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Synthesis of 3-Cyano-6-hydroxy-5-[2-(perfluoroalkyl)phenylazo]-2-pyridones and Their Application for Dye Diffusion Thermal Transfer Printing

Masaki Matsui,* Bharati Joglekar, Yoshinao Ishigure,† Katsuyoshi Shibata, Hiroshige Muramatsu, and Yuukichi Murata††
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-11
† Gifu Prefectural Industrial Technology Research Center, Kitaoyobi 47, Kasamatsu, Hashima, Gifu 501-61
†† Research Center, Mitsubishi Chemical Industries Ltd., Kamoshida 1000, Midori-ku, Yokohama 227

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New fluorine-containing azopyridone dyes, 3-cyano-6-hydroxy-5-[2-(perfluoroalkyl)phenylazo]-2-pyridones, have been synthesized. Though the introduction of a long perfluoroalkyl group lowered film forming ability and sensitivity, 5-[2-(trifluoromethyl)phenylazo]- and 5-[2-(perfluorobutyl)phenylazo]-3-cyano-4-methyl-6-hydroxy-2-pyridones showed good photostability.

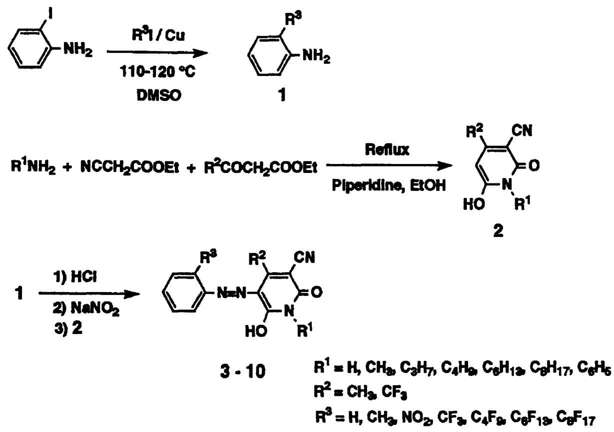
Application of dyes to high technology has been attracting much attention.[1] Dyes are used in various fields such as printing, electronic photography, color formers, liquid crystal displays, laser technology, data storage, and solar energy conversion. Dye diffusion thermal transfer (D2T2) system is one of the important non-impact thermal printing technology. Color hard copy prints can be obtained from video sets by the D2T2 technology. Principle of D2T2 printing is transfer of dye from a dyesheet to a receiver paper by heating.[2] Since the amounts of dye transfered are controlled by the supplied heat energy, continuous tone can be regenerated. Full-color print can be produced using a yellow, magenta, and cyan trichromat color sheet. Essential requirements of dyes for D2T2 printing are good thermal stability, good film forming ability, good ability of transferability by heating (sensitivity), excellent light fastness, and high optical density. Dyes used for D2T2 printing are such as quinophthalones, anthraquinones, monoazo dyes, and naphthoquinones.[3]

Introduction of fluorine atoms, trifluoromethyl-, and perfluoro(or polyfluoro)alkyl groups into organic molecules changes the property of the compounds.[4,5] For example, CI Acid Red 266 having a trifluoromethyl group at the *ortho* position for the azo bond and 3-perfluoroalkyl coumarins have been reported to show good stability for light.[6,7] Arylethenes exhibit excellent thermal and photochromic stabilities.[8] Fluorine-substituted phthalocyanines show good solubility.[9]

Therefore, it is of interest to synthesize dyes containing a perfluoroalkyl group and examine their properties. In this report, synthesis and evaluation of 3-cyano-6-hydroxy-5-[2-(perfluoroalkyl)phenylazo]-2-pyridones for D2T2 printing have been investigated.

Results and Discussion

Scheme 1 shows the process of synthesis of azopyridone dyes. New 2-(perfluoroalkyl)anilines **1** were prepared by the reaction of 2-iodoaniline with a perfluoroalkyl iodide in the presence of copper, as described in a literature.[10] 3-Cyano-5-hydroxy-2-pyridones (**2**) were synthesized by the reaction of amine with ethyl cyanoacetate and ethyl acetoacetate in the presence of piperidine.[11] Compounds **2** were used as coupling components, without further purification, to give azopyridone dyes **3**—**10** in moderate to good yields.



Scheme 1.

