



## Two near-UV and visible chromophores of CpCo(Dithiolene) complexes with pyridinium-dicyanomethylide group

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### ABSTRACT

Tetracyanoethylene oxide (TCNEO) reacted with [CpCo(dithiolene)] (Cp =  $\eta^5$ -cyclopentadienyl) complexes having 4-pyridyl or 3-pyridyl group to undergo a dicyanomethylation to the nitrogen atom on the pyridyl group. The reaction of [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>4</sup>Py)<sub>2</sub>)] (**1**) with TCNEO formed both the monodicyanomethylated [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>4</sup>Py)(<sup>4</sup>Py–C(CN)<sub>2</sub>)] (**1a**) and bisdicyanomethylated [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>4</sup>Py–C(CN)<sub>2</sub>)<sub>2</sub>)] (**1b**). [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>2</sup>Py)(<sup>4</sup>Py))] (**2**) reacted with TCNEO to give [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>2</sup>Py)(<sup>4</sup>Py–C(CN)<sub>2</sub>)] (**2a**) but no dicyanomethylation occurred on the 2-pyridyl group. **2** reacted with excess TCNEO to form the only dicyanomethylated acetylene derivative <sup>2</sup>Py–C≡C–(<sup>4</sup>Py–C(CN)<sub>2</sub>) (**2c**), followed by a dissociation of the CpCoS<sub>2</sub> fragment. The monodicyanomethylated [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>n</sup>Py–C(CN)<sub>2</sub>)(2-thienyl))] (*n* = 4 (**4a**) or 3 (**5a**)) complexes were also prepared from [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>n</sup>Py)(2-thienyl))] (*n* = 4 (**4**) or 3 (**5**)) and TCNEO. **1b** was structurally characterized by X-ray diffraction study. The all dicyanomethylated [CpCo(dithiolene)] complexes showed the dithiolene LMCT absorption in the range of 605–644 nm ( $\epsilon$  = 7000–9200 M<sup>-1</sup> cm<sup>-1</sup>) and very strong absorption due to their pyridinium-dicyanomethylide moieties in near-UV region (e.g. **1b**:  $\lambda_{\text{max}}$  = 470 nm,  $\epsilon$  = 43,400 M<sup>-1</sup> cm<sup>-1</sup>). The CV of the all dicyanomethylated complexes exhibited two reduction waves. The first reduction is due to Co<sup>III</sup>/Co<sup>II</sup> and the second one is due to the reduction of the pyridinium-dicyanomethylide moiety. The reduced **1b**<sup>-</sup> is stable enough for several minutes according to the visible spectroelectrochemical measurement. The ESR spectrum of **1b**<sup>-</sup> indicated eight hyperfine splittings due only to the interaction with the nuclear spin of cobalt (*I* = 7/2).

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### 1. Introduction

Tetracyanoethylene oxide (TCNEO) is a precursor of malononitrile derivatives [1] and is one strong electrophile to undergo a dipolar addition, dicyanomethylation and so on. TCNEO normally shows two types of electrophilic reaction. One is the reaction with multiple C–C bonds, including those in aromatic compounds to give five-membered tetracyanotetrahydrofurans by a cleavage of the C–C bond of the epoxide ring [2,3]. The other is the reaction with pyridine derivatives or sulfide derivatives to afford stable pyridinium-dicyanomethylides or sulfonium-dicyanomethylides, respectively [4]. In addition, the reactions of TCNEO with heterocycles have been well developed [5]. Since the metalladithiolene ring (MS<sub>2</sub>C<sub>2</sub>) has been one important five-membered heterocycle

containing one metal, the reaction of metal dithiolene complex with TCNEO has been interesting for us to obtain dicyanomethylated dithiolene complexes.

To our knowledge, metal dithiolene complexes have both aromaticity and unsaturation in the metallacycle [6]. In fact, we developed some electrophilic substitutions, radical substitutions [7] and Suzuki-Miyaura cross-coupling reactions [8] by the aromaticity of metalladithiolene ring. On the other hand, addition reactions due to the unsaturation have been much more developed [9–16]. An olefin undergoes a cycloaddition reaction on the dithiolene ligand in the square-planar [M(dithiolene)<sub>2</sub>] complexes (M = Ni, Pd, Pt). Furthermore, half-metallocene dithiolene complexes, which are generally formulated as [CpM(dithiolene)] (M = Co, Rh, Ir; Cp =  $\eta^5$ -cyclopentadienyl) [12], undergo both nucleophilic and electrophilic addition reactions on the central metal or M–S bond [13–16] (Chart 1, left). These nucleophiles initially attack the coordinatively unsaturated central metal.

In addition, the reactions of [CpCo(dithiolene)] complexes with an activated alkyne [17] or TCNEO [18] as electrophiles to afford

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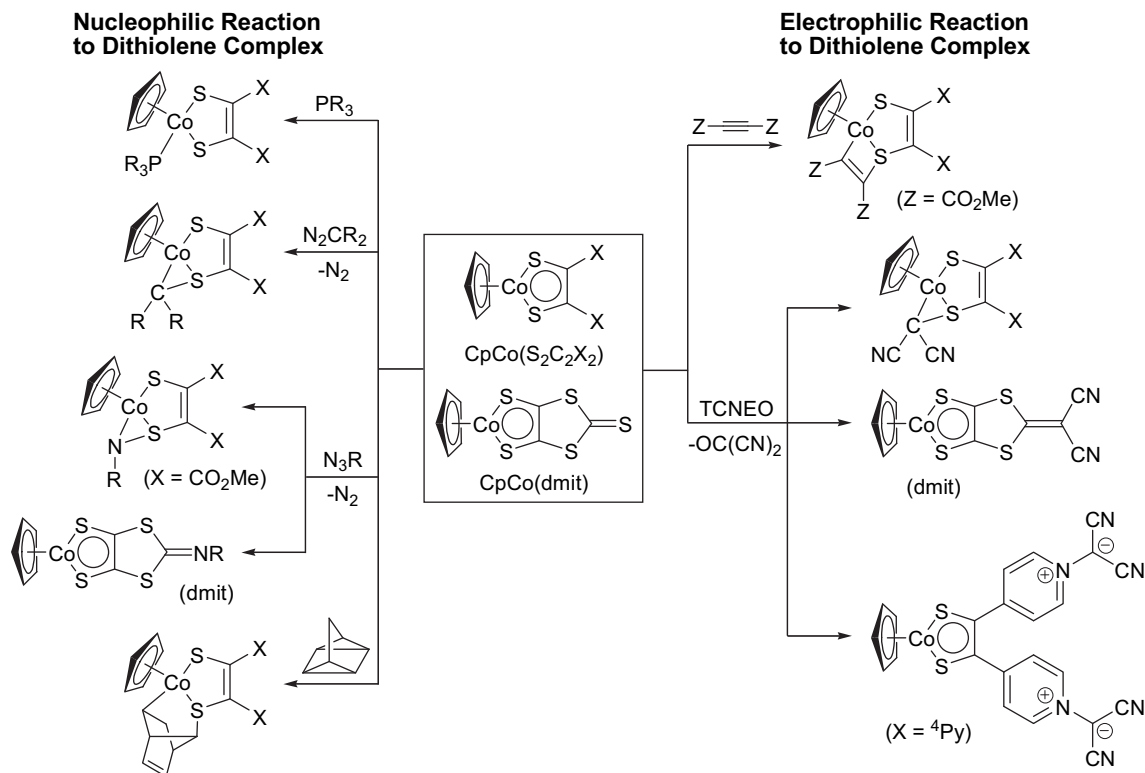


Chart 1.

