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Molecular Design and Synthesis of Fluorinated Polyethers toward Organic Materials with High Dielectric Constants and Ferroelectricity

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Molecular design and synthesis of organic ferroelectric materials with a –$OCH_2CF_2CH_2O$– moiety as the basic molecular structure were conducted in order to improve the high coercive field value of poly(vinylidene fluoride) (PVDF). The synthesis of the designed molecules were based on the half ester 2,2-difluoro-1,3-propanediol *N*,*N*-diethylcarbamamic acid. The sequence of alkylation of alcohol, deprotection, and the second alkylation efficiently produced the desired polyethers except in the case of the Williamson ether synthesis, which occurs between a fluorinated alcohol and a fluorinated tosylate. The dielectric constants of the prepared polyethers at room temperature were relatively high, although no ferroelectric properties were observed. Another method had functional groups at the end of the molecules for intermolecular interaction. Hydrogen-bonded bisacetamide showed dielectric relaxation and ferroelectricity.

Ferroelectric materials are substances that respond to changes in the applied electric field and memorize them, and they are widely used in electric and electronic devices, such as capacitors, transducers, actuators, ferroelectric random access memory (FeRAM) devices, etc.[1,2] Electrically and mechanically stable inorganic ferroelectric materials, such as $BaTiO_3$ and lead zirconate titanate (PZT), are commonly used in such electronic devices. Organic ferroelectric materials[3] are also known, and the macromolecular PVDF and its copolymer with trifluoroethene (PVDF–PTrFE) are superior to the inorganic materials with regard to processability.[4] However, since the ferroelectric properties of PVDF or PVDF–PTrFE result from parallel alignment of dipoles that are due to alternating fluorinated and hydrogenated carbons of the polymer backbone, switching of the polarity requires rotation of the individual polymer molecules in the tangled van der Waals network. Consequently, a higher voltage than that for inorganic materials must be applied. Recently, a new organic ferroelectric material consisting of cocrystals of π-conjugated molecules with a low coercive field (E_c) value has been reported. Nevertheless, the ferroelectric phase only occurs at temperatures below 250 K.[5]

We have previously proposed an alternative molecular structure, 2,2-difluoropropane-1,3-dioxy group (–$OCH_2CF_2CH_2O$–) for organic materials with a high dielectric constant and ferroelectric materials.[6] The ether functionality forms a dipole similar to the –CF_2– bond as shown in Fig. 1. Although the dipole moment is smaller than the PVDF skeleton, the flexibility of the ether bonds[7] is expected to assist molecular motion by alternating the electric field.

In this paper, we report the molecular design and synthesis of fluorinated polyethers with relatively high dielectric constants. While most of the synthesized materials were not ferroelectric, a hydrogen-bonded compound showed dielectric relaxation and ferroelectricity at room temperature.

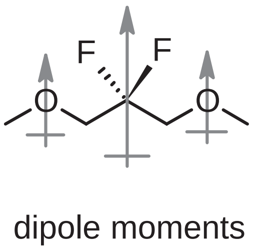

Fig. 1. Dipole alignment of 2,2-difluoropropane-1,3-dioxy group structure under electric poling.

Results and Discussion

We have reported the synthesis of a *m*-xylylene-connected polyether **1**.[6] In this molecule, there are two major dipoles (–CF_2–) and four minor dipoles (–O–) across the molecular axis. Under an electric field, these dipoles can be aligned in parallel as shown in Fig. 1. In a similar manner, an alkyl-chain-terminated molecule **2**, a tripod molecule **3**, and a molecule with integrated 2,2-difluoropropane-1,3-dioxy units (four major dipoles and six minor dipoles: **4**) were designed (Chart 1). In the design of these molecules, the *m*-xylylene backbone structure was incorporated in order to maintain a linear conformation of the polyether moieties, instead of employing the *p*-xylylene structure, which would cause an anti-parallel alignment of the dipoles. We anticipated, in part, π-stacking effects and also ease of etherification of benzyl bromides.

Preparation of the polyether **1** was started with the radical addition of 2,2-difluoroethenyl *N*,*N*-diethylcarbamate (**5**) to 2,2-dimethyl-1,3-dioxolane,[8] and the half-protected 2,2-difluoro-1,3-propanediol **6**,[6] which is an important synthetic intermediate, was used. For the preparative scale experiments, the preparation sequence for **6** was slightly changed, as shown in Scheme 1. The radical reaction of the fluorinated olefin **5** was initiated by dibenzoyl peroxide in 2-ethyl-2-methyl-1,3-

