Luminescent Metal Complexes. Part 2.[1] A Model for the Luminescence Properties of the Tris-chelates of Substituted 2,2'-Bipyridyls with Ruthenium(II)

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A three-state model is presented to explain the variations in the quantum efficiencies within a series of complexes formed from 26 2,2'-bipyridyl ligands with ruthenium(II). The radiative rate constants are shown to vary with the molar absorptivity for the singlet $d \longrightarrow \pi^*$ transitions. Ln k_N (non-radiative rate constant) for complexes bearing $+M$ $-I$ and $+M$ $+I$ groups at the 4- and 4,4'-positions of the ligands vary with the energy gap. A parallel is noted between the metal-to-ligand charge-transfer process and the charge-transfer transition from a metal ion impurity to the conducting band of a semiconducting lattice.

In the preceding paper[1] we have described the synthesis of a wide range of tris-chelate complexes of the general type $Ru(bipy)_3^{2+}$ in which substituents have been introduced into the 2,2'-bipyridyl ring systems. Also reported are the luminescence properties of these complexes under a variety of different environmental conditions, that is, in a variety of solvents and plastic matrices, and in the absence and presence of oxygen. Our objective was to find a compound with a high luminous efficiency at room temperature for various photophysical applications. However, having amassed a comprehensive set of spectroscopic parameters including molar absorptivities, quantum efficiencies, and lifetimes we have noted some systematic variations in these properties. In this paper we provide an interpretation of these figures using a simplifed three-state model. We have been particularly interested in understanding the substituent effects upon the room temperature luminous efficiencies.

The luminescence properties of $Ru(bipy)_3^{2+}$ and closely related compounds have been intensively investigated by other workers.[2] Studies have been made in ethanol–methanol glasses, poly(methyl methacrylate) matrices, and single crystals over the temperature range 77—*ca.* 1.6 K.[3–10] The quantum yields and decay times showed a marked change with temperature, the former dropping sharply and the latter rising by about two orders of magnitude. All compounds examined behaved in a similar qualitative manner. The largest change in decay rate takes place below *ca.* 10 K. It is now clear that there are a set of closely spaced energy states that provide a manifold of emitting levels with very different individual decay times. It is the change in relative population of these levels which leads to the temperature dependence of the luminescence parameters. There is disagreement about the exact ordering and symmetry properties of the emitting levels.[2,9–13] However, it is accepted that the manifold of emitting states are the formally spin-forbidden metal-to-ligand charge-transfer (CT) states. The spin-allowed counterparts of these transitions lie in the visible region of the spectrum and are responsible for the colour of these compounds.

In view of the controversy about the detailed nature of the emitting manifold we have interpreted our data on the basis of a simplifed three-state model in order to understand the luminescence properties at room temperature. There is detailed evidence to suggest that the level ordering both within the singlet-allowed transition and the triplet manifold is invariant to ligand substitution. Thus the form of the temperature dependence of the luminescence lifetimes and the quantum efficiencies down to 1.6 K are of the same qualitative nature.[3–7]

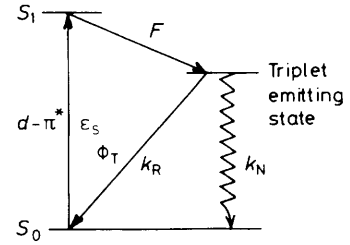

Figure 1. Schematic representation of the three-state model; terms defined in text

We have extended these measurements to a number of the new compounds reported in the preceding paper and find a similar behaviour.[14] The polarised crystal spectra of some compounds have been measured and suggested an unchanging pattern. We have also surveyed the magnetic circular dichroism (m.c.d.) spectra of a range of our new compounds and compared them with the spectra of the unsubstituted derivative.[14] In low-temperature (4.2 K) alcoholic glasses the m.c.d. spectra show a number of well resolved bands which have been assigned satisfactorily. The spectra confirm that the level ordering of the singlets remain unchanged.

As a result we expect that in the high-temperature regime there will be a systematic and gradual, rather than an abrupt, change in the luminescence parameters with change in ligand substituents. Such systematic variations are indeed observed and form the basis of the interpretation given here.

