mechanism of conductivity is quite complex and that further study will be required to understand and optimize the conductivity process.

Although monotonic trends are observed in the activation energies (Table IV), we note that within each set the values are similar, suggesting that the conduction mechanism is the same in all compounds, which in turn suggests, in line with Kilner and Brook's arguments,[25] that the nature of the crystal structure is the dominant factor in determining migration energies.

In summary, high oxide ion conductivity has been observed for $Ln_5Mo_3O_{16.5-y}$ (Ln = Nd, Pr, Sm, and Gd) which have a fluorite-related structure. The highest ionic conductivity was found in $La_5Mo_3O_{16.5-y}$ ranging from 10^{-6} at 275 °C to about 10^{-2} $(\Omega\ cm)^{-1}$ at 670 °C. Yttrium-stabilized zirconias show oxide ion conductivities of about the same order of magnitude in this temperature range. However, the variable oxygen stoichiometry of the $Ln_5Mo_3O_{16+x}$ phases and the sensitivity of the ionic conductivity to oxygen content suggests that these materials might prove to be good oxygen sensors.

Acknowledgment. We thank Prof. John Sheats of Rider College and Prof. Charles Dismukes of Princeton University for the ESR measurements and Dr. S. Tanase, Visiting Research Scientist from GERIO, Japan, for useful discussions. This work was supported by the ONR (M.T. and M.G.) and the National Science Foundation's Research in Undergraduate Institutions (RUI) Program, Solid State Chemistry Grant DMR-88-42788 (W.H.McC.).

Polyquinoline-Supported Ruthenium Catalysts: Selective Oxidation of Alcohols with Coated Electrodes

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Two ruthenium complexes containing the novel 2-(2-pyridyl)-4-phenylquinoxaline ligand (qpy), $[Ru(trpy)(qpy)OH_2]^{2+}$ (11) and $[Ru(bpy)(qpy)pyOH_2]^{2+}$ (18) (trpy = 2,2′,2″-terpyridyl, bpy = 2,2′-bipyridyl, py = pyridine), were prepared as models for complexes supported on polyquinolines (**9**) containing qpy units in the backbone. These polymer complexes, $[Ru(trpy)(polymer\ 9)OH_2]^{+}$ (**13**) and $[Ru(bpy)(polymer\ 9)pyOH_2]^{2+}$ (**20**), were synthesized by a sequence of ligand-replacement reactions on $Ru(trpy)Cl_3$ and $[Ru(bpy)py_4]Cl_2$, respectively. Complexes **11** and **18** were catalytically active for the electrochemical oxidation of secondary alcohols to ketones and allylic or benzylic primary alcohols to aldehydes. Unactivated primary alcohols were not oxidized. Polyquinoline-containing ruthenium complexes **13** and **20** coated on electrodes were more selective and were not catalytically active in the electrochemical oxidation of secondary alcohols (or unactivated primary alcohols), but oxidation of benzylic and allylic alcohols to aldehydes took place. None of the catalysts carried the oxidation further to the corresponding carboxylic acids. Catalytic currents as high as 1 mA were observed.

Ruthenium oxides containing terpyridyl (trpy) and bipyridyl (bpy) ligands, for example, $[Ru(trpy)(bpy)O]^{2+}$ and $[Ru(bpy)_2pyO]^{2+}$, oxidize primary alcohols and allylic and benzylic methyl groups to carboxylic acids; secondary alcohols are oxidized to ketones.[1] These oxides can be generated by the electrochemical oxidation of the corresponding monoaquo complexes $[Ru(trpy)(bpy)OH_2]^{2+}$ (**1**) and $[Ru(bpy)_2pyOH_2]^{2+}$ (**2**). The oxidation reactions of the organic substrates can be effected catalytically with respect to **1** by carrying out the oxidation in a bulk electrolysis cell in which the anode reoxidizes the ruthenium(II) product.

To attach such a ruthenium catalyst to the electrode surface and thereby realize some of the advantages of the modified electrode, a polymer analogue of **2** was developed by coordination of the ruthenium complex to poly(vinylpyridine) (PVP).[2,3] The initial cyclic voltammogram (CV) of this complex, $[Ru(bpy)_2(PVP)OH_2]^{2+}$, on a glassy carbon electrode was similar to the CV of **2**, but after successive scans, the growth of a new wave was apparent at the expense of previous couples, probably as a result of the oxidation of the benzylic carbon on PVP.[1,3]

The utilization of a chemically stable polymer such as a polyquinoline that has no available oxidation sites was therefore of interest in the preparation of ruthenium-modified electrodes. The synthesis of high molecular weight polyquinolines, obtained by the acid-catalyzed condensation of aromatic *o*-amino ketones with aromatic ketomethylene compounds,[4] can be tailored to incorporate a variety of structural features.[5] In the synthesis of such a polymer support, the incorporation of bipyridyl-like ligands in the polymer backbone was of particular interest, since these ligands should mimic the bpy ligand in ruthenium complexes **1** and **2**.

Results and Discussion

Synthesis of a Polyquinoline Support. To ensure that the acid-catalyzed condensation reaction with the 2-acetylpyridine-type ketomethylene monomer would take place and to obtain a model ligand analogous to that

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[1] (a) Thompson, M. S.; Giovani, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1981**, *49*, 4972. (b) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5070.

[2] Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 307.

[3] Thompson, M.S. Dissertation, University of North Carolina, 1981.

[4] Cheug, C. C.; Yan, S. J. *Org. React.* **1982**, *28*, 37.

[5] Stille, J. K. *Macromolecules* **1981**, *14*, 870.

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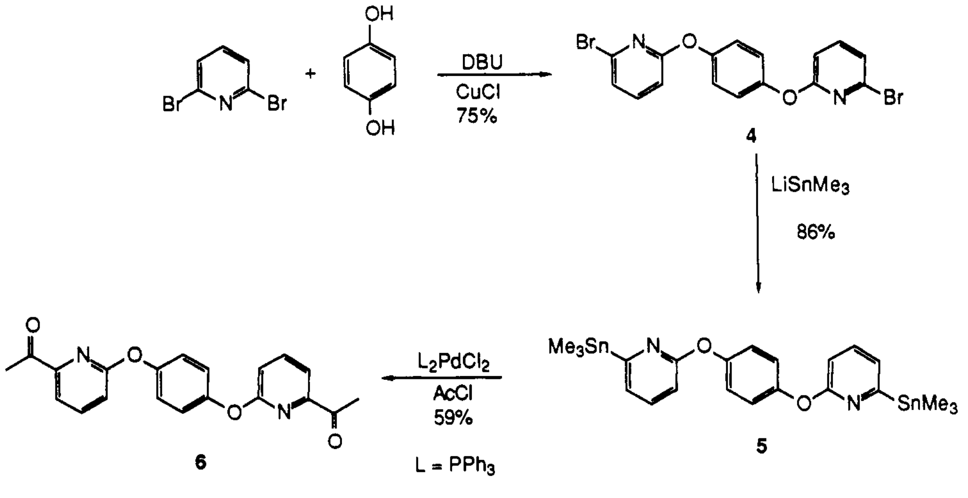
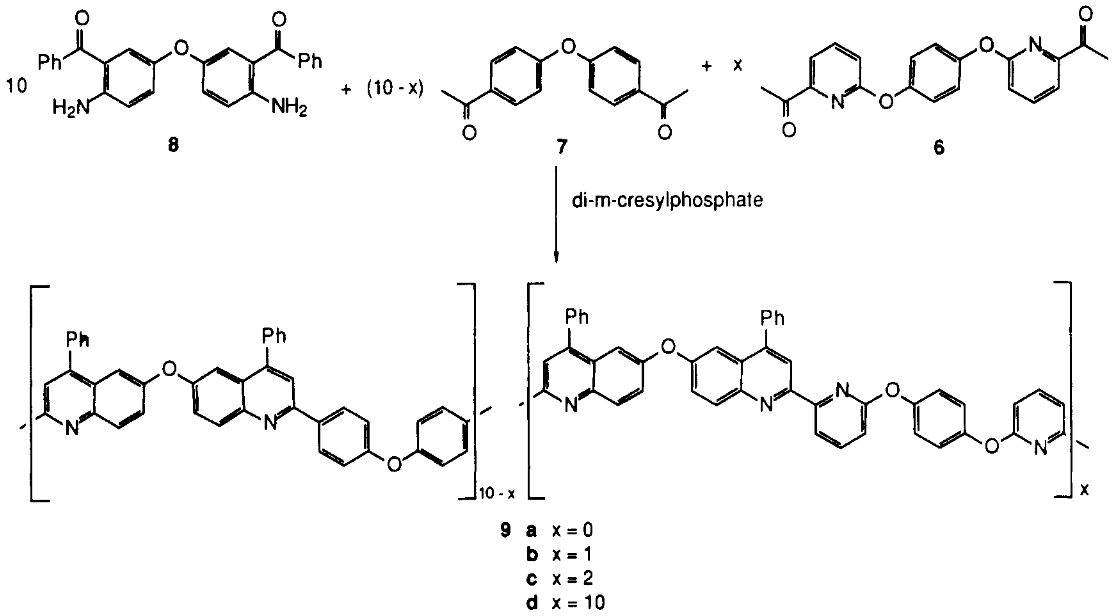
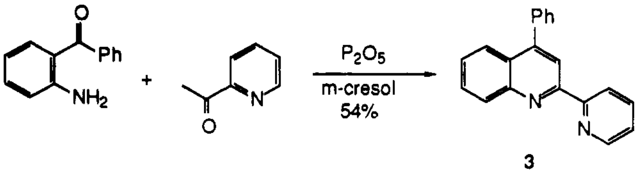
Scheme I



Scheme II



present in the polymer backbone, the condensation of 2-acetylpyridine with *o*-aminobenzophenone was carried out to yield 2-(2′-pyridyl)-4-phenylquinoline (**3**).



