Perfluoroalkylquinones. Synthesis Using Bis(perfluoroalkanoyl) Peroxides, Absorption Bands, and Solubility

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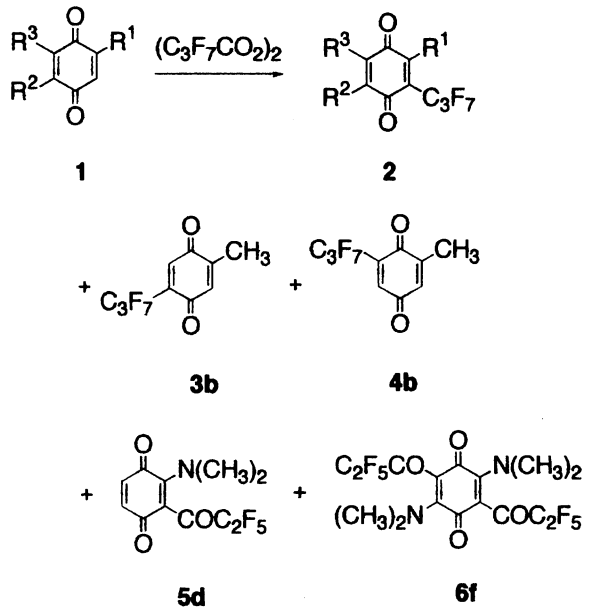
The reactions of 1,4-benzo-, naphtho-, and 9,10-anthraquinones with bis(perfluoroalkanoyl) peroxides gave the corresponding perfluoroalkylated derivatives. Those of 2-methyl- and 2-[4-(chloroanilino)]-1,4-naphthoquinones with bis(oxaperfluoroalkanoyl) peroxides afforded the dichloromethyl and trifluoromethyl derivatives, respectively. Absorption bands of the perfluoroalkylated naphtho- and anthraquinone dyes showed a slight hypsochromic shift. The solubilities of the perfluoroalkylated anthraquinone dyes into hexane were much more higher than those of the non-perfluoroalkylated ones.

Quinones are used in various drugs and dyes. To invent excellent blood coagulators and antimalariants, the alkylations of 2-methyl-1,4-naphthoquinone (Vitamin K) and 2-hydroxy-1,4-naphthoquinone have already been performed.[1] 1,4-Naphthoquinones and 9,10-anthraquinones also play a very important role in the field of dye chemistry. 2-(4-Chloroanilino)-1,4-naphthoquinone (CI Vat Yellow 5) is a useful dyestuff for dyeing of silk and wool. Such 9,10-anthraquinone dyes, having yellow, magenta, or cyan hue, can be used not only as a dyestuff but also as organic functional materials in data storage, information recording, and information display systems.[2] The introduction of fluorine atoms or a trifluoromethyl group alters the absorption bands, stability for heat and UV irradiation, and solubility of the dye molecule.[3] Therefore, it is of interest to synthesize perfluoroalkylquinones and examine their properties. Bis(perfluoroalkanoyl) and bis(oxaperfluoroalkanoyl) peroxides are useful perfluoroalkylation reagents for electron-rich substrates such as olefins, homoaromatics, heteroaromatics, and polymers.[4]

In our continuing study on the syntheses and properties of perfluoroalkylated compounds,[5] perfluoroalkylquinones have been synthesized by using bis(perfluoroalkanoyl) and bis(oxaperfluoroalkanoyl) peroxides as perfluoroalkylating reagents; their absorption bands and solubility are examined in this report.

Results and Discussion

Perfluoroalkylation of 1, 4- Benzoquinones. The reaction of 1,4-benzoquinones **1** with bis(perfluorobutyryl) peroxide is shown in Scheme 1 and Table 1. Quinones **1a—c**, **1e**, and **1g** reacted with the peroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon® 113) to give the corresponding 3-(perfluoropropyl)-1,4-benzoquinones **2** in low yields accompanied by the formation of unidentified products unable to be developed by column chromatography (Runs 1—3, 5, 7). In the reaction of **1b**, a mixture of two unseparable isomers **3b** and **4b** was also obtained. Those of **1d** and **1f**, having one or more strong electron-donating dimethylamino group(s), afforded the perfluoropropionyl derivatives **5d** and **6f**, respectively (Runs 4 and 6). The formed perfluoropropyl derivatives would react with a hydroxide ion followed by loss of hydrogen fluoride to produce the perfluoropropionyl derivatives during the isolation process of the products (Scheme 2).



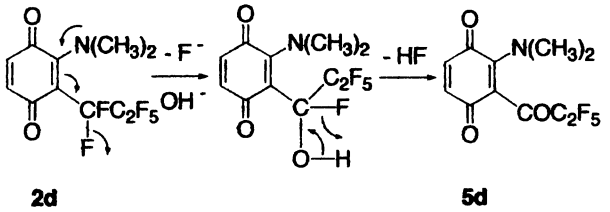
Scheme 1.

Perfluoroalkylation of Naphthoquinones.

Table 1. Perfluoropropylation of Benzoquinones[a)]

Run	Compd	R^1	R^2	R^3	IP[b)]/V	Conv. %	Yield/% 2	Others
1	**a**	H	H	H	>2.50	48	11	
2	**b**	CH_3	H	H	>2.50	78	8	**3b**+**4b** (7%)[c)]
3	**c**	C_6H_5	H	H	>2.50	56	10	
4	**d**	$N(CH_3)_2$	H	H	0.68	82	0	**5d** (9%)
5	**e**	CH_3	CH_3	H	>2.50	56	17	
6	**f**	$N(CH_3)_2$	$N(CH_3)_2$	H	0.68	85	0	**6f** (6%)
7	**g**	CH_3	H	CH_3	>2.50	62	16	

a) Refluxing under nitrogen atmosphere for 4 h. b) Onset ionization potential (Ag/Ag^+) in acetonitrile. c) Total yield of two isomers. Identified by GC-MS and NMR analyses and determined by the NMR spectrum of the mixture (**3b**:**4b**=1:1).

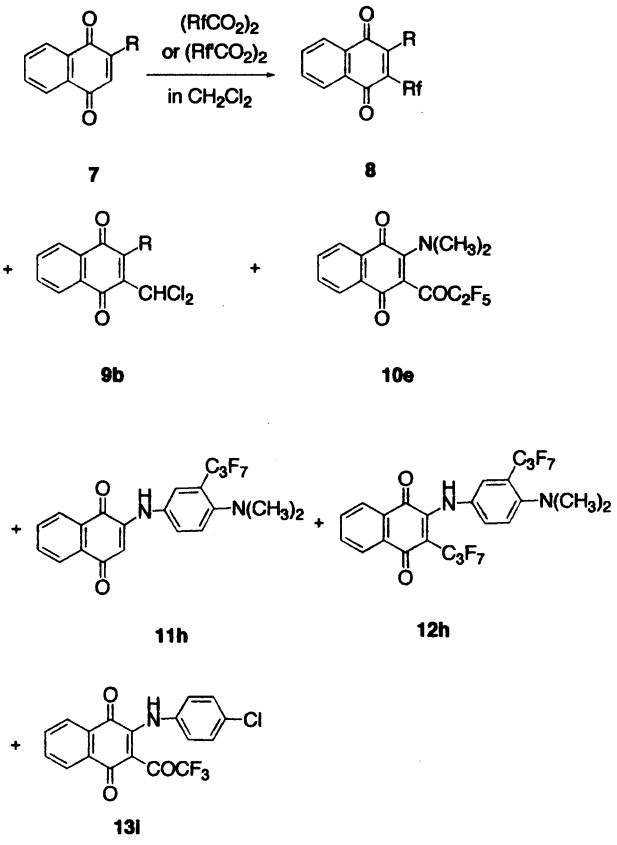


Scheme 2.

