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Syntheses of the Terpyridine−Bipyridine Linked Binary Ligands and Structural and Redox Properties of Their Cobalt Complexes

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New binary ligands consisting of 2,2′:6′,2″-terpyridine and 2,2′-bipyridine were synthesized through the linkage of various lengths of the polymethylene chain (**1a**−**1d**; $n=3-6$, where n is the number of CH_2 units). Their Co(II) complexes, **2a**−**2d** (Cl complexes) and **2a**′−**2d**′ (H_2O complexes), were synthesized. They exclusively formed mononuclear complexes, which could be oxidized to Co(III) complexes in aqueous solutions after prolonged exposure to the air. The single crystals of **2b** and Co(III) complex **2c**″ were obtained, and their crystal structures were determined. Cyclic voltammograms of the Co(II) complexes showed the redox processes of the terpyridine, Co(II)/Co(I), and Co(III)/Co(II). The redox waves of Co(II)/Co(I) in **2a** and **2a**′ were slightly different from those of other complexes because of the short polymethylene chain.

Introduction

Polypyridyl ligands, such as 2,2′:6′,2″-terpyridine (trpy), 2,2′-bipyridine (bpy), and 1,10-phenanthroline (phen), are intriguing ligands for constructing various photo- and redox-active complexes.[1] Among these, terpyridine derivatives are particularly unique from the viewpoint of structural coordination chemistry. Because of their planar nature, the terpyridine derivatives function almost exclusively as meridional tridentate ligands, and the structural changes are restricted when the oxidation state of the center changes. On the basis of these characteristics, one effective use of terpyridine ligands is to combine them with other "auxiliary" ligands and to form "mixed-ligand" complexes.[2] In these complexes, the terpyridine ligands tune the various properties of the complexes. The auxiliary ligands are often bidentate, so that one of the octahedral coordination sites can be vacant and utilized for catalytic reactions.

These mixed-ligand terpyridine complexes are synthesized with various 4d and 5d metal ions such as ruthenium, rhodium, osmium, and iridium.[2] As for the 3d metal ions, the mixed-ligand complexes should be more difficult to isolate, because of the high tendency of ligand substitution of 3d metals in comparison with that of the 4d and 5d metals. Nevertheless, the mixed-ligand complexes of 3d metals should be worth investigating, because they are likely to present interesting characteristics hitherto unknown.

In order to synthesize the stable mixed-ligand complexes with the substitution labile 3d metals, a certain artifice is necessary in the ligand part. The most common approach is to use small-ring (five- or six-membered) chelates involving the metal ions; this approach generally gives metal complexes with substantial chemical stability and conformational rigidity.[3] However, although these characteristics are useful for physical applications such as electron transport or luminescence, they are less attractive when catalytic chemistry is concerned, where conformational flexibility often plays an important role. An alternative approach is to connect the terpyridine and auxiliary ligands by polymethylene linkers. In such "binary" ligands, the two different ligands are

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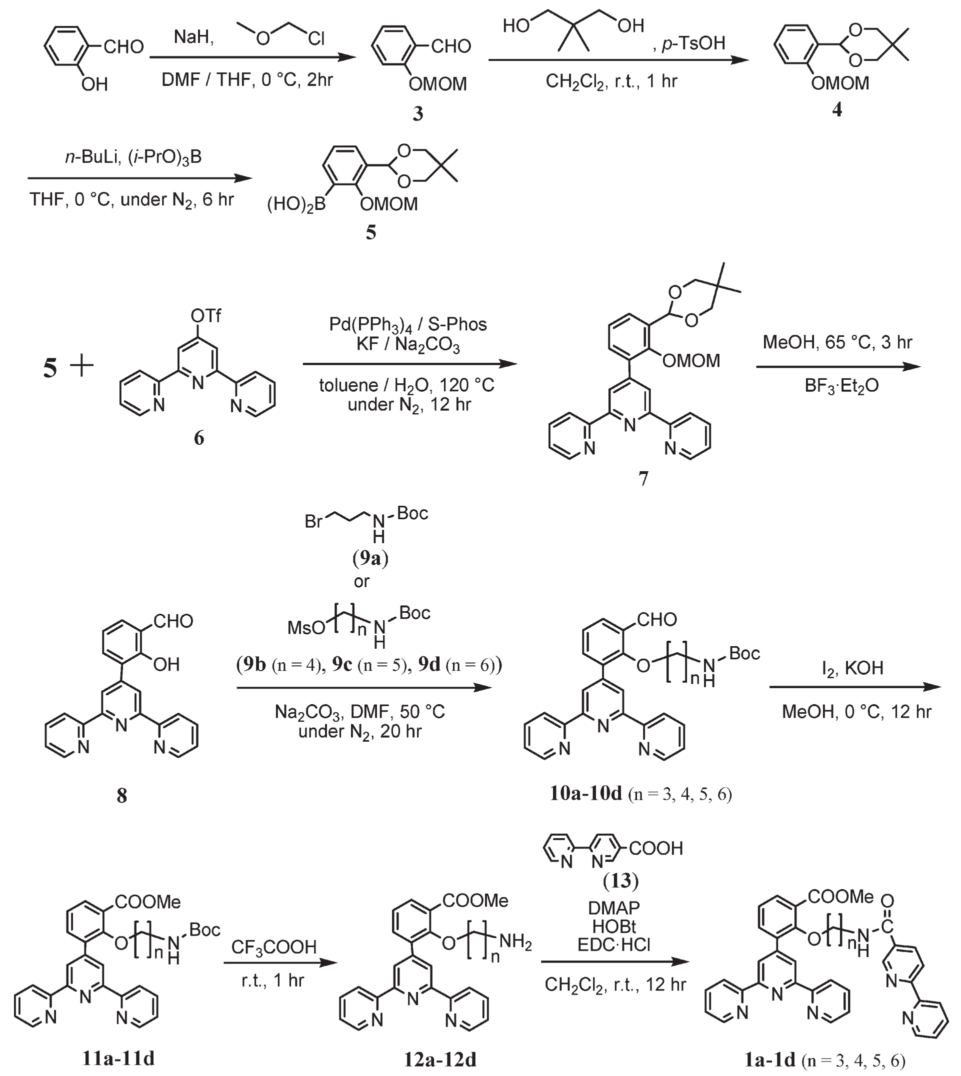
Scheme 1. Synthetic Routes for **1a**−**1d**



arranged closely so that the construction of mixed-ligand complexes is made easy and, at the same time, the connection is flexible enough for the complex to acclimate to the change of the chemical environments.

Among the 3d metals, we are currently interested in cobalt complexes. There are very few examples of mixed-ligand cobalt complexes containing terpyridines,[4] so that binary ligands should be effective. In our previous work, we synthesized the terpyridine−catechol−Co(III) complexes and discussed their structural and redox properties.[5] However, we would also like to work with Co(II) and Co(I) complexes, because Co(II) and Co(I) complexes exhibit various interesting chemistries, such as hydrogen production, the formation of metal−carbon bonds, reversible O_2 adsorption, and so on.[6] On the other hand, the mixed-ligand Co(II) (and Co(I)) complexes pose a greater challenge than the Co(III) complexes, because these ions are more labile toward ligand substitution than Co(III).

In this paper, we wish to report the syntheses of new terpyridine-based binary ligands, **1a**−**1d**, and their Co(II) complexes, **2a**−**2d** and **2a′**−**2d′**. We use bipyridine as the auxiliary ligand, which is more suitable for Co(II) systems than catechol. Because the bipyridine and terpyridine are used, the ligands act as the penta-dentate ligands, and one coordination site will be vacant. As we will see later, the ligand exchange at this site is crucial for the redox properties of the complexes. The crystal structures and redox properties of these complexes are also reported.

Results and Discussion

Ligand Design. The binary ligands **1a**−**1d** (Scheme 1) consist of the terpyridine and bipyridine units linked by polymethylene linkers of various lengths, which enables the change in the distance between the terpyridine and bipyridine units. The 1,2-phenylene group at the 4′ position of terpyridine acts as a fulcrum for the polymethylene linker and allows the conformational variation of the

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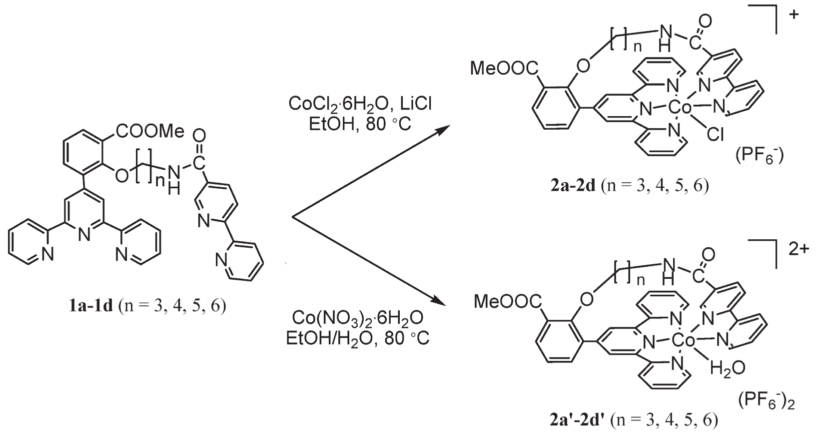
Scheme 2. Syntheses of Co(II) Complexes **2a**−**2d** and **2a′**−**2d′**



linker via the rotation along the phenylene−terpyridine bond.[7] The carboxylic ester group on the phenylene ring is intended for a connection of yet another functional group with additional capability (such as photoactivity). As a side effect, we later found that this group was also useful in restricting the conformation of the polymethylene linker.

