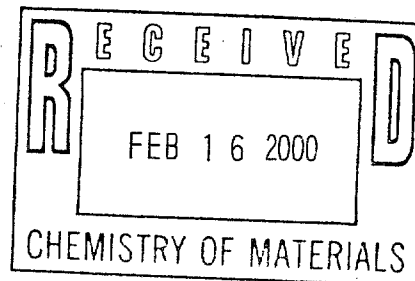


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Supporting Information



Preparation of Ligands. See figure for ligand structures. **4,4'-dicarboxaldehyde-2,2'-**

bipyridine was prepared from 5.0 g (0.027 moles) of 4,4'-dimethyl-2,2'-bipyridine and

9.0 g (.081 moles) selenium dioxide by the method of Furue.¹ The starting material was removed from the product mixture by chromatography on silica gel with ethyl acetate as

eluent. However, repeated attempts to isolate the dicarboxaldehyde product from 4-methyl-4'-carboxaldehyde-2,2'-bipyridine via chromatography (in various solvents and

solvent mixtures) were unsuccessful. Thus, 600 mg of the unpurified mixture were

reacted with 643 mg (17.0 mmol) sodium borohydride according to Furue.¹ The product

4,4'-hydroxymethyl-2,2'-bipyridine was isolated by chromatography on silica gel,

eluting as the second band in a gradient of 2-5% methanol in CHCl₃. It was then

recrystallized from ethanol. NMR (δ from TMS, d-DMSO): δ 4.62 (s, 2 H), δ 5.5 (br, 1

H), δ 7.36 (d of d, 1 H), δ 8.37 (m, 1 H), δ 8.58 (d of d, 1 H). **4,4'-Bis(diethyl**

methylphosphonate)-2,2'-bipyridine was prepared from 4,4'-dimethyl-2,2'-bipyridine

as previously reported, with comparable yield.^{2,3} It was hydrolyzed to **4,4'-**

Bis(methylphosphonic acid)-2,2'-bipyridine by refluxing in 48% HBr according to

Bonhôte.⁴ It was converted to the tetrasodium salt by neutralization with saturated

Na₂CO₃. NMR (δ from TMS, D₂O): δ 2.91 (d, 2 H), δ 7.33 (d, 1 H), δ 7.78 (s, 1 H),

δ 8.39 (d, 1 H). **(4,4'-Bis(diethyl phosphonate)-2,2'-bipyridine)** was prepared according to the procedure of Hirao⁵, using 557.1 mg (1.77 mmol) 4,4'-dibromo-2,2'-bipyridine⁶, 619 μ L triethylamine, 572 μ L diethyl phosphite and 208 mg tetrakis(triphenylphosphine) palladium(0). The product was chromatographed on silica gel using 1:1 acetone:CH₂Cl₂. Although TLC often indicated complete conversion of the dibrominated ligand to the bis(diethyl phosphonate), the yield after column chromatography was typically ~65%. It was then hydrolyzed to **4,4'-Bis(phosphonic acid)-2,2'-bipyridine** by refluxing in 48% HBr.⁴ It was converted to **Tetrasodium 4,4'-diphosphonate-2,2'-bipyridine** by neutralization with saturated Na₂CO₃ and then extracted into hot methanol. The methanol was evaporated off and the product dried at 105°C. NMR (δ from TMS, D₂O): δ 7.74 (d of d, 1 H), δ 8.22 (d, 1 H), δ 8.66 (d of d, 1 H). **5,5'-dicarboxylic acid-2,2'-bipyridine** was a gift of Professor C. Michael Elliott.⁷

Preparation of Complexes. All complexes were characterized by optical and electrochemical measurements and these data are given in Tables 1 and 2. Selected complexes were also characterized by elemental analyses. **[Fe(4,4'-dicarboxylic acid-2,2'-bipyridine)₂(CN)₂]** was prepared as described previously.⁸ To purify the complex, it was first converted to the tetra-TBA⁺ salt by the stoichiometric addition of 1 M TBAOH in methanol, then chromatographed on Sephadex LH-20 using methanol eluent.