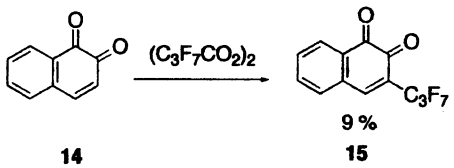
Scheme 3 and Table 2 summarize the reaction of 1,4-naphthoquinones **7** with bis(perfluoroalkanoyl) and bis(oxaperfluoroalkanoyl) peroxides. Quinones **7a**—**d**, **7f**, **7g**, **7i** reacted with bis(perfluorobutyryl) peroxide to afford the 3-perfluoroalkyl derivatives **8** in low to good yields (Runs 1—4, 9—11, 13, 14, 16). 1,4-Naphthoquinone **7c**, having a low ionization potential (IP), reacted more smoothly with the peroxide than **7a** and **7b** which have rather high IP values (Runs 1—4, 9, 10). This suggests the single electron transfer (SET) mechanism for the perfluoroalkylation. In the case of **7h**, the corresponding 3-perfluoroalkylated derivative **8h** was not obtained, but **11h** and **12h** were isolated (Run 15). This result indicates that the 3-position of the 4-(dimethylamino)anilino moiety is more reactive toward the peroxide than the 3-position of the naphthoquinone skeleton. 1,4-Naphthoquinone **7e** bearing a dimethylamino group reacted with bis(perfluorobutyryl) peroxide to give the 3-perfluoropropionyl derivative **10e** (Run 12), as in the cases of 1,4-benzoquinones **1d** and **1f**. The reaction of **7b** and **7i** with bis(perfluoroalkanoyl) peroxides gave the corresponding 3-perfluoroalkyl derivatives **8′b**, **8″b**, **8′i**, and **8″i**, respectively (Runs 5, 6, 17, 18). Interestingly, the reactions with bis(oxaperfluoroalkanoyl) peroxides afforded the corresponding 3-(dichloromethyl) and 3-(trifluoroacetyl) derivatives **9b** and **13i**, respectively (Runs 7, 8, 19, 20).

The reaction of 1,2-naphthoquinone (**14**) (IP: >2.50 V) with bis(perfluorobutyryl) peroxide gave 3-(perfluoropropyl)-1,2-naphthoquinone (**15**) in 9% yield (Scheme 4).

Perfluoroalkylation of 9,10-Anthraquinones. Scheme 5 and Table 3 exhibit the reaction of 1-substituted anthraquinones **16** with bis(perfluorobutyryl)



Scheme 3.



Scheme 4.

peroxide. The reactivity (conversion) was in the order of the substituent R: H (16%)<OH (42%)<NH_2 (90%), $NHCH_3$ (97%), NHC_2H_5 (100%), NHC_6H_5 (95%), suggesting an SET mechanism for the perfluoroalkylation

Table 2. Perfluoroalkylation of Naphthoquinones[a)]

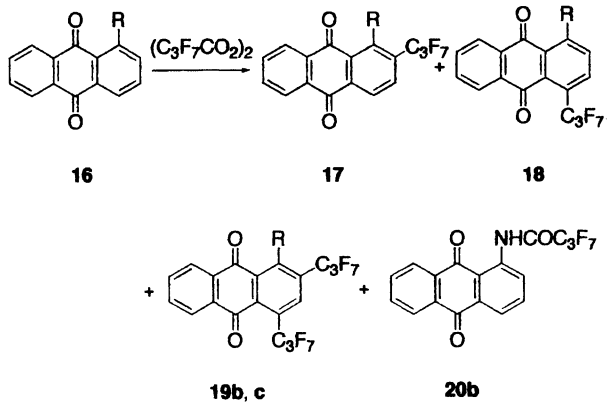
Run	Compd	R	IP[b)]/V	Rf (Rf′)	Conv. %	Yield/% 8	Others
1	**a**	H	>2.50	C_3F_7	25	Trace	
2	**a**	H		C_3F_7	99[c)]	15[c)]	
3	**b**	CH_3	>2.50	C_3F_7	50	17	
4	**b**	CH_3		C_3F_7	84[c)]	54[c)]	
5	**b**	CH_3		CF_3	19	3	
6	**b**	CH_3		C_6F_{13}	88	41	
7	**b**	CH_3		$CF(CF_3)OC_3F_7$	65	0	**9b** (22%)
8	**b**	CH_3		$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	54	0	**9b** (33%)
9	**c**	$NHCH_3$	1.03	C_3F_7	99	76	
10	**c**	$NHCH_3$		C_3F_7	99[c)]	71[c)]	
11	**d**	NHC_2H_5	0.99	C_3F_7	97	70	
12	**e**	$N(CH_3)_2$	0.86	C_3F_7	84	0	**10e** (30%)
13	**f**	NHC_6H_5	0.96	C_3F_7	92	75	
14	**g**	$NHC_6H_4OCH_3$ (*p*)	0.46	C_3F_7	78	58	
15	**h**	$NHC_6H_4N(CH_3)_2$ (*p*)	0.15	C_3F_7	55	0	**11h** (6%), **12h** (8%)
16	**i**	NHC_6H_4Cl (*p*)	0.99	C_3F_7	88	67	
17	**i**	NHC_6H_4Cl (*p*)		CF_3	76	31	
18	**i**	NHC_6H_4Cl (*p*)		C_6F_{13}	90	67	
19	**i**	NHC_6H_4Cl (*p*)		$CF(CF_3)OC_3F_7$	65	0	**13i** (30%)
20	**i**	NHC_6H_4Cl (*p*)		$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	65	0	**13i** (50%)

a) Stirring at 0 °C under nitrogen atmosphere for 4 h. b) Onset ionization potential (Ag/Ag^+) in acetonitrile.
c) Refluxing under nitrogen atmosphere for 4 h.

Table 3. Perfluoropropylation of 1-Substituted Anthraquinones[a)]

Run	Compd	R	IP[b)]/V	Conv. %	Yield/% 17	Yield/% 18	Selectivity[c)]	Others
1	**a**	H	>2.50	16	2	0		
2	**b**	NH_2	0.96	90	22	19	1.16	**19b** (18%), **20b** (9%)
3	**c**	$NHCH_3$	0.84	97	10	53	0.19	**19c** (12%)
4	**d**	NHC_2H_5	0.88	100	0	22	0	**18b** (6%)
5	**e**	NHC_6H_5	0.75	95	0	34	0	
6	**f**	$N(CH_3)_2$	0.64	67	0	15	0	**16c** (6%), **18c** (23%), **19c** (2%)
7	**g**	OH	>2.50	42	25	0		

a) Stirring at 0 °C under nitrogen atmosphere for 4 h. b) Onset ionization potential (Ag/Ag^+) in acetonitrile.
c) Defined on the basis of the yields of **17** : **18**.



Scheme 5.

of 9,10-anthraquinones. Both the 2- and 4-perfluoropropyl derivatives **17** and **18** were produced. The selectivity (**17**/**18**) was drastically changed by the substituent R: NHC_2H_5, NHC_6H_5, $N(CH_3)_2 < NH_2$, $NHCH_3 < H$, OH. The less was the bulkiness of the substituent, the larger was the formation of 2-perfluoroalkyl derivatives **17**. Thus the selectivity can be attributed to a steric effect of R on the 2-position of the anthraquinone skeleton. Amide **20b** is formed by the reaction of perfluorobutyric acid, produced as shown in Scheme 9, with **16b**.

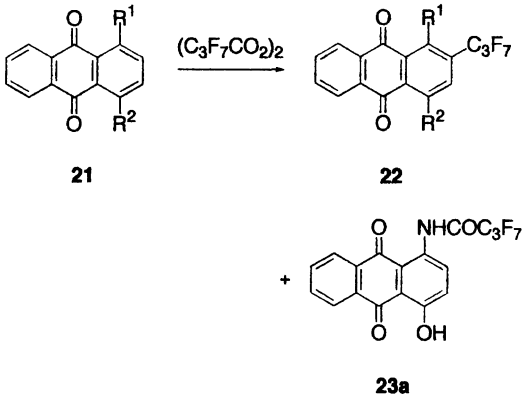
Scheme 6 and Table 4 show the perfluoropropylation of 1,4-disubstituted anthraquinones **21**. In these reactions, the reactivities of **21** with the peroxide were medium to high and 2-perfluoropropyl derivatives **22** were mainly obtained. The reaction of 1,4-bis(methylamino)-9,10-anthraquinone (IP: 0.20 V) with the peroxide gave several products in low yields (conversion: 85%).

