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Selenium-linked liquid crystal dimers for twist-bend nematogens

Yuki Arakawa,* and Hideto Tsuji

Abstract

The recently discovered twist-bend nematic (N_{TB}) phase has become an intensively studied topic in supramolecular chemistry and condensed matter science. Herein, a new molecular design for twist-bend nematogens employing selenoether (C-Se-C) linkage, instead of the conventional methylene or ether linkages, is introduced. We synthesized CBSenSeCB dimers, consisting of two cyanobiphenyl (CB) units connected by two selenoether linkers sandwiching an odd-numbered alkylene spacer (n = 3, 5, 7, and 9)and revealed their phase transitions and mesomorphism. CBSenSeCB (n = 5, 7, and 9)can potentially form mesophases; notably, CBSe7SeCB formed the N_{TB} phase from the conventional uniaxial nematic phase, which was cooled to below room temperature. The structure of the all-trans model of CBSe7SeCB, optimized by density functional theory, suggests that the molecular bend angle between the para axes of the cyanobiphenyl moieties is about 90°, which is more bent than those of previously reported twist-bend nematogens. Such a keen curvature is ascribed to the small C-Se-C angle of about 101°. In addition, the molecular bend angles of the twist-bend dimers, including the present and previously reported ones, correlate linearly with their phase-transition temperatures. The present study paves the way for the molecular design of new twist-bend nematic liquid crystals based on chalcogen linkages.

Introduction

The breaking of chiral symmetry in achiral molecules is among the most fascinating phenomena in supramolecular chemistry and condensed matter science. Liquid crystals, which have properties between those of anisotropic solids and isotropic liquids, offer rich sources of such phenomena. Over the past few decades, bent achiral liquid crystals have gained impetus because of the discoveries of ferroelectric [1] and spontaneous chiral segregation [2].

On the other hand, liquid crystal dimers composed of two rigid mesogenic parts connected by an odd-numbered alkylene spacer that gives rise to a bent molecular geometry have also gained much interest [3]. Furthermore, the most recently reported emergent liquid crystal phase for such a bent dimer, the twist-bend nematic (N_{TB}) phase, has attracted a great deal of attention. This phase, which was predicted by Meyer [4] and Dozov [5], is formed by right- and left-handed helical nanostructured molecular aggregation and is based on symmetry breaking in achiral systems. The phase transition from uniaxial nematic (N_U) to another nematic (N_X) , which was subsequently characterized as N_{TB} [6], was experimentally observed in several bent dimers [7] and polymers [8]. Freeze-fracture transmission electron microscopy [9] and resonant X-ray scattering [10] experiments disclosed that the N_{TB} phase usually has a relatively short (10 nm) helical pitch. Inspired by the recent discovery of the N_{TB} phase, the development of new twist-bend nematogens has become a major focus of supramolecular and liquid crystal chemistry research [11]. Very recently, twist-bend nematogens have been expanded to some oligomers [12] and polymers [8,13]. Moreover, several applications based on the N_{TB} phase have also been reported [14].

The molecular designs of liquid crystal dimers or oligomers that exhibit the N_{TB} phase are based on three parts: rigid mesogenic parts, spacers, and the linkers between them. One of the determinants in the molecular design that induces the N_{TB} phase is the molecular bend or interarm angle (χ) between the para axes of the two mesogenic parts, as shown in Figure 1, which is strongly dominated by the linker. Mandle and coworkers have widely explored the structure-property relationships of dimers with various χ values [15]. For example, although a few methylene-linked cyanobiphenyl (CB) dimers (CB*n*CB, where *n* denotes the odd number of carbon atoms in the alkylene spacer) with $\chi = 111^{\circ}$ form the N_{TB} phase, with the exception of CBO5OCB with its very narrow N_{TB}-phase range [16], their ether-linked counterparts, CBO*n*OCB, with $\chi = 144^{\circ}$ are almost conventional nematogens [17]. The difference in angle is mainly attributed to the difference in the bond angles of the linkers, specifically ~111° for methylene (C–CH₂–C) and ~117° for ether (C–O–C). Consequently, the methylene- and ether-linked dimers,

