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Application of polyfluorophenazines to dichroic fluorescent dyes in guest–host liquid crystal displays

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Novel dichroic fluorescent 2- and 2,7-disubstituted perfluorophenazines exhibit emission maxima in the range 570–600 nm in MLC-2039. The order parameter of fluorescence was observed in the range 0.29–0.49.

1. Introduction

Although many kinds of dichroic dyes, such as azo and anthraquinone derivatives, have been used in guest–host liquid crystal displays [1], fewer kinds of dichroic fluorescent dyes are known. Only perylenes [2], naphthalimides [3–5], thiadiazoles [6], oligothiophenes [7], dilactone derivatives [8] and 3-aminobenzanthrones [9] have been reported. Recently, we found that novel polyfluorophenazines, obtained by the reaction of octafluorophenazine with nucleophiles, were fluorescent compounds. In our continuing study on dichroic dyes [10–16], we considered that these compounds might be used as dichroic fluorescent dyes. Here we report the application of polyfluorophenazines to fluorescent dichroic dyes in guest–host liquid crystal displays.

2. Results and discussion

2.1. *Synthesis*

The preparation of the polyfluorophenazines used in this study is shown in the scheme 1. Perfluorophenazines **1** and **2** were obtained by the oxidation of perfluoroanilines as described in the literature [17]. Octafluorophenazine (**1**) reacted with nucleophiles **3** in DMF in the presence of triethylamine (TEA) to afford the 2-substituted products **4** in good yields. The 2-monosubstituted products **4b** and **4d** reacted with another molar amount of nucleophiles **3b** and **3d** to give the 2,7-disubstituted derivatives **5b** and **5d**, respectively, in good yields. Details of the synthesis are reported elsewhere.

2.2. *UV-vis absorption and fluorescence spectra of polyfluorophenazines*

Typical UV-vis absorption and fluorescence spectra of polyfluorophenazines (here, compound **4b**) in hexane are shown in figure 1. The absorption and fluorescence maxima ($\lambda_{\max}$ and λ_{em}) of **4b** were observed at 471 and 560 nm, respectively. The UV-vis absorption and fluorescence spectra of compounds **1**, **2**, **4**, and **5** are indicated in the table, together with other physical data.

The chromophoric system of 2-substituted polyfluorophenazine **4b** was analysed by the PPPMO method (PiSystem 98). The schemetic representation of LUMO, HOMO, and change in electron density accompanied by first excitation are shown in figure 2. This compound showed an intramolecular charge-transfer chromophoric system from the amino to quinoxaline moiety. Since the electron-donating ability of phenylthio groups is lower than that of amino group, the $\lambda_{\max}$ of phenylthio derivative **4f** (394 nm) was more hypsochromic than the amino derivatives **4a**–**e** (456–478 nm).

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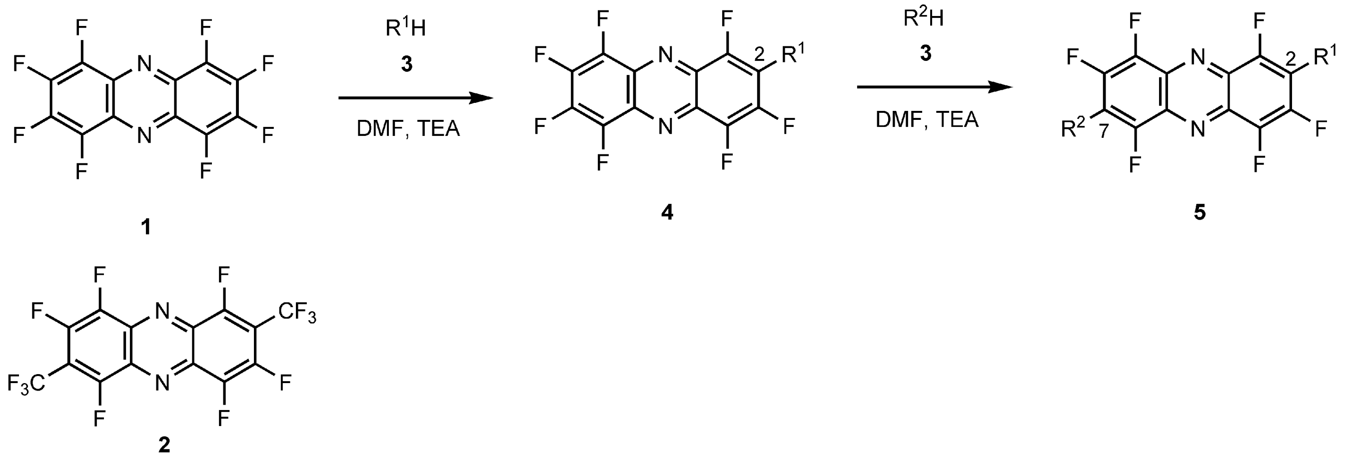


Scheme 1.

