Disulfide-Functionalized 3-, 4-, 5-, and 6-Substituted 2,2′-Bipyridines and Their Ruthenium Complexes

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The self-assembly of ruthenium complexes of bipyridine thiols was studied by Obeng and Bard in 1991.[1] They used a complex containing 4-methyl-4′-(dodecyl-1-thiol)-2,2′-bipyridine deposited on gold and indium-doped tin oxide surfaces. More recently, Yamada and co-workers[2] used a sulfide-functionalized chain also attached to the 4-position of a ruthenium-complexed 2,2′-bipyridine.

This paper reports the synthesis of nine 2,2′-bipyridines that were substituted on the 3-, 4-, 5-, and 6-positions with chains containing disulfide functional groups. The chains varied from four to twelve atoms in length between the disulfide and the bipyridine nucleus and incorporated ester or amide linkages. The latter moiety has been known to stabilize self-assembled monolayers (SAMs) through interchain hydrogen bonding.[3] All of the 2,2′-bipyridines were unsymmetrically substituted. Six were converted to their redox active ruthenium(II) complexes which were submitted to electrochemical evaluation on antimony-doped tin oxide (ATO) electrodes. The work described below resulted in the following conclusions regarding the effects of some key features of molecular design on the electrochemical properties of the modified electrodes. First, the surface coverages for these bipyridine disulfide complexes were found to be comparable to those measured for bipyridine thiols by Obeng and Bard.[1] The best coverages were observed with those complexes with the longest carbon chains between the bipyridine nucleus and the disulfide group. However, the complexes with short chains had lower oxidation potentials. Last, for complexes immobilized on gold electrodes, the highest electron-transfer rates were obtained with the 4-substituted bipyridines. In short, SAMs prepared from the disulfide derivatives of ruthenium bipyridine complexes have few advantages or disadvantages compared to those of the corresponding thiols.

The unsymmetrically substituted 2,2′-bipyridines prepared in this work were synthesized using modifications of a method that was first used by Bailey for the preparation of biaryls[4] and later applied by Ghadiri et al. to the synthesis of ethyl 2,2′-bipyridine-5-carboxylate.[5] It involved the palladium-catalyzed coupling of a pyridyltrimethylstannane with a pyridyl halide. We have found this procedure to be well suited for making all of our unsymmetrically substituted 2,2′-bipyridines. This paper describes the first syntheses of the ruthenium complexes of disulfide-functionalized 2,2′-bipyridines.

Methyl 6-chloropyridine-2-carboxylate[6] was prepared from the commercial 6-hydroxypyridine-2-carboxylic acid and was then coupled with trimethylstannylpyridine[7] to afford the known methyl 2,2′-bipyridine-6-carboxylate (**1a**).[8,9] The ester, **1a**, was reduced to the hydroxymethylbipyridine (**2a**) which was then esterified with 3,3′-dithiodipropanoic acid to yield the bipyridine disulfide ester (**3a**). The methyl 2-chloropyridine-5- and 4-carboxylates were similarly treated to afford **3b** and **3c**, respectively. The overall yields of **3a**, **b**, and **c** from trimethylstannylpyridine and the methyl chloropyridinecarboxylates were, respectively, 18, 23, and 7% (Scheme 1).

Four examples of the 5-substituted 2,2′-bipyridine disulfides (**3b**, **5b** $n = 2$, **5b** $n = 10$, **8**) were prepared. They differed mainly in the length of the side chains (from five to twelve atoms) which incorporated amide or ester groups. As with all of the bipyridines, these were synthesized from the appropriate methyl chloropyridinecarboxylates and trimethylstannylpyridines. Methyl 2,2′-bipyridine-5-carboxylate (**1b**) was prepared from commercially available 2-chloropyridinecarboxylic acid (6-chloronicotinic acid) following the procedure that Ghadiri[5] reported for the ethyl ester, except that the reaction mixture was refluxed for 6−7 h in *m*-xylene instead of 24 h in THF. This modification increased the yield of the ester from 45 to 84%. After saponification of the bipyridyl ester, **1b**, the resultant 2,2′-bipyridine-5-carboxylic acid (**4b**) was converted to the amide of cystamine, **5b** ($n =$ 2), under Schotten-Baumann conditions (see Scheme 2). The di(10-aminodecyl) disulfide ($n = 10$) was synthesized by a three-step procedure[10] which began with the preparation of *N*-(10-bromodecyl)phthalimide. Treatment of the latter with benzyltriethylammonium tetrathiomolybdate[11] converted it to the di(10-phthalimidyldecyl) disulfide which was deprotected with hydrazine to afford the amino disulfide ($n = 10$). This was condensed with the 2,2′-bipyridine-5-carboxylic acid chloride to give the long-chain bipyridyl disulfide, **5b** ($n = 10$). The methyl 2-chloropyridine-4-carboxylate, needed for the syntheses of the 4-substituted 2,2′-bipyridines (**1c**), was prepared by a route that included the chlorination of pyridine *N*-oxide 4-carboxylic acid.[12,13] Methyl 2-chloropyridine-3-carboxylate was made from the commercial carboxylic acid and then condensed with 2-trimethylstannylpyridine

