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

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ABSTRACT

4′-(4-{2-[6,7-Bis-dodecyloxy-3-(2-substituted-phenyl-vinyl)-quinoxalin-2-yl]-vinyl}-phenyl)-[2,2′:6′,2″]terpyridine was prepared by the Horner–Wadsworth–Emmons reaction of 4-[2,2′:6′,2″]terpyridin-4′-yl-benzaldehyde with various quinoxaline derivatives. The absorption and fluorescence maxima of the compounds were observed at 398–443 nm and 484–586 nm, respectively; the compounds offer potential as optical sensors for protons and metal ions.

1. Introduction

Quinoxalines [1,2] are a well known class of fluorescent compounds with high quantum yields and have attracted much attention due to their potential for specialty and high-technology applications. Futhermore, fluorophores containing a heterocyclic system are potentially useful as biologically active compounds and for diagnostic methods.

Quinoxaline itself is a weak base, while quinoxalines onto which electron-donating substituents have been introduced are protonated easily at the 1,4-positions. These protonated quinoxalines have electron-accepting properties and different optical properties compared to their unprotonated counterparts. It is well known that the characteristics of quinoxalines can be controlled by modifying the type and location of substituents. Several substituted quinoxalines have been utilized as fluorescence probes in various complex chemosensors [3,12].

On the other hand, most of the chemical sensors based on π-conjugated systems have been designed to have electron-donating properties, for the detection of analytes, such as protons and metal ions [4–9]. Terpyridines, which form metal complexes with a variety of transition metal ions, have wide applications in fields such as macromolecular chemistry, biochemistry and photophysics [10,11]. In these ligands with built-in fluorescence the metal ion binding may affect intramolecular charge transfer, and consequently induce spectral changes, both in absorption and in emission. The above may also be applicable to the sensing of metal ions.

In a previous study, we synthesized a series of novel quinoxaline compounds containing styryl groups [12]. They all exhibited strong fluorescence. Consequently, the work herein comprises an investigation of the synthesis and properties of new quinoxaline compounds each containing a terpyridine moiety. The effects of protonation and deprotonation on their absorption and emission spectra in solution are studied. Moreover, the capability of these compounds to chelate metal ions is assessed.

2. Results and discussion

2.1. Synthesis

Quinoxaline derivatives (**1**) and 4-[2,2′:6′,2″]terpyridin-4′-yl-benzonitrile were synthesized by a method previously described in the literature [3,12–14]. The long linear alkyl ether moiety was chosen to improve the solubility of the resulting quinoxaline fluorescent compounds in common organic solvents. The reaction of compound **1** with one equivalent of a 4-substituted benzaldehyde, in the presence of one equivalent of potassium *tert*-butoxide, gave the monostyryl intermediate **2**.

4-[2,2′:6′,2″]Terpyridin-4′-yl-benzaldehyde (**3**) was synthesized by the reaction of 4-[2,2′:6′,2″]terpyridin-4′-yl-benzonitrile and diisobutylaluminum hydride (DIBAL-H). The aldehyde group of **3**

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was confirmed by ^{1}H NMR spectroscopy with a signal at δ 10.12, and by FT-IR. The absorption peak at around 1697 cm^{-1} corresponds to the stretching vibration of the aldehyde (C=O) group, which is normally present at 1725 cm^{-1}. This shift of the vibration absorption region from 1725 to 1697 cm^{-1} is due to conjugation between the carbonyl and aryl groups.

The Horner–Wadsworth–Emmons (HWE) reaction of compounds **2** and **3**, 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 (**4a**). The reaction pathways are summarized in Scheme 1.

The synthesized quinoxalines were characterized by UV–visible spectroscopy, MALDI-TOF-MS (matrix-assisted laser desorption ionization time-of-flight mass spectroscopy) and ^{1}H NMR spectroscopy. Fig. 1 shows the spectrum of **4a** in $CDCl_3$ at 25 °C, which provides structural information. In the aliphatic region, a sharp triplet resonance corresponding to the *O*-methylene proton is observed. Ethylene protons appeared as a doublet at 7.97 and 7.50 ppm and revealed a *trans*-configuration with coupling constants of 15.6 Hz. In addition, the protons of terminal N–CH_3 and O–CH_2 are singlets at 3.04, and triplets at 4.22 ppm, respectively. The two H_a protons in the terpyridinyl group of **4** can be observed as a singlet at 8.80 ppm.

