz, Ar*H*), 6.83 (8H, d, *J*=8.8 Hz, Ar*H*), 6.66 (4H, d, *J*=8.8 Hz, Ar*H*), 3.70 (12H, s, OCH_3).

4.3.16. 4,4′-Bis[tris(4-hydroxyphenyl)methyl]biphenyl (**26**)

1,4-Bis[bis(4-methoxyphenyl)-4-hydroxyphenylmethyl]-benzene **24** (0.72 g, 0.91 mmol) was placed in a 100 ml two-neck flask equipped with mechanical stirrer and argon system. Dry CH_2Cl_2 (50 ml) was added and the mixture was kept at −78 °C. A 1.0 M solution of BBr_3 in methylene chloride (4.0 ml, 4.0 mmol) was slowly added. The temperature was slowly raised to 25 °C and the mixture was stirred for 12 h at 25 °C. The reaction was quenched with water at 0 °C and generated precipitate was filtered. Reddish brown solid was obtained by washing with water and chloroform (0.59 g, 88%). The compound was used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.34 (6H, s, O*H*), 7.55 (4H, s, Ar*H*), 7.12 (4H, d, *J*=8.4 Hz, Ar*H*), 6.88 (12H, d, *J*=8.8 Hz, Ar*H*), 6.65 (12H, d, *J*=8.8 Hz, Ar*H*); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.10, 146.96, 137.52, 136.79, 131.50, 130.97, 125.46, 114.19, 62.06; *m*/*z* (MALDI-TOF) 734.05 (calcd $[M]^+$=734.27); IR (KBr): 3360, 1609, 1594, 1507, 1437, 1362, 1237, 1177, 1111, 1014, 1004, 825, 583 cm^{-1}.

4.3.17. 1,4-Bis[tris(4-(3,4,5-tridodecyloxybenzyloxy)phenyl)-methyl]biphenyl (**6**)

To a DMF (15 ml) solution of 4,4′-bis[tris(4-hydroxyphenyl)-methyl]biphenyl **26** (60 mg, 0.082 mmol) and 3,4,5-tridodecyloxybenzyl chloride (0.40 g, 0.60 mmol) was added K_2CO_3 (0.28 g, 2.0 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture, water (150 ml) was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane–ethyl acetate=20:1) gave a white highly viscous oil (0.23 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (4H, d, *J*=8.4 Hz, Ar*H*), 7.24 (4H, d, *J*=8.4 Hz, Ar*H*), 7.12 (12H, d, *J*=8.8 Hz, Ar*H*), 6.88 (12H, d, *J*=8.8 Hz, Ar*H*), 6.62 (12H, s, Ar*H*), 4.90 (12H, s, ArCH_2O), 3.99–3.91 (36H, m, CH_2CH_2O), 1.87–1.70 (36H, m, $CH_2CH_2CH_2$O), 1.52–1.37 (36H, br, $CH_2CH_2CH_2CH_2$O), 1.37–1.19 (288H, br, CH_2), 0.89–0.85 (54H, m, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.79, 153.24, 146.48, 139.59, 137.92, 137.71, 132.04, 131.75, 131.47, 125.67, 113.44, 106.23, 73.35, 69.02, 62.71, 31.92, 31.89, 30.32, 29.73, 29.71, 29.68, 29.61, 29.59, 29.37, 29.34, 26.11, 26.08, 22.67, 22.66, 14.08; *m*/*z* (MALDI-TOF) 4594.9 (calcd $[M+H]^+$=4594.3); IR (neat): 2922, 2852, 1590, 1505, 1467, 1439, 1377, 1334, 1294, 1239, 1182, 1116, 1004, 824, 721, 592, 529 cm^{-1}; Anal. Calcd for $C_{308}H_{506}O_{24}$: C, 80.54; H, 11.10. Found: C, 80.39; H, 11.29.

