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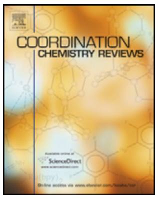

Review

Photochemistry of immobilized photoactive compounds

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ABSTRACT

The development of responsive molecular based materials and surfaces requires the incorporation of functional molecular components. In this regard thermo-, electro- and photochromic systems are of considerable interest. In this review, the immobilization of photoactive inorganic complexes is focused upon with attention directed to highlighting general issues presented by immobilization compared with photochemistry in solution; not least the effect of surface confinement on reactivity together with the stability of these systems in operation, e.g., the involvement or otherwise of the surface employed in perturbing molecular properties and the effect of surface confinement on essentially bimolecular solution photochemistry. In this review several demonstrative examples of photoactive molecular inorganic systems in which the photochemistry has been explored in the immobilized state under ambient conditions and especially on electroactive surfaces will be discussed including self-assembled monolayers, polymers and sol gel systems.

1. Introduction

Although photochemistry has been demonstrated frequently in solution for a wide range of photoactive coordination complexes, key challenges are encountered in moving from solution based to surface confined and polymer and sol–gel immobilized systems. In this review, several approaches taken to immobilizing inorganic photoactive systems will be discussed using selected examples that demonstrate important aspects, specifically the effect of immobilization of photoactive coordination complexes on the photochemistry due to changes in mass transfer kinetics, e.g., confinement in polymer matrices where diffusion of charges and small molecules is limited and the opportunities presented by immobilization in terms of addressability. The scope of this review is restricted to those photoactive molecular systems in which the photochemistry has been explored in the immobilized state under ambient conditions and especially on electroactive surfaces [1]. Although most discussion will focus on inorganic systems, especially ruthenium(II) based systems, selected comparisons will be drawn from wholly organic photo- and electroactive systems reported recently.

2. Photoactive self-assembled monolayers (SAMs)

The preparation of self-assembled monolayers has focused primarily on the affinity of pyridyl and sulfur moieties for the noble metals, with platinum and gold being the electrode materials of choice. A distinct drawback with this approach is the very limited amount of material that is available in the SAM (typically 10^{-11} to 10^{-9} mol cm^{-2}). This has required highly sensitive spectroscopic equipment, which has only become widely available in

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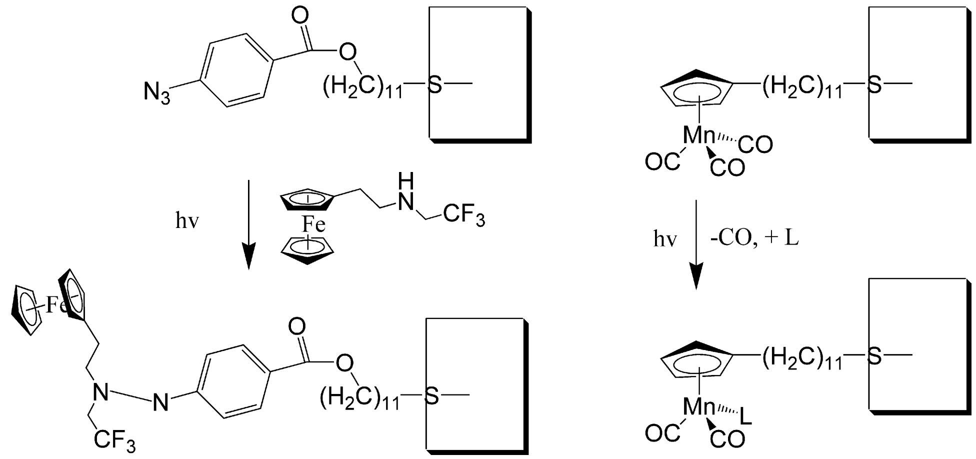


Fig. 1. Two approaches to building SAMs by first attaching a photoactive molecule to the surface followed by photolabilisation of a ligand (e.g., CO) or formation of a nitrene followed by reaction of the photoactivated surface with a second unit to increase the functionality of the surface [5].

recent years. Such sensitivity issues are easily overcome by electrochemical methods and hence most of studies of the photochemistry of SAMs have focused on electrochemical detection rather than spectroscopic detection [2]. A distinct advantage of forming monolayers of active molecular systems on conducting surfaces is the ability to address the entire sample rapidly by an electrochemical perturbation and moreover a precise control of the ‘doping’ of a monolayer with molecules in a higher or lower oxidation state simple by controlling the potential applied. More recently nanoparticles, in particular gold and silver, have been employed to raise the effective concentration available for spectroscopic examination [3] and semiconductor surfaces have received considerable attention due to their importance in photovoltaic applications [4].

2.1. Photochemically reactive SAMs

The photochemistry of cyclopentadienyl manganese tricarbonyls ([HS-$C_{11}H_{22}$-CpMn$(CO)_3$] and azides has been harnessed by Wrighton and coworkers [5] to prepare photoactive surfaces which can, via photosubstitution reactions, be used as substrates for high resolution lateral image patterning. In the case of the azide group the photochemistry is used to attach secondary amines to the surface, in the example in Fig. 1, a redox active substituted ferrocene unit, while for the manganese tricarbonyl photolysis of the Mn–CO bond to release carbon monoxide allows for coordination of a phosphine ligand. This approach gives access to a wide range of molecularly modified surfaces with functionalities which are incompatible with the synthetic procedures required to produce the thiol tether unit and to control the modification of the surface in a spatial manner.

The photochemistry of ruthenium(II) polypyridyl complexes has been examined extensively since the first observations of the photoreactivity of $[Ru(bpy)_3]^{2+}$ by van Houten and Watts in the early 1970s [6]. In particular the photochemically induced exchange of ligands with solvent has proven to be particularly interesting in the generation of photoactive surfaces. A recent example of this is photosubstitution of a chlorido ligand for an aqua ligand in a Ru(II) polypyridyl complex $[Ru(bpy)_2(bpe)Cl]^+$,