Table 1 summarizes the synthesis, absorption spectra, and melting points of the azopyridone dyes. It is known that dyes used for D2T2 printing should possess melting points in the range of 100 to 200 °C. Melting points of the azopyridone dyes were remarkably affected by a R^1 substituent. A long alkyl chain substituent lowered the melting points of azopyridones dyes (Runs 1—6). The melting point of 3-cyano-6-hydroxy-4-methyl-1-phenyl-5-phenylazo-2-pyridone (**9a**) was relatively high (Run 7). Those of 4-trifluoromethyl azopyridone dyes ($R^2 = CF_3$) were slightly lower than the corresponding 4-methyl derivatives ($R^2 = CH_3$) (Runs 5, 8—20).

The alkyl substituent at the 1-position (R^1) did not affect the absorption maxima of azopyridone dyes (Runs 1—7). Azopyridone dyes containing an electron-withdrawing trifluoromethyl and nitro group on the phenyl moiety showed small hypsochromic shifts compared with those containing an electron-releasing methyl group (Runs 8—10, 15—17). No remarkable differences of absorption maxima were observed among 5-[2-(perfluoroalkyl)phenylazo]pyridone dyes (Runs 17—20). These results suggest that azopyridone dyes have

Table 1. Synthesis, Absorption Spectra,[a] and Melting Points of Azopyridone Dyes

Run	Compd	R^1	R^2	R^3	Yield	Mp	λ_{max}	ε
					%	°C	nm	
1	**3a**	H	CH_3	H	65	297	430	35400
2	**4a**	CH_3	CH_3	H	75	261	429	9500
3	**5a**	C_3H_7	CH_3	H	46	191	431	34600
4	**6a**	C_4H_9	CH_3	H	70	184	431	39200
5	**7a**	C_6H_{13}	CH_3	H	66	159	432	35000
6	**8a**	C_8H_{17}	CH_3	H	93	156	432	41100
7	**9a**	C_6H_5	CH_3	H	52	280	430	25000
8	**7b**	C_6H_{13}	CH_3	CH_3	69	173	439	31000
9	**7c**	C_6H_{13}	CH_3	NO_2	70	210	432	42700
10	**7d**	C_6H_{13}	CH_3	CF_3	47	174	418	29000
11	**7e**	C_6H_{13}	CH_3	C_4F_9	56	169	418	38000
12	**7f**	C_6H_{13}	CH_3	C_6F_{13}	27	177	419	37600
13	**7g**	C_6H_{13}	CH_3	C_8F_{17}	63	183	419	31000
14	**10a**	C_6H_{13}	CF_3	H	60	145	431	35600
15	**10b**	C_6H_{13}	CF_3	CH_3	49	165	451	33600
16	**10c**	C_6H_{13}	CF_3	NO_2	86	156	434	33800
17	**10d**	C_6H_{13}	CF_3	CF_3	45	120	424	37800
18	**10e**	C_6H_{13}	CF_3	C_4F_9	43	136	420	33600
19	**10f**	C_6H_{13}	CF_3	C_6F_{13}	84	158	423	30100
20	**10g**	C_6H_{13}	CF_3	C_8F_{17}	63	170	420	37000

a) UV spectra were measured in EtOH.

the intramolecular charge-transfer chromophoric system.

Application of azopyridone dyes to D2T2 printing was examined. Three important parameters for D2T2 printing are shown in Table 2. These are film forming ability of dyes, sensitivity (amounts of dye transferred from a dye sheet to a receiver paper by heating) and photostability of dyes transferred.

The film forming ability was decreased depending on the length of perfluoroalkyl chain in 5-(2-substituted phenylazo)pyridones, due to low affinity of perfluoroalkyl chain moiety to resin.

Figure 1 represents the relationship between heating time at constant temperature and color density of image on a receiver paper. Continuous tone can be obtained by changing the heating time on the dye sheet. To evaluate the thermal transfer sensitivity of dye, color density of the receiver paper was measured after heating for 13 ms. No remarkable differences of sensitivity between 4-methyl- (**7**) and 4-trifluoromethyl-2-pyridone series (**10**) were observed. However, the introduction of long perfluoroalkyl group lowered the sensitivity in both 4-methyl-, and 4-trifluoromethyl derivatives.

