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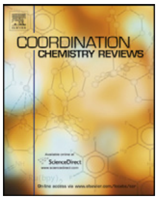

Review

Molecular devices featuring sequential photoinduced charge separations for the storage of multiple redox equivalents

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ABSTRACT

The present review focuses on one facet of artificial photosynthesis: the charge photo-accumulation function, which has been much less investigated than photoinduced energy or electron transfer reactions. However, charge accumulation is certainly of fundamental importance to perform reactions involving multiple redox equivalents, such as most fuel making reactions. Indeed, the charge photo-accumulation function is specifically relevant to the efficiency of artificial photosynthetic devices and represents an essential property of the photosystem II in oxygenic photosynthetic organisms. We introduce the general concept of charge photo-accumulation, which consists in the collection of multi-redox equivalents at specific sites upon consecutive multiple photon absorptions. We survey the existing artificial molecular systems capable of multiple charge storage upon successive light excitations and new directions for future developments in this area are presented.

1. Introduction

Climate change due to the greenhouse effect and the ever increasing global energy demand have prompted a growing interest in the development of carbon zero energy resources in order to replace our major dependence on fossil fuels [1,2]. Solar energy certainly represents one of the most realistic and appealing solutions to this crucial challenge since it is a colossal and inexhaustible source of energy. The sun's activity is estimated to last for another 5 billion years and it annually provides about 100 000 TW. Photosynthesis produces more than 100 billions tons of biomass which represents an energy storage of about 100 TW. Currently, the rate of global energy consumption is a bit less than 14 TW, therefore 1 h of sunlight brings the equivalent to all the energy consumed in one year by mankind. Alternatively, natural photosynthesis produces more than seven times the global energy demand of 2010. The storage of solar energy into chemical bonds is a very attractive strategy to produce and store environmentally free energy and this strategy is demonstrated at large scale with photosynthetic organisms. In natural photosynthesis low energy inorganic starting materials such as carbon dioxide and water are respectively reduced and oxidized into carbohydrates and dioxygen. Similarly, an integral artificial photosynthetic system produces energy rich substances, such as dihydrogen or methanol, from low energy materials (such as water, carbon dioxide) activated by solar energy [3–11]. The mimicry of the natural photosynthesis process by artificial systems, refereed as the field of artificial photosynthesis, represents one of the most challenging endeavours and perhaps the Holy Grail of this century [10,12–16]. Today, there are considerable information about the structure and the operation principle of natural photosynthetic systems [17–21]. Moreover, scientists have dedicated important research efforts towards artificial photosynthesis; first to understand and then to duplicate the functional features of the natural photosynthetic apparatus with man-made

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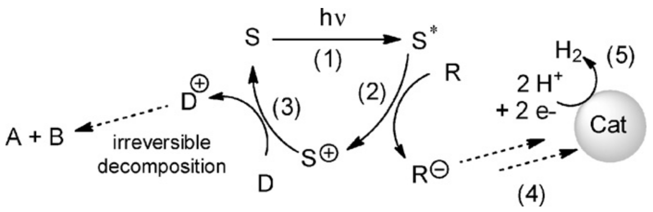
devices. A molecular system capable of transducing solar energy into chemical potentials, that is producing fuels, can be viewed as a multi-functional system performing several distinct acts in series. First, sunlight is harvested by highly absorbing pigments and then transformed into a charge separated state. These first two functions are relatively well-mastered in artificial molecular systems since antenna systems made of chromophoric arrays can efficiently collect solar energy and convert it into a long-lived charge separated state with quite high quantum yields [3,22–28]. However, the ultimate goal of artificial photosynthesis is to produce fuels and towards this objective another crucial step is required. It involves the use of the charge separated state to perform oxidation and reduction reactions [4,6,7,14,29]. At this stage, it is important to underline that most fuel making reactions require more than a single electron to operate, while photoinduced charge separation is a monoelectronic process in essence. For example, proton reduction into dihydrogen involves two reducing equivalents, while carbon dioxide reduction into methanol requires six. These reactions will be difficult to achieve with single electron/single hole charge separated states. Therefore, an efficient molecular system for multielectron catalysis should be able to deliver several redox equivalents to a substrate in a concerted manner, because the alternative stepwise monoelectronic pathway will inevitably be uphill and therefore more energy demanding. A strategy to overcome the poor stoichiometry matching between the photoinduced process and a multielectron fuel making reaction would be to couple single photon charge separation to a multiple charges storage function, which is referred thereafter as charge photo-accumulation. This rarely addressed function represents another paradigm of solar conversion. The natural photosynthetic apparatus, which is the most efficient molecular system for the transformation of solar energy into chemical potentials, has indeed developed, over the evolution, the capability to store multiple oxidizing equivalents in the photosystem II (PSII) in order to oxidize water into dioxygen. To integrate a charge accumulation function into a photomolecular device, charge pools or charge reservoirs should be placed in the vicinities of the terminal electron and hole acceptors in order to temporarily store the redox equivalents produced upon successive photoinduced charge separations (Scheme 4). A reservoir is therefore a molecule able to collect multiple electrons (or holes) within a narrow potential range and to subsequently deliver them in a concerted manner to a catalyst or directly to a substrate to drive a multiredox process. At this stage, it is certainly useful to recall the general approach used so far to design molecular photocatalysts for light driven fuel production. This strategy was developed in the late seventies [30–37] and still governs the operation of most recent published systems [9,38–40]. Herein, we will discuss a system for hydrogen evolution, but the same conceptual approach is clearly involved to drive other redox processes, such as carbon dioxide reduction [41–43] or water oxidation [44–46], except that in the latter case, the sensitizer is reductively quenched with an electron donor relay and that sacrificial electron donors are replaced by sacrificial electron acceptors. Molecular photocatalytic systems for dihydrogen production are generally composed of four functional components: the sensitizer (S), which is generally a highly absorbing dye in the visible region, an electron relay (R), which is often a viologen derivative, a sacrificial electron donor (D) (typically triethanolamine) and an electrocatalyst (Cat), which is often colloidal platinum. The operation mechanism is shown in Scheme 1 and can be summarized as follows: (1) the sensitizer excited-state (S^*) is generated upon photon absorption, (2) S^* is oxidatively quenched by the electron relay R to produce the first ion pair (S^+ and R^-), (3) the oxidized sensitizer is restored back to its original state by the sacrificial electron donor (D), (4) the reduced relay R^- diffuses to the electrocatalyst (Cat) to donate its electron. Finally, once two reducing equivalents are collected by the catalyst, the transformation of two protons into dihydrogen can occur (act 5). Catalysis can only take place when two electron relay molecules have supplied two reducing equivalents to the hydrogen evolution catalyst. This requires that two relay molecules effectively each shuttle one electron to the catalyst. In the simple conventional approach, shown in Scheme 1, energy wasting charge recombination reactions (for example of R^- with S^+ or S^*) could compete with the intermolecular electron transfer step (4) of R^- to the catalyst. This drawback becomes even more pronounced if one envisions getting rid of the sacrificial reagent D, because D^+ represents a supplementary potential deleterious quencher of R^- or S^*.

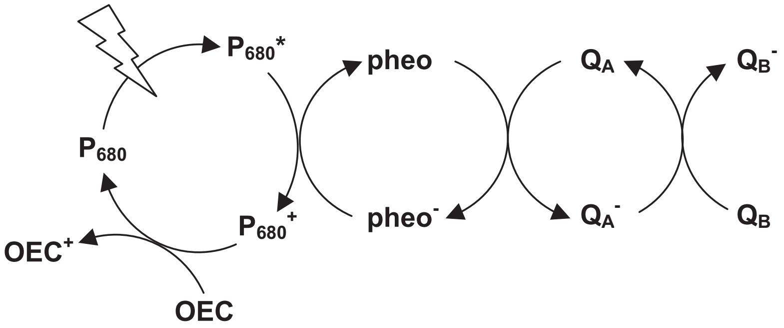


Scheme 1. General operation principle involved in photocatalytic systems for dihydrogen production.

In photosystem II, all the active components are rigidly organized in a protein matrix and their movements are restricted to a low amplitude. As a result, the quantum yield of all the electron transfer reactions approaches unity, because the charge carriers have very little chance to exchange electrons in a counterproductive manner, that is, with other components than those positioned in their vicinity. Accordingly, the linking and the organization of all the components will most certainly be a decisive advantage to improve the efficiency of future molecular photocatalytic devices. Indeed, the direct wiring of the sensitizer to the electrocatalyst [47–52] or of the electron relay to the electrocatalyst [53], as shown in recent photomolecular devices for hydrogen production, proved to afford higher efficiencies compared to the simple mixture of separate components. There are several reviews on the topic of artificial photosynthesis [4,5,9,10,14,29,54–56], but in this article we specifically emphasize the function of charge photo-accumulation at the molecular level. The focus of this review is therefore to highlight some of the experimental works which have appeared in the recent literature concerning the development of molecular systems for the photo-driven production and storage of multiple redox equivalents on single molecular units. The review is organized as follows. Starting with a brief description of the photosystem II in natural photosynthetic organisms, we highlight the importance of charge photo-accumulation to conduct a multi-electron reaction such as water oxidation. Then, we define the general principles for the design and molecular engineering of an integral artificial photosystem, including the function of charge photo-accumulation, which is rarely clearly discussed. The next two parts survey the existing molecular systems capable of photodriven hole or electron storage. Finally, we end with some perspectives in this new area.

2. Hole photo-accumulation in the oxygenic photosynthetic reaction centre

Over 3 billion years of evolution, Nature has developed in photosynthetic organisms an elegant molecular machinery which solves all the key features of solar energy transformation into chemical potentials and particularly the function of charge photo-accumulation. Natural photosynthesis allows green plants, algae and cyanobacteria to metabolize carbon dioxide and water; these endergonic reactions are fuelled by solar light as the one and only source of energy. The latter is transformed into usable energy by a complex assembly of proteins, capable of performing a tremen-



Scheme 2. Photoinduced charge separation and subsequent electron transfer steps in PSII.

dous number of poly-electronic redox reactions. Among them, the photo-oxidation of water into molecular dioxygen (Eq. (6)) is particularly studied. A mere glance at Eq. (6) suffices to realize that no less than four electrons are exchanged in this chemical reaction, putting premium on the unavoidable necessity for any photosynthetic organism to be able to collect several holes and electrons.

$$2H_2O + h\nu \rightarrow 4H^+ + O_2 + 4e^- \qquad (6)$$

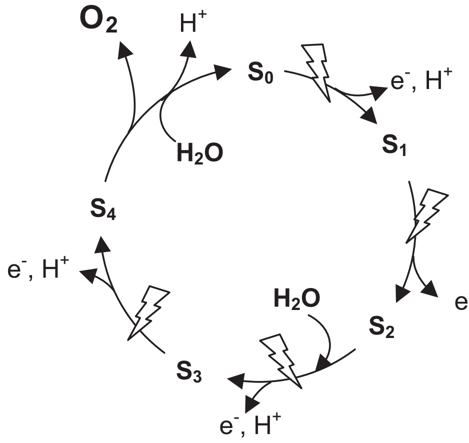
To give a detailed expose of the functioning of natural photosynthesis is off the subject of this review, but a brief account of the mechanistic ways found by Nature to realize charge photo-accumulation will be given in this section.

