Artificial Photosynthesis: Water Cleavage into Hydrogen and Oxygen by Visible Light

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In the present era of depleting fossil fuel reserves, the development of alternative energy supplies has become a research subject of high priority.[1] One topic that has fascinated and aroused the imagination of scientists from many different fields[2] is the photolysis of water using solar radiation. The practical potential of devices achieving this process is of course enormous. For example, Zamaraev and Parmon have calculated[3] that the equivalent of the total annual consumption of electrical energy of the USSR could be provided by covering a 65×65 km area of desert in Middle Asia with a solar converter operating at 20% efficiency. According to recent conservative estimates[4] water splitting devices with 16% optical conversion efficiency[5] appear to be feasible.

In order to achieve the goal of decomposing water into hydrogen and oxygen by visible light

$$H_2O \xrightarrow{h\nu} H_2 + 0.5O_2 \qquad (1)$$
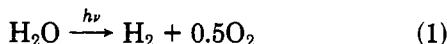
different strategies have been applied. A straightforward solution would be the coupling of a photovoltaic device with a water electrolyzer. However, the cost of such an installation based on the current price of silicon solar cells would be prohibitively high. Also it would operate at relatively low efficiency due to overvoltage losses (30–40% in today's commercial electrolyzers) and the fact that combination of at least two silicon cells is required to afford the threshold voltage required for water decomposition.

An alternative approach is based on the concept of wet photovoltaics, i.e., the illumination of a semiconductor in contact with an aqueous electrolyte. Here hydrogen and oxygen production from water can occur directly and without intervention of an electrolysis cell. This field has experienced an astonishingly fast development over the last 20 years which is documented by a series of excellent reviews that have appeared recently.[6] Honda and collaborators have shown that photoelectrolysis of water can indeed be achieved with TiO_2 as a photoanode.[7] However this material absorbs only UV light, which makes it unsuitable for solar application, and so far no smaller band gap semiconductor electrode has been found which could replace TiO_2.

This Account deals with yet another concept of photoinduced water cleavage based on microheterogeneous photochemistry and redox catalysis. Recently there has been a tremendous explosion of information

and work on this subject.[3,8] It is attempted to design and develop microscopic units, frequently invisible to the eye, which would mimic the function of chloroplasts in photosynthesis. The first task is to achieve light-induced charge separation. Here micelles or vesicles can substitute the distinct microenvironment found in the biological membranes and kinetically control the photoredox events. An even simpler method is the use of colloidal semiconductor particles as light-absorbing units. The next step is to combine the photoprocess with the generation of hydrogen using water as an electron source. This presents a formidable problem since water oxidation as well as reduction are multistep electron-transfer processes that proceed through stages of highly reactive and energetic intermediates. The success in this domain has therefore largely been determined by the development of redox catalysts mediating hydrogen and oxygen formation and thus avoiding these radical intermediates. In fact, only through drastic improvement of previously known and discovery of new redox catalysts has the design of a cyclic water decomposition system operating on four quanta of visible light become feasible. For this reason catalytic aspects will be emphasized in the following report.

Light-Harvesting Units

From the thermodynamic point of view, cleavage of water should be possible with light of wavelength ≤1000

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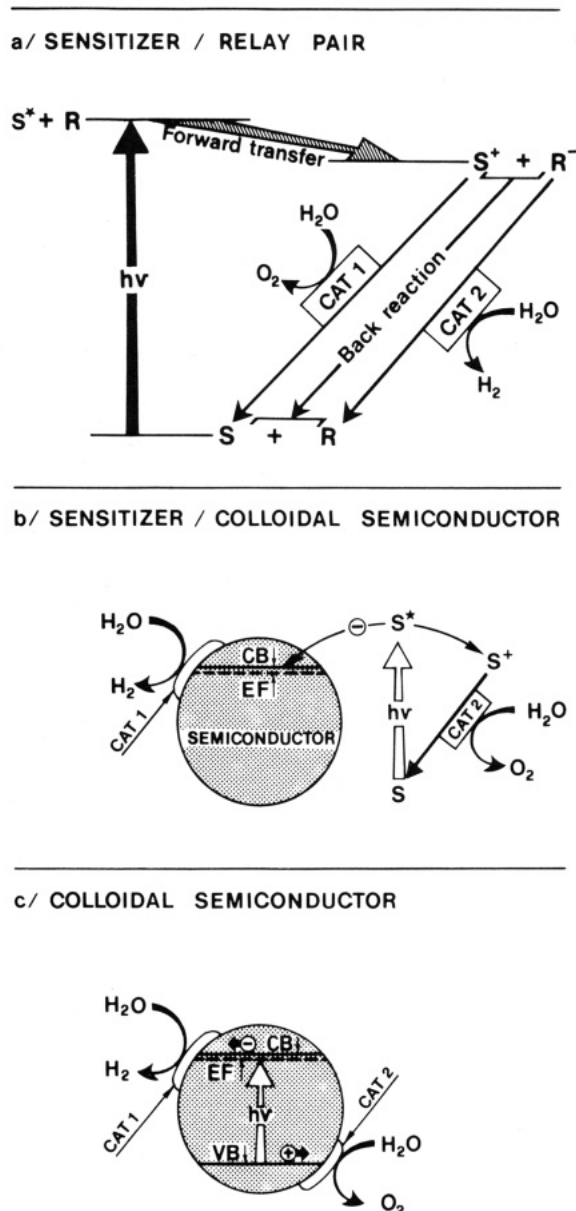
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a/ SENSITIZER / RELAY PAIR

b/ SENSITIZER / COLLOIDAL SEMICONDUCTOR

c/ COLLOIDAL SEMICONDUCTOR

Figure 1. Schematic illustration of light-harvesting units employed in photochemical water splitting devices.

nm if four photons are used to produce one molecule of oxygen. As water is transparent to visible and near-UV light, these photons have to be absorbed by additives which must be selected such that excitation energy is ultimately transmitted to the aqueous medium to generate hydrogen and oxygen. In view of the complexity of the processes involved in water photolysis, it is highly unlikely that a single dye molecule can accomplish this task. (Metal ions such as Fe^{2+} and Ce^{3+} in aqueous solution do generate H_2 and O_2 under illumination.[9] However, these compounds absorb only in the UV region, and quantum yields are very small. The same holds for Kallman and Pope's system where water is decomposed by illumination of anthracene crystals.[10])