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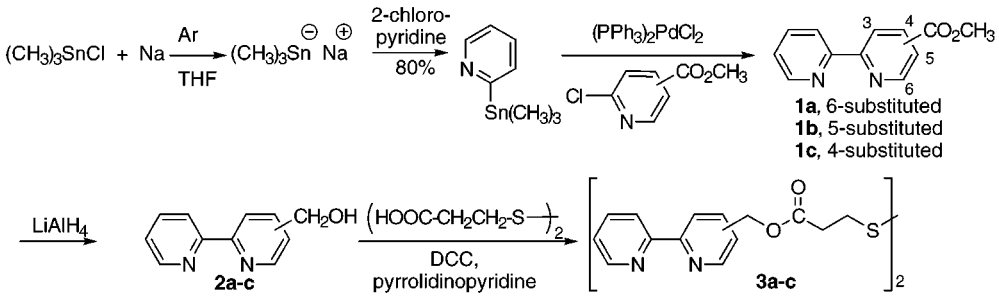
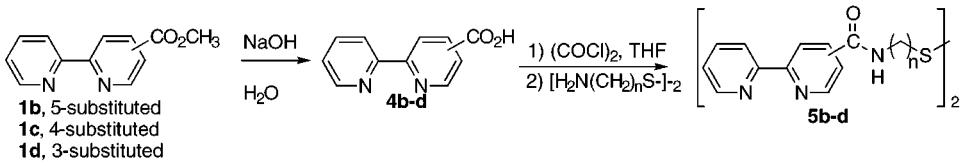
Scheme 1



Scheme 2



Scheme 3

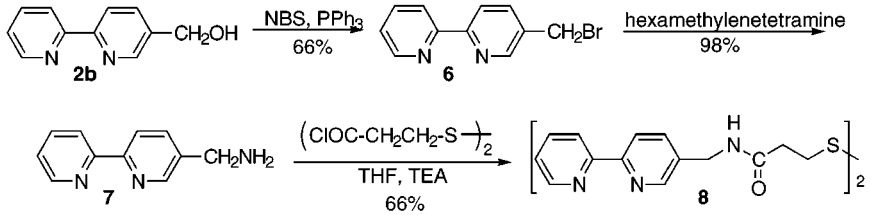


Table 1. The Syntheses of Methyl 2,2′-Bipyridine-6-, 5-, 4-, and 3-carboxylates (1a−d) from Trimethylstannylpyridine and Methyl Chloropyridinecarboxylates

product no.[a]	solvent	temp, °C	heating, h	symmetrical byproduct yield, %	product yield, %	mp, °C	lit. mp, °C	IR, ν cm^{-1}
1a	DMF	130	12	0	61	77−79	83.5−84.0[c]	1722
1b	*m*-xylene	135	7	0	84	108−110	*d*	1722
1c	*m*-xylene	135	12	0	52	79−80	*d*	1731
1c[b]	*m*-xylene	120	12	0	40			
1c	dioxane	100	20	2	46			
1c	THF	68	36	8	21			
1c	THF	68	24	7	18			
1d	dioxane	100	16	0	86	55−56	53−55[e]	1722

[a] Five mole % of $(PPh_3)_2PdCl_2$ used. [b] Three mole % of $(PPh_3)_2PdCl_2$ used. [c] Reference 8. [d] Only the ethyl esters are known.[14] [e] Reference 15.

Table 2. The Syntheses of 6-, 5-, and 4-(Hydroxymethyl)-2,2′-bipyridines (2a, b, and c) from Methyl 2,2′-Bipyridinecarboxylates (1a, b, and c) and $LiAlH_4$

product no.	yield, %	IR (film), ν cm^{-1}	^{1}H NMR ($CDCl_3$), δ
2a	86	3424 (br), 3046, 2930, 1582, 1430	8.57 (d, 1H), 8.32−8.21 (m, 2H), 8.05 (d, 1H), 7.72 (m, 2H), 7.21 (m, 1H), 4.60 (s, 2H)
2b[a]	92	3619, 2941, 1590, 1555, 1461, 1017, 926	8.64 (dq, 1H), 8.56 (d, 1H), 8.32−8.26 (m, 2H), 7.84−7.7 (m, 2H), 7.3 (s, 1H), 4.72 (2H)
2c	58	3323, 3022, 2970, 1587, 1559, 1403, 1226, 1049	8.53 (br d, 1H), 8.45 (d, 1H), 8.19 (m, 2H), 7.7 (br t, 1H), 7.2 (m, 2H), 4.65 (s, 2H)

[a] Reference 16.

in dioxane to afford **1d**. The overall yields of **5b**, **c**, and **d** (n = 2) from the methyl chloropyridinecarboxylates were, respectively, 40, 29, and 29%. For products **5b** and **c** (n = 10), the overall yields were 43 and 30%, respectively.

The 5-(hydroxymethyl)-2,2′-bipyridine (**2b**) was also used to prepare 2,2′-bipyridine disulfide with a five-atom amide side chain (**8**) (Scheme 3).

The methods of Bailey[4] and Ghadiri[5] were found to be well-suited to the preparations of the methyl 2,2′-bipyridine-6-, 5-, 4-, and 3-carboxylates (**1a**−**d**) which are important precursors of the 2,2′-bipyridine disulfides. Table 1 summarizes the experimental results of this synthetic step; further results are given in Tables 2−6.

Six of the 2,2′-bipyridine disulfides were converted to their ruthenium complexes by treating each of them with *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate in ethanol solution (**3a** → **9**; **5b** → **10**, **11**; **5c** → **12**, **13**; **5d** → **14**). The complexes were precipitated as hexafluorophosphate salts, purified on neutral alumina, and recrystallized from acetone/ether or acetonitrile/ether. The yields ranged from 65 to 80%. The UV−vis spectra

