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PAPER

Generation of biaxiality in smectic A phases by introduction of intermolecular perfluoroarene–arene and C–H/F interactions, and the non-odd–even effect of the molecules in their transition temperatures and layer distances[†]

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Compounds **1a–j**, 4-alkoxy-4'-pentafluorobenzoyloxybiphenyls, were synthesized to investigate the biaxiality in the smectic A phases of rod-like molecules possessing both perfluorinated and non-fluorinated benzene rings. The phase behaviors of the compounds and the molecular packing structures of their smectic A phases were investigated by polarized optical microscopy (POM), differential scanning colorimetry (DSC), and X-ray diffraction (XRD). As a result, it was found that the plot of the transition temperatures against the number of carbon atoms in the terminal alkyl chains did not show a clear odd–even effect, and an unique effect "*tgg*-effect" was observed in the plots of their layer distances against the number of carbon atoms. In the detailed 1D- and 2D-XRD studies of the smectic A phases, lateral directional orders in each layer were observed. It is assumed that these results originate from the biaxiality of the smectic A phases and slow rotation of the molecules around their molecular long axes.

Introduction

In rod-like molecules, smectic A phases are known as common thermal liquid crystal phases and have layered superstructures. In uniaxial smectic A phases, the molecular long axes are on average parallel to the layer normal and the molecules have no directional order in their lateral directions.¹⁻³ On the other hand, biaxial smectic A phases have a lateral directional order and the phases have a possibility to realize new high-responsive LC display devices.⁴ The study of biaxial smectic A phases is also important to understand the mechanisms for generation of biaxiality in nematic phases.5 However, realization of biaxial smectic A phases is so difficult that the examples are still limited. To generate the lateral directional order, laterally anisotropic molecular shapes such as bent rods6,7 or boards8 have been used for the molecular designs in most cases. Side-chain polymers with laterally attached rod-like mesogenic units have also been used for generation of biaxial smectic A phases.9 Those shape-assisted and covalent bond-assisted approaches are thought to be necessary for generation of biaxial smectic A phases, and it is still difficult to realize them by using straight rod-like molecules with low molecular weight. In this study, we indicate an interactionassisted approach to realize laterally ordered smectic A phases of low molecular weight straight rod-like molecules by introducing strong lateral intermolecular interactions. As a result, these molecules showed local biaxiality in the smectic A phases and unique phenomena in the transition temperatures and layer distances depending on their alkyl chain lengths.

As shown in Fig. 1, we planned to introduce two different kinds of benzene rings into one rod-like molecule. If both intermolecular face-to-face (A) and edge-to-edge (B) interactions simultaneously interact, a laterally ordered structure (C) is generated by these two kinds of interactions. For this purpose,



Fig. 1 Concept for generation of a laterally ordered structure.

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we selected the interactions between perfluorinated and nonfluorinated benzene rings. It is known that perfluoroarene–arene (PFA–A)^{10–15} and C–H/F¹⁶ interactions interact as face-to-face and edge-to-edge manners, respectively. Based on this concept, a pentafluorobenzoyloxy group was introduced at the 4-position of a biphenyl moiety (Scheme 1).

Further, to stabilize the liquid crystallinity, a flexible alkoxy chain was introduced at the other terminal of the biphenyl moiety.

Result and discussion

Synthesis and phase identification of liquid crystalline compounds 1a–j

Compounds 1a-i were synthesized by condensation of pentafluorobenzoic acid and the corresponding 4-(4-alkoxyphenyl) phenol. Their phase behaviors were identified by POM and DSC. As shown in Table 1, all compounds in this study showed a stable smectic A phase. The microphotograph of **1a** is shown in Fig. 2. It shows fan-like textures with dark lines parallel to the directions of the crossed polarizers that were observed as the typical textures of smectic A phases which indicated that the phases had layer structures and the molecules were parallel to the layer normal. These compounds also showed dark homeotropic textures, indicative of the optically uniaxial phases.¹⁷ In Fig. 3, the clearing and melting points are plotted against the number of carbon atoms in the substituted normal alkyl chain. A distinctive odd-even chain length effect18 is not observed in these compounds. It is known that the odd-even effects on the clearing points in rod-like liquid crystalline compounds originate from the excluded volumes during rotation of the molecules around the molecular long axes. Rapid rotational movements of molecules around their long axes enhance the population of all-transconformers to make their excluded volumes smaller, which causes an odd-even effect.19 Accordingly, no odd-even effect for these molecules strongly suggests that the rotation of the molecules is highly suppressed by their strong intermolecular interactions. The clearing point of 1d (n = 10) is lower than those of the homologues 1c (n = 9) and 1e (n = 11), while the melting point of 1d is higher than those of 1c and 1e. It is difficult to explain this discontinuity in the clearing and melting points. It is assumed that the volume balance between the core and the chain