The reaction of 1,5-disubstituted anthraquinones **24** with bis(perfluorobutyryl) peroxide is indicated in

Table 4. Perfluoropropylation of 1,4-Disubstituted Anthraquinones[a)]

Run	Compd	R^1	R^2	IP[b)]/V	Conv.	Yield/%	Others
					%	**22**	
1	**a**	NH_2	OH	0.56	81	14	**23a** (12%)
2	**b**	OH	OH	>2.50	49	9	

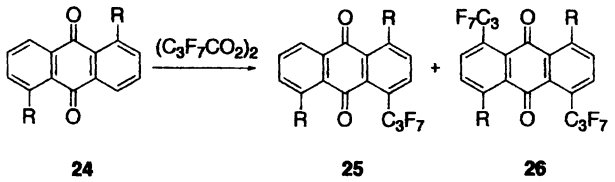
a) Stirring at 0 °C under nitrogen atmosphere for 4 h. b) Onset ionization potential (Ag/Ag^+) in acetonitrile.



Scheme 6.

Scheme 7 and Table 5. To make the reaction proceed satisfactorily, two equimolar amounts of the peroxide were required, producing both the mono- and bis(perfluoropropyl)anthraquinones **25** and **26**. Similarly, 1,8-bis(dimethylamino)anthraquinone **27** (IP: 0.76 V) affords the mono- and bis(perfluoroalkyl) derivatives **28** and **29** in 6 and 16% yields (Scheme 8).

Perfluoroalkylation Mechanism. Plausible reaction mechanisms of two kinds of 1,4-naphthoquinones **7**, having high and low IP, with bis(perfluoroalkanoyl) and bis(oxaperfluoroalkanoyl) peroxides are shown in Schemes 9, 10, 11, and 12. The perfluoroalkylation of naphthoquinones **7c**—**g** and **7i** having low IP values with bis(perfluoroalkanoyl)peroxides is depicted in Scheme 9. For these compounds, SET from the substrate to the peroxides can mainly proceed to form the radical cation and radical anion. The radical anion decomposes to afford the perfluoroalkyl radical, which attacks the electron-rich moiety of the radical cation to produce the perfluoroalkylated product **8** and (perfluoroalkyl)alkanoic acid.[4)] In the case of **7h**, the perfluoroalkyl radical attacks the 3-position of the 4-(dimethylamino)anilino moiety.

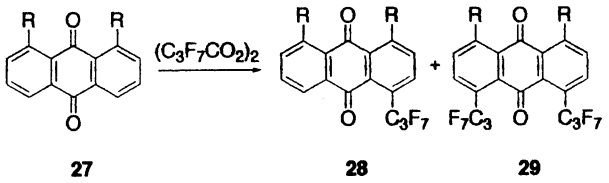


Scheme 7.

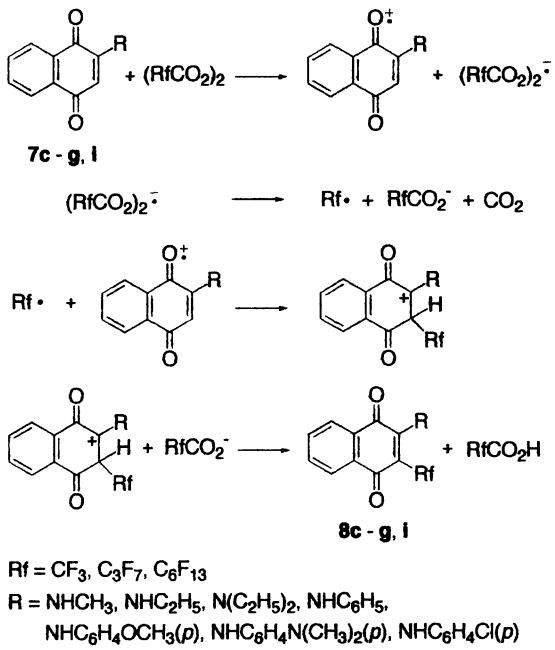
Table 5. Perfluoropropylation of 1,5-Disubstituted Anthraquinone[a)]

Run	Compd	R	IP[b)]/V	Conv.	Yield/%	
				%	**25**	**26**
1	**a**	$NHCH_3$	0.84	47	4	14
2	**b**	NHC_2H_5	0.65	52	7	19

a) To a dichloromethane solution (40 ml) of quinone **24** (2 mmol) was added a Freon® 113 solution of bis(perfluorobutyryl) peroxide (4 mmol) and stirred at 0 °C under nitrogen atmosphere for 4 h. b) Onset ionization potential (Ag/Ag^+) in acetonitrile.



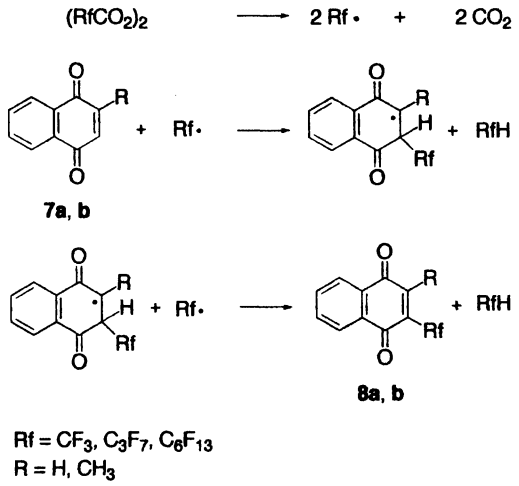
Scheme 8.



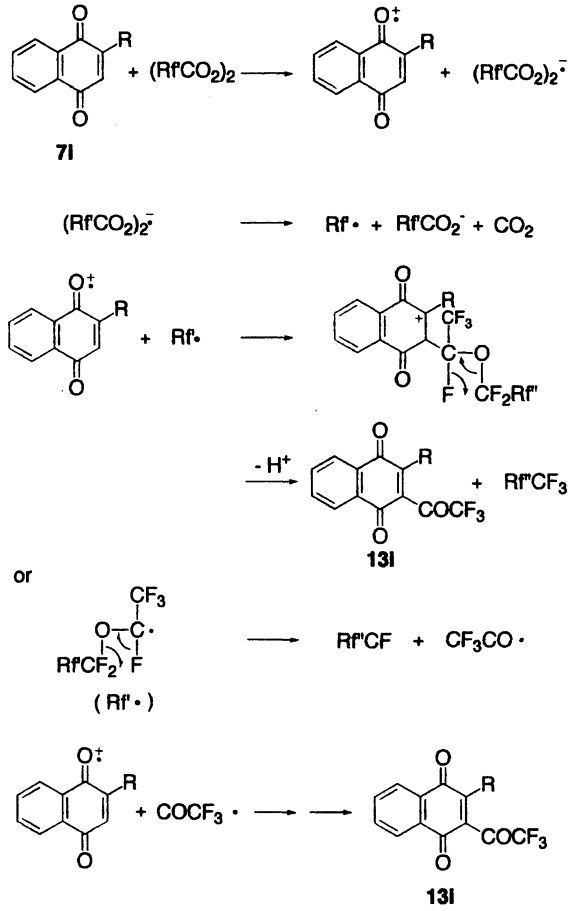
Scheme 9.

Scheme 10 shows the reaction of naphthoquinones having a high IP (>2.50 V) such as **7a** and **7b** with bis(perfluoroalkanoyl) peroxides. The perfluoroalkyl radical is formed by thermal decomposition of the peroxides, which can react with the substrate to give perfluoroalkylated products **8a** and **8b**.