Polyfluorophenazine (0.5 wt%) was dissolved in MLC-2039, and the mixture solution filtered. The cell (thickness about 50 μm) was prepared by filling the solution between two glass plates attached with transparent electrodes, on which polyimide was applied and rubbed. The UV-vis absorption and emission spectra of polyfluorophenazines were measured by irradiating the cell with polarized light. Figure 3 shows the typical UV-vis absorption and emission spectra obtained. The $\lambda_{\max}$ and λ_{em} of **4b** were observed at 470 and 590 nm, respectively.

The order parameter of absorption (S_A) is calculated by the following equation:

$$S_A = (A_{//} - A_{\perp}) / (A_{//} + 2A_{\perp})$$

where $A_{//}$ and $A_{\perp}$ represent the absorbance of light polarized parallel and perpendicular, respectively, to the direction of the alignment of the molecule in the liquid crystal. S_F is calculated from the relationship $S_F = (F_{//} - F_{\perp}) / (F_{//} + 2F_{\perp})$, where $F_{//}$ and $F_{\perp}$ represent the fluorescence intensity of light polarized parallel and perpendicular, respectively, to the direction of the alignment of the molecule in the liquid crystal.

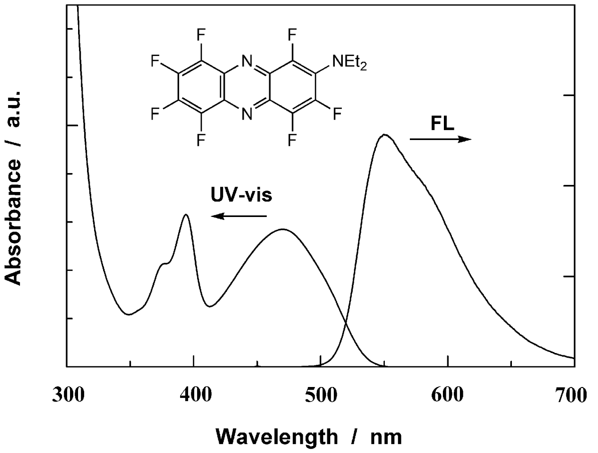


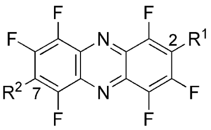
Figure 1. UV-vis absorption and fluorescence spectra of **4b** in hexane.

The S_A and S_F values of **4b** in MLC-2039 were calculated to be 0.37 and 0.38, respectively. The results for other compounds are shown in the table. The $\lambda_{\max}$ and λ_{em} were observed in the range 380–490 and 570–600 nm, respectively. The S_A and S_F values were calculated to be in the range 0.08–0.39 and 0.29–0.49, respectively.

Dichroism was analysed by calculating the deviation of angle θ between the direction of the transition moment and of the long axis, and the l/d ratio, where l and d represent the length of the long axis and the diameter of the circumscribed cylinder of the molecule, respectively. The θ values and l/d ratios in the optimized structure of polyfluorophenazines were calculated. A typical example is depicted in figure 4. The calculated θ value of **4b** was 48.60°. The l and d values were calculated to be 14.629 and 8.693 Å, respectively, the l/d ratio being 1.68. The results for the other derivatives are indicated in the table.

The relationship between the S value and the l/d ratio is shown in figure 5. That of selected azo derivatives is also indicated in the figure for reference [16]. The l/d ratios of azo derivatives are large, in the range 2.56–4.68. This indicates that the molecule can be well oriented in liquid crystals. The θ values of the azo derivatives are 2.90–24.02° [16], suggesting that the orientation is almost parallel to the direction of the liquid crystals. Thus, large S values for azo dyes arises from their good orientation in liquid crystals. Meanwhile, the l/d ratios of polyfluorophenazines **4** and **5** were calculated to be in the range 1.09–1.75, smaller than those of azo dyes. The θ values for **4** and **5** varied

Table. UV-vis absorption and fluorescence spectra of phenazines, and dichroic data.