The first protein system that is prompted in the whole process of photosynthesis is called photosystem II (PSII), and is responsible for the photo-oxidation of water into dioxygen (Scheme 2). All the photosynthetic processes are sparked off by the absorption of light. An impressive collection of pigments is in charge of this function, among them, carotenes and, of course, chlorophylls [19,20,57]. First and foremost, all these dyes take on the protection of the reactive heart of PSII, shielding the latter from the potential damages caused by direct solar illumination [5]. But there is a lot more to the role of this pigment shell. Indeed, taken separately, these pigments display rather narrow absorption bands and cover therefore a too small wavelength domain of the solar spectrum. All together however, they can spread over the whole visible spectrum. All absorbed photons from the visible wavelength domain are thus absorbed by the pigments located in this antenna and the resulting excitation energy is directed by a series of very efficient energy transfer steps to the ultimate destination: the special pair which is the energy sink of the system.

In one of the most studied photosynthetic bacteria *thermosynechoccocus elongatus*, P_{680} is a crown-shaped, supramolecular arrangement of four chlorophyll dyes, and is the very place where photonic energy is converted into chemical energy [58,59]. When funnelled solar energy finally reaches P_{680}, an electron is transferred from the latter towards the vicinal pheophytin acceptor (pheo), hence producing a charge separated state. Thus is accomplished the transformation of photonic energy into redox, usable energy, yielding a strong oxidant ($P_{680}{}^+$) and a reductant (pheo$^-$). The amount of energy that is accumulated in PSII at this moment of the process is quite considerable (ca. 1.8 eV) [60], and the potential of $P_{680}{}^+$, estimated around 1.25 V/ENH is more than sufficient to realize water oxidation, from a thermodynamic point of view.

In addition to this, the practical use of a charge separated state is always subjected to the kinetics of the back electron transfer. A charge recombination between the hole on P_{680} and the electron on pheo is a highly thermodynamically favourable process, which would unfortunately dissipate the energy acquired by P_{680} before it could be involved in a redox reaction. In order to avoid this quenching process, the distance between the photo-produced hole and electron is quickly increased *via* secondary electron transfers, lowering the probability of charge recombination: the extra electron located on pheo is transferred to the quinone acceptors Q_A, then Q_B, thanks to the adequacy of their redox potentials. Concomitantly, the hole on P_{680} is conveyed to the adjacent tyrosine residue Tyr_Z through oxidation of the latter by $P_{680}{}^+$. In the course of this process, Tyr_Z releases its phenolic proton in favour of the closely lying histidine residue His_{190}, yielding a stable tyrosyl radical, $Tyr_Z{}^{ox}$ [61,62]. PSII is now more or less 20 ns older since the first charge separation, and the lifetime of the $Q_{A,\,red} - Tyr_Z{}^{ox}$ is worth tens of microseconds [62,63]. This very long-lived state is mandatory to give enough time for the following, rather sluggish steps. $Tyr_Z{}^{ox}$ is subsequently reduced by electron transfer from a cluster of four manganese ions. Its role is to collect four holes and to catalyze water oxidation into dioxygen. Indeed, this tetranuclear complex (noted Mn_4 thereafter) is the very catalytic site where water molecules are oxidized into molecular oxygen. The latter and the Tyrosine/Histidine pair are gathered under the evocative name of Oxygen Evolving Centre (OEC). Finally, the distance between the photo-produced hole and electron has reached an impressive value superior to 20 Å, definitely curbing the probability for charge recombination and other quenching pathways. On the other hand, these electron transfers have been realized at the cost of a loss in the initially acquired energy, a problem that is solved within PSI through the "Z-scheme". With an electron on Q_B and a hole on Mn_4, the physical boundaries of PSII are reached.

To sum up, the absorption of one photon by P_{680} has led to a charge separated state, described as one extra electron on the acceptor Q_B, and one extra hole on Mn_4. No chemical reaction can be performed at this stage: for instance, the manganese cluster requires the accumulation of four holes to catalyze water oxidation. The chain of steps we have described so far must therefore be performed three more times in order to photo-accumulate the necessary redox payload on the polynuclear complex. The manganese tetranuclear cluster cycles through five redox states S_n ($n = 0, 1, 2, 3$ and 4), gathered under the name of "Kok cycle" (Scheme 3): the initial state is S_0 (no hole accumulated); after absorption of a photon by P_{680}, one more hole is accumulated on the manganese cluster, provoking the passage from S_n to S_{n+1}. When S_4 is reached, enough energy is gathered and the release of molecular oxygen takes place, entailing the return of Mn_4 to S_0, and a new cycle can begin with the absorption of a photon by PSII. With the advent of the long desired 2.9-Å resolution X-ray structure of PSII, a rather clear picture of the evolution of the OEC through the Kok cycle is at hand, even if there remains matter for debate. From a redox point of view, the charges are spread over the manganese ions and a bridging oxido ligand, step by step [60,64]. Concomitant proton losses to the lumen are observed, allowing for coulombic relaxation. During the catalytic process, substrate water molecules are progressively altered, being implied in the very structure of the manganese cluster itself



Scheme 3. Illustration of the five redox states of Mn_4 (Kok cycle) produced upon stepwise photon absorption by PSII [60].

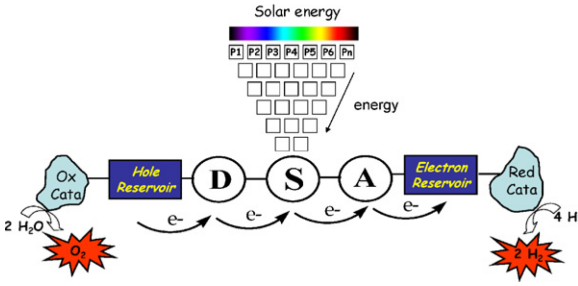
as molecular bridges until energy constraints eventually provoke the formation of an O–O bond and subsequent evolution of dioxygen (S_4 to S_0). In other words, each accumulated charge on Mn_4 is used to create a new species from substrate water molecules, one step closer to molecular oxygen as we proceed through the Kok cycle. Accordingly, this "S state cycle" is the most blatant feature to illustrate the why's and how's of charge photo-accumulation in photoinduced chemistry.

On the opposite side of PSII, electron photo-accumulation takes place: Q_B is able to accumulate two electrons after two consecutive photon absorptions. Once doubly reduced, Q_B is protonated (producing Q_BH_2) and is released from its binding site, being replaced by a plastoquinone from the quinone pool in the thylakoid membrane. Meantime, Q_BH_2 diffuses towards protein b6f, the last check point before PSI for photo-produced electrons.

To summarize, the neat outcome of PSII from the photo-redox point of view is the accumulation of four holes on the OEC and the accumulation of twice two electrons on the relaying quinone Q_B, triggered by the absorption of four photons. In PSII, the tool box for charge photo-accumulation contains: (1) the antenna effect, allowing PSII to massively harvest photons, and therefore maximize the probability for charge separation, the starting point of charge photo-accumulation; (2) a very long lived charge separation state over a great distance, to allow sluggish catalytic reactions to take place without competition from charge recombination; (3) a proton coupled electron transfer at the level of the tyrosine/histidine pair, bringing further stability to the charge separated state; (4) versatile, self-adapting electron and hole reservoirs. The relaxation of the manganese cluster through the S state cycle is a critical feature of charge photo-accumulation in PSII. Therefore, apart from light collection and its transformation into a charge separated state, an essential property of PSII is to form and to collect multi-redox equivalents on a single molecular unit: the tetramanganese cluster of the OEC.

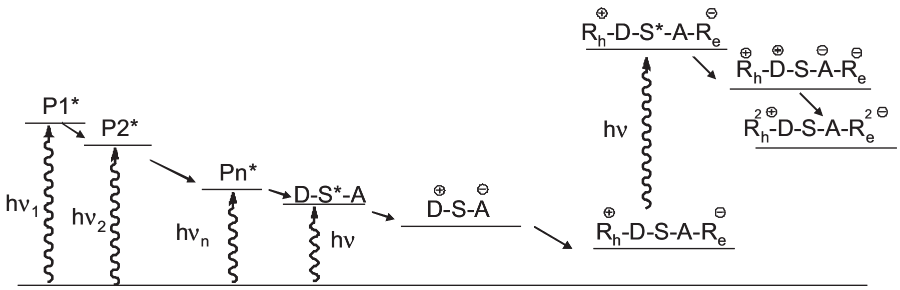
3. Conceptual approach for the design of artificial photosynthetic systems

As illustrated above in the natural photosynthetic centre, the overall process of photosynthesis necessitates performing a number of different processes, which should work in concert. Balzani [22,23] and others [4,7,29] have established the general rules and analyzed the basic functions to integrate for the construction of an artificial molecular system for solar fuels production (Scheme 4).

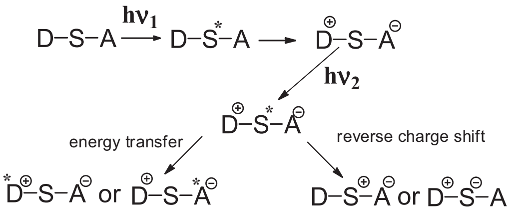


Scheme 4. Schematic representation of an artificial photosynthetic system with the four basic functions.