1:1 bridging adducts as well (Chart 1, right). These electrophiles initially attack the nucleophilic sulfur atom in the dithiolene ligand. On the basis of our previous works, TCNEO shows further diverse reactivities with [CpCo(dithiolene)] complexes. The reaction of TCNEO with [CpCo(dmit)] (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) undergoes a sulfur replacement reaction on the terminal C=S bond [19]. Moreover, the reaction of TCNEO with [CpCo(S<sub>2</sub>C<sub>2</sub>(<sup>4</sup>Py)<sub>2</sub>)] (<sup>4</sup>Py = 4-pyridyl) forms the [CpCo(dithiolene)] complex with pyridinium-dicyanomethylidene group (Chart 1), that has been briefly reported in a short communication [18]. A strong near-UV absorption has been expected in this dithiolene system, because the pyridinium-dicyanomethylidene group is one strong near-UV chromophore around 380–400 nm [20].

According to the photochemical research background, many dithiolene complexes are also well known as strong near-IR [21] and visible chromophores [22], that have been already applied for photo-functional materials [23–26]. Generally, the near-IR absorption has been observed in the homoleptic [M(dithiolene)<sub>2</sub>]<sup>n-</sup> complexes (M = Ni, Pd, Pt; n = -1, 0) based on the ligand-to-ligand charge transfer. Molar extinction coefficients (ε) as high as 80,000 M<sup>-1</sup> cm<sup>-1</sup>

were even reported in the neutral [M(R,R'timdt)<sub>2</sub>]<sup>0</sup> (R,R'timdt = N,N'-disubstituted imidazolidine-2,4,5-trithione) complexes (Chart 2) [27]. On the other hand, heteroleptic dithiolene complexes exhibit electronic absorption in visible region. Eisenberg et al. have developed the photochemical properties of [(diimine)Pt(dithiolene)] (diimine = bpy, phen) complexes (Chart 2) and their MMLL/CT (mixed-metal/ligand-to-ligand charge transfer) electronic absorption in visible region [24].

Recently, multinuclear dithiolene complexes have been frequently reported and they have been usually strong chromophores [28–32]. The dinuclear [Cp\*<sub>2</sub>M<sub>2</sub>(btt)] (λ<sub>max</sub> = 677 nm (Co), 586 nm (Rh), 474 nm (Ir); btt = 1,2,4,5-benzenetetrathiolate) [28,29] and trinuclear [Cp\*<sub>3</sub>M<sub>3</sub>(bht)] (λ<sub>max</sub> = 704 nm (Co), 590 nm (Rh), 499 nm (Ir); bht = benzenehexathiolate) [30] complexes have shown strong visible absorption based on the LMCT in dichloromethane solution (ε > 30,000 M<sup>-1</sup> cm<sup>-1</sup>). Gray and Donahue group have reported that multimetallic complexes with the btt ligand (M = group 10 metals) exhibiting strong near-IR absorption (1159–1177 nm, ε = 12,400–16,000 M<sup>-1</sup> cm<sup>-1</sup>) [31]. However, no strong near-UV chromophore of dithiolene complex has been

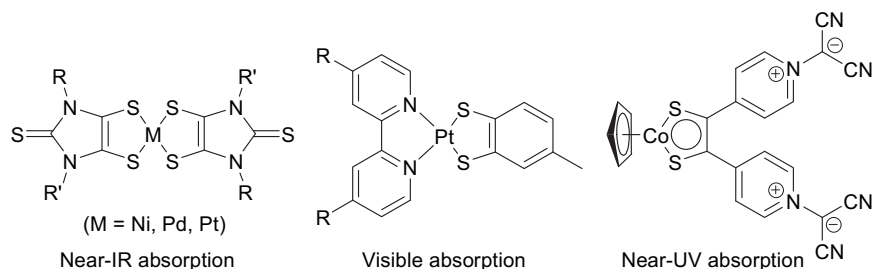


Chart 2.

reported yet. Thus, we are interested in the dithiolene complex with pyridinium-dicyanomethylide group as a strong near-UV chromophore, which can be synthesized by the electrophilic reaction of TCNEO with  $[\text{CpCo}(\text{S}_2\text{C}_2(^n\text{Py})_2)]$  complexes. This paper describes the crystal structure of one dicyanomethylated product, the reactions of TCNEO with dithiolene complexes having pyridyl isomers (e.g.  $^3\text{Py}$  and  $^2\text{Py}$  instead of  $^4\text{Py}$ ), their electrochemical behavior and electronic absorption (UV–vis) of the dicyanomethylated products as well. In this work, we observed very strong near-UV absorption up to  $\epsilon = 43,400 \text{ M}^{-1} \text{ cm}^{-1}$  using a mono-nuclear–monodithiolene complex.

## 2. Results and discussion

### 2.1. Reactions of $[\text{CpCo}(\text{dithiolene})]$ complexes with TCNEO

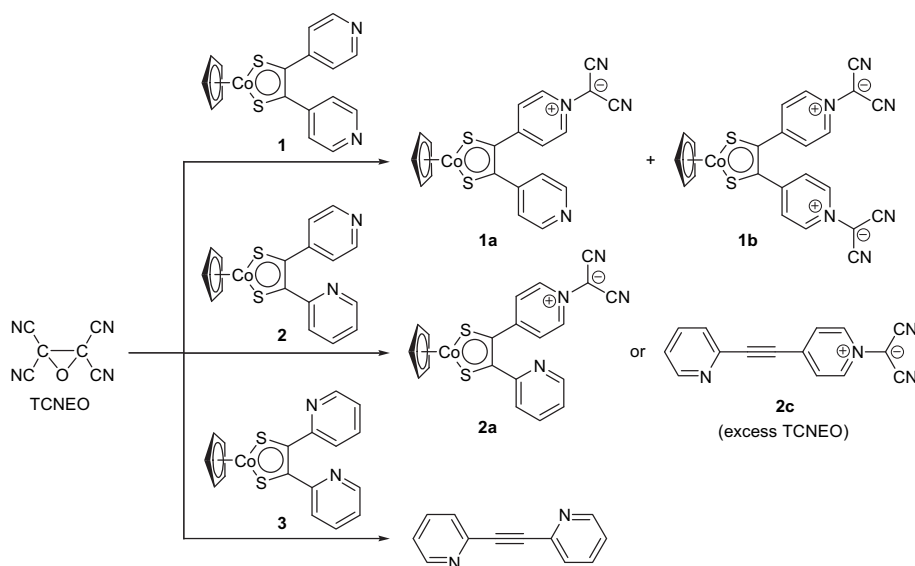
The reaction of  $[\text{CpCo}(\text{S}_2\text{C}_2(^4\text{Py})_2)]$  (**1**) with 2 equiv of TCNEO in refluxing THF has produced  $[\text{CpCo}(\text{S}_2\text{C}_2(^4\text{Py})(^4\text{Py}-\text{C}(\text{CN})_2))]$  (**1a**) with one dicyanomethylide group and  $[\text{CpCo}(\text{S}_2\text{C}_2(^4\text{Py})-\text{C}(\text{CN})_2)_2]$  (**1b**) with two dicyanomethylide groups in 21% and 59% yields, respectively (Scheme 1). Both complexes have been already identified with NMR data and elemental analyses [18]. In this work, the reaction of  $[\text{CpCo}(\text{S}_2\text{C}_2(^2\text{Py})_2)]$  (**3**) with TCNEO was performed but no dicyanomethylation occurred. The only product, which could be identified, was the corresponding di-2-pyridylacetylene ( $^2\text{Py}-\text{C}\equiv\text{C}-^2\text{Py}$ ) in c.a. 30% yield (Scheme 1). In addition,  $[\text{CpCo}(\text{S}_2\text{C}_2(^2\text{Py})(^4\text{Py}))]$  (**2**) reacted with 1 equiv of TCNEO to form  $[\text{CpCo}(\text{S}_2\text{C}_2(^2\text{Py})(^4\text{Py}-\text{C}(\text{CN})_2))]$  (**2a**) having one dicyanomethylide group in 28% yield. However, the reaction of **2** with 2 equiv of TCNEO gave only dicyanomethylated acetylene derivative  $^2\text{Py}-\text{C}\equiv\text{C}-(^4\text{Py}-\text{C}(\text{CN})_2)$  (**2c**) in 73% yield but no **2a** was obtained. **2c** was directly prepared by the reaction of  $^2\text{Py}-\text{C}\equiv\text{C}-^4\text{Py}$  with TCNEO (46% yield). One-pot synthesis of **2a** was performed by  $[\text{CpCo}(\text{CO})_2]$ , elemental sulfur and **2c** in 71% yield. On the other hand, one-pot reaction of  $[\text{CpCo}(\text{CO})_2]$ , elemental sulfur and  $^2\text{Py}-\text{C}\equiv\text{C}-^4\text{Py}$  gave **2** in 40% yield. These two one-pot reactions suggest that the electron-withdrawing dicyanomethylene group on **2c** can activate the electrophilic acetylene carbons, that can smoothly react with nucleophilic  $[\text{Cp}_4\text{Co}_4\text{S}_n]$  intermediate ( $n = 4$  or 6) [33].

