SYNTHESIS OF 2,2'-BIPYRIDINES BEARING AMINO OR CARBOXYL GROUP AT THE SIDE CHAIN AND PHYSICAL PROPERTIES OF THEIR RUTHENIUM(II) COMPLEXES†

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Abstract —— The synthesis of unsymmetrical 2,2'-bipyridines, in which one pyridine ring of bipyridine is linked to the amino or carboxyl group through the alkyl chain as the side chain became possible by the regioselective *O*-alkylation of pyridyl-2(1*H*)-pyridinones. Synthetic tris(bipyridine)ruthenium(II) showed characteristic metal-to-ligand charge transfer (MLCT) bands at around 480 nm. The standard redox potentials of new $[Ru(bpy)_3]^{2+}$ were about 200 mV lower than that of the parent $[Ru(bpy)_3]^{2+}$. The *p*-substituent effect of the benzene ring upon the redox potential was observed.

It is well known that tris(bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, plays an important role in the photochemical systems for solar energy conversion.[1-3] Recent research in this field has been directed toward the construction of hybrid compounds, in other word, supramolecules, in order to improve the catalytic efficiency by assembling two or more different functions in a molecule.[4-9] Meyer and co-workers, for example, have demonstrated that the supramolecular system incorporating $[Ru(bpy)_3]^{2+}$ as a photosensitizer, phenothiazine as a electron donor, and 1,1'-dimethyl-4,4'-bipyridinium salt (paraquat) as an electron acceptor in a molecule attains a long-lived charge-separated state.[7] Under these situations, it seems to be very important to develop a new synthetic method for unsymmetrical 2,2'-bipyridines, in

† Dedicated to Dr. Bernhard Witkop on the occasion of his 80th birthday.

which some kind of functional group is attached to one of the two pyridine rings, in order to design and synthesize hybrid compounds.

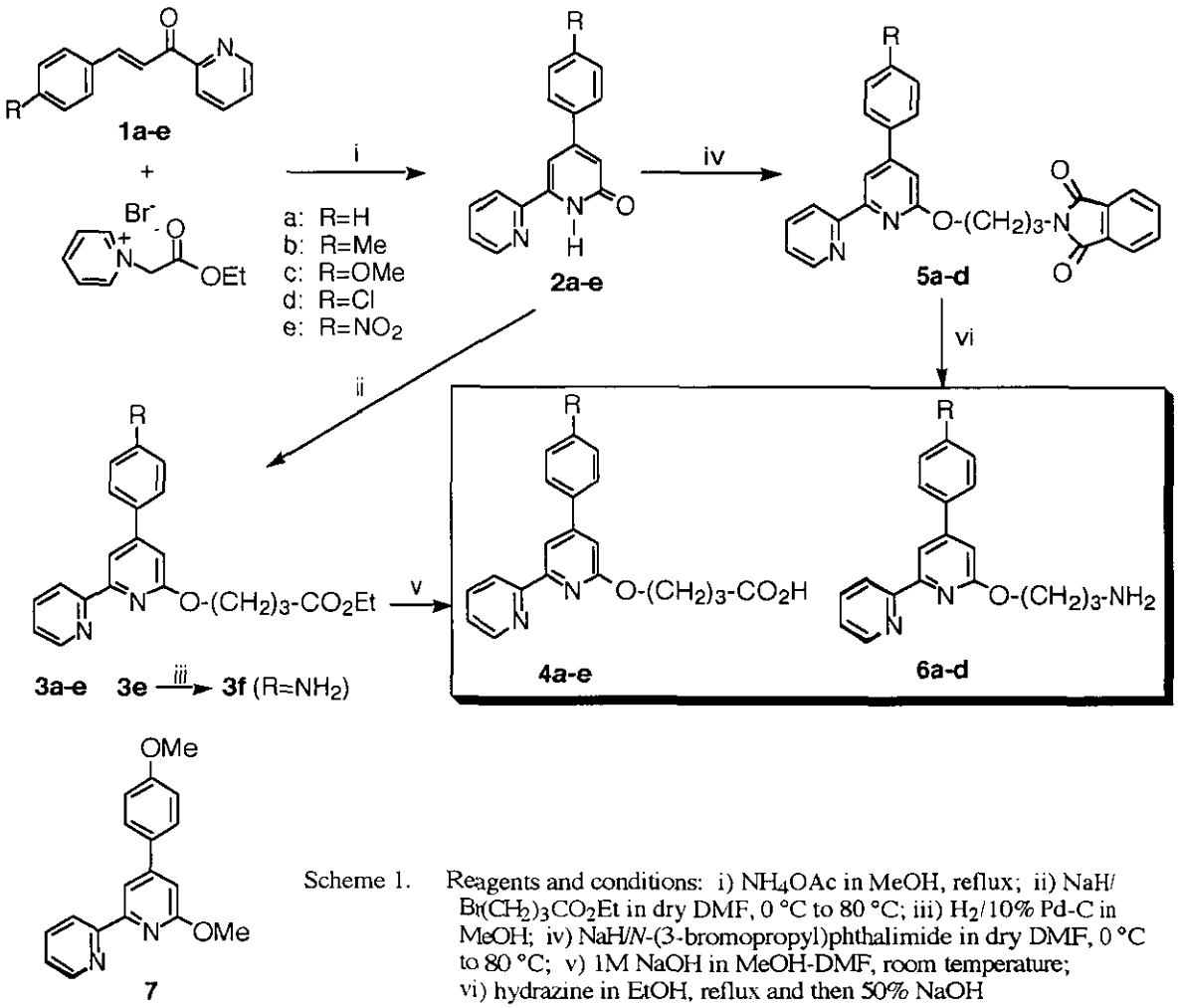
Synthetic methods was classified into four categories, although a number of papers concerning synthesis of unsymmetrical 2,2'-bipyridines have been reported. The most widely used method is the monolithiation of the methyl group. The deprotonation of methyl group of 4,4'- or 6,6'-dimethyl-2,2'-bipyridine with a strong base and subsequent treatment with various electrophiles afforded the hydroxy, amino, or carboxyl group-containing bipyridines.[10-17] The reaction of 6,6'-dimethyl-2,2'-bipyridine with *m*-chloroperbenzoic acid, treatment of the resulting mono *N*-oxide with acetic anhydride, followed by acidic hydrolysis gave hydroxymethyl group-containing 2,2'-bipyridine.[18] The direct oxidation of 4,4'-dimethyl-2,2'-bipyridine with SeO_2[19] or $KMnO_4$[20] gave 4'-methyl-2,2'-bipyridine-4-carboxylic acid. Further, Raney nickel-catalyzed coupling of nicotinic acid ethyl ester and subsequent partial hydrolysis gave the carboxyl group-containing 2,2'-bipyridine.[21] However, these methods have some disadvantages. For example, it is often difficult to separate a mixture of mono- and disubstituted products. The coupling reaction proceeds in only 23% yield.[21] On the contrary, no papers concerning the synthesis of unsymmetrical 2,2'-bipyridines by the direct *O*-alkylation of pyridyl-2(1*H*)-pyridinones have been reported, to the best of our knowledge. The present *O*-alkylation method has some advantages: i) all steps are easy in handling; ii) since two pyridine rings show different reactivities, the introduction of the functional groups at the side chain become possible by the regioselective *O*-alkylation. Further, it is possible to examine the *p*-substituent effect of the benzene ring attached to 2,2'-bipyridine ring.