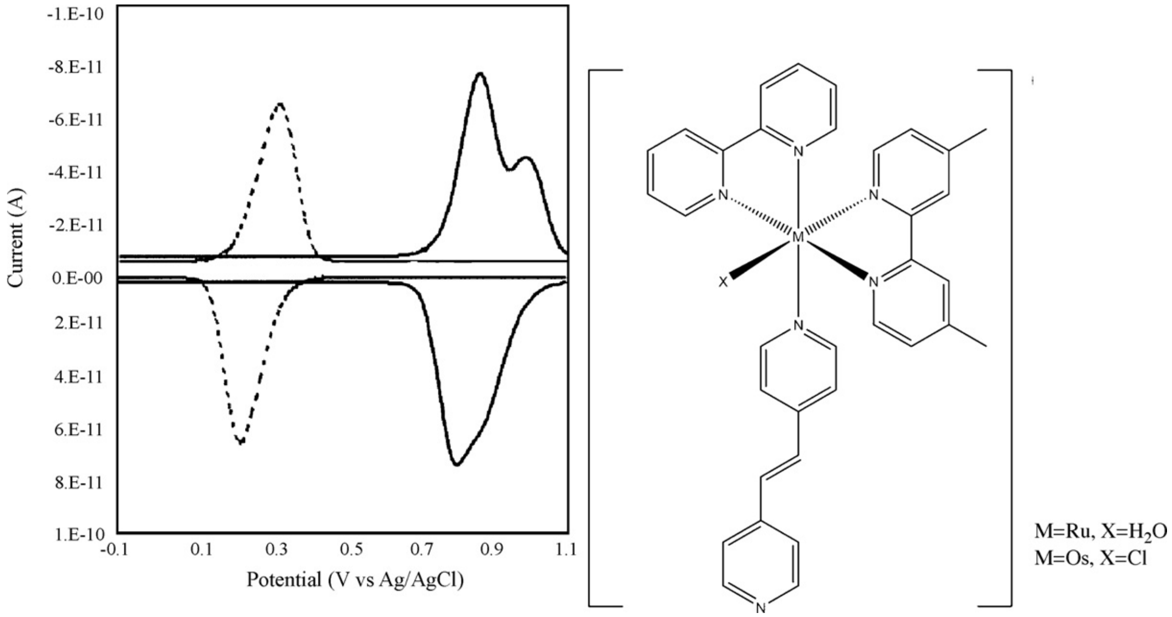


Fig. 2. Cyclic voltammograms for $[Ru(bpy)_2(bpe)H_2O]^{2+}$ (solid line) and $[Os(bpy)_2(bpe)Cl]^+$ (dashed line) self-assembled monolayers adsorbed spontaneously on a 5 mm platinum disk electrode (0.1 M $HClO_4$, 1.0 V s^{-1}). Reproduced from Ref. [7], copyright ACS 2000.

reported by Forster et al. [7] (Fig. 2). The complex undergoes loss of either the bpe ligand or the chlorido ligand depending on the solvent employed with aqueous solvents favoring loss of the latter ligand. For the corresponding osmium complex the SAMs formed are completely photo-inert. The electrochemical response of the osmium(II) chlorido complex is characterised by a simple heterogeneous one electron transfer reaction. For the corresponding Ru(II) aqua complex not only is the redox chemistry strongly dependent on pH, there is also a contribution of the high effective surface concentration on the disproportionation of Ru(III) centres, formed by oxidation, to the Ru(IV) and Ru(II) state:

$$2[\mathrm{Ru^{II}(bpy)_2(bpe)OH_2}]^{2+} \rightarrow 2[\mathrm{Ru^{III}(bpy)_2(bpe)OH}]^{2+} + 2\mathrm{H}^+ + 2\mathrm{e}^- \quad (1)$$

$$2[\mathrm{Ru^{III}(bpy)_2(bpe)OH}]^{2+} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpe)OH_2}]^{2+} + [\mathrm{Ru^{IV}(bpy)_2(bpe)O}]^{2+} \quad (2)$$

The pH dependence of this process is interesting and reflects the complexity [8] of the system. The acidity of the Ru(II) centre increases upon oxidation to the Ru(III) state and subsequently to the Ru(IV) state resulting in deprotonation following oxidation of the metal center. However, the deprotonation of the complex serves to lower the redox potential and provides the driving force for disproportionation. In solution the rate of disproportionation is diffusion controlled whereas in the densely packed SAM the rate is enhanced considerably due to the proximity of the redox centers. This is an excellent example of a major difference in the kinetics of intermolecular interactions between SAMs and dilute solutions.

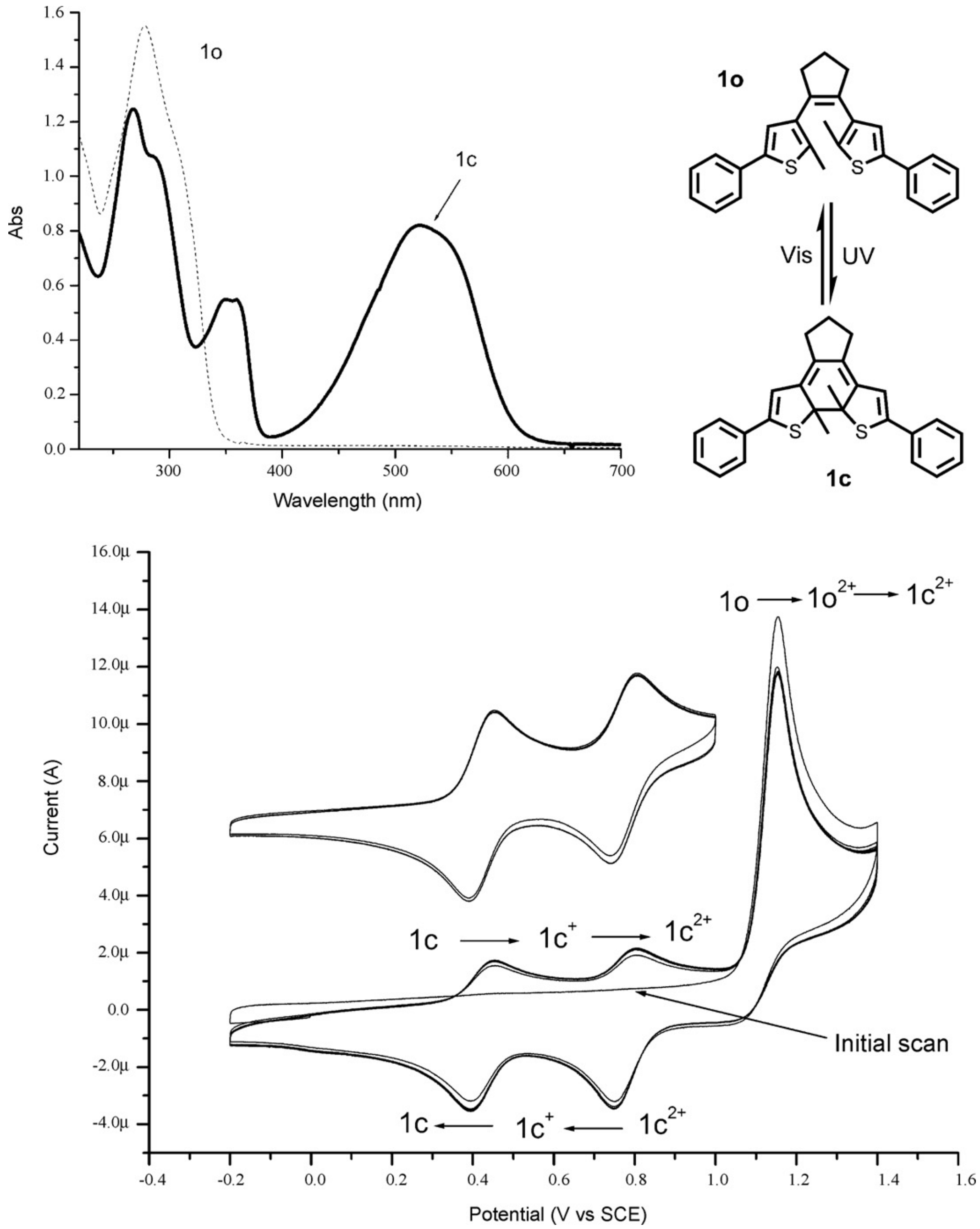


Fig. 3. UV–vis absorption spectra and cyclic voltammetry of a dithienylcyclopentene in its open (**1o**) and closed (**1c**) form in $CH_2Cl_2/TBAPF_6$ (0.1 M), 0.1 V s^{-1} adapted with permission from [12d]. Copyright RSC 2006.