4.3.18. 5,5′-Bis[bis(4-methoxyphenyl)hydroxymethyl]-2,2′-bipyridyl (**28**)

In an oven-dried 50 ml three-necked flask equipped with a condenser, mechanical stirrer, and argon system were placed 4-bromoanisole (0.90 g, 4.8 mmol) with dry THF (30 ml). A 1.6 M solution of buthyllithium in hexane (3.3 ml, 5.3 mmol) was added dropwise at −78 °C. After the reaction was kept for 1 h, the temperature of the reaction mixture was raised to 0 °C. Dimethyl 2,2′-bipyridyl-5,5′-dicarboxylate **27** (0.24 g, 0.80 mmol) was added and the mixture was stirred overnight under argon. The reaction mixture was neutralized with 5 wt % HCl aq and extracted with $CHCl_3$. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The filtrate was concentrated and chromatographed on silica with $CHCl_3$–methanol (10:1) to afford compound **28** as a white solid (0.13 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (2H, s, Py*H*), 8.31 (2H, d, *J*=8.4 Hz, Py*H*), 7.78 (2H, d, *J*=8.4 Hz, Py*H*), 7.19 (8H, d, *J*=9.6 Hz, Ar*H*), 6.85 (8H, d, *J*=8.8 Hz, Ar*H*), 3.81 (12H, s, OCH_3), 2.76 (12H, s, O*H*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.15, 153.73, 148.65, 143.07, 138.81, 135.87, 128.76, 119.44, 112.72, 54.84; *m*/*z* (MALDI-TOF) 641.66 (calcd $[M+H]^+$=641.27); IR (KBr): 3299, 2955, 2835, 1608, 1509, 1463, 1298, 1254, 1175, 1035, 915, 830, 747, 608, 589 cm^{-1}.

4.3.19. 5,5′-Bis[bis(4-methoxyphenyl)-4-hydroxyphenylmethyl]-2,2′-bipyridyl (**29**)

In a 100 ml flask equipped with a condenser, mechanical stirrer, and argon system were placed 5,5′-bis[bis(4-methoxyphenyl)hydroxymethyl]-2,2′-bipyridyl **28** (0.13 g, 0.20 mmol) with phenol (0.38 g, 4.0 mmol). A few drops of methanesulfonic acid were added with gentle heating. A deep-red solution was obtained. The reaction mixture was stirred for 18 h at 120 °C. Reprecipitation with methanol–H_2O (1:1) afforded compound **29** as a white solid (0.11 g, 67%). ^{1}H NMR (400 MHz, DMSO-d_6: $CDCl_3$=1:10): δ 8.49 (2H, s, Py*H*), 8.23–8.19 (4H, m, O*H* and Py*H*), 7.63 (2H, d, *J*=6.0 Hz, Py*H*), 7.08 (8H, d, *J*=8.8 Hz, Ar*H*), 6.98 (4H, d, *J*=8.8 Hz, Ar*H*), 6.78 (8H, d, *J*=8.8 Hz, Ar*H*), 6.74 (4H, d, *J*=8.4 Hz, Ar*H*), 3.79 (12H, s, OCH_3).

4.3.20. 5,5′-Bis[tris(4-hydroxyphenyl)methyl]-2,2′-bipyridyl (**30**)

5,5′-Bis[bis(4-methoxyphenyl)-4-hydroxyphenylmethyl]-2,2′-bipyridyl **29** (50 mg, 0.063 mmol) was placed in a 100 ml two-neck flask equipped with mechanical stirrer and argon system. Dry CH_2Cl_2 (20 ml) was added and the mixture was kept at −78 °C. A 1.0 M solution of BBr_3 in methylene chloride (1.0 ml, 1.0 mmol) was slowly added. The temperature was slowly raised to 25 °C and the mixture was stirred for 12 h at 25 °C. The reaction was quenched with water at 0 °C and generated precipitate was filtered. A pale yellow solid was obtained by washing with water and chloroform (30 mg, 65%). The compound was used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.41 (6H, s, O*H*), 8.31 (2H, s, Py*H*), 8.28 (2H, d, *J*=8.4 Hz, Py*H*), 7.69 (2H, d, *J*=8.4 Hz, Py*H*), 6.87 (12H, d, *J*=8.4 Hz, Ar*H*), 6.67 (12H, d, *J*=8.0 Hz, Ar*H*); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.64, 148.06, 146.63, 146.27, 142.19, 135.88, 131.31, 121.82, 114.75, 60.79; *m*/*z* (MALDI-TOF) 737.48 (calcd $[M+H]^+$=737.27); IR (KBr): 3283, 1609, 1546, 1509, 1469, 1436, 1374, 1262, 1177, 1113, 1013, 829, 733, 587 cm^{-1}.