Compound	R^1	R^2	$\frac{\lambda^a_{max}}{nm}$	ε^a	$\frac{\lambda^b_{ex}}{nm}$	$\frac{\lambda^b_{em}}{nm}$	RFI_b	$\frac{\lambda^c_{max}}{nm}$	$S_A{}^c$	$\frac{\lambda^c_{em}}{nm}$	$S_F{}^c$	θ	l	d	l/d
1	F	F	357	3000	365	465	4	380	0.08	—[d]	—[d]	90.16	12.184	8.121	1.50
2	CF_3	CF_3	414	3000	412	490	4	400	0.14	—[d]	—[d]	50.28	14.099	8.116	1.74
4a	EtNH	F	456	4800	452	522	95	460	0.33	570	0.30	41.44	14.819	8.488	1.75
4b	Et_2N	F	471	5100	487	560	100	470	0.37	590	0.38	48.60	14.629	8.693	1.68
4c	*cyclo*-$C_6H_{11}NH$	F	460	7100	454	526	116	460	0.25	570	0.32	56.21	16.709	10.521	1.59
4d	*p*-(*n*-Bu)C_6H_4NH	F	472	9100	460	565	17	430	0.37	—[d]	—[d]	25.55	18.237	16.691	1.09
4e	*p*-$MeOC_6H_4NH$	F	478	7300	478	611	1	490	0.30	—[d]	—[d]	37.04	18.162	10.471	1.73
4f	PhS	F	394	9400	392	489	14	380	0.24	—[d]	—[d]	80.70	16.412	12.031	1.36
5b	Et_2N	Et_2N	459	7500	485	558	142	480	0.34	600	0.29	46.00	15.467	8.981	1.72
5d	*p*-(*n*-Bu)C_6H_4NH	*p*-(*n*-Bu)C_6H_4NH	460	16000	511	557	124	470	0.39	590	0.49	57.71	25.460	17.104	1.49

[a] Measured in hexane. 7-Diethylamino-4-methylcoumarin: $\lambda_{max} = 350$ nm, $\varepsilon = 22000$ in hexane.
[b] Measured in hexane at 25°C (1×10^{-5} mol dm^{-3}, 7-diethylamino-4-methylcoumarin: $\lambda_{ex} = 347$ nm, $\lambda_{em} = 392$ nm, $RFI = 285$).
[c] Measured in MLC-2039.
[d] No fluorescence.

in the range 25.5–90.16°. These results indicate that the orientation of polyfluorophenazines in liquid crystals is legs distinct. Therefore the S_A and S_F values are lower than the S values of azo derivatives. The large difference in θ values for **4** and **5** may affect the S_A and S_F values of polyfluorophenazines whose l/d ratios are small, to show relatively large ranges of S_A and S_F values (0.08–0.49) in spite of the small range of l/d ratios (1.09–1.75).

3. Conclusion

Novel dichroic fluorescent 2- and 2,7-disubstituted polyfluorophenazines exhibit λ_{em} in the range 570–600 nm in MLC-2039 solution. S_F values were calculated to be in the range 0.29–0.49. Dichroic analysis of the polyfluorophenazines showed that the shape of the molecules was less slim, and the deviation of the transition moment from the long axis larger, than those of typical dichroic azo dyes.

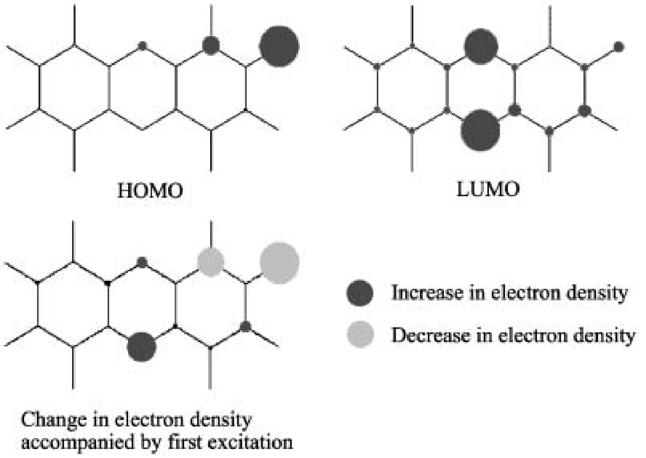


Figure 2. Schematic representation of HOMO, LUMO and change in electron density accompanied by first excitation in **4b** calculated by the PPPMO method.