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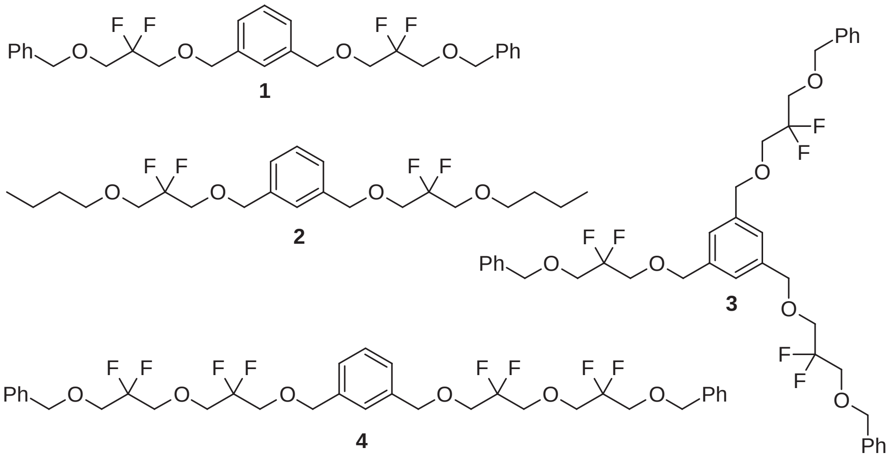
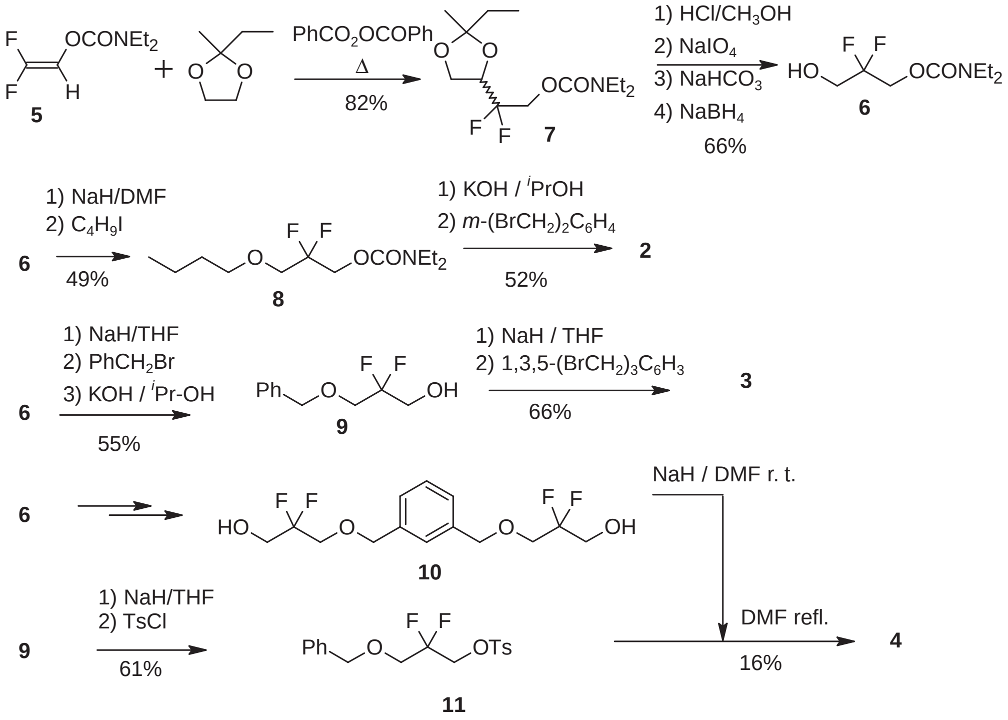


Chart 1.



Scheme 1.

dioxolane, which can be readily prepared from 2-butanone and ethylene glycol,[9] and gave a 1:1 mixture of the addition product stereoisomers **7** in 82% yield. The roughly isolated stereoisomeric mixture of adducts **7** was treated with hydrochloric acid in methanol, sodium periodate for glycol cleavage, $NaHCO_3$ for neutralization, and finally $NaBH_4$ for reduction of the aldehyde in a one-pot reaction to give monoalcohol **6** in 66% yield.

For the preparation of alkyl-chain-terminated compound **2**, alcohol **6** was first alkylated with NaH and 1-iodobutane, deprotected with alkaline hydrolysis, and then reacted with NaH and *m*-bis(bromomethyl)benzene (52%). Tripod molecule **3** was synthesized starting from alcohol **6** to convert it into alcohol **9** (55%), which was then successively reacted with 1,3,5-tris(bromomethyl)benzene (66%). In the case of the synthesis of polyether **4**, alcohol **9** was first tosylated, affording tosylate **11**, and **11** was reacted with previously reported diol **10**.[6] While the reaction of sodium alkoxide of diol **10** and tosylate **11** is a typical condition of the Williamson ether synthesis, it was unusually sluggish because of the retarded reactivities of both the reactants which had electron-withdrawing fluorine substituents. The reaction in refluxing DMF gave polyether **4** in low yield (16%).

In Table 1, the relative dielectric constants of polyethers **1**–**4** recorded at room temperature (100 Hz) are summarized. The experimental dielectric constants were corrected using the value for *o*-dichlorobenzene as a standard. As expected, all four polyethers **1**–**4** had relatively high dielectric constants and were comparable to a typical high-dielectric-constant compound, nitrobenzene. This implies that molecular design of the organic materials with a high dielectric constant based on the 2,2-difluoropropane-1,3-dioxy structure is reliable.

Since the dielectric constants of 2,2-difluoropropane-1,3-dioxy containing compounds **1**–**4** were all comparable and independent of the molecular structure, the contribution of the fluorinated ether structure to the high dielectric constants was concluded to be determined by the content of the fluorinated ether moiety in the molecule.