4.3.21. 5,5′-Bis[tris(4-(3,4,5-tridodecyloxybenzyloxy)phenyl)-methyl]-2,2′-bipyridyl (**7**)

To a DMF (15 ml) solution of 4,4′-bis[tris(4-hydroxyphenyl)-methyl]biphenyl **30** (50 mg, 0.068 mmol) and 3,4,5-tridodecyloxybenzyl chloride (0.33 g, 0.49 mmol) was added K_2CO_3 (0.30 g, 2.2 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture, water (150 ml) was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane–ethyl acetate=10:1) gave a white highly viscous oil (0.12 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (2H, s, Py*H*), 8.26 (2H, d, *J*=8.0 Hz, Py*H*), 7.65 (2H, d, *J*=8.4 Hz, Py*H*), 7.00 (12H, d, *J*=8.0 Hz, Ar*H*), 6.88 (12H, d, *J*=8.8 Hz, Ar*H*), 6.62 (12H, s, Ar*H*), 4.90 (12H, s, ArCH_2O), 3.99–3.92 (36H, m, CH_2CH_2O), 1.85–1.70 (36H, m, $CH_2CH_2CH_2$O), 1.52–1.37 (36H, br, $CH_2CH_2CH_2CH_2$O), 1.37–1.19 (288H, br, CH_2), 0.89–0.85 (54H, m, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.06, 153.27, 153.09, 151.81, 143.09, 138.87, 138.56, 137.97, 131.85, 131.63, 119.44, 113.76, 106.26, 73.38, 70.45, 69.05, 61.25, 31.92, 31.90, 30.32, 29.96, 29.74, 29.71, 29.68, 29.63, 29.40, 29.38, 29.35, 26.11, 26.08, 22.68, 22.66, 14.09; *m*/*z* (MALDI-TOF) 4595.7 (calcd $[M]^+$=4595.3); IR

(neat): 2922, 2852, 1733, 1589, 1505, 1464, 1436, 1378, 1334, 1238, 1181, 1115, 1012, 825, 721, 595 cm^{-1}; Anal. Calcd for $C_{306}H_{504}N_2O_{24}$: C, 79.98; H, 11.05; N, 0.61. Found: C, 79.69; H, 11.23; N, 0.64.

*4.3.22. Bis(4-methoxyphenyl)-4-bromophenylmethanol (**32**)*

In an oven-dried 50 ml three-necked flask equipped with a condenser, mechanical stirrer, and argon system were placed magnesium turnings (0.50 g, 21 mmol) with dry THF (30 ml). 4-Bromoanisole (3.0 g, 16 mmol) was added dropwise with gentle heating until the reaction was started. The reaction was allowed to go for 1 h. A brown color was observed. Ethyl 4-bromobenzoate **31** (1.8 g, 7.6 mmol) was added. The mixture was stirred overnight under argon. The reaction mixture was neutralized with 5 wt % HCl aq and extracted with $CHCl_3$. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The filtrate was concentrated and chromatographed on silica with 20% ethyl acetate in hexane to afford compound **13** as a reddish oil (2.5 g, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (2H, d, J=8.8 Hz, Ar*H*), 7.17 (2H, d, J=8.8 Hz, Ar*H*), 7.14 (4H, d, J=8.8 Hz, Ar*H*), 6.83 (4H, d, J=8.8 Hz, Ar*H*), 3.80 (6H, s, OCH_3), 2.70 (1H, s, O*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.44, 146.31, 138.78, 130.64, 129.48, 128.92, 120.89, 113.07, 80.90, 55.01; IR (neat): 3486, 2955, 2836, 1605, 1463, 1243, 1116, 1072, 1009, 905, 826, 733, 585 cm^{-1}; Anal. Calcd for $C_{21}H_{19}BrO_3$: C, 63.17; H, 4.80. Found: C, 62.95; H, 4.79.