The compounds **1a**−**1d** are designed with synthetic versatility in mind. The precursors of **1a**−**1d** are **11a**−**11d**, which have a *tert*-butoxycarbonyl (Boc) protected amino group at the end of the polymethylene linker, and the ester-protected carboxylic acid at the phenylene group. Consequently, various derivatives of **11a**−**11d** can be easily made by well-established synthetic methods of amino acids.[8]

Ligand Syntheses. The synthetic route of the binary ligands, **1a**−**1d**, is shown in Scheme 1. The key step is the introduction of the diprotected phenyl group at the 4′ position of terpyridine by the Suzuki−Miyaura coupling of **5** and **6**.[9] In our first attempt, we followed the procedure that we used in our previous work[5] (Pd(OAc)$_2$/P(*o*-tol)$_3$/Na$_2$CO$_3$/toluene/H$_2$O/MeOH); however, only a trace amount of **7** was obtained together with unchanged **5** and the hydrolyzed product **4**. After optimization of the reaction conditions, the best results were obtained when Pd(PPh$_3$)$_4$/S-Phos[10] and KF/Na$_2$CO$_3$ were used as the catalyst and the base, respectively. Under these conditions, product **7** was obtained very effectively and reproducibly.

Another step worth mentioning is the conversion of the formyl group to the carboxylic ester group (i.e., **10** to **11**). It was necessary that this reaction proceeded without the deprotection of the Boc group. In addition, the use of metal-based oxidants should be avoided if possible, because the formation of terpyridine-metal complexes might complicate the workup process. The reagents of choice were I$_2$ and KOH,[11,12] with careful control of the reaction temperature (see the Experimental Section).

The syntheses of the binary ligands were completed by the deprotection of *t*-butoxycarbonyl group and the condensation with 2,2′-bipyridine-4-carboxylic acid (**13**). The binary ligands **1a**−**1d** were purified by column chromatography and recrystallization and obtained as analytically pure, crystalline solids.

Syntheses of the Co(II) Complexes. The cobalt(II) complexes, **2a**−**2d** and **2a′**−**2d′**, were prepared from **1a**−**1d** by treatment with CoCl$_2$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O, respectively (Scheme 2). The compounds **2a**−**2d** were chloro complexes, whereas **2a′**−**2d′** were aqua complexes. These complexes were mononuclear complexes with 1:1 (metal/ligand) stoichiometry; neither the multinuclear complexes nor complexes with multiple ligands (like bis-terpyridine) were produced, as proven by the electrospray ionization (ESI)-mass spectrometry (vide infra).

Recrystallization of **2b** was performed by the diffusion of CH$_3$CN/MeOH over several weeks, and single crystals of [Co(**1b**)Cl](PF$_6$)·2CH$_3$OH (**2b**·2CH$_3$OH) were obtained. On the other hand, when recrystallization of **2c** was performed through the slow evaporation of a CH$_3$CN/H$_2$O mixed solvent over a few months, the obtained crystals were the Co(III) complexes, [Co(**1c**)-OH](PF$_6$)$_2$·H$_2$O (**2c″**·H$_2$O), as proven by the X-ray crystallographic analysis and ESI-mass spectrometry (vide infra). We assume that the oxidation took place during the prolonged exposure to the air. In fact, when a basic solution of **2c′** in EtOH/H$_2$O was exposed to O$_2$ for 1 day, the same Co(III) complex **2c″** was generated.

Structures of the Co Complexes. The crystal structures of **2b** and **2c″** are shown in Figures 1 and 2. Details of the crystallographic parameters and the structure refinements are listed in Table 1, and the selected bond distances and angles are given in Table 2.

These two compounds were mononuclear Co complexes with six-coordinate octahedral geometry. It is notable that, in both structures, the Co center binds two

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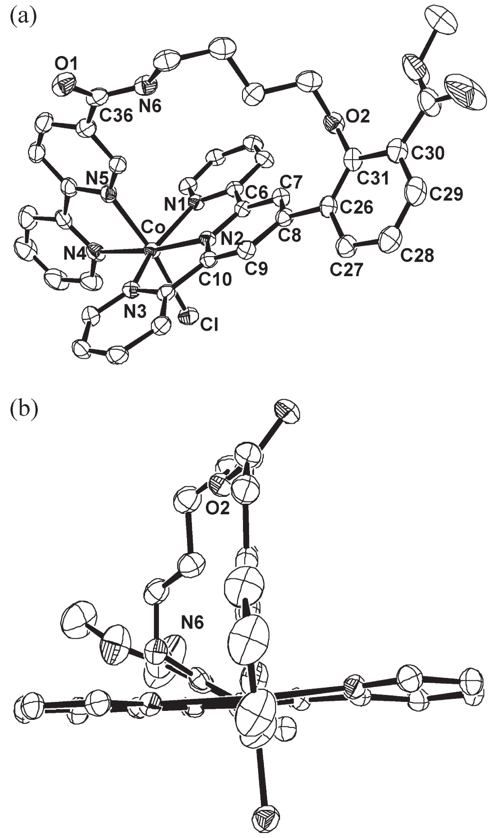

Figure 1. ORTEP drawing of the complex cation of **2b**: (a) overall view and (b) side view from the Co−N4 axis.

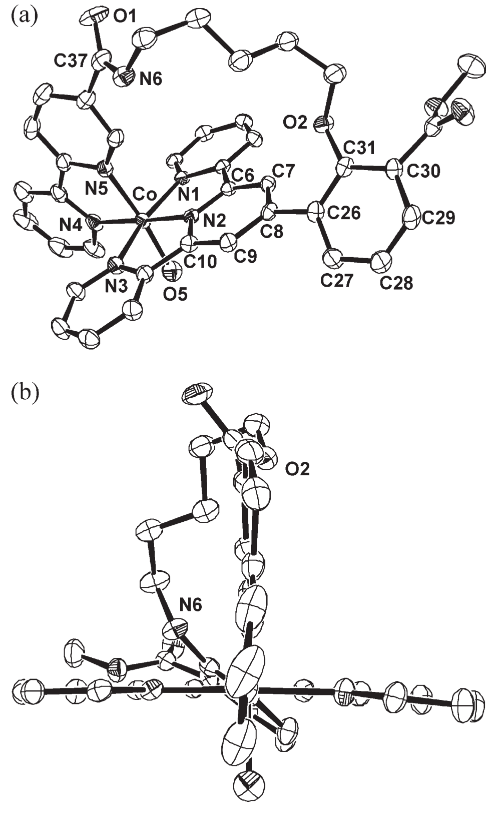

Figure 2. ORTEP drawing of the complex cation of **2c**″: (a) overall view and (b) side view from the Co−N4 axis.

Table 1. Crystallographic Data for **2b**·$2CH_3OH$ and **2c**″·H_2O

	2b·$2CH_3OH$	**2c**″·H_2O
formula	$C_{40}H_{40}N_6O_6CoClPF_6$	$C_{39}H_{37}N_6O_6CoP_2F_{12}$
M_w	940.14	1034.62
temp/°C	−100	−100
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a/Å	18.270(14)	12.100(5)
b/Å	8.975(7)	13.696(6)
c/Å	24.559(19)	14.426(6)
α/deg	90	111.920(5)
β/ deg	95.662(13)	90.574(4)
γ/ deg	90	108.828(2)
V/Å^3	4007(5)	2075.8(15)
Z	4	2
μ/cm^{-1}	6.913	6.005
d_{calcd}/g cm^{-3}	1.558	1.655
no. obsd reflns ($I > 2\sigma(I)$)	22158	14219
no. unique reflns (R_{int})	8426 (0.037)	8943 (0.018)
no. params	581	628
GOF	1.037	1.199
R1, wR2	0.0647, 0.1505	0.0580, 0.1405

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2b**·$2CH_3OH$ and **2c**″·H_2O

2b·$2CH_3OH$		**2c**″·H_2O	
	bond distances		
Co1−Cl1	2.4318(5)	Co1−O5	1.9023(14)
Co1−N1	2.1832(14)	Co1−N1	1.9491(17)
Co1−N2	2.0763(15)	Co1−N2	1.8563(19)
Co1−N3	2.1875(14)	Co1−N3	1.9502(19)
Co1−N4	2.1095(17)	Co1−N4	1.938(2)
Co1−N5	2.1499(14)	Co1−N5	1.9626(17)
	bond angles		
Cl1−Co1−N1	93.76(3)	O5−Co1−N1	91.02(7)
Cl1−Co1−N2	93.04(4)	O5−Co1−N2	91.69(7)
Cl1−Co1−N3	93.08(3)	O5−Co1−N3	88.16(7)
Cl1−Co1−N4	94.76(4)	O5−Co1−N4	90.39(7)
Cl1−Co1−N5	170.52(4)	O5−Co1−N5	172.58(7)
N1−Co1−N2	75.44(5)	N1−Co1−N2	82.36(7)
N1−Co1−N3	150.10(5)	N1−Co1−N3	164.54(8)
N1−Co1−N4	101.71(6)	N1−Co1−N4	97.24(8)
N1−Co1−N5	90.18(5)	N1−Co1−N5	91.40(7)
N2−Co1−N3	75.15(5)	N2−Co1−N3	82.26(8)
N2−Co1−N4	171.87(5)	N2−Co1−N4	177.89(7)
N2−Co1−N5	96.30(5)	N2−Co1−N5	95.58(7)
N3−Co1−N4	106.68(6)	N3−Co1−N4	98.21(8)
N3−Co1−N5	87.75(5)	N3−Co1−N5	91.36(7)
N4−Co1−N5	75.98(6)	N4−Co1−N5	82.33(8)

different polypyridyl ligands (terpyridine and bipyridine). Although such structures are commonly observed in 4d and 5d metals,[13] they are less common in 3d metals. In fact, only two such complexes are known for cobalt.[4b] Obviously, this demonstrates the advantage of the binary ligands.