Discussion

Model for the Luminescence Properties.—The measured quantities are the quantum efficiency of luminescence, φ_m, the measured lifetime, τ_m, and the molar absorptivity of the main absorption band, ε_S. A simplifed three-state model is used to relate these experimental parameters to one another, Figure 1. It is recognised that the states shown as singlets and triplets have several components. Thus they should be interpreted as closely spaced manifolds of energy levels. Additional parameters are defined with the aid of this model. They are F, the fractional intersystem crossing probability, k_R, the radiative transition rate, and k_N, the non-radiative transition rate from the triplet manifold. Hence relationship (1) holds, under conditions where

$$\varphi_m = \varphi_T F = k_R \tau_m F \qquad (1)$$

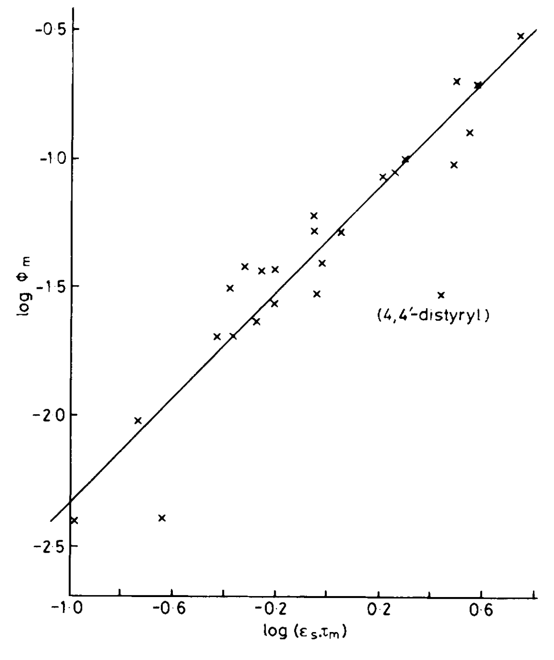

Figure 2. Plot of log φ_m against log ($\varepsilon_S.\tau_m$)

oxygen quenching and self quenching are absent, where φ_T is the quantum efficiency of triplet emission and $\tau_m = (k_R + k_N)^{-1}$. By rearrangement the relationships (2) and (3) are obtained.

$$\varphi_m/\tau_m = k_R \cdot F \qquad (2)$$

$$(1 - \varphi_m)/\tau_m = F \cdot k_N + (1 - F)/\tau_m \qquad (3)$$

Only φ_m and τ_m relate directly to the efficiency of emission of the triplet whereas there are three unknowns, namely, k_R, k_N, and F. Hence there are insufficient data to determine all the required parameters. Therefore we make some assumptions in order to proceed further.

We assume that spin–orbit interactions are constant across the complete series of compounds. This is not unreasonable since the substitutions made in the 2,2'-bipyridyl ring system all involve light atoms. We further assume that the triplet intensity arises from spin–orbit mixing with the lowest energy singlet states. This assumption has been verified with the aid of the magnetic circular dichroism (m.c.d.) spectra of some members of the series.[14]

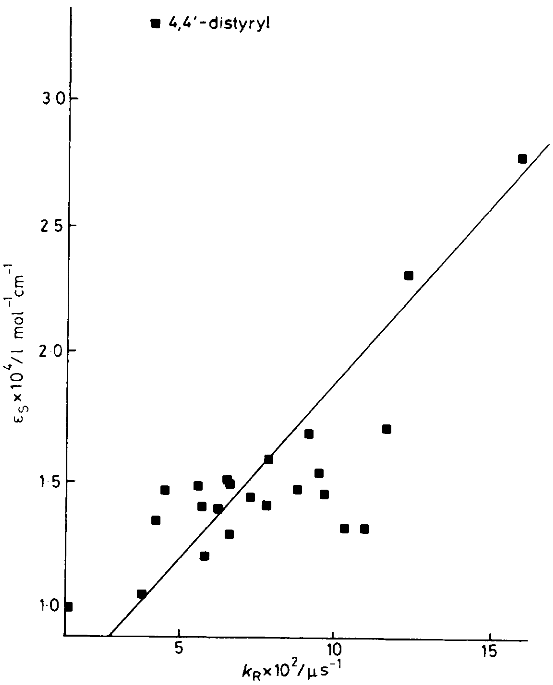

Figure 3. Plot of ε_S against k_R

Table. Radiative and non-radiative lifetimes τ_R, τ_N and rate constants k_R, k_N for Ru^{II} tris-2,2'-bipyridyl complexes measured in ethanol–methanol (4:1) solution