These results noted above indicate that the dicyanomethylene group can be introduced on the 4-pyridyl group. We assume that

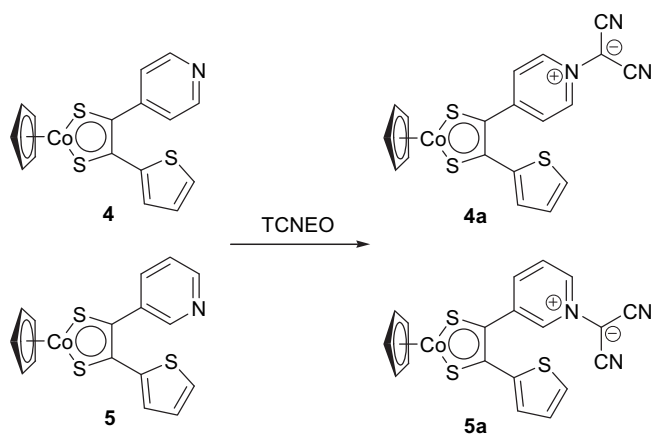
the electrophilic dicyanomethylene group in TCNEO may attack the 2-pyridyl group but may cause a decomposition of the dithiolene moiety. One reason for instability is probably a steric effect of the transient 2-pyridinium-dicyanomethylide. In the reaction of **2** with 2 equiv of TCNEO, extra amount of TCNEO can attack the 2-pyridyl group of **2a** to form **2c**. No formation of a dicyanomethylene-bridged adduct to the Co–S bond indicates that the any pyridyl groups are more nucleophilic than the sulfur atom of the dithiolene ligand in **1–3**. Such dicyanomethylene-bridged adduct has been formed while the complex has a weakly nucleophilic group such as methoxycarbonyl ( $\text{CO}_2\text{Me}$ ) or phenyl group [18] (Chart 1).

Some new CpCo dithiolene complexes,  $[\text{CpCo}(\text{S}_2\text{C}_2(^4\text{Py})(2\text{-thienyl}))]$  (**4**) or  $[\text{CpCo}(\text{S}_2\text{C}_2(^3\text{Py})(2\text{-thienyl}))]$  (**5**), were prepared in 10% or 14% yield from the one-pot reaction of  $[\text{CpCo}(\text{CO})_2]$ , elemental sulfur and *n*-(2-thienylethynyl)pyridines ( $n = 3$  or 4). These one-pot reactions relatively gave lower yield than the case of **2**. Probably, an electron-donating thienyl group could reduce the electrophilicity of the acetylene precursors. The reactions of TCNEO (2 equiv) with **4** or **5** in refluxing THF successfully formed the corresponding dicyanomethylated complex  $[\text{CpCo}(\text{S}_2\text{C}_2(^4\text{Py}-\text{C}(\text{CN})_2)(2\text{-thienyl}))]$  (**4a**) (32% yield) or  $[\text{CpCo}(\text{S}_2\text{C}_2(^3\text{Py}-\text{C}(\text{CN})_2)(2\text{-thienyl}))]$  (**5a**) (32% yield), respectively (Scheme 2). A bridging reaction of dicyanomethylene group to the Co–S bond did not occur. Note that the formation of **4a** suggests that the dicyanomethylene group can be also introduced on the 3-pyridyl group without any steric effects. A dicyanomethylated acetylene derivative was not obtained. This fact may indicate that TCNEO does not attack the 2-thienyl group of **4** or **5**.

Crystal structure of **1b** was obtained by the X-ray diffraction study. **1b** crystallized in the triclinic system with space group *P*-1. This crystal contained one cocrystallized dichloromethane in the unit cell. Fig. 1 exhibits the ORTEP drawing of **1b** and definitely prove that there are two dicyanomethylene groups on the 4-pyridyl groups. The central cobalt atom has formally coordinative unsaturation with 16-electron. This is a typical two-legged piano stool geometry, because the cobaltadithiolene plane is located at a perpendicular position with respect to the Cp ligand. Some selected bond lengths and angles are shown in Fig. 1 caption. The Co–S bond lengths are 2.098(4) and 2.105(3) Å that are slightly shorter than those of typical  $\text{Co}^{\text{III}}-\text{SR}$  bond lengths (2.25–2.48 Å) [34] because of a strong  $\pi$ -donation from sulfur to the electron-



Scheme 1.



Scheme 2.

poor cobalt atom [35]. The all bond lengths in the pyridinium-dicyanomethylide moieties of **1b** are comparable with those of free pyridinium-dicyanomethylide [36]. Namely, we can expect a strong near-UV absorption in **1b** due to the strong chromophore groups.

