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Red solid-state fluorescent aminoperfluorophenazines

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ABSTRACT

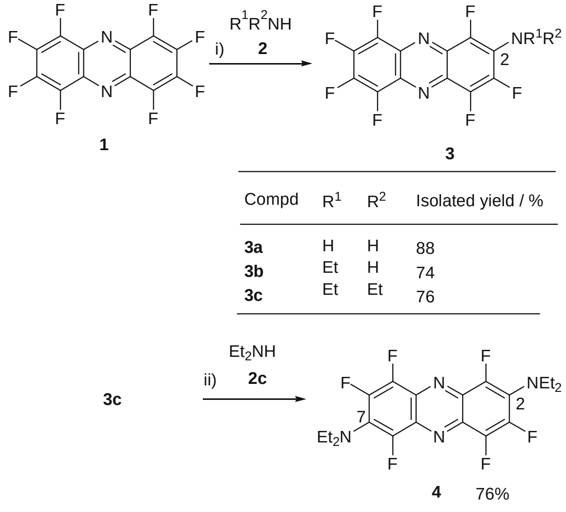
The solid-state fluorescence of 2-amino-, 2-ethylamino, 2-diethylamino-, and 2,7-bis(diethylamino)perfluorophenazines was examined. They showed their fluorescence maxima in the range of 584–637 nm. The solid-state fluorescence quantum yield of 2-diethylamino derivative was highest among these derivatives, there being 0.22. X-ray crystallographic analysis suggests that the 2-diethylamino derivative has no strong intermolecular interactions among adjacent molecules to show intense fluorescence, whereas the other derivatives have network NH/F hydrogen, π–π, and CH/F interactions to reduce solid-state fluorescence intensity.

Survey of solid-state fluorescent compounds is of significance from the viewpoint of their application to emitters in OLED, solid dye laser, and security materials. Though many organic compounds show red fluorescence in solution, fewer compounds show fluorescence in solid state, because of intermolecular interactions in the condensed and solid states. Dicyanopyrazines,[1] dicyanodiazepines,[2] α,β-dicyanostilbenes,[3] 4-(dicyanomethylene)-2-methyl-6-[4-(dimethylamino)styryl]-4*H*-pyrans,[4] and diphenylaminospirobifluorenylfumaronitriles[5] have been reported to show red solid-state fluorescence. Meanwhile, fewer studies on the solid-state fluorescence of fluorine-containing compounds have been reported in spite of their potential applications to advanced materials. To our knowledge, only trifluoromethyl-substituted α,β-dicyanostilbenes,[3] pyrromethenes,[6] bis(pentafluorobenzoyloxy)-substituted anthracene,[7] perfluoroalkyl-substituted coumarins,[8] and perfluoroalkenyloxy-substituted naphtho oxazines[9] have been reported to show solid-state fluorescence. No solid-state fluorescence of perfluoroaromatic compounds have been reported so far. Therefore, it is of importance to examine the effect of aromatic fluorine atom(s) on solid-state fluorescence. In our previous paper, perfluorophenazine has been reported to regiospecifically react with amines to give fluorescent 2-amino derivatives.[10] We report herein red solid-state fluorescent aminoperfluorophenazines.

2-Aminoperfluorophenazines **3** were prepared by the reaction of perfluorophenazine (**1**) with amines **2** in the presence of triethylamine (TEA) as shown in Scheme 1. 2,7-Bis(diethylamino)perfluorophenazine (**4**) was prepared by the reaction of **3c** with another molar amount of diethylamine.[10]

The UV–vis absorption and fluorescence spectra of **3a**, **3b**, **3c**, and **4** in hexane are shown in Figure 1a. The results are also summarized in Table 1. The absorption maximum (λ_{max}) of **3** was more bathochromic with increasing electron-donating ability of the amino group at the 2-position: **3c** (471) > **3b** (456) > **3a** (437).