Substituents	τ_R/μs	$k_R \times 10^2$/μs^{-1}	τ_N/μs	$k_N \times 10^2$/μs^{-1}
None	12.83	7.8	1.26	79.1
4-Bromo	15.77	6.3	0.87	115.6
4-Chloro	22.37	4.5	0.69	144.7
4-Methoxy	17.20	5.8	0.70	143.4
4-Benzyloxy	11.32	8.8	0.63	157.8
4-Amino	16.67	6.0	0.36	279.7
4-Dimethylamino	15.22	6.6	0.36	279.1
4,4'-Dinitro	*ca.* 125	0.8	0.25	399.2
4,4'-Bisethoxycarbonyl	8.25	12.1	2.06	48.5
4,4'-Dibromo	8.67	11.5	0.56	178.8
4,4'-Dichloro	11.11	9.0	0.42	235.3
4,4'-Diphenyl	6.37	15.7	2.81	35.6
4,4'-Distyryl	24.00	4.2	0.74	134.7
4,4'-Dibenzyl	12.76	7.8	1.39	72.2
4,4'-Dimethyl	11.05	9.1	1.04	95.9
4,4'-Diphenoxy	9.21	10.9	0.36	276.8
4,4'-Diethoxy	15.00	6.7	0.31	326.6
4,4'-Dibenzyloxy	9.69	10.3	0.32	312.3
4,4'-Bisacetamido	15.19	6.6	0.42	237.3
4,4'-Diamino	25.00	4.0	0.10	996.0
4,4'-Bis(diethylamino)	13.00	7.7	0.13	761.5
5,5'-Bisethoxycarbonyl	57.50	1.7	0.23	433.4
5,5'-Dimethyl	9.46	10.6	0.36	274.5
5,5'-Bisacetamido	19.05	5.3	2.75	36.4
None, (4,4'-diPh)$_2$	21.68	4.6	2.35	42.5
(None)$_2$, 4,4'-diPh	9.77	10.2	2.40	41.7

Then we can write expression (4), where k is a constant

$$k_R \approx k\varepsilon_S \qquad (4)$$

related to the magnitude of spin–orbit coupling. Using the relationship given earlier we obtain expression (5). Therefore a

$$\varphi_m \approx k(\varepsilon_S \cdot \tau_m)F \qquad (5)$$

plot of log φ_m against log ($\varepsilon_S.\tau_m$) will be a line of unit slope and intercept log $k.F$, if both k and F are constant. The data for 25 compounds are plotted in Figure 2. A clear correlation exists with all the compounds, except for the complex derived from 4,4'-distyryl-2,2'-bipyridyl, falling close to the line of slope unity. A linear least-squares fit of the points, excluding the styryl derivative, gave a line of gradient 1.02, with a correlation of 0.976. We conclude therefore that the assumption of constant intersystem crossing probability for all the compounds (except possibly the styryl derivative) is valid. Demas and Crosby[3] reported that this parameter is unity for the parent (unsubstituted) complex, a conclusion based primarily on the quantum efficiency of luminescence being independent of excitation wavelength. Taking F as unity over the whole series enables us to equate φ_m with φ_T and hence to calculate k_R and k_N, see the Table, from the empirical parameters φ_m and τ_m

reported in the preceding paper.[1] In view of the demonstration of the approximate constancy of both F and k (above) it is valid to seek trends in the values of k_N and k_R which depend upon the electronic properties of the substituents. We discuss these dependencies in the subsequent sections.

k_R *Values.*—In spite of uncertainties in some of the k_R data, particularly for those compounds having low φ_m or τ_m values, there is a reasonable correlation between k_R and ε_S, Figure 3. This is to be expected from the preceding discussion. Since spin–orbit coupling between the singlet and triplet states appears to remain constant, the value k_R should depend linearly on ε_S to a first approximation. As with the log φ_m *versus* log $\varepsilon_S.\tau_m$ plot, the styryl derivative falls well clear of the most acceptable straight line. However, for the remainder of the series we conclude that the substituent dependence of k_R is essentially a manifestation of the effect of the substituent on ε_S, a discussion of which was presented in the preceding paper.