## 2.2. Electronic absorption and electrochemical behavior

The UV–vis absorption spectra of dithiolenes complexes were obtained in dichloromethane solution (Fig. 2). The spectral data ( $\lambda_{\max}$ /nm and  $\epsilon/M^{-1}\text{cm}^{-1}$ ) are summarized in Table 1. The all complexes showed electronic absorption in the range of 605–644 nm based on the LMCT [37] and exhibited very strong absorption in the range of 413–470 nm (near-UV) due to the pyridinium-dicyanomethylide moiety [20]. Similar near-UV absorption was found in the dithiolenes-free compound **2c** (462 nm). While focused on the LMCT absorption, the  $\lambda_{\max}$  values of the dicyanomethylated complexes (**1a**, **1b**, **2a**, and **4a**) are lower energy than

those of the corresponding dicyanomethylene-free [CpCo(dithiolenes)] complexes (**1**, **2**, and **4**) except **5** (617 nm) vs **5a** (605 nm). One reason for that is difference of the dicyanomethylated position (<sup>4</sup>Py vs <sup>3</sup>Py). While focused on the near-UV absorption, the bisdicyanomethylated complex **1b** ( $\epsilon = 43,400\text{ M}^{-1}\text{cm}^{-1}$ ) has much higher  $\epsilon$  value than those of the monodicyanomethylated complexes ( $\epsilon = 23,600\text{--}32,300\text{ M}^{-1}\text{cm}^{-1}$ ). In the CpM dithiolenes complexes of the group 9 metals, the LMCT absorption energy becomes lower in order of the  $\text{Co} > \text{Rh} > \text{Ir}$  complexes. The blue shift of the LMCT band with an increase in atomic number is due to the d-orbital energy level of the metal. In fact, [Cp\*Ir(dithiolenes)] complexes have exhibited near-UV absorption based on the LMCT (dithiolenes =  $\text{S}_2\text{C}_2(\text{H})(\text{Ph})$  (450 nm,  $8800\text{ M}^{-1}\text{cm}^{-1}$ ),  $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2$  (416 nm,  $8000\text{ M}^{-1}\text{cm}^{-1}$ ) [38], but those  $\epsilon$  values have been much smaller compared with those near-UV absorption of the all dicyanomethylated complexes in this work.

The cyclic voltammograms (CVs) of [CpCo(dithiolenes)] complexes and the dicyanomethylated complexes are shown in Fig. 3 and their redox potentials are summarized in Table 2. The dicyanomethylene-free [CpCo(dithiolenes)] complexes **1**, **2**, **4** and **5** showed single reversible reduction waves at  $-1.17\text{ V}$ ,  $-1.25\text{ V}$ ,  $-1.19\text{ V}$  and  $-1.22\text{ V}$  (vs Fc/Fc<sup>+</sup>), respectively. These are attributed to  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  redox couples. On the other hand, the all complexes displayed irreversible oxidation waves around  $+0.5\text{ V}$ . In addition, the all dicyanomethylated complexes showed second reduction waves. Note that the second reduction wave of the bisdicyanomethylated complex **1b** at  $-1.70\text{ V}$  is almost twice larger than the first reduction wave at  $-0.93\text{ V}$  (Fig. 3(c)). This result suggests that probably the second wave is two-electron reaction in **1b** and is corresponding to the reductions at the two pyridinium-dicyanomethylide moieties. In fact, the second reduction waves of monodicyanomethylated complexes **1a**, **2a**, **4a** and **5a** supported one-electron waves at  $-2.08\text{ V}$ ,  $-2.19\text{ V}$ ,  $-2.13\text{ V}$  and  $-2.26\text{ V}$ , respectively. The first reduction potentials of the all dicyanomethylated complexes became more positive than those of the corresponding dicyanomethylene-free complexes, because of an electron-withdrawing effect of the dicyanomethylene group.

The spectroelectrochemical measurement of **1b** was performed using an optically transparent thin-layer electrode (OTTLE) cell. Fig. 4 shows visible spectral changes during electrolysis at  $-1.3\text{ V}$  (vs Fc/Fc<sup>+</sup>) for **1b**<sup>-</sup>. The initial absorption with  $\lambda_{\max} = 644\text{ nm}$ , which is attributed to the LMCT in the dithiolenes ring, decreased during 2 min with isosbestic points at 428 and 516 nm (Fig. 4(a)).

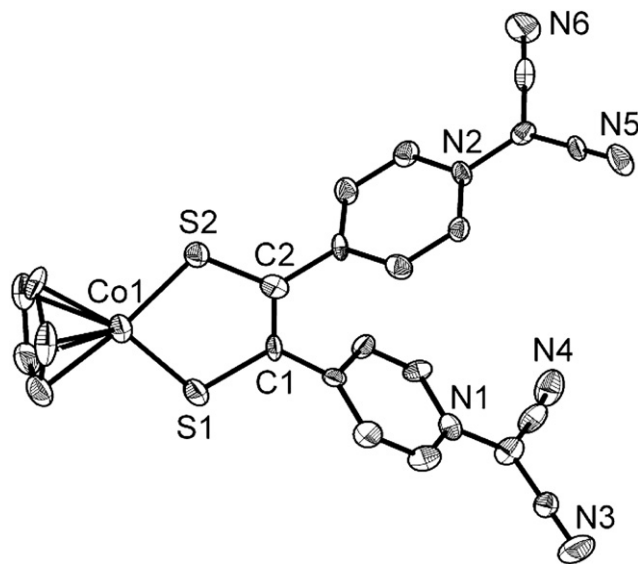


Fig. 1. Molecular structure of **1b**. Thermal ellipsoids are drawn at 30% probability. Co-crystallized dichloromethane is not shown for simplicity. Selected bond lengths (Å): Co1–S1 = 2.098(4), Co1–S2 = 2.105(3), S1–C1 = 1.734(11), S2–C2 = 1.710(13), C1–C2 = 1.344(17). Selected bond angles (°): S1–Co–S2 = 91.93(14), Co–S1–C1 = 104.3(4), Co–S2–C2 = 105.5(4), S1–C1–C2 = 119.7(10), S2–C2–C1 = 118.5(9). Selected dihedral angles (°): Co–dithiolenes/Cp = 92.299. Co–dithiolenes/4-Py = 59.478, 61.487.

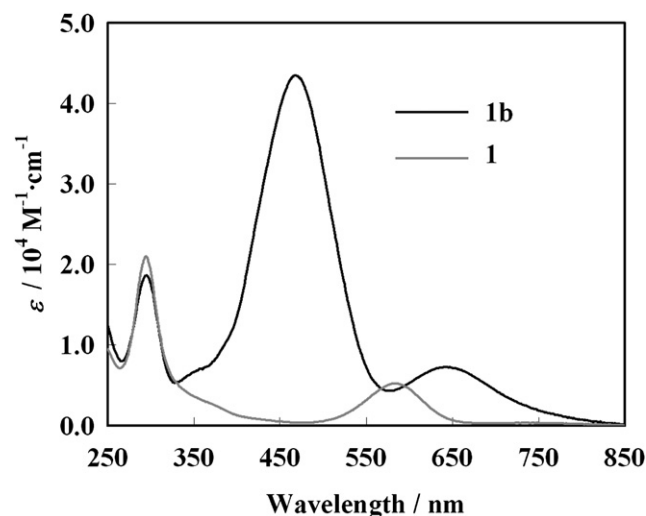


Fig. 2. UV–vis spectra of **1** (gray) and **1b** (black) in dichloromethane solution at room temperature.

