Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Transition Metal Complexes as Mediators in Photochemical and Chemiluminescence Reactions

Vincenzo Balzani[a]; Fabrizio Bolletta[a]
[a] Istituto Chimico "G. Ciamician" dell'Università and Istituto FRAE-CNR, Bologna, Italy

To cite this Article Balzani, Vincenzo and Bolletta, Fabrizio(1983) 'Transition Metal Complexes as Mediators in Photochemical and Chemiluminescence Reactions', Comments on Inorganic Chemistry, 2: 5, 211 — 226
To link to this Article: DOI: 10.1080/02603598308078119
URL: http://dx.doi.org/10.1080/02603598308078119

Transition Metal Complexes as Mediators in Photochemical and Chemiluminescence Reactions

Transition metal complexes can play the role of photosensitizers in light driven electron transfer reactions and the role of chemiluminescence inducers in exoergonic electron transfer reactions. A unifying view of these processes is given and their relevance concerning the interconversion of light, chemical energy and electrical energy is emphasized. Ru(*bpy*) is presently the most used photosensitizer and chemiluminescence inducer. Several specific processes mediated by Ru $(bpy)_3^{2+}$ (including water splitting by solar energy, generation of light from the reaction between lead dioxide and oxalic acid and "firefly" type emission from the oscillating Belousov–Zhabotinskii reaction) are described.

INTRODUCTION

Recent developments in chemical research have shown that transition metal complexes can play the role of photosensitizers in light driven chemical reactions[1–4] and of luminescence inducers in exoergonic chemical reactions.[5–7] Since these processes are extremely important for theoretical reasons (i.e., for the elucidation of the interaction between light and chemical compounds) as well as for practical applications (e.g., photochemical conversion of solar energy,[8,9] electronic display devices,[10] etc.), it seems worthwhile to present a unified view of the principles on which these processes are based. Our discussion will be limited to electron transfer reactions because the best known and most important light driven and light generating chemical reactions belong to this category.

Comments Inorg. Chem.
1983, Vol. 2, No. 5, pp. 211–226
0260-3594/83/0205-0211/$18.50/0

PHOTOCHEMICAL AND CHEMILUMINESCENT ELECTRON TRANSFER REACTIONS

In electron transfer processes light can participate as a reactant [photochemical reactions, Eq. (1)] or it can be generated as a product [chemiluminescent reactions, Eq. (2)]. In both cases the involvement of light occurs via the formation of electronically excited states, which are usually denoted by an asterisk.

Photoinduced Electron Transfer Reaction

$$A + h\nu \rightarrow {}^*A \qquad \text{light absorption} \qquad (1a)$$

$$^*A + B \rightarrow A^+ + B^- \qquad \text{electron transfer} \qquad (1b)$$

Electron Transfer Generated Chemiluminescence

$$A^+ + B^- \rightarrow {}^*A + B \qquad \text{electron transfer} \qquad (2a)$$

$$^*A \rightarrow A + h\nu \qquad \text{light emission} \qquad (2b)$$

As is well known to photochemists,[11,12] an excited state is a new chemical species compared with the corresponding ground state molecule. As far as photoinduced and chemiluminescent electron transfer processes are concerned, two excited-state properties, namely redox potentials and luminescence emission, are particularly relevant and thus they will be briefly reviewed.

An excited state is 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[1,2]:

$$E^0(^*A/A^-) \simeq E^0(A/A^-) + E(^*A), \qquad (3)$$

$$E^0(^*A/A^+) \simeq E^0(A/A^+) + E(^*A), \qquad (4)$$

where $E^0(A/A^-)$ and $E^0(A/A^+)$ 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 reagents, although their participation in redox processes may be prevented when their lifetime is too short.[1,2] Figure 1 shows the redox potentials of the ground and the lowest excited state of $Ru(bpy)_3^{2+}$ (*bpy* = 2,2′-bipyr-

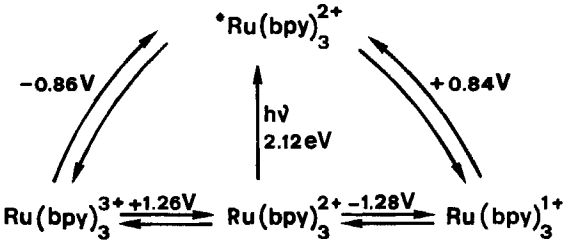

FIGURE 1 Redox potentials for the ground and lowest excited states of Ru(*bpy*)$_3^{2+}$.

idine), a complex that is extensively used in photoinduced and chemiluminescent electron transfer reactions.