The lowest k_R value reported is that for the complex of 4,4′-dinitro-2,2′-bipyridyl. This compound is not included on the plot because insufficient material was available at the later stages of the project to measure ε_S with accuracy. A low value would be expected should the compound behave normally.

k_N *Values.*—Inspection of the Table shows that the values of k_N vary over a markedly wider range than those of k_R. Therefore non-radiative relaxation pathways play a major role in governing the variation in the quantum yield. The compounds which have the highest value of k_N are, in general, those in which the emission band is shifted to longer wavelength. This suggested that an energy gap may be operating as has been demonstrated by Meyer and his co-workers for a series of Os^{II} bis-2,2′-bipyridyl and bis-1,10-phenanthroline compounds.[15]

The energy gap law[16] predicts that radiationless processes are facilitated by a lowering of the energy gap between the excited and ground states. It is based upon a model of radiationless decay which is largely determined by vibrational overlap between the ground and excited states. Thus k_N is a function of parameters which include the electron tunnelling matrix element, the frequency of the de-activating vibrational mode, and the energy gap. For a series of closely related compounds a linear correlation is expected between ln k_N and the emission energy. Such a plot is shown in Figure 4. There is an obvious correlation for the complexes of the ligands substituted in the 4- and 4,4′-positions with $+M$ $-I$ atoms or groups and this extends also to the methyl group (correlation coefficient 0.951, number of points 16). We conclude therefore that within this sub-series of complexes the effect of the substituent on the rate of non-radiative decay is primarily a consequence of the substituent effect upon the energy of the emitting state(s). As discussed in Part 1,[1] the position of both $\lambda_{max.}$(em.) and $\lambda_{max.}$(abs.) are particularly sensitive to the mesomeric electron-donating capabilities of the substituent.

There are a number of assumptions inherent in the derivation of the energy gap law expression. One important assumption is that the electron tunnelling matrix element is constant or nearly so for a given series of complexes.[15] It has been estimated that for the series of bis-complexes of bipyridyl or phenanthroline with osmium(II) the variation in the electron tunnelling matrix element is too small to affect the linearity of the energy gap law plot.[15] In the present series it appears that 5,5′-substituents lead to a different value of the tunnelling matrix element from that of the 4,4′-substituents. The other complexes which lie off the line are those bearing 4,4′-substituents which extend substantially the conjugation of the π system (*i.e.*, styryl, phenyl, ethoxycarbonyl, and nitro groups). We return to discussion of these below.

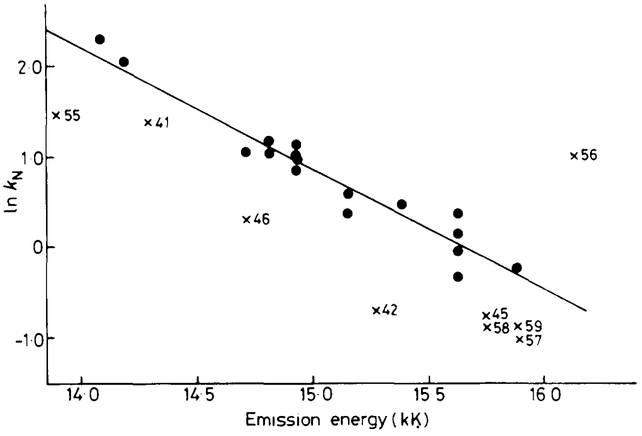

Figure 4. Plot of ln k_N against emission energy (1 kK = 1 000 cm^{-1}). Line corresponds to a correlation through points, (●), for the parent compound and derivatives bearing $+M$ $-$ I and $+M$ $+$ I substituents at the 4- and 4,4′-sites (17 points, slope −1.36, correlation coefficient 0.967). Points denoted × are for complexes substituted thus: (**41**) 4,4′-dinitro; (**42**) 4,4′-bisethoxycarbonyl; (**45**) 4,4′-diphenyl; (**46**) 4,4′-distyryl; (**55**) 5,5′-bisethoxycarbonyl; (**56**) 5,5′-dimethyl; (**57**) 5,5′-diacetamido; (**58**) none, (4,4′-diphenyl)$_2$; (**59**) (none)$_2$, 4,4′-diphenyl; (numbering as in ref. 1)

We note that the gradient of the line in Figure 4 is −1.36, which can be compared with a value of −0.9 obtained by Meyer and co-workers[15] for the Os^{II} complexes referred to above. These workers argued that the dominant deactivating mode is likely to be a vibrational frequency of *ca.* 1 300 cm^{-1}, a skeletal stretching mode of the ligand which appears strongly in the low-temperature emission spectrum and is therefore strongly coupled to the electronic transition giving rise to the emission. A vibrational progression of similar frequency is also seen in the low-temperature luminescence spectra of the compounds investigated here.[14] It seems likely that the same modes are active in dissipating the electronic excitation energy.

