to that of NH_3, reflecting the predominantly σ-donor nature of these alkenes.

The products $Fe(C_2H_4)$, $Fe_2(C_2H_4)_2$, and $Fe_p(C_2H_4)_p$ all have similar isomer shifts and quadrupole splittings, implying similar electronic configurations. Thus, it would appear that addition of further $Fe-C_2H_4$ units to $Fe(C_2H_4)$ itself causes only a small perturbation to the iron atom. This is in agreement with the results of the GVB-CI study of $Ni_2(C_2H_4)$.[12]

One of the unexpected findings of this research was the presence of small amounts (~10%) of unreacted iron atoms in pure C_2H_4 at 4.2 K in addition to $Fe(C_2H_4)$. Although unreacted atoms in a pure reactive matrix are surprising, they are not unknown. Cobalt[9] and copper[8] atoms have been observed by ultraviolet spectroscopy (UV) in pure C_2H_4 at 12 K. Chromium and vanadium[32] atoms have been observed by UV in pure N_2 at 4.2 K. In the case of iron, unreacted atoms have been detected by Mössbauer spectroscopy in pure N_2 (also by UV[3]), in CO,[5] and in CH_4.[33] So it would appear that the persistence of bare atoms in pure, reactive matrices is apparently not uncommon. This points to the existence of a small activation energy. Our results show that this energy can be supplied either thermally or photolytically. In the latter case whether the mechanism is direct reaction of an excited-state atom or just a local heating of the matrix is difficult to say.

To our knowledge there have been no surface vibrational studies of the iron/ethylene system. Part of the reason for the paucity of data is that iron surfaces are notoriously difficult to clean. However, recent work[34] appears to have overcome this problem. From a study[35] of ethylene on the α-Fe(100) surface using low-energy electron diffraction and ultraviolet photoemission spectroscopy, it was concluded that ethylene is molecularly absorbed at 77 K. Cleavage of the double bond to surface methylene groups started to occur at 98 K and by 123 K was complete. Our matrix isolation study gave no evidence for C=C cleavage at any temperature up to the highest annealing temperature used (50 K), the only reaction being clustering of the iron/alkene complexes. (There have been no reports of cleavage of C=C bonds by matrix-isolated atoms or clusters.) Thus, while both iron clusters and iron surfaces can molecularly bond alkenes, the small clusters are unable to cleave the double bond. Whether this is due to the temperature being too low to provide the necessary activation energy for the process, or to a fundamental difference between clusters and surfaces, is a question we are unable to answer.

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Preparation, Spectroscopic Characterization, and Photochemical and Electrochemical Properties of Some Bis(2,2′-bipyridyl)ruthenium(II) and Tetracarbonyltungsten(0) Complexes of 6-*p*-Tolyl-2,2′-bipyridyl and of 6-*p*-Styryl-2,2′-bipyridyl and Its Copolymers[1]

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Received March 3, 1983

The syntheses of 6-*p*-styryl-2,2′-bipyridyl (6-stybpy) (**1**), 6-*p*-tolyl-2,2′-bipyridyl (6-tolbpy) (**2**), 6,6′-di-*p*-tolyl-2,2′-bipyridyl (**3**), $W(CO)_4$(6-stybpy) (**4**), $[Ru(bpy)_2(\text{6-stybpy})](PF_6)_2$ (**5**), and $[Ru(bpy)_2(\text{6-tolbpy})](PF_6)_2$ (**6**) are described. ^1H NMR spectra of **5** and **6** taken between 0 and 75 °C reveal that in these complexes the rotation of the phenylene group is hindered. In contrast to $[Ru(bpy)_3]^{2+}$, **5** and **6** are only weakly luminescent at room temperature in fluid solution. Copolymers of **1** with styrene, methyl methacrylate (MMA), or maleic anhydride and copolymers of **4** and **5** with styrene have been prepared by radical-initiated copolymerization. Polymer-bound $Ru(bpy)_2$ complexes of poly(6-stybpy-*co*-MMA) are formed by reaction of $[Ru(bpy)_2(OH_2)Cl]^+$ and a poly(6-stybpy-*co*-MMA) copolymer. The luminescence and photochemical properties of this polymer-bound $Ru(bpy)_2$ complex and also of poly(sty-*co*-$[Ru(bpy)_2(\text{6-stybpy})]^{2+}$) differ quite markedly from those reported for $Ru(bpy)_2$ derivatives of bipyridylated polystyrene, possibly indicating that in this latter material the bipyridyl function is bound to the polystyrene through its 4-position.

Introduction

Research into the properties of polymer-bound compounds has been stimulated inter alia by their usefulness as reagents or as catalysts[2-4] and as electrode coatings.[5-7] The aim of our work in this area has been to determine how the photochemical and photophysical properties of metal complexes such as metal carbonyls,[8] (bipyridyl)ruthenium complexes,[9,10] and porphyrins[10] are modified upon binding to polymers. It is hoped that this information may lead to the design of more efficient

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(1) Throughout this paper a compound number may designate either the neutral complex or its cation.

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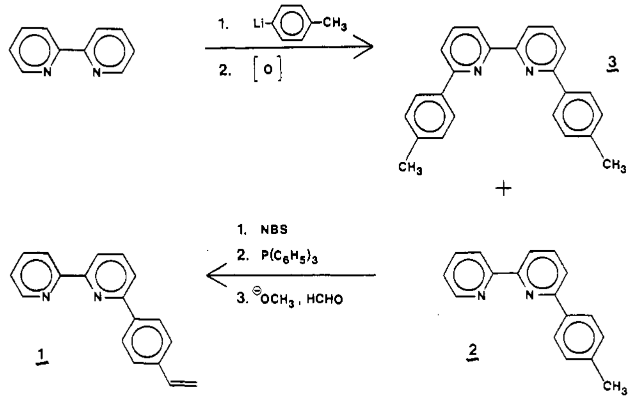
Scheme I



