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Synthesis and properties of (*E*)-1,2-difluoroethylene derivatives: improvement of the ultraviolet light stability

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The synthesis and properties of (*E*)-α,β-difluorostilbene derivatives were studied. In particular, we investigated three suppression methods of (*E*)–(*Z*) isomerisation by shortening the molecular conjugation length, which included the introduction of a fluorine atom into the *ortho* or *para* position of the benzene ring or the replacement of the benzene ring with a cyclohexane ring. The relationship between the molecular structure of liquid crystals and the level of isomerisation by ultraviolet (UV) light was discussed.

Keywords: (*E*)-α,β-difluorostilbene derivatives; isomerisation; UV photostability; molecular conjugation length

1. Introduction

High birefringence (Δn) liquid crystals (LCs) are useful not only in conventional display devices, but also in the scattering type of polymer-dispersed liquid crystal displays (PDLCDs) (*1*, *2*) and cholesteric liquid crystal displays (LCDs) (*3*, *4*) as reflective LCDs with low power consumption. The response time (τ) of twisted nematic (TN) LCDs is proportional to the product of the LC's rotational viscosity (γ_1) and the cell gap (*d*) squared (*5*):

$$\tau_{\text{on}} = \gamma_1 \times d^2/\varepsilon_0 \times \Delta\varepsilon(V^2 - V_c^2) \qquad (1)$$

and

$$\tau_{\text{off}} = \gamma_1 \times d^2/\varepsilon_0 \times \Delta\varepsilon V_c^2, \qquad (2)$$

where τ_{on} is the switching-on time and τ_{off} is the switching-off time, ε_o is the static dielectric constant and $\Delta\varepsilon$ is dielectric anisotropy, V is the operating voltage and V_c is Frederik's threshold voltage.

The transmittance (*T*) of the TN-LCD is represented in (*6*)

$$T = \sin^2(\pi/2 \times (1 + u^2)^{1/2}) \times (1 + u^2)^{-1}, \qquad (3)$$

where $u = 2d\Delta n/\lambda$ and λ is the wavelength of the transmitted radiation.

In the Gooch–Tarry curve for a wavelength equal to 550 nm, it is necessary for the *u* value to equal root 3 (first minimum), or root 15 (second minimum) for the high contrast ratio of brightness (*6*). This means that the product of Δn and *d* is constant. Therefore, for high-speed responses, high Δn LC materials are useful for making the cell gap (*d*) smaller.

A high Δn value can be achieved by increasing the molecular conjugation length (*7*). A considerable number of π-conjugated compounds have been developed as high Δn LCs (*8*). Molecules that contain highly-polarisable groups with a high electron density, such as benzene rings or acetylene linking groups, will therefore have large optical anisotropies. Tolane-based LCs exhibit a reasonably high Δn value, comparatively low viscosity and good chemical, photo and thermal stability (*9*). We synthesised various (*E*)-α,β-difluorostilbene (DFS) compounds (Figure 1) and discovered them to have characteristic properties, such as high Δn values and extremely low viscosity (*10*, *11*). Googby *et al.* investigated these materials to show great promise as host materials for ferroelectric mixtures (*12*).

However, there is a problem with using these compounds in LCDs, as they isomerise to (*Z*)-structures in several per cent by ultraviolet (UV) light. The existence of slight (*Z*)-1,2-DFS affects the properties of the LC mixture because these compounds have no LC properties. Therefore, the improvement of the UV photo stability of (*E*)-structure compounds is essential. We studied three suppression methods of (*E*)–(*Z*) isomerisation by shortening the molecular conjugation length as shown in Figure 2.

In this paper, we report on the synthesis of novel (*E*)-1,2-difluoroethylene compounds **2**–**4** derived from iodotrifluoroethylene or tetrafluoroethylene, and the

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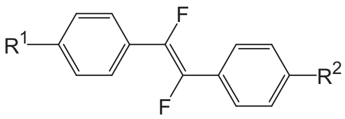


R^1,R^2: Alkyl, Alkoxy, CN, OCF_3 groups

Figure 1. (*E*)-α,β-DFS compounds.

properties of these compounds and the UV photo stability are discussed.

2. Results and discussion

2.1 *Excited state potential energy curves of α,β-DFS*

There have been many studies of *cis*-*trans* photo-isomerisation of stilbene (*13*); for example, the excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) plays an important role (*14*, *15*). In this study, the minimum energy structure of α,β-DFS was obtained by the PM3 method, based on the semi-empirical molecular orbital method (*16*), and the excitation energies of the ground state and the excited state were obtained by a Gaussian 90,92 program based on the *ab initio* molecular orbital method (*17*). The excited potential energy curves as a function of the C=C bond rotation were calculated. The results are shown in Figure 3.

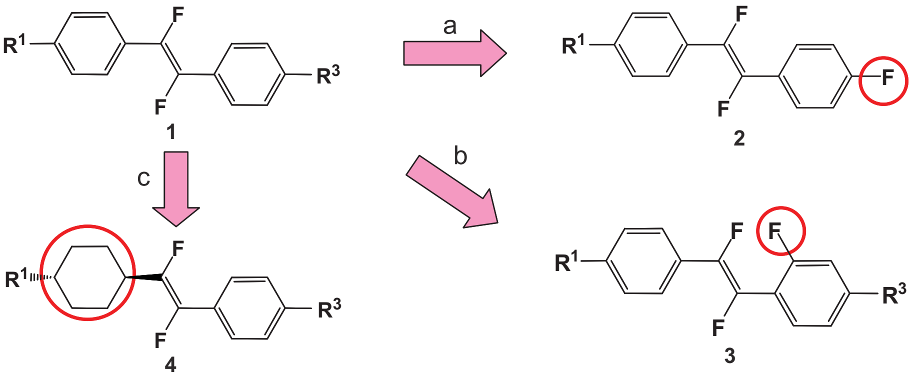
In the ground state, because there is a 120 kJ mol^{-1} barrier at 90 degrees of the dihedral angle, the isomerisation reaction cannot proceed. On the other hand, in the singlet excited state, there is no energy barrier, and the *cis* form is 50 kJ mol^{-1} more stable than the *trans* form. This means that the photo-isomerisation reaction from the *trans* form to the *cis* form takes place. Therefore, we investigated the suppression methods of (*E*)–(*Z*) isomerisation by decreasing the absorbance of UV light.