Table 3. The Syntheses of Di[(2,2′-bipyridin-6-, 5-, and 4-yl)methyl] 3,3′-Dithiodipropanoates (3a, b, and c) from 6-, 5-, and 4-(Hydroxymethyl)-2,2′-bipyridines (2a, b, and c) and 3,3-Dithiodipropanoic Acid

product no.	mp, °C	yield, %	IR (film), ν cm^{-1}	^{1}H NMR ($CDCl_3$), δ	Anal. Calcd for $C_{28}H_{26}N_4O_4S_2$ (546.7): C, 61.52; H, 4.79; N, 10.25; S, 11.73. Found:
3a	101−102	34	2925, 1738, 1582, 1430, 1270, 744	8.66 (dd, 1H), 8.43 (d, 1H), 8.31 (d, 1H), 7.83 (m, 2H), 7.38−7.26 (m, 2H), 5.34 (s, 2H), 3.01 (t, 2H), 2.89 (t, 2H).	C, 61.40; H, 4.82; N, 10.32; S, 11.64
3b	101−102	30	1738, 1590, 1558, 1462, 1273, 1236, 882	8.7 (m, 2H), 8.4 (m, 2H), 7.85 (m, 2H), 7.34 (m, 1H), 5.2 (s, 2H), 2.95 (t, 2H), 2.84 (t, 2H)	C, 61.26; H, 4.82; N, 9.90; S, 11.49
3c	oil	23	2990, 1740, 1659, 1597, 1462, 1224	8.67 (d, 2H), 8.36 (m, 2H), 7.83 (ddd, 1H), 7.25 (m, 2H), 5.2 (s, 2H), 2.97 (t, 2H), 2.88 (t, 2H)	C, 61.42; H, 4.82; N, 10.25; S, 11.73

Table 4. The Syntheses of 2,2′-Bipyridine-5-, 4-, and 3-carboxylic Acids (4b, c, and d) from the Saponification of the Methyl 2,2′-Bipyridinecarboxylates (1b, c, and d)

product no.	mp, °C	yield, %	IR (film), ν cm^{-1}	^{1}H NMR ($CDCl_3$), δ
4b	196−198	80	3448−3096 (br), 1678, 1654, 1534, 1458, 1398, 1016, 749	(in DMSO) 9.2 (d, 1H), 8.78 (dd, 1H), 8.4−8.5 (m, 3H), 8.0 (ddd, 1H), 7.5 (m, 1H)
4c	233−234	89	3448−3000 (br), 2900, 1670, 1654, 1534, 1458, 1398, 1314, 1016, 749	(in DMSO) 9.0 (d, 1H), 8.85 (m, 2H), 8.64 (d, 1H), 8.3 (t, 1H), 8.0 (d, 1H), 7.7 (m, 1H)
4d	108−109	77	3440 (br), 1680, 1552, 1480	8.83 (m, 2H), 8.79 (dd, 1H), 8.60 (d, 1H), 8.12 (ddd, 1H), 7.61 (m, 1H), 7.52 (dd, 1H)

Table 5. The Syntheses of Di[2-(2,2′-bipyridine-5-, 4-, and 3-carboxamido)ethyl] Disulfides (5b, c, and d, $n = 2$) from 2,2′-Bipyridine-5-, 4-, or 3-carboxylic Acid (4b, c, and d) and Cystamine Dihydrochloride

product no.	mp, °C	yield, %	IR ($CHCl_3$), ν cm^{-1}	^{1}H NMR ($CDCl_3$), δ	Anal. Calcd for $C_{26}H_{24}N_6O_2S_2$ (516.7): C, 60.04; H, 4.68; N, 16.26; S, 12.42
5b $n = 2$	203−204	59	3442, 2927, 1672, 1585, 1552, 1518, 1459, 1268	9.15 (d, 1H, J = 1.7 Hz), 8.68 (ddd, 1H, J = 0.83, 1.8, 5.0 Hz), 8.46 (m, 2H), 8.29 (dd, 1H, J = 1.7, 8.27 Hz), 7.84 (ddd, 1H, J = 1.8, 7.8, 7.8 Hz), 7.35 (m, 2H), 3.86 (q, 2H), 3.05 (t, 2H)	semihydrate; Calcd: C, 59.42; H, 4.76; N, 16.26; S, 12.19. Found: C, 59.43; H, 4.55; N, 16.04; S, 12.17
5c $n = 2$	178−180	63	(KBr) 3442, 2927, 1672, 1585, 1552, 1518, 1459, 1268	9.1 (d, 1H), 8.97 (dd, 1H), 8.72 (d, 1H), 8.44 (m, 1H), 8.35 (dd, 1H), 8.0 (d, 1H), 7.5 (m, 1H), 6.8 (t, 1H), 3.85 (q, 2H), 3.0 (t, 2H)	hydrate; Calcd: C, 58.41; H, 4.52; N, 15.72; S, 12.01. Found: C, 58.71; H, 4.69; N, 15.50; S, 12.56
5d $n = 2$	120−123	43	3429, 2921, 1659, 1504, 1508, 1429, 770	8.69 (dd, 1H, J = 1.5, 4.7 Hz), 8.57(br d, 1H, J = 4.7 Hz), 7.98(d, 1H, J = 7.8 Hz), 7.9 (dd, 1H, J = 1.5, 7.7 Hz), 7.82 (ddd, 1H, J = 1.4, 7.7, 7.8 Hz), 7.44 (t, 1H), 7.32 (dd, 2H, J = 4.7, 7.7 Hz), 2.098 (t, 2H), 1.998 (t, 2H)	Found: C, 59.59; H, 4.83; N, 15.95; S, 12.25