**Table 1**  
UV–vis spectral data.

	Pyridinium-dicyanomethylide		Dithiolene LMCT	
	$\lambda_{\max}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\max}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$
<b>1a</b>	454	26,200	616	7500
<b>1b</b>	470	43,400	644	7300
<b>1</b>	–	–	585	5200
<b>2a</b>	459	23,600	615	7000
<b>2c</b>	462	33,200	–	–
<b>2</b>	–	–	584	8000
<b>4a</b>	461	32,300	638	9200
<b>4</b>	–	–	611	6900
<b>5a</b>	413	29,700	605	9000
<b>5</b>	–	–	617	6400

Reoxidation of the reduced species perfectly recovered the original spectrum for the neutral **1b** upon electrolysis for 2 min at  $-0.5$  V (Fig. 4(b)). This complete reversibility explains that the reduced **1b<sup>-</sup>** is stable enough for several minutes. Furthermore, visible spectral measurements were carried out at  $-2.0$  V with the second reduction for the trianion **1b<sup>3-</sup>** during 1 min. The absorption totally decreased (Fig. 4(c)) and the spectrum was not recovered after reoxidation at  $-1.3$  V (Fig. 4(d)). Although there was enough reversibility of the **1b<sup>3-</sup>/1b<sup>-</sup>** process on the CV measurement time scale (Fig. 3(c)), the spectroelectrochemical measurement indicated that the reduced trianion **1b<sup>3-</sup>** was unstable during several minutes. An early paper has described electrochemical reduction of free pyridinium-dicyanomethylide, and has proposed that the reduced species undergoes either a dimerization or C–N bond cleavage [39]. However, we assume that a following chemical reaction of **1b<sup>3-</sup>** is not simple to discuss because the remarkable absorption of dithiolene ring (644 nm) was never recovered again.

According to the OTTL spectral measurement,  $1e^-$  reduced species is stable enough for any spectroelectrochemical measurements with bulk electrolysis. The ESR spectra of electrochemically

**Table 2**  
Redox potentials (vs Fc/Fc<sup>+</sup>)

	$E_{1/2}(\text{red})/\text{V}^a$	$E_{1/2}(2\text{red})/\text{V}^a$
<b>1</b>	-1.17	– <sup>b</sup>
<b>1a</b>	-1.02	-2.08
<b>1b</b>	-0.93	-1.70
<b>2</b>	-1.25	– <sup>b</sup>
<b>2a</b>	-1.09	-2.19
<b>4</b>	-1.19	– <sup>b</sup>
<b>4a</b>	-1.07	-2.13
<b>5</b>	-1.22	– <sup>b</sup>
<b>5a</b>	-1.10	-2.26

<sup>a</sup>  $E_{1/2}$ , half-wave potential =  $|E_{\text{pc}} + E_{\text{pa}}|/2$ .

<sup>b</sup> Not found.

generated **1<sup>-</sup>**, **1a<sup>-</sup>** and **1b<sup>-</sup>** were obtained (Fig. 5). In this work, we also measured the ESR of electrochemically formed  $[\text{CpCo}^{\text{II}}(\text{mnt})]^-$  (mnt = maleonitrile-1,2-dithiolate) for a sake of comparison. The all **1<sup>-</sup>**, **1a<sup>-</sup>** and **1b<sup>-</sup>** showed eight hyperfine splittings due only to the interaction with the nuclear spin of cobalt ( $I = 7/2$ ) and not to that of nitrogen atom ( $I = 1$ ). Those  $g_{\text{iso}}$  and  $A_{\text{iso}}$  values are as follows (Table 3):  $g_{\text{iso}} = 2.094$ ,  $A_{\text{iso}} = 4.1$  mT (**1<sup>-</sup>**),  $g_{\text{iso}} = 2.092$ ,  $A_{\text{iso}} = 4.2$  mT (**1a<sup>-</sup>**) and  $g_{\text{iso}} = 2.092$ ,  $A_{\text{iso}} = 4.2$  mT (**1b<sup>-</sup>**). These data are clearly due to  $\text{Co}^{\text{II}}$  species and comparable with the electrochemically generated  $[\text{CpCo}^{\text{II}}(\text{mnt})]^-$  (Table 3) and other  $[\text{CpCo}^{\text{II}}(\text{dithiolene})]$  complexes as previously reported [40]. Namely, the first reduction sites of **1a** and **1b** are the  $\text{Co}^{\text{III}}$  centers but are not pyridinium-dicyanomethylide moiety. The all  $g_{\text{iso}}$  values are larger than those of the paramagnetic neutral  $[\text{CpNi}(\text{dithiolene})]^0$  complexes ( $g_{\text{iso}} = 2.041$ – $2.053$ ) (Table 3) [41]. Delocalized spin densities in  $[\text{CpNi}(\text{dithiolene})]^0$  complexes were theoretically observed and mostly occupied on the dithiolene and Cp ligand with little metal contribution [42]. On the other hand, relatively larger metal contribution is plausible in the electrochemically generated  $[\text{CpCo}^{\text{II}}(\text{dithiolene})]^-$  complexes.

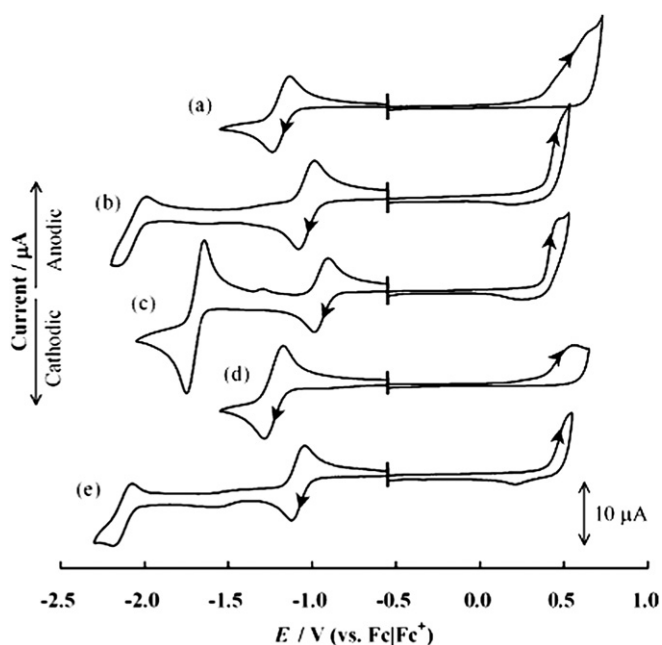
### 3. Conclusion

In this work, some dicyanomethylated  $[\text{CpCo}(\text{dithiolene})]$  complexes were synthesized and they showed strong near-UV absorption ( $\epsilon = 23,600$ – $43,400$   $\text{M}^{-1}\text{cm}^{-1}$ ) due to the pyridinium-dicyanomethylide moiety and visible absorption ( $\epsilon = 7000$ – $9200$   $\text{M}^{-1}\text{cm}^{-1}$ ) based on the LMCT. Therefore, this system involves two near-UV and visible chromophores. The absorption intensity of the near-UV almost depends on the number of the pyridinium-dicyanomethylide group and we nicely developed new chromophores using a mononuclear–monodithiolene system. Here we can propose how we can introduce more pyridinium-dicyanomethylide group to a dithiolene complex, thus; bisdithiolene  $[\text{M}(\text{dithiolene})_2]$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{Au}$ ) [43] or trisdithiolene  $[\text{M}(\text{dithiolene})_3]$  ( $\text{M} = \text{Mo}, \text{W}$ ) [44] complexes can include four or six pyridinium-dicyanomethylide groups on the dithiolene ligands with more than  $\epsilon = 10^5$   $\text{M}^{-1}\text{cm}^{-1}$  as expected.