For the organic ferroelectric materials, the dielectric constants depend on the measuring frequency.[10] However, the dielectric constants of compounds **1**–**4** and the applied frequency (10–100 kHz) showed almost no correlation. These compounds are all light oil materials at room temperature because of the weak intermolecular interactions, which are peculiar to fluorinated organic compounds.[11] In the case of the PVDF, the accumulated van der Waals interaction of individual polymer molecules forces the dipole-aligned conformation to be maintained against electric field switching (high E_c values).[3] This suggests a strategy for the molecular design of new organic ferroelectric materials. If each molecule has two or more interactive functional groups that are stronger than the van der Waals bonding, the motion of the dipole-aligned molecules should be restricted, and thus a bulk ferroelectric property is expected. As a basic molecular structure, we selected polyether **1**. Instead of the benzyl groups in compound **1**, 4-nitrobenzyl (**12**), 4-aminobenzyl (**13**), and 4-acetamidobenzyl (**14**) groups (see Scheme 2), were employed as terminal groups for the intermolecular polar interactions. 4-Nitrobenzylation of diol **10** was carried out by treatment with 4-nitrobenzyl bromide and Ag_2O in refluxing benzene to give **12** in 31% yield.[12] Diamine **13** was obtained by the catalytic hydrogenation of **12** (58%) with palladium on carbon (Pd/C), and acetylation of **13** with acetic anhydride yielded bisacetamide **14** (73%). In comparison to the prototype compound **1**, bifunctional compounds **12**–**14** have the higher viscosities at room temperature indicating enhanced intermolecular interactions. Particularly, bisacetamide **14** is an extremely viscous fluid at room temperature resulting from a strong hydrogen-bonding, which appears stronger than that of aniline derivative **13** on the basis of the estimated hydrogen-bond energies of aniline[13] and acetanilide.[14]

In Table 1, the dielectric constants of **12**–**14** are also shown (100 Hz). Unexpectedly, the dielectric constants of nitro and amino compounds **12** and **13** were lower than **1**, probably because of the unfavorable dipoles resulting from the added functional groups. However, bisacetamide **14** ($\varepsilon' = 43$) had the highest dielectric constant among all our compounds.

The frequency dependence of the dielectric constants of **12**–**14** and **1** were evaluated at 100 Hz, 1 kHz, 10 kHz, and 100 kHz and are summarized in Fig. 2. The dielectric constants of **1**, **12**, and **13** were affected slightly by changes in the mea-

Table 1. Relative Dielectric Constants of Benzene Derivatives with $-OCH_2CF_2CH_2O-$ Substructure at Room Temperature (100 Hz)

Entry	Compounds	Relative dielectric constants (ε')
1	**1**	36.8
2	**2**	38.7
3	**3**	36.1
4	**4**	34.1
5	**12**	29.1
6	**13**	21.9
7	**14**	43.7
8	*o*-Dichlorobenzene (experimental standard)	10.12[a)]
9	Nitrobenzene	34.74[a)]

a) Literature values (Ref. 16).

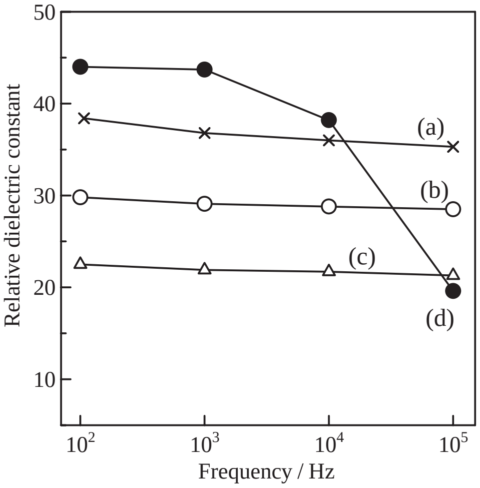
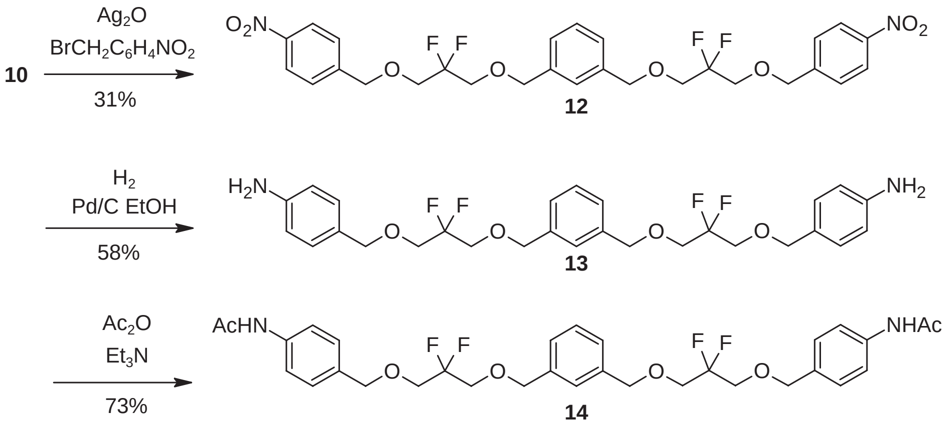


Fig. 2. Frequency dependence of relative dielectric constants of ethers (a) **1**, (b) **12**, (c) **13**, and (d) **14**.