We would like to describe here synthesis of unsymmetrical 2,2'-bipyridines bearing amino or carboxyl group at the side chain and physical properties of their ruthenium(II) complexes, including spectroscopic and electrochemical behaviors.

Results and Discussion

Synthesis of Unsymmetrical 2,2'-Bipyridines. The synthetic procedure for unsymmetrical 2,2'-bipyridines is depicted in Scheme 1. 3-(*p*-Substituted phenyl)-1-(2-pyridyl)-2-propen-1-ones (**1a-e**) were allowed to react with *N*-ethoxycarbonylmethylpyridinium bromide in the presence of ammonium acetate under reflux to afford 6-(2-pyridyl)-4-(*p*-substituted phenyl)-2(1*H*)-pyridinones (**2a-e**) in good yields. Compound (**2a**) was treated with ethyl 4-bromobutyrate in the presence of NaH in dry DMF to give the *O*-alkylated product. In this reaction, both *N*- and *O*-alkylation are possible by virtue of ambient anion, but only *O*-alkylation product (**3a**) was isolated. In IR spectrum, the absorption band due to C=O stretching

vibration of the lactam moiety of the starting material disappeared. Further, on ^{1}H NMR spectrum, the methylene protons adjacent to the oxygen atom was observed at 4.54 ppm, and C-3 and C-5 protons of 2(1*H*)-pyridinone ring were shifted to lower magnetic field by aromatization. Similarly, treatment of other 6-(2-pyridyl)-2(1*H*)-pyridinones (**2b-e**) with ethyl 4-bromobutyrate gave new 2,2'-bipyridines (**3b-e**). 4-Aminophenyl-2,2'-bipyridine (**3f**) was obtained by the catalytic hydrogenation of the corresponding 4-nitrophenyl one (**3e**). Compounds (**3a-e**) were subjected to hydrolysis with aqueous NaOH solution to afford unsymmetrical 2,2'-bipyridines (**4a-e**) bearing the carboxyl group at the side chain.



Scheme 1. Reagents and conditions: i) NH_4OAc in MeOH, reflux; ii) NaH/ $Br(CH_2)_3CO_2Et$ in dry DMF, 0 °C to 80 °C; iii) H_2/10% Pd-C in MeOH; iv) NaH/*N*-(3-bromopropyl)phthalimide in dry DMF, 0 °C to 80 °C; v) 1M NaOH in MeOH-DMF, room temperature; vi) hydrazine in EtOH, reflux and then 50% NaOH

On the other hand, 6-(2-pyridyl)-2(1*H*)-pyridones (**2a-d**) were treated with *N*-(3-bromopropyl)phthalimide in the presence of NaH and subsequent removal of the phthaloyl protecting group of compounds (**5a-d**) with hydrazine hydrate in aqueous 50% NaOH[12] solution to give 2,2-bipyridines (**6a-d**) bearing the amino group at the side chain. From these experiments, the synthesis of new unsymmetrical 2,2'-bipyridines bearing amino or carboxyl group at the side chain became possible by the regioselective *O*-alkylation of 6-(2-pyridyl)-2(1*H*)-pyridinones. These new 2,2'-bipyridines seems to be quite useful as building blocks on design of hybrid compounds.

UV-Vis Spectra and X-Ray Crystallographic Analysis. UV-Vis spectra of new 2,2'-bipyridines (**3a-e**) were measured in MeCN, and λ_{max} and log ε are summarized in Table 1, together with a data of the parent 2,2'-bipyridine as a reference. All new compounds showed bathochromic shifts compared to the parent 2,2'-bipyridine owing to the participation of a lone-pair electron of oxygen atom at the C-2 position to the conjugated system.

Table 1. UV-Vis Spectral Data of New 2,2'-Bipyridines and Their Ru(II) Complexes

Compound	λ_{max} nm (log ε) in MeCN		
3a	242 (4.5)	270 (4.2)	308 (4.1)
3b	246 (4.5)	269 (4.3)	310 (4.1)
3c	251 (4.4)	280 (4.4)	308 (4.2)
3d	246 (4.5)	260 (4.4)	311 (4.1)
3e	202 (4.5)	223 (4.3)	289 (4.4)
bpy[a)]		236 (4.1)	280 (4.2)
8a	249 (4.8)	316 (4.7)	476 (4.0)
8b	257 (4.8)	315 (4.9)	477 (4.2)
8c	271 94.7)	315 (4.8)	478 (4.2)
$[Ru(bpy)_3]^{2+}$		290 (4.8)	452 (4.1)

a) 2,2'-bipyridine.

Treatment of 6-(2-pyridyl)-2(1*H*)-pyridinone (**2c**) with methyl iodide instead of ethyl 4-bromobutyrate afforded 6-methoxy-2,2'-bipyridine (**7**) as pale yellow needles suitable for X-Ray crystallographic analysis. The ORTEP view of compound (**7**) is shown in Figure 1, together with crystal data (Tables 2 and 3). The following two structural features are revealed in the crystalline state: i) two nitrogen atoms of the bipyridine ring are *trans*-positioned each other, and one pyridine ring is nearly co-planar to the other

pyridine one (dihedral angle between two planes: *ca.* 4 °); ii) the benzene ring is nearly co-planar to the bipyridine ring (*ca.* 3 °), and thus all three aromatic rings lie in the almost same plane.

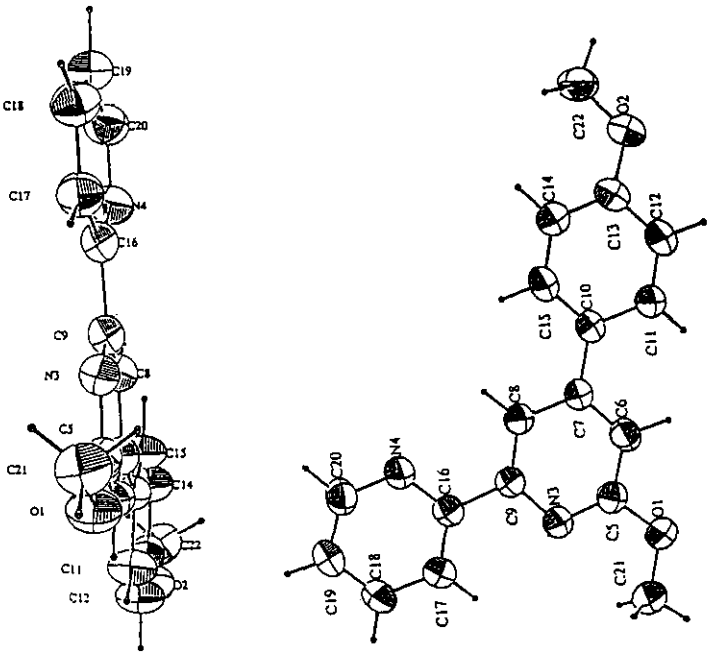


Figure 1. ORTEP drawings of 2,2'-bipyridine (**7**) showing 50% probability *displacement elipsoides*; parallel to molecular plane (right) and perpendicular to right (left).

