SYNTHESIS AND PHASE TRANSITIONS OF FLUORINATED 4,4'-BIPHENYL DERIVATIVES

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ABSTRACT: Symmetrical fluoroalkylated 4,4'-biphenyl derivatives were synthesized starting from 4,4'-biphenol and characterized. In these compounds, the perfluoroalkyl chain is separated from biphenyl core by two kinds of spacers: allyloxy or ethyl[(3-propyloxy)sulfanyl]acetate moiety. Their thermotropic properties have been examined by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). It has been found that compounds having longer fluoroalkyl chain exhibit higher transition temperatures and melting points. Compounds whose spacer is an allyloxy group exhibit smectic phases, whereas those bearing ethyl[(3-propyloxy)sulfanyl]acetate moiety, show nematic phases.

Keywords: Biphenyl; Fluorine; Liquid crystal.

RESUME: Deux séries de composés symétriques bis(*F*-alkylés) dérivés du 4,4'-biphényle ont été synthétisées à partir du 4,4'-biphénol. Les chaînes *F*-alkylées sont couplées au biphényle par l'intermédiaire de deux types d'espaceurs: allyloxy ou 3-propyloxysulfanylacetate d'éthyle. Les propriétés mésophases de ces composés ont été étudiées par analyse calorimétrique différentielle à balayage constant (DSC) et au microscope optique polarisé (MOP). Les températures de transitions et d'isotropization de ces composés augmentent avec la longueur des chaînes *F*-alkylées. Les mésophases de ces composés sont smectiques lorsque le bras espaceur est un groupe allyloxy et nématiques lorsque le bras est un groupe 3-propyloxysulfanylacetate d'éthyle.

Mots clés: Biphényle; Fluor; Cristal liquide.

1. INTRODUCTION

Biphenyl derivatives have been extensively studied [1-8] because of their applications in liquid crystal displays. Perfluorinated groups were incorporated to enhance the liquid crystal character of such derivatives [9,10], e.g. the introduction of the perfluorinated chain could be considered as an interesting alternative for obtaining smectic phases [4,7,11,12]. The stability of the liquid crystal mesophase is strongly influenced by the nature of the spacer separating the perfluorinated tail and the biphenyl rigid core. Thus, when the perfluorinated chain is directly linked to 4-biphenyl group, no mesomorphic property has been observed [13]. In the same way, linkers such as amide, thioether or hemithioacetal derivatives lead to complete suppression of the smectic character of monosubstituted biphenyl compounds [3,4].

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We describe herein the synthesis and the liquid crystalline properties of new symmetrical 4,4’-biphenyl derivatives containing two perfluoalkyl chains linked to biphenyl rigid core by allyloxy or ethyl[(3-propyloxy)sulfanyl]acetate groups (Figure 1).

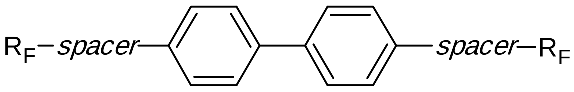
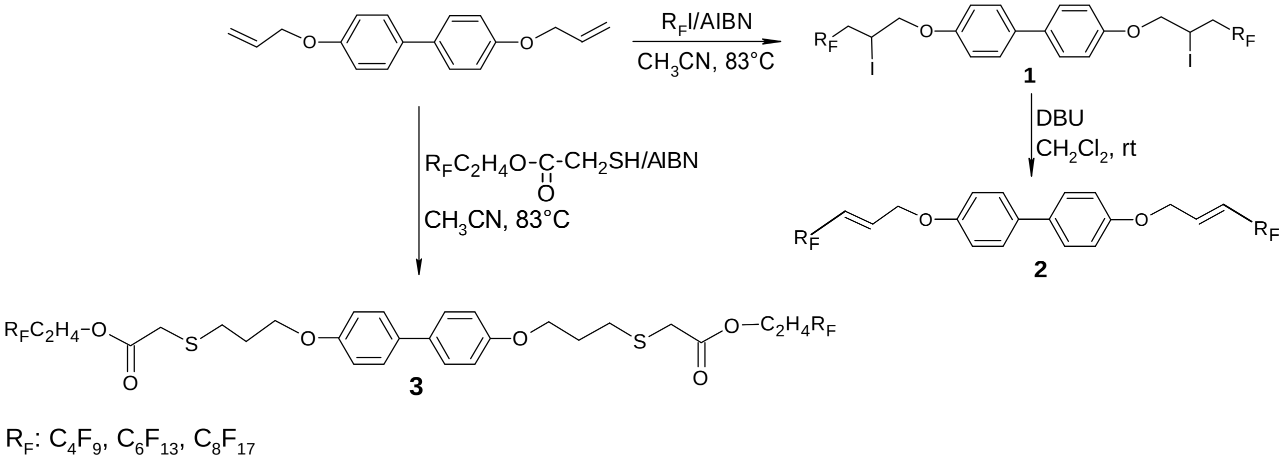


