

Synthesis and UV/Vis Absorption Spectra of Novel Azo Dyes Derived from Polyfluoro- and Perfluoroazobenzenes

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Novel mono- and intermolecularly substituted, cyclized, and disazo dyes have been synthesized by the reaction of 4′-dimethylamino-2,3,4,5,6-pentafluoroazobenzene and perfluoroazobenzene with bifunctional heteroatom nucleophiles, such as 1,2-benzenedithiol, 2-aminobenzenethiol, 2-aminophenol, 1,2-ethanedithiol, ethylenediamine, and 2-aminoethanol. The kinds of bifunctional nucleophiles and the reaction conditions drastically affected the distribution of the product. The absorption maxima and the molar absorption coefficients of these dyes were observed in the range of 323–485 nm and 15000–60000 dm mol^{-1} cm^{-1}, respectively.

Azo compounds are important due to their applications to dyes, pigments, and functional materials.[1] Fluorine-containing dyes are of interest because of their reactivity with nucleophiles and their unique properties.[2] However, papers concerning the synthesis and properties of polyfluoro and perfluoro derivatives are limited. The synthesis of polyfluoro- and perfluoroazobenzenes,[3–8] their X-ray crystallography,[9–12] the UV/vis absorption spectra of fluorine-containing azobenzenes,[13] the *cis–trans* isomerization[14] and the photochemical reaction[15] of perfluoroazobenzene have been reported. Nonafluoroazobenzen-2- and -4-ol have been reported to act as inhibitors for androgen.[16] The syntheses of azoxy and benzotriazole derivatives of polyfluoro- and perfluoroazobenzenes have also been reported.[17] Though the reactions of polyfluoro- and perfluoroazobenzenes with amines and alkoxides have been reported,[7,18] those with bifunctional nucleophiles have not been published so far. When fluorine-containing azobenzenes react with bifunctional heteroatom nucleophiles, new azo dyes can be obtained. We report here on the synthesis and UV/vis absorption spectra of novel azo compounds.

Results and Discussion

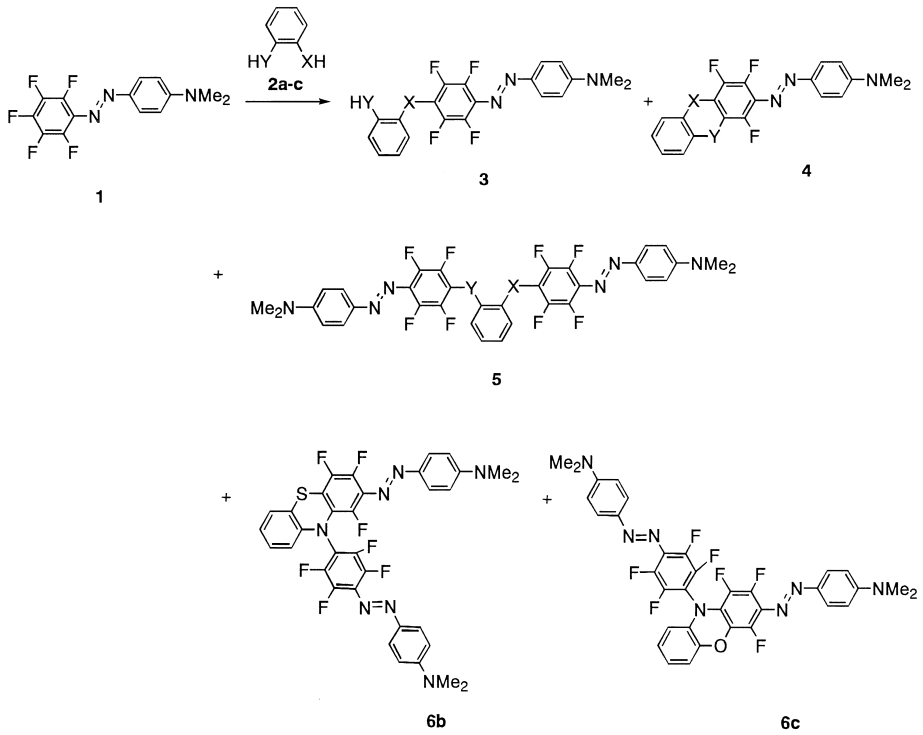
The reaction of 4′-dimethylamino-2,3,4,5,6-pentafluoroazobenzene (**1**) with aromatic bifunctional heteroatom nucleophiles **2a–c** is summarized in Scheme 1 and Table 1. The kinds of bifunctional nucleophiles and the reaction conditions drastically affected the product distribution. The reaction of **1** with 1,2-benzenedithiol (**2a**) gave both cyclized and intermolecularly substituted products, **4a** and **5a** (run 1). A monosubstituted product **3a** was not provided due to the high reactivity of another mercapto moiety under the reaction conditions. The reaction in ethanol was slower than that in DMF to give **4a** and **5a** (run 2). The yield of cyclized product **4a** increased by ten-fold volume of DMF (run 3).