2.2 *spectra data of UV absorption and (Z) isomer formation ratio*

In order to shorten the molecular conjugation length compared with (*E*)-1,2-difluoro-1,2-bis(4-propylphenyl)ethylene (**1**), we synthesised three types of (*E*)-1,2-difluoroethylene compounds: (*E*)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-propylphenyl)ethylene (**2b**), (*E*)-1,2-difluoro-1-(2-fluoro-4-methylphenyl)-2-(4-propylphenyl)ethylene (**3**) and (*E*)-1,2-difluoro-1-(4-propylphenyl)-2-(4-*trans*-propylcyclohexyl)ethylene (**4a**). The conformation models are shown in Figure 4.

The spectral data of UV light absorption (λ_{max}), HOMO and LUMO energy levels, and the relative formation ratio of the (*Z*) isomer after the UV irradiation test for 300 hours are summarised in Table 1. The HOMO and LUMO energy levels were calculated using the semiempirical quantum chemical PM3 method (*17*).

Compound **2b** achieves low hyperconjugation of the π–σ bond between the benzene ring and the alkyl group by introducing a fluorine atom in one of benzene rings instead of an alkyl group. In compound **3**, in addition to the low hyperconjugation mentioned above, the repulsion between the introduced fluorine atom in the benzene ring and the fluorine atom on the ethylene bond causes the twisting conformation, which makes the resonance between the benzene ring and the ethylene bond reasonably weak. The compound **4a** has a cyclohexane ring instead of a benzene ring. In the



a: Introduction of 4-fluorophenyl group
b: Introduction of 2-fluoro-4-alkylphenyl group
c: Introduction of *trans*-4-alkylcyclohexyl group

Figure 2. Methods of decreasing the molecular conjugation length.

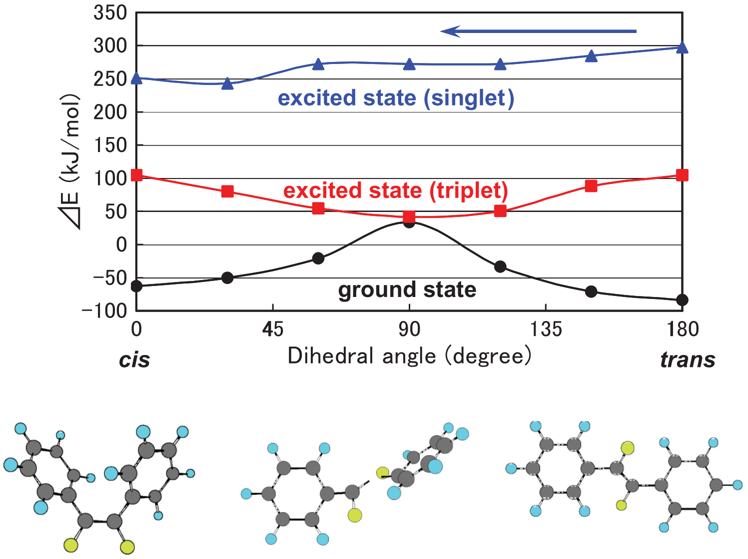


Figure 3. Potential curves of α,β-DFS.

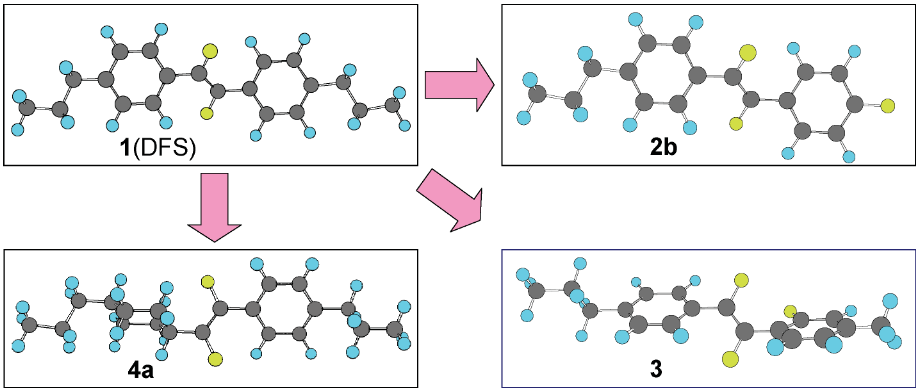
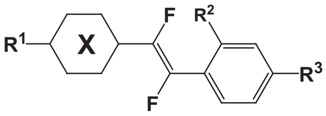


Figure 4. Structure of (*E*)-1,2-difluoroethylene compounds.

Table 1. Physical properties of (*E*)-1,2-difluoroethylene compounds.