Three suitable light-harvesting units which serve to capture photons, convert their energy into chemical potential, and use it to decompose water are shown in

Figure 1. Case a represents a two-component system containing a sensitizer (S) and an electron relay (R). Light promotes electron transfer from S to R whereby the energy-rich radical ions S^+ and R^- are produced. Thus, light functions here as an electron pump operating against a gradient of chemical potential. A similar process may be conducted in a system where the sensitizer acts as electron acceptor in the excited state and the electron relay is oxidized. Such photoinduced redox reactions have been studied in great detail both from the experimental[11] and the theoretical[12] point of view. The rate of electron transfer between excited sensitizer and relay is expected to approach the diffusion-controlled limit as soon as the driving force for the reaction exceeds a few hundred millivolts. Conversely, the backward electron transfer between S^+ and R^- which is thermodynamically strongly favored is almost always diffusion controlled. This poses a severe problem for the use of such systems in energy conversion devices as it limits the lifetime of the radical ions to at most several milliseconds under solar light intensity. Below we shall give examples of how suitable molecular assemblies may be developed that allow the retardation of this undesired back-reaction.

With regard to the choice of the sensitizer and the relay, compounds have to be found that are suitable from the viewpoints of both light absorption and redox potentials and undergo no chemical side reactions in the oxidation states of interest. The sensitizer should have good absorption features with respect to the solar spectrum. Also its excited state should be formed with high quantum yield and have a reasonably long lifetime and the electron-transfer reaction must occur with high efficiency, viz., good solvent cage escape yield of the redox products. The redox properties of the donor–acceptor relay must obviously be tuned to the fuel producing transformation envisaged. If, for example, water cleavage by light is to be achieved, then the thermodynamic requirements are such that $E°(S^+/S)$ > 1.23 V (NHE/ and $E°(R/R^-)$ < 0 V under standard conditions. In the design of sensitizer/relay couples suitable for photoinduced water decomposition considerable progress has been made over the last few years.[13] A number of systems converting more than 90% of the threshold light energy required for excitation of the sensitizer into chemical potential have been explored. Also, in several cases the reduced relay and oxidized sensitizer are thermodynamically capable of generating H_2 and O_2 from water:

$$R^- + H_2O \rightarrow 0.5H_2 + OH^- + R \qquad (2)$$

$$2S^+ + H_2O \rightarrow 0.5O_2 + 2H^+ + 2S \qquad (3)$$
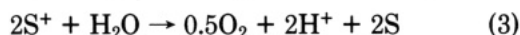
Noteworthy examples are sensitizers such as Ru-$(bpy)_3^{2+}$,[14] porphyrin derivatives,[15] and acridine dyes,

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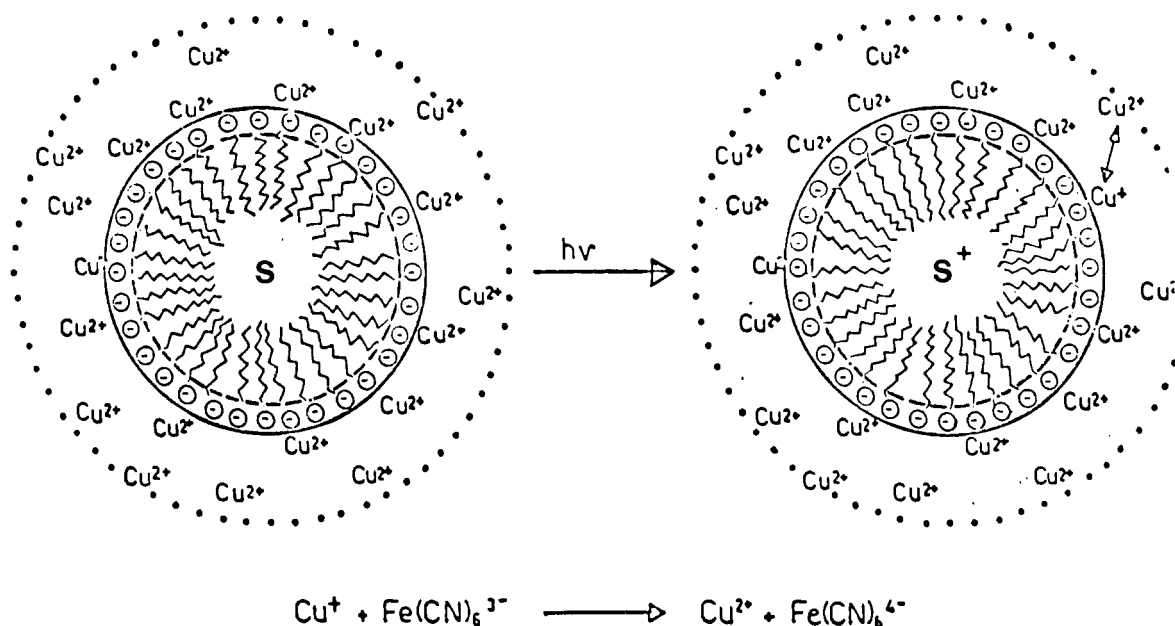(10) Kallmann, H.; Pope, M. *Nature (London)* **1960**, *188*, 935.

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(13) Compare ref 1, 2, and 8.

$$Cu^+ + Fe(CN)_6{}^{3-} \longrightarrow Cu^{2+} + Fe(CN)_6{}^{4-}$$

Figure 2. Light-induced charge separation in functional micelles. Surfactant $Cu(LS)_2$, S = sensitizer.

e.g., proflavin.[16] Among the electron relay compounds investigated, it is worth mentioning the viologens,[17] Eu^{3+} and V^{3+}, and their respective salicylate complexes,[18] $Ru(bpy)_3{}^{3+}$,[19] and cobalt complexes.[20]

A second type of light-harvesting unit suitable for water cleavage by visible light is illustrated in Figure 1b. The sensitizer is adsorbed onto a colloidal semiconductor particle, and no electron relay is required. The excited state of the sensitizer injects an electron into the conduction band of the semiconductor where it is channelled to a catalytic site for hydrogen evolution. A second ultrafine catalyst, codeposited onto the colloidal particle, mediates oxygen generation from S^+ and H_2O whereby the original form of the sensitizer is regenerated.