Scheme 1 Molecular structures of 1a-j.

Table	1	Phase	transition	behaviours	of	the	4-alkoxy-4'-pentafluoro-		
benzoyloxybiphenyls ^a									

Compound	n	Phase transition/°C (kcal/mol ⁻¹)
1a	7	Cr $\xrightarrow{116(5.4)}$ SmA $\xrightarrow{156(1.0)}$ Iso
1b	8	Cr $\xrightarrow{116 (4.6)}$ SmA $\xrightarrow{155 (0.8)}$ Iso
1c	9	Cr <u>117 (9.7)</u> <u>100 (-9.8)</u> SmA <u>153 (1.6)</u> <u>150 (-1.5)</u> Iso
1d	10	Cr $\xrightarrow{122 (12.7)}_{112 (-12.4)}$ SmA $\xrightarrow{141 (1.4)}_{139 (-1.4)}$ Iso
1e	11	Cr $\xrightarrow{119(12.4)}_{103(-12.7)}$ SmA $\xrightarrow{150(1.9)}_{148(-1.8)}$ Iso
1f	12	$Cr \xrightarrow{119 (9.3)}_{103 (-9.5)} SmA \xrightarrow{148 (1.4)}_{146 (-1.3)} Iso$
1g	13	Cr $\xrightarrow{121 (9.8)}_{107 (-10.3)}$ SmA $\xrightarrow{146 (1.3)}_{144 (-1.2)}$ Iso
1h	14	Cr $\xrightarrow{121 (12.4)}_{107 (-12.5)}$ SmA $\xrightarrow{144 (1.7)}_{143 (-1.6)}$ Iso
1i	15	Cr $\xrightarrow{122 (11.0)}_{110 (-11.5)}$ SmA $\xrightarrow{143 (1.3)}_{141 (-1.2)}$ Iso
1j	16	$Cr \xrightarrow{121 (14.0)}_{111 (-14.4)} SmA \xrightarrow{140 (1.7)}_{138 (-1.6)} Iso$

^{*a*} The transition temperatures (°C) and transition enthalpies (kcal mol⁻¹) were determined by DSC (5 °C min⁻¹) and are given above and below the arrows. Cr, SmA, Iso indicate crystal, smectic A, and isotropic liquid phases, respectively.

parts is not appropriate for molecular packing in the liquid crystalline state.

1D-XRD study of 1a-j

Fig. 4 shows the observed layer distances d(100) in the 1D-XRD of **1a–j** and their molecular lengths calculated as the all-*trans*



Fig. 2 Polarized light microphotograph of 1a (130 °C, \times 300). The directions of the crossed polarizers were indicated by the crossed arrows. The scale bar is 100 μ m.



Fig. 3 Plots of clearing and melting points of **1a–j** (n = 7-16) against *n* (*n*: number of carbon atoms in the alkyl chain). The temperature rate is 5 °C min⁻¹.