Scheme 11 indicates a reaction mechanism of 1,4-



Scheme 10.



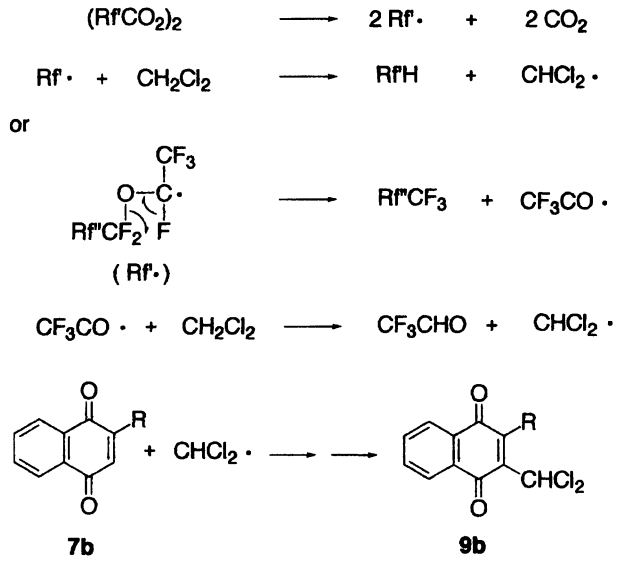
Scheme 11.

naphthoquinones having low IP values with bis(oxaperfluoroalkanoyl) peroxides. The energy level of LUMO of bis[perfluoro(2-methyl-3-oxahexanoyl)] and bis [perfluoro(2,5-dimethyl-3,6-dioxanonanoyl)] peroxides calculated by MNDO-PM3 semiempirical MO method with MOPAC 6.01 program (JCPE #049) were −2.491 and −2.707 eV, respectively. These values are similar to those of bis(perfluoroalkanoyl) peroxides (Rf=CF_3: −2.384 eV, C_3F_7: −2.525 eV, C_6F_{13}: −2.552 eV). The energy level of HOMO of **7i** (IP: 0.99 V) calculated to be −8.946 eV implies that an SET process can proceed to give the radical cation of the quinone and radical anion of the peroxide, as in the reaction with bis(perfluoroalkanoyl) peroxides. Trifluoroacetyl derivative **13i** can be obtained by two paths. One possibility is that the oxaperfluoroalkyl moiety of Rf'-adduct is decomposed during the reaction and/or treatment of the reaction mixture. The other is the attack of trifluoroacetyl radical, produced by loss of a Rf"CF_3 molecule from Rf' radical during the reaction, at the radical cation of the substrate.

The reaction mechanism of naphthoquinones having high IP values such as **7b** with bis(oxaperfluoroalkanoyl) peroxides (IP: >2.50 V) is proposed in Scheme 12. The calculated energy level of HOMO of **7b** (IP: >2.50 V) was −10.254 eV (IP: >2.50 V). This value is fairly low compared with that of **7i**, suggesting the attack of perfluoroalkyl radical formed by thermal decomposition of the peroxides occurs. Either an oxaperfluoroalkyl radical or a trifluoroacetyl radical abstracts a hydrogen atom from dichloromethane used as a solvent to form a dichloromethyl radical, which reacts with **7b** to afford **9b**.

An identical mechanism can be proposed for the perfluoroalkylation of 1,4-benzo-, 1,2-naphtho-, and 9,10-anthraquinones.

Absorption Bands and Solubility of Perfluoro-



Scheme 12.

alkylated Naphtho-, and Anthraquinone Dyes. The absorption bands of naphthoquinone dyes are indicated in Table 6. Naphthoquinone dyes substituted with a perfluoroalkyl group at the 3-position were more hypsochromic than the unsubstituted ones. The first excitation band of naphthoquinone dyes consists of an intramolecular charge transfer system from the substituents at the 3- and 4-positions to the carbonyl moieties. Therefore, introduction of the electron-withdrawing perfluoroalkyl or perfluoroacyl group can cause hypsochromic shift.

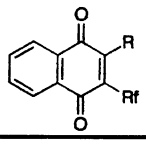
Table 7 lists the absorption bands, solubility, and melting points of anthraquinone dyes. Absorption bands of perfluoroalkyl derivatives were more hypsochromic than the corresponding unsubstituted ones. It is known that the first excitation bands of 1,5- and 1,8-diaminoanthraquinone dyes are π–π^* transitions of the intramolecular charge transfer system from anilino to central quinone moieties.[6] The hypsochromic shift is due to the introduction of the electron-withdrawing perfluoropropyl group on the anilino moieties. Introduction of perfluoropropyl group(s) into anthraquinone dyes improved the solubility and lowered the melting points, suggesting that the intermolecular interactions in anthraquinone dyes affect the solubility.

Experimental

Instruments. Melting points were measured with a Yanagimoto micro melting point apparatus. NMR, mass and UV spectra were taken on JEOL JNM-270GX, Shimadzu 9020-DF, and Shimadzu UV-160A spectrometers, respectively. Ionization potentials were measured with a Nikko NPGF-2501A instrument.

Materials. Bis(perfluoroalkanoyl) and bis(oxaperfluoroalkanoyl) peroxides were prepared as described in the literature.[7] Quinones **1a**, **7a**, **7b**, and **16b** were purchased from Nacalai Tesque Co., Ltd. Quinones **1b**, **1c**, **1e**, **1g**, **14**, **16a**, **16b**, **16c**, **16g**, **21a**, **21b**, and **21c** were purchased from Tokyo Kasei Co., Ltd. Quinones **1d**,[8] **1f**,[9] **7c**,[10] **7d**,[10] **7e**,[11] **7f**,[10] **7g**,[10] **7h**,[12] **7i**,[10] and **16d**[13] were synthesized as described in the literature. Quinones **16e**, **16f**, **24a**, and **27** were prepared by the reaction of a chloroanthraquinone with an amine.

Table 6. Absorption Bands of Naphthoquinone Dyes[a]



Compd	R	Rf	λmax[a] nm
7c	$NHCH_3$	H	448
8c	$NHCH_3$	C_3F_7	424
7e	$N(CH_3)_2$	H	460
10e	$N(CH_3)_2$	COC_2F_5	435
7f	NHC_6H_5	H	465
8f	NHC_6H_5	C_3F_7	446
7g	$NHC_6H_4OCH_3$ (*p*)	H	481
8g	$NHC_6H_4OCH_3$ (*p*)	C_3F_7	462
7i	NHC_6H_4Cl (*p*)	H	463
8′i	NHC_6H_4Cl (*p*)	CF_3	453
8i	NHC_6H_4Cl (*p*)	C_3F_7	446
8″i	NHC_6H_4Cl (*p*)	C_6F_{13}	442
13i	NHC_6H_4Cl (*p*)	$COCF_3$	448

a) Measured in ethanol.

Reaction of Quinones with Bis(perfluoroalkanoyl) and Bis(oxaperfluoroalkanoyl) Peroxides. To a dichloromethane solution (60—300 cm^3) of quinone (2.0 mmol) was added a Freon® 113 solution of the peroxide. The mixture was stirred under nitrogen atmosphere. After the reaction, the solution was washed with brine (100 cm^3), 10% aqueous sodium hydrogencarbonate solution (100 cm^3), and again brine (100 cm^3). Products were extracted with dichloromethane (100 $cm^3 \times 3$) and dried over anhydrous sodium sulfate. After evaporation of the solvent, the products were separated by column chromatography (SiO_2; CH_2Cl_2, $CHCl_3$, C_6H_6, CCl_4). The physical and spectral data are shown below.

2-(Perfluoropropyl)-1,4-benzoquinone (2a): Oil; ^1H NMR ($CDCl_3$) δ=6.89—6.91 (m, 2H), 7.12—7.14 (m, 1H); EIMS (70 eV) *m/z* (rel intensity) 276 (M^+; 28), 248 (10), 127 (56), 53 (100); MLMS Found: *m/z* 276.0011. Calcd for $C_9H_3F_7O_2$: M, 276.0022.