Figure 2 shows a typical example of DTA-TG analysis of azopyridone dye **7a**, which did not sublime and decomposed around 270 °C. In this D2T2 printing system, melting and diffusion process of azopyridone dyes play an important role. Therefore, the perfluoroalkylated dyes having higher molecular weight lowers the diffusion rate of the dye molecule from a dye sheet to a receiver paper and then results low sensitivity.

Photostability of 4-methylpyridones **7** was better than that of 4-trifluoromethyl derivatives **10**. Especially, 5-[2-(trifluoromethyl)phenylazo]- and 5-[2-(perfluorobutyl)phenylazo]-4-methyl-2-pyridones showed good photostability.

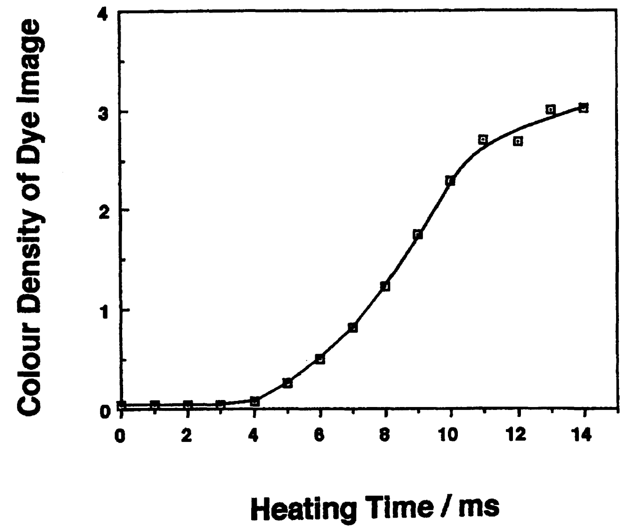


Fig. 1. Relationship between heating time and color density of dye image of 3-cyano-1-hexyl-6-hydroxy-4-methyl-5-phenylazo-2-pyridone (**7a**).

Experimental

Instruments. NMR spectra were taken on a JEOL JNM-270 GX spectrometer and mass spectra on a Shimadzu 9020-DF spectrometer. Thermal analysis was performed with a Rigaku TAS-200 instrument.

Synthesis of 2-(Perfluoroalkyl)anilines. To a DMSO solution (40 ml) of 2-iodoaniline (10 mmol) was

Table 2. Evaluation of 5-(2-Substituted Phenylazo)-3-Cyano-6-hydroxy-2-pyridones for D2T2 Printing

Run	Compd	R^1	R^2	R^3	Film forming ability	Sensitivity	Photostability
1	**7a**	C_6H_{13}	CH_3	H	1.42	3.00	16.8
2	**7b**	C_6H_{13}	CH_3	CH_3	1.37	2.84	67.4
3	**7c**	C_6H_{13}	CH_3	NO_2	1.24	2.70	5.4
4	**7d**	C_6H_{13}	CH_3	CF_3	0.56	2.69	2.0
5	**7e**	C_6H_{13}	CH_3	C_4F_9	0.37	2.13	5.8
6	**7f**	C_6H_{13}	CH_3	C_6F_{13}	—[a]	—[a]	—[a]
7	**7g**	C_6H_{13}	CH_3	C_8F_{17}	—[a]	—[a]	—[a]
8	**10a**	C_6H_{13}	CF_3	H	1.67	2.89	7.0
9	**10b**	C_6H_{13}	CF_3	CH_3	0.53	2.11	12.6
10	**10c**	C_6H_{13}	CF_3	NO_2	1.64	2.89	7.0
11	**10d**	C_6H_{13}	CF_3	CF_3	0.57	1.88	16.5
12	**10e**	C_6H_{13}	CF_3	C_4F_9	0.51	2.03	19.9
13	**10f**	C_6H_{13}	CF_3	C_6F_{13}	0.33	0.97	47.7
14	**10g**	C_6H_{13}	CF_3	C_8F_{17}	0.08	0.35	22.7

a) These were not evaluated due to low film forming ability.