The reaction of **1** with 2-aminobenzenethiol (**2b**) at 25 °C provided only a monosubstituted product **3b** (runs 4–7). Meanwhile, when **1** reacted with **2b** at 153 °C (refluxing DMF), both the monosubstituted and cyclized products, **3b** and **4b**, were obtained (runs 8–10). The reaction of **1** with monosubstituted product **3b** at 153 °C in the presence of potassium carbonate provided not an intermolecularly substituted product **5b**, but a cyclyzed product **4b** in 53% yield. This result suggests that the aromatic bifunctional nucleophiles react with **1** to produce cyclized products **4** due to the stability of an extended π-conjugated electron system of the products. The reaction of **1** with 2-aminophenol (**2c**) at 25 °C was slow and preferentially provided a monosubstituted product **3c** (run 12). Compound **1** also reacted with **2c** at 153 °C to afford both monosubstituted and cyclized products, **3c** and **4c** (run 13). Interestingly, the reactions of **1** with a half molar amount of **2b** and **2c** at 153 °C produced the corresponding disazo derivatives, **6b** and **6c**, respectively (runs 11 and 14). Actually, both compounds **4b** and **4c** reacted with an equimolar amount of **1** in the presence of potassium carbonate at 153 °C to give disazo derivatives, **6b** and **6c**, in 53 and 31% yields, respectively. The reactivity of **2b** with **1** was higher than that of **2c** with **1**.

The reaction of **1** with *o*-phenylenediamine at 153 °C in the presence of potassium carbonate was very complicated, giving several unidentified products in very low yields.

The reaction of **1** with aliphatic bifunctional nucleophiles **2d–f** is shown in Scheme 2 and Table 1. The reaction of **1** with 1,2-ethanedithiol (**2d**) provided mono- and intermolecularly substituted products, **3d** and **5d** (run 15). Ethylenediamine (**2e**) also reacted with **1** to give mono and intermolecular substitution products, **3e** and **5′e** (run 16). The reaction of **1** with 2-aminoethanol (**2f**) afforded only monosubstituted products, **3f** and **3f′** (run 17). No intermolecular substitution product **5f** was isolated, because of the low nucleophilicity of the oxygen atom in **3f**. No formation of cyclized products **4** was observed in the reaction of **1** with the aliphatic bifunctional nucleophiles, **2d**, **2e**, and **2f**. Thus, the product distribution in the reaction of **1** with aromatic bifunctional nucleophiles **2** mainly depended on the reaction temperature. The kind of bases scarcely affected the product distribution.

To prepare new dicyclized azo dyes, the reaction of **4** with **2a** was examined. The results are indicated in Scheme 3 and



Scheme 1.

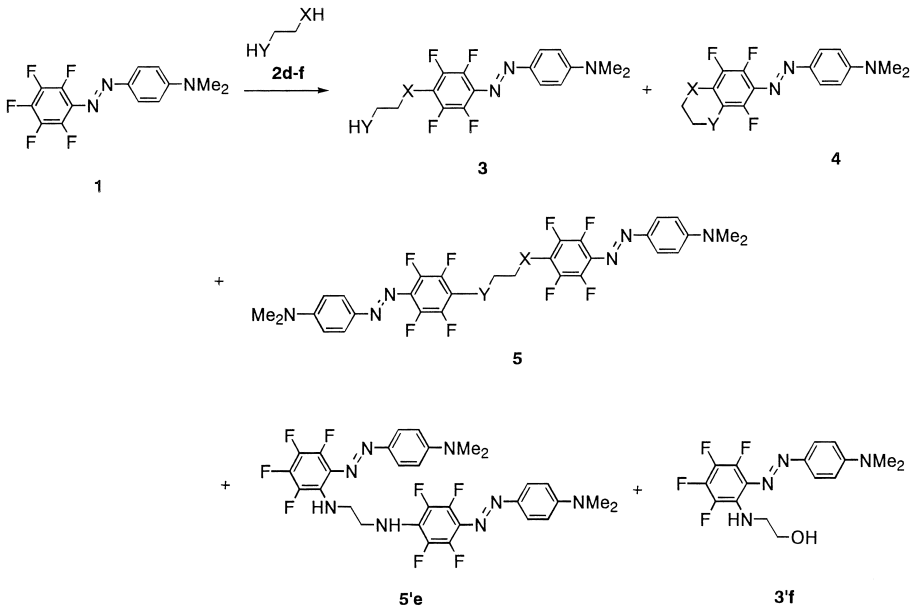
Table 1. Reaction of 4′-Dimethylamino-2,3,4,5,6-pentafluoroazobenzene (**1**) with Bifunctional Nucleophiles **2**