Compound	R^1	X	R^2	R^3	λ_{max} (nm)	HOMO (eV)	LUMO (eV)	Δ*E* (eV)	Relative formation ratio[a]
1	*n*-C_3H_7	*p*-Phenylene	H	*n*-C_3H_7	305	−8.655	−0.789	7.866	1.0
2b	*n*-C_3H_7	*p*-Phenylene	H	F	300	−8.798	−0.768	8.030	0.64
3	*n*-C_3H_7	*p*-Phenylene	F	CH_3	284	−8.761	−0.601	8.160	0.33
4a	*n*-C_3H_7	*trans*-1,4-Cyclohexylene	H	*n*-C_3H_7	258	−8.874	−0.259	8.615	0.04

[a] Relative formation ratio of *Z* isomer after UV irradiation test for 300 hours.

spectral data of UV absorption, the maximum wavelength (λ_{max}) of compounds **2b**, **3** and **4a** are shifted to a shorter wavelength in that order. Moreover, the LUMO energy level increases of the same order of the molecule conformation that transforms the plane structure into the twisted structure. Therefore, the isomerisation reaction was suppressed in these novel compounds; in particular, compound **4a** was almost stable with regard to (*E*)–(*Z*) isomerisation.

2.3 Synthesis and performances of (E)-1,2-difluoroethylene compounds

The melting point (T_m), phase transition temperature (T_{ni}), kinematic viscosity (ν) and optical anisotropy value (Δn) of each compound were measured as a 20 wt% mixture to the host LC (ZLI-1565^{TM}). The extrapolation data of each LC material were calculated by following (*18*):

$$\begin{aligned} T_{ni \text{ measured}} &= 0.8 \times T_{ni \text{ ZLI-1565}} \\ &\quad + 0.2 \times T_{ni \text{ liquid crystal}} \\ \log_{10}(\nu_{\text{measured}}) &= 0.8 \times \log_{10}(\nu_{\text{ZLI-1565}}) \\ &\quad + 0.2 \times \log_{10}(\nu_{\text{liquid crystal}}) \\ \Delta n_{\text{measured}} &= 0.8 \times \Delta n_{\text{ZLI-1565}} + 0.2 \times \Delta n_{\text{liquid crystal}}. \end{aligned}$$

The results are summarised in Table 2.

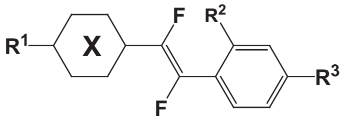
2.3.1 Synthesis and properties of (E)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-alkylphenyl)ethylenes (2a–2e)

New LC compound **2a–2e** was synthesised. The symmetric type of α,β-DFSs were synthesised by the reaction of phenyllithium reagents and tetrafluoroethylene (*19–23*) and other reactions (*24*). The stereoselective preparation method is published in (*25*). For synthesis of the antisymmetric type, the palladium-catalysed cross-coupling reaction of perfluoroalkenylzinc reagents with aryl iodides is a useful method (*26*, *27*). The reaction of trifluoroethenylzinc iodide with 1-fluoro-4-iodobenzene and Pd(PPh_3)$_4$ gave 1-(4-fluorophenyl)-1,2,2-trifluoroethylene. Subsequent nucleophilic replacement reaction with 4-alkylphenyllithium gave an *E* and *Z* mixture of 1,2-difluoro-1-(4-fluorophenyl)-2-(4-alkylphenyl)ethylene. The mixture was purified by recrystallisation from ethanol to give (*E*)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-alkylphenyl)ethylene (Scheme 1). The results of the cross-coupling reactions are shown in Table 3.

In the case of using 1-(4-fluorophenyl)-1,2,2-trifluoroethylene, stereoselectivity (*E*/*Z*) is about 80:20. In the nucleophilic replacement reaction with phenyllithium, two types of anion are formed, which are the unstable *cis* structure and the stable *trans* structure. In using 1-(4-fluorophenyl)-1,2,2-trifluoroethylene, the stereoselectivity (*E*/*Z* = 80:20) would be determined by the selectivity of this anion formation, because the rate of defluorination reaction is high (Figure 5). The gaps of heat of formation (ΔE) between the *cis*-form anion and the *trans*-form anion were calculated using the semiempirical quantum chemical PM3 method (MOPAC 6.0 package) (*17*).

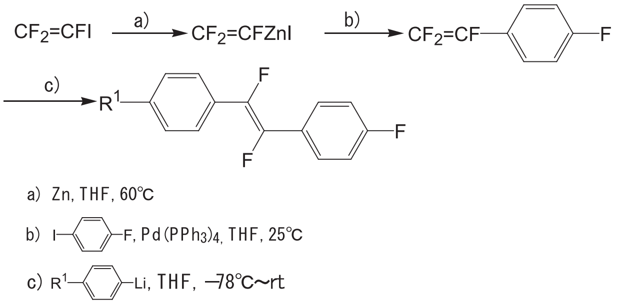
The compounds **2a**–**2e**, introducing a fluorine atom in the 4-position of the benzene ring, have kept high Δn in the range 0.21–0.25. It was found that the introduced fluorine atom affected the Δn values

Table 2. Physical properties of (*E*)-1,2-difluoroethylene compounds.



