Electrochemical Homocoupling of 2-Bromomethylpyridines Catalyzed by Nickel Complexes

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2,2′-Bipyridine (bpy) and a series of dimethyl-2,2′-bipyridines were synthesized from 2-bromopyridine and 2-bromomethylpyridines, respectively, using an electrochemical process catalyzed by nickel complexes. The method is simple and efficient, with isolated yields between 58 and 98% according to the structure. We first studied the influence of the presence and the position of the methyl group on the yield, using *N*,*N*-dimethylformamide (DMF) or acetonitrile (AN) as the solvent, $NiBr_2$bpy as the catalyst, and Zn as the sacrificial anode, in an undivided cell and at ambient temperature. On the basis of a better understanding of the reaction mechanism based on electroanalytical studies, we could improve the dimerization both by substituting the catalyst ligand (bpy) by the reagent itself, i.e., 2-bromomethylpyridine or 2-bromopyridine, and by using Fe instead of Zn as the sacrificial anode.

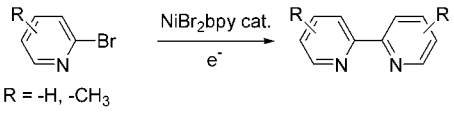
Introduction

The nickel-catalyzed homocoupling of aryl halides has recently received considerable attention[1] because the reactions proceed under mild conditions, as compared to the classical Ullmann reaction conditions, to give the corresponding biaryls in good to high yields. The yield of biaryls has notably been found to be dependent on a suitable choice of the low-valent nickel complex and the solvent. Iyoda and co-workers have thus reported an efficient homocoupling of aryl halides using $Ni(PPh_3)Br_2$ as catalyst precursor, along with Zn as the reducing agent, THF as the solvent, and in the presence of Et_4NI.[2]

Nickel complexed to the ligand 2,2′-bipyridine (bpy) has also been studied as a catalyst in the electroreductive homocouplings and cross-couplings of aryl, alkenyl, and alkyl halides.[3] The electrochemical procedure is very simple and efficient, giving notably very good yields of the respective dimers in the homocoupling reactions. In addition, the use of a sacrificial anode makes possible the implementation of an undivided electrochemical cell. Several anode metals may be used such as Mg, Al, Fe, and Zn and are selected according to both the reduction potential of the organic halide and the type of reaction.[4]

Recently we reported the successful electrochemical dimerization of 2-bromo-6-methylpyridine, yielding 75% of the isolated product, 6,6′-dimethyl-2,2′-bipyridine[5] (Scheme 1). The method uses $NiBr_2$bpy as the catalyst precursor, DMF as the solvent, and Zn as the sacrificial anode.

Scheme 1



Because of the interest in substituted bipyridines as precursors of chelates for transition-metal complexes,[6] we decided to investigate this electrochemical route more deeply in order to explore its scope and limitations. In this paper we describe the influence on yield of the methyl substituent position in 2-bromomethylpyridines, using first the reaction conditions previously applied to the synthesis of 6,6′-dimethylbipyridine. This study has led us to a better understanding of the catalytic cycle and to ways of improving the preparation of bipyridines.

Results and Discussion

We thus first conducted a series of experiments with 2-bromopyridine and the various 2-bromomethylpyridines with the reaction conditions previously used for the dimerization of 2-bromo-6-methylpyridine:[5] that is, in DMF, at room temperature, with a current intensity of 100 mA, and having a zinc rod as the sacrificial anode. Results are given in Table 1.

The reactions were run until the full consumption of the starting reagent. There is clearly an influence of the position of the methyl groups on the efficiency of the dimerization. Thus, 3,3′-dimethyl-2,2′-bipyridine is obtained in the same yield as bipyridine, while 4,4′- and 5,5′-dimethyl-2,2′-bipyridines are obtained in a higher yield, 45%, and 6,6′-dimethyl-2,2′-bipyridine gives the highest yield, 75%.

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Table 1. Nickel-Catalyzed Electrochemical Homocoupling of 2-Bromomethylpyridines and 2-Bromopyridine, in DMF and in Acetonitrile, Using $NiBr_2Bpy$ as Catalyst[a]

		yield[b] (%)	
entry	reagent	in DMF	in acetonitrile
1	2-bromo-3-methylpyridine (**1**)	35	23
2	2-bromo-4-methylpyridine (**2**)	45	43
3	2-bromo-5-methylpyridine (**3**)	44	48
4	2-bromo-6-methylpyridine (**4**)	75	69
5	2-bromopyridine (**5**)	32	see text

[a] Conditions: aryl halide (5 mmol), $NiBr_2bpy$ (0.35 mmol), DMF (20 mL), constant current intensity (100 mA), room temperature. [b] Isolated yields.