3

qpy

For generation of a bipyridyl-like unit in the polymerization yielding a polyquinoline, the synthesis of a bis-ketomethylene monomer containing the 2-acetylpyridine functional group was necessary. The reaction of hydroquinone with a 10-fold excess of 2,6-dibromopyridine under basic conditions (2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU) with a catalytic amount of cuprous chloride[6] gave dibromide **4** (Scheme I). The reaction of **4** with trimethyltin anion gave the ditin compound **5**, which was coupled with acetyl chloride in the presence of a palladium catalyst to yield the bis(6-acetyl-2-pyridyl)-1,4-bisoxyphenylene monomer (**6**).

Table I. Molecular Weights of Polyquinolines 9

9	*x*	[η], dL/g[a]	M_v[b]
a	0	2.35	150 000
b	1	1.92	110 000
c	2	1.05	44 300
d	10	0.167	2 700

[a] Determined by viscosity in $CHCl_3$ at 25 °C. [b] Calculated by the relation $[\eta] = KM_v^a$, where $K = 9 \times 10^{-4}$ and $a = 0.66$ for **9a**.[7]

The pyridine-containing monomer (**6**) was incorporated into the polyquinoline by its substitution for 4,4′-diacetyldiphenyl ether (**7**) in various amounts in a polymerization reaction with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**8**, Scheme II). The ratio of **6** to **7** was varied while keeping the combined equivalents of the diacetyl monomers equal to the bis(amino ketone). As the ratio of **6** to **7** increased, the molecular weight of the polymer (**9b**–**d**) decreased; the reason for this decrease is not apparent (Table I).

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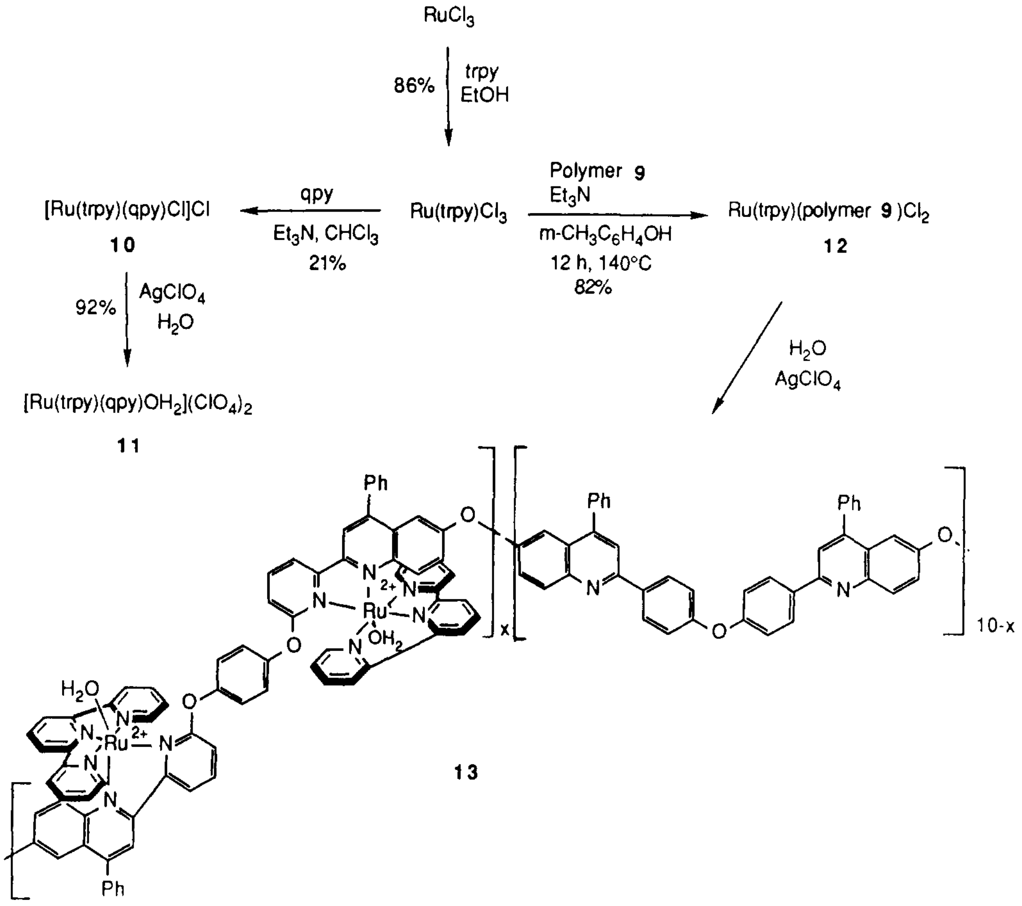
(6) (a) Moroz, A. A.; Shvartsberg, M. S. *Russ. Chem. Rev.* **1974**, *43*, 679. (b) Williams, A. L.; Kinney, R. E.; Bridger, R. F. *J. Org. Chem.* **1967**, *32*, 2501. (c) Kovalev, S. E.; Shershukou, V. M.; Krasovitsky, B. M.; Andreevskaya, O. I.; Valoarsky, L. B. *Isv. Sib. Otd. Akad. Nauk SSR, Ser. Khim. Nauk* **1973**, 104. (d) Litvak, V. V.; Shein, S. M. *J. Org. Chem., USSR* **1973**, *9*, 329.

(7) Norris, S. O.; Stille, J. K. *Macromolecules* **1976**, *9*, 496.

Scheme III



Ruthenium Complexes. Ruthenium complexes containing the quinoline analogue (**3**, qpy) and the polymeric quinoline analogue (**9b–d**) of bipyridyl were synthesized. By following the route utilized for the preparation of **1**,[3,8] the complex $[Ru(trpy)(qpy)OH_2]^{2+}$ (**11**) could be synthesized starting with ruthenium trichloride (Scheme III). The reaction of $RuCl_3$ with terpyridyl gave a brown, insoluble salt that was not purified but was carried on to the ruthenium(II) salt (**10**) by reaction with the qpy ligand (**3**) in the presence of triethylamine. Chloride was replaced by water with use of silver perchlorate to yield the desired complex **11**.

The analogous polymer complex was prepared by the reaction of $Ru(trpy)Cl_3$ with **9**. The reaction temperature needed to prepare polymer complex **12** was higher than that required for **10**. At temperatures below 120 °C, a dark blue, insoluble polymer complex precipitated. Presumably, ruthenium cross-links the polymer by coordination to the quinoline nitrogen sites. This mode of cross-linking is supported by the fact that the reaction of $Ru(trpy)Cl_3$ with polyquinoline **9a** (which does not contain the qpy-type site) formed a similar product. When the temperature is increased, this cross-linked product is dissolved, and the desired chelating qpy-type coordination occurred. Because silver ion coordinates to polyquinolines, causing it to precipitate from solution, the conversion of **12** to the aquo complex could not be effected with silver perchlorate. Thus polymer complex **12** was coated on the electrodes, and the aquo complex was formed in situ by dipping the electrode into a silver perchlorate solution to yield **13**.

The direct, sequential substitution of ligands onto ruthenium by procedures used to prepare $[Ru(bpy)_2pyOH_2]^{2+}$ (**2**) could not be used to prepare the qpy derivative, $[Ru(bpy)(qpy)pyOH_2]^{2+}$ (**18**), or its polyquinoline analogue (**20**), primarily because the qpy analogues would not elute from ion-exchange resins and because of the problems associated with the use of silver ion in the presence of polyquinoline. However, it is known that pyridine can be displaced from $[Ru(bpy)_2py_2]Cl_2$, either thermally or photolytically.[9,10]

The reaction of ruthenium trichloride with 2,2′-bipyridine in 1 N HCl gave the insoluble ruthenium(IV) salt (**14**), which was converted to **15** by its reaction with pyridine (Scheme IV). In practice, **15** was not isolated, but instead the reaction mixture was diluted with water and used as a stock solution. The qpy ligand was introduced by its reaction with **15** followed by precipitation with sodium perchlorate to yield **16**. Higher reaction temperatures were needed to coordinate qpy and bpy than reported[11] for the coordination of bpy by displacement of two pyridine ligands from **15**. The purple product (**16a**, λ_{max} = 545 nm) obtained from this sequence of reactions was accompanied by a second orange complex, $[Ru(bpy)(qpy)_2](ClO_4)_2$ (**17**, λ_{max} = 490 nm). It was not possible to convert **16a** cleanly to the aquo complex by UV irradiation; however, aquo complex **18** was obtained by dissolving **16b** in 75% aqueous ethanol and heating the solution to reflux.

The polymer complex $[Ru(bpy)(polymer\ 9)py_2](PF_6)_2$ (**19**) was prepared from **15** in a manner similar to that used for the preparation of the model complex. Under these

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(8) Wale, D. C.; Lay, P. A.; Taube, H. *Inorg. Synth.* **1986**, *24*, 299.

(9) Clear, J. M.; Kelly, J. M.; Pepper, D. C.; Vos, J. G. *Inorg. Chim. Acta* **1979**, *33*, L139.

(10) Pinnick, P. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.