*4.3.23. 4-[Bis(4-methoxyphenyl)-4-bromophenylmethyl]-phenol (**33**)*

In a 100 ml flask equipped with a condenser, mechanical stirrer, and argon system were placed bis(4-methoxyphenyl)-4-bromophenylmethanol **32** (4.5 g, 11 mmol) with phenol (6.0 g, 64 mmol). A few drops of methanesulfonic acid were added with gentle heating. A deep-red solution was obtained. The reaction mixture was stirred for 18 h at 120 °C. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was dried with sodium sulfate and concentrated. The crude compound was chromatographed on silica with 25% ethyl acetate in hexane to afford compound **33** as a reddish oil (3.4 g, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (2H, d, J=8.4 Hz, Ar*H*), 7.07–6.98 (6H, m, Ar*H*), 6.78 (2H, d, J=9.2 Hz, Ar*H*), 6.71 (2H, d, J=8.8 Hz, Ar*H*), 3.79 (6H, s, OCH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.50, 153.58, 146.66, 139.05, 138.90, 132.68, 132.10, 131.89, 130.41, 119.85, 114.27, 112.75, 62.54, 55.18; *m*/*z* (MALDI-TOF) 474.54 (calcd $[M]^+$=474.08); IR (neat): 3868, 3033, 2834, 1606, 1505, 1247, 1177, 1034, 1009, 907, 817, 752, 580, 539 cm^{-1}.

*4.3.24. Tris(4-methoxyphenyl)-4-bromophenylmethane (**34**)*

4-[Bis(4-methoxyphenyl)-4-bromophenylmethyl]phenol **33** (3.4 g, 7.2 mmol) and K_2CO_3 (2.0 g, 15 mmol) were placed in a 100 ml two-neck flask equipped with mechanical stirrer and argon system. Dry DMF (50 ml) and methyliodide (2.0 g, 14 mmol) were added and the reaction mixture was stirred at 25 °C for 12 h. The reaction mixture was neutralized with 5 wt % HCl aq and extracted with $CHCl_3$. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The filtrate was concentrated and chromatographed on silica with $CHCl_3$–hexane (1:1) to afford compound **34** as a white solid (2.4 g, 68%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (2H, d, J=8.4 Hz, Ar*H*), 7.07–7.03 (8H, m, Ar*H*), 6.78 (6H, d, J=9.2 Hz, Ar*H*), 3.79 (6H, s, OCH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.53, 146.72, 138.91, 132.69, 131.89, 130.41, 119.85, 112.74, 62.54, 55.15; IR (KBr): 3035, 2948, 2834, 1605, 1576, 1508, 1457, 1392, 1292, 1250, 1180, 1034, 1009, 822, 580 cm^{-1}.

*4.3.25. 4,4″-Bis[tris(4-methoxyphenyl)methyl]-[1,1′,4′,1″]-terphenyl (**35**)*

A mixture of tris(4-methoxyphenyl)-4-bromophenylmethane **34** (0.40 g, 0.82 mmol), 1,4-phenyldiboronic acid (65 mg, 0.39 mmol), $Pd(PPh_3)_4$ (100 mg), and sodium carbonate (0.54 g, 5.1 mmol) in 10 ml of THF and 2.5 ml of water was degassed and stirred at 80 °C for 48 h. The mixture was cooled to room temperature and diluted with 100 ml of chloroform. The organic layer was collected, washed with water, dried over sodium sulfate, and then the solvent was removed. The residue was chromatographed on silica with chloroform and then obtained solid was washed with ethyl acetate to give the desired compounds as a white solid (0.21 g, 60%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 ppm (4H, s, Ar*H*), 7.52 (4H, d, J=8.8 Hz, Ar*H*), 7.25 (4H, d, J=8.8 Hz, Ar*H*), 7.13 (12H, d, J=9.2 Hz, Ar*H*), 6.80 (12H, d, J=8.4 Hz, Ar*H*), 3.80 (18H, s, OCH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.44, 146.74, 139.39, 139.32, 137.74, 132.02, 131.39, 127.19, 125.76, 112.65, 62.67, 55.16; IR (KBr): 3030, 2949, 2834, 1605, 1581, 1507, 1488, 1462, 1442, 1304, 1288, 1252, 1182, 1117, 1034, 823, 812, 590, 581 cm^{-1}.

