Photoinduced Charge Accumulation in Molecular Systems

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Abstract: Fuel-forming reactions such as CO_2 reduction or water splitting require multiple redox equivalents. When aiming at light-driven production of energy-rich chemicals, nowadays often referred to as solar fuels, it therefore becomes important to master the photoinduced accumulation of electrons or holes on individual molecular components. Featured in this short review are some of the key molecular systems explored in this emerging field of research. This includes for example a trinuclear Ru(II)-Rh(III)-Ru(III) complex or an Ir(III)-sensitized polyoxotungstate hybrid, but also several systems in which electron or hole collection occurs at organic moieties such as perylenebis(dicarboximide), quinone-containing or oligotriarylamine-based units. In many cases the photodriven accumulation of charge requires the use of sacrificial electron donors, but there exist also a handful of studies in which redox equivalents can be accumulated without the use of such additives.

Keywords: Electron transfer · Photochemistry · Proton transfer · Solar fuel · Transient absorption

1. Introduction

Photoinduced electron transfer in molecular systems has been investigated very thoroughly over the past few decades. While many early studies focused on understanding basic aspects of electron transfer such as its driving-force or distance dependence,[1,2] more recent work on photoinduced electron transfer is often put into the greater context of light-to-chemical energy conversion.[3] The primary charge-separation events in natural photosynthesis have been mimicked with artificial (synthetic) systems many times, and there are numerous examples of photogenerated electron-hole pairs which have lifetimes on the order of microseconds and beyond.[1,4] In principle such lifetimes are long enough in order to perform useful secondary chemistry, but fuel-forming reactions usually require more than one redox equivalent and often must occur coupled to proton transfer events. Probably the most frequently cited specific example in this context is water splitting which involves two electrons and two protons for the reductive half-reaction and four holes and four protons for the oxidative half-reaction. Thus, as has been pointed out many times before, a single electron-hole pair is insufficient for the production of so-called solar fuels.

Against this background researchers explore photoinduced electron transfer reactions which are either coupled to proton transfer events, *i.e.* so-called proton-coupled electron transfer (PCET),[3,5–7] or which are followed by a secondary photoinduced electron transfer leading to the accumulation of two redox equivalents on a given molecular unit. In nanoparticles the light-driven accumulation of multiple charge carriers is readily possible,[8] and such materials are of course highly promising for application purposes. In purely molecular systems, photoinduced charge accumulation is more difficult to achieve, and until now there have been comparatively few studies which have succeeded in this regard. While most molecular systems are far less robust than systems based on inorganic nanoparticles, the former are attractive for basic research because one can work with structurally and electronically very well defined molecules.

Comprehensive reviews of photoinduced charge accumulation in molecular systems have been published recently,[9–11] yet for this invited short article it seemed useful to highlight a few specific case studies in order to increase awareness of this timely research subject.

2. A Few Specific Case Studies of Photoinduced Charge Accumulation

An interesting case of functioning photoinduced charge accumulation in a molecular system was reported by the Brewer group in 1994.[12] Two ruthenium complexes were attached to a central iridium(III) species with 2,3-bis(2-pyridyl)-benzoqui-noxaline (dpb) ligands, the peripheral ruthenium complexes were equipped with 2,2'-bipyridine (bpy) chelating agents (Fig. 1a). When irradiated with visible light in CH_3CN in the presence of an electron donor such as *N,N*-dimethylaniline, the $[(bpy)_2Ru(dpb)ClIrCl(dpb)Ru(bpy)_2]^{5+}$ complex is reduced by two electrons. Each of the two dpb ligands acts as an acceptor for one electron in this case, *i.e.* the two additional charges remain spatially somewhat separated but are at least accumulated in the coordination sphere of the iridium(III) center.