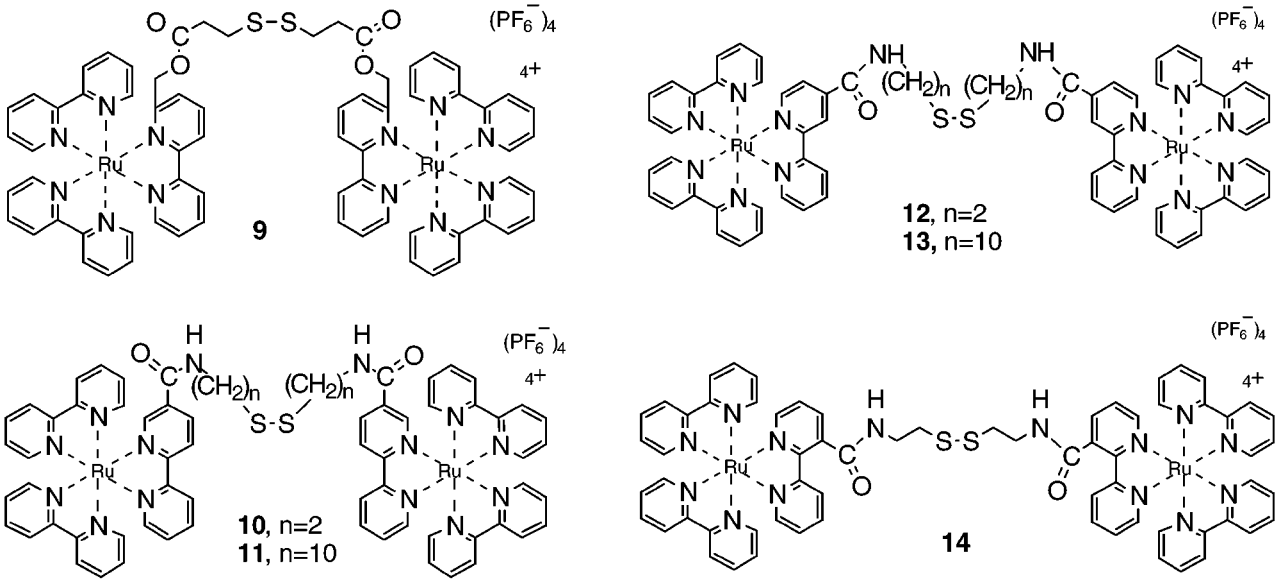
Table 6. The Syntheses of Di[10-(2,2′-bipyridine-5- and 4-carboxamido)decyl] Disulfides (5b, and c, $n = 10$) from 2,2′-Bipyridine-5- and 4-carboxylic Acid (4b, and c) and Di(10-aminodecyl) Disulfide[10]

product no.	mp, °C	yield, %	IR (KBr), ν cm^{-1}	^{1}H NMR ($CDCl_3$), δ	Anal. Calcd for $C_{42}H_{56}N_6O_2S_2$ (750.1): C, 66.45; H, 7.43; N, 11.00; S, 8.44
5b $n = 10$	131−133	64	3452, 2929, 2856, 1660, 1590, 1523, 1459	9.0 (d, 1H, J = 2.1 Hz), 8.69 (d, 1H, J = 4.8 Hz), 8.43 (dd, 2H, J = 8.2, 8.2 Hz), 8.18 (dd, 1H, J = 2.1, 8.2 Hz), 7.83 (ddd, 1H, J = 1.8, 7.8, 8.2 Hz), 7.34 (m, 1H), 6.17 (t, 1H), 3.8 (q, 2H), 2.67 (t, 2H), 1.6 (m, 4H), 1.3−1.2 (m, 12H)	semihydrate; Calcd: C, 67.25; H, 7.52. Found: C, 67.13; H, 7.93
5c $n = 10$	109−110	64	3414, 3297, 2913, 2844, 1630, 1525	8.78 (d, 1H), 8.68 (dd, 1H, J = 1.8, 4.77 Hz), 8.6 (d, 1H, J = 1.6 Hz), 8.44 (dd, 1H, J = 1.5, 7.7 Hz), 7.85 (ddd, 1H, J = 1.89, 7.75, 7.7 Hz), 7.76 (dd, 1H, J = 1.64, 4.9 Hz), 7.36 (m, 1H), 6.65 (t, 1H), 3.5 (q, 2H), 2.65 (t, 2H), 1.7 (m, 4H), 1.4−1.0 (m)	Found: C, 66.78; H, 7.81; N, 10.44; S, 8.36

showed absorptions at 446−452 nm for the d−π* metal-to-ligand charge-transfer transitions. The most intense peaks at 298−301 nm were assigned to the intraligand $\pi-\pi$* transitions.

Self-assembled monolayers of compounds **9**−**14** (Chart 1) were prepared on gold(111) substrates and examined with cyclic voltammetry in 1.0 M $HClO_4$. However, these surface-bound complexes produced poorly defined voltammetric responses due to the concurrent oxidation of the gold surface. Similar results were reported by Obeng and Bard[1] for a thiol-functionalized tris(bipyridyl)ruthenium(II) complex immobilized on gold similar to those examined here. Thus, it was necessary to use Sb-doped SnO_2 (ATO) substrates (Corning Pyrex brand infrared reflecting glass) in order to obtain good quality voltammograms. All of the tris(2,2′-bipyridyl)ruthenium(II) complexes listed above chemisorbed on ATO, some to a greater extent than others. Figure 1 shows a typical cyclic voltammogram of an ATO substrate modified with **13**. For a series of voltammograms similar to that shown in Figure 1, a plot of the voltammetric oxidation peak current varied linearly with the scan rate as expected for a surface-bound redox center.[17] Voltammetric data for complexes **9**−**14** chemisorbed on ATO substrates are

Chart 1



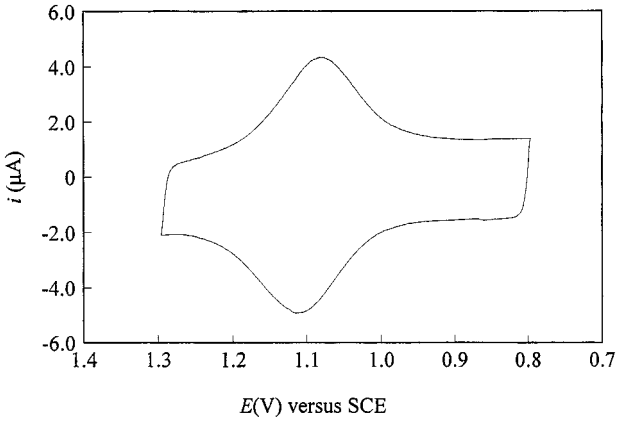


Figure 1. Cyclic voltammogram of the 2,2′-bipyridylruthenium complex with di[10-(2,2′-bipyridine-4-carboxamido)decyl] disulfide (**13**).