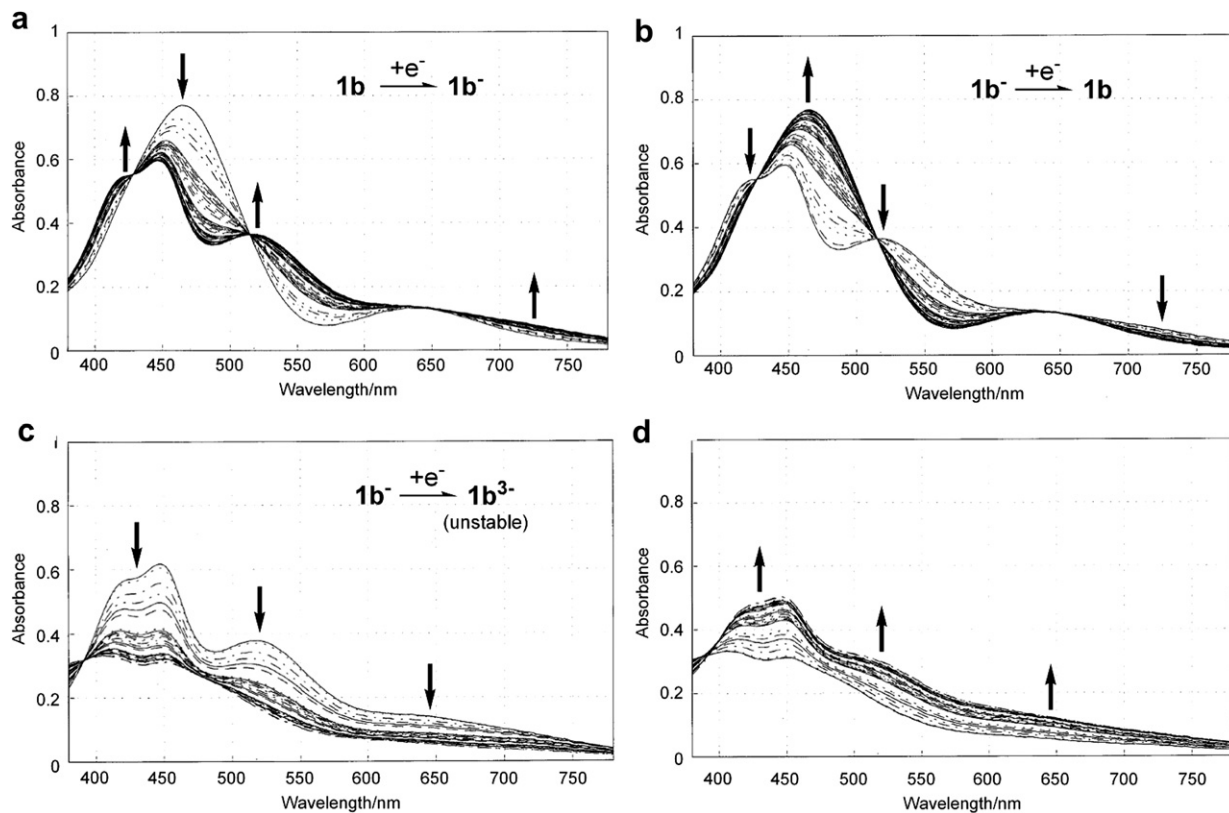
### 4. Experimental section

#### 4.1. General remarks

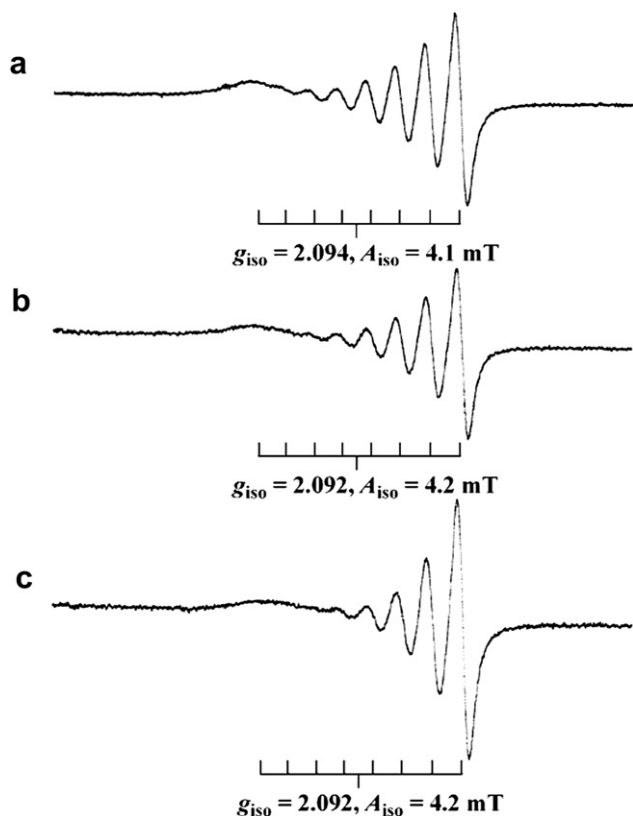
All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. All solvents for reactions (THF and xylene) were purified by distillation from Na-benzophenone. Silica gel (Wakogel C-300) was obtained from Wako Pure Chemical Industries, Ltd. TCNEO was obtained from Tokyo Chemical Industry Co., Ltd.  $[\text{CpCo}(\text{CO})_2]$  [45], **1**, **2**, **3** [46], **1a** and **1b** [18], 4-(2-thienylethynyl)pyridine and 3-(2-thienylethynyl)pyridine



**Fig. 3.** Cyclic voltammograms of (a) **1**, (b) **1a**, (c) **1b**, (d) **2**, and (e) **2a** in dichloromethane solution ( $c = 1 \times 10^{-3}$   $\text{mol dm}^{-3}$ ,  $v = 100$   $\text{mV s}^{-1}$ ,  $\phi = 1.6$  mm Pt disk as a working electrode) containing  $0.1$   $\text{mol dm}^{-3}$  tetra-*n*-butylammonium perchlorate (TBAP) at room temperature.



**Fig. 4.** The visible spectral changes of complex **1b** during (a) 1st reduction at  $-1.3$  V for 2 min, (b) reoxidation of  $1b^-$  at  $-0.5$  V for 2 min, (c) 2nd reduction at  $-2.0$  V for 1 min after 1st reduction for 2 min, and (d) reoxidation at  $-1.3$  V for 1 min after (c) using OTTE cell.



**Fig. 5.** ESR spectra of electrochemically generated (a)  $1^-$ , (b)  $1a^-$  and (c)  $1b^-$  in TBAP-dichloromethane solution at room temperature.

[47] were prepared by literature methods. Mass and IR spectra were recorded on a JEOL JMS-D300 and a Shimadzu model FTIR 8600PC, respectively. NMR spectra were measured with a JEOL LA500 spectrometer. UV–vis spectra were recorded on a Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument.

#### 4.2. Reaction of $[CpCo(S_2C_2(^2Py)(^4Py))]^-$ (**2**) with TCNEO

**2** (100 mg, 0.27 mmol) reacted with TCNEO (39 mg, 0.27 mmol) in refluxing THF (50 ml) for 3 h. An initial blue solution was changed to greenish-brown. Solvent was removed under reduced pressure, and the mixture was separated by column chromatography on silica gel (eluent = dichloromethane). A resulted green product was further purified by recrystallization from dichloromethane and *n*-hexane. **2a** was obtained in 28% yield (34 mg).