Compound	R^1	X	R^2	R^3	T_m (°C)	T_{ni}^a (°C)	$\nu^{a,b}$ (mm^2 s^{-1})	$\Delta n^{a,b}$	$\Delta n^{a,c}$
1	n-C_3H_7	*p*-Phenylene	H	n-C_3H_7	74.8	84.1	4.9	0.261	–
2a	C_2H_5	*p*-Phenylene	H	F	60.6	51.4	2.8	0.238	0.232
2b	n-C_3H_7	*p*-Phenylene	H	F	37.4	61.6	3.7	0.233	0.232
2c	n-C_5H_{11}	*p*-Phenylene	H	F	50.5	65.5	5.2	0.228	0.213
2d	CH_2=$CHCH_2CH_2$	*p*-Phenylene	H	F	38.2	70.5	3.3	0.230	–
2e	*trans*-CH_3CH=$CHCH_2CH_2$	*p*-Phenylene	H	F	60.2	94.8	4.3	0.255	0.248
3	n-C_3H_7	*p*-Phenylene	F	CH_3	49.0	18.4	9.3	0.198	–
4a	n-C_3H_7	*trans*-1,4-Cyclohexylene	H	n-C_3H_7	32.0	60.5	10.1	0.128	–
4b	n-C_3H_7	*trans*-1,4-Cyclohexylene	H	Cl	46.9	60.9	8.1	0.170	0.149
ZLI-1565[d]	–	–	–	–	–	86[e]	14.5[e]	0.124[e]	–

[a]Extrapolation data, [b]Measured at 25°C, [c]Measured at (0.85 × $T_{ni \text{ mixture}}$)°C, [d]Host mixture, [e]Measured data using ZLI-1565 only.



Scheme 1. Synthetic route of compound **2**.

significantly. The Δn value of compound **2b** was slightly smaller than that of compound **1**. Moreover, compounds **2a**–**2e** have very low viscosity, less than 10 mm^2 s^{-1}, as do compound **1**. In particular, compound **2e**, introducing the *trans*-3-pentenyl group, has a high T_{ni} temperature while keeping a high Δn and low viscosity (Table 2).

2.3.2 *Synthesis and properties of (E)-1,2-difluoro-1-(4-propylphenyl)-2-(2-fluoro-4- methylphenyl)ethylene (3)*

New LC compound **3** was synthesised. The reaction of trifluoroethenylzinc iodide with 4-propyliodobenzene in the presence of Pd(PPh$_3$)$_4$ gave 1-(4-propylphenyl)-1,2,2-trifluoroethylene. The subsequent nucleophilic replacement reaction with 2-fluoro-4-methylphenyllithium gave an *E* and *Z* mixture of 1,2-difluoro-1-(4-propylphenyl)-2-(2-fluoro-4-methylphenyl)ethylene. The mixture was purified by recrystallisation from ethanol to give (*E*)-1,2-difluoro-1-(4-propylphenyl)-2-(2-fluoro-4-methylphenyl)ethylene (Scheme 2).

Compound **3** has a low T_{ni} temperature and low Δn values compared with compound **1** because of its structure being twisted by the repulsion between the introduced fluorine atom in the benzene ring and the fluorine atom on the ethylene bond mentioned in Section 2.2 (Table 2).

2.3.3 *Synthesis and properties of (E)-1,2-difluoro-1-(*trans*-4-propylcyclohexyl)-2-(4-alkylphenyl)ethylenes (4a–4b)*

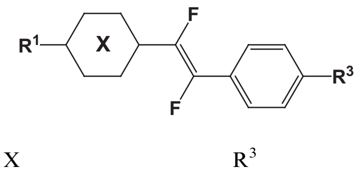
New LC compound **4a–4b** was synthesised. The reaction of 4-propyl-1-chlorocyclohexane with lithium 4,4′-di-*t*-butylbiphenyl (Li-DBB) and tetrafluoroethylene gave 1-(*trans*-4-propylcyclohexyl)-1,2,2-trifluoroethylene. In this case, the *trans* and *cis* mixture (*trans*/*cis* = 55:45) of the starting material can be used. The 4-propylcyclohexyllithium has *trans* and *cis* isomers in equilibrium state. The anion obtained from the *cis* isomer and tetrafluoroethylene is unstable due to the steric repulsion between the axial hydrogen atoms on the cyclohexane ring and the fluorine atom, and is hard to form. On the other hand, the anion obtained from the *trans* isomer and tetrafluoroethylene is stable, and is easy to form (Figure 6).

Therefore, 1-(*trans*-4-alkylcyclohexyl)-1,2,2-trifluor oethylene was obtained in high stereoselectivity (*trans*/*cis* = 98:2). The subsequent nucleophilic replacement reaction with 4-alkylphenyllithium gave (*E*)-1,2-difluoro-1-(*trans*-4-propylcyclohexyl)-2-(4-alkylphenyl) ethylenes after recrystallisation (Scheme 3).

With respect to stereoselectivity (*E*/*Z*), in using 1-(*trans*-4-propylcyclohexyl)-1,2,2-trifluoroethylene, the *trans*-form anion is more stable than the *cis*-form anion because of the repulsion between the benzene ring and the cyclohexane ring. The stereoselectivity (*E*/*Z* = 95:5) is determined by the selectivity of anion formation and the degree of anion isomerisation (Figure 5).

Although the compounds **4a** and **4b** have good UV stability, their Δn values were lower than that of compound **1** because of the shortening of the molecular conjugation length by the introduction of the cyclohexane ring instead of one of the benzene rings (Table 2).

Table 3. Preparation of (*E*)-1,2-difluoroethylene compounds.