(11) Krause, R. A. *Inorg. Chim. Acta* **1977**, *22*, 209.

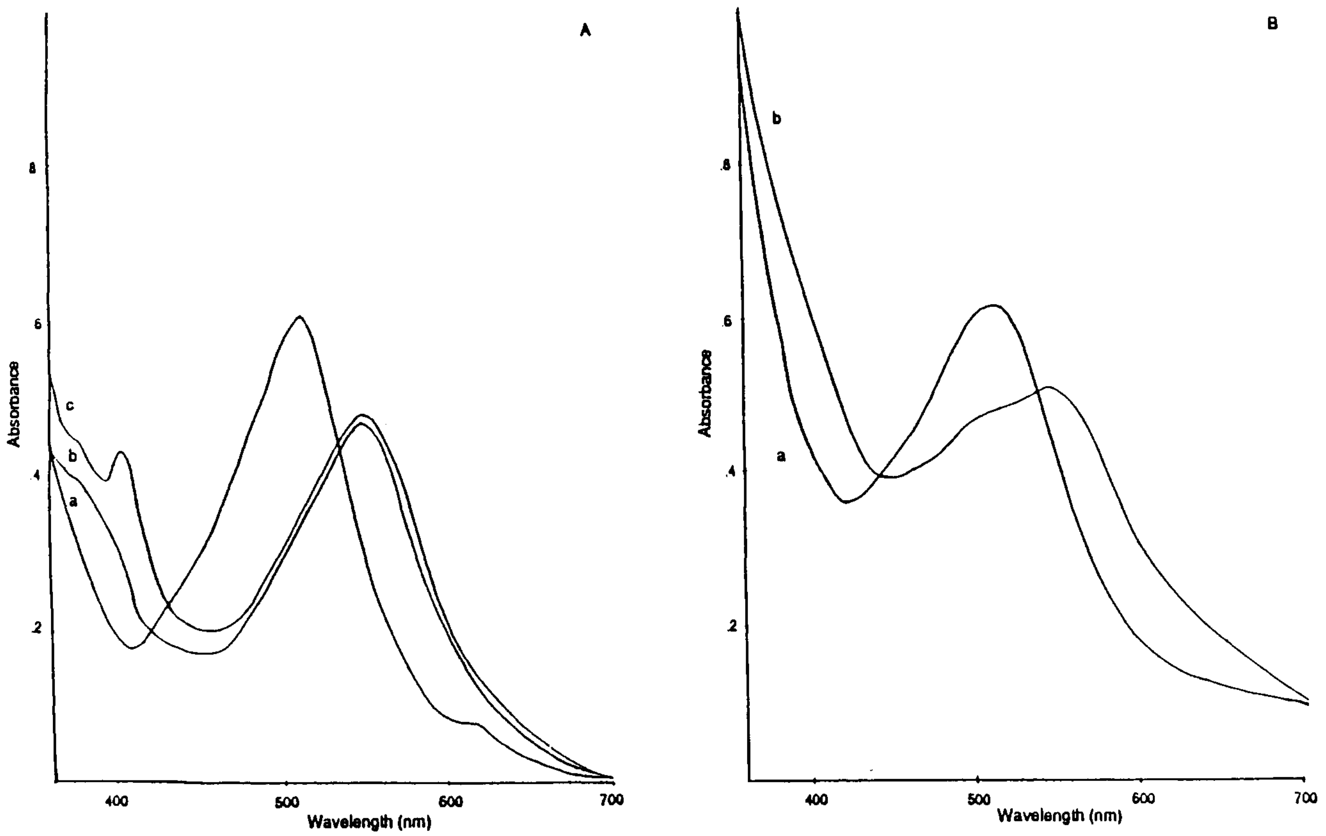

Figure 1. Visible spectra, 50% acetone/water with pH adjusted by using $HClO_4$ or NaOH. A. 1.2×10^{-4} M $[Ru(trpy)(qpy)OH_2](ClO_4)_2$ (11): a, pH 1–7; b, pH 9; c, pH 13. B. 1.7×10^{-4} M $[Ru(bpy)(qpy)pyOH_2](ClO_4)_2$ (18): a, pH 6; b, pH 8.

reaction conditions, the molecular weight of the polymer was reduced. Polymer complex **19** was isolated by precipitation in a 10% triethylamine/ether mixture and was purified by exhaustive washing with water and ethanol. Solutions of **19** in 50% chloroform/ethanol were used to coat the electrode. The polymer was then converted to the aquo complex (**20**) by dipping the coated electrode into boiling water.

Properties of Ruthenium Complexes. The visible spectra of $[Ru(trpy)(qpy)OH_2](ClO_4)_2$ (**11**) and $[Ru(bpy)(qpy)pyOH_2](ClO_4)_2$ (**18a**) show a broad, intense band at 510 nm, red shifted approximately 30 nm from the absorptions of **1** and **2** as a result of the fact that the qpy ligand is more easily reduced, taking less energy for promotion of an electron to the π^* orbital of qpy from the metal (Figure 1). At pH > 8–9, λ_{max} for both **11** and **18a** shift to approximately 530 nm as a result of the loss of a proton from coordinated water.[3] The spectra of the corresponding polymer complexes **13** and **20**, as expected,[1,12,13] were similar, with absorption maxima at 545 nm but with broader bands.[14]

In the infrared, the five-band series centered at 769 cm^{-1} in **11**, **13**, **18**, and **20** was identified as the ring-adjacent hydrogen deformation resulting from coordinated qpy-type ligands. Bipyridine has a deformation band at 759 cm^{-1}.[11] Bands at 447 and 403–405 cm^{-1} were assigned qpy out-of-plane deformations by analogy to those bands for bpy[11,15] (Table II). Weak absorptions at 334–344 cm^{-1} were assigned to Ru–N stretching for qpy.[16] The assignment of the absorption bands for Ru–N stretching for pyridine is controversial.[15,17]

Table II. Far-IR Stretches of Ruthenium Pyridine Complexes (cm^{-1})

	bpy[a]	qpy[a]	Ru–N(py)	Ru–N(qpy)
$Ru(bpy)py_4(ClO_4)_2$	423		310, 301 277, 280	344 337 (sh)
$Ru(bpy)_2py_2(ClO_4)_2$	423		301, 310 (sh) 277, 279, 288	344 (br)
$Ru(bpy)(qpy)py_2(ClO_4)_2$	424	403, 447	276, 307 (br)	334 (br)
$Ru(bpy)(polymer)py_2Cl_2$	423	405 (br)	300, 310 279, 277	340 (br)

[a] bpy and qpy out-of-plane deformations.

Table III. Potentials of Electrochemical Oxidation Catalysts

catalyst	$E_{1/2}$ potentials, V vs SCE	
$Ru(trpy)(bpy)OH_2^{2+}$ (1)		
50% acetone/water (Ph 6.8)	0.74	0.52
water (pH 6.8)[a]	0.62	0.49
water (pH 1)[a]	0.93	0.81
$Ru(bpy)_2pyOH_2^{2+}$ (2)		
70% acetone/water (pH 6.8)	0.71	
water (pH 7)	0.53	0.42
water (pH 1)	0.99	0.76
$Ru(trpy)(qpy)OH_2^{2+}$ (11)		
70% acetone/water (pH 6.8)	0.77	
70% acetone/water (pH 1)	0.81[b]	
$Ru(bpy)(qpy)pyOH_2^{2+}$ (18)		
50% acetone/water (pH 6.8)	0.71	
70% acetone/water (pH 1)	0.75	

[a] References 3 and 8. [b] Average of the two waves.

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(12) Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3978.

(13) Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 27.

(14) (a) Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 4895. (b) Tait, D.; Vess, T. M.; DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. *J. Chem. Soc., Dalton Trans.* **1987**, 2467. (c) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(15) Clark, R. J. H.; Williams, C. S. *Inorg. Chem.* **1965**, *4*, 350.

(16) Poizat, O.; Sourisseau, P. *J. Phys. Chem.* **1977**, *22*, 209.