Table 2. Crystal Data for 2,2'-Bipyridine (**7**)

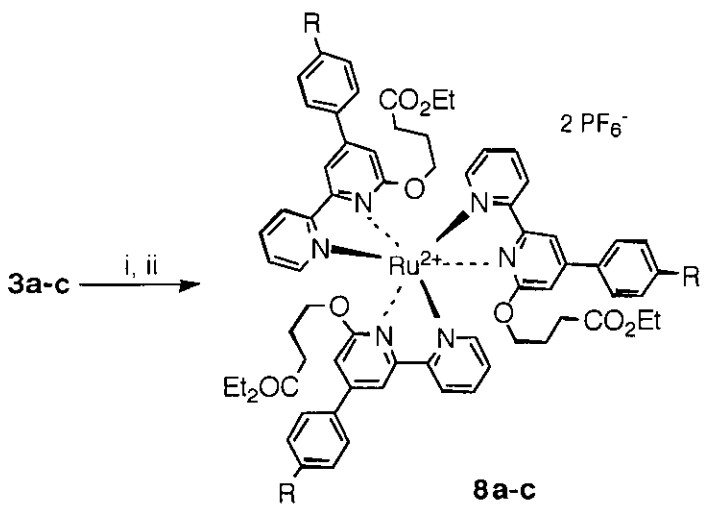
Formula	$C_{18}H_{16}N_2O_2$	Crystal size/nm	0.7x0.4x0.3
FW	292.34	μ(Mo $K\alpha$)/cm^{-1}	0.8
Habit	needle	Radiation	Mo $K\alpha$ (λ=0.71073Å)
Temp/K	298	Diffractometor	Enraf-Nonius CAD4
Crystal system	Monoclinic	Monochrometor	Graphite crystal
Space group	$P2_1/a$	Scan type	ω–2θ
a/Å	16.216(2)	2θ_{max}/deg	50.0
b/Å	5.426(1)	Scan speed/deg min^{-1}	1-5
c/Å	16.758(2)	No. of unique reflns	2887
β/deg	95.55(1)	No. of reflns used	1818($\|F_o\|>3\alpha(F_o)$)
V/Å^3	1467.7	No. of variables	199
Z	4	R	0.049
d_{calcd}/g cm^{-3}	1.32	R_w	0.065

Table 3. Bond Distances (Å) and Angles (deg) for 2,2'-Bipyridine (**7**)[a)]

			Bond distances		
O(1)-O(5)	1.361(2)	O(1)-C(21)	1.425(3)	O(2)-C(13)	1.361(3)
O(2)-C(22)	1.422(3)	N(3)-C(5)	1.316(3)	N(3)-C(9)	1.352(3)
N(4)-C(16)	1.339(3)	N(4)-C(20)	1.329(3)	C(5)-C(6)	1.396(3)
C(6)-C(7)	1.373(3)	C(7)-C(8)	1.405(3)	C(7)-C(10)	1.487(3)
C(8)-C(9)	1.375(3)	C(9)-C(16)	1.491(3)	C(10)-C(11)	1.394(3)
C(10)-C(15)	1.390(3)	C(11)-C(12)	1.372(3)	C(12)-C(13)	1.378(3)
C(13)-C(14)	1.376(3)	C(14)-C(15)	1.378(3)	C(16)-C(17)	1.389(3)
C(17)-C(18)	1.380(3)	C(18)-C(19)	1.369(3)	C(19)-C(20)	1.373(3)
			Bond angles		
C(5)-O(1)-C(21)	117.6(2)	C(13)-O(2)-C(22)	117.4(2)	C(5)-N(3)-C(9)	116.0(2)
C(16)-N(4)-C(20)	117.5(2)	O(1)-C(5)-N(3)	119.5(2)	O(1)-C(5)-N(3)	119.5(2)
N(3)-C(5)-C(6)	124.9(2)	C(5)-C(6)-C(7)	119.2(2)	C(6)-C(7)-C(8)	116.5(2)
C(6)-C(7)-C(10)	121.5(2)	C(8)-C(7)-C(10)	122.0(2)	C(7)-C(8)-C(9)	120.1(2)
N(3)-C(9)-C(8)	123.2(2)	N(3)-C(9)-C(16)	115.4(2)	C(8)-C(9)-C(16)	121.4(2)
C(7)-C(10)-C(11)	122.1(2)	C(7)-C(10)-C(15)	122.3(2)	C(11)-C(10)-C(15)	115.7(2)
C(10)-C(11)-C(12)	122.1(2)	C(11)-C(12)-C(13)	120.7(2)	O(2)-C(13)-C(12)	116.4(2)
O(2)-C(13)-C(14)	125.0(2)	C(12)-C(13)-C(14)	118.6(2)	C(13)-C(14)-C(15)	120.1(2)
C(10)-C(15)-C(14)	122.7(2)	N(4)-C(16)-C(9)	116.8(2)	N(4)-C(16)-C(17)	122.0(2)
C(9)-C(16)-C(17)	121.2(2)	C(16)-C(17)-C(18)	119.0(2)	C(17)-C(18)-C(19)	119.1(2)
C(18)-C(19)-C(20)	118.2(2)	N(4)-C(20)-C(19)	124.2(2)		

a) Number of the atom refers to that in the ORTEP drawing (Figure 1).

UV-Vis and Fluorescence Spectra of Ru(II) Complexes. New Ru(II) complexes (**8a-f**) were prepared by reaction of 2,2'-bipyridines (**3a-f**) with ruthenium(III) chloride in EtOH under reflux conditions and subsequent treatment with ammonium hexafluorophosphate (NH_4PF_6) according to Scheme 2.



Scheme 2. Reagents and conditions: i) $RuCl_3$ in EtOH, reflux; ii) an excess of NH_4PF_6 in H_2O, room temperature

Unfortunitely, attempts to purify Ru(II) complexes (**8d-f**) by recrystallization or gel chromatography on Sephadex LH-20 were unsuccessful. Therefore, UV-Vis spectra of Ru(II) complexes (**8a-c**) were measured in MeCN, and λ_{max} and log ε are also summarized in Table 1, together with a data of the parent $[Ru(bpy)_3]^{2+}$. In all cases, characteristic MLCT bands were observed at around 480 nm in addtion of two absorption bands due to π-π* transitions. It was found that MLCT bands of these new Ru(II) complexes showed the bathochromic shift about 30 nm attributable to the attachment of an auxochromic oxygen atom at the C-2 position of the bipyridine ring. Further, the fluorescence emission spectrum of Ru(II) complex (**8a**) was measured in MeCN. This complex showed an emission band at 705 nm when the excitation wavelength of 480 nm was applied.

