

Syntheses and Thermal Properties of 5,10-Disubstituted-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines and Polymeric Porphyrazines Derived from 2,3-Dichloro-5,6-dicyanopyrazine

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Abstract: Intermolecular cyclization of 2-alkylamino-3-chloro-5,6-dicyanopyrazine **2** in the presence of tributylamine in N,N-dimethylformamide (DMF) gave 5,10-disubstituted-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines **3**, which showed strong mesomorphic property and were anticipated as new chromophoric system for functional dye materials. Absorption spectra, fluorescent properties and other physical properties were correlated with their chemical structures. Vanadyl oligomeric porphyrazine with long alkyl groups synthesized from **3** had satisfactory solubility in tetrahydrofuran (THF), diethyl ether and dimethylsulfoxide (DMSO). The syntheses and characterization of vanadyl polymeric porphyrazines derived from **3** with long alkyl groups are reported.

Keywords: Dicyanopyrazine, Porphyrazine, Intramolecular charge-transfer chromophore, Polymeric phthalocyanine, Aggregation

Introduction

Pyrazine has two nitrogen atoms at 1,4-positions to replace carbon atoms in benzene ring, and is anticipated to have many functionalities and reactivities in comparison with their benzene analogues. 2,3-Dichloro-5,6-dicyanopyrazine has been applied to synthesize a wide variety of heterocycles useful as bioactive substances and as coloring matters[1-3]. 2,3-Dicyanopyrazine moiety acts as a very powerful electron acceptor and is especially suitable building block of strong intramolecular charge-transfer chromophoric system for dye materials. These dyes have an ability to give strong intermolecular $\pi - \pi$ interactions for molecular stacking. They also have additional functionalities such as higher polarizability, higher melting point and higher solubility in polar solvents compared with those of their benzene analogues.

Tetrapyrazinoporphyrazines with long alkyl groups have push-pull intramolecular charge-transfer chromophoric systems and have good solubility in most of organic solvents. Their absorption spectra changes by molecular aggregation depending on the polarity of solvent and temperature have been reported previously[4,5]. These dyes showed red fluorescence with a small Stokes shift indicating less structure changes in the excited state and high efficiency of energy transformation of the absorbed light energy to the fluorescence. Polymeric phthalocyanines synthesized from bifunctional reactants preferentially formed two dimensional network polymers[6]. However, these materials never reached any industrial application, and limited data are available on their optical properties because of their insolubility in common solvents due to the relatively high

molecular weight. Introduction of long alkyl groups into the porphyrazine nucleus enhances their solubility in organic solvents. Vanadyl oligomeric porphyrazines with long alkyl groups synthesized from 5,10-disubstituted-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines **3** have satisfactory solubility in tetrahydrofuran (THF), diethyl ether and dimethylsulfoxide (DMSO).

In this paper, 2-alkylamino-3-chloro-5,6-dicyanopyrazines **2** were synthesized by the nucleophilic substitution of 2,3-dichloro-5,6-dicyanopyrazine **1** with amines, and intermolecular cyclization of **2** in the presence of tributylamine in N,N-dimethylformamide (DMF) gave 5,10-disubstituted-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines **3**. We also report the synthesis of some vanadyl polymeric porphyrazines with long alkyl groups, and evaluate their thermal properties with respect to substituent effect.

Experimental

Materials and Characterization

All chemicals were reagent grade and used without further purification unless otherwise specified.

Identifications of compounds and measurements of properties were carried out in general procedures using following equipments; Melting points were determined on a Yanagimoto micro melting point apparatus without correction. The pmr spectra were taken on FT-NMR QE 300 MHz GEC spectrometer. The ms spectra were recorded on M-80 B Hitachi and Shimadzu GCM S-QP 5000 mass spectrometer. The visible and fluorescence spectra were measured on U-3410 Hitachi spectrophotometer and Shimadzu RF-5000 fluorescence spectrophotometer. Microanalysis was conducted with a Yanaco CHN MT-3 recorder.

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Syntheses of 2

To a solution of **1** (10 mmol) in tetrahydrofuran (15 ml) was dropwise added the amine (20 mmol) in tetrahydrofuran (30 ml) at 0~5°C, and then the mixture was stirred at the room temperature until all of **1** disappeared by tlc. The reaction solution was poured into 100 ml of water. The precipitated solid was filtered, washed with water and dried. The crude product was recrystallization from cyclohexane to give **2** as pale yellow solids.