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The average bond length of Co−N in **2b** was 2.14 Å, whereas in **2c″**, the average bond length of N−Co was 1.93 Å. This difference strongly suggests that the valence of cobalt is different, namely, Co(II) in **2b** and Co(III) in **2c″**. Indeed, the individual bond lengths and angles of Co^{II}(trpy) and Co^{II}(bpy) moieties in **2b** were consistent with those of previously reported complexes, respectively.[14] Similarly, the bond lengths and angles of **2c″** were consistent with those of Co^{III}(trpy) or Co^{III}(bpy).[14b,14c,15] The bond length of Co−Cl (2.4318 Å) is also consistent with other Co(II) complexes (2.37−2.46 Å).[14d,16] On the other hand, the Co−O bond length in **2c″** is 1.9023(14) Å, which is close to the distance of Co(III)−O̲H (1.89−1.90 Å)[17] rather than that of Co(III)−O̲H_2 (1.93−1.95 Å).[18] This indicates that the sixth ligand coordinating to the Co ion is not aqua but hydroxo. The formulation of Co(III)−OH requires that the complex cation has a +2 charge, which is consistent with the observed crystallographic unit cell, including two PF_6^- anions per complex cation.

Apart from the differences of the Co−N distances, the overall structures of Co(trpy)(bpy) moieties are very similar for **2b** and **2c″**. However, there are characteristic differences in the structures of the linker part, which are attributed to the different lengths of the polymethylene chains. First, the plane of the amide bond (−NHCO−) in **2b** is tilted in the opposite direction from the 4′-phenylene ring, but in **2c″** they are in the same direction (Figures 1b and 2b). This is because the distance between the two termini of the polymethylene chain (N6−O2) is shorter in **2b** (5.156 Å, four methylenes) than in **2c″** (5.428 Å, five methylenes).

Second, the para-carbon atom of the 4′-phenylene ring was bent out of the terpyridine plane, and the displacement was larger in **2c″** than that in **2b** (Figure 3). The out-of-plane distances of the C29 atom from the central pyridyl ring of the terpyridine were 0.1724 Å and 0.5030 Å in **2b** and **2c″**, respectively. Such a difference is caused by the C_5 chain in **2c″** requiring more space than the C_4 chain in **2b**. These facts indicate that a small difference in the length of the polymethylene chain of only one carbon can result in significant modification of the structures of these complexes.

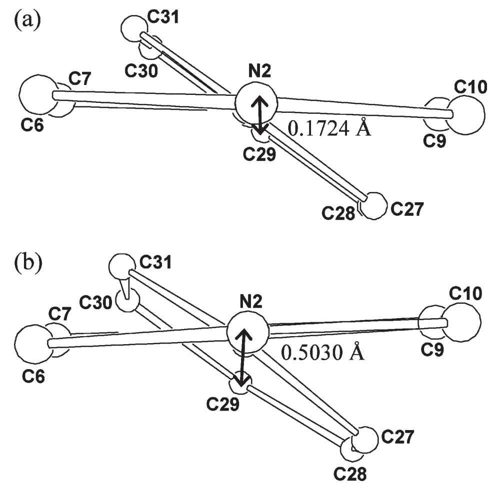

Figure 3. Partial structures of (a) **2b** and (b) **2c″**, showing the deformation of the 4′-phenylene ring from the terpyridine plane.

ESI-Mass Spectra. The ESI-mass spectra of these complexes measured in CH_3CN showed the characteristic dependence on the "sixth" ligand (see the Supporting Information, Figure S1). The spectrum of **2a** shows only one major peak at $m/z = 716$, and the isotope patterns are consistent with the theoretical patterns calculated for **2a** ($[Co^{II}(\mathbf{1a})Cl]^+$). In addition, other fragment peaks at $m/z =$ 340.5, 358, and 361 are the divalent ion peaks, and the mass numbers and the isotope patterns are consistent with $[Co^{II}(\mathbf{1a})]^{2+}$, $[Co^{II}(\mathbf{1a})Cl]^{2+}$, and $[Co^{II}(\mathbf{1a})(CH_3CN)]^{2+}$, respectively. The mass numbers and peak patterns of **2a′** are also consistent with its theoretical patterns. The main divalent ion peak at $m/z = 340.5$ is $[Co^{II}(\mathbf{1a})]^{2+}$, and other fragment peaks at m/z = 361 and 826 are $[Co^{II}(\mathbf{1a})(CH_3CN)]^{2+}$ and $[Co^{II}(\mathbf{1a})(PF_6)]^+$, respectively. The difference in the major peak can be reasonably explained since the neutral H_2O ligand in **2a′** is more easily detached from the complex than the anionic chloro ligand in **2a**. Importantly, the ESI-mass spectra of all these complexes showed only one major peak corresponding to the mononuclear complex; that is, the dinuclear or higher multinuclear complexes were not produced.

The Co(III) complex, $[Co^{III}(\mathbf{1c})(OH)](PF_6)_2$ (**2c″**), was confirmed with ESI-mass spectrometry. The transition of ESI-mass spectra from **2c′** to **2c″** is shown in Figure 4. Figure 4a−c represent the spectrum of **2c′**, the spectrum after the exposure of **2c′** to O_2 gas for 12 h, and the spectrum of **2c″**, respectively.[19] In Figure 4a, the major peak at $m/z =$ 354.5 corresponds to the fragment peak of $[Co^{II}(\mathbf{1c})]^{2+}$ and the peak at $m/z = 854$ to $[Co^{II}(\mathbf{1c})(PF_6)]^+$. Figure 4b shows the peaks at $m/z = 354.5$, 363, 770, and 787, which are assigned to the fragments $[Co^{II}(\mathbf{1c})]^{2+}$, $[Co^{III}(\mathbf{1c})(OH)]^{2+}$, $[Co^{II}(\mathbf{1c})(NO_3)]^+$, and $[Co^{III}(\mathbf{1c})(OH)(NO_3)]^+$, respectively. Finally, the spectrum of Figure 4c shows the peaks derived from **2c″** at m/z = 363 and 871, which are assigned to $[Co^{III}(\mathbf{1c})(OH)]^{2+}$ and $[Co^{III}(\mathbf{1c})(OH)(PF_6)]^+$, respectively.

All of these results show the exclusive formation of the 1:1 (metal/ligand) complexes. This is ascribed to an

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[19] Figure 4a and c show the spectra of **2c′** and **2c″**, which were isolated Co(II) and Co(III) complexes as PF_6 salts, respectively. The spectrum of Figure 4b was measured by the reaction mixture of $Co(NO_3)_2 \cdot 6H_2O$ and **1c** in EtOH/H_2O directly.

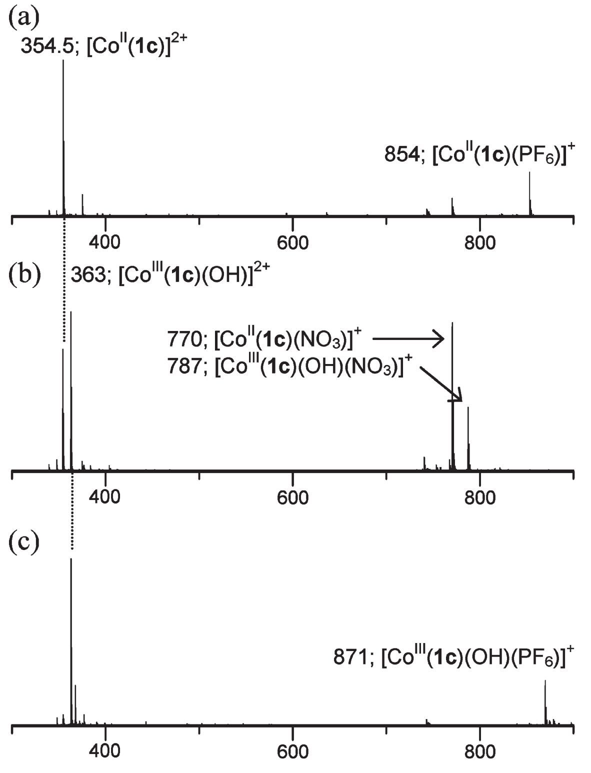

Figure 4. ESI-mass spectra of (a) **2c′**, (b) after the exposure of **2c′** to O_2 gas for 12 h, and (c) **2c″**.

entropy effect, because the formation of the 1:1 complex generally causes a smaller loss of entropy than the formation of 2:2 or higher complexes. This entropy effect may be offset by the loss of enthalpy when the polymethylene chain is too short and the formation of a mononuclear complex causes large intramolecular strain. However, in the case **1a**−**1d**, such offsets by the enthalpy term should be small, given the observation of only the mononuclear complexes.

