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The synthesis and optical characterization of quinoxalines bearing 2,2′:6′,2″-terpyridine

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Abstract

4′-(4-{2-[6,7-Bis-dodecyloxy-3-(2-*p*-substituted phenyl-vinyl)-quinoxalin-2-yl]-vinyl}-phenyl)-[2,2′:6′,2″] terpyridine was prepared by the Horner–Wadsworth–Emmons (HWE) reaction of 4-[2,2′:6′,2″]terpyridin-4′-yl-benzaldehyde and quinoxaline derivatives. The absorption and fluorescence maximum of these compounds were observed at 398–443 nm and 484–586 nm, respectively. The compounds were characterized by ^{1}H NMR spectroscopy and MALDI-TOF-MS, and their recognition properties for metal ions were evaluated using both absorption and emission spectroscopy.

Keywords: 2,2′:6′,2″-Terpyridine; Quinoxaline; Chemosensor; Heterocycles; Chelating; Multi-function

1. Introduction

Fluorescent heterocyclic compounds are of interest as functional materials in the following fields: emitters for electroluminescence devices [1], molecular probes for biochemical research [2] and in traditional textile and polymer fields [3]. Quinoxalines are well known fluorescent compounds with high quantum yields and have attracted much attention due to their potential functions for specialty and high technology applications [4,5]. These compounds have been utilized as fluorescence probes in some elaborated chemosensors.

Quinoxalines are, in general, comparatively easy to prepare, and numerous derivatives have been designed and prepared for potential use as biologically active materials [6]. The classical synthesis of quinoxalines involves the condensation of an aromatic 1,2-diamine with a 1,2-dicarbonyl compound. The reaction is facile and it is the most widely used method for synthesizing both quinoxaline itself and its derivatives [7].

On the other hand, most chemical sensors based on π-conjugated systems have been designed to have electron-donating properties for the recognition of analytes such as protons and metal ions [8–10]. Terpyridines, which form metal complex with a variety of transition metal ions, have wide application in fields such as macromolecular chemistry, biochemistry and photophysics [11,12].

In this study, we designed and synthesized several quinoxaline derivatives containing substituents with different electron-donating abilities, in order to investigate the effects of their recognition properties to metal ions.

2. Experimental

2.1. General

Flash chromatography was performed with Merck-EM Type 60 (230–400 mesh) silica gel (flash). Melting points were obtained from a capillary melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker DRX-300 FT-NMR spectrometer. The UV–visible and fluorescence spectra were measured on UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometer. MALDI-TOF-MS spectra were obtained on a Waters Limited MALDI-TOF spectrometer with dithranol as matrix. Reagents and solvents used

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for the synthesis were all synthetic grades and used without any purification. Chemicals used for spectroscopic analysis were all analytical reagent grades.

*2.2. Typical procedure to synthesize [4-(2-{6,7-bis-(dodecyloxy)-3-[2-(4-[2,2′:6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-quinoxalin-2-yl}-vinyl)-phenyl]-dimethyl-amine (**6a**)*

[4-(2-{6,7-Bis-(dodecyloxy)-3-[2-(4-[2,2′:6′,2″]terpyridin-4′-yl-phenyl)-vinyl] quinoxalin-2-yl}-vinyl)-phenyl]-dimethyl-amine (**6a**) was synthesized by the condensation reaction of [3-[2-(4-dimethylamino-phenyl)-vinyl]-6,7-bis-(dodecyloxy)-quinoxalin-2-ylmethyl]-phosphonic acid diethyl ester (**4a**) and 4-[2,2′:6′,2″]terpyridin-4′-yl-benzaldehyde (**5**). A reaction mixture of **4a** (0.7 mmol) and sodium ethoxide (0.87 mmol) in ethanol (20 mL) was stirred until it dissolved. After dissolving, added **5** (0.98 mmol), refluxed for ca. 1.5 h and monitored by thin layer chromatography (silica gel, ethyl acetate:*n*-hexane = 1:4). The solution was filtered and a yellow solid was obtained. And the solid was recrystallized from acetone to give [4-(2-{6,7-bis-dodecyloxy-3-[2-(4-[2,2′:6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-quinoxalin-2-yl}-vinyl)-phenyl]-dimethyl-amine (**6a**) as a bright yellow solid. M.p.: 117–119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) of **6a**: 8.80 ppm (s, 2H, Py), 8.76–8.74 ppm (d, 2H, Py), 8.71–8.68 ppm (d, 2H, Py), 7.97–7.92 ppm (d, 2H, $J = 15.6$ Hz, ethylene), 7.89–7.78 ppm (m, 4H, Py, ArH), 7.62–7.59 ppm (d, 2H, ArH), 7.50–7.45 ppm (d, 2H, $J = 15.6$ Hz, ethylene), 7.37–7.30 ppm (m, 6H, ArH, Py, quinoxaline), 6.78–6.75 ppm (d, 2H, ArH), 4.22–4.17 ppm (t, 4H, OCH_2), 3.04 ppm (s, 6H, NCH_3), 1.97–1.92 ppm (m, 4H, CH_2) 1.54 ppm (m, 4H, CH_2), 1.28 ppm (m, 32H, CH_2), 0.89–0.86 ppm (t, 6H, CH_3). Calcd.: for $C_{65}H_{80}N_6O_2$: C, 79.88; H, 8.25; N, 8.60; found: C, 79.95; H, 8.30; N, 8.54.; MALDI-TOF-mass-spectrum: *m*/*z*: 978.00 (100%, M^+, calcd. 977.37).