2-chloro-3-(*n*-octylamino)-5,6-dicyanopyrazine 2a

mp: 105-107°C; m/z 293 (M+2)⁺; ¹H nmr (CDCl₃) δ 0.87 (3H, t, *J* 6.6, CH₃), 1.26~1.78 (12H, m, CH₂), 3.40 (2H, t, *J* 6.6, CH₂), 8.68 (1H, br. t, NH).

Anal. Calcd. for C₁₄H₁₈N₅Cl: C, 57.63; H, 6.22; N, 24.00.
Found: C, 57.55; H, 6.14; N, 24.10.

2-chloro-3-(*n*-laurylamino)-5,6-dicyanopyrazine 2b

mp: 99-101°C; m/z 349 (M+2)⁺; ¹H nmr (CDCl₃) δ 0.88 (3H, t, *J* 6.6, CH₃), 1.26~1.78 (20H, m, CH₂), 3.39 (2H, t, *J* 6.6, CH₂), 8.70 (1H, br. t, NH).

Anal. Calcd. for C₁₈H₂₆N₅Cl: C, 62.15; H, 7.53; N, 20.13.
Found: C, 62.37; H, 7.55; N, 19.89.

2-chloro-3-(*n*-hexadecylamino)-5,6-dicyanopyrazine 2c

mp: 103-105°C; m/z 405 (M+2)⁺; ¹H nmr (CDCl₃) δ 0.87 (3H, t, *J* 6.6, CH₃), 1.26~1.78 (28H, m, CH₂), 3.37 (2H, t, *J* 6.6, CH₂), 8.69 (1H, br. t, NH).

Anal. Calcd. for C₂₂H₃₄N₅Cl: C, 65.41; H, 8.48; N, 17.34.
Found: C, 65.40; H, 8.55; N, 17.28.

Syntheses of 3

A solution of **2** (5 mmol) and tributylamine (10 mmol) in N,N-dimethylformamide (10 ml) was refluxed for 7 hr and poured into aqueous 5% hydrochloric acid (50 ml). The precipitate was filtered, washed with water and dried. The crude product was recrystallized from N,N-dimethylformamide to give **3** as yellow solids.

5,10-bis(*n*-octyl)-2,3,7,8-tetracyano-5,10-dihydrodipyrazino [2,3-*b*:2',3'-*e*]pyrazines 3a

m/z 510 (M)⁺; ¹H nmr (CDCl₃) δ 0.89 (6H, t, *J* 6.9, CH₃), 1.26~1.42 (20H, m, CH₂), 1.57 (4H, br. s, CH₂), 3.88 (4H, t, *J* 6.9, CH₂); ν_{\max} (KBr)/cm⁻¹ 3420, 2950, 2922, 2857, 2235, 1583, 1534, 1473, 1349, 1270, 698.

Anal. Calcd. for C₂₈H₃₄N₁₀: C, 65.86; H, 6.71; N, 27.43.
Found: C, 65.54; H, 6.86; N, 27.20.

5,10-bis(*n*-lauryl)-2,3,7,8-tetracyano-5,10-dihydrodipyrazino [2,3-*b*:2',3'-*e*]pyrazines 3b

m/z 62 (M)⁺; ¹H nmr (CDCl₃) δ 0.87 (6H, t, *J* 6.9, CH₃), 1.26~1.42 (36H, m, CH₂), 1.58 (4H, br. s, CH₂), 3.88 (4H, t, *J* 6.9, CH₂); ν_{\max} (KBr)/cm⁻¹ 3422, 2952, 2918, 2852, 2233, 1583, 1533, 1471, 1347, 1262, 694.

Anal. Calcd. for C₃₆H₅₀N₁₀: C, 69.42; H, 8.09; N, 22.49.
Found: C, 69.49; H, 8.34; N, 22.50.