Electrochemical Properties of Ru(II) Complexes. The electrochemical properties of Ru(II) complexes were determined by means of cyclic voltammetry. The platinum electrode was used together with a standard calomel electrode (SCE) as a reference in the presence of tetrabutylammonium perchlorate as a electrolyte in dry MeCN. At sequential scans, cyclic voltammograms of Ru(II) complexes did not change, indicating that Ru(II) complexes (**8a-c**) were electrochemically stable. Further, the plots of the square root of the scan rate V vs. i_p gave the straight line, suggesting that the electron transfer process proceeds at the difusion control. The standard redox potentials of other new Ru(II) complexes are summarized in Table 4 together with that of the parent $[Ru(bpy)_3]^{2+}$.

Table 4. The Standard Redox Potentials of Ru(II) Complexes

	8a	**8b**	**8c**	**$[Ru(bpy)_3]^{2+}$**
$E_{1/2}$ $Ru^{II/III}$ (V)	1.10	1.07	1.06	1.29
$E_{1/2}$ $Ligand^{0/-}$ (V)	-1.36	-1.37	-1.40	-1.33

The standard redox potentials of these complexes were about 200 mV lower than that of the parent complex. It may be attributable for the contribution of the electron-donating oxygen atom attached directly to the bipyridine ring. Further, it was indicated that the *p*-substituents of the benzene ring at C-4 position of the bipyridine ring affected the standard redox potentials, although the degree was fairly small.

EXPERIMENTAL

Melting points were measured with a Mel-Temp apparatus in open capillaries and are uncorrected. IR spectra were recorded on a JIR-3510 FT-IR spectrophotometer. UV-Vis and fluorescence spectra were

taken on JASCO Ubest V-550 and FP-777 fluorescence spectrophotometers, respectively. ^{1}H NMR spectra were obtained with a JEOL GX-270NMR spectrometer and are reported in ppm (δ) downfield from internal Me_4Si. Thin layer chromatography (TLC) analysis was performed on silica gel 60F-254 with a 0.2 mm layer thickness. Column chromatography was carried out with Merck Kieselgel 60 (230-400 mesh). High performance liquid chromatography (HPLC) was carried out with a JASCO 880-PU and 875-UV equipped with a JASCO 807-IT integrator by using a column packed with a Finepak $SILC_{12}S$. Combustion analysis was performed on a Perkin Elmer 2400 CHNS/O analyser. Compounds (**1a-e**) were prepared by the aldol condensation of the corresponding *p*-substituted benzaldehydes with 2-acetylpyridine according to literature methods.[22-24]

General Procedure for Synthesis of 4-(4-Substituted phenyl)-6-(2-pyridyl)-2(1*H*)-pyridinones (2a-e): A Typical Example, 4-Phenyl-6-(2-pyridyl)-2(1*H*)-pyridinone (2a): A mixture of 2-propen-1-one (**1a**) (2.0 g, 9.56 mmol), *N*-ethoxycarbonylmethylpyridinium bromide (2.35 g, 9.56 mmol) and NH_4OAc (7.2 g, 93 mmol) in EtOH (20 mL) was heated at 60 °C for 5 h. The reaction mixture was cooled to 0 °C in a refrigerator. The resulting solid was washed with cold AcOEt (120 mL) and then recrystallized from AcOEt-petroleum ether mixture to give the pure product (**2a**) as colorless powders; mp 190-191 °C; yield 1.15 g (57%); IR (KBr) 3370, 1645, 766 and 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.82 (1H, d, *J*=1.5 Hz), 7.06 (1H, d, *J*=1.5 Hz), 7.35-7.40 (1H, m), 7.46-7.52 (3H, m), 7.64 (2H, d, *J*=9.5 Hz), 7.84 (1H, t, *J*=7.7 Hz), 7.92 (1H, d, *J*=7.7 Hz), 8.67 (1H, d, *J*=4.9 Hz), 10.68 (1H, br s). *Anal.* Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.26; H, 4.88; N, 11.28.

6-(2-Pyridyl)-4-*p*-tolyl-2(1*H*)-pyridinone (2b): as pale yellow needles; mp 203-205 °C; yield 81%; IR (KBr) 3390, 1650, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.43 (3H, s), 6.81 (1H, s), 7.06 (1H, s), 7.30 (2H, d, *J*=8.7 Hz), 7.38 (1H, m), 7.54 (2H, d, *J*=8.7 Hz), 7.83 (1H, t, *J*=7.9 Hz), 7.92 (1H, d, *J*=7.9 Hz), 8.67 (1H, d, *J*=4.7 Hz), 10.62 (1H, br s). *Anal.* Calcd for $C_{17}H_{14}N_2O$: C, 77.57; H, 5.70; N, 10.64. Found: C, 77.63; H, 5.71; N, 10.45.

4-(4-Methoxyphenyl)-6-(2-pyridyl)-2(1*H*)-pyridinone (2c): as brown needles; mp 227-230 °C; yield 77%; IR (KBr) 3420, 1650, and 833 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=3.86 (3H, s), 6.68 (1H, s), 7.04 (2H, d, *J*=8.9 Hz), 7.45 (2H, t, *J*=8.1 Hz), 7.74 (2H, d, *J*=8.9 Hz), 7.91 (1H, t, *J*=8.1 Hz), 8.13 (1H, s), 8.27 (1H, d, *J*=8.1 Hz), 8.69 (1H, d, *J*=4.6 Hz), 10.76 (1H, br s). *Anal.* Calcd for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.08; N, 10.06. Found: C, 73.29; H, 5.03; N, 10.02.

4-(4-Chlorophenyl)-6-(2-pyridyl)-2(1*H*)-pyridinone (2d): as colorless needles; mp 225-226 °C; yield 57%; IR (KBr) 3370, 1650, and 825 cm^{-1}; ^1H NMR (DMSO-d_6) δ=6.78 (1H, s), 7.45-7.52 (2H, m), 7.54 (2H, d, *J*=8.7 Hz), 7.83 (2H, d, *J*=8.7 Hz), 7.96 (1H, t, *J*=7.9 Hz), 8.31 (1H, d, *J*=7.9 Hz), 8.70 (1H, d, *J*=5.2 Hz), 11.00 (1H, br s). *Anal.* Calcd for $C_{16}H_{11}N_2OCl$: C, 67.97; H, 3.93; N, 9.90. Found: C, 68.07; H, 3.94; N, 10.01.

4-(4-Nitrophenyl)-6-(2-pyridyl)-2(1*H*)-pyridinone (2e): as greenish plates (recrystallization from DMF); 315-318 °C (lit.,[25] mp 310 °C); yield 62%; IR (KBr) 3432, 1654, 1533, 1350, and 825 cm^{-1}. *Anal.* Calcd for $C_{16}H_{11}N_3O_3$: C, 65.52; H, 3.79; N, 14.32. Found: C, 65.30; H, 3.76; N, 14.71.

