

## Synthesis of Organic-Metallic Hybrid Polymers Using Novel Bis-terpyridines Bearing Alkoxy Chains

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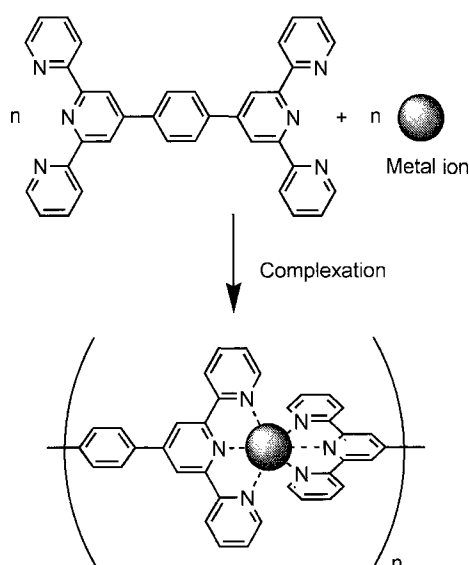
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We synthesized a linear structure of organic-metallic hybrid polymers by complexation of iron(II) acetate with novel bis-terpyridines bearing alkoxy chains as an electro-releasing group. Introduction of alkoxy groups to bis-terpyridines was achieved during a reaction of bromo-substituted bis-terpyridines with sodium alkoxide in DMF. When we use alkane-diol as a starting material, a unique bis-terpyridine with a cyclic structure obtained *via* intramolecular cyclization. Formation of the corresponding hybrid polymers based on complexation of the organic module with iron(II) ions was confirmed as increase of a MLCT absorption in the UV-vis spectral measurements. We found that a blue shift of the MLCT absorption is caused by introduction of electro-releasing groups to the organic modules.

Key words: organic-metallic hybrid polymers, complexation, bis-terpyridines, alkoxy chains, MLCT absorption

### 1. INTRODUCTION

Complexation of metal ions with organic modules bearing two coordination sites gives a linear structure of organic-metallic hybrid polymers.<sup>1</sup> The polymers are expected as a novel kind of polymers to be applied for electronic devices or displays because of their unique electronic, photonic, and magnetic properties.<sup>2</sup> Such properties are caused by electrochemical and/or steric interaction between metal ions and the organic module. Therefore, modification of the organic modules will be effective in order to control their properties. Bis-terpyridines are useful as an organic module for making hybrid polymers due to their high coordination ability for various metal ions such as iron, cobalt, and ruthenium (Scheme 1).<sup>3</sup>



**Scheme 1.** Formation of organic-metallic hybrid polymers by complexation of bis-terpyridines with metal ions.

However, synthetic methods to modify terpyridines are limited, and especially, introduction of electro-releasing groups at a 2-position of the pyridine units in bis-terpyridines has not been reported as far as we know. We herein report synthesis of novel bis-terpyridine bearing alkoxy chains as electro-releasing groups, and the corresponding hybrid polymers by complexation with iron(II) ions. In addition, we discuss chromic properties based on the metal-to-ligand charge transfer (MLCT) absorption of the polymers.

### 2. EXPERIMENTAL SECTION

#### 2.1 Generals

All reagents were reagent grade and were used without purification. De-ionized H<sub>2</sub>O was used in the experiment where required. <sup>1</sup>H NMR spectra were recorded at 300 MHz on a JEOL AL 300/BZ instrument. Chemical shifts were given relative to TMS. Mass spectra (MS) were measured by using AXIMA-CFR, Shimadzu/Kratos TOF Mass spectrometer. High resolution mass spectra (HRMS) were measured by using Shimadzu LCMS-IT-TOF spectrometer. UV-vis spectra were measured by using Shimadzu UV-vis spectrometer. Analytical thin layer chromatography (TLC) were Merck aluminium oxide 60 F<sub>254</sub> neutral or silica gel 60 F<sub>254</sub> coated on 25 TCC aluminium sheets (20 x 20 cm). Flash column chromatographic separations were performed on silica gel 60 N (neutral, 40-100 μM), Kanto Chemical Co. Inc., or activated alumina oxide (75 μM), Wako.