Although quenching of electronically excited states is encountered frequently in SAMs of photoactive compounds on noble metals, this is not necessarily always the case. Bertoncello et al. have prepared SAMs of the complex $[Ru(bpy)_2(bpySH)](PF_6)_2$, where bpy is 2,2′-bipyridyl and bpySH is 5,5′-bis(mercaptomethyl)-2,2′-bipyridine, which retain some of the luminescent properties on gold [9]. However, the luminescence properties of dry monolayers are similar to that of solid samples rather than that observed in solution. Brennan et al. [10] have studied SAMs of the complex $[Ru(dpp)_2(Qbpy)]^{2+}$ (where dpp = 4,7-diphenyl-1,10-phenanthroline and Qbpy is 4,7-di(4′-pyridyl)-1,10-phenanthroline). The monolayers formed by this complex retain their emissive behavior. This system offers a good opportunity to probe both the rate of lateral electron transfer between the electronically excited states of the Ru(II) complex and Ru(III) species introduced electrochemically and of the redox properties of the Ru(II) complex in the excited state by high speed cyclic voltammetry coupled with excitation of the immobilized complex by a nanosecond laser pulse. These studies demonstrate that the immobilization of photoactive systems on surfaces allows for entire samples to be addressed at sufficiently high rates to allow for even transient excited state populations to be examined.

The effect of immobilization on the rates of bimolecular reactions in particular electron transfer reactions, e.g., disproportionation, can prove useful in extending the functionality of molecular systems. However, the approach taken to anchoring the functional unit to a surface and indeed the surface itself is of equal importance. The photochemistry and more recently the electrochemistry of the dithienylcyclopentene class of compounds have been the subject of several detailed studies [11,12]. These functional systems can exist in two thermally stable forms; the so-called ‘open’ colorless form and the ‘closed’ colored form (Fig. 3).

The majority of investigations have focused on the intrinsic molecular properties of these systems in solution, however, to interface them with non-molecular systems (and the outside world) their immobilization on surfaces is essential. Recently the covalent self-assembly of diarylethenes on an ITO (Fig. 4a) [13] and gold [14] surfaces was demonstrated. The photo-and redoxactive system **1o/1c**, which undergoes switching between the open and closed form by UV and visible irradiation, respectively, can only be closed electrochemically in solution. That is electrochemical switching in these systems is unidirectional in solution, the direction of which can be controlled by tuning of the molecular structure [12e]. By contrast when immobilized on a surface electrochemical switching in both directions can be achieved in a fully reversible manner (Fig. 4) [13]. As for the ruthenium(II) system described above, the change in the behavior of the dithienylethene when immobilized is not due to a change in its intrinsic electrochemical properties. Instead it demonstrates the importance of the changes in the rates of bimolecular reactions, such as disproportionation, on going from solution to the densely packed monolayers. Again as for ruthenium based oxidation catalysts, such as those reported recently by Meyer and coworkers [15], immobilization on a surface such as ITO allows for the entire sample to be addressed rapidly electrochemically. In the case of the photochromic dithienylethenes the ‘added value’ gained upon immobilization on a surface is that the entire sample can be addressed rapidly. Whereas the neutral compound is thermally stable in both the open and closed states in the dicationic