General Procedure for Synthesis of 6-[3-(Ethoxycarbonyl)propoxy]-4-(4-substituted phenyl)-2,2'-bipyridines (3a-e): A Typical Example, 6-[3-(Ethoxycarbonyl)propoxy]-4-phenyl-2,2'-bipyridine (3a): NaH (60% in oil, 200 mg, 5 mmol) was washed with distilled hexane. To a suspension of NaH in dry DMF (10 mL) was added dropwise a solution of compound (**2a**) (1.12 g, 4.5 mmol) in dry DMF (30 mL). After 15 min, a solution of ethyl 4-bromobutyrate (965 mg, 4.95 mmol) in dry DMF (10 mL) was added to the mixture. The reaction mixture was stirred for 1 h at rt tunder nitrogen atmosphere and then heated on an oil bath (80-100 °C) for another 6 h. After removal of the solvent, the residue was dissolved in AcOEt (300 mL). The organic layer was washed with H_2O (50 mL x 3) and then dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel with $CHCl_3$-acetone (100:4) mixture and subsequent recrystallization from petroleum ether to give the pure product (**3a**) as colorless needles; mp 50-52 °C; yield 939 mg(58%); IR(KBr) 1733 and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, *J*=7.1 Hz), 2.20 (2H, quint, *J*=7.1 Hz), 2.56 (2H, t, *J*=7.1 Hz), 4.15 (2H, q, *J*=7.1 Hz), 4.54 (2H, t, *J*=7.1 Hz), 6.99 (1H, d, *J*=1.3 Hz), 7.26 and 7.34 (1H, dd, *J*=7.8 and 3.9 Hz), 7.40-7.52 (3H, m), 7.74 (2H, d, *J*=7.8 Hz), 7.84 (1H, t, *J*=7.8 Hz), 8.33 (1H, d, *J*=1.3 Hz), 8.42 (1H, d, *J*=7.8 Hz), 8.69 (1H, d, *J*=3.9 Hz). *Anal.* Calcd for $C_{22}H_{22}N_2O_3$: C,72.91; H, 6.12; N, 7.73. Found: C, 72.99; H, 6.18; N, 7.51.

6-[3-Ethoxycarbonyl)propxy]-4-*p*-tolyl-2,2'-bipyridine (3b) : as colorless needles; mp 77-78 °C; yield 65%; IR (KBr) 1736 and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (3H, t, *J*=7.2 Hz), 2.15 (2H, quint, *J*=7.2 Hz), 2.56 (2H, t, *J*=7.2 Hz), 3.87 (3H, s), 4.16 (2H, q, *J*=7.2 Hz), 4.53 (2H, t, *J*=7.2 Hz), 6.94 (1H, d, *J*=1.2 Hz), 7.00 (2H, d, *J*=8.5 Hz), 7.25-7.33 (1H, m), 7.71 (2H, d, *J*=8.5 Hz), 7.81 (1H, t, *J*=8.0 Hz), 8.28 (1H, d, *J*=1.4 Hz), 8.41 (1H, d, *J*=8.0 Hz), 8.68 (1H, d, *J*=5.1 Hz). *Anal.* Calcd for $C_{23}H_{24}N_2O_3$: C, 73.40; H, 6.38; N, 7.45. Found: C, 73.60; H, 6.43; N, 7.36.

6-[3-(Ethoxycarbonyl)propoxy]-4-(4-methoxyphenyl)-2,2'-bipyridine (3c) : as colorless needles; mp 95-97 °C; yield 76%; IR (KBr) 1733 and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (3H, t, *J*=7.2 Hz), 2.20 (2H, quint, *J*=7.2 Hz), 2.56 (2H, t, *J*=7.2 Hz), 3.87 (3H, s), 4.16 (2H, q, *J*=7.2 Hz), 4.53 (2H, t, *J*=7.2 Hz), 6.94 (1H, d, *J*=1.4 Hz), 7.00 (2H, d, *J*=8.5 Hz), 7.25-7.33 (1H, m), 7.71 (2H, d, *J*=8.5 Hz), 7.81 (1H, t, *J*=8.0 Hz), 8.28 (1H, d, *J*=1.4 Hz), 8.41 (1H, d, *J*=8.0 Hz), 8.68 (1H, d, *J*=5.1 Hz). *Anal.* Calcd for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 6.96. Found: C, 70.13; H, 6.15; N, 6.96.

4-(4-Chlorophenyl)-6-[3-(ethoxycarbonyl)propoxy]-2,2'-bipyridine (3d): as colorless needles; mp 92-93 °C; yield 79%; IR (KBr) 1732 and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, *J*=6.8 Hz), 2.17 (2H, quint, *J*=6.8 Hz), 2.56 (2H, t, *J*=6.8 Hz), 4.15 (2H, q, *J*=6.8 Hz), 4.54 (2H, t, *J*=6.8 Hz), 6.94 (1H, d, *J*=1.3 Hz), 7.26-7.33 (1H, m), 7.45 (2H, d, *J*=8.7 Hz), 7.68 (2H, t, *J*=8.7 Hz), 7.83 (1H, t, *J*=7.8 Hz), 8.26 (1H, d, *J*=1.3 Hz), 8.41 (1H, d, *J*=7.8 Hz), 8.68 (1H, d, *J*=4.6 Hz). *Anal.* Calcd for $C_{22}H_{21}N_2O_3Cl$: C, 66.58; H, 5.33; N, 7.06. Found: C, 66.29; H, 5.49; N, 7.06.

6-[3-(Ethoxycarbonyl)propoxy]-4-(4-nitrophenyl)-2,2'-bipyridine (3e): as pale yellow needles; mp 120-121 °C; yield 62%; IR (KBr) 1734 and 847 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, *J*=7.1 Hz), 2.21 (2H, quint, *J*=6.8 Hz), 2.56 (2H, t, *J*=6.8 Hz), 4.16 (2H, q, *J*=7.1 Hz), 4.56 (2H, t, *J*=6.8 Hz), 6.99 (1H, d, *J*=1.5 Hz), 7.31and 7.37 (1H, dd, *J*=7.7 and 5.1 Hz), 7.83 (1H, t, *J*=7.7 Hz), 7.88 (2H, d, *J*=8.8 Hz), 8.31 (1H, d, *J*=1.5 Hz), 8.34 (2H, d, *J*=8.8 Hz), 8.42 (1H, d, *J*=7.7 Hz), 8.68 (1H, d, *J*=5.1 Hz). *Anal.* Calcd for $C_{22}H_{21}N_3O_5$: C, 64.85; H, 5.21; N, 10.31. Found: C, 64.91; H, 5.44; N, 10.06.