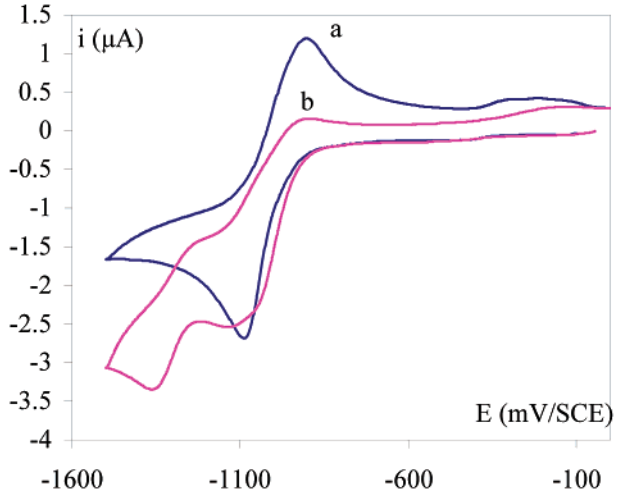

Figure 1. Cyclic voltammograms in DMF + 0.1 M NBu_4BF_4, at a gold-disk microelectrode (0.25 mm diameter) at $v = 0.2$ V s^{-1} and at room temperature: (a) 10^{-2} M $NiBr_2bipy$; (b) 10^{-2} M $NiBr_2bipy$ in the presence of 10^{-2} M 2-bromopyridine.

In looking for ways to improve these coupling reactions, we first checked the effect of the reaction temperature on the homocoupling of 2-bromo-3-methylpyridine (**1**) in DMF. It was observed that below room temperature the electric resistance of the medium becomes too high and the solubility of the nickel complex is low; therefore, the reaction is less efficient than at room temperature. No improvement was obtained at 50 °C, either. Thus, ambient temperature seems to be the most appropriate.

We then used acetonitrile as the solvent. As shown in Table 1, the yields are similar to those obtained in DMF. Actually, the main limitation in acetonitrile is the low solubility of the Ni complex catalyst. In addition, the reaction with 2-bromopyridine (**5**) gave no product because of the insolubility of the catalyst in the presence of this reagent.

The central question therefore involves the nature of the effect of the methyl group, as well as its position on the ring, on the efficiency of the dimerization. This effect is likely related to one or more step(s) of the catalytic cycle.

We can reasonably assume that the catalytic cycle involved in this reaction is similar to the one operating in the dimerization of aryl[7] or alkenyl halides.[8] Indeed, we have found that the cyclic voltammogram obtained in the case of 2-bromopyridine (**5**) (2-BrPy) in the presence of Ni(bpy) (Figure 1) is very close to that obtained with C_6H_5Br.[7] This clearly shows that the steps of the catalytic cycle are similar in nature: i.e., in the first step

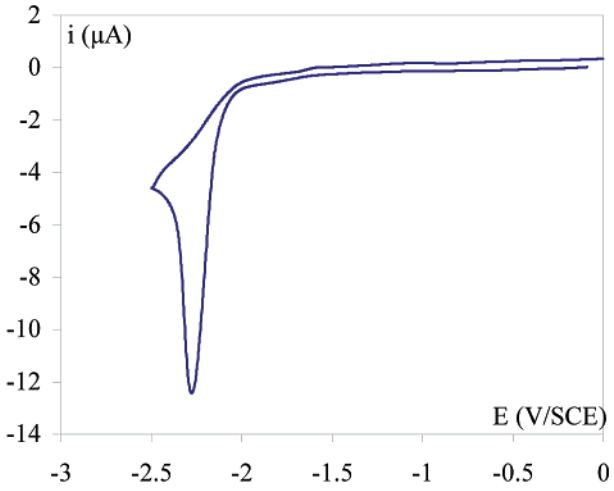

Figure 2. Cyclic voltammogram in DMF + 0.1 M NBu_4BF_4, at a gold-disk microelectrode (0.25 mm diameter) at $v = 0.2$ V s^{-1} and at room temperature, of 10^{-2} M 2-bromopyridine.

the low-valent nickel complex generated at the cathode at −1.1 V/SCE reacts with 2-BrPy to give the $PyNi^{II}Br$ intermediate, which is further reduced into $PyNi^{I}$ at a slightly lower potential before reacting with another molecule of 2-BrPy. The $Py_2Ni^{III}Br$ thus formed leads to 2,2′-bipyridine by reductive elimination, along with Ni(I), which re-enters the catalytic cycle (Scheme 2). As shown in Figure 2, the reduction of 2-BrPy (**5**) occurs at the low −2.25 V/SCE.