Naturally, the primary function is to collect light over the widest spectroscopic window and store the incident photons, *via* energy transfers, in the form of a single excited-state localized on a single molecular unit (sensitizer: S). As presented above, this feature is achieved in natural photosynthetic systems with the antenna units, which are composed of several pigments spanning different absorption bands in order to cover a broader spectrum of wavelengths than those of the special pair (SP). The special pair is the terminal energy acceptor of the antenna light harvester and the first electron donor of the electron transfer chain. Each SP is surrounded by several hundreds of antenna pigments [19,20]. The large number of pigments per SP increases the frequency of electronic energy feed of the special pair than that resulting of its own spontaneous direct absorption. Indeed, under regular sun's irradiance the spontaneous photon absorption occurs at a rate of about 10^{-3}–10^{-2}/s, which means that for a given molecule, one excited state is generated about every 100–1000 s [15]. The charge separated state being a meta-stable state, its lifetime is usually very short (1 s at most); therefore to achieve effective charge photo-accumulation, the charge separation events should be brought about at a relatively high frequency, in order to compete with the back recombination reaction. In other words, the sensitizer excited-state should be populated at a higher rate than the sun's fluence. Accordingly, the presence of a large number of pigments (Pn), within the light absorber system, is certainly a prerequisite to increase the frequency of sensitizer excited-state formation within the same molecular array. As a result, multi-chromophoric dendritic architectures are certainly valuable systems to achieve such feature (see below). The second key function is the photoinduced charge separation trigged by the sensitizer excited-state. The ultimate goal is to produce the longer-lived charge separated state with the highest quantum yield. An effective strategy to retard charge recombination is to separate the negative and the positive charge over a large distance thanks to an electron transfer cascade through charge shift reactions, with electron donor (D) and acceptor (A) linked to the sensitizer (Schemes 4 and 5). With such strategy, the two charges are geographically separated over a large distance [22,23]. The third function is the storage of the electrons and holes, formed upon successive photoinduced charge separations, on specific molecular units, which will be named charge reservoirs. These reservoirs have the role to temporarily store the reducing and oxidizing equivalents prior to their deliveries, in a concerted manner, to the substrates *via* the redox catalysts. This charge collection feature is essential to drive multi-redox fuel making reactions. Indeed to couple the one electron/one hole nature of single photon charge separation to multi-electron processes, it is crucial to interface a charge accumulation function. The possibility to deliver in "one go" multi-redox equivalents to perform multi-electron reactions is undoubtedly a thermodynamic and kinetic advantage over single electron pathways. Knowing that the accumulation of pair-wise charges on a same molecular unit, therefore at close proximity, induces electrostatic repulsions, the introduction of several charges at an almost constant redox potential or in a narrow range of potentials implies that a charge compensating



Scheme 5. Schematic photophysical processes involved in the artificial photosynthetic device for charge photo-accumulation. Pi: pigment of the antenna. R_h: hole reservoir. R_e: electron reservoir.



Scheme 6. Illustration of the potential counter-productive quenching processes upon second excitation of the sensitizer.

process comes into play. Proton-coupled electron transfer is most certainly the solution [65,66], since the removal (or the addition) of the electrons could be compensated by the departure (or the introduction) of protons during an oxidation (reduction) process. At this stage, it is also important to realize that the reservoirs should be also clearly physically and electronically separated from the sensitizer to avoid counter-productive reactions. Indeed, upon reduction (or oxidation) the charge storage unit becomes an electron rich (or electron deficient) unit and therefore is transformed into a strong electron donor (or strong electron acceptor). As a result, this unit could quench the sensitizer excited-state by a reverse charge shift [67–71]. Furthermore, radical anions and radical cations are generally strongly coloured species with low lying excited-states [72], implying that the reservoirs could also quench the sensitizer excited-state by energy transfer [68,69]. These two latter processes are counter productive and should be therefore absolutely avoided (Scheme 6).

This is certainly possible, by decoupling these two competing processes from the desired reactions (charge separations with the nearby electron donor and electron acceptor units D and A) either by controlling the electronic coupling (choosing the suitable spacer) or the distance between the sensitizer and the reservoirs. Towards this goal, the presence of D and A which play the role of intermediate charge relays could enable to place the charge pool in a remote position from the sensitizer. A strategy, that Nature seems to have used in PSII, since the OEC is significantly separated from the special pair (SP) by the tyrosine serving as a hole relay and probably avoiding direct quenching of SP* by the OEC. Finally, multi-redox catalysts will probably be necessary to achieve acceptable rates for the reduction and the oxidation reactions aiming at transforming the low energy substrates into fuels. Indeed, most useful fuel making reactions such as proton or carbon dioxide reduction or water oxidation necessitate catalysts to operate at sufficient rates [43,73].

Overall these key functions will be ensured by specific molecular subunits, which will be assembled together *via* covalent or supramolecular bonds to build the multi-functional device. The complete device could be a homogenous system or a heteromolecular architecture linked to a surface such as metal conductor or inorganic semi-conductor.

4. Synthetic systems featuring photo-accumulation of oxidizing equivalents

When one beholds the clever ways Nature had to imagine in order to perform charge photo-accumulation, we understand what a dramatic challenge this is to design and synthesize an artificial device that will be capable of the same achievements.

All PSII's mimics share the same overall structure, built on the assembly of a photo-sensitizer (S) and an electron donor (D), and/or an electron acceptor (A). The resulting D–S–A polyads abound in the literature, in particular S–A and S–D dyads, and the natures of S, A and D have been widely explored. A great many of such systems can sustain photoinduced electron/hole transfer (mimicking, say, the S_0 to S_1 step in PSII) but dramatically fewer are capable of performing at least a second photoinduced charge transfer on the same molecular assembly. The reasons for this experimental fact have been exposed above (competing energy or back electron transfer kinetics). Given the complexity of the issues to address, the research activity concerning artificial photosynthesis has been severed into two distinct problems: on one hand, electron photo-accumulation (modelling P_{680}-pheo-Q_A-Q_B cofactors) and on the other hand hole photo-accumulation (modelling P_{680}-Tyr/His-Mn_4 cofactors). We will now give a quick overview of the achievements realized in the latter field.

All the molecular mimics of P_{680}-Tyr/His-Mn_4 presented in this part rely on the interaction between a photo-sensitizer (P_{680} mimic, S) and a hole reservoir (OEC mimic, R_h). In a typical experiment, the obtained S–R_h system is irradiated in the presence of a sacrificial electron acceptor in solution (A). An intermolecular electron transfer quenching takes place (Eq. (8)), leading to the oxidation of S^* into S^+ and reduction of A into A^-. If the photo-produced S^+ is sufficiently oxidizing, a second, intramolecular electron transfer may occur from R_h to S^+ (or a hole transfer from S^+ to Rh, Eq. (9)), leading overall to the neat oxidation of R_h by light, assisted by S and A. The objective of charge photo-accumulative systems is to perform this round of charge transfers at least a second time (Eqs. (10)–(12)).

$$\mathrm{S{-}R_h} + h\nu \rightarrow \mathrm{S*{-}R_h} \tag{7}$$

$$\mathrm{A} + \mathrm{S*{-}R_h} \rightarrow \mathrm{A^-} + \mathrm{S^+{-}R_h} \tag{8}$$

$$\mathrm{S^+{-}R_h} \rightarrow \mathrm{S{-}R_h}^+ \tag{9}$$

$$\mathrm{S{-}R_h}^+ + h\nu \rightarrow \mathrm{S*{-}R_h}^+ \tag{10}$$

$$\mathrm{A} + \mathrm{S*{-}R_h}^+ \rightarrow \mathrm{A^-} + \mathrm{S^+{-}R_h}^+ \tag{11}$$

$$\mathrm{S^+{-}R_h}^+ \rightarrow \mathrm{S{-}R_h}^{2+} \tag{12}$$

$$\mathrm{S*{-}R_h}^+ \rightarrow \mathrm{S{-}R_h}^{+*} \tag{13}$$

$$\mathrm{S*{-}R_h}^+ \rightarrow \mathrm{S^+{-}R_h} \tag{14}$$

From Eqs. (7)–(12), the main difficulties to circumvent in order to achieve hole photo-accumulation appear obviously as: energy transfer from S^* to R_h^+ entailing a fast quenching of S excited state

(Eq. (13)) and the thermodynamically favourable photoinduced back electron transfer between reductive S* and oxidative R_h^+ (Eq. (14)), both in competition with the rather sluggish bimolecular reduction of A by S* (Eq. (11)). Let us add that charge recombination with A^-, although slow (ms scale), could compete as well with hole photo-accumulation. This issue was addressed with the use of irreversible sacrificial electron acceptors, such as $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ (noted "Co^{III}") or aryldiazonium salts ArN_2^+.

With this in mind, S–D systems were synthesized with the aim to realize charge photo-accumulation. Among all the possible photosensitizers, the well-known ruthenium–polypyridine chromophore stood out thanks to its numerous advantages: broad absorption in the visible domain, photo-stability, synthetic versatility, long-lived excited state with a charge separation state character, and rather strong photo-reducing power ($E^0(Ru^{III}/Ru^{II*}) \approx -1$ V/ENH for $[Ru^{II}(bpy)_3]^{2+}$). To fish out a proper model for the OEC, being a particularly intricate molecular assembly, was a harder task. Pre-requisites are: (1) accessible oxidation potentials, i.e. at least two oxidation steps at potentials below that of S^+, to allow photo-accumulation of two holes; (2) resilience to all the aforementioned, highly thermodynamically favoured quenching processes. Though the X-ray structure of PSII has remained elusive until the advent of the new millennium, the fact that PSII's catalytic centre was constituted of four manganese ions was unanimously acknowledged. This, plus the well-known versatility of manganese redox chemistry, lead the scientific community to choose manganese complexes as hole reservoirs in the first place. Historically speaking, the first systems to model the hole photo-accumulative function of PSII are based on the covalent assembly of the $[Ru(bpy)_3]^{2+}$ photosensitizer with mono and polynuclear manganese complexes.

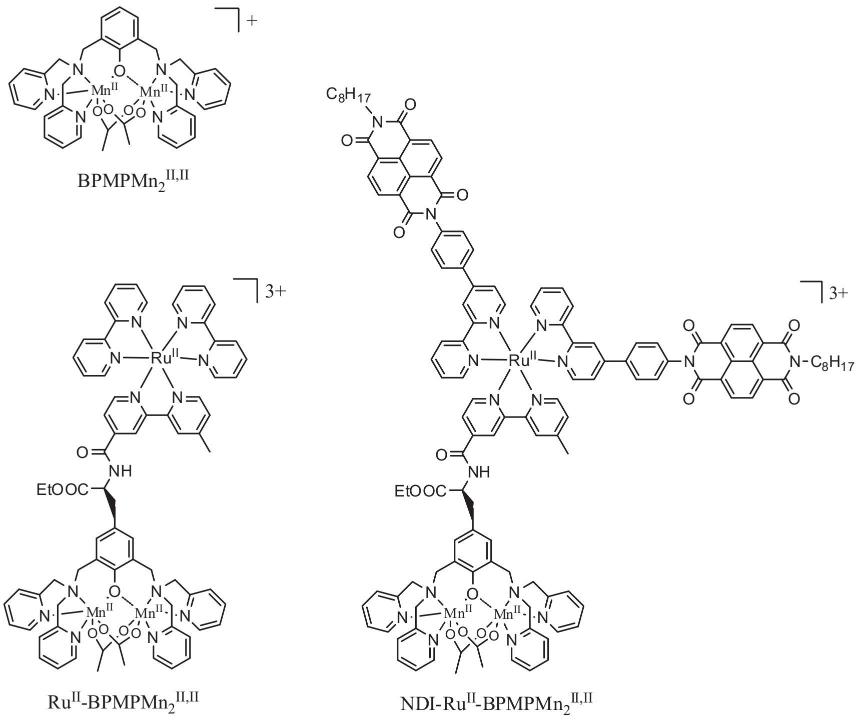
Wieghardt and co-workers [74,75], and Akermark and co-workers [8,76–80] thereby developed mixed ruthenium–manganese complexes where a mononuclear manganese unit was covalently appended to a $[Ru^{II}(bpy)_3]^{2+}$ like chromophore (noted thereafter Ru^{II}-bpy) In the presence of a sacrificial electron acceptor, namely methylviologen or Co^{III}, the excited-state of the ruthenium sensitizer is efficiently oxidatively quenched by bimolecular electron transfer. The resulting Ru^{III}-bpy species, with a high oxidizing potential of +1.2–1.3 V/SCE, is regenerated by intramolecular electron transfer from the manganese complex. However, no charge photo-accumulation was observed upon further illumination. Three main reasons can be invoked: first of all, accumulation of two holes on a mononuclear manganese complex does not seem probable without coulombic relaxation (through proton loss for instance). Polynuclear manganese complexes were proposed by Wieghardt and colleagues but charge photo-accumulation was not investigated. Second, the manganese complexes appeared to efficiently quench the excited state of the ruthenium–polypyridine chromophore by energy transfer, depending on the size and nature of the spacer linking the two units [76,79]. Finally, the stability of some mixed ruthenium–manganese species appeared to be a primal issue to address for the durability of such PSII mimics [80].