#### 2.2 Synthesis of dibutoxy-bis(terpyridyl)benzene 2

With dried *n*-hexane was washed 55wt% sodium hydride (625 mg, 7.16 mmol) beforehand, and suspended in DMF (200 ml). 1-Butanol (0.66 ml, 7.16 mmol) was added to the solution, and stirred for 30 min at room temperature. Dibromo-bis(terpyridyl)benzene 1 (500 mg, 0.72 mmol) was further added, and stirred for 2 days at 70 °C. For

quenching, de-ionized water (200 ml) was added to the reaction mixture. After filtration, the residue was washed with de-ionized water, methanol, and hexane. Dibutoxy-bis(terpyridyl)benzene **2** (282 mg, a 58% yield) was obtained by re-crystallization in acetic acid. *Spectral data*:  $^1\text{H NMR}$  ( $\text{CF}_3\text{COOD}$ )  $\delta = 9.03\text{--}8.97$  (2H, m),  $8.95\text{--}8.89$  (2H, m),  $8.87\text{--}8.73$  (6H, m),  $8.67\text{--}8.59$  (2H, m),  $8.37\text{--}8.30$  (2H, m),  $8.24\text{--}8.15$  (2H, m),  $8.09$  (4H, s),  $7.62\text{--}7.55$  (2H, m),  $4.60$  (4H, t,  $J = 7.3$  Hz),  $1.98$  (4H, quintet,  $J = 7.3$  Hz),  $1.52$  (4H, sextet,  $J = 7.3$  Hz),  $1.01$  (6H, t,  $J = 7.3$  Hz).  $^{13}\text{C NMR}$  ( $\text{CF}_3\text{COOD}$ )  $\delta = 154.1$ ,  $150.3$ ,  $148.6$ ,  $147.8$ ,  $147.1$ ,  $146.8$ ,  $144.6$ ,  $142.0$ ,  $137.9$ ,  $128.6$ ,  $128.2$ ,  $125.0$ ,  $123.7$ ,  $123.3$ ,  $111.7$ ,  $74.0$ ,  $29.8$ ,  $18.0$ ,  $11.7$ . IR (KBr,  $\text{cm}^{-1}$ ): 2956, 2930, 2873, 1583, 1457, 1419, 796. HRMS: Calcd for  $\text{C}_{44}\text{H}_{41}\text{N}_6\text{O}_2$ : ( $\text{M}+\text{H}^+$ ) 685.3286, found:  $m/z$  685.3294.

### 2.3 Synthesis of dihexadecanoxy-bis(terpyridyl)benzene **3**

With dried *n*-hexane was washed 55wt% sodium hydride (625 mg, 7.16 mmol) beforehand, and suspended in DMF (200 ml). 1-Hexadecanol (1.74 g, 7.16 mmol) was added to the solution, and stirred for 30 min at room temperature. Dibromo-bis(terpyridyl)benzene **1** (500 mg, 0.72 mmol) was further added, and stirred for 2 days at 70 °C. For quenching, de-ionized water (200 ml) was added to the reaction mixture. After filtration, the residue was washed with de-ionized water, methanol, and hexane. Dihexadecanoxy-bis(terpyridyl)benzene **3** (328 mg, a 44% yield) was obtained by re-crystallization in acetic acid. *Spectral data*:  $^1\text{H NMR}$  ( $\text{CF}_3\text{COOD}$ )  $\delta = 8.99\text{--}8.92$  (2H, m),  $8.91\text{--}8.84$  (2H, m),  $8.82\text{--}8.68$  (6H, m),  $8.63\text{--}8.52$  (2H, m),  $8.32\text{--}8.25$  (2H, m),  $8.19\text{--}8.10$  (2H, m),  $8.04$  (4H, s),  $7.57\text{--}7.49$  (2H, m),  $4.54$  (4H, t,  $J = 6.9$  Hz),  $1.96$  (4H, quintet,  $J = 6.9$  Hz),  $1.52\text{--}1.08$  (52H, m),  $0.75$  (6H, t,  $J = 6.0$  Hz).  $^{13}\text{C NMR}$  ( $\text{CF}_3\text{COOD}$ )  $\delta = 154.2$ ,  $150.4$ ,  $148.6$ ,  $147.9$ ,  $147.2$ ,  $146.9$ ,  $144.6$ ,  $142.1$ ,  $138.0$ ,  $128.7$ ,  $128.2$ ,  $125.0$ ,  $123.7$ ,  $123.4$ ,  $111.7$ ,  $74.3$ ,  $31.6$ ,  $29.31$ ,  $29.29$ ,  $29.22$ ,  $29.1$ ,  $29.0$ ,  $28.7$ ,  $27.9$ ,  $24.9$ ,  $22.2$ ,  $12.5$ . IR (KBr,  $\text{cm}^{-1}$ ): 2920, 2851, 1583, 1419, 795. HRMS: Calcd for  $\text{C}_{68}\text{H}_{89}\text{N}_6\text{O}_2$ : ( $\text{M}+\text{H}^+$ ) 1021.7042, Found:  $m/z$  1021.7016.