Luminescence emission is in principle a deactivation pathway available to each excited state. In practice, however, luminescence can only be observed when it can kinetically compete with radiationless deactivation processes which are usually very fast. In general, for transition metal complexes luminescence is only observed from the lowest excited state and only when this state is not strongly distorted compared to the ground state. The best known families of luminescent transition metal complexes are those of the polypyridine complexes of Ru(II), Os(II), Rh(III) and Ir(II) where the emitting state is either charge transfer or ligand localized, and that of the Cr(III) complexes where the emitting excited state is an intraconfigurational metal centered state.[1,2,13]

In photoinduced processes [Eq. (1)] light can play two distinct roles which are illustrated in Figure 2. The upper scheme (Figure 2a) corresponds to the case of a $A^+ + B^-$ reaction which is strongly endoergonic. Under such conditions the chemical equilibrium between A + B and $A^+ + B^-$ in the dark is strongly displaced toward the left-hand side for thermodynamic reasons. Light excitation of reagent A causes the formation of the excited state *A which, as we have seen before, is a much stronger reductant than A, so that the reaction $*A + B \rightarrow A^+ + B^-$ is now thermodynamically allowed. In systems of this type light plays a thermodynamic role and part of the light energy is converted into free chemical energy of the products. The lower scheme (Figure 2b) corresponds to an exoergonic reaction which in the dark is slow for kinetic reasons (high activation energy). Again, light excitation of reactant A leads to *A, a much stronger reductant than A. The reaction

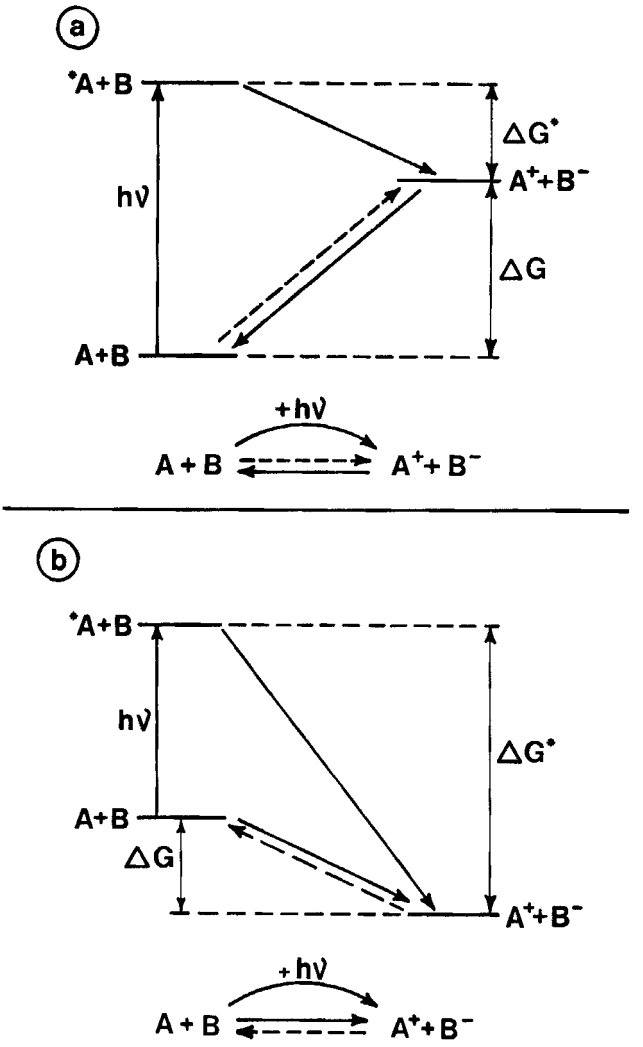

FIGURE 2 Schematic energy diagrams for photoinduced electron transfer reactions.

between *A and B is thus much more exoergonic than the reaction between A and B. Since the activation energy usually decreases with increasing exoergonicity,[14] the reaction involving the excited state will be much faster than that involving the ground state.† In a system of this kind light is simply used to overcome a kinetic barrier and plays the role of a catalyst.

Chemiluminescent reactions can take place when the energy situation is like that depicted in Figure 3. In this case the energy content of A^+ and B^- is not only higher than that of A + B but also higher than that of *A + B, so that the reaction from left to right can be driven neither thermally nor photochemically. Under such conditions, if A^+ and B^- are prepared in some other way (e.g., electrochemically) and mixed together the reaction from left to right may occur either directly with complete dissipation of the free energy into heat, or via the intermediate formation of *A + B and the subsequent radiative deactivation (luminescence) of *A to A. In the latter case part of the free energy change is converted into light energy, i.e., photons are generated as reaction products.