After this first round of studies, it became apparent that mixed Ru–Mn systems in the presence of a sacrificial electron acceptor could indeed support charge shift reactions, but hole photo-accumulation requested the hole reservoir be a polynuclear manganese complex, in order to arrange several redox states which could be reached by oxidation by the photo-generated Ru^{III}-bpy entity. Moreover, special care was brought to the linker between the chromophore and the OEC mimic, supporting the internal electron transfers. Indeed, the alkyl floppy linkers used in Akermark's models allow counter-productive folding of the S–R_h molecule, entailing a great deal of uncertainty for the distance between S and Rh, the latter being a crucial parameter on which depends the extent of the electron (and energy) transfer [79].

Taking in account all the information gathered, a new mixed ruthenium–manganese dyad was soon prepared by Akermark and colleagues [81]. The latter consists in the assembly of a well-known manganese(II) dinuclear complex, $BPMPMn_2^{II,II}$ with the same Ru^{II}-bpy moiety. First of all, the manganese dinuclear complex on its own ($BPMPMn_2^{II,II}$) exhibits a very rich anodic electrochemical behaviour [82]; two well defined, reversible, one electron oxidation waves are monitored at 0.45 and 0.9 V/SCE in water free acetonitrile, assigned to stepwise Mn^{II} to Mn^{III} transitions ($Mn_2^{II,II} \rightarrow Mn_2^{II,III}$ and $Mn_2^{II,III} \rightarrow Mn_2^{III,III}$, respectively). Crucially, these electrochemical processes occur at lower potentials than $E^0(Ru^{III}/Ru^{II})$ (roughly 1.25 V/ECS), thermodynamically authorizing the intramolecular transfer of at least two electrons from $BPMPMn_2^{II,II}$ towards photo-produced Ru^{III}-bpy in the presence of a sacrificial electron acceptor, and paving the way for hole photo-accumulation. Second, special attention was given to the nature of the spacer sustaining the electronic communication between the P_{680} and OEC models. A more rigid amide bond links the Ru^{II}-bpy core to the $BPMPMn_2^{II,II}$ hole reservoir. Moreover, the latter is constructed *via* a Mannich condensation on the tyrosine amino-acid itself, in an effort to mimic the Tyr_Z cofactor which acts as a redox relay and, in cooperation with the histidine residue His_{190}, plays a pivotal role in charge photo-accumulation within PSII [61–63].

This approach proved to be crowned with success [83]. First of all, a "collisional" approach was explored: $[Ru(bpy)_3]^{2+}$ and plain $BPMPMn_2^{II,II}$ were mixed together with the sacrificial acceptor Co^{III}. The mixture was subsequently irradiated with flashes of light and probed by X-band EPR spectroscopy. Continuous formation of a Co^{II} species was monitored, testifying to the oxidative quenching of $[Ru^{II}(bpy)_3]^{2+}$ excited state by Co^{III}, while the typical $Mn_2^{II,II}$ signal gradually vanished. Eventually, the unmistakable spectroscopic signature of a $Mn_2^{III,IV}$ dimer was observed, synonymous with the accumulation of three holes onto the Mn dinuclear cluster. The covalent assembly of a Ru^{II}-bpy beacon with $BPMPMn_2^{II,II}$, Ru^{II}-$BPMPMn_2^{II,II}$ (Fig. 1) behaved in a similar manner in that a Ru^{II}-$BPMPMn_2^{III,IV}$ species was unveiled by EPR spectroscopy after irradiation, indicating that three holes were photo-accumulated in the manganese cluster. However, a lesser yield of $Mn_2^{III,IV}$ species was formed than in the "collisional approach" due to competing quenching by energy transfer from the excited ruthenium chromophore to the manganese dimer.

These results must now be substantiated by a few comments. First of all, in both collisional and covalent approaches, the triple photo-oxidation of the manganese cluster is accompanied with considerable changes in the coordination sphere of the manganese dinuclear complex. It is inferred that, in the presence of water, the $Mn_2^{III,III}$ state is unstable and μ-oxido bridges are formed between manganese ions, while μ-acetato ligands are released [55,84]. This ligand shift is believed to play a crucial role in the third and last photo-oxidation step leading to the $Mn_2^{III,IV}$ state; moreover, the μ-oxido ligands stem from water molecules, which endure deprotonation in a very biomimetic way, reminiscent of the OEC coulombic relaxation. Second, manganese complexes exhibit in general a rather high internal reorganization energy λ_{in}, estimated around 1 eV for the $Mn_2^{II,III}/Mn_2^{II,II}$ couple in $BPMPMn_2^{II,II}$ [85]. According to Marcus theory, this feature entails slow kinetics for electron transfers involving this redox state. Although this looks like a considerable drawback for the first photoinduced intramolecular hole shift, it appears to be a positive boon regarding charge recombination: the latter being therefore strongly activated, it cannot compete with the bimolecular oxidative quenching of the Ru^{II}-bpy* moiety, hence favouring hole photo-accumulation. Furthermore, λ has reached the spectacular value of 2 eV in the case of the perfected NDI-Ru-$BPMPMn_2^{II,II}$ triad (Fig. 1), yielding an impressively long lived charge separated state NDI^--Ru-$BPMPMn_2^{II,III}$ of 600 μs in average [85]. Never-


$BPMPMn_2^{II,II}$

Ru^{II}-$BPMPMn_2^{II,II}$

NDI-Ru^{II}-$BPMPMn_2^{II,II}$

Fig. 1. Akermark and co-workers' hole photoaccumulative systems [81,82].

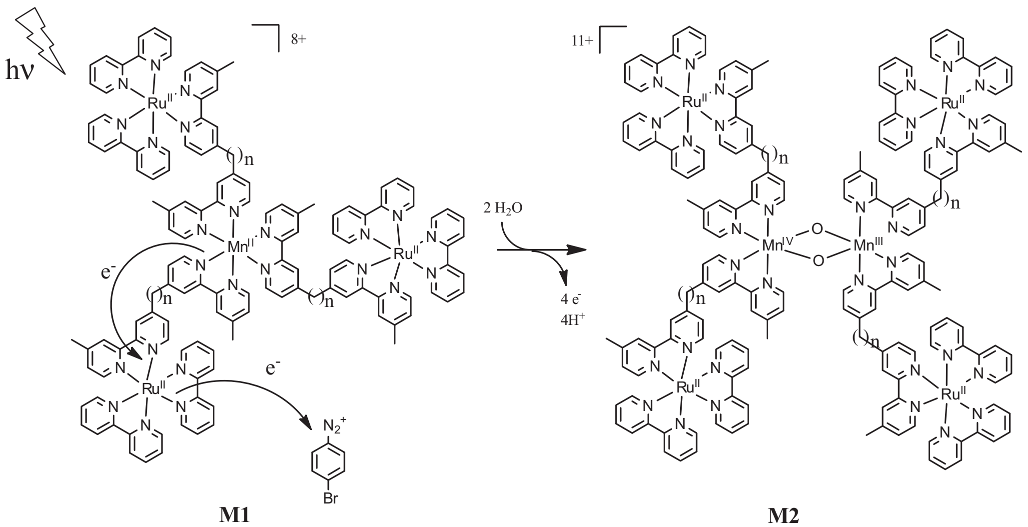
theless, rapid kinetics for electron transfer from the manganese based OEC models towards the photo-oxidized ruthenium photosensitizer remain essential to insure a high-performance artificial system (in particular with a view to overriding competing energy transfer processes). This justifies the presence of a redox relay, like tyrosine. Simple models of the P_{680}-Tyr_Z have been investigated and were capable of mimicking the proton coupled electron transfer taking place in PSII [86–89]. At no time however was monitored the presence of a transient phenoxyl radical during the study of Ru-$BPMPMn_2^{II,II}$ and related systems. Yet, the authors underline the fact that the electron transfer from the $Mn_2^{II,II}$ dimer is surprisingly fast (less than 100 ns) and may involve the bound phenolate. However, the main weakness of this system is that it is not regenerative. Since no dioxygen evolution is observed upon extensive irradiation, the μ-oxido manganese dimer is the final state in which the molecule is "stuck" and cannot be released to its initial state, to perform a new round of hole photo-accumulation.

A similar approach has been proposed by Deronzier et al. with a variable-geometry ruthenium–manganese system (Fig. 2) [90,91]. Three ruthenium–polypyridine chromophores are bound to a mononuclear $Mn^{II}(bpy)_3$ unit. In the presence of ArN_2^+ as a sacrificial electron acceptor, photo-oxidation of the manganese (II) ion takes place, yielding a very unstable Mn^{III} species that dissociates and eventually forms a di μ-oxido bridged $Mn_2^{III,IV}$ dimer, quantitatively. Formally, the passage from **M1** to **M2** has claimed three electrons and four protons. Further illumination of **M2** allowed the latter to accumulate a fourth hole, yielding the corresponding μ-oxido bridged $Mn_2^{IV,IV}$ dimer. Like in the previous case exposed in this review, this artificial photosystem is nevertheless unable to evolve dioxygen and cannot therefore return to its initial state **M1**.

Irreversible hole photo-accumulation is at hand, but a balance must be found between stabilization of the hole reservoirs during photo-oxidation, and storage of a sufficient amount of energy to use the latter in a chemical process and therefore start a whole photo-catalytic cycle.