Scheme 2.

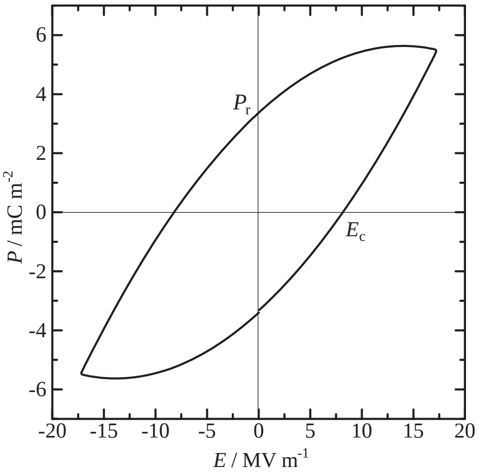


Fig. 3. Electric field–polarization profile of bisamide **14**.

surement frequency. However, the dielectric constant of bisacetamide **14** considerably decreased from $\varepsilon' = 43$ at 100 Hz to $\varepsilon' = 19$ at 100 kHz. Such dielectric relaxation behavior has often been observed in ferroelectric liquid crystals[15] and suggests that the molecular motion is restricted at higher frequencies by the intermolecular hydrogen bonding.

The ferroelectric property of the most promissing compound **14** was evaluated using a cell between indium tin oxide (ITO) glass electrodes with a 25-µm-thick film spacer of poly(ethylene terephthalate) (PET) at room temperature in the range of ±450 V bias voltages at 1 Hz. As shown in Fig. 3, a ferroelectric hysteresis loop of the polarization–electric field (P–E) characteristic was observed at this frequency. Unfortunately, the polarization did not reach a saturated value due to an insulation failure in the liquid film at higher bias voltages. Thus, the residual polarization ($P_r = 3.3\,\mathrm{mC\,m^{-2}}$) was considerably smaller than PVDF (ca. $60\,\mathrm{mC\,m^{-2}}$),[3] but the coercive field ($E_c = 8.2\,\mathrm{MV\,m^{-1}}$) was close to the saturated value according to the P–E characteristics profile of PVDF.[3] As expected, the effect of substituting part of the difluoromethylene groups of the PVDF molecular structure with oxygen atoms caused a decrease in the coercive field, which was ca. 20% of that of PVDF ($E_c = 45\,\mathrm{MV\,m^{-1}}$).[3]

In summary, we designed a fluorinated polyether structure for preparing organic ferroelectric materials. The designed 2,2-difluoropropane-1,3-dioxy group structure was highly oriented under an electric field, while a disorder of the dipole alignment rapidly occurred when the applied electric field was switched off. Intermolecular hydrogen bonding helped to maintain the ordered structure and bisacetamide **14** showed ferroelectricity at room temperature. For fine tuning the molecular design of this type of new organic ferroelectric materials, it is essential that the following two molecular structural factors must be balanced: 1) there must be a high population of the flexible –$OCH_2CF_2CH_2O$– moieties for the alignment of the dipoles, and 2) it must have relatively constrained intermolecular bonds that intervene in the rapid molecular motion. The lower coercive field value of the non-crystalline organic ferroelectric material observed here is an important factor for application in low-voltage operating electronic devices used at ambient temperatures.

Experimental

^{1}H NMR spectra were recorded on a 300 MHz spectrometer with $Si(CH_3)_4$ as an internal standard, and ^{19}F NMR spectra were recorded on a 282 MHz spectrometer with CF_3COOEt as an internal standard (δ −75.75 from $CFCl_3$).

4-[2-(*N*,*N*-Diethylcarbamoyloxy)-1,1-difluoroethyl]-2-ethyl-2-methyl-1,3-dioxolane (7). To a refluxing solution of 2,2-difluoroethenyl *N*,*N*-diethylcarbamate (**5**) (12.6 g, 70 mmol) in 2-ethyl-2-methyl-1,3-dioxolane (220 mL, 1.76 mol), solid dibenzoyl peroxide was added portionwise in a rate of 20 mg in every 5–10 min (totally 2.7 g, 11 mmol). When the amount of unreacted **5** was less than 10% of the initial amount, the solvent was recovered by distillation. The cooled residue was dissolved in Et_2O, and the solution was washed with saturated aqueous $NaHCO_3$ to remove benzoic acid. The solution was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on an SiO_2 column (hexane:AcOEt = 5:1) to give a diastereomer mixture (1:1) of dioxolane **7** as a colorless oil: 17.0 g (82%); IR (neat film) 2977, 2937, 1715, 1429, 1276, 1166, 1084 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (1.5H, t, $J = 7.5$ Hz), 0.94 (1.5H, t, $J = 7.5$ Hz), 1.14 (6H, t, $J = 7.2$ Hz), 1.31 (1.5H, s), 1.38 (1.5H, s), 1.61–1.76 (2H, m), 3.24–3.36 (4H, m), 3.88–3.99 (2H, m), 4.08–4.52 (3H, m); ^{19}F NMR ($CDCl_3$) δ −115.2 (1F × 0.5, dtd, $J = 261$, 16, 5 Hz), −115.9 (1F × 0.5, dtd, $J = 261$, 17, 5 Hz), −123.1 (1F × 0.5, dddd, $J = 261$, 22, 12, 7 Hz), −123.2 (1F × 0.5, dddd, $J = 261$, 17, 10, 7 Hz); EI-MS m/z (%) 295 (0.2, M$^+$), 280 (11), 266 (29), 100 (100), 73 (11), 72 (20), 57 (30), 56 (20), 55 (14). Anal. Found: C, 53.02; H, 8.04; N, 4.91%. Calcd for $C_{13}H_{23}F_2NO_4$: C, 52.87; H, 7.85; N, 4.74%.