A third configuration where the colloidal semiconductor absorbs itself visible light is shown in Figure 1c. An electron–hole pair is formed through band gap excitation. The former affords hydrogen formation while the latter gives rise to oxygen generation from water, both processes being again mediated by suitable catalysts.

The light-harvesting units delineated under (b) and (c) have the advantage over the simple sensitizer–relay pair presented in (a) that light-induced charge separation and redox catalysis are concentrated in a very small

and confined reaction space. Thus all the water-splitting events can take place on a single colloidal semiconductor particle, eliminating the need for bulk phase diffusion of the reactants. If very active catalysts are employed, these processes can become extremely fast, thus dominating over undesired cross-reactions whose rates as a rule are limited by bulk diffusion.

Light-Induced Charge Separation, Functional Micelles, and Amphiphilic Redox Relays

A great deal of knowledge concerning the design of microscopic functional units suitable for water photolysis can be derived from studying colloidal model systems such as micelles,[21] microemulsions,[21] and vesicles.[22] These devices are microheterogeneous in character, providing compartmented reaction space of minute dimensions. In these systems fast redox processes do not obey the fundamental rate laws of homogeneous kinetics, and new theories had to be conceived to account for the experimental observations.[23] Some kinetic features characteristic for micellar assemblies will be discussed in the following section.

Micelles are surfactant aggregates that form spontaneously in aqueous solution[24] above a critical concentration (cmc). They are of approximately spherical structure (radius 15–30 Å), the polar head groups being exposed to the aqueous bulk phase while the hydrocarbon tails protrude in the interior. The micellar core region is thus apolar, allowing for the solubilization of hydrophobic species. The electrical double layer formed around ionic micelles gives rise to surface potentials

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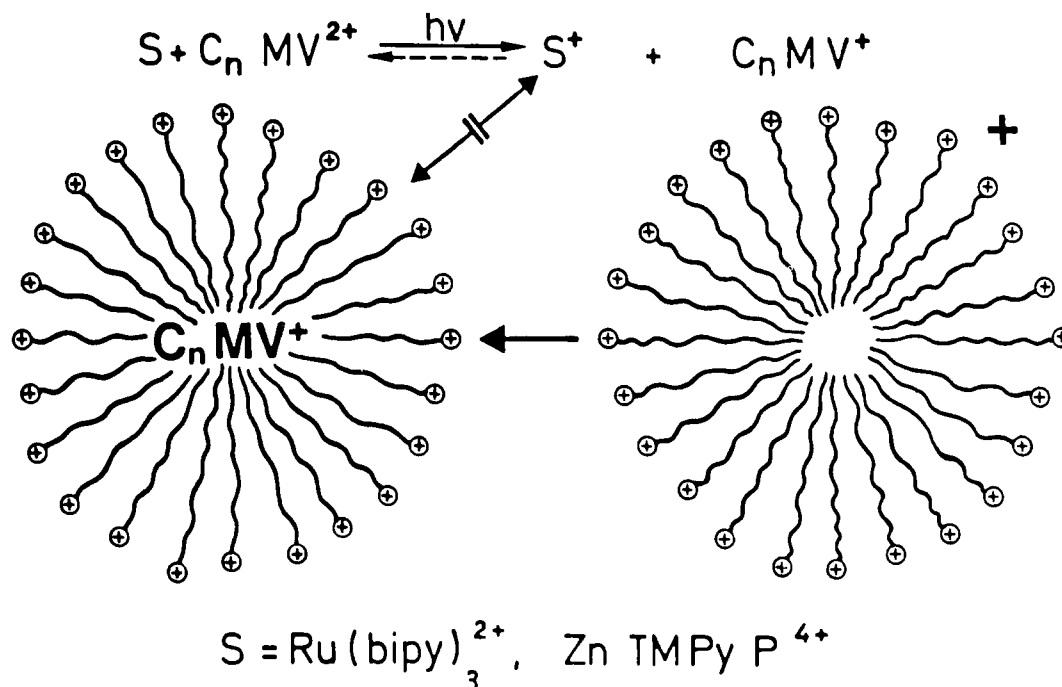
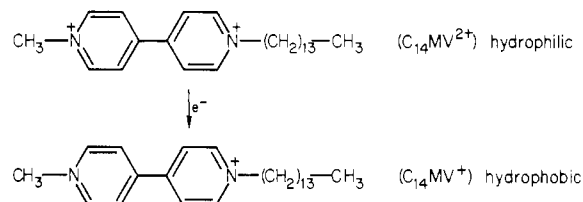**Figure 3.** Light-induced charge separation with amphiphilic redox relays.

frequently exceeding values of 150 mV.[25] This charged lipid–water interface provides a microscopic barrier for the prevention of thermal electron back-transfer and hence is comparable to the depletion or accumulation layer present at the semiconductor/electrolyte interface. The following examples illustrate this point:

Consider first a light-driven electron-transfer reaction in a functional micellar unit formed by a surfactant such as copper lauryl sulfate ($Cu(LS)_2$) (Figure 2). The term functional is used here to indicate that part of the micelle, i.e., the Cu^{2+} counterion atmosphere, participates in the redox events. A sensitizer (S) is solubilized in the interior of the aggregate and upon excitation transfers an electron to Cu^{2+}, thereby producing Cu^+ and S^+. The detailed laser analysis shows that the electron transfer is very fast and occurs here in less than a nanosecond.[26] Thus it can compete efficiently with other radiative and nonradiative deactivation processes of the exicted sensitizer. This is a consequence of the fact that through the micellar organization S and Cu^{2+} are held in close proximity and that the latter is present at high local concentration. (The counterion concentration in the micellar Stern layer is between 3 and 6 M.) The Cu^+ ion escapes in the solution bulk via exchange with Cu^{2+} before intramicellar back-reaction can occur. There it may be used to react with an electron acceptor such as $Fe(CN)_6^{3-}$, which in the reduced state is negatively charged and through Coulombic repulsion can no longer approach the anionic micelle. As a result, this system achieves electron/hole separation since the oxidized sensitizer (S^+) remains associated with the micellar aggregate.