On the other hand, we encountered an interesting observation when we examined the variant binary ligand **14a**, which lacks the methoxycarbonyl group adjacent to the polymethyleneoxy group. When **14a** was allowed to react with $CoCl_2 \cdot 6H_2O$, a 2:2 complex, **15a** ([(Co(**14a**)Cl)$_2$](PF$_6$)$_4$), was obtained (the chemical structures of **14a** and **15a** and the preliminary crystal structure of **15a** are shown in the Supporting Information).[20] Furthermore, the fragment peaks derived from the 2:2 complex were observed in the ESI-mass spectrum.[21] This striking difference between **1a** and **14a** is likely to be caused by the degree of internal freedom of the metal-free ligand. When the ligand has a large internal freedom (like polymethylene linkers in **1a**−**1d** and **14a**), the formation of the 1:1 complex will cause a significant loss of entropy due to the restriction of the internal movement, and the loss will be much larger for the 1:1 complex than the higher complexes. Therefore, it is possible that the ligand with larger internal freedom has a stronger tendency to form the 2:2 or higher complexes in preference to the 1:1 complex. The methoxycarbonyl group in **1a** causes restriction on the conformation of the polymethylene linker in comparison with **14a**, which is beneficial for the formation of the 1:1 complex. This kind of "remote" control is a novel concept for designing metal complexes and will be useful in constructing complicated metal-containing systems.

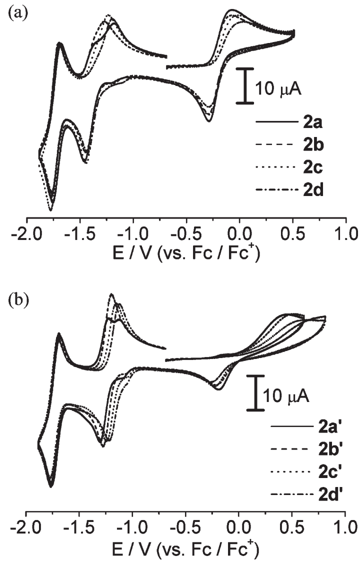

Figure 5. Cyclic voltammograms for (a) **2a**−**2d** and (b) **2a′**−**2d′**.

Cyclic Voltammograms. The cyclic voltammograms (CVs) of **2a**−**2d** and **2a′**−**2d′** are shown in Figure 5, and the redox potentials are listed in Table 3.

For **2a**, only one reversible wave at -1.72 V and irreversible and quasi-reversible waves around -1.4 V and -0.2 V were observed. The reversible wave was assigned to the redox process of terpyridine, and the others were assigned to the redox couples Co(II)/Co(I) and Co(III)/Co(II). These potentials were consistent with those of analogous compounds, such as $[Co(trpy)_2]^{2+}$ and $[Co(bpy)_3]^{2+}$ in previous literature reports.[14f,22] The CVs of **2b**−**2d** showed very similar waves as **2a**, except that the waves at -1.3 V were quasi-reversible in **2b**−**2d** and was distinctly irreversible in **2a**. These differences are ascribed to the different response to the change of the oxidation state of the Co center, which is caused by the differences of the length of the polymethylene linker. Before the reduction of the complexes, the coordination geometry of the Co(II) center is six-coordinate octahedral.[23] On the other hand, the coordination geometry of Co(I) complexes is generally four-coordinate tetrahedral or five-coordinate bipyramidal.[3b] Accordingly, after the reduction of Co(II) to Co(I), the coordination geometry was generally expected to change. The Co(II) mononuclear

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[20] Although the high-quality crystals could not be obtained, the crystal structure of **15a** was observed as the dinuclear complex. See Figure S2 and Tables S1 and S2 in the Supporting Information.

[21] Among the observed signals, the following peaks were attributed to fragments derived from [(Co(**14a**)Cl$_2$)]: 328.5, [(Co(**14a**)Cl)$_2$]$^{4+}$; 438, [(Co(**14a**)Cl)$_2$]$^{3+}$; 735.5, [(Co(**14a**)(CH$_3$CN))$_2$Cl(PF$_6$)]$^{2+}$; 753, [(Co(**14a**)-(CH$_3$CN))$_2$(PF$_6$)]$^{2+}$. See Figure S3 (Supporting Information).

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[23] The resting potentials were ca. -0.3 V (vs Fc/Fc$^+$, **2a**−**2d**) and -0.2 V (vs Fc/Fc$^+$, **2a′**−**2d′**), and the oxidation waves of Co(III)/Co(II) were observed at the first sweep to the positive potential. These facts indicate that the valence of Co is divalent.

Table 3. Redox Potentials of the Complexes. (V vs. Fc/Fc^+)

	trpy$^{0/-}$		Co$^{II/I}$			Co$^{III/II}$		
	$E_{1/2}$	(ΔE_p)	E_{pc}	(ΔE_p)	E_{pa}	E_{pc}	(ΔE_p)	E_{pa}
2a	−1.72	(0.07)	−1.46		−1.35, −1.18	−0.28	(0.20)	−0.08
2b	−1.74	(0.07)	−1.45	(0.18)	−1.27	−0.29	(0.20)	−0.09
2c	−1.74	(0.07)	−1.45	(0.21)	−1.24	−0.29	(0.25)	−0.04
2d	−1.74	(0.07)	−1.43	(0.23)	−1.20	−0.28	(0.28)	0.00
2a′	−1.72	(0.07)	−1.30		−1.23, −1.11	−0.19	(0.63)	0.44
2b′	−1.73	(0.07)	−1.27	(0.07)	−1.20	−0.21	(0.71)	0.50
2c′	−1.74	(0.07)	−1.24	(0.08)	−1.16	−0.23	(0.81)	0.58
2d′	−1.74	(0.07)	−1.21	(0.09)	−1.12	−0.25	(0.96)	0.71

complex **2a** was not suitable for the structural change following the reduction, whereas **2b**−**2d** were more adaptive for the structural change because of the longer methylene chain. This argument is consistent with the observation that the redox wave of **2a** around −1.4 V was irreversible, whereas the corresponding waves of **2b**−**2d** were quasi-reversible. On the other hand, the voltammograms remained almost unchanged after several cycles, suggesting that these complexes were chemically invariable during the redox processes. The peak-to-peak separations (ΔE_p) for the Co(II)/Co(I) couples (except for **2a**) and the Co(III)/Co(II) couples become larger with longer polymethylene chains. The larger ΔE_p corresponds to slower electron transfer, which is likely to be caused by the large structural change of the longer polymethylene chain.

The CVs of **2a′**−**2d′** show similar trends to those of **2a**−**2d**. The notable difference was that the redox potentials for the Co(II)/Co(I) and Co(III)/Co(II) couples were slightly shifted to the positive, reflecting the difference in the ligand, chloro or aqua. In the CV of **2a′**, the redox wave at −1.2 V was irreversible, as with **2a**. This is also attributed to the short length of the polymethylene chain. The ΔE_p's for the Co(III)/Co(II) couples of **2a′**−**2d′** are much larger than those of **2a**−**2d**. Such differences can be explained by assuming that the oxidation of the Co(II)−OH_2 complex is accompanied by deprotonation to give the Co(III)−OH complex. This interpretation is also consistent with the observation of the Co(III)−OH complex described above. The voltammograms of **2a′**−**2d′** were also invariant after several cycles, suggesting that the proton-coupled redox process (Co(III)−OH/Co(II)−OH_2) is chemically reversible.

In summary, we synthesized binary ligands consisting of terpyridine and bipyridine groups linked with polymethylene chains. These ligands exclusively formed 1:1 complexes with Co(II) ion, and the redox properties were consistent with the linker lengths. These characteristics will be useful for constructing complicated, multimolecular systems containing metal complexes.

Experimental Section

General. Reagents were purchased from Wako, Nacalai, and Aldrich. All reagents were used without further purification unless otherwise noted. The following compounds were prepared according to literature procedures: 4′-((trifluoromethanesulfonyl)oxy)-2,2′:6′,2″-terpyridine (**6**),[24] *t*-butoxycarbonylaminopropyl bromide (**9a**),[25] *t*-butoxycarbonylaminoalkyl mesylate (**9b**−**9d**),[26] and 2,2′-bipyridine-4-carboxylic acid (**13**).[27]

^1H NMR spectra were measured at room temperature with a JEOL LA400 spectrometer. ESI-mass spectra were recorded on a Waters Micromass LCT.