### 2.4 Synthesis of hexadecane-dioxy-1,4-bis(terpyridyl)benzene **4**

With dried *n*-hexane was washed 55wt% sodium hydride (125 mg, 2.86 mmol) beforehand, and suspended in DMF (200 ml). 1,16-Hexadecane-diol (74 mg, 0.29 mmol) was added to the solution, and stirred for 30 min at room temperature. Dibromo-bis(terpyridyl)benzene **1** (200 mg, 0.29 mmol) was further added, and stirred for 24 h at 70 °C. For quenching, de-ionized water (200 ml) was added to the reaction mixture. After filtration, the residue was washed with de-ionized water, methanol, and hexane. Hexadecane-dioxy-1,4-bis(terpyridyl)benzene **4** (75 mg, a 33% yield) was obtained by re-crystallization in chloroform/hexane. *Spectral data*:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta = 8.78\text{--}8.67$  (8H, m),  $8.31\text{--}8.26$  (2H, m),  $8.05$  (2H, s),  $7.93\text{--}7.86$  (2H, m),  $7.81\text{--}7.74$  (2H, m),  $7.40\text{--}7.33$  (2H, m),  $6.85\text{--}6.78$  (2H, m),  $4.51$  (4H,  $J = 7.0$  Hz),  $1.87$  (4H, quintet,  $J = 7.0$  Hz),  $1.52$  (4H, quintet,  $J = 7.0$  Hz),  $1.15\text{--}1.45$  (20H, m).  $^{13}\text{C NMR}$  ( $\text{CF}_3\text{COOD}$ )  $\delta = 153.7$ ,  $150.3$ ,  $148.9$ ,  $148.7$ ,  $147.3$ ,  $146.8$ ,  $146.2$ ,  $142.1$ ,  $137.9$ ,  $128.6$ ,  $128.2$ ,  $124.7$ ,  $124.4$ ,  $122.2$ ,  $117.6$ ,  $111.3$ ,  $74.0$ ,  $29.3$ ,  $29.24$ ,  $29.22$ ,  $29.18$ ,  $28.9$ ,  $28.2$ ,  $25.6$ . IR (KBr,

$\text{cm}^{-1}$ ): 2924, 2852, 1584, 1454, 1419, 806, 792. HRMS: Calcd for  $\text{C}_{52}\text{H}_{55}\text{N}_6\text{O}_2$ : ( $\text{M}+\text{H}^+$ ) 795.4381, Found:  $m/z$  795.4359.

### 2.5 Synthesis of tetramethoxy-1,4-bis(terpyridyl)benzene **6**

With dried *n*-hexane was washed 55wt% sodium hydride (1.27 g, 29.2 mmol) beforehand, and suspended in DMF (200 ml). Methanol (0.96 ml, 23.4 mmol) was added to the solution, and stirred for 30 min at room temperature. Tetrabromo-bis(terpyridyl)benzene **5** (500 mg, 0.58 mmol) was further added, and stirred for 12 h at 70 °C. For quenching, de-ionized water (200 ml) was added to the reaction mixture. After filtration, the residue was washed with de-ionized water, methanol, and hexane. Tetramethoxy-1,4-bis(terpyridyl)benzene **6** (170 mg, a 44% yield) was obtained by re-crystallization in acetic acid. *Spectral data*:  $^1\text{H NMR}$  ( $\text{CF}_3\text{COOD}$ )  $\delta = 8.74$  (4H, m),  $8.70\text{--}8.62$  (4H, m),  $8.40\text{--}8.34$  (4H, m),  $8.08$  (4H, s),  $7.63\text{--}7.57$  (4H, m),  $4.37$  (12H, m).  $^{13}\text{C NMR}$  ( $\text{CF}_3\text{COOD}$ )  $\delta = 153.9$ ,  $150.6$ ,  $147.3$ ,  $144.7$ ,  $138.0$ ,  $128.6$ ,  $123.4$ ,  $111.0$ ,  $58.6$ . IR (KBr,  $\text{cm}^{-1}$ ): 3009, 2947, 1576, 1551, 1470, 803, 765. HRMS: Calcd for  $\text{C}_{40}\text{H}_{33}\text{N}_6\text{O}_4$ : ( $\text{M}+\text{H}^+$ ) 661.2558, Found:  $m/z$  661.2538.

