

Preparation and Immobilization of 6-Amino-2,3-di(2-pyridyl)quinoxaline. New Fluorescent Chemosensory Materials for Heavy Metal Ions

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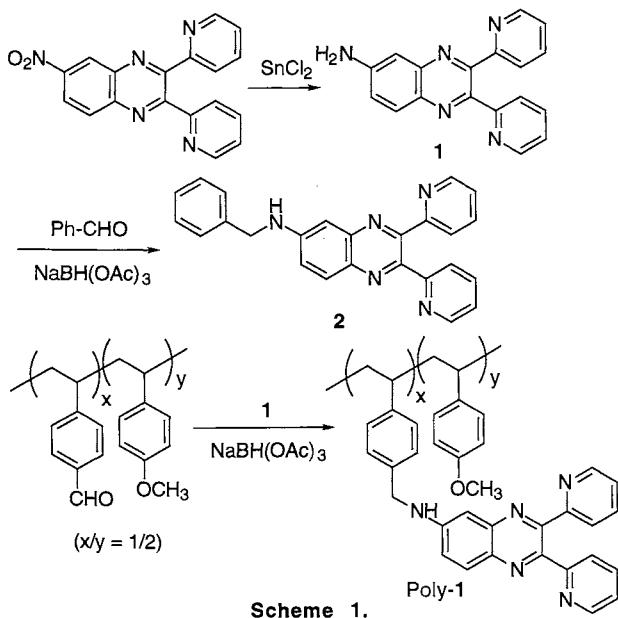
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6-Amino-2,3-di(2-pyridyl)quinoxaline and its derivatives were synthesized and immobilized to polymer support, and the interaction with metal ions was examined. The spectroscopic data predict promising chemosensory materials.

Selective and sensitive fluorescent sensory materials have attracted a great deal of interest for both fundamental and applied significance, and a large number of attempts on the molecular design and construction of fluorescent chemosensors have been reported.¹ On the other hand, aminoquinoxaline derivatives exhibit strong fluorescent properties in visible region, and have been utilized as fluorescent whiteners, disperse dyes, and fluorescence derivatization reagents for carboxylic acids.² Meanwhile, 2,3-di(2-pyridyl)quinoxaline (dpq) is an important bridging ligand, and various mono and bimetallic complexes with dpq have been prepared and characterized.³ However, to our knowledge, there is no report on preparation of 6-amino-dpq and its derivatives. We here report synthesis of new fluorescent dpq derivatives, 6-amino-2,3-di(2-pyridyl)quinoxaline (**1**), 6-benzylamino-2,3-di(2-pyridyl)quinoxaline (**2**), and polymer-supported **1** (Poly-**1**), and preliminary results of the changes in their fluorescence behaviors on the addition of several metal ions.

The synthetic procedures of **1**, **2**, and Poly-**1** are depicted in Scheme 1. **1** was prepared via reduction of 6-nitro-dpq³ⁱ with SnCl₂.⁴ Then, reductive amination of benzaldehyde with **1** using sodium triacetoxyborohydride (NaBH(OAc)₃) gave **2**.⁵ Poly-**1** was also prepared by the reductive amination of poly(*p*-formylstyrene-*co*-*p*-methoxystyrene) (P(FSt-*co*-MeOST))⁶ with **1**.⁷ ¹H NMR and elemental analysis data indicate the introduction



of **1** into the side chain of P(FSt-*co*-MeOST) smoothly proceeds to afford Poly-**1** with 0.85 of degree of substitution.⁸

1 is soluble in water, and **1** and **2** are soluble in common organic solvents such as acetone, tetrahydrofuran, N,N-dimethylformamide, and chloroform. **1** and **2** exhibit strong fluorescence in chloroform with a peak at 490 nm, when irradiated with a light of 395 and 405 nm, respectively. The fluorescence quantum yields of **1** and **2** are both about 0.3.⁹

UV-vis absorption spectrum of a mixture of chloroform-ethanol (9/1, v/v) solution of **2** exhibits two absorption peaks at 295 and 410 nm. Figure 1 shows changes in the absorption

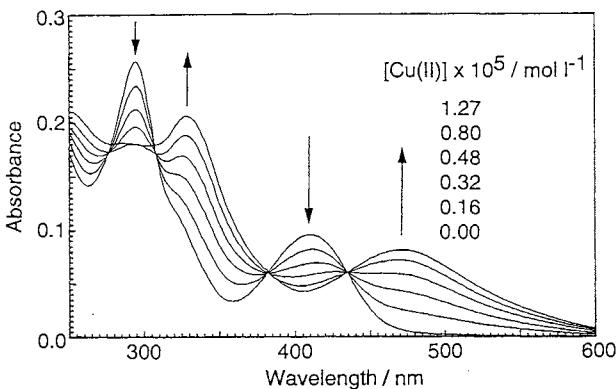


Figure 1. Changes in the absorption spectrum of a CHCl₃/ethanol (9/1, v/v) solution of **2** (5×10^{-6} M) with increasing concentration of CuCl₂.

spectrum of the solution of **2** titrated with an ethanol solution of CuCl₂.¹⁰ The addition of CuCl₂ led to a decrease of the bands at 295 and 410 nm and an appearance of new bands at 328 and 473 nm with two isosbestic points at 382 and 435 nm. The maximum absorbance ($\epsilon = 7860 \text{ M}^{-1} \text{ cm}^{-1}$) at 473 nm was observed at an approximately equivalent of CuCl₂ for **2**. Similar changes in the absorption spectrum of **1** upon an addition of CuCl₂ were observed. These results suggest that the bathochromic effect is accompanied by the formation of mononuclear complexes of **1** or **2** with Cu(II).