Run	Nucleophiles			Conditions					Conv	Yield[a)]/%			
	Compd	X	Y	Mol amt of nucleophiles	Additive (mol amt)	Temp/°C	Time/h	Solvent (mL)	%	**3**	**4**	**5**	**6**
1				1	TEA (2)	25	1	DMF (20)	100	0	20	39	—
2	**2a**	S	S	1	TEA (2)	25	1.5	EtOH (20)	75	0	5	42	—
3				1	TEA (2)	25	1	DMF (200)	94	0	41	25	—
4				1	TEA (2)	25	1.5	DMF (20)	100	97	0	0	0
5				1	NaH (2)	25	0.25	DMF (20)	96	80	0	0	0
6				1	LDA (2)	25	1	DMF (20)	90	90	0	0	0
7	**2b**	S	NH	1	K_2CO_3 (2)	25	4	DMF (20)	78	75	0	0	0
8				1	NaH (2)	153	1	DMF (20)	98	16	7	0	0
9				1	LDA (2)	153	1	DMF (20)	90	67	8	0	0
10				1	K_2CO_3 (2)	153	1	DMF (20)	100	37	26	0	0
11				0.5	K_2CO_3 (2)	153	1	DMF (20)	93	25	10	0	41
12				1	TEA (2)	50	100	DMF (20)	30	15	0	0	0
13	**2c**	NH	O	1	K_2CO_3 (2)	153	2	DMF (20)	100	22	49	0	0
14				0.5	K_2CO_3 (1)	153	2	DMF (20)	100	trace	28	0	35
15	**2d**	S	S	1	TEA (2)	0	3	DMF (20)	87	36	0	27	—
16	**2e**	NH	NH	1	TEA (2)	25	8	DMF (20)	89	60	0	4[b)]	—
17	**2f**	NH	O	1	TEA (2)	25	72	DMF (20)	92	83[c)]	0	0	—

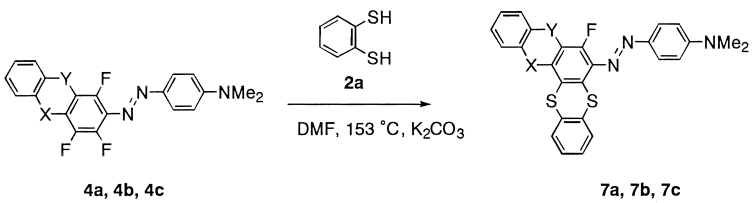
a) Isolated yields. b) **5e**: 0%, **5′e**: 4%. c) **3f**: 46%, **3′f**: 37%.

Table 2. The cyclized derivatives (**4a**, **4b**, and **4c**) reacted with an equimolar amount of **2a** in the presence of potassium carbonate at 153 °C to afford the dicyclized products (**7a**, **7b**, and **7c**) in low-to-moderate yields (runs 1–3). Thus, the fluorine atoms in compounds **4** were sufficiently active to react with another bifunctional nucleophile to give dicyclized derivatives.

The reactions of perfluoroazobenzene (8) with bifunctional nucleophiles 2 were also examined. The results are shown in Scheme 4 and Table 3. The reaction of 8 with ethylenediamine (2e) afforded an intermolecular substitution product 10e (run 1). That of 8 with 2-aminoethanol (2f) provided monosubstituted products, 9f and 9′f (run 2). The reactions of 8 with other



Scheme 2.

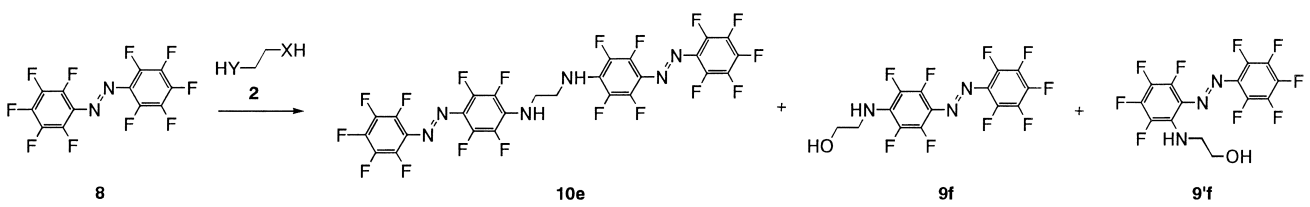


Scheme 3.

Table 2. Reaction of Cyclized Derivatives **4** with 1,2-Benzenedithiol (**2a**)

Run	Starting material	X	Y	Conv/%	Yield of **7**[a)]/%
1	**4a**	S	S	100	46
2	**4b**	S	NH	89	20
3	**4c**	NH	O	97	8

a) Isolated yields.