### 2.6 Synthesis of organic-metallic hybrid polymers using bis-terpyridines

Typical synthetic procedures of organic-metallic hybrid polymers using bis-terpyridines are as follows: bis-terpyridine as an organic module is dissolved in acetic acid under argon atmosphere (1 ml of acetic acid is used per 1 mg of an organic module). If solubility of the organic module for acetic acid is low, the organic modules are totally dissolved by heating. To the solution is added iron(II) acetate suspended in methanol. A molar ratio of the organic module and iron(II) acetate used in this complexation is exactly 1:1. A color of the solution changes to purple based on the complexation. The reaction mixture was refluxed for 24 h. After cooling, the reaction mixture is filtrated, and the filtrate is concentrated. The crude product is dissolved again in methanol, and a slight amount of the free ligand is removed by filtration. The hybrid polymer is obtained quantitatively by concentration of the filtrate.

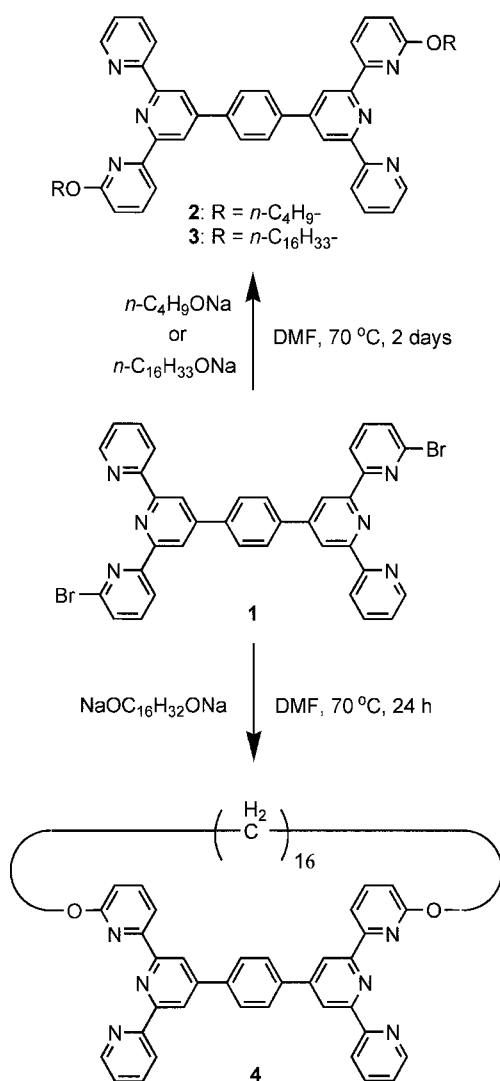
## 3 RESULTS AND DISCUSSION

### 3.1 Synthesis of novel bis-terpyridines with alkoxy groups

Since terpyridines have high coordination ability for various metal ions such as iron or cobalt ions, complexation of bis-terpyridines with metal ions gives a linear structure of organic-metallic hybrid polymers.<sup>4</sup> The hybrid polymers have a specific color based on a metal-to-ligand charge transfer (MLCT) absorption, and we revealed that the polymer formed by complexation of bis(terpyridyl)benzene with iron(II) ions has excellent electrochromic functions. The color of the polymer will be changed, if LUMO potential of the organic modules is controlled, because the color depends on energy band-gap between LUMO potential of organic ligands and HOMO of metal ions. One of the best ways to change the LUMO potential of bis-terpyridines is introduction of electro-releasing or -withdrawing groups to the pyridine units, especially to the 2-position of the pyridine units,

because the substituent effect is expected to be strongest at the position. However, modification methods of bis-terpyridines are limited. We succeeded to synthesize novel bis-terpyridines bearing butoxy and hexadecanoxy groups as an electro-releasing group, **2** and **3**, via a reaction of dibromo-substituted bis(terpyridyl)benzene **1** with sodium butoxide and hexadecanoxide, respectively, in DMF (Scheme 2). They were isolated with 58 and 44% yields, respectively, using re-crystallization in acetic acid, and identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and HRMS.

