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Electrochromic devices based on thin metallopolymeric films

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Recent work from our own lab on electrochromic thin-film metallopolymers is surveyed and summarized. The survey includes discussion of (1) new electrochemical synthetic methods based on reductive halide loss or oxidative activation for nucleophilic attack, (2) spatially selective, multicomponent film formation based on semiconductor bandgap illumination, followed by electropolymerization, (3) spatially selective film formation based on solution-phase (monomer) photoredox chemistry, and (4) reversible electrochromic image recording, based on a combination of semiconductor electrode illumination and polymer-phase metal–metal bond chemistry.

1. Introduction

Coordination complexes of transition metals are attractive as building blocks for electrochromic devices on account of their intense coloration, ample redox reactivity and well established preparative chemistry. In coordination complexes, chromophoric properties can arise from metal-to-ligand charge transfer (MLCT), intervalence charge transfer, intraligand excitation, and related visible-region electronic transitions. Because these transitions involve valence electrons, chromophoric characteristics are altered or eliminated upon complex oxidation or reduction. While these properties alone (visible light absorption and susceptibility to oxidation or reduction) are sufficient for direct use of monomeric species in primitive electrochromic applications, more advanced device applications require solid (preferably polymeric) chemical systems. Our research has emphasized the development of new synthetic routes – especially electrochemical routes – to thin-film metallopolymeric materials. It has also emphasized the construction of chromophoric macrostructures and microstructures which may be of unique value in advanced device applications, especially electrochromic applications. Some examples drawn from our current and recent research are outlined in the sections below.

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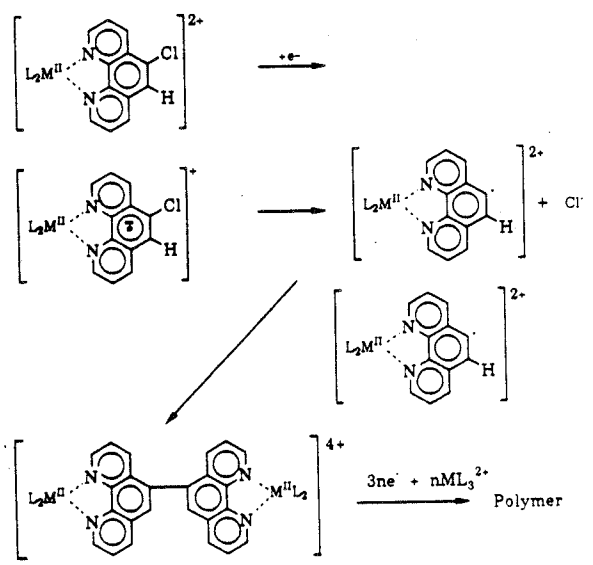
2. New synthetic methods

We have developed two new routes – one reductive and one oxidative – to metallopolymeric films. These complement a variety of existing routes which have been reviewed by Abruña [1], Murray [2] and Deronzier [3]. The reductive polymerization chemistry uncovered in our lab [4] relies upon electrochemically initiated carbon–halide bond cleavage and radical generation and is illustrated by scheme 1. As suggested by scheme 1, radical generation provides an efficient route to carbon–carbon bond formation and metal-complex oligomerization. Oligomers above a critical (as yet, ill defined) size are insoluble. Because the oligomers are created at or near an electrode surface, insolubility leads to electrode film formation.

Depending on the nature of the metal center, we find that polymeric films can be obtained in orange (ruthenium), red (iron) or green (osmium) form [4]. Film-based metal oxidation ($M^{II} \rightarrow M^{III}$) leads reversibly to very pale, nearly transparent, films (see fig. 1). Film-based ligand reduction, on the other hand, leads reversibly to dark purple films.

As suggested by table 1, the reductive halide-loss chemistry can be generalized. The table also lists some ligand combinations involved in oxidative polymerization [5,6]. Fig. 2 shows an example of an electrochemical "growth cycle" for a thin-film metallopolymer derived from oxidation of $Os(phen)_2(BPA)_2^{2+}$ (phen is 1,10-phenanthroline; BPA is bis(pyridyl)ethane). We find that films of this type are both reductively and oxidatively electrochromic. For example, an oxidatively grown copolymer of $Ru(phen)_2(4,4'\text{-bpy})_2^{2+}$ and $Os(phen)_2(4,4'\text{-bpy})_2^{2+}$ (4,4′-bpy is 4,4′-bipyridine) displays four distinct color states corresponding to four different combi-



Scheme 1.