The TBA⁺ form of the complex was recrystallized by adding 1:1 diethyl ether: petroleum ether to a nearly saturated methanolic solution of the complex. The oily product was skimmed off the top with a disposable pipet. The fully protonated form could be recovered by dissolution and re-precipitation in water, followed by recrystallization from concentrated sulfuric acid.⁹ Elemental analysis: C, 49.61; H, 3.16; N, 11.46. Calculated for [Fe(4,4'-dicarboxylic acid-2,2'-bipyridine)₂(CN)₂] \cdot 2H₂O as FeC₂₆H₂₀N₆O₁₀: C, 49.39; H, 3.19; N, 13.29.¹⁰

Preparation of [Fe(5,5'-dicarboxylic acid-2,2'-bipyridine)₂(CN)₂]. The ligand 5,5'-dicarboxylic acid-2,2'-bipyridine (252 mg, 1.03 mmol) and (NH₄)₂Fe(SO₄)₂ \cdot 6H₂O (135 mg, 0.344 mmol) were combined in a 50 mL E. flask and 20 mLs distilled water were added. The aqueous solution turned light pink with the formation of the tris-ligated complex. Upon addition of 1.03 mLs of 2 M aqueous KOH, the solution became dark purple. It was then heated to boiling. A solution of KCN (344.5 mg, 5.30 mmol) in ~ 3 mLs water was added; the reaction was boiled for an additional 5 minutes, and then allowed to cool overnight. The pH was lowered with 1 M H₂SO₄ until a blue product precipitated. It is essential that this step be performed in a hood because HCN is produced. The solid was collected on 0.45 μ m filter paper and rinsed with water. The fully protonated product (as collected) was converted to the TBA⁺ salt via addition of a 1

M methanolic solution of TBAOH and purified on Sephadex LH-20, using methanol as eluent. Yields of purified complex ranged from 50-70%.

Preparation of $[\text{Fe}(4,4'\text{-bis(hydroxymethyl)-2,2'-bipyridine)}_2(\text{CN})_2]$. To 90.4 mg 4,4'-hydroxymethyl-2,2'-bipyridine (0.419 mmol) and 57.4 mg $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.140 mmol) in a 50 mL E. flask was added 7 mLs distilled water. The solution was heated and ~2 mLs acetone were added to completely dissolve the ligand. After the acetone had boiled off with heating, 137 mg KCN (2.1 mmol) dissolved in ~1 mL distilled water was added. The solution was heated in air just below boiling for approximately 30 minutes. The reaction was allowed to cool and the crystalline purple product was collected on a 0.2 μm nylon filter paper, rinsed with water, and dried in air at 100°C. The yield was ~70 mg (~87%).

Preparation of $[\text{TBA}^+]_8[\text{Fe}(4,4'\text{-Bis(methylphosphonate)-2,2'-bipyridine)}_2(\text{CN})_2]$.

To 10 mLs distilled water in a 125 mL E. flask was added tetrasodium (4,4'-bis(methylphosphonate)-2,2'-bipyridine (371 mg, 0.860 mmol, but containing excess NaBr^4). A solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (112 mg, 0.286 mmol) in ~ 5 mLs distilled water was added all at once. The solution turned red immediately and a salty precipitate appeared (it was not filtered). A solution of 280 mg NaCN (5.72 mmol) in ~ 2 mLs water

was added and the mixture was heated near boiling for ~15 minutes. It was then cooled and stirred at room temperature for approximately four hours. The solution was orange. The pH was lowered to ~2.5 with 1 M H₂SO₄ (in a hood) and the precipitate was collected on 0.45 µm filter paper and rinsed with water. The precipitate was put into methanol and 1 M TBAOH in methanol was added; the resulting TBA⁺ salt of the product was chromatographed on Sephadex LH-20 using methanol as eluent. The yield was not calculated since the exact starting stoichiometry was not known.

Preparation of [TBA⁺]₈[Fe(4,4'-diphosphonate-2,2'-bipyridine)₂(CN)₂]. To a mixture of 15 mLs water and 5 mLs acetone in a 50 mL E. flask was added sodium 4,4'-bis(phosphonate)-2,2'-bipyridine (814.5 mg, 1.77 mmol, but containing excess NaBr⁴). A solution of (NH₄)₂Fe(SO₄)₂•6H₂O (231 mg, 0.59 mmol) in 2 mLs water was subsequently added. The solution turned red immediately and a precipitate appeared (it was not filtered). A solution of NaCN (578 mg, 11.8 mmol) in ~5 mLs water was added and the aqueous reaction mixture was heated near boiling for approximately one hour. It was then covered and allowed to sit overnight. The pH was lowered to ~4 with 1 M H₂SO₄. It is essential that this step be performed in a hood because HCN is released. The reaction mixture was rotary evaporated to dryness then re-dissolved in methanol and

chromatographed on Sephadex LH-20 with methanol eluent. Yields were not calculated because the starting stoichiometry was uncertain.