Ligand Syntheses. 2-(Methoxymethoxy)benzaldehyde (3). A solution of salicylaldehyde (17.5 g, 0.14 mol) in N,N-dimethylformamide (DMF; 20 mL) was added dropwise to a suspension of NaH (6.4 g, 0.16 mol) in dry tetrahydrofuran (THF; 20 mL) at 0 °C with stirring. After 30 min, a solution of chloromethyl methyl ether (18.3 mL, 0.16 mmol) in dry THF (40 mL) was added dropwise to the solution kept at 0 °C with stirring. After 2 h, hexane was added, and the mixture was washed with H_2O and then washed thrice with NaOH (aq., 20%). The organic phase was separated, dried over Na_2SO_4, evaporated, and dried in a vacuum. Yield: 22.6 g (0.136 mol, 98%). ^1H NMR ($CDCl_3$): δ 10.48 (s, 1H, −C*H*O), 7.81 (dd, 1H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 1.6$ Hz, 6-Ar), 7.50 (dt, 1H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 2.0$ Hz, 4-Ar), 7.19 (d, 1H, $^3J_{H,H} = 8.4$ Hz, 3-Ar), 7.05 (t, 1H, $^3J_{H,H} = 7.2$ Hz, 5-Ar), 5.28 (s, 2H, −OCH_2O−), 3.49 (s, 3H, −OCH_3).

2-(2-Methoxymethoxyphenyl)-5,5-dimethyl-1,3-dioxane (4). A mixture of **3** (6.73 g, 40.4 mmol), 2,2-dimethyl-1,3-propanediol (6.73 g, 64.6 mmol), and *p*-toluenesulfonic acid monohydrate (407.1 mg, 2.14 mmol) in CH_2Cl_2 was stirred for 30 min at room temperature. The resulting solution was washed with saturated $NaHCO_3$ (aq.), dried over Na_2SO_4, and evaporated. The pale yellow oil was dried in a vacuum. Yield: 9.37 g (37.2 mmol, 92%). ^1H NMR ($CDCl_3$): δ 7.65 (dd, 1H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, 6-Ar), 7.26 (dt, 1H, $^3J_{H,H} = 8.0$ Hz, $^3J_{H,H} = 1.6$ Hz, 4-Ar), 7.06 (d, 1H, $^3J_{H,H} = 7.2$ Hz, 3-Ar), 7.03 (t, 1H, $^3J_{H,H} = 7.2$ Hz, 5-Ar), 5.77 (s, 1H, acetal-CH), 5.18 (s, 2H, -OCH_2O−), 3.70 (ABquartet, 4H, $^4J_{H,H} = 11.2$ Hz, acetal-CH_2), 3.47 (s, 3H, -OCH_3), 1.31 (s, 3H, acetal-Me), 0.77 (s, 3H, acetal-Me).

3-(4,4-Dimethyl-2,6-dioxacyclohexyl)-2-methoxymethoxyphenylboronic Acid (5). A 1.6 M hexane solution of *n*-BuLi (33 mL, 52.8 mmol) was added dropwise to the solution of **4** (9.17 g, 36.4 mmol) in dry THF (80 mL) at 0 °C under N_2. After 3 h of

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stirring at 0 °C, triisopropyl borate (16 mL, 69.3 mmol) was added at once to the mixture and stirred for 2 h. The solution of NH_4Cl (9 g, 168 mmol) in H_2O (90 mL) was added to the resulting solution, and the mixture was stirred for 12 h at room temperature. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The organic solutions were combined and dried over Na_2SO_4. Evaporating the solvent gave pale yellow oil, and hexane was added to this oil with stirring. The resulting mixture was left to stand in a freezer overnight. The white crystals were collected by filtration and washed with hexane. This compound should be kept in a freezer because it slowly decomposes at room temperature. Yield: 6.16 g (20.8 mmol, 57%). ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 2H, 4-Ar, 6-Ar), 7.24 (t, 1H, $^3J_{H,H} = 7.6$ Hz, 5-Ar), 6.01 (s, 2H, $-\mathrm{B(O}H)_2$), 5.61 (s, 1H, acetal-CH), 5.09 (s, 2H, $-\mathrm{OC}H_2\mathrm{O}-$), 3.70 (ABquartet, 4H, $^4J_{H,H} = 11.2$ Hz, acetal-CH_2), 3.51 (s, 3H, $-OCH_3$), 1.32 (s, 3H, acetal-Me), 0.79 (s, 3H, acetal-Me).

4′-(3-(4,4-Dimethyl-2,6-dioxacyclohexyl)-2-methoxymethoxyphenyl)-2,2′:6′,2″- terpyridine (7). Compounds **5** (1.57 g, 5.30 mmol), **6** (1.57 g, 4.12 mmol), $Pd(PPh_3)_4$ (62.8 mg, 0.054 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-phos,[10] 195.2 mg, 0.48 mmol), KF (1.8 g, 31 mmol), and Na_2CO_3 (3.2 g, 30 mmol) were suspended in toluene/H_2O (30 mL/5 mL). The mixture was purged with N_2 gas and heated at 120 °C for 12 h under N_2. After the reaction mixture was allowed to cool to room temperature, CH_2Cl_2 and water were added, and the organic phase was separated and dried over Na_2SO_4. The organic solution was concentrated to remove CH_2Cl_2, and then hexane was added to the remaining solution and left to stand overnight. The orange-pink crystals were collected by filtration. Yield: 1.86 g (3.86 mmol, 93%). Anal. Found: C, 71.75; H, 6.05; N, 8.61%. Calcd for $C_{29}H_{29}N_3O_4$: C, 72.03; H, 6.04; N, 8.69%. ^{1}H NMR ($CDCl_3$): δ 8.71 (d, 2H, $^3J_{H,H} = 4.4$ Hz, trpy-6-H, trpy-6″-H), 8.69 (s, 2H, trpy-3′,5′-H), 8.66 (d, 2H, $^3J_{H,H} = 8.0$ Hz, trpy-3-H, trpy-3″-H), 7.87 (dt, 2H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 2.0$ Hz, trpy-5-H, trpy-5″-H), 7.81 (dd, 1H, $^3J_{H,H} = 7.8$ Hz, $^3J_{H,H} = 1.6$ Hz, 4-Ar), 7.56 (dd, 1H, $^3J_{H,H} = 7.6$ Hz, 6-Ar), 7.34 (dt, 2H, $^3J_{H,H} = 7.6$ Hz, $^3J_{H,H} = 1.2$ Hz, trpy-4-H, trpy-4″-H), 7.32 (t, 1H, $^3J_{H,H} = 7.6$ Hz, 5-Ar), 5.89 (s, 1H, acetal-CH), 4.74 (s, 2H, $-\mathrm{OC}H_2\mathrm{O}-$), 3.75 (ABquartet, 4H, $^4J_{H,H} = 11.2$ Hz, acetal-CH_2), 3.19 (s, 3H, $-OCH_3$), 1.37 (s, 3H, acetal-Me), 0.82 (s, 3H, acetal-Me).

4′-(3-Formyl-2-hydroxyphenyl)-2,2′:6′,2″-terpyridine (8). Compound **7** (483.6 mg, 1.00 mmol) and $BF_3\cdot Et_2O$ (1.5 mL, 12 mmol) were dissolved in MeOH (20 mL), and the mixture was heated at 65 °C. After 3 h, the solution was neutralized by saturated $NaHCO_3$ (aq.), evaporated to remove MeOH, and filtered. Yield: 361.3 mg (1.02 mmol, 102%). ^{1}H NMR (DMSO-d_6): δ 11.61 (br, 1H, $-\mathrm{O}H$), 10.16 (s, 1H, $-\mathrm{C}H\mathrm{O}$), 8.92 (d, 2H, $^3J_{H,H} = 8.0$ Hz, trpy-6-H, trpy-6″-H), 8.86 (d, 2H, $^3J_{H,H} = 4.4$ Hz, trpy-3-H, trpy-3″-H), 8.80 (s, 2H, trpy-3′, 5′-H), 8.35 (dt, 2H, $^3J_{H,H} = 7.6$ Hz, $^3J_{H,H} = 1.2$ Hz, trpy-5-H, trpy-5″-H), 7.99 (two overlapping doublets, 2H, $^3J_{H,H} = 7.6$ Hz, 4-Ar, 6-Ar), 7.78 (t, 2H, $^3J_{H,H} = 6.4$ Hz, trpy-4-H, trpy-4″-H), 7.31 (t, 1H, $^3J_{H,H} = 7.6$ Hz, 5-Ar).