Thus in this functional micellar unit light-induced charge separation is achieved by (a) exploiting the high local concentration of electron relay (Cu^{2+}) to drive the forward electron transfer at high rate which would be

difficult to obtain if bulk diffusion of the reactants was involved, (b) making use of a cooperative effect, i.e., the exchange of Cu^{2+} and Cu^+ at the micellar surface, which assists electron–hole separation, and (c) taking advantage of the charged micelle water interface which provides a local potential barrier to prevent the thermal back-reaction.

A different strategy to accomplish light-induced charge separation is based on the use of amphiphilic electron relays such as *N*-tetradecyl-*N*-methylviologen. In the oxidized state this compound exhibits a pronounced hydrophilic character while in the reduced state it has hydrophobic properties.

$$CH_3-\overset{+}{N}\!\!\!\diagdown\!\!\!\diagup\!\!\!\overset{+}{N}\!\!-(CH_2)_{13}-CH_3 \quad (C_{14}MV^{2+}) \text{ hydrophilic}$$

$$\downarrow e^-$$

$$CH_3-N\!\!\!\diagdown\!\!\!\diagup\!\!\!\overset{+}{N}\!\!-(CH_2)_{13}-CH_3 \quad (C_{14}MV^+) \text{ hydrophobic}$$

Consider now the reduction of $C_{14}MV^{2+}$ by a water-soluble sensitizer S in the presence of cationic micelles (Figure 3). The forward reaction occurs here in the aqueous phase. In the reduced state the viologen acquires hydrophobic properties, leading to rapid solubilization in the cationic micelles. As the oxidized sensitizer is prevented from approaching the micelles by their positive surface potential, the back-reaction is drastically retarded. When $Ru(bpy)_3^{2+}$ or porphyrin derivatives are used as a sensitizer 400-fold inhibition of the back-reaction has been achieved.[27]

Redox Catalysis, Artificial Equivalents of the Water-Splitting Enzyme

The kinetic control of light-driven redox reactions by micellar and other multiphase systems is only a first

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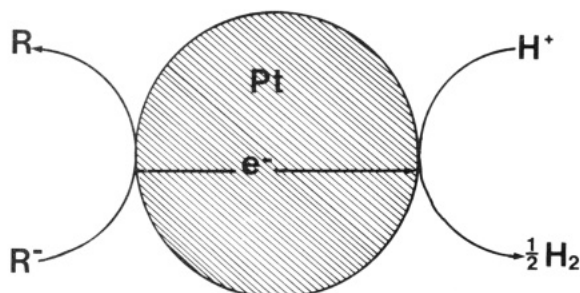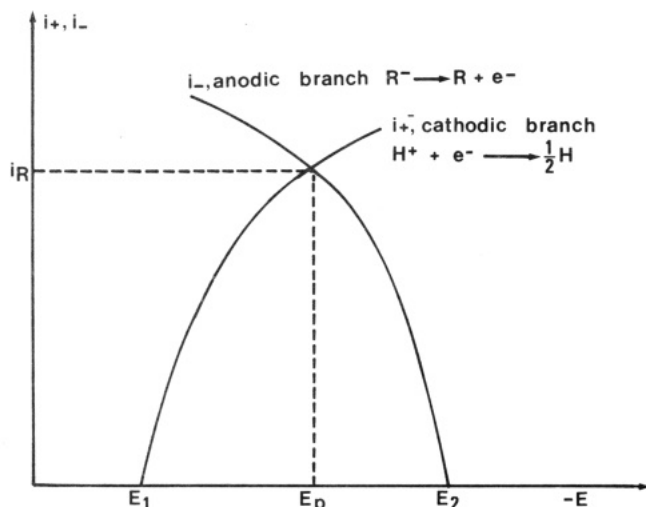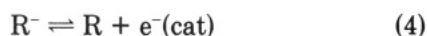
Figure 5. Mediator function of the colloidal TiO$_2$ particle, loaded with Pt in the light-induced H$_2$ generation from water. Electron injection from the reduced relay into the TiO$_2$ conduction band.

distinguished by a small overvoltage for hydrogen generation from water.[29] The second concerns the influence of the size of the colloidal particle on the rate of water reduction. From diffusion and electrokinetic theory it is expected that the rate constant for reaction 2 when mediated by a noble metal colloid should increase proportionally to $(1/r)^n$ where r is the particle radius and n is a constant[30] ($1 \leq n \leq 2$).

Both predictions have found ample experimental confirmation. It was already recognized many decades ago that colloidal Pt catalyzes water reduction by agents such as Cr^{2+}, V^{2+}, and the methylviologen radical.[31] This fact has been exploited more recently to develop photochemical systems that produce hydrogen under illumination.[32] Typically, Ru(bpy)$_3^{2+}$ or a porphyrin[15] are employed as the sensitizer which upon excitation reduces the electron relay, i.e., methylviologen (MV^{2+}).

$$\text{Ru(bpy)}_3^{2+} + \text{MV}^{2+} \underset{}{\overset{h\nu}{\rightleftharpoons}} \text{MV}^+ + \text{Ru(bpy)}_3^{3+} \quad (6)$$
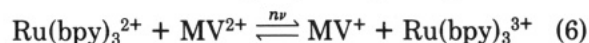
In the presence of Pt, water reduction occurs.

$$\text{MV}^+ + \text{H}_2\text{O} \xrightarrow{\text{(Pt)}} \text{MV}^{2+} + \text{OH}^- + 0.5\text{H}_2 \quad (7)$$
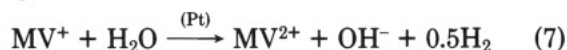
Ru(bpy)$_3^{3+}$ is reduced back to the 2+ state by a donor such as EDTA. As the latter is consumed in the photoreactions, these systems are sacrificial in that an organic compound instead of water is used as an electron source.

Despite their sacrificial character, these systems have nevertheless had great value in that they allowed for the optimization of the water reduction catalyst. Thus the hypothesis could be fully confirmed[33,34] that the catalytic activity increases with decreasing size of the noble metal particle.[35] To date, ultrafine Pt colloids are available[36] with a mean particle diameter of only 32 Å that allow for photochemical H$_2$ production with a

Figure 4. Current–voltage diagram for coupled electron-transfer processes occurring on a Pt particle. The overall reaction is hydrogen generation from the reaction of the reduced relay with water.

achievement on the way to conversion of solar light into chemical energy. A crucial problem to be solved is the coupling of the electron-transfer events with fuel producing steps, i.e., water decomposition according to eq 2 and 3. This can be brought about by a colloidal redox catalyst capable of mediating hydrogen and oxygen generation from water. The catalytic mechanism operative in these systems is now briefly discussed.