Fig. 1: Structure of target compounds

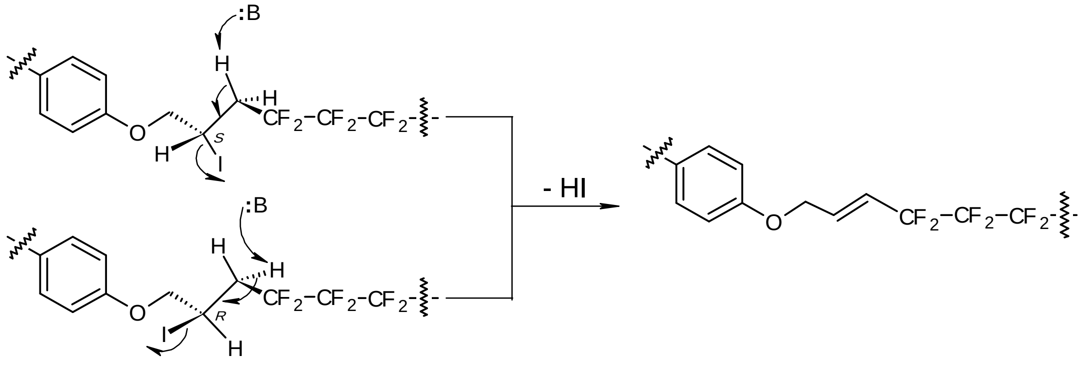
2. RESULTS AND DISCUSSION

The starting material, i.e. 4,4’-bis(allyloxy)biphenyl [14] was prepared according to the literature [15]. This compound reacted with perfluoroalkyl iodide [16-22] to give adduct **1**, as a *syn*/*anti* mixture in ca. 1:1 ratio (Scheme 1).



Scheme 1: Conversion of 4,4'-bis(allyloxy)biphenyl into diolefins **2** and diesters **3**

Next, dehydroiodination of **1** with DBU [23] furnished, as depicted in Scheme 1, the diolefins **2** almost as an *EE* isomer. The obtained diolefins are listed in Table 1. In the same way, 4,4’-bis(allyloxy)biphenyl reacted with *F*-alkylethyl sulfanylacetate [22,24-26] to give diesters **3** in good yields (Scheme 1, Table 1).



Scheme 2: Dehydroiodination of **1**

Among the three expected *EE*, *EZ* and *ZZ* isomers from the dehydroiodination reaction of **1**, only the *EE* one was obtained [27] as observed by ^{1}H NMR. This selectivity may be rationalized if we assume that while undergoing anti-elimination, compound **1** adopts the suitable conformation where the perfluoroalkyl and the biphenyl groups are anti to each other, to minimize repulsive interactions and steric hindrance when base B attacks [28] (Scheme 2).

Table 1: Yields of fluorinated 4,4'-biphenyl derivatives **2** and **3**

Diolefins **2** and diesters **3**	R_F	Yield (%)
2a	C_4F_9	86
2b	C_6F_{13}	85
2c	C_8F_{17}	88
3a	C_6F_{13}	88
3b	C_8F_{17}	84

The mesomorphic properties of 4,4'-biphenyl derivatives **2** and **3** have been studied by polarizing optical microscopy observation using a heating-cooling stage. Phase transition temperature (T_t), melting temperatures (T_i) and enthalpy (ΔH_t) were obtained by differential scanning calorimetry (DSC) (Table 2).