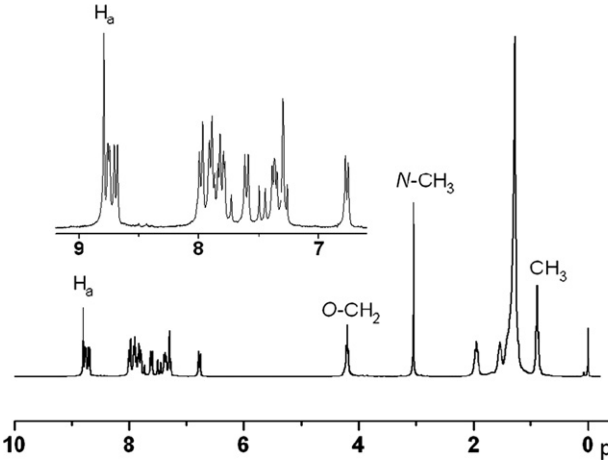


Fig. 1. ^{1}H NMR (300 MHz) spectra of **4a** in $CDCl_3$.

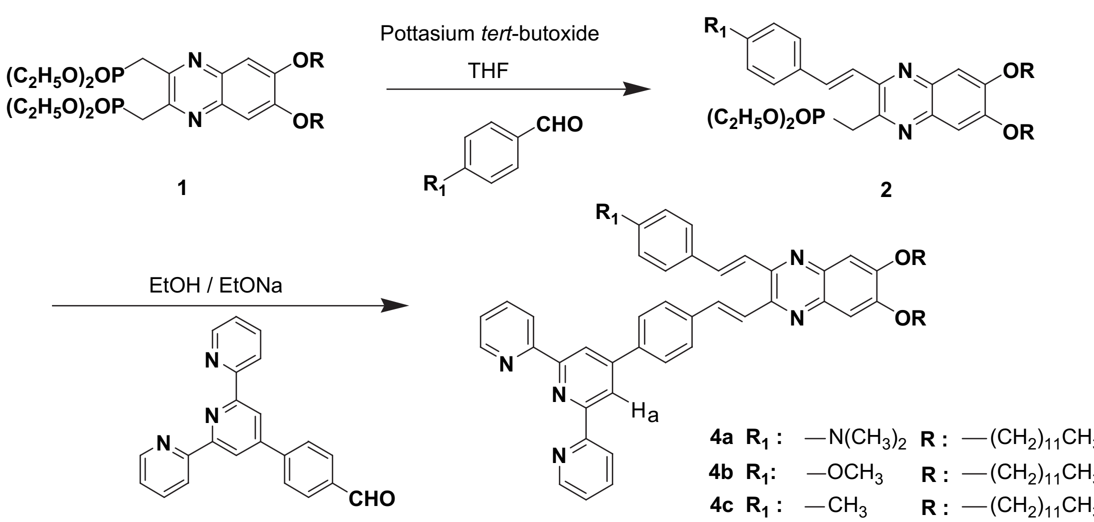
2.2. Optical properties (absorption and emission spectra)

The UV–visible spectra of the synthesized quinoxalines in chloroform/methanol (9/1) were measured by varying the mole ratio of quinoxaline/*p*-toluenesulfonic acid, as shown in Fig. 2. The quinoxaline derivatives showed bathochromic shifts with increased proportions of *p*-toluenesulfonic acid. The original yellow solutions of **4c** became increasingly orange colored with increasing concentration of *p*-toluenesulfonic acid. When the concentration of *p*-toluenesulfonic acid (PTC) was increased, the absorption maximum at 398 nm decreased, and a new absorption band appeared at 492 nm. Also, in the absorption spectra of **4a**, the absorption maximum at 443 nm decreased, and a new absorption band appeared at 603 nm, increasing in intensity as the PTC was increased. The color of **4a** (in solution) changed from yellow to green with increasing PTC.