Structurally similar Ru-Rh-Ru complexes did later permit electron accumulation at the central metal site, thereby reducing the initially present Rh(III) to a Rh(I) center.[13–15] The bridging ligand between Ru and Rh metals in this case was 2,3-bis(2-pyridyl)pyrazine (dpp) to result in the $[(bpy)_2Ru(dpp)BrRhBr(dpp)Ru(bpy)_2]^{5+}$ molecular construct shown in Fig. 1b. Analogous trimetallic complexes with chloro-ligands at the Rh center were also explored.[16] In the course of two-electron reduction, the Rh center is thought to release its two halide ligands to produce a four-coordinate Rh(I) intermediate which reduces aqueous protons to H_2 under suitable conditions. Specifically, when using CH_3CN with 1.5 M *N,N*-dimethylaniline and water acidified with triflic acid to pH 2 and irradiating at 470 nm with an LED, 38 catalytic turnovers were observed in 4 h for the system shown in Fig. 1b. The quantum yield for this photocatalytic process was estimated to ~0.01.

The trimetallic complex in Fig. 1b is one out of many molecular systems that have been explored in recent years in the context of light-driven reduction of aque-

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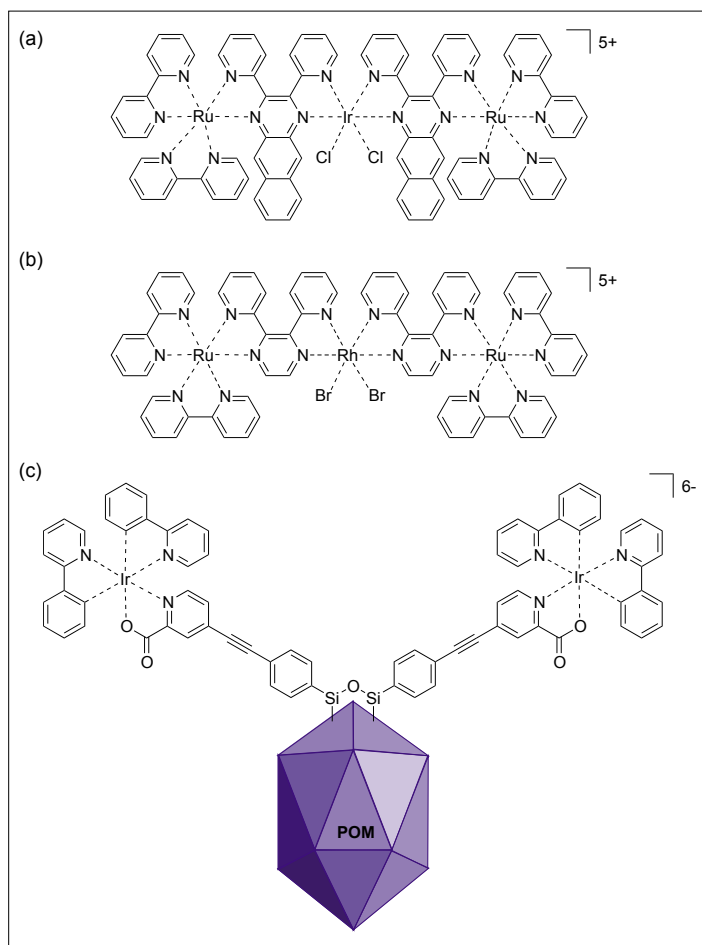E-mail: oliver.wenger@unibas.ch

Fig. 1. Trimetallic Ru(II)-Ir(III)-Ru(II) and Ru(II)-Rh(III)-Ru(II) systems and an Ir(III)-POM hybrid for which photoinduced charge accumulation at the central unit was observed when using sacrificial electron donors.[10–16,20]

ous protons with sacrificial electron donors.[11,17] This large field of research is beyond the scope of the present article; the system from Fig. 1b is merely mentioned here because it represents a further development of an early functioning system for photodriven charge accumulation. A key issue in this sub-discipline is always whether the catalytically active species is indeed a molecular compound or whether it is a colloid resulting from (photo) decomposition.[18,19] In this regard, the charge accumulating systems presented in this article are far better characterized because their one- and two-electron reduced (or oxidized) forms are usually identifiable unambiguously on the basis of optical spectroscopic investigations.