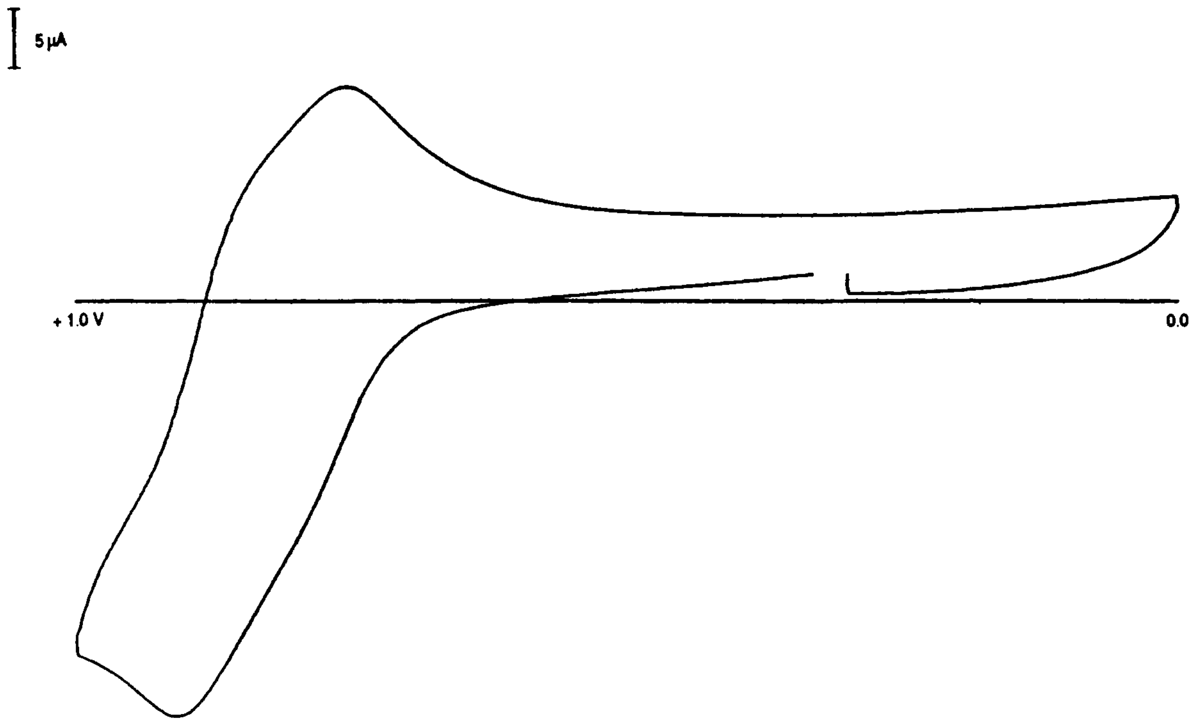

Figure 2. Cyclic voltammogram of $[Ru(trpy)(qpy)OH_2]^{2+}$ (11). Taken in 70% acetone/0.1 M $HClO_4$, sweep rate = 50 mV/s, concentration approximately 5 × 10^{-4} M.

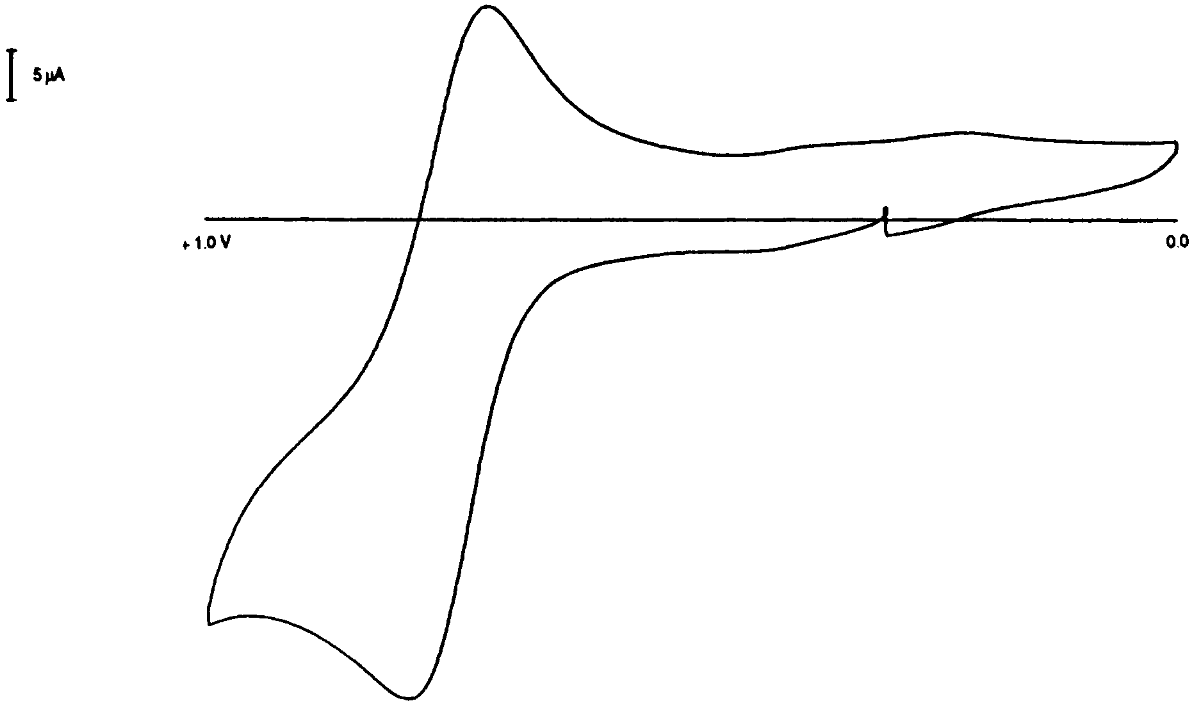

Figure 3. Cyclic voltammogram of $[Ru(bpy)(qpy)pyOH_2]^{2+}$ (18). Taken in 70% acetone/0.1 M $HClO_4$, sweep rate = 50 mV/s, concentration approximately 5 × 10^{-4} M.

To establish the potentials necessary to oxidize the ruthenium(II) species containing qpy-like ligands to the active ruthenium(IV) state, the electrochemistry of the model and polymer complexes was studied. The potentials obtained by cyclic voltammetry for the model complexes exhibited a solvent dependence (Table III) as a result of the occurrence of chemical steps (proton transfer) as well as electron transfers.[18] Because complexes 11 and 18 were not soluble in water, acetone–water mixtures were used. This mixed solvent causes the potentials of 1 and 2 to increase 120–180 mV above those observed in water, as a result of a lower equilibrium concentration of the more easily oxidized hydroxy complex.[1b,3,8] The $E_{1/2}$ of complexes 11 and 18 containing the qpy ligands are not significantly different from those for 1 and 2, but the electrochemistry of 11 and 18 is considerably more complex. At pH 7 in 70% acetone/water, the CVs of 11 and 18 have only one wave. In an effort to force the expected +4/+3 and +3/+2 couples to resolve, the electrochemistry was examined in 70% acetone/0.1 M $HClO_4$ (Figures 2 and 3). The potentials increased slightly at lower pH, but two

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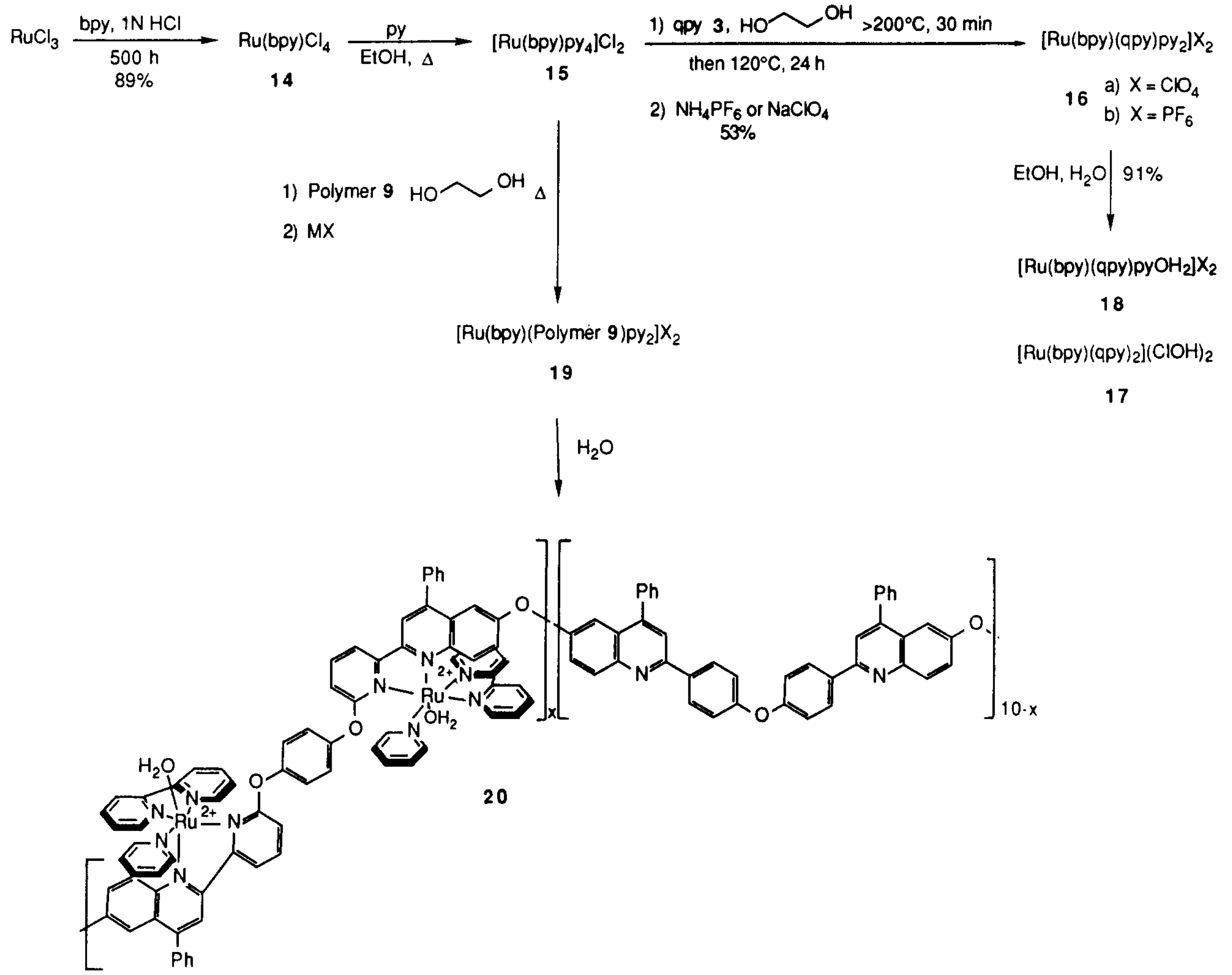
(17) Wajcla, S.; Rachlewicz, K. *Inorg. Chim. Acta* **1978**, *31*, 35.