**Table 3**

ESR data of paramagnetic  $[CpM(\text{dithiolene})]$  ( $M = Co^{II}$  and  $Ni^{III}$ ) complexes

Complex	$g_{iso}$	$A_{iso}/mT$	Ref.
<b>1<sup>-</sup></b>	2.094	4.1	This work
<b>1a<sup>-</sup></b>	2.092	4.2	This work
<b>1b<sup>-</sup></b>	2.092	4.2	This work
$[CpCo^{II}(mnt)_2]^-$	2.093	4.1	This work
$[CpCo^{II}(S_2C_2(CO_2Me)_2)]^-$	2.11	3.84	[40]
$[CpCo^{II}(S(SMe)C_2(CO_2Me)_2)]^0$	2.11	2.70	[40]
$[CpNi^{III}(mnt)]^0$	2.0487	— <sup>a</sup>	[41]
$[CpNi^{III}(S_2C_2(CO_2Me)_2)]^0$	2.0460	— <sup>a</sup>	[41]

<sup>a</sup> Not detected.

#### 4.3. Reaction of $[\text{CpCo}(\text{S}_2\text{C}_2(^2\text{Py})(^4\text{Py}))]$ (**2**) with excess TCNEO

A solution of **2** (110 mg, 0.3 mmol) and TCNEO (86 mg, 0.6 mmol) in THF (70 ml) was refluxed for 3 h. After the reaction, solvent was removed under reduced pressure. Resulted residue was separated by column chromatography on silica gel (eluent = dichloromethane). Orange solids  $^2\text{Py}-\text{C}\equiv\text{C}-(^4\text{Py}-\text{C}(\text{CN})_2)$  (**2c**) were obtained in 73% yield.

**2a.** Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 432 ( $[\text{M}^+]$ , 36), 368 ( $[\text{M}^+ - \text{C}(\text{CN})_2]$ , 100), 304 ( $[\text{M}^+ - \text{S}_2\text{C}(\text{CN})_2]$ , 36), 188 ( $[\text{CpCoS}_2^+]$ , 85), 124 ( $[\text{CpCo}^+]$ , 31).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.49 (d,  $J$  = 1.0 Hz, 1H, Py), 8.13 (d,  $J$  = 7.0 Hz, 2H, Py), 7.69 (t,  $J$  = 1.0 Hz, 1H, Py), 7.45 (d,  $J$  = 7.0 Hz, 2H, Py), 7.34 (d,  $J$  = 6.0 Hz, 1H, Py), 7.45 (t,  $J$  = 2.0 Hz, 1H, Py), 5.49 (s, 5H, Cp).  $^{13}\text{C}$  NMR (DMSO, 125 MHz)  $\delta$  = 161.4, 158.2 (dithiolene-C), 149.5, 145.8, 136.9, 137.1, 130.8, 126.1, 124.2, 123.2 (Py), 118.1 (CN), 80.6 (Cp), 58.7 (C(CN) $_2$ ). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 615 (7000), 459 (23,600), 294 (21,100). IR (KBr disk) 2185, 2145  $\text{cm}^{-1}$  (C $\equiv$ N). Anal. Calcd. For  $\text{C}_{20}\text{H}_{13}\text{CoN}_4\text{S}_2$ : C, 55.55; H, 3.03; N, 12.96. Found: C, 55.63; H, 3.09; N, 12.68.

#### 4.4. Reaction of $^2\text{Py}-\text{C}\equiv\text{C}-^4\text{Py}$ with TCNEO

A solution of  $^2\text{Py}-\text{C}\equiv\text{C}-^4\text{Py}$  (200 mg, 1.12 mmol) and TCNEO (320 mg, 2.24 mmol) was reacted in refluxing THF (50 ml) for 3 h. After removing solvent, resulted residue was separated by column chromatography on silica gel (eluent = dichloromethane). An orange product  $^2\text{Py}-\text{C}\equiv\text{C}-(^4\text{Py}-\text{C}(\text{CN})_2)$  (**2c**) was obtained in 46% (113.4 mg) yield.

**2c.** Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 244 ( $[\text{M}^+]$ , 36), 180 ( $[\text{M}^+ - \text{C}(\text{CN})_2]$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.68 (d,  $J$  = 1.0 Hz, 1H, Py), 8.36 (d,  $J$  = 7.0 Hz, 2H, Py), 7.77 (t,  $J$  = 1.0 Hz, 1H, Py), 7.62 (d,  $J$  = 7.0 Hz, 2H, Py), 7.42 (d,  $J$  = 6.0 Hz, 1H, Py), 7.36 (t,  $J$  = 2.0 Hz, 1H, Py).  $^{13}\text{C}$  NMR (DMSO, 125 MHz)  $\delta$  = 150.7, 141.5, 136.6, 130.4, 129.3, 127.9, 125.2, 124.3 (Py), 116.5 (CN), 97.6, 84.2 (C $\equiv$ C), 67.1 (C(CN) $_2$ ). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 462 (33,200), 300 (6600). IR (KBr disk) 2188, 2150  $\text{cm}^{-1}$  (C $\equiv$ N). Anal. Calcd. For  $\text{C}_{15}\text{H}_8\text{N}_4$ : C, 73.76; H, 3.30; N, 22.94. Found: C, 73.57; H, 3.21; N, 22.66.

#### 4.5. One-pot reaction of $[\text{CpCo}(\text{CO})_2]$ , elemental sulfur and **2c**

The mixture of  $[\text{CpCo}(\text{CO})_2]$  (0.041 ml, 0.29 mmol), elemental sulfur (20 mg, 0.57 mmol) and **2c** (70 mg, 0.29 mmol) were reacted in refluxing xylene (60 ml) for 17 h. An initial brown solution was changed to dark blue. After the reaction, solvent was removed under reduced pressure. The resulted mixture was separated by column chromatography on silica gel (eluent = dichloromethane/*n*-hexane). A blue product (**2a**) was isolated in 71% yield.

#### 4.6. Syntheses of $[\text{CpCo}(\text{S}_2\text{C}_2(^4\text{Py})(2\text{-thienyl}))]$ (**4**) and $[\text{CpCo}(\text{S}_2\text{C}_2(^3\text{Py})(2\text{-thienyl}))]$ (**5**) by one-pot reaction

$[\text{CpCo}(\text{CO})_2]$  (1.17 g, 0.92 ml, 6.50 mmol), elemental sulfur (0.416 g, 13.0 mmol) and (2-thienylethynyl)pyridine (1.20 g, 6.5 mmol) were reacted in refluxing xylene (50 ml) for 17 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography on aluminium oxide (eluent: *n*-hexane:dichloromethane = 2:5). Resulted product was further purified by recrystallization from dichloromethane/*n*-hexane. Dark blue products **4** and **5** were obtained in yields of 10% and 14%, respectively.

**4.** Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 373 ( $[\text{M}^+]$ , 100), 309 ( $[\text{M}^+ - \text{S}_2]$ , 25), 188 ( $[\text{CpCoS}_2^+]$ , 45), 185 ( $[\text{M}^+ - \text{CpCoS}_2]$ , 50), 124 ( $[\text{CpCo}^+]$ , 18).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.56 (m, 2H, Py), 7.26 (m, 2H, Py), 7.25 (d,  $J$  = 3.7 Hz, 1H, thienyl), 6.84 (dd,  $J$  = 3.7 Hz, 1H, thienyl), 6.74 (d,  $J$  = 3.7 Hz, 1H, thienyl), 5.41 (s, 5H, Cp).

UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 611 (6900), 342 (7300). HR-mass Calcd. For  $\text{C}_{16}\text{H}_{12}\text{CoNS}_3$ : 372.9464. Found: 372.9468.