Recently, Artero and coworkers presented a polyoxometalate-photosensitizer (POM-PS) hybrid comprised of a polyoxotungstate covalently attached to two Ir(III) photosensitizers (Fig. 1c).[20] Upon irradiation with visible light ($\lambda > 400$ nm) the excited Ir(III) photosensitizer reduces the POM, resulting in the formation of a first charge-separated state. In presence of excess triethylamine as sacrificial electron donor, the oxidized photosensitizer was re-reduced, enabling further charge separation upon continuing excitation. The reduced POM species could easily be identified due to their d-d and intervalence

charge transfer bands at 840 nm for 1e−-reduced POM and at 710 nm for 2e−-reduced POM. The redox properties of the POM could be influenced by the addition of acetic acid. Even with a large excess of acid (500 equiv.) the POM-PS hybrid remained stable in solution for days, and the charge accumulating step was facilitated and accelerated. Furthermore, in a DMF solution of the hybrid with added acetic acid and triethylamine, H_2 evolution was observed.

The system remained active for up to seven days and showed superior efficiency to the corresponding multi-component system in which POM and photosensitizers are not linked to each other covalently.

MacDonnell and coworkers investigated two molecular compounds which behave in a conceptually similar way to the Ru-Ir/Rh-Ru complexes reported earlier by Brewer.[21] Specifically, they focused on dinuclear ruthenium(II) 1,10-phenanthroline (phen) complexes with tetraazatetrapyridopentacene (tatpp) and tetraazatetrapyridopentacene-quinone (tatpq) bridging ligands (Fig. 2).[22] Absorption of visible light induces MLCT excitation leading to reduction of the bridging ligand. In the presence of triethylamine or triethanolamine, the resulting Ru(III) center is re-reduced to Ru(II) and subsequent excitation then leads to charge accumulation on the tatpp or tatpq ligands. In alkaline solution, there is only electron accumulation but under acidic conditions one observes proton-coupled multi-electron transfer. In particular, the [(phen)$_2$Ru(tatpp) Ru(phen)$_2$]$^{4+}$ complex (Fig. 2a) accepts up to four electrons and two protons on the bridging ligand *via* chemical reduction and protonation whereas under visible light irradiation it can formally take up an H_2 molecule.[23] Electrons and protons are thought to be located on one of the two pyrazine units of the bridging tatpp ligand, thereby converting a pyrazine to a dihydropyrazine. In de-oxygenated CH_3CN in presence of 0.35 M triethylamine, irradiation of [(phen)$_2$Ru(tatpq)Ru(phen)$_2$]$^{4+}$ (Fig. 2b) with visible light first leads to reduction of the central quinone moiety to its hydroquinone form. Continued irradiation then converts one of the pyrazine units of the bridging ligand to a dihydropyrazine. The overall result is storage of four electrons and four protons on the tatpq
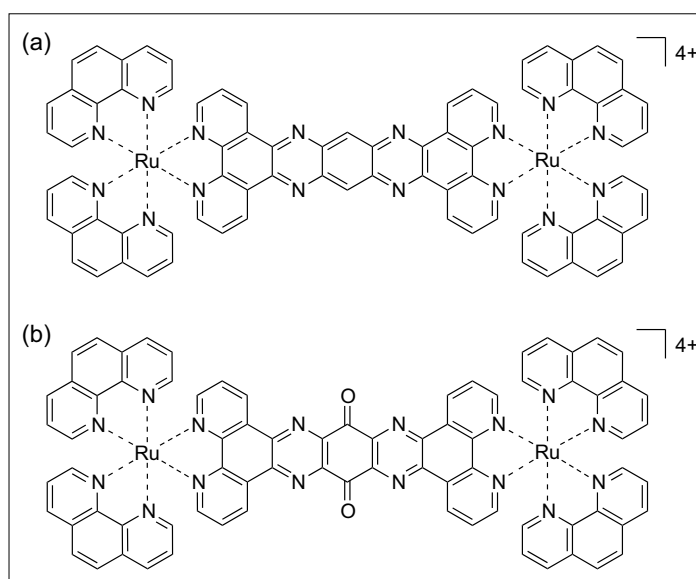