2-Methyl-3-(perfluoropropyl)-1,4-benzoquinone (2b): Oil; ^1H NMR ($CDCl_3$) δ=2.29 (t, J=3.5 Hz, 3H), 6.80 (d, J=10.1 Hz, 1H), 6.91 (d, J=10.1 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 290 (M^+; 33), 262 (26), 143 (82), 82 (100). MLMS Found: *m/z* 290.0180. Calcd for $C_{10}H_5F_7O_2$: M, 290.0178.

2-(Perfluoropropyl)-3-phenyl-1,4-benzoquinone (2c): Mp 88—91 °C; ^1H NMR ($CDCl_3$) δ=6.92 (d, J=10.1 Hz, 1H), 6.97 (d, J=10.1 Hz, 1H), 7.06—7.11 (m, 2H), 7.39—7.42 (m, 3H); EIMS (70 eV) *m/z* (rel intensity) 352 (M^+; 100), 304 (36), 233 (89). Found: C, 51.15; H, 2.01%. Calcd for $C_{15}H_7F_7O_2$: C, 51.15; H, 2.00%.

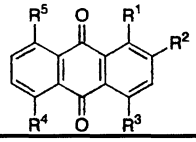
2,5-Dimethyl-3-(perfluoropropyl)-1,4-benzoquinone (2e): Oil; ^1H NMR ($CDCl_3$) δ=2.10 (d, J=1.5 Hz, 3H), 2.26 (t, J=3.7 Hz, 3H), 6.75 (q, J=1.5 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 304 (M^+; 71), 276 (23), 157 (100), 69 (39), 68 (97), 67 (59). MLMS Found: *m/z* 304.0335. Calcd for $C_{11}H_7F_7O_2$: M, 304.0334.

2,6-Dimethyl-3-(perfluoropropyl)-1,4-benzoquinone (2g): Oil; ^1H NMR ($CDCl_3$) δ=2.10 (d, J=1.5 Hz, 3H), 2.29 (t, J=3.7 Hz, 3H), 6.64 (q, J=1.5 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 304 (M^+; 40), 276 (64), 157 (99), 69 (32), 68 (100), 67 (52). MLMS Found: *m/z* 304.0349. Calcd for $C_{11}H_7F_7O_2$: M, 304.0334.

2-(Dimethylamino)-3-(perfluoropropionyl)-1,4-benzoquinone (5d): Oil; ^1H NMR ($CDCl_3$) δ=3.16 (s, 6H), 6.65 (d, J=10.3 Hz, 1H), 6.71 (d, J=10.3 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 297 (M^+; 100), 178 (78), 150 (46), 82 (61). MLMS Found: *m/z* 297.0418. Calcd for $C_{11}H_8F_5NO_3$: M, 297.0424.

2,5-Bis(dimethylamino)-3,6-bis(perfluoropropionyl)-1,4-benzoquinone (6f): Mp 185 °C (decomp); ^1H NMR ($CDCl_3$) δ=3.33 (s, 12H); EIMS (70 eV) *m/z* (rel intensity) 486 (M^+; 100), 471 (28), 459 (19), 228 (15), 96 (73); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−1.55 (6F), −37.65 (4F). Found: C, 39.41; H, 2.53; N, 5.72%. Calcd

Table 7. Absorption Bands, Solubility, and Melting Points of Anthraquinone Dyes



Compd	R^1	R^2	R^3	R^4	R^5	λ_{max}[a] / nm	Solubility[b] / mmol dm^{-3}	Mp / °C
16b	NH_2	H	H	H	H	450	0.04	261–262
17b	NH_2	C_3F_7	H	H	H	448	0.33	129–130
18b	NH_2	H	C_3F_7	H	H	429	0.82	128–129
19b	NH_2	C_3F_7	C_3F_7	H	H	432	1.62	132–134
16c	$NHCH_3$	H	H	H	H	487	0.11	173–174
18c	$NHCH_3$	H	C_3F_7	H	H	462	0.43	151–153
16e	NHC_6H_5	H	H	H	H	494	0.41	135–136
18e	NHC_6H_5	H	C_3F_7	H	H	466	1.19	128–129
24a	$NHCH_3$	H	H	$NHCH_3$	H	516	0.39	280–282
25a	$NHCH_3$	H	C_3F_7	$NHCH_3$	H	500	7.52	227–229
26a	$NHCH_3$	H	C_3F_7	$NHCH_3$	C_3F_7	462	11.06	201–203
27a	$NHCH_3$	H	H	H	$NHCH_3$	516	0.52	277–279
28	$NHCH_3$	H	C_3F_7	H	$NHCH_3$	496	6.33	230–232
29	$NHCH_3$	H	C_3F_7	C_3F_7	$NHCH_3$	471	16.01	193–195

a) Measured in hexane. b) Measured in hexane at 25 °C.

for $C_{16}H_{12}F_{10}N_2O_4$: C, 39.52; H, 2.49; N, 5.76%.

2-(Perfluoropropyl)-1,4-naphthoquinone (8a): Mp 55—58 °C; ^{1}H NMR ($CDCl_3$) δ=7.32 (s, 1H), 7.83—7.88 (m, 2H), 8.10—8.19 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 326 (M^+; 56), 207 (20), 179 (74), 104 (100). MLMS Found: *m/z* 326.0197. Calcd for $C_{13}H_5F_7O_2$: M, 326.0178.

2-Methyl-3-(perfluoropropyl)-1,4-naphthoquinone (8b): Mp 69—71 °C; ^{1}H NMR ($CDCl_3$) δ=2.42 (t, *J*=4.0 Hz, 3H), 7.76—7.80 (m, 2H), 8.09—8.14 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 340 (M^+; 72), 221 (52), 193 (97), 104 (100). Found: C, 49.22; H, 1.76%. Calcd for $C_{14}H_7F_7O_2$: C, 49.43; H, 2.07%.

2-Methyl-3-(trifluoromethyl)-1,4-naphthoquinone (8′b): Oil; ^{1}H NMR ($CDCl_3$) δ=2.43 (q, *J*=3.7 Hz, 3H), 7.76—7.81 (m, 2H), 8.11—8.14 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 240 (M^+; 92), 115 (67), 104 (89), 76 (100). MLMS Found: *m/z* 240.0396. Calcd for $C_{12}H_7F_3O_2$: M, 240.0398.

2-Methyl-3-(perfluorohexyl)-1,4-naphthoquinone (8″b): Mp 95—97 °C; ^{1}H NMR ($CDCl_3$) δ=2.43 (t, *J*=3.7 Hz, 3H), 7.76—7.81 (m, 2H), 8.11—8.14 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 490 (M^+; 75), 221 (100), 193 (97), 104 (71). Found: C, 41.45; H, 1.23%. Calcd for $C_{17}H_7F_{13}O_2$: C, 41.66; H, 1.44%.

2-(Methylamino)-3-(perfluoropropyl)-1,4-naphthoquinone (8c): Mp 167—169 °C; ^{1}H NMR ($CDCl_3$) δ=3.22 (d, *J*=5.5 Hz, 3H), 6.96 (br, 1H), 7.66 (t, *J*=7.6 Hz, 1H), 7.79 (t, *J*=7.6 Hz, 1H), 8.07 (d, *J*=7.6 Hz, 1H), 8.16 (d, *J*=7.6 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 355 (M^+; 91), 236 (82), 216 (100). Found C, 47.58; H, 2.00; N, 3.93%. Calcd for $C_{14}H_8F_7NO_2$: C, 47.34; H, 2.27; N, 3.94%.