Scheme 4.

Table 3. Reaction of Perfluoroazobenzene (**8**) with Bifunctional Nucleophiles **2e** and **2f**

Run	Nucleophiles			Conditions					Conv	Yield[a)]/%	
	Compd	X	Y	Mol amt of nucleophiles	Additive (mol amt)	Temp/°C	Time/h	Solvent (mL)	%	**9**	**10**
1	**2e**	NH	NH	1	TEA (2)	0	4	DMF (20)	100	0	34
2	**2f**	NH	O	1	TEA (2)	0	7	DMF (20)	100	75[b)]	0

a) Isolated yields. b) **9f**: 69%, **9′f**: 6%.

Table 4. UV/Vis Absorption Spectra of Azo Derivatives[a)]

Compds	λ_{max} (ε)/nm (dm mol^{-1} cm^{-1})
1	439 (28000)
3b	448 (22000)
3c	438 (24000)
3d	448 (33000)
3e	425 (22000), 455 (21000)
3f	425 (24000), 454 (24000)
3′f	467 (24000), 482 (24000)
4a	446 (18000)
4b	477 (19000)
4c	472 (29000)
5a	458 (60000)[b)]
5d	449 (57000)[b)]
5e	457 (46000)[b)]
6b	454 (54000)[b)]
6c	465 (59000)[b)]
7a	445 (30000)[b)]
7b	321 (10000), 404 (13000), 484 (16000)[b)]
7c	400 (shoulder), 485 (13000)[b)]
8	312 (20000)
9f	392 (29000)
9′f	323 (15000)
10e	397 (55000)

a) Measured in ethanol. b) Measured in chloroform.

bifunctional nucleophiles 2a–d were very complicated to give several unidentified products in very low yields. This may be attributed to the stronger electron-withdrawing nature and many more reaction positions in the perfluoro derivative 8 than in the pentafluoro derivative 1.

The UV/vis absorption spectra of the products are indicated in Table 4. The absorption maxima (λ_{max}) of **1**, **3**, **4**, **5**, **6**, and **7** were observed in the range of 438–485 nm, being orange to red in color. The molar absorption coefficients (ε) of **5** and **6** were as ca. two-times as intense as that of **1** due to two azo chromophores in a molecule. The azo dyes, **9** and **10**, derived from **8** showed their absorption maxima in the range of 323–397 nm.

Conclusions

We have synthesized novel azo dyes by the reaction of fluorine-containing azobenzenes with bifunctional nucleophiles.

In the reactions of 4′-dimethylamino-2,3,4,5,6-pentafluoroazobenzene with the bifunctional nucleophiles, the product distribution drastically changed based on the kinds of nucleophiles and reaction conditions to produce mono- and intermolecularly substituted, cyclized, and disazo derivatives. 1,2-Benzenedithiol was very active to give both cyclized and intermolecularly substituted derivatives even at 25 °C. The reactions with 2-aminobenzenethiol and 2-aminophenol at 25 °C preferentially afforded mono-substituted derivatives. The reaction at 153 °C provided both the mono-substituted and cyclized products. Disazo derivatives were also produced by the reaction of the cyclized products with 4′-dimethylamino-2,3,4,5,6-pentafluoroazobenzene.

The reaction of perfluoroazobenzene with the aromatic bifunctional nucleophiles was usually complicated. The reaction with aliphatic bifunctional nucleophiles gave mono- and intermolecularly substituted derivatives.

The absorption maxima of these novel azo compounds derived from the fluorine-containing azobenzenes were observed in the range of 323–485 nm.

Experimental

Instruments. The melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were recorded on a JEOL α-400 spectrometer. Mass spectra were taken on a Shimadzu QP-1000 spectrometer. UV/vis absorption spectra were measured with a Shimadzu UV-160A spectrometer.

Materials. *N*,*N*-Dimethyl-*p*-phenylenediamine, 1,2-benzenedithiol (**2a**), 2-aminobenzenethiol (**2b**), 2-aminophenol (**2c**), 1,2-ethanedithiol (**2d**), ethylenediamine (**2e**), 2-aminoethanol (**2f**) were purchased from Tokyo Kasei Co., Ltd. Perfluoroazobenzene (**8**) was prepared as described in the literature.[7]