Table 2: DSC thermograms data of fluorinated 4,4'-biphenyl derivatives **2** and **3**

Compound	Heating		Cooling		T_i(°C)
	T_t(°C)	ΔH_t(kJ.mol^{-1})	T_t(°C)	ΔH_t(kJ.mol^{-1})	
2a	108.9	-7.67	111.4	4.68	128.2
2b	116.2	-9.64	118.5	7.20	147.3
2c	134.6	-16.84	136.5	2.32	177.5
-	155.3	-3.00	156.7	10.24	-
3a	86.2	-39.46	74.0	32.74	128.6
3b	110.4	-85.64	97.0	62.42	166.5

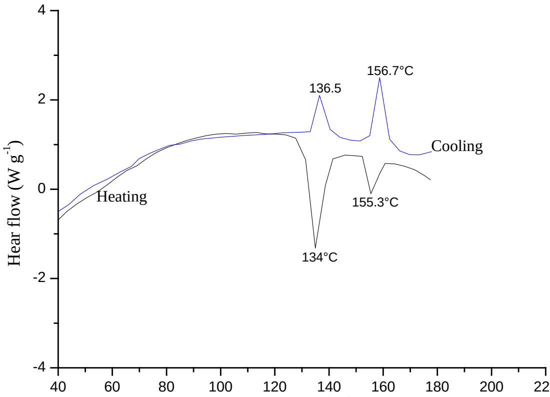


Fig. 2: DSC thermogram of **2c** during heating and cooling cycles (ΔT = 10°Cmin^{-1}).

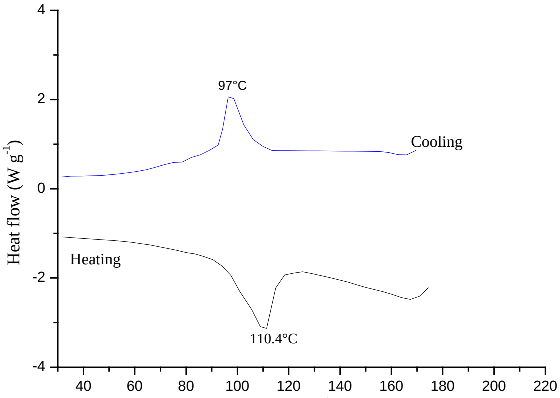


Fig. 3: DSC thermogram of **3b** during heating and cooling cycles (ΔT = 10°Cmin^{-1}).

It is noteworthy to mention that the temperature T_i leading to the isotropic phase increases as fluoroalkyl chain length become longer in both compounds **2** and **3**. On the other hand, thermograms of diolefin **2c** (Figure 2) exhibit two phase transitions on heating or cooling whereas the other compounds **2a**, **2b** and **3** show only one transition (Figure 3).

Diolefins **2** and diesters **3** exhibited optical anisotropy when heated or cooled; this suggests that compounds **2** and **3** were liquid crystalline. Figures 4, 5, 6, 7 and 8 show microphotographs of mesomorphic textures of compounds **2** and **3** taken under a polarized optical microscope. On cooling from the isotropic liquid, **2a** and **2b** showed a batonnet –like smectic A phase which exhibited focal-conic fan textures (Figures 4 and 5).

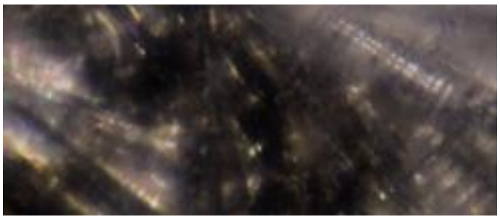


Fig. 4: Optical texture (x200) of **2a** at 116°C observed on cooling from isotropic liquid

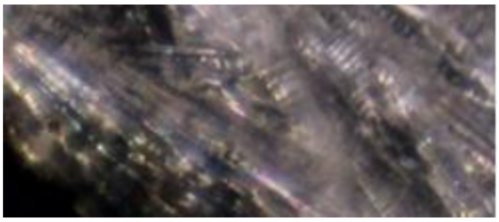


Fig. 5: Optical texture (x200) of **2b** at 125°C observed on cooling from isotropic liquid

Figure 6 shows the polarized optical microphotograph of compound **2c** textures during cooling process from the isotropic state to room temperature. Fig. 6a is the typical perfect focal-conic fan texture of the smectic A phase at 170°C, in which lines can be seen. Further lowering of the temperature, leads to smectic B phase [13,29] which appears at 145°C. Texture of smectic B is quite different from the smectic A one as shown in Figure 6b.