From the above discussion it is clear that a chemiluminescent process is just the reverse of a photochemical process:

$$\underset{\text{photochemistry}}{A + B + h\nu \rightleftarrows {}^*A + B \rightleftarrows A^+ + B^-}, \qquad (5)$$

chemiluminescence

and that the equilibrium represented by Eq. (5) will move from left to right or from right to left depending on whether the situation is that depicted in Figure 2 or Figure 3. When *A + B and $A^+ + B^-$ are almost isoenergetic, as in the case of A = $Cr(4,7\text{-}bpy)_3^{3+}$ and B = $Ru(bpy)_3^{2+}$, both processes can be studied for the same system.[16]

It is interesting to note that when A^+ and/or B^- are involved in redox processes at electrodes or are themselves appropriate (semiconductor) electrodes, Reaction (5) can allow the interconversion between light energy and electrical energy. For example, when an aqueous solution containing A = $Ru(bpy)_3^{2+}$, B = Fe^{3+} and a Pt electrode is excited

†An excited state reaction can be faster than the corresponding ground state reaction, also for electronic reasons.[15]

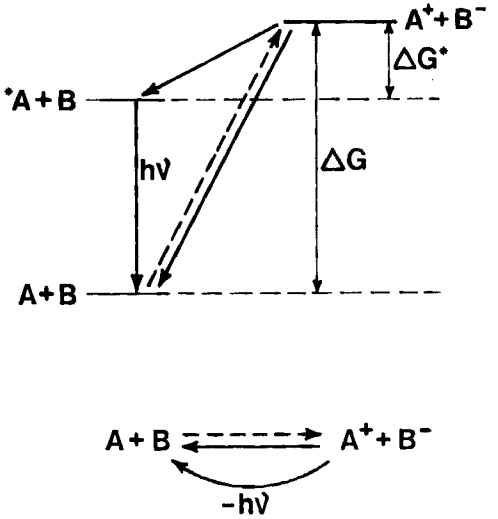

FIGURE 3 Schematic energy diagram for an electron transfer chemiluminescent reaction.

with visible light, an electrical potential is generated between the Pt electrode and another Pt electrode immersed in an identical solution kept in the dark[17] (photogalvanic effect).[18] As another example, when B^+ is $Ru(bpy)_3^{3+}$ and A^- is a SiC electrode, $*Ru(bpy)_3^{2+}$ is formed by electron transfer from the conduction band of SiC to $Ru(bpy)_3^{3+}$ and luminescence from $*Ru(bpy)_3^{2+}$ is observed.[19]

APPLICATION TO ENERGY CONVERSION

The processes described by Eq. (1) [or by Eq. (5) from left to right] are important from a theoretical and also from an applied perspective because they may allow the conversion of light into chemical energy. For example, it is possible to convert solar radiation into free chemical energy using A = $Ru(bpy)_3^{2+}$ and B = MV^{2+} (MV^{2+} is a short hand notation for methylviologen, which is 4,4′-dimethylbipyridine)[20]:

$$Ru(bpy)_3^{2+} + h\nu \rightarrow *Ru(bpy)_3^{2+}, \tag{6a}$$

$$*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+}, \tag{6b}$$

$$Ru(bpy)_3^{3+} + MV^{+} \rightarrow Ru(bpy)_3^{2+} + MV^{2+}. \tag{6c}$$

Reaction (6c) is exoergonic by 1.70 eV, so that 80% of the spectroscopic energy of $*Ru(bpy)_3^{2+}$ (2.12 eV, Figure 1) is converted into free chemical energy.

In practice, however, it would be imposible to convert substantial amounts of solar energy into free energy of very complicated and expensive compounds like $Ru(bpy)_3^{3+}$ and MV^+.† For practical purposes, the conversion (and storage) of solar energy into a real energy resource requires the transformation of an abundant and low cost raw material into a fuel. Simple economical, ecological and energetic considerations show that the most attractive raw materials are water, carbon dioxide and nitrogen, from which one could obtain excellent fuels like hydrogen, methanol and ammonia in endoergonic processes which require ~1.2 eV.[21,22] In principle, such processes can be driven by solar radiation, which essentially consists of visible light (3.1 eV > $Nh\nu$ > 1.6 eV).‡ However, water, carbon dioxide and ammonia are not able to absorb visible radiation and thus their transformation into fuels by a *direct* photochemical process cannot occur. Consider, for example, the splitting of water into hydrogen and oxygen[23]:

$$\tfrac{1}{2}\,H_2O \rightarrow \tfrac{1}{2}\,H_2 + \tfrac{1}{4}\,O_2 \qquad \Delta G = +1.23\ \text{eV}. \tag{7}$$