No significant difference in λ_{max} was observed between **3c** (471) and **4** (478). The fluorescence maximum (F_{max}) was also more bathochromic in the following order of aminoperfluorophenazines: **4** (562), **3c** (553) > **3b** (541) > **3a** (521). Their fluorescence quantum yields (Φ_f) were observed in the range of 0.63–0.97. The fluorescence spectra of **3a**, **3b**, **3c**, and **4** in the solid state (powder) are shown in Figure 1b. The results are also listed in Table 1. The F_{max} was observed in the range of 584–637 nm, there being more bathochromic compared with that in hexane (521–562), indicating



Compd	R^1	R^2	Isolated yield / %
3a	H	H	88
3b	Et	H	74
3c	Et	Et	76

Scheme 1. Synthesis of aminoperfluorophenazines. Reagents and conditions: (i) **2** (1.2 equiv), TEA, DMF, 0 °C, 24 h; (ii) **2c** (1.2 equiv), DMF, rt, 24 h.

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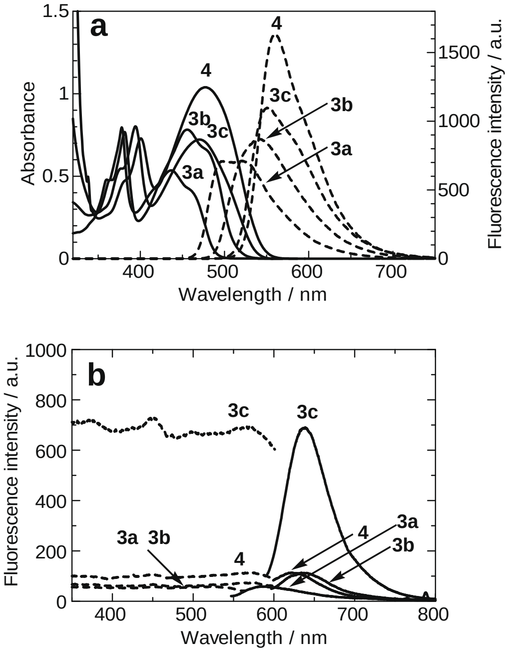


Figure 1. (a) UV–vis absorption and fluorescence spectra of **3a**, **3b**, **3c**, and **4** in hexane measured at the concentration of 1×10^{-5} mol dm^{-3} at 25 °C. (b) Solid-state fluorescence spectra of **3a**, **3b**, **3c**, and **4**.

Table 1
Optical properties of aminoperfluorophenazines

Compound	In hexane[a]			Solid state	
	λ_{max} (ε) (nm)	F_{max} (nm)	Φ_f[b]	F_{max} (nm)	Φ_f[b]
3a	437 (5360)	521	0.63	584	0.02
3b	456 (7820)	541	0.76	632	0.05
3c	471 (7220)	553	0.86	637	0.22
4	478 (10,390)	562	0.97	621	0.03

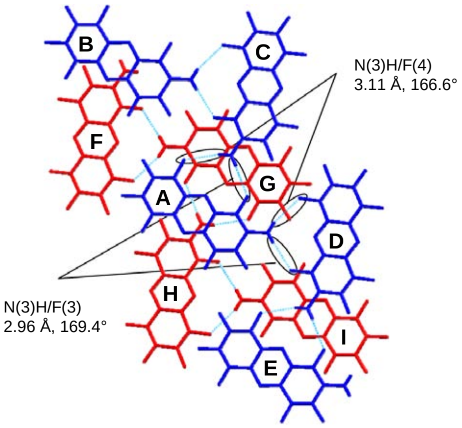
[a] Measured at the concentration of 1.0×10^{-5} mol dm^{-3} at 25 °C.
[b] Determined by absolute PL quantum yield measurement system C9920-02.

intermolecular interactions in the solid state. The fluorescence intensity significantly changed by the kinds of amino substituent(s), whereas no drastic difference in Φ_f was observed in solution. The Φ_f of **3c** (0.22) in the solid state was exceptionally high compared with those of **3b** (0.05), **4** (0.03), and **3a** (0.02).

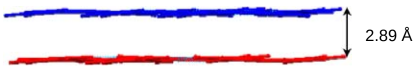
To examine the difference of fluorescence intensity in the solid state, the X-ray crystallographic analysis of **3a**, **3b**, **3c**, and **4** was performed.[11]

The X-ray crystallography of **3a** is shown in Figure 2. The molecules are arranged in a ‘herring-bone’ fashion. Figure 2a and b shows that blue molecules, A, B, C, D, and E, are located on the same plane. Red ones, F, G, H, and I, are also located on the same plane. Molecule A has four NH/F interactions with C and D. Fluorine interactions have been reviewed.[12] The side view indicates that the interplanar distance between blue and red molecules is 2.89 Å. However, the top view depicts that there are little π–π overlapping between blue and red molecules. Thus, compound **3a** has network NH/F interactions forming planar structure to show least intense solid-state fluorescence.