collected in Table 7. The equilibrium surface coverage (Γ) of each monolayer was estimated from the charge under the voltammetric wave after correction for the charging current. Voltammetric waves consistent with surface-confined **14** could be detected; however, the surface coverage of this complex was so small that meaningful electrochemical data could not be extracted from these voltammograms. However, the surface coverages of the remaining complexes were comparable to that reported by Obeng and Bard,[1] $\sim 1.8 \times 10^{-11}$ mol/cm^2. This value is attributed to about 10% of a full monolayer (1.8×10^{-10} mol/cm^2). Although no clear trend can be seen, the highest surface coverages appear to favor those complexes with the longest side chains (**11** and **13**); the long alkyl tethers probably facilitate surface packing. The formal potential ($E°$) of each of the surface-confined complexes is also listed in Table 7 along with its solution counterpart. These potentials indicate that those complexes with shorter tethers (**10** and **12**) are 30−40 mV easier to oxidize than those with the longer tethers (**11** and **13**). The voltammetric peak separation, ΔE_p, is inversely proportional to the electron-transfer rate of redox couples in solution or immobilized on electrode surfaces. For a Nernstian redox couple confined to a surface, ΔE_p approaches 0 V, whereas for a freely diffusing species in solution, ΔE_p should be close to 0.059 V at 25 °C. The data in Table 7 show that ΔE_p exceeds these theoretical expectations for all of the complexes investigated both in solution and immobilized on gold electrodes. Among the surface-bound species, the most facile electron transfer was observed for films prepared from **13**. However, in solution, **13** exhibited the slowest electron-transfer rate. The voltammetric oxidation peak-width at half-maximum, E_{fwhm}, is a measure of the lateral interactions between adjacent surface-bound redox centers.[18] It should be 90.3/n mV, where n is the number of electrons involved in the redox reaction. Despite the relatively low surface coverages found for **9**−**13**, the values of E_{fwhm} are considerably larger than the 90.3 mV value expected for an ideal one-electron surface reaction, indicating substantial repulsive interactions between adjacent redox centers.

Table 7. Electrochemical Results of Substituted 2,2′-Bipyridylruthenium Complexes

		SAMs on ATO electrodes[a]				in solution[b]	
product no.	subst. position	$E°$ (V)	ΔE_p (mV)	ΔE_{fwhm} (mV)	Γ^c (mol/cm^2)	$E°$ (V)	ΔE_p (mV)
9	6	1.08	51	110	3.6×10^{-12}		
10	5	1.07	61	163	1.0×10^{-11}	1.31	86
11	5	1.11	47	140	1.6×10^{-11}	1.30	86
12	4	1.08	46	141	8.3×10^{-12}	1.31	94
13	4	1.11	34	130	2.7×10^{-11}	1.30	96
14	3				very low	1.30	83

[a] Versus SCE as determined by cyclic voltammetry in aqueous 1.0 M $HClO_4$; the scan rates were 100 mV/s. [b] Versus SCE as determined by cyclic voltammetry at a Pt disk working electrode in acetonitrile containing 0.1 M [n-Bu_4N]PF_6, the scan rates were 100 mV/s. [c] Equilibrium surface coverages of **9**−**14** on antimony-doped tin oxide.

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Table 8. Spectra and Analyses of the 2,2′-Bipyridylruthenium Complexes Prepared in This Work

complex (mp °C)	source	^{1}H NMR (CD_3CN), δ, J (Hz)	UV (CH_3CN), abs λ (nm)	analyses (%)
9 (169−173)	**3a**	8.6−8.51 (m, 6H), 8.1−8.09 (m, 6H), 7.81−7.35 (m, 11H), 4.75 (d, 1H, J = 14.1), 4.21 (d, 1H, J = 14.1), 2.79 (t, 2H), 2.60 (t, 2H)	210, 300, 431, 446	Calcd for $C_{68}H_{58}F_{24}N_{12}O_4P_4Ru_2S_2$: C, 41.81; H, 2.99; N, 8.60; S, 3.28. Found: C, 41.85; H, 3.12; N, 8.17; S, 3.31
10 (214−216)	**5b** n = 2	8.57−8.54 (m, 5H), 8.1 (m, 6H), 7.8 (m, 6H), 7.45 (m, 7H), 2.9 (t, 2H), 2.8 (t, 2H)	210, 241, 298, 452	Calcd for $C_{66}H_{56}F_{24}N_{14}O_2P_4Ru_2S_2$: C, 41.22; H, 2.93; N, 10.14; S, 3.33. Found: C, 41.57; H 3.36; N, 9.74; S, 3.63
11 (189−191)	**5b** n = 10	8.60−8.54 (m, 6H), 8.33 (m, 1H) 8.13−8.02 (m, 6H), 7.83−7.7 (m, 5H), 7.47−7.43 (m, 5H), 7.18 (t, 1H), 3.48 (q, 2H), 2.75−2.70 (t, 2H), 1.68−1.66 (m, 2H), 1.51−1.31 (m, 16H)	220, 300, 448	Calcd for $C_{82}H_{88}F_{24}N_{14}O_2P_4Ru_2S_2 \cdot 1H_2O$: C, 45.50; H, 4.14; N, 9.06; S, 2.96. Found: C, 45.13; H, 4.16; N, 9.00; S, 3.33
12 (237−239)	**5c** n = 2	8.83 (d, 1H), 8.55 (br d, 1H), 8.57−8.54 (br d, 4H), 8.15−8.08 (m, 5H), 7.9 (d, 1H), 7.78−7.44 (m, 7H), 7.48−7.44 (m, 5H), 3.79 (q, 2H), 3.01 (t, 2H)	299, 320, 450	Calcd for $C_{66}H_{56}F_{24}N_{14}O_2P_4Ru_2S_2 \cdot 1H_2O$: C, 40.85; H, 3.01; N, 10.10; S, 3.33. Found: C, 40.85; H 3.06; N, 9.86; S, 3.53
13 (172−174)	**5c** n = 10)	8.8 (d, 1H), 8.6 (d, 1H), 8.56 (m, 4H), 8.14 (m, 5H), 7.91 (d, 1H), 7.7 (m, 7H), 7.47 (m, 5H), 3.4 (t, 2H), 2.7 (t, 2H), 1.7 (m, 4H), 1.6 (m, 12H)	210, 240, 301, 451	Calcd for $C_{82}H_{88}F_{24}N_{14}O_2P_4Ru_2S_2$: C, 45.50; H, 4.14; N, 9.06. Found: C, 45.77; H, 4.46; N, 8.51
14 (228−230)	**5d**	8.6−8.5 (m, 4H), 8.4 (m, 1H), 8.2−7.9 (m, 6H), 7.89−7.7 (m, 6H), 7.55−7.45 (m, 6H), 3.95−3.8 (t, 2H), 3.1 (t, 2H)	200, 298, 450	Calcd for $C_{66}H_{56}F_{24}N_{14}O_2P_4Ru_2S_2$: C, 41.22; H, 2.93; N, 10.14; S, 3.33. Found: C, 40.88; H 3.09; N, 9.79; S, 3.62