Preparation of $[\text{Fe}(\text{4,4'}\text{-Bis}(\text{diethyl methylphosphonate})\text{-2,2'}\text{-bipyridine})_2(\text{CN})_2]$.

The ligand 4,4'-Bis(diethyl methylphosphonate)-2,2'-bipyridine (187.0 mg, 0.470 mmol) and ~5 mLs acetone were placed in a 125 mL E. flask and warmed to dissolve. A solution of 61.3 mg (0.156 mmol) $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ~10 mLs water was added, and the reaction was heated to evaporate acetone. Then 141 mg (2.88 mmol) NaCN dissolved in ~ 5 mLs water were added and the solution was heated near boiling for approximately 15 minutes. The reaction was stirred for approximately 30 minutes at room temperature, then rotary evaporated to dryness. The product was dissolved in methanol and chromatographed on Sephadex LH-20 with methanol eluent. Yield of product after separation was approximately 75 mg (~51%).

Preparation of $[\text{Fe}(\text{4,4'}\text{-dimethyl-2,2'}\text{-bipyridine})_2(\text{CN})_2]$. In a 125 mL E. flask, 532

mg (2.89 mmol) 4,4'-dimethyl-2,2'-bipyridine, 377 mg (0.961 mmol)

$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and ~30 mLs water were mixed. Acetone (~5 mLs) was added to promote dissolution and reaction of remaining ligand, then it was evaporated from the aqueous solution by heating. A solution of 994 mg (15.3 mmol) KCN in 4 mLs water

was then added all at once. The reaction was heated near boiling for approximately 30 minutes, then allowed to cool overnight. The precipitated product (~400 mg, ~80%) was collected by vacuum filtration and rinsed with water and diethyl ether. Elemental analysis: C, 60.32; H, 5.50; N, 15.84. Calculated for $[\text{Fe}(\text{4,4'}\text{-dimethyl-2,2'}\text{-bipyridine})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ as $\text{FeC}_{26}\text{H}_{28}\text{N}_6\text{O}_2$: C, 60.95; H, 5.51; N, 16.4.

Preparation of $[\text{Fe}(\text{4,4'}\text{-dimethyl-2,2'}\text{-bipyridine})_3][\text{PF}_6]_2$. The complex was prepared according to Serr et al.¹¹

Preparation of $\{\text{Fe}[\text{4,4'}\text{-(COO)}\text{-2,2'}\text{-bipyridine}]_3\}[\text{TBA}^+]_4$. 71.3 mg 4,4'-dicarboxylic acid-2,2'-bipyridine (0.292 mmol), 584 μL 1M TBAOH (methanol), 50 mLs methanol, and 25 mLs acetone were placed in a 125 mL E. flask and brought to a boil. $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (44 mg, 0.11 mmol) dissolved in ~10 mLs distilled water were added all at once. An additional 20 mLs distilled water were added and the methanol and acetone were boiled off. The water was removed by rotary evaporation and the reaction mix dissolved in methanol and filtered through 0.45 μm filter paper. The product was then chromatographed on Sephadex LH-20 using methanol as eluent. Yield after separation was approximately 60% (102 mg).

Preparation of $\{\text{Fe}[5,5'-(\text{COO}^-)-2,2'\text{-bipyridine}]_3\}[\text{TBA}^+]_4$. The complex was prepared analogously to $\{\text{Fe}^{\text{II}}[4,4'-(\text{COO}^-)-2,2'\text{-bipyridine}]_3\}[\text{TBA}^+]_4$. Isolated as a dried solid, it appeared to be unstable; absorption spectra indicated excess free ligand absorption, i.e. that the iron had fallen out.

Preparation of $[\text{TBA}^+]_{10}[\text{Fe}(4,4'\text{-Bis(methylphosphonate)-2,2'\text{-bipyridine}})_3]$. The complex was obtained as a byproduct in the separation of $[\text{TBA}^+]_8[\text{Fe}(4,4'\text{-Bis(methylphosphonate)-2,2'\text{-bipyridine}})_2(\text{CN})_2]$.

Preparation of $[\text{Na}^+]_4[\text{H}^+]_6[\text{Fe}(4,4'\text{-diphosphonate-2,2'\text{-bipyridine}})_3]$. To a solution of $[\text{Na}]_4[4,4'\text{-diphosphonate-2,2'\text{-bipyridine}]$ (50 mg, 0.11 mmol) in 10 mLs water was added 14.2 mg (.036 mmol) $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Upon concentration by boiling, a precipitate formed, which was collected by vacuum filtration and rinsed with water (pH 2.5). Yield was 30 mg (~66%).