One main limitation of most reported molecular systems for charge photo-accumulation is the necessity to consumate sacrificial electron acceptors. This problem could be solved by chemisorption of the photocatalyst on a semiconductor such as TiO_2, which oxidatively quenches the sensitizer by electron injection in its conduction band (CB) and then shuttle them towards an external electrode, where the reduction reaction could operate in the presence of a catalyst (Fig. 3). Recently, the use of dye sensitized TiO_2, within photo-electrochemical cells (PEC), has opened the gate to overall water splitting [10]. The principle of such a device is presented in Fig. 3. Summarily, a photosensitizer chemisorbed on mesoporous TiO_2 is photo-oxidized upon irradiation, resulting in a charge separated state TiO_2^-–S^+. The hole on S is then transferred to a catalyst (Cat) and the cycle can be reproduced again until enough holes are accumulated within the catalyst, performing water oxidation and returning the whole system to the initial state. Meanwhile, the electrons are carried away from the CB of TiO_2 towards a catalytically active cathode where protons can be reduced into molecular hydrogen. From the design point of view, a covalent bond between S and Cat seems mandatory, to insure fast intramolecular electron transfers and achieve hole photo-accumulation. Special care is therefore to be given to the choice of the linker between S and Cat. A few systems have been prepared, showing great promises for the future of water photolysis. For example, the groups of Mallouk, Gust and Moore have recently reported an interesting system giving a proof of concept of this valuable approach [92]. The photosensitizer is a ruthenium bipyridine complex functionalized by phosphonic acid anchoring groups, which enable relatively stable linkage in aqueous solution, and linked to iridium oxide nanoparticles (IrO_2, n H_2O) *via* a malonate binding handle.

Hole accumulation into the IrO_2 nanoparticles is indicated by the evolution of molecular oxygen at the photo-anode upon irradiation of the ruthenium sensitizer, while the electrons are collected at the platinum cathode which catalyses hydrogen evolution. Importantly, a slight yet significant potential must be applied to the PEC in order to operate it. This provides the necessary driving force to empty the CB of TiO_2 as electrons are photo-injected, and convey the latter towards the Pt cathode. This prototype exhibits a rather low yield of dioxygen production, certainly because the hole shift



M1 **M2**

Fig. 2. hole photoaccumulation in a "variable geometry" mixed Ru–Mn complex [90,91].

reaction from the Ru(III) to the iridium oxide particle is too slow to compete with the recombination reaction (electron in TiO_2 and hole on Ru(III)), but this system is among the few published devices capable of realizing water splitting into its elemental constituents. A similar system was reported by Spiccia and co-workers, but in which the iridium oxide particule was replaced by a bioinspired manganese cubane, as for oxygen evolving catalyst [93]. The latter was not covalently connected to the ruthenium trisbipyridine sensitizer, but embedded in a Nafion membrane. The absence of external bias to drive the whole process of water splitting represents an important feature of this new system.

A similar approach was employed by Meyer and co-workers, grounded in the extensive activity of this research group devoted to water oxidation by ruthenium based catalysts [94–96]. A ruthenium polypyridine photosensitizer was chemisorbed on TiO_2, and thanks to the simple homoditopic bipyrazine ligand, linked to a ruthenium Mebimpy water oxidation catalyst. Primary photophysical experiments have revealed the stepwise photo-oxidation of the $Ru^{II}(H_2O)$-Mebimpy into $Ru^{III}(OH)$-Mebimpy following excitation of the TiO_2 anchored Ru-bpy chromophore [95,97]. This PCET is the first step of a well described catalytic cycle that leads to the oxidation of water into molecular oxygen. The charge separated state can be formulated TiO_2^{-}–Ru^{II}–Ru^{III}–OH, and recombines on a long timescale (>1 μs), potentially allowing further excitation of this charge separated state. Encouragingly, oxidation of dihydroquinone into quinone by the photo-produced $Ru^{III}(OH)$-Mebimpy has already been reported, together with reduction of the released protons into dihydrogen at the cathode. However, to our knowledge, this PEC has not been tested for water splitting yet.

5. Synthetic systems featuring photo-accumulation of reducing equivalents

The first example of double reduction of a single molecular unit upon two successive photoinduced electron transfers was reported by Wasielewski and co-workers in 1992 with a perylene bis(carboxyimide) (PBDCI) electron acceptor functionalized with two peripheral free base porphyrins as sensitizers (H2P-PBDCI-P2H; Fig. 4) [98]. With a high laser pulse excitation, it is possible to generate the singlet excited-states of

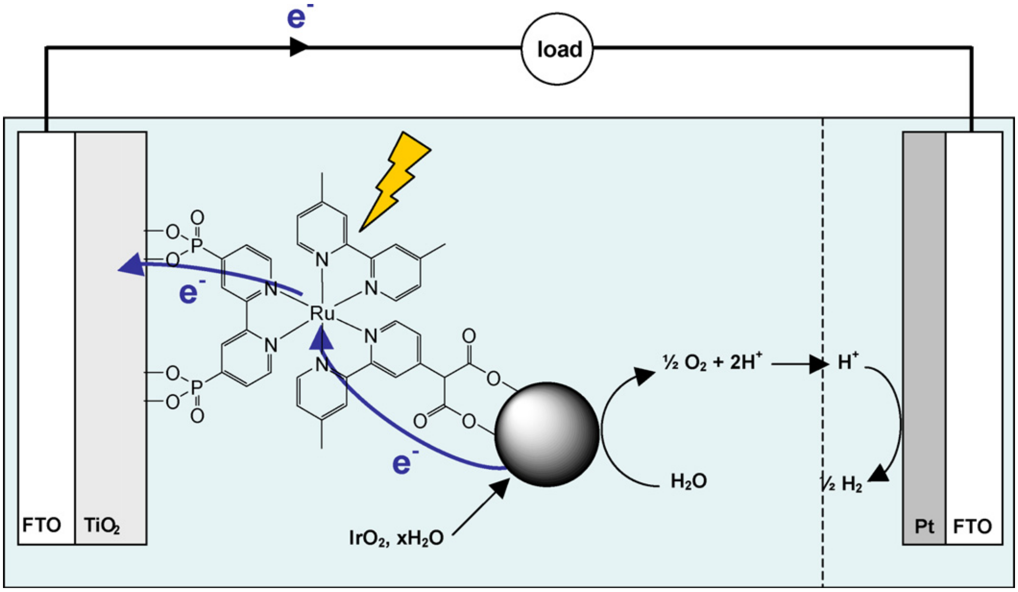


Fig. 3. Illustration of the water splitting PEC by Mallouk and co-workers [92].

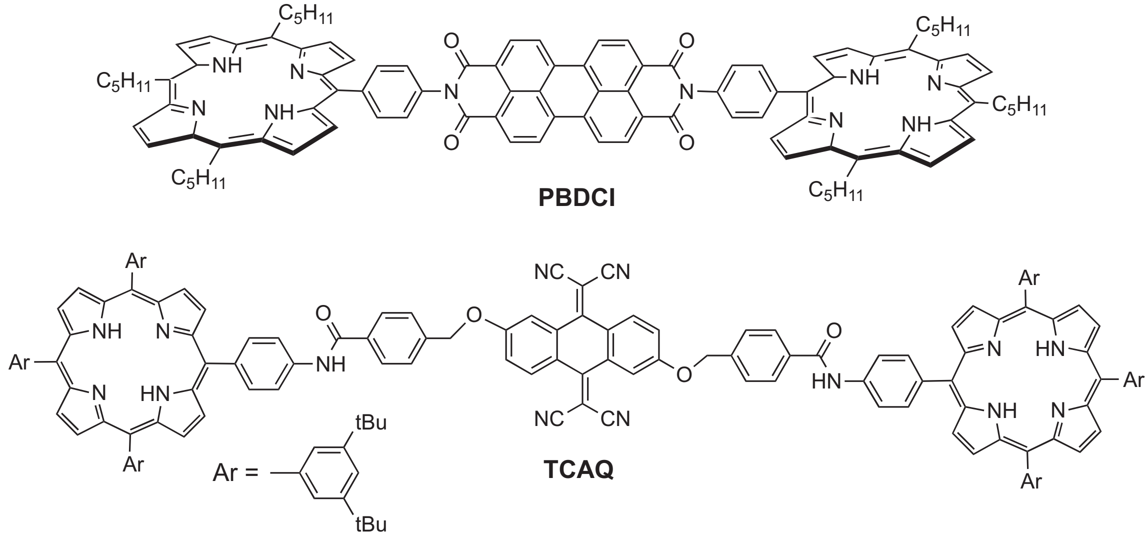
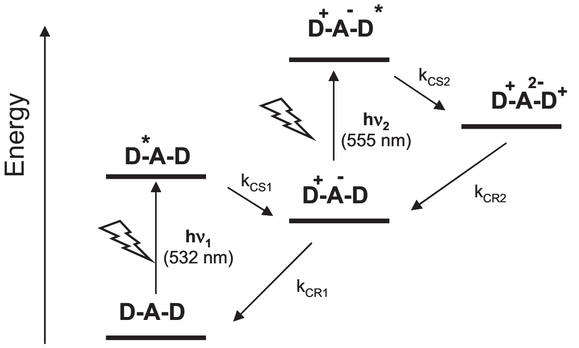


Fig. 4. Structures of the triads H2P-PBDCI-P2H [98] and H2P-TCAQ-P2H [99].

two porphyrins within the same molecule (^{1*}H2P-PBDCI-P2H^{1*}). The latter subsequently decay by two successive electron transfers to form the doubly reduced perylene bis(carboxyimide) according to the following route: ^{1*}H2P-PBDCI-P2H^{1*} → $^{+}$H2P-PBDCI^{-}-P2H* → $^{+}$H2P-PBDCI^{2-}-P2H^{+}. Interestingly, the doubly reduced acceptor exhibits a longer lifetime (~5 ns) than the singly reduced one (~120 ps).

The formation of PBDCI^{2-} was clearly indicated by transient absorption spectroscopy and could not be confused with that of PBDCI^{-}, since these two species display very distinct absorption spectra. This system was presented as a light intensity-dependent optical switch and could be potentially used to perform logic operations, since the outcome of the system (final charge separated state and therefore photochromic absorbance changes) could be triggered by the intensity of the initial light pulse.

A similar system was then reported by Imahori and co-workers in which the electron acceptor (PBDCI) was replaced by a tetracyanoanthraquinomethane (TCAQ, Fig. 4) [99]. In this study, the doubly reduced TCAQ^{2-} was photogenerated upon two independent and successive pump pulses delayed by 233 ps, instead of a single pulse as in the preceding example. The first laser pulse was set at 532 nm while the second at 555 nm to ensure better selectivity, since the absorbance at 555 nm of the non-excited free base porphyrin is the highest relative to those of the other transient species. The relatively similar absorption characteristics of the singly (TCAQ^{-}) and doubly reduced tetracyanoanthraquinomethane (TCAQ^{2-}) makes it difficult to distinguish their respective formation in the transient absorption spectroscopy experiments. However, the rate constants for the first ($1/k_{CS1} = 200$ ps) and the second ($1/k_{CS2} = 400$ ps) electron transfer steps and for the charge recombination reactions from TCAQ^{-} ($1/k_{CR1} = 1500$ ps) and from TCAQ^{2-} ($1/k_{CR2} = 1200$ ps) could be extracted from the data (Scheme 7).