Figure 3 shows the X-ray crystallography of **3b**. Blue, red, and green molecules are located almost on the same plane, respectively. They form a head-to-tail dimer with two F/F interactions. They are packed in parallel, there being the interplanar distance of 3.36 Å. The top view shows that almost a half part of the aromatic moiety is overlapped.

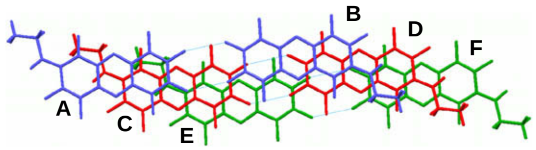


(a) Top view

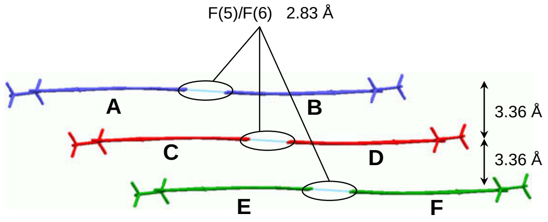


(b) Side view

Figure 2. X-ray crystallography of **3a**.



(a) Top view



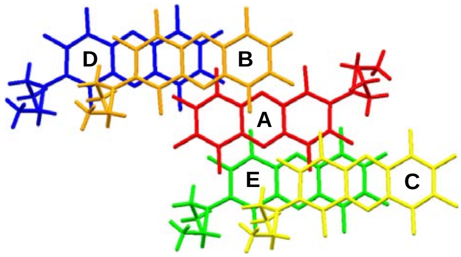
(b) Side view

Figure 3. X-ray crystallography of **3b**.

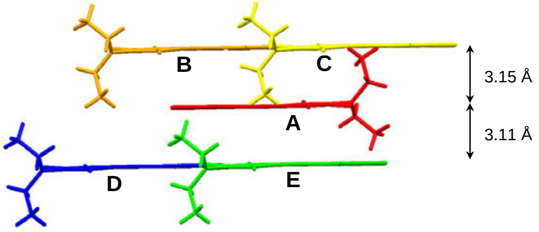
The X-ray crystallography of **3c** is shown in Figure 4. The side view shows that molecules B and C are located on the same plane. The top view shows no strong interactions between B and C. The interplanar distance between A and C is 3.15 Å and that of A and E is 3.11 Å. However, the top view clearly shows that no π–π overlapping is observed among B, A, and E. Thus, compound **3c** has no strong intermolecular interactions with adjacent molecules.

Figure 5 shows the X-ray crystallography of **4**. Molecules B, C, and D are located almost on the same plane. Molecules E, F, and G are also located almost on the same plane. Figure 5a and b shows that molecule A is surrounded by B, C, D, E, F, and G. Molecule A has 12 CH/F interactions with these adjacent molecules. No π–π overlapping is observed among A, B, and G. Thus, compound **4** has network CH/F interactions to show less intense solid-state fluorescence.

In conclusion, 2-(diethylamino)perfluorophenazine exceptionally showed intense fluorescence at 637 nm in the solid state with Φ_f 0.22. The X-ray crystallography suggests that this compound has no strong intermolecular interactions with adjacent molecules to show intense solid-state fluorescence, whereas the other derivatives have NH/F, π–π, and CH/F network interactions. This is the

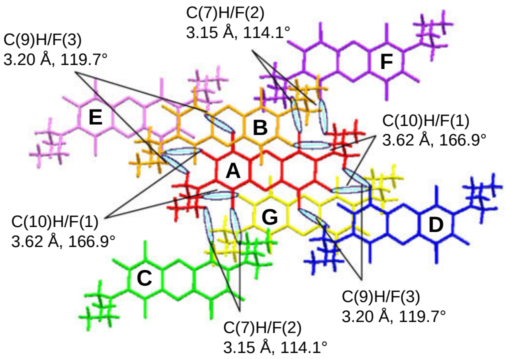


(a) Top view

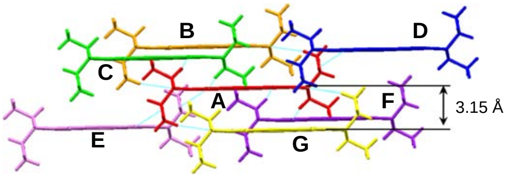


(b) Side view

Figure 4. X-ray crystallography of **3c**.