In aromatic hydrocarbons it is the highest frequency vibrational modes, that is the C–H stretch at *ca.* 3 000 cm^{-1}, which are primarily responsible for dissipating the electronic excitation energy.[16] As a consequence there is a large deuteron effect on the k_N values for these organic systems.[16] There is no such marked isotope effect for the present series of compounds when, for example, the bipyridyl ring is per-deuteriated.[1] This observation was first reported for $Ru(bipy)_3{}^{2+}$ by Van Houten and Watts,[17] and is confirmed in this work. This shows that C–H modes of the heteroaromatic ring system are not effective as accepting modes. This is most surprising and presumably implies that the electron coupling with the C–H modes is extremely weak.

There is however a marked solvent dependence of the quantum efficiency with a change of solvent from H_2O to D_2O causing an increase in quantum yield for the parent complex of 140%. Hence the vibrational modes of the solvent play a most significant role in the deactivating process. The importance of the medium is also apparent from data obtained in various other solvents and may be a contributing factor to the general enhancement of the quantum yields in plastic medium compared with the solution phase.[1]

A Phenomenological Model of the Rate Law.—The nature of the low lying emitting states of $Ru(bipy)_3{}^{2+}$ and related complexes is the subject of debate between two groups of workers.[2,13] Both agree that the emitting manifold consists of a number of closely spaced electronic states each with rather different radiative lifetimes. However, there is sharp disagreement about the number of states involved and also about the orbital origins of them. We have designated this manifold of states 'triplets' and have treated it as a set of thermally averaged states whose relative thermal populations stay invariant to substituent at room temperature.

One interesting aspect of the Hipps–Crosby model is that it suggests an excited state in which a $Ru^{3+}(d^5)$ core is weakly coupled to the excited electron occupying an orbital of large radius, extending over the three bipyridyl ligands. This picture of a transition metal impurity embedded at the centre of a large molecular framework is physically analogous to the situation of isolated transition metal impurities in covalent semiconductor crystals, where the semiconductor lattice may be considered as an infinitely large ligand system. In that case the crystal conduction band (CB) is formed from antibonding orbital combinations in the semiconductor lattice, and is therefore equivalent to the antibonding orbital combinations in the bipyridyl complexes. Accordingly the excitation proposed by Hipps and Crosby, equation (6), is formally analogous to

$$Ru^{2+}(d^6) \longrightarrow [Ru^{3+}(d^5)]\,.\,e(\text{ligand }\psi) \qquad (6)$$

impurity-to-conduction band charge-transfer transitions recently reported by one of us for Co^{2+} impurities in the semiconductor ZnSe, equation (7).[18] The magneto-optical

$$Co^{2+}(d^7) \longrightarrow [Co^{3+}(d^6)]\,.\,e(\text{CB}) \qquad (7)$$

properties of the excited state in the latter case have been interpreted in terms of a weakly localised electron interacting with the residual $Co^{3+}(d^6)$ core *via* a small exchange interaction.[19] The success of the weak coupling model in this case makes more plausible the corresponding Hipps–Crosby model for $Ru(bipy)_3^{2+}$ complexes. The ordering of the lowest excited states in all the complexes is determined by a weak interaction between the $Ru^{3+}(d^5)$ core and an excited electron in a large-radius orbital of ψ-symmetry, and hence the state ordering is expected to be relatively insensitive to ligand substituents, as observed. The effect of interaction with the heavy metal core is to mix, *via* spin–orbit coupling, excitations involving metal orbitals of $t_2(a_1)$ and $t_2(e)$ character, and hence to make partially allowed the otherwise forbidden $\psi(a_1) \longrightarrow t_1(a_1)$ lowest energy transition. Furthermore, if the core-electron coupling is weak, only small splittings of the excited configurations will result which accounts for the steep temperature dependence of the measured lifetimes observed only at very low temperature.[5,8,13]

