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Synthesis of perfluorobutyl-substituted ester-disazo dyes and their application to guest–host liquid crystal displays

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Ester-disazo dyes having perfluorobutyl and diethylamino groups in their molecules have been prepared. Their absorption maxima were observed in the range $\lambda = 483\text{--}529\text{ nm}$ in a liquid crystal solvent. The solubility in terms of dye structure was in the order: monoester-disazo > trisazo > diester-disazo. The solubility of the diester-disazo dyes in terms of the substituents at the terminal end was in the order: $\text{C}_4\text{F}_9 > \text{C}_4\text{H}_9 > \text{H}$. The introduction of the 4-diethylaminonaphthylene moiety was also effective in improving the solubility. The order parameter of the dye host systems was in order of the dye structures: trisazo > diester-disazo > monoester-disazo. The order parameter for the diester-disazo dyes was calculated to be 0.79–0.82, high enough for practical use.

1. Introduction

Studies of dichroic dyes are again attracting much attention due to the recent development of reflection-type guest–host liquid crystal displays. Azo dyes have been proposed as positive dichroic dyes for use in the displays [1], and the improvement of the solubility and the dichroism of dyes is a challenging subject in this field. Perfluoroalkyl-substituted disazo dyes have been reported to show larger solubilities than the corresponding alkyl derivatives [2], and perfluoro-*p*-phenylene disazo dyes have also been reported to show higher solubility than the corresponding *p*-phenylene derivatives [3]. Aroyloxy disazo dyes too have been reported to be more soluble than trisazo dyes [4]. The slimmer the molecular structure of azo dyes, the higher the dichroism becomes and the lower is the solubility. The order parameters (*S*) of perfluoroalkyl-substituted disazo dyes have been reported to be higher than those of the alkyl-substituted derivatives [2], and the order parameters of tris-, tetrakis-, and pentakis-azo dyes having two

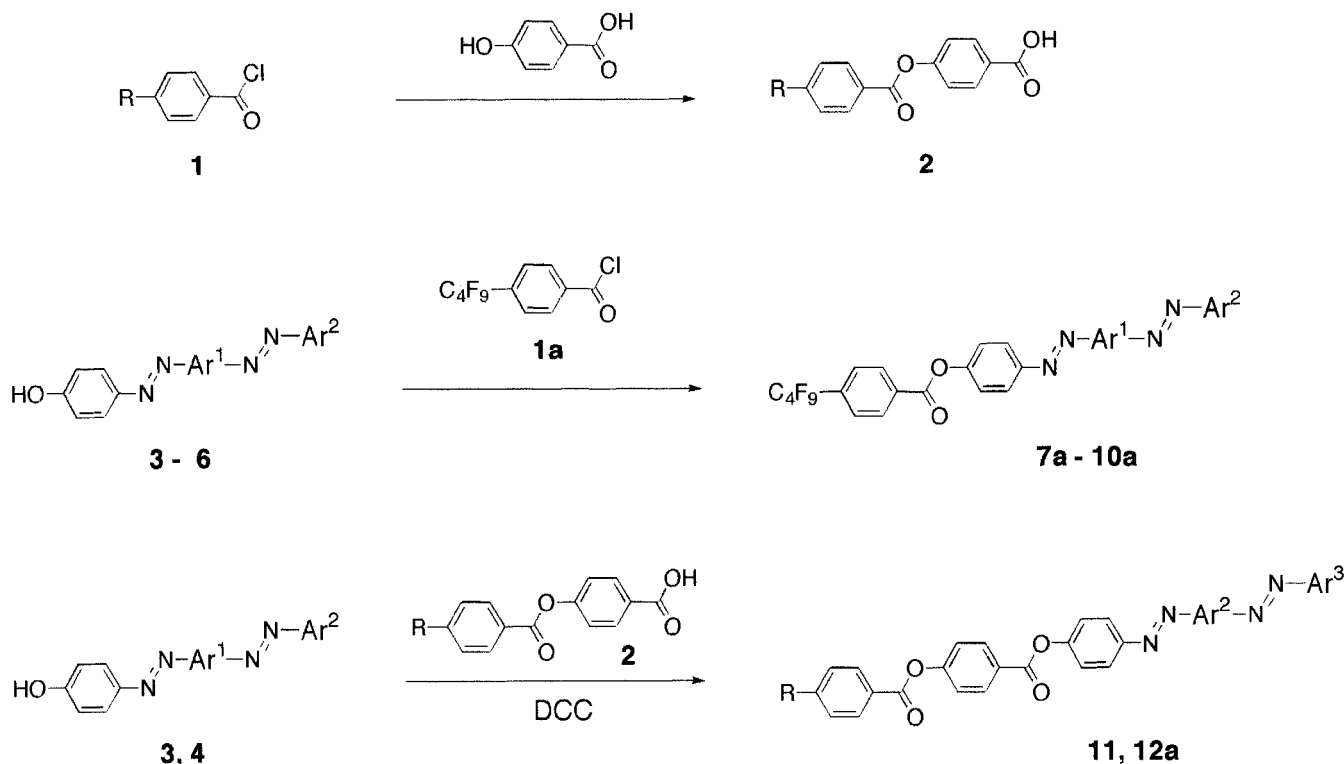
terminal butyl groups in the molecules were calculated to be 0.66–0.81 [5]. This result indicates that the dichroism of polyazo dyes without polar substituents such as dialkylamino groups are not as high as would be expected in spite of their slim structures. Therefore, it is supposed that the introduction of both the polar dialkylamino and perfluoroalkyl groups into the molecule is essential to improve the solubility and dichroism of azo dyes. We report here the synthesis, solubility, and dichroism of ester-disazo dyes having perfluorobutyl and diethylamino groups.