2,2-Difluoro-3-(*N*,*N*-diethylcarbamoyoxy)-1-propanol (6). Dioxolane **7** (16.3 g, 55 mmol) was dissolved in methanol (100 mL), and conc. HCl (12 mL) was added to the resulting solution. The solution was stirred overnight at room temperature. To the solution, $NaIO_4$ (14 g, 65 mmol) and water (20 mL) were added, and the mixture was stirred for 3 h at room temperature. To the mixture, solid $NaHCO_3$ was carefully added portionwise to neutralize the mixture. Solid $NaBH_4$ (4 g, 106 mmol) was added portionwise to the ice-cooled mixture. The resulting mixture was stirred for 30 min at room temperature. After filtration and removal of the solvent under reduced pressure, the residue was dissolved to water. The aqueous solution was extracted with Et_2O, and the combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was distilled to obtain alcohol **6** as a colorless oil: 7.65 g (66%); bp 124–126 °C (3 mmHg). Spectral data of this material were identical with an authentic sample.[6]

***m*-Bis[(3-butoxy-2,2-difluoropropoxy)methyl]benzene (2).** NaH (60% oil dispersion, 1.00 g, 25 mmol) was suspended to anhydrous DMF (10 mL), and then to the ice-cooled suspension, alcohol **6** (4.06 g, 19 mmol) dissolved in anhydrous DMF (20 mL) was added dropwise under N_2 atmosphere. After H_2 evolution had stopped, 1-iodobutane (4.3 mL, 39 mmol) was added, and the resulting mixture was refluxed for 8 h. The cooled mixture was poured onto water and extracted with Et_2O. The combined extracts were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on an SiO_2 column (hexane:EtOAc = 5:1) to give pure 2,2-difluoro-4-oxaoctyl *N*,*N*-diethylcarbamate (**8**): 2.51 g (49%); IR (neat film) 2963, 2917, 1713, 1428, 1273, 1166, 1131 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, $J = 7.5$ Hz), 1.14 (6H, t, $J = 7.2$ Hz), 1.37 (2H, sextet, $J = 7.8$ Hz), 1.57 (2H, quintet, $J = 7.5$ Hz), 3.26–3.30 (4H, m), 3.54 (2H, t, $J = 6.6$ Hz), 3.68 (2H, t, $J = 12.6$ Hz), 4.37

(2H, t, $J = 12.9$ Hz); ^{19}F NMR ($CDCl_3$) δ −113.6 (quintet, $J = 12$ Hz); EI-MS m/z (%) 267 (0.5, M^+), 180 (24), 116 (23), 100 (20), 72 (12), 58 (16), 57 (100). Anal. Found: C, 53.99; H, 8.86; N, 5.19%. Calcd for $C_{12}H_{23}F_2NO_3$: C, 53.92; H, 8.67; N, 5.24%.

This carbamate **8** (2.51 g, 9.4 mmol) was dissolved in 2-propanol (70 mL). To the solution, KOH (5.60 g, 100 mmol) was added, and the resulting mixture was refluxed for 20 h. To the mixture, water was added, and the solution was neutralized by addition of dilute hydrochloric acid. The mixture was extracted with EtOAc, and the combined extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure to give crude 2,2-difluoro-4-oxaoctan-1-ol, which was used at the next step without purification: 1.22 g (77%): ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, t, $J = 7.2$ Hz), 1.37 (2H, sextet, $J = 7.2$ Hz), 1.58 (2H, quintet, $J = 7.2$ Hz), 3.55 (2H, t, $J = 6.6$ Hz), 3.74 (2H, t, $J = 12.3$ Hz), 3.87 (2H, t, $J = 12.9$ Hz); ^{19}F NMR ($CDCl_3$) δ −115.1 (quintet, $J = 12$ Hz).