On the other hand, the UV–visible spectra of **4c** showed a maximum shift of absorption band at the mole ratio of 1:40. For **4a**, the maximum shift of absorption band dramatically shifted in the molecular range from 1:0 to 1:17. This was attributed to the electron-donating abilities of the substituents. In the case of **4a**, the 1,4-position nitrogen atoms of the quinoxaline ring were easily saturated with electrons because of electron-donating ability of *N*,*N*-dimethylamino phenyl substituent, therefore the 1,4-position nitrogen atoms could be protonated by a lower concentration of *p*-toluenesulfonic acid than for **4c**. Consequently, the electron density of the protonated nitrogen would be decreased with a concomitant increase in the electron-withdrawing ability of quinoxaline unit. Predictably, the quinoxaline derivatives with different electron-donor substituents will have different responses and absorption spectra under acidic conditions.

The substituent effects of the donor group on the visible and fluorescence spectra are summarized in Table 1. The electronic character of the substituents in dyes **4a**–**4c** strongly affect their absorption spectra, by producing a bathochromic shift. The extent of this shift depends on the electron-donating abilities of the substituents.

For fluorescence spectroscopy, the concentration of solutions of dye **4** were in the range of 10^{-7} M. The fluorescence maxima under non-acidic conditions are observed at 586 nm (**4a**), 484 nm (**4b**) and 490 nm (**4c**), but those under acidic conditions are observed at 712 nm (**4a**), 575 nm (**4b**) and 548 nm (**4c**). The difference in



Scheme 1. Synthetic route of quinoxaline bearing 2,2′:6′,2″-terpyridine.

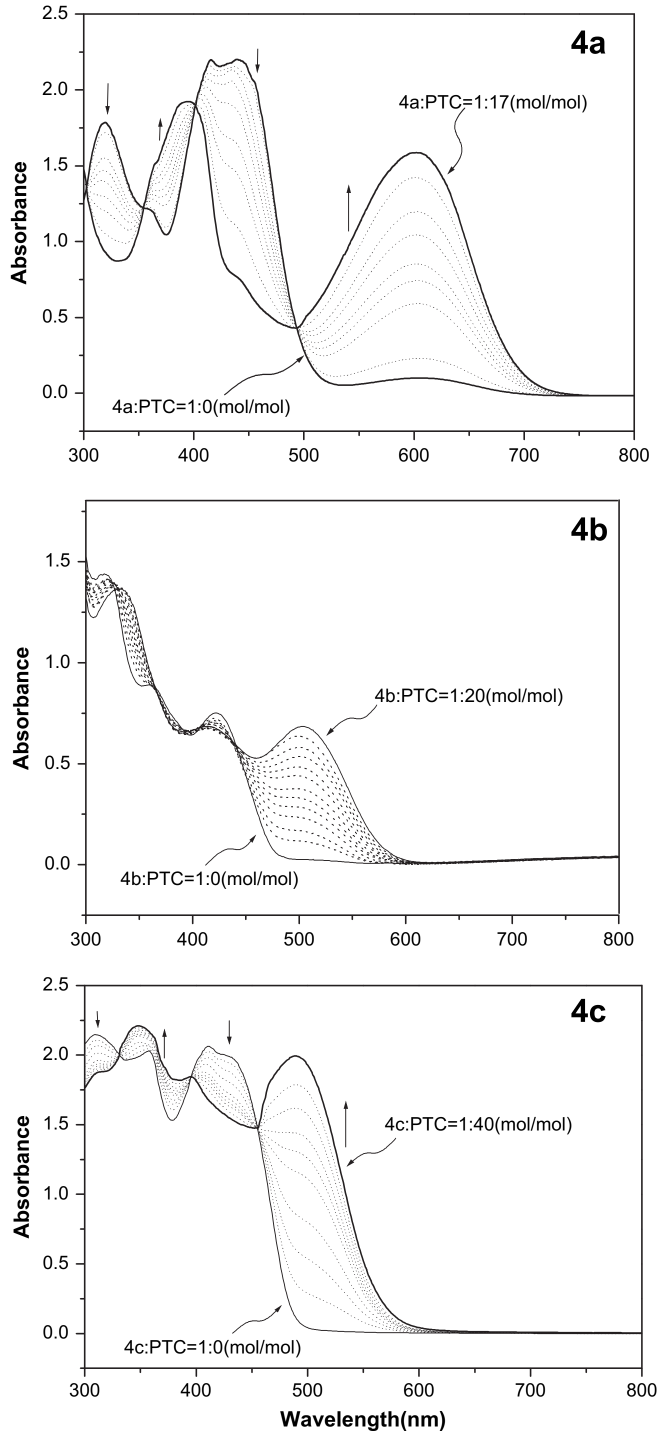


Fig. 2. The effect of *p*-toluenesufonic acid (PTC) on the absorption spectra of **4a** (2.0×10^{-4} M), **4b** (4.96×10^{-5} M) and **4c** (2.14×10^{-4} M) in $CHCl_3$/MeOH = 9/1.