systems for photoinduced reactions such as the photodissociation of water. As $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) has been shown to be a promising material for water photodissociation,[11] the effect of incorporating $[Ru(bpy)_3]^{2+}$ in organic polymeric media such as cellulose,[12] sulfonated polystyrene,[13] and Nafion perfluorosulfonated polymers[14] has been studied by several groups. There has also been considerable interest in sensitizers of the $[Ru(bpy)_3]^{2+}$ type in which the complex is covalently linked to the polymer backbone. Thus $Ru(bpy)_2$ complexes of polymeric derivatives of vinylpyridine,[7,9,10,15,16] 4-methyl-4′-vinyl-2,2′-bipyridyl,[15a,17-23] 6-vinyl-2,2′-bipyridyl,[24] 4-methyl-4′-(hydroxyethyl)-2,2′-bipyridyl,[25] 4-methyl-4′-(styrylethyl)-2,2′-bipyridyl,[26] 4,4′-dicarboxy-2,2′-bipyridyl,[27] and bipyridylated polystyrene[28] have been prepared. This latter polymer was originally synthesized by Card and Neckers[29] from cross-linked polystyrene by ring bromination, lithiation with butyllithium, and subsequent reaction with 2,2-′bipyridyl. It was later shown that metal carbonyl derivatives of this polymer are active reagents for hydrogenation and metathesis of olefins,[29-31] and Kaneko et al. have described the light-induced electron-transfer reactions of its $Ru(bpy)_2$ derivative in the presence of methylviologen.[28] A difficulty with this kind of material is that the synthetic procedure used leads to a polymer whose composition is rather ill-defined. Indeed, although the binding of the polymer to the bipyridyl is generally supposed to be through the C(6) position, by analogy with the known reactivity of 2,2′-bipyridyl with other aryllithium compounds,[32] no definitive evidence for this has been given. An alternative route to polymers of this type would be via 6-*p*-styryl-2,2′-bipyridyl (6-stybpy) (**1**). With this well-characterized monomer, a range of bipyridyl-containing copolymers may be prepared, allowing considerable control of the physical, and possibly of the chemical, properties of the product. In this paper we describe the preparation of **1** and of its copolymers with styrene, methyl methacrylate, and maleic anhydride. Some examples of metallopolymers containing $Ru(bpy)_2$ or $W(CO)_4$ groups have been prepared either by reaction of a copolymer with a metal complex or by copolymerization of $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ or $W(CO)_4$(6-stybpy) with styrene or methyl methacrylate, and preliminary data on their photophysicochemical properties are presented in this publication. It has also been shown by ^1H NMR that in the $Ru(bpy)_2$ complexes there is appreciable steric hindrance to rotation of the styryl group, and it is probable that this steric interaction is responsible for the difference between the photophysical properties of these complexes and those of $[Ru(bpy)_3]^{2+}$.

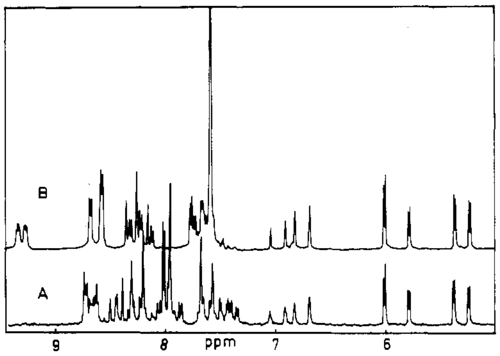


Figure 1. 80-MHz ^1H NMR spectra of (A) 6-*p*-styryl-2,2′-bipyridyl (**1**) and (B) $W(CO)_4$(6-stybpy) (**4**) in acetone-d_6.

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Table I. ^{1}H NMR Data of $[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$ (6) (19.4 mg/mL) at 30 °C and of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ at 29 °C in Acetone-d_6 Measured on a Varian SC300 Spectrometer (300 MHz)

	chem shift of pyridyl protons, ppm				coupling const, Hz					
ring	6	5	4	3	$J_{5,6}$	$J_{4,6}$	$J_{3,6}$	$J_{4,5}$	$J_{3,5}$	$J_{3,4}$
				$[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$[a]						
1	7.24	7.01	7.82	8.32	5.6	1.5	0.7	7.6	1.4	8.0
2	7.68	7.41	8.07	8.63	5.7	1.5	0.8	7.7	1.3	8.2
3	8.11^5	7.60	8.27^5	8.71	5.7	1.4	0.7	7.6	1.3	8.2
4	8.35	7.69	8.21	8.71	5.7	1.5	0.7	7.7	1.4	8.2
5	7.88^5	7.50	8.21	8.87	5.7	1.5	0.7	7.7	1.3	8.2
6	*p*-tolyl	7.50^5	8.30	8.90				7.7	1.4	8.3
				$[Ru(bpy)_3]Cl_2$						
	8.08	7.60	8.23^5	8.95	5.7	1.4	0.8	7.7	1.2	8.2

[a] $\delta(CH_3)$ 2.13.

Table II. ^{1}H NMR Data of $[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ (5) in Acetone-d_6 (16.0 mg/mL) at 30 °C Measured on a Varian SC300 Spectrometer (300 MHz)

Pyridyl Protons

	chem shift, ppm				coupling const, Hz					
ring	6	5	4	3	$J_{5,6}$	$J_{4,6}$	$J_{3,6}$	$J_{4,5}$	$J_{3,5}$	$J_{3,4}$
1	7.25	6.92	7.25^5	8.28	5.7	1.4	0.7	7.6	1.3	8.1
2	7.68^5	7.41	8.07^5	8.63	5.7	1.4	0.8	7.7	1.3	8.2
3	8.11^5	7.60^5	8.28	8.71^5	5.7	1.4	0.7	7.6	1.3	8.1
4	8.39	7.69	8.22^5	8.71^5	5.6	1.4	0.7	~7.6	1.4	~8
5	7.89	7.50^5	8.21^5	8.88^5	5.8	1.4	0.7	7.6	1.3	8.1
6	*p*-styryl	7.53^5	8.31^5	8.91^5				7.7	1.4	8.3

Vinylic Protons

chem shift, ppm			coupling const, Hz		
H_a	H_b	H_c	J_{ab}	J_{ac}	J_{bc}
6.56	5.69	5.28	17.6	10.9	0.8

Results and Discussion

I. Preparation of 6-*p*-Styryl-2,2′-bipyridyl (1) and 6-*p*-Tolyl-2,2′-bipyridyl (2). 6-*p*-Styryl-2,2′-bipyridyl (1) was synthesized by the method outlined in Scheme I. The initial step involving the reaction of tolyllithium with 2,2-′bipyridyl and subsequent mild oxidation give the desired 6-*p*-tolyl-2,2′-bipyridyl (2) in 25% yield with the disubstituted derivative 3 as minor product. This yield is substantially higher than that reported for the formation of 6-phenyl-2,2′-bipyridyl from phenyllithium[32] and is similar to that recorded for the reaction of 2,2′-bipyridyl with lithiated polystyrene.[30] Subsequent free-radical bromination with *N*-bromosuccinimide (NBS) of the methyl group of 6-tolylbipyridyl (2), formation of the Wittig reagent, and reaction with formaldehyde give 1.

