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ELECTRON TRANSFER REACTIONS INVOLVING LIGHT

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Electron Transfer Reactions Involving Light

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A substantial fraction of the chemical literature is currently dealing with reactions involving light. Electron transfer reactions, which are fundamental to all chemistry, are particularly important for the connection between chemistry and light. In this paper we will discuss the involvement of light in electron transfer reactions, with particular emphasis on the important role that can be played in these processes by suitable chemical species called sensitizers.

Fundamental Principles

Light can be involved in many electron transfer processes. The best known cases are those in which light is used as a *reactant* (photochemical reactions, eqn. (1)) (*1*), while less known are perhaps the cases in which light is generated as a *product* (chemiluminescence reactions, eqn. (2)) (*2*).

$$A + B + h\nu \rightarrow A^- + B^+ \tag{1}$$

$$A^- + B^+ \rightarrow A + B + h\nu \tag{2}$$

Of course, the involvement of light in both processes occurs via the formation of electronically excited states. Assuming that the light absorbing species in reaction 1 is reactant A and that light emitting species in reaction 2 is an excited state of A, $^*A$, the two processes may be reformulated as follows.[1]

$$A + B + h\nu \rightarrow {}^*A + B \rightarrow A^- + B^+ \tag{3}$$

$$A^- + B^+ \rightarrow {}^*A + B \rightarrow A + B + h\nu \tag{4}$$

An electronically excited state usually differs from the corresponding ground state molecule for having an electron in a high energy (antibonding) orbital and a hole in a low energy (bonding) orbital (*1*, *3*). For these reasons an excited state is expected to be both a better reductant and a better oxidant than the corresponding ground state molecule. To a first approximation, the reduction and oxidation potentials of an excited state are given by the following equations (*3*).

$$E^\circ({}^*A/A^-) = E^\circ(A/A^-) + E({}^*A) \tag{5}$$

$$E^\circ({}^*A/A^+) = E^\circ(A/A^+) + E({}^*A) \tag{6}$$

where $E^\circ(A/A^-)$ and $E^\circ(A/A^+)$ are the reduction and oxidation potentials of the ground state molecule and $E({}^*A)$ is the one electron potential corresponding to the zero-zero spectroscopic energy of the excited state. Thus, the excited states are potentially excellent redox reactants but their participation to redox processes may be prevented by their short lifetimes (*3*).[2]

Figure 1 shows schematically three possible energetic situations for electron transfer reactions (eqn. (7)) and underlines the

$$A + B \rightleftarrows A^- + B^+ \tag{7}$$

different roles that can be played by light when it is involved in these processes. The first scheme (Fig. 1a) corresponds to an exoergonic electron transfer process which requires a high activation energy. Light excitation of reactant A leads to an excited state ($^*A$) which, as we have seen above, is a much stronger oxidant than the corresponding ground state molecule. The reaction between $^*A$ and B is thus much more exoergonic than the reaction between A and B. Since the activation energy generally decreases with increasing exoergonicity, the reaction involving the excited state may be much faster than that involving the ground state. In these systems light is simply used to overcome a kinetic barrier and plays the role of a catalyst.

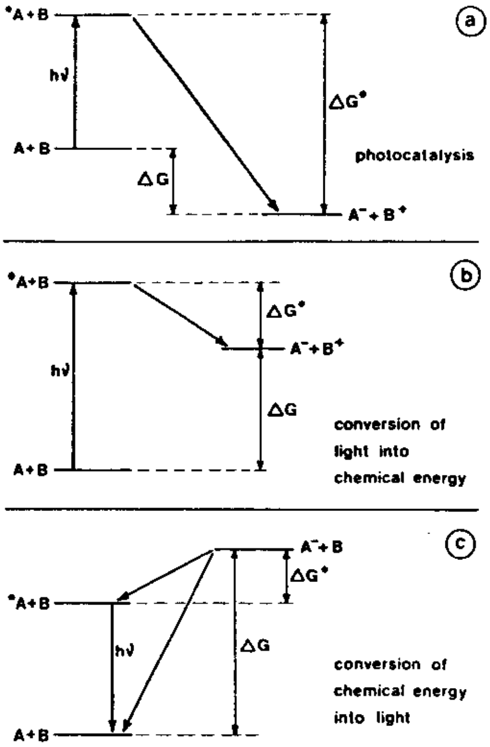

Figure 1. Schematic diagram showing three possible ways in which light can be involved in electron transfer processes.