Table 1
Visible and fluorescence spectra of compounds **4a**–**4c**

Compound	$\lambda_{max}{}^{a}$ (nm)	$\lambda_{max}{}^{b}$ (nm)	$F_{max}{}^{c}$ (nm)	$F_{max}{}^{d}$ (nm)	SS[e]
4a	443	603	586	712	143
4b	422	503	484	575	62
4c	398	492	490	548	92

[a] In $CHCl_3/CH_3OH$ (9/1).
[b] In acidic condition.
[c] Fluorescence maximum excited at $\lambda_{max}{}^{a}$ value.
[d] Fluorescence maximum excited at $\lambda_{max}{}^{b}$ value.
[e] Stokes shift ($F_{max}{}^{c} - \lambda_{max}{}^{a}$).

fluorescence maxima in response to changes in acidity suggests that these compounds could be used in chemical sensor devices.

The integration of receptors with chromophores and fluorophores has been shown to produce highly efficient chemosensor responses to target analytes [15]. The terpyridine ligands possess an excellent ability to coordinate to a large number of metal ions, and these ligands have been utilized as a receptor in chemosensors for metal ions. The binding affinity of 4′-[4-(2-{6,7-bis-dodecyloxy-3-[2-(4-substituted-phenyl)-vinyl]-quinoxalin-2-yl}-vinyl)-phenyl]-[2,2′:6′,2″]terpyridine (**4**) toward transition metal ions, Co^{2+}, Ni^{2+}, Cu^{2+} and Fe^{3+}, was evaluated by absorption and emission spectroscopy measurements. Upon addition of these metal ions, the absorption and emission spectra of the quinoxaline derivative change in a similar manner. The intensity of the absorption spectra was increased at around 422 nm when the concentration of the several metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}) was increased, as shown in Fig. 3.

In contrast to the fluorescence of **4b** in $CHCl_3$/MeOH (9/1) solution, the gradual addition of metal ions (Fe^{3+}) to a $CHCl_3$/MeOH (9/1) solution of **4b** leads to a continuous decrease in the intensity of the fluorescence maximum (484 nm) as shown in Fig. 4. This is likely to be due to an electron or energy transfer between the metal cation and the fluorophore, which is known as fluorescence quenching.

Fig. 5 shows the spectral change of **4b** solution ($CHCl_3$/MeOH = 9/1) by the presence of both Co^{2+} ion and PTC. Comparison of Fig. 5 with Figs. 2–4 clearly indicates that the spectral change of **4b** solution by the presence of both Co^{2+} ion and PTC is almost identical with the spectra when the ions and acid are added into the **4b** solution, individually. It shows that the effect of Co^{2+} ion on the spectra independently occurred in the non-acidic solution of **4b**.

In summary, quinoxaline-linked terpyridines were synthesized and their characteristics investigated. These compounds have been utilized as fluorescence probes in some elaborate chemosensors based on π-conjugated systems, designed to have electron-donating properties. The absorption and fluorescence maxima of these compounds **4** were observed at 398–443 nm and 484–586 nm, respectively. The quinoxaline containing terpyridine could be used as an optical sensor for both protons and metal ions.

3. Experimental

General. Flash chromatography was performed with Merck-EM Type 60 (230–400 mesh) silica gel (flash). Melting points were obtained from capillary melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded using a Bruker DRX-300 FT-NMR spectrometer. The UV–visible and fluorescence spectra were measured using UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometers, respectively. MALDI-TOF-MS spectra were obtained using a Waters Limited MALDI-TOF spectrometer with dithranol as the matrix. The reagents and solvents used for the syntheses were all synthetic grade, and were used as received. The chemicals used for spectroscopic analysis were all of analytical reagent grade.