4-(4-Aminophenyl)-6-[3-(ethoxycarbonyl)propoxy]-2,2'-bipyridine (3f): A suspension of 10% Pd-C (25 mg) in dry MeOH (40 mL) was prehydrogenated for 30 min under hydrogen atmosphere. To this suspension was added a solution of compound (**3e**) (244 mg, 0.60 mmol) in dry MeOH (20 mL). The reaction mixture was hydrogenated for 1.5 h under hydrogen atmosphere. After removal of the catalyst, the solvent was evaporated to give the crude product, which was recrystallized from AcOEt-petroleum ether to give the pure product (**3f**) as pale yellow solids; yield 196 mg (87%); mp 131-132 °C; IR (KBr) 3456, 1734, and 827 cm^{-1}, ^1H-NMR ($CDCl_3$) δ=1.25 (3H, t, *J*=7.2 Hz), 2.19 (2H, quint, *J*=7.2 Hz), 2.55 (2H, t, *J*=7.2 Hz), 3.84 (2H, s), 4.15 (2H, q, *J*=7.2 Hz), 4.52 (2H, t, *J*=7.2 Hz), 6.76 (2H, d, *J*=8.5 Hz), 6.93 (2H, d, *J*=1.3 Hz), 7.26 and 7.31 (1H, dd, *J*=7.8 and 3.9 Hz), 7.60 (2H, d, *J*=8.5 Hz), 7.80 (1H, t, *J*=7.8 Hz), 8.26 (1H, d, *J*=1.3 Hz), 8.40 (1H, d, *J*=7.8 Hz), 8.67 (1H, d, *J*=3.9 Hz). *Anal.* Calcd for $C_{22}H_{23}N_3O_3$: C, 70.0; H, 6.15; N, 11.13. Found: C, 70.26; H, 6.13; N, 11.44.

General Procedure for Synthesis of 6-(3-Carboxypropoxy)-4-(4-substituted phenyl)-2,2'-bipyridines (4a-e): A Typical Example, 6-(3-Carboxypropoxy)-4-phenyl-2,2'-bipyridine (4a). A solution of compound (**3a**) (254 mg, 0.70 mmol) and 1M NaOH (8 mL, 8 mmol) in MeOH-DMF (3:1) mixture (60 mL) was stirred for 6 h at rt. After evaporation of the solvent under reduced pressure, H_2O (50 mL) was added to the residue. The aqueous solution was adjusted to pH 2.0 with 1M HCl and extracted with AcOEt (100 mL x 3). The combined organic layers were washed with H_2O (60 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was recrystallized from AcOEt-petroleum ether mixture to give the pure product (**4a**) as colorless needles; mp 172-174 °C; yield 176 mg (75%); IR (KBr) 3000 (br), 1710, 735, and 669 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.14 (2H, quint, *J*=6.9 Hz), 2.62 (2H, t, *J*=6.9 Hz), 4.56 (2H, t, *J*=6.9 Hz), 7.00 (1H, d, *J*=0.8 Hz), 7.30 and 7.37 (1H, dd, *J*=6.6 and 3.3 Hz), 7.41-7.52 (3H, m), 7.75 (2H, d, *J*=7.2 Hz), 7.87 (1H, t, *J*=6.6 Hz), 8.30 (1H, d, *J*=0.8 Hz), 8.42 (1H, d, *J*=6.6 Hz), 8.78 (1H, d, *J*=3.3 Hz). *Anal.* Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.67; H, 5.58; N, 8.16.

6-(3-Carboxypropoxy)-4-*p*-tolyl-2,2'-bipyridine (4b): as colorless needles; mp 167-169 °C; yield 78%; IR (KBr) 3000 (br), 1712, and 816 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.19 (2H, quint, *J*=6.7 Hz), 2.42 (3H, s), 2.39 (2H, t, *J*=6.7 Hz), 4.56 (2H, t, *J*=6.7 Hz), 6.99 (1H, d, *J*=1.5 Hz), 7.28 (2H, d, *J*=8.9 Hz), 7.31-7.37 (1H, m), 7.65 (2H, d, *J*=8.9 Hz), 7.85 (1H, t, *J*=7.6 Hz), 8.26 (1H, d, *J*=1.5 Hz), 8.40 (1H, d, *J*=7.6 Hz), 8.73-8.82 (1H, m). *Anal.* Calcd for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.23; H, 5.81; N, 7.98.

6-(3-Carboxypropoxy)-4-(4-methoxyphenyl)-2,2'-bipyridine (4c): as colorless needles; mp 149-150 °C; yield 70%; IR (KBr) 3000 (br), 1716 and 831 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.21 (2H, quint, *J*=6.7 Hz), 2.62 (2H, t, *J*=6.7 Hz), 3.85 (3H, s), 4.54 (2H, t, *J*=6.7 Hz), 6.94 (1H, d, *J*=1.4 Hz), 6.98 (2H, d, *J*=8.9 Hz), 7.24-7.32 (1H, m), 7.69 (2H, d, *J*=8.9 Hz), 7.80 (1H, t, *J*=9.0 Hz), 8.24 (1H, d, *J*=1.4 Hz), 8.38 (1H, d, *J*=9.0 Hz), 8.69 (1H, d, *J*=6.0 Hz). *Anal.* Calcd for $C_{21}H_{20}N_2O_4$: C, 69.21; H, 5.54; N, 7.68. Found: C, 69.11; H, 5.56; N, 7.53.

6-(3-Carboxypropoxy)-4-(4-chlorophenyl)-2,2'-bipyridine (4d): as colorless needles; mp 183-185 °C; yield 84%; IR (KBr) 3000 (br), 1714, and 827 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.06 (2H, quint, *J*=7.0 Hz), 2.45 (2H, t, *J*=7.0 Hz), 4.49 (2H, t, *J*=7.0 Hz), 7.15 (1H, s), 7.44 (1H, m), 7.56 (2H, d, *J*=7.6 Hz), 7.86 (2H, d, *J*=7.6 Hz), 7.95 (1H, t, *J*=8.6 Hz), 8.28 (1H, s), 8.40 (1H, d, *J*=8.6 Hz), 8.70

ppm (1H, d, *J*=4.3 Hz). *Anal.* Calcd for $C_{20}H_{17}N_2O_3Cl$: C, 65.13; H, 4.64; N, 7.60. Found: C, 65.13; H, 4.78; N, 7.34.

6-(3-Carboxypropoxy)-4-(4-nitrophenyl)-2,2'-bipyridine (4e) : as colorless needles; mp 168-170 °C; yield 88%; IR (KBr) 3000 (br), 1730, and 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.16 (2H, quint, *J*=6.9 Hz), 2.46 (2H, t, *J*=6.9 Hz), 4.50 (2H, t, *J*=6.9 Hz), 7.00 (1H, d, *J*=1.5 Hz), 7.40 (1H, m), 7.84 (1H, t, *J*=7.7 Hz), 7.88 (2H, d, *J*=8.8 Hz), 8.31 (1H, d, *J*=1.5 Hz), 8.35 (2H, d, *J*=8.8 Hz), 8.42 (1H, d, *J*=8.8 Hz), 8.70 (1H, d, *J*=4.6 Hz). *Anal.* Calcd for $C_{20}H_{17}N_3O_5$: C, 63.32; H, 4.52; N, 11.08. Found: C, 63.13; H, 4.38; N, 11.37.