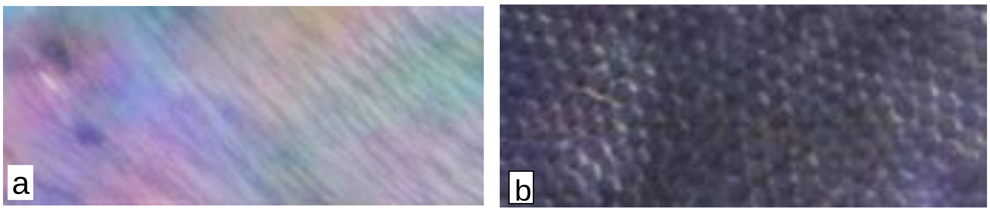


Fig. 6: Optical textures (x200) of **2c** (a) at 170°C and (b) at 145°C observed on cooling from the isotropic liquid.

Compounds **3** exhibit monotropic nematic mesophase, which has been identified by the typical nematic droplets [30,31] on cooling from the isotropic liquid (Figures 7 and 8). Similar mesomorphic properties were previously reported for biphenyl derivatives having thioether a moiety as linker [3,4].

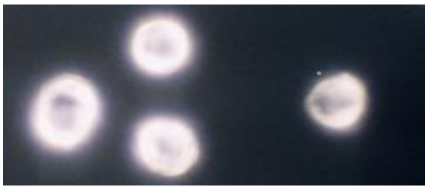


Fig. 7: Optical texture (x200) of **3a** at 95°C observed on cooling from isotropic liquid

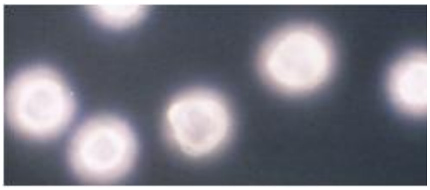


Fig. 8: Optical texture (x200) of 3**b** at 130°C observed on cooling from isotropic liquid

3. CONCLUSION

In summary, symmetrical 4,4'-biphenyl derivatives containing two perfluoroalkyls chain attached to a rigid core *via* allyloxy or ethyl[(3-propyloxy)sulfanyl]acetate groups, were synthesized and characterized. Thermotropic phase behaviors of these compounds have been investigated by DSC and POM. The obtained results show that the fluoroalkyl chain length of these compounds influences transition temperatures. The anisotropic mesophase is observed on heating or cooling from isotropic state to room temperature. The anisotropic mesophase is smectic when the spacer is an allyloxy group whereas it is nematic with ethyl[(3-propyloxy)sulfanyl]acetate group as a spacer.

4. EXPERIMENTAL

The ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Brüker AC 300 at 300, 75 and 282 MHz, respectively. TMS was used as a standard reference for ^1H and ^{13}C NMR spectra and $CFCl_3$ for ^{19}F NMR. The IR spectra were recorded on a Brüker IFS 66V/S spectrometer. High resolution mass spectra (HRMS) were taken on AMD-604 apparatus. Differential scanning calorimetry (DSC) was performed on a Metler DSC-30 instrument. Thermograms were recorded at 10°Cmin^{-1} heating/cooling scan rate. Texture observation was performed using a polarizing optical microscope (magnification 200x).

Preparation of 4,4'-bis(allyloxy)biphenyl

4,4'-biphenol (1.862 g, 10 mmol) in dry dimethylformamide (10 mL) was added dropwise under nitrogen to a solution of NaH (0.62 g, 30 mmol) in dry dimethylformamide (10 mL) at 0°C. Allyl bromide (3.629 g, 30 mmol) was added dropwise to the resulting solution at 0°C. The mixture was stirred at room temperature for 12 h (TLC ethyl acetate/cyclohexane: 1/1). Cold water was added to the solution and the mixture was extracted with CH_2Cl_2 (3x40 mL). The organic layer was washed with water, dried (Na_2SO_4) and then evaporated under reduced pressure. Purification of the crude product by column chromatography (CH_2Cl_2/CCl_4: 1/9) furnished 2.55 g of 4,4'-bis(allyloxy)biphenyl (yield: 96%).