Consider first the generation of hydrogen from the reduced relay R$^-$ and water (eq 2). The role of the catalyst particle is to couple oxidation of R$^-$

$$\text{R}^- \rightleftharpoons \text{R} + \text{e}^-(\text{cat}) \quad (4)$$

to water reduction

$$\text{e}^-(\text{cat}) + \text{H}_2\text{O} \rightleftharpoons 0.5\text{H}_2 + \text{OH}^- \quad (5)$$

The current–voltage curves corresponding to these processes are depicted in Figure 4. As the net current across the particle/solution interface is zero, the potential E_p assumed by the particle under stationary conditions is given by the intersection of the two $i(E)$ curves. At this point the anodic and cathodic current are equal, and their value corresponds to i_R. The latter parameter defines the overall reaction rate. From this concept[28] two important predictions can be made. The first concerns the choice of the catalyst material: noble metals appear to be suitable candidates as they are

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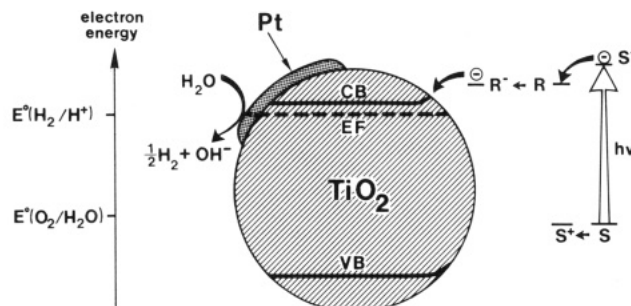
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(34) (a) Miller, D.; Bard, A. J.; McLendon, G.; Ferguson, J. *J. Am. Chem. Soc.* **1981**, *103*, in press. (b) Frank, A. J.; Stevenson, K. L. *J. Chem. Soc., Chem. Commun.* **1981**, 593. (c) Toshima, N.; Kuriyama, M.; Yamada, Y.; Hirai, H. *Chem. Lett.* **1981**, 793.
(35) Only one recent publication (Keller, P.; Moradpour, A. *J. Am. Chem. Soc.* **1980**, *102*, 7193) appears to contradict this fundamental principle of electrocatalysis. Hydrogen generation in a sacrificial system was claimed to be independent of catalyst particle size. Presumably, these effects arise from agglomeration of the colloid and/or interference of the protective agent with catalytic sites.
(36) Turkevich, J.; Aika, K.; Ban, L. L.; Okura, I.; Namba, S. *J. Res. Inst. Cat. Hokkaido Univ.* **1976**, *24*, 54.

quantum yield exceeding 30%.[37]

A further remarkable increase in activity is observed when these ultrafine Pt aggregates are deposited on a colloidal semiconductor such as TiO_2. In this case the cross section of the reaction of the reduced relay R^- with the catalyst is greatly increased as the support itself can act as an electron acceptor (Figure 5). The electron is injected into the conduction band of the semiconductor from where it migrates to Pt sites where hydrogen generation from water takes place. By using laser photolysis techniques, it was possible to directly monitor the kinetics of hydrogen formation from reduced methylviologen and water in such a system.[38] We observed a reaction rate constant of $k_7 = 3 \times 10^{-5}$ s^{-1} at 20 mg/L Pt supported by 500 mg/L colloidal TiO_2. Furthermore, it was shown that the colloidal particles interacted selectively with the MV^+, while no or very slow reaction occurred with the oxidized sensitizer $Ru(bpy)_3^{3+}$. This finding is of crucial importance for the design of a cyclic water decomposition system where specificity of interaction is mandatory and high rates of water reduction required to successfully intercept the back-reaction and to compete with oxygen reduction via

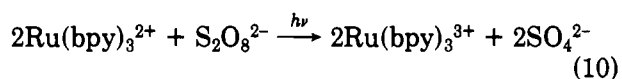$$MV^+ + O_2 \rightarrow MV^{2+} + O_2^- \qquad (8)$$
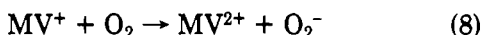
The photodecomposition of water became feasible in a regenerative way only after oxygen-generating catalysts had been developed. In 1978, it was discovered in our laboratory[39] that noble metal oxides such as PtO_2, IrO_2, and RuO_2 in macrodisperse or colloidal form are capable of mediating water oxidation by agents such as Ce^{4+}, $Ru(bpy)_3^{3+}$, and $Fe(bpy)_3^{3+}$. RuO_2 has subsequently been most widely investigated.[40] An impression of the improvement of the activity of RuO_2-based catalysts may be gained from the following comparison: Three years ago, in order to effect water oxidation by $Ru(bpy)_3^{3+}$

$$4Ru(bpy)_3^{3+} + 2H_2O \rightarrow 4Ru(bpy)_3^{2+} + O_2 + 4H^+ \qquad (9)$$
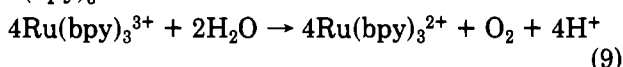
within a time domain of several minutes we required 1 g/L RuO_2 powder. Today, by using an ultrafine deposit of RuO_2 on colloidal TiO_2 particles, a half-lifetime of 5–10 ms can be obtained[41] with only 3 mg/L RuO_2. Thus, by decrease of the particle size of RuO_2 and stabilization of the catalyst on a suitable carrier a more than 10^6-fold increase in the catalytic activity has been achieved.