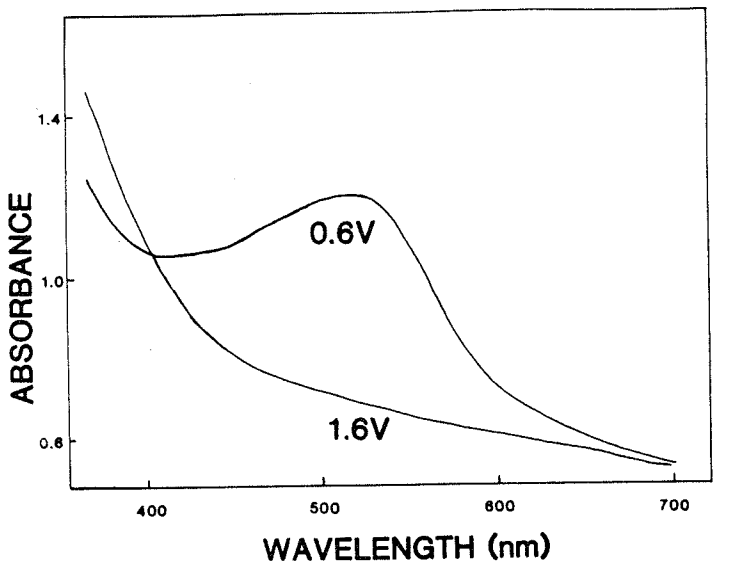
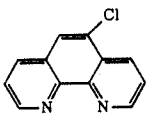
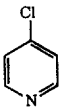
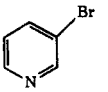
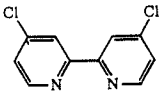
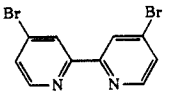
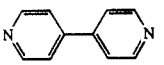
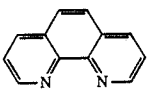
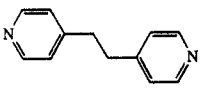
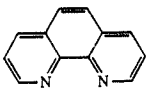
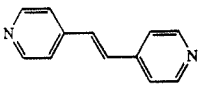
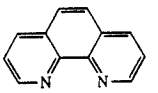


Fig. 1. Potential dependence (versus SCE) of the visible region absorption spectrum of a film derived from Fe(5-chlorophenanthroline)$_3^{2+}$. The electrode material is indium–tin-oxide coated glass. It should be noted that the large apparent absorption remaining at 1.6 V (oxidized film; $A \approx 0.4$–0.6) is due primarily to polymer particle scattering and substrate electrode effects, not metallopolymer absorption effects.

Table 1
New polymerizable ligands

	,		and 	Reductive
		and		Reductive
		with		Oxidative
		with		Oxidative
		with		Both

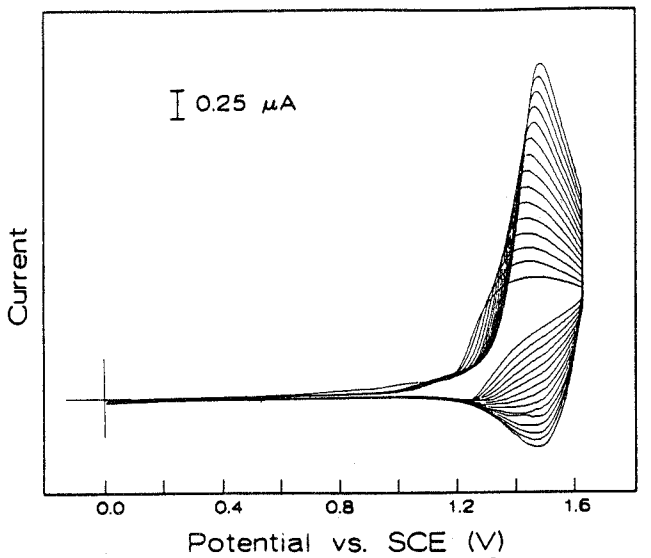


Fig. 2. Consecutive cyclic voltammograms for 1 mM $Ru(phen)_2(BPA)_2^{2+}$ at a platinum disk electrode in contact with an acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrode. The scan rate was 100 mV/s.