This reaction can in principle be driven by light of $Nh\nu$ > 1.23 eV ($\lambda \leq 1000$ nm), but the onset of the absorption spectrum of water is above 6.5 eV (190 nm). The reaction

$$\tfrac{1}{2}\,H_2O + h\nu \rightarrow \tfrac{1}{2}\,H_2 + \tfrac{1}{4}\,O_2, \tag{8}$$

where 6.5 eV > $Nh\nu$ > 1.23 eV can be considered as a *potential* photochemical reaction, since it is allowed on energy grounds but cannot occur because the reactant is unable to use light energy.

Analogous problems arise as far as chemiluminescent reactions are concerned. Nice chemiluminescent reactions usually involve expensive reactants and thus cannot be of practical interest:

$$Ru(bpy)_3^{3+} + NaBH_4 \rightarrow *Ru(bpy)_3^{2+} + \text{products}, \tag{9a}$$

$$*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu. \tag{9b}$$

†It should also be noted that the energy converted by Reactions (6a) and (6b) cannot be stored because Reaction (6c) is extremely fast.[20]

‡$Nh\nu$ is a mole of photons and is called an Einstein. The energy of one Einstein of visible light varies from 1.6 eV (800 nm) to 3.1 eV (400 nm).

Other reactions involving less expensive materials are sufficiently exoergonic to generate light but only produce heat because the species involved do not meet the necessary requirements for light emission. Consider the reaction between lead dioxide and oxalate ion:

$$\tfrac{1}{2}\,PbO_2 + \tfrac{1}{2}\,C_2O_4^{2-} + 2H^+ \rightarrow \tfrac{1}{2}\,Pb^{2+} + CO_2 + H_2O \qquad \Delta G \simeq -2\ \text{eV}. \quad (10)$$

This reaction is exoergonic by ~2 eV and thus it could emit light of $\lambda \gtrsim 620$ nm. However, all its exoergonicity is degraded to heat. Reactions of this type can be considered as *potential* chemiluminescent processes, in the same way as Eq. (8) is a potential photochemical process. In the next sections we will see that potential photochemical processes and potential chemiluminescent processes can be induced by appropriate mediators.

TRANSITION METAL COMPLEXES AS PHOTOSENSITIZERS IN POTENTIAL PHOTOCHEMICAL REACTIONS

Potential photochemical electron transfer reactions [Eq. (8)] can be induced by species having appropriate spectroscopic and redox properties. Such species, which are called photosensitizers (PS), play the role of mediators between light and molecules which are not able to use light energy. Consider a potential photochemical reaction,

$$C + D + h\nu \rightarrow C^+ + B^-, \quad (11)$$

which does not occur because neither C nor D are able to absorb photons that would make the process thermodynamically allowed. The role of a photosensitizer, as illustrated in Figure 4a, is first that of absorbing light so as to give an excited state which can be oxidized (or reduced) by one of the reactants of Eq. (11). Then, the oxidized (reduced) form of the potosensitizer obtained from the excited state reaction must be able to oxidize (reduce) the other reactant in order to complete the redox process indicated by Eq. (11) and to regenerate the initial form of the photosensitizer. Since small amounts of photosensitizers are usually needed and since in principle the photosensitizer is not destroyed, expensive compounds can also be used to play this role.

A molecule should meet several specific requirements in order to be a useful photosensitizer for electron transfer processes. It should have