Application of combined flash photolytic and fast conductometric technique made it possible to probe the mechanistic details of the oxygen evolution reaction. Thus, $Ru(bpy)_3^{3+}$ was produced via the photoredox reaction[41]

$$2Ru(bpy)_3^{2+} + S_2O_8^{2-} \xrightarrow{h\nu} 2Ru(bpy)_3^{3+} + 2SO_4^{2-} \qquad (10)$$

and the kinetics of oxygen production via reaction 9 were studied in the presence of a catalyst consisting of a transparent TiO_2 sol loaded with RuO_2. A comparison of the temporal behavior of the $Ru(bpy)_3^{3+}$ absorption decay and the increase in conductivity associated with water oxidation was made. Both events were found to occur simultaneously, indicating that hole transfer from $Ru(bpy)_3^{3+}$ to RuO_2 is immediately followed by release of protons and oxygen from water. Thus the particle couples reduction of $Ru(bpy)_3^{3+}$ to water oxidation. This experimental observation provides a direct proof that the concept of redox catalysis, considering the RuO_2 colloid as microelectrodes, is valid for water oxidation as well as for water reduction. Moreover, the RuO_2 particles can be regarded as artificial analogues of the water-splitting enzyme in photosystem II, present in chloroplasts. Both are capable of transferring four oxidation equivalents from a suitable solute to water, releasing oxygen and protons. The RuO_2 mediator affords water oxidation within milliseconds at surprisingly low concentration. This proved to be extremely valuable in energy conversion systems where water is the source of photodriven uphill electron flow.

Cyclic Water Cleavage with Coupled Redox Catalysts

Since photogenerated MV^+ and $Ru(bpy)_3^{3+}$ can be used for water reduction and oxidation, respectively, it is tempting to examine a system where the two catalytic processes can take place simultaneously following photoinduced electron transfer. As was pointed out above, the RuO_2 and Pt catalysts have to be active enough to intercept the back-reaction. Also, their intervention has to be specific in that MV^+ reacts selectively with the Pt particles while $Ru(bpy)_3^{2+}$ interacts with RuO_2. Cross-reactions have to be avoided since they lead to short circuitry of the back-reaction.

A first successful attempt to split water photochemically this way was made by us in 1979.[42] A copolymer of maleic anhydride and styrene was used as a protective agent for the Pt sol. This is suitable to achieve selectivity since it provides functions with pronounced hydrophobicity. Of the redox products formed in the light reaction, MV^+ is relatively hydrophobic and will therefore interact with the Pt. $Ru(bpy)_3^{3+}$, on the other hand, is prone to interact with the hydrophilic and negatively charged RuO_2 surface. One disadvantage of this system is that the quantum yield of water splitting is small ($\sim 0.1\%$) and that the photoreaction stops in a closed vessel after a few hours of irradiation. One encounters here a fundamental problem which is inherent to all devices that attempt to produce photolytically H_2 and O_2 without local separation: The presence of oxygen will severely limit the quantum yield of water splitting as both depolarization of the cathodically tuned Pt particles and reoxidation of the reduced relay according to eq 8 will interfere with hydrogen generation. Using computer simulation, Infelta[43] has elaborated the detailed kinetics of the processes occurring in the $Ru(bpy)_3^{2+}/MV^{2+}$ system under illumination. By taking into account the rate parameters for all relevant reactions including catalytic H_2 and O_2 production, he arrives at the conclusion that water

(37) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* 1980.

(38) Duonghong, D.; Borgarello, E.; Grätzel, M. *J. Am. Chem. Soc.* 1981, *103*, 4685.

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(41) Humphry-Baker, R.; Lilie, J.; Grätzel, M. *J. Am. Chem. Soc.* 1981, *103*, in press.

(42) Kalyanasundaram, K.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 701.
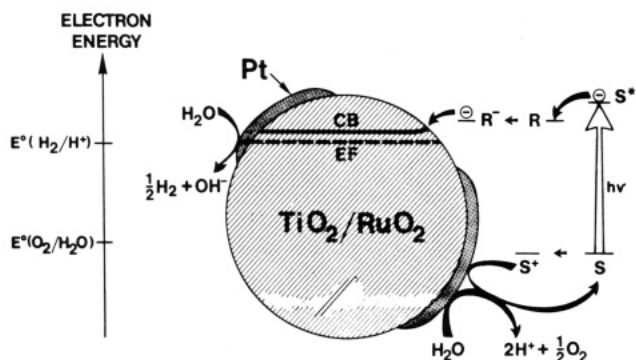
(43) Infelta, P. P., to be published.

Figure 6. Schematic illustration of the intervention of a colloidal TiO₂ based bifunctional redox catalyst in the cleavage of water by visible light.

splitting will cease once the oxygen concentration builds up in solution.

This problem has been overcome only recently through the development of bifunctional redox catalysts.[44] The latter are distinguished by the fact that Pt and RuO₂ are loaded onto the same mineral carrier particle. Colloidal TiO₂ was the first material to be used as a support. It fulfills four different functions in the water-splitting system (Figure 6): (1) It serves as a carrier for Pt and RuO₂ and maintains these catalysts in a highly dispersed state. (2) The TiO₂ conduction band accepts electrons from the reduced relay or the excited sensitizer. These are channeled to Pt sites where hydrogen generation occurs. As the whole TiO₂ particle is reactive, the cross section and hence the rate of electron capture are greatly increased with respect to systems in which polymer protected Pt particles are used as catalysts. (3) RuO₂ catalyzes oxygen production from water. (4) TiO₂ serves as an adsorbent for O₂ produced during the photolysis. Some adsorption will take place spontaneously; however, the main part is photoinduced: Electrons injected into the conduction band are used to reduce O₂ to O₂⁻ which is strongly attached to the TiO₂ surface.[45] Assuming monolayer coverage 1 g of TiO₂ with a surface area of 200 m² can adsorb ca. 50 mL of O₂. Through this mechanism the amount of O₂ in solution is kept very low, which benefits greatly the efficiency of water photolysis.