Synthesis of 4′-Dimethylamino-2,3,4,5,6-pentafluoroazobenzene (1). To a toluene solution (48 mL) of pentafluoronitrosobenzene[19] (0.985 g, 5 mmol) was added an acetic acid solution (2 mL) of *N*,*N*-dimethyl-*p*-phenylenediamine (0.680 g, 5 mmol). The mixture was heated at 75 °C for 30 h. After the reaction was completed, the mixture was poured into water (200 mL). The product was extracted with dichloromethane, purified by column chromatography (SiO_2, hexane–toluene = 1:2), and recrystallized from hexane. The physical and spectral data of **1** are shown below. Yield 1.085 g (69%); mp 149.0–149.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.13 (s, 6H), 6.74 (d, J = 9.5 Hz, 2H), 7.87 (d, J = 9.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −85.50 to −85.36 (m, 2F), −78.90 (t, J = 21.0 Hz, 1F), −74.12 to −74.03 (m, 2F); EIMS (70 eV) *m*/*z* (rel intensity) 315 (M^+; 60), 121 (100), 120 (68), 77 (49).

Reaction of Fluoroazobenzenes 1 and 8 with Nucleophiles 2. To a solution (15 mL) of fluoroazobenzenes **1** or **8** (0.5 mmol) were added a solution (5 mL) of nucleophile **2** and an additive. The mixture was stirred. After the reaction, the mixture was poured into water (200 mL). The resulting precipitate was collected by filtration. The products were isolated by column chromatography (SiO_2, **4a**, **5a**, **4b**, **3b**, and **10e**: hexane–toluene = 1:2; **3c**, **4c**, **3d**, **5d**, **6b**, and **6c**: toluene; **5e**, **3f**, **3′f**, **9f**, and **9′f**: dichloromethane; **3e**: acetone) and recrystallized (**4a**, **5a**, **3b**, **9f**, and **9′f**: hexane; **4b**, **3c**, **4c**, **3d**, **5d**, **3e**, **5e**, **3f**, **3′f**, **6b**, and **6c**: toluene; **10e**: chloroform–hexane).

2-[4-(Dimethylamino)phenylazo]-1,3,4-trifluorothianthrene (4a). mp 210.5–211.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.12 (s, 6H), 6.74 (d, J = 8.9 Hz, 2H), 7.30–7.33 (m, 2H), 7.54–7.57 (m, 2H), 7.87 (d, J = 8.9 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −69.10 (d, J = 11.3 Hz, 1F), −60.09 (dd, J = 21.4 and 11.3 Hz, 1F), −45.44 (d, J = 21.4 Hz, 1F); EIMS (70 eV) *m*/*z* (rel intensity) 417 (M^+; 58), 148 (24), 120 (100), 105 (22), 77 (28). Anal. Found: C, 57.84; H, 3.44; N, 10.02%. Calcd for $C_{20}H_{14}F_3N_3S_2$: C, 57.54; H, 3.38; N, 10.07%.

1,2-Bis{4-[4-(dimethylamino)phenylazo]-2,3,5,6-tetrafluorophenylthio}benzene (5a). mp 235.5–236.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.13 (s, 12H), 6.74 (d, J = 9.3 Hz, 4H), 7.15–7.21 (m, 4H), 7.89 (d, J = 9.3 Hz, 4H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −73.41 to −73.33 (m, 4F), −55.97 to −55.88 (m, 4F); EIMS (70 eV) *m*/*z* (rel intensity) 732 (M^+; 12), 148 (26), 120 (100), 105 (19), 104 (13), 77 (22). Anal. Found: C, 56.11; H, 3.37; N, 11.18%. Calcd for $C_{34}H_{24}F_8N_6S_2$: C, 55.73; H, 3.30; N, 11.47%.

2-{4-[4-(Dimethylamino)phenylazo]-2,3,5,6-tetrafluorophenylthio}aniline (3b). mp 200.0–202.0 °C; ^{1}H NMR ($CDCl_3$) δ

3.12 (s, 6H), 4.45 (br s, 2H), 6.67–6.72 (m, 2H), 6.73 (d, J = 9.0 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.86 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −73.87 to −73.78 (m, 2F), −57.25 to −57.16 (m, 2F); EIMS (70 eV) *m/z* (rel intensity) 420 (M^+; 58), 148 (19), 120 (100), 105 (21), 77 (28). Anal. Found: C, 57.22; H, 3.89, N, 13.01%. Calcd for $C_{20}H_{16}F_4N_4S$: C, 57.14; H, 3.84; N, 13.33%.

2-[4-(Dimethylamino)phenylazo]-1,3,4-trifluorophenothiazine (4b). mp 194.5–195.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.10 (s, 6H), 6.62 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 9.3 Hz, 2H), 6.89 (t, J = 7.6 Hz, 1H), 6.98–7.06 (m, 2H), 7.82 (d, J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −87.75 (dd, J = 19.1 and 10.3 Hz, 1F), −70.95 (dd, J = 19.1 and 5.4 Hz, 1F), −48.73 (dd, J = 10.3 and 5.4 Hz, 1F); EIMS (70 eV) *m/z* (rel intensity) 400 (M^+; 48), 148 (32), 120 (100), 105 (19), 77 (22). Anal. Found: C, 59.75; H, 3.96; N, 13.72%. Calcd for $C_{20}H_{15}F_3N_4S$: C, 59.99; H, 3.78; N, 13.99%.