Preparation of $[\text{Fe}(4,4'\text{-bis(hydroxymethyl)-2,2'\text{-bipyridine}})_3][\text{PF}_6]_2$. The complex was prepared from 54.7 mg (0.253 mmol) of 4,4'-bis(hydroxymethyl)-2,2'-bipyridine and 39.3 mg $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ according to Serr.¹¹ Yield was 61.8 mg (74%).

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- 10) Repeated attempts at elemental analysis always yielded values for nitrogen that were low. Numerous purification and recrystallization methods were tried, always resulting in low elemental analyses for nitrogen. The low value cannot be explained. However, our confidence in the purity of complex is substantiated by chromatographic purity and the electrochemical and spectral data.
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Table 1a. Oxidation Potentials ($\text{Fe}^{2+/3+}$), $\text{FeL}_2(\text{CN})_2$ vs. ferrocene ($\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$).

L =	Ethanol	CH_3CN	DMSO
4,4'-dimethyl-2,2'-bipyridine	+110 mV	-94	
4,4'-dicarboxylic acid-2,2'-bipyridine	+213		+596
4,4'-dicarboxylate-2,2'-bipyridine ²	+209	-77	+386
5,5'-dicarboxylate-2,2'-bipyridine ²	+99	-129	
4,4'-diphosphonate-2,2'-bipyridine ^{1,3}	+132 ¹		
4,4'-Bis(methylphosphonate)-2,2'-bipyridine ²	+19		
4,4'-bis(hydroxymethyl)-2,2'-bipyridine	+109	-85	
4,4'-Bis(diethyl methylphosphonate)-2,2'-bipyridine	+62		-123

¹A drop of water was added to solubilize the complex. ²Complex isolated as TBA^+ salt.³Complex isolated as Na^+ salt.Table 1b. Oxidation Potentials ($\text{Fe}^{2+/3+}$), FeL_3 vs. ferrocene.

L =	CH_3CN	DMSO
4,4'-dimethyl-2,2'-bipyridine	+510 mV	
4,4'-dicarboxylate-2,2'-bipyridine	~+638	
5,5'-dicarboxylate-2,2'-bipyridine	~+638	
4,4'-bis(hydroxymethyl)-2,2'-bipyridine	+497	+441

Table 2a. Absorbance Data, $\text{FeL}_2(\text{CN})_2$. Absorbance wavelength in nm (relative extinction, see text).

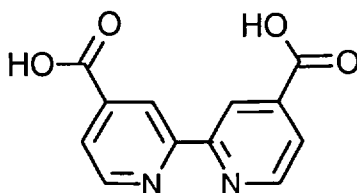
L =	Ethanol	CH_3CN	DMSO
4,4'-dimethyl-2,2'-bipyridine	567 (1.0) 367 (1.1) 297 (5.8)		614 (1.0) 385 (1.1) 301 (5.7)
4,4'-dicarboxylic acid-2,2'-bipyridine	610 (1.0) 426 (1.0) 318 (2.2)		655 (1.3) 455 (1.0) 314 (3.3)
4,4'-dicarboxylate-2,2'-bipyridine	590 (1.1) 404 (1.0) 302 (5.8)	627 (1.0) 420 (1.0) 301 (5.2)	
5,5'-dicarboxylate-2,2'-bipyridine	605 (1.0) 377 (1.4) 306 (13.5)	620 (1.0) 383 (1.2) 310 (9.9)	627 (1.0) 387 (1.3) 310 (11.1)
4,4'-diphosphonate-2,2'-bipyridine	581 (1.0) 392 (1.1) 296 (6.11)		
4,4'-Bis(methylphosphonate)-2,2'-bipyridine	567 (1.0) 371 (1.1) 301 (6.7)		
4,4'-bis(hydroxymethyl)-2,2'-bipyridine	571 (1.0) 371 (1.1) 299 (5.7)		616 (1.0) 388 (1.8) 302 (8.5)
4,4'-Bis(diethyl methylphosphonate)-2,2'-bipyridine	574 (1.0) 344 (1.1) 290 (5.9)		609 (1.0) 386 (1.1) 293 (6.6)

Table 2b. Absorption data, FeL_3 complexes. Absorbance wavelength in nm (relative extinction, see text). All complexes measured in acetonitrile.