The scheme of Figure 1b corresponds to the case of a strongly endoergonic reaction. In this case the equilibrium between A + B and $A^- + B^+$ (eqn. (7)) is strongly displaced toward the left-hand side in the dark. Light excitation causes the formation of $^*A$ which is an oxidant much stronger than A. Light can thus drive A + B to $A^- + B^+$ via $^*A$ + B and in such a process a fraction of light energy is converted into chemical energy of the products. When A^- and B^+ undergo the back electron transfer reaction leading to A + B the converted energy is released.

The third scheme (Fig. 1c) corresponds to the case in which the energy content of A^- and B^+ is not only higher than that of A + B, but also than that of $^*A$ + B. In such a case the reaction from A + B to $A^- + B^+$ can be driven neither thermally nor photochemically. Under this condition the reverse reaction can be studied when A^- and B^+ can be prepared in some other

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[1] In practical cases the excited state obtained upon light absorption is often different from that emitting light.

[2] For an accurate thermodynamic discussion of photochemical processes, see ref. (*4*).

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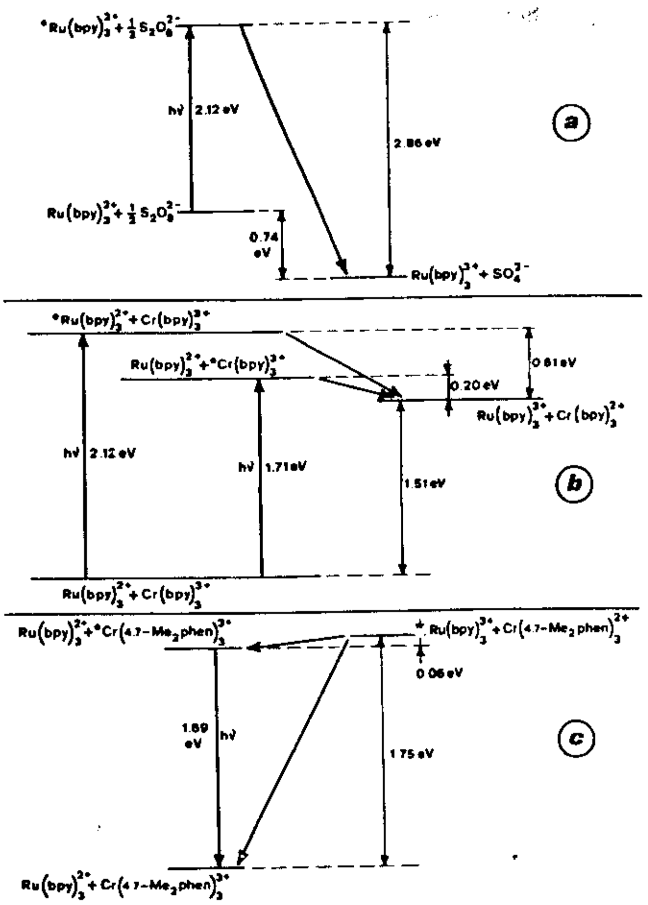

Figure 2. Examples of photocatalytic process (a), conversion of light into chemical energy (b), and conversion of chemical energy into light (c).

way (e.g., electrochemically). As shown in Fig. 1c, such a reverse reaction can occur directly, with complete dissipation of the free energy difference between $A^- + B^+$ and $A + B$. Alternatively, the reaction can occur via the intermediate formation of $^*A + B$ and subsequent radiative deactivation of $^*A$ to A. In the latter case part of the free energy change is converted into light energy.