The parallel we wish to emphasise between the nature of the metal to ligand $d \longrightarrow \pi^*$ charge-transfer transition and a charge-transfer transition involving a metal ion impurity in a conducting lattice provides a basis for rationalising the anomalous behaviour of compounds where the substituents extend the conjugation. The excitation process transfers an electron from a metal to a ligand orbital, creating a 'hole' in the t_2 shell to produce the $Ru^{3+}(t_2{}^5)$ core. It is likely that electron-withdrawing groups in the 4-position and extended conjugation will tend to increase the spatial separation between the density of the excited electron and the density of the 'hole' left on the ruthenium ion. We have invoked this spatial effect (see Part 1 [1]) and suggested that it accounts for an increase in the transfer length, $|R|$, which appears in the 'transfer term' for the magnitude of the charge-transfer intensity. In semiconductor crystals it is well known that the rate of recombination of electrons and holes spatially separated in the lattice becomes smaller as the spatial separation increases, because of a decrease in wavefunction overlap.[20] The dependence on distance of electron–hole separation often takes an exponential form, equation (8),[20] where W_r is the observed rate of recombination

$$W_r = W_o e^{-r/r_o} \qquad (8)$$

of electrons and holes separated by a distance r, and W_o and r_o are parameters determined by the detailed nature of the wavefunctions.

We suggest that a similar phenomenon can be expected in the case of the excited states of the $Ru(bipy)_3^{2+}$ complexes. For simplicity we shall assume that the rate of recombination of the excited electron with the hole on the Ru^{3+} core, which determines k_N, also depends exponentially on the spatial separation of electron and hole. We further suppose that this spatial separation is proportional to $|R|$, so that the non-radiative electron–hole recombination rate takes the form of equation (9).

$$k_N = W_o' e^{R\,r_o} \qquad (9)$$

The term W_o' now includes the energy-gap dependence, equation (10), where E_M is the energy of the emitting state.

$$W_o' = k_N{}^o e^{\gamma E_M} \qquad (10)$$

Hence we can write a phenomenological rate expression for k_N as given in equation (11). The term in brackets represents the

$$k_N = [k_N{}^o e^{R/R_o}]\, e^{\gamma E_M} \qquad (11)$$

electronic (tunnelling) matrix element, and includes a dependence on distance of separation $|R|$ of electron and hole in the excited state. When R exceeds some critical separation R_o, the rate tends to decrease rapidly with increasing separation R; when $R < R_o$ the tunnelling rate tends to a constant value $k_N{}^o$. The last term accounts for the energy-gap law demonstrated above. The energy gap determines the general trend in values of k_N throughout the series of complexes, but for those compounds where substituents tend to increase the electron–hole separation in the excited state beyond some average value R_o the non-radiative rate can be significantly decreased through a reduction in the electronic (tunnelling) matrix element *via* the term e^{R/R_o}.

Conclusions

We draw together our conclusions as follows.

1. The three-level model proposed gives an adequate description of variation of the room temperature values of ε_S, k_N, k_R, and φ_T with change in ligand substituent, provided that the intersystem crossing probability, F, and the spin–orbit coupling, k, remains constant.
2. The quantum efficiency, φ_T, is most sensitive to k_N.
3. k_N can be expressed as a product of terms, as given in equation (11). This involves an electronic term, which depends upon the unusual electronic (tunnelling) matrix element but also includes an exponential term to account for the dependence of the non-radiative rate upon the spatial separation of the electron and hole. The second term is the classic energy-gap law and is particularly important.
4. The substituents determine the energy gap, E_M (see Part 1 [1]).
5. With the exception of data for the styryl compound there is a correlation between ε_S and k_R.
6. The 4,4′-diphenyl and 4,4′-bisethoxycarbonyl substituted compounds show a high φ_T because the substituents (*i*) raise the value of ε_S and (*ii*) extend the conjugation so lowering k_N through a reduction in recombination (tunnelling) at large electron–hole separation.
7. Our formulation for the achievement of a high quantum efficiency in this series of compounds appears to be the simultaneous attainment of (*i*) a high-energy luminescence band, to increase the band gap and (*ii*) a high molar absorptivity. The requirement (*i*) prevents the utilisation of the

widest spectral range for absorption of solar photons in solar energy collector devices.

Acknowledgements

We thank the Ministry of Defence Procurement Executive (C.V.D.), for funds in support of this work and the S.E.R.C. for a research studentship (A. P. L.) and a C.A.S.E. award sponsored by R.S.R.E., Malvern (G. S. G. M.). We also thank Dr. K. J. Harrison (R.S.R.E., Malvern) for helpful discussion.

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Received 21*st July* 1983; *Paper* 3/1247