3.1. General procedure to synthesize 2

The procedure by Horner–Wadsworth–Emmons (HWE) reaction was modified as follows. To a solution of [3-(diethoxyphosphorylmethyl)-6,7-bis-dodecyloxy-quinoxalin-2-yl methyl] phosphonic acid diethyl ester (0.05 mol) and 4-substituted benzaldehyde (0.05 mol) in THF (60 ml) was added potassium *tert*-butoxide (0.05 mol) at 0–5 °C, and the mixture was stirred for 1 h. The concentrating 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 **2**.

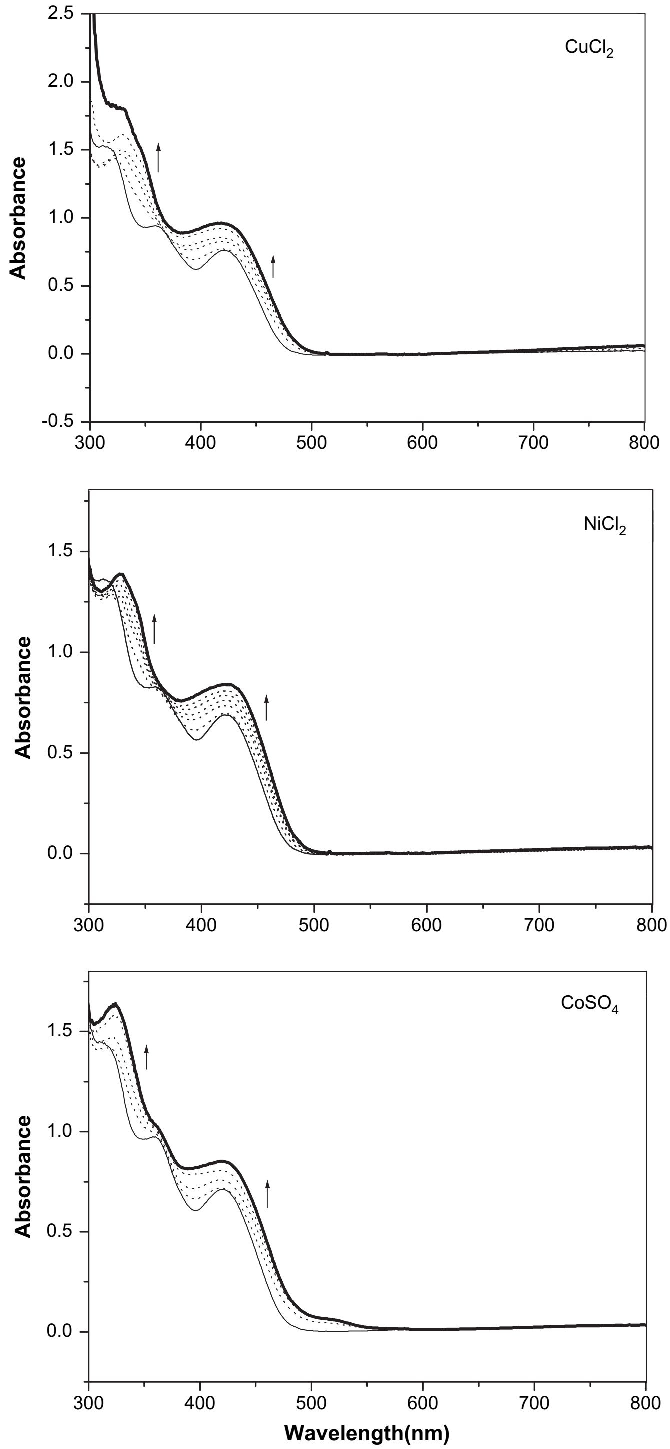


Fig. 3. The effect of metal ion type on the absorption spectra of **4b** (4.96×10^{-5} M) in $CHCl_3$/MeOH = 9/1.