nations of metal and ligand oxidation or reduction. As expected, the color states can be repetitively interconverted by repetitively scanning the electrode potential. The ranges of color stability are the following: purple (below −1.0 V), deep brown (−0.9 to +0.8 V), orange (+1.0 to +1.5 V) and transparent (above +1.6 V).

Although the mechanism of polymerization in fig. 2 has yet to be established with certainty, the available evidence [7] suggests that it proceeds by nucleophilic attack of a pyridyl moiety at the central ring of a metal-bound phenanthroline, leading to reductive elimination of a hydrogen atom and efficient carbon–nitrogen bond formation.

3. Multicomponent polymer macrostructures

One of the limitations to electrochemical methods of polymer film formation is lack of macroscopic spatial selectivity: film dimensions and shape are defined entirely by the dimensions and shape of the underlying electrode. Furthermore, only one type (or color) of coating can be displayed on an electrode at a time. Obviously both characteristics could represent shortcomings in at least some electrochromic device applications (e.g. multicolor alphanumeric displays, etc.). We have sought, therefore, to devise methods of assembling multicomponent polymeric films in a spatially defined way. Two methods have yielded results; both rely upon light input to initiate polymerization. With these methods, spatial

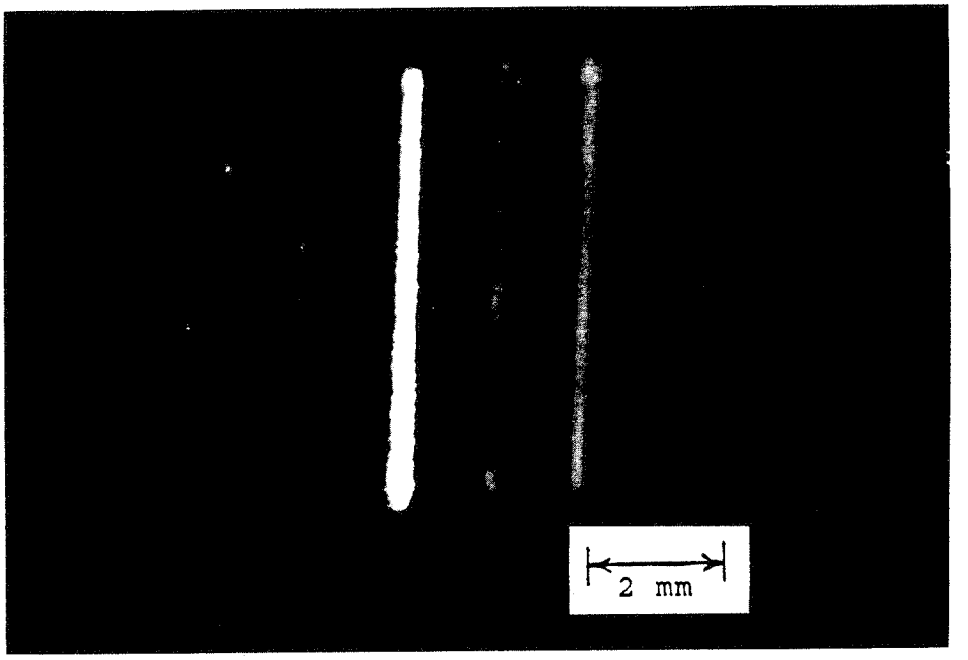


Fig. 3. Side-by-side structures on p-silicon. Left: $Re(CO)_3(vbpy)(Cl)$ (yellow); center: $Fe(vbpy)_3^{2+}$ (red); right: $Ru(vbpy)_3^{2+}$ (orange) [8].

(lateral) control of film growth becomes largely a matter of controlling photolysis beam dimensions.