CB6OCB [18] and CB8OCB [17], also form N_{TB} phases. Watanabe et al. described a comparative of mesogenic abilities on two-typed opposite-directed ester (COO and OCO)-linked dimers and the N_{TB} phase incidence [19]. In the literature, they noted that the former has more bent molecular curvature with $\chi = 97^{\circ}$, which is a candidate for twist-bend nematogens, and revealed that some analogues of cyclohexylbenzene-based dimers form N_{TB} phase. While, the latter opposite ester-linked dimers (or alkanedioates) showing exclusive N_U phase tendency [20] have a relatively large χ of 139°, which is comparable to that of the ether-linked conventional nematogen CBOnOCB dimers. Dawood et al. revealed that the dimer with the Schiff-base linkage and the shortest propylene spacer forms transitioned directly from the isotropic (Iso) phase (the novel N_{TB} -Iso sequence), which differs to that of the usual N_{TB} - N_{U} -Iso sequence [21]. This is consistent with the theory that a shorter spacer is reflected in increased molecular curvature. Consequently, χ was suggested to be a factor responsible for the incidence of the N_{TB} phase. Thus far, among the large variety of twist-bend nematogenic dimers or oligomers that have been recently developed, the atoms introduced at the linking point have solely been carbon or oxygen.

On the other hand, while we have been homing in on the development of alkylsulfanyl- or thioether-containing mesogens [22], we recently investigated thioether-linked cyanobiphenyl dimers that exhibit the N_{TB} phase, specifically, CBS*n*SCB and CBS*n*OCB with odd-numbered alkylene spacers of length *n* (Figure 1) [23]. This is because thioether (R–S–R) has a relatively small bond angle of ~103°, CBS*n*SCB and CBS*n*OCB have molecular geometries that are more bent (bend angles of 109° and 126°, respectively) than the conventional ether-linked nematogen, CBO7OCB. In addition, a thioether is believed to be more flexible because it has a lower rotation barrier than alkylene or ether. Such curvature and flexibility would assist the induction of the N_{TB} phase. Consequently, our research showcased the potential of a "chalcogen-based linkage" in the development of new twist-bend nematogens.

In this paper, we report, for the first time, twist-bend nematogens containing the selenoether or C–Se–C. We designed and synthesized a homologous series of selenoether-linked cyanobiphenyl dimers, CBSenSeCB, with an odd number of carbon atoms (n = 3, 5, 7, and 9) (Figure 1). Their phase transition behavior and mesomorphism were unlocked by polarizing light microscopy (PLM) and differential scanning calorimetry (DSC), and the optimized molecular structure of one of these structures was studied by density functional theory (DFT). In addition, these dimers were compared with other twist-bend nematogens and the correlation between molecular bend angle and phase-transition temperature determined.



Figure 1. Molecular design concept based on chalcogen-linked liquid crystal dimers to induce N_{TB} phase. Ether-linked conventional nematogens CBOnOCB (a), thioether-linked twist-bend nematogen CBSnSCB (b) and the present selenoether-linked dimers CBSenSeCB (c).

Results and Discussion

CBSenSeCB was synthesized according to the procedure shown in Figure 2. First, 4,4'-dibromodiselenide (1) was prepared by reacting selenium with 4-bromoiodobenzene [24]. Bis(4-bromophenyl)diselenide was reduced with NaBH₄ in ethanol to afford a colorless solution of the selenide anion [25], which was subsequently reacted with the α,ω -dibromoalkane at room temperature to afford disubstituted product 1,7-bis[(4-bromophenyl)seleno]heptane along with the monosubstituted product. Finally, the disubstituted compound was subjected to Suzuki–Miyaura coupling [26] with the pinacol ester of 4-cyanophenylboronic acid to afford the target CBSenSeCB. A

representative synthetic procedure for CBSe7SeCB and its characterization data is available in the Experimental section, and those for the other dimers are provided in the supporting information.

The phase sequence, transition temperature, and change in enthalpy (ΔH) for CBSenSeCB are tabulated in Table 1. The CBSenSeCB dimers (n = 5, 7, and 9) exhibit mesophases, whereas CBSe3SeCB does not form any mesophase and has a single melting temperature of 147.4 °C. CBSe5SeCB does not exhibit a mesophase during heating but formed the monotropic N_U phase during cooling, commencing at ~59 °C with subsequent crystallization starting at about 49 °C upon cooling. The emergence of the N_U phase is supported by the photomicrographs show in Figure S1. However, the formation of the N_U phase was not clearly evident by DSC owing to prior crystallization at 75.5 °C with $\Delta H = 22.1$ kJ mol⁻¹, as shown in Figure S4. Notably, CBSe7SeCB forms a N_U phase as well as the N_{TB} phase, with unusual phase-transition behavior, which is independently described in detail below. CBSe9SeCB also exhibits a monotropic N_U phase between 61.7 and 75.9 °C Whereas, it does not form the N_{TB} phase at a fast rate of 20 °C min⁻¹ although some molecules can only induce N_{TB} phase at a fast rate [23].