II. Complexes of 6-*p*-Styryl-2,2′-bipyridyl (1) and 6-*p*-Tolyl-2,2′-bipyridyl (2). $W(CO)_4(6\text{-stybpy})$ (4). This was prepared from $W(CO)_6$ by a route similar to that previously employed for other tetracarbonylmetal complexes[33] (eq 1 and 2). The carbonyl stretching frequencies and the visible absorption spectrum are closely similar to those of $W(CO)_4(bpy)$.[33] The ^{1}H NMR (Figure 1) is consistent with that expected for complexed styrylbipyridyl, and no broadening of any peak is observed.

$$W(CO)_6 \xrightarrow[Et_2O]{h\nu} W(CO)_5(Et_2O) + CO \quad (1)$$

$$W(CO)_5(Et_2O) + \mathbf{1} \xrightarrow{\Delta} \underset{\mathbf{4}}{W(CO)_4(6\text{-stybpy})} + Et_2O + CO \quad (2)$$

$[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ (5) and $[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$ (6). These complexes were prepared from $Ru(bpy)_2Cl_2$ and either 1 or 2 in refluxing aqueous methanol. The reaction (eq 3) is conveniently monitored by observing the disappearance of the visible bands of $[Ru(bpy)_2Cl(H_2O)]^+$ (formed on dissolution of $Ru(bpy)_2Cl_2$ in the solvent) and their replacement by those of 5 or 6 at about 450 nm.

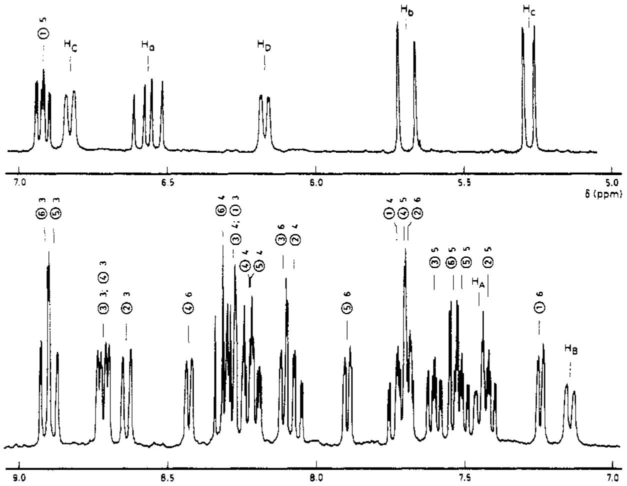

Figure 2. 300-MHz ^{1}H NMR spectrum of $[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ in acetone-d_6 at 0 °C. The chemical shifts of the protons are identified according to the system used in Tables II and III.

$$[Ru(bpy)_2Cl(H_2O)]^+ + L \xrightarrow[MeOH/H_2O]{\Delta} [Ru(bpy)_2L]^{2+} + Cl^- \quad (3)$$

5, L = 6-stybpy
6, L = 6-tolbpy

The ^{1}H NMR spectra of 5 and 6 exhibit the complexity expected for bipyridyls in the cis configuration and for complexed 1 and 2 (e.g., Figure 2). Their chemical shifts and

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Table III. Chemical Shifts and Coupling Constants of the Arene Ring Protons (Ortho H_A and H_D; Meta H_B and H_C) of $[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ (5) and $[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$ (6) in Acetone-d_6 at 0 °C Measured on a Varian SC300 Spectrometer (300 MHz)

	chem shifts, ppm				coupling const, Hz	
compd	H_A	H_B	H_C	H_D	$J_{AD} \simeq J_{BC}$	$J_{AB} \simeq J_{CD}$
6	7.34	6.84	6.52	6.03	1.9	7.9
5	7.46	7.15	6.83	6.16	2.0	8.0

coupling constants are summarized in Tables I and II and compared with those of $[Ru(bpy)_3]Cl_2$. The most striking features of the spectra at room temperature however are the broad signals observed for the protons of the arene ring. To study this further, the spectra of **5** and **6** were taken over a temperature range 0–75 °C, in either $(CD_3)_2CO$ or $(CD_3)_2SO$. The NMR spectrum of $[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$ in $(CD_3)_2SO$ at 75 °C shows a poorly resolved broad signal for the tolyl ring protons. At lower temperatures this signal broadens and splits into four signals of equal intensity. The coalescence temperature, T_c, for the meta protons (H_B and H_C) is 51 ± 1 °C; for the ortho protons (H_A and H_D), T_c could not be established. Qualitatively similar results were obtained with $[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$, but T_c could not be accurately determined, since the relevant signals of individual rotamers are not well separated from some pyridyl protons (Tables II and III). In contrast to these large chemical shift differences of the ring protons of the tolyl (styryl) group, the δ values of the protons of the bipyridyl moieties remain nearly temperature independent. The temperature dependence of the NMR spectra points to a fast-exchange process of the aryl ring protons at high temperatures. This mode of conformational change can be explained by assuming that the 6-aryl substituent rotates around its bond to the bipyridyl system on one and the same side of the plane of the bipyridyl moiety. The free energies of activation for the exchange process observed ($\Delta G_c^{\ddagger}$) at the coalescence temperature T_c have been calculated from the Eyring equation, taking the transmission coefficient as unity because the occurrence of an intermediate is improbable:

$$\Delta G_{rot}^{\ddagger} = RT_c \ln \frac{k_B T_c \tau_c}{h} \tag{4}$$

(where τ_c = lifetime of exchange, k_B = Boltzmann's constant, h = Planck's constant, T_c = coalescence temperature (K), and R = gas constant). Hence

$$\Delta G_c^{\ddagger} = 19.12T_c(10.32 + \log (T_c\tau_c)) \text{ kJ mol}^{-1} \tag{5}$$

For this purpose, exchange rate constants ($k_c = \tau_c^{-1}$) at T_c were determined with the approximate formula

$$k_c = \frac{\pi[(\nu_B - \nu_C)^2 + 6J_{BC}^2]^{1/2}}{2^{1/2}} \tag{6}$$

in which exchanging protons H_B and H_C are mutually coupled. The calculated values for $\Delta G_c^{\ddagger}$ are summarized in Table IV. In both compounds rather large differences between δ values of individual ortho as well as meta protons are found at lower temperatures; those lying opposite to a terminal ring of a bipyridyl moiety experience strong shielding and give rise to signals at higher field; those lying in the deshielding cone of a nitrogen atom of the pyridyl ring are found at the lowest field. The signals of the pyridyl protons opposite to the 6-aryl substituent (likely ring 1) are shifted upfield over 0.4–0.6 ppm in comparison with those of $[Ru(bpy)_3](PF_6)_2$ because of shielding by the aryl substituent.