Compound	R^1	X	R^3	Formation ratio (*E*/*Z*)	Isolated yield (%)
2a	C_2H_5	*p*-Phenylene	F	78/22	60
2b	*n*-C_3H_7	*p*-Phenylene	F	81/19	62
4a	*n*-C_3H_7	*trans*-1,4-Cyclohexylene	*n*-C_3H_7	96/4	84
4b	*n*-C_3H_7	*trans*-1,4-Cyclohexylene	Cl	95/5	76

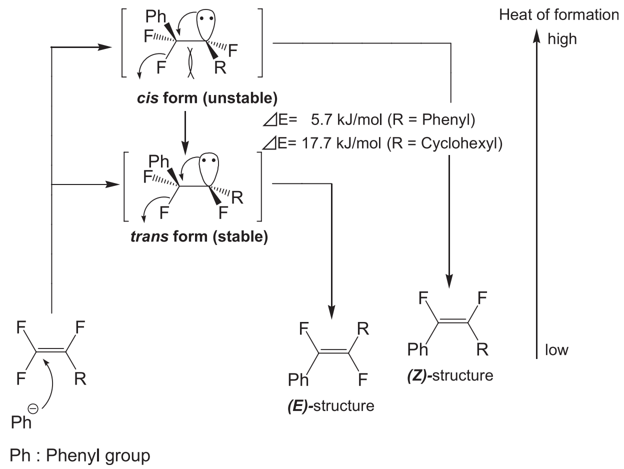
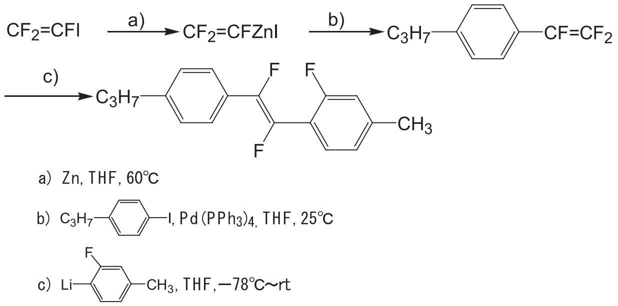


Figure 5. Stereoselectivity of cross-coupling reaction in 1,2,2-trifluoroetylene derivatives.



Scheme 2. Synthetic route of compound **3**.

2.3.4 *Improvement of UV stability*

We investigated three suppression methods of (*E*)–(*Z*) isomerisation by shortening the molecular conjugation length, which included the introduction of a fluorine atom into the *ortho* or *para* position of the benzene ring or the replacement of the benzene ring with a cyclohexane ring. An UV irradiation test was carried out by the following method. LC cells with polarised film containing LC mixture were irradiated with UV light in a long life fade meter for 300 hours. The injected mixture was composed of 20 wt% of the synthesised novel compound and 80 wt% of the host LC (ZLI-1565$^{\mathrm{TM}}$). After irradiation, the amount of (*Z*) isomer in the mixture was analysed by gas chromatography (GC). The relative formation ratio of (*Z*) isomers compared with compound **1** is shown in the last column of Table 1. It was found that the introduction of fluorine atoms in the 4-position and the 2-position of the benzene ring gave good UV stability compared with compound **1** because of low hyperconjugation of the π–σ bond between the benzene ring and the fluorine atom in one of the benzene rings, instead of the alkyl group mentioned in Section 2.2.. In the case of **3**, in addition to the lowered hyperconjugation, the repulsion between the fluorine atom in the benzene ring and the difluoroethylene bond causes the twisted conformation, which makes the resonance between the benzene ring and the ethylene bond reasonably weak, hence the UV absorption is blue-shifted. Moreover, compound **4a**, which was obtained by the introduction of a cyclohexane ring instead of one of the benzene rings, had high UV stability because of the shortening of the conjugation length, so as to be assumed by the HOMO and LUMO energy level calculated using the semiempirical quantum chemical PM3 method mentioned in Section 2.2.

3. Conclusion

We studied three suppression methods of (*E*)–(*Z*) isomerisation by shortening the molecular conjugation length in (*E*)-1,2-difluoroethylene compounds compared with (*E*)-α,β-DFS **1**. We synthesised three

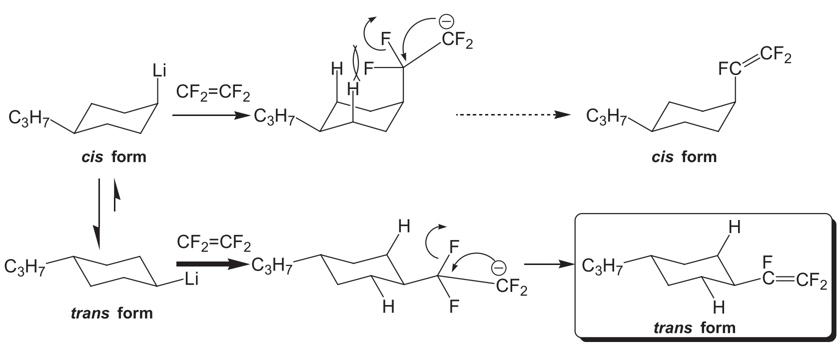
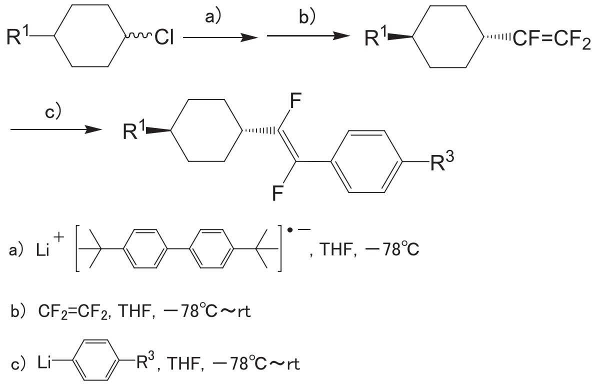


Figure 6. Selective formation of *trans* form.