Typical Examples

Numerous processes of the types illustrated by Figure 1 are reported in the recent chemical literature. Such processes play a fundamental role in several fields of pure and applied chemistry including new synthetic routes (*1*, *5*), solar energy conversion (*1e*, *3*, *4*), analytical methods (*2d*, *2e*), environmental problems (*1c*, *2d*), electronic display devices (*6*), theory of electron transfer reactions (*3*), and biological problems (*1c*, *1e*, *2d*, *2e*). We will now examine some examples in which the species interacting with light are complexes of the M(LL)$_3^{z+}$ type, where M is a transition metal and LL are ligands like 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) or their derivatives.

In an aqueous solution containing Ru(bpy)$_3^{2+}$ and $S_2O_8^{2-}$ (Fig. 2a) (*7*), the energetic situation is like that shown in Figure 1a, because the reduction potentials of the Ru(bpy)$_3^{3+}$/Ru(bpy)$_3^{2+}$ and ½ $S_2O_8^{2-}$/SO_4^{2-} couples are +1.26 and +2.0 V, respectively. The reaction, however, is slow ($k < 10^{-3} M^{-1} s^{-1}$) for the high intrinsic barrier of the one-electron reduction of $S_2O_8^{2-}$. Upon light absorption by Ru(bpy)$_3^{2+}$ the reaction becomes very fast ($k = 5.3 \times 10^8 M^{-1} s^{-1}$) because the Ru(bpy)$_3^{2+}$ excited state, whose zero-zero spectroscopic energy is 2.12 eV, is a much better reductant than the ground state (eqn. (6)). Interestingly, this photoreaction has been used to determine the quantum yield of formation of the lowest excited state of Ru(bpy)$_3^{2+}$ (*7*).

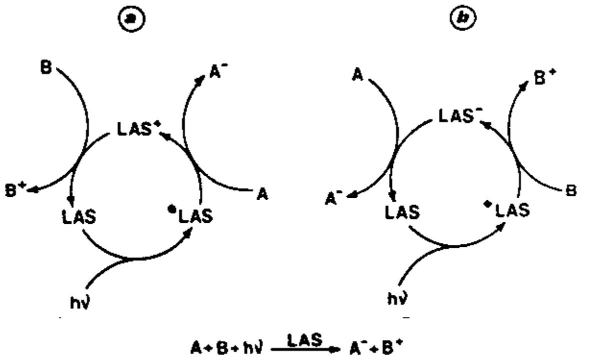

Figure 3. Light driven electron transfer process via the intermediacy of a light absorption sensitizer (LAS). Scheme *a* shows the oxidative cycle and scheme *b* the reductive cycle.

Ru(bpy)$_3^{2+}$ and Cr(bpy)$_3^{3+}$ in aqueous solution are in equilibrium with their one-electron oxidation and reduction species, respectively (Fig. 2b). In the dark, the equilibrium is strongly displaced toward the left-hand side because Cr(bpy)$_3^{3+}$ (E°_{red} = −0.25 V) is a much weaker oxidant than Ru(bpy)$_3^{3+}$ (E°_{red} = 1.26 V). Light absorption can lead Ru(bpy)$_3^{2+}$ and/or Cr(bpy)$_3^{3+}$ to their lowest excited states, *Ru(bpy)$_3^{2+}$ and *Cr(bpy)$_3^{3+}$, whose spectroscopic energies are 2.12 and 1.71 eV, respectively (*8*). By using eqns. (5) and (6) one can see that *Ru(bpy)$_3^{2+}$ is a reductant strong enough to reduce Cr(bpy)$_3^{3+}$ and that *Cr(bpy)$_3^{3+}$ is an oxidant strong enough to oxidize Ru(bpy)$_3^{2+}$. Light can thus drive the reaction toward the right-hand side (*8*). In such photochemical processes a substantial fraction of the excited state energy of *Ru(bpy)$_3^{2+}$ or *Cr(bpy)$_3^{3+}$ is converted into chemical energy. This converted energy, however, is only transiently stored because Ru(bpy)$_3^{3+}$ and Cr(bpy)$_3^{2+}$ undergo a rapid back-electron transfer reaction which regenerates Ru(bpy)$_3^{2+}$ and Cr(bpy)$_3^{3+}$. As we will see later, storage of the converted energy can be obtained when these complexes are used as sensitizers.