*4.3.26. 4,4″-Bis[tris(4-hydroxyphenyl)methyl]-[1,1′,4′,1″]-terphenyl (**36**)*

4,4″-Bis[tris(4-methoxyphenyl)methyl]-[1,1′,4′,1″]-terphenyl **35** (0.72 g, 0.91 mmol) was placed in a 100 ml two-neck flask equipped with mechanical stirrer and argon system. Dry CH_2Cl_2 (50 ml) was added and the mixture was kept at −78 °C. A 1.0 M solution of BBr_3 in methylene chloride (4.0 ml, 4.0 mmol) was slowly added. The temperature was slowly raised to 25 °C and the mixture was stirred for 12 h at 25 °C. The reaction was quenched with water at 0 °C and generated precipitate was filtered. Reddish brown solid was obtained by washing with water and chloroform (0.59 g, 88%). The compound was used without further purification. ^1H NMR (400 MHz, DMSO-d_6): δ 9.33 (6H, s, O*H*), 7.75 (4H, s, Ar*H*), 7.64 (4H, d, J=8.8 Hz, Ar*H*), 7.16 (4H, d, J=8.8 Hz, Ar*H*), 6.90 (12H, d, J=8.8 Hz, Ar*H*), 6.66 (12H, d, J=8.4 Hz, Ar); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 155.09, 147.22, 138.42, 137.50, 136.52, 131.49, 131.02, 126.93, 125.40, 114.20, 62.08; IR (KBr): 3559, 1699, 1610, 1593, 1507, 1488, 1440, 1362, 1235, 1177, 1111, 1014, 1004, 823, 579 cm^{-1}.

*4.3.27. 4,4″-Bis[tris(4-(3,4,5-tridodecyloxybenzyloxy)phenyl)-methyl]-[1,1′,4′,1″]-terphenyl (**8**)*

To a DMF (10 ml) solution of 4,4″-bis[tris(4-hydroxyphenyl)-methyl]-[1,1′,4′,1″]-terphenyl **36** (50 mg, 0.062 mmol) and 3,4,5-tridodecyloxybenzyl chloride (0.30 g, 0.44 mmol) was added K_2CO_3 (0.14 g, 1.0 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture, water (100 ml) was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na_2SO_4, and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, $CHCl_3$, 3.8 ml min^{-1}) and column chromatography (silicagel, hexane–ethyl acetate=10:1) gave a colorless oil (0.14 g, 49%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (4H, s, Ar*H*), 7.53 (4H, d, J=8.8 Hz, Ar*H*), 7.26 (4H, m, Ar*H*), 7.14 (12H, d, J=8.4 Hz, Ar*H*), 6.88 (12H, d, J=8.8 Hz, Ar), 6.61 (12H, s, Ar*H*), 4.91 (12H, s, ArCH_2O), 3.99–3.92 (36H, m, CH_2CH_2O), 1.85–1.70 (36H, m, $CH_2CH_2CH_2$O), 1.52–1.37 (36H, br, $CH_2CH_2CH_2CH_2$O), 1.37–1.19 (288H, br, CH_2), 0.89–0.85 (54H, m, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.80, 153.26, 146.66, 139.59, 139.28, 137.93, 137.77, 132.04, 131.78, 131.39, 127.16, 125.74, 113.49, 106.24, 73.37, 70.38, 69.04, 62.74, 31.92, 31.90, 30.32, 29.74, 29.72, 29.68, 29.63, 29.62, 29.60, 29.40, 29.38, 29.35, 26.12, 26.08, 22.66, 14.09; *m*/*z* (MALDI-TOF) 4676.8 (calcd $[M+Li]^+$=4676.3); IR (neat): 2923, 1591, 1505, 1439, 1377, 1334, 1238, 1181, 1116, 1004, 908, 824, 721, 635, 593, 540 cm^{-1}; Anal. Calcd for $C_{314}H_{510}O_{24}$: C, 80.77; H, 11.01. Found: C, 80.67; H, 11.14.