NaH (60% oil dispersion, 200 mg, 5 mmol) was suspended in anhydrous DMF (5 mL). To the ice-cooled mixture, a solution of the above alcohol (1.0 g, 5.9 mmol) in anhydrous DMF (5 mL) was added. After evolution of H_2 had stopped, a solution of α,α'-dibromo-*m*-xylene (530 mg, 2 mmol) in anhydrous DMF (5 mL) was added at room temperature. The resulting mixture was stirred overnight at room temperature. The mixture was diluted with water and extracted with Et_2O. The combined extracts were dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on an SiO_2 column (hexane:EtOAc = 10:1) to give polyether **2** as a colorless oil: 587 mg (67%); IR (neat film) 2977, 2917, 2873, 1461, 1295, 1117, 988, 792, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (6H, t, $J = 7.5$ Hz), 1.36 (4H, sextet, $J = 7.5$ Hz), 1.56 (4H, quintet, $J = 7.5$ Hz), 3.53 (4H, t, $J = 6.6$ Hz), 3.71 (4H, t, $J = 12.6$ Hz), 3.74 (4H, t, $J = 12.6$ Hz), 4.63 (4H, s), 7.26–7.36 (4H, m); ^{19}F NMR ($CDCl_3$) δ −113.1 (quintet, $J = 12$ Hz); EI-MS m/z (%) 270 (41), 213 (20), 151 (29), 119 (100). Anal. Found: C, 60.53; H, 7.99%. Calcd for $C_{22}H_{34}F_4O_4$: C, 60.26; H, 7.82%.

2,2-Difluoro-5-phenyl-4-oxapentan-1-ol (9). Alcohol **6** (4.64 g, 22 mmol) and NaH (60% oil dispersion: 1.07 g, 27 mmol) were dissolved in THF (20 mL). After H_2 evolution had stopped, benzyl bromide (4.2 g, 24 mmol) was added dropwise under ice-cooling. The resulting mixture was stirred at room temperature overnight. A small amount of water was added into the mixture, and the mixture was extracted with Et_2O. The combined extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residual mixture was purified with SiO_2 column chromatography (hexane:EtOAc = 5:1) to afford 2,2-difluoro-5-phenyl-4-oxapentyl *N*,*N*-diethylcarbamate (4.56 g; 69%): colorless oil; IR (neat film) 2976, 1713, 1479, 1429, 1275, 1167, 1097, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (6H, t, $J = 7.5$ Hz), 3.18–3.31 (4H, m), 3.71 (2H, t, $J = 12.5$ Hz), 4.40 (2H, t, $J = 12.8$ Hz), 4.62 (2H, s), 7.27–7.38 (5H, m); ^{19}F NMR ($CDCl_3$) δ −113.7 (quintet, $J = 12$ Hz); EI-MS m/z (%) 301 (0.12, M^+), 195 (10), 180 (28), 160 (21), 116 (34), 100 (26), 91 (100), 72 (11). Anal. Found: C, 59.72; H, 7.19; N, 4.50%. Calcd for $C_{15}H_{21}F_2NO_3$: C, 59.79; H, 7.02; N, 4.65%.

This benzyl derivative (7.0 g, 23 mmol) was dissolved in 2-propanol (30 mL). To the solution, KOH (5.60 g, 100 mmol) was added, and the resulting mixture was refluxed for 24 h. To the mixture, water was added, and the mixture was extracted with EtOAc. The combined extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on an SiO_2 column (hexane:EtOAc = 5:1) to obtain pure alcohol **9**: 3.70 g (79%): IR (neat film) 3401, 3066, 2936, 1455, 1299, 1211, 1106, 1078, 906, 741, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.98 (1H, t, $J = 7.1$ Hz), 3.77 (2H, t, $J = 12.5$ Hz), 3.89 (2H, t, $J = 12.5$ Hz), 4.63 (2H, s), 7.30–7.40 (5H, m); ^{19}F NMR ($CDCl_3$) δ −115.3 (quintet, $J = 12$ Hz); EI-MS m/z (%) 202 (59, M^+), 108 (11), 107 (78), 92 (23), 91 (100), 79 (30), 77 (24), 65 (42), 51(35). Anal. Found: C, 59.72; H, 6.34%. Calcd for $C_{10}H_{12}F_2O_2$: C, 59.40; H, 5.98%.

1,3,5-Tris(4,4-difluoro-7-phenyl-2,6-dioxaheptyl)benzene (3). Alcohol **9** (1.65 g, 8.2 mmol) and NaH (60% oil dispersion: 250 mg, 6.2 mmol) were dissolved in anhydrous THF (5 mL). After H_2 evolution had stopped, a THF solution (10 mL) of 1,3,5-tris-(bromomethyl)benzene (712 mg, 2.0 mmol) was added dropwise. The resulting mixture was stirred for 24 h. A small amount of water was added into the mixture, and the mixture was neutralized with hydrochloric acid. The mixture was extracted with Et_2O. The combined extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on an SiO_2 column (hexane:EtOAc = 5:2) to give pure polyether **3** as a colorless oil: 956 mg (66%); IR (neat film) 3032, 2917, 2857, 1604, 1454, 1109, 1000, 740, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.78 (6H, t, $J = 12.5$ Hz), 3.76 (6H, t, $J = 12.5$ Hz), 4.57 (6H, s), 4.60 (6H, s), 7.20 (3H, s), 7.28–7.35 (15H, m); ^{19}F NMR ($CDCl_3$) δ −112.9 (quintet, $J = 12$ Hz); EI-MS m/z (%) 517 (2.2), 427 (20), 337 (20), 317 (32), 303 (23), 227 (19), 209 (12), 202 (15), 201 (100), 193 (15), 181 (14), 123 (14), 119 (12), 107 (39), 105 (15). Anal. Found: C, 64.73; H, 6.06%. Calcd for $C_{39}H_{42}F_6O_6$: C, 64.99; H, 5.87%.

