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VIOLOGEN BASED ELECTROACTIVE POLYMERS AND COMPOSITES FOR DURABLE ELECTROCHROMIC SYSTEMS

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''Knowledge can only be got in one way, the way of experience;
there is no other way to know.''

- Swami Vivekananda

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II **Bhushan Gadgil**, Pia Damlin, Markku Heinonen & Carita Kvarnström, A facile one step electrostatically driven electrocodeposition of polyviologen–reduced graphene oxide nanocomposite films for enhanced electrochromic performance, *Carbon* **89** (2015), 53-62.

III **Bhushan Gadgil**, Pia Damlin, Timo Ääritalo, Jouko Kankare & Carita Kvarnström, Electrosynthesis and characterization of viologen cross linked thiophene copolymer, *Electrochimica Acta* **97** (2013), 378– 385.

IV **Bhushan Gadgil**, Pia Damlin, Evgenia Dmitrieva, Timo Ääritalo & Carita Kvarnström, ESR/UV-Vis-NIR spectroelectrochemical study and electrochromic contrast enhancement of a polythiophene derivative bearing a pendant viologen, *RSC Advances* **5** (2015), 42242–42249.

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Contributions of the Author

Paper **I-IV**: The author did all the experimental work except the synthesis of precursors and wrote the first draft of the manuscripts and finalized it together with co-authors.

LIST OF OTHER RELATED PUBLICATIONS

Bhushan Gadgil, Pia Damlin, Timo Ääritalo & Carita Kvarnström, Electrosynthesis of viologen cross-linked polythiophene in ionic liquid and its electrochromic properties, *Electrochimica Acta* **133** (2014) 268–274.

Bhushan Gadgil, Pia Damlin, Antti Viinikanoja, Markku Heinonen & Carita Kvarnström, One-pot synthesis of an Au/Au_2S-viologen hybrid nanocomposite for efficient catalytic applications, *Journal of Materials Chemistry A* **3** (2015), 9731–9737.

Cecilia Lete, **Bhushan Gadgil** & Carita Kvarnström, The electrochemistry of copolymer films based on azulene and 3-thiophene acetic acid, *Journal of Electroanalytical Chemistry* **742** (2015) 30–36.

Bhushan Gadgil, Pia Damlin & Carita Kvarnström, Graphene vs. reduced graphene oxide: A comparative study of graphene based nanoplatforms on electrochromic switching kinetics, *Carbon* **96** (2016) 377-381.

Bhushan Gadgil, Pia Damlin, Evgenia Dmitrieva, Timo Ääritalo & Carita Kvarnström, Exploring amide linkage in a polyviologen derivative towards simultaneous voltammetric determination of Pb(II), Cu(II) and Hg(II) ions, *Electrochimica Acta* **192** (2016) 482-488.

ABBREVIATIONS

ACN	Acetonitrile
Ag/AgCl	Silver/Silver Chloride
CCD	Charge-coupled device
CCE	Composite coloration efficiency
CE	Coloration efficiency
CE	Counter electrode
CPQ	Cyanophenyl paraquat
CR	Contrast ratio
CRT	Cathode ray tube
CV	Cyclic voltammetry
CW	Continuous-wave
DMP	9,10-dimethylphenazine
EC	Electrochromic
ECD	Electrochromic device
EQCM	Electrochemical quartz-crystal microbalance
ESR	Electron spin resonance
EtV	Ethyl viologen
FTIR	Fourier transform infrared
FTO	Fluorine doped tin oxide
GC	Glassy carbon
GO	Graphene oxide
GQD	Graphene quantum dot
HD	High definition
HV	Heptyl viologen
IBM	International Business Machines Corporation
ICI	Imperial Chemical Industries
ITO	Indium Tin oxide
KCl	Potassium Chloride

LCD	Liquid crystal display
MV	Methyl viologen
NIR	Near Infrared
NVS	Night Vision Safety
OD	Optical density
OTE	Optically transparent electrode
PB	Prussian blue
PBV	poly (butyl viologen)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PET	Polyethylene terephthalate
poly(AMPS)	poly(2-acrylamido-2-methyl-1-propanesulfonic acid
PV	Polyviologen
PXV	poly(hexyl viologen)
rGO	reduced graphene oxide
SEM	Scanning electron microscopy
TCO	Transparent conducting oxide
THF	Tetrahydrofuran
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
V	Viologen
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction

ABSTRACT

Electrochromism, the phenomenon of reversible color change induced by a small electric charge, forms the basis for operation of several devices including mirrors, displays and smart windows. Although, the history of electrochromism dates back to the 19th century, only the last quarter of the 20th century has its considerable scientific and technological impact. The commercial applications of electrochromics (ECs) are rather limited, besides top selling EC anti-glare mirrors by Gentex Corporation and airplane windows by Boeing, which made a huge commercial success and exposed the potential of EC materials for future glass industry. It is evident from their patents that viologens (salts of 4,4′-bipyridilium) were the major active EC component for most of these marketed devices, signifying the motivation of this thesis focusing on EC viologens.

Among the family of electrochromes, viologens have been utilized in electrochromic devices (ECDs) for a while, due to its intensely colored radical cation formation induced by applying a small cathodic potential. Viologens can be synthesized as oligomer or in the polymeric form or as functionality to conjugated polymers. In this thesis, polyviologens (PVs) were synthesized starting from cyanopyridinium (CNP) based monomer precursors. Reductive coupling of cross-connected cyano groups yields viologen and polyviologen under successive electropolymerization using for example the cyclic voltammetry (CV) technique. For further development, a polyviologen-graphene composite system was fabricated, focusing at the stability of the PV electrochrome without sacrificing its excellent EC properties. High electrical conductivity, high surface area offered by graphene sheets together with its non-covalent interactions and synergism with PV significantly improved the electrochrome durability in the composite matrix. The work thereby continued in developing a CNP functionalized thiophene derivative and its copolymer for possible utilization of viologen in the copolymer blend. Furthermore, the viologen functionalized thiophene derivative was synthesized and electropolymerized in order to explore enhancement in the EC contrast and overall EC performance. The findings suggest that such electroactive viologen/polyviologen systems and their nanostructured composite films as well as viologen functionalized conjugated polymers, can be potentially applied as an active EC material in future ECDs aiming at durable device performances.

TIIVISTELMÄ

Elektrokromismi on ilmiö, jossa pienellä sähköisellä varauksella saadaan aikaan palautuva värinmuutos. Monien laitteiden, kuten peilien, näyttöjen tai älykkäiden ikkunoiden, toiminta perustuu tähän ilmiöön. Historiallisesti elektrokromismi on tunnettu 19. vuosisadalta asti, mutta vasta 20. vuosisadan viimeinen neljännes on osoittanut ilmiön huomattavan tieteellisen ja teknologisen merkityksen. Näiden elektrokromismiin perustuvien tekniikoiden kaupallinen hyödyntäminen on vielä melko vähäistä. Tähän asti myydyimpiä tuotteita ovat olleet häikäisysuojatut peilit (Gentex Corporation) ja lentokoneen ikkunat (Boeing), jotka olivat valtavia kaupallisia menestyksiä osoittaen tekniikan mahdollisuudet tulevaisuuden lasiteollisuudessa. Patenteista selviää, että viologeenit (4,4′-bipyridiniumin suolat) ovat yleisimpiä aktiivisia komponentteja useimmissa markkinoilla olevissa sovelluksissa, minkä perusteella tässä väitöskirjassa keskitytään viologeeneihin.

Erilaisista sähköväriaineista viologeenejä on käytetty elektrokromisissa laitteissa jo jonkin aikaa johtuen niiden voimakkaan värisestä radikaalikationista, joka saadaan syntymään pienellä katodisella jännitteellä.Viologeenejä voidaan syntetisoida oligomeerinä tai polymeerinä, sekä toiminnallisena ryhmänä osana konjugoitua polymeeriä. Tässä väitöskirjassa polyviologeenit syntetisoitiin käyttämällä lähtöaineena syanopyridinium-pohjaista monomeeriä. Ristiinkytkettyjen syanoryhmien pelkistävä kytkeytyminen tuottaa viologeeniä ja polyviologeeniä peräkkäisissä sähköpolymerisaatioreaktioissa, mikä voidaan toteuttaa käyttämällä menetelmänä esimerkiksi syklistä voltammetriaa. Systeemiä kehitettiin edelleen siten, että polyviologeenistä ja grafeenista valmistettiin komposiitti, jossa parannettiin polyviologeenin stabiilisuutta, menettämättä sen erinomaisia elektrokromisia ominaisuuksia. Grafeenilevyjen hyvä sähköinen johtavuus ja suuri pinta-ala yhdistettynä ei-kovalenttisiin vuorovaikutuksiin ja synergiaetuihin PV:n kanssa paransi huomattavasti komposiittimatriisin elektrokromista kestävyyttä. Työtä jatkettiin kehittämällä CNP:llä funktionalisoitu tiofeenijohdos ja vastaava polymeeri, mikä mahdollisti viologeenin hyödyntämisen kopolymeeriseoksessa. Lisäksi syntetisoitiin ja sähköpolymeroitiin viologeenillä funktionalisoitu tiofeenijohdos, jonka avulla tutkittiin elektrokromisen kontrastin ja kokonaissuorituskyvyn parantumista. Havainnot osoittavat, että sähköisesti aktiivisia viologeeni/polyviologeenisysteemejä ja niistä valmistettuja nanorakenteisia komposiittikalvoja, sekä myös viologeenillä funktionalisoituja konjugoituja polymeerejä on mahdollista hyödyntää aktiivisena elektrokromisena materiaalina tulevissa suorituskyvyltään kestävissä elektrokromisissa laitteissa.

1. INTRODUCTION

In today's world, major reforms are essential towards energy consumption, storage and utilization, which will impact on the quality of life, global economic welfare, productivity and sustainability [1]. In particular, renewable energy storage technologies are beneficial if they are environmentally friendly. By now, glazing materials are well-known, which selectively controls the spectral aspect of radiation [2]. Although the primary function of the glass is to transmit light, a low-emitting thin coating layer provides control over the heat transmitted, thereby rejecting unwanted solar infrared [3,4]. This is particularly important due to a significantly high demand of using electrically driven air conditioning in most parts of the world, which ultimately require higher energy and is expensive [5]. Switchable glass thus controls incoming and outgoing light and heat to increase energy-saving effects, especially beneficial in buildings and construction industry. The term 'smart windows' was introduced for this kind of fenestration in 1984 [6]. Dynamic windows not only promise energy savings but also enhance the outside view in high-glare sun orientations [7]. Moreover, such windows reflect or transmit both visible and infrared light, thus improving the energy efficiency and indoor comfort by reducing lighting, heating or cooling **(Fig. 1)** [8]. These effects are due to a particular type of smart material, known as 'chromogenics' that can be used for large area glazing in buildings, automobile sunroofs, plane windows, and for certain types of electronic displays [9].

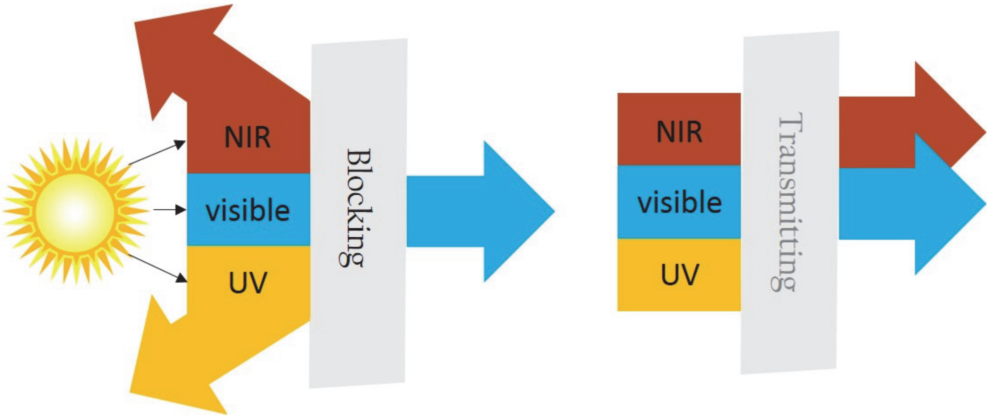


Fig. 1. A principle of window technology, where the window blocks solar heat (left) during warm weather conditions, without a noticeable change in visible light. During cold weather periods, near infrared (NIR) solar heat passes through the window (right).

1.1. Chromogenic materials

Chromogenic materials, usually described as “chameleonic”, change their color reversibly as a response to the changes in the environmental conditions (e.g. temperature, light, pressure etc.) or by externally induced stimuli [10]. Such change in color is associated with the change in the electronic state of the molecule, mainly π or d electron state, often induced by a stimulus, consequently resulting in modified optical properties, such as absorption, reflection, transmission or emission [11]. When the stimulus ceases, the material returns to its original electronic state, restoring the original optical properties, hence the initial color or transparency [12]. Chromogenic materials are thus grouped according to the external stimulus or energy source used which incites the change in optical properties [13]. A general frame of reference of the most important chromogenic categories is given below.

Photochromic materials exhibit color change when exposed to UV light. The commercial applications of photochromism are in ophthalmic products like photochromic lenses and sunglasses [14]. Various polymer based materials are used for this purpose.

Thermochromic materials change their color with temperature. Besides liquid crystals, aerospace industry has been particularly benefited by the thermochromic technology altering the emission properties of the surfaces upon heating [15]. A well-known product in this category is a ceramic mug which changes color when a hot drink is poured in and the coloration fades slowly when the mug cools down to room temperature, attaining its original state [16]. Some transition metal oxides like vanadium dioxide (VO_2) possess thermochromic properties [17].

Gasochromic materials alter their optical properties in response to exposed gases like H_2. Gasochromic films consist of a gasochromic layer and a very thin film of catalyst where the gas adsorbs and dissociates, consequently giving color to the gasochromic material [18]. Tungsten oxide (WO_3) is widely used as gasochromic material [19]. An inexpensive layer configuration and a high solar transmittance make these materials suitable for large window applications [20].

Electrochromic materials show a change in color in response to an external applied electric field. Electrochromism is probably today’s most versatile chromogenic technology due to its easy color control mechanism. Additionally, it can easily be used in combination with several external stimuli such as stress or temperature [21]. Switchable antiglare mirrors are dominating the market for electrochromic technology and several companies making millions of dollars.

In addition to those mentioned above: Chemochromic (depending on chemical changes) [22], mechanochromic (depending on mechanical stimulus like stress) [23], solvatochromic (depending on change in solvent) [24] and biochromic (depending on biological stimulus) [25] materials are recognized in the class of chromogenics.

A recent study from the Madison Gas and Electric, a US-based company provided a brief overview of energy index for cooling and for electric lighting of different chromogenic-based glazing types, as demonstrated in **Fig. 2** [26]. Obviously, clear glass lets in both solar heat and visible light, and therefore needs a small electrical lighting energy, however is disadvantageous with regard to cooling energy. In contrary, tinted or reflective glass need less cooling energy but increases the demand for lighting. Among the different chromogenic technologies, electrochromic glazings are found to have strong advantages to improve performance in both parameters, i.e. for cooling energy and for electric lighting energy.

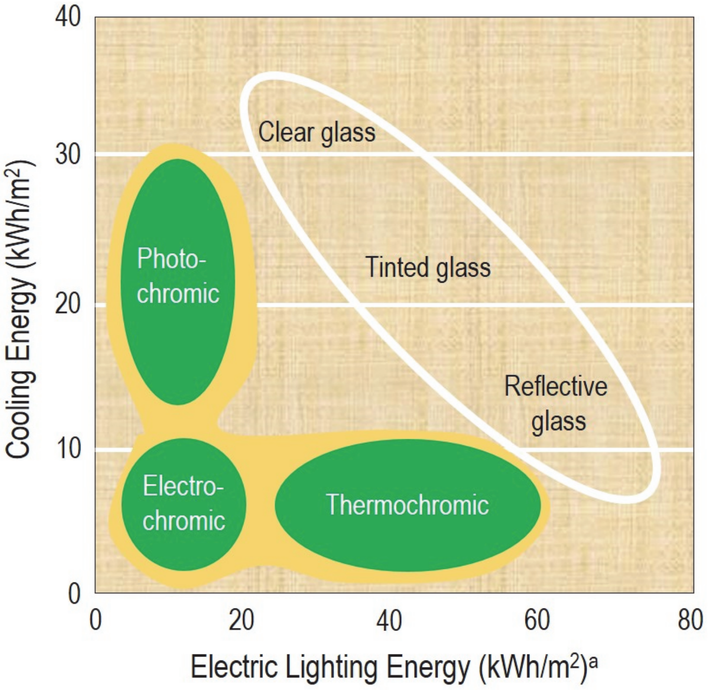


Fig. 2. Lighting energy vs. cooling energy for different types of glazing. ([a] Lighting savings assume the use of a switched or dimmable electric lighting control.)

1.2. Electrochromic materials

Electrochromic (EC) materials possess the property of evocation or alteration of color induced either by an electron-transfer (redox) process or by a sufficient electrochemical potential [27]. Electrochromism is thus a result of switching between redox states that generates different electronic absorption bands in the visible spectral region. A spectral absorption arise either from a moderate internal electronic excitation or an intervalence optical charge transfer where the chemical species have two centers of differing valence or oxidation state, as given in eq. 1.

$$O + n\, e^{-} \leftrightarrow R \qquad (1)$$

The color change is commonly between a transparent (bleached) state and a colored state. Despite the discovery of electrochromism in 19th century by S.K. Deb and J.A. Chopoorian (in 1968), only the last quarter of the 20th century could really see the potential of EC materials, evident by increasing number of reviews and scientific publications [28-37]. Though materials are thought to be electrochromic when noticeable visible color changes are observed under applied electric potential, with time, the definition of electrochromism is getting broader [38]. Recent studies on EC materials suggests the modulation of electromagnetic radiation in the near infrared (NIR) [39-42] and microwave regions [43-45], and the perceived color is a response of detectors to these multispectral radiations. The electrochromic technology leaning on tuning of light either reflected or transmitted, has already been commercially utilized in several applications. Some of these applications are smart windows and antiglare mirrors for cars and buildings [46], active optical filters (e.g. sunglasses) [47], controllable aircraft canopies [48], camouflage materials [49], chameleonic fabrics [50], spacecraft thermal control [51], reusable price labels [52], frozen food monitoring displays [53] and optical information and storage [54]. Of these, self-darkening car rear-view mirrors designed by Gentex Corporation (USA) have already achieved astonishing commercial success and are operating in several millions of cars till date [55,56]. Gentex also supplies adjustable darkening windows to The Boeing Company [57-60], as a result, Boeing's 787 Dreamliner passenger aircraft windows are all electrochromic. A very recent forecast by 'research and markets' suggests a rapid growth in the electrochromic devices market at a CAGR of 12.27% from 2014 to 2020 and expected to reach $5.81 billion by 2020 [26]. The advancement of the new technologies accompanied by high demands from developing countries accounts for the growth of the electrochromic glass market. The key players in this industry include SAGE Electrochromics, Inc.(U.S.), ChromoGenics AB (Sweden), RavenBrick LLC (U.S.), Asahi Glass Company (Japan), Gentex Corporation (U.S.), EControl-Glas (Germany), Magna Glass & Window, Inc. (U.S.) , Guardian Industries (U.S.), PPG Industries (U.S.), and View, Inc. (U.S.).

The electrochromic window is based on an optical switching technology that can vary its transmittance. Under the application of a voltage, a window tints from clear to a dark shade in a given time. The process is reversible and when the voltage source is removed, the window restores its original color state. In comparison to low-emissive windows, electrochromic windows are used both for solar radiation control and fenestration [61]. The electrochromic windows are still relatively expensive with current market price ranging somewhere between \$50-\$100/ft^2 [62]. The projections indicate that the price of window under \$20/ft^2 is needed. Smart windows based on electrochromic technology can eliminate the need for and cost of interior or exterior shading devices, somewhat offsetting their higher costs.

There are a vast number of chemical compounds that exhibit electrochromism [21]. The most important classes of chemical species which demonstrate electrochromic effects are: metal oxides and hydroxides, metal hexacyanometallates like Prussian blue, metal coordination complexes, metallopolymers, metal pthalocyanines, conjugated conducting polymers and the viologens, summarized in **Table 1.**

Table 1. Summary of different chemical classes of electrochromic materials with examples and possible applications.

Class of EC material	Examples	Possible applications
Metal oxides/hydroxides	WO_3, NiO, MoO_3, V_2O_5, Nb_2O_5, $Ir(OH)_3$	Smart windows, thermal control of satellites, EC paper
Metal hexacyanometallates	Prussian blue, Fe_4^{III} $[Fe^{II}(CN)_6]_3$ Ruthenium purple, $Fe_4^{III}[Ru^{II}(CN)_6]_3$	Displays
Metal coordination complexes, Metallopolymers	Nitrosyl/oxo Mo (V) complexes, $[M^{II}(bipy)_3]^{2+}$ complexes (M=Fe, Ru, Os), poly$[Ru^{II}(vbpy)_2(py)_2]Cl_2$	NIR switching, switchable mirrors
Metal pthalocyanines	$[Lu(Pc)_2]$, Co(II) pthalocyanine	EC displays
Conjugated polymers	Polypyrrole, Polythiophene, PANI	Smart windows and displays
Viologens	Methyl viologen, Benzyl viologen	Car rear-view mirrors, displays

Depending on the physical state at room temperature, three different types of electrochromes can be distinguished, as given in **Table 2** [63]. Type I electrochromic materials are soluble in its redox states and remain in the electrolyte solution during usage. Type II electrochromic materials are soluble typically in their colorless state and form a solid colored film at the electrode surface after electron transfer, whereas type III electrochromic materials are solid in all redox states during usage.

Table 2. Three simple types of EC materials on the basis of the solubility of each redox state.

Type	Physical state	Examples
Type I	Soluble in both the reduced state and oxidized state	Methyl viologen, metal complexes, organic redox indicators
Type II	Soluble in one redox state, but forms a solid film on electrode surface following electron transfer	Heptyl viologen in water
Type III	Solid in both or all redox states	Polyviologens, Prussian blue, WO_3, conjugated polymers, metallopolymers

In another classification, electrochromes are divided into two categories [64]: i) the materials that can switch upon intercalation of small (e.g. Li^+ or Na^+) ions into the thin films of metal oxides (WO_3, TiO_2, NiO etc.) or ii) a color change is attained upon electrochemical oxidation/reduction (redox) reaction; e.g. deep blue color in methyl viologen solution upon electroreduction or multicolored electrochromism in conjugated polymers upon oxidation/reduction. All the above mentioned classifications of electrochromic materials are somehow interrelated and eventually divided into two broad categories: organic EC materials and inorganic EC materials.

1.3. Electrochromic films and devices

Electrochemical redox systems that show promising electrochromic properties are generally first studied as a film or as an electroactive solute, at an electrochemically inert single 'working' electrode, under potentiostatic or galvanostatic control using three-electrode circuitry, with 'counter' and 'reference' electrodes completing the electrical circuit. Conventional electrochemical techniques such as cyclic voltammetry (CV), chronoamperometry and coulometry, all partnered by, as appropriate, in situ spectroscopic measurements are employed for characterization.

After successful initial trials in a three electrode cell, an electrochromic device (ECD) can be constructed comprising a simple two-electrode system in a sandwich configuration (**Fig. 3**) [65]. The basic operating principle of an ECD is similar to that of an electrochemical cell or battery. The

ECD consists of five superimposed layers sandwiched between two transparent substrates, most commonly glass or flexible plastic (PET; polyethylene terephthalate) coated by a very thin layer of an optically transparent conducting oxide (TCO), e.g. tin-doped indium oxide (ITO), antimony-doped tin oxide or F-doped tin oxide (FTO). One of these transparent electrodes is coated by an electrochromic (EC) film and the other by an ion storage layer, often referred to as counter electrode (CE). An ion conducting colorless electrolyte (solid, gel or liquid) is typically in the middle of the ECD adjoining the EC and CE layer on transparent conducting oxide coated glass/PET. The device is typically sealed with epoxy and other sealants (e.g. acrylic tape) in order to avoid any leakage of the electrolyte from the device. When an appropriate voltage is applied between two transparent electrodes, charge is transported between the EC and CE layers, altering the transparency of ECD. A voltage of opposite polarity or short-circuiting reverses the phenomenon and the ECD goes back to its original state. ECDs are aimed to operate in absorptive/transmissive manner or in reflective modes. In recent progress, 'all polymer' ECDs have been designed, having PEDOT-PSS as the electrically conducting film coated on commercial PET substrates, replacing TCO [66].

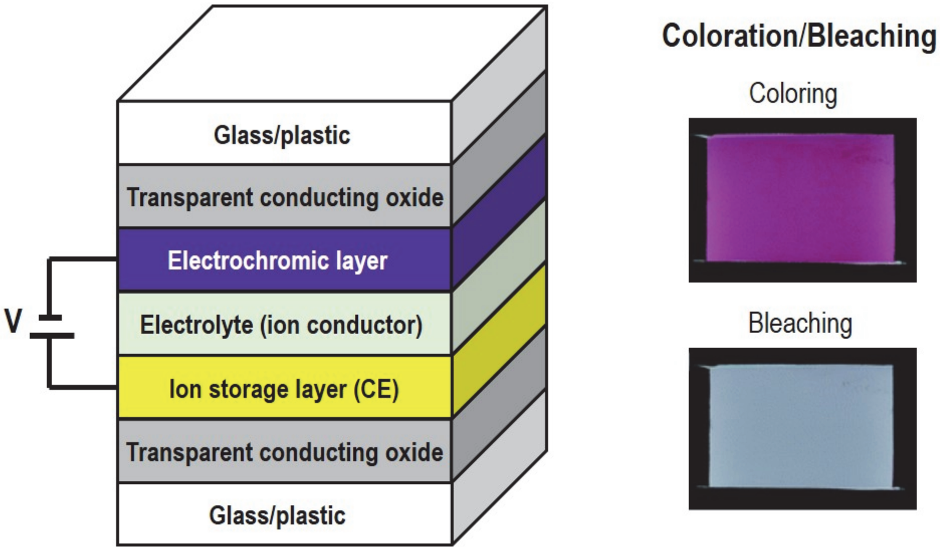


Fig. 3. Typical setup of an electrochromic device (ECD) (left) and photographs of ECP-Magenta/MCCP ECD with colored and bleached states, as a result of applied voltages of −0.6 V and 1.4 V, respectively (right) [67].

1.4. Electrochromic performance parameters

Contrast ratio (CR)

The contrast ratio (CR) of an EC material, a measure commonly employed refers to the intensity of the color formed during electrochemical switching [68], measuring light transmission or reflectance of ECD. The change in CR is given as:

$$CR = \frac{R_0}{Rx} \text{ or } \frac{\%T_0}{\%Tx} \tag{2}$$

where R_0 or $\%T_0$ is the intensity of light reflected or transmitted at bleached/transparent state and R_x or $\%T_x$ is the intensity of light reflected diffusely through or transmitted from the darkened /colored state of EC materials, respectively. The higher the contrast ratio, the stronger the perceived color change achieved. For materials where CR<3, it is practically impossible to see the color change by naked eye.

Response times (τ)

For a given EC material or ECD, the response time (τ) is the time required to change from bleached to colored state or vice versa [69]. In practice, response times are calculated as the time required for the film to achieve 90% of its full electrochromic response. Depending on the application, the response time value plays a crucial role in determining device performance. For instance, display devices switch rapidly and require a fast response time [63]. On the other hand, a relatively slow response time is suitable for large area smart office windows [46]. Inorganic electrochromic materials are in general slower in response time compared to the organic ones [70]. Nevertheless, one cannot generalize or compare the response times of different EC materials stated in the scientific literature due to the lack of consistency in the reporting and precise determination of switching kinetic data. There are several parameters affecting the τ values, for example, double layer capacitance at the electrochrome-electrolyte interface, substrate (ITO) resistance, resistance at the bleached state of electrochrome etc. In recent years, several methods were employed to enhance the response times, e.g. use of modified electrode substrates that minimizes the electrical resistance, combining two or more electrochromes, applying potential pulses to speed up the coloration, etc. [71].

Write-Erase efficiency

The write–erase efficiency of an ECD, generally expressed as a percentage, is the fraction of the originally formed color that can subsequently be electro-bleached [69]. In the ideal case, the efficiency must approach 100% for a high performing display, which is a stringent test of device fabrication and design. For example, in case of methyl viologen, the write-erase efficiency is always lower on a realistic time scale due to the aging process and slowest step of diffusion to and from the electrode through solution [72]. The easiest way to enhance the write-erase efficiency is to use a type-II and III electrochrome, since between the write and erase parts, the colored form of the electrochrome is not lost from the electrode by diffusion. In case of viologens, the improvement is done in two ways: i) chemical tethering of the viologen to the surface of e.g. TiO_2 modified electrode, thereby retarding the diffusion rates, or by immobilizing the viologen species within a semi-solid electrolyte like poly (AMPS) and (ii) by choosing asymmetric viologens or its derivatized analogue, which yield solid radical cations [72].

Cycle life

One of the major factors that limits the use of electrochromic materials in real applications is the long term stability, in other words 'cycle life'. For a given EC material, cycle life demonstrates the number of write-erase cycles that can be performed during the voltage switching before any significant extent of degradation occurs [73]. The cycle life of an ECD is nothing but the durability of the electrochrome. Needless to say, cycle life of electrochromes has to be superior for efficient device performance.

There are several reasons related to the cycle life of electrochrome leading to ECD device failure. They are most commonly related to the components utilized in the fabrication of device. This includes: conducting electrodes, electrolyte, EC layer, ion exchange layer etc. Failing of all or just one of the aforementioned parameters will result in deterioration of the device [74]. The most common issues for low cycle life are related to the organic materials (electrochrome or electrolyte) used in the device built-up, that are very sensitive towards photo-degradation [75]. Another issue, mainly concerning type-II and type III electrochromes, is associated with the continuous recrystallizations of solid electrochromes. In improving the durability of ECD, the following criteria's need to be carefully addressed:

1. The environment for a specific application, which clearly dictates the device operation speed.

2. The optimum upper and lower temperatures for operation of the device; the climate of the region plays a key role.

3. The robustness of the device towards climate; controlling stresses effected in a device by 'thermal shock' when it cools/warms rapidly.

4. The influence of solar light (e.g. UV) on the deterioration of device.

5. The effect of surplus stresses such as changes in humidity and mechanical shock for optimum performance. For rough handling, strong frames are needed and special care towards device encapsulation is required.

Power consumption and memory effect

An ECD is switched to its colored/bleached state by repetitive charging/discharging cycles. Once the color change is achieved, the new redox state persists, with no or little power. Such retention of coloration between write and erase cycles without power input is referred to 'memory effect' [72]. For instance, the coloration of the viologen radical cation can be observed as remaining undimmed over a long time period in the absence of oxidizing agents/O_2. At some point, any ECD will eventually fade unless it is charged to the colored state again, alike the battery. ECDs require less power than CRT displays or mechanical devices to operate. The consumed power is so small that lately, a solar powered ECD has been reported [76].

Coloration efficiency (CE or η)

In simple electrochemical reactions, the amount of deposited material is proportional to the electrochemical charge passed, according to Faraday's first law. In a similar way, one can correlate the color centers formed by the electrode reaction [69], and hence is the change in absorbance (ΔA) in direct proportion to the amount of charge (Q) passed.

$$\Delta A \ \propto Q \tag{3}$$

The coloration efficiency (CE or η) is thus given as

$$\Delta A \ \propto \eta Q \tag{4}$$

where the proportionality factor η, the 'coloration efficiency', is a quantitative measure of the amount of color being formed per unit injected charge measured at a fixed monochromatic wavelength (λ_{max}). In practice, a plot of change of the absorbance or optical density (ΔA/ΔOD) vs. injected charge as a function of electrode area (Q_d), accurately gives the CE or the η value as the gradient expressed as area per unit charge, $cm^2\ C^{-1}$. The higher the CE, the more efficient is the ECD. In an ideal case, the device should exhibit large %T change by virtue of a small amount of charge. Generally, η value is positive if the color is cathodically generated and negative if the color is anodically generated [72]. In recent studies, Reynolds et al. proposed composite coloration efficiency (CCE) for accurately measuring CE of organic conjugated polymers [77]. CCE provides detailed insight into the reasons for high efficiencies as well as structure-property relationship in organic polymer systems. Similarly as the response times, the coloration efficiencies of inorganics; particularly metal oxide electrochromes are lower compared to their organic counterparts.

Table 3 gives a detailed comparison between inorganic and polymer based electrochromic materials with respect to their method of preparation, processability, cost of final device, obtainable colors and various performance parameters [78].

Table 3. Comparison between inorganic and polymeric EC materials [78].

Sr. No.	Property	Inorganic materials	Polymers
1	*Method of preparation*	Needs sophisticated techniques such as vacuum evaporation, spray pyrolysis, sputtering, etc.	The material can be easily prepared by simple chemical, electrochemical polymerization and the films can be obtained by simple techniques such as dip-coating, spin coating, etc.
2	*Processability of the materials*	The materials are poor in processability	The materials can be processed very easily
3	*Cost for making the final device*	High as compared to the polymer based devices	Low cost as compared to the inorganic materials
4	*Colors obtainable*	Limited number of colors are available from a given material	Colors depend on the doping percentage, choice of the monomer, operating potential, etc. Hence, large number of colors are available with the polymeric materials
5	*Contrast*	Contrast is moderate	Very high contrast can be obtained
6	*Switching time (ms)*	10–750	10–120
7	*Lifetime*	10^3–10^5	10^4–10^6 cycles

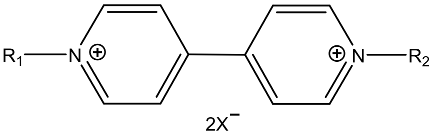
1.5. Organic electrochromic materials

As can be expected from the enormous width of the organic synthetic chemistry, many organic materials exhibit electrochromism in the course of electrochemical redox reaction [79]. In particular, two main characteristics of organic electrochromes need to be highlighted: the ease in processability via solution based low cost processes and diversity in the color palette. Main classes of organic electrochromic materials, include the viologens, conjugated polymers, metallopolymers and metallopthalocyanines [72]. While the latter two also belong to the inorganic class, they are mentioned here due to the coloring properties of organic ligands bound to the metal centers. Other organic EC materials to be mentioned are electroactive polymers or compounds containing redox active molecules like nitroxyl [80], phenoxyl [81], carbazole [82], cyanines [83], quinones [84], hydrazyl triarylamine [85], methoxybiphenyl [86], thiazine [87], pyrazoline [88], tetracyano-quinodimethane (TCNQ) [89], tetrathiafulvalene (TTF) [90], 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [91], etc.. In this thesis, the main focus is on the viologen based organic EC materials.

1.6. The viologens

Introduction

A major group in the organic electrochromes is the bipyridilium species [92]. The diquaternization reaction of 4,4′ -bipyridyl yields 1,1′-disubstituted-4,4′-bipyridilium salts (**I**). The localized positive charge seen on N is better viewed as being delocalized over the respective rings. The counter anion (X^-) need not be monovalent and can be a part of the polymer backbone.

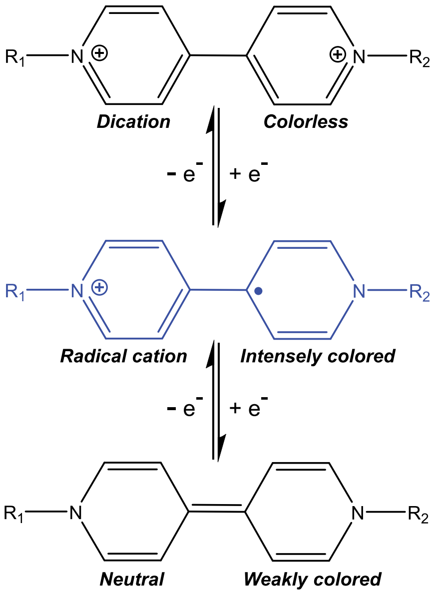


I

The most appropriate abbreviation for any bipyridyl system irrespective of its redox state is ‘bipm’, with its charge indicated, for instance the dication can be assigned as bimp^{2+}. In the literature, these compounds hold several trivial, non IUPAC names. The most common is ‘viologen’, originating from Michaelis’s work on 1,1′-dimethyl-4,4′-bipyridilium [93], when he noticed the violet color formation during one-electron reduction, subsequently naming the compound as ‘methyl viologen’ (MV) in this nomenclature. Similarly, other such bipyridilium compounds are named as *substituent* viologen, e.g. ethyl viologen, heptyl viologen, benzyl viologen, etc. Another widely used name is 'paraquat' (PQ), a brand name for methyl viologen, which was developed by Imperial Chemical Industries (ICI) for herbicidal use.

Redox chemistry of viologens

There are three well defined redox states of viologen (V): a dication (V^{2+}), a radical cation ($V^{\bullet+}$) and a di-reduced neutral form (V^0), as shown in **Scheme 1**. Of these three, the dication salt is the most stable one and is colorless in its pure form. Reductive electron transfer to the dication produces a radical cation ($V^{\bullet+}$) which is intensely colored and highly stable among organic radicals. The strong color in $V^{\bullet+}$ is owing to the intramolecular optical charge transfer process. The viologen radical is very sensitive to oxidizing agents or molecular oxygen [92]. The stability of the radical cation is governed by the delocalization of the radical electron along the π-framework of the bipyridyl nucleus, part of the charge is weakly carried by the 1 and 1′ substituents [94]. Further reduction of $V^{\bullet+}$ gives neutral di-reduced viologens (V^0), decaying the intense color of radicals. The neutral form of viologen is extremely reactive, hence often termed as bi-radicals [72]. Studies have shown that bi-radicals are diamagnetic in nature at solid state and the spins are paired. V^0 is often weakly colored as there is no optically assisted charge transfer or any accessible internal transition corresponding to the visible wavelength [69].



Scheme 1. Different redox states of viologen.

Electrochromism in viologens

Most of the viologen compounds exhibit electrochromism due to its ability of forming highly colored radical cation. As discussed before, such coloration is arising from the delocalization of positive charge in the radical cation form accompanied by an optical charge transfer process. Hence, the origin of the color is perhaps better viewed as an intramolecular photo-effected electronic excitation [72]. Desired color can be tuned by choosing suitable nitrogen substituent, thereby attaining the appropriate molecular orbital energy levels. Simple alkyl groups offer a blue-violet coloration to the radicals [95]. As the chain length increases, color transforms into crimson due to the increased dimerization, as the dimer is generally red colored. On the other hand, aryl groups such as 4-cyanophenyl usually imparts a green hue to the viologen radical cation [95]. The color properties of the radical cation also depend on the counter ion and solvent used [72]. The major advantage of viologen electrochromes lies in their ease in molecular design, relatively high charge efficiency, and quick response time. Unlike inorganic materials, viologen absorption spectrum is sharp and can be located anywhere in the visible wavelength region. Poor consistency and unexpected side reactions leading to further degradation have been the major problems in the viologen EC system. Besides all the mentioned liabilities, viologens are by far the most intensively studied organic electrochromes for research and commercialization purposes [72].

1.7. Type I viologen electrochromes

The most extensively studied viologen electrochrome to-date is 1,1′-dimethyl-4,4′-bipyridilium, i.e. methyl viologen. In device application, methyl viologen as type-I electrochrome is studied and commercially used for several years by now [72]. The best example of such an electrochromic system is Gentex automatic dimming interior mirror, world’s best-selling type-I ECD where the primary electrochrome is a viologen [55]. In the context of device performance, write-erase efficiency of type-I electrochrome based on short alkyl chain viologens is generally quite low as both the dication and radical cation are soluble in polar solvents like water [96]. To avoid the complicated electrochemistry of viologens in aqueous solvents, they are often dissolved in non-aqueous solvents such as acetonitrile, propylene carbonate or γ-butyrolactone. The write-erase efficiency in such cases has been improved reasonably over the observation period. Another improvement is achieved by retarding the rate of radical cation diffusion away from the electrode and into the bulk electrolyte [95]. Generally, type-I electrochromes tend to have poor response times if the optimum contrast ratio is anticipated. As a consequence, most type-I electrochromes are suited for applications such as anti-glare mirrors or long term data displays, where slow response times are enough [72].

1.8. Type II viologen electrochromes

The viologen materials become type-II electrochrome when the nitrogen substituents are long alkyl chains or aryl groups. The problems concerning solubility-diffusion and slow response time in type-I electrochrome can be avoided in type-II systems, where viologen species are dissolved in aqueous solvents, and the colored radical cation product, produced by an electron transfer reaction, is insoluble [69]. This insolubility is driven by long chain alkyl substituents or aryl chain. Such a process is called electrodeposition. The mechanism for such electrodeposition is a three step process: radical cation being formed at the electrode, followed by acquisition of an anion X^- in solution and thereafter precipitation of the radical salt from solution [95], as given in eq. 5.

$$V^{\bullet+}\,(aq) + X^{-}\,(aq) \rightarrow V^{\bullet+}X^{-}\,(s) \tag{5}$$

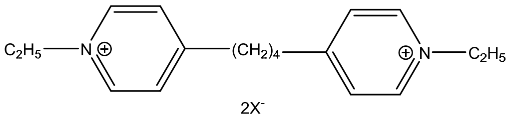
The obtained viologen is essentially a solution-to solid type II electrochrome. Heptyl viologen (HV; 1,1'-diheptyl-4,4'-bipyridilium) is the best example of this type, where its dibromide or bipthalate salt has been thoroughly studied for display applications [97]. Its dication is water soluble, but, upon reductive one-electron transfer, forms a crimson radical salt insoluble in the solvent, obtained on the surface of the electrode. An ECD developed by the Philips Laboratories in Holland, which was never commercialized, used HV electrochrome for their display [97]. When tested, it was found to have a contrast ratio of 20:1, very fast response times (~10-50 ms), with a cycle life of 10^5 cycles between its redox states. In 1971, ICI Ltd. submitted a first patent on the use of aryl-substituted viologen 'cyanophenyl paraquat' (CPQ), which electro-precipitates to a green colored radical [98]. The choice of CPQ over HV is owing to its greater extinction coefficient and therefore its faster response time per injected charge. The electrodeposition process follows eq. 5 for precipitating $CPQ^{\bullet+}$. Following the successful initial trials, a first full flex ECD was promoted as a data display device in the early 1970s. However, the slow kinetics in type-II device from ICI could not resist the competition from fast switching liquid-crystal displays (LCDs) entering the market at about the same time. Fletcher et al. reported a nucleation-assisted reduction mechanism for HV type II systems [99]. Once the nucleation is initiated, the crystal-growth starts which is controlled by mass transport and is a very rapid process. The study also inferred hemispherical diffusion that creates a diffusion zone, subsequently multiplying into semi-infinite planar diffusion. In brief, the process can be summarized as electron transfer → nucleation → hemispherical diffusion → linear diffusion. However, the kinetic process is much more complicated when developing a precise mathematical model of deposition for specific application.

Viologen radical cation dimerization/comproportionation

Most viologen species have tendency to form dimers by spin-pairing their radical cations. The process often termed as 'comproportionation' [92]. For example, the MV radical-cation monomer is blue (λ_{max}=600 nm) while the dimer is red (λ_{max}=550, 900 nm) in aqueous solutions [79]. Very often, the absorption spectrum shows presence of both the monomeric and dimeric form of radical cation. Electrochemical oxidation of the radical-cation dimer $(V^{\bullet +})_2$ is quasi-reversible and very slow, meaning that the bleaching process is really sluggish. This particularly affects write/erase efficiency of viologens in device applications. Monk et al. showed how widely the comproportionation occurs in several viologen redox systems [92]. In the case of heptyl viologen (HV), a maroon colored film precipitates after radical cation formation. Since the alkyl substituted viologens generally produce blue colored radical cation, the maroon color implies comproportionation reaction in HV.

There are a couple of options to avoid the dimerization of radicals and subsequently improve the write-erase efficiency. These are either to employ non-aqueous solutions or to add redox mediators into the dication-containing solution [100]. Redox couples such as hydroquinones, ferrocyanide, ferrous ions or ferrocene in acetonitrile were employed for this purpose [100,101]. The process can be illustrated as follows: V^{2+} gets reduced to $V^{\bullet +}$following one electron transfer. During re-oxidation, the mediator, e.g. ferrocyanide is oxidized at the electrode to ferricyanide (Fe^{3+}), allowing chemical oxidation of $V^{\bullet +}$ back to V^{2+}, thereby inhibiting the dimerization process. Most of the type-II electrochromes based on alkyl or aryl viologens uses mediator assisted electro-oxidation of radical cation species [72].

In the case of HV type-II systems, the as deposited maroon colored salt is amorphous, but soon after precipitation, slight crystallization occurs and the film looks patchy; the phenomenon normally referred as 'aging' of an electrochrome [72]. Such patchy films are more difficult to oxidize, a higher applied potential is required. An addition of auxiliary redox couple like ferrocene eases the aging problem. Another effective strategy to avoid the aging process is to add another spacer between two pyridine rings (**II**) or to use asymmetric substituents at ring nitrogen group (**III**) [102,103]. The molecular asymmetry inhibits the crystallization of viologen radical cation salts. Furthermore, it has also been found that the ECDs based on certain viologen compounds form a yellowish brown stain on the electrode surface after prolonged color/bleach switching cycles. A careful investigation suggests that this stain is due to the dimerization of viologen radicals or else comprises both radical and dication in the intervalent form [104]. In order to understand these processes of recrystallization and comproportionation of cation radicals, many techniques are employed including in situ UV–Vis spectroelectrochemistry [105-107], ESR spectroscopy and spectroelectrochemistry [108], Raman spectroscopy [109,110], photoacoustic spectroscopy [111], photothermal spectroscopy [112] and the electrochemical quartz-crystal microbalance (EQCM) technique [113].



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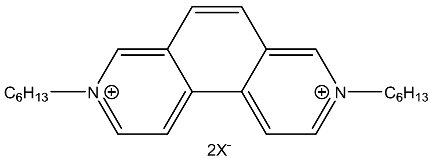


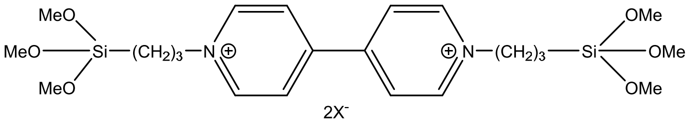
III

Despite all the above mentioned downsides, many prototypes of viologens ECDs have been made. For example, IBM laboratories fabricated 64 x 64 pixels integrated ECD with 8 levels of grey tone on a 1 inch square silicon chip utilizing heptyl viologen chromophore [114].

1.9. Type-III viologen electrochromes

In this type, the electrochrome is essentially an insoluble solid over all the redox states and generally studied as a thin film on electrode surface. In such systems, the precursor for electrochrome is dissolved in an electrolyte solution and the electrochrome is deposited as film on the electrode. Alternatively, an electrochrome dispersion in proper solvents can be drop cased on the surface of the electrode and dried for further use. Once the desired redox state is achieved, no further charge is needed to retain a new electrochromic state, such systems have optical memory [72]. This is a clear advantage over type-I ECD that need a constant flow of current to diffuse back the electrochrome towards the electrode.

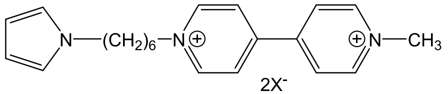
Using type-III electrochromes, the write–erase efficiency of viologen ECDs is significantly improved. There are two main approaches in this method: either by retarding the rate at which the radical cation salt diffuses away from the electrode, into the bulk solution, following the electron transfer or by completely preventing the diffusion process altogether. The former strategy is best achieved by immobilizing the viologen species into the semi-crystalline electrolyte. The electrolytes used for this purpose are e.g. poly(2-acrylamido-2-methylpropanesulfonic acid) (poly(AMPS)) [115], several carboxylate polymers [116], styrene [117] or succinonitrile [91]. The latter approach is best achieved via immobilizing viologens by tethering the dication to the surface of an electrode, thereby forming a chemically modified, in other words 'derivatized' electrode. Wrighton et al. utilized tethering of short alkyl chain terminating in the trimethoxysilyl group to the oxide lattices of ITO surface (**IV**) [118]. This way, attachment of viologen species in achieved on the electrode surface exclusively.



IV

1.10. Viologen functionalized conjugated polymers

Another little different approach of tethering viologens is reported by Wrighton et al., where a viologen nucleus is attached to the pyrrole monomer, separated by short alkyl chain (**V**) [119]. Anodic polymerization of pyrrole yields a poly(pyrrole) film derivatising the electrode surface, thereby attaching viologen units. Similar structural modifications were later reported by H. Lee et al. by using different thiophene based monomers containing a pendant viologen group, that were polymerized to polythiophene (**VI**) [120], poly(cyclopentadithiophene) (**VII**) [121] and PEDOT (**VIII**) [122], all bearing the viologen electrochrome. Though the electroactivity of a pendant viologen moiety is very high, that of the polymer backbone degraded after continuous scanning. Such approach has also been utilized for improving the overall contrast and multicolored electrochromism of the conjugated polymeric heterocycles. This thesis also provides detailed structural analysis and EC property investigations on similar structures [123,124].



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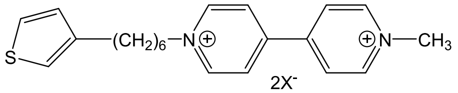

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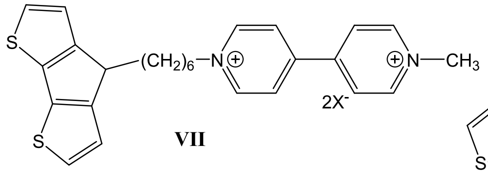

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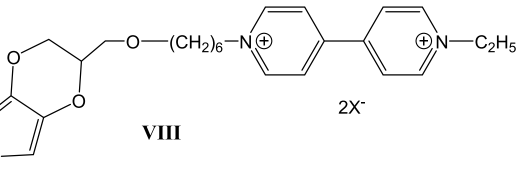
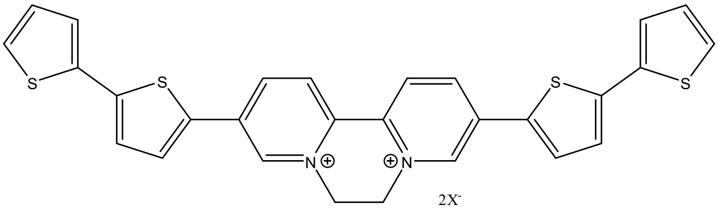


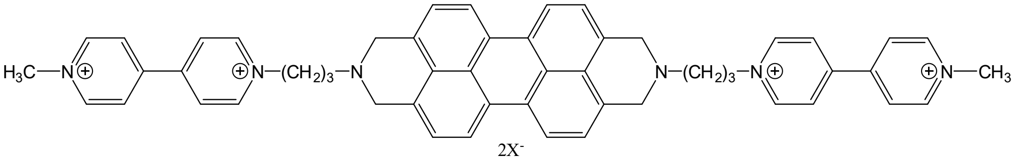
VIII

Earlier, N.S. Sariciftci et al. reported spectroelectrochemical investigations of different poly (3-alkylthiophene) derivatives bearing pendant viologen [125,126]. Similarly, P. Bäuerle et al. provided tunable synthesis as well as structural insights of polythiophenes possessing viologen side groups [127]. Recently, Krompiec et al. developed an electropolymerizable block copolymer containing alternating quaterthiophene and diquat (viologen-like moiety) blocks derived from bis-bithiophenyl derivative of diquat (**IX**) [128]. This conjugated polymer with redox viologen moiety was reported to be very stable, showing decent electrochromic properties.



IX

Kim at al. synthesized a new electrochromic molecule, viologen–perylenediimide diad (**X**) and utilized it in the fabrication of layer-by-layer (LBL) self-assembled multilayers with (PEDOT:PSS) [129]. A dual type ECD with P3HT-coated ITO as a counter electrode exhibited a sharp color change between deep red and dark blue when switched between +2.0 and −2.0 V.



X

Recently, Bhandari et al. reported dual type flexible ECD, composed of viologen doped PEDOT polymer, electropolymerized at a deposition potential of +1.8 V with Prussian blue (PB) as counter electrode in ionic liquid based electrolyte [130]. The films could be switched between +1.5 V and -1.5 V giving pale and deep purple coloration respectively, with faster response times and coloration efficiency (CE) of 187 $cm^2\ C^{-1}$ in the visible region (**Fig. 4**).

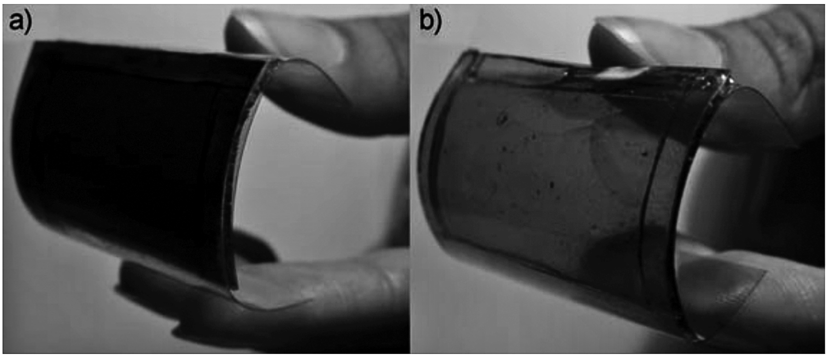


Fig. 4. Photographs of the flexible PEDOT-Viologen-IL gel-PB device in the a) colored (-1.5 V) and b) bleached (+1.5 V) states [130].

1.11. Polymeric viologens or Polyviologens

Electrochromic polymeric viologens; named poly (viologen) or polyviologen (PV) is again a perfect example of type-III electrochromes [95]. A precursor monomer of viologen is dissolved in solution and the cation radical is adhered on the surface of an electrode substrate by the electrodeposition method. Stepp et al. reported self-assembled electrochromic multilayers of a poly (butanyl viologen) dibromide (PBV) and poly (styrene sulfonate) (PSS) using an alternating polyion solution deposition technique [131]. The prepared films were robust, easy to synthesize and strongly colored. DeLongchamp et al. prepared poly (hexyl viologen) (PXV) and PEDOT:PSS multilayers using LBL technique. The 40- or 50-layer-pair films were found to exhibit a contrast of 82.1% at 525 nm, one of the highest reported for polymer electrochromes [132]. Jain et al. reported ionic self-assembled multilayers of polyviologen and poly (AMPS) [133]. 40 bilayer films of PV/poly (AMPS) on ITO electrode showed high contrast ($\Delta T=61\%$) with color changes from transparent yellow to dark violet and CE of 57 $cm^2 C^{-1}$. Ho et al. recently reported all solid state complementary ECD, based on poly (butyl viologen) (PBV) and Prussian blue (PB) using $LiBF_4$-succinonitrile as solid electrolyte [134]. The device can reversibly be switched from colorless to purplish-blue, with decent EC performance and cycle life up to 4000 cycles. Saika et al. synthesized six bis(4-cyano-1-pyridinio) derivatives and electropolymerized to EC PV films with blue/red violet coloration [135]. Such a coupling of cyanopyridyl radicals to viologen was reported much before by Kosower et al. in 1964 [136] and later explored by several researchers [137-139]. Based on similar phenomenon, this thesis also reports preparation of PV films from cyanopyridinium based monomers [140].

1.12. Hybrid electrochromic composite systems

Viologen-metal oxides EC composites

In recent years, nanostructured EC materials have been employed to improve the viability of smart windows [141]. Especially, hybrid organic-inorganic electrochromic systems have been developed aiming at enhancing the EC performance parameters. Fitzmaurice et al. for the first time reported the adsorption of viologens on transition metal oxide layers [142]. Following this work, NTera Ltd., who developed a so-called NanoChromics™ display device using viologen-TiO_2 (anatase) hybrid owing to the high surface area of anatase and ease of making thin films. Several other workers later reported improved electrochromic performance of viologens modified with mesoporous anatase nanostructures [143-146]. Sun et al. adsorbed viologens on ZnO nanowire as a thin film coated on ITO glass electrode [147]. Their ECD had fast response times (170 ms) with CE of 196 cm^2C^{-1}.

Viologen-graphene EC composites

Graphene, a 2D allotrope of carbon, has attracted enormous interest in recent years, especially after the mid 2000's. Other than many of its extraordinary physicochemical properties, the richness in optical and electronic properties of graphene is particularly significant towards electronics related applications. Regarding EC applications, graphene has been employed by two main ways: as an electrode substrate material owing to its low sheet resistance, high transparency and flexibility or as a functional component in a composite assembly together with active electrochrome. There are few reports on using graphene analogues with several electrochromic materials for improving the EC performance parameters. In a very recent works, researchers exploited both the functions of graphene materials for enhancing the electrochromic properties of viologens (**Fig. 5**). Hwang et al. fabricated flexible ECD prototype using electrostatically strong methyl viologen (MV) and graphene quantum dot (GQD) nanocomposite [148]. The resulting device exhibited excellent operational stability over 3000 s when switched between 0 and -2.8 V, with faster switching rates, in comparison to the bare MV device. Palenzuela et al., on the other hand, electrodeposited reduced graphene oxide (rGO) films on the ITO coated PET substrate, and the resulting flexible transparent electrodes have been employed in making ECDs of ethyl viologen (EtV) [149]. The electrochromic performances were compared with bare ITO-PET electrodes. Upon continuous cycling, rGO gets oxidized and dispersed in the electrochromic mixture, thus required lower switching voltages and exhibited higher optical contrast compared to EtV-ECD without rGO films. The findings encouraged designing of ECDs integrated with a second component like graphene having electrocatalytic properties, requiring low operational voltages, thereby preventing undesired degradation or side reactions in viologens. This thesis also elaborates the improved electrochromic properties of viologens in assembled composite thin films with graphene [150].

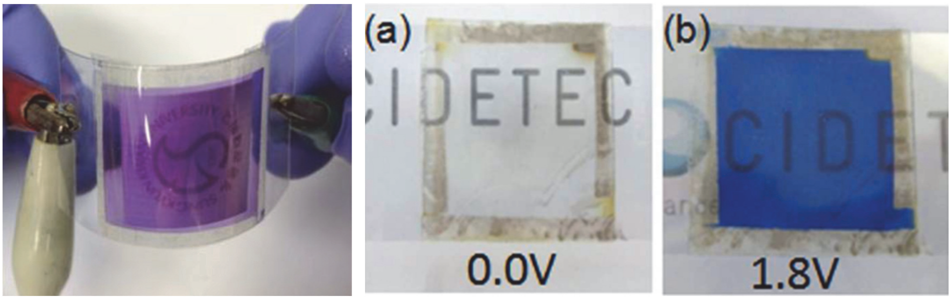


Fig. 5. Photograph of MV^{2+}-GQD bent ECD using ITO-on-PET (left) [148]. Photographs of an EtV^{2+}-RGO ECD in the (a) bleached and (b) colored state (right) [149].

1.13. Viologen based ECDs in market

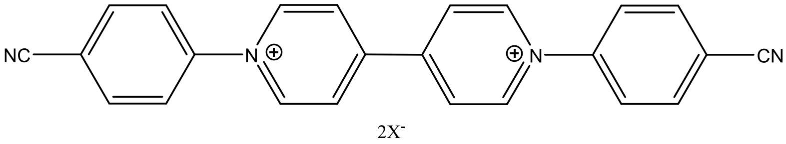
Following is a list of commercial viologen based ECDs marketed by different industrial groups in the order of their arrival in patents or marketable products. Few of these devices are already mentioned in the previous sections, they are summarized here.

The Philips Device

The Philips device, reported by Schoot et al. in 1973, might be the first viologen based ECD projected [97]. The Philips labs were seemed to have started making ECDs at some time during the mid-1960s. The first patent by Philips in 1970 reports use of heptyl viologen (HV) type-II electrochrome system [151]. HV is soluble in water in the dicationic form. After one electron transfer, it forms a crimson colored insoluble film of $HV^{\bullet+}$ strongly adhered on the electrode surface. The final ECD device has contrast ratio of 20:1, rapid erasing time (10-50 s) and switching durability of more than 10^5 cycles. The HV was chosen among the viologen based electrochromes owing to its ease in the film formation and durability. The Philips ECD was never marketed.

The ICI device

Imperial Chemical Industries Limited (ICI) submitted their first patent on the use of the aryl-substituted viologen 1,1′-bis(p-cyanophenyl)-4,4′-bipyridilium, ‘cyanophenyl paraquat’ (CPQ, **XI**), which electro-precipitates to an intense olive-green colored radical [98]. The preference of CPQ over other simpler bipyridiliums like HV, in ICI device, was due to its greater extinction coefficient leading to a device with higher CE and faster switching time. The ECD followed type-II electro-coloration mechanism, according to eq. 5 and found to be more resistant to aerial oxidation. The reduction potential was limited to -0.4 V (vs. Ag/AgCl), as further reduction would yield the pale-red species CPQ^0. A reverse oxidative potential of +1.0 V vanished the electro-generated color. The ICI ECD was first marketed as a data display device in the early 1970s. At about the same time, ultra-fast switching LCD entered the electronic market and overwhelmingly captured an unassailable market share. The ICI’s ECD falls to this competition, mainly because of its slower switching kinetics. Since the electrolyte layer was gelled with agar (5%) to improve the stability, after many write-erase cycles, a yellow-brown oil eventually stains the electrode surface. Such gelling (oiling) of electrochrome was found to be a reason for slower switching rates.



XI

The IBM device

The IBM laboratories, in 1970, developed an impressive ECD using HV electrochrome on a 64 × 64 pixel integrated device [114]. The one inch square silicon chip contained eight levels of grey tone of HV, capable of giving detailed images. These devices were not exploited further, obviously again due to competition from LCDs. However, they promised a great potential in the large-sized devices.

The Gentex Device

The most well-known device, Gentex's best-selling automatic dimming 'Night Vision Safety' (NVS®) mirror entirely functions on the principle of type-II/solution electrochromism [152-154]. As illustrated in **Fig. 6,** NVS® mirror comprises two electrodes: a front ITO coated-glass electrode and a reflective metallic rear electrode, spaced by a sub-millimeter gap, thus forming the basis of two electrode cell. The solution containing two electroactive molecules that function both as electrochrome and supporting electrolyte filled the cell cavity. The two electroactive chemical species are cathodically coloring substituted viologen (V) and anodically coloring 9,10-dimethylphenazine (DMP) [152]. After switching the mirror on, primary electrochrome viologen reductively forms colored $V^{\bullet+}$ via ohmic mass transport of the positively charged uncolored precursor propelling the viologen towards the cathode. On the other hand, the secondary electrochrome, neutral DMP electro-oxidized at the anode and provides a complementary color to the viologen. Electro-oxidation of DMP^0 depletes the solution of uncharged species, so mass transport in this case occurs only by diffusion. The dual electro-coloration process can be expressed as the color forming viologen reduction and complementary oxidation of DMP, according to eq. 6 and 7:

$$V^{2+} + e^- \rightarrow V^{\bullet+} \tag{6}$$

$$DMP \rightarrow DMP^{\bullet+} + e^- \tag{7}$$

Once the dual electrochromic coloration process has started, the products diffuse away from their corresponding electrodes and meet in the intervening solution, where their mutual reaction occurs according to eq. 8:

$$DMP^{\bullet+} + V^{\bullet+} \rightarrow DMP + V^{2+} \tag{8}$$

The reaction regenerates both the original uncolored species in solution so that the coloration process can start again. The mechanism is explained schematically in **Fig. 6**, with a photograph of the auto-dimming mirror. This type of ECD thus needed a continuous small current for the renewal of the colored electroactive species that were vanished during their mutual redox reaction in solution. Bleaching of the device occurs at open or short circuit by homogeneous electron transfer in the bulk of the solution.

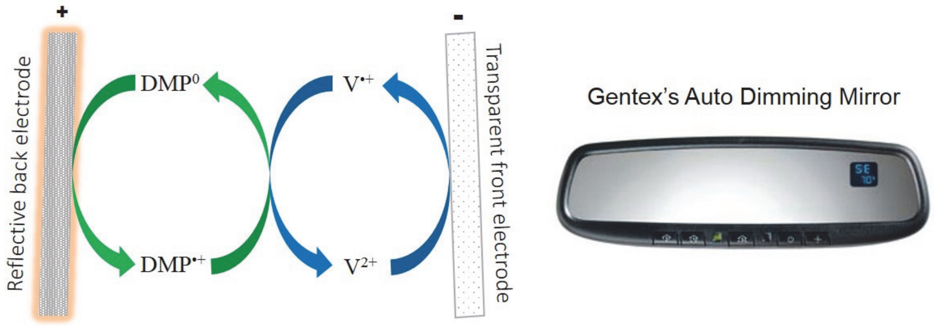


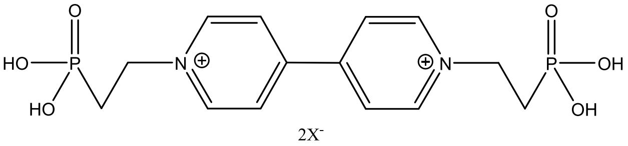
Fig. 6. Schematic representation of the redox cycles occurring within the Gentex NVS® mirror (left). Coloration occurs electrochemically at both electrodes; bleaching occurs chemically midway between the two parallel electrodes by a process of radical annihilation. A photograph of Gentex auto dimming mirror with inbuilt Homelink® press button for outside temperature and compass (right).

The NTERA device

The NTERA Ltd., a Dublin based spin off from the Grätzel cell, devised a new ECD in 1997 developed by Fitzmaurice and co-workers, based on layered/thin film electrodes composed of nanostructured anatase [155]. The rough surface of the porous TiO_2 consists of an interconnected network of oxide nanocrystals with high surface area. As a result, a high number of viologen molecules could be fitted in a relatively small area, leading to a high CE. Owing to their electron deficiency, viologen molecules adsorb strongly on the surface of TiO_2 modified electrode. Because of their strong surface confinement, the viologen electrochromes need not diffuse to the electrode surface, leading to the shorter response times. Such electrode systems have long been investigated in dye-sensitized photo-electrochemical solar cells [156].

The NanoChromics Cell

Fitzmaurice et al. later developed a 'next generation display technology' so-called NanoChromics™ displays, following the initial field trials [157,158]. The device was claimed as 'paper quality' meaning high definition (HD) display as demonstrated in **Fig. 7** [159]. NanoChromics ECD comprises of two metal oxide coated FTO electrodes. In a typical cell assembly, the negative FTO-glass electrode was coated by a wide band gap TiO_2 film, followed by a self-assembled monolayer of chemisorbed phosphonated viologen electrochrome, bis(2-phosphonoethyl)-4,4'-bipyridilium dichloride (**XII**) [158,160]. The positive counter electrode FTO-glass was coated by a heavily doped antimony tin oxide (SnO_2:Sb), followed by a self-assembled monolayer of chemisorbed phosphonated phenothiazine molecules. The TiO_2 film was further modified by a monolayer of viologen **XII**. The γ-butyrolactone solvent mixed with $LiClO_4$ and ferrocene served as electrolyte. The trial experiments of this device showed CE of $170 cm^2C^{-1}$ and stability over 10^4 switch cycles. By applying a potential of -1.2 V, viologen gets reduced to the blue colored radical while phenothiazine oxidizes from its pale yellow color to red. The overall color change virtually appeared as colorless to blue-red purple. The display was said to be ultra-fast, owing to its faster switching speed, where an absorbance change of 0.6 was attained in just one second.



XII

NTera demonstrated a NanoChromics™ display operating in a converted *iPod* and 'consumer product reference designs' for digital clocks and an eight-digit calculator [161]. The flexible prototype display was also stated to be applicable to several products including windows, mirrors, flexible electronic displays, dimmable window laminates, games and toys.

Fig. 7. Picture of Nanochromics™ 'paper quality' devices (left) [159]. Prototype of a fast switching, high-contrast blue-red colored ECD viewed at a low angle (right) [160].

The Grätzel Device

Grätzel et al. prepared display and shutter devices using series of alkyl and aryl substituted viologens [162]. The viologen molecules were decorated at a TiO_2 surface by using different anchoring groups such as benzoate, salicylate or phosphonate. The ECD cell geometry is: OTE | TiO_2-poly(viologen) | glutaronitrile-$LiN(SO_2CF_3)_2$ | Prussian blue | OTE [163]. An optical density change up to 2 units with color alterations between transparent to blue or yellowish to green and red-brown (at higher potential) were reported for this device having switching times in the range of 1–3 s. A construction of reflective type display with very fast switching times was also reported, by modifying ECD cell geometries.

Based on a similar principle, Pettersson et al. constructed a very attractive reflective type ECD made of nanocrystalline titania electrodes with chemisorbed viologen electrochromes [164]. The device comprises viologen-TiO_2 electrode in combination with nanocrystalline, capacitive, porous antimony-doped tin oxide counter electrodes, a white reflective layer and lithium triflate ($LiCF_3SO_3$) in polyethylene glycol electrolyte. The final ECD acts as a direct-driven display with promising stability and attractive paper-like visual qualities.

The viologen based electrochromics is a well-established field by now in the context of their basic properties and structural investigations, as well as their successful device applications. The recent developments in the viologen based ECDs mainly focusses on enhancing the coloration rate and cycle life. The nanostructured materials and integrated systems are being employed for this purpose.

2. AIMS OF THE THESIS

The aim of the thesis was to design viologen based redox polymers for electrochromic (EC) investigations. Since viologen EC materials have been commercially used in smart windows (e.g. self-darkening car mirrors from Gentex Corporation), but lacks good cyclic stability, the aim was to elevate some of the important electrochromic performance parameters of viologens. For this reason, polymeric viologens, viologen functionalized polythiophene and polyviologen- reduced graphene oxide (PV-rGO) composite films were studied. Electrochemical polymerization and deposition techniques were employed for assembling viologen based EC thin films. All deposited films were thoroughly characterized using different instrumental as well as electrochemical techniques. Finally, the electrochromic properties of these films casted on transparent conducting electrodes were tested using spectroelectrochemical methods.

For each publication, the specific aims were:

I. To synthesize a cyanopyridinium based monomer precursor CNP, study its reductive electropolymerization to polyviologen thin films at an electrode surface and to study its structural analysis. Understand the mechanism of formation of viologens from CNP, using electrochemical and spectroelectrochemical characterization methods.

II. To fabricate polyviologen-reduced graphene oxide composite films in order to explore the effect of grafting a secondary component like graphene on the electrochromic performance of polyviologens. Thorough characterization of the composite films using different spectroscopic, microscopic and electrochemical analytical methods. Investigate the interactions between two electroactive components within the composite matrix.

III. To synthesize a thiophene monomer with a cyanopyridinium moiety at the side chain and perform electropolymerization of the thiophene derivative and reductively cross-link the polymers by the CNP to viologen. Copolymerize this monomer with another thiophene monomer and monitor the spectral changes using UV-Vis spectroelectrochemistry. Understand the structural differences between homopolymers and copolymer and examine EC properties.

IV. As a comparison, synthesize a thiophene monomer bearing viologen functionality and perform the electrochemical polymerization. Detailed structure analysis using spectral techniques and in situ ESR-UV-Vis-NIR spectroelectrochemistry. Investigate the EC performances of the polythiophene films and possible improvement in the EC properties after the viologen functionalization.

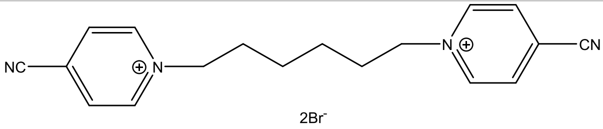
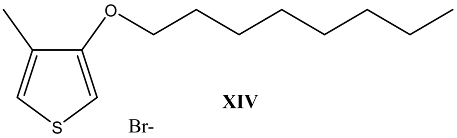
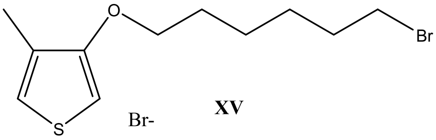
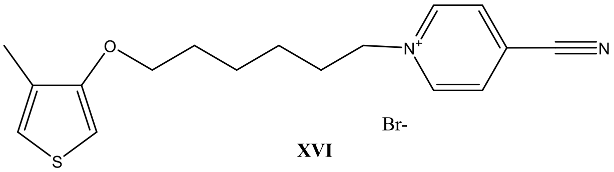
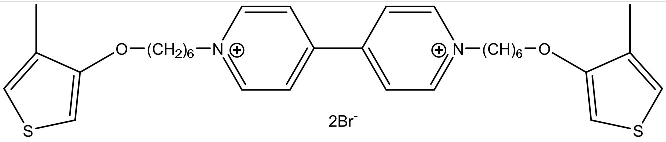
3. MATERIALS AND METHODS

A detailed description of materials employed in each work is given in the list of original publications (**I-IV**). A brief summary with some additional details is presented here.

3.1 Synthesis of monomers

Table 4 provides a brief list of monomer structures employed in each publication.

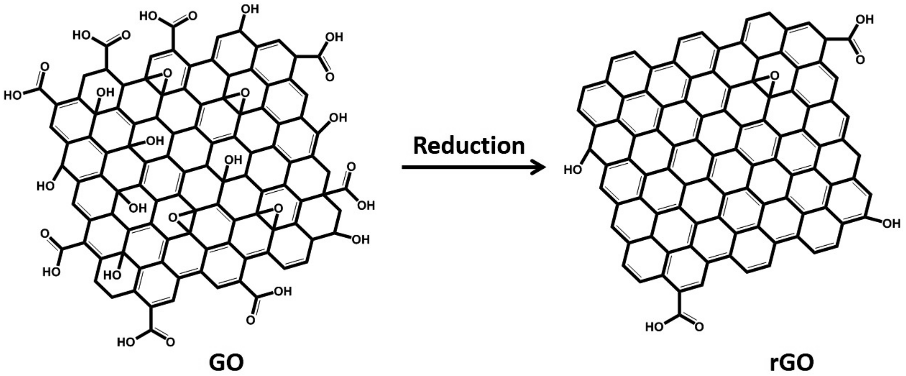
Table 4. List of monomers employed in each publication.

Publication	Monomer structure and name	Abbrev.
I & II	 **XIII** Pyridinium, 1,1′-(1,6-hexanediyl) bis (4-cyano) dibromide	**CNP**
III	 **XIV** 3-octyloxy-4-methylthiophene bromide  **XV** 3-[(6-bromohexyloxy)-4-methyl] thiophene bromide  **XVI** 1-[6-[(4-methyl-3-thienyl) oxy] hexyl]-4-cyanopyridinium bromide	**OOT** **HOT** **HOT-CNP**
IV	 **XVII** N,N′-bis{[6-(4-methyl-3-thienyl)oxy]hexyl}-4,4′-bipyridinium dibromide	**Th-V**

3.2 Synthesis of graphene oxide (GO) and its reduction

GO is produced by oxidation of graphite using a modified Hummers method [165]. In brief, natural graphite flakes (2 g) were suspended in a mixture of conc. H_2SO_4 (68 mL) and $NaNO_3$ (1.5 g) in a three-necked round bottom flask equipped with a thermometer and a gas trap. $KMnO_4$ (9 g) was then added slowly over ½ h in the above mixture, cooled under ice bath and then continuously stirred for ~2 h. The reaction mixture was then allowed to warm to room temperature under continuous stirring. After a day, the mixture becomes two thick to stir. It was allowed to react further for 4 days. During this time, the reaction temperature was not allowed to rise above 35 °C. Next, the oxidation reaction was terminated by adding dropwise 5 wt.% H_2SO_4 in the mixture, in an ice bath and the unreacted $KMnO_4$ was removed by addition of 30% H_2O_2 (6 mL) at room temperature. The brown colored mixture was then centrifuged after which the precipitate was dispersed in water and centrifuged again. The process was repeated several times until desired pH was achieved. The dispersion was then placed in a cellulose dialysis tubing and kept in a bathtub containing double distilled water. The bath solution was changed twice a day until no significant UV–vis absorbance was noticed in the outer solution. The final dispersion from the dialysis tube was collected as GO, with concentration ~4.4 mg/mL and pH=2.5, and used thereof.

The produced GO thus facilitates the solution processing of graphene; however the harsh oxidation conditions employed on graphite eradicates most of its important physical properties like conductivity. Therefore, reduction of graphene oxide is desired to partially recover the π-conjugated network of graphite, thereby restoring some of its excellent properties like electrical conductivity. Kauppila et al. discussed several methods for the reduction of GO in great details [166]. For electrochemical applications, electroreduction of GO is favored, since it does not involve any harsh chemicals reductants and can be directly performed on the GO-coated electrode by simply passing sufficient electrical voltage [167]. Such electrochemical reduction has been proven to be effective green strategy for removing most of the oxygenated surface groups on GO, as illustrated in **Scheme 2**. In the case of graphene composites with polymers, the monomers or precursors are usually dispersed in the GO suspension with/without electrolyte and electropolymerization is carried out. Following the deposition of films, electro-reduction of deposited GO is carried out by applying suitable reduction potential. Similarly, pristine GO films can be casted at the electrode surface and reduced thereafter. However, after electroreduction, the resulting physical changes in the material causes detachment of the rGO from the electrode surface, limiting its further use. Therefore, at least in the case of polymer-GO composites, mixing monomer precursors in the GO dispersion is an effective strategy and after the deposition, the electrodeposited GO within the composite film can be reduced in situ. The non-covalent forces between resulting polymer and GO stabilize the composite matrix, and adhere at electrode surface firmly. In Publication **II**, a CNP monomer is mixed with the as prepared GO aqueous dispersion and the electrocodeposition is carried out for synthesizing PV-rGO composite.



Scheme 2. Reduction of graphene oxide (GO) to reduced graphene oxide (rGO).

3.3 Electrochemical synthesis and characterization of electroactive thin films

All the electrosynthesis/electropolymerization experiments were carried out in a conventional three-electrode one-compartment cell, performing cyclic voltammetry (CV) measurement using a Autolab (PGSTAT101) potentiostat. The working electrodes employed were a glassy carbon (GC) or gold (Au) electrode (d=1 mm) or fluorine doped tin oxide (FTO) (K Glass-Pilkington, sheet resistance=8.1 $\Omega\square^{-1}$, active d=10 mm) or indium doped tin oxide (ITO) (Delta-technology Inc., sheet resistance=100 $\Omega\square^{-1}$, active d=10 mm) on glass. GC or Au electrodes were polished mechanically with diamond paste containing polyethylene glycol (DP-Paste-P by Struers) of different grain sizes (0.25, 1, 3, 7, 15 μm) before use. FTO or ITO electrodes were cleaned successively in acetone, ethanol and water using ultra- sonication before use. A Pt wire and Ag wire coated with AgCl served as counter electrode and quasi-reference electrode, respectively. The Ag/AgCl wire was calibrated vs. ferrocene (Fe/Fe^+) ($E_{1/2}$(Fe/Fe^+) = 0.45 V) and all the potentials mentioned are vs. Ag/AgCl electrode. The monomers or mixtures of appropriate concentrations were dissolved in supporting electrolyte solution (acetonitrile or water) containing electrolyte salts ($TBAPF_6$, $LiClO_4$ or KCl). The electropolymerization experiments were performed in a specific potential window depending on the electroactivity of the material under study. For thiophenes, the potential was scanned in anodic direction while for the viologens, the potential scanning was performed in cathodic direction, mostly between 0 and -1.2 V. The scan rate was after optimization set to 50 mVs^{-1} for all polymerization and electrodeposition experiments since it provides well defined voltammogramms. For the copolymerization's, different feed ratios of monomers were tested to achieve optimum monomer proportions in the final copolymer. All the given solutions were deaerated by dry nitrogen (N_2) stream for 15 min before each CV experiment and a slight N_2 overpressure was maintained during the reaction.

After each deposition, polymer films were rinsed, generally with the solvent used in the electrolyte, several times in order to remove electrolyte residues or unreacted monomers. The deposited films were then placed in a monomer-free supporting electrolyte solution and CVs of the film-coated electrodes were recorded. In order to check the reversibility of the electrochemical system, the films were further subjected to CV scanning at different scan rates.

3.4 Spectroscopic & surface characterization techniques

FTIR spectra of samples dispersed in KBr pellet were recorded using a dry-air