General Procedure for Synthesis of 4-(4-Substituted phenyl)-6-(3-phthalimidopropoxy)-2,2'-bipyridines (5a-d): A Typical Example, 4-Phenyl-6-(3-phthalimidopropoxy)-2,2'-bipyridine (5a): NaH (60% in oil, 208 mg, 5 mmol) was washed with distilled hexane. To a suspension of NaH in dry DMF (10 mL) was added dropwise a solution of compound (**2a**) (1.12 g, 4.5 mmol) in dry DMF (30 mL). After 15 min, a solution of *N*-(3-bromopropyl)phthalimide (1.34 g, 5 mmol) in dry DMF (10 mL) was added to the mixture. The reaction mixture was stirred for 6 h at rt under nitrogen atmosphere and then heated for another 3 h on an oil bath (80-100 °C) for another 3 h. After removal of the solvent, the residue was dissolved in AcOEt (250 mL). The organic layer was washed with H_2O (50 mL x 3), saturatred NaCl (80 mL), and then dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by column chromatography on silica gel with $CHCl_3$-acetone-EtOH (100:10:2) mixture to give the pure product (**5a**) as colorless powders; mp 142-143 °C; yield 1.58g (81%); IR (KBr) 1762, 1707, 734, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.28 (2H, quint, *J*=6.6 Hz), 3.97 (2H, t, *J*=6.6 Hz), 4.58 (2H, t, *J*=6.6 Hz), 6.83 (1H, d, *J*=1.5 Hz), 7.26-7.30 (1H, m), 7.41-7.46 (3H, m), 7.66-7.70 (4H, m), 7.77 (1H, t, *J*=7.6 Hz), 7.81-7.85 (2H, m), 8.23 (1H, d, *J*=1.5 Hz), 8.36 (1H, d, *J*=7.8 Hz), 8.66 (1H, d, *J*=3.9 Hz). *Anal.* Calcd for $C_{27}H_{21}N_3O_3$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.51; H, 5.01; N, 9.62.

6-(3-Phthalimidopropoxy)-4-*p*-tolyl-2,2'-bipyridine (5b): as colorless powders; mp 131-132 °C; yield 81%; IR (KBr) 1774, 1708, and 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.28 (2H, quint, *J*=6.4 Hz), 2.41 (3H, s), 3.96 (2H, t, *J*=6.4 Hz), 4.57 (2H, t, *J*=6.4 Hz), 6.82 (1H, d, *J*=1.5 Hz), 7.26 (2H, d, *J*=8.3 Hz), 7.26-7.30 (1H, m), 7.59 (2H, d, *J*=8.3 Hz), 7.69 (2H, d, *J*=5.6 Hz), 7.74-7.80 (1H, m), 7.83 (2H, d, *J*=8.5 Hz), 8.26 (1H, d, *J*=1.5 Hz), 8.36 (1H, d, *J*=8.1 Hz), 8.66 (1H, d, *J*=3.9 Hz).

Anal. Calcd for $C_{28}H_{23}N_3O_3 \cdot 0.5H_2O$: C, 73.35; H, 5.28; N, 9.16. Found: C, 73.13; H, 5.15; N, 9.06.

4-(4-Methoxyphemyl)-6-(3-phthalimidopropoxy)-2,2'-bipyridine (5c): as colorless powders; mp 145-146 °C; yield 81%; IR (KBr) 1774, 1712, 1180, and 734 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.28 (2H, quint, *J*=6.5 Hz), 3.87 (3H, s), 3.96 (2H, t, *J*=6.5 Hz), 4.57 (2H, t, *J*=6.5 Hz), 6.79 (1H, s), 6.98 (2H, d, *J*=7.3 Hz), 7.26-7.30 (1H, m), 7.63-7.71 (4H, m), 7.78 (1H, t, *J*=6.7 Hz), 7.84 (2H, d, *J*=7.3 Hz), 8.25 (1H, s), 8.36 (1H, d, *J*=7.8 Hz), 8.67 (1H, d, *J*=4.5 Hz). *Anal.* Calcd for $C_{28}H_{23}N_3O_4$: C, 72.25; H, 4.98; N, 9.03. Found: C, 72.02; H, 4.96; N, 8.92.

4-(4-Chlorophenyl)-6-(3-phthalimidopropoxy)-2,2'-bipyridine (5d): as yellow powders; mp 108-110 °C; yield 71%; IR (KBr) 1771, 1709, and 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.28 (2H, quint, *J*=5.9 Hz), 3.96 (2H, t, *J*=5.9 Hz), 4.57 (2H, t, *J*=5.9 Hz), 6.78 (1H, s), 7.27-7.31 (1H, m), 7.43 (2H, d, *J*=8.5 Hz), 7.62 (1H, d, *J*=8.5 Hz), 7.67-7.70 (2H, m), 7.74-7.81 (1H, m), 7.82-7.85 (2H, m), 8.23 (1H, s), 8.36 (1H, d, *J*=8.3 Hz), 8.66 (1H, d, *J*=4.9 Hz). *Anal.* Calcd for $C_{27}H_{20}N_3O_3Cl$: C, 69.01; H, 4.29; N, 8.94. Found: C, 69.38; H, 4.49; N, 8.61.

General Procedure for Synthesis of 6-(3-Aminopropoxy)-4-(4-substituted phenyl)-2,2'-bipyridines (6a-d): A Typical Example, 6-(3-Aminopropoxy)-4-phenyl-2,2'-bipyridine (6a): A mixture of compound (**5a**) (306 mg, 0.7 mmol) and 80% hydrazine monohydrate (125 mg, 2 mmol) in EtOH (10 mL) was refluxed for 6 h, and then cooled to room rt. The reaction mixture was poured into saturated NaCl solution (35 mL), basified with 50% NaOH to pH 12, and then extracted with $CHCl_3$ (30 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was recrystallized from AcOEt-petroleum ether mixture to give the pure product (**6a**) as yellow powders; mp 71-72 °C; yield 185 mg (86%); IR(KBr) 3332 and 698 cm^{-1}; ^1H NMR ($CDCl_3$)δ=2.03 (2H, quint, *J*=6.5 Hz), 2.96 (2H, t, *J*=6.5 Hz), 4.60 (2H, t, *J*=6.5 Hz), 6.99 (1H, d, *J*=1.5 Hz), 7.28-7.33 (1H, m), 7.45-7.48 (3H, m), 7.73-7.76 (2H, m), 7.82 (1H, d, *J*=7.8 Hz), 8.30 (1H, d, *J*=1.5 Hz), 8.41 (1H, d, *J*=8.1 Hz), 8.69 (1H, d, *J*=4.1 Hz). *Anal.* Calcd for $C_{19}H_{19}N_3O \cdot H_2O$: C, 70.57; H, 6.54; N, 12.99. Found: C, 70.21; H, 6.84; N, 12.85.