If in the previous system we replace Cr(bpy)$_3^{3+}$ with Cr(4,7-Me$_2$phen)$_3^{3+}$ (excited state energy = 1.69 eV, E°_{red} = −0.49 V), the energetic situation concerning the chromium complex (Fig. 2c) is of the type previously discussed in Figure 1c. As expected, light emission from Cr(4,7-Me$_2$phen)$_3^{3+}$ can be obtained on mixing solutions of Ru(bpy)$_3^{3+}$ and Cr(4,7-Me$_2$phen)$_3^{2+}$ (*9*).

Light Absorption Sensitizers (LAS)

There are "potential" photochemical reactions which do not occur because the reactants are not able to absorb light. For example, the reduction of methylviologen (MV^{2+}) by triphenylamine (NPh_3) (eqn. (8)) would be made thermodynamically allowed by absorption of visible light:[3]

$$MV^{2+} + NPh_3 \rightarrow MV^+ + NPh_3^+ \qquad \Delta G = +1.45 \text{ eV} \qquad (8)$$

The reaction, however, cannot be driven by visible light because neither MV^{2+} nor NPh_3 absorb in this spectral region (*10*). More important for practical applications, the splitting of water into hydrogen and oxygen (eqn. (9)) by visible light would also be thermodynamically possible but it does not occur because

$$\tfrac{1}{2}H_2O \rightarrow \tfrac{1}{2}H_2 + \tfrac{1}{4}O_2 \; \Delta G = +1.23 \text{ eV} \qquad (9)$$

water is transparent in the visible region (*11*).

A thermodynamically allowed photochemical reaction which is not able to occur because of light absorption problems can be induced by a suitable *light absorption sensitizer* (LAS). As one can see from Figure 3, the role of LAS in an

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[3] The energy of one einstein (i.e., one mole of photons) of visible light varies from 1.56 eV (800 nm) to 3.12 eV (400 nm).

electron transfer process is that of absorbing light so as to give an excited state which can be oxidized or reduced by one of the reactants of the electron transfer process. The oxidized or reduced form of LAS obtained in this way must then be able to oxidize or reduce the other reactant in order to complete the redox process and regenerate LAS.[4]

The best known LAS is currently the previously discussed $Ru(bpy)_3^{2+}$ complex which is able to drive reactions (8) (*10*) and (9) (*12*) as well as many other "potential" photochemical reactions by using visible light. For the light driven reaction (9), the energetics of the various steps is as follows (at pH 7).

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu(<600\ nm)} {}^*Ru(bpy)_3^{2+} \quad \Delta G = +2.12\ eV \qquad (9a)$$

$${}^*Ru(by)_3^{2+} + H^+ \rightarrow Ru(bpy)_3^{3+} + \tfrac{1}{2}H_2 \quad \Delta G = -0.44\ eV \qquad (9b)$$

$$Ru(bpy)_3^{3+} + \tfrac{1}{2}H_2O \rightarrow Ru(bpy)_3^{2+} + H^+ + \tfrac{1}{4}O_2 \quad \Delta G = -0.45\ eV \qquad (9c)$$

In practice, steps (9b) and (9c) are slow for kinetic reasons related to the multi-electron nature of the water splitting process and thus they can occur efficiently only under appropriate experimental conditions (i.e., via the intermediacy of relay species and catalysts (*12*)).

The conversion of light energy into electrical energy (photogalvanic effect (*13*) is also possible by using LAS's. Consider, for example, a cell consisting of two identical compartments separated by a sintered glass disk and containing a Pt electrode and an aqueous solution of $Ru(bpy)_3^{2+}$ and Fe^{3+} (*14*). If one of the compartments is illuminated and the other is kept in the dark, an electrical potential is generated which depends on the incident light intensity. This potential is due to the difference in the composition of the solutions in the dark and illuminated compartments caused by the following reactions.