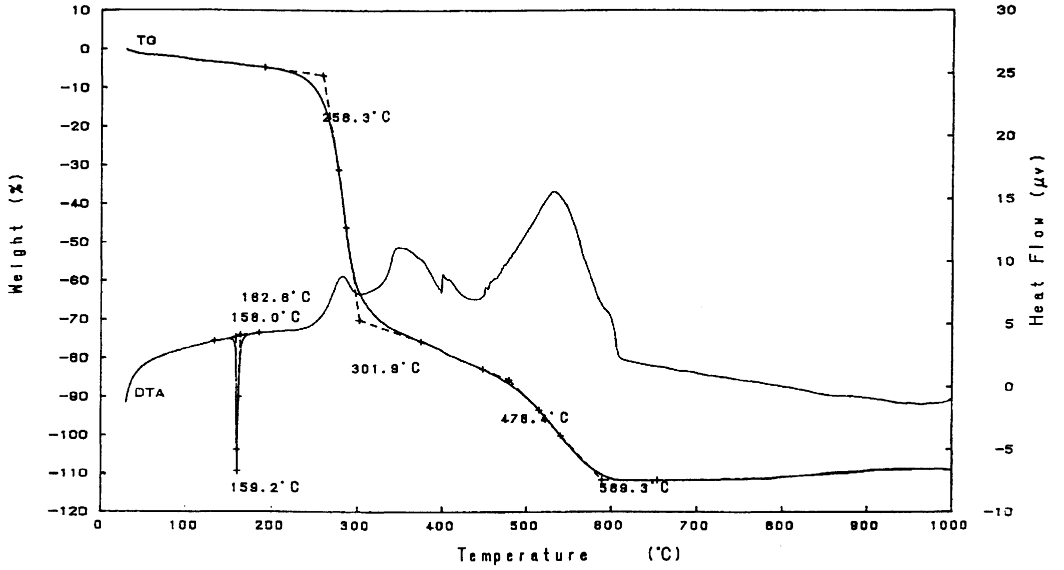


Fig. 2. Thermal analysis of 3-cyano-1-hexyl-6-hydroxy-4-methyl-5-phenylazo-2-pyridone (**7a**).

added a perfluoroalkyl iodide (10 mmol) and copper powder (1.5 g). The mixture was heated at 110—120 °C overnight in an autoclave. After the reaction, the mixture was poured into water (300 ml). The product was extracted with ether (100 ml×3). The extract was washed with brine and dried over anhydrous sodium sulfate. The product was distilled under reduced pressure. The physical and spectral data are shown below.

2-(Perfluorobutyl)aniline: Yield 65%; bp 95—98 °C/3300 Pa; ^{1}H NMR ($CDCl_3$) δ=4.21 (br s, 2H), 6.71 (d, J=7.7 Hz, 1H), 6.79 (t, J=7.7 Hz, 1H), 7.29—7.32 (m, 2H); MS (70 eV) m/z (rel intensity) 311 (M^+, 74), 142 (100). Found: C, 38.14; H, 1.73; N, 4.62%. Calcd for $C_{10}H_6F_9N$: C, 38.60; H, 1.94; N, 4.50%.

2-(Perfluorohexyl)aniline: Yield 43%; bp 119—121 °C/3600 Pa; ^{1}H NMR ($CDCl_3$) δ=4.17 (br s, 2H), 6.61 (d, J=8.1 Hz, 1H), 6.73 (t, J=8.1 Hz, 1H), 7.20 (t, J=8.1 Hz, 1H), 7.29 (d, J=8.1 Hz, 1H); MS (70 eV) m/z (rel intensity) 411 (M^+, 60), 142 (100), 69 (13). Found: C, 35.41; H, 1.51; N, 3.36%. Calcd for $C_{12}H_6F_{13}N$: C, 35.05; H, 1.47; N, 3.41%.

2-(Perfluorooctyl)aniline: Yield 63%; bp 135—142 °C/3300 Pa; ^{1}H NMR ($CDCl_3$) δ=4.21 (br s, 2H), 6.41 (d, J=7.3 Hz, 1H), 6.79 (d, J=7.3 Hz, 1H), 7.30—7.32 (m, 2H); MS (70 eV) m/z (rel intensity) 511 (M^+, 46), 142 (100), 69 (13). Found: C, 32.89; H, 1.26; N, 2.41%. Calcd for $C_{14}H_6F_{17}N$: C, 32.90; H, 1.18; N, 2.74%.