We have successfully synthesized nine new 2,2′-bipyridines substituted at four different positions with disulfide-terminating chains. Six of them were complexed with ruthenium II and the resultant products were fabricated into self-assembled monolayers. Certain electrochemical parameters were evaluated with respect to the position of the disulfide substituent and the length of the carbon chain between the disulfide and the redox center.

Experimental Section

General Electrochemistry. Acetonitrile (Fisher Optima grade) was distilled from CaH_2 under nitrogen, passed through activated alumina, and stored in a tightly capped bottle over 4 Å molecular sieves until needed. Dehydrated absolute ethanol was used as received from McCormick Distilling Co., Inc. Tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) was synthesized and purified according to standard procedures. Standard glass microscope slides (Fisher cat. no. 12-549) served as gold substrates; they were cleaned by ultrasonication in successive baths of piranha solution (1:3 by volume 30% H_2O_2/concentrated H_2S0_4), distilled water, and 2-propanol (Fisher Optima grade). The oven-dried microscope slides were coated with 50 Å of chromium followed by 1500 Å of gold by thermal evaporation at a base pressure of 7×10^{-7} Torr by using an Edwards Auto 306 vacuum coater equipped with a Sycon Model STM-100/MF thin film monitor. After coating was complete, the vacuum chamber was back-filled with high-purity nitrogen gas. The gold films prepared by this method were found by X-ray diffraction analysis to exhibit strong Au {111} crystallographic texture.[19] The gold electrodes were taken directly from the vacuum coater and immersed in solutions containing **9**−**14**. Cyclic voltammetric measurements were made in a three-electrode cell with an EG & G Princeton Applied Research Corp. (PARC) Model 283 potentiostat/galvanostat employing PARC Model 270 Electrochemistry Analysis Software running on an IBM-compatible 386 computer. For studies with self-assembled monolayers, the gold-coated substrates served as the working electrodes. They were clamped to an O-ring joint attached to the side of the cell. The O-ring provided a liquid-tight seal and defined the area of the working electrode, which was ca. 1.54 cm^2. For electrochemical experiments involving solutions in acetonitrile, a small Kel-F shrouded platinum disk electrode (area = 0.0214 cm^2) served as the working electrode. The reference electrode for all experiments was an EG&G saturated calomel electrode (SCE) separated from the working electrode compartment by means of a Luggin capillary. All potentials mentioned in this paper were measured with respect to this reference electrode. The counter electrode was a platinum wire spiral. The electrolyte solutions used for aqueous experiments were 1.0 M aqueous $HClO_4$ and a pH = 7.2 phosphate buffer solution (Aldrich Chemical Co.). Nonaqueous experiments were conducted in anhydrous acetonitrile containing 0.1 M [*n*-Bu_4N]PF_6. All measurements were conducted at ca. 24 °C. The solutions in the electrochemical cells were deaerated with high purity N_2 before each experiment, and an atmosphere of N_2 was maintained over the solution in the cell during measurements. Electronic resistance compensation was employed during all experiments. The equilibrium surface coverage, Γ, reported for each monolayer was estimated from the charge under the appropriate voltammetric oxidation or reduction wave after subtraction of the residual current.

General Synthetic Chemistry. The following techniques were followed unless otherwise stated. All reactions sensitive to air and moisture were carried out in flame-dried apparatus, under a dry nitrogen atmosphere using either magnetic or mechanical stirring. All melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were recorded using KBr pellets or thin liquid films. ^{1}H and ^{13}C NMR spectra were determined on a 300 MHz spectrometer using $CDCl_3$, DMSO-d_6, acetone-d_6, or CD_3CN with tetramethylsilane (Me_4Si) as the internal standard. Column chromatography was carried out by gravity using 80−200 mesh neutral alumina (Fisher, A-540−3) or E. Merck silica gel (9385). Thin-layer chromatography was performed on Analtech neutral alumina plates (2.5 cm × 10 cm, no. 47031) with a fluorescence indicator. TLC spots were visualized either by exposure to iodine vapors or by irradiation with UV light. Table 8 lists the spectroscopic and analytical data of the major products. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Atlantic Microlab, Inc., Norcross, GA.