5,10-bis(*n*-hexadecyl)-2,3,7,8-tetracyano-5,10-dihydrodipyrazino [2,3-*b*:2',3'-*e*]pyrazines 3c

m/z 734 (M)⁺; ¹H nmr (CDCl₃) δ 0.87 (6H, t, *J* 6.9, CH₃), 1.26~1.43 (52H, m, CH₂), 1.58 (4H, br. s, CH₂), 3.88 (4H, t, *J* 6.9, CH₂); ν_{\max} (KBr)/cm⁻¹ 3422, 2953, 2924, 2854, 2233, 1583, 1533, 1469, 1348, 1260, 696.

Anal. Calcd. for C₄₄H₆₆N₁₀: C, 71.90; H, 9.05; N, 19.06.
Found: C, 71.57; H, 9.11; N, 19.02.

Syntheses of 4a and 4c

A solution of **3a** (2.5 mmol) and vanadium chloride (VCl₃, 1.2 mmol) in quinoline (10 ml) in the presence of ammonium metavanadate (NH₄VO₃, 0.02 g) was stirred at 145~155°C for 2 hr and then refluxed for 4 hr. The reaction mixture was cooled to room temperature, poured into 5% aqueous hydrochloric acid (50 ml) and then filtered. The collected solid was washed with water (3 × 50 ml), 10% aqueous ammonia (2 × 50 ml), methanol (3 × 50 ml), acetone (3 × 50 ml), and N,N-dimethylformamide (2 × 50 ml) and then dried, to give **4a** as black solids.

Vanadyl polymeric porphyrizine 4a

ν_{\max} (KBr)/cm⁻¹ 2948, 2919, 2850, 1778, 1723, 1558, 1430, 1280, 1239, 1001, 861, 743, 704, 668.

Vanadyl polymeric porphyrizine 4c

ν_{\max} (KBr)/cm⁻¹ 2945, 2919, 2849, 1781, 1723, 1558, 1437, 1290, 1242, 1007, 860, 745, 706, 662.

Synthesis of 4b

A solution of **3b** (2.5 mmol) and vanadium chloride (VCl₃, 1.2 mmol) in quinoline (15 ml) in the presence of ammonium metavanadate (NH₄VO₃, 0.02 g) was stirred at 125~135°C for 2 hr and then slowly warmed to 150~155°C for 1 hr. The reaction mixture was cooled to room temperature, poured into 5% aqueous hydrochloric acid (50 ml) and then filtered. The collected solid was washed with water (3 × 50 ml), 10% aqueous ammonia (2 × 50 ml), methanol (3 × 50 ml), acetone (3 × 50 ml), and N,N-dimethylformamide (2 × 50 ml) and then dried, to give **4b** as black solids.

ν_{\max} (KBr)/cm⁻¹ 2945, 2922, 2851, 1781, 1748, 1567, 1446, 1296, 1244, 1009, 863, 748, 686.

Results and Discussion

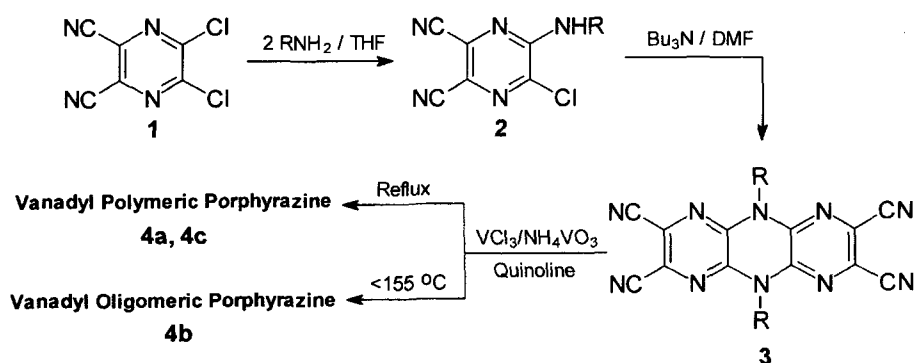
In previous paper[7], nucleophilic substitutions of 2,3-chloro-5,6-dicyanopyrazine **1** with various nucleophiles such as amines, enamines and thiocarbonyl compounds gave the desired 2- and 2,3-disubstituted pyrazines in good yields.