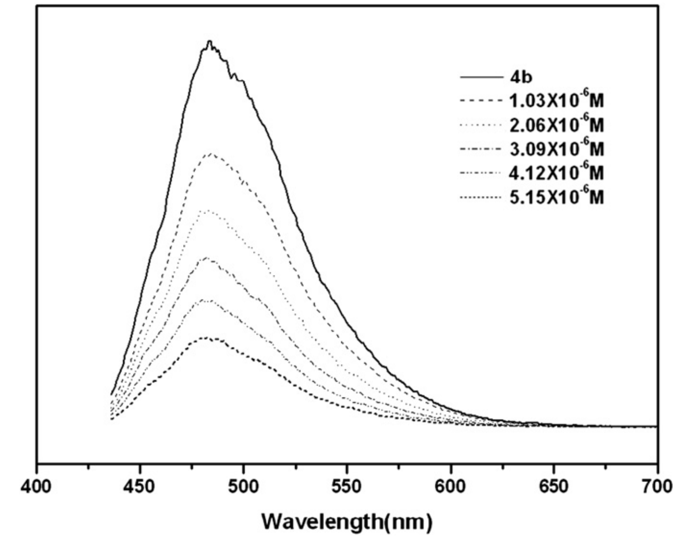


Fig. 4. The effect of metal ion (Fe^{3+}) concentration on the emission intensity of **4b** (2.48×10^{-7} M) in $CHCl_3$/MeOH = 9/1. Excitation wavelength = 422 nm.

3.1.1. *{3-[2-(4-Dimethylaminophenyl)-vinyl]-6,7-bis-dodecyloxy-quinoxalin-2-ylmethyl}-phosphonic acid diethyl ester (**2a**)*

Yield 65%; m.p. 48–50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 ppm (d, 1H, J = 15.0 Hz, ethylene), 7.55 ppm (d, 2H, J = 9.0 Hz, ArH), 7.39 ppm (d, 1H, J = 15.0 Hz, ethylene), 7.28 ppm (s, 2H, quinoxaline), 6.73 ppm (d, 2H, J = 9.0 Hz, ArH), 4.19–4.09 ppm (m, 8H, OCH_2), 3.77 ppm (d, 2H, J = 24.0 Hz, PCH_2), 3.03 ppm (s, 6H, NCH_3), 1.94–1.90 ppm (m, 4H, CH_2), 1.59–1.52 ppm (m, 4H, CH_2), 1.27–1.22 ppm (m, 38H, CH_2, CH_3), 0.88 ppm (t, 6H, J = 9.0 Hz, CH_3); Calcd. for $C_{47}H_{76}N_3O_5P$: C, 71.09; H, 9.65; N, 5.29, found: C, 71.23; H, 9.66; N, 5.17; MALDI-TOF-mass-spectrum: m/z: 795.00 (100%, M^+, calcd. 794.01).

3.1.2. *{6,7-Bis-dodecyloxy-3-[2-(4-methoxy-phenyl)-vinyl]-quinoxalin-2-ylmethyl}-phosphonic acid diethyl ester (**2b**)*

Yield 60%; m.p. 41–43 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 ppm (d, 1H, J = 15.0 Hz, ethylene), 7.62 ppm (d, 2H, J = 9.0 Hz, ArH), 7.49 ppm (d, 1H, J = 15.0 Hz, ethylene), 7.29 ppm (s, 2H, quinoxaline), 6.94 ppm (d, 2H, J = 9.0 Hz, ArH), 4.20–4.10 ppm (m, 8H, OCH_2), 3.85 ppm (s, 3H, OCH_3), 3.72 ppm (d, 2H, J = 24.0 Hz, PCH_2), 1.93–1.91 ppm (m, 4H, CH_2), 1.53–1.51 ppm (m, 4H, CH_2), 1.27–1.21 ppm (m, 38H, CH_2, CH_3), 0.88 ppm (t, 6H, J = 6.0 Hz, CH_3); Calcd. for $C_{46}H_{73}N_2O_6P$: C, 70.74; H, 9.42; N, 3.59, found: C, 71.05; H, 9.51; N, 3.46; MALDI-TOF-mass-spectrum: m/z: 782.00 (100%, M^+, calcd. 781.06).

3.1.3. *{6,7-Bis-dodecyloxy-3-[2-(4-methyl-phenyl)-vinyl]-quinoxalin-2-ylmethyl}-phosphonic acid diethyl ester (**2c**)*

Yield 62%; m.p. 40–42 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 ppm (d, 1H, J = 15.0 Hz, ethylene), 7.63 ppm (d, 2H, J = 9.0 Hz, ArH), 7.77 ppm (d, 1H, J = 15.0 Hz, ethylene), 7.37 ppm (m, 4H, ArH, quinoxaline), 4.22–4.10 ppm (m, 8H, OCH_2), 3.91 ppm (d, 2H, J = 24.0 Hz, PCH_2), 2.40 ppm (s, 3H, $ArCH_3$), 1.98–1.90 ppm (m, 4H, CH_2), 1.61–1.54 ppm (m, 4H, CH_2), 1.27–1.20 ppm (m, 38H, CH_2, CH_3), 0.88 ppm (t, 6H, J = 6.0 Hz, CH_3); Calcd. for $C_{46}H_{73}N_2O_5P$: C, 72.22; H, 9.62; N, 3.66, found: C, 71.95; H, 9.57; N, 3.57; MALDI-TOF-mass-spectrum: m/z: 766.00 (100%, M^+, calcd. 765.06).