(18) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106.

Scheme IV



waves did not appear at pH 1, even for **2**. A single, quasi-reversible wave with ΔE_{peak} independent of the scan rate was observed; the 86 mV observed is greater than the 59 mV expected for a one-electron reversible oxidation or the 28 mV expected for a two-electron process. For **1**, the CV in 70% acetone/0.1 M $HClO_4$ showed two unresolved waves, with the wave shape dependent on the scan rate.

Rotating disk voltammetry in 50% acetone/water with a ruthenium concentration of 5×10^{-4} M was conducted to determine the number of electrons involved in the oxidation. $Ru(bpy)_3Cl_2$ was used as a standard since it is known to undergo a one-electron oxidation and is approximately the same size as complexes **11** and **18**. Plots of the square root of rotation rate vs limiting current were linear for $Ru(bpy)_3Cl_2$ and **18** but not for **11** (Figure 4). The observed currents for **18** were 1.25 times greater than those for $Ru(bpy)_3Cl_2$, lower than expected for a two-electron oxidation but too high for a one-electron oxidation. The nonlinear behavior for **11** indicates a lack of hydrodynamic control of the current, probably due to slow kinetics of the associated chemical reactions.[19]

Reproducible CVs of thin films of polymer-supported catalysts on platinum, glassy carbon, and pyrolytic graphite electrodes could not be obtained; little activity was shown by **12**, **19**, and the corresponding aquo complexes in a number of solvents and solvent mixtures.

Catalysis. The oxidation of aqueous solutions of benzyl alcohol by model complexes **11** and **18** gave benzaldehyde. Catalytic currents and the production of benzaldehyde were observed only when the ruthenium complexes were present. No benzoic acid was detected.

Platinum gauze electrodes were coated with solutions of **12** or **19**, followed, in the case of **12**, by dipping the electrode into 1% silver perchlorate solution or, in the case of **19**, into boiling water, to convert the polymer complexes to their aquo complexes, **13** and **20**, respectively. In spite of the electrochemical inactivity shown in the CV studies, both **13**- and **20**-coated electrodes catalyzed the oxidation of benzyl alcohol to benzaldehyde! No catalytic activity was observed for electrodes coated with **12** or **19**.

In general, model complexes **11** and **18** oxidized unhindered secondary alcohols to ketones, but simple primary alcohols and hindered secondary alcohols such as 1-phenylethanol were not oxidized. Activated primary alcohols such as benzyl alcohol, cinnamyl alcohol, and 3-methyl-2-butenol were readily oxidized to the corresponding aldehydes at rates as much as 4 times greater than the rate of oxidation of 2-propanol (Table IV). No further oxidation to carboxylic acids was observed. Alkyl side chains on aromatics are not oxidized. Thus toluene, toluic acid, and 4-isopropylbenzoic acid were recovered unchanged. These catalysts apparently are sensitive not only to steric effects (secondary alcohols oxidize slowly, but more hindered secondary alcohols not at all) but also to the oxidation potential of the alcohol, since only acti-

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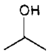
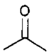
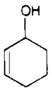
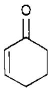
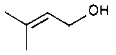
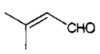
[19] (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; John Wiley & Sons: New York, 1980; Chapter 11. (b) Pickup, P. G.; Kunter, W.; Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1991.

Table IV. Catalytic Oxidation of Alcohols

		catalytic currents, mA (yields)			
substrate	product	Ru(trpy)-(qpy)OH_2^{2+} (**11**)	Ru(trpy)-(polymer **9**)-OH_2^{2+} (**13**)	Ru(bpy)(qpy)-pyOH_2^{2+} (**18**)	Ru(bpy)-(polymer **9**) pyOH_2^{2+} (**20**)
		0.677 (39)^b	NR	7.50^e	NR
$PhCH_2OH$	PhCHO	1.85 (69)^b	0.579^c 1.10^d	0.536	0.200
$PhCH{=}CHCH_2OH$	$PhCH{=}CHCHO$	3.01 (65)	0.535 (65)	4.60 (30)	0.755 (30)
		0.654 (im)^b	NR	0.351 (im)	NR
		0.633 (im)	0.225 (im)	0.541	0.121

^{a} Electrolyses performed in 0.1 M phosphate buffer solutions (pH 7) and 0.1 M substrate concentration. Yields based on mol of product found by HPLC analysis/mol of charge passed. NR = no reaction, im = immeasurable because peak occurs as a shoulder or fused to starting material peak. ^{b} GC analysis. ^{c} pH 7. ^{d} pH 1; initial catalytic current over 1 h was 2.1 mA. ^{e} 1 M 2-propanol solution and 100 μL of acetone were added.

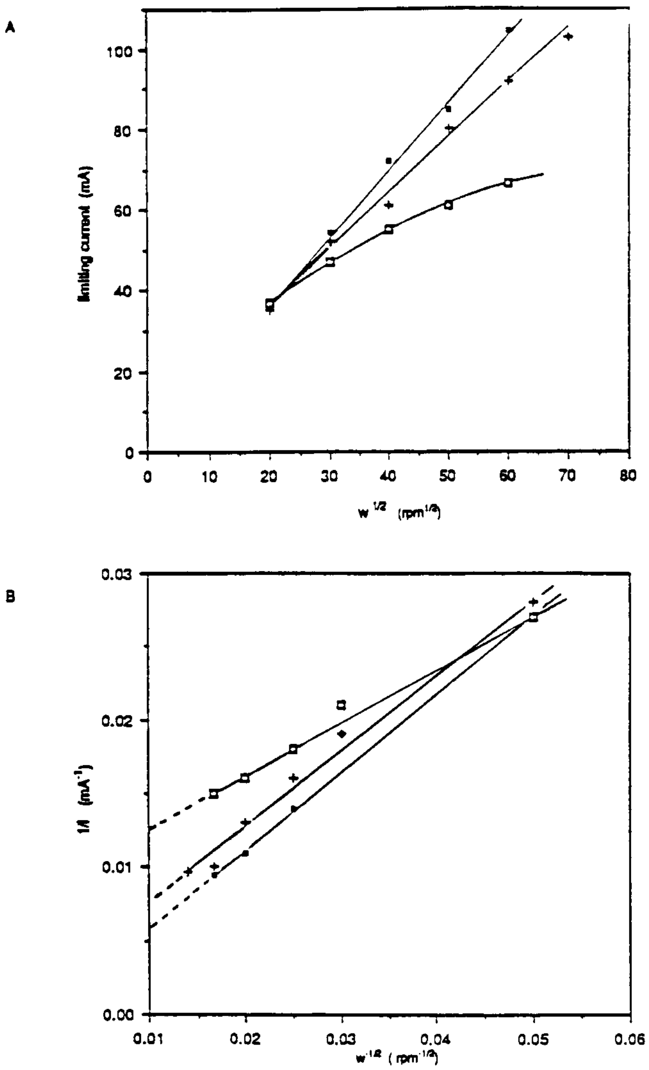


Figure 4. Plots of rotation rate versus limiting current. Performed in 50% acetone/0.1 M $HClO_4$: A, square root of rotation rate versus limiting current; B, reciprocal square root of rotation rate versus reciprocal limiting current. (+) $Ru(bpy)_3Cl_2$, (■) $[Ru(bpy)(qpy)pyOH_2](ClO_4)_2$, (□) $[Ru(trpy)(qpy)OH_2](ClO_4)_2$.

vated primary alcohols (benzylic and allylic) undergo oxidation.

The catalytic activity of the polymer-modified electrodes was similar to that of the model complexes. Primary benzylic and allylic alcohols were oxidized to aldehydes and substrates that were not oxidized by model complexes **11** and **18** were not oxidized by the polymer-modified electrodes. Unlike the model complexes, the polymer-modified electrodes did not oxidize secondary alcohols, indicating a greater sensitivity to steric effects. The rates of oxidation of substrates were 6.5 times greater for the polymer-modified electrodes than for the homogeneous catalysts (~1.0 × 10^{-3} M) for equal concentrations of substrate at pH 1; benzyl alcohol oxidation by **13** was nearly twice as fast as oxidation at pH 7. At pH 1, polyquinolines are protonated at the quinoline nitrogen, and the resulting intrachain repulsion expands the film, allowing more facile proton, substrate, and counterion diffusion. A similar effect of pH has been noted in the oxidation of 2-propanol with the poly(vinylpyridine) complex $[Ru(bpy)(PVP)OH_2]^{2+}$.[1] Use of a large platinum basket as the electrode gave a catalytic current of 5–7 mA for the oxidation of benzyl alcohol, while a small platinum flag gave a current of 0.5 mA. The observed currents have a linear dependence (0.05 mA/cm^2) on the electrode area for the same solution of benzyl alcohol substrate. One shortcoming of the polymer-coated electrode was that the polymer tended to come off the electrode.

There are several striking differences between the model complexes containing bpy ligands, $[Ru(trpy)(bpy)OH_2]^{2+}$ (**1**) and $[Ru(bpy)_2pyOH_2]^{2+}$ (**2**), and the qpy-containing complexes, $[Ru(trpy)(qpy)OH_2]^{2+}$ (**11**) and $[Ru(bpy)(qpy)pyOH_2]^{2+}$ (**18**). First, the currents for **1** and **2** are typically 10 times larger than the 5–0.5 mA currents observed for **11** and **18** under roughly similar conditions. Second, complexes **1** and **2** are more reactive and oxidize many types of substrates, usually to carboxylic acids in the case of primary alcohols. Complexes **11** and **18** are more selective and oxidize primary alcohols to aldehydes. Finally, complexes **1** and **2** are more efficient, with 80–100% of the passed current forming product, while the efficiencies of complexes **11** and **18** are only 30–60%.