2. Results and discussion

2.1. Synthesis

The scheme shows the synthesis of disazo dyes **7a–12a** extended with ester linkages. 4-Aroyloxybenzoic acids **2** were prepared by the reaction of 4-aroyle chlorides **1** with 4-hydroxybenzoic acid. 4-Hydroxyazobenzene **3–6** were synthesized by the diazotization of the arylamines followed by coupling with phenol. Monoester-disazo dyes **7a–10a** were obtained by the esterification of 4-hydroxyazobenzene **3–6** with 4-perfluorobutylbenzoyl chloride (**1a**) in low to moderate yields. Diester-disazo

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Scheme.

dyes **11** and **12a** were synthesized by the reaction of 4-hydroxyazobenzenes **3** and **4** with 4-aryloxybenzoic acids **2** in the presence of dicyclohexylcarbodiimide (DCC) in low to moderate yields.

2.2. Physical properties

The physical properties of azo dyes **7a-12a** are shown in the table. Those of tris-azo dye **13a** are shown for reference. The absorption maxima (λ_{\max}) of **7a-12a** were observed in the range 453–502 nm in hexane. The λ_{\max} of **7a-12a** in the liquid crystal solvents shown were observed in the range 483–536 nm; the values show bathochromic shifts compared with those using hexane due to the higher polarity of the liquid crystal solvents. Thus, the colour of dyes **7a-12a** was orange to red in the liquid crystal solvents.

The solubility of diester-disazo dyes in hexane could be improved by introducing a perfluorobutyl group. The solubility was in order of the terminal substituents: C_4F_9 (**11a**: $0.03 \text{ mmol dm}^{-3}$) > C_4H_9 (**11b**: < 0.01) > H (**11c**: insoluble). The solubility in order of the dye structures was: monoester-disazo (**7a**: 0.41) > trisazo (**13a**: 0.08) > diester-disazo (**11a**: 0.03). The solubilities of dyes **7a**, **8a**, **9a**, and **10a** in hexane were 0.41, 0.66, 0.47, and $0.72 \text{ mmol dm}^{-3}$, respectively. These results indicate that the introduction of the naphthylene moiety adjacent to the diethylamino group is also effective

in improving the solubility. Actually, the solubility of diester-disazo dye **12a** having both the perfluorobutyl and 4-diethylaminonaphthylene moieties in the molecule was found to be 0.19, much more soluble than **11a** and **11b**.

The S values for the order parameter were in order of the dye structures: trisazo (**13a**: 0.82) > diester-disazo (**11a**, **11b**, **11c**, and **12a**: 0.78–0.82) > monoester-disazo (**7a-10a**: 0.73–0.79). Trisazo dye **13a** showed the highest order parameter probably because of the fixed *trans*-configuration of the molecule, whereas the ester linkages in dyes **7-12** may rotate in the liquid crystal and give lower order parameters than **13a**. The S values of **11a**, **11b**, and **11c** were in the range 0.79–0.82. Thus, no remarkable effect of a perfluorobutyl group on the dichroism was observed in the diester-disazo dyes **11**. The S values of monoester-naphthylene derivatives **8a**, **9a**, and **10a** were rather low compared with that for the corresponding phenylene derivative **7a**. The dichroism of diester-naphthylene derivative **12a** was similar to that of the diester-phenylene derivative **11a**.