Fig. 4 Plots of the observed layer distances (filled squares) and calculated molecular lengths²⁰ with all-*trans*-forms (open triangles) against *n* in **1a–j** (n = 7-16, *n*: number of carbon atoms in the alkyl chains) at 130 °C.

conformers.²⁰ Their layer distances observed are significantly shorter than the corresponding molecular lengths calculated. It suggests that the alkyl chains also have gauche-forms. Further, the layer distances against the number of carbon atoms (n) have a periodicity. The layer distances of compounds 1a (n = 7), 1d (n= 10), 1g (n = 13), and 1j (n = 16) are particularly short compared to their molecular lengths. It means that the ratios of the layer distances to the calculated lengths become smaller for every three carbon atoms added. To the best of our knowledge, this phenomenon has not been reported. It is assumed that this originated in the suppression of the rotational movements of the rod-like molecules by the strong lateral intermolecular interactions. It is not necessary that their alkyl chains have trans-forms to make the excluded volumes small, because they are not rotating rapidly. As shown in Scheme 2, there is a possibility that the alkyl chains of 1a, 1d, 1g, and 1j in the smectic A phases have



Scheme 2 The most probable conformations of the alkyl chains of 1a, 1d, 1g, and 1j estimated from periodicity in the layer distance measured by XRD in the series of 1a–j. The alkyl chains of 1a, 1d, 1g, and 1j have *tggtgg-*, *tggtggtgg-*, *tggtggtggtgg-*, and *tggtggtggtgg-*forms (*t: trans, g: gauche*) to attain the tight packing. The covalent bonds with *trans-*(*t*) and *gauche-*(g) forms were indicated in red and black, respectively.

tggtgg-, *tggtggtgg-*, *tggtggtggtgg-*, and *tggtggtggtgg-*forms (*t: trans, g: gauche*) as their averaged conformations to be packed tightly in the layers, respectively.

Fig. 5 shows molecular models for a **1d** molecule possessing a decyl group with *tggtggtgg*-form which is suitable for the dense



Fig. 5 Molecular models (stick and space-fill models) of 1d with a *tggtggtgg*-form.

packing in the smectic layer structure. This "tgg-effect" explains the periodicity in the plots of the layer distances against the n in the alkyl chains.

In Fig. 6, the 1D-XRD profile of **1a** is shown. In the small angle region, it has a large sharp d(100) peak with small sharp d (200) and d(300) peaks, which is indicative of a well-organized layer structure. The magnified chart in the inset has the four broad peaks b (= 7.8 Å), c (= 5.6 Å), d (= 4.5 Å), and e (= 3.9 Å). It is assumed that the peaks b, c, and e indicate the repeat distances in the lateral directions in each layer. The broad peak d originates in the molten alkyl chains.

2D-XRD study of 1a

Compound **1a** was sealed in a glass capillary of 1.5 mm diameter. The sample was aligned by heating up to 170 °C followed by cooling slowly down to 120 °C. The 2D-XRD profile at 120 °C (smectic A phase) is shown in Fig. 7. The sets of d(100) and d(200) peaks are observed clearly only on the equator, which means that there is a well aligned layer structure, and some broad peaks are shown on the meridian. It suggests that the rod-like molecules are parallel to the layer normal and are also ordered laterally in each layer.

In comparison with the result of the 1D-XRD of **1a**, the broad peaks b (= 7.8 Å), c (= 5.6 Å), d (= 4.5 Å), and e (= 3.9 Å)observed in 1D-XRD were depicted on the 2D-XRD profile, and the broad peaks in the 1D-XRD profile almost agree with those on the meridian in the 2D-XRD profile. In addition, the most intensive broad peak $a \approx 11 \text{ Å}$ was observed in the 2D-XRD, which is difficult to distinguish from d(200) in the 1D-XRD profile.

Estimation of the packing structure in the smectic A phase. To estimate the most stable conformation of 1, the conformation of the homologue, 4-methoxy-4'-pentafluorobenzoyloxy-biphenyl,



Fig. 6 XRD profile of **1a** at 120 °C. The d(100) and d(200) are indicated at the top of the peaks. The magnified profile is shown in the inset, and the d(200), d(300), and broad peaks (a, b, c, d, and e) are indicated by the arrows.