2-[4-(Dimethylamino)phenylazo]-10-{4-[4-(dimethylamino)-phenylazo]-2,3,5,6-tetrafluorophenyl}-1,3,4-trifluorophenothiazine (6b). mp 221.5–222.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.10 (s, 6H), 3.13 (s, 6H), 6.69 (d, J = 9.3 Hz, 2H), 6.72 (d, J = 9.3 Hz, 2H), 6.93 (d, J = 7.8 Hz, 1H), 7.02–7.17 (m, 2H), 7.85 (d, J = 9.3 Hz, 2H), 7.90 (d, J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −76.91 (dd, J = 18.3 and 9.4 Hz, 1F), −70.22 (d, J = 18.3 Hz, 1F), −66.29 to −66.20 (m, 2F), −49.50 (d, J = 9.4 Hz, 1F); EIMS (70 eV) *m/z* (rel intensity) 695 (M^+; 37), 148 (22), 120 (100), 77 (16). Anal. Found: C, 58.88; H, 3.64; N, 13.93%. Calcd for $C_{34}H_{24}F_7N_7S$: C, 58.70; H, 3.48; N, 14.09%.

2-{4-[4-(Dimethylamino)phenylazo]-2,3,5,6-tetrafluorophenylamino}phenol (3c). mp 139.0–140.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.13 (s, 6H), 4.40 (br s, 2H), 6.67–6.72 (m, 2H), 6.75 (d, J = 9.3 Hz, 2H), 6.82–6.84 (m, 1H), 6.96–9.97 (m, 1H), 7.89 (d, J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −78.38 to −78.29 (m, 2F), −74.65 to −74.56 (m, 2F); EIMS (70 eV) *m/z* (rel intensity) 404 (M^+; 66), 148 (14), 120 (100), 105 (17), 77 (22). Anal. Found: C, 59.24; H, 4.13; N, 13.87%. Calcd for $C_{20}H_{16}F_4N_4O$: C, 59.41; H, 3.99; N, 13.86%.

3-[4-(Dimethylamino)phenylazo]-1,2,4-trifluorophenoxazine (4c). mp 211.5–212.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.10 (s, 6H), 5.56 (br s, 1H), 6.52–6.54 (m, 1H), 6.73 (d, J = 9.0 Hz, 2H), 6.77–6.87 (m, 3H), 7.83 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −89.27 (dd, J = 19.8 and 8.6 Hz, 1F), −76.73 (dd, J = 19.8 and 3.4 Hz, 1F), −72.94 (dd, J = 8.6 Hz, 1F); EIMS (70 eV) *m/z* (rel intensity) 384 (M^+; 100), 148 (21), 120 (73). Anal. Found: C, 63.22; H, 4.25; N, 13.72%. Calcd for $C_{20}H_{15}F_3N_4O$: C, 62.50; H, 3.93; N, 14.58%.

3-[4-(Dimethylamino)phenylazo]-10-{4-[4-(dimethylamino)-phenylazo]-2,3,5,6-tetrafluorophenyl}-1,2,4-trifluorophenoxazine (6c). mp 221.5–223.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.11 (s, 6H), 3.15 (s, 6H), 6.37 (d, J = 8.1 Hz, 1H), 6.74 (d, J = 9.4 Hz, 2H), 6.76 (d, J = 9.4 Hz, 2H), 6.85 (t, J = 8.1 Hz, 1H), 6.70–6.90 (m, 2H), 7.85 (d, J = 9.4 Hz, 2H), 7.92 (d, J = 9.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −83.25 (dd, J = 19.8 and 8.4 Hz, 1F), −76.58 (dd, J = 19.8 and 3.1 Hz, 1F), −74.13 to −74.04 (m, 2F), −73.21 (dd, J = 8.4 and 3.1 Hz, 1F); EIMS (70 eV) *m/z* (rel intensity) 679 (M^+; 7), 148 (31), 120 (100), 77 (14). Anal. Found: C, 60.21; H, 3.86; N, 14.31%. Calcd for $C_{34}H_{24}F_7N_7O$: C, 60.09; H, 3.56; N, 14.43%.