Figure 2. Synthetic pathway of CBSenSeCB.

n	Process	Phase sequence					
3	2nd heat	Cr 147.4 (35.8) Iso					
	1st cool	Cr 105.8 (27.6) Iso					
5	2nd heat	Cr 122.8 (27.5) Iso					
	1st cool ^a	Cr 49 (-) ^a N _U 59 (-) ^a Cr 75.5 (22.1) Iso					
7	1st heat	Cr' 80.8 (34.3) Iso' 86.3 (6.96) Cr" 100.6 (9.6) Iso					
	1st cool	G 2.39 Cr ^{***} 32.4 (12.4) ^c N _{TB} 43.1 (-) N _U 71.9 (1.1) Iso					
	2nd heat ^b	G 2.2 N _{TB} 32.0 (6.8) Cr ^{**} 64.9 (5.9) Cr ^{**} 100.6 (36.0) Iso					
9	2nd heat	Cr 89.5 (40.8) Iso					
	1st cool	Cr 61.7 (33.1) N _U 75.9 (1.5) Iso					

Table 1. Phase transition temperatures (°C) and enthalpy changes (kJ mol⁻¹) at a rate of 10 °C min⁻¹.

^a Observed by POM but not clear on DSC, ^b N_U region emerged between around 69 and 75 °C from Cr" region, ^c Imperfect crystallization.



Figure 3. Photomicrographs of CBSe7SeCB for the N_U phase at 70 °C (a), the N_{TB} phase at 42 °C (b) and at 30°C (c) in an untreated cell, and for the N_U phase at 45 °C (d), the N_{TB} phase at 42 °C (e) and at 30°C (f) in an uniaxially-rubbed planarly-aligned cell with the thickness of 3 µm. Crossed arrows and diagonal arrow represent polarizers and rubbing directions, respectively.

We next examined the phase-transition behavior of CBSe7SeCB in detail. Photomicrographs of the untreated, as well as uniaxially and planarly aligned cells upon

cooling, are shown in Figure 3. Figure 3(a) reveals the N_U phase with typical schlieren textures at ~70 °C. At about 43 °C, the N_U texture gradually changes to other ellipsoidal, rope-like, and focal conic textures with partially crystallized regions [Figures 3(b) and 3(c)]. These textural changes are distinct in the images of the uniaxially and planarly aligned cells. A monochroic birefringent texture is observed in the N_U phase region, which secures its uniaxial alignment in the N_U phase [Figure 3(d)]. A line in the rubbing direction gradually appears at 43 °C, resulting in a stripe texture, as shown in Figures 3(e) and 3(f). These optical textural changes strongly support the incidence of the N_{TB} phase. The striped texture is maintained with partial crystallization upon cooling to ambient temperature. By acquiring the DSC curve at 10 °C min⁻¹, the transition from the N_U to the N_{TB} phase (N_U-N_{TB}) at 43 °C, and the glass transition at 2.3 °C, become discernible, as shown in Figure 4(a), which supports the persistence of the N_{TB} phase to room temperature. Interestingly, CBSe7SeCB exhibits unusual phase- transition behavior during heating, as shown in Figure 4(b). During the first heating, CBSe7SeCB melts to the Iso phase (abbreviated as Iso') at 80.8 °C, which is immediately subjected to cold crystallization to Cr" at 86.3 °C, subsequently giving rise to melting to the Iso phase transition at 100.6 °C. During the second heating, after first cooling to below -10 °C, cold crystallization (to Cr''') is observed at 32 °C [Figures 4 and 5(b)]; this Cr''' phase undergoes an exothermic transition to Cr'' [Figures 4 and 5(c)]. Moreover, it is interesting to note that an additional N_U phase emerges from the remaining Cr" region at