6-(3-Aminopropoxy)-4-*p*-tolyl-2,2'-bipyridine (6b): as colorless powders; mp 91-94 °C, IR(KBr) 3369 and 1548 cm^{-1}; ^1H NMR ($CDCl_3$)δ=2.02 (2H, quint, *J*=6.5 Hz), 2.43 (3H, s), 2.95 (2H, t, *J*=6.5 Hz), 4.59 (2H, t, *J*=6.5 Hz), 6.98 (1H, d, *J*=1.4 Hz), 7.27-7.31 (1H, m), 7.29 (2H, d, *J*=8.5 Hz), 7.67 (2H, d, *J*=8.5 Hz), 7.82 (1H, t, *J*=7.7 Hz), 8.30 (1H, d, *J*=1.4 Hz), 8.42 (1H, d, *J*=8.5 Hz),

8.67 (1H, d, *J*=4.1 Hz). *Anal.* Calcd for $C_{20}H_{21}N_3O \cdot 1.7H_2O$: C, 68.72; H, 7.02; N, 12.0. Found: C, 68.63; H, 6.80; N, 11.71.

6-(3-Aminopropoxy)-4-(4-methoxyphenyl)-2,2'-bipyridine (6c): as yellow powders; mp 122-125 °C; IR(KBr) 3367, 1550, and 1180 cm^{-1}; ^1H NMR ($CDCl_3$)δ=2.07 (2H, quint, *J*=6.5 Hz), 3.00 (2H, t, *J*=6.5 Hz), 3.86 (3H, s), 4.59 (2H, t, *J*=6.5 Hz), 6.96 (1H, d, *J*=1.3 Hz), 6.99 (2H, d, *J*=8.8 Hz), 7.29-7.32 (1H, m), 7.70 (1H, d, *J*=8.8 Hz), 7.81 (1H, t, *J*=6.8 Hz), 8.21 (1H, d, *J*=1.3 Hz), 8.36 (1H, d, *J*=8.1 Hz), 8.70 (1H, d, *J*=4.9 Hz). *Anal.* Calcd for $C_{20}H_{21}N_3O_2 \cdot H_2O$: C, 67.97; H, 6.56. Found: C, 68.28; H, 6.64.

6-(3-Aminopropoxy)-4-(4-chlorophenyl)-2,2'-bipyridine (6d): as yellow oil; IR(neat) 3379, 1549, and 756 cm^{-1}; ^1H NMR ($CDCl_3$)δ=1.82 (2H, quint, *J*=5.9 Hz), 2.77 (2H, t, *J*=5.9 Hz), 4.37 (2H, t, *J*=5.9 Hz), 6.72 (1H, s), 7.04-7.11 (1H, m), 7.21 (2H, d, *J*=8.3 Hz), 7.44 (2H, d, *J*=8.3 Hz), 7.55-7.63 (1H, m), 8.07 (1H, s), 8.22 (1H, d, *J*=6.5 Hz), 8.49 (1H, d, *J*=4.4 Hz). *Anal.* Calcd for $C_{19}H_{18}N_3OCl \cdot H_2O$: C, 63.78; H, 5.63; N, 11.74. Found: C, 63.52; H, 5.84; N, 11.63.

6-Methoxy-4-(4-methoxyphenyl)-2,2'-bipyridine (7): Similarly, the reaction of compound (**2c**) (557 mg, 2.0 mmol) with methyl iodide (426 mg, 3.0 mmol) in the presence of NaH (60% in oil, 88 mg, 2.2 mmol) in dry DMF (20 mL) afforded the pure product (**7**) as pale yellow needles; mp 110-112 °C; yield 400 mg (70%); IR (KBr) 856 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.87 (3H, s), 4.09 (3H, s), 6.97 (2H, s), 7.00 (2H, d, *J*=7.7 Hz), 7.27-7.35 (1H, dd, *J*=7.9 and 4.7 Hz), 7.72 (2H, d, *J*=7.7 Hz), 7.84 (1H, t, *J*=7.9 Hz), 8.31 (1H, s), 8.46 (1H, d, *J*=7.9 Hz), 8.69 (1H, d, *J*=4.7 Hz). UV-Vis (MeCN), λ_{max} nm (log ε): 251 (4.36), 280 (4.32), and 310 (sh. 4.13).

General Procedure for Synthesis of Tris[6-(3-ethoxycarbonylpropoxy)-4-(4-substituted phenyl)-2,2'-bipyridine]ruthenium(II) Bis(hexafluorophosphate)s (8a-c): A Typical Example, Tris[6-(3-ethoxycarbonylpropoxy)-4-phenyl-2,2'-bipyridine]ruthenium(II) Bis(hexafluorophosphate) (8a): To a solution of 2,2'-bipyridine (**3a**) (217 mg, 0.60 mmol) in 95% EtOH (10 mL), was added "dried" $RuCl_3$ (37 mg, 0.18 mmol). The deep brown mixture was refluxed for 48 h. After evaporation of the solvent, the residue was treated in distilled H_2O (200 mL). For removal of unreacted ligand, the aqueous solution was washed with AcOEt (30 mL x 3). A 10-fold molar excess (293 mg) of NH_4PF_6 was added to the aqueous solution, and then the red precipitate was collected by filtration. The crude product was washed with distilled H_2O (10 mL x 3), benzene (15 mL x 3) and then dried *in*

vacuo to give the pure Ru(II) complex (**8a**) as dark red solids; yield 160 mg (73%). *Anal.* Calcd for $C_{66}H_{66}N_6O_9F_{12}P_2Ru$: C, 53.62; H, 4.51; N, 5.68. Found: C, 53.63; H, 4.75; N, 6.03.

Tris[6-(3-ethoxycarbonylpropoxy)-4-p-tolyl-2,2'-bipyridine]ruthenium(II) bis(hexafluorophosphate) (8b): *Anal.* Calcd for $C_{69}H_{72}N_6O_9F_{12}P_2Ru$: C, 54.51; H, 4.77; N, 5.53. Found: C, 54.58; H, 4.93; N, 5.89.

Tris[6-(3-ethoxycarbonylpropoxy)-4-(4-methoxyphenyl)-2,2'-bipyridine]ruthenium(II) bis(hexafluorophosphate) (8c): *Anal.* Calcd for $C_{69}H_{72}N_6O_{12}F_{12}P_2Ru \cdot H_2O$: C, 52.24; H, 4.70; N, 5.30. Found: C, 52.23; H, 4.76; N, 5.60.

Electrochemical Measurement: Tetrabutylammonium perchlorate (Bu_4NClO_4) as supporting electrolyte was recrystallized from dry AcOEt and dried *in vacuo* for 6 h. A three-electrode system was employed. A BAS MF-2013 platinum-disk electrode (2.01 mm^2 electrode area) was used as the working electrode, along with a platinum-wire as the auxiliary electrode and a BAS RE-2 saturated calomel electrode (SCE) as the reference electrode in the presence of Bu_4NClO_4 (0.1 M) in MeCN. Cyclic voltammetry was carried out using a HECS 311B potentiostat, a HECS 321B potential sweep unit (Fusô-Seisakusyo Co. Ltd.) and an F-35 X-Y recorder (Riken Denshi Co. Ltd.). All experiments were performed at a scan rate of 100 mV/s at 23.0 ± 1.0 °C in the solution purged with N_2 for 20 min before measurement.

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