*Preparation of iodoperfluoroalkylated compounds **1**: general procedure*

In a 25 mL round bottomed flask, was placed under N_2 atmosphere a mixture of 4,4'-bis(allyloxy)biphenyl (0.532 g, 2 mmol), perfluoroalkyl iodide (5 mmol), AIBN (0.131 g, 0.8 mmol) and 2 mL of dry CH_3CN. The mixture was then stirred at 83°C for 18 h (TLC CH_2Cl_2/CCl_4: 1/9). After cooling to room temperature, the solvent was removed under vacuum and the obtained compound was purified on a column chromatography (CH_2Cl_2/CCl_4: 1/9).

*Preparation of F-alkylated ethers **2**: general procedure*

DBU (0.300 g, 2 mmol) was added to a solution of compound **1** (0.5 mmol) in CH_2Cl_2 at room temperature. The mixture was stirred for 6 h (TLC CH_2Cl_2/CCl_4: 1/9) and then quenched with aqueous NH_4Cl (5 mL). It was extracted with CH_2Cl_2 (3x40 mL) and the organic layer was washed with aqueous K_2CO_3 and then with water. After drying (Na_2SO_4), the solvent was removed under vacuum. The crude product was purified on a column chromatography (**2a**) ($CHCl_3/CCl_4$: 1/3), or by crystallization from $CHCl_3/CCl_4$ (**2b** and **2c**).

4,4'-bis(3-Nonafluorobutylallyloxy)biphenyl (**2a**). IR (cm^{-1}) $\nu_{C\text{-}F}$ = 1186, $\nu_{C=C}$ = 1607, $\nu_{C=Carom}$ = 1498, ^1H NMR ($CDCl_3$) δ(ppm) 4.60 (d, 4H, $2OC\underline{H}_2CHCH$, $^3J_{HH}$ = 6.36 Hz), 6.03 (m, 2H, $2CHC\underline{H}CF_2$), 6.58 (dt, 2H, $2OCH_2C\underline{H}CH$, J^{trans}_{HH} = 13.59 Hz, $^3J_{HH}$ = 6.36 Hz), 6.95, 7.50 (2d 8H, H_{arom}, $^3J_{HH}$ = 8.82 Hz), ^{13}C NMR ($CDCl_3$) δ(ppm) 66.17 (s, 2C, $2O\underline{C}H_2CHCH$), 117.22 (t, 2C, $2CH\underline{C}HCF_2$, $^2J_{CF}$ = 20.52 Hz), 133.63 (s, 2C, $2OCH_2\underline{C}HCH$), 115.00, 127.95, 134.16, 157.75 (4s, 12C, C_{arom}), ^{19}F NMR ($CDCl_3$) δ(ppm) -82.12 (m, 6F, $2CF_3$), -113.04 (m, 4F, $2CF_{2\alpha}$), -125.10 (m, 4F, $2CF_{2\beta}$), -126.68 (m, 4F, $2CF_{2\omega}$), HRMS (ESI) calculated for: $(C_{26}H_{16}F_{18}O_2Na)^+$: 725.0755, found: 725.0753.