 $^{\circ}$ G9 °C, as shown in Figures 5 (c) and (d); in such a thermal process, it eventually undergoes a transition to Cr" transition [Figures 5 (e) and (f)]. In other words, CBSe7SeCB has a tendency toward a kinetics-dominated enantiotropic N_U phase. Considering the above phase-transition behavior, Cr" phases upon the first and second heating are similar but Cr' and C"" are derived from different crystalline species to one another, and Cr" upon heating and cooling is similar. Upon the other thermal heating process after cooling to 30 °C from Iso phase, whereas, the following three transitions such as the N_{TB} to N_U transition with cold crystallization (Cr"") at 43 °C, the Cr" to N_U transition at $^{\circ}$ 69 °C, and the N_U phase to other Iso (Iso") phase transition at around 75 °C were clearly captured as shown in Figure 6. That is, CBSe7SeCB has an enantiotropic N_U phase between ca. 69 and 75 °C in which the latter temperature is considered as the N_U to Iso transition of CBSe7SeCB used in the bend angle dependency later. A repeat DSC experiment after leaving the sample for two weeks shows almost only melting at $^{\circ}$ 100 °C with a subtle peak at $^{\circ}$ 79 °C, too, as shown in Figure S7, with which the former is highly analog to that upon the second heating. This

suggests that the prior melting at ~81 °C during the first cooling or Cr' is ascribable to the crystalline species that developed predominantly during solution crystallization.



Figure 4. DSC curves of CBSe7SeCB at a rate of 10 °C min⁻¹ upon first cooling (a) and upon first and second heating (b). $N_{TB}G$: N_{TB} glassy, Cr, Cr', Cr'' and Cr''': each crystal phase, N_{TB} : twist-bend nematic phase, N_U : uniaxial nematic phase, and Iso and Iso': each isotropic phase.



Figure 5. Photomicrographs of CBSe7SeCB at -10 °C for the $N_{TB}G$ (a), at 34 °C for the N_{TB} phase with cold crystallization to Cr^{'''} (b), at 67 °C for the Cr^{'''} to Cr^{''} transition (c), at 72 °C (d) and at 73 °C (e) for the N_U emergence in the middle to Cr^{''} transition, and at 77 °C for Cr^{''} phase (f) in an untreated cell upon heating at a rate of 10 °C min⁻¹ from

-10 °C.



Figure 6. Photomicrographs of CBSe7SeCB at 30 °C for the N_{TB} region (a), at 46 °C for the N_U region subjected to cold crystallization to Cr^{'''} (b), at 73 °C the emergent N_U phase from the Cr^{'''} region in the middle of the Cr^{''} transition (c), and at 77 °C for the

 N_U to the Iso transition (d) in an untreated cell upon heating at a rate of 10 °C min⁻¹.

Finally, the molecular geometry of CBSe7SeCB with an all-trans spacer was optimized by DFT calculations at the B3LYP [27]/6-31G(d) level using the Gaussian 16 software (Figure 7) [28]. The selenoether has an out-of-plane conformation with respect to the benzene ring, in contrast to its in-plane conformation in the same chalcogen family of ether- or thioether-linked dimers, in which the in-plane conformation is due to π - π interaction between a lone pair on an O or S and the phenyl ring. On the other hand, such an out-of-plane conformation for selenoether is rather similar to those observed for methylene-linked dimers, which exhibit a σ - π interaction between the methylene C-H and the phenyl ring. On the other hand, the χ value between the para axes of the two cyanobiphenyl moieties is about 90°; intriguingly, this value is markedly smaller or more bent than those of a conventional nematogen, namely CBO7OCB (144°) [15], as well as twist-bend nematogens, such as CB9CB (111°) [15], CB8OCB (128°) [15], CBS7SCB (109°) [24], and CBS7OCB (126°) [24], which have a total of nine atoms in the spacer and linker along each chain line. The smaller χ of CBSe7SeCB is mainly attributed to the C-Se-C bond angle of 101°. The transition temperatures for the $N_{TB}-N_U$ and N_U -Iso phase transitions [$T(N_{TB}-N_U)$ and $T(N_U$ -Iso), respectively] of CBSe7SeCB, CB9CB, CBO7OCB, CB8OCB, CBS7SCB, and CBS7OCB are summarized in Table 2 and plotted against χ in Figure 8. The $T(N_{TB}-N_U)$ and $T(N_U-Iso)$ values of CB9CB, CB07OCB and CB8OCB are taken from the literature [15]. Notably, although methylene, ether, thioether and selenoether have distinct intermolecular interactions, the transition temperatures, especially $T(N_{\rm U}$ -Iso), correlate almost linearly with χ ; that is, they decrease with decreasing χ . This observation may be an efficient embodiment of the molecular geometry facilitated by the linkage in each aggregated state. Although the phase-transition behavior and incidence of the N_{TB} phase also depend on other factors, χ provides useful plausible insight into the observed phenomena.