The first approach to spatially defined metallopolymer growth entails photolytic activation of a semiconductor electrode [8]. The electrode material initially chosen was p-type silicon. Under dark conditions this material is insulating, in an electrochemical sense. Under visible region illumination, however, valence-band/conduction-band excitation occurs, with concurrent electron/hole pair generation. For the p-type electrode, electrons can then be delivered to the electrode surface for use as reducing equivalents. If the species reduced is susceptible to electropolymerization then film growth can be achieved during illumination. The key, however, is that electrode activation and electropolymerization occur only on that specific portion of the electrode surface exposed to visible radiation, a point that has been appreciated also by workers in the organic conducting polymer area [9,10]. Successive irradiation in different monomer solutions provides a means for multicomponent film fabrication. Fig. 3 shows an example of differently colored (yellow, red and orange) side-by-side structures obtained by this scheme. The monomeric precursors to the film structures were $Re(CO)_3(vbpy)(Cl)$, $Fe(vbpy)_3^{2+}$ and $Ru(vbpy)_3^{2+}$ where vbpy is 4-methyl-4′-vinylbipyridine [11], a ligand well known to undergo efficient electroreductive polymerization [12,13].

Fig. 4 shows that site-selective redox responses (electrochromic responses) can be obtained from appropriate multicomponent structures [8]. The electrode mate-

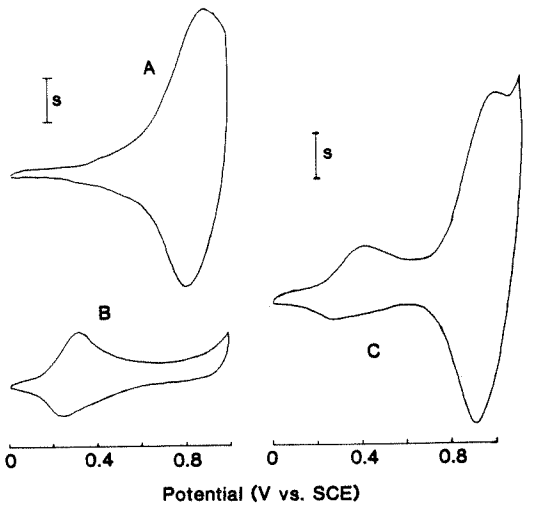


Fig. 4. Cyclic voltammograms of RuL_3^{2+}- and OsL_3^{2+}-based spot films (L = 5-amino-1,10-phenanthroline) on an n-$MoSe_2$ electrode in an acetonitrile solution containing 0.1 M tetraethylammonium perchlorate. $S = 20\ \mu A$, sweep rate = 100 mV/s, light source = Hg–Xe lamp (450 W) with 550 nm cutoff filter. (A) Selective illumination of RuL_3^{2+}-based spot film, (B) selective illumination of OsL_3^{2+}-based spot film and (C) entire electrode illuminated [8].

rial in this case is n-type $MoSe_2$. An electroactive side-by-side structure was developed by sequential (photo)oxidative electropolymerization [14] of Ru(5-amino-1,10-phenanthroline)$_3^{2+}$. Subsequent illumination of the electrode on the poly-osmium side leads to an electrochemical response for Os(II/III) (green/transparent), while illumination of the poly-ruthenium side leads exclusively to that of Ru(II/III) (orange/transparent). An expanded beam experiment gives the sum of the responses from the two sites.

A second approach to spatially defined film growth involves *solution phase* photochemistry. We note that many of the film precursor complexes described above possess long-lived photo-excited states (MLCT states). Furthermore these states can often be quenched by bimolecular electron transfer. If the quenching reaction is irreversible, or if back electron transfer is slow, then an opportunity exists for polymer formation from the reduced (or oxidized) chromophoric form. In order to obtain polymers in thin-film form, solutions can be photolyzed via backside illumination of a transparent surface (for example, indium–tin-oxide coated glass). Fig. 5 shows an example based on reductive quenching (scheme 2) of excited Ru(vbpy)$_3^{2+}$ by *n*-hexyltriphenylborate, a species which has previously been shown to be an effective reductive quencher of photo-excited cyanine dyes [14]. As implied by the figure, spatial selectivity in film growth can readily be achieved by simply restricting the illumination area. Furthermore, multicomponent structures can again be generated by repeating the photolysis in successive monomer solutions.