2-{4-[4-(Dimethylamino)phenylazo]-2,3,5,6-tetrafluorophenylthio}ethanethiol (3d). mp 114.0–114.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.71 (q, J = 8.3 Hz, 2H), 3.14 (s, 6H), 3.14 (t, J = 8.3 Hz, 1H), 6.75 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −73.81 to −73.72 (m, 2F), −57.04 to −56.96 (m, 2F). EIMS (70 eV) *m/z* (rel intensity) 389 (M^+; 100), 148 (20), 120 (91), 105 (16), 77 (18). Anal. Found: C, 49.02; H, 3.85, N, 10.43%. Calcd for $C_{16}H_{15}F_4N_3S_2$: C, 49.35, H, 3.88; N, 10.79%.

1,2-Bis{4-[4-(dimethylamino)phenylazo]-2,3,5,6-tetrafluorophenylthio}ethane (5d). mp 230.5–231.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.12 (s, 4H), 3.13 (s, 12H), 6.74 (d, J = 9.1 Hz, 4H), 7.88 (d, J = 9.1 Hz, 4H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −73.64 to −73.55 (m, 4F), −57.01 to −56.93 (m, 4F); EIMS (70 eV) *m/z* (rel intensity) 684 (M^+; 7), 148 (20), 120 (100), 105 (15), 77 (19). Anal. Found: C, 52.93; H, 3.63; N, 11.86%. Calcd for $C_{30}H_{24}F_8N_6S_2$: C, 52.63; H, 3.53; N, 12.27%.

4′-Dimethylamino-4-(2-aminoethylamino)-2,3,5,6-tetrafluoroazobenzene (3e). mp 179.0–178.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.46 (br s, 2H), 2.98 (t, J = 5.9 Hz, 2H), 3.09 (s, 6H), 3.50 (q, J = 5.9 Hz, 2H), 4.60 (br s, 1H), 6.73 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −84.67 to −84.63 (m, 2F), −75.37 to −75.28 (m, 2F); EIMS (70 eV) *m/z* (rel intensity) 355 (M^+; 9), 148 (16), 120 (100), 105 (17), 77 (21). Anal. Found: C, 53.72; H, 5.11; N, 20.08%. Calcd for $C_{16}H_{17}F_7N_5$: C, 54.08; H, 4.82; N, 19.71%.

***N*-2-[4-(Dimethylamino)phenylazo]-3,4,5,6-tetrafluorophenyl-*N*′-4-[4-(dimethylamino)phenylazo]-2,3,5,6-tetrafluorophenylethylenediamine (5′e).** mp 225.5–226.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.03 (s, 6H), 3.11 (s, 6H), 3.69 (br s, 4H), 6.64 (d, J = 9.3 Hz, 2H), 6.74 (d, J = 9.3 Hz, 2H), 7.63 (d, J = 9.3 Hz, 2H), 7.83 (d, J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −96.29 (td, J = 21.6 and 5.0 Hz, 1F), −83.93 to −93.89 (m, 2F), −82.58 to −82.51 (m, 1F), −77.16 (td, J = 21.6 and 5.0 Hz, 1F), −74.64 to −74.56 (m, 2F), −70.31 to −70.22 (m, 1F); EIMS (70 eV) *m/z* (rel intensity) 650 (M^+; 0.7), 135 (100), 120 (38), 105 (19), 77 (23). Anal. Found: C, 53.79; H, 4.08; N, 17.44%. Calcd for $C_{30}H_{26}F_8N_8$: C, 55.39; H, 4.03; N, 17.21%.

2-{4-[4-(Dimethylamino)phenylazo]-2,3,5,6-tetrafluorophenyl}aminoethanol (3f). mp 198.5–199.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.10 (s, 6H), 3.56–3.64 (m, 2H), 3.81–3.88 (m, 2H), 4.42 (br s, 1H), 6.73 (d, J = 9.3 Hz, 2H), 7.83 (d, J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −84.03 to −83.94 (m, 2F), −75.07 to −74.95 (m, 2F); EIMS (70 eV) *m/z* (rel intensity) 356 (M^+; 90), 121 (100). Anal. Found: C, 53.70; H, 4.48; N, 15.48%. Calcd for $C_{16}H_{16}F_4N_4O$: C, 53.93; H, 4.53; N, 15.72%.

2-{2-[4-(Dimethylamino)phenylazo]-3,4,5,6-tetrafluorophenyl}aminoethanol (3′f). mp 204.5–205.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.09 (s, 6H), 3.60–3.65 (m, 2H), 3.82–3.85 (m, 2H), 6.73 (d, J = 9.3 Hz, 2H), 7.80 (d, J = 9.3 Hz, 2H), 9.37 (br s, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −97.18 to −97.04 (m, 1F), −82.56 to −82.44 (m, 1F), −77.29 to −77.17 (m, 1F), −70.74 to −70.63 (m, 1F); EIMS (70 eV) *m/z* (rel intensity) 356 (M^+; 14), 136 (100), 121 (11). Anal. Found: C, 54.02; H, 4.48; N, 15.46%. Calcd for $C_{16}H_{16}F_4N_4O$: C, 53.93; H, 4.53; N, 15.72%.