4,4'-bis(3-Tridecafluorohexylallyloxy)biphenyl (**2b**). IR (cm^{-1}) $\nu_{C\text{-}F}$ = 1143, $\nu_{C=C}$ = 1608, $\nu_{C=Carom}$ =1504, ^1H NMR ($CDCl_3$) δ(ppm) 4.73 (d, 4H, $2OC\underline{H}_2CHCH$, $^3J_{HH}$ = 7.82 Hz), 6.10 (m, 2H, $2CHC\underline{H}CF_2$), 6.61 (dt, 2H, $2OCH_2C\underline{H}CH$, J^{trans}_{HH} = 15.31 Hz, $^3J_{HH}$ = 7.82 Hz), 6.95, 7.48 (2d, 8H, H_{arom}, $^3J_{HH}$ = 8.82 Hz), ^{13}C NMR ($CDCl_3$) δ(ppm) 66.32 (s, 2C, $2O\underline{C}H_2CHCH$), 117.53 (t, 2C, $2CH\underline{C}HCF_2$, $^2J_{CF}$ = 19.6 Hz), 133.72 (s, 2C, $2\underline{C}HCHCF_2$), 115.04, 128.02 134.16, 158.14 (4s, 12C, C_{arom}), ^{19}F NMR ($CDCl_3$) δ(ppm) -81.89 (6F, $2CF_3$), 112.80 (m, 4F, $2CF_{2\alpha}$), -122.82 (m, 4F, $2CF_{2\beta}$), -124.07 (m, 4F, $2CF_{2\gamma}$), -124.02 (m, 4F, $2CF_{2\delta}$), -127.29 (m, 4F, $2CF_{2\omega}$), HRMS (ESI) calculated for: $(C_{30}H_{16}F_{26}O_2Na)^+$: 925.0627, found: 925.0624.

4,4'-bis(3-Heptadecafluorooctylallyloxy)biphenyl (**2c**). IR (cm^{-1}) $\nu_{C\text{-}F}$ = 1148, $\nu_{C=C}$ = 1608, $\nu_{C=Carom}$ =1504, ^1H NMR ($CDCl_3$) δ(ppm) 4.72 (d, 4H, $2OC\underline{H}_2CHCH$, $^3J_{HH}$ = 8.16 Hz), 6.11 (m, 2H, $2CHC\underline{H}CF_2$), 6.62 (dt, 2H, $2OCH_2C\underline{H}CH$, J_{HH}^{trans} = 15.81 Hz, $^3J_{HH}$ = 8.16 Hz), 6.95, 7.48 (2d, 8H, H_{arom}, $^3J_{HH}$ = 8.82 Hz), ^{13}C NMR ($CDCl_3$) δ(ppm) 66.17 (s, 2C, $2O\underline{C}H_2CHCH$), 117.73 (t, 2C, $2CH\underline{C}HCF_2$, $^2J_{CF}$ = 19.31 Hz), 133.36 (s, 2C, $2\underline{C}HCHCF_2$), 114.97, 127.84, 133.86, 156.97 (4s, 12C, C_{arom}), ^{19}F NMR ($CFCl_3$) δ(ppm) -81.62 (m 6F, $2CF_3$), -112.876 (m, 4F, $2CF_{2\alpha}$), -122.34 (m, 4F, $2CF_{2\beta}$), -122.75 (m, 8F, $4CF_{2\gamma}$), -123.10 (m, 4F, $2CF_{2\delta}$), -124.21 (m, 4F, $2CF_{2\xi}$), -124.02 (m, 4F, $2CF_{2\omega}$), HRMS (ESI) calculated for: $(C_{34}H_{16}F_{34}O_2Na)^+$: 1125.0499, found: 1125.0497.

*Preparation of compound **3**: general procedure*

In a 25 mL round bottomed flask was placed under N_2 atmosphere a mixture of 4,4'-bis(allyloxy)biphenyl (0.532 g, 2 mmol), *F*-alkylethyl sulfanylacetate (5 mmol), AIBN (0.131 g, 0.8 mmol) and 2 mL of dry CH_3CN. The mixture was then stirred at 83°C for 18 h (TLC CH_2Cl_2/CCl_4: 1/9). After cooling to room temperature, the solvent was removed under vacuum and the crude compound **3** was purified on a column chromatography (silicagel, ethyl acetate/hexane: 1/3) (**3a**), or by crystallization from ethanol (**3b**).