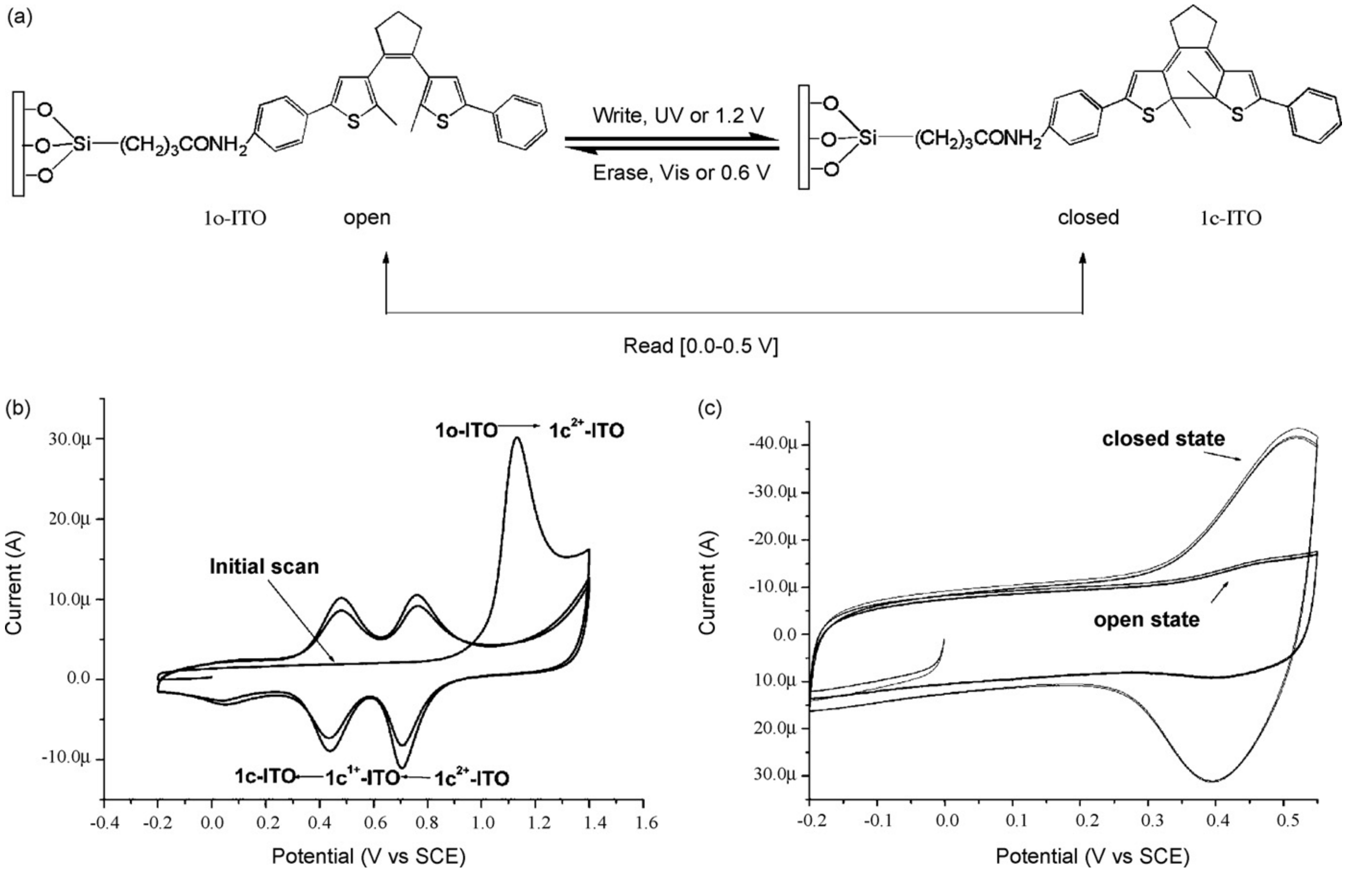


Fig. 4. (a) Schematic of a dithienylethene molecular switch **1o** immobilized on ITO using triethoxysilyl anchors. (b) Electrochemical ring closing of **1o**-ITO to **1c**-ITO by cyclic voltammetry. (c) Electro- and photochemical write and erase functions with readout achieved non-destructively through cyclic voltammetry. Adapted with permission from Ref. [13]. Copyright The Royal Society of Chemistry 2006.

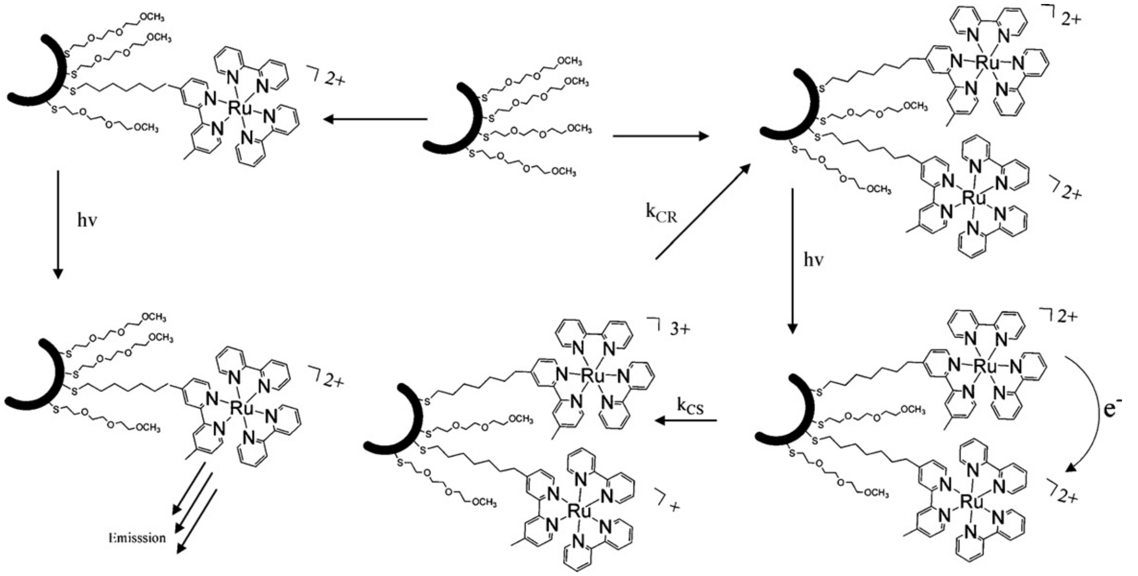


Fig. 5. Light-induced Processes on ruthenium polypyridyl modified gold nanoparticles. k_{CS} and k_{CR} are the rate of charge separation and recombination, respectively [18].

state the open and closed forms are in thermal equilibrium. Hence by cycling electrochemically between 0.0 and 1.2 V (i.e. the potential at which the both the open and closed forms are oxidised) the entire sample can be converted first to the stable dicationic closed state and on reduction to the neutral closed state. However, if electrochemical cycling is carried out only between 0.0 and 0.6 V the only the closed form will be oxidised. This can be used to drive conversion from the closed to the open state. At 0.6 V the closed form will be converted to the dicationic state. This will convert partially to the (dicationic) open form which at this potential is reduced immediately. Therefore, although the dicationic open and closed forms are in thermal equilibrium in favor of the closed state, the reaction will nevertheless be driven towards the neutral open state at this potential.

2.2. Photochemically reactive modified nanoparticles

The immobilization of photoactive molecules to generate 'functional' surfaces in which molecular species can be interfaced with the non-molecular bulk materials, in particular with a view to incorporation into electronic devices, has brought with it considerable challenges as well as opportunities. The formation of stable chemical bonds between the surface and the molecule of interest and the control of the orientation of the molecule with respect to the surface are in themselves two challenging aspects: however, even with high surface densities the total amount of the compound of interest that is available for analysis is at the nanomol/cm^2 level and lower. As a consequence metallic surfaces, in particular gold, have received most attention due in part to their conductivity and hence suitability for surface analysis by X-ray photoelectron spectroscopy (XPS) [16], scanning tunnelling microscopy (STM), surface enhanced Raman spectroscopy [17], electrochemistry [2] etc., and in part due to ease with which relatively simple ligands can be employed as anchors, i.e., pyridine and thiolates. Metal nanoparticles, however, offer a compromise between solution and surface in that the size of the nanoparticles means that the molecule sees, effectively, a bulk surface but the total amount of material which is available of characterisation by electronic spectroscopy approaches that available in solution.

This point is exemplified in the study of Ru(II) polypyridyl complexes immobilized on gold nanoparticles by Pramod et al. [18] The particles were modified by a place exchange reaction (Fig. 5) in which the density of the ruthenium complexes on the gold nanoparticles could be tuned. Whereas in solution and at low surface concentrations on the nanoparticles excited state decay was primarily via the non-radiative/radiative pathways ($\tau = 1.1\ \mu s$), for nanoparticles modified with high $[Ru(bpy)_3]^{2+}$/nanoparticle ratios, electron transfer quenching became the dominant deactivation pathway reducing the emission lifetime to less than 5 ns. In this example the immobilization of the luminophore has had no effect on its inherent photophysical properties but has changed the rate at which various bimolecular processes can proceed.

Similar phenomena were observed in the photochemistry of $[Fe(CO)_5]$ adsorbed onto single crystal and roughened silver at 89 K [19]. Photodissociation leads to CO loss in both the gas and adsorbed phases however the photochemical quantum yield was found to be larger for multilayer coverage in part assigned to dark reactions between the photoproduct and $[Fe(CO)_5]$ which are assisted by immobilization, i.e. they are no longer diffusion rate limited.