1,3-Bis(4,4,8,8-tetrafluoro-11-phenyl-2,6,10-trioxaundecyl)-benzene (4). To an ice-cooled suspension of NaH (60% oil dispersion: 1.08 g, 27 mmol) in anhydrous THF (15 mL), a solution of alcohol **9** (5.16 g, 25 mmol) in THF (15 mL) was added. After evolution of hydrogen stopped, a solution of *p*-toluenesulfonyl chloride (6.18 g, 32 mmol) in THF (20 mL) was added, and the resulting mixture was stirred overnight. The mixture was diluted with water and extracted with Et_2O. The combined extracts were dried with $MgSO_4$, and the solvent was removed under reduced pressure. The crude tosylate **11** was used without further purification (5.56 g, 61%).

Already reported $\beta,\beta,\beta',\beta'$-tetrafluoro-1,3-benzenebis(δ-oxapentanol) (**10**) (1.95 g, 6.0 mmol) and NaH (60% oil dispersion: 520 mg, 13 mmol) were dissolved in anhydrous DMF (10 mL). To the mixture, a DMF solution (40 mL) of above-mentioned tosylate (5.56 g, ca. 15 mmol) was added dropwise at room temperature. The mixture was refluxed for 21 h. A small amount of water was added into the mixture, and the mixture was neutralized with hydrochloric acid. The mixture was extracted with Et_2O. The combined extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was successively chromatographed on SiO_2 columns (hexane:EtOAc = 10:1–5:1) to give pure polyether **4** as a pale yellow oil. Yield: 650 mg (16%); IR (neat film) 3032, 2977, 2917, 2874, 1454, 1122, 913, 738, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (8H, t, $J = 12.4$ Hz), 3.73 (8H, t, $J = 12.6$ Hz), 4.63 (8H, s), 7.30–7.36 (14H, m); ^{19}F NMR ($CDCl_3$) δ −113.2 (quintet, $J = 12$ Hz); EI-MS m/z (%) 295 (29, $C_6H_5CH_2(OCH_2CF_2CH_2)_2O^+$), 201 (50), 183 (33), 107 (100), 105 (41). Anal. Found: C, 59.04; H, 5.77%. Calcd for $C_{34}H_{38}F_8O_6$: C, 58.79; H, 5.51%.

1,3-Bis[4,4-difluoro-7-(4-nitrophenyl)-2,6-dioxaheptyl]benzene (12). Diol **10** (1.0 g, 3.1 mmol) and *p*-nitrobenzyl bromide (2.6 g, 12 mmol) was dissolved in benzene (15 mL), and then Ag_2O (2.3 g, 10 mmol) was added in one portion. The mixture was refluxed with vigorous stirring for 36 h. The cooled mixture was filtered, and the solvent of the filtrate was removed under reduced pressure. The residue was chromatographed on an SiO_2 column (hexane:EtOAc = 5:1–1:1) to give pure polyether **13** as a pale orange-colored highly viscous liquid: 567 mg (31%); IR (neat film) 3077, 2928, 2857, 1610, 1526, 1460, 1347, 1118, 1022, 916, 855, 810, 749, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.78 (4H, t, $J =$ 12.5 Hz), 3.83 (4H, t, $J =$ 12.5 Hz), 4.62 (4H, s), 4.71 (4H, s), 7.25–7.36 (4H, m), 7.46 (4H, d, $J =$ 8.4 Hz), 8.18 (4H, d, $J =$ 8.4 Hz); ^{19}F NMR ($CDCl_3$) δ -112.9 (quintet, $J =$ 12 Hz); EI-MS m/z (%) 230 (70), 152 (52), 106 (92), 104 (100). Anal. Found: C, 56.60; H, 4.89; N, 4.63%. Calcd for $C_{28}H_{28}F_4N_2O_8$: C, 56.38; H, 4.73; N, 4.70%.

1,3-Bis[7-(4-aminophenyl)-4,4-difluoro-2,6-dioxaheptyl]benzene (13). Nitrobenzyl derivative **12** (567 mg, 0.95 mmol) was dissolved in EtOAc (5 mL). To the solution, palladium/carbon (10% Pd, 11 mg, 0.01 mmol) was added. The resulting mixture was vigorously stirred overnight under H_2 (1 atm) at room temperature. The mixture was filtered, and the solvent was removed under reduced pressure. The residue was almost pure diamine **13** (a pale orange-colored highly viscous liquid): 300 mg (58%); IR (neat film) 3460, 3373, 3226, 3032, 2917, 2875, 1622, 1518, 1454, 1290, 1103, 994, 916, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.02 (4H, brs), 3.70 (4H, t, $J =$ 12.4 Hz), 3.75 (4H, t, $J =$ 12.5 Hz), 4.48 (4H, s), 4.58 (4H, s), 6.65 (4H, d, $J =$ 8.4 Hz), 7.10 (4H, d, $J =$ 8.4 Hz), 7.23–7.36 (4H, m); ^{19}F NMR ($CDCl_3$) δ -112.8 (quintet, $J =$ 12 Hz); EI-MS m/z (%) 536 (3.9, M^+), 430 (17), 216 (21), 123 (18), 106 (100). Anal. Found: C, 62.53; H, 6.05; N, 5.19%. Calcd for $C_{28}H_{32}F_4N_2O_4$: C, 62.68; H, 6.01; N, 5.22%.