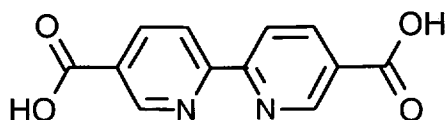
L =	λ in nm (rel ext)
4,4'-dimethyl-2,2'-bipyridine	528 (1.2) 355 (1.0) 292 (7.2)
4,4'-dicarboxylate-2,2'-bipyridine	535 (1.0) 358 (1.2) 297 (9.0)
4,4'-bis(hydroxymethyl)-2,2'-bipyridine	528 (1.2) 355 (1.0) sh 297 (6.6)

Table 3. Absorbance maxima and molar absorption coefficients.

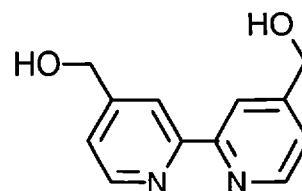
Complex	λ in nm ($\text{M}^{-1}\text{cm}^{-1}$)
$\text{Fe}(4,4'\text{-dimethyl-2,2'-bipyridine})_3(\text{PF}_6)_2$ in acetonitrile	528 (8300) 355 (7200) 292 (52000)
$\text{Fe}(4,4'\text{-dimethyl-2,2'-bipyridine})_2(\text{CN})_2$ in acetonitrile	606 (4800) 382 (5100) 298 (25000)
$\text{Fe}(4,4'\text{-dicarboxylic acid-2,2'-bipyridine})_2(\text{CN})_2$ in ethanol	610 (8400) 426 (8300) 318 (27000)



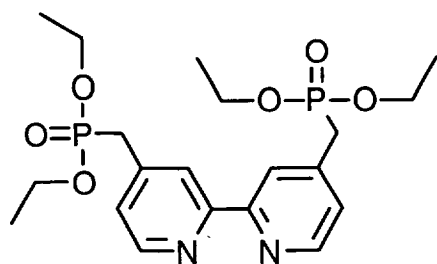
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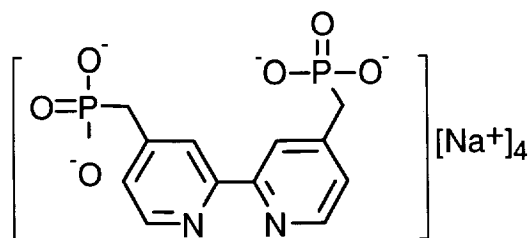
5,5'-dicarboxylic acid-2,2'-bipyridine



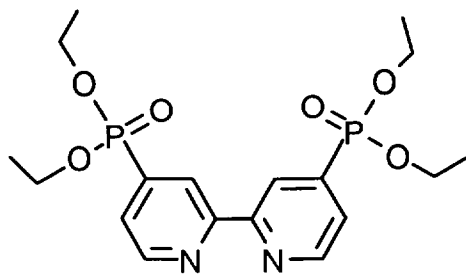
4,4'-hydroxymethyl-2,2'-bipyridine



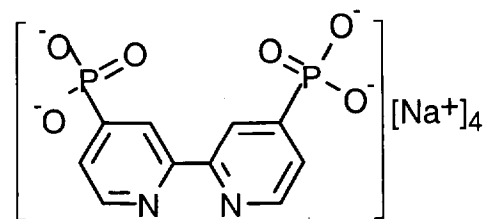
4,4'-Bis(diethyl methylphosphonate)-
2,2'-bipyridine



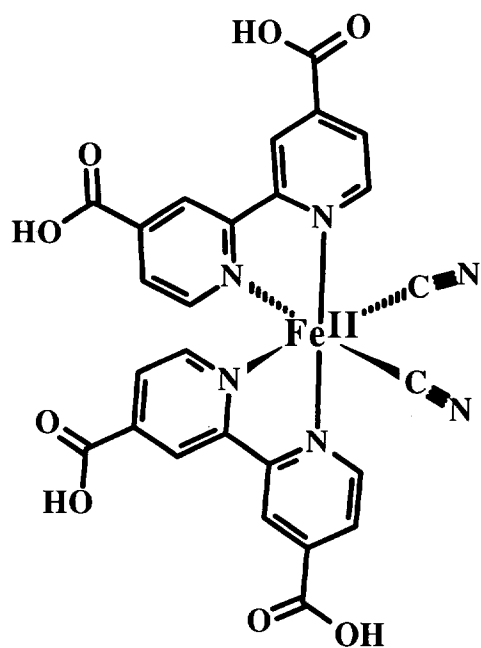
Tetrasodium 4,4'-Bis(methylphosphonate)-
2,2'-bipyridine



4,4'-Bis(diethylphosphonate)-
2,2'-bipyridine



Tetrasodium 4,4'-diphosphonate-
2,2'-bipyridine



Structure, [Fe(4,4'-dicarboxylic acid)-2,2'-bipyridine)₂(CN)₂]