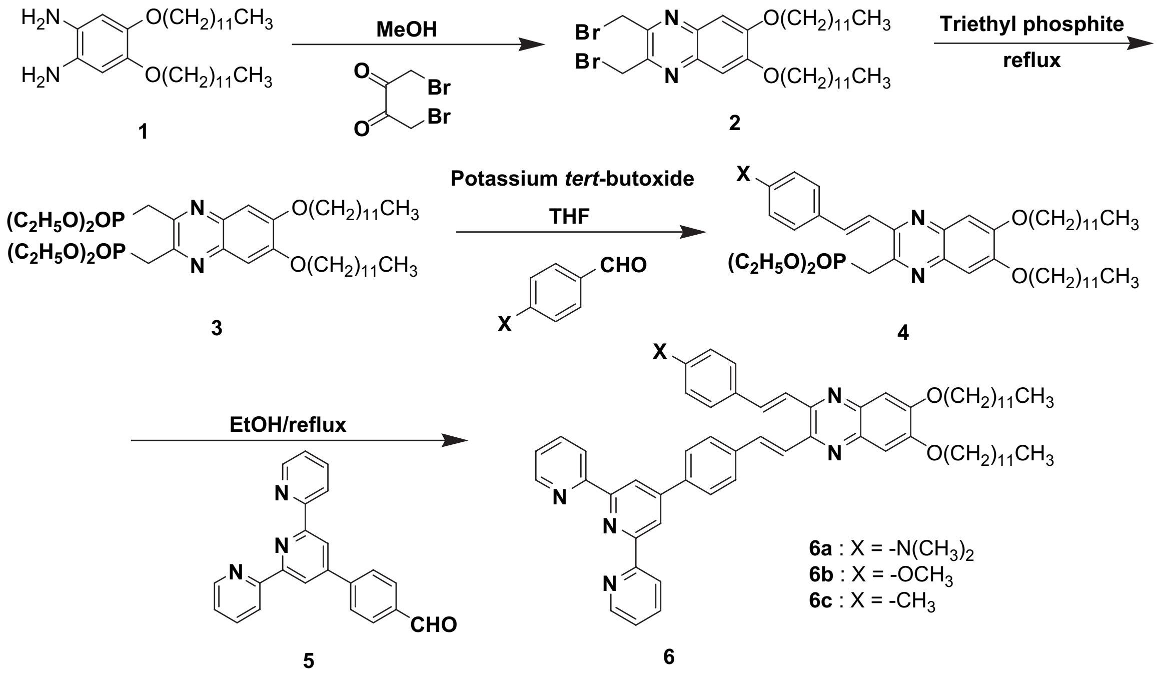
3. Result and discussion

Quinoxaline derivatives (**2** and **3**) and 4-[2,2′:6′,2″] terpyridin-4′-yl-benzonitrile were synthesized by the method described in the literature [13–15]. The linear long alkyl ether moiety was chosen to improve the solubility of the resulting fluorescent quinoxaline compounds in common organic solvents.

Potassium *tert*-butoxide (0.05 mol) was added to a solution of [3-(diethoxyphosphorylmethyl)-6,7-bisdodecyloxy-quinoxalin-2-yl methyl] phosphonic acid diethyl ester (**3**, 0.05 mol) and 4-substituted benzaldehyde (0.05 mol) in tetrahydrofuran (THF, 60 ml) at 0–5 °C, and the mixture was stirred for 1 h. The concentration of the mixture under reduced pressure afforded a crude product, which was purified by flash chromatography (silica gel, ethyl acetate:*n*-hexane = 1:1) to give **4** (60–65%).

The Horner–Wadsworth–Emmons (HWE) reaction of compounds **4** and **5** in ethanol under reflux conditions gave 4′-(4-{2-[6,7-bis-dodecyloxy-3-(2-*p*-substituted phenyl-vinyl)-quinoxalin-2-yl]-vinyl}-phenyl)-[2,2′:6′,2″] terpyridine (**6**) (64–69%). The reaction pathways are summarized in Scheme 1.

The formation of **6** was verified with ^{1}H NMR spectroscopy. For example, the ^{1}H NMR spectra of **6a** indicated that ethylene protons appeared as a doublet at 7.45 and 7.92 ppm and revealed a *trans*-configuration with coupling constants, 15.6 Hz. In addition, quinoxaline protons and protons of terminal N–CH_3 are singlets at 7.35 and 3.04 ppm, respectively.



Scheme 1. Reaction routes of quinoxaline compounds with terpyridine.