Figure 7. The optimized structure of CBSe7SeCB from its all-*trans* spacer model and the molecular bend angle value (χ).

Table 1. Molecular bend angles (χ) and transition temperatures $T(N_{TB}-N_U)$ and $T(N_U-Iso)$ upon cooling.

	Compd.	χ (°)	$T(N_{TB}-N_U)$ (°C)	$T(N_U-Iso)$ (°C)	Refs.
	CB9CB	111	105.4	121.5	15
	CBO7OCB	144	-	181.3	15
	CB8OCB	128	109.9	153.3	15
	CBS7SCB	109	88.3	115.2	23
	CBS7OCB	126	95.9	146.7	23
	CBSe7SeCB	90	43.1	75 ^a	Present
^a Observed by POM.					



Figure 8. $T(N_{TB}-N_U)$ and $T(N_U-Iso)$ plots against molecular bend angles (χ).

Conclusions

In summary, the present study offers a new molecular design for twist-bend nematogens

based on a selenoether linkage. Selenium-linked CBSenSeCB cyanobiphenyl dimers were synthesized and their phase transitions and mesomorphism revealed. CBSe7SeCB forms an N_U phase, as well as an N_{TB} phase, which was stable down to room temperature. The DFT-optimized geometry of CBSe7SeCB revealed a χ of 90°, which is markedly smaller than those of liquid crystalline dimers with other types of linkage. In addition, linear correlations between the phase transition temperatures (N_{TB}-N_U

transition and isotropic temperatures) and χ were observed. The present study provides structural insight into phase transitions from the viewpoint of χ , and paves the way for the molecular design of new twist-bend nematogens based on chalcogen linkages. The selenoether-based twist-bend nematogens could exert a beneficial effect in structural analyses by resonant X-ray scattering at the selenium K-edge [10(c)]. Furthermore, since selenium-containing mesogens are highly rare [30], the present discussion could be useful to design the new molecular selenium-based ones. We will further explore selenoether-based twist-bend nematogens and mesogens in future studies.

Experimental

Chemicals

All chemicals were obtained from commercial suppliers and used without further purification. Selenium and copper(I) oxide (CuO) were purchased from FUJIFILM Wako Co., Pure Chemical Ltd. (Tokyo, Japan). 4-Bromoiodobenzene, 4-cyanophenylboronic acid pinacol ester (Bpin-benzonitrile), each α, ω -dibromoalkane, sodium borohydride $(NaBH_4),$ and tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), while hexane, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dichloromethane (DCM,) and methanol (MeOH) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Anhydrous ethanol (EtOH), potassium hydroxide (KOH), potassium carbonate (K_2CO_3) and cesium carbonate (Cs_2CO_3) were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

Synthesis

The synthesis procedure and ¹H and ¹³C NMR (JEOL JNM ECS 500) characterization data for CBSe7SeCB are presented below, with those for the other compounds provided in the supporting information.

Synthesis of bis(4-bromophenyl)diselenide

Selenium powder (3.34 g, 42.4 mmol), 4-bromo-iodobenzene (6.0 g, 21.2 mmol), CuO (0.338 g, 4.24 mmol), and KOH (2.38 g, 42.4 mmol) were placed in a flask, after which dry DMSO (25 mL) was added under an argon atmosphere. The resulting mixture was stirred at 90 °C for 5 h. After the reaction was complete, as evidenced by TLC, the mixture was cooled to ambient temperature and filtered to remove the insoluble portion. The filtrate was extracted with DCM, the extract washed with water and brine, and dried over MgSO₄. The volatiles were removed under reduced pressure, and the crude product

was purified by silica-gel column chromatography (eluent: 1:10 DCM/hexane) to afford 1 as a yellow solid (2.48 g, 50%). ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* = 7.2 Hz, 4H), 7.39 (d, *J* = 7.2 Hz, 4H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 133.4, 133.4, 133.4, 133.4, 133.4, 133.4, 132.3, 132.3, 132.3, 132.3, 129.4, 129.4, 122.4, 122.4 ppm.