2-(3-(*tert*-Butoxycarbonylamino)propyloxy)-3-methoxycarbonylphenyl-2,2′:6′,2″- terpyridine (11a). Compound **8** (530.7 mg, 1.50 mmol), **9a** (520.9 mg, 2.19 mmol), K_2CO_3 (940.2 mg, 7.03 mmol), and KI (519.4 mg, 3.13 mmol) were suspended in DMF (10 mL), and the solution was stirred for 12 h at 50 °C under N_2. Saturated NaCl (aq.) and CH_2Cl_2 were added to the reaction mixture, and the organic phase was separated. The organic solution was washed twice with H_2O and dried over Na_2SO_4. Evaporating the solvent gave **10a** as orange oil. Subsequently, the orange oil (**10a**) was dissolved in MeOH (20 mL) and cooled to 0 °C. KOH (365.2 mg, 6.52 mmol) was added to the solution and stirred for 5 min; then, I_2 (419.0 mg, 3.30 mmol) was added and stirred for 6 h at 0 °C. Aqueous $KHSO_4$ was added to the reaction mixture to neutralize it. To the mixture CH_2Cl_2 and $NaHSO_3$ (aq.) were added, and the separated organic phase was further washed with $NaHSO_3$ (aq.) and H_2O. The organic phase was dried over Na_2SO_4, evaporated, and dried in a vacuum. The purification was performed by chromatography on an alumina column with CH_2Cl_2/hexane. Yield: 561.8 mg (1.04 mmol, 69%). Anal. Found: C, 68.80; H, 5.80; N, 10.28%. Calcd for $C_{31}H_{32}N_4O_5$: C, 68.87; H, 5.97; N, 10.36%. ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 2H, trpy-3′-H, trpy-5′-H), 8.71 (d, 2H, $^3J_{H,H} = 5.2$ Hz, trpy-6-H, trpy-6″-H), 8.67 (d, 2H, $^3J_{H,H} = 8.0$ Hz, trpy-3-H, trpy-3″-H), 7.89 (dt, 2H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 1.6$ Hz, trpy-4-H, trpy-4″-H), 7.86 (dd, 1H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, 4-Ar), 7.73 (dd, 1H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 1.6$ Hz, 6-Ar), 7.35 (dt, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.2$ Hz, trpy-5-H, trpy-5″-H), 7.29 (t, 1H, $^3J_{H,H} = 7.6$ Hz, 5-Ar), 5.42 (br, 1H, $-\mathrm{N}H\mathrm{CO}-$), 3.96 (s, 3H, COOMe), 3.75 (t, 2H, $^3J_{H,H} = 5.6$ Hz, $-\mathrm{OC}H_2\mathrm{CH_2}-$), 3.18 (q, 2H, $^3J_{H,H} = 6.4$ Hz, $-\mathrm{CH_2C}H_2\mathrm{NH}-$), 1.71 (m, 2H, $-\mathrm{OCH_2C}H_2\mathrm{CH_2}-$), 1.32 (s, 9H, Boc-Bu). [Note: Although the literature suggested the reaction at 50 °C,[11] the reaction hardly proceeded at this temperature in our case. At 0 °C, the reaction proceeded smoothly.[12] However, if the temperature rose to room temperature before workup, the hydrolysis reaction of the ester group took place. The failure of the reaction at 50 °C is probably due to the instability of the active species derived from I_2 and KOH. Furthermore, it was necessary to remove residual I_2 as much as possible, so that the reaction mixture was washed with $NaHSO_3$ (aq.); otherwise, unidentified byproducts were formed.]

2-(4-(*tert*-Butoxycarbonylamino)butoxy)-3-methoxycarbonylphenyl-2,2′:6′,2″-terpyridine (11b). This compound was synthesized by a similar procedure using **8** (590.9 mg, 1.67 mmol), **9b** (700.0 mg, 2.78 mmol), K_2CO_3 (1.1 g, 7.97 mmol), and KI (488.0 mg, 2.94 mmol) in DMF (30 mL), then KOH (493.0 mg, 8.80 mmol) and I_2 (544.4 mg, 4.29 mmol) in MeOH (20 mL). Yield: 600.0 mg (1.08 mmol, 65%). Anal. Found: C, 69.42; H, 6.24; N, 9.98%. Calcd for $C_{32}H_{34}N_4O_5$: C, 69.30; H, 6.18; N, 10.10%. ^{1}H NMR ($CDCl_3$): δ 8.72 (d, 2H, $^3J_{H,H} = 4.0$ Hz, trpy-6-H, trpy-6″-H), 8.71 (s, 2H, trpy-3′-H, trpy-5′-H), 8.67 (d, 2H, $^3J_{H,H} = 7.6$ Hz, trpy-3-H, trpy-3″-H), 7.88 (dt, 2H, $^3J_{H,H} = 7.8$ Hz, $^4J_{H,H} = 1.6$ Hz, trpy-4-H, trpy-4″-H), 7.86 (dd, 1H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, 4-Ar), 7.71 (dd, 1H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 2.0$ Hz, 6-Ar), 7.35 (dt, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, trpy-5-H, trpy-5″-H), 7.28 (t, 1H, $^3J_{H,H} = 7.6$ Hz, 5-Ar), 4.43 (br, 1H, $-\mathrm{N}H\mathrm{CO}-$), 3.94 (s, 3H, COOMe), 3.67 (t, 2H, $^3J_{H,H} = 6.0$ Hz, $-\mathrm{OC}H_2\mathrm{CH_2}-$), 2.88 (q, 2H, $^3J_{H,H} = 6.4$ Hz, $-\mathrm{CH_2C}H_2\mathrm{NH}-$), 1.52 (m, 2H, $-\mathrm{OCH_2C}H_2\mathrm{CH_2}-$), 1.38 (s+m, 11H, $-\mathrm{OCH_2CH_2C}H_2-$, Boc-Bu).

2-(5-(*tert*-Butoxycarbonylamino)pentyloxy)-3-methoxycarbonylphenyl-2,2′:6′,2″-terpyridine (11c). This compound was prepared similarly to **11a** using **8** (209.6 mg, 0.59 mmol), **9c** (257.3 mg, 0.91 mmol), K_2CO_3 (437.7 g, 3.17 mmol), and KI (236.8 mg, 1.43 mmol) in DMF (8 mL), then KOH (205.9 mg, 3.65 mmol) and I_2 (232.7 mg, 1.83 mmol) in MeOH (10 mL). Yield: 216.1 mg (0.38 mmol, 64%). Anal. Found: C, 69.68; H, 6.39; N, 9.88%. Calcd for $C_{33}H_{36}N_4O_5$: C, 69.70; H, 6.38; N, 9.85%. ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 2H, trpy-3′-H, trpy-5′-H), 8.70 (d, 2H, $^3J_{H,H} = 6.0$ Hz, trpy-6-H, trpy-6″-H), 8.68 (d, 2H, $^3J_{H,H} = 8.0$ Hz, trpy-3-H, trpy-3″-H), 7.89 (dt, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 2.0$ Hz, trpy-4-H, trpy-4″-H), 7.86 (dd, 1H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 1.6$ Hz, 4-Ar), 7.70 (dd, 1H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 2.0$ Hz, 6-Ar), 7.35 (dt, 2H, $^3J_{H,H} = 6.0$ Hz, $^4J_{H,H} = 1.2$ Hz, trpy-5-H, trpy-5″-H), 7.28 (t, 1H, $^3J_{H,H} = 7.6$ Hz, 5-Ar), 4.41 (br, 1H, $-\mathrm{N}H\mathrm{CO}-$), 3.94 (s, 3H, COOMe), 3.65 (t, 2H, $^3J_{H,H} = 5.6$ Hz, $-\mathrm{OC}H_2\mathrm{CH_2}-$), 2.76 (m, 2H, $-\mathrm{CH_2C}H_2\mathrm{NH}-$), 1.51 (m, 2H, $-\mathrm{OCH_2C}H_2\mathrm{CH_2}-$), 1.41 (s, 9H, Boc-Bu), 1.16 (m, 4H, $-\mathrm{CH_2C}H_2\mathrm{C}H_2\mathrm{CH_2NH}-$).

2-(6-(*tert*-Butoxycarbonylamino)hexyloxy)-3-methoxycarbonylphenyl-2,2′:6′,2″-terpyridine (11d). This compound was prepared similarly to **11a** using **8** (202.9 mg, 0.58 mmol), **9d** (262.5 mg, 0.89 mmol), K_2CO_3 (427.9 g, 3.10 mmol), and KI

(206.1 mg, 1.24 mmol) in DMF (8 mL), then KOH (198.6 mg, 3.55 mmol) and I_2 (209.8 mg, 1.65 mmol) in MeOH (10 mL). Yield: 217.7 mg (0.37 mmol, 65%). Anal. Found: C, 69.91; H, 6.62; N, 9.69%. Calcd for $C_{34}H_{38}N_4O_5$: C, 70.08; H, 6.57; N, 9.62%. ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 2H, trpy-3′-H, trpy-5′-H), 8.70 (d, 2H, $^3J_{H,H}$ = 6.0 Hz, trpy-6-H, trpy-6″-H), 8.68 (d, 2H, $^3J_{H,H}$ = 8.0 Hz, trpy-3-H, trpy-3″-H), 7.89 (dt, 2H, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz, trpy-4-H, trpy-4″-H), 7.86 (dd, 1H, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 2.0 Hz, 4-Ar), 7.70 (dd, 1H, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 2.0 Hz, 6-Ar), 7.35 (dt, 2H, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.2 Hz, trpy-5-H, trpy-5″-H), 7.27 (t, 1H, $^3J_{H,H}$ = 7.6 Hz, 5-Ar), 4.40 (br, 1H, −N*H*CO−), 3.94 (s, 3H, COOMe), 3.65 (t, 2H, $^3J_{H,H}$ = 6.4 Hz, $-\mathrm{OC}\mathit{H}_2\mathrm{CH}_2-$), 2.83 (m, 2H, $-\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{NH}-$), 1.49 (m, 2H, $-\mathrm{OCH}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2-$), 1.43 (s, 9H, Boc-Bu), 1.07 (m, 6H, $-\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2\mathrm{NH}-$).