The following reagents were prepared as follows: 2-trimethylstannylpyridine, by the method of Yamamoto;[7] methyl 2-chloropyridine-2-carboxylate (mp 96 °C), via esterification of 6-hydroxypicolinic acid (Aldrich); methyl 2-chloropyridine-3-carboxylate (mp 64−65 °C), via esterification of the free acid (Maybridge-Ryan Scientific); methyl 2-chloropyridine-4-carboxylate (mp 38−40 °C), via esterification of 2-chloroisonicotinic acid;[13] methyl 2-chloropyridine-5-carboxylate, via esterification of the free acid (Maybridge-Ryan Scientific).

General Procedure for the Preparation of Methyl 2,2′-Bipyridinecarboxylates (1). A mixture of one of the methyl chloropyridinecarboxylates (2.9 mmol), 2-trimethylstannylpyridine (3.3 mmol), and $(PPh_3)_2PdCl_2$ (0.15 mmol) in 10 mL of an

(19) He, Z.; Bhattacharyya, S.; Cleland, W. E. J.; Hussey, C. L. *J. Electroanal. Chem.* **1995**, *397*, 305.

anhydrous solvent was heated for a period of time (see Table 1). During the course of this reaction, the color changed from yellow to black as Pd° was formed. The solvent was removed, and the residue was dissolved with CH_2Cl_2 and filtered through a bed of silica gel and Celite. The pale yellow eluate was evaporated and the residue was purified on a neutral alumina column.

General Procedure for the Preparation of (Hydroxymethyl)-2,2′-bipyridines (2). To a solution of one of the methyl 2,2′-bipyridinecarboxylates (**1a**, **b**, or **c**) (5 mmol) in anhyd THF (20 mL) at −78 °C was added lithium aluminum hydride (5 mmol). The mixture was stirred at this temperature for 0.5 h and was warmed slowly to −20 °C, at which temperature, a homogeneous solution was obtained. The reaction was monitored with TLC on alumina, and the complete disappearance of the starting material was noted after 1 h. The reaction mixture was cooled to −78 °C and quenched very slowly with 10 mL of 10% aqueous THF. After being warmed to room temperature, the reaction mixture was stirred with Celite for 15 min and then filtered. The filtrate was concentrated and extracted with methylene chloride, and the extract was dried over anhyd $MgSO_4$. Evaporation of the solvent yielded **2a**, **b**,[16] and **c** as yellow oils. They were homogeneous by TLC and were used, as is, for further transformations. See Table 2 for yields and spectral data.

General Procedure for the Preparation of Di[(2,2′-bipyridinyl)methyl] 3,3′-Dithiodipropanoates (3). A mixture of one of the 6-, 5-, or 4-(hydroxymethyl)-2,2′-bipyridines (**2a**, **b**, or **c**) (0.6 mmol), dicyclohexylcarbodiimide (0.6 mmol), 3,3-dithiodipropanoic acid (0.3 mmol), and pyrrolidinopyridine (0.1 mmol) was stirred in dry CH_2Cl_2 (10 mL) at room temperature for about 2 days. Dicyclohexylurea precipitated and was filtered. The filtrate was concentrated to an oil, and this was purified on a neutral alumina column to yield a white solid. Recrystallization from EtOAc/hexane afforded **3a** and **b** as white crystals and **3c** as an oil. See Table 3 for data on these products.

General Procedure for the Preparation of the 2,2′-Bipyridinecarboxylic Acids (4). Five mmol of one of the methyl 2,2′-bipyridine-5, 4, or 3-carboxylates (**1b**, **c**, or **d**) was dissolved in hot methanol (5 mL) to which was added 1 N NaOH (5 mL) and the reaction mixture was stirred at room temperature for 3−5 h. A TLC was used to check for any remaining starting material. The solvent was removed under reduced pressure, and the aqueous phase was acidified with 0.5 N HCl to pH 3.5−4.0. A white precipitate separated upon cooling. It was collected by filtration, washed with water, and air-dried. Pure white crystals were obtained. See Table 4 for data on these products.

General Procedure for the Preparation of the Di[2-(2,2′-bipyridinecarboxamido)ethyl] Disulfides (5, $n = 2$). Oxalyl chloride (5 mmol) in 2.5 mL of CH_2Cl_2 was added to a stirred solution of 2,2′-bipyridine-5-, 4-, or 3-carboxylic acid (2.5 mmol, **4b**, **c**, or **d**) in THF (8 mL). The mixture immediately turned green and a precipitate formed. This mixture was refluxed for 2 h. The solvent and the excess oxalyl chloride were removed under reduced pressure. The acid chloride was dissolved in 3 mL of dry THF and was added to a solution of cystamine dihydrochloride (1.25 mmol) in 2.5 equiv of aqueous NaOH. The mixture was stirred at room temperature for 3 h and refluxed for an additional 3 h. The solvent was removed, and the residue was dissolved in water. The pH of the solution was made slightly alkaline and the product precipitated as a brown solid. This crude product was purified by column chromatography on neutral alumina using 0.5 parts of MeOH:4.0 parts of CH_2Cl_2:6.0 parts of hexane for **5b**, 0.5 parts of MeOH:5.0 parts of CH_2Cl_2:6.0 parts of hexane for **5c**, and 1.0 parts of EtOAc:1.0 parts of CH_2Cl_2:10 parts of hexane for **5d**. Recrystallization from CH_2Cl_2/hexane afforded a white solid product. See Table 5 for data on these products.