Table IV. Free Energies of Activation for the Exchange Process in the Compounds $[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$ (6) and $[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ (5)

compd	solvent	protons used	$\Delta\nu$, Hz	J, Hz	T_c, K	$\Delta G_c^{\ddagger}$, kJ mol^{-1}
6	acetone-d_6	H_{meta}	94.6	1.9	324	64.8
	acetone-d_6	H_{ortho}	393.3	1.9		
	Me_2SO-d_6	H_{meta}	101.0	1.9	324	64.8
	Me_2SO-d_6	H_{ortho}	406.0	1.9		
5	acetone-d_6	H_{meta}	96.0	2.0	ca. 326	~65.2
	acetone-d_6	H_{ortho}	390.3	2.0		
	Me_2SO-d_6	H_{meta}	103.0	2.0	ca. 328	~65.6
	Me_2SO-d_6	H_{ortho}	400.0	2.0		

Table V. Absorption and Emission Properties of $[Ru(bpy)_2L]^{2+}$ [L = bpy, 6-stybpy, 6-tolbpy, and poly(6-stybpy-*co*-MMA)] in Acetone Solution

	absorption		emission	
complex	λ_{max}	$\log \epsilon$	λ_{max}[a]	rel peak intens[b]
$[Ru(bpy)_3](PF_6)_2$	451	4.20	613	1.00
$[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ (5)	450	4.14	616	0.007
$[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$ (6)	450	4.13	618	0.004
poly(MMA-*co*-$[Ru(bpy)_2$-(6-stybpy)$](PF_6)_2$) (10)	453		620	0.007

[a] Uncorrected for photomultiplier sensitivity. [b] All solutions had OD of 0.50 at excitation wavelength (451 nm).

III. Polymeric Derivatives of 6-Styryl-2,2′-bipyridyl (1), $W(CO)_4$(6-stybpy) (4), and $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ (5). **1** shows the propensity to polymerize expected of a styrene derivative, and as examples, three types of copolymers were prepared by radical polymerization using AIBN as initiator. The copolymer (**7**) of **1** and maleic anhydride was insoluble in most common solvents. However, copolymers of **1** with methyl methacrylate (MMA) (**8**) or styrene (**9**) dissolve in a range of organic solvents, and **8** is also soluble in water/methanol mixtures. The solubility of **8** in aqueous solvent mixtures is particularly useful as it allows the preparation of poly(MMA-*co*-$[Ru(bpy)_2(stybpy)]^{2+}$) copolymers (**10**) (eq 7).

$$\underset{\mathbf{8}}{\text{poly(6-stybpy-}co\text{-MMA)}} + Ru(bpy)_2Cl_2 \xrightarrow[MeOH/H_2O]{\Delta} \underset{\mathbf{10}}{\text{poly(MMA-}co\text{-}[Ru(bpy)_2(6\text{-stybpy})]^{2+})} \tag{7}$$

Copolymer complex (**10**) was isolated from solution by addition of a dilute aqueous solution of NH_4PF_6, which precipitates the polymer while nonpolymer complexes, e.g. $[Ru(bpy)_2Cl(OH_2)]^+$ or $[Ru(bpy)_3]^{2+}$, remain in solution. Further purification was effected by precipitation from dichloromethane solution using hexane. The visible absorption spectrum (see Table V) is rather similar to that of $[Ru(bpy)_3]^{2+}$, and no evidence was found for species such as polymer-bound $[Ru(bpy)(6\text{-stybpy})Cl(OH_2)]^+$. As the styrene–6-styrylbipyridyl copolymer (**9**) is insoluble in water or alcohols, an analogous experiment to that shown in eq 7 cannot be carried out in the same solvent. Attempts to prepare a poly(sty-*co*-$[Ru(bpy)_2(6\text{-stybpy})]^{2+}$) copolymer by refluxing a THF/methanol (1:1 v/v) solution of the copolymer **9** and $Ru(bpy)_2Cl_2$ were unsuccessful, as judged by changes in the visible absorption spectrum. In this connection it may be noted that preparation of polystyrene-bound $[Ru(bpy)_3]^{2+}$ type complexes by refluxing methanolic THF solutions of $Ru(bpy)_2Cl_2$ and bipyridylated polystyrene has been reported.[28] It was however suggested that some ligand exchange takes place under these reaction conditions as polymer-bound $Ru(bpy)_2Cl_2$ centers were also observed.[28]

Polymer-bound metal complexes have also been prepared by AIBN-initiated copolymerization of styrylbipyridine com-

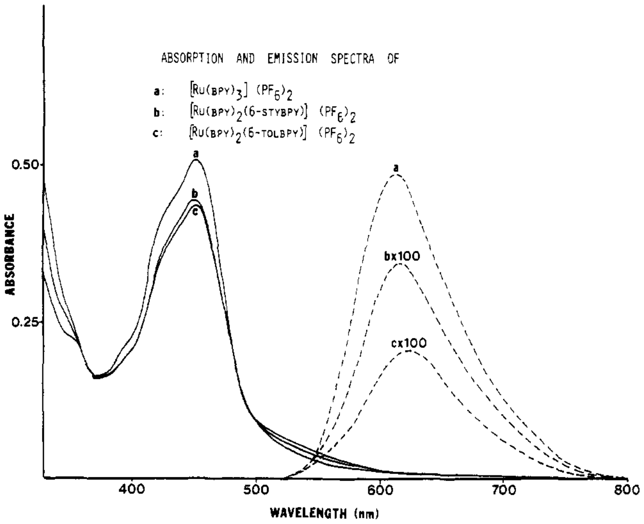

Figure 3. Visible absorption spectra (—) of 3.26×10^{-5} M acetone solutions of $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ (**5**), and $[Ru(bpy)_2(6\text{-tolbpy})]^{2+}$ (**6**) and room-temperature emission spectra (- - -) of same recorded following excitation of each at 451 nm.

plexes **4** or **5** with other vinyl monomers. The copolymers (**11** or **12**) of $W(CO)_4$(6-stybpy) (**4**) with MMA or styrene have ν_{CO} stretching frequencies in a position similar to that found by Neckers and co-workers[30] for the $W(CO)_4$ complex of bipyridylated polystyrene, and the λ_{max} of the visible absorption band is shifted slightly to shorter wavelengths compared to that of **4**. Copolymers poly(sty-*co*-$[Ru(bpy)_2(6\text{-stybpy})]^{2+}$) (**13**) were prepared by radical-induced polymerization of monomer complex **5** with styrene in a stoichiometric ratio 1:20. ^{1}H NMR measurements confirmed that the vinyl group of **5** had indeed reacted, and a comparison of the integrated signal intensities for the bipyridyl ring protons with those of the polymerized styrene indicated a ratio of 6-stybpy:styrene in the polymer of 1:20, in good agreement with the composition of the reaction mixture. The near-UV/visible spectrum of the copolymer is closely similar to that of the monomer complex (**5**).