Scheme 3. Synthetic route of compound **4**.

types of novel compounds: (*E*)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-alkylphenyl)ethylenes (**2a**–**e**), (*E*)-1,2-difuluoro-1-(4-alkylphenyl)-2-(2-fluoro-4-methylphenyl)ethylene (**3**) and (*E*)-1,2-difluoro-1-(*trans*-4-alkylcyclohexyl)-2-(4-alkylphenyl)ethylenes (**4a,b**). They had better UV photo stability than compound **1**; in particular compound **2** had low viscosity and high Δn, as did compound **1**. Moreover, (*E*)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-*trans*-3-pentenylphenyl)ethylenes (**2e**) had the best performances for LCs because of having high T_{ni} temperatures.

4. Experimental

4.1 Instrumentation and materials

The synthesised compounds were characterised using the following conditions and instruments. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR: Jeol JSM-AL300 NMR spectrometer (300 MHz): Tetramethyl silane was used as the internal standard in ^{1}H NMR and ^{13}C NMR, and fluorotrichloromethane was used as the internal standard in ^{19}F NMR. The purity of the compounds was measured by GC: Agilent Technologies Agilent 6850.MS data were obtained with EI (70 eV) on a Shimadzu GCMS-2010 spectrometer. Infrared spectra were obtained using a Shimadzu FT-IR 8300 Fourier transform infrared spectrometer in the range of 400–4000 cm^{-1}. Phase transition temperatures: a Perkin Elmer DSC 7 differential scanning calorimeter and a Nikon Optiphot polarising microscope with a Mettler FP82HT hot stage. Kinematic viscosity (ν) measured at 25°C: Shibayama Scientific Ostwald's viscometer SS-290S. Optical anisotropy (Δn) measured at 25°C and (0.85 × T_{ni} of the mixture)°C: an Atago 1T Abbe refractometer. UV irradiation test: LC cells with a polarised seat (Q12-35: Nitto Denko) were irradiation by an UV long life fade mater (FAL-5: Suga Test Instruments) for 300 hours. The physical properties of the host mixture ZLI-1565 (Merck) are T_{ni} = 86°C, Δn = 0.124 and $\Delta\varepsilon$ = 6.7.

4.1.1 1-(4-fluorophenyl)-1,2,2-trifluoroethylene

A solution of 4-fluoroiodobenzene (51 g, 0.23 mol) in tetrahydrofuran (THF) (60 ml) at 60°C was added dropwise to a mixture of iodotrifluoroethylene (62 g, 0.30 mol), Zn (25.4 g, 0.39 mol) and Pd(PPh$_3$)$_4$ (2.66 g, 0.002 mol) in THF (600 ml). After being stirred for 4 h at 60°C, the reaction mixture was cooled to 0°C and zinc powder was filtered off. The mixture was acidified with dilute hydrochloric acid, followed by extraction with methyl *t*-butyl ether. The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure, and the remaining mixture was distilled, b.p. 60–61°C at 6.93 kPa, to give 1-(4-fluorophenyl)-1,2,2-trifluoroethylene (29.1 g, 72%). ^{1}H NMR (CDCl$_3$) δ 7.03–7.14 (2H, m), 7.38–7.43 (2H, m). ^{19}F NMR (CDCl$_3$) δ –101.1 (1F, dd, J_{FF} = 32.7 Hz, J_{FF} = 73.5 Hz), –111.9 (1F, s), –116.1 (1F, dd, J_{FF} = 73.5, 110.3 Hz), –176.4 (1F, dd, J_{FF} = 32.7, 110.3 Hz). ^{13}C NMR (CDCl$_3$) δ 115.9 (d, J = 22.4 Hz), 116.1 (d, J = 27.1 Hz), 126.5 (m), 130.0 (dt, J = 9.3, 32.8 Hz), 153.8 (dd, J = 3.8, 7.3 Hz), 161.4 (d, J = 247.2 Hz).

*4.1.2 (E)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-propylphenyl)ethylene (**2b**)*

A solution of 4-propylphenyllithium (0.024 mol) in THF (40 ml) at –78°C was added dropwise to a solution of 1-(4-fluorophenyl)-1,2,2-trifluoroethylene (3.52 g, 0.02 mol) in THF (100 ml). After being stirred for 2 h at –78°C, and then for 1 h at room temperature, the mixture was acidified at 0°C with dilute hydrochloric acid, followed by extraction with methyl *t*-butyl ether. The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the remaining mixture was purified by recrystallisation from ethanol to give (*E*)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-propylphenyl)ethylene (3.4 g, 62%). Purity 99.4% by GC. MS (EI, 70 eV) *m*/*z* 276 (M^{+}, 55), 247 (100), 233 (4), 214 (3). IR (KBr) $\nu_{\max}$ (cm^{-1}) 2970, 2940, 2876, 1920, 1900, 1604, 1514, 1410, 1228, 1055, 833. ^{1}H NMR (CDCl$_3$) δ 0.91 (3H, t, J = 7.3 Hz), 1.62 (2H, m), 2.55 (2H, t, J = 7.9 Hz), 7.02 (2H, t, J = 8.7 Hz), 7.17 (2H, d, J = 8.2 Hz), 7.59–7.67 (4H, m). ^{19}F NMR (CDCl$_3$) δ –111.9 (1F, m), –152.5 (1F, d, J_{FF} = 120.7 Hz), –152.9 (1F, d, J_{FF} = 120.7 Hz), ^{13}C NMR (CDCl$_3$) δ 13.7, 24.3, 37.8, 115.5 (d, J = 22.8 Hz), 125.7 (t, J = 8.7 Hz), 126.6 (dd, J = 2.1, 16.7 Hz), 127.5 (d, J = 14.6 Hz), 127.7 (q, J = 8.7 Hz), 128.5, 143.8, 148.0 (dd, *J* = 140.3, 150.2 Hz), 148.5 (dd, *J* = 96.5, 280.8 Hz), 162.6 (d, *J* = 250.3 Hz).