Detailed investigations have meanwhile been carried out with the TiO₂-based redox catalyst with the Ru(bpy)₃²⁺/MV²⁺ couple as a sensitizer/relay pair. Apart from the composition of the catalyst (n doping, RuO₂ and Pt loading), the quantum yield of water splitting depends strongly on TiO₂ concentration, pH, and temperature.[46] Under optimum conditions, the efficiency for hydrogen production ($\phi(H_2)$) is 6% (75 °C). A study of the kinetics of H₂ and O₂ generation showed that over the initial period of 10–20-h irradiation time the gas released from the solution is pure hydrogen, oxygen being retained in the solution through adsorption on TiO₂. This finding is important in that it points at a way to separate hydrogen from oxygen which presents a problem for practical applications of such systems. The capacity of the carrier must be made high enough to adsorb the quantity of oxygen produced from 1-day

Figure 7. Processes involved in the photodecomposition of water in a relay free system. An amphiphilic Ru(bpy)₃²⁺ derivative is used as a sensitizer.

solar irradiation. In such a system daylight production of hydrogen would alternate with O₂ release during the night.[47]

Cyclic water cleavage by visible light was also achieved in electron relay free systems. In this case the fraction of sensitizer that is adsorbed onto the particle surface is photoactive and electron injection occurs directly from its excited state into the TiO₂ conduction band. With the surfactant–ruthenium complex depicted in Figure 7, a quantum yield of 7% was obtained for the water-splitting process.[48]

A third type of water photolysis system is based on band gap excitation of colloidal semiconductors, as depicted in Figure 1c. Photoinduced electron–hole separation is followed by H₂ production from conduction band electrons catalyzed by Pt. Holes in the valence band are used to generate oxygen. Previous studies have been carried out with TiO₂ or SrTiO₃ as support material.[49] However, UV irradiation is required to excite these particles, and efficiencies are usually small. An exception is made by the bifunctional redox catalyst which splits water with surprising efficiency under near-UV illumination (λ > 300 nm). Thus, from irradiating 25 mL of water containing 12.5 mg of

(44) Kiwi, J.; Borgarello, E.; Pelizzetti, E.; Visca, M.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 646.
(45) Munuera, G.; Rives-Arnau, V.; Saucedo, A. *J. Chem. Soc., Faraday Trans 1* **1979**, 736.
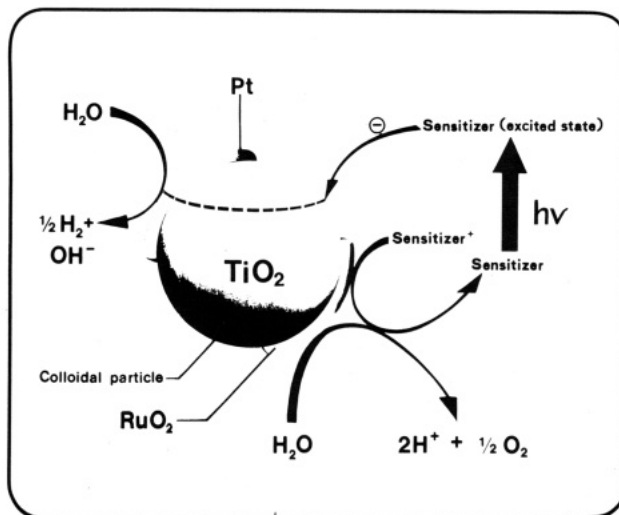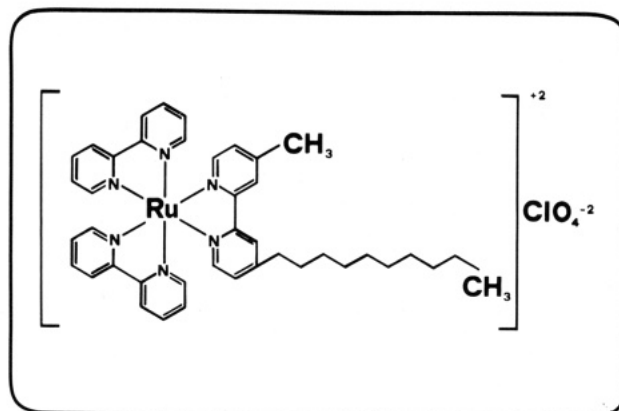(46) Borgarello, E.; Kiwi, J.; Pellizzetti, E.; Visca, M.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 0000.

(47) Oxygen release can be brought about for example by exposing the TiO₂ solution to sodium phosphate.
(48) Borgarello, E.; Kiwi, J.; Pelizzetti, E.; Visca, M.; Grätzel, M. *Nature (London)* **1981**, *289*, 158.
(49) (a) Kawai, T.; Sakata, T. *Chem. Phys. Lett.* **1980**, *72*, 87. (b) Sati, S.; White, J. *J. Chem. Phys. Lett.* **1980**, *72*, 83.

TiO$_2$ loaded with Pt and RuO$_2$ with a Xe lamp one obtains hydrogen at a rate of 2 mL/h, which corresponds to a quantum yield of ca. 30%. A key role to achieve this high efficiency is played by the RuO$_2$ deposit on the TiO$_2$ particle which greatly facilitates the transfer of holes from the valence band of the semiconductor to the solution bulk.

This catalytic effect of RuO$_2$ has been exploited recently to stabilize small band gap semiconductor particles which from their absorption properties are more suitable for solar energy conversion than TiO$_2$. An undesirable property of these materials is that they undergo photocorrosion under illumination. Holes produced in the valence band migrate to the surface where photocorrosion occurs, i.e.

$$CdS + 2h^+ \rightarrow Cd^{2+} + S \qquad (11)$$
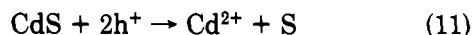
Recently, we discovered[50] that loading of colloidal or macrodisperse CdS particles with an ultrafine deposit of RuO$_2$ prevents photodecomposition through promotion of water oxidation according to

$$4h^+ (CdS) + 2H_2O \xrightarrow{(RuO_2)} O_2 + 4H^+ \qquad (12)$$
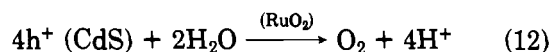
Sustained water cleavage by visible light is observed when CdS particles loaded simultaneously with Pt and RuO$_2$ are used as photocatalyst. Again, hydrogen and oxygen are generated by conduction band electrons[51] and valence band holes, respectively, produced by band gap excitation. Thus irradiation of a 25-mL solution containing 2.5 mg of colloidal CdS loaded with 0.5 mg of Pt and 0.2 mg of RuO$_2$ yields 2.8 mL of H$_2$ and 1.4 mL of O$_2$ after 44 h of irradiation with the visible output of a 450-W xenon lamp. The quantum yield is still significantly below that observed with the TiO$_2$/Pt/RuO$_2$ sol in the presence of a suitable sensitizer, and further development is required to improve the performance of this system.