Scheme 2. Mechanism of the Ni-Catalyzed Electrochemical Dimerization of Aryl Halides

$$Ni^{II} + 2\ e^- \rightarrow Ni^0 \quad (1)$$

$$Ni^0 + \text{2-BrPy} \rightarrow PyNi^{II}Br \quad (2)$$

$$PyNi^{II}Br + e^- \rightarrow PyNi^{I} + Br^- \quad (3)$$

$$PyNi^{I} + \text{2-BrPy} \rightarrow Py_2Ni^{III}Br \quad (4)$$

$$Py_2Ni^{III}Br \rightarrow Py{-}Py + Ni^{I} \quad (5)$$

$$Ni^{I} + e^- \rightarrow Ni^0 \quad (6)$$

We also know from previous studies in these laboratories that the coordinatively saturated 18-electron nickel complex $Ni(bpy)_2$ is poorly reactive toward the oxidative addition to ArBr[7b,9] and leads mostly to the reduction product, instead of the dimer Ph−Ph, from PhBr. Thus, the catalytic species in the dimerization reaction is very likely the 14-electron Ni(bpy) complex. It is therefore obvious that, in the dimerization of 2-bromopyridine (**5**), the product 2,2′-bipyridine itself coordinates to Ni, thus shifting the equilibrium in Scheme 3 toward the less reactive $Ni(bpy)_2$ complex.

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Scheme 3

$$Ni^0(bpy) + bpy \rightleftharpoons Ni^0(bpy)_2$$

As a consequence, the yield at the end of the electrolysis does not exceed 32%, and the main product is the reduction product pyridine.

However, the discrepancy in the results according to the presence and the position of CH_3 on the pyridine ring prohibits one from applying a single explanation to all compounds. We have therefore to address two more questions. (i) Are all compounds involved in the oxidative addition step at the same rate? (ii) Is the ligand affinity to Ni different from one to another bipyridine?

We have readily established by cyclic voltammetry that all 2-bromomethylpyridines react with Ni^0(bpy) at roughly the same rate as 2-bromopyridine (**5**) does. This means that a methyl substituent on the pyridine ring has no great influence on the reactivity toward Ni^0(bpy), whatever its position.

The affinity of bpy and each dimethylbipyridine toward Ni has been determined semiquantitatively by cyclic voltammetry in the following way. The reduction of $NiBr_2$ in DMF, in the absence of ligand, displays a reduction peak at −1.3 V/SCE, along with a large intense peak at 0.2 V/SCE on the reverse scan which corresponds to the dissolution of the Ni metal formed at the electrode (Figure 3a). In contrast, in the presence of 1 equiv of bpy (Figure 3b), we obtain a quasi-reversible wave corresponding to the Ni^0/Ni^{II} system. The increase in the number of equivalents of bpy vs Ni leads to a quite reversible system. In the presence of 1 equiv of 6,6′-dimethyl-2,2′-bipyridine, such a stable complex does not form, and we observe a behavior (Figure 4a) similar to that found in the absence of ligand. This may be due to a steric effect of the two CH_3 groups attached to carbons 6 and 6′, i.e., on each side of the bipyridine structure, which prevents the formation of the square-planar complex Ni(bpy)$_2$, and this may account for the efficiency in the dimerization of 2-bromo-6-methylpyridine (**4**) as compared to 2-bromopyridine (**5**). In the presence of 1 equiv of each of the three other isomers, we obtained a medium stabilization similar to that observed for 4,4′-dimethyl-2,2′-bipyridine (Figure 4b), which is in keeping with yields in the range of 40−50%, at least for 2-bromo-4-methylpyridine (**2**) and 2-bromo-5-methylpyridine (**3**).