3.2. *4-[2,2′:6′,2″]Terpyridin-4′-yl-benzaldehyde (**3**)*

Diisobutylaluminum hydride (DIBAL-H) (1.0 M in hexane, 18.0 mmol) was slowly added to a solution of 4-[2,2′:6′,2″] terpyridin-4′-yl-benzonitrile (17 mmol) in ether (30 ml), at −20 °C. The reaction mixture was kept at −20 °C, and stirred for 10 h. The reaction mixture was quenched with 18% hydrochlroic acid (20 ml), diluted with dichloromethane (30 ml), and washed with distilled water (2 × 60 ml); the organic layer was dried over sodium sulfate. The solvent was removed to give the crude product. Purification of this crude product by flash chromatography (alumina, dichloromethane) produced the desired product **3** (in an yield of 38%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.12 ppm (s, 1H, aldehyde), 8.78 ppm (s,

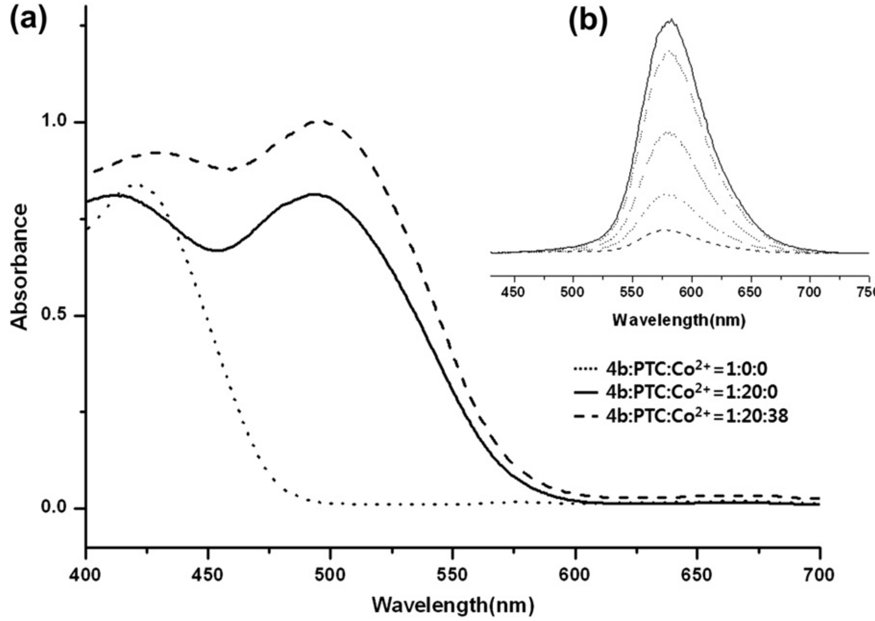


Fig. 5. The absorption (a) and emission spectra (b) of **4b** [(a) 4.96×10^{-5} M, (b) 4.96×10^{-7} M] in the presence of both Co^{2+} and PTC. Excitation wavelength = 484 nm.

2H, pyridine), 8.75 ppm (d, 2H, $J = 6.0$ Hz, pyridine), 8.71 ppm (d, 2H, $J = 6.0$ Hz, pyridine), 8.01–8.10 ppm (m, 4H, ArH), 7.94–7.88 ppm (t, 2H, $J = 6.0$ Hz, ArH), 7.41–7.36 ppm (t, 2H, $J = 6.0$ Hz, pyridine); Calcd. for $C_{22}H_{15}N_3O$: C, 78.32; H, 4.48; N, 12.46; found: C, 78.36; H, 4.41; N, 12.40.