Fig. 2. Dinuclear Ru(II) complexes with central redox-active tetraazatetrapyridopentacene (tatpp) and tetraazatetrapyridopentacene-quinone (tatpq) ligands which can accumulate multiple electrons and protons upon photoexcitation in the presence of sacrificial electron donors and proton sources.[21–23]

ligand entirely driven by light, but of course on the basis of sacrificial electron donors. (Triethylamine is also the proton source in this instance. After oxidation, triethylamine decomposes and liberates protons.[24]) The individual redox and protonation products were identified unambiguously on the basis of complementary studies using either spectroelectrochemistry or chemical reductants such as cobaltocene/NaBH$_4$ and suitable acids.[23]

Fujita, Tanaka, and coworkers focused on a molecular charge accumulation system which is bio-inspired in the sense that it contains a structural element that aims to mimic the enzymatic NAD$^+$/NADH redox couple. Its molecular structure is shown in Fig. 3 and contains a Ru(bpy)$_2$ moiety chelated by a 2-(2-pyridyl)benzo[b]-1,5-naphthyridine (pbn) ligand. This complex was originally developed as a catalyst for the electrochemical reduction of acetone to 2-propanol.[25] Later it was found that when the excited-state of [Ru(bpy)$_2$(pbn)]$^{2+}$ is quenched reductively by an amine, one obtains a stable one-electron reduced species in dry organic solvents.[26] The reduced species is a pbn radical anion. When using continuous excitation ($\lambda > 300$ nm), the [Ru(bpy)$_2$(pbn)]$^{2+}$ complex can be converted to [Ru(bpy)$_2$(pbnH$_2$)]$^{2+}$ with a quantum yield of 0.21 for $\lambda = 355\pm6$ nm. Alternatively, the same species can be generated by reacting [Ru(bpy)$_2$(pbn)]$^{2+}$ with two equivalents of Na$_2$S$_2$O$_4$ in CH$_3$CN/H$_2$O, thereby making unambiguous assignment of the spectral features observed in the course of the photochemical conversion possible. The decay pathways of the one-electron reduced pbn radical intermediate were investigated in considerable detail,[27,28] and it is thought that disproportionation of the singly reduced, singly protonated intermediate to form a π-stacked dimer of [Ru(bpy)$_2$(pbnH)]$^{2+}$ is a key step in the formation of [Ru(bpy)$_2$(pbnH$_2$)]$^{2+}$ out of [Ru(bpy)$_2$(pbn)]$^{2+}$. Related work by Dietzek and coworkers recently reported on the possibility of storing two electrons in a suitably designed ligand of a mononuclear ruthenium complex.[29]

Various mono- and dinuclear metal complexes, also containing earth-abundant metals (Ni, Co), have been explored in the context of direct fuel formation or CO$_2$ reduction. A prerequisite hereby is again the accumulation of redox equivalents.[30]

Fox and coworkers investigated purely organic systems for light-driven charge accumulation. A central methylviologen unit was connected via benzyl spacers to peripheral naphthalene units in dendritic molecular structures.[31] In the system shown in Fig. 4, 16 naphthyl groups are linked to a single methyl viologen unit via 14 benzyl spacers. Excitation of the naphthyl groups with a pulsed laser at 266 nm produces the
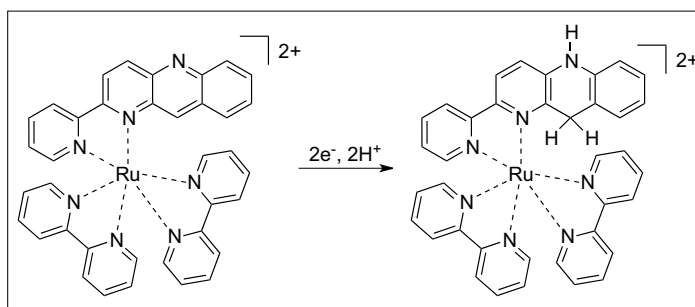