Scheme 7. Energy diagram of H2P-TCAQ-P2H. D and A stand for PH2 and TCAQ, respectively.

Brewer and co-workers were pioneers in the construction of heteropolymetallic complexes such as [bpy$_2$Ru^{II}-BL-M^{III}Cl$_2$-BL-Ru^{II}bpy$_2$]$^{5+}$ (BL = bridging ligand, M = Ir^{III} or Rh^{III}) for photodriven electron collection (Fig. 5) [100–105]. In these trinuclear complexes, the rhodium(III) or the iridium(III) complex is the electron reservoir and the two peripheral ruthenium complexes act as the sensitizers to direct the electron towards the reservoir. Light excitation, into the ruthenium MLCT absorption band, promotes intramolecular electron transfer to the BL resulting in the formation of the intermediate [bpy$_2$Ru^{III}-BL-M^{II}Cl$_2$-BL-Ru^{II}bpy$_2$]$^{5+}$. In the presence of dimethylaniline (DMA), the ruthenium(III) is reduced

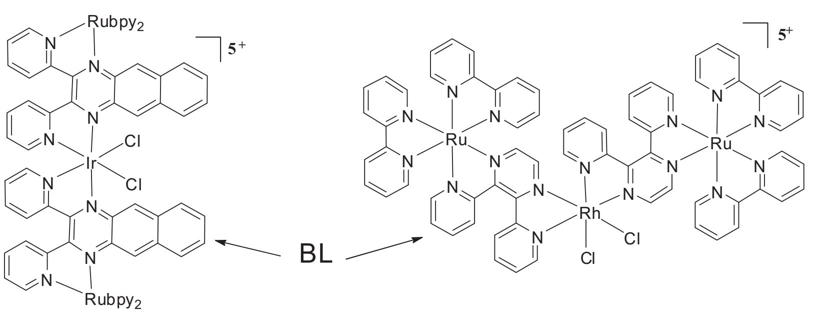


Fig. 5. Heteronuclear complexes [bpy$_2$Ru^{II}-BL-M^{III}Cl$_2$-BL-Ru^{II}bpy$_2$]$^{5+}$ developed by Brewer and co-workers [100,101].

and affords the singly reduced complex $[bpy_2Ru^{II}\text{-BL-}M^{II}Cl_2\text{-BL-}Ru^{II}bpy_2]^{5+}$. In the case of the rhodium complex (M^{III}=Rh^{III}), the Rh^{II} intermediate disproportionates to form the Rh^{III} and Rh^{I} complexes with the loss of two chloro ligands [101]. As far as the iridium complex is concerned, the singly reduced species is a ligand-based process and the species is therefore stable. A second photon absorption by the ruthenium sensitizer and its subsequent quenching by DMA can occur and it yields to the doubly reduced species (also ligand-based). This state is not stable in the presence of the unreduced species, therefore it comproportionates to the singly reduced species [100]. As a result, the build-up of the doubly reduced species occurs only after the system was quantitatively singly reduced. The formation of the reduced species could be monitored by absorption spectrometry because the decrease of electron withdrawing ability of the bridging ligand, as the electrons accumulate on the central complex, induces a clear blue-shift of the MLCT absorption band of the ruthenium sensitizers.

The above rhodium system lies among the rare examples in which the photo-driven electron collection could be successfully coupled with protons reduction into dihydrogen. Photolysis of the trinuclear $\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ (dpp = 2,3-bis(2-pyridyl)pyrazine) complex at 470 nm in a mixture of CH_3CN/H_2O in the presence of dimethylaniline, as sacrificial electron donor, leads to hydrogen evolution with a turnover of 30 and a quantum efficiency of 0.01 [51]. Very interestingly, the mixture of the two monometallic components $((bpy)_2Ru(dpp)](PF_6)_2$ and $[Rh(dpp)RhCl_2](PF_6)_2)$ displays a lower efficiency for hydrogen evolution than the trinuclear complex. This attests to the beneficial effect of collecting multiple reductive equivalents before conducting a bielectronic reaction. Indeed, the first step of the process consists in the photoreduction of the Rh(III) into Rh(I) and subsequent loss of the two chloro ligands. The second step is the oxidation of the unsaturated Rh(I) centre by water to form dihydrogen.

Another class of very interesting dinuclear ruthenium complexes performing multi-electron photo-accumulation was reported by MacDonnell and co-workers [106–108]. These systems are composed of a fused bis-phenanthroline bridging ligand incorporating a multi-reduction site such as a tetraazatetrapyridopentacene (**TATPP**) as two electron acceptor or a tetraazatetrapyridoquinone (**TATPQ**) [109] as four electron acceptor flanked by two ruthenium bisbipyridine complexes at the extremities (Fig. 6).

Light excitation in the MLCT absorption band of the ruthenium complexes ejects an electron into the bridging ligand moiety to form the first charge separated state. Then, sacrificial donor (triethylamine TEA or triethanolamine TEOA) reduces the ruthenium(III) centre to regenerate the initial state of the sensitizer. Next, the reduced bridging ligand pulls-up the proton released by the TEA or TEOA oxidation and is restored back to a neutral state to afford the singly reduced system. This charge compensation mechanism, upon protonation or the reduced reservoir, is certainly essential to keep the value of the second reduction potential close to the first one and subsequently enables the second reduction to take place on the same molecular component. Upon photolysis in acetonitrile solution, this sequence of reactions could be repeated twice with the **TATPP** system or four times with the **TATPQ** until two electrons and two protons or four electrons and four protons are respectively stored in the form of reduced bridging units (Fig. 6). The kinetic and the assignment of the transient species formed upon sequential electron reduction of the bridging ligands were monitored with an extensive and detailed spectro-electrochemical study. In aqueous solution, the influence of the pH on the mechanism of ligand reduction was also elucidated [110]. Under basic conditions, sequential single electron reduction was observed while in neutral or slightly acidic conditions proton-coupled multielectron transfer is the major pathway. This property is certainly important for the design of multielectron photocatalysts, since it represents an energy advantage for the system and is found in most natural photosynthetic processes. A theoretical quantum chemistry study of these systems revealed important information [106]. First, the Ru d orbitals are weakly coupled to the lowest energy lying π^* orbital (LUMO), which is localized on the inner part of the bridging ligand (pyrazine or quinone). Second, the d Ru orbitals, however, overlap significantly with the LUMO+1 orbital, which spans more on phenanthroline-like portion of the bridging ligand. Accordingly, the LUMO + 1 is involved in the MLCT transition, while the LUMO rather corresponds to the ultimate site of reduction of the system. As a result, the site of electron storage is distinct and electronically decoupled from the initially populated orbital upon light excitation. This feature is certainly essential for the electron photo-accumulation function and probably prevents counter-productive reverse electron transfer once the first electron is stored on the system. These dinuclear ruthenium complexes represent valuable systems capable of multielectron storage following proton-coupled electron transfer mechanisms, but the utilization of such photocatalysts to perform multielectron reduction reactions has not been reported yet.

More recently, Tanaka and co-workers synthesized a polypyridine ruthenium complex containing a bipyridine benzonaphthyridine ligand (pbn) which could undergo photodriven bisreduction (Fig. 7) [111,112]. Benzo-naphthyridine ligand is reminiscent of the nicotinamide adenine dinucleotide (NAD^+) cofactor which transports two electrons in biological systems. In the presence of a sacrificial electron donor (TEOA), the complex $bpy_2Ru^{II}(pbn)$ could be reduced photochemically and can even catalyze the reduction of acetone into 2-propanol, like the enzymatic reaction with the $NADH/NAD^+$ couple. Similarly to the

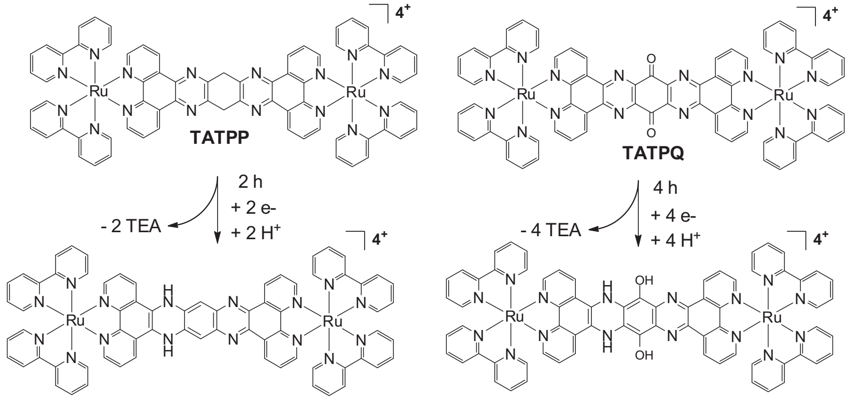


Fig. 6. Structures of two dinuclear ruthenium complexes reported by MacDonnell and their photodriven reduction products [106–108].

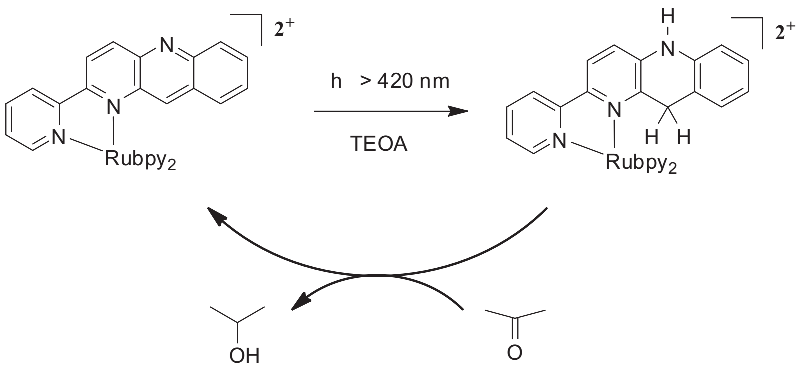


Fig. 7. Polypyridine ruthenium complex reported by Tanaka and co-workers [111].