However, the yield is still lower with 2-bromo-3-methylpyridine (**1**), thus indicating that this compound is a very specific case. Indeed, the product 3,3′-dimethyl-2,2′-bipyridine can moderately stabilize the low-valent nickel despite the absence of planarity in the bpy structure, and we could expect a product yield in the range of 40−50%. A low 35% yield could therefore be due to a steric effect of CH_3 in the second oxidative addition to the first formed 3-MePyNi^{I}: i.e., step 4 in Scheme 2. We could also even have another mechanism, which has been reported to be notably operating at low current intensity (which is the case for results of Table 1): that is, the slow disproportionation between two 3-MePyNiBr intermediates, according to Scheme 4.

It comes out from this study that the medium-sized yield, 45%, in the preparation of 4,4′- and 5,5′-dimethylbipyridine is mainly due to the decrease in the concentration of the active catalytic species, the 14-electron nickel complex, as the reaction proceeds, because of the equilibrium shift to the unreactive 18-electron nickel

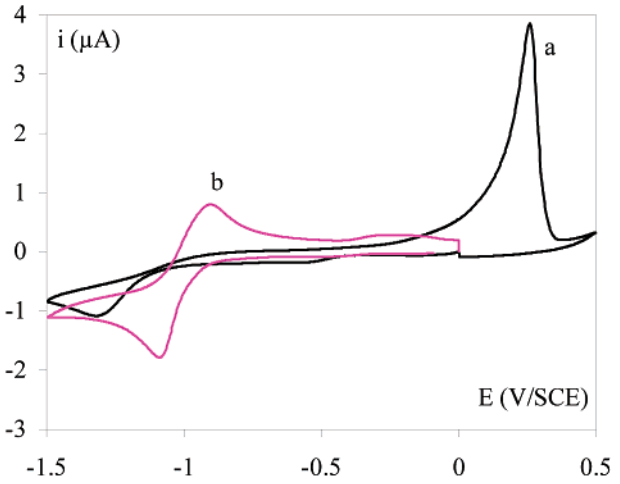

Figure 3. Cyclic voltammograms in DMF + 0.1 M NBu_4BF_4, at a gold-disk microelectrode (0.25 mm diameter) at $v = 0.2$ V s^{-1} and at room temperature (a) 10^{-2} M $NiBr_2$; (b) in the presence of 10^{-2} M 2,2′-bpy.

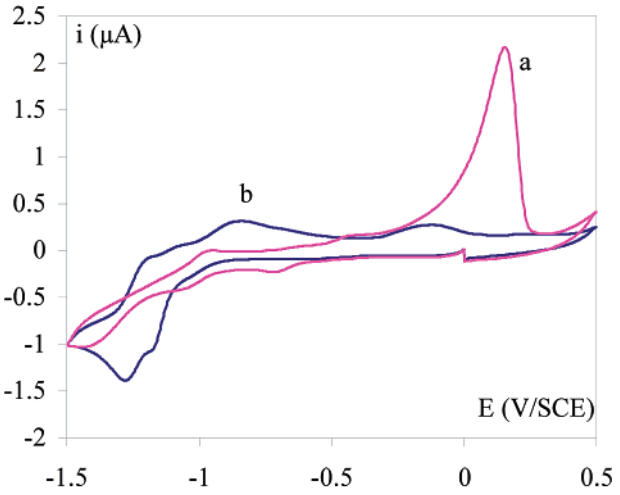

Figure 4. Cyclic voltammograms in DMF + 0.1 M NBu_4BF_4, at a gold-disk microelectrode (0.25 mm diameter) at $v = 0.2$ V s^{-1} and at room temperature: (a) 10^{-2} M $NiBr_2$ in the presence of 10^{-2} M 6,6′-dimethyl-2,2′-bipyridine; (b) 10^{-2} M $NiBr_2$ in the presence of 10^{-2} M 4,4′-dimethyl-2,2′-bipyridine.

complex (Scheme 3). This led us first to try to run all reactions without bipyridine at the beginning of the electrolysis. Actually, we have already shown that pyridine itself can sufficiently stabilize a low-valent nickel species, which can react quickly in the presence of the substrate. Thus, a series of runs were done in DMF using $NiBr_2$ as the catalyst precursor.