2.3. Dye based solar cells

The advent of dye based solar cells in the early 1990s [20] marked a new direction in how surfaces modified with molecular systems were viewed. In particular, the concept of a heterosupramolecular assembly [21] where photoactive molecular systems came to be viewed as active components in a system rather than as isolated systems. A detailed review of this area is beyond the scope of the present discussion; however there are key issues which arose in this field which are immediately relevant. The effect of immobilization of photoactive compounds, not least the complex $[(LL)_2Ru(SCN)_2]^-$ [22], is a case in point. This complex undergoes photoinduced ligand labialization in solution whereas when immobilized on nanocrystalline TiO_2 in Li^+ containing electrolytes the complex showed excellent photostability. In this case the change in the behavior of the complex is not due to perturbation of its electronic structure upon surface immobilization but rather due to quenching of the electronically excited state within less than a picosecond after excitation by charge injection into the TiO_2 substrate. In the absence of Li^+ ions the valence and conduction band levels of the TiO_2 do not facilitate rapid heterogeneous electron transfer and photochemical ligand loss is observed for the complex [23]. In this case the proximity to the surface changes the relative rates of competing processes (charge injection vs. photoinduced ligand loss) and thereby the properties of the molecule immobilized.

3. Photoactive polymer films

Immobilization of photoactive complexes in polymer matrices enables the study of the electro- and photochemistry of species in non-diffusive conditions, i.e. where the complex itself does not diffuse. Perhaps the simplest method to form polymer modified electrodes is to spin-coat a polymer film on an electrode where either the electro- and photoactive complex covalently attached (*vide infra*) or as intimate mixtures. Such systems have seen widespread application in polymer based solid state electrochemoluminescent [24] and dye based solar cell systems [25] in recent years. A recent example of this is the report by Moran-Mirabal et al. [24] whom have embedded $[Ru(bpy)_3]^{2+}$ in polyethylene oxide by electrospinning [26] thin films onto gold interdigitated electrodes. This example demonstrates that electrochemoluminescence seen in solution can be achieved in an immobilized system also, however the restriction the non-conducting matrix places on conductivity limits the dimensions of the active regions on the spin cast film. Such a limitation is, in this case, advantages as it allows for localisation of the electroluminescence. Haas et al. [27] employed polyvinylpyridine decorated with $[Ru(bpy)_2(L)Cl]^+$ groups (where L is a pyridyl unit of the polymer itself) [28] to enable the photosubstitution reactions of this class of complex to be probed by electrochemistry (Fig. 6). As for the related monolayer systems discussed above, upon irradiation photolysis of the Ru–Cl bond was observed followed by substitution with either CH_3CN or H_2O. Notably although the initial photosubstitution or the chlorido ligand for an aqua or acetonitrile ligand is observed by the disappearance in the redox wave at 0.64 V and the appearance of new redox waves at 0.84 and 1.135 V, respectively, in the case of the acetonitrile complex it is clear that the complex remains photoactive. The difference in the photochemistry of the chlorido and acetonitrile complexes is remarkable and shows that essentially irreversible substitution reactions can be rendered reversible by tuning of the relative stability of the reactant and the product. In the case of the chlorido complex the ligand substitution yields a complex which is thermodynamically more stable and hence a driving force for reforming the chlorido complex is absent. In the case of the acetonitrile complex the photosubstitution yields a complex which is thermally less stable and reversion is observed once irradiation ceases. This approach to photoactive polymer films is not limited to polyvinylpyridine based polymers but can be extended to other systems such as the more pH sensitive polyvinylimidazoles [29].

An alternative approach to preparing polymer modified electrodes is to spin-coat polymerizable monomers onto a substrate (electrode or otherwise) followed by *in situ* polymerization by application of UV light or the redox generation of radical initiators (Fig. 7) [30]. This approach allows for patterning of the photoactive polymer using masking technologies.

A further issue with regard to the stability of Ru(II) complexes immobilized in polymer matrices is that of oxygen reactivity. Fuller et al. suggested that whereas in solution quenching by $^3O_2$ serves to decrease the level of ligand photodissociation by competitive deactivation of the electronically excited state, in polymer matrices the inability of $^1O_2$ to diffuse away from the complex subsequent to energy transfer may increase its destructive affect, the so-called cage effect. Indeed in increasingly more viscous polyethylene glycol media the effect of $^3O_2$ changed from reducing the rate of photochemical decomposition to increasing it [31]. Hartmann [32] has proposed that the effect of photobleaching of ruthenium(II) complexes absorbed on silica or dissolved in polymer matrices is due to reaction of the $^1O_2$, generated by energy transfer quenching, with the polypyridyl ligands. In particular whereas bipyridyl based complexes were found to be photostable, complexes based on phenanthroline type ligands exhibited photodegradation with changes in emission lifetimes and spectral features being consistent with attack at the reactive 5,6-position of the phenanthroline (Fig. 8). The extent of the effects observed were found to be dependent on the both oxygen concentration and the dye concentration. The ligand oxidized complexes absorb and emit at lower energy than the parent phenathroline complexes and hence at higher concentrations energy transfer from parent complex to the product of the reaction is observed resulting in an amplification of the effect of the oxidation.