IV. Electrochemical Properties of $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ (5) and $[Ru(bpy)_2(6\text{-tol-bpy})]^{2+}$ (6). Cyclic voltammograms of complexes **5** (and **6**), measured at a platinum electrode in acetone solution (ca. 8×10^{-4} M) with a scan speed 200 mV s^{-1}, exhibit one oxidation wave at 1.53 V (1.49 V) and three reduction waves at −1.12 V (−1.11 V), −1.37 V (−1.36 V), and −1.73 V (−1.66 V) vs. an Ag/AgCl reference electrode. The values of these redox potentials are confirmed by normal-pulse polarography and differential-pulse polarography. Compared with those of the well-studied parent compound $[Ru(bpy)_3]^{2+}$,[34] the data show that introduction of an aryl substituent at the 6-position makes the reduction potentials 20–160 mV more negative. Cyclic voltammetry shows that the oxidations and reductions are not completely chemically reversible, as i_f/i_b ratios for the oxidation are about 0.8. Furthermore, after repeated scans some new oxidation and reduction peaks grow, indicating that decomposition products are also formed.

As expected, strontium titanate photoanodes could be sensitized by $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ and by poly(sty-*co*-$[Ru(bpy)_2(6\text{-stybpy})]^{2+}$) (**13**) films in 0.5 M H_2SO_4 solutions, in agreement with previous reports.[35]

Table VI. Comparative Rates for the Reduction of Methylviologen by $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ and Its Copolymers Excited by Visible Light in Homogeneous Solution in the Presence of Triethanolamine or EDTA

sensitizing complex	initial rate, mol dm^{-3} min^{-1}
Aqueous Acetone Solution[a]	
$[Ru(bpy)_3](PF_6)_2$	1.8×10^{-4}
$[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ (5)	2.4×10^{-6}
poly(MMA-*co*-$[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$) (10)	2.0×10^{-6}
none	1.1×10^{-6}
Aqueous Dimethylformamide Solution[b]	
$[Ru(bpy)_3](PF_6)_2$	2.4×10^{-5}
poly(sty-*co*-$[Ru(bpy)_2(6\text{-stybpy})](PF)_6)_2$) (13)	6.5×10^{-7}
none	3.8×10^{-7}

[a] Ruthenium complex 4×10^{-5} M; TEOA 0.125 M; MV^{2+} 1.0×10^{-2} M; 9:1 pH 9 buffer/acetone (v/v). [b] Ruthenium complex 4×10^{-5} M; EDTA 1.0×10^{-3} M; MV^{2+} 2.0×10^{-3} M; 4:1 DMF/water (v/v).

V. Excited-State Properties of $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ (5), $[Ru(bpy)_2(6\text{-tolbpy})]^{2+}$ (6), and Copolymers of 5. The main feature of the visible absorption spectra of **5**, **6**, and copolymers of **5** (i.e., an absorption band at ca. 450 nm) is rather similar to that of $[Ru(bpy)_3]^{2+}$ (Figure 3 and Table V). The emission properties, however, are different. Each of **5**, **6**, or the copolymers luminesces only weakly in acetone solution at room temperature, the intensity in each case being less than 1% that of $[Ru(bpy)_3]^{2+}$.[36] The luminescence intensity is, however, much higher in frozen alcohol glasses at 77 K. Strong emission is also observed from the copolymers when they are cast as films on glass slides. Although the low quantum yields in solution could be caused by the different electron-donating properties of the substituent, it is more likely that they are a consequence of steric hindrance caused by the arene group in the 6-position. This steric interaction could lead to a longer Ru–N bond length in the 6-arylbipyridyl complexes and a resultant lowering of the excited-state ligand field $t_{2g}{}^5e_g$ level, allowing a more rapid deactivation of the emissive MLCT state. A reduction of the emission quantum yields of other $Ru(bpy)_2$ derivatives of 6-substituted 2,2′-bipyridyls compared with $[Ru(bpy)_3]^{2+}$ has previously been reported.[37]

Complexes **5** and **6** are quite photostable in methanol or acetone ($\Phi < 10^{-4}$). In acetonitrile, photosolvation of **5** [giving $[Ru(bpy)_2(MeCN)_2]^{2+}$ or possibly $[Ru(bpy)(6\text{-stybpy})(MeCN)_2]^{2+}$] takes place with low efficiency (Φ at 436 nm $= 8 \times 10^{-4}$; under the same conditions, Φ for $[Ru(bpy)_3]^{2+}$ $= 2 \times 10^{-4}$).

The ability of the excited states of **5** or its methyl methacrylate copolymer **10** to act as electron-transfer agents was compared to that of $[Ru(bpy)_3]^{2+}$ by monitoring spectrophotometrically the rate of production of the radical cation MV^+ from methylviologen MV^{2+} in degassed buffered (pH 9.1) aqueous acetone solution (reaction 8). The back-reaction

$$[Ru(bpy)_2(bpy\text{-}R)]^{2+} + MV^{2+} \xrightarrow{h\nu} [Ru(bpy)_2(bpy\text{-}R)]^{3+} + MV^+ \quad (8)$$

was suppressed by scavenging the Ru(III) complex with triethanolamine (TEOA).[38] Under the conditions used (see Experimental Section), MV^+ was produced rapidly in the sample containing $[Ru(bpy)_3]^{2+}$ whereas, under identical

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[34] (a) Tinnemans, A. H. A.; Timmer, K.; Reinten, M.; Kraaijkamp, J. G.; Alberts, A. H.; van der Linden, J. G. M.; Schmitz, J. E. J.; Saaman, A. A. *Inorg. Chem.* **1981**, *20*, 3698. (b) Saji, J.; Aoyagui, S. *J. Electrochem. Soc.* **1975**, *58*, 401. (c) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.

[35] (a) Mackor, A.; Schoonman, J. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 71. (b) Tinnemans, A. H. A.; Mackor, A. *Ibid.* **1981**, *100*, 295.

[36] The possibility that even this emission is due to impurities cannot be completely excluded at the moment, particularly as luminescent complexes could possibly be formed if ligand-exchange reactions of the type reported by others[28] were to take place to a small extent.

[37] Fabian, R. H.; Klassen, D. M.; Sonntag, R. W. *Inorg. Chem.* **1980**, *19*, 1977.

[38] Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1979**, *62*, 1345.

conditions with **5** or **10**, the rate of production of MV^+ was only slightly greater than that observed in the absence of any ruthenium complex (Table VI). This observation may be contrasted with that of Kaneko[28] in DMF/H_2O (4:1 v/v) where the rate of production of MV^+ using the $Ru(bpy)_2$ derivative of bipyridylated polystyrene was found to be ca. 24% of that obtained with $[Ru(bpy)_3]^{2+}$. To investigate whether these contrasting results could be caused by the different solvent systems employed, the photoreduction of MV^{2+} sensitized by poly(sty-*co*-$[Ru(bpy)_2(6\text{-stybpy})]^{2+}$) (**13**) was studied in DMF/H_2O (4:1 v/v). In this case also it was found that the efficiency of production of MV^+ is very low (Table VI.) In summary, our observations reveal that $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ (**5**) and its copolymers (**10** and **13**) are poor sensitizers for the photoreduction of MV^{2+}, probably because of the short lifetime of their excited states. The difference between these results and those obtained with $Ru(bpy)_2$ derivatives of bipyridylated polystyrene[28] probably lies in the different structure of the complexes and especially in the site of attachment of the styryl group to the bipyridyl ligand. This is quite definitely at the 6-position in **5**, **10**, and **13**, whereas in the bipyridylated polystyrene the site of substitution is uncertain and it is possible that this could be at the sterically less hindered 4-position.

Conclusions

The results reported here indicate that it should be possible to prepare a range of complexes of polymer-bound 6-styryl-2,2′-bipyridyl, allowing the properties of the polymers (e.g., solubility, loading, etc.) to be varied in a controlled fashion. Although only selected examples have been prepared, it is clear that complexes can be prepared either from copolymers by reaction with some suitable reactive metal complex precursor or by copolymerization of a 6-stybpy complex. It would appear that the materials obtained by these routes are better defined than those prepared from modified polystyrene as (i) no intermediates of the modification procedure (e.g., brominated polystyrene groups) are present and (ii) it is certain that the styryl group is attached to the bipyridyl through the 6-position.

The attachment of the styryl group at the 6-position causes steric interaction between this group and other ligands in the complex, and this is reflected in the hindered rotation of the styryl group observed in the ^1H NMR of $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ and $[Ru(bpy)_2(6\text{-tolbpy})]^{2+}$. In agreement with the findings of other authors,[37] 6-substitution on the bipyridyl group has a marked effect on the photophysical properties of the $[Ru(bpy)_2(bpy\text{–}R)]^{2+}$ complex. Thus, Fabian et al.[37] have found that the luminescence quantum yield of $[Ru(bpy)_2(6\text{-Mebpy})]^{2+}$ and $[Ru(bpy)_2(6,6'\text{-}Me_2bpy)]^{2+}$ in alcohol glasses at 77 K is substantially reduced (to 28% and 8%, respectively) compared to that of $[Ru(bpy)_3]^{2+}$. It has also been reported[24] that the luminescence of polymer complexes poly(6-vbpy-*co*-$[Ru(bpy)_2(6\text{-vbpy})]^{2+}$) (6-vbpy = 6-vinylbipyridyl) is substantially weaker than that of $[Ru(bpy)_3]^{2+}$ although this was ascribed to quenching of the excited state because of the high local concentration of the ruthenium centers. Concentration quenching of this type is clearly not the reason for the low luminescence yield with the complexes described here as the effect is found also for the monomer complexes in dilute solution. For $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ and its copolymers, we believe that the most probable reason for the low emission yield is a shortening of the excited-state lifetime compared to that of $[Ru(bpy)_3]^{2+}$. This could be a result of an enhanced rate of radiationless deactivation of the emissive MLCT state via the $t_{2g}{}^5e_g$ ligand field excited state, which is expected to be at lower energy than in $[Ru(bpy)_3]^{2+}$ because of a lengthening of the Ru–N bond due to steric interaction of the 6-substituent.

The most disappointing of our observations is the inability of $[Ru(bpy)_2(6\text{-stybpy})]^{2+}$ or its copolymers to produce reduced methylviologen upon irradiation, probably as a consequence of the short lifetime of their excited states. This finding means that this type of complex will be unsuitable as an intermediary for light-induced hydrogen production, and our attention is now focused on polymeric derivatives of 4-substituted 2,2′-bipyridyls.[23]

Experimental Section

Materials. $Ru(bpy)_2Cl_2{\cdot}2H_2O$ was prepared as described by Whitten et al.,[39] methylviologen was analytical grade (ICI), and vinyl monomers were distilled before use. Reagent grade solvents were purified by standard methods; other chemicals for synthesis were reagent grade and used as received.

General Procedures. ^1H NMR spectra were recorded on a Bruker WP-80 80-MHz or Varian SC-300 300-MHz instrument. Tetramethylsilane was used as internal standard, and all spectra are recorded in δ units. UV/vis spectra were recorded on a Unicam SP8-200 spectrometer, IR spectra on a Perkin-Elmer 599 spectrometer, and luminescence spectra on a Perkin-Elmer 44B spectrofluorimeter. (Luminescence spectra were not corrected for instrumental response.) Elemental analyses were carried out in the TNO analytical department (W. J. Buis) or in the microanalytical laboratory at University College, Dublin. The electrochemical measurements were performed as described in ref 34a.

6-*p*-Tolyl-2,2′-bipyridyl (2). To a thoroughly cooled solution of phenyllithium [3.1 g (0.45 mol) of lithium and 38.1 g (0.22 mol) of *p*-bromotoluene] in 250 mL of ether was slowly added, with vigorous stirring, a solution of 25 g (0.16 mol) of 2,2′-bipyridine in 150 mL of dry toluene. After the mixture was stirred for 1 h under reflux, the ether was distilled off and the residual mixture stirred at 100 °C for 4 h. The mixture was hydrolyzed with cold dilute HCl and the water layer extracted with ether. The acid extracts were basified and extracted with ether. After removal of the solvent, 40 mL of nitrobenzene was added. The solution was heated at 150 °C for 1.5 h. After the solution was cooled, ca. 150 mL of ether was added. This caused the separation of a small quantity of a precipitate, which was removed by filtration, and the filtrate was extracted with 10% hydrochloric acid. The acid solution was washed with ether and neutralized with concentrated ammonia. The dark oil that separated was taken up in ether and dried over anhydrous sodium sulfate. After removal of the solvent and most of the excess nitrobenzene, the dark residue was purified by column chromatography over silica gel.

From the combined fractions, 0.55 g (1.6 mmol) of compound **3** crystallized, after removal of most of the solvent. The desired monotolyl derivative **2** was isolated by repeated column chromatography over silica gel, followed by crystallization from methanol (9.85 g, 0.040 mol, 25%); mp 68–70 °C. ^1H NMR ($CDCl_3$): δ 2.40 (s, CH_3), 7.28^5 and 8.23^5 (AA′BB′, $J_{AB} \sim 8.3$ Hz, 4 H_{tolyl}), 7.27 ($H_{5'}$), 7.70 (H_5), 7.80 ($H_{4'}$), 7.82 (H_4), 8.34 (H_3), 8.62 ($H_{3'}$), 8.67 ($H_{6'}$); $J_{5',6'} = 4.8$ Hz, $J_{4',6'} = 1.8$ Hz, $J_{3',6'} = J_{3,5} = 0.9$ Hz, $J_{4',5'} = 7.6$ Hz, $J_{3',5'} = 1.0$ Hz, $J_{3',4'} = 8.0$ Hz, $J_{4,5} = J_{3,4} = 7.8$ Hz. Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 83.00; H, 5.81; N, 11.33.

6,6′-Di-*p*-tolyl-2,2′-bipyridyl (3): Mp 224 °C. ^1H NMR ($CDCl_3$): δ 2.43 (s, 2 CH_3), 7.74 (dd, 7.8 and 1.5 Hz, $H_{5,5'}$), 7.89 (t, ~7.6 Hz, $H_{4,4'}$), 7.32 and 8.07 (AA′BB′, $J_{AB} \simeq 8.2$ Hz, 4 H_{tolyl}), 8.57 (dd, 7.3 and 1.6 Hz, $H_{3,3'}$). Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.18; H, 6.02; N, 8.14.

6-*p*-Styryl-2,2′-bipyridyl (1). To a solution of 7.38 g (0.03 mol) of **2** in 225 mL of CCl_4 were added 5.34 g (0.03 mol) of freshly crystallized *N*-bromosuccinimide (NBS) and a few milligrams of azoisobutyronitrile (AIBN). The mixture was irradiated (Philips IR-1000) and refluxed until the NBS was consumed. The reaction mixture was cooled to room temperature, filtered to remove the succinimide, and concentrated to give crude 6-(*p*-(bromomethyl)-phenyl)-2,2′-bipyridyl in 85% yield by NMR. A solution of the bromomethyl aromatic compound and 7.86 g (0.03 mol) of triphenylphosphine in 200 mL of xylene was refluxed for 8 h. After the mixture was cooled, the precipitated phosphonium salt was filtered, washed with hexane and absolute ether, and dried. It was subjected to the Wittig reaction without further purification.

To a stirred solution of 18.5 g (0.031 mol) of the phosphonium salt in 150 mL of a mixture of dried MeOH/DMF (5:1) was added in

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(39) Sprintschnik, G.; Sprintschnik, G. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.

small portions 2.04 g of sodium methoxide. The red brownish solution was treated with a methanolic solution of formaldehyde[40] (70 mL, large excess). After the mixture was stirred overnight, the solvent was removed under reduced pressure, and water was added. After extraction with chloroform, washing of the combined extracts with water, and drying over anhydrous Na_2SO_4, the residue was purified by repeated column chromatography over silica gel (63–100 mesh). Elution with chloroform/petroleum ether (bp 40–60 °C) mixtures of increasing ratio (1:9 → 2:8) gave 6.3 g (77%) of **1**, which was crystallized from methanol/chloroform; mp 92–94 °C. ^1H NMR ($CDCl_3$): vinylic protons at δ 5.11, 5.61, and 6.62. Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.47; N, 10.84. Found: C, 83.74; H, 5.56; N, 10.73.

$W(CO)_4$(6-stybpy) (4). A 0.50-g (1.42-mmol) sample of $W(CO)_6$ in 150 mL of nitrogen-flushed diethyl ether solution was photolyzed for 8 h in a Pyrex photochemical reactor using a Philips HPK 125-W lamp. After photolysis, 0.37 g (1.42 mmol) of **1** was added to this photolysate, and the resulting solution was refluxed under a nitrogen atmosphere. After 3 min of reflux, the color of the solution had changed from orange to dark red. After 1 h, the solvent was removed under reduced pressure. The crude product was purified by chromatography on neutral alumina using acetone as eluant, and **4** was recrystallized from a toluene/chloroform mixture. ^1H NMR [$(CD_3)_2CO$, 80 MHz]: δ 5.23–5.39 (dd, 1 H), 5.78–6.03 (dd, 1 H), 6.69–7.06 (q, 1 H), 7.55–7.8 (m, 6 H), 8.1–8.4 (m, 2 H), 8.56–8.69 (dd, 2 H), 9.25–9.36 (m, 1 H). IR (PhMe): ν_{CO} 2004 (w), 1889 (br, s), 1854 (sh). Vis ($CHCl_3$): λ_{max} (log ϵ) 502 nm (3.70). Anal. Calcd for $C_{22}H_{14}N_2O_4W$: C, 47.69; H, 2.52; N, 5.05. Found: C, 47.20; H, 2.30; N, 5.10.

[Ru(bpy)$_2$(6-stybpy)]$(PF_6)_2$·CH_3COCH_3 (5·CH_3COCH_3). A 0.30-g (1.16-mmol) sample of **1** and 0.40 g (0.77 mmol) of $Ru(bpy)_2Cl_2·2H_2O$ were refluxed for 43 h in 225 mL of methanol/H_2O mixture (3:1 v/v). The reaction was followed by taking UV/vis spectra of aliquots. A finely divided precipitate, which later settled as a glue, was obtained upon addition of an aqueous solution containing 1 g of NH_4PF_6. All the solvent was taken off and the remaining solid redissolved in acetone. Some water (with 0.05 g of NH_4PF_6) was then added, and the mixture was left overnight. Upon evaporation of the acetone, bright orange crystals were formed. The compound could also be purified by passing down a column of neutral alumina, using acetone as eluant. Yields were in excess of 50%; for ^1H NMR and UV/vis data, see Tables II and V. Anal. Calcd for $C_{41}H_{36}F_{12}N_6OP_2Ru$: C, 48.29; H, 3.55; F, 22.36; N, 8.24; P, 6.07. Found: C, 48.26; H, 3.61; F, 22.00; N, 8.07; P, 5.91.

[Ru(bpy)$_2$(6-tolbpy)]$(PF_6)_2$ (6). **6** was prepared by a method similar to that for **5**. ^1H NMR and UV/vis data are given in Tables I and V. Anal. Calcd for $C_{37}H_{30}F_{12}N_6P_2Ru$: C, 46.80; H, 3.18; F, 24.00; N, 8.85; P, 6.52. Found: C, 46.86; H, 3.16; F, 23.90; N, 8.78; P, 6.06.

Copolymer (7) of 1 with Maleic Anhydride. To a solution of 0.275 g (2.8 mmol) of maleic anhydride and 0.725 g (2.8 mmol) of **3** in 15 mL of dried benzene was added 0.0092 g (0.056 mmol) of AIBN. Under vigorous stirring, the reaction mixture, kept under nitrogen atmosphere, was heated for 3 h at 70 °C and, subsequently, for 2 h at 80 °C. The precipitate was filtered, thoroughly washed with benzene, and dried. Analysis of the colorless powder (0.60 g) revealed a 0.96:1 ratio. Anal. Calcd for 1:1 copolymer: N, 7.86. Found: N, 7.59.

Copolymer (8) of 1 with Methyl Methacrylate. A 0.060-g (0.23-mmol) sample of **1** was added to 0.5 mL (5.0 mmol) of freshly distilled MMA and 0.04 g of AIBN. The reaction mixture was heated at 80 °C for 1 h. The copolymer (**8**) was purified by dissolution in CH_2Cl_2 and reprecipitation in hexane. ^1H NMR ($CDCl_3$, 80 MHz): 0.5–2.3 (m, 99 H, CCH_3, CH, CH_2), 3.60 (s, 59 H, CO_2CH_3), 7.0–8.8 (m, 11 H, poly(stybpy)), giving calcd stybpy:MMA in copolymer (**8**) of 1:19.5.

Copolymer (9) of 1 with Styrene. A 0.099-g (0.38-mmol) sample of **1** was dissolved in 0.44 mL (3.8 mmol) of styrene. A 0.024-g portion of AIBN was added and the reaction mixture heated at 70 °C under nitrogen atmosphere. The resulting polymer (**9**) was dissolved in CH_2Cl_2 and reprecipitated with hexane. ^1H NMR ($CDCl_3$, 80 MHz): 1.0–2.3 (broad m, 29 H, $CHCH_2$), 6.4–7.4 (broad d, 45 H, poly(sty)), 7.4–8.9 (m, 11 H, poly(stybpy)), giving calcd stybpy:sty in copolymer (**9**) of 1:8.8.

Copolymer Poly(MMA-*co*-[Ru(bpy)$_2$(6-stybpy)]$^{2+}$) (10). A 0.147-g sample of the poly(6-stybpy-*co*-MMA) (**8**) was dissolved in 60 mL of EtOH/H_2O (68:32 v/v) by refluxing for 15 min. Then 0.110 g (0.21 mmol) of $Ru(bpy)_2Cl_2·2H_2O$ was added and the reaction mixture heated at reflux for 140 h. The reaction progress was monitored spectrophotometrically by taking aliquots. Addition of an aqueous NH_4PF_6 solution to the cooled reaction mixture yielded an orange-brown solid, whereas the excess $Ru(bpy)_2Cl_2$ present in the reaction mixture remained in solution. After filtration and drying, the product (**10**) was further purified by dissolution in CH_2Cl_2 and reprecipitation in hexane. The final product was pure according to TLC. UV/vis (CH_2Cl_2): λ_{max} 452 nm. ^1H NMR ($CDCl_3$, 80 MHz): 0.5–2.3 (m, 120 H, CCH_3, CH, CH_2), 3.61 (s, 65 H, CO_2CH_3), 7.2–8.8 (m, 27 H, poly(stybpy) + bpy), giving calcd [Ru(bpy)$_2$(6-stybpy)]$^{2+}$:MMA in copolymer (**10**) of 1:22.

Copolymer (13) of [Ru(bpy)$_2$(6-stybpy)]$(PF_6)_2$ (5) and Styrene. A 0.10-g (0.098-mmol) sample of **5** was dissolved in 0.5 mL of CH_3CN, and 0.20 g (1.9 mmol) of styrene was added. After addition of 0.013 g of AIBN, the reaction mixture was heated at 75 °C for 1 h. The resulting polymer (**13**) was dissolved in CH_2Cl_2 and reprecipitated with hexane. UV/vis (CH_2Cl_2): λ_{max} 453 nm. ^1H NMR ($CDCl_3$, 80 MHz): 1.4–2.0 (broad, m, 64 H, $CHCH_2$), 6.4–7.3 (broad d, 100 H, polysty), 7.3–9.0 (m, 27 H, poly(stybpy) + bpy), giving calcd [Ru(bpy)$_2$(6-stybpy)]$^{2+}$:sty in copolymer (**13**) of 1:20.

Copolymers (11 and 12) of $W(CO)_4$(6-stybpy) (4) with Methyl Methacrylate or Styrene. A 0.05-g (0.090-mmol) sample of **4** was dissolved in a minimum volume of chloroform together with 1 mL (9.4 mmol) of methyl methacrylate or 1 mL (8.7 mmol) of styrene and 0.01 g of AIBN. The resulting solution was heated for 1 h at 80 °C. After the solution was cooled to room temperature, the crude polymers were dissolved in dichloromethane and precipitated in 500 mL of *n*-hexane. Poly[MMA-*co*-$W(CO)_4$(6-stybpy)] (**11**) UV/vis (CH_2Cl_2): λ_{max} 498 nm. IR (KBr, cm^{-1}): 2002 (w), 1890 (m), 1830 (m). Poly[sty-*co*-$W(CO)_4$(6-stybpy)] (**12**) UV/vis (CH_2Cl_2): λ_{max} 496 nm. IR (KBr, cm^{-1}): 2001 (w), 1895 (m), 1835 (m).

Photochemical Procedures. Quantum yields were determined by steady-state irradiation using the 436-nm line isolated, from a Thorn MED 250W medium-pressure mercury lamp, by an Applied Photophysics High Radiance monochromator with 5-nm slit settings. Light intensities at 436 nm were measured before and after each determination using potassium ferrioxalate actinometry assuming a quantum yield of ferrous ion formation of 1.11.[37]

Solutions for study of photoinduced electron transfer contained either (a) 4×10^{-5} M Ru-complex sensitizer, 1.0×10^{-2} M methylviologen (MV^{2+}), and 0.125 M triethanolamine (TEOA) in 9:1 (v/v) borate buffer (pH 9.1)/acetone or (b) 4×10^{-5} M Ru-complex sensitizer, 2.0×10^{-3} M MV^{2+}, and 1.0×10^{-3} M EDTA in 4:1 (v/v) DMF/H_2O (see Table VI). For polymer-bound derivatives, the concentration was such that the optical density at λ_{max}(MLCT) was the same as that for 4×10^{-5} M $[Ru(bpy)_3]^{2+}$. Blank experiments were also carried out by using both mixtures a and b, but in the absence of any sensitizer. Aliquots (5 mL) were degassed by three freeze–pump–thaw cycles and irradiated with a 150-W high-pressure xenon arc lamp with filters to remove the IR and UV light (λ < 400 nm). The rate of reaction was monitored by following changes in absorbance at 603 nm (characteristic of MV^+).

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Registry No. **1**, 68965-73-1; **2**, 86696-22-2; **3**, 86696-23-3; **4**, 86696-16-4; **5**, 86696-28-8; **6**, 86696-18-6; **7**, 86696-19-7; **8**, 86696-20-0; **9**, 86696-21-1; **11**, 86696-25-5; **12**, 86696-26-6; **13**, 86696-29-9; bpy, 366-18-7; HCHO, 50-00-0; *p*-tolyllithium, 2417-95-0; 6-[*p*-(bromomethyl)phenyl]-2,2′-bipyridyl, 86696-24-4.

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