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References and notes

1. Hamley, I. W. *Introduction to Soft Matter*; Wiley: Chichester, UK, 2000.
2. (a) Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, 1998; (b) Collings, P. J.; Hird, M. *Introduction to Liquid Crystals*; Taylor & Francis: London, 1997; (c) Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B. *Ferroelectric Liquid Crystals: Principles, Properties and Applications*; Gordon & Breach: Philadelphia, 1991.
3. Thematic issue on liquid crystals: *Chem. Soc. Rev.* **2007**, *36*, 1845–2128.
4. Thematic issue on liquid crystals: *J. Mater. Chem.* **2001**, *11*, 2631–2886.
5. Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38–68.
6. Kato, T. *Science* **2002**, *295*, 2414–2418.
7. Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogol, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832–4887.
8. Tschierske, C. *J. Mater. Chem.* **2001**, *11*, 2647–2671.
9. Lee, M. S.; Cho, B.-K.; Zin, W.-C. *Chem. Rev.* **2001**, *101*, 3869–3892.
10. Goodby, J. W.; Mehl, G. H.; Saez, I. M.; Tuffin, R. P.; Mackenzie, G.; Auzély-Velty, R.; Benvegnu, D.; Plusquellec, D. *Chem. Commun.* **1998**, 2057–2070.
11. Donnio, B.; Bruce, D. W. *Struct. Bonding (Berlin)* **2000**, *95*, 194–217.
12. Guillon, D. *Struct. Bonding (Berlin)* **2000**, *95*, 42–74.
13. (a) Cheng, X.; Das, M. K.; Tschierske, C. *Langmuir* **2002**, *18*, 6521–6529; (b) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855–9866.
14. (a) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159–1160; (b) Komori, T.; Shinkai, S. *Chem. Lett.* **1993**, 1455–1456; (c) Budig, H.; Lunkwitz, R.; Paschke, R.; Tschierske, C.; Nütz, U.; Diele, S.; Pelzl, G. *J. Mater. Chem.* **1996**, *6*, 1283–1289; (d) Percec, V.; Glodde, M.; Johansson, G.; Balagurusamy, V. S. K.; Heiney, P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4338–4342; (e) Sawamura, S.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702–705; (f) Matsuo, Y.; Muramatsu, A.; Kamimawa, Y.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9586–9587.
15. (a) Nguyen, H.-T.; Destrade, C.; Malthête, J. *Adv. Mater.* **1997**, *9*, 375–388; (b) Yasuda, T.; Kishimoto, K.; Kato, T. *Chem. Commun.* **2006**, 3399–3401.
16. Kato, T.; Matsuoka, T.; Nishii, M.; Kamikawa, Y.; Kanie, K.; Nishimura, T.; Yashima, E.; Ujiie, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1969–1972.
17. Kamikawa, Y.; Nishii, M.; Kato, T. *Mol. Cryst. Liq. Cryst.* **2005**, *435*, 755–765.
18. Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061–11070.
19. Borisch, K.; Diele, S.; Göring, P.; Kresse, H.; Tschierske, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2087–2089.
20. Kato, T.; Mizoshita, N. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 579–587.
21. (a) Hatano, T.; Kato, T. *Chem. Commun.* **2006**, 1277–1279; (b) Yoshio, M.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2004**, *126*, 994–995; (c) Yoshio, M.; Ichikawa, T.; Shimura, H.; Kagata, T.; Hamasaki, A.; Mukai, T.; Ohno, H.; Kato, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1836–1841.
22. Destro, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B* **1980**, *36*, 2495–2497.
23. Dutta, A. K.; Misra, T. N.; Pal, A. J. *J. Phys. Chem.* **1994**, *98*, 12845–12848.
24. (a) Pistrolis, G. *Chem. Phys. Lett.* **1999**, *304*, 371–377; (b) Sumiyoshi, T.; Takahashi, I.; Tsuboi, Y.; Miyasaka, H.; Itaya, A.; Asahi, T.; Masuhara, H. *Thin Solid Films* **2000**, *370*, 285–293.
25. Camerel, F.; Bonardi, L.; Schmutz, M.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 4548–4549.
26. Chen, Z.; Swager, T. M. *Org. Lett.* **2007**, *9*, 997–1000.
27. Sivacova, S.; Rowan, S. J. *Chem. Commun.* **2003**, 2428–2429.
28. Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Scmidt, M.; Gerle, M.; Möller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley, D. J. P. Y. *J. Am. Chem. Soc.* **1998**, *120*, 8619–8631.
29. Aprahamian, I.; Yasuda, T.; Ikeda, T.; Saha, S.; Dichtel, W. R.; Isoda, K.; Kato, T.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 4675–4679.
30. Aprahamian, I.; Miljanić, O. Š.; Dichtel, W. R.; Isoda, K.; Yasuda, T.; Kato, T.; Stoddart, J. F. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1856–1869.
31. Baranoff, E. D.; Voignier, J.; Yasuda, T.; Heitz, V.; Sauvage, J.-P.; Kato, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4680–4683.
32. Terazzi, E.; Bourgogne, C.; Welter, R.; Gallani, J.-L.; Guillon, D.; Rogaz, G.; Donnio, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 490–495.
33. Venema, F.; Neilssen, H. F. M.; Berthault, P.; Birlirakis, N.; Rowam, A. E.; Feiters, M. C.; Nolte, R. J. M. *Chem.—Eur. J.* **1998**, *4*, 2237–2250.