Synthesis of 2,3,7,8-tetracyano-5,10-dimethyl-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine from reaction of **1** with

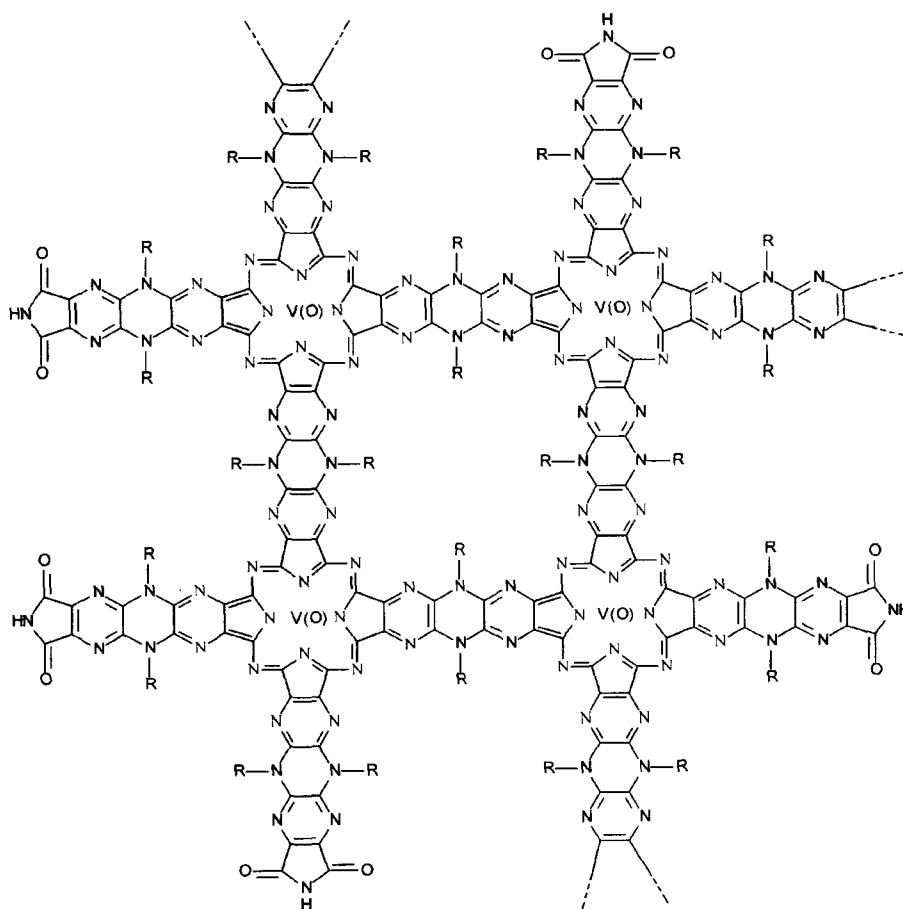
2,3-bis(*N*-methylamino)-5,6-dicyanopyrazine has been previously reported by author[3], but target compound was obtained in less than 5% yield. However, intermolecular cyclization of 2-*n*-octylamino-3-chloro-5,6-dicyanopyrazine **2a** in the presence of base gave 5,10-bis(*n*-octyl)-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines **3a** in moderate yields. The yields were improved when the reaction was carried out in *N,N*-dimethylformamide (DMF) under reflux reaction in the presence of two equiv. of tributyl-

Table 1. Syntheses of dipyrazino[2,3-*b*:2',3'-*e*]pyrazines and polymeric porphyrazines

Compound	R	mp (°C)	Yield (%)
3a	-(CH ₂) ₇ CH ₃	221-223	46
3b	-(CH ₂) ₁₁ CH ₃	177-180	50
3c	-(CH ₂) ₁₅ CH ₃	175-178	49
4a	-(CH ₂) ₇ CH ₃	> 300	93
4b	-(CH ₂) ₁₁ CH ₃	> 300	90
4c	-(CH ₂) ₁₅ CH ₃	> 300	88



Scheme 1.



Scheme 2.

lamine.

Treatment of **3a** and **3c** with 0.5 equivalent of vanadium chloride (VCl_3) in the presence of ammonium metavanadate (NH_4VO_3) in quinoline under reflux conditions afforded vanadyl polymeric porphyrazines **4a** and **4c** in good yields. Vanadyl polymeric porphyrazines **4a** and **4c** had very low solubility in almost all organic solvents caused by the high molecular weight. Moreover, vanadyl oligomeric porphyrazine **4b** was also obtained under mild reaction condition (reaction temperature $< 155^\circ C$) using **3b** in quinoline. Vanadyl oligomeric porphyrazine **4b** had satisfactory solubility in tetrahydrofuran, diethyl ether and dimethylsulfoxide (DMSO). The results are summarized in Scheme 1 and Table 1.