Fig. 3. Ru(II) complex with an NAD$^+$/NADH-type ligand.[26–28]

typical spectroscopic signature of methyl viologen monocation. When increasing the laser power, less strongly absorbing doubly reduced viologen is formed. The number of 266-nm photons absorbed at the highest laser fluences (>6 mJ) was estimated to be more than 12 per dendrimer. Thus, by exploiting the antenna effect brought about by the multitude of photosensitizers present in this system, Fox and coworkers were able to perform photoinduced charge accumulation without the use of a sacrificial reactant, and this is in clear contrast to the studies reported above.

An early case of photoinduced charge accumulation did not rely on sacrificial reagents either. Already in 1992 Wasielewski and coworkers reported on a donor-acceptor-donor molecule in which a central perylenebis(dicarboximide) unit (PBDCI) was linked covalently to two peripheral porphyrin (P) moieties (Fig. 5a).[32] When using low excitation densities, one detects primarily the P$^+$-PBDCI$^-$-P photoproduct by picosecond transient absorption spectroscopy. However, when increasing the laser excitation density above 5 photons per molecule, the lifetime of this photoproduct markedly decreases and the characteristic spectroscopic signature of two-electron reduced PBDCI can be detected. Remarkably, the P$^+$-PBDCI^{2-}-P$^+$ photoproduct decays with a lifetime of 5

ns whereas the P$^+$-PBDCI$^-$-P photoproduct has a lifetime of only 5 ps at low excitation densities. An alternative possible reaction product resulting from two-photon excitation would be P$^+$-PBDCI-P$^-$, but this species appears to be formed far less efficiently than P$^+$-PBDCI^{2-}-P$^+$. A key feature of the system from Fig. 5a is the presence of unambiguous spectroscopic signatures for the PBDCI$^-$ and PBDCI^{2-} ions, combined with favorable reduction potentials.

Imahori and coworkers reported a related donor-acceptor-donor system (Fig. 5b) which is based on a central tetracyanoanthraquinodimethane (TCAQ) unit flanked by two Zn(II) porphyrin moieties (ZnP).[33] In the visible spectral range there are rather small differences between TCAQ$^-$ and TACQ^{2-} hence identification of two-electron photoproducts is somewhat complicated in this instance. Yet, upon consecutive excitation of both ZnP chromophores with two laser pulses which were temporally delayed by 233 ps, it was possible to detect spectral changes which are compatible with the formation of doubly reduced TCAQ. This species decayed with a time constant of 1.2 ns in dioxane.

Hammarström and Odobel recently reported on photoinduced charge accumulation in a donor-photosensitizer-acceptor system (Fig. 6a).[34,35] The donor was an oligotriarylamine (OTA) unit, the photo-