Fig. 7 2D-XRD profile of **1a** (120 °C). The peaks of interlayer distances (d(100) and d(200)) are pointed by arrows, and the areas of the lateral repeat distances (a, b, c, d, and e) are indicated by oval and crescent moon shapes drawn with black (a, b, c, and e) and yellow (d) broken lines, respectively.

was calculated by the DFT (B3LYP6-31G(d)) method.²¹ As shown in Fig. 8, the π -faces of pentafluorophenyl and the ester linked phenyl of biphenyl are almost in the same plane. The torsion angle between the two benzene rings of the biphenyl group was about 38°. The molecule has a board-like shape, and the fluorine atoms at the 2, 3, 5, 6-positions of the pentafluorophenyl and all hydrogen atoms of the biphenyl moiety are at the sides of the board-like molecule, which are suitable for the intermolecular PFA–A and C–H/F interactions, respectively.

In Fig. 9a (molecular model of 1) and Fig. 9b (the top view of the layer), the lateral repeat distances in 1D- and 2D-XRD profiles, ca. 11, 7.8, 5.6, and 3.9 Å, are indicated as a, b, c, and e. The two different benzene rings alternately stack and this packing structure generates the repeat distances e and b corresponding to once and twice the stacking distance of 3.9 Å which is close to the value 3.7 Å reported as the inter-centroid distance in co-crystals of hexafluorobenzene and benzene.¹¹ The molecules aligned laterally in each layer generate the repeat distances a and c. The alkyl chains are interdigitated between the adjacent two layers (Fig. 9c), and they are tightly packed not to make leave space by having both trans- and gauche-conformations. The π -faces of the molecules direct one direction in each of the layers, and the long axes of the rod-like cores are perpendicular to the layer normal. The rotation of the rod-like molecules around the molecular long axes is strongly suppressed by the



Fig. 8 Most stable conformation of 4-methoxy-4'-pentafluorobenzoyloxybiphenyl calculated by the DFT (B3LYP6-31G(d)) method.²¹ The fluorine, carbon, oxygen, and hydrogen atoms are colorized yellow, gray, red, and white, respectively.

(a) (b) a = c(c) $d(100) \approx L$

Fig. 9 Schematic representations of (a) the molecular model of 1 (*L*: molecular length), (b) the top view of a part of the layer (the alkyl chains are omitted for clarity, the four repeat distances *a*, *b*, *c*, and *e* are indicated), and (c) the layer structure of 1 in the smectic A phase (d(100): layer distance observed in XRD).

PFA–A and C–H/F interactions. It is assumed that these smectic A phases are locally biaxial in each layer, they have no macroscopic biaxiality from the observation of the POM in the smectic A phase which gave dark homeotropic textures.

Conclusion

We demonstrated an interaction assisted approach for realization of biaxiality in smectic A phases, and indicated the effectiveness of the PFA-A and CH/F interactions as the intermolecular interactions. The 1D- and 2D-XRD studies indicated that the molecules in the smectic A phases have lateral directional order in each layer, and it is assumed to originate from the local biaxiality of the smectic A phases. Further, the slow rotation of the molecules showed unique phenomena such as no clear odd-even effect in their clearing and melting points, and a "*tgg*-effect" in the plots of their layer distances against the number of carbon atoms in the terminal alkyl chains.

Experimental

Synthesis of 4-(4-alkoxyphenyl)phenol (synthesis of 2)

To 4,4'-biphenol (1.00 g, 5.37 mmol), K_2CO_3 (0.740 g, 5.37 mmol), and potassium iodide (0.090 g, 0.54 mmol) in a 200 mL three necked round bottom flask equipped with a Dimroth condenser and a CaCl₂ tube was added acetone (30 mL). The solution was refluxed with stirring and 1-bromoalkane (5.37 mmol) was added dropwise. The solution was refluxed for 24 h with stirring. After cooling, ethyl acetate (100 mL) was added and the solution was dried over anhydrous MgSO₄, filtered with suction, and concentrated *in vacuo*. The product was purified by recrystallization from hexane–ethyl acetate to give 4-(4-alkoxyphenyl)phenol **2** as a white powder crystal. Compounds **2a–j** were prepared by the abovementioned procedure. The yields of

2a–j were 74.5, 65.3, 25.5, 50.9, 58.4, 48.4, 64.6, 26.3, 29.1, and 33.4%, respectively.