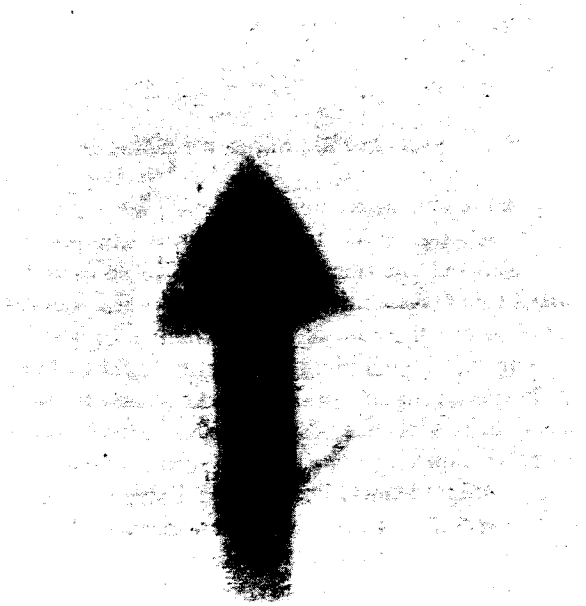
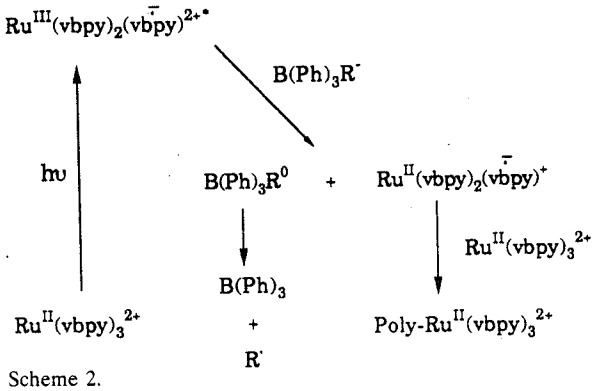


Fig. 5. Spatially structured film of poly-$Ru(vbpy)_3^{2+}$ grown on antimony–tin-oxide coated glass via scheme 2.

Among the potential advantages of scheme 2 in comparison to the semiconductor approach described above, are (1) the ability (because of the transparent substrate) to employ any desired background color (externally) in display applica-



Scheme 2.

tions, and (2) the ability to project electrochromic images by simple light transmission.

4. Optically addressable electrochromic image recording devices

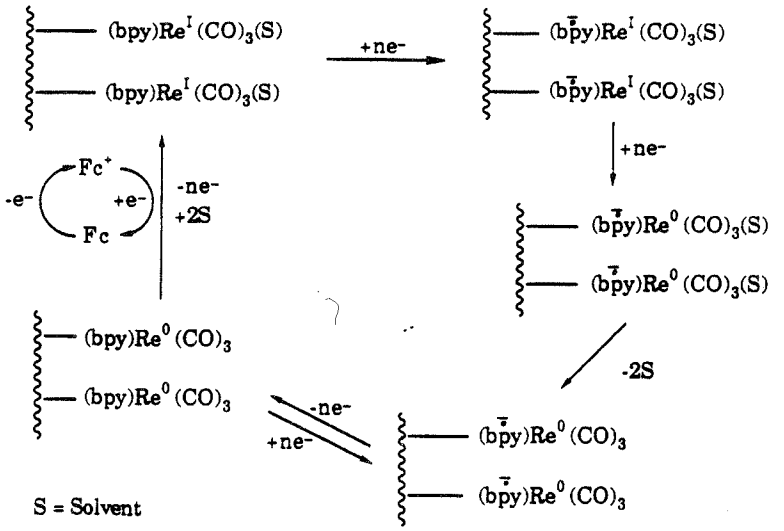
The most advanced electrochromic device we have constructed is a light-addressable image recording device based on an organometallic material, poly-$Re(CO)_3(vbpy)(Cl)$. (See also the recent work of O'Toole et al. [15].) The key to its operation is electrochromic bistability, i.e. the ability for two color states to exist (and co-exist) over a common range of electrochemical potential. Chemically the bistability effect is achieved by coupling electron transfer to follow-up steps which render the transfer energetically irreversible. In the reductive direction ($Re^I \rightarrow Re^0$) the coupled chemical step is polymer-phase metal–metal bond (dimer) formation. In the oxidative direction, on the other hand, electron transfer necessarily involves cleavage of the metal–metal bond. The chemical step which follows cleavage is uptake of a solvent molecule to form a substitutionally inert complex (an 18-electron species). This species can then be reactivated only by reduction. The end result is that the reduction and re-oxidation of a pair of rhenium sites are separated in energy by an amount corresponding to a rhenium–rhenium single bond (≈ 1.6 V $\times$ 2 electrons). Within the 1.6 V range both Re(I) (monomeric) and Re(0) (dimeric) species can exist, while beyond it, only one form is found. Electrochromic possibilities exist because the monomeric species is bright yellow and the dimeric species dark green.