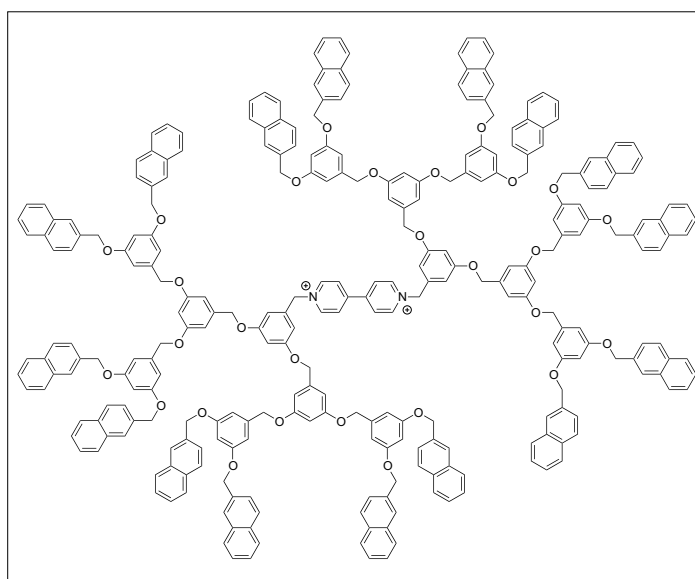

Fig. 4. Dendrimer system for the photoinduced accumulation of two electrons at the central methylviologen unit by exploitation of the antenna effect.[31]
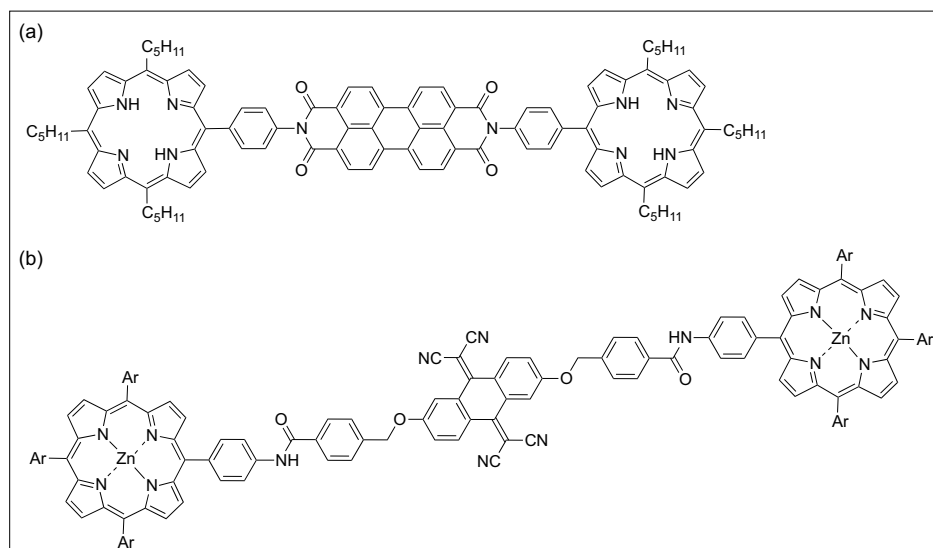
Fig. 5. Donor-acceptor-donor triads for the light-driven accumulation of electrons at the central acceptor site without the use of sacrificial reagents.[32,33]

sensitizer was a ruthenium(II) α-diimine complex which was attached to the surface of nanocrystalline TiO$_2$ acting as a terminal electron acceptor. To some extent, the resulting construct resembles what is often used in dye-sensitized solar cells,[36] but there are of course important conceptual differences in the photophysics and photochemistry. By using two-photon excitation with two temporally delayed laser pulses it was possible to detect OTA^{2+} unambiguously, which is clear evidence for the formation of a charge-separated state of the type OTA^{2+}-Ru(II)-TiO$_2$$^{2-}$.[34,35] Under the conditions used for this experiment, ~30% of all OTA-Ru(II)-TiO$_2$ units were excited by the first of the two laser pulses, and out of this fraction another ~30% was then excited by the second laser pulse. The fraction of OTA^{2+} detected by transient absorption after the second pulse was ~10%, and this leads to the conclusion that the formation of OTA^{2+}-Ru(II)-TiO$_2$$^{2-}$ occurs with nearly quantitative yield. This is truly remarkable and most likely is owed to the fact that charge injection into TiO$_2$ is extremely rapid, whereas reverse (energy-wasting) electron transfer processes are very slow in comparison. Interestingly, the OTA^{2+}-Ru(II)-TiO$_2$$^{2-}$ photoproduct was also observed in single-pulse high-photon flux laser experiments, *i.e.* multiple excitations of the same Ru(II) photosensitizer can occur in a single 10-ns laser pulse.