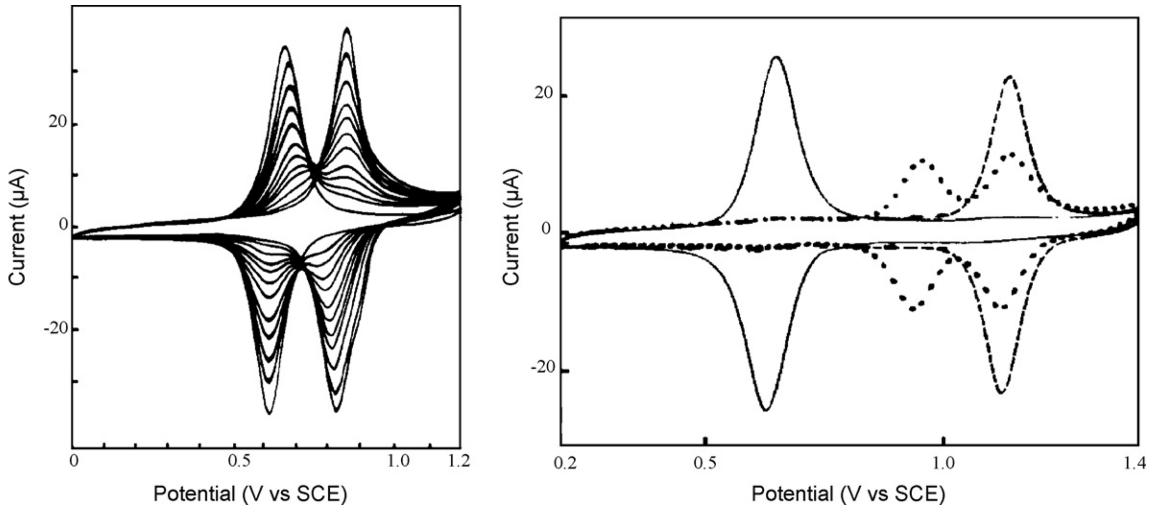


Fig. 6. Left: Cyclic voltammetry of a glassy carbon electrode modified with a $[Ru(bpy)_2(L)Cl]^+$ containing polyvinylpyridine film (supporting electrolyte 1.0 M $HClO_{4(aq)}$) under continuous irradiation. The intensity of the redox wave at 640 mV decreases with the concomitant increase in the redox wave at 840 mV. Right: Cyclic voltammetry of a glassy carbon electrode modified with a $[Ru(bpy)_2(L)Cl]^+$ containing polyvinylpyridine film (supporting electrolyte 0.5 M $LiClO_4$ in CH_3CN) under continuous irradiation. The intensity of the redox wave at 640 mV decreases with the concomitant increase in the redox waves at 840 mV and 1.135 V. In this case the redox wave at 840 mV was observed only upon irradiation. From Ref. [27], copyright ACS 1981.

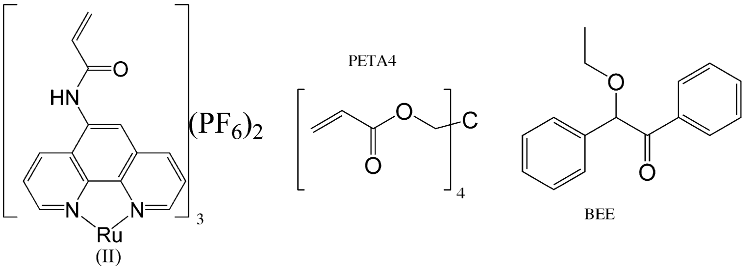


Fig. 7. Mixture of ruthenium modified and non-modified (PETA4) monomers and initiator (BEE) used for photopolymerization to form photoactive polymer films [30].

The use of polymerization as a method for immobilizing electrocatalysts has and continues to receive considerable attention. The benefits of immobilization are perhaps obvious in that the effective rate of electron transfer between the catalyst and the electrode support is potentially higher than in solution and the immobilized layer can be addressed completely quickly relative to that achieved by diffusion of a dissolved catalyst; the effect of the polymer on catalytic activity is often considerable as the diffusion of reactants and products into and out of the polymer film is very sensitive both to the nature of the polymer (e.g., hydrophobicity) and the polymer structure (e.g., porosity). Meyer and coworkers [33,34] have employed reductive electropolymerization to immobilize Ru(II) based electrocatalysts for water oxidation. *cis*-$[Ru(vinyl\text{-}bpy)_2(py)_2](PF_6)_2$ (where vinyl-bpy = 4-methyl-4′-vinyl-2,2′-bipyridine and py = pyridine) was employed to generate the polymer by reductive polymerization of the vinyl moiety [35] on glassy carbon electrodes. The immobilized complex was activated by photochemical ligand dissociation of the pyridine ligands to yield poly-*cis*-$[Ru(vinyl\text{-}bpy)_2(OH_2)_2](PF_6)_2$. Although ligand loss could be achieved, the efficiency of the photolysis was markedly reduced in comparison to that observed in solution. The redox chemistry and the film structure of the electropolymer modified electrodes can be varied considerably through the conditions under which electropolymerization takes place and the solution composition. In this example the electrocatalytic oxidation of alcohols was examined.

The increasing efficiency of solar cell technology based on dye sensitized photoanode electrodes and the possibility of reducing carbon dioxide directly at related photocathodes has seen increasing attention in recent years. Hirose et al. [36] have reported an immobilized polymer for the photocatalytic reduction of carbon dioxide. In contrast to the previous systems where the metal complex catalysts were immobilized by electropolymerization, in this system $[Ru(bpy)_3]^{2+}$ are immobilized electrostatically using a cation exchange polymer (Nafion 112) with $[Co(bpy)_3]^{2+}$ as a homogenous component. The system shows very modest turnover numbers (8.3) but does operate at atmospheric pressure and demonstrates that electrostatic immobilization can be useful in accessing immobilized systems more rapidly. However, in this case a sacrificial electron donor was employed and to make the system catalytic the reduction of the ruthenium(III) complex should be achieved electrochemically. The difficulties inherent in achieving a working system of this type have been demonstrated by Stoessel and Stille [37], who used a novel polyquinoline system to immobilize Ru(II) complexes as a photosensitiser in a photocatalytic system for water photolysis. Although the photocatalyst was demonstrated to be able to function in the polymer film, diffusion through the polymer film both of material and electrons was insufficient to allow the system to be applied in a working device.

A further aspect of immobilization of photoactive units within polymer matrices over and above charge transport issues is the inherent inhomogenity of the systems obtained. Meyer and coworkers [38] have reported the preparation of low polydispersity copolymers (see Fig. 9) through anionic polymerization of 4{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene followed by partial derivatization with $[Ru(bpy)_2(4\text{-}CO_2H\text{-}bpy)]^{2+}$ through amide coupling. The electronic absorption and emission spectra are essentially the same as the model complex $[Ru(bpy)_2(4\text{-}CO_2NHPh\text{-}bpy)]^{2+}$, the emission quantum yields and excited state decay lifetimes show a modest dependence on the extent of loading of the polymer with the Ru(II) complex. At higher loading levels the decay kinetics became non-exponential but could be fit using a modified Williams–Watts distribution function [39] indicating that in the restricted environment of the polymer, increasing the loading of the complex lead to increased contributions of intermolecular interactions between the luminophores.

Whereas for wholly organic photoactive systems reversible unimolecular photo-isomerization has and continues to receive widespread attention [40], inorganic photochemistry is dominated largely by either energy and electron transfer [41] or by ligand dissociation through population of ligand field centered excited states, which require re-coordination of, e.g., solvent or electrolytes to reverse the process if such a reversal is thermodynamically favored. Nevertheless the of photo and redox triggered linkage isomerization of nitrosyl [42] and sulfoxyl [43] inorganic complexes serves to demonstrate that the versatility seen in organic photochemistry can be, potentially, matched by inorganic systems.