The ability of RuO$_2$ to promote hole transfer from the conduction band of CdS to solution species can be exploited for processes other than water oxidation. Thus, CdS suspensions loaded with RuO$_2$ decompose H$_2$S into hydrogen and sulfur very efficiently under visible light irradiation:[52]

$$H_2S \xrightarrow{h\nu} H_2 + S \qquad (13)$$

The quantum yield obtained for reaction 13 is as high as 35%. The role of RuO$_2$ in this system is to enhance the rate of sulfide oxidation by holes produced in the valence band through band gap excitation. Thus electron–hole recombination is intercepted efficiently, and high quantum yields are obtained. Electrons in the conduction band are used to reduce protons to hydrogen. Important with respect to practical application is the fact that no Pt catalyst is required to promote hydrogen formation. This is due to a cathodic shift of the flatband potential of CdS caused by adsorption of sulfide ions. Therefore the driving force for water reduction to hydrogen is increased, making the use of a

Pt catalyst superfluous. The decomposition of hydrogen sulfide is an energy-storing process that could become an important alternative to water cleavage as a source for hydrogen production from sunlight. H$_2$S is an abundant waste product in coal- and petrol-related industry that could be made use of in this way.

Dynamics of Interfacial Charge Transfer Processes in Colloidal Semiconductor Solutions

Colloidal semiconductors have the advantage of yielding optically transparent solutions when dispersed in a liquid. This allows for ready kinetic analysis of interfacial charge-transfer processes by laser photolysis techniques, opening up the way to direct determination of rate parameters and yields for oxidation and reduction reactions involving conduction band electrons or valence band holes, respectively.

We have recently initiated investigations in this direction by applying laser photolysis techniques to the study of light-induced charge-transfer processes in colloidal TiO$_2$ and CdS solutions.[53] Consider, for example, the reduction of viologen by conduction band electrons of CdS. The laser provides a short light pulse ($\sim$5 ns) to excite the colloidal CdS particle, producing an electron–hole pair. The electron migrates to the phase boundary where it reduces the viologen to the blue radical ion. An analysis of the temporal behavior of the radical absorption at 602 nm showed that the appearance of the absorption follows essentially the profile of the laser pulse. Thus the electron transfer from the conduction band of CdS to the viologen appears to be a very rapid process. In the absence of oxygen the viologen radical is stable, giving rise to the appearance of an intense blue color under illumination.[54] The complementary hole reaction involves oxidation of CdS to sulfur. The quantum yield of MV$^+$ formation is increased about 5 times when hole scavengers such as sulfide ions are added to the solution. This indicates that electron–hole recombination occurs at a rate which is significantly faster than viologen reduction. Work involving a series of different electron donors or acceptors is now in progress. This should yield a wealth of information on the detailed mechanism of charge-transfer processes across a semiconductor/electrolyte interface.

Conclusions

Colloidal semiconductors, molecular assemblies such as micelles or vesicles, and ultrafine redox catalysts provide suitable microscopic organization to accomplish the difficult task of light-induced water cleavage. Work in the future will will be directed to improve the efficiency of such devices by identifying new photocatalysts and solving the problem of hydrogen/oxygen separation. Colloidal semiconductors will certainly play a primordial role in this development. Together with other functional organizations they have the key advantage that light-induced charge separation and catalytic events leading to fuel production can be coupled without intervention of bulk diffusion. Thus a single colloidal semiconductor particle can be treated with appropriate catalysts so that different regions function

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(51) Hydrogen production from illumination of CdS in the presence of EDTA has been shown by: Darwent, J. R.; Porter, G. *J. Chem. Soc., Chem. Commun.* 1981, 145.
(52) Borgarello, E.; Kalyanasundaram, K.; Grätzel, M.; Pelizzetti, E. submitted for publication.

(53) Duonghong, D.; Ramsden, J.; Grätzel, M., submitted to *J. Am. Chem. Soc.*
(54) Saeva, F. D.; Olin, G. R.; Harbour, J. R. *J. Chem. Soc., Chem. Commun.* 1980, 401.

as anodes and cathodes. It appears that this wireless photoelectrolysis could be the simplest means of large scale solar energy harnessing and conversion.

Lanthanide Ion Luminescence Probes of the Structure of Biological Macromolecules

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Approximately a third of all proteins require metal ions for their activity or contain bound metal ions in their native states.[1-3] Some of these metal ions, e.g., Cu, Fe, Mo, exhibit useful spectroscopic or magnetic probe properties, while others, e.g., Zn, Mg, Ca, do not. When the native metal ion is devoid of useful properties, it is often possible to substitute an ion with useful characteristics. Some examples are the replacement of Zn(II) by Co(II)[4,5] or Ca(II) by the trivalent lanthanide ions.[6-10] This latter substitution is the principal concern of this Account.

In any study in which a biomolecule is modified, it is important to establish what, if any, changes occur upon substitution. The ideal probe will leave the macromolecule virtually indistinguishable from the native species except for the spectroscopic "handle". For enzymes, the retention of at least some degree of biological activity is evidence that the native conformation has not been drastically altered. Lanthanide ions (symbolically Ln(III)) have been reported to activate the following systems to their biological function in the absence of Ca(II): aequorin,[11] concanavalin A,[12] trypsinogen,[13] phospholipase A$_2$,[14] α-amylase,[15] galactosyltransferase,[16] and prothrombin (activation by activated factor X).[17] In the cases of staphylococcal nuclease,[18] phosphoglycerate kinase,[19] and calcium ATPase[20] and in the activation of bovine factor X by the coagulant protein of Russell's viper venom,[21] Ln(III) ions act as inhibitors of the Ca(II) or Mg(II) ion functions. Ln(III) ion substitution has no effect on the enzymatic activity of thermolysin[22] and elastase.[23] In addition, Ln(III) ions have been shown by X-ray crystallographic techniques to substitute isomorphously for Ca(II) in thermolysin[24] and parvalbumin.[25,26] It can be argued that replacement of a metal by one of similar size represents a smaller perturbation of a macromolecule than the chemical modification of a polypeptide side chain using, say, a nitroxide spin-label.

The trivalent ions of the 14 stable elements from La(III) through Lu(III) have ionic radii ranging from slightly greater to slightly smaller than that of Ca(II).[27]

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