Synthesis of 3-Cyano-6-hydroxy-2-pyridones 2. They were synthesized as described in a literature.[11]

Synthesis of 5-(2-Substituted Phenylazo)-3-cyano-6-hydroxy-2-pyridones (3—10). To a 10% aqueous hydrochloric acid solution (3.6 ml) of an aniline (10 mmol) was added a 20% aqueous solution (3.5 ml) of sodium nitrite (0.7 g, 10 mmol) at 0 °C. The mixture was stirred for 45 min at 0 °C. To the solution was added a water–acetone solution (1 : 1, 30 ml) of a 3-cyano-6-hydroxy-2-pyridone (10 mmol).

The mixture was stirred for 4 h at 0 °C. The pH value of the solution was adjusted to 7.0. After the reaction, resultant precipitate was filtered, washed with water, and dried. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from chloroform–hexane. The physical and spectral data are shown below.

3-Cyano-6-hydroxy-4-methyl-5-phenylazo-2-pyridone (3a): Mp 297 °C (lit,[11] 288.1 °C).

3-Cyano-1,4-dimethyl-6-hydroxy-5-phenylazo-2-pyridone (4a): Mp 261 °C (lit,[11] 264.8 °C).

3-Cyano-6-hydroxy-4-methyl-5-phenylazo-1-propyl-2-pyridone (5a): ^{1}H NMR ($CDCl_3$) δ=0.97 (t, J=7.3 Hz, 3H), 1.59—1.71 (m, 2H), 2.62 (s, 3H), 3.94 (t, J=7.6 Hz, 2H), 7.43—7.51 (m, 5H), 15.04 (br s, 1H); MS (70 eV) m/z (rel intensity) 296 (M$^+$, 71), 254 (41), 177 (41), 77 (100), 65 (48). Found: C, 65.19; H, 5.42; N, 19.14%. Calcd for $C_{16}H_{16}N_4O_2$: C, 64.85, H, 5.44; N, 18.91%.

1-Butyl-3-cyano-6-hydroxy-4-methyl-5-phenylazo-2-pyridone (6a): ^{1}H NMR ($CDCl_3$) δ=0.96 (t, J=7.3 Hz, 3H), 1.41 (sextet, J=7.6 Hz, 2H), 1.62 (pentet, J=7.1 Hz, 2H), 2.62 (s, 3H), 3.97 (t, J=7.6 Hz, 2H), 7.30—7.49 (m, 5H), 15.04 (br s, 1H); MS (70 eV) m/z (rel intensity) 310 (M$^+$, 53), 293 (63), 254 (37), 177 (31), 77 (100), 65 (50). Found: C, 65.78; H, 5.87; N, 17.82%. Calcd for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85; N, 18.05%.

3-Cyano-1-hexyl-6-hydroxy-4-methyl-5-phenylazo-2-pyridone (7a): ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=5.5 Hz, 3H), 1.33 (br, 8H), 2.62 (s, 3H), 3.94 (t, J=5.5 Hz, 2H), 7.38 (s, 5H), 15.05 (br s, 1H); MS (70 eV) m/z (rel intensity) 338 (M$^+$, 16), 151 (100), 93 (28), 55 (45). Found: C, 67.23; H, 6.44; N, 16.68%. Calcd for $C_{19}H_{22}N_4O_2$: C, 67.44; H, 6.55; N, 16.56%.

3-Cyano-6-hydroxy-4-methyl-5-phenylazo-1-octyl-2-pyridone (8a): ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=5.8 Hz, 3H), 1.27—1.32 (m, 10H), 1.60—1.65 (m, 2H), 2.62 (s, 3H), 3.96 (dd, J=7.8 and 7.8 Hz, 2H), 7.29—7.49 (m, 5H), 15.04 (br s, 1H); MS (70 eV) m/z (rel intensity) 366 (M$^+$, 61), 349 (69), 254 (63), 177 (35), 105 (32), 93 (100), 92 (50), 77 (94), 65 (43). Found: C, 69.20; H, 7.44; N, 15.47%. Calcd for $C_{21}H_{26}N_4O_2$: C, 68.83; H, 7.15; N, 15.29%.