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \qquad (10a)$$

$${}^*Ru(bpy)_3^{2+} + Fe^{3+} \rightarrow Ru(bpy)_3^{3+} + Fe^{2+} \qquad (10b)$$

More efficient photogalvanic cells can be obtained when selective electrodes are used (*13b*).

LAS can also be used to convert light into electrical energy and, at the same time, to carry on a net redox process. For example, photocurrents can be obtained from a cell where the net reaction involves the photochemical oxidation of water by $Co(C_2O_4)_3^{3-}$. The reaction mechanism is as follows (*15*).

Cathodic Compartment

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \qquad (11a)$$

$${}^*Ru(bpy)_3^{2+} + Co(C_2O_4)_3^{3-} \rightarrow Ru(bpy)_3^{3+} + Co^{2+} + 3C_2O_4^{2-} \qquad (11b)$$

$$Ru(bpy)_3^{3+} + e^- \xrightarrow{Pt\ cathode} Ru(bpy)_3^{2+} \qquad (11c)$$

Anodic Compartment

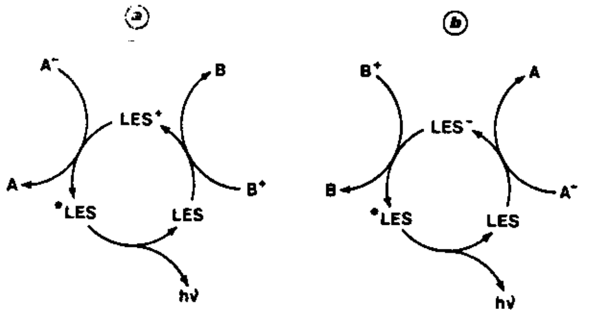
$$OH^- \xrightarrow{Pt\ anode} e^- + \tfrac{1}{2}H_2O_2$$

Light Emission Sensitizers (LES)

There are "potential" chemiluminescent reactions which do not occur because the reaction products do not meet the necessary requirements for light emission. For example, the reaction between lead dioxide and oxalate (eqn. (12)) is sufficiently exoergonic to

$$\tfrac{1}{2}PbO_2 + \tfrac{1}{2}C_2O_4^{2-} + 2H^+ \rightarrow \tfrac{1}{2}Pb^{2+} + CO_2 + H_2O \quad \Delta G \simeq -2\ eV \qquad (12)$$

generate visible light, but actually it only produces heat.



$$A^- + B^+ \xrightarrow{LES} A + B + h\nu$$

Figure 4. Light generating electron transfer process via the intermediacy of a light emission sensitizer (LES). Scheme *a* shows the oxidative cycle and scheme *b* the reductive cycle.

In the same way that a "potential" photochemical reaction may be induced by a light absorption sensitizer, a "potential" chemiluminescence reaction may be induced by a suitable *light emission sensitizer* (LES). As one can see from Figure 4, the role of LES in an electron transfer process is that of being oxidized or reduced by one of the two reactants. The oxidized or reduced form of LES should then be reduced or oxidized by the other reactant to give an excited state of LES which then emits. The exoergonicity of the redox reaction is thus partly channelled to light emission.

Light emission sensitizers are less known than light absorption sensitizers but they are presently the object of many investigations. Most (but not all) of the requirements to be met are the same for LAS and LES, so that it is not surprising that presently $Ru(bpy)_3^{2+}$ is also the best known LES. Recently it has been found (*16*) that part of the energy dissipated in reaction (12) can be converted into light when $Ru(bpy)_3^{2+}$ is present. The reaction mechanism is as follows:

$$Ru(bpy)_3^{2+} + \tfrac{1}{2}PbO_2 + 2H^+ \rightarrow Ru(bpy)_3^{3+} + \tfrac{1}{2}Pb^{2+} + H_2O \qquad (13a)$$