2a: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.91 (t, J = 7.0 Hz, 3H), 1.26–1.52 (m, 8H), 1.80 (quint, J = 7.0 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 4.77 (s, 1H), 6.88 (d, J = 2.7 Hz, 2H), 6.94 (d, J = 2.9 Hz, 2H), 7.43 (m, 4H).

2b: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.89 (t, J = 6.8 Hz, 3H), 1.31–1.56 (m, 10H), 1.80 (quint, J = 7.0 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 4.70 (s, 1H), 6.91 (m, 4H), 7.44 (m, 4H).

2c: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.89 (t, J = 6.8 Hz, 3H), 1.28–1.55 (m, 12H), 1.80 (quint, J = 7.0 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 4.80 (s, 1H), 6.88 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 7.43 (m, 4H).

2d: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.91 (t, J = 6.9 Hz, 3H), 1.30–1.55 (m, 14H), 1.80 (quint, J = 7.0 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 4.77 (s, 1H), 6.91 (m, 4H), 7.43 (m, 4H).

2e: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.88 (t, J = 6.6 Hz, 3H), 1.26–1.47 (m, 16H), 1.79 (quint, J = 7.0 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 4.74 (s, 1H), 6.91 (m, 4H), 7.43 (m, 4H).

2f: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.88 (t, J = 6.8 Hz, 3H), 1.26–1.46 (m, 18H), 1.80 (quint, J = 7.3 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 4.70 (s, 1H), 6.90 (m, 4H), 7.43 (m, 4H).

2g: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.88 (t, J = 6.8 Hz, 3H), 1.36 (m, 20H), 1.80 (quint, J = 7.0 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 4.78 (s, 1H), 6.91 (m, 4H), 7.43 (m, 4H).

2h: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.88 (t, J = 6.6 Hz, 3H), 1.26–1.56 (m, 22H), 1.80 (quint, J = 6.9 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 4.69 (s, 1H), 6.91 (m, 4H), 7.44 (m, 4H).

2i: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃): 0.91 (t, J = 6.9 Hz, 3H), 1.25–1.55 (m, 24H), 1.80 (quint, J = 7.0 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 4.77 (s, 1H), 6.88 (d, J = 2.7 Hz, 2H), 6.94 (d, J = 0.29 Hz, 2H), 7.43 (m, 4H).

2j: $R_f = 0.7$ (hexane : ethyl acetate = 1 : 1); ¹H NMR (300.22 MHz, CDCl₃) 0.88 (t, J = 6.2 Hz, 3H), 1.24–1.55 (m, 26H), 1.79 (quint, J = 6.9 Hz, 2H), 3.98 (t, J = 6.2 Hz, 2H), 4.68 (s, 1H), 6.91 (m, 4H), 7.43 (m, 4H).

Synthesis of compound 1

Compound 2 (3.99 mmol), pentafluorobenzoic acid (0.85 g, 4.0 mmol), and dry THF (20 mL) were placed in a 200 mL threenecked flask equipped with a CaCl₂ tube. The solution was stirred at 0 °C, and DIPC (0.74 mL, 4.8 mmol) and DMAP (0.05 g, 0.4 mmol) were added and stirred at room temperature for 24 h. The solution was concentrated *in vacuo*, and chloroform (100 mL) was added. The solution was washed with water (100 mL \times 3), and dried over anhydrous MgSO₄. The solution was filtered and the filtrate was concentrated. The product was purified by silica gel column chromatography eluting with chloroform, and then the product was purified by recrystallization from chloroform-hexane to give 1 as a white crystal. Compounds 1a–j were obtained by the same procedure. The yields of 1a–j were 47.3, 49.2, 42.4, 37.2, 38.0, 44.7, 34.2, 30.8, 24.0, and 26.8%. **1a**: $R_{\rm f} = 0.27$ (hexane : chloroform = 1 : 1); IR (KBr) 2914, 2770, 1748, 1653, 1497, 1216, 1010 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃): 0.91 (t, J = 6.8 Hz, 3H), 1.26–1.48 (m, 8H), 1.80 (m, 2H), 4.00 (t, J = 6.3 Hz, 2H), 6.96 (m, 2H), 7.30 (m, 2H), 7.49 (m, 2H), 7.64 (m, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.55, 23.07, 26.48, 29.53, 29.73, 32.25, 68.57, 109.87, 115.30, 121.86, 128.33, 128.58, 132.75, 135.02, 137.82, 148.96, 149.12, 149.30, 159.41, 166.59; HRMS (FAB) calcd for $C_{26}H_{23}F_5O_3Na$ [(M + Na)⁺] 501.1443, found 501.1460.