As seen in Table 2, there is no improvement with only 7% of the catalyst. However, the increase of the amount of $NiBr_2$ to 30% enables us to highly increase the yield, at least in the case of 2-bromo-4-methylpyridine (**2**) and 2-bromo-5-methylpyridine (**3**), to ca. 93−95%. The increase in yield is, however, lower with 2-bromopyridine (**5**) and much lower with 2-bromo-3-methylpyridine (**1**). Actually, from 2-bromopyridine (**5**), the dimer remains an overly favorable ligand for Ni, and the yield is no more than twice the yield of $NiBr_2$ used. On the other hand, the explanation given above for 2-bromo-3-methylpyridine **1** remains: that is, that the presence of CH_3 at carbon 3 induces a steric effect in a further step of the catalytic cycle. Finally, as compared with the reaction

Scheme 4

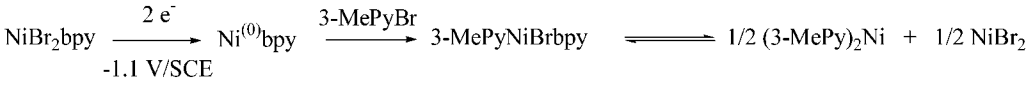

Table 2. Nickel-Catalyzed Electrochemical Homocoupling of 2-Bromomethylpyridines and 2-Bromopyridine in DMF, Using $NiBr_2$ as Catalyst, in the Presence of a Zinc Anode[a]

entry	reagent	amt of $NiBr_2$ (%)	yield[b] (%)
1	**1**	7	25
2	**1**	15	35
3	**1**	30	42
4	**1**	50	47
5	**2**	7	47
6	**2**	15	72
7	**2**	30	93
8	**3**	7	49
9	**3**	15	73
10	**3**	30	95
11	**4**	7	65
12	**4**	15	68
13	**4**	30	82
14	**5**	7	48
15	**5**	15	64
16	**5**	30	71

[a] Conditions: aryl halide (5 mmol), DMF (20 mL), constant current intensity (100 mA), room temperature. [b] Isolated yields.

conductedin the presence of Ni(bpy), the yield in 6,6′-dimethylbipyridine in only slightly improved from 75% (Table 1) to 82% (Table 2).

Though this was already a good improvement of the dimerization, we thought it preferable, however, to keep the amount of nickel as low as possible. This has been obtained on the basis of the following. We know that, in these reactions, the reagents and more importantly the products are medium to good ligands of nickel. Therefore, if we had in the reaction medium an electrochemically inactive species which could pick up the product and thus store it till the end of the reaction, this could prevent the loss of the active catalyst in the form of the inactive 18-electron complex. Zinc salts generated from the anode, according to the reaction conditions reported above, are not efficient enough. In contrast, iron ions have good affinity for nitrogen ligands, and in addition, we have already shown that iron anodes can be advantageously used in combination with nickel-catalyzed as well as cobalt-catalyzed electrochemical couplings.[10] We thus performed the homocouplings in the presence of an iron sacrificial anode. The reactions have been conducted at room temperature under a current intensity of 200 mA, without any pre-electrolysis. Results obtained under these new reaction conditions are given in Table 3.

We can see that yields have been greatly improved as compared to those in Table 1, notably in the cases of 3-, 4-, and 5-methylated bromopyridines. Under these reaction conditions, 2-chloropyridine was also dimerized in 89% isolated yield.

Conclusion

In conclusion, we have found an efficient method of dimerization of substituted 2-bromopyridines. The main difficulty when dealing with heterocyclic substrates is the ability of reagents and products to form stable complexes with transition-metal catalysts. The method we have developed offers a very good demonstration of the advantage of the electrochemical approach based on the combination of the nickel complex catalysis and the sacrificial anode. Indeed, the efficiency of the process is clearly based on a cooperative effect where the advantage of generating iron ions is not simply to enable the use of an undivided cell but also to produce a species that can operate within the catalytic cycle to pick up the product, thus allowing the efficient recycling of the active catalytic species. In addition, it should be noted that iron ions are produced continuously, at a rate that matches that of the formation of the product.

Table 3. Nickel-Catalyzed Electrochemical Homocoupling of 2-Bromomethylpyridines and 2-Bromopyridine, Using $NiBr_2$ as Catalyst and Iron as Sacrificial Anode[a]

entry	reagent	yield (%)[b]	entry	reagent	yield (%)[b]
1	**1**	58[c]	4	**4**	98
2	**2**	81	5	**5**	83
3	**3**	86			

[a] Conditions: aryl halide (10 mmol), $NiBr_2$ (0.7 mmol), DMF (40 mL), constant current intensity (200 mA), room temperature, Fe anode. [b] Isolated yields after passing a charge of 1500 C. [c] Yield obtained after a charge of 3000 C, the reaction being not complete after 1500 C.