The relationship between the S values and the l/d ratios, where l and d represent the lengths of the molecular long axes and the diameters of the circumscribed cylinders of revolution of the molecules, respectively, is shown in the figure. It is clear that the slimmer the molecule, the higher is the dichroism. To obtain dichroic azo dyes

Table. Physical properties of azo dyes.

Compd	Structure	Solubility ^a		ZLI-1565 ^c		ZLI-4792 ^c		θ°	<i>l</i>	<i>d</i>	<i>l/d</i>
		mmol dm ⁻³	λ_{\max}^b /nm	λ_{\max} /nm	<i>S</i>	λ_{\max} /nm	<i>S</i>				
7a		0.41	462 (31000)	500	0.79	499	0.79	5.22	33.876	8.053	4.21
8a		0.66	453 (31000)	486	0.77	489	0.78	5.72	33.792	13.176	2.56
9a		0.47	502 (17000)	536	0.77	533	0.78	5.69	33.737	13.084	2.58
10a		0.72	484 (21000)	525	0.73	529	0.75	24.02	33.902	12.457	2.72
11a		0.03	462 (30000)	500	0.79	493	0.80	7.03	39.992	8.568	4.67
11b		<0.01	456 (19000)	497	0.80	492	0.80	6.26	39.316	8.399	4.68
11c		insoluble	495 ^d (31000)	499	0.82	496	0.81	6.18	34.323	8.399	4.09
12a		0.19	488 (22000)	483	0.78	487	0.79	6.48	40.013	13.149	3.04
13a		0.08	490	530	0.82	527	0.82	2.90	33.75	8.237	4.10

^a Measured in hexane at 25°C.^b Measured in hexane.^c ZLI-1565 and ZLI-4792 are commercial liquid crystals from E. Merck.^d Measured in chloroform.

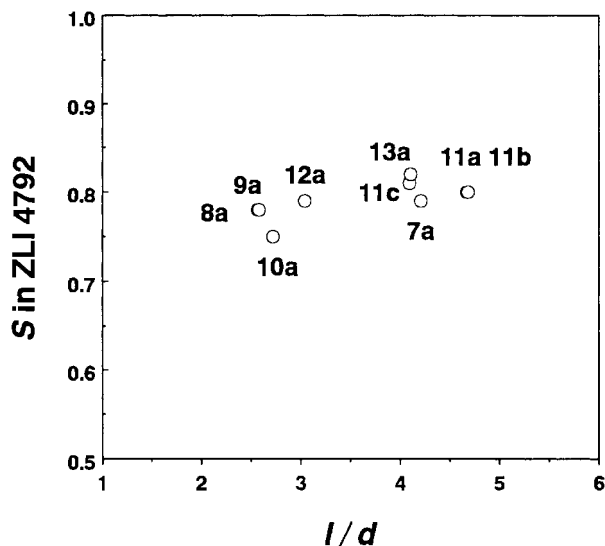


Figure 1. Relationship between order parameter (S) and l/d ratio.

showing a dichroism higher than 0.85, the l/d value is required to be larger than *c.* 6.0, that is for hexakisazo dyes. Some new ideas may be required to obtain slim, polar, and soluble polyazo dyes.

3. Conclusions

We have synthesized novel disazo dyes containing the ester moiety. Their UV-Vis absorption bands were observed in the range of λ 483–529 nm using liquid crystal solvents. The solubility was in order of the dye structures: monoester-disazo > trisazo > diester-disazo. However, the solubilities of diester-disazo dyes were improved by introducing perfluorobutyl and terminal naphthylene moieties in the molecule. The order parameters of the diester-disazo dyes were 0.79–0.82, high enough to be of practical use.

4. Experimental

4.1. Characterization

Melting points were measured using a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were recorded using a Jeol α -400 spectrometer and mass spectra with a Shimadzu QP-1000 spectrometer. UV-Vis absorption spectra were measured with a Shimadzu UV-160A spectrometer.