1b: $R_{\rm f} = 0.27$ (hexane : chloroform = 1 : 1); IR (KBr) 2921, 2769, 1750, 1652, 1607, 1505, 1275, 996 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃): 0.89 (t, J = 6.8 Hz, 3H), 1.29–1.47 (m, 10H), 1.80 (m, 2H), 3.99 (t, J = 6.3 Hz, 2H), 6.93 (m, 2H), 7.30 (m, 2H), 7.47 (m, 2H), 7.64 (m, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.57, 23.12, 26.51, 29.72, 29.87, 32.33, 68.57, 109.97, 115.29, 121.87, 128.08, 128.33, 132.76, 134.34, 139.23, 147.81, 148.02, 149.30, 158.64, 165.34; HRMS (FAB) calcd for $C_{27}H_{25}F_5O_3$ [M⁺] 492.1688, found 492.1718.

Ic: $R_{\rm f} = 0.27$ (hexane : chloroform = 1 : 1); IR (KBr) 2933, 2851, 1750, 1652, 1607, 1503, 1229, 989 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃): 0.89 (t, J = 6.6 Hz, 3H), 1.28–1.47 (m, 12H), 1.80 (m, 2H), 3.99 (t, J = 6.3 Hz, 2H), 6.95 (m, 2H), 7.29 (m, 2H), 7.50 (m, 2H), 7.62 (m, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.57, 23.13, 26.52, 29.72, 29.87, 30.00, 32.33, 68.57, 110.12, 115.30, 121.86, 128.08, 128.33, 132.75, 135.87, 139.90, 145.90, 149.26, 149.83, 157.56, 165.28; HRMS (FAB) calcd for $C_{28}H_{28}F_5O_3Na$ [(M + H + Na)⁺] 530.1805, found 530.1851.

1d: $R_{\rm f} = 0.27$ (hexane : chloroform = 1 : 1); IR (KBr) 2919, 2851, 1751, 1652, 1607, 1491, 1234, 990 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃): 0.89 (t, J = 6.6 Hz, 3H), 1.28–1.47 (m, 14H), 1.80 (m, 2H), 3.99 (t, J = 6.3 Hz, 2H), 6.95 (m, 2H), 7.32 (m, 2H), 7.48 (m, 2H), 7.63 (m, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.58, 23.14, 26.52, 29.73, 29.78, 29.87, 30.02, 30.05, 32.36, 68.57, 110.03, 115.29, 122.15, 128.08, 128.92, 132.75, 133.74, 139.24, 146.77, 147.84, 148.46, 158.63, 165.25; HRMS (FAB) calcd for $C_{29}H_{28}F_5O_3$ [(M–H)⁺] 519.1959, found 519.1953.

1e: $R_{\rm f} = 0.25$ (hexane : chloroform = 1 : 1); IR (KBr) 2918, 2850, 1750, 1653, 1607, 1490, 1234, 990 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃): 0.88 (t, J = 6.6 Hz, 3H), 1.27–1.47 (m, 16H), 1.79 (m, 2H), 3.99 (t, J = 6.3 Hz, 2H), 6.96 (m, 2H), 7.31 (m, 2H), 7.49 (m, 2H), 7.62 (m, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.56, 23.12, 26.49, 29.70, 29.74, 29.79, 29.85, 30.02, 30.05, 32.34, 68.55, 107.84, 115.27, 121.85, 128.06, 128.57, 132.78, 134.23, 140.16, 147.75, 149.27, 150.66, 159.38, 167.13; HRMS (FAB) calcd for $C_{30}H_{31}F_5O_3$ [M⁺] 534.2182, found 534.2188.