Polyquinoline-supported catalysts **13** and **20** show catalytic currents greater than those of the poly(vinylpyridine) complexes for similar conditions.[2] In addition, polyquinoline-supported complexes are chemically inert, showing continued catalytic activity after 12 h of electrolysis.

Experimental Section

All solvents were distilled from calcium hydride just prior to use except for the following materials: chloroform was distilled from phosphorus pentoxide, xylene was distilled from sodium/benzophenone, tetrahydrofuran (THF) was distilled from molten potassium, and tetrachloroethane and *m*-cresol were fractionally distilled. Absolute ethanol (Midwest Solvents) was USP grade and was used as obtained unless specified otherwise. Electrochemical solvents (Burdick and Jackson) were used as obtained except water, which was triply distilled from potassium permanganate. All other reagents were used as obtained from commercial suppliers unless otherwise noted.

Alumina (Aldrich) used for chromatography was neutral Brockmann I, 150 mesh, CAMAG 507C-I. Thin-layer chromatography was performed with plastic-backed Baker-flex alumina 1B-F plates, and the solvent system was 10% isopropyl alcohol/dichloromethane unless otherwise noted. Silica chromatography utilized Absorbenzien Woelm (Universal Scientific), 32-63 silica gel. High-performance liquid chromatography (HPLC) was performed on a Waters HPLC system consisting of a Model 6000A and M-45 solvent delivery system, U6K injector, Model 660 solvent programmer, and Model 440 absorbance detector interfaced with a Waters Model 730 data module. Analyses were done by using a C-18 Bondapak reverse-phase column with a 55% acetonitrile/water mixture as solvent. Solutions of authentic samples of known concentrations were used as external standards. Gas chromatography (GC) was performed on a Varian 3700 gas chromatograph with an SE-30 packed glass capillary column (50 m × 0.25 mm) or a Varian 2800 Aerograph with 50/80 mesh Carbowax column (2 m × 0.125 in.).

NMR spectra were recorded on an IBM WP-270-SY (270 MHz ^{1}H, 68 MHz ^{13}C) in deuterochloroform with tetramethylsilane (0.00 ppm ^{1}H) or chloroform (77.00 ppm ^{13}C) as internal standards, unless otherwise noted. Both near and far IR were recorded on a Nicolet 60-SX interferometer or a Beckman 4240 with potassium bromide (1% concentration of complex) for near IR and cesium iodide (50% concentration) for far IR as diluents unless otherwise noted. UV–vis spectra were recorded on a Perkin-Elmer 552A spectrophotometer or Varian Techtron 536. Thermal analyses were recorded on a Du Pont 990 thermal analyzer coupled with a Du Pont differential scanning calorimeter with the sample under a nitrogen atmosphere. Dilute solution viscosities were measured in chloroform at 25 °C with a Cannon size 50 Ubbelohde viscometer at concentrations of 0.50, 0.40, 0.31, and 0.25 g/dL. The electrochemical apparatus has been previously described.[20] Irradiations were performed with a 275 W GE Suntanner lamp or 250 W Hanovia lamp.

Melting points were obtained on a Mel-Temp melting apparatus and are uncorrected. Ruthenium analyses were performed with a Tracor-5000 energy dispersive X-ray fluorescence spectrometer with a 0.63-mm Cu filter.[21] Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

The following reagents were prepared or purified by literature procedures: 4,4′-diamino-3,3′-dibenzoyldiphenyl ether,[7] 4,4′-diacetyldiphenyl ether,[22] di-*m*-cresyl phosphate,[23] trimethylstannyl chloride,[24] bis(triphenylphosphine)palladium dichloride,[25] tris(2,2′-bipyridyl)ruthenium bis(hexafluoro)phosphate,[26] tetrabutylammonium hexafluorophosphate,[27] [Ru(trpy)(bpy)OH$_2$](ClO$_4$)$_2$,[3] and [Ru(bpy)$_2$pyOH$_2$](ClO$_4$)$_2$.[28]

4-Phenyl-2-(2-pyridyl)quinoline (3). Under a static argon atmosphere, a solution of 10.0 g (50.7 mmol) of *o*-aminobenzophenone, 5.68 mL (6.13 g, 50.7 mmol) of 2-acetylpyridine, 21.5 g (199 mmol) of di-*m*-cresyl phosphate, and 10 mL of *m*-cresol was heated to 135–137 °C for 24 h. The reaction was allowed to cool and poured into 500 mL of 10% NaOH, and the resulting precipitate was filtered. The solid was washed with 250 mL of water. The material was dissolved in dichloromethane and dried over MgSO$_4$, and the solvent was removed under reduced pressure to yield 13.3 g of a brown powder. The powder was recrystallized twice from toluene with charcoal to yield 7.8 g (54%) of pale yellow needles: mp 154–155 °C; IR (KBr) 1585, 793, 773, 758, 730, 706, 674 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.71 (t, J = 3.4 Hz, 2 H), 8.52 (d, J = 3.1 Hz, 1 H), 8.26 (d, J = 2.4 Hz, 1 H), 8.22 (s, 1 H), 7.96–7.86 (m, 2 H), 7.73 (br s, 1 H), 7.57–7.49 (m, 6 H), 7.35 (q, J = 4 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 156.49, 155.64, 149.10, 148.56, 138.52, 136.67, 130.28, 129.64, 129.22, 128.37, 128.22, 126.84, 126.67, 125.73, 123.83, 121.81, 119.24. Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.06; H, 5.00; N, 9.92. Found: C, 85.04; H, 5.03; N, 9.90.

Bis(6-bromo-2-pyridyl)-1,4-bisoxyphenylene (4). A dry pressure bottle was charged with 2.0 g (18 mmol) of hydroquinone, 86.0 g (260 mmol) of 2,6-dibromopyridine, 5.4 g (36 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene, and 0.02 g (0.2 mmol) of CuCl and then purged with argon for 30 min. The bottle was sealed and heated to 150 °C for 24 h. For the last hour of heating, the neck of the bottle was raised above the oil bath to allow the excess dibromopyridine to distill from the reaction. The bottle was allowed to cool, and the seal was broken. The excess dibromopyridine was scraped from the sides of the bottle and removed. The residue was dissolved in dichloromethane and absorbed onto 50 g of silica gel. The silica gel was placed on top of a 200-g, 30 cm × 5 cm column of silica gel and eluted with 25% dichloromethane/hexane until all the starting material had eluted. The product was then eluted with 10% ethyl acetate/dichloromethane. The solvent was removed under reduced pressure to yield 5.7 g (75%) of a white powder: mp 173–174.5 °C; IR (paraffin oil) 1580 (m), 1455 (s), 1270 (s), 1180 (s), 1150 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.815 (d, 1 H), 7.17–7.26 (m, 3 H), 7.53 (t, 1 H); ^{13}C NMR (CDCl$_3$) δ 163.05, 150.71, 141.08, 139.35, 122.58, 121.99, 109.69. Anal. Calcd for $C_{16}H_{10}Br_2N_2O_2$: C, 45.53; H, 2.39; N, 6.63. Found: C, 45.50; H, 2.43; N, 6.57.

Bis(6-(trimethylstannyl)-2-pyridyl)-1,4-bisoxyphenylene (5). To 3.76 g (542 mmol) of clean Li/1% Na wire (which had been flattened into leaves) was added 40 mL of dry THF. The mixture was cooled in an ice bath, and then a solution of 10.8 g (54.2 mmol) of trimethyltin chloride in 40 mL of THF was added dropwise over 1 h.[29] The reaction was dark green at this point. This mixture was then cannulated into 8.00 g (19.0 mmol) of bis(6-bromo-2-pyridyl)-1,4-bisoxyphenylene (4) in 30 mL of THF that had been cooled to −78 °C. The reaction was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The reaction was quenched with 50 mL of saturated NH$_4$Cl. The mixture was poured into water and extracted with 3 × 150 mL of dichloromethane. The organic layers were collected, combined, and washed with 1 × 150 mL of 10% NaOH, 1 × 250 mL of water, and 1 × 250 mL of brine. The solution was dried over MgSO$_4$, and the solvent was removed under reduced pressure to yield 11.421 g of a cloudy oil which crystallized upon standing. The solid was distilled (bulb-to-bulb) at 200 °C/0.25 mmHg to give 9.6 g (86%) of a white solid: mp 83–85 °C; IR (mull): 1585, 1561, 1250, 1180 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 7.59 (t, J = 6.9 Hz, 1 H), 7.24 (d, J = 6.1 Hz, 1 H), 7.21 (s, 4 H), 7.15 (d, J = 7.0 Hz, 1 H), 0.32 (quintet, J = 28.2 Hz, 9 H); ^{13}C NMR (CD$_2$Cl$_2$) δ 172.19, 163.86, 151.37, 137.46, 127.49, 122.37, 122.24, 110.16, −9.41. An analytical sample was carefully distilled at 100 °C to yield white needles: mp 90–91 °C. Anal. Calcd for $C_{22}H_{28}N_2O_2Sn_2$: C, 44.80; H, 4.78; N, 4.75. Found: C, 44.89; H, 4.80; N, 4.73.