(**3a**). IR (cm^{-1}) $\nu_{C\text{-}F}$ = 1141, $\nu_{C=Carom}$ = 1511, $\nu_{C=O}$ = 1734, ^1H NMR ($CDCl_3$) δ(ppm) 2.15 (m, 4H, $2OCH_2C\underline{H}_2CH_2S$), 2.51 (m, 4H, $2OCH_2C\underline{H}_2CF_2$), 2.9 (t, 4H, $2OCH_2CH_2C\underline{H}_2S$, $^3J_{HH}$ = 6.83 Hz), 3.20 (s, 4H, $2CO_2C\underline{H}_2S$), 4.15 (t, 4H, $2OC\underline{H}_2CH_2CH_2S$, $^3J_{HH}$ = 6.58 Hz), 4.42 (t, 4H, $2OC\underline{H}_2CH_2CF_2$, $^3J_{HH}$ = 6.51 Hz), 6.96, 7.46 (2d, 8H, H_{arom}, $^3J_{HH}$ = 8.43 Hz), ^{13}C NMR ($CDCl_3$) δ(ppm) 28.76 (s, 2C, $2OCH_2\underline{C}H_2CH_2S$), 28.80 (s, 2C, $2OCH_2CH_2\underline{C}H_2S$), 33.44 (s, 2C, $2CO_2\underline{C}H_2S$), 30.48 (t, 2C, $2OCH_2\underline{C}H_2CF_2$, $^2J_{CF}$ = 22.03 Hz), 66.01 (s, 2C, $2O\underline{C}H_2CH_2CH_2S$), 57.18 (s, 2C, $2O\underline{C}H_2CH_2CF_2$), 170.12 (s, 2C, $2\underline{C}O_2$), 114.78, 127.74, 133.57, 157.92 (4s, 12C, C_{arom}), ^{19}F NMR ($CFCl_3$) δ(ppm) -81.70 (m, 6F, $2CF_3$), -114.48 (m, 4F, $2CF_{2\alpha}$), -122.82 (m, 4F, $2CF_{2\beta}$), -123.82 (m, 4F, $2CF_{2\gamma}$), -124.54 (m, 4F, $2CF_{2\delta}$), -127.13 (m, 4F, $2CF_{2\omega}$), HRMS (ESI) calculated for: $(C_{38}H_{32}F_{26}O_6S_2Na)^+$: 1165.1117, found: 1165.1114.

(**3b**). IR (cm^{-1}) $\nu_{C\text{-}F}$ = 1146, $\nu_{C=Carom}$ = 1507, $\nu_{C=O}$ = 1730, ^1H NMR ($CDCl_3$) δ(ppm) 2.15 (m, 4H, $2OCH_2C\underline{H}_2CH_2S$), 2.54 (m, 4H, $2OCH_2C\underline{H}_2CF_2$), 2.92 (t, 4H, $2CH_2C\underline{H}_2S$, $^3J_{HH}$ = 6.83 Hz), 3.15 (s, 4H, $2CO_2C\underline{H}_2S$), 4.10 (t, 4H, $2OC\underline{H}_2CH_2CH_2S$, $^3J_{HH}$ = 6.58 Hz), 4.45 (t, 4H, $2OC\underline{H}_2CH_2CF_2$, $^3J_{HH}$ = 6.51 Hz), 6.98, 7.46 (2d, 8H, H_{arom}, $^3J_{HH}$ = 8.43 Hz), ^{13}C NMR ($CDCl_3$) δ(ppm) 28.77 (s, 2C, $2OCH_2\underline{C}H_2CH_2S$), 29.39 (s, 2C, $2OCH_2CH_2\underline{C}H_2S$), 33.46 (s, 2C, $2CO_2\underline{C}H_2S$), 30.50 (t, 2C, $2OCH_2\underline{C}H_2CF_2$, $^2J_{CF}$ = 21.73 Hz), 66.02 (s, 2C, $2O\underline{C}H_2CH_2CH_2S$), 57.20 (s, 2C, $2O\underline{C}H_2CH_2CF_2$), 170.13 (s, 2C, $2\underline{C}O_2$), 114.78, 127.57, 133.63, 157.92 (4s, 12C, C_{arom}), ^{19}F NMR ($CFCl_3$) δ(ppm) -81.90 (m, 6F), -114.48 (m, 4F, $2CF_{2\alpha}$), -122.61 (m, 4F, $2CF_{2\beta}$), -122.90 (m, 8F, $4CF_{2\gamma}$), -123.63 (m, 4F, $2CF_{2\delta}$), -124.48 (m, 4F, $2CF_{2\xi}$), -127.04 (m, 4F, $2CF_{2\omega}$), HRMS (ESI) calculated for: $(C_{42}H_{32}F_{34}O_6S_2Na)^+$: 1365.0989, found: 1365.0987.

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