2-(Ethylamino)-3-(perfluoropropyl)-1,4-naphthoquinone (8d): Mp 134—135 °C; ^{1}H NMR ($CDCl_3$) δ=1.41 (t, *J*=7.3 Hz, 3H), 4.20 (quintet, *J*=7.3 Hz, 2H), 6.03 (br, 1H), 7.70 (t, *J*=7.9 Hz, 1H), 7.83 (t, *J*=7.9 Hz, 1H), 8.12 (d, *J*=7.9 Hz, 1H), 8.19 (d, *J*=7.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−1.67 (3F), −28.32 (2F), −47.08 (2F); EIMS (70 eV) *m/z* (rel intensity) 369 (M^+; 61), 347 (37), 228 (41), 222 (100). Found: C, 48.58; H, 2.91; N, 3.80%. Calcd for $C_{15}H_{10}F_7NO_2$: C, 48.79; H, 2.73; N, 3.79%.

2-Anilino-3-(perfluoropropyl)-1,4-naphthoquinone (8f): Mp 83—85 °C; ^{1}H NMR ($CDCl_3$) δ=7.10—7.18 (m, 2H), 7.27—7.39 (m, 3H), 7.67 (t, *J*=7.3 Hz, 1H), 7.79 (t, *J*=7.3 Hz, 1H), 7.84 (br, 1H), 7.97 (d, *J*=7.3 Hz, 1H), 8.15 (d, *J*=7.3 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 417 (M^+; 96), 278 (100), 248 (47). Found: C, 55.06; H, 2.38; N, 3.35%. Calcd for $C_{19}H_{10}F_7NO_2$: C, 54.69; H, 2.42; N, 3.36%.

2-(4-Anisidino)-3-(perfluoropropyl)-1,4-naphthoquinone (8g): Mp 126—128 °C; ^{1}H NMR ($CDCl_3$) δ=3.82 (s, 3H), 6.89 (d, *J*=9.2 Hz, 2H), 7.05 (d, *J*=9.2 Hz, 2H), 7.67 (t, *J*=7.6 Hz, 1H), 7.79 (t, *J*=7.6 Hz, 1H), 7.80 (br, 1H), 7.98 (d, *J*=7.6 Hz, 1H), 8.17 (d, *J*=7.6 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 447 (M^+; 65), 407 (34), 379 (20), 308 (100). Found: C, 53.97; H, 2.45; N, 3.10%. Calcd for $C_{20}H_{12}F_7NO_3$: C, 53.70; H, 2.70; N, 3.13%.

2-(4-Chloroanilino)-3-(perfluoropropyl)-1,4-naphthoquinone (8i): Mp 135—137 °C; ^{1}H NMR ($CDCl_3$) δ=7.06 (d, *J*=9.2 Hz, 2H), 7.34 (d, *J*=9.2 Hz, 2H), 7.70 (br, 1H), 7.71 (t, *J*=7.3 Hz, 1H), 7.82 (t, *J*=7.3 Hz, 1H), 8.00 (d, *J*=7.3 Hz, 1H), 8.17 (d, *J*=7.3 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 451 (M^+; 47), 411 (29), 383 (25), 312 (100). Found: C, 50.59; H, 1.83; N, 3.05%. Calcd for $C_{19}H_9ClF_7NO_2$: C, 50.52; H, 2.01; N, 3.10%.

2-(4-Chloroanilino)-3-(trifluoromethyl)-1,4-naphthoquinone (8′i): Mp 211—213 °C; ^{1}H NMR ($CDCl_3$) δ=7.14 (d, *J*=8.5 Hz, 2H), 7.35 (d, *J*=8.5 Hz, 2H), 7.74 (t, *J*=7.6 Hz, 1H), 7.86 (t, *J*=7.6 Hz, 1H), 8.03 (br, 1H), 8.16 (d, *J*=7.6 Hz, 1H), 8.22 (d, *J*=7.6 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 351 (M^+; 100), 296 (34), 282 (81), 268 (30). Found: C, 58.45; H, 2.57; N, 3.97%. Calcd for $C_{17}H_9ClF_3NO_2$: C, 58.06; H, 2.58; N, 3.98%.

2-(4-Chloroanilino)-3-(perfluorohexyl)-1,4-naphthoquinone (8″i): Mp 133—135 °C; ^{1}H NMR ($CDCl_3$) δ=7.05 (d, J=9.2 Hz, 2H), 7.34 (d, J=9.2 Hz, 2H), 7.69 (br, 1H), 7.71 (t, J=7.3 Hz, 1H), 7.82 (t, J=7.3 Hz, 1H), 7.99 (d, J=7.3 Hz, 1H), 8.17 (d, J=7.3 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 601 (M^+; 47), 362 (15), 312 (100). Found: C, 44.15; H, 1.35; N, 2.33%. Calcd for $C_{22}H_9ClF_{13}NO_2$: C, 43.91; H, 1.51; N, 2.33%.

2-(Dichloromethyl)-3-methyl-1,4-naphthoquinone (9b): Mp 164—166 °C; ^{1}H NMR ($CDCl_3$) δ=2.60 (s, 3H), 7.37 (s, 1H), 7.74—7.79 (m, 2H), 8.09—8.17 (m, 2H); EIMS (70 eV) m/z (rel intensity) 254 (M^+; 69), 218 (100), 191 (49), 155 (42). Found: C, 56.13; H, 2.91%. Calcd for $C_{12}H_8Cl_2O_2$: C, 56.50; H, 3.16%.

2-(Dimethylamino)-3-(perfluoropropionyl)-1,4-naphthoquinone (10e): Mp 118—119 °C; ^{1}H NMR ($CDCl_3$) δ=3.26 (s, 6H), 7.68 (t, J=7.3 Hz, 1H), 7.78 (t, J=7.3 Hz, 1H), 7.97 (d, J=7.3 Hz, 1H), 8.12 (d, J=7.3 Hz, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−0.88 (3F), −37.82 (2F); EIMS (70 eV) m/z (rel intensity) 347 (M^+; 56), 228 (100). Found: C, 51.94; H, 2.87; N, 4.11%. Calcd for $C_{15}H_{10}F_5NO_3$: C, 51.88; H, 2.92; N, 4.03%.

2-[4-(Dimethylamino)-3-(perfluoropropyl)anilino]-1,4-naphthoquinone (11h): Mp 223—225 °C; ^{1}H NMR ($CDCl_3$) δ=2.66 (s, 6H), 6.30 (s, 1H), 7.40 (s, 1H), 7.49—7.52 (m, 3H), 7.69 (t, J=7.3 Hz, 1H), 7.78 (t, J=7.3 Hz, 1H), 8.10—8.15 (m, 2H); EIMS (70 eV) m/z (rel intensity) 460 (M^+; 100), 341 (12). Found: C, 54.56; H, 2.93; N, 5.87%. Calcd for $C_{21}H_{15}F_7N_2O_2$: C, 54.79; H, 3.28; N, 6.09%.

2-[4-(Dimethylamino)-3-(perfluoropropyl)anilino]-3-(perfluoropropyl)-1,4-naphthoquinone (12h): Mp 145—147 °C; ^{1}H NMR ($CDCl_3$) δ=2.66 (s, 6H), 7.26—7.30 (m, 2H), 7.44 (d, J=7.9 Hz, 1H), 7.72 (t, J=7.3 Hz, 1H), 7.80 (br, 1H), 7.84 (t, J=7.3 Hz, 1H), 8.02 (d, J=7.3 Hz, 1H), 8.19 (d, J=7.3 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 628 (M^+; 74), 606 (27), 489 (100). Found: C, 46.27; H, 2.24; N, 4.39%. Calcd for $C_{24}H_{14}F_{14}N_2O_2$: C, 45.88; H, 2.25; N, 4.46%.

2-(4-Chloroanilino)-3-(trifluoroacetyl)-1,4-naphthoquinone (13i): Mp 156—160 °C; ^{1}H NMR ($CDCl_3$) δ=7.07 (d, J=8.5 Hz, 2H), 7.40 (d, J=8.5 Hz, 2H), 7.76 (t, J=6.7 Hz, 1H), 7.88 (t, J=6.7 Hz, 1H), 8.10 (d, J=6.7 Hz, 1H), 8.20 (d, J=6.7 Hz, 1H), 9.62 (br, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−4.65 (s, 3F); EIMS (70 eV) m/z (rel intensity) 379 (M^+; 40), 310 (100), 282 (25). Found: C, 56.79; H, 2.29; N, 3.60%. Calcd for $C_{18}H_9ClF_3NO_3$: C, 56.94; H, 2.39; N, 3.69%.