3-Cyano-6-hydroxy-4-methyl-1-phenyl-5-phenylazo-2-pyridone (9a): ^{1}H NMR ($CDCl_3$) δ=2.72 (s, 3H), 7.38—7.47 (m, 5H), 7.42—7.59 (m, 5H), 14.91 (br s, 1H); MS (70 eV) m/z (rel intensity) 330 (M$^+$, 93), 93 (62), 77 (100), 65 (52), 51 (52). Found: C, 68.83; H, 3.93; N, 17.02%. Calcd for $C_{19}H_{14}N_4O_2$: C, 69.08; H, 4.27; N, 16.96%.

3-Cyano-1-hexyl-6-hydroxy-4-methyl-5-(2-methylphenylazo)-2-pyridone (7b): ^{1}H NMR ($CDCl_3$) δ=0.89 (s, 3H), 1.33 (br s, 8H), 2.49 (s, 3H), 2.64 (s, 3H), 3.98 (t, J=7.6 Hz, 2H), 7.21—7.36 (m, 3H), 7.76 (d, J=7.9 Hz, 1H), 15.23 (br s, 1H); MS (70 eV) m/z (rel intensity) 352 (M$^+$, 100), 351 (61), 334 (50), 106 (42). Found: C, 68.32; H, 6.50; N, 15.81%. Calcd for $C_{20}H_{24}N_4O_2$: C, 68.16; H, 6.86; N, 15.90%.

3-Cyano-1-hexyl-6-hydroxy-4-methyl-5-(2-nitrophenylazo)-2-pyridone (7c): ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=5.4 Hz, 3H), 1.32 (br, 8H), 2.66 (s, 3H), 4.01 (t, J=7.6 Hz, 2H), 7.37 (t, J=6.7 Hz, 1H), 7.78 (t, J=6.7 Hz, 1H), 8.13 (d, J=6.7 Hz, 1H), 8.33 (d, J=6.7 Hz, 1H), 15.91 (br s, 1H); MS (70 eV) m/z (rel intensity) 383 (M$^+$, 100), 366 (72), 313 (28), 299 (40), 177 (53), 55 (66). Found: C, 59.79; H, 5.17; N, 18.13%. Calcd for $C_{19}H_{21}N_5O_4$: C, 59.52; H, 5.52; N, 18.27%.

3-Cyano-1-hexyl-6-hydroxy-4-methyl-5-[2-(trifluoromethyl)phenylazo]-2-pyridone (7d): ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=5.4 Hz, 3H), 1.32 (br, 8H), 2.63 (s, 3H), 4.00 (t, J=7.6 Hz, 2H), 7.37 (t, J=7.8 Hz, 1H), 7.69 (t, J=7.8 Hz, 1H), 7.70 (d, J=7.8 Hz, 1H), 7.96 (d, J=7.8 Hz, 1H), 15.31 (br s, 1H); MS (70 eV) m/z (rel intensity) 406 (M$^+$, 61), 389 (40), 177 (70), 161 (70), 55 (70). Found: C, 59.26; H, 5.01; N, 13.84%. Calcd for $C_{20}H_{21}F_3N_4O_2$: C, 59.11; H, 5.21; N, 13.79%.

3-Cyano-1-hexyl-6-hydroxy-4-methyl-5-[2-(perfluorobutyl)phenylazo]-2-pyridone (7e): ^{1}H NMR ($CDCl_3$) δ=0.89 (s, 3H), 1.32 (br, 8H), 2.63 (s, 3H), 4.00 (d, J=7.6 Hz, 2H), 7.40 (t, J=7.9 Hz, 1H), 7.62 (d, J=8.0 Hz, 1H), 7.70 (t, J=7.9 Hz, 1H), 8.00 (d, J=8.0 Hz, 1H), 15.34 (br s, 1H); MS (70 eV) m/z (rel intensity) 556 (M$^+$, 55), 539 (36), 311 (41), 177 (100), 44 (61). Found: C, 49.72; H, 3.74; N, 9.94%. Calcd for $C_{23}H_{21}F_9N_4O_2$: C, 49.65; H, 3.80; N, 10.07%.