4.1.3 *(E)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-ethylphenyl)ethylene (**2a**)*

Following the procedure for **2b**, **2a** (60%) was obtained from 1-(4-fluorophenyl)-1,2,2-trifluoroethylene and 4-ethylphenyllithium. Purity 99.2% by GC. MS (EI, 70 eV) *m*/*z* 262 (M$^+$, 92), 247 (100), 233 (14), 214 (4). IR (KBr) ν_{max} (cm^{-1}) 2966, 2937, 2870, 1930, 1905, 1600, 1512, 1410, 1232, 1012, 835. ^{1}H NMR ($CDCl_3$) δ 1.20 (3H, t, *J* = 7.6 Hz), 2.61 (2H, q, *J* = 7.6 Hz), 7.01 (2H, t, *J* = 8.7 Hz), 7.18 (2H, d, *J* = 8.2 Hz), 7.58–7.66 (4H, m). ^{19}F NMR ($CDCl_3$) δ –111.9 (1F, m), –152.4 (1F, d, J_{FF} = 119.8 Hz), –153.0 (1F, d, J_{FF} = 119.8 Hz), ^{13}C NMR ($CDCl_3$) δ 15.2, 28.7, 115.4 (d, *J* = 22.8 Hz), 125.7 (t, *J* = 8.2 Hz), 126.6 (dd, *J* = 2.9, 18.5 Hz), 127.5 (d, *J* = 14.5 Hz), 127.6 (q, *J* = 7.9 Hz), 127.9, 145.3, 148.0 (dd, *J* = 100.4, 394.3 Hz), 148.4 (dd, *J* = 121.4, 166.4 Hz), 162.6 (d, *J* = 249.4 Hz).

4.1.4 *(E)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-pentylphenyl)ethylene (**2c**)*

Following the procedure for **2b**, **2c** (64%) was obtained from 1-(4-fluorophenyl)-1,2,2-trifluoroethylene and 4-pentylphenyllithium. Purity 99.5% by GC. MS (EI, 70 eV) *m*/*z* 304 (M$^+$, 60), 247 (100), 233 (3), 214 (2). IR (KBr) ν_{max} (cm^{-1}) 2964, 2940, 2854, 1930, 1905, 1600, 1503, 1406, 1236, 1013, 835. ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, *J* = 7.0 Hz), 1.30 (4H, m), 1.59 (2H, m), 2.57 (2H, t, *J* = 7.9 Hz), 7.02 (2H, t, *J* = 8.8 Hz), 7.17 (2H, d, *J* = 8.2 Hz), 7.59–7.68 (4H, m). ^{19}F NMR ($CDCl_3$) δ –111.9 (1F, m), –152.5 (1F, d, J_{FF} = 120.4 Hz), –153.0 (1F, d, J_{FF} = 120.4 Hz), ^{13}C NMR ($CDCl_3$) δ 14.0, 22.7, 30.9, 31.6, 35.8, 115.5 (d, *J* = 21.0 Hz), 125.7 (t, *J* = 8.4 Hz), 126.7 (dd, *J* = 2.4, 17.4 Hz), 127.4 (d, *J* = 16.7 Hz), 127.7 (q, *J* = 8.7 Hz), 128.5, 144.1, 148.0 (dd, *J* = 134.9, 155.5 Hz), 148.5 (dd, *J* = 94.6, 283.7 Hz), 162.6 (d, *J* = 249.6 Hz).

4.1.5 *(E)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-(3-butenyl)phenyl)ethylene (**2d**)*

Following the procedure for **2b**, **2d** (61%) was obtained from 1-(4-fluorophenyl)-1,2,2-trifluoroethylene and 4-(3-butenyl)phenyllithium.

4.1.6 *(E)-1,2-difluoro-1-(4-fluorophenyl)-2-(4-*trans*-3-pentenyl)phenyl)ethylene (**2e**)*

Following the procedure for **2b**, **2e** (58%) was obtained from 1-(4-fluorophenyl)-1,2,2-trifluoroethylene and 4-(*trans*-3-pentenyl)phenyllithium. Purity 99.5% by GC. MS (EI, 70 eV) *m*/*z* 302 (M$^+$, 24), 247 (100), 233 (2), 214 (1). IR (KBr) ν_{max} (cm^{-1}) 3037, 2920, 2864, 1924, 1904, 1600, 1512, 1414, 1238, 1017, 836. ^{1}H NMR ($CDCl_3$) δ 1.62 (3H, m), 2.27 (2H, m), 2.64 (2H, t, *J* = 7.3 Hz), 5.43 (2H, m), 7.03 (2H, t, *J* = 8.8 Hz), 7.17 (2H, d, *J* = 8.3 Hz), 7.59–7.68 (4H, m). ^{19}F NMR ($CDCl_3$) δ –111.8 (1F, m), –152.4 (1F, d, J_{FF} = 119.8 Hz), –152.9 (1F, d, J_{FF} = 119.8 Hz), ^{13}C NMR ($CDCl_3$) δ 17.8, 34.1, 35.8, 115.5 (d, *J* = 21.9 Hz), 125.6, 125.7 (t, *J* = 8.2 Hz), 126.6 (dd, *J* = 3.9, 18.5 Hz), 126.7 (d, *J* = 8.9 Hz), 127.7 (q, *J* = 8.8 Hz), 128.5, 130.2, 143.3, 147.3 (dd, *J* = 94.7, 278.0 Hz), 148.5 (dd, *J* = 92.5, 277.4 Hz), 162.6 (d, *J* = 249.6 Hz).