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + CO_2 + CO_2^- \qquad (13b)$$

$$Ru(bpy)_3^{3+} + CO_2^- \rightarrow {}^*Ru(bpy)_3^{2+} + CO_2 \qquad (13c)$$

$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu \qquad (13d)$$

Reduced or oxidized species can readily be generated electrochemically. The involvement of LES in electrochemical processes may allow the conversion of electrical energy into light. This phenomenon, which is the reverse of the photogalvanic effect seen above, is called electrogenerated chemiluminescence (ecl). For example (*17*), an acetonitrile solution containing $Ru(bpy)_3^{2+}$ and 10-methylphenothiazine (MP) shows luminescence when cyclic square waves at a frequency of 0.2 Hz between potentials of formation of $Ru(bpy)_3^+$ and MP^+ are applied at a Pt electrode immersed in the solution. The reaction mechanism is the following.

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^+ \qquad (14a)$$

$$Mp - e^- \rightarrow Mp^+ \qquad (14b)$$

$$Ru(bpy)_3^+ + MP^+ \rightarrow {}^*Ru(bpy)_3^{2+} + MP \qquad (14c)$$

$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu \qquad (14d)$$

Interestingly, ecl is also obtained with solutions containing only $Ru(bpy)_3^{2+}$ if the cyclic square waves are applied between potentials of formation of $Ru(bpy)_3^+$ and $Ru(bpy)_3^{3+}$ (*17*).

Finally, LES can also serve to produce light by the combined use of chemical and electrical energy, which is in some way the reverse of the third LAS induced process (eqn. (11)) described above. For example, light can be obtained upon

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[4] For a more detailed description of the requirements needed for LAS, see ref. (*3*).

electrochemical oxidation of $C_2O_4^{2-}$ (eqn. (15)) (*16*) or electrochemical reduction of $S_2O_8^{2-}$ (eqn. (16)) (*18*) when $Ru(bpy)_3^{2+}$ is present.

$$C_2O_4^{2-} - 2e^- \xrightarrow{Ru(bpy)_3^{2+}} 2CO_2 + h\nu \qquad (15)$$

$$S_2O_8^{2-} + 2e^- \xrightarrow{Ru(bpy)_3^{2+}} 2SO_4^{2-} + h\nu \qquad (16)$$

The reaction mechanism of eqn. (16) is presumably the following (*18*).

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+} \qquad (16a)$$

$$Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + SO_4^{2-} + SO_4^{-} \qquad (16b)$$

$$Ru(bpy)_3^{+} + SO_4^{-} \rightarrow {}^*Ru(bpy)_3^{2+} + SO_4^{2-} \qquad (16c)$$

$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu \qquad (16d)$$

Conclusions

Electron transfer reactions can often be driven by light (photochemical reactions) or can produce light (chemiluminescent reactions). The involvement of light occurs via the participation of an electronically excited state as a reactant or the formation of an (emitting) electronically excited state as a product. In photochemical reactions light can play a thermodynamic or kinetic role depending on the energetics of the ground state process. Potential photochemical reactions that cannot occur because the reactants are not able to absorb light can be induced by suitable light absorption sensitizers (LAS). In the same way, potential chemiluminescent reactions that cannot occur because the products are not able to emit can be induced by suitable light emission sensitizers (LES). $Ru(bpy)_3^{2+}$ is presently the most commonly used LAS and LES. For example, it can photochemically drive the water splitting reaction using visible light, and it can produce light from the oxidation of $C_2O_4^{2-}$ by PbO_2. Electron transfer processes (particularly, those based on LAS and LES) are most suitable for converting light into chemical and/or electrical energy as well as for converting chemical and/or electrical energy into light.[5] In view of their numerous and important fields of applications, studies concerning LAS's and LES's should be strongly encouraged.[6]

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[5] For the conversion of light into chemical or electrical energy by irradiation of semiconductor materials, see ref. (*19*).

[6] *Note added proof:* In a more recent paper (V. Balzani and F. Bolletta, *Comments in Inorganic Chemistry*, in press) *light absorption sensitizers* (LAS's) have been called *photosensitizers* (PS's) and *light emission sensitizers* (LES's) have been called *chemiluminescence inducers* (CLI's).