The fluorescence emission from **1** and **2** was also monitored as several metal ions were titrated into the chloroform-ethanol solutions of **1** and **2**. When LiCl, MgCl₂, and CaCl₂ were added in the solutions, the changes in the fluorescence spectra were scarcely observed. In contrast, an addition of CuCl₂, NiCl₂, CoCl₂, and ZnCl₂ to the solutions led to efficient fluorescence quenching (Figure 2).¹⁰ The fluorescence quenching was linked to the formation of complexes, and it would be caused by a metal-ligand charge transfer between metal and **1** or **2**.

We also studied the metal ion-response for a thin film of Poly-**1** formed by spin-casting from a chloroform solution on a quartz plate. Figure 3 shows changes in the fluorescence spectrum of the film of Poly-**1** caused by immersion in an ethanol solution of

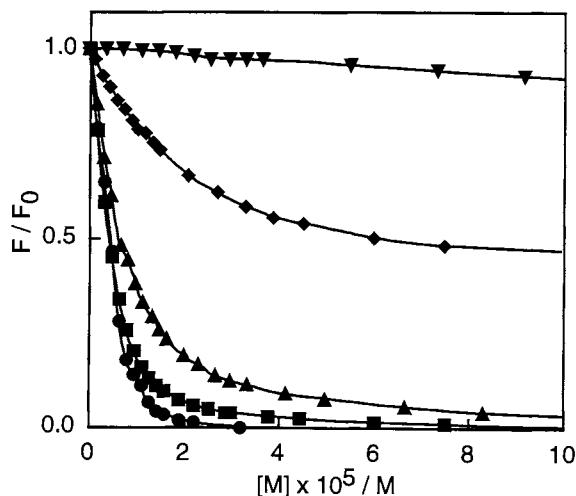


Figure 2. Plots of fluorescence intensities of **2** (5×10^{-6} M in CHCl_3 /ethanol (9/1, v/v)) at 510 nm ($\lambda_{\text{ex}} = 410$ nm) versus the concentration of metal ions; (●) Cu(II), (■) Ni(II), (▲) Co(II), (◆) Zn(II), and (▼) Mn(II).

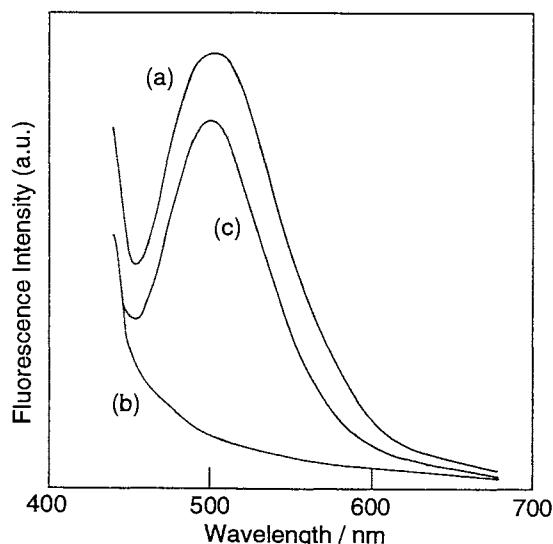


Figure 3. Fluorescence spectra of a film of Poly-1 on a quartz plate ($\lambda_{\text{ex}} = 415$ nm): a) before immersion. b) after immersion in an ethanol solution of CuCl_2 (3×10^{-5} M). c) after immersion in an ethanol/aqueous ammonia.

CuCl_2 . The fluorescence was rapidly quenched within a few seconds. The fluorescence intensity fairly recovered without any observable damage when the film was immersed in a mixture of ethanol-aqueous ammonia.

As described above, **1**, **2**, and Poly-1 are able to coordinate with several heavy metal ions with significant changes in the absorption as well as fluorescence spectra, while the response to alkali and alkaline earth metal ions is negligible. The fluorescence properties of the film of Poly-1 predict a reusable sensory material. Although the fluorescence behaviors in aqueous conditions and selectivity for various metal ions are not clear in the present study, 6-amino-dpq derivatives are expected to provide new fluorescence sensory materials for heavy metal ions. Further studies are in progress, including immobilization of **1** to

other polymer supports and their fluorescence behaviors with several metal ions under various conditions.