1f: $R_f = 0.25$ (hexane : chloroform = 1 : 1); IR (KBr) 2917, 2850, 1750, 1653, 1607, 1489, 1235, 989 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃): 0.87 (t, J = 6.6 Hz, 3H), 1.26–1.46 (m, 18H), 1.80 (quint, J = 7.0 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.55, 23.11, 26.51, 29.70, 29.76, 29.82, 30.04, 30.06, 30.12, 32.27, 68.53, 110.49, 115.30, 121.86, 128.08, 128.92, 133.75, 134.09, 138.76, 147.49, 148.57, 149.77, 158.65, 166.67; HRMS (FAB) calcd for C₃₁H₃₃F₅O₃ [M⁺] 548.2335, found 548.2344.

1g: $R_{\rm f} = 0.25$ (hexane : chloroform = 1 : 1); IR (KBr) 2917, 2849, 1750, 1653, 1607, 1490, 1234, 989 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃) 0.88 (t, J = 6.8 Hz, 3H), 1.26–1.47 (m, 20H), 1.81 (quint, J = 7.3 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 6.97 (d, J = 9.0

Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.57, 23.15, 26.51, 29.72, 29.81, 29.86, 30.05, 30.09, 30.12, 32.37, 68.57, 111.17, 115.30, 121.86, 128.33, 128.58, 132.74, 136.19, 139.74, 147.39, 149.28, 150.04, 159.41, 162.78; HRMS (FAB) calcd for $C_{32}H_{35}F_5O_3$ [M⁺] 562.2497, found 562.2501.

1h: $R_{\rm f} = 0.25$ (hexane : chloroform = 1 : 1); IR (KBr) 2917, 2850, 1750, 1653, 1607, 1490, 1234, 989 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃): 0.88 (t, J = 6.6 Hz, 3H), 1.26–1.47 (m, 22H), 1.81 (quint, J = 7.0 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.57, 23.15, 26.51, 29.72, 29.81, 29.86, 30.00, 30.04, 30.06, 30.11, 32.38, 68.57, 109.88, 115.30, 121.86, 128.33, 128.58, 132.75, 134.36, 137.98, 146.94, 147.46, 149.30, 159.41, 164.97; HRMS (FAB) calcd for C₃₃H₃₇F₅O₃ [M⁺] 576.2656, found 576.2657.

1i: $R_{\rm f} = 0.25$ (hexane : chloroform = 1 :1); IR (KBr) 2917, 2849, 1750, 1652, 1607, 1490, 1235, 989 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃) 0.88 (t, J = 6.8 Hz, 3H), 1.26–1.47 (m, 24H), 1.80 (quint, J = 7.0 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H); ¹³C NMR (75.48 MHz, CDCl₃): 14.56, 23.14, 26.51, 29.72, 29.83, 29.86, 30.04, 30.06, 30.12, 32.37, 68.57, 109.37, 115.30, 121.86, 128.33, 128.57, 132.74, 134.33, 140.12, 145.91, 148.47, 149.30, 159.40, 165.52; HRMS (FAB) calcd for C₃₄H₃₉F₅O₃ [M⁺] 590.2811, found 590.2814.

1j: $R_{\rm f} = 0.25$ (hexane : chloroform = 1 : 1); IR (KBr) 2917, 2849, 1750, 1653, 1607, 1490, 1234, 990 cm⁻¹; ¹H NMR (300.22 MHz, CDCl₃) 0.88 (t, J = 6.6 Hz, 3H), 1.26–1.49 (m, 26H), 1.81 (quint, J = 7.3 Hz, 2H), 4.00 (t, J = 7.3 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 7.29 (m, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.61 (m, 2H); ¹³C NMR (75.48 MHz, CDCl₃) 14.57, 23.15, 26.51, 29.72, 29.82, 29.86, 30.04, 30.06, 30.12, 30.14, 32.38, 68.57, 109.69, 115.29, 121.86, 128.33, 128.58, 132.74, 136.36, 140.11, 145.47, 147.21, 149.30, 159.40, 164.37; HRMS (FAB) calcd for $C_{35}H_{41}F_5O_3$ [M⁺] 604.2965, found 604.2970.

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