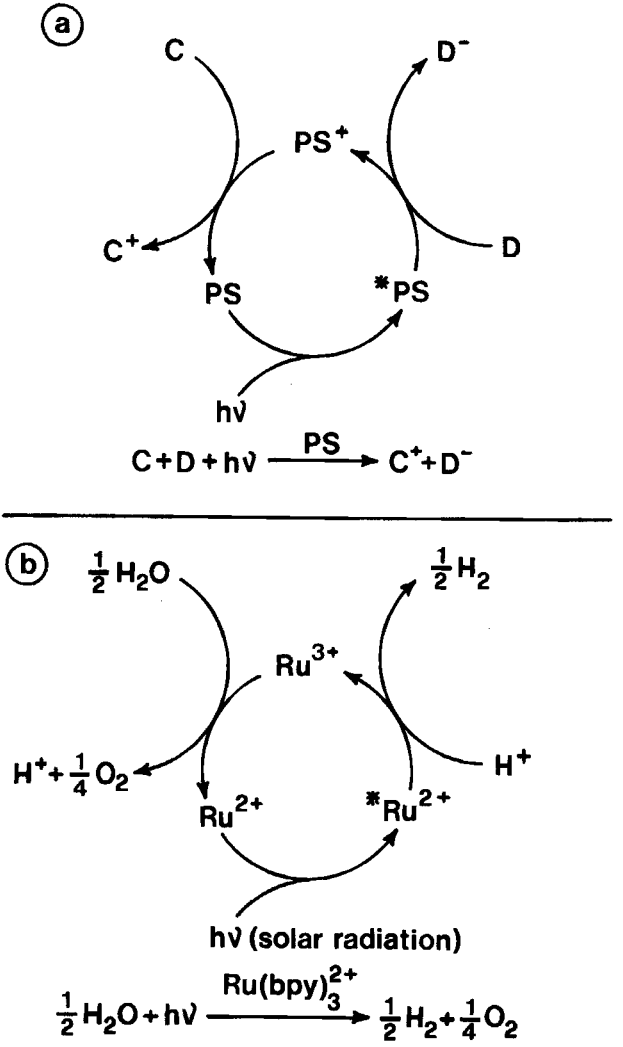

FIGURE 4 (a) Scheme showing the role played by a photosensitizer (PS) in a photoinduced electron transfer reaction. (b) Schematic representation of the water splitting reaction by solar energy using $Ru(bpy)_3^{2+}$ as a photosensitizer.

a high extinction coefficient in the desired spectral range and its excited state should have a sufficiently long lifetime to encounter the reaction partner and a sufficiently high reduction (oxidation) power to induce the electron transfer process. It should also be stable towards photodecomposition and its oxidation (reduction) product should be a good oxidant (reductant) and should also be stable towards side reactions.

Most of these requirements are more easily met by transition metal complexes than by organic molecules or transition metal ions. The best known and more commonly used photosensitizer is the previously discussed (Figure 1) $Ru(bpy)_3^{2+}$ complex.[1–4,24] Several other transition metal complexes including polypyridine complexes of Ru(II), Rh(III), Os(II) and Cr(III),[1,2] prophyrins,[25] phthalocyanines,[26] quinolinolates[27] and polynuclear Mo, Re and Rh compounds[28] exhibit spectroscopic and redox properties suitable for use as photosensitizers. Figure 4b schematizes the use of $Ru(bpy)_3^{2+}$ as a photosensitizer for water splitting reactions. The two-electron transfer reactions involved [Eqs. (11) and (12)] are both thermodynamically allowed at pH 7:

$$*Ru(bpy)_3^{2+} + H^+ \rightarrow Ru(bpy)_3^{3+} + \tfrac{1}{2} H_2$$

$$\Delta G = -0.44 \text{ eV}, \tag{11}$$

$$Ru(bpy)_3^{3+} + \tfrac{1}{2} H_2O \rightarrow Ru(bpy)_3^{2+} + H^+ + \tfrac{1}{4} O_2$$

$$\Delta G = -0.45 \text{ eV}. \tag{12}$$

However, they are slow for kinetic reasons related to the multielectron nature of the water splitting process, so that actual systems for water splitting also involve the intermediacy of relay species and catalysts.[8,9,29]

In the previously mentioned photogalvanic effect the absorbing species practically plays the role of a photosensitizer which mediates the conversion of light into electrical energy. Photosensitizers can also be used to convert light into electrical energy and at the same time carry on a net photoredox process. For example, photocurrent can be obtained from a cell where the net reaction involves the photochemical reduction of water by a reductant S (which may be cysteine or EDTA) according to the following mechanism[30]:

Anodic Compartment

$$Ru(bpy)_3^{2+} + h\nu \rightarrow *Ru(bpy)_3^{2+}, \tag{13a}$$

$$*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^+, \tag{13b}$$

$$Ru(bpy)_3^{3+} + S \rightarrow Ru(bpy)_3^{2+} + S_{ox}, \quad (13c)$$

$$MV^+ \xrightarrow{Pt} MV^{2+} + e^-, \quad (13d)$$

Cathodic Compartment

$$H^+ + e^- \rightarrow \tfrac{1}{2} H_2. \quad (13e)$$

TRANSITION METAL COMPLEXES AS CHEMILUMINESCENCE INDUCERS IN POTENTIAL CHEMILUMINESCENCE REACTIONS

Potential chemiluminescent reactions [e.g., Reaction (10)] can be transformed into effective chemiluminescent reactions by species having appropriate spectroscopic and redox properties. Such species, which may be called *chemiluminescence inducers* (CLI), play the role of mediators between chemical energy and light energy. Consider a potential chemiluminescent reaction which does not occur either because the excited states of E or F are too high in energy to be obtained or because, if they are obtained, they do not emit light:

$$E^+ + F^- \rightarrow E + F + h\nu. \quad (14)$$

The role of the chemiluminescence inducer, as illustrated in Figure 5a, is that of being oxidized (or reduced) by one of the reactants of Eq. (14) to yield CLI^+ which then is reduced (oxidized) by the other reactant to yield an excited state of CLI, *CLI, which undergoes radiative deactivation, regenerating CLI. In this way part of the exoergonicity of the electron transfer reaction between E^+ and F^- is channelled to light emission.

Chemiluminescence inducers are less known than photosensitizers but they are presently the object of many investigations. The redox properties that a molecule must have in order to be a useful chemiluminescence inducer are qualitatively the same as those needed for being a photosensitizer. From the spectroscopic point of view the requirements are somewhat different (e.g., a CLI does not need to have high extinction coefficients), but slow radiationless deactivation of the excited state is a fundamental requirement in both cases because a photosensitizer must have a long excited state lifetime and a chemiluminescence inducer has to have a high emission efficiency. Thus, it is not surprising that the

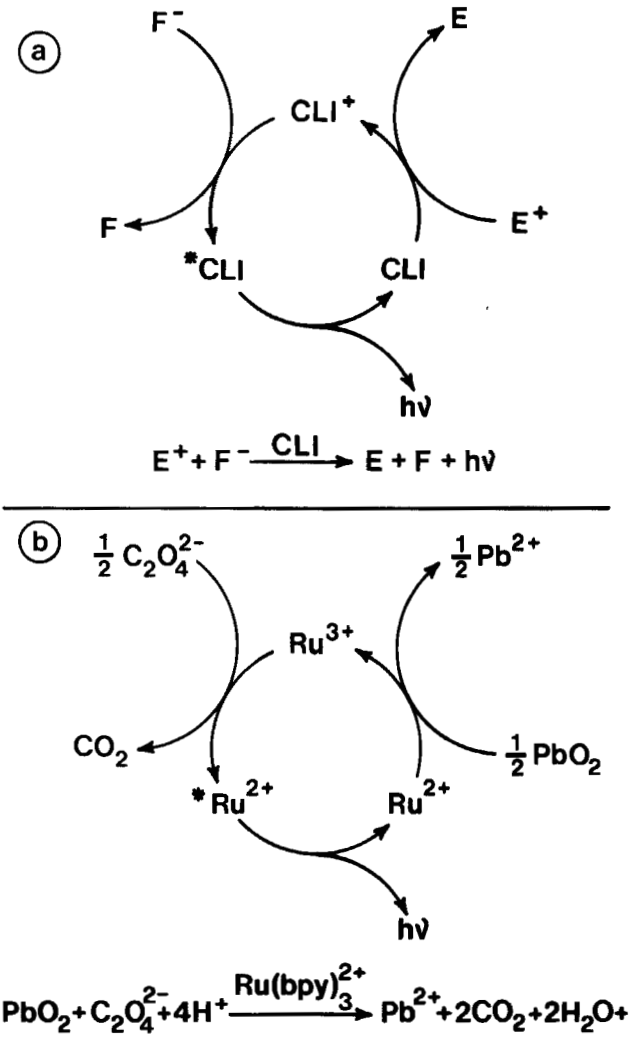

FIGURE 5 (a) Scheme showing the role played by a chemiluminescence inducer (CLI) in an exoergonic electron transfer reaction. (b) Schematic representation of the process leading to chemiluminescence emission when oxidation of $C_2O_4^{2-}$ by PbO_2 is performed in the presence of $Ru(bpy)_3^{2+}$. See text for details.

best known chemiluminescence inducers are the same transition metal complexes that are used as photosensitizers. In particular, $Ru(bpy)_3^{2+}$ is an excellent chemiluminescence inducer for many reactions. One of the most interesting examples is the induction of chemiluminescence from Reaction (11), which takes place according to the following mechanism[5]:

$$Ru(bpy)_3^{2+} + \tfrac{1}{2}\,PbO_2 + 2H^+ \rightarrow Ru(bpy)_3^{3+} + \tfrac{1}{2}\,Pb^{2+} + H_2O, \quad (15a)$$