Table 1
Visible and fluorescence spectra of compound **6**

Compound	λ_{max}[a]	F_{max}[b]	SS[c]
6a	443	586	143
6b	422	484	62
6c	398	490	92

[a] In $CHCl_3/CH_3OH$ (9:1).
[b] Fluorescence maximum excited at λ_{max} value.
[c] Stoke's shift ($F_{max} - \lambda_{max}$).

The substituent effects of the donor group on the visible and fluorescent spectra are summarized in Table 1. The electronic character of the substituents in **6** strongly affects their absorption spectra, producing a bathochromic shift to an extent which depends on their electron-donating ability. Compound **6c** absorbs at 398 nm and emits at 490 nm in $CHCl_3$. As the electron-donating ability of the donor group increases from the methyl to the dimethylamine derivatives (**6a**), the λ_{max} and F_{max} values show bathochromic shifts attaining the maximum values of 443 nm ($\Delta\lambda = 45$ nm) and 586 nm ($\Delta F = 96$ nm) for **6a**, respectively.

Binding affinities of 4′-[4-(2-{6,7-bis-dodecyloxy-3-[2-(4-substituted-phenyl)-vinyl]-quinoxalin-2-yl}-vinyl)-phenyl]-[2,2′:6′,2″]terpyridine (**6**) toward transition metal ions, Co^{2+}, Ni^{2+}, Cu^{2+} and Fe^{3+}, were evaluated by the absorption and the emission spectroscopy measurements. Upon addition of these metal ions, the absorption and the emission spectra of quinoxaline derivative **6b** changes in a similar manner as shown in Figs. 1 and 2. In contrast to the fluorescence of **6b** in $CHCl_3$/MeOH (9/1) solution, the gradual addition of metal ion (Ni^{2+}) to a $CHCl_3$/MeOH (9/1) solution of **6b** leads to a continuous decrease in the intensity of the fluorescence maximum (484 nm), probably because there is an electron or energy transfer between metal cation and fluorophore, which is known as the fluorescence quenching mechanism. However, the intensity of the absorption spectra was increased at 422 nm (λ_{max}).

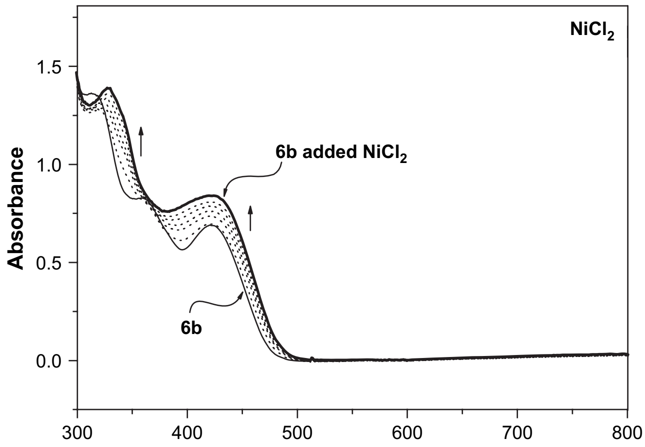


Fig. 1. The effect of metal ion (Ni^{2+}) on the absorption spectra of **6b** in $CHCl_3$/MeOH = 9/1.

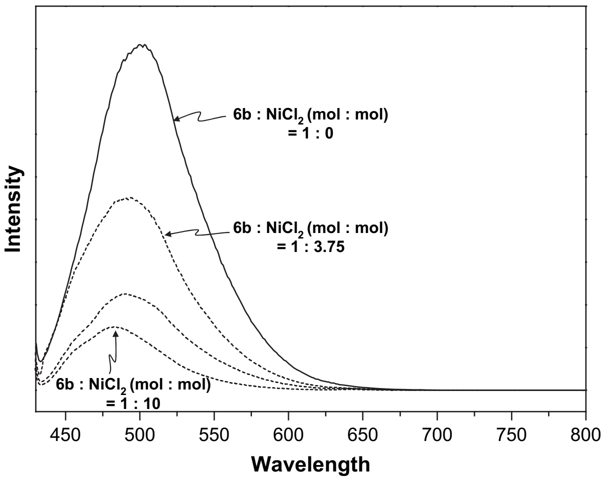


Fig. 2. The effect of metal ion (Ni^{2+}) on the emission spectra of **6b** in $CHCl_3$/MeOH = 9/1.

4. Conclusion

Quinoxalines have attracted much attention due to their potential functions as organic chemosensors. 4′-(4-{2-[6,7-Bis-dodecyloxy-3-(2-*p*-substituted phenyl-vinyl)-quinoxalin-2-yl]-vinyl}-phenyl)-[2,2′:6′,2″] terpyridine (**6**) was prepared by the Horner−Wadsworth−Emmons (HWE) reaction of 4-[2,2′:6′,2″]terpyridin-4′-yl-benzaldehyde (**5**) and quinoxaline derivatives (**4**). These compounds have been utilized as fluorescence probes in some elaborated chemosensors. The typical absorption and emission change of quinoxalines (**6**) with increasing concentration of metal ions was observed.

Acknowledgements

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