References and Notes

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- 4 A mixture of 6-nitro-dpq (4 mmol) and SnCl_2 (15 mmol) in ethanol (60 cm^3) was refluxed for 5 h. The solution was evaporated and washed with a conc. NaOH aqueous solution. Purification of **1** was carried out by column chromatography (65% yield). Anal. Found: C, 71.88; H, 4.63; N, 22.41%. Calcd for $\text{C}_{18}\text{H}_{13}\text{N}_5$: C, 72.22; H, 4.38; N, 23.40%. IR (KBr, cm^{-1}): 3345, 3227, 3050, 1619, 1590, 1567, 1500, 1476, 1444, 1360, 1260, 1224, 1143, 1083, 1004, 832, 789, 746; ^1H NMR (CDCl_3 , ppm): 88.37 (2H, dd), 7.86 (1H, d), 7.80 (2H, dd), 7.71 (2H, m), 7.13 (2H, m), 7.07 (1H, d), 7.03 (1H, dd), 4.51 (2H, s); ^{13}C NMR (CDCl_3 , ppm): 8157.6, 157.5, 151.9, 148.9, 148.3, 147.8, 142.9, 136.3, 136.2, 135.8, 129.9, 124.1, 123.9, 122.6, 122.3, 107.3.
- 5 $\text{NaBH}(\text{OAc})_3$ (1 mmol) was added to a mixture of **1** (1 mmol) and benzaldehyde (0.5 mmol) in 1,2-dichloroethane (5 cm^3), and the reaction mixture was stirred at 25 °C for 5 h. The reaction mixture was quenched by adding a NaOH aqueous solution (1 M) and extracted with CHCl_3 . Purification of **2** was carried out by column chromatography (85% yield). Anal. Found: C, 76.57; H, 5.07; N, 17.36%. Calcd for $\text{C}_{25}\text{H}_{19}\text{N}_5$: C, 77.10; H, 4.92; N, 17.98%. IR (KBr, cm^{-1}): 3307, 3061, 1618, 1588, 1567, 1514, 1468, 1449, 1362, 1273, 1229, 1139, 1084, 1001, 825, 793, 748, 705; ^1H NMR (CDCl_3 , ppm): 88.39 (2H, dd), 7.94 (1H, d), 7.78 (2H, m), 7.72 (2H, m), 7.42-7.07 (9H, m), 4.84 (1H, s), 4.45 (2H, d); ^{13}C NMR (CDCl_3 , ppm): 8157.9, 157.7, 152.2, 149.5, 148.7, 148.6, 147.8, 143.7, 137.9, 136.4, 136.3, 136.2, 130.0, 128.7, 127.5, 124.3, 124.1, 122.7, 122.4, 103.8, 47.9.
- 6 P(FSt-co-MeOSt) ($x/y = 1/2$, $M_n = 24000$ calibrated by GPC) was prepared by radical copolymerization of 4-formylstyrene and 4-methoxystyrene in the presence of AIBN in benzene at 60 °C under N_2 . Since poly(*p*-formylstyrene) exhibited poor solubility in 1,2-dichloroethane, P(FSt-co-MeOSt) was used as the polymer support.
- 7 Introduction of **1** to the polymer support was also carried out by reductive amination of P(FSt-co-MeOSt) (0.5 mmol of formyl unit) with **1** (1 nmol). Purification of Poly-1 was carried out by reprecipitation from CHCl_3 /ether (89% yield). Anal. Found: C, 78.46; H, 6.17; N, 9.24%. Calcd for $[(\text{C}_{27}\text{H}_{21}\text{N}_5)\text{O}_5 + (\text{C}_9\text{H}_8\text{O})_0.15 + (\text{C}_9\text{H}_{10}\text{O})_2]_n$: C, 79.22; H, 6.14; N, 9.28%. $M_n = 32000$ (calibrated by GPC). IR (KBr, cm^{-1}): 3360, 3060, 2915, 2833, 1620, 1587, 1566, 1511, 1472, 1440, 1361, 1246, 1177, 1146, 1081, 1036, 1001, 822, 748, 688; ^1H NMR (CDCl_3 , ppm): 88.40, 7.88-7.48, 7.18-6.63, 6.63-6.08, 4.88, 4.27, 3.70, 1.82, 1.36; ^{13}C NMR (CDCl_3 , ppm): 8157.9, 157.7, 157.4, 152.2, 149.8, 148.6, 147.6, 144.7, 143.8, 137.2, 136.6, 136.4, 136.2, 135.2, 130.0, 128.5, 124.3, 124.1, 122.7, 122.4, 113.3, 103.4, 55.1, 47.7, 39.5.
- 8 The degree of substitution was calculated from C/N ratios on the basis of the charged amount of formyl unit.
- 9 The fluorescence quantum yield of **1** and **2** in solutions was estimated by a literature method using quinine bisulfate as a standard; J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971); W. H. Melhuish, *J. Phys. Chem.*, **64**, 762 (1960).
- 10 M. Kimura, T. Horai, K. Hanabusa, and H. Shirai, *Adv. Mater.*, **10**, 459 (1998). The concentration of metal ions in solutions was measured by ICP-AES.