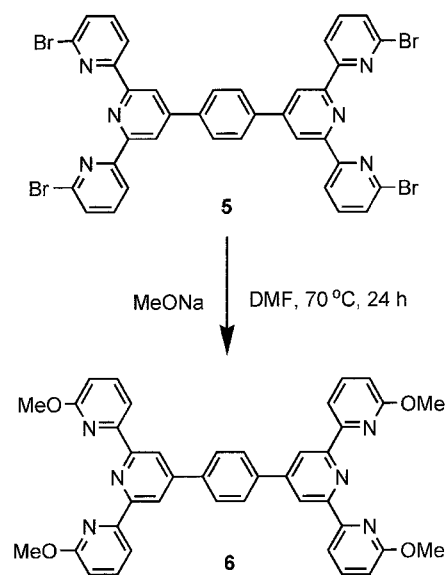
On the other hand, the reaction of **1** with alkane diols is expected to cause the formation of unique organic modules such as cyclic oligo-terpyridines and we tried a reaction of **1** with sodium 1,16-hexadecane-dioxide (Scheme 2). Interestingly, novel bis-terpyridine bridged by a dioxo-hexadecane group between the two terpyridine moieties **4** was obtained in a 33% yield as a main product, probably because the intra-molecular cyclization is much faster than intermolecular reactions.



**Scheme 2.** Synthesis of bis-terpyridine derivatives having alkoxy chains.

In addition, tetramethoxy-bis(terpyridyl)benzene **6** was prepared via a reaction of tetrabromo-substituted

bis(terpyridyl)benzene **5** with sodium methoxide (Scheme 3). In conclusion, we first synthesized some kinds of bis(terpyridyl)benzene derivatives with alkoxy groups using bromo-substituted bis-terpyridines as a starting material.



**Scheme 3.** Synthesis of bis-terpyridine derivatives having four methoxy groups.

### 3.2 Formation of organic-metallic hybrid polymers

Bis-terpyridines work as an organic module to form organic-metallic hybrid polymers by complexation with metal ions (Scheme 1). The polymers have a specific color based on MLCT absorption. We confirmed formation of hybrid polymers by the color change of the solution to blueish purple, which was caused by the MLCT absorption, during reflux of a reaction mixture of the bis-terpyridines bearing alkoxy groups and iron(II) acetate in acetic acid.

### 3.3 UV-vis spectra of the hybrid polymers

A color of a hybrid polymer obtained by complexation of bis(terpyridyl)benzene with iron(II) acetate is purple in methanol. On the other hand, colors of the polymers consisted of alkoxy-substituted bis(terpyridyl)benzenes, **3**, **4**, and **6** and iron(II) ions were blueish purple. We investigated UV-vis spectra of the polymers in detail. An UV-vis spectrum of a hybrid polymer consisted of bis(terpyridyl)benzene and iron(II) ions have a MLCT absorption around 580 nm, but the  $\lambda_{\text{max}}$ s of the absorption of the polymers consisted of **3**, **4**, and **6** were 578, 571, 568 nm, respectively. These results clearly show that increase of the number of alkoxy groups in the bis-terpyridines causes stronger blue shift of the MLCT absorption, because of an electro-releasing effect of alkoxy groups introduced to bis-terpyridines.

## 4. CONCLUSION

We synthesized novel bis-terpyridine derivatives with alkoxy group as an electro-releasing substituent by a reaction of bromo-substituted bis-terpyridines with sodium alkoxides. Novel organic-metallic hybrid polymers were formed by complexation of the novel

organic modules with iron(II) acetate in an acetic acid. During the complexation, a color of the solution became blueish purple due to an MLCT absorption. UV-vis spectral measurements of the polymers showed a blue shift of the absorption around 580 nm based on a MLCT absorption. We revealed that stronger blue shift of the MLCT absorption is caused by increase of the number of alkoxy groups in the bis-terpyridines, due to the electro-releasing effect.

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