4.2. Materials

4-Hydroxybenzoic acid, 4-butylbenzoyl chloride (**1b**), and benzoyl chloride (**1c**) were purchased from the Tokyo Kasei Co., Ltd. 4-(Perfluorobutyl)benzoyl chloride (**1a**) [4], 4-(benzoyloxy)benzoic acid (**2c**) [6], 4-{4-[4-(diethylamino)phenylazo]phenylazo}phenol (**3**) [4] and 4-perfluorobutylphenyl 4-{4-[4-(diethylamino)phenylazo]-

phenylazo}benzoate (**7a**) [4], were prepared as described in the previous papers indicated.

4.3. Synthesis of 4-aryloxybenzoic acids **2a** and **2b**

To a THF solution (20 ml) of the benzoyl chloride **1** (11.4 mmol) were added 4-hydroxybenzoic acid (1.4 g, 10.4 mmol) and triethylamine (1.2 g, 11.4 mmol). The mixture was stirred for 1 h at room temperature. After reaction was complete, the resulting white precipitate was filtered off and recrystallized from chloroform–hexane. In the case of **2b**, the precipitate was used without further purification. The physical and spectral data for **2a** are shown below.

4.3.1. 4-[4-(Perfluorobutyl)benzoyloxy]benzoic acid **2a**

Yield 30%; m.p. 208–209°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.73 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H), 8.24 (d, J = 8.3 Hz, 2H), 8.30 (d, J = 8.3 Hz, 2H); EI MS (70 eV) m/z (rel. intensity, %) 460 [M^+] (3), 443 (1), 323 (100), 295 (7), 137 (8).

4.4. Synthesis of 4-hydroxyazo compounds **4–6**

To an acetone solution (10 ml) of the 4-arylamine (2.5 mmol, 0.53 g) was added conc. hydrochloric acid (7.5 mmol, 0.64 ml) and the mixture cooled to 0°C. An aqueous solution (20 ml) of sodium nitrite (2.5 mmol, 0.16 g) was added at 0°C and the whole stirred for 2 h. The mixture was then added to an acetone solution (20 ml) of *N,N*-diethylaniline (2.5 mmol, 0.17 mg) and stirring continued overnight at 0°C with adjustment of the pH to 5.0 using aqueous sodium hydrogen carbonate. After the reaction was complete, the mixture was poured into water. The resulting precipitate was filtered off, washed with water, dried, and purified by column chromatography (SiO_2 , CH_2Cl_2). The physical and spectral data for **4–6** are shown below.

4.4.1. 4-{4-[4-(Diethylamino)naphthylazo]phenylazo}phenol **4**

Yield 15%; m.p. 129.5–131.0°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 1.14 (t, J = 7.1 Hz, 6H), 3.36 (q, J = 7.1 Hz, 4H), 5.25 (br s, 1H), 6.98 (d, J = 9.1 Hz, 2H), 7.18 (d, J = 8.3 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.65 (t, J = 7.9 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 9.1 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H), 8.14 (d, J = 8.3 Hz, 2H), 8.29 (d, J = 7.9 Hz, 1H), 9.03 (d, J = 7.9 Hz, 1H); EI MS (70 eV) m/z (rel. intensity, %) 423 [M^+] (100), 408 (33), 198 (38), 93 (38).

4.4.2. 4-{4-[4-(Diethylamino)phenylazo]naphthylazo}phenol **5**

Yield 12%; m.p. 204–205°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 1.27 (t, J = 6.8 Hz, 6H), 3.50 (q, J = 6.8 Hz, 4H), 5.20 (br s, 1H), 6.78 (d, J = 8.8 Hz, 2H), 7.00

(d, $J = 8.3$ Hz, 2H), 7.68–7.70 (m, 2H), 7.87 (t, $J = 8.3$ Hz, 1H), 7.90 (t, $J = 8.3$ Hz, 1H), 8.01–8.04 (m, 4H), 8.99–9.02 (m, 2H); EI MS (70 eV) m/z (rel. intensity, %) 423 [M^+] (100), 148 (68), 93 (59).