Synthesis of 1,7-bis[(4-bromophenyl)seleno]heptane

Bis(4-bromophenyl)diselenide (0.30 g, 0.638 mmol), NaBH₄ (96.5 mg, 2.55 mmol), and anhydrous EtOH (4.0 mL) were placed in a two-necked round-bottomed flask under argon, and the resultant mixture was stirred at 0 °C for 15 min. After a colorless solution had formed, 1,7-dibromoheptane (0.108 mL, 0.638 mmol) in anhydrous EtOH (0.5 mL) was added dropwise to the reaction mixture with cooling at 0 °C, after which it was stirred at room temperature for 2 h. The reaction mixture was extracted with DCM, the extract washed with water and brine, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatograph (eluent: 1:5 DCM/hexane) to afford the target compound (0.260 g, 72%) together with the mono-substituted biproduct as a colorless solid. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 7.2 Hz, 4H), 7.33 (d, *J* = 7.2 Hz, 4H), 2.87 (t, *J* = 5.8 Hz, 4H), 1.66 (tt, *J* = 5.8 and 6.2 Hz, 4H), 1.37 (tt, *J* = 5.6 and 6.2 Hz, 4H), 1.32-1.24 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 134.0, 134.0, 134.0, 134.0, 132.0, 132.0, 132.0, 132.0, 129.5, 129.5, 120.8, 120.8, 29.9, 29.9, 29.5, 29.5, 28.4, 28.4, 28.1, 28.1 ppm.

Synthesis of 1-(4-cyanobiphenyl-4'-ylseleno)-7-(4-cyanobiphenyl-4'-ylseleno)heptane (CBSe7SeCB)

1,7-Bis[(4-bromophenyl)seleno]heptane (0.232 g, 0.408 mmol), 4-cyanophenylboronic acid pinacol ester (0.215 g, 0.938 mmol), Pd(PPh₃)₄ (0.108 g, 93.8 µmol), and Cs₂CO₃ (0.611 g, 1.88 mmol) were placed in a two-way flask, after which THF (9 mL, degassed by argon bubbling) was added under argon. After stirring for 6 h under reflux, the reaction mixture was extracted with DCM and the organic layer was washed with water and brine and dried over MgSO₄. After the volatiles were removed under reduced pressure, the crude product was purified by silica-gel column chromatography (eluent: DCM) and recrystallized from MeOH/DCM to afford CBSe7SeCB as a colorless solid (0.120 g, 48%). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 6.8 Hz, 4H), 7.66 (d, *J* = 6.8 Hz, 4H), 7.55 (d, *J* = 6.8 Hz, 4H), 7.47 (d, *J* = 6.8 Hz, 4H), 2.96 (t, *J* = 5.8 Hz, 4H), 1.74 (tt, *J* = 5.8 and 6.2 Hz, 4H), 1.43 (tt, *J* = 5.6 and 6.2 Hz, 4H), 1.38-1.29 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 144.9, 144.9, 137.2, 137.2, 132.7, 132.7, 132.7, 132.7, 132.3, 132.3, 132.3, 132.3, 132.1, 132.1, 127.7, 127.7, 127.7, 127.7, 127.4, 127.4, 127.4,

127.4, 127.4, 118.9, 118.9, 110.9, 110.9, 29.9. 29.9, 29.6, 29.6, 28.5, 27.7, 27.7 ppm.

Mesophase characterization

Phase transitions were identified by variable-temperature PLM using an Olympus BX50 microscope equipped with a Linkam LK-600 PM hot stage. Detailed phase-transition temperatures and ΔH values were obtained using a Shimadzu DSC-60 differential scanning calorimeter with 10 °C min⁻¹ heating/cooling/heating cycles under a 50 mL min⁻¹ flow of nitrogen gas.

Molecular modeling

The structure of CBSe7SeCB in its all-*trans* spacer form was optimized at the B3LYP/6-

31G(d) [27] (DFT) level of theory using Gaussian 16 [28]. Gauss View 6 [29] was used for visualization. The atom coordinates and absolute energy level obtained from the calculations for CBSe7SeCB are provided in the supporting information.

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CCC RANK



Figure 1







Figure 4







Figure 7



Figure 8