Experimental Section

2-Bromopyridine and 2-bromomethylpyridines were purchased from Aldrich. Acetonitrile, DMF, and CH_2Cl_2 were used as received. Water was Milli-Q grade. The supporting electrolyte tetrabutylammonium tetrafluoroborate (NBu_4BF_4) was purchased from Merck. 2,2′-Bipyridine (bpy), used as a ligand for Ni complexes, and nickel bromide were obtained from Aldrich. ^1H NMR spectra were measured with a Varian Unity Plus (300 MHz) spectrometer. Chemical shifts are expressed in ppm, using tetramethylsilane and/or residual chloroform (δ 7.24) as internal standards. Mass spectra were taken with a Finnigan GC-MS instrument.

A. Preparative Electrolyses. The controlled-current preparative electrolyses were carried out in undivided cells of 20−50 mL. The sacrificial anode used was a Zn or Fe metallic bar of 8.0 mm diameter. A Ag/AgCl reference electrode (3 M KCl), placed in parallel and separated from solution by Vycor, allowed us to monitor the potential of the working electrode. Nickel foam (12 cm × 4 cm) from Nitech was used as the working electrode. The Ni electrode may be reused about 20 times, after cleaning with a 6 M HCl solution. The same solution was used to clean the anode.

For experiments involving Ni(bpy) as catalyst, the catalyst precursor $NiBr_2$bpy was either prepared separately according to the literature[11] or formed in situ by stirring a 2 mL DMF solution containing $NiBr_2$ and 2,2′-bipyridine (bpy) for 2 h before starting the electrolysis.

The electrolytic cell was charged with the solvent and the supporting electrolyte. The pyridyl bromide was then added, and a constant current was applied until the full consumption of the starting reagent. The solvent was removed at reduced pressure, the residue was dissolved in CH_2Cl_2, and this solution was washed with several portions of a diluted am-

(10) See for example: (a) Condon Gueugnot, S.; Dupré, D.; Nédélec, J.-Y.; Périchon, J. *Synthesis* **1997**, 1457. (b) Gosmini, C.; Nédélec, J.-Y.; Périchon, J. *Tetrahedron Lett.* **2000**, *41*, 5039.

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monia solution until the organic layer became yellow. After drying with Na_2SO_4, the solvents were removed under reduced pressure.

The products were purified and characterized as follows. Chemical Abstracts registry numbers are given in brackets.

2,2′-Bipyridine [366-18-7]. The crude product was chromatographed on silica gel (75−230 mesh, Aldrich), using benzene/ether as eluent to give 2,2′-bipyridine, Mp: 70−71 °C (lit.[2] mp 71−72 °C).

3,3′-Dimethyl-2,2′-bipyridine [1762-32-9]. This compound was purified by chromatography using silica gel (75−230 mesh) and ethyl acetate as eluent followed by $CHCl_3$. The $CHCl_3$ fraction containing the product was evaporated, and the yellow liquid was analyzed by GC-MS: *m*/*z* (relative intensity) 184 (M^+, 37), 169 (100). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (d, J = 5.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.22 (dd, J = 5.0 and 8.0 Hz, 2H), 2.18 (s, 6H).

4,4′-Dimethyl-2,2′-bipyridine [1134-35-6]. The crude product was washed with 20 mL of ethyl acetate and dissolved in 5 mL of CH_2Cl_2. The mixture was maintained at room temperature, and the slow evaporation afforded crystals. The product was analyzed by GC-MS: *m*/*z* (relative intensity) 184 (M^+, 100). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (d, J = 16.0 Hz, 2H), 8.24 (s, 2H), 7.15 (d, J = 16.0 Hz, 2H), 2.45 (s, 6H).

5,5′-Dimethyl-2,2′-bipyridine [1762−34−1]. The solid product obtained from extraction was dissolved in 5 mL of ethyl acetate and the solution filtered. The mixture was maintained at room temperature, and slow evaporation gave white crystals. The product was analyzed by GC-MS: *m*/*z* (relative intensity) 184 (M^+, 100). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 2H), 8.24 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 2.45 (s, 6H).

6,6′-Dimethyl-2,2′-bipyridine [4471−80−7] was isolated as described previously.[5]

B. Analytical Experiments. Cyclic voltammetry studies were carried out in DMF at room temperature under argon in a three-electrode cell using an EG&G 273A potentiostat. The reference electrode was SCE, separated from the solution by a bridge compartment filled with the same solvent−supporting electrolyte solution as that used in the cell. The working electrode was a gold disk (0.25 mm diameter), and the counter electrode was a gold wire.

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