4.4.3. 4-{4-[4-(Diethylamino)naphthylazo]naphthylazo}phenol **6**

Yield 7%; m.p. 177.0–178.0°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 1.14$ (t, $J = 7.0$ Hz, 6H), 3.39 (q, $J = 7.0$ Hz, 4H), 5.28 (br s, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 1H), 7.56–7.60 (m, 1H), 7.66–7.68 (m, 1H), 7.73–7.77 (m, 2H), 7.95 (d, $J = 8.3$ Hz, 1H), 8.01 (d, $J = 8.8$ Hz, 2H), 8.09 (d, $J = 8.3$ Hz, 1H), 8.19 (d, $J = 8.1$ Hz, 1H), 8.29–8.31 (m, 1H), 9.02–9.04 (m, 1H), 9.12–9.15 (m, 2H); EI MS (70 eV) m/z (rel. intensity, %) 473 [M^+] (31), 247 (13), 198 (25), 121 (27), 93 (100).

4.5. Synthesis of monoester disazo dyes **8a–10a**

To a pyridine solution (5 ml) of the phenol **4**, **5** or **6** (0.51 mmol) was added aroyl chlorides **1** (1.5 mmol) and the mixture stirred for 2 h at 100°C. After reaction was complete, the mixture was poured into aqueous hydrochloric acid. The resulting precipitate was filtered off, washed with water, and dried. The product was purified by column chromatography (SiO_2 , toluene) and recrystallized from chloroform–hexane.

4.5.1. 4-{4-[4-(Diethylamino)naphthylazo]phenylazo}phenyl 4-perfluorobutylbenzoate **8a**

Yield 25%; m.p. 153.5–154.5°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 1.14$ (t, $J = 7.0$ Hz, 6H), 3.37 (q, $J = 7.0$ Hz, 4H), 7.18 (d, $J = 8.3$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.66 (t, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.94 (d, $J = 8.3$ Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 2H), 8.12 (d, $J = 9.0$ Hz, 2H), 8.17 (d, $J = 9.0$ Hz, 2H), 8.29 (d, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 8.3$ Hz, 2H), 9.04 (d, $J = 8.0$ Hz, 1H); EI MS (70 eV) m/z (rel. intensity, %) 745 [M^+] (11), 422 (23), 323 (100), 295 (12), 198 (80), 176 (10). Elemental analysis: calc. for $\text{C}_{37}\text{H}_{28}\text{F}_9\text{N}_5\text{O}_2$ C 59.60, H 3.78, N 9.39; found C 59.23, H 4.01, N 9.51%.

4.5.2. 4-{4-[4-(Diethylamino)phenylazo]-1-naphthylazo}phenyl 4-perfluorobutylbenzoate **9a**

Yield 36%; m.p. 173.5–175.0°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 1.28$ (t, $J = 7.1$ Hz, 6H), 3.51 (q, $J = 7.1$ Hz, 4H), 6.79 (d, $J = 9.1$ Hz, 2H), 7.45 (d, $J = 8.8$ Hz, 2H), 7.70–7.73 (m, 2H), 7.80 (d, $J = 8.1$ Hz, 2H), 7.88 (d, $J = 7.9$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 8.04 (d, $J = 9.1$ Hz, 2H), 8.18 (d, $J = 8.8$ Hz, 2H), 8.39 (d, $J = 8.1$ Hz, 2H), 9.01–9.03 (m, 2H); EI MS (70 eV) m/z (rel. intensity, %) 745 [M^+] (76), 323 (100), 302 (17), 295 (11), 176 (18), 148 (93). Elemental analysis: calc. for $\text{C}_{37}\text{H}_{28}\text{F}_9\text{N}_5\text{O}_2$ C 59.60, H 3.78, N 9.39; found C 60.28, H 3.81, N 9.71%.

4.5.3. 4-[4-(4-Diethylamino-1-naphthylazo)-1-naphthylazo]phenyl 4-perfluorobutylbenzoate **10a**

Yield 21%; m.p. 169.0–170.0°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 1.17$ (t, $J = 7.2$ Hz, 6H), 3.40 (q, $J = 7.2$ Hz, 4H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 8.7$ Hz, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.76–7.78 (m, 2H), 7.80 (d, $J = 8.7$ Hz, 2H), 8.02 (d, $J = 8.6$ Hz, 1H), 8.08 (d, $J = 8.6$ Hz, 1H), 8.11 (d, $J = 8.0$ Hz, 1H), 8.21 (d, $J = 8.7$ Hz, 2H), 8.30 (d, $J = 7.5$ Hz, 1H), 8.40 (d, $J = 8.7$ Hz, 2H), 9.04–9.07 (m, 1H), 9.13–9.15 (m, 2H); EI MS (70 eV) m/z (rel. intensity, %) 795 [M^+] (37), 472 (16), 352 (4), 323 (100), 226 (2), 198 (46). Elemental analysis: calc. for $\text{C}_{41}\text{H}_{30}\text{F}_9\text{N}_5\text{O}_2$ C 61.89, H 3.80, N 8.80; found C 62.54, H 3.46, N 8.86%.