We recently explored two rhenium(I)-oligotriarylamine molecules with a view to obtaining doubly reduced and doubly oxidized charge-separated states in purely molecular systems without the use of nanoparticles or sacrificial donors or acceptors.[37] A molecular triad with an oligotriarylamine (OTA) donor, a rhenium(I) tricarbonyl diimine photosensitizer, and an anthraquinone (AQ) acceptor (Fig. 6b) did

show a relatively long-lived charge-separated state of the type OTA$^+$-Re(I)-AQ$^-$ but no evidence could be found for OTA^{2+} or AQ^{2-} using single-pulse laser experiments. A key problem of this system was its comparatively low photo-damage threshold at the laser excitation wavelength of 355 nm. Interestingly, the lifetime of the above-mentioned charge-separated state lengthened significantly upon addition of excess organic acid to the CH$_3$CN solution. In de-aerated CH$_3$CN the OTA$^+$-Re(I)-AQ$^-$ photoproduct did exhibit a lifetime of 205 ns but when 0.2 M chloroacetic acid was

present, the lifetime increased to 3.7 μs under oxygen-free conditions. This was attributed to the formation of the semiquinone (AQH) in the presence of acid, similar to what is observed in the presence of hydrogen-bond donating solvents.[38,39] Thus, the proton-coupled electron transfer (PCET) chemistry of quinones holds some promise for further investigations in the context of light-driven charge accumulation in purely molecular systems.

While the relatively short wavelengths which are necessary for excitation of rhenium(I) tricarbonyl diimine photosensitizers were problematic for the rhenium(I)-oligotriarylamine molecules mentioned above, Ishitani and coworkers recently reported on successful charge accumulation in ring-shaped molecules based on the same photosensitizer, albeit with sacrificial electron donors.[40]

3. Conclusions

A very large body of literature exists on the subject of photoinduced electron transfer, but the number of molecular systems in which an electron donor is oxidized more than once or in which an electron acceptor is reduced more than once by photoinduced electron transfer is very limited. While this short review is not comprehensive, it features some of the key systems investigated in the field of photoinduced charge accumulation in molecular systems. Work in this area is important in the
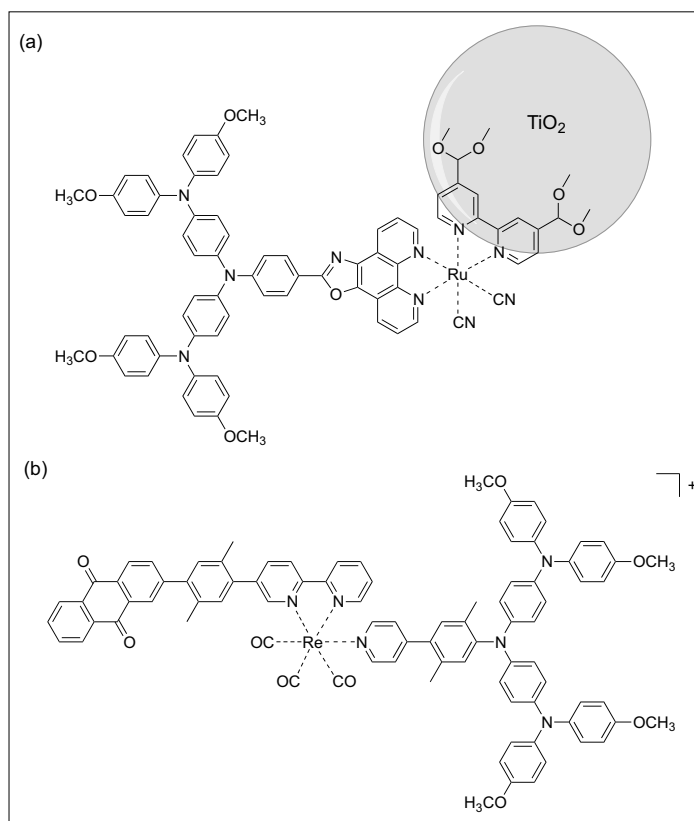

Fig. 6. Oligotriarylamine-based systems explored in the context of photo-induced charge accumulation.[34,35,37]

context of light-to-chemical energy conversion because many of the most interesting fuel-forming reactions require multiple redox equivalents. The molecular systems presented herein offer the advantage that they are chemically and electronically very well defined species, and the identification of two-electron reduced or oxidized reaction products usually occurs unambiguously on the basis of transient absorption spectroscopy and complementary spectro-electrochemical experiments.

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