3-Cyano-1-hexyl-6-hydroxy-4-methyl-5-[2-(perfluorohexyl)phenylazo]-2-pyridone (7f): ^{1}H NMR ($CDCl_3$) δ=0.87 (t, J=6.7 Hz, 3H), 1.31 (m, 6H), 1.60 (m, 2H), 2.63 (s, 3H), 3.96 (t, J=8.0 Hz, 2H), 7.40 (t, J=8.0 Hz, 1H), 7.62 (d, J=8.0 Hz, 1H), 7.70 (t, J=8.0 Hz, 1H), 7.86 (d, J=8.0 Hz, 1H), 15.63 (br s, 1H); MS (70 eV) m/z (rel intensity) 656 (M$^+$, 36), 177 (100). Found: C, 45.33; H, 2.93; N, 8.38%. Calcd for $C_{25}H_{21}F_{13}N_4O_2$: C, 45.74; H, 3.22; N, 8.54%.

3-Cyano-1-hexyl-6-hydroxy-4-methyl-5-[2-(perfluorooctyl)phenylazo]-2-pyridone (7g): ^{1}H NMR ($CDCl_3$) δ=0.92 (t, J=6.7 Hz, 3H), 1.33—1.64 (br, 8H), 2.63 (s, 3H), 3.99 (t, J=7.6 Hz, 2H), 7.32 (t, J=7.9 Hz, 1H), 7.66 (d, J=7.9 Hz, 1H), 7.73 (t, J=7.9 Hz, 1H), 7.92 (d, J=7.9 Hz, 1H), 15.49 (br s, 1H). Found: C, 42.96; H, 2.52; N, 7.23%. Calcd for $C_{27}H_{21}F_{17}N_4O_2$: C, 42.87; H, 2.80; N, 7.41%.

3-Cyano-1-hexyl-6-hydroxy-5-phenylazo-4-trifluoromethyl-2-pyridone (10a): ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=6.7 Hz, 3H), 1.22—1.39 (m, 6H), 1.58—1.66 (m, 2H), 4.00 (dd, J=7.6 and 7.6 Hz, 2H), 7.34—7.55 (m, 5H), 15.26 (br s, 1H); MS (70 eV) m/z (rel intensity) 392 (M$^+$, 94), 375 (42), 105 (68), 93 (68), 77 (100), 55 (31). Found: C, 58.08; H, 4.80; N, 14.11%. Calcd for $C_{19}H_{19}F_3N_4O_2$: C, 58.16; H, 4.88; N, 14.28%.

3-Cyano-1-hexyl-6-hydroxy-5-(2-methylphenylazo)-4-trifluoromethyl-2-pyridone (10b): ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=6.8 Hz, 3H), 1.26—1.33 (m, 6H), 1.58—1.64 (m, 2H), 2.50 (s, 3H), 4.03 (dd, J=7.3 and 7.3 Hz, 2H), 7.29—7.38 (m, 3H), 7.78 (br s, 1H), 15.5 (br s, 1H); MS (70 eV) m/z (rel intensity) 406 (M$^+$, 54), 389 (30), 336 (15), 119 (23), 107 (33), 91 (100), 86 (33), 84 (51). Found: C, 59.30; H, 5.27; N, 13.32%. Calcd for $C_{20}H_{21}F_3N_4O_2$: C, 59.11; H, 5.21; N, 13.79%.

3-Cyano-1-hexyl-6-hydroxy-5-(2-nitrophenylazo)-4-trifluoromethyl-2-pyridone (10c): ^{1}H NMR ($CDCl_3$) δ=0.91 (t, J=6.7 Hz, 3H), 1.29—1.44 (m, 6H), 1.61—1.72 (m, 2H), 4.02 (t, J=7.6 Hz, 2H), 7.47 (t, J=7.0 Hz, 1H), 7.83 (t, J=7.3 Hz, 1H), 8.11 (d, J=7.3 Hz, 1H), 8.35 (d, J=8.5 Hz, 1H), 16.08 (br s, 1H); MS (70 eV) m/z (rel intensity) 437 (M$^+$, 22), 231 (42), 81 (100). Found: C, 52.22; H, 4.08; N, 16.22%. Calcd for $C_{19}H_{18}F_3N_5O_4$: C, 52.18; H, 4.15; N, 16.01%.