***N*,*N*′-Bis[2,3,4,5,6-tetrafluoro-4-(pentafluorophenylazo)-phenyl]ethylenediamine (10e).** mp 193.0–194.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.85–3.86 (m, 4H), 4.63 (br s, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −84.66 to −84.52 (m, 6F), −74.60 to −74.49 (m, 4F), −72.74 to −72.65 (m, 4F), −70.59 to −70.48 (m, 4F); EIMS (70 eV) *m/z* (rel intensity) 744 (M^+; 17), 373 (100), 177 (65). Anal. Found: C, 41.83; H, 1.10; N, 11.47%. Calcd for $C_{26}H_6F_{18}N_6$: C, 41.95; H, 0.81; N, 11.29%.

2-{[2-(Pentafluorophenyl)azo-3,4,5,6-tetrafluorophenyl]-amino}ethanol (9f). mp 103.0–104.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.74 (q, J = 4.8 Hz, 2H), 3.91 (q, J = 4.8 Hz, 2H), 4.90 (br s, 1H);

^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −84.71 (d, J = 13.7 Hz, 2F), −84.51 to −84.42 (m, 2F), −74.97 (t, J = 17.9 Hz, 1F), −72.74 (d, J = 17.9 Hz, 2F), −70.71 (d, J = 13.7 Hz, 2F); EIMS (70 eV) *m/z* (rel intensity) 403 (M^+; 100), 372 (46), 177 (58), 167 (20); Anal. Found: C, 41.90; H, 1.66; N, 10.49%. Calcd for $C_{14}H_6F_9N_3O$: C, 41.70; H, 1.50; N, 10.42%.

2-{[(2-Pentafluorophenyl)azo-3,4,5,6-tetrafluorophenyl]-amino}ethanol (9′f). mp 165.0–166.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.78 (q, J = 5.1 Hz, 2H), 3.88 (q, J = 5.1 Hz, 2H), 9.71 (br s, H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −96.39 (t, J = 18.3 Hz, 1F), −84.04 to −83.94 (m, 2F), −82.33 (d, J = 18.3 Hz, 1F), −74.78 (t, J = 18.3 Hz, 1F), −72.51 (d, J = 18.3 Hz, 2F), −68.70 (t, J = 18.3 Hz, 1F), −66.11 (d, J = 18.3 Hz, 1F); EIMS (70 eV) *m/z* (rel intensity) 403 (M^+; 15), 372 (35), 191 (55), 182 (100), 167 (21), 155 (16).

Reaction of 4 with 2a. To a DMF solution (15 mL) of **4** (0.5 mmol) were added a DMF solution (5 mL) of **2a** (0.5 mmol) and potassium carbonate (138 mg, 1.0 mmol). The mixture was refluxed (**7a**, **7b**: 3 h; **7c**: 4 h). After the reaction, the mixture was poured into brine (200 mL). The resulting precipitate was corrected by filtration. The products were isolated by column chromatography (SiO_2, toluene). The crude product was recrystallized from an ethyl acetate-hexane mixed solution. The physical and spectral data are shown below.

7a. mp 297.5–198.0 °C; ^{1}H NMR (DMSO-d_6) δ 3.13 (s, 6H), 6.90 (d, J = 9.3 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.42–7.45 (m, 3H), 7.66–7.74 (m, 3H), 7.86 (d, J = 9.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −43.29 (s, 1F); EIMS (70 eV) *m/z* (rel intensity) 519 (M^+; 67), 120 (100). Anal. Found: C, 60.55; H, 3.52; N, 7.87%. Calcd for $C_{26}H_{18}FN_3S_4$: C, 60.09; H, 3.49; N, 8.09%.

7b. mp 223.5–224.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.12 (s, 6H), 6.68 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.85 (t, J = 7.6 Hz, 1H), 6.98–7.05 (m, 3H), 7.18–7.22 (m, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −44.99 (s, 1F); EIMS (70 eV) *m/z* (rel intensity) 502 (M^+; 47), 120 (100). Anal. Found: C, 61.90; H, 3.97; N, 11.42%. Calcd for $C_{26}H_{18}FN_4S_3$: C, 62.13; H, 3.81; N, 11.05%.

7c. mp 245.0–245.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.12 (s, 6H), 6.15 (s, 1H), 6.58 (d, J = 7.8 Hz, 1H), 6.73–6.84 (m, 3H), 6.79 (d, J = 8.8 Hz, 2H), 7.18 (t, J = 7.8 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ −68.21 (s, 1F); EIMS (70 eV) *m/z* (rel intensity) 486 (M^+; 28), 120 (100).

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