The formation of the dipyrzino[2,3-*b*:2',3'-*e*]pyrazine **3** was confirmed by 1H NMR, IR and microanalyses. The IR spectrum of **3** showed sharp peak at around 2233 cm^{-1} due to four of the CN stretching absorption. On the other hand, the planar polymeric porphyrazine **4** can be regarded as planar sheets of monomeric units connected to each other by pyrazine rings with imide end groups (Scheme 2). The band at 2920 and 2851 cm^{-1} were assigned to the C-H stretching of the long alkyl group. The strongest band at 1296 cm^{-1} was characteristic of the isoindole ring, with a large contribution of C-N stretching in the 16-membered inner ring. The IR spectra of **4** agreed reasonably well with those reported for the planar polymeric phthalocyanine[8] and clearly showed the presence of imide end groups as indicated by the imide C=O stretching at $1770\text{--}1780\text{ cm}^{-1}$. Five typical bands were detected in the following ranges; $1446\text{--}1437$, $1245\text{--}1240$, $1115\text{--}1112$, $864\text{--}860$, $750\text{--}705\text{ cm}^{-1}$.

The thermal properties of **3** and **4** were investigated by means of DSC (differential scanning calorimetry), TG (thermal gravimetric) and DT (differential thermal) analysis. Dihydrodipyrzino[2,3-*b*:2',3'-*e*]pyrazines **3** showed two endothermic peak, one near $105^\circ C$ and the other at temperatures of $171\text{--}178^\circ C$ (Figure 1). The endothermic peak at $105^\circ C$ is presumably derived from the solid-solid phase transition. The endothermic peak at $171\text{--}178^\circ C$ is considered as the melting point, which is consistent with melting point determined by a capillary tube method.

On the other hand, vanadyl polymeric porphyrazines **4** did

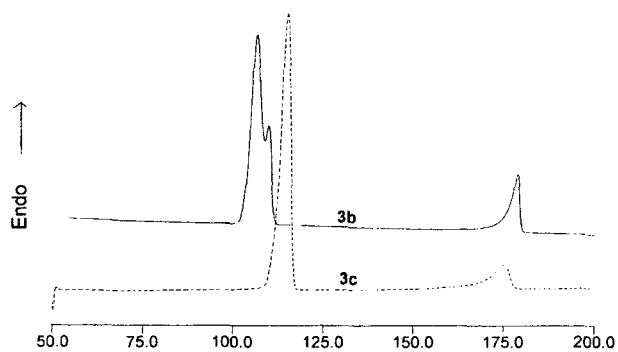


Figure 1. DSC thermograms of **3b** and **3c**.

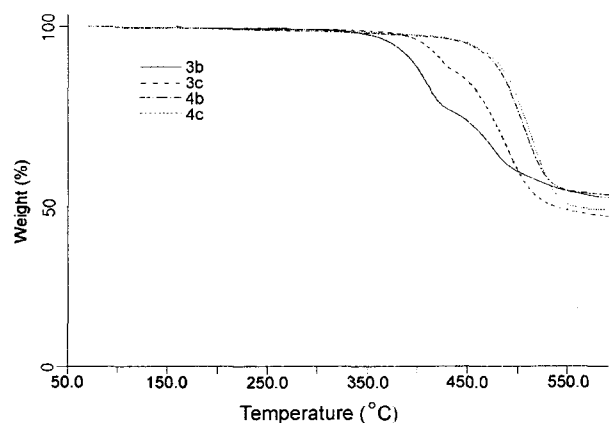


Figure 2. TGA curves of **3b**, **3c**, **4b**, and **4c**.

not exhibit any endothermic peak and appeared to decompose at temperature above $300^\circ C$. From the DSC thermograms, we also noted that polymer **4** did not exhibit any liquid crystalline phases. This is probably due to the rigid structure of the network polymer.