3-Cyano-1-hexyl-6-hydroxy-4-trifluoromethyl-5-[2-(trifluoromethyl)phenylazo]-2-pyridone (10d): ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.9 Hz, 3H), 1.26—1.34 (m, 6H), 1.57—1.65 (m, 2H), 4.02 (t, J=7.6 Hz, 2H), 7.34 (t, J=7.8 Hz, 1H), 7.72 (t, J=7.8 Hz, 1H), 7.73 (d, J=7.8 Hz, 1H), 7.97 (d, J=7.8 Hz, 1H), 15.53 (br s, 1H); MS (70 eV) m/z (rel intensity) 460 (M^+, 60), 251 (31), 161 (79). Found: C, 52.43; H, 3.95; N, 11.95%. Calcd for $C_{20}H_{18}F_6N_4O_2$: C, 52.18; H, 3.94; N, 12.17%.

3-Cyano-1-hexyl-6-hydroxy-5-[2-(perfluorobutyl)phenylazo]-4-trifluoromethyl-2-pyridone (10e): ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.7 Hz, 3H), 1.28—1.39 (br, 6H), 1.62 (br, 2H), 4.04 (dd, J=7.6 and 7.6 Hz, 2H), 7.48 (t, J=7.8 Hz, 1H), 7.65 (d, J=7.8 Hz, 1H), 7.74 (d, J=7.8 Hz, 1H), 8.02 (d, J=7.8 Hz, 1H), 15.54 (br s, 1H); MS (70 eV) m/z (rel intensity) 610 (M^+, 27), 311 (30), 86 (61), 84 (100). Found: C, 45.60; H, 2.65; N, 9.17%. Calcd for $C_{23}H_{18}F_{12}N_4O_2$: C, 45.26; H, 2.97; N, 9.18%.

3-Cyano-1-hexyl-6-hydroxy-5-[2-(perfluorohexyl)phenylazo]-4-trifluoromethyl-2-pyridone (10f): ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.7 Hz, 3H), 1.23—1.38 (m, 6H), 1.59—1.70 (m, 2H), 4.01 (t, J=7.6 Hz, 2H), 7.48 (t, J=7.6 Hz, 1H), 7.65 (d, J=7.3 Hz, 1H), 7.74 (t, J=7.6 Hz, 1H), 8.02 (d, J=8.5 Hz, 1H), 15.55 (br s, 1H); MS (70 eV) m/z (rel intensity) 710 (M^+, 10), 423 (30), 395 (41), 145 (100). Found: C, 42.61; H, 2.41; N, 7.78%. Calcd for $C_{25}H_{18}F_{16}N_4O_2$: C, 42.27%; H, 2.55; N, 7.89%.

3-Cyano-1-hexyl-6-hydroxy-5-[2-perfluorooctyl)phenylazo]-4-trifluoromethyl-2-pyridone (10g): ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.7 Hz, 3H), 1.25—1.65 (m, 8H), 4.01 (t, J=7.6 Hz, 2H), 7.47 (t, J=8.1 Hz, 1H), 7.65 (d, J=8.1 Hz, 1H), 7.74 (t, J=8.1 Hz, 1H), 8.02 (d, J=8.1 Hz, 1H), 15.55 (br s, 1H); MS (70 eV) m/z (rel intensity) 810 (M^+, 60), 511 (70), 231 (73), 145 (42), 142 (100), 83 (70), 81 (77), 69 (92). Found: C, 39.90; H, 2.16; N, 6.79%. Calcd for $C_{27}H_{18}F_{20}N_4O_2$: C, 40.02; H, 2.24; N, 6.91%.

Evaluation of 5-(2-Substituted Phenylazo)-3-cyano-1-hexyl-6-hydroxy-2-pyridones for D2T2 Printing. Ink was prepared by mixing the dye (0.6 part) with toluene (9.0 part) containing resin (1.0 part). Films (dye sheet) were prepared by coating the ink on a thin layer of poly(ethylene terephthalate) using a draw bar technique. After drying the films, the film forming ability was evaluated by measuring the color density of the films (thickness: about 0.5 µm).

D2T2 process was examined using a test printer (thermal head: 0.3 W dot^{-1}, heating time: 1—14 ms). The thermal transfer sensitivity is defined by measuring the color density of dye image on the receiver paper (main component: poly(vinyl chloride)) after heating for 13 ms. Color density of the films and the dye images were measured by a color densitometer using blue filter.

Photostability of dye transferred is evaluated by color difference ($\Delta E^* ab$) between the dye images on the receiver paper before and after irradiation for 80 h with a xenon fademater. Color difference ($\Delta E^* ab$) is defined by the following equation.[12,13]

$$\Delta E^* ab = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2}$$

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