Given these unusual characteristics, we reasoned that electrochromic *images* could be generated (green on yellow or yellow on green) provided that (1) the color sites were immobilized (polymerized) and (2) color changes could be made to occur in a spatially restricted fashion. To achieve the latter, we chose to grow poly-$Re(CO)_3(vbpy)(Cl)$ on n-type $MoSe_2$, a small bandgap semiconductor. In principle, photo-oxidation (via bandgap excitation) could then be employed to convert poly-"dimeric" Re^0 (green) to poly-"monomeric" Re^I (yellow).

The scheme is perfect, but for one overwhelming flaw: only the innermost layer of polymer can be oxidized (or reduced) directly by the electrode. In simple metallopolymers, this difficulty is overcome by ordinary electron hopping: electrons are readily shuttled to or from the outer polymeric layers and the electrode by passage through (i.e. reversible oxidation or reduction of) the intervening polymeric layer or layers. Unfortunately, for the more complex material considered here, charge transport by electron hopping is an energetically forbidden process. Thus each hopping event entails the destruction and concurrent re-creation (one site removed) of one half of a metal–metal bond. Consequently we find that poly-$Re(CO)_3(vbpy)(Cl)$, once reduced, cannot be reoxidized directly by an electrode even under conditions which are highly favorable thermodynamically.

To overcome this problem we have turned to film-permeable redox mediators or charge carriers, the prototypical mediator or carrier being ferrocenium/ferrocene. Thus, electrogenerated ferrocenium present even in trace amounts is capable of

Fig. 6. A bistable electrochromic recording device based on poly-$Re(CO)_3(vbpy)(Cl)$ coated on n-$MoSe_2$ and placed in contact with an acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate and $\approx 5\times10^{-5}$ M ferrocene. Top panel: initially prepared green film obtained by repetitive dark cycling between -0.6 and -1.6 V versus SCE in a solution containing monomeric $Re(CO)_3(vbpy)(Cl)$. Center panel: bistable (yellow/green) film obtained by illuminating the electrode with a bar image while maintaining the potential at 0.2 V. Bottom panel: yellow film obtained after full area illumination while maintaining the potential at 0.3 V. The overall electrode dimensions are ≈ 2.5 mm $\times$ 4.5 mm. The width of the yellow line in the center panel is ≈ 0.5 mm.



Scheme 3.

rapidly converting the reduced rhenium polymer (green) to its oxidized (yellow) form. In principle, the reverse reaction (yellow to green) should also require mediation. In all likelihood it does; however, the mediator couple employed is apparently vbpy/vbpy$^-$ which is already present in the polymer in ligated form. The complete reaction sequence is summarized in scheme 3.

To complete the description, fig. 6 provides an experimental illustration of the electrochromic image recording scheme. In the top panel is the initial (reduced) green state. In the center is the same film after selective exposure to a bar of visible light. The key point is that a yellow bar now exists on the green background of the film. The image is stable indefinitely (i.e. hours). It can be readily erased, however, by either dark reduction (to regenerate all green) or by exposure to an expanded light beam (to generate all yellow; bottom panel). While the device can be driven for only a few optical write and erase cycles before suffering degradation, it does provide an indication of the level of electrochromic versatility and sophistication one may hope to achieve by utilizing metallopolymers in color generation schemes.

Acknowledgments

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