General Procedure for the Preparation of the Di[10-(2,2′-bipyridinecarboxamido)decyl] Disulfides (5, $n = 10$). A stirred solution of 2,2′-bipyridine-5 or 4-carboxylic acid (0.8 mmol, **4b** or **c**) in THF (5 mL) was treated with 3 equiv of oxalyl chloride. The resulting green precipitate was refluxed for 2 h at 70 °C and the solvents were evaporated under vacuum. In another flask, a solution of di(10-aminodecyl) disulfide[10] was prepared by dissolution of the dihydrochloride (0.35 mmol) in water (0.5 mL) and NaOH (1.0 mmol). The acid chloride was added dropwise to this mixture. The formation of a precipitate was noted as the acid chloride was added, and the resulting mixture was stirred at room temperature for 2 h and refluxed for an additional 2 h. An orange-red precipitate or oil was obtained after evaporation of the solvents. This residue was dissolved in water, and the solution was made just slightly alkaline with dilute hydrochloric acid to give a light yellow solid. The crude solid, **5b**, was purified by several recrystallizations from CH_2Cl_2/hexane mixtures and finally from hot chloroform. Crude **5c** was a brown oil which was purified by chromatography over a neutral alumina column using a 1.0 parts of EtOAc:1.0 parts of CH_2Cl_2:10 parts of hexane. Recrystallization from chloroform afforded the product. See Table 6 for data on these products.

5-(Aminomethyl)-2,2′-bipyridine (7). This procedure was reported by Ziessel and Lehn for the preparation of 6-(aminomethyl)-2,2′-bipyridine.[20] A 25-mL round-bottom flask fitted with a reflux condenser was charged with hexamethylenetetramine (0.39 g, 2.8 mmol) and methylene chloride (5 mL). The mixture was heated to reflux, and a solution of 5-(bromomethyl)-2,2′-bipyridine (**6**)[16] (0.6 g, 2.4 mmol) in CH_2Cl_2 (1 mL) was added dropwise and refluxed an additional 3 h. The deposited white solid was filtered, dried, and suspended in EtOH (10 mL) and concentrated HCl (2 mL). The mixture was stirred at 80 °C for 20 h during which time the solid dissolved. The solution was cooled to room temperature, and the solvents were evaporated under reduced pressure. Water (5 mL) and chloroform (10 mL) were added to the residue, and the mixture was adjusted to pH 13 with a solution of NaOH. The aqueous phase was extracted with methylene chloride (3 × 20 mL), and the combined organic extracts were dried over anhyd $MgSO_4$. The crude amine (440 mg, 98%) was obtained after evaporation of the solvents. It was used as is or was stored as the hydrochloride salt. ^{1}H NMR (free amine) ($CDCl_3$): δ 8.68 (dq, 1H), 8.62 (d, 1H), 8.37 (2H), 7.8 (overlapping ddd, 2H), 7.29 (m, 1H), 3.96 (s, 2H), 1.64 (s, 2H).

Di{N-[(2,2′-bipyrid-5-yl)methyl]}-3,3′-dithiodipropanamide (8). A mixture of 3,3-dithiodipropanoic acid (0.17 g, 0.81 mmol), THF (5 mL), and oxalyl chloride (1.6 mmol, 0.8 mL of a 2 M solution in CH_2Cl_2) was stirred at room temperature overnight and then refluxed for 2 h. The volatile components were evaporated under a stream of nitrogen at reduced pressure, and the residue was dissolved in anhyd THF (5 mL). To this mixture was added 5-(aminomethyl)-2,2′-bipyridine (**7**) (0.39 g, 1.62 mmol) dropwise, the whole reaction mixture was stirred at room temperature for 6 h, and then refluxed for an additional 2 h. The solvent was evaporated under vacuum, the residue was dissolved in water, and the pH was adjusted to 8. The product precipitated as a light brownish solid that weighed 0.35 g. It was then recrystallized from hot methanol and a cream-colored solid, **8**, was obtained (0.29 g, 66%), mp 164−165 °C. IR (KBr): ν 3438, 3013, 2926, 1731, 1686, 1514, 1461, 1194, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.64 (dd, 1H, $J = 0.7$, 4.0 Hz), 8.54 (d, 1H, $J =$ 2.0 Hz), 8.28 (br t, 2H, $J = 7.9$, 8.1 Hz), 7.76 (ddd, 1H, $J = 0.7$, 7.8, 7.9 Hz), 7.69 (dd, 1H, $J = 2.0$, 8.1 Hz), 7.29 (dd, 1H, $J =$ 4.0, 7.8 Hz), 6.9 (t, 1H, $J = 5.9$ Hz), 4.43 (d, 2H, $J = 5.9$ Hz), 2.96 (t, 2H), 2.60 (t, 2H). Anal. Calcd For $C_{28}H_{28}N_6O_2S_2$: C, 61.74; H, 5.18; N, 15.42; S, 11.77. Found: C, 61.72; H, 5.36; N, 14.99; S, 11.38.

General Method for the Preparation of Six 2,2′-Bipyridylruthenium Complexes with Disulfide-Functionalized 2,2′-Bipyridines. In a typical experiment, *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate (2 equiv) was suspended in ethanol solution to which was added 1 equiv of the appropriate ligand. The resulting mixture was deaerated with N_2 for about 15 min using a syringe needle, and the mixture was heated at reflux for 6−12 h with vigorous magnetic stirring. After the reflux period, the dark red-orange solution was evaporated to one-third of the initial volume, and water (20 mL) was added. The unreacted *cis*-Ru(bipy)$_2$Cl$_2$·2H$_2$O was removed by filtration. An excess of ammonium hexaflurophosphate was added, and the flocculent orange-to-red precipitate that appeared was collected. The product was washed with copious amounts of water followed by ether and was air-dried. The complexes were purified initially

(20) Ziessel, R.; Lehn, M.-J. *Helv. Chim. Acta* **1990**, *73*, 1149.

by column chromatography on neutral alumina using 9:1 CH_2Cl_2:MeOH followed by a few recrystallizations from acetone-ether or acetonitrile-ether mixtures. Crude yields ranged from 80 to 95% and the purified yields were about 70−85%. See Table 8 for data on these red/orange complexes.

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