3-(Perfluoropropyl)-1,2-naphthoquinone (15): Oil; ^{1}H NMR ($CDCl_3$) δ=7.57 (d, J=7.6 Hz, 1H), 7.69 (t, J=7.6 Hz, 1H), 7.78 (t, J=7.6 Hz, 1H), 7.88 (s, 1H), 8.20 (d, J=7.6 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 298 (M^+−CO; 26), 179 (100), 151 (27); CIMS (isobutane) m/z (rel intensity) 327 (MH^+; 100). MLMS Found: m/z 326.0157. Calcd for $C_{13}H_5F_7O_2$: M, 326.0178.

2-(Perfluoropropyl)anthraquinone (17a): Mp 166—168 °C; ^{1}H NMR ($CDCl_3$) δ=7.83—7.90 (m, 2H), 8.02 (d, J=8.6 Hz, 1H), 8.32—8.38 (m, 2H), 8.48 (d, J=8.6 Hz, 1H), 8.57 (s, 1H); EIMS (70 eV) m/z (rel intensity) 376 (M^+; 49), 257 (100), 229 (48). Found: C, 54.67; H, 1.83%. Calcd for $C_{17}H_7F_7O_2$: C, 54.27; H, 1.88%.

1-Amino-2-(perfluoropropyl)anthraquinone (17b): Mp 129—130 °C; ^{1}H NMR ($CDCl_3$) δ=7.63 (d, J=7.9 Hz, 1H), 7.71 (d, J=7.9 Hz, 1H), 7.71—7.83 (m, 2H), 8.20—8.29 (m, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−1.29 (3F), −31.14 (2F), −47.17 (2F); EIMS (70 eV) m/z (rel intensity) 391 (M^+; 49), 272 (100), 244 (20), 69 (1). Found: C, 52.53; H, 1.83; N, 3.52%. Calcd for $C_{17}H_8F_7NO_2$: C, 52.19; H, 2.06; N, 3.58%.

1-(Methylamino)-2-(perfluoropropyl)anthraquinone (17c): Mp 133—134 °C; ^{1}H NMR ($CDCl_3$) δ=3.02 (t, J=3.4 Hz, 3H), 7.69—7.83 (m, 4H), 8.21—8.30 (m, 2H), 9.02 (br, 1H); EIMS (70 eV) m/z (rel intensity) 405 (M^+; 32), 388 (100), 269 (41), 69 (8). Found: C, 53.56; H, 2.26; N, 3.42%. Calcd for $C_{18}H_{10}F_7NO_2$: C, 53.35; H, 2.49; N, 3.46%.

1-Hydroxy-2-(perfluoropropyl)anthraquinone (17g): Mp 183—185 °C; ^{1}H NMR ($CDCl_3$) δ=7.86 (d, J=3.4 Hz, 1H), 7.88 (d, J=3.4 Hz, 1H), 7.92—7.93 (m, 2H), 8.31—8.38 (m, 2H), 13.50 (s, 1H); EIMS (70 eV) m/z (rel intensity) 392 (M^+; 30), 273 (100), 245 (17), 169 (15). Found: C, 52.45; H, 1.66%. Calcd for $C_{17}H_7F_7O_3$: C, 52.06; H, 1.80%.

1-Amino-4-(perfluoropropyl)anthraquinone (18b): Mp 128—129 °C; ^{1}H NMR ($CDCl_3$) δ=6.97 (d, J=9.2 Hz, 1H), 7.63 (d, J=9.2 Hz, 1H), 7.70—7.78 (m, 2H), 8.10—8.20 (m, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−1.76 (3F), −19.67 (2F), −40.90 (2F); EIMS (70 eV) m/z (rel intensity) 391 (M^+; 23), 272 (100), 250 (25), 69 (13). Found: C, 52.17; H, 1.72; N, 3.51%. Calcd for $C_{17}H_8F_7NO_2$: C, 52.19; H, 2.06; N, 3.58%.

1-(Methylamino)-4-(perfluoropropyl)anthraquinone (18c): Mp 151—153 °C; ^{1}H NMR ($CDCl_3$) δ=3.05 (d, J=5.5 Hz, 3H), 7.02 (d, J=9.2 Hz, 1H), 7.67—7.76 (m, 2H), 7.71 (d, J=9.2 Hz, 1H), 8.07—8.16 (m, 2H), 9.97 (s, 1H); EIMS (70 eV) m/z (rel intensity) 405 (M^+; 45), 286 (100), 69 (6). Found: C, 53.11; H, 2.26; N, 3.35%. Calcd for $C_{18}H_{10}F_7NO_2$: C, 53.35; H, 2.49; N, 3.46%.

1-(Ethylamino)-4-(perfluoropropyl)anthraquinone (18d): Mp 116—117 °C; ^{1}H NMR ($CDCl_3$) δ=1.43 (t, J=7.3 Hz, 3H), 3.42 (quintet, J=7.3 Hz, 2H), 7.05 (d, J=7.3 Hz, 1H), 7.70 (d, J=7.3 Hz, 1H), 7.75 (t, J=7.3 Hz, 2H), 8.10 (d, J=7.3 Hz, 1H), 8.17 (d, J=7.3 Hz, 1H), 10.02 (s, 1H); EIMS (70 eV) m/z (rel intensity) 419 (M^+; 85), 404 (100), 300 (49), 272 (39). Found: C, 54.18; H, 2.91; N, 3.57%. Calcd for $C_{19}H_{12}F_7NO_2$: C, 54.43; H, 2.88; N, 3.34%.

1-Anilino-4-(perfluoropropyl)anthraquinone (18e): Mp 128—129 °C; ^{1}H NMR ($CDCl_3$) δ=7.32 (m, 3H), 7.43 (m, 3H), 7.63 (d, J=9.2 Hz, 1H), 7.77 (m, 2H), 8.15 (d, J=7.0 Hz, 1H), 8.23 (d, J=7.0 Hz, 1H), 11.67 (s, 1H); EIMS (70 eV) m/z (rel intensity) 467 (M^+; 87), 348 (100). Found: C, 58.87; H, 2.77; N, 3.21%. Calcd for $C_{23}H_{12}F_7NO_2$: C, 59.11; H, 2.59; N, 3.00%.

1-(Dimethylamino)-4-(perfluoropropyl)anthraquinone (18f): Oil; ^{1}H NMR ($CDCl_3$) δ=3.02 (s, 6H), 7.23 (d, J=9.5 Hz, 1H), 7.63 (d, J=9.5 Hz, 1H), 7.64—7.74 (m, 2H), 8.07—8.16 (m, 2H); EIMS (70 eV) m/z (rel intensity) 419 (M^+; 100), 402 (77), 382 (59), 300 (31), 285 (23), 257 (16), 233 (26), 84 (24), 69 (12). This compound was not pure enough for elemental analysis.

1-Amino-2,4-bis(perfluoropropyl)anthraquinone (19b): Mp 132—134 °C; ^{1}H NMR ($CDCl_3$) δ=7.74—7.83 (m, 2H), 7.86 (s, 1H), 8.09—8.22 (m, 2H), 10.35 (s, 2H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−1.26 (3F), −1.79

(3F), −19.79 (2F), −31.61 (2F), −41.02 (2F), −47.31 (2F); EIMS (70 eV) m/z (rel intensity) 559 (M^+; 22), 440 (100), 321 (84), 69 (8). Found: C, 43.06; H, 1.06; N, 2.28%. Calcd for $C_{20}H_7F_{14}NO_2$: C, 42.95; H, 1.26; N, 2.50%.