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + CO_2 + CO_2^-, \quad (15b)$$

$$Ru(bpy)_3^{3+} + CO_2^- \rightarrow {}^*Ru(bpy)_3^{2+} + CO_2, \quad (15c)$$

$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu. \quad (15d)$$

A practical chemiluminescence device based on this reaction has also been proposed.[5]

Reduced and oxidized species easily can be generated electrochemically. The involvement of chemiluminescence inducers in electrochemical processes may allow the conversion of electrical energy into light. This phenomenon, which is the reverse of the previously seen photogalvanic effect, is called electrogenerated chemiluminescence (ECL). The most noticeable example is that described by Bard *et al.* concerning $Ru(bpy)_3^{2+}$ in acetonitrile solution.[31] When cyclic square waves between potentials of formation of $Ru(bpy)_3^+$ and $Ru(bpy)_3^{3+}$ (Figure 1) are applied at a Pt electrode immersed in the solution, a beautiful luminescence is observed which continues indefinitely if the electrical potential is maintained. The reaction mechanism is as follows[31]:

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

$$Ru(bpy)_3^{2+} - e^- \rightarrow Ru(bpy)_3^{3+}, \quad (16b)$$

$$Ru(bpy)_3^+ + Ru(bpy)_3^{3+} \rightarrow {}^*Ru(bpy)_3^{2+} + Ru(bpy)_3^{2+}, \quad (16c)$$

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

Chemiluminescence inducers can also be used to produce light by the combined use of chemical and electrical energy, which is in some way the reverse of the process described above, where a photosensitizer is used to convert light into electrical *and* chemical energy. For example, light can be obtained when electrochemical reduction of $S_2O_8^{2-}$ is carried

out in the presence of $Ru(bpy)_3^{2+}$. The reaction mechanism involves the formation of the SO_4^- radical which is a very strong oxidant that can oxidize $Ru(bpy)_3^{+}$ to the excited $^*Ru(bpy)_3^{2+}$ complex[6]:

$$Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+}, \tag{17a}$$

$$Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + SO_4^{-\,-} + SO_4^-, \tag{17b}$$

$$Ru(bpy)_3^{+} + SO_4^- \rightarrow {}^*Ru(bpy)_3^{2+} + SO_4^{-\,-}, \tag{17c}$$

$$^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu. \tag{17d}$$

A very interesting case of chemiluminescence induction has been recently reported. It has been found[32] that $Ru(bpy)_3^{2+}$ can play the role of CLI in the oscillating Belousov–Zhabotinskii reaction (oxidation of malonic acid by bromate, catalyzed by a redox couple).[33] In this system a very complex set of reactions causes an oscillation in the $Ru(bpy)_3^{3+}$ concentration and since $Ru(bpy_3^{3+}$ is engaged in a luminescent reaction an oscillating luminescence emission is observed (Figure 6):

$$Ru(bpy)_3^{3+} + \text{red} \rightarrow {}^*Ru(bpy)_3^{2+} + \text{ox}, \tag{18a}$$

$$^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\nu. \tag{18b}$$

This system can be considered a nonbiological firefly.

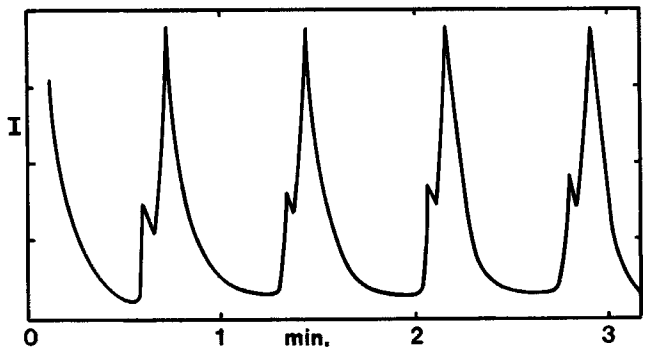

FIGURE 6 An artificial firefly: oscillating chemiluminescence emission in the Belousov–Zhabotinskii reaction catalyzed by $Ru(bpy)_3^{2+}$.

CONCLUSIONS

Electron transfer reactions involving electronically excited states can be used to interconvert light, chemical energy and electrical energy. Transition metal complexes can be substrates for these reactions and they can also be used to mediate processes of this type based on other substrates. More specifically, transition metal complexes having suitable electrochemical and spectroscopic properties can play the role of photosensitizers in potential photochemical reactions and the role of chemiluminescence inducers in potential chemiluminescent reactions. The most extensively used photosensitizer and chemiluminescence inducer is presently $Ru(bpy)_3^{2+}$. Processes of these types are very interesting from a theoretical point of view because they contribute to the elucidation of the interaction mechanisms between light and matter. They are also extremely important for several applications, including the photochemical conversion of solar energy and the production of "cold light" from chemical reactions.