2-(3-(2,2′-Bipyridin-4-ylcarbonylamino)propyloxy)-3-methoxycarbonylphenyl-2,2′:6′,2″-terpyridine (1a). A solution of **11a** (420.6 mg, 0.78 mmol) in trifluoroacetic acid (10 mL) was stirred for 2 h at room temperature. The solution was neutralized by saturated $NaHCO_3$ (aq.). The white solids deposited, which were collected by filtration to obtain deprotected product **12a**. Subsequently, **12a**, 4-dimethylaminopyridine (DMAP; 207.7 mg, 1.70 mmol), 1-hydroxybenzotriazole (HOBt; 228.5 mg, 1.69 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl; 298.0 mg, 1.56 mmol), and **13** (152.8 mg, 0.76 mmol) were dissolved in CH_2Cl_2 (15 mL), and the mixture was stirred for 14 h at room temperature. The reaction mixture was washed with water, and then with saturated $NaHCO_3$ (aq.). The separated organic phase was dried over Na_2SO_4 and evaporated to give pale yellow oil. The purification was performed by chromatography on an alumina column and recrystallization from CH_2Cl_2/hexane. Yield: 356.5 mg (0.57 mmol, 74%). Anal. Found: C, 71.13; H, 4.84; N, 13.44%. Calcd for $C_{37}H_{30}N_6O_4$: C, 71.37; H, 4.86; N, 13.50%. ^{1}H NMR ($CDCl_3$): δ 9.13 (d, 1H, $^4J_{H,H}$ = 2.4 Hz, bpy-6-H), 8.79 (s, 2H, trpy-3′-H, trpy-5′-H), 8.69 (d, 1H, $^3J_{H,H}$ = 4.4 Hz, bpy-6′-H), 8.66 (d, 2H, $^3J_{H,H}$ = 8.0 Hz, trpy-6-H, trpy-6″-H), 8.63 (d, 2H, $^3J_{H,H}$ = 4.8 Hz, trpy-3-H, trpy-3″-H), 8.42 (d, 1H, $^3J_{H,H}$ = 8.8 Hz, bpy-3′-H,), 8.40 (d, 1H, $^3J_{H,H}$ = 8.4 Hz, bpy-3-H), 8.23 (dd, 1H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.4 Hz, bpy-4-H), 7.94 (dd, 1H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.6 Hz, 4-Ar), 7.79−7.88 (m, 5H, trpy-4-H, trpy-4″-H, bpy-4′-H, bpy-5′-H, 6-Ar), 7.31−7.35 (m, 4H, trpy-5-H, trpy-5″-H, 5-Ar, −N*H*CO−), 3.95 (s, 3H, −COOMe), 3.84 (t, 2H, $^3J_{H,H}$ = 5.6 Hz, $-\mathrm{OC}\mathit{H}_2\mathrm{CH}_2-$), 3.68 (q, 2H, $^3J_{H,H}$ = 6.0 Hz, $-\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{NH}-$), 1.83 (m, 2H, $-\mathrm{OCH}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2-$).

2-(4-(2,2′-Bipyridin-4-ylcarbonylamino)butoxy)-3-methoxycarbonylphenyl-2,2′:6′,2″-terpyridine (1b). This compound was synthesized by a procedure similar to that of **1a**, using **11b** (183.8 mg, 0.33 mmol) and trifluoroacetic acid (8 mL), and then DMAP (78.3 mg, 0.64 mmol), HOBt (79.6 mg, 0.59 mmol), EDC·HCl (115.2 mg, 0.60 mmol), **13** (64.1 mg, 0.32 mmol), and CH_2Cl_2 (10 mL). Yield: 143.8 mg (0.23 mmol, 68%). Anal. Found: C, 71.45; H, 5.20; N, 13.16%. Calcd for $C_{34}H_{38}N_4O_5$: C, 71.68; H, 5.07; N, 13.20%. ^{1}H NMR ($CDCl_3$): δ 8.96 (d, 1H, $^4J_{H,H}$ = 2.0 Hz, bpy-6-H), 8.71 (dd, 1H, $^3J_{H,H}$ = 4.8 Hz, $^4J_{H,H}$ = 0.8 Hz, bpy-6′-H), 8.70 (s, 2H, trpy-3′-H, trpy-5′-H), 8.65 (dd, 2H, $^3J_{H,H}$ = 4.8 Hz, $^4J_{H,H}$ = 1.2 Hz, trpy-6-H, trpy-6″-H), 8.62 (d, 2H, $^3J_{H,H}$ = 8.0 Hz, trpy-3-H, trpy-3″-H), 8.46 (dd, 1H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 0.8 Hz, bpy-3′-H,), 8.41 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, bpy-3-H), 8.08 (dd, 1H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.4 Hz, bpy-4-H), 7.90 (dd, 1H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.6 Hz, 4-Ar), 7.85 (dt, 1H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.6 Hz, bpy-4′-H), 7.83 (dt, 2H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 2.0 Hz, trpy-4-H, trpy-4″-H), 7.72 (dd, 1H, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,H}$ = 2.0 Hz, 6-Ar), 7.36 (t, 1H, bpy-5′-H), 7.27−7.32 (m, 3H, trpy-5-H, trpy-5″-H, 5-Ar), 6.56 (br, 1H, −N*H*CO−), 3.93 (s, 3H, −COOMe), 3.75 (t, 2H, $^3J_{H,H}$ = 5.6 Hz, $-\mathrm{OC}\mathit{H}_2\mathrm{CH}_2-$), 3.25 (q, 2H, $^3J_{H,H}$ = 6.0 Hz, $-\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{NH}-$), 1.55−1.68 (m, 4H, $-\mathrm{OCH}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2-$).

2-(5-(2,2′-Bipyridin-4-ylcarbonylamino)pentyloxy)-3-methoxycarbonylphenyl-2,2′:6′,2″-terpyridine (1c). This compound was synthesized by a procedure similar to that of **1a**, using **11c** (169.6 mg, 0.30 mmol) and trifluoroacetic acid (8 mL), and then DMAP (79.2 mg, 0.65 mmol), HOBt (85.6 mg, 0.63 mmol), EDC·HCl (159.0 mg, 0.68 mmol), **13** (59.8 mg, 0.30 mmol), and CH_2Cl_2 (10 mL). Yield: 165.9 mg (0.26 mmol, 85%). Anal. Found: C, 71.92; H, 5.34; N, 12.86%. Calcd for $C_{39}H_{34}N_6O_4$: C, 71.98; H, 5.27; N, 12.92%. ^{1}H NMR ($CDCl_3$): δ 9.02 (d, 1H, $^4J_{H,H}$ = 2.0 Hz, bpy-6-H), 8.72 (d, 1H, $^3J_{H,H}$ = 4.8 Hz, bpy-6′-H), 8.69 (s, 2H, trpy-3′-H, trpy-5′-H), 8.68 (d, 2H, $^3J_{H,H}$ = 4.8 Hz, trpy-6-H, trpy-6″-H), 8.63 (d, 2H, $^3J_{H,H}$ = 7.6 Hz, trpy-3-H, trpy-3″-H), 8.47 (d, 1H, $^3J_{H,H}$ = 8.8 Hz, bpy-3′-H,), 8.45 (d, 1H, $^3J_{H,H}$ = 9.2 Hz, bpy-3-H), 8.13 (dd, 1H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 2.4 Hz, bpy-4-H), 7.81−7.90 (m, 4H, 4-Ar, bpy-4′-H, trpy-4-H, trpy-4″-H), 7.69 (dd, 1H, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,H}$ = 2.0 Hz, 6-Ar), 7.37 (t, 1H, bpy-5′-H), 7.26−7.34 (m, 3H, trpy-5-H, trpy-5″-H, 5-Ar), 6.40 (br, 1H, −N*H*CO−), 3.92 (s, 3H, −COOMe), 3.70 (t, 2H, $^3J_{H,H}$ = 6.0 Hz, $-\mathrm{OC}\mathit{H}_2\mathrm{CH}_2-$), 3.12 (q, 2H, $^3J_{H,H}$ = 5.6 Hz, $-\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{NH}-$), 1.56 (m, 2H, $-\mathrm{OCH}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2-$), 1.30−1.32 (m, 4H, $-\mathrm{OCH}_2\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2-$).