In contrast to photoinduced exchange of ligands where solvent coordination is involved, in systems where the same ligand presents two alternate coordination modes, such as in the sulfoxide ligand

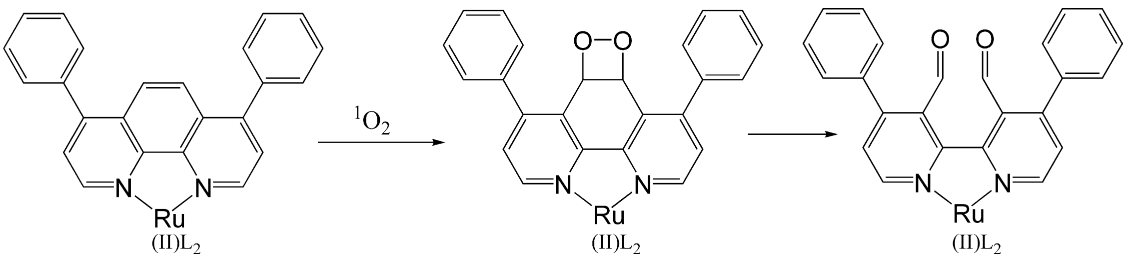


Fig. 8. Proposed mechanism [32] for photobleaching of Ru(II) complexes containing phenanthroline type ligands. The $^1O_3$ generated by energy transfer quenching subsequently oxidises the 5,6-position of the phenanthroline ligand.

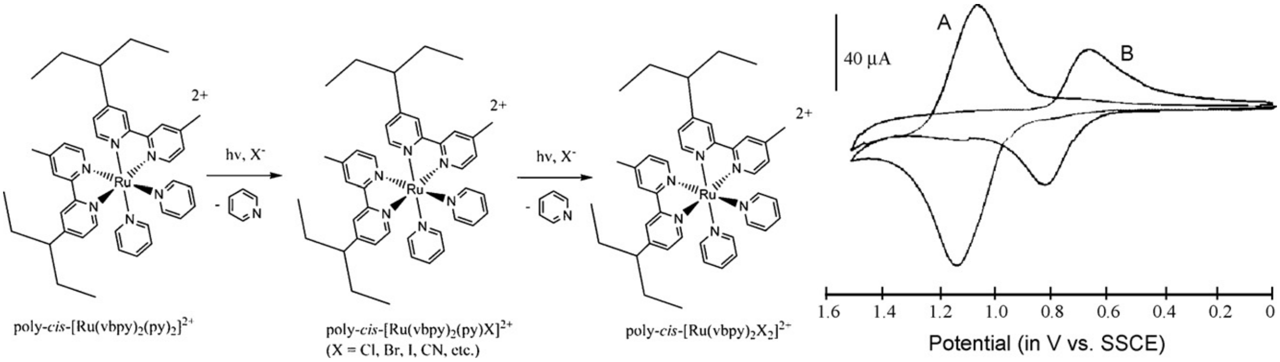


Fig. 9. Left: Sequential photosubstitution of pyridine ligands. Right: Cyclic voltammetry of poly-*cis*-[Ru(vbpy)$_2$(py)$_2$]$^{2+}$ on 3 mm Glassy Carbon electrode (Γ 5.0×10^{-9} mol cm^{-2}) (A) before (in 0.1 M TBAPF$_6$ in CH$_3$CN) and (B) after photoaquation to *cis*-[Ru(vbpy)$_2$(H$_2$O)$_2$]$^{2+}$ (in 0.1 M HClO$_4$). Reproduced from Ref. [34], copyright ACS 1996.

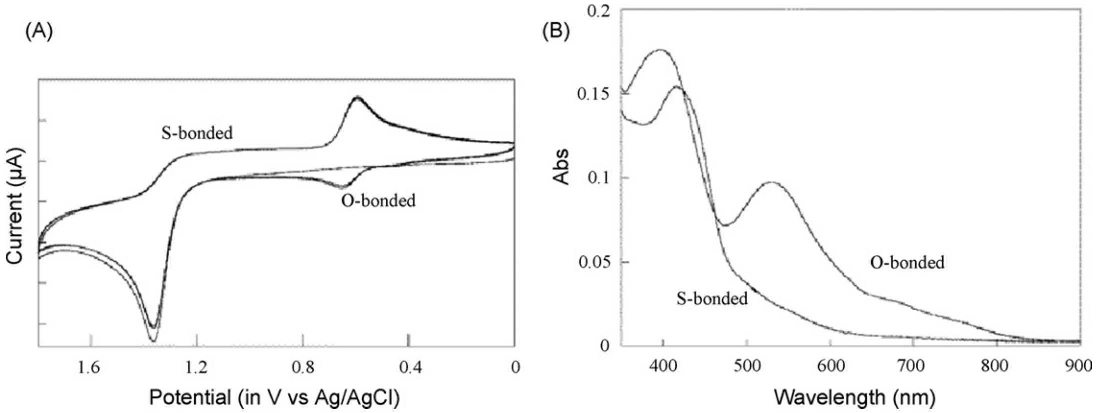
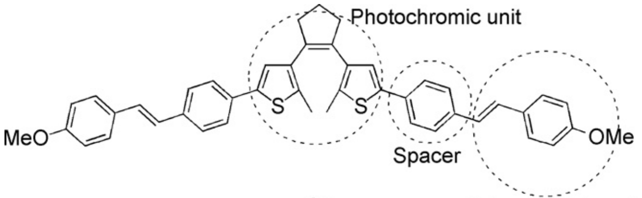


Fig. 10. Cyclic voltammetry and UV–vis absorption spectra of two interconvertable forms of a light/redox switchable complex [Ru$^{\text{II}}$(tpy)(pic)(DMSO)]$^+$. From Ref [43], copyright ACS 2004.

of the complex [Ru$^{\text{II}}$(tpy)(pic)(DMSO)]$^+$ (where tpy = terpyridine and pic = picolinic acid, Fig. 10), the rate of the photoinduced process is less sensitive to the immediate environment and hence when immobilized in polymer films the rate of diffusion of solvent becomes a minor issue if it remains an issue at all [43].

The choice of the polymer backbone used to immobilize the photoactive unit is non-trivial. The monomer employed in forming the polymer and the polymerization process must be compatible with the photo/electroactive unit. For the ruthenium(II) polypyridyl systems described above the inherent chemical stability of the functional unit provides considerable freedom in the choice of polymerization method, e.g., anionic polymerization, UV light initiated radical polymerization, oxidative and reductive electropolymerization, etc. For less robust photoactive systems, consideration should be given to both the effect the polymer matrix has not only on the properties of the photoactive unit itself but on the stability during operation also.

For example, immobilization of a photo/electrochromic dithienylcyclopentene (similar to that described above) can be achieved through electropolymerization of a methoxystyryl unit attached to the photoactive unit (**2o**, Fig. 11) [44]. The oxidative electropolymerization of the methoxystyryl unit produces thin films (<10 nm), which can undergo complete switching between the open form (poly-**2o**) and the closed form (poly-**2c**) electrochemically and by irradiation with UV and visible light (*vide supra*). However, although the photochromic unit, the dithienylcyclopentene, operates in the polymer matrix in the same manner as in the SAMs described above (Fig. 12), the stability is much lower. Oxidation of the closed form at slow scan rates or irradiation with UV light leads to rapid destruction of the photochromic functional unit due to reactions with the methoxystyryl polymer component.