1-(Methylamino)-2,4-Bis(perfluoropropyl)anthraquinone (19c): Mp 71—72 °C; ^{1}H NMR ($CDCl_3$) δ=3.03 (s, 3H), 7.69—7.80 (m, 2H), 7.89 (s, 1H), 8.05—8.16 (m, 2H), 8.76 (br, 1H); EIMS (70 eV) m/z (rel intensity) 573 (M^+; 39), 556 (100), 536 (44), 454 (27), 427 (21), 402 (52), 286 (37), 69 (20). Found: C, 43.61; H, 1.60; N, 2.56%. Calcd for $C_{21}H_9F_{14}NO_2$: C, 44.00; H, 1.58; N, 2.44%.

1-[(Perfluoropropionyl)amino]anthraquinone (20b): Mp 167—170 °C; ^{1}H NMR ($CDCl_3$) δ=7.83—7.87 (m, 3H), 8.22 (d, J=8.5 Hz, 1H), 8.29—8.37 (m, 2H), 9.07 (d, J=8.5 Hz, 1H), 13.58 (s, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ=−3.72 (3F), −43.97 (2F); EIMS (70 eV) m/z (rel intensity) 369 (M^+; 18), 250 (100), 151 (25), 69 (19). Found: C, 55.16; H, 1.96; N, 3.69%. Calcd for $C_{17}H_8F_5NO_3$: C, 55.30; H, 2.18; N, 3.79%.

1-Amino-4-hydroxy-2-(perfluoropropyl)anthraquinone (22a): Mp 123—124 °C; ^{1}H NMR ($CDCl_3$) δ=1.57 (s, 2H), 7.49 (s, 1H), 7.76—7.88 (m, 2H), 8.31—8.38 (m, 2H), 13.08 (s, 1H); EIMS (70 eV) m/z (rel intensity) 407 (M^+; 100), 288 (56), 260 (11). Found: C, 50.47; H, 1.86; N, 3.46%. Calcd for $C_{17}H_8F_7NO_3$: C, 50.14; H, 1.98; N, 3.44%.

1,4-Dihydroxy-2-(perfluoropropyl)anthraquinone (22b): Mp 180—182 °C; ^{1}H NMR ($CDCl_3$) δ=7.60 (s, 1H), 7.86—7.93 (m, 2H), 8.35—8.41 (m, 2H), 12.61 (s, 1H), 13.63 (s, 1H); EIMS (70 eV) m/z (rel intensity) 408 (M^+; 100), 289 (61), 261 (11). Found: C, 49.93; H, 1.56%. Calcd for $C_{17}H_7F_7O_4$: C, 50.02; H, 1.73%.

1-Hydroxy-4-[(perfluorobutyryl)amino]anthraquinone (23a): Mp 158—159 °C; ^{1}H NMR ($CDCl_3$) δ=7.44 (d, J=9.2 Hz, 1H), 7.85—7.92 (m, 2H), 8.23—8.38 (m, 2H), 9.03 (d, J=9.2 Hz, 1H), 13.22 (s, 1H), 13.56 (s, 1H); EIMS (70 eV) m/z (rel intensity) 385 (M^+; 54), 266 (100), 238 (26), 69 (11). Found: C, 53.33; H, 1.87; N, 3.55%. Calcd for $C_{17}H_8F_5NO_4$: C, 53.00; H, 2.09; N, 3.64%.

1,5-Bis(methylamino)-4-(perfluoropropyl)anthraquinone (25a): Mp 227—229 °C; ^{1}H NMR ($CDCl_3$) δ=3.02 (d, J=5.0 Hz, 3H), 3.05 (d, J=5.0 Hz, 3H), 6.95 (d, J=9.0 Hz, 2H), 7.45 (d, J=9.0 Hz, 1H), 7.54 (t, J=9.0 Hz, 1H), 7.72 (d, J=9.0 Hz, 1H), 8.90 (br s, 1H), 10.02 (br s, 1H); EIMS (70 eV) m/z (rel intensity) 434 (M^+; 23), 394 (36), 275 (100). Found: C, 52.88; H, 3.14; N, 6.31%. Calcd for $C_{19}H_{13}F_7N_2O_2$: C, 52.55; H, 3.02; N, 6.45%.

1,5-Bis(ethylamino)-4-(perfluoropropyl)anthraquinone (25b): Mp 185—187 °C; ^{1}H NMR ($CDCl_3$) δ=1.41 (t, J=7.0 Hz, 6H), 3.39 (q, J=7.0 Hz, 4H), 6.97 (d, J=9.0 Hz, 2H), 7.33 (d, J=9.0 Hz, 1H), 7.48 (t, J=9.0 Hz, 1H), 7.65 (d, J=9.0 Hz, 1H), 9.14 (br s, 1H), 9.91 (br s, 1H); EIMS (70 eV) m/z (rel intensity) 462 (M^+; 42), 433 (100), 415 (32). Found: C, 54.71; H, 3.57; N, 6.00%. Calcd for $C_{21}H_{17}F_7N_2O_2$: C, 54.55; H, 3.71; N, 6.05%.

1,5-Bis(methylamino)-4,8-bis(perfluoropropyl)anthraquinone (26a): Mp 201—203 °C; ^{1}H NMR ($CDCl_3$) δ=3.04 (d, J=5.0 Hz, 3H), 3.07 (d, J=5.0 Hz, 3H), 6.97 (d, J=9.0 Hz, 2H), 7.66 (d, J=9.0 Hz, 2H), 8.89 (br s, 2H); EIMS (70 eV) m/z (rel intensity) 602 (M^+; 10), 443 (37), 149 (100). Found: C, 43.72; H, 2.12; N, 4.67%. Calcd for $C_{22}H_{12}F_{14}N_2O_2$: C, 43.87; H, 2.01; N, 4.65%.

1,5-Bis(ethylamino)-4,8-bis(perfluoropropyl)anthraquinone (26b): Mp 158—160 °C; ^{1}H NMR ($CDCl_3$) δ=1.41 (t, J=6.9 Hz, 6H), 3.38 (q, J=6.0 Hz, 4H), 6.93 (d, J=9.0 Hz, 2H), 7.55 (d, J=9.0 Hz, 2H), 9.44 (br s, 2H); EIMS (70 eV) m/z (rel intensity) 630 (M^+; 27), 601 (100), 583 (23). Found: C, 45.64; H, 2.42; N, 4.33%. Calcd for $C_{24}H_{16}F_{14}N_2O_2$: C, 45.73; H, 2.56; N, 4.44%.

1,8-Bis(methylamino)-4-(perfluoropropyl)anthraquinone (28): Mp 230—232 °C; ^{1}H NMR ($CDCl_3$) δ=3.02 (d, J=5.0 Hz, 3H), 3.05 (d, J=5.0 Hz, 3H), 6.96 (d, J=8.0 Hz, 2H), 7.45 (d, J=8.0 Hz, 1H), 7.54 (t, J=8.0 Hz, 1H), 7.72 (d, J=8.0 Hz, 1H), 8.89 (br s, 1H), 9.97 (br s, 1H); EIMS (70 eV) m/z (rel intensity) 434 (M^+; 90), 414 (66), 394 (100). Found: C, 52.91; H, 3.00; N, 6.75%. Calcd for $C_{19}H_{13}F_7N_2O_2$: C, 52.55; H, 3.02; N, 6.45%.

1,8-Bis(methylamino)-4,5-bis(perfluoropropyl)anthraquinone (29): Mp 193—195 °C; ^{1}H NMR ($CDCl_3$) δ=3.05 (d, J=5.0 Hz, 6H), 6.94 (d, J=9.0 Hz, 2H), 7.66 (d, J=9.0 Hz, 2H), 8.88 (br s, 2H); EIMS (70 eV) m/z (rel intensity) 602 (M^+; 72), 587 (34), 483 (100), 468 (56). Found: C, 44.03; H, 2.06; N, 4.29%. Calcd for $C_{22}H_{12}F_{14}N_2O_2$: C, 43.87; H, 2.01; N, 4.65%.

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