4.6. Synthesis of diester disazo dyes **11** and **12a**

To a dichloromethane solution (5 ml) of the 4-hydroxyazobenzenes **3** or **4** (0.1 mmol) were added *N,N*-dicyclohexylcarbodiimide (DCC, 0.11 mmol, 23 mg), the aroyloxybenzoic acids **2** (0.1 mmol), and 4-pyrrolidinopyridine (0.01 mmol, 15 mg). The mixture was stirred for 24 h at room temperature. After the reaction was complete, the mixture was poured into water. The product was extracted into dichloromethane, purified by column chromatography (SiO_2 , CH_2Cl_2), and recrystallized from chloroform–hexane. The physical and spectral data for the products are shown below.

4.6.1. 4-{4-[4-(Diethylamino)phenylazo]phenylazo}phenyl 4-[4-(perfluorobutyl)benzoyloxy]benzoate **11a**

Yield 4% m.p. 205.5–206.5°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 1.26$ (t, $J = 7.1$ Hz, 6H), 3.48 (q, $J = 7.1$ Hz, 4H), 6.75 (d, $J = 9.3$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.90 (d, $J = 9.3$ Hz, 2H), 7.98 (d, $J = 8.8$ Hz, 2H), 8.050 (d, $J = 8.8$ Hz, 2H), 8.052 (d, $J = 8.8$ Hz, 2H), 8.35 (d, $J = 8.8$ Hz, 2H), 8.37 (d, $J = 8.3$ Hz, 2H); EI MS (70 eV) m/z (rel. intensity, %) 815 [M^+] (4), 443 (22), 372 (6), 323 (100), 295 (5), 148 (30). Elemental analysis: calc. for $\text{C}_{40}\text{H}_{30}\text{F}_9\text{N}_5\text{O}_2$ C 58.90, H 3.71, N 8.59; found C 59.36, H 3.98, N 8.89%.

4.6.2. 4-{4-[4-(Diethylamino)phenylazo]phenylazo}phenyl 4-(4-butylbenzoyloxy)benzoate **11b**

Yield 3% m.p. 163.5–165.0°C; ^1H NMR (400 MHz, CDCl_3) $\delta = 0.96$ (t, $J = 7.6$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 6H), 1.39 (sextet, $J = 7.6$ Hz, 2H), 1.66 (quintet, $J = 7.6$ Hz, 2H), 2.73 (t, $J = 7.6$ Hz, 2H), 3.48 (q, $J = 7.1$ Hz, 4H), 6.75 (d, $J = 9.3$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 7.40 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.90 (d, $J = 9.3$ Hz, 2H), 7.98 (d, $J = 8.8$ Hz, 2H), 8.04–8.06 (m, 4H), 8.14 (d, $J = 8.3$ Hz, 2H), 8.32 (d, $J = 8.8$ Hz, 2H); EI MS (70 eV) m/z (rel. intensity, %) 653 [M^+]

(8), 281 (11), 161 (100), 148 (14). Elemental analysis: calc. for $C_{40}H_{39}N_5O_4$ C 73.49, H 6.01, N 10.71; found C 73.90, H 5.71, N 10.59%.

4.6.3. 4-{4-[4-(Diethylamino)phenylazo]phenylazo}phenyl 4-benzoyloxybenzoate **11c**

Yield 60% m.p. 222.0–222.5°C; 1H NMR (400 MHz, $CDCl_3$) δ = 1.26 (t, J = 7.1 Hz, 6H), 3.48 (q, J = 7.1 Hz, 4H), 6.75 (d, J = 9.3 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.53–7.70 (m, 3H), 7.91 (d, J = 9.3 Hz, 2H), 7.98 (d, J = 8.8 Hz, 2H), 8.03–8.04 (m, 4H), 8.22–8.24 (m, 2H), 8.33 (d, J = 8.8 Hz, 2H); EI MS (70 eV) m/z (rel. intensity, %) 597 [M^+] (40), 372 (15), 225 (32), 148 (30), 105 (100). Elemental analysis: calc. for $C_{36}H_{31}N_5O_4$ C 72.35, H 5.23, N 11.72; found C 72.76, H 5.62, N 11.37%.