2-(6-(2,2′-Bipyridin-4-ylcarbonylamino)hexyloxy)-3-methoxycarbonylphenyl-2,2′:6′,2″-terpyridine (1d). This compound was synthesized by a procedure similar to that of **1a**, using **11d** (190.2 mg, 0.33 mmol) and trifluoroacetic acid (8 mL), and then DMAP (80.3 mg, 0.66 mmol), HOBt (87.1 mg, 0.65 mmol), EDC·HCl (125.0 mg, 0.65 mmol), **13** (62.1 mg, 0.31 mmol), and CH_2Cl_2 (10 mL). Yield: 154.1 mg (0.23 mmol, 71%). Anal. Found: C, 72.16; H, 5.59; N, 12.42%. Calcd for $C_{40}H_{36}N_6O_4$: C, 72.27; H, 5.46; N, 12.64%. ^{1}H NMR ($CDCl_3$): δ 9.04 (d, 1H, $^4J_{H,H}$ = 2.0 Hz, bpy-6-H), 8.68−8.72 (m, 3H, bpy-6′-H, trpy-6-H, trpy-6″-H), 8.69 (s, 2H, trpy-3′-H, trpy-5′-H), 8.64 (d, 2H, $^3J_{H,H}$ = 7.6 Hz, trpy-3-H, trpy-3″-H), 8.46 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, bpy-3′-H,), 8.45 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, bpy-3-H), 8.19 (dd, 1H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 2.4 Hz, bpy-4-H), 7.82−7.87 (m, 4H, 4-Ar, bpy-4′-H, trpy-4-H, trpy-4″-H), 7.66 (dd, 1H, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,H}$ = 1.6 Hz, 6-Ar), 7.23−7.37 (m, 4H, bpy-5′-, trpy-5-H, trpy-5″-H, 5-Ar), 6.44 (br, 1H, −N*H*CO−), 3.94 (s, 3H, −COOMe), 3.68 (t, 2H, $^3J_{H,H}$ = 5.6 Hz, $-\mathrm{OC}\mathit{H}_2\mathrm{CH}_2-$), 3.21 (q, 2H, $^3J_{H,H}$ = 6.0 Hz, $-\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{NH}-$), 1.52 (m, 2H, $-\mathrm{OCH}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2-$), 1.08−1.26 (m, 6H, $-\mathrm{OCH}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2-$).

Syntheses of Co(II) Complexes. [CoCl(1a)](PF$_6$) (2a). The ligand **1a** (50.6 mg, 0.081 mmol) and LiCl (11.8 mg, 0.28 mmol) were suspended in EtOH (10 mL), and the solution was heated at 80 °C to dissolve **1a**. A solution of $CoCl_2 \cdot 6H_2O$ (19.3 mg, 0.081 mmol) in EtOH (5 mL) was added to the hot EtOH solution, and the mixture was refluxed for 2 h. The reaction mixture was cooled; NH_4PF_6 was added to the solution and left to stand overnight. The pale brown powder was collected by filtration and dried at 100 °C in a vacuum. Yield: 67.4 mg (0.078 mmol, 96%). Anal. Found: C, 49.48; H, 3.75; N, 9.26%. Calcd for $C_{37}H_{30}N_6O_4ClCoF_6P \cdot 2H_2O$: C, 49.49; H, 3.82; N, 9.36%.

[Co(1a)H$_2$O](PF$_6$)$_2$ (2a′). The ligand **1a** (47.1 mg, 0.076 mmol) was suspended in EtOH (10 mL), and the solution was heated at 80 °C. The aqueous solution (5 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (21.6 mg, 0.074 mmol) was added to the hot EtOH solution, and the mixture was refluxed for 2 h. The reaction mixture was cooled; NH_4PF_6 was added to the solution and left to stand overnight. The micro brown crystals were collected by filtration and dried at 100 °C in a vacuum. Yield: 56.1 mg (0.057 mmol, 77%). Anal. Found: C, 44.38; H, 3.14; N, 8.34%. Calcd for $C_{37}H_{32}N_6O_5CoF_{12}P_2 \cdot H_2O$: C, 44.11; H, 3.40; N, 8.34%.

[CoCl(1b)](PF$_6$) (2b). This complex was synthesized by the same procedure as for **2a** by using **1b** (45.7 mg, 0.072 mmol), LiCl (12.7 mg, 0.30 mmol), and $CoCl_2 \cdot 6H_2O$ (17.3 mg, 0.073 mmol). Yield: 62.8 mg (0.071 mmol, 99%). Anal. Found: C, 51.05; H, 4.28; N, 9.12%. Calcd for $C_{38}H_{32}N_6O_4ClCoF_6P \cdot 2CH_3OH$: C, 51.10; H, 4.29; N, 8.94%.

[Co(1b)H$_2$O](PF$_6$)$_2$ (2b′). This complex was synthesized by the same procedure as for **2a′** by using **1b** (42.7 mg, 0.067 mmol) and Co(NO$_3$)$_2\cdot$6H$_2$O (19.9 mg, 0.068 mmol). Yield: 46.2 mg (0.046 mmol, 69%). Found: C, 44.23; H, 3.33; N, 8.09%. Calcd for $C_{38}H_{34}N_6O_5CoF_{12}P_2\cdot 1.5H_2O$: C, 44.29; H, 3.62; N, 8.15%.

[CoCl(1c)](PF$_6$) (2c). This complex was synthesized by the same procedure as for **2a** by using **1c** (42.4 mg, 0.065 mmol), LiCl (9.3 mg, 0.22 mmol), and CoCl$_2\cdot$6H$_2$O (15.5 mg, 0.065 mmol). Yield: 52.8 mg (0.059 mmol, 91%). Found: C, 51.03; H, 3.84; N, 9.27%. Calcd for $C_{39}H_{34}N_6O_4ClCoF_6P\cdot 1.5H_2O$: C, 51.08; H, 4.06; N, 9.16%.

[Co(1c)H$_2$O](PF$_6$)$_2$ (2c′). This complex was synthesized by the same procedure as for **2a′** by using **1c** (48.4 mg, 0.075 mmol) and Co(NO$_3$)$_2\cdot$6H$_2$O (22.0 mg, 0.076 mmol). Yield: 55.2 mg (0.054 mmol, 73%). Found: C, 45.11; H, 3.56; N, 7.99%. Calcd for $C_{39}H_{36}N_6O_5CoF_{12}P_2\cdot H_2O$: C, 45.23; H, 3.70; N, 8.12%.

[CoCl(1d)](PF$_6$) (2d). This complex was synthesized by the same procedure as for **2a** by using **1d** (35.6 mg, 0.054 mmol), LiCl (7.6 mg, 0.18 mmol), and CoCl$_2\cdot$6H$_2$O (14.3 mg, 0.060 mmol). Yield: 43.9 mg (0.049 mmol, 90%). Anal. Found: C, 52.10; H, 4.02; N, 9.14%. Calcd for $C_{40}H_{36}N_6O_4ClCoF_6P\cdot H_2O$: C, 52.10; H, 4.15; N, 9.11%.

[Co(1b)H$_2$O](PF$_6$)$_2$ (2d′). This complex was synthesized by the same procedure as for **2a′** by using **1d** (34.1 mg, 0.051 mmol) and Co(NO$_3$)$_2\cdot$6H$_2$O (15.4 mg, 0.053 mmol). Yield: 38.6 mg (0.037 mmol, 74%). Anal. Found: C, 45.80; H, 3.66; N, 7.99%. Calcd for $C_{40}H_{38}N_6O_5CoF_{12}P_2\cdot H_2O$: C, 45.77; H, 3.84; N, 8.01%.

Electrochemical Methods. Cyclic voltammograms were measured with an ALS/CHI Model 660 voltammetric analyzer at a scan rate of 100 mV/s. The working and counter electrodes were a platinum disk and a platinum wire, respectively. The sample solutions (ca. 0.001 M) in 0.1 M *n*-Bu$_4$NClO$_4$/DMF were deoxygenated with a stream of nitrogen gas. All values of redox potentials are reported in reference to Fc/Fc$^+$ (Fc = ferrocene); in practice, a Ag/Ag$^+$ electrode was used as a reference (−0.15 V vs Fc/Fc$^+$).

X-Ray Diffraction Studies. Suitable single crystals of **2b** were obtained from the diffusion of CH$_3$CN/MeOH, and those of **2c″** were obtained from the slow evaporation of a solution of **2c′** in a CH$_3$CN/H$_2$O mixed solvent, respectively. The measurements were performed at −100 °C. Data collection was made on a Mercury CCD area detector coupled with a Rigaku/MSC diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å) by use of the CrystalClear software.[28] All of the calculations were carried out on the CrystalStructure software.[29] The structures were solved by direct methods and expanded by Fourier and difference Fourier techniques. The crystals contained methanol or water molecules as crystal solvents. Details of crystal parameters and structure refinement are given in Table 1. Selected bond lengths and angles are shown in Table 2.

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Supporting Information Available: Crystallographic data for **1b** and **1c″** in CIF format; the ESI-mass spectra of **2a**, **2a′**, and **15a**; and the preliminary X-ray structure of **15a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] *CrystalClear*; Rigaku Corp.: Tokyo, 1999.

[29] *CrystalStructure*, ver. 3.8.2; Rigaku Corp.: Tokyo, 2007.