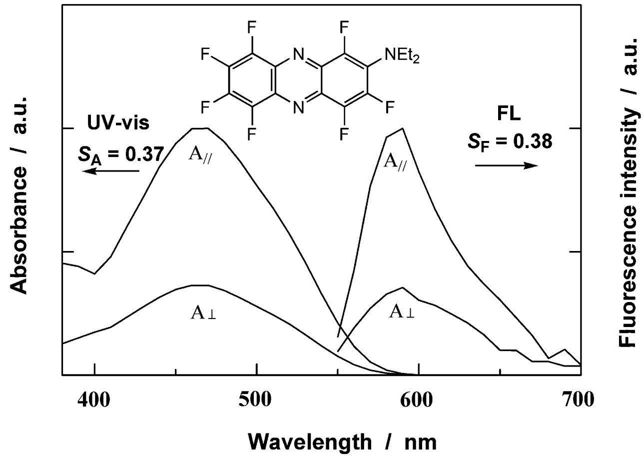


Figure 3. UV-vis absorption and fluorescence spectra of **4b** in MLC-2039.

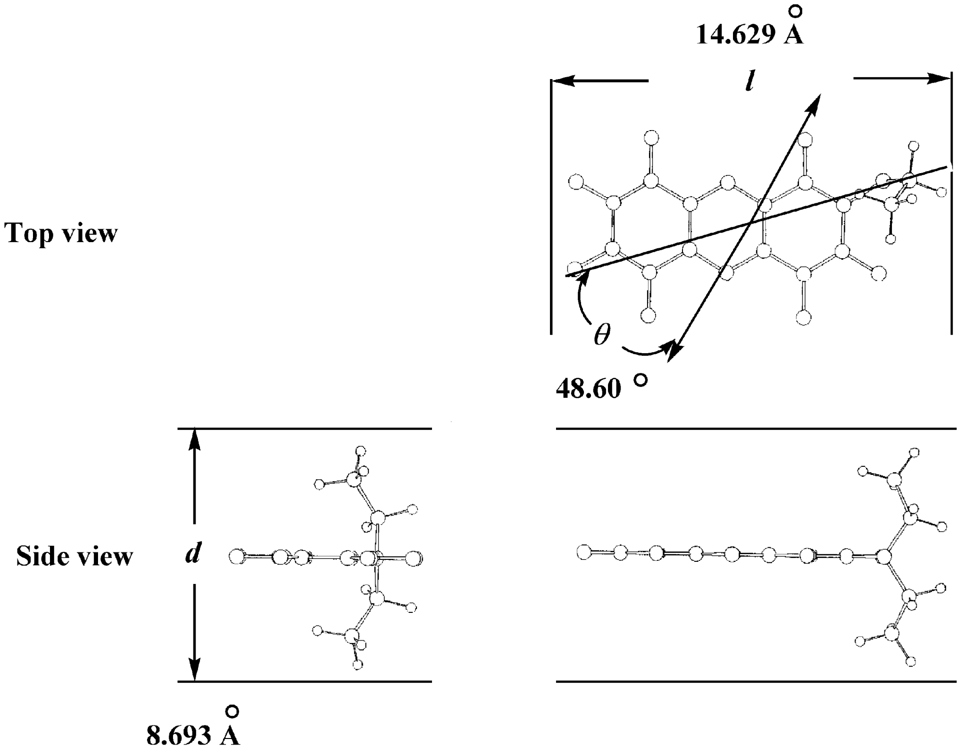


Figure 4. Analysis of compound **4b**.

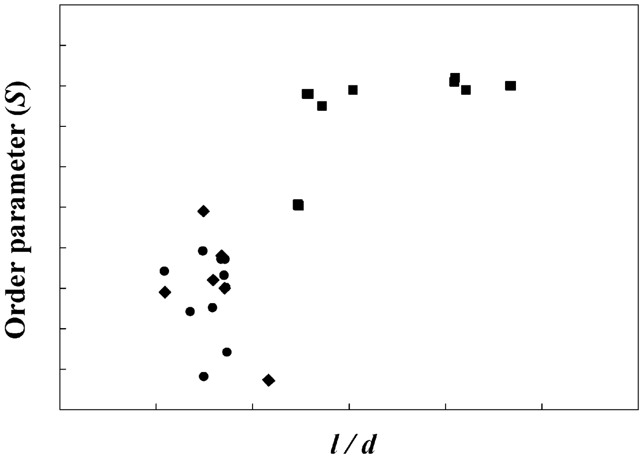


Figure 5. Relationship between S value and l/d ratio.

4. Experimental

4.1. *MO calculation*

θ values and l/d ratios were calculated from the geometry of the most stable conformer by the MNDO-PM3 method [18] in the MOPAC97 program [19]. The heat of formation of any conformations of a molecule was calculated; then, the transition moment of the optimized conformer was calculated by the CNDO/S method [20]. The van der Waals radius was taken into account in calculating the l and d values.

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