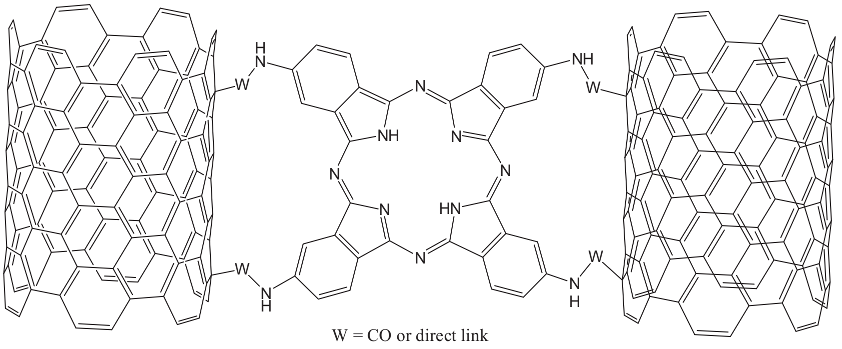


Fig. 8. Single wall carbon nanotubes functionalized by phthalocyanines [113,114].

system reported by Brewer and co-workers, the photochemical reduction of the $bpy_2Ru(pbn)$ starts with the promotion of one electron onto the bpn, since this ligand displays the lowest energy LUMO of the complex. This is followed by the irreversible oxidation of TEOA by Ru(III) to generate $bpy_2Ru^{II}(pbn^-)$. The latter species undergoes protonation of the ligand to afford $bpy_2Ru^{II}(pbn^{\bullet}H)$. Two such monoreduced complexes diffuse to one another and dimerize to form a π–π intermediate dinuclear complex which disproportionates into the bisreduced $bpy_2Ru^{II}(pbnH_2)$ and $bpy_2Ru^{II}(pbn)$. This bisreduced species results from two successive photon absorptions and stores two reducing equivalents in the form of a hydride donor. Summarily, upon excitation into the MLCT absorption band, $bpy_2Ru^{II}(pbn)$ exhibits proton coupled electron transfer with catalytic activity towards acetone reduction and represents therefore an interesting bioinspired system sharing similarities with the NADH natural co-enzyme [111].

In a relatively different system, Zhang and co-workers took advantage of the multi-electron storage ability of single wall carbon nanotubes (SWNTs) [113,114]. These materials, can accept many electrons in a narrow potential range since the empty orbitals are separated by very weak energy gaps creating thus an almost continuous energy band. Carboxylated SWNTs, prepared by partial oxidation with nitric acid, were coated by amino phthalocyanine sensitizers mainly *via* amide bonds (Fig. 8). The binding through direct –NH– bonds was also suggested. The authors estimated that about 120 phthalocyanines (Pcs) were grafted per 1 μm SWNT length.

Upon an intense laser pulse excitation, simultaneous absorption of several photons by many Pcs prompted the formation of a multitude of singlet excited states, which induce synchronous (one step multi-electron transfer) or sequential multi-electron transfers (stepwise single electron transfer) into the SWNT. The multireduced SWNT was indicated by kinetic analyses and by transient absorption spectroscopy by the presence of the characteristic signals of the multicharged anions $SWNT^{n-}$. The decay of the charge separated state obeys a multiexponential law with a 3.5 ms short-lived component and a 42 ms long-lived component. This study raises the question of a theory ruling the kinetic of synchronous multi-electron transfer and recombination, since classical Sutin-Marcus theory essentially deals with single electron exchange. In conclusion, the attachment of a large number of sensitizers to a multiple electron acceptor (such as SWNT) enables the formation of multi-reduced species upon high energy pulse excitation thanks to the generation of multiple excited-states within a short interval.

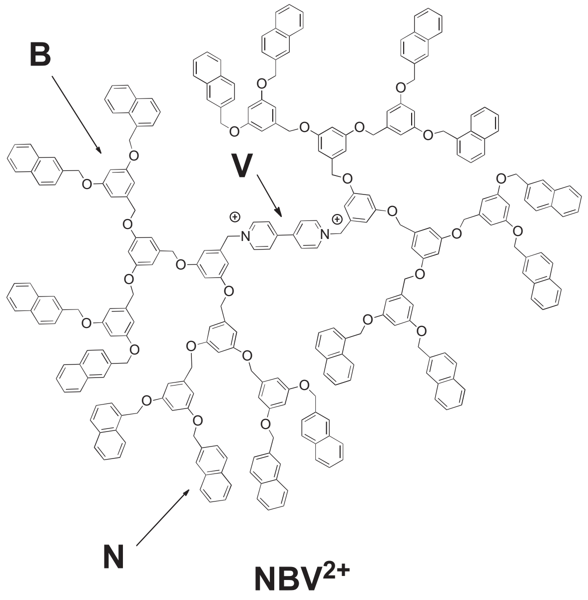


Fig. 9. Structure of a dendrimer incorporating a single viologen redox active unit as electron reservoir [115].

The dendritic architecture provides an unique scaffold to realize multielectron processes induced by multiple excitations of the chromophores embedded in the dendrimer. In this context, Fox and co-workers were pioneers by reporting a dendrimer **NBV^{2+}** consisting of a viologen (V^{2+}) at the core and naphthalene groups (N) at the periphery and connected together by benzyl ether (B) spacers (Fig. 9) [115].

Excitation of the dendrimer **NBV^{2+}** with a strong laser pulse at 266 nm yields the excitation of multiple chromophores at different sites (both B* and N*) but within the same molecule. For example, more than 12 photons could be absorbed, hence generating 12 excited chromophores, within the same dendrimer molecule when the laser intensity is higher than 6 mJ. The chromophore excited-states then undergo intramolecular oxidative quenching by electron transfer to the viologen core to initially form V^{+} then, before the charge recombination takes place from V^{+}, a second electron transfer can occur to afford V^{0}. This is a very elegant strategy to produce a doubly reduced viologen, but the present system requires a high laser pulse excitation and in the UV region, which is far from the solar conditions at the surface of the earth.

Other interesting examples of viologen-based dendrimers were published by Stoddart and co-workers, such as molecule **A21^{42+}** which contains 21 viologens units within the same structure (Fig. 10) [116–118]. It can be considered as a real electron sponge, since this system can accept many electrons (up to 14) upon electrochemical reduction or photoinduced electron transfers with external dyes. This polycationic dendrimer naturally exhibits a strong affinity to anionic compounds and can form host-guest complexes by electrostatic interactions. For example, dianionic eosin (EY^{2-}) can associate in dichloromethane with each viologen unit in the dendrimer **A21^{42+}**. A valuable feature of these viologen-based dendrimers relies on their charge pooling property upon light excitation. For example, photolysis of a solution of **A21^{42+}** with methyl-anthracene in the presence of a sacrificial electron donor (such as TEOA) results in colour changes highlighting the reduction of the viologen units of the dendrimers. The mechanism involves a first intermolecular electron transfer of the photoexcited methyl-anthracene to a viologen in **A21^{42+}** followed by the regeneration of the oxidized dye by TEOA (Scheme 8). Upon steady-state irradiation, such multiple electron transfer acts occur until several viologens (V^{+}) within the same dendrimer are reduced and therefore store several reducing equivalents. However, in such systems the number of electrons stored within the dendrimer **A21^{42+}** (8.5 hence only 41%) is lower than the total number of viologens (21) present inside the molecule. This phenomenon can be rationalized by the fact that the internal viologen units are tightly associated with the counter-anions (PF_6^-) and are therefore more difficult to reduce, thus preventing electron diffusion from the external viologen to those at the heart of the dendrimer.

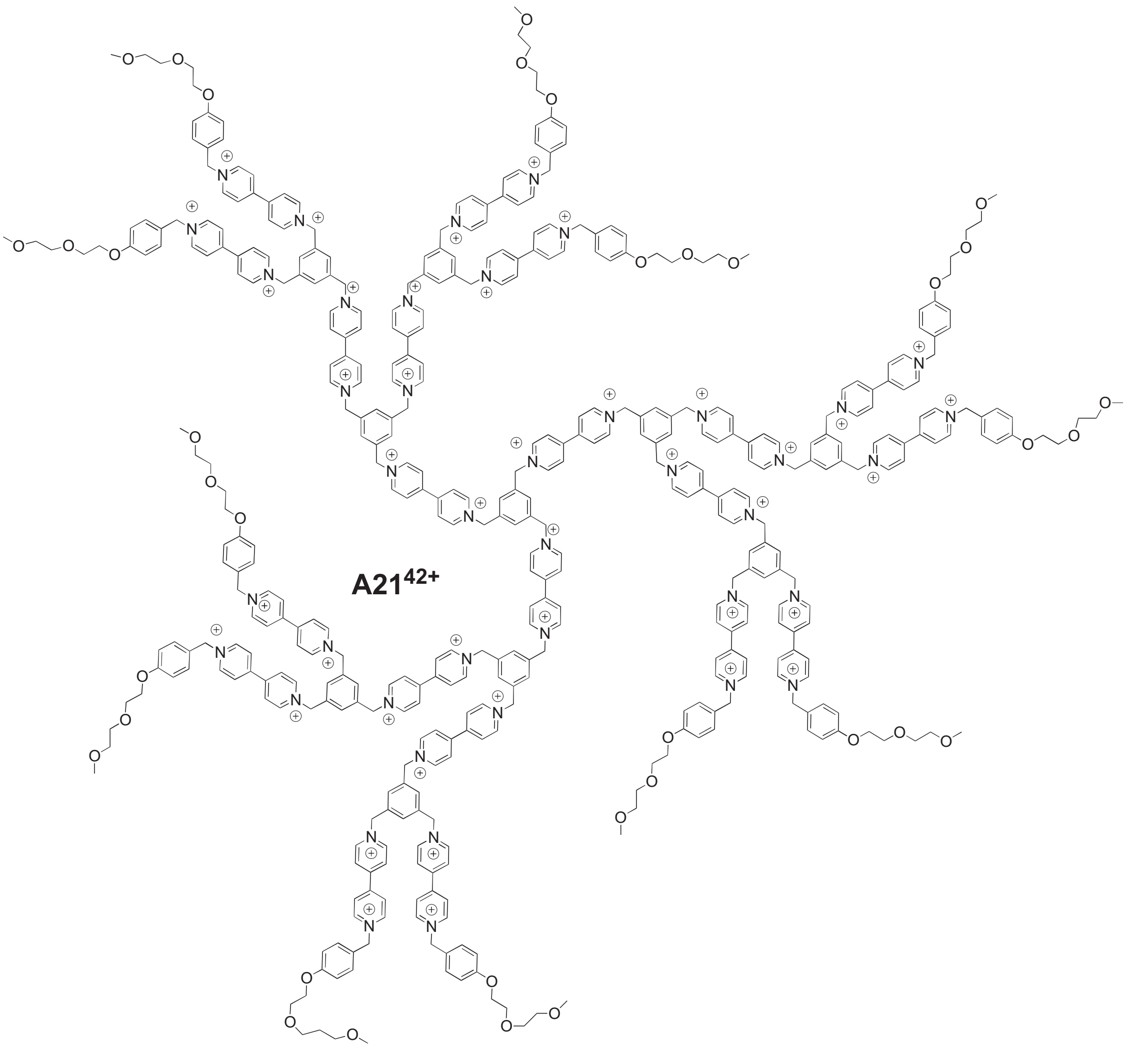
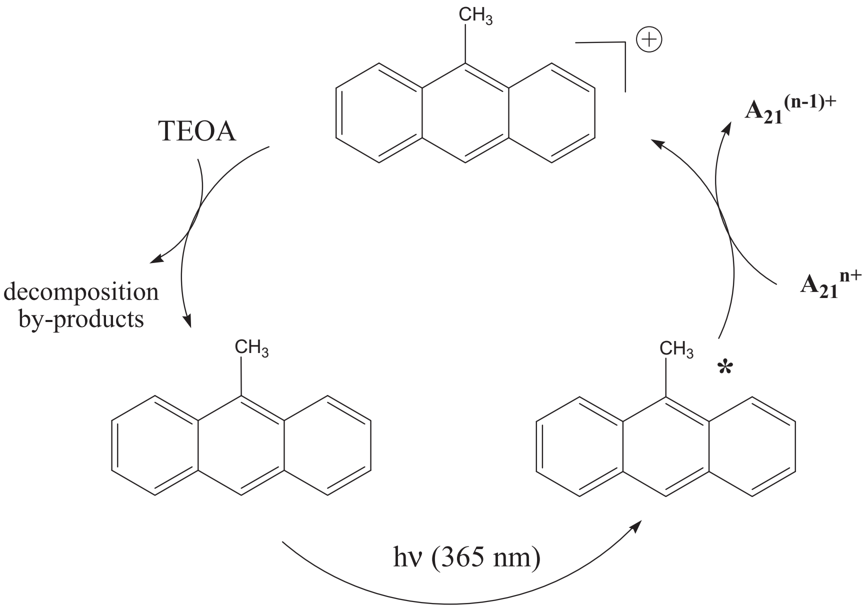