An alternate procedure was carried out as follows. Under an argon atmosphere, a solution of 3.10 mL (14.3 mmol) of hexamethylditin and 140 mL of dry THF was cooled to −23 °C, and 10.6 mL (14.5 mmol) of 1.36 M methyllithium was added dropwise over 20 min.[30] The reaction was cooled to −78 °C, and a solution of 3.0 g (7.1 mmol) of bis(6-bromo-2-pyridyl)-1,4-bisoxyphenylene (4) in 30 mL of THF was added dropwise over 45 min. The reaction was stirred for 1 h at −78 °C, and allowed to warm to room temperature. The reaction was quenched with saturated NH$_4$Cl solution, and the mixture was poured into water and

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extracted with dichloromethane. The organic layers were collected, combined, washed with water and brine, and dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield a cloudy oil. The oil was distilled (bulb-to-bulb) at 140 °C/0.05 mmHg to give a clear oil which solidified upon standing. The total yield was 2.7 g (65%): mp 61–62 °C.

Bis(6-acetyl-2-pyridyl)-1,4-bisoxyphenylene (6). To 1.0 g (1.7 mmol) of bis(6-(trimethylstannyl)-2-pyridyl)-1,4-bisoxyphenylene (**5**), 0.290 mL (4.08 mmol) of acetyl chloride, 0.059 g (0.085 mmol) of bis(triphenylphosphine)palladium dichloride, 0.022 g (0.085 mmol) of triphenylphosphine, and 17 mL of dry xylene were combined under an argon atmosphere. The mixture was subjected to three freeze–thaw cycles, and the tube was sealed under vacuum. The tube was completely immersed in a 120 °C oil bath for 24 h. The tube was cooled, and the seal was broken. The reaction mixture was poured into 250 mL of water. The mixture was extracted with 2 × 100 mL of dichloromethane. The organic layers were collected and combined, and washed with 1 × 200 mL of water and 1 × 200 mL of brine. The solution was dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield a yellow solid. The material was recrystallized from absolute ethanol with charcoal three times to yield 0.34 g (57%) of a pale tan solid: mp 153.5–154 °C; IR (paraffin oil) 1691 (s), 1587 (s), 1240 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (t, J = 8.6 Hz, 1 H), 7.76 (d, J = 7.2 Hz, 1 H), 7.25 (s, 2 H), 7.12 (d, J = 7.9 Hz, 1 H), 2.49 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.11, 162.89, 151.67, 150.58, 140.17, 122.30, 116.35, 115.24, 25.38. Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.81; H, 4.67; N, 7.99.

Poly[2,2′-(4,4′-diphenyl ether)-2,2′-(6,6′-(1,4-bisoxyphenylene)pyridine)-6,6′-bis(4-phenylquinolinyl) ether] (9c). This procedure illustrates a polymerization reaction involving the formation of a copolymer containing bis(6-acetyl-2-pyridyl)-1,4-bisoxyphenylene (**6**). A solution of 1.0212 g (2.5000 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 0.5086 g (2.000 mmol) of 4,4′-diacetyldiphenyl ether, 0.1742 g (0.5000 mmol) of bis(6-acetyl-2-pyridyl)-1,4-bisoxyphenylene, 16.5 g (59.5 mmol) of di-*m*-cresyl phosphate in 5.5 mL of *m*-cresol was heated to 135–137 °C for 24 h under a static argon atmosphere. The reaction was allowed to cool slightly and then poured into a vigorously stirring solution of 300 mL of 95% ethanol and 30 mL of triethylamine. The polymer was chopped in a blender and filtered. The polymer was then continuously extracted with 95% ethanol and a small amount of triethylamine for 24 h and dried under reduced pressure at 100 °C for 24 h to yield 1.42 g (93%) of polymer: $[\eta]$ ($CHCl_3$, 25 °C) = 1.05 dL/g; M_V = 44 300;[7] T_g (DSC) = 207 °C; IR (film) 1595, 1235, 1210, 765, 735 (w) cm^{-1}. Anal. Calcd for $C_{214}H_{132}N_{12}O_{11}$: C, 84.34; H, 4.37; N, 5.52. Found: C, 84.18; H, 4.42; N, 5.47.

(2,2′,2″-Terpyridyl)ruthenium(III) Trichloride. Under a static argon atmosphere were combined 0.56 g (2.1 mmol) of ruthenium trichloride trihydrate, 0.50 g (2.1 mmol) of 2,2′,2″-terpyridine, and 125 mL of absolute ethanol, and the reaction was heated to reflux for 24 h. The reaction was cooled in the freezer overnight. The mixture was filtered, and the resulting solid was washed with ethanol until the washings were colorless. The solid was then washed with ether and dried in air to yield 0.75 g (86%) of a black solid.

(4-Phenyl-2-(2-pyridyl)quinoline)(2,2′,2″-terpyridyl)ruthenium(II) Dichloride (10). Under a static Ar atmosphere, 0.088 g (0.31 mmol) of 4-phenyl-2-(2-pyridyl)quinoline, 0.10 g (0.23 mmol) of 2,2′,2″-terpyridylruthenium trichloride, 1 mL (9 mmol) of triethylamine, and 30 mL of chloroform were combined and heated to reflux for 24 h. The reaction was poured into 400 mL of chloroform, and the mixture was washed with 1 × 250 mL of water and 1 × 150 mL of 10% HCl. The aqueous phases were collected, combined, and back-extracted with 1 × 100 mL of chloroform. The organic layers were combined, washed with 2 × 250 mL of water and 1 × 250 mL of brine, and dried over K_2CO_3, and the solvent was removed to yield 0.17 g of a purple solid. The material was recrystallized by slow precipitation from a chloroform solution by the addition of pentane. The mother liquor was decanted, and the solid was washed with ether and air dried to give 50 mg (21%) of purple crystals that were pure by TLC: UV–vis (CH_2Cl_2) 535 (ϵ = 8390 cm^{-1} M^{-1}), 380 (5777), 324 (35 070), 280 nm (27 235). An analytical sample was prepared by precipitating the complex from ethanol as the monohexafluorophosphate salt. Anal. Calcd for $C_{35}H_{29}ClF_6N_5O_2PRu$: C, 50.46; H, 3.51; N, 8.40. Found: C, 50.61; H, 3.31; N, 8.61.

(4-Phenyl-2-(2-pyridyl)quinoline)(2,2′,2″-terpyridyl)aquoruthenium(II) Diperchlorate (11). A solution of 20 mg (0.030 mmol) of $Ru(trpy)(qpy)Cl_2$ and 15 mg (0.06 mmol) of $AgClO_4{\cdot}H_2O$ in 25 mL of degassed 75% acetone/water was heated to reflux for 1.5 h under an argon atmosphere. The reaction was allowed to cool, and then it was filtered. The filtrate was collected, and the solvent was evaporated under reduced pressure until precipitation just started. The mixture was then placed in the refrigerator and left overnight. The resulting solid was filtered and washed with 2 mL of ice-cold water and then ether. The solid was dried in air to yield 23 mg (92%) of a dark solid: UV–vis (CH_2Cl_2) 510 nm (ϵ = 8305 M^{-1} cm^{-1}); near-IR (KBr) 3500, 3100, 1600, 1450, 1090, 766, 730 cm^{-1}; far-IR (CsI) 445, 425, 408, 377 (sh), 373 cm^{-1}. Anal. Calcd for $C_{35}H_{27}Cl_2N_5O_9Ru$: C, 50.43; H, 3.29; N, 8.40. Found: C, 51.46; H, 3.87; N, 8.16.

(2,2′,2″-Terpyridyl)(poly[2,2′-(4,4′-diphenyl ether)-2,2′-(6,6′-(1,4-bisoxyphenylene)pyridine)-6,6′-bis(4-phenylquinoline) ether])ruthenium(II) Dichloride (12). Under a static argon atmosphere were combined 0.12 g (0.039 mmol) of **9c**, 0.035 g (0.079 mmol) of (2,2′,2″-terpyridyl)ruthenium trichloride, 0.50 mL (3.5 mmol) of triethylamine, and 10 mL of *m*-cresol, and the mixture was heated to 140 °C for 24 h. The reaction was allowed to cool and then was poured into a vigorously stirred solution of 150 mL of ether and 10 mL of triethylamine. The resulting precipitate was filtered, washed with 95% ethanol and ether, and dried under reduced pressure to yield 0.13 g (83%) of a deep purple powder: UV–vis ($CHCl_3$) 545 nm. Anal. Calcd for $C_{244}H_{154}Cl_4N_{16}O_{11}Ru_2$: C, 76.52; H, 4.05; N, 5.85. Found: C, 79.83; H, 4.63; N, 5.81. X-ray analysis: calcd for Ru, 5.28%; found, 5.41%.

(2,2′-Bipyridyl)ruthenium(IV) Tetrachloride (14). This material was prepared by a literature procedure.[11] To 1.0 g (3.8 mmol) of ruthenium trichloride trihydrate were added 0.22 g (3.8 mmol) of 2,2′-bipyridine and 5.0 mL (5.0 mmol) of 1.0 N HCl. The mixture was stirred for 30 min and then allowed to stand in a stoppered flask for 3 weeks. The reaction was filtered, washed with water and ether, and allowed to dry in air to yield 1.5 g (100%) of a brown solid.