4.6.4. 4-[4-(4-Diethylamino-1-naphthylazo)phenylazo]-phenyl 4-(4-perfluorobutylbenzoyloxy)benzoate **12a**

Yield 17% m.p. 141.0–143.0°C; 1H NMR (400 MHz, $CDCl_3$) δ = 1.14 (t, J = 7.3 Hz, 6H), 3.37 (q, J = 7.3 Hz, 4H), 7.18 (d, J = 7.9 Hz, 1H), 7.42–7.44 (m, 4H), 7.57 (t, J = 8.8 Hz, 1H), 7.66 (t, J = 8.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 8.8 Hz, 2H), 8.38 (d, J = 8.8 Hz, 2H), 9.04 (d, J = 8.8 Hz, 1H); EI MS (70 eV) m/z (rel. intensity, %) 865 [M^+] (6), 422 (12), 323 (100), 198 (31). Elemental analysis: calc. for $C_{44}H_{32}F_9N_5O_4$ C 61.04, H 3.73, N 8.09; found C 60.67, H 3.53, N 8.39%.

4.7. Solubility measurement

A saturated hexane solution of an azo dye was allowed to stand overnight at 25°C. The solubility was calculated on the basis of the ϵ value of the azo dye.

4.8. Measurement of dichroism

Dye (about 0.2 wt%) was dissolved in the liquid crystal. The cell (thickness: about 9 μ m) was prepared

by filling the solution between two glass plates fitted with transparent electrodes, onto which polyimide had been applied and rubbed. The absorption of the solution was measured. The order parameter (S) was calculated on the basis of the following equation: $S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$, where A_{\parallel} and A_{\perp} represent the absorbance of light polarized parallel and perpendicular, respectively, to the direction of alignment of the dye molecules in the liquid crystal medium.

4.9. MO calculation

θ values and l/d ratios were calculated as described in our previous papers [2–5].

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References

- [1] (a) ZOLLINGER, H., 1991, *Colour Chemistry* (Weinheim: VCH); (b) GREGORY, P., 1991, *High-Technology Application of Organic Colorants* (New York: Plenum Press); (c) NOVOSELETSKI, N. V., DOROZHKINA, G. N., TORGOVA, S. I., and UMANSKI, B. A., 2001, *Mol. Cryst. liq. Cryst. Sci. Technol., A*, **352**, 27; (d) GRIFFITHS, J., and FENG, K.-C., 1999, *J. mater. Chem.*, **9**, 2333; (e) UMANSKI, B., PRUDNIKOVA, E., and TORGOVA, S., 1999, *Mol. Cryst. liq. Cryst. Sci. Technol., A*, **332**, 2537.
- [2] (a) MATSUI, M., NAKAGAWA, H., JOGLEKAR, B., SHIBATA, K., MURAMATSU, H., ABE, Y., and KANEKO, M., 1996, *Liq. Cryst.*, **21**, 669; (b) MATSUI, M., KAMINO, Y., HAYASHI, M., FUNABIKI, K., SHIBATA, K., MURAMATSU, H., ABE, Y., and KANEKO, M., 1998, *Liq. Cryst.*, **25**, 235.
- [3] MATSUI, M., TANAKA, N., ANDOH, N., FUNABIKI, K., SHIBATA, K., MURAMATSU, H., ISHIGURE, Y., KOHYAMA, E., ABE, Y., and KANEKO, M., 1998, *Chem. Mater.*, **10**, 1921.
- [4] MATSUI, M., TANAKA, N., NAKAYA, K., FUNABIKI, K., SHIBATA, K., MURAMATSU, H., ABE, Y., and KANEKO, M., 1997, *Liq. Cryst.*, **23**, 217.
- [5] MATSUI, M., SHIRAI, K., TANAKA, N., FUNABIKI, K., MURAMATSU, H., SHIBATA, K., ABE, Y., and OHGOMORI, Y., 1999, *J. mater. Chem.*, **9**, 2755.
- [6] BALLAUFF, M., WU, C., and FLORY, P. J., 1984, *Ber. Bunsenges, Phys. Chem.*, **88**, 524.