Fig. 10. Structure of an electron sponge incorporating viologen redox units in the branches of a dendrimer [116–118].



Scheme 8. Photochemical reduction of dendrimer **A21^{42+}** [116–118].

A more recent successful example of charge photo-accumulation using a dendritic architecture makes use of porphyrins as light collectors and a polyoxometallate as electron reservoir (Fig. 11) [119]. An interesting feature of this new system resides in the fact that it undergoes a two-electron reduction of the POM upon steady-state irradiation with visible light and therefore does not request high intensity laser pulse nor UV light. Besides, the polyoxometalates represent appealing moieties to be used as charge reservoirs, since they exhibit catalytic properties for reduction of protons into dihydrogen [120] and for oxidation of water into dioxygen [121,122]. Excitation of the external zinc porphyrins induces a first energy transfer to the free base porphyrin with a quantitative efficiency. The singlet excited-state of the free base porphyrin is a sufficiently powerful reductant to transfer up to two electrons on the POM, whose characteristic broad absorption band could be monitored during the photolysis experiments in DMF solutions. In this study, the presence of TEOA as sacrificial electron donor is also essential to regenerate the

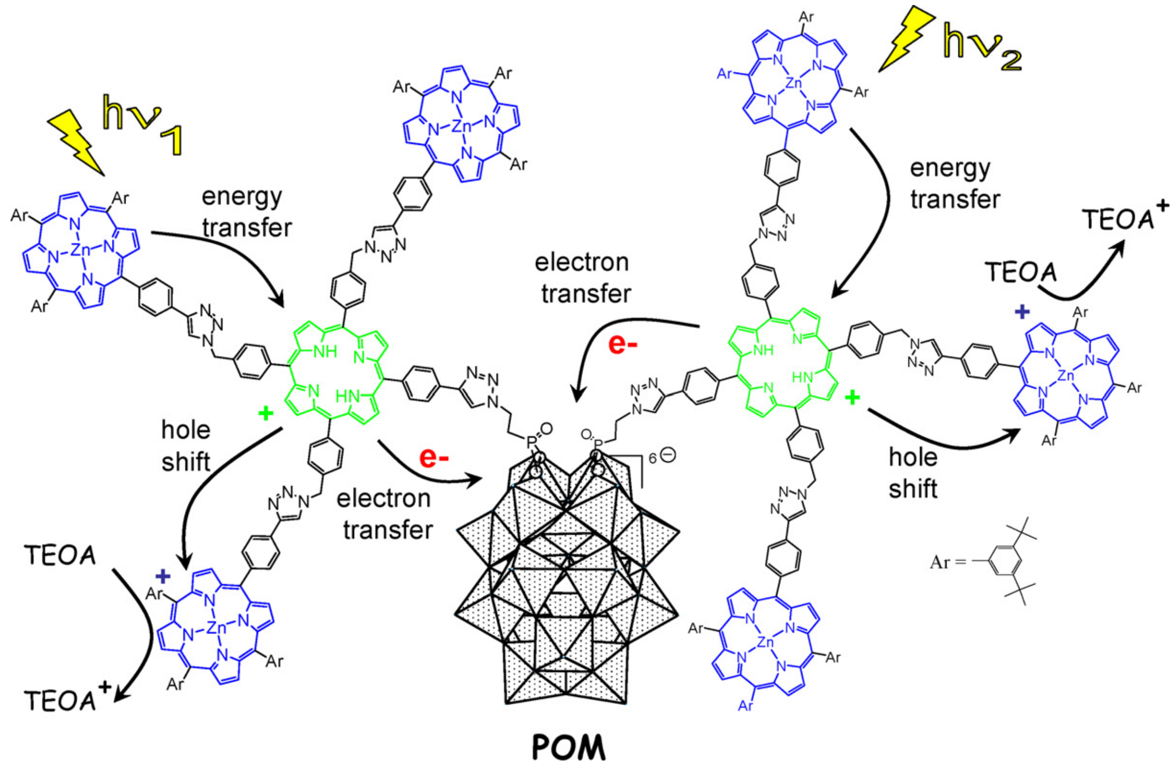


Fig. 11. Structure of the porphyrin-based dendrimer organized around a polyoxometallate leading to photodriven two-electron accumulation (POM) [119].

ground state of the oxidized porphyrins formed upon electron transfers.

The above dendrimers highlight their real potential for charge photo-accumulation. In these systems, we cannot miss a certain analogy with the antenna systems found in the natural photosynthetic system, in which many chromophoric units (chlorophylls and carotenoids) are placed in a circular symmetry and whose role is to power the special pair with incident solar energy. The latter brings about successive charge separation events until several reducing and oxidizing equivalents are stored in the proximity. In multi-chromophoric dendritic architectures, multiple excitations could be achieved within the same molecule with a relatively high probability owing to the large number of absorbing species. The occurrence of multi-photon absorption events at different sites is the prerequisite to bring about multiple charge separation reactions and to funnel several charges to a single molecular unit (reservoir). Alternatively, dendrimers consisting of repeating electro-active species such as viologen or ferrocene, also represent appealing charge storage systems behaving like molecular capacitors [123,124].

6. Conclusion and perspectives

The identification of the specific scientific challenges of charge photo-accumulation and the elucidation of the molecular engineering rules to rationally design efficient systems certainly represent an important step for photodriven catalysis of multiredox processes, such as water splitting or carbon dioxide reduction. Note that such systems have also potential applications for information storage or processing. During the past two decades, single electron transfer systems have been abundantly described in the literature. For example a triad made of a sensitizer S connected to an electron donor D and an electron acceptor A on the other side can produce an ion pair with a high quantum yield and a long lifetime upon light excitation. However, it is certainly crucial to attach a hole and an electron reservoir, whose role is to temporally store the charges in order to couple this one electron/one hole charge separated state to a multi-electron fuel making reaction. Artificial molecular systems exhibiting charge photo-accumulation are seldom and were reported only recently. Basically, the existing man made molecular systems featuring charge photo-accumulation are based on two main approaches. The first one consists in connecting a redox active molecule, playing the role of charge reservoir, to a photosensitizer. Photolysis of the photosensitizer induces a charge separation reaction with a sacrificial reagent, which rapidly and irreversibly decomposes. Then, the oxidatively or reductively quenched sensitizer donates its charge to the nearby reservoir. If this sequence of reactions is repeated several times on a single molecular system, this will naturally lead to the storage of multiple charges (or redox equivalents) on the reservoir. This is the strategy found in most published systems and constitutes a first step to reproduce charge-photo-accumulation. However, this strategy requires the use of sacrificial electron donors or electron acceptors, and therefore does not represent a realistic strategy for the design of economically viable photocatalytic systems. The second strategy makes use of a multi-chromophoric array (generally dendrimer), which is photo-excited by a strong laser pulse. This induces the formation of a multitude of photo-excited chromophores within a single molecule. The multiple chromophores decay by intramolecular photoinduced charge separation to a single electron acceptor or single electron donor unit. This implies that the latter should undergo multiple reductions or multiple oxidations in a narrow potential range so the chromophore excited-state always lies above the multi-reduced or multi-oxidized charge separated-state. However, this approach only works under intense laser excitation and not with natural light, limiting again its practical use. The above analysis therefore illustrates new challenges to take up in order to improve the existing systems. One certainly valuable innovation would be the development of new systems operating under low energy irradiance such as the terrestrial solar influence and without sacrificial reagent. Intense laser pulse excitations are undoubtedly useful for the fundamental studies of charge photo-accumulation, but if the multiple charge storage function cannot be achieved under daylight, the artificial systems will be of poor utility for solar energy transformation. Another crucial step would be the integration, in a single molecular system, of both an electron and a hole reservoir in order to simultaneously store reducing and oxidizing equivalents at each side of the single molecular system. Indeed, all artificial systems reported so far for charge photo-accumulation contain only a single reservoir (holes or electrons). Consequently, they require the utilization of sacrificial reagents to scavenge the holes or the electrons produced at the other side of the system. However, the consumption of sacrificial electron donor or acceptor reagents should be avoided for practical applications, especially if cost effective fuel production is envisioned. This will only be possible when reducing and oxidizing equivalents are simultaneously stored on different units of an individual molecular system. The ultimate goal of artificial photosynthesis being the production of fuels, another important step is therefore the practical use these new artificial charge storing systems to perform multi-electron fuel making reactions in order to prove that multiple redox equivalent storage improves the quantum efficiency of the overall photocatalytic process, as already demonstrated by Brewer and co-workers with a trimetallic Ru_2Rh complex [51]. Towards this goal the association of an electrocatalyst at proximity to the reservoir to rapidly remove the stored charges might be necessary if the latter, itself, does not present any catalytic activity. In this vein, the discovery of molecular entities which can be highly reduced or oxidized at relatively accessible potentials and with catalytic properties, such as polyoxometalates, will be valuable to develop reservoirs. This new emerging area of artificial photosynthesis is therefore full of challenges; many exciting developments remain to be done and we can foresee that they will contribute to the design of more efficient molecular devices for artificial photosynthesis.

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