Results of TGA plotted in Figure 2 reveal that thermal stability of **4** is higher than that of **3**. And the thermal stability of **4a**, **4c**, and **4b** are almost identical, suggesting that length of the flexible moiety hardly affects the thermal stability of dipyrzino[2,3-*b*:2',3'-*e*]pyrazine unit. Dye **3** reveals two step decomposition behavior, while polymeric porphyrazines **4** have only one step decomposition. The two step decomposition may be attributed to the different decomposition rate of the two linear long alkyl groups in the dipyrzino[2,3-*b*:2',3'-*e*]pyrazine ring.

The high molecular weight of polymeric phthalocyanine has prevented early investigators from studying their absorption spectra in common solvents or in the vapour phase since polymeric phthalocyanine do not sublime.

We have reported the absorption spectra of 2,9,16,23-tetra(4-*n*-hexadecylphenyl)tetrpyrazinoporphyrazinato vanadium oxide **5** which exhibited splitted Q bands in the Q band region ($630\text{--}740\text{ nm}$). The Soret band observed at around $360\text{--}450\text{ nm}$ consisted of a prominent peak near 365 nm and a well-defined shoulder around 435 nm [5]. Vanadyl polymeric porphyrazines **4** have a push-pull intramolecular charge-transfer chromophoric system in which the alkyl amino groups work as donor moieties and the pyrazine rings as acceptor moieties. The absorption spectra of **4b** in THF showed the similar pattern as that of the aggregate species of 2,9,16,23-tetra(4-*n*-hexadecylphenyl)tetrpyrazinoporphyrazinato vanadium oxide[5]. The absorption spectra of **4b** exhibited a well-resolved splitting of Q_x/Q_y and B_x/B_y bands in the $570\text{--}675\text{ nm}$ ($\pi\text{--}\pi^*$ transition) and $420\text{--}445\text{ nm}$ ($n\text{--}\pi^*$ transition) region, respectively (Figure 3). The presence of the two bands in both the Q and B regions, both x/y polarized, suggests that there are two main π^* states, both degenerate. However, vanadyl oligomeric porphyrazine

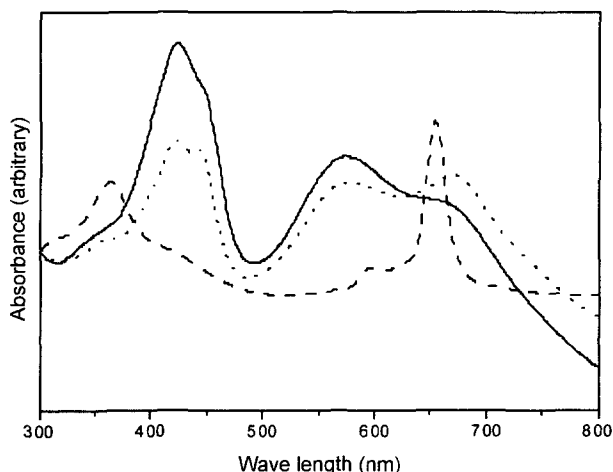


Figure 3. Absorption spectra of **4b** and **5**; **4b** in DMSO (solid line), **4b** in THF (dotted line), **5** in THF (dashed line).

4b in DMSO exhibited some band broadening in the Q band region, and much less splitting in the B band region than that in THF. It is caused by an excitation coupling between pairs of degenerate $n-\pi^*$ and $\pi-\pi^*$ excited states of the porphyrazine rings. The extent of band broadening is also related to the degree of coupling between the porphyrazine units. Mizuguchi *et al.*, recently reported that the molecular distortion of titanylphthalocyanine in solid state produced the doubly degenerate excited level, to give the splitted absorption bands[8]. Reduction in molecular symmetry on going from the monomeric state to the dimeric state resolves the doubly degenerate level of the LUMO and gives the two $\pi-\pi^*$ transitions whose transition moments are on the

molecular plane and octagonal.

On the other hand, the absorption and fluorescence maxima of **3** in chloroform were observed at 397 nm and 517 nm, respectively. Dye **3** had fluorescence in solution and on solid state, but polymer **4** did not show any fluorescence. The weight-average molecular weight (M_w) of **4b** was measured with gel permeation chromatography (GPC) using calibration curves for polystyrene. The measuring temperature was 30°C. THF was eluted at 0.3 ml/min flow rate. GPC chromatogram of **4b** showed a broad peak at the retention time of 45-53 min. The M_w was 18,905 corresponding to the oligomer with ten porphyrazine units.

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