4.1.7 *(E)-1,2-difluoro-1-(2-fluoro-4-methylphenyl)-2-(4-propylphenyl)ethylene (**3**)*

Following the procedure for **2b**, **3** (70%) was obtained from 1-(4-propylphenyl)-1,2,2-trifluoroethylene and 4-(2-fluoro-4-methyl)phenyllithium. ^{19}F NMR ($CDCl_3$) δ –111.7 (1F, m), –144.5 (1F, dd, J_{FF} = 13.4, 128.8 Hz), –152.2 (1F, dd, J_{FF} = 24.1, 128.8 Hz).

4.1.8 *1-(*trans*-4-propylcyclohexyl)-1,2,2-trifluoroethylene*

Lithium (7.41 g, 1.07 mol), at room temperature under argon atmosphere, was added to a solution of 4,4′-di-*tert*-butylbiphenyl (199.1 g, 0.747 mol) in THF (1300 ml) and *n*-hexane (1300 ml). After being stirred for 2 h, the mixture was cooled to –70°C. A solution of 1-chloro-4-propylcyclohexane (57.1 g, 0.356 mol) in THF (50 ml) at –70°C was added dropwise to the deep green-coloured THF solution. After being stirred for 2 h, tetrafluoroethylene (40 g, 0.4 mol) was added to the mixture at the same temperature. After being stirred for 1 h, the mixture was poured into 0.1 M HCl, and was extracted with hexane. The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the remaining mixture was distilled, b.p. 57–58°C at 5.33 × 10^{-1} kPa, to give 1-(*trans*-4-propylcyclohexyl)-1,2,2-trifluoroethylene (51.3 g, 70%). ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t), 1.13–1.40 (6H, m), 1.47–1.85 (4H, m), 2.00–2.05 (3H, m), 2.10–2.81 (1H, m). ^{19}F NMR ($CDCl_3$) δ –107.5 (1F, dd, J_{FF} = 91.5, 31.1 Hz), –125.4 (1F, dd, J_{FF} = 91.5, 113.3 Hz), –182.4 (1F, ddd), J_{FH} = 28.3, 31.1, 113.3 Hz). ^{13}C NMR ($CDCl_3$) δ 14.3, 20.0, 25.4, 29.1, 32.0, 33.4, 39.2, 126.6, 126.9.

4.1.9 *(E)-1,2-difluoro-1-(4-chlorophenyl)-2-(*trans*-4-propylcyclohexyl)ethylene (**4b**)*

A solution of 4-chlorophenyllithium (0.024 mol) in THF (40 ml) at –78°C was added dropwise to a solution of 1-(*trans*-4-propylcyclohexyl)-1,2,2-trifluoroethylene (4.12 g, 0.02 mol) in THF (50 ml). After being stirred for 1 h at –78°C, the mixture was stirred for 2 h at room temperature. After cooling to 0°C, the mixture was acidified with dilute hydrochloric acid and extracted with methyl *t*-butyl ether. The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the remaining mixture was purified by recrystallisation from ethanol to give (*E*)-1,2-difluoro-1-(4-chlorophenyl)-2-(4-*trans*-propylcyclohexyl)ethylene (4.7 g, 76%). Purity 99.4% by GC. MS (EI, 70 eV) *m*/*z* 300 (M$^+$ + 2, 10), 298 (M$^+$, 30), 280 (3), 278 (7), 263 (3), 156 (100). IR (KBr) $\nu_{\max}$ (cm^{-1}) 2940, 2860, 1914 1700, 1489, 1450, 1217, 1087, 833. ^{1}H NMR (CDCl$_3$) δ 0.88 (3H, t, *J* = 7.3 Hz), 1.00 (2H, dt, *J* = 2.9, 11.6 Hz), 1.12–1.37 (4H, m), 1.47–1.61 (2H, dq, *J* = 4.2, 13.6 Hz), 1.78–1.84 (4H, m), 2.61–2.82 (1H, m), 7.30 (2H, d, *J* = 8.5 Hz), 7.50 (2H, dt, *J* = 2.4, 8.8 Hz). ^{19}F NMR (CDCl$_3$) δ –154.3 (1F, dd, J_{FF} = 120.9, 30.5 Hz), –161.4 (1F, dd, J_{FF} = 120.9, 5.5 Hz). ^{13}C NMR (CDCl$_3$) δ 14.3, 20.0, 28.7 (d, *J* = 1.8 Hz), 32.6, 36.6, 36.7 (d, *J* = 22.3 Hz), 39.6, 126.3 (dd, *J* = 7.8, 9.7 Hz), 128.5 (d, *J* = 2.0 Hz), 128.9 (*d*, *J* = 6.5 Hz), 133.9 (*d*, *J* = 3.0 Hz), 144.9 (*dd*, *J* = 44.9, 233.2 Hz), 156.2 (dd, *J* = 54.6, 250.6 Hz).

*4.1.10 (E)-1,2-difluoro-1-(4-propylphenyl)-2-(4-*trans*-propylcyclohexyl)ethylene (**4a**)*

Following the procedure for **4b**, **4a** (84%) was obtained from 1-(*trans*-4-propylcyclohexyl)-1,2,2-trifluoroethylene and 4-propylphenyllithium.

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