1,3-Bis[7-(4-acetamidophenyl)-4,4-difluoro-2,6-dioxaheptyl]benzene (14). Diamine **13** (38 mg, 0.07 mmol) was dissolved in EtOAc (3 mL). To the solution, acetic anhydride (10 µL, 0.10 mmol) and triethylamine (10 µL, 0.08 mmol) were added, and the resulting solution was stirred at room temperature for 2 h. The solution was washed with a small amount of H_2O and dried with Na_2SO_4. After removal of the solvent, the residue was chromatographed on an SiO_2 column (EtOAc) to give pure **14** as a faintly yellow and highly dense liquid: 32 mg (73%); IR (neat film) 3307, 3193, 3124, 2961, 2921, 2872, 1668, 1604, 1537, 1410, 1316, 1106, 1004, 827, 791 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.17 (6H, s), 3.72 (4H, t, $J =$ 12.6 Hz), 3.75 (4H, t, $J =$ 12.5 Hz), 4.55 (4H, s), 4.57 (4H, s), 7.23 (4H, d, $J =$ 8.5 Hz), 7.24 (2H, br s), 7.28–7.35 (4H, m), 7.46 (4H, d, $J =$ 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ -112.8 (quintet, $J =$ 12 Hz); EI-MS m/z (%) 621 (0.7), 620 (0.6, M^+), 148 (28), 136 (15), 119 (24), 106 (100). Anal. Found: C, 61.79; H, 6.15; N, 4.36%. Calcd for $C_{32}H_{36}F_4N_2O_6$: C, 61.93; H, 5.85; N, 4.51%.

Measurement of Relative Dielectric Constants of Compounds 1, 2, 3, 4, 12, 13, and 14, and *P–E* Characteristics of Bisacetamide 14. Relative dielectric constants were measured using liquid film cells (5–10 cm^2) sandwiched between two ITO glass cover plates with a 25-µm- or 50-µm-thick PET film spacer, and they were recorded on an impedance analyzer at several frequencies at room temperature. The acquired dielectric constant data were calibrated by using the literature data for *o*-dichlorobenzene ($\mathcal{E}' = 10.12$).[16] The cell with a 25-µm-thick film spacer was also used to obtain a *P–E* field characteristic of bisacetamide **14** at 1 Hz by applying several bias voltages until 450 V at room temperature.

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References

1 a) E. Fatuzzo, W. J. Merz, *Ferroelectricity*, North-Holland Publishing, Amsterdam, **1967**. b) M. E. Lines, A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon Press, Oxford, **1977**.

2 *Ferroelectric Random Access Memories: Fundamentals and Applications*, ed. by H. Ishikawa, M. Okayama, Y. Arimori, Springer-Verlag, Berlin, **2004**.

3 T. Furukawa, *Phase Transitions* **1989**, *18*, 143.

4 W. Jillek, W. K. C. Young, *Int. J. Adv. Manuf. Technol.* **2005**, *25*, 350.

5 S. Horiuchi, F. Ishii, R. Kumai, Y. Okimoto, H. Tachibana, N. Nagaosa, Y. Tokura, *Nat. Mater.* **2005**, *4*, 163.

6 T. Okano, A. Nakajima, S. Eguchi, *Synlett* **2001**, 1449.

7 a) R. G. Snyder, G. Zerbi, *Spectrochim. Acta, Part A* **1967**, *23*, 391. b) S. E. Ulic, H. Oberhammer, *J. Phys. Chem. A* **2004**, *108*, 1844.

8 A. J. Bennett, J. M. Percy, M. H. Rock, *Synlett* **1992**, 483.

9 H. J. Dauben, Jr., B. Lölen, H. J. Ringold, *J. Am. Chem. Soc.* **1954**, *76*, 1359.

10 R. Casalini, C. M. Roland, *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 1975.

11 K. Reichenbächer, H. I. Süss, J. Hulliger, *Chem. Soc. Rev.* **2005**, *34*, 22.

12 K. Kukase, H. Tanaka, S. Torii, S. Kusumoto, *Tetrahedron Lett.* **1990**, *31*, 389.

13 J. H. Landy, K. B. Whetsel, *J. Phys. Chem.* **1964**, *68*, 1001.

14 G. L. Perlovich, T. V. Volkova, A. Bauer-Brandl, *J. Pharm. Sci.* **2006**, *95*, 2158.

15 S. K. Prasad, S. M. Khened, *Moderen Topics in Liquid Crystals*, ed. by A. Buka, World Scientific, Singapore, **1993**, pp. 271–284.

16 C. Wohlfarth, *Landolt-Börnstein Numerical Data and Functional Relationship in Science and Technology, gr. IV*, ed. by O. Madelung, Springer-Verlag, Berlin, **1991**, Vol. 6.