(2,2′-Bipyridyl)tetrakis(pyridine)ruthenium(III) Dichloride (15). This material was prepared by a literature procedure.[11] Under an argon atmosphere, 1.5 g (3.8 mmol) of $Ru(bpy)Cl_4$ and 3 mL (38 mmol) of pyridine were dissolved in 120 mL of 25% ethanol/water. The reaction was heated to reflux for 24 h. The mixture was allowed to cool and then was filtered. The filtrate was collected and diluted with 30 mL of water to form a 0.025 M solution.

Bis(2,2′-bipyridyl)bis(pyridine)[4-phenyl-2-(2-pyridyl)quinoline]ruthenium(II) Diperchlorate (16a). A 20-mL aliquot of the above solution was evaporated to dryness under reduced pressure (using a little absolute ethanol as a rinse). The residue was washed three times with copious amounts of ether and then dried again under reduced pressure. The residue was combined with 0.078 g (0.50 mmol) of 2,2′-bipyridine and 6 mL of ethylene glycol under a static nitrogen atmosphere. The mixture was quickly heated to reflux in a 230 °C sand bath. Reflux was maintained for 10 min, and then the reaction was placed in a 120 °C oil bath for 12 h. The reaction was allowed to cool, and 4 mL of water was added. The mixture was heated to boiling, and 2 mL of 10% sodium perchlorate solution was added. The mixture was allowed to cool and left to stand overnight. The reaction was filtered, and the resulting brown solid was recrystallized from 10% ethanol (under nitrogen) to yield a brown solid: UV–vis (CH_3CN) 475, 342; IR (KBr) 762, 755, 738 (w), 725, 691 cm^{-1}. The spectra were identical with those reported.[4] Anal. Calcd for $C_{40}H_{32}N_6Cl_2O_8Ru$: C, 53.58; H, 3.60. Found: C, 59.36; H, 3.68.

(2,2′-Bipyridyl)[4-phenyl-2-(2-pyridyl)quinoline]bis(pyridine)ruthenium(II) Dihexafluorophosphate (16b). A 10-mL aliquot of $Ru(bpy)py_4Cl_2$ solution was evaporated to dryness under reduced pressure (using a little absolute ethanol as a rinse). The residue was washed three times with copious amounts of ether and then dried again under reduced pressure. The residue was dissolved in 3 mL of ethylene glycol, and the solution was placed under an argon atmosphere. To the solution was added 0.036 g (0.13 mmol) of 4-phenyl-2-(2-pyridyl)quinoline. The mixture was quickly heated to reflux in a 230 °C sand bath. Reflux was maintained for 30 min, and then the reaction was placed in a 120 °C oil bath for 24 h. The reaction was allowed to cool. Saturated ammonium hexafluorophosphate (4 mL) and 2 mL of water were then added to the reaction. The mixture was filtered, and the resulting solid was washed with water until the washings were colorless. The solid was then washed with ether and allowed to dry in air. The solid was dissolved in a small amount of dichloromethane. A small amount of neutral alumina was added, and the mixture was placed atop a 28 cm × 2.5 cm column of neutral alumina. The column was eluted with 2% isopropyl alcohol/dichloromethane, and the fractions were separated by color. The purple band was collected, and the solvent was removed under reduced pressure to yield 0.023 g (54%) of a purple solid: UV–vis (CH_2Cl_2) 550 ($\epsilon = 6545\ M^{-1}\ cm^{-1}$), 330 nm (21 163); near-IR (KBr) 1600, 1080, 765, 726, 696 cm^{-1}; far-IR (CsI) 447, 424, 403, 334, 307 (br), 276 cm^{-1}. Anal. Calcd for $C_{40}H_{32}F_{12}N_6P_2Ru$: C, 48.64; H, 3.27; N, 8.51. Found: C, 50.87; H, 4.12; N, 8.55.

(2,2′-Bipyridyl)(poly[2,2′-(4,4′-diphenyl ether)-2,2′-(6,6′-(1,4-bisoxyphenylene)pyridine)-6,6′-bis(4-phenylquinoline) ether])bis(pyridine)ruthenium(II) Dihexafluorophosphate (19). In a procedure identical with the above, a 10-mL aliquot of $Ru(bpy)py_4Cl_2$ solution was treated with 0.37 g (0.12 mmol) of **9c**, 5 mL of *m*-cresol, and 1 mL of ethylene glycol. The reaction was worked up by pouring the cool reaction mixture into 150 mL of ether. The mixture was filtered, and the resulting solid was washed with 50 mL of ether, 150 mL of absolute ethanol, and an additional 100 mL of ether. The solid was dried under reduced pressure at 100 °C for 24 h to yield 0.37 g (76%) of a blue solid: UV–vis (CH_2Cl_2) 550 nm; IR (CsI) 452, 406 (br), 340 (b), 310 (w), 301, 280, 277 cm^{-1}.

(2,2′-Bipyridyl)(4-phenyl-2-(2-pyridyl)quinoline)(pyridine)aquoruthenium(II) Diperchlorate (18a). A solution of 0.10 g (0.11 mmol) of $[Ru(bpy)(qpy)py_2](ClO_4)_2$ in 30 mL of 25% ethanol/water was heated to reflux for 1 h under an argon atmosphere. A solution of 1.3 g (11 mmol) of sodium perchlorate in 5 mL of water was then added to the reaction. The mixture was boiled for 1 min and then allowed to cool. The reaction was placed in the freezer for 2 days. The resulting solid was filtered, washed with cold water and ether, and dried under reduced pressure for 24 h to yield 0.091 g (99%) of a dark purple solid: UV–vis (CH_2Cl_2) 510 nm ($\epsilon = 2550\ M^{-1}\ cm^{-1}$); near-IR (KBr) 3500, 3050, 1600, 1100, 790, 769, 702 cm^{-1}; far-IR (CsI) 457, 452, 448 (sh), 426, 420, 402. Anal. Calcd for $C_{35}H_{29}Cl_2N_5O_9Ru$: C, 50.31; H, 3.50. Found: C, 53.47; H, 4.79.

Electrolyses. Catalysis studies were done in a three-compartment cell. The working and auxilliary electrodes were platinum gauze. The area of the working electrode was approximately 7.0 cm^2. The reference electrode was the standard saturated calomel electrode (SCE). The electrolyses were conducted in 0.1 M phosphate buffer, pH 6.8. The substrate concentration was 0.1 M, and in the case of water-insoluble compounds, 1 equiv of acetone was also added. The total volume of the working solution was approximately 5 mL. Homogeneous catalyst concentrations were typically millimolar.

Large-scale electrolyses were conducted in a cell having a total volume of approximately 150 mL. The working electrode was a platinum basket with an approximate area of 182.8 cm^2. The auxilliary electrode was a platinum coil.

Polymer-modified electrodes were prepared by dipping the bare electrodes into a polymer solution (5 mg in 0.5 mL of 50% chloroform/ethanol). The film was allowed to dry, and then the electrode was weighed. Typically, 1 mg of polymer was deposited on the electrode. When polymer **19** was used, the coated electrode was placed into boiling water for 30 min to convert it to **20**. When polymer **13** was used, the coated electrode was placed in a 1% silver perchlorate solution for 10 min. The electrode was rinsed with distilled water, and the silver treatment was repeated twice more. Finally, the electrode was rinsed with distilled water several times and then patted dry with tissue before being used for an electrolysis. The large platinum basket was coated with polymer **13** by painting the electrode with the polymer solutions with a nylon brush. Typically, 18 mg of polymer was coated onto the electrode. The coated electrode was then treated with silver perchlorate in a manner identical with that used for the small electrode; however, a white or yellow precipitate was occasionally observed upon the first dipping.

The electrolyses were performed at a fixed applied potential of 0.9 mV vs SCE. The reaction was monitored for approximately 2.5 h with the passed charge and time being noted. Large cells were run for periods as long as 12 h. The working solutions were then analyzed by HPLC or GC. Product assignment was then confirmed by submitting dichloromethane extractions of the working solutions for GC/MS.

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Registry No. **3**, 20364-46-9; **4**, 118537-61-4; **5**, 118537-62-5; **6**, 118537-63-6; **6·7·8** copolymer, 118537-64-7; **10**, 118537-65-8; **11**, 118537-67-0; **14**, 63338-26-1; **15**, 110635-40-0; **16a**, 118537-69-2; **16b**, 118537-70-5; **18a**, 118537-72-7; Pt, 7440-06-4; $(CH)_2CHOH$, 67-63-0; $PhCH_2OH$, 100-51-6; $PhCH{=}CHCH_2OH$, 104-54-1; $(CH_3)_2C{=}CHCH_2OH$, 556-82-1; $(CH_3)_2C{=}O$, 67-64-1; PhCHO, 100-52-7; $PhCH{=}CHCHO$, 104-55-2; $(CH_3)_2C{=}CHCHO$, 107-86-8; *o*-aminobenzophenone, 2835-77-0; 2-acetylpyridine, 1122-62-9; hydroquinone, 123-31-9; 2,6-dibromopyridine, 626-05-1; acetyl chloride, 75-36-5; 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 59827-14-4; 4,4′-diacetyldiphenyl ether, 2615-11-4; (2,2′,2″-terpyridyl)ruthenium(III) trichloride, 72905-30-7; ruthenium trichloride, 10049-08-8; 2,2′,2″-terpyridine, 1148-79-4; 2,2′-bipyridine, 366-18-7; 2-cyclohexen-1-ol, 822-67-3; 2-cyclohexen-1-one, 930-68-7.