**5.** Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 373 ( $[\text{M}^+]$ , 100), 309 ( $[\text{M}^+ - \text{S}_2]$ , 18), 188 ( $[\text{CpCoS}_2^+]$ , 48), 185 ( $[\text{M}^+ - \text{CpCoS}_2]$ , 44), 124 ( $[\text{CpCo}^+]$ , 21).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.84 (m, 1H, Py), 8.63 (m, 1H, Py), 7.83 (d,  $J$  = 7.5 Hz, 1H, Py), 7.58 (d,  $J$  = 7.9 Hz, 1H, Py), 7.23 (d,  $J$  = 5.0 Hz, 1H, thienyl), 6.83 (dd,  $J$  = 5.0 Hz, 1H, thienyl), 6.81 (d,  $J$  = 5.0 Hz, 1H, thienyl), 5.41 (s, 5H, Cp). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 617 (6400), 341 (6600). HR-mass Calcd. For  $\text{C}_{16}\text{H}_{12}\text{CoNS}_3$ : 372.9464. Found: 372.9469.

#### 4.7. Reaction of $[\text{CpCo}(\text{S}_2\text{C}_2(^4\text{Py})(2\text{-thienyl}))]$ (**4**) or $[\text{CpCo}(\text{S}_2\text{C}_2(^3\text{Py})(2\text{-thienyl}))]$ (**5**) with TCNEO

Complex **4** (50 mg, 0.13 mmol) reacted with TCNEO (39 mg, 0.27 mmol) in refluxing THF (30 ml) for 3 h. Solvent was removed under reduced pressure, and the mixture was separated by chromatography on aluminium oxide (eluent = dichloromethane). A blue green product **4a** was obtained in 32% yield (18 mg). **5a** was obtained from **5** with TCNEO in 32% yield.

**4a.** Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 437 ( $[\text{M}^+]$ , 35), 373 ( $[\text{M}^+ - \text{C}(\text{CN})_2]$ , 100), 188 ( $[\text{CpCoS}_2^+]$ , 86), 124 ( $[\text{CpCo}^+]$ , 18).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.13 (d,  $J$  = 6.5 Hz, 2H, Py), 7.42 (d,  $J$  = 6.5 Hz, 1H, Py), 7.33 (d,  $J$  = 1.6 Hz, 1H, thienyl), 6.92 (t,  $J$  = 1.6 Hz, 1H, thienyl), 6.82 (d,  $J$  = 1.6 Hz, 1H, thienyl), 5.43 (s, 5H, Cp). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 638 (9200), 461 (32,300). IR (KBr disk) 2181, 2140  $\text{cm}^{-1}$  (C $\equiv$ N). HR-mass Calcd. For  $\text{C}_{19}\text{H}_{12}\text{CoN}_3\text{S}_3$ : 436.9525. Found: 436.9520.

**5a.** Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 437 ( $[\text{M}^+]$ , 40), 373 ( $[\text{M}^+ - \text{C}(\text{CN})_2]$ , 100), 188 ( $[\text{CpCoS}_2^+]$ , 78), 124 ( $[\text{CpCo}^+]$ , 26).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.42 (s, 1H, Py), 8.33 (d,  $J$  = 5.3 Hz, 1H, Py), 7.37 (m, 1H, Py), 7.36 (m, 1H, thienyl), 7.28 (m, 1H, Py), 6.98 (t,  $J$  = 3.7 Hz, 1H, thienyl), 6.93 (d,  $J$  = 1.3 Hz, 1H, thienyl), 5.50 (s, 5H, Cp). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 605 (9000), 413 (29,700). IR (KBr disk) 2180, 2139  $\text{cm}^{-1}$  (C $\equiv$ N). HR-mass Calcd. For  $\text{C}_{19}\text{H}_{12}\text{CoN}_3\text{S}_3$ : 436.9525. Found: 436.9519.

#### 4.8. CV measurements

All electrochemical measurements were performed under an argon atmosphere. Dichloromethane for electrochemical measurements were dried by molecular sieve 4A before use. A platinum wire served as a counter electrode, and the reference electrode Ag/AgCl was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc $^+$ ) couple. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode. The Model CV-50W instrument from BAS Co. was used for cyclic voltammetry (CV) measurements. CVs were measured in 1  $\text{mmol} \cdot \text{dm}^{-3}$  dichloromethane solutions of complexes containing 0.1  $\text{mol} \cdot \text{dm}^{-3}$  tetra-*n*-butylammonium perchlorate (TBAP) at 25 °C.

#### 4.9. Visible absorption spectral measurements during electrolysis

The visible absorption spectra were obtained during electrolysis for 0.5  $\text{mmol} \cdot \text{dm}^{-3}$  dichloromethane solutions of complexes containing 0.2  $\text{mol} \cdot \text{dm}^{-3}$  TBAP at 25 °C in an optically transparent thin-layer electrode (OTTLE, thin-layer thickness = 0.4 mm) [48] cell. Measurements were made with MCPD-7000 rapid scan spectrometer and MC-2530 of Otsuka Electronics Co., Ltd. The working electrode was stationary platinum mesh in thin-layer form.

#### 4.10. ESR measurements

ESR spectra were obtained for ca. 5  $\text{mmol} \cdot \text{dm}^{-3}$  dichloromethane solutions of complexes containing 0.1  $\text{mol} \cdot \text{dm}^{-3}$  TBAP at

**Table 4**  
Crystallographic data

Compound	<b>1b</b> ·(CH <sub>2</sub> Cl <sub>2</sub> )
Formula	C <sub>24</sub> H <sub>15</sub> Cl <sub>2</sub> CoN <sub>6</sub> S <sub>2</sub>
FW (g mol <sup>-1</sup> )	581.38
Crystal color	Greenish brown
Crystal shape	Platelet
Crystal size (mm)	0.07 × 0.07 × 0.02
Crystal system	Triclinic
Space group	P-1 (No. 2)
T (K)	298
a (Å)	8.665(4)
b (Å)	10.692(6)
c (Å)	13.714(7)
α (°)	88.471(14)
β (°)	77.756(12)
γ (°)	84.600(13)
V (Å <sup>3</sup> )	1236.1(11)
Z	2
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.562
μ (mm <sup>-1</sup> )	1.105
Total refls.	9862
Unique refls. (R <sub>int</sub> )	5422 (0.088)
Unique refls. (I > 2σ(I))	2974
R <sub>1</sub> , wR <sub>2</sub> (I > 2σ(I))	0.0506, 0.1142
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.1069, 0.2487
Goodness-of-fit	1.029

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}.$$

293 K by electrolysis. ESR spectra were recorded on a JEOL X-band JES-3X ESR spectrometer. Microwave frequencies and the magnetic field were directly determined by using a microwave counter, ADVANTEST TR5212, and a field measurement unit, JEOL NMR field meter ES-FC-5, respectively.

#### 4.11. X-ray diffraction study

The single crystal of **1b**·(CH<sub>2</sub>Cl<sub>2</sub>) was obtained from recrystallization by vapor diffusion of hexane into the dichloromethane solution. Crystal was mounted on the top of a thin glass fiber. Measurement was made on Rigaku Mercury CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and expanded Fourier techniques [49]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and these were not refined. Absorption corrections were applied. All calculations for **1b**·(CH<sub>2</sub>Cl<sub>2</sub>) were performed using the Crystal Structure software package [50]. Crystallographic data are summarized in Table 4.

#### Appendix A. Supplementary material

CCDC No. 772,632 contains crystallographic data for the structural analysis of compound **1b**·CH<sub>2</sub>Cl<sub>2</sub>. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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