3.3. General procedure to synthesize *4*

To a solution of **2** (0.5 mmol) and 4-[2,2′:6′,2″]terpyridin-4′-yl-benzaldehyde (0.9 mmol) in ethanol (20 ml), sodium ethoxide (0.87 mmol) was added. The resulting mixture was refluxed for 1.5 h. The concentrating of the mixture under reduced pressure afforded the crude product, which was purified by flash chromatography (silica gel, ethyl acetate:*n*-hexane = 1:5) to give **4**.

3.3.1. [4-(2-{6,7-Bis-dodecyloxy-3-[2-(4-[2,2′:6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-quinoxalin-2-yl}-vinyl)-phenyl]-dimethylamine (*4a*)

Yield 67%; m.p. 117–119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 ppm (s, 2H, Py), 8.75 ppm (d, 2H, $J = 6.0$ Hz, Py), 8.70 ppm (d, 2H, $J = 9.0$ Hz, Py), 7.97 ppm (d, 2H, $J = 15.6$ Hz, ethylene), 7.89–7.78 ppm (m, 4H, Py, ArH), 7.62 ppm (d, 2H, $J = 6.0$ Hz, ArH), 7.50 ppm (d, 2H, $J = 15.6$ Hz, ethylene), 7.37–7.30 ppm (m, 6H, ArH, Py, quinoxaline), 6.76 ppm (d, 2H, $J = 9.0$ Hz, ArH), 4.22 ppm (t, 4H, $J = 6.0$ Hz, 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), 0.88 ppm (t, 6H, $J = 6.0$ Hz, 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).

3.3.2. 4′-[4-(2-{6,7-Bis-dodecyloxy-3-[2-(4-methoxy-phenyl)-vinyl]-quinoxalin-2-yl}-vinyl)-phenyl]-[2,2′:6′,2″]terpyridine (*4b*)

Yield 66%; m.p. 96–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 ppm (s, 2H, Py), 8.74 ppm (d, 2H, $J = 6.0$ Hz, Py), 8.69 ppm (d, 2H, $J = 9.0$ Hz, Py), 7.96–7.51 ppm (m, 8H, ethylene, Py, ArH), 7.57 ppm (d, 2H, $J = 15.6$ Hz, ethylene), 7.39–7.29 ppm (m, 6H, ArH, Py, quinoxaline), 6.97 ppm (d, 2H, $J = 9.0$ Hz, ArH), 4.19 ppm (t, 4H, $J = 6.0$ Hz, OCH_2), 3.87 ppm (s, 3H, OCH_3), 1.98–1.92 ppm (m, 4H, CH_2) 1.54 ppm (m, 4H, CH_2), 1.28 ppm (m, 32H, CH_2), 0.88 ppm (t, 6H, $J = 6.0$ Hz, CH_3); Calcd. for $C_{64}H_{77}N_5O_3$: C, 79.71; H, 8.05; N, 7.26, found: C, 79.77; H, 8.01; N, 7.22; MALDI-TOF-mass-spectrum: *m*/*z*: 965.00 (100%, M^+, calcd. 964.33).

3.3.3. 4′-(4-{2-[6,7-Bis-dodecyloxy-3-(2-p-tolyl-vinyl)-quinoxalin-2-yl]-vinyl}-phenyl)-[2,2′:6′,2″]terpyridine (*4c*)

Yield 69%; m.p. 95–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 ppm (s, 2H, Py), 8.79 ppm (d, 2H, $J = 6.0$ Hz, Py), 8.72 ppm (d, 2H, $J = 9.0$ Hz, Py), 7.96–7.51 ppm (m, 10H, ethylene, Py, ArH), 7.39–7.20 ppm (m, 8H, ArH, Py, quinoxaline), 4.19 ppm (t, 4H, $J = 6.0$ Hz, OCH_2), 2.38 ppm (s, 3H, $ArCH_3$), 1.96–1.93 ppm (m, 4H, CH_2) 1.54 ppm (m, 4H, CH_2), 1.27 ppm (m, 32H, CH_2), 0.88 ppm (t, 6H, $J = 6.0$ Hz, CH_3); Calcd. for $C_{64}H_{77}N_5O_2$: C, 81.06; H, 8.18; N, 7.38, found: C, 81.10; H, 8.17; N, 7.34; MALDI-TOF-mass-spectrum: *m*/*z*: 949.00 (100%, M^+, calcd. 948.33).

Acknowledgements

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