(a) Top view



(b) Side view

Figure 5. X-ray crystallography of **4**.

first report that not only π–π interactions and hydrogen bonds but also NH/F and CH/F interactions decrease solid-state fluorescence intensity.

Supplementary data

Supplementary data (synthesis of **3a**, ORTEP, and overall packing of **3a**, **3b**, **3c**, and **4**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.095.

References and notes

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11. Single crystals were obtained by diffusion method using dichloromethane and hexane. In the case of **3a**, the diffraction data were collected by using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods SIR97 and refined by fill-matrix least-squares calculations. In the cases of **3b**, **3c**, and **4**, the diffraction data were collected by using graphite-monochromated Cu Kα radiation. The structure was solved by SHELX97 method. Crystal data for **3a**: $C_{12}H_2N_3F_7$, $M_w = 321.17$, orthorhombic, *Pbca*, $Z = 8$, $a = 9.512(4)$, $b = 19.479(8)$, $c = 11.332(5)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $D_{calcd} = 2.032$ g cm^{-3}, $T = 123(2)$ K, $F(0\,0\,0) = 1264$, μ(Mo Kα) = 0.213 mm^{-1}, 15,693 reflections were corrected, 2390 unique ($R_{int} = 0.0305$). 2390 observed ($I > 2\sigma(I)$), 207 parameters, $R_1 = 0.0533$, $wR_2 = 0.1124$. Crystal data for **3b**: $C_{14}H_6N_3F_7$, $M_w = 349.21$, monoclinic, $P21/n$, $Z = 4$, $a = 5.391(3)$, $b = 12.168(7)$, $c = 19.82(1)$ Å, $\alpha = 90°$, $\beta = 86.99(3)°$, $\gamma = 90°$, $D_{calcd} = 1.786$ g cm^{-3}, $T = 296$ K, $F(0\,0\,0) = 696.0$, μ(Cu Kα) = 1.623 mm^{-1}, 10,700 reflections were corrected, 2207 unique ($R_{int} = 0.062$). 2207 observed ($I > 2\sigma(I)$), 223 parameters, $R_1 = 0.0520$, $wR_2 = 0.1330$. Crystal data for **3c**: $C_{16}H_{10}N_3F_7$, $M_w = 377.26$, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.338(10)$, $b = 10.26(2)$, $c = 11.580(19)$ Å, $\alpha = 111.78°$, $\beta = 10.26(2)°$, $\gamma = 105.33(9)°$, $D_{calcd} = 1.621$ g cm^{-3}, $T = 296$ K, $F(0\,0\,0) = 380.0$, μ(Cu Kα) = 1.411 mm^{-1}, 5852 reflections were corrected, 5852 unique ($R_{int} = 0.068$). 5852 observed ($I > 2\sigma(I)$), 245 parameters, $R_1 = 0.0792$, $wR_2 = 0.1631$. Crystal data for **4**: $C_{20}H_{20}N_4F_6$, $M_w = 430.40$, triclinic, $P\bar{1}$, $Z = 1$, $a = 5.1945(11)$, $b = 9.3306(18)$, $c = 10.250(2)$ Å, $\alpha = 108.024(12)°$, $\beta = 92.710(13)°$, $\gamma = 94.339(13)°$, $D_{calcd} = 1.521$ g cm^{-3}, $T = 93$ K, $F(0\,0\,0) = 222.0$, μ(Cu Kα) = 1.170 mm^{-1}, 4883 reflections were corrected, 1637 unique ($R_{int} = 0.086$). 1637 observed ($I > 2\sigma(I)$), 137 parameters, $R_1 = 0.0626$, $wR_2 = 0.1713$. These crystallographic data **3a** (CCDC 722763), **3b** (CCDC 297182), **3c** (CCDC 722764), and **4** (CCDC 297183) have been also deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.
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