Acknowledgments

This work was supported by the Progetto Finalizzato Chimica Fine e Secondaria of the Italian National Research Council (CNR) and by the European Communities (Contract ESD-025-I).

VINCENZO BALZANI and FABRIZIO BOLLETTA
Istituto Chimico "G. Ciamician" dell'Università
and Istituto FRAE-CNR,
Bologna, Italy

References

1. V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri, Top. Curr. Chem. **75,** 1 (1978).
2. N. Sutin and C. Creutz, Pure Appl. Chem. **52,** 2717 (1980).
3. D. G. Whitten, Acc. Chem. Res. **13,** 83 (1980).
4. M. Grätzel, Acc. Chem. Res. **14,** 376 (1981).
5. I. Rubistein and A. J. Bard, J. Am. Chem. Soc. **103,** 512 (1981).
6. F. Bolletta, M. Ciano, V. Balzani and N. Serpone, Inorg. Chim. Acta **62,** 207 (1982).

7. V. Balzani, F. Bolletta, M. Ciano and M. Maestri, J. Chem. Ed., in press.
8. J. S. Connolly (Ed.), *Photochemical Conversion and Storage of Solar Energy* (Academic, New York, 1981).
9. J. Rabani (Ed.), *Photochemical Conversion and Storage of Solar Energy* (Weizmann Press, Israel, 1982).
10. D. Laser and A. J. Bard, J. Electrochem. Soc. **122,** 632 (1975).
11. V. Balzani and V. Carassiti, *Photochemistry of Coordination Compounds* (Academic, London, 1970).
12. N. J. Turro, *Modern Molecular Photochemistry* (Benjamin, Menlo Park, California, 1978).
13. M. K. De Armond and C. M. Carlin, Coord. Chem. Rev. **36,** 325 (1981).
14. F. Scandola and V. Balzani, J. Am. Chem. Soc. **101,** 6140 (1979).
15. V. Balzani and F. Scandola, Ref. 8, p. 97.
16. V. Balzani and F. Bolletta, J. Photochem. **17,** 479 (1981).
17. C. T. Lin and N. Sutin, J. Phys. Chem. **80,** 97 (1976).
18. M. D. Archer and M. I. C. Ferreira, Ref. 8, p. 201.
19. M. Gleria and R. Memming, Z. Phys. Chem. (Neue Folge) **101,** 171 (1976).
20. C. R. Bock, T. J. Meyer and D. G. Whitten, J. Am. Chem. Soc. **97,** 2909 (1975).
21. J. R. Bolton and D. O. Hall, Ann. Rev. Energy **4,** 353 (1979).
22. V. Balzani and F. Scandola, in *Energy Resources by Photochemistry and Catalysis,* edited by M. Grätzel (Academic, New York), in press.
23. V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta and M. Gleria, Science **189,** 852 (1975).
24. K. Kalyanasundaram, Coord. Chem. Rev. **46,** 159 (1982).
25. A. Harriman, G. Porter and M. C. Richoux, J. Chem. Soc. Faraday Trans. **2, 77,** 833 (1981).
26. A. Harriman, G. Porter and M. C. Richoux, J. Chem. Soc. Faraday Trans. **2, 77,** 1175 (1981).
27. F. Scandola, R. Ballardini and T. Indelli, in *Photochemical, Photoelectrochemical, and Photobiological Processes,* edited by D. O. Hall and V. Palz (Reidel, Dordrecht, 1982).
28. H. B. Gray and A. Maverick, Science **214,** 1201 (1981).
29. K. Kalyanasundaram and M. Grätzel, Angew. Chem. Int. Ed. Engl. **18,** 701 (1979).
30. W. J. Dressick, T. J. Meyer, B. Durham and D. P. Rillema, Inorg. Chem. **21,** 3451 (1982).
31. N. E. Tokel-Takvoryan, R. E. Hemingway and A. J. Bard, J. Am. Chem. Soc. **95,** 6582 (1973). W. L. Wallace and A. J. Bard, J. Phys. Chem. **83,** 1350 (1979).
32. F. Bolletta and V. Balzani, J. Am. Chem. Soc. **104,** 4250 (1982).
33. H. Degn, J. Chem. Ed. **49,** 302 (1972).