2o

Fig. 11. A bifunctional molecule incorporating photo/electrochromic dithienylethene and electropolymerizable methoxystyryl units (**2o**).

4. Photochemistry in gels and viscous matrices

Although gels and viscous matrices can be viewed as bearing more of a resemblance to solutions than to surfaces, the effect of immobilization on photochemistry is worth mentioning here if only briefly. Pankasem et al. [45] employed pyrene and [Ru(bpy)$_3$]$^{2+}$ as probes in polymer microgels to study the temperature dependence of the gel's morphology, in particular shrinkage at elevated temperatures in which the rate of diffusional quenching was used to probe the location of the luminophore, i.e. within the gel fibers or in the aqueous component. More systematic studies of the photochemistry of [Ru(bpy)$_3$]$^{2+}$ in sol–gels, in particular those based on the condensation of tetramethoxysilane (TMOS) to form SiO$_2$ glasses were reported shortly after by Matsui and Momose [46]

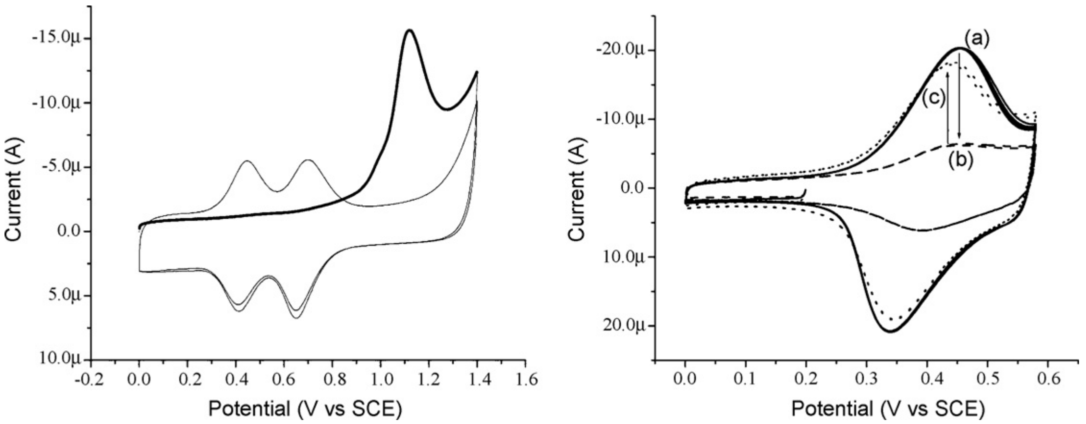


Fig. 12. Left: Cyclic voltammetry of poly-**2o** on a glassy carbon electrode prepared by visible irradiation (>420 nm) of poly-**2c** in monomer free solution at 0.1 V s^{-1} in DCM (0.1 M $TBAClO_4$). First cycle is indicated by an arrow. Right: Cyclic voltammetry of poly-**2c** on a glassy carbon electrode at 0.75 V s^{-1} in DCM (0.1 M $TBAClO_4$) before (a) and after (b) photochemical ring opening by visible irradiation (>420 nm) of poly-**2c** in monomer free solution, and after (c) oxidative ring closure. Reproduced from Ref. [44] Copyright ACS 2008.

and Vos and coworkers [47]. Matsui and Momose [46] reported that the luminescence spectrum of the complex underwent a blue-shift upon ageing of the sol–gels, similar to that observed upon formation of low temperature (77 K) glasses, attributed to the reduction in the ability of the local environment of the complex to reorient to stabilize the $[Ru(bpy)_3]^{2+}$ excited state. In a further study, Mongey et al. [47] examined the effective of immobilization of a series of trisheteroleptic Ru(II) complex $[Ru(LL)_3]^{2+}$, where LL = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 4,7-diphenyl, l,10-phenanthroline (ph_2phen) and found that although the blue-shift in the luminescence spectrum and the increased decay lifetime was observed in all cases, for $[Ru(ph_2phen)_3]^{2+}$ the effect was markedly less than for the other complexes. The differences were assigned to the shielding of the complex by the phenyl groups, with the increase in emission lifetime being assigned to a reduction in the diffusion rate of O_2 as the gels aged and shrank.

In contrast to the polymer immobilized systems discussed above addressing sol/gel based systems electrochemically is more challenging with diffusion of charge being severely limited. Nevertheless Kanaizuka et al. have demonstrated that ruthenium(II) complexes immobilized in zirconium based sol–gels formed by the dip coating technique do show adequate redox responses for thin films (<12 layers) [48].

Photochemistry in the solid state, where a significant change in molecular structure takes place, is of considerable interest due to the possibility of changing unit cell dimensions reversibly. Irie and coworkers [49] and Uchida et al. [50] have shown that thin single crystals of photochromic diarylethenes can be made to bend and even ‘roll up’ and uncurl by application of UV and visible light, respectively. The reason the thin crystals show this phenomenon under excitation with light of different wavelengths is by taking advantage of what is otherwise seen as a problem in the photochromic switching of solid materials. For a solid material photochromic switching from a colorless to a colored state is limited by inner filter effects arising from conversion of the top layer of a material [51]. Therefore, irradiation of a thin crystal will cause only the molecules on one side to change shape, i.e. contract, which induces the crystal to bend (and eventually roll up). The reverse process, that of ring opening of the diarylethene, leads to a transparent state so complete recovery of the open stretched state can be achieved. At one and the same time these studies demonstrate that when moving from solution to the solid state with photoactive systems one should recognise that changes in behavior will be observed but equally that these differences between solution and the solid state should not be seen only as a problem but as an opportunity.

5. Prospects for molecular based photo-responsive systems

The immobilization of inorganic complexes that are both redox and photochemically active on conductive surfaces is particularly advantageous, due to the tunability of the response that can be achieved not least with the versatile metal polypyridyl family of complexes in applications from dye based solar cells to sensors [52] and molecular electronics. In any application, however, it is clear that the perturbation of molecular properties by the immobilization itself, such as quenching of electronically excited states may be of less importance than the effect immobilization has on kinetics, in terms of both charge and mass transfer. Indeed it is perhaps these latter considerations that in the end determine the suitability of a particular approach to immobilization. In SAMs and densely modified polymers for example the rates of intermolecular energy and electron transfer become appreciably higher than under diffusion controlled conditions in solution. On the other hand the diffusion of reactants and products into and out off polymer matrices remains a challenge to be overcome in applying this strategy to immobilizing (photo)catalytic systems. Overall perhaps, it is important to realize that the approach taken in immobilizing can be viewed positively as an additional tool over and above tuning of molecular structure in achieving control over molecular properties.

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