Luminescent Metal Complexes. Part 1. Tris-chelates of Substituted 2,2′-Bipyridyls with Ruthenium(II) as Dyes for Luminescent Solar Collectors

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Ruthenium(II) and osmium(II) complexes of 2,2′-bipyridyls (bipy) and 1,10-phenanthrolines (phen) are identified as feasible dyes for use in luminescent solar collectors. Twenty-seven $Ru^{II}(bipy)_3^{2+}$ complexes are prepared and the absorption and emission spectra of their solutions in EtOH–MeOH at room temperature are reported. Quantum efficiencies, which are sensitive to oxygen quenching, vary between 0.002 and 0.306 depending upon substituents. The effect of the medium on the spectral properties of selected compounds has also been investigated. Measured quantum yields of non-aqueous solutions are higher than those for aqueous solutions but lower than for doped plastic films.

Luminescent solar concentrators, LSCs, offer the possibility of concentrating both direct and diffuse sunlight for use in light displays and for conversion into electrical energy.[1] The collector operates on the principle of light absorption by fluorescent molecules, dissolved in a transparent plastic sheet, followed by re-emission which is trapped by total internal reflection within the sheet. Although an attractive prospect, practical realisation is not yet possible since ideal fluorescent dyes are unavailable. The properties required for such an application are not yet found in any dye. The demands are stringent. Thus the dye must have intense absorption in the visible region to absorb sunlight, emission with a quantum efficiency close to unity, and a large Stokes shift between the absorption peak and the emission maximum in order to minimise re-absorption of luminescence. Much effort in this area so far has been directed towards the use of the organic dyes developed for laser application.[1] But these dyes suffer from the severe disadvantage of a small Stokes shift and hence strong re-absorption of emitted radiation. This prevents a sheet of significant surface area being useful.

We have begun a programme of synthetic work and spectral evaluation of luminescent materials in an effort to overcome some of the defects of dyes already tested. The molecular systems chosen for evaluation are based upon the well known tris-chelates of 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) with divalent ruthenium and osmium. The electronic spectra of these complexes have been under intensive investigation over the last few years[2] and there are features that make them worthy of research for use in LSCs. Thus there is intense absorption in the u.v. which extends into the visible down to 500 nm in the case of Ru^{II} complexes and to 700 nm for the Os^{II} series. The luminescence arises from the formally spin forbidden counterparts of the transitions responsible for the visible region absorption, resulting in significant apparent Stokes† shifts. Thus for $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ the emission maxima occur between *ca.* 550 and 650 nm and for the Os^{II} complexes the maxima are at *ca.* 720 nm. The quantum efficiency of $Ru(bipy)_3^{2+}$ is susceptible to oxygen quenching,[3] temperature, and the fluidity of the medium. The value is only 0.042 in aqueous solution at 25 °C[4] but is as high as 0.386 in alcoholic glass at 77 K:[5] it also approaches this value in poly(methylmethacrylate) at 77 K.[6] The quantum efficiency for $Ru(phen)_3^{2+}$ is 0.584 in alcoholic glass at 77 K, though values for the Os^{II} analogues are much lower.[5]

The great scope for introducing ring substituents in this class of compounds also offers the possibility of tuning the optical properties to those required for the proposed application. Few studies are available which delineate the effect of substituents on the photophysics of the systems. Those reported to date are based largely on complexes obtained from ligands available commercially or *via* short synthetic pathways.[5,7] We have now carried out a systematic synthetic programme making both new and known ligands in the 2,2′-bipyridyl and 1,10-phenanthroline series and preparing their Ru^{II} and Os^{II} complexes for spectral evaluation. This has furnished a large amount of data from which we have noted a number of interesting trends. The present paper reports that part of our work which is concerned with the preparation and investigation of the optical properties of substituted 2,2′-bipyridyls tris-chelated with Ru^{II} in a variety of solvents and plastics. In the subsequent paper[8] we describe a simple three-state model that can account for the trends observed in the quantum efficiencies, radiative and non-radiative rates.

Results and Discussion

Preparation of Ligands.—Routes to most of the ligands have been described previously but we frequently found it necessary to modify reported reaction conditions to achieve acceptable yields. 4-Substituted 2,2′-bipyridyls were obtained from bipyridyl (**1**) *via* 4-nitro-2,2′-bipyridyl 1-oxide (**2**) using adaptations of Jones' scheme.[9] In our hands attempted deoxygenation of (**2**) using phosphorus trichloride[9] gave a mixture of products which included the desired nitrobipyridyl (**3**) and also the 4-chloro derivative (**4**). Triphenylphosphine proved a cleaner deoxygenating agent although the yield of (**3**) remained low. Our preferred route to (**4**) involved refluxing (**2**) with acetyl chloride *prior to*, rather than *with*, phosphorus trichloride treatment, a modification which raised the yield from 55[9] to 93%. However, for the conversion of (**2**) into 4-bromo-2,2′-bipyridyl (**5**), deoxygenation of the isolated intermediate 4-bromo-1-oxide (**6**) was more successful than a one-pot procedure. We were unable to obtain the 4-methoxy compound (**7**) from (**4**) using sodium methoxide.[9] However, we obtained (**7**) by displacement of the nitro group from (**2**)

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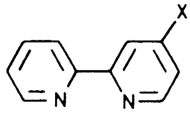
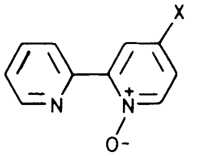
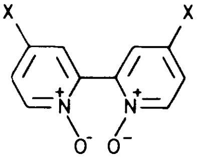
† The term Stokes shift refers to the energy separation between the absorption and fluorescence maxima and properly applies only when the absorbing and emitting states are the same. In the present case the intense absorbing transitions are not the same as the emitting ones. Hence we refer to the energy separation between the two as an apparent Stokes shift.



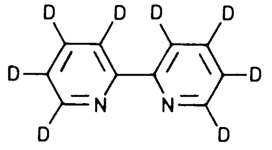
(1) X = H
(3) X = NO_2
(4) X = Cl
(5) X = Br
(7) X = OMe
(9) X = OCH_2Ph
(10) X = NH_2
(11) X = NMe_2



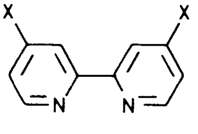
(2) X = NO_2
(6) X = Br
(8) X = OMe



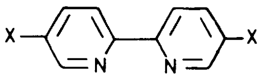
(12) X = H
(14) X = NO_2



(13)



(15) X = NO_2
(16) X = Cl
(17) X = Br
(18) X = OEt
(19) X = OBz
(20) X = OPh
(21) X = NH_2
(22) X = NHAc
(23) X = NEt_2
(24) X = Me
(25) X = CH_2Ph
(27) X = CH=CHPh(*E*)
(28) X = CO_2Et



(26) X = Me
(29) X = CO_2Et
(30) X = NH_2
(31) X = NHAc
(32) X = NMe_2

followed by deoxygenation of the 4-methoxy-1-oxide (**8**). The 4-benzyloxy derivative (**9**) was prepared similarly. The 4-amino and 4-dimethylamino compounds (**10**) and (**11**) were obtained, the former in low yield, from (**2**) and (**4**), respectively, using literature conditions.[9,10]

Further substituted 2,2′-bipyridyls were obtained *via* the 1,1′-dioxide (**12**). The compound readily underwent base-catalysed hydrogen–deuterium exchange and this, followed by deoxygenation, afforded a convenient route to [$^2H_8$]-2,2′-bipyridyl (**13**). Dinitration of (**12**) afforded (**14**) but deoxygenation of the latter to 4,4′-dinitro-2,2′-bipyridyl (**15**) proved troublesome. Maerker and Case[11] achieved this using PCl_3 in chloroform but we recovered only starting material when using their conditions. However, satisfactory yields of (**15**), *i.e.* >50%, were obtained when a larger volume of solvent was used but, even so, the reaction only proceeded well when performed on a small scale. Triphenylphosphine, phosphorus tribromide, trimethyl phosphite, and triphenyl phosphite all proved ineffectual as deoxygenating agents for (**14**).[10] In our hands, the conversion of (**14**) into the dichloro compound (**16**) using PCl_3 under Haginawa's conditions[12] also proved unreliable but the method devised above for preparing the monochloro analogue (**4**) gave satisfactory results. The 4,4′-disubstituted compounds (**17**)—(**23**) were obtained by literature routes[11] or standard procedures: the reduction of (**14**) to the diamino compound (**21**) using iron in acetic acid[11] was found to be dependent on the iron used, the yield varying from 20% for iron filings to 54% for reduced iron powder.[10]

4,4′-Dimethyl-, 4,4′-dibenzyl-, and 5,5′-dimethyl-2,2′-bipyridyls, (**24**), (**25**), and (**26**), respectively, were obtained by coupling the corresponding pyridine over W7-J Raney nickel. An attempt[10] to prepare 5,5′-dimethyl-4,4′-diphenyl-2,2′-bipyridyl using the coupling reaction was unsuccessful. Using literature procedures (**24**) was converted into (**27**) and (**28**), and (**26**) converted through to (**29**)—(**32**).

Preparation of Complexes.—Various methods are available for the preparation of tris-2,2′-bipyridyl complexes of ruthenium(II) and several were utilised in the preparation of the complexes (**33**)—(**59**), Table 1. The chelating abilities of the ligands vary substantially which enabled us to test the generality of some existing methods and to modify them when appropriate. The original Burstall method[13] involving the direct high-temperature reaction between ruthenium chloride and a large excess of ligand (method A, Table 1) afforded complexes (**33**) and (**34**) from 2,2′-bipyridyl[10] and [$^2H_8$]-2,2′-bipyridyl (**13**), respectively, but the method is wasteful of ligand and this discouraged us from using it further. Heating the reactants in refluxing ethanol, method B after Palmer and Piper,[14] improved the yield of (**33**) and satisfactory yields were also obtained from ligands substituted with electron-donating groups (4,4′-diethoxy) and electron-withdrawing substituents (4,4′-dibromo and 5,5′-bisethoxycarbonyl). However, the strongly deactivated ligand 4,4′-dinitro-2,2′-bipyridyl (**15**) failed to react under these conditions. The problem was circumvented using potassium aquapentachlororuthenate(III) in the higher boiling solvent ethanediol, the complex being precipitated as the tetrafluoroborate salt. In a further modification the 4,4-distyryl ligand (**27**) was complexed in refluxing glycerol.

A standard alternative method involves reaction of potassium aquapentachlororuthenate(III) with excess of ligand in refluxing aqueous DMF, the Ru^{III} complex so formed then being reduced with an added reducing agent.[15,16] In one of our preliminary experiments using this scheme, we experienced difficulty in separating the complex from excess of ligand and subsequently we showed that the reaction proceeds smoothly using stoicheiometric amounts of the reactants, the isolated product showing only one spot on t.l.c. This procedure (method C in Table 1) proved very versatile; disappointing results were obtained only with the distyryl ligand (**27**), which gave a mixture of tris- and bis-chelates, and the 5,5′-diamino- and 5,5′-bis(dimethylamino)-bipyridyls (**30**) and (**32**). The last two are apparently readily reoxidised to the Ru^{III} state. Thus addition of Raney nickel to solutions containing the products gave rise to detectable orange fluorescence which faded within minutes of removal of the reductant.[10]

The two mixed complexes, (**58**) and (**59**), were prepared by reacting an equivalent of one ligand with an equivalent of the appropriate bisbipyridyl ruthenium(II) complex, formed from ruthenium trichloride and two equivalents of the second ligand.

Complexes formed from 4-substituted 2,2′-bipyridyls can exist as two geometrical isomers and these can be detected by n.m.r. spectrometry.[17] Where signal integration is possible, it shows that the ratio of the facial to meridional isomers is *ca.* 1 : 3, in accord with the statistical probability for their formation. As yet, it has not proved possible to separate the isomers and thus

Table 1. Preparation of ruthenium(II) trisbipyridyl complexes, $Ru(bipy)_3{}^{2+}X^-{}_2$

Compound		Preparation						Analytical data (%)							
								Found				Requires			
No.	Substituent	Anion	Method[a]	Time (h)	Yield (%)	Recrystallisation solvent	Formula	C	H	N	Hal.	C	H	N	Hal.
(33a)	None	I^-	C	0.25	50	H_2O	$C_{30}H_{24}N_6RuI_2{\cdot}4H_2O$	40.1	3.5	9.2		40.2	3.5	9.4	
(33b)	None	Cl^-	C	0.25	80	H_2O	$C_{30}H_{24}N_6RuCl_2{\cdot}2.5H_2O$	52.7	4.0	12.3		52.6	4.3	12.3	
(34)	Octadeuterio	Cl^-	A	4.5	57	D_2O									
(35)	4-Bromo	I^-	C	0.25	74	H_2O	$C_{30}H_{21}Br_3N_6RuI_2{\cdot}3.5H_2O$	31.4	2.1	7.7		32.0	2.5	7.5	
(36)	4-Chloro	I^-	C	0.25	37	H_2O	$C_{30}H_{21}Cl_3N_6RuI_2{\cdot}5H_2O$	35.1	2.7	8.1	10.8[b]	35.4	3.0	8.3	10.5
(37)	4-Methoxy	I^-	C	0.25	59	H_2O	$C_{33}H_{30}N_6RuI_2{\cdot}4H_2O$	41.5	3.9	8.8	27.3	41.5	4.0	8.8	26.6
(38)	4-Benzyloxy	I^-	C	0.25	79	H_2O–EtOH	$C_{51}H_{42}N_6RuI_2{\cdot}1.5H_2O$	52.5	4.1	7.1	21.0	52.4	3.9	7.2	21.7
(39)	4-Amino	I^-	C	0.25	33	H_2O–EtOH	$C_{30}H_{27}N_9RuI_2{\cdot}2H_2O$	39.6	3.5	13.8		39.8	3.5	13.9	
(40)	4-Dimethylamino	I^-	C	0.25	77	H_2O–EtOH	$C_{36}H_{39}N_9RuI_2{\cdot}3.5H_2O$	42.9	4.2	11.9		42.9	4.2	11.8	
(41)	4,4′-Dinitro	BF_4^-	B[c]	2.5	41	H_2O wash	$C_{30}H_{18}N_{12}RuB_2F_8{\cdot}3H_2O$	34.0	2.1	15.4		33.8	2.3	15.75	
(42)	4,4′-Bisethoxycarbonyl	BF_4^-	B[c]	3.25	30	H_2O–EtOH	$C_{48}H_{48}N_6O_{12}RuB_2F_8{\cdot}6H_2O$	45.0	4.3	6.4		44.9	4.7	6.5	
(43)	4,4′-Dibromo	I^-	B	65	56	H_2O wash	$C_{30}H_{18}N_6Br_6RuI_2$	27.9	1.5	6.3		27.8	1.4	6.5	
(44)	4,4′-Dichloro	I^-	B	69	49	H_2O	$C_{30}H_{18}N_6Cl_6RuI_2{\cdot}H_2O$	34.4	1.5	7.8		34.4	1.9	8.0	
(45)	4,4′-Diphenyl	Cl^-	A	3	48	1N-HCl	$C_{66}H_{48}N_6RuCl_2{\cdot}4H_2O$	67.55	4.5	7.2		67.8	4.8	7.2	
(46)	4,4′-Distyryl	Cl^-	B[d]	1.5	75	H_2O wash	$C_{78}H_{60}N_6RuCl_2{\cdot}6H_2O$	69.2	5.0	6.0	5.0	68.8	5.3	6.2	5.2
(47)	4,4′-Dibenzyl	Cl^-	C	0.25	83	H_2O wash	$C_{72}H_{60}N_6RuCl_2{\cdot}3H_2O$	69.55	4.9	6.75	5.8	70.0	5.4	6.8	5.7
(48)	4,4′-Dimethyl	I^-	C	0.25	39	H_2O wash	$C_{36}H_{36}N_6RuI_2{\cdot}1.5H_2O$	45.9	3.9	8.9	28.15	46.3	4.2	9.0	27.15
(49)	4,4′-Diphenoxy	Cl^-	C	0.25	64	DMF–1N-HCl	$C_{66}H_{48}N_6O_2RuCl_2{\cdot}5H_2O$	61.9	4.2	6.9	6.2	61.8	4.6	6.55	5.5
(50)	4,4′-Diethoxy	I^-	B	73	49	DMF–H_2O	$C_{48}H_{48}N_6O_6RuI_2{\cdot}6H_2O$	41.9	4.9	6.9		42.2	5.0	7.0	
(51)	4,4′-Dibenzyloxy	Cl^-	C	0.25	98	EtOH	$C_{72}H_{60}N_6RuCl_2{\cdot}1H_2O$	66.4	4.6	6.4	5.3	66.8	4.8	6.5	5.5
(52)	4,4′-Biscetamido	I^-	C	0.25	73	H_2O wash	$C_{42}H_{42}N_{12}O_6RuI_2{\cdot}3H_2O$	39.6	4.1	13.1	20.4	39.6	4.3	13.2	19.9
(53)	4,4′-Diamino	I^-	C	0.25	52	H_2O wash	$C_{30}H_{30}N_{12}RuI_2{\cdot}5H_2O$	35.5	3.7	16.4		35.3	4.0	16.7	
(54)	4,4′-Bis(diethylamino)	Cl^-	B	0.4	50	H_2O wash	$C_{54}H_{78}N_{12}RuCl_2{\cdot}4H_2O$	56.8	7.3	14.5	6.2	56.9	7.6	14.7	6.2
(55)	5,5′-Bisethoxycarbonyl	I^-	B	89	35	H_2O–EtOH	$C_{48}H_{48}N_6O_{12}RuI_2$	45.6	3.9	6.6	20.2	45.9	3.9	6.7	20.2
(56)	5,5′-Dimethyl	Cl^-	C	0.25	76	H_2O	$C_{36}H_{36}N_6RuCl_2{\cdot}3.5H_2O$	54.65	5.2	10.6	9.7	54.9	5.5	10.7	9.0
(57)	5,5′-Bisacetamido	I^-	C	0.25	74	H_2O wash	$C_{42}H_{42}N_{12}O_6RuI_2{\cdot}3H_2O$	41.2	4.25	13.6	20.7	41.35	4.0	13.8	20.8
(58)	None, (4,4′-diphenyl)$_2$	I^-	[e]		59	H_2O wash	$C_{54}H_{40}N_6RuI_2{\cdot}2H_2O$	55.8	3.6	6.9		55.7	3.8	7.2	
(59)	(None)$_2$, 4,4′-diphenyl	I^-	[e]		37	H_2O wash	$C_{42}H_{32}N_6RuI_2{\cdot}3.5H_2O$	48.3	3.4	8.0		48.6	3.6	8.1	

[a] For details see Experimental section. [b] Chlorine analysis. [c] Prepared by a variant of B using potassium aquapentachlororuthenate(III) in ethanediol. [d] As [c] but using glycerol as solvent. [e] Prepared in a two-step synthesis *via* a bis-complex of Ru^{II}, see Experimental section.

Table 2. Spectroscopic properties of ruthenium(II) trisbipyridyl complexes in EtOH–MeOH (4:1 v v) solution at 20 °C

Compound no.	Substituent	$\lambda_{max.}$(abs.)/ nm	$\lambda_{max.}$(em.)/ nm	$\varepsilon_S \times 10^4$	φ_m'	φ_m	τ_m/ μs
(33)	None	450	630	1.43	0.029	0.089	1.15
(34)	Perdeuterio	448	630		0.031	0.096	
(35)	4-Bromo	457	640	1.40	0.018	0.052	0.82
(36)	4-Chloro	454	640	1.35	0.014	0.030	0.67
(37)	4-Methoxy	461	660	1.41	0.014	0.039	0.67
(38)	4-Benzyloxy	460	650	1.48	0.017	0.053	0.60
(39)	4-Amino	472.5	675	1.21	0.006	0.021	0.35
(40)	4-Dimethylamino	475	680	1.50	0.006	0.023	0.35
(41)	4,4′-Dinitro	473	700		0.001	0.002	0.25
(42)	4,4′-Bisethoxycarbonyl	464	655	2.33	0.076	0.200	1.65
(43)	4,4′-Dibromo	465	660	1.73	0.028	0.060	0.52
(44)	4,4′-Dichloro	465	670	1.55	0.020	0.036	0.40
(45)	4,4′-Diphenyl	473	635	2.80	0.058	0.306	1.95
(46)	4,4′-Distyryl	487	680	3.30	0.009	0.030	0.72
(47)	4,4′-Dibenzyl	460	640	1.61	0.030	0.098	1.25
(48)	4,4′-Dimethyl	455	640	1.70	0.027	0.086	0.95
(49)	4,4′-Diphenoxy	479	670	1.34	0.018	0.038	0.35
(50)	4,4′-Diethoxy	477	675	1.30	0.009	0.020	0.30
(51)	4,4′-Dibenzyloxy	476	670	1.35	0.015	0.032	0.31
(52)	4,4′-Bisacetamido	479	670	1.50	0.014	0.027	0.41
(53)	4,4′-Diamino	504	705	1.05	0.002	0.004	0.10
(54)	4,4′-Bis(diethylamino)	518	700	1.45	0.005	0.010	0.13
(55)	5,5′-Bisethoxycarbonyl	495	720	0.99	0.003	0.004	0.23
(56)	5,5′-Dimethyl	440	620	1.47	0.015	0.037	0.35
(57)	5,5′-Bisacetamido	445	630	1.49	0.021	0.126	2.40
(58)	None, (4,4′-diPh)$_2$	465	635	1.47	0.025	0.098	2.125
(59)	(None)$_2$, 4,4′-diPh	457.5	630	1.97	0.041	0.197	1.925

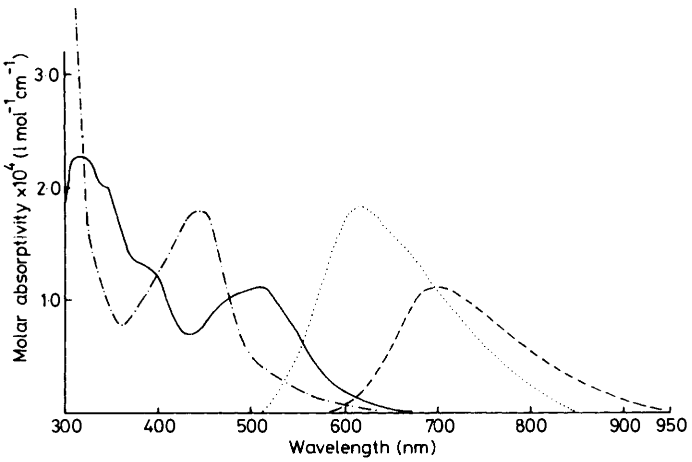


Figure. Representative electronic spectra. Absorption (——) and emission (– – –) spectra of **(54)**, absorption (–·–) and emission (···) spectra of **(56)**

spectroscopic data reported below for **(35)**—**(40)** refer to the mixtures.

Absorption Spectra.—All the complexes investigated in our study, **(33)**—**(59)**, show an intense metal $d \longrightarrow$ ligand π^* charge-transfer (CT) transition in the wavelength region 420—520 nm, Table 2. The Figure gives examples of the absorption and emission spectra of complexes with the most red- and blue-shifted CT absorption spectra, *viz.* **(54)** and **(56)**.

The assignment of the lowest-energy singlet transitions has been discussed by Ceulemans and Vanquickenborne.[18] Their conclusions are that two one-electron transitions lie within the envelope of the main absorption band. These involve transitions from the d-orbitals of e symmetry, under the point group D_3, to the a_2 and e components of the φ combination of π^* ligand orbitals. These assignments are now broadly confirmed by the crystal spectra and theoretical studies of Ferguson and Herren[2] and by low-temperature m.c.d. spectra of alcoholic glasses.[19] Substitution of the ligand causes both wavelength shifts and intensity changes in these transitions. We discuss each property in turn.

The substituents borne by the six complexes, **(35)**—**(40)**, derived from monosubstituted 2,2′-bipyridyls are of the $+M$, $-I$ category. All shift the charge-transfer band to longer wavelength and the trend is qualitatively similar to their effect on $\lambda_{max.}$ within monosubstituted benzenes.[20] Thus substituents having a large mesomeric effect give rise to larger shifts in $\lambda_{max.}$ and we note a reasonable correlation between $1/\lambda_{max.}^{H} - 1/\lambda_{max.}^{sub.}$ and the Hammett substituent constant σ_R (*i.e.*, $\sigma_p - \sigma_m$). This parameter provides an approximate measure of the relative mesomeric contribution of the substituent.[21] [slope = −1 938, correlation coefficient 0.971 for six points (H, Cl, Br, OMe, NH$_2$, NMe$_2$; we were unable to locate a reliable value for OCH$_2$Ph).]

A wider range of substituents is available within the series of complexes **(31)**—**(54)** derived from 4,4′-disubstituted 2,2′-bipyridyls and includes two $-M$, $-I$ groups (NO$_2$ and CO$_2$Et). Once again, all the complexes show a band maximum shifted to longer wavelength compared with the parent complex and this in itself essentially precludes an all embracing single substituent parameter correlation with $1/\lambda_{max.}^{H} - 1/\lambda_{max.}^{sub.}$. As before, however, there is a correlation between $1/\lambda_{max.}^{H} - 1/\lambda_{max.}^{sub.}$ with σ_R for groups of the $+M$, $-I$ category and this extends also to the Me group, slope −4 616, correlation coefficient 0.968. The benzyl, phenyl, and styryl substituents induce a shift to longer wavelength which is larger than would be expected simply on the basis of their small negative σ_R values: data for the NO$_2$ and CO$_2$Et derivatives, where the substituents have positive σ_R values, provide the remaining points which are not included in the correlation. From the slopes of the two $1/\lambda_{max.}^{H} - 1/\lambda_{max.}^{sub.}$ *versus* σ_R plots, it is apparent that the introduction of the second $+M$, $-I$ substituent has a marginally larger effect than the introduction of the first substituent. Sequential replacement of a 2,2′-bipyridyl ligand by a 4,4′-diphenyl-2,2′-bipyridyl ligand causes a linear change in $1/\lambda$ (correlation coefficient 0.999).

Of the three complexes (**55**)—(**57**) obtained from the 5,5′-disubstituted 2,2′-bipyridyls, the two substituted with electron-donating groups, (**56**) and (**57**), show $\lambda_{max.}$ for the charge-transfer band at shorter wavelength than for the parent. In contrast, the complex (**55**) derived from 5,5′-bisethoxycarbonyl-2,2′-bipyridyl shows a very substantial shift in $\lambda_{max.}$ to longer wavelength relative to both the parent complex and the complex (**42**) derived from 4,4′-bisethoxycarbonyl-2,2′-bipyridyl.

We do not attempt to provide a detailed molecular orbital interpretation of these substituent-induced energy shifts as Day and Sanders[22] have done for the methyl-substituted 1,10-phenanthroline complexes with Fe^{II}, Fe^{III}, and Cu^{I}. This is beyond the scope of the present work. We do wish to draw attention to the striking empirical correlation between the energy of the CT bands and the electron-withdrawing and -donating effects of the substituents.

The effect of substituents upon the molar absorptivities, ε_S, defined at $\lambda_{max.}$ of the CT band, involves a variation between values of 0.99 to 3.30 × 10^4 l mol^{-1} cm^{-1} (for the 4,4′-diamino- and 4,4′-distyryl-substituted complexes). Apart from the styryl compound (**46**) the largest values for ε_S are found for the 4,4′-diphenyl and 4,4′-bisethoxycarbonyl derivatives. Systematic replacement of a 4,4′-diphenyl substituted ligand by 2,2′-bipyridyl, that is, series (**45**), (**58**), (**59**), (**33**), does not show a sequential change in ε_S. Thus the mixed complex (**58**) has a lower value of ε_S than the parent (**33**). Low values for the molar absorptivity are found for the 5,5′-bisethoxycarbonyl compound (**55**) and the 4,4′-diamino derivatives. Within the sub-series of compounds bearing $+M$, $-I$ substituents in the 4,4′-positions there are marked variations in the values of ε_S with the electron-donating character of the substituent. Thus ε_S increases over the series of complexes bearing NH_2, OR, H, Cl, and Br atoms or groups. In this respect the high molar absorptivity for the 4,4′-bis(diethylamino) derivative (**54**) is seen to be anomalous. Variations in ε_S for the 4-monosubstituted derivatives are much smaller.

The major source of intensity lies in the 'transfer term' as discussed by Day and Sanders.[22] This term is proportional to the square of the d-φ orbital mixing coefficient, C. The relative intensities of the allowed singlet transitions are given by Ceulemans and Vanquickenborne[18] as $3K^2/2$ where $K = C \cdot q|R|$ and $q \cdot |R|$ is a measure of the dipole moment of the transferred charge. Hence the intensity of the singlet transition can be affected by changes (*i*) in the mixing coefficient C and (*ii*) in the effective transfer length $|R|$. The former is expected to change as the basicity of the nitrogen atom co-ordinated to Ru^{II} varies since this factor will alter the energy separation between the d and φ orbitals. We suggest it is this factor which contributes to the variation of ε_S with the electron-donor properties of the $+M$, $-I$ substituents noted above. The second factor, the effective transfer length $|R|$, is likely to be increased for ligands with extended conjugation and appears to be responsible for the relatively large ε_S values of the styryl, 4,4′-diphenyl, and 4,4′-bisethoxycarbonyl derivatives.

Emission Spectra.—Watts and Crosby[5,23] reported the spectra of $Ru(bipy)_3^{2+}$ and of the complex of the 4,4′-diphenyl-substituted ligand at 77 K. There are a number of closely spaced emission bands. Under the conditions of the present series of measurements, the fine structure is lost and luminescence is recorded as a broad band. The $\lambda_{max.}$(em.) values, Table 2, therefore refer to a maximum resulting from a series of overlapping transitions.

The data reported at 77 K show that the phenyl substituents shift the emission to longer wavelength.[5,23] The present solution-phase data, Table 2, confirm this shift and show that the band is indeed shifted to a longer wavelength for all the complexes derived from 4-substituted and 4,4′-disubstituted ligands. Styryl groups in the 4,4′-positions produce a somewhat larger shift but extended conjugation of the π system is but one factor controlling the position of $\lambda_{max.}$(em.). Thus substituents with large $+M$ (NH_2, NEt_2, NMe_2) and $-M$ (NO_2) effects induce still larger shifts. For the $+M$, $-I$ substituents the trend induced in the shift of the emission band is qualitatively similar to that induced in the absorption band maximum although substituents having larger $+M$ effects have a larger effect on the latter. Thus the apparent Stokes shift [$1/\lambda_{max.}$(abs.) − $1/\lambda_{max.}$(em.)] for complexes bearing $+M$, $-I$ substituents in the 4,4′-positions decreases in the series Cl, H, Br, OEt, OPh, NHAc, NH_2, NEt_2. Among other substituents in these positions, a small apparent Stokes shift is induced by phenyl groups and the largest by nitro groups.

When the substituents are attached to the 5,5′-position their effects on the optical properties are rather different. Methyl groups induce a shift in $\lambda_{max.}$(em.) to shorter wavelength, [complex (**56**)], relative to the parent, giving a large apparent Stokes shift, acetamido groups cause no wavelength shift but induce a large Stokes shift, and bisethoxycarbonyl groups induce the largest shift in $\lambda_{max.}$(em.) found within all the complexes studied but, energetically, this is essentially matched by the shift in the absorption band.

Quantum Efficiency and Lifetime Measurements.—Demas and Adamson[3] reported that the emission from $Ru(bipy)_3^{2+}$ is sensitive to oxygen quenching but that bubbling of nitrogen or argon through solutions to be irradiated is sufficient to limit oxygen quenching to less than 1%. However, in work on related Ru^{II} complexes of 1,10-phenanthroline derivatives we have found that the quantum yields for certain compounds are extremely sensitive to the presence of oxygen.[24] For some materials it was found that deoxygenation of solutions by vacuum deaeration at 10^{-6} Torr, using freeze–pump–thaw cycles, raised the quantum efficiency relative to that measured following simple nitrogen flushing techniques. Using vacuum deaeration conditions, oxygen quenching is effectively eliminated. In the present work we measured quantum yields for the bipy complexes both before, φ_m' values, and after freeze–pump–thaw treatment, φ_m values. Data so obtained are given in Table 2. Quantum yields for the parent complex as both the chloride (**33a**) and iodide (**33b**) salt were in satisfactory agreement to within experimental error, showing that the halide ion has no effect. Values for (**33**) and its perdeuterio-analogue are higher than those reported by Van Houten and Watts[4] who measured these compounds in aqueous solution. The present data, however, confirm their observation that replacement of C–H bonds by bonds of lower vibrational frequency enhances the quantum efficiency only slightly.

The ratio $\varphi_m : \varphi_m'$ varies within the series between about 2 to over 5, demonstrating that the sensitivity of the quantum efficiency to oxygen quenching depends upon substituent. The highest value is found for the 4,4′-diphenyl-substituted compound (**45**). However, in general, the values are smaller than those found within the Ru^{II} $(phen)_3^{2+}$ series.[24]

The lifetime measurements, τ_m (see Experimental section), listed in Table 2 refer to data obtained after vacuum deaeration. Comparison with the limited range of values we measured after nitrogen bubbling show that lifetimes are raised by a value of 2—3 when greater attention is given to removal of oxygen from the solution. The value τ_m = 1.15 μs for $Ru(bipy)_3^{2+}$ in EtOH–MeOH compares with literature values measured in water of 0.66,[3] 0.58,[4] and 0.59 μs.[25]

Table 3. Solvent dependence of the quantum efficiency and absorption and emission maxima

Compound No.	Compound Substituent	Solvent	φ_m'	φ_m	$\lambda_{max.}$(abs.)/ nm	$\lambda_{max.}$(em.)/ nm
(**33**)	None	H_2O	0.033	0.062	452	640
		D_2O	0.058	0.089	451	635
		EtOH–MeOH	0.029	0.089	450	630
		Glycerol	0.099	0.127	452	625
		CH_3CN	0.032	0.122	450	630
		DMSO	0.050	0.131	454	645
		DMF	0.028	0.129	453	640
(**34**)	Perdeuterio	H_2O	0.036	0.071	451	640
		D_2O	0.067	0.106	450	635
		EtOH–MeOH	0.031	0.096	448	630
(**45**)	4,4′-Diphenyl	H_2O	0.070	0.112	473	650
		EtOH–MeOH	0.058	0.306	473	635
		Glycerol	0.237	0.243	476	640
		CH_3CN	0.033	0.291	473	640
		DMSO	0.082	0.246	478	655
		DMF	0.043	0.234	477	650

Table 4. Quantum efficiency and absorption and emission maxima for $Ru(bipy)_3^{2+}$ complexes in plastic

Compound No.	Compound Substituents	Plastic[a]	Approximate concentration (M)	φ_m[b]	$\lambda_{max.}$(abs.)/ nm	$\lambda_{max.}$(em.)/ nm
(**33**)	None	PVA	6.0×10^{5}	0.237	450	630
(**34**)	Perdeuterio	PVA	6.2×10^{5}	0.404	448	630
		PVC	1.9×10^{4}	0.356	450	620
		PMMA	8.9×10^{4}	0.230	448	630
(**43**)	4,4′-Dibromo	PVA	8.0×10^{5}	0.118	463	645
(**45**)	4,4′-Diphenyl	PVC	7.6×10^{5}	0.544	475	610
		PVC	6.0×10^{4}	0.535	475	610
(**46**)	4,4′-Distyryl	PVC		0.094	485	665

[a] PVA = poly(vinyl acetate), PVC = poly(vinyl chloride), PMMA = poly(methyl methacrylate). [b] Measured relative to Rhodamine B, $\varphi_m = 0.73$.

Medium Effects on φ_m.—The apparent contrast between φ_m for the parent complex (**33**) in EtOH–MeOH, Table 2, and in aqueous media[4] encouraged us to investigate further the variation of the quantum yield with solvent. Results obtained for (**33**), the perdeuterio analogue (**34**), and the 4,4′-diphenyl-substituted derivative (**45**) are summarised in Table 3. As before, φ_m' and φ_m values refer to data measured before and after deaeration, respectively. The φ_m values obtained for (**33**) and (**34**) in H_2O and D_2O are somewhat larger than those reported by Van Houten and Watts.[4] Both sets of data show, however, that deuteriation of the solvent has a larger effect on the quantum yield than ligand deuteriation, demonstrating the importance of radiationless dissipation of energy through the O–H vibrations of the medium.

For all three complexes φ_m' is lower in EtOH–MeOH than in water. However, following vacuum deaeration, the quantum yields become higher (φ_m values) in the alcoholic medium. This reversal arises presumably from greater oxygen quenching (under the conditions of the φ_m' measurements) in EtOH–MeOH; we note that the solubility of oxygen in these alcohols is about eight times higher than in water.[26] Oxygen solubility is expected to be a factor in determining the ratio $\varphi_m : \varphi_m'$ for the parent complex and the diphenyl derivative in the other solvents studied, Table 3. However, oxygen quenching may also be a function of solvent viscosity, a view which finds support in the low $\varphi_m : \varphi_m'$ ratio obtained for the most viscous solvent, glycerol. Under conditions of no oxygen quenching and in solvents other than water, the quantum yield shows a modest dependence on the medium. Trends are qualitatively comparable with those reported recently by Nakamaru.[27] Though EtOH–MeOH and glycerol contain O–H bonds there is a greater number of C–H bonds and the principal mode of energy dissipation among the non-aqueous solvents may well be *via* C–H bond vibrations. However, in the absence of values of the non-radiative transition rates we do not wish to pursue this argument further at the present time. Furthermore, the sensitivity of $\lambda_{max.}$(abs.) and $\lambda_{max.}$(em.) to change in solvent indicates that the nature, and presumably polarity, of the solvation sphere is a second factor which affects the finer detail of the photophysical processes.

Five complexes were incorporated into plastic as part of the programme to evaluate them for application in LSC devices, Table 4. The emission spectra are broadly similar to those recorded of solutions but there is some indication of a shift in the emission band to shorter wavelength. There is a general enhancement of the quantum yield over those measured for the solution phase and the data for the perdeuterio derivative (**34**) show variations from one plastic to another. Values for the parent compound (**33**) and the 4,4′-diphenyl-substituted analogue (**45**) are somewhat lower than those obtained in poly(methyl methacrylate) (PMMA) at 77 K by Hager and Crosby.[6]

Of particular note is the observation that the quantum efficiencies in poly(vinyl chloride) (PVC) are significantly higher than in PMMA. In view of the finding that the solvent vibrational properties play an important role in the deactivating process it is tempting to conclude that it is the lower density of high frequency vibrational modes in PVC, particularly the absence of methyl C–H bonds, that is responsible for higher quantum efficiencies in this medium.

Conclusions

It has been demonstrated that the absorption bands arising from the $d \longrightarrow \pi^*$ charge-transfer transitions and the associated emission bands have energies, transition intensities, and quantum efficiencies which are sensitive to the nature and site of substitution of ring substituents. Substituents in the 4- and 4,4′-series all shift the bands to longer wavelengths compared with the unsubstituted parent compound. The quantum efficiencies of luminescence are dependent upon vacuum deaeration and also sensitively dependent upon the nature of the medium in which the complexes are dissolved. A complex with a quantum efficiency greater than 0.5 in plastic medium has been discovered. This, together with the considerable apparent Stokes shift, suggests that some of these materials may find a useful application as dyes for luminescent solar concentrators and for fluorescence-activated liquid crystal displays.

Experimental

Materials.—2,2′-Bipyridyl (**1**) and 4,4′-diphenyl-2,2′-bipyridyl were obtained as commercial samples. The following ligands were prepared using literature procedures: 4-benzyloxy-2,2′-bipyridyl[9] (**9**), m.p. 90—91 °C (lit.,[9] 92 °C), 4-amino-2,2′-bipyridyl[10] (**10**), m.p. 127 °C (lit.,[9] 129 °C), 4-dimethylamino-2,2′-bipyridyl[9] (**11**), m.p. 80 °C (lit.,[9] 100 °C) (Found: C, 72.35; H, 6.6; N, 21.0. Calc. for $C_{12}H_{13}N_3$: C, 72.3; H, 6.6; N, 21.0%), 4,4′-Dinitro-2,2′-bipyridyl[11] (**15**), m.p. 193—195 °C (lit.,[11] 191.5—194 °C), 4,4′-dibromo-2,2′-bipyridyl[11] (**17**), m.p. 138—139 °C (lit.,[11] 141—142 °C), 4,4′-diethoxy-2,2′-bipyridyl[11] (**18**), m.p. 118—121 °C (lit.,[11] 122 °C), 4,4′-diphenoxy-2,2′-bipyridyl[11] (**20**), m.p. 155—158 °C (lit.,[11] 156.5—157.5 °C), 4,4′-diamino-2,2′-bipyridyl[11] (**21**), m.p. 275—280 °C (lit.,[11] 277—278 °C), 4,4′-bis(diethylamino)-2,2′-bipyridyl[11] (**23**), m.p. 152 °C (lit.,[11] 155—156 °C), 4,4′-dimethyl-2,2′-bipyridyl[27] (**24**), m.p. 168—172 °C (lit.,[28] 171—172 °C), 4,4′-dibenzyl-2,2′-bipyridyl (**25**) under the conditions of ref. 28, yield 21%, m.p. 131—132 °C (lit.,[29] 133 °C), 5,5′-dimethyl-2,2′-bipyridyl[28] (**26**), m.p. 114—116 °C (lit.,[28] 114.5—115 °C), 4,4′-distyryl-2,2′-bipyridyl[28] (**27**), m.p. 266—268 °C (lit.,[28] 268.5—269.5 °C), 4,4′-bisethoxycarbonyl-2,2′-bipyridyl[30] (**28**), m.p. 157—158 °C (lit.,[30] 159—160.5 °C), 5,5′-bisethoxycarbonyl-2,2′-bipyridyl[28] (**29**), m.p. 148—149 °C (lit.,[28] 148—149 °C), 5,5′-diamino-2,2′-bipyridyl[31] (**30**), m.p. 205—206 °C (lit.,[31] 208—210 °C), 5,5′-bisacetamido-2,2′-bipyridyl[31] (**31**), m.p. 329 °C (lit.,[31] 331—333 °C), 5,5′-bis(dimethylamino)-2,2′-bipyridyl[32] (**32**), m.p. 225—229 °C (lit.,[32] 228—230 °C).

4-*Nitro*-2,2′-*bipyridyl* (**3**). 4-Nitro-2,2′-bipyridyl 1-oxide[33] (1 g) and triphenylphosphine (4 g) in chloroform (25 ml) were heated in a sealed tube, at 140 °C for 5 days. The solution was evaporated to dryness and the residue extracted with ether. The ether extracts were combined and evaporated to dryness, giving a residue which was chromatographed over silica (CH_2Cl_2 as eluant). The separated product (**3**) was recrystallised from ethanol (0.1 g, 11%), m.p. 118 °C (lit.,[9] 114 °C).

4-*Chloro*-2,2′-*bipyridyl* (**4**). 4-Nitro-2,2′-bipyridyl 1-oxide[34] (1 g) was refluxed with acetyl chloride (30 ml) for 1 h. The reaction mixture was cooled to 0 °C and phosphorus trichloride (5 ml) was added dropwise. The solution was heated to reflux for a further 2 h, cooled to room temperature, poured into ice (150 g), and neutralised (20% sodium hydroxide) to give a colourless precipitate which was extracted with dichloromethane (3 × 75 ml). The extracts were dried (Na_2SO_4) and evaporated to dryness to afford 4-chloro-2,2′-bipyridyl as colourless needles (0.8 g, 93%), m.p. 70—71 °C (from light petroleum) (lit.,[9] 84 °C) (Found: C, 62.9; H, 3.5; N, 14.7; Cl, 18.3. Calc. for $C_{10}H_7ClN_2$: C, 63.0; H, 3.7; N, 14.7; Cl, 18.6%).

4-*Bromo*-2,2′-*bipyridyl* (**5**). To a solution of 4-bromo-2,2′-bipyridyl 1-oxide[9] (0.9 g) in anhydrous chloroform (15 ml) at −5 °C was added phosphorus tribromide (4 ml). The mixture was refluxed with stirring for 2 h, cooled to room temperature, poured into ice (25 g), and neutralised (20% aqueous NaOH). The colourless precipitate was extracted with dichloromethane (3 × 50 ml). The extracts were dried (Na_2SO_4) and evaporated to dryness to afford 4-bromo-2,2′-bipyridyl as colourless needles (0.35 g, 41%), m.p. 51 °C (from H_2O–EtOH) (lit.,[9] 52 °C).

4-*Methoxy*-2,2′-*bipyridyl* (**7**). 4-Methoxy-2,2′-bipyridyl 1-oxide[9] was deoxygenated under the conditions used for 4-bromo-2,2′-bipyridyl 1-oxide but using phosphorus trichloride. 4-Methoxy-2,2′-bipyridyl (72%) was obtained as colourless needles, m.p. 65 °C (from light petroleum) (lit.,[9] 61 °C).

[$^2H_8$]-2,2′-*Bipyridyl* (**13**). 2,2′-Bipyridyl 1,1′-dioxide[11] (1.88 g) in NaOD–D_2O (1N in NaOD, 32 ml) was heated at 150 °C for 65 h in a sealed tube. From the filtered, concentrated, and cooled solution [$^2H_8$]-2,2′-bipyridyl 1,1′-dioxide (1.4 g) separated as colourless needles. The material was dissolved in phosphorus trichloride (10 ml) and heated under reflux for 1.5 h. The cooled, neutralised (20% aqueous KOH) solution was extracted with ether. The extracts were dried ($MgSO_4$), the solvent evaporated, and [$^2H_8$]-2,2′-bipyridyl (1.04 g), m.p. 65—69 °C, collected by sublimation of the residue. I.r. (Nujol), ν_{C-D} 2 250—2 295 cm^{-1}.

4,4′-*Dichloro*-2,2′-*bipyridyl* (**16**). 4,4′-Dinitro-2,2′-bipyridyl 1,1′-dioxide[11] (0.5 g) was heated with acetyl chloride (30 ml) for 1 h at reflux. To the chilled solution at 0 °C was added phosphorus trichloride (5 ml). The mixture was heated under reflux for 2 h, cooled to room temperature, poured onto ice (100 g), and neutralised (30% NaOH). The colourless precipitate was extracted with dichloromethane (2 × 100 ml). The organic solution was dried ($MgSO_4$) and the solvent evaporated to afford 4,4′-dichloro-2,2′-bipyridyl (0.34 g, 84%), m.p. 131—132 °C, as colourless plates (from aqueous EtOH).

4,4′-*Dibenzyloxy*-2,2′-*bipyridyl* (**19**). 4,4′-Dibenzyloxy-2,2′-bipyridyl 1,1′-dioxide[12] (0.5 g) was deoxygenated using phosphorus trichloride (15 ml) in chloroform (50 ml), following the procedure for (**5**) above. 4,4′-*Dibenzyloxy*-2,2′-*bipyridyl* (0.35 g, 76%), m.p. 194—196 °C, was obtained as buff coloured needles (from EtOH) (Found: C, 78.4; H, 5.55; N, 7.4. $C_{24}H_{20}N_2O_2 \cdot H_2O$ requires C, 78.2; H, 5.5; N, 7.6%).

4,4′-*Bisacetamido*-2,2′-*bipyridyl* (**22**). 4,4′-Diamino-2,2′-bipyridyl (**21**) was acylated under standard conditions using glacial acetic acid (4 ml) in acetic anhydride (20 ml) at reflux temperature for 1 h. 4,4-*Bisacetamido*-2,2′-*bipyridyl* (1.5 g, 95%), m.p. 320 °C (from H_2O), was isolated as colourless needles (Found: C, 62.0; H, 5.2; N, 20.6. $C_{14}H_{14}N_4O_2$ requires C, 62.2; H, 5.2; N, 20.7%).

Complexes.—Ligands were chelated using the following procedures, see Table 1.

Method A. In a typical experiment, ruthenium trichloride monohydrate (0.1 g) and [$^2H_8$]-2,2′-bipyridyl (0.88 g) were heated to 250—260 °C for 4.5 h. Excess of ligand and some impurities were removed from the dark brown mixture by exhaustive washing with hot toluene. The remaining yellow-brown residue was extracted with D_2O and the aqueous solution evaporated until crystallisation commenced. The complex was collected and recrystallised one further time from D_2O; yield 0.2 g (57% based on $RuCl_3 \cdot H_2O$).

Method B. In a typical procedure, a solution of ruthenium trichloride monohydrate (0.50 g) and 4,4′-diethoxy-2,2′-bipyridyl (2.59 g) in 95% ethanol (300 ml) was heated under reflux for 72 h. The deep orange-red solution was filtered hot and evaporated to a small volume. Water (60 ml) was added and the solution extracted with toluene to remove excess of ligand. Potassium iodide solution was added to the aqueous solution and the precipitated *tris*-4,4′-*diethoxy*-2,2′-*bipyridylruthenous* *iodide* was collected by filtration and recrystallised from DMF–water. The preparation of **(54)** was worked up by precipitation of the complex as the chloride using sodium chloride, recrystallisation (from aqueous EtOH), followed by chromatography over alumina (CH_3CN as eluant).

In one variant, complexes **(41)** and **(42)** were prepared by treating the ligand with potassium aquapentachlororuthenate in refluxing ethanediol, with precipitation of the complex as the fluoroborate salt using $NaBF_4$. In a second variant, **(46)** was prepared from 4,4′-distyryl-2,2′-bipyridyl **(27)** and potassium aquapentachlororuthenate in refluxing glycerol with precipitation of the complex as the chloride using 6N-HCl.

Method C. In a typical experiment, a solution of potassium aquapentachlororuthenate(III) (0.186 g) in hot water (19 ml) containing one drop of 6N-HCl was added to a solution containing three equivalents of 4,4′-dibenzyl-2,2′-bipyridyl (0.50 g) in DMF (11 ml). The mixture was heated to reflux for 0.25 h and treated with phosphinic acid (30%, 4.5 ml) neutralised with 2N-NaOH (*ca.* 1.2 ml). The solution was maintained at reflux for a further 30 min, filtered hot, and treated with 6N-HCl (4 ml). The volume of solution was reduced by evaporation to encourage crystallisation. When cold, *tris*-4,4′-*dibenzyl*-2,2′-*bipyridylruthenous chloride* was collected by filtration, washed with water, and dried (100 °C at 0.1 mmHg).

In variants, complexes were precipitated as the iodide by addition of potassium iodide.

Bis-2,2′-bipyridylruthenous chloride. A solution of ruthenium trichloride trihydrate (1.56 g) and 2,2′-bipyridyl (1.87 g) in DMF (80 ml) was heated under reflux for 3 h. The purple solution was reduced in volume using a rotavapor and left to stand at 0 °C overnight. The black crystals were filtered off, washed well with cold water, and extracted into boiling water. Lithium chloride (30 g) was added to the hot solution which was then cooled to 0 °C. The bis-bipyridyl complex was collected by filtration, washed with cold water, and dried *in vacuo* (P_2O_5) (2.3 g, 78%).

4,4′-Diphenyl-2,2′-bipyridyl-bis-2,2′-bipyridylruthenous iodide. A solution of bis-2,2′-bipyridylruthenous chloride (0.43 g) from above and 4,4′-diphenyl-2,2′-bipyridyl (0.27 g) in absolute ethanol (200 ml) was heated to reflux for 16 h. Addition of excess of potassium iodide solution to the red alcoholic solution caused the precipitation of an orange-red solid. *Bis*-2,2′-*bipyridyl* 4,4′-*diphenyl*-2,2′-*bipyridylruthenous iodide* was filtered off, washed with a small volume of water, and dried (90 °C at 0.1 mmHg) (0.43 g, 47%).

Bis-4,4′-diphenyl-2,2′-bipyridylruthenous chloride. Ruthenium trichloride trihydrate (0.78 g) and 4,4′-diphenyl-2,2′-bipyridyl (1.85 g) were allowed to react together in refluxing DMF for 3 h. Lithium chloride (15 g) dissolved in water was then added and the purple-black complex filtered off, washed with water, and dried (100 °C at 0.1 mmHg) (2.33 g, 95%).

2,2′-Bipyridyl-bis-4,4′-diphenyl-2,2′-bipyridylruthenous iodide. Bis-4,4′-diphenyl-2,2′-bipyridylruthenous chloride (0.6 g) and 2,2′-bipyridyl (0.11 g) were heated in refluxing ethanol for 16 h. The solution was filtered hot and to the filtrate was added excess of potassium iodide solution. The red precipitate of *bis*-4,4′-*diphenyl*-2,2′-*bipyridylruthenous iodide* was collected by filtration, washed with water, and dried (60 °C at 0.1 mmHg) (0.53 g, 62%).

Incorporation of Materials into Plastic Films.—To viscous solutions of plastics [poly(vinyl acetate) (PVA) in ethanol, poly(methyl methacrylate) (PMMA) in chloroform, poly(vinyl chloride) (PVC) in chlorobenzene] was added with stirring the complex dissolved in the corresponding solvent (except for addition to PVC where a solvent such as acetone or acetonitrile was used). The resultant homogeneous solutions were contained in moulds and the solvent evaporated in air over several days, affording doped plastic film *ca.* 0.5—1 mm in thickness.

Spectroscopic Measurements.—Absorption spectra have been measured either with a Cary model 17 spectrophotometer or Pye–Unicam SP8-400 spectrophotometer.

Luminescence spectra were recorded on an instrument constructed in this laboratory consisting of the following major components. A source of monochromatic radiation is supplied by a 450 W xenon arc lamp, powered by a current-stabilised d.c. supply, in combination with a double-grating monochromator (D330/331, Hilger and Watts). The grating blaze is 300 nm. Order sorting and stray light control is achieved by Corning edge filters appropriately chosen. Luminescence from the sample is collected by suitable mirror optics and analysed by a monochromator (Monospek D600, Hilger and Watts) containing a single grating (102 × 102 mm, blaze wavelength 750 nm). Detection is made with a GaAs photomultiplier (RCA type C31034) cooled in a housing (Model TE-182TS-RF, Products for Research, Inc.). The signal is measured in the photon counting mode with a quantum photometer (type 9511, Brookdeal Electronics Ltd.) and displayed on a chart recorder.

The spectral response curve of the monochromator–photomultiplier combination was measured using the method described by Parker and Rees.[35] A thermopile (type FT 16.1 Hilger and Watts) was used to determine the photon output of the excitation monochromator. This was, in turn, employed as a source of known spectral distribution. Light from this monochromator was reflected with a plane mirror into the emission monochromator. A spectral sensitivity curve was constructed in this way and used to correct all luminescence spectra. The validity of the correction procedure was tested using luminescent materials with known fluorescence spectra.

Quantum efficiencies have been measured relative to Rhodamine B as a standard using the procedure of Melhuish.[33] For the determination of solution quantum efficiencies the standard and unknown solutions were placed in a 10 mm path Spectrosil cell which fitted into a holder rigidly held with respect to the excitation beam and emission collecting optics. Excitation was of the front face of the cell from which emission was also collected. The Rhodamine B standard was prepared from material twice recrystallised from ethanol made up in ethanol. The standard was fully aerobic. The unknown sample was placed in a special cell fitted with a side-arm through which evacuation could be effected and also with an ion gauge (type IG5G, Edwards Vacuum Products) so that the gas pressure above the solution could be measured. For de-aeration of the sample the following procedure was adopted. The sample was cooled to 77 K and the space above the frozen solid evacuated to 10^{-6} Torr as measured by the ion gauge within the sample space. The stopcock to the pump was closed and the solution allowed to warm to room temperature in order to degas into the space above it. The gas space was pumped before the sample was refrozen. This was found necessary to obtain quantum efficiencies that were independent of freeze–pump–thaw cycles. If the sample is frozen in the presence of any oxygen above its surface then oxygen becomes trapped in the solution and is impossible to remove by pumping. Hence the procedure described was adopted. Since some loss of solvent inevitably takes place when the solution is pumped in the fluid state it is necessary to monitor carefully the absorbance of the sample solution in order to determine the change in concentration brought about by pumping. Samples were degassed a sufficient number of times until a constant pressure reading of 10^{-6} Torr had been achieved at the ion gauge.

Quantum efficiencies of dyes in plastic sheet have been determined in the following manner. A piece of plastic sheet was mounted in a holder that held a slit before and behind the sample. Excitation light was passed through the sheet from the rear and emission was collected from the slit at the front of the sample. The sheet was replaced by a standard of Rhodamine B solution in a 1 mm path cell. The same slits were present before and behind the cell. In this way the collection and excitation geometries of sample and standard were made equivalent. The absorbances of the plastic sheets were adjusted during preparation to give values low enough to avoid re-absorption or inner filter errors.

A quantum efficiency for Rhodamine B of 0.73 has been assumed throughout this work.[35,36] Two values have been reported for the efficiency of this standard namely 0.97, when excited at 535 nm in ethanol, and 0.73, relative to quinine bisulphate in dilute H_2SO_4, excited at 366 nm.[36] We take the lower value to be the more prudent choice for our purposes.

Luminescence lifetime measurements were made at the Royal Signals and Radar Establishment, Great Malvern, using the following apparatus assembled in the laboratory. The excitation source is a nitrogen laser (Lambda Physik) operating at 10 KV with 30 pulses per second. The excitation wavelength is 337 nm. The exciting beam is led to the sample with plane mirrors and focused by a convex lens onto the centre of the sample. The emitted light is collected at 90° to the exciting beam *via* a filter, to remove the exciting light, and a lens by a grating monochromator (SPEX minimate). The detector is a photomultiplier (EMI 9569 QB). The photocurrent is led to earth *via* a 470 ohm resistor to generate a voltage which is monitored by a field effect transistor probe (Tektronic 6201). The latter serves as a buffer amplifier of gain unity and enables the detected signal to be viewed without distorting the original wave-form. The detected signal is observed on an oscilloscope and optimised by scanning the emission monochromator. The signal amplitude required was obtained by adjustment of the high tension voltage (600—800 V) of the photomultiplier power supply. The detected waveform is fed to a transient recorder (Biomation 1024 channels) and then to a Nicolet signal averager and finally to an $X-Y$ plotter. The transient recorder is triggered by the laser pulses. Curves were plotted as intensity (I) *versus* time and replotted as log I against time. In all cases exponential curves were obtained and lifetimes quoted (τ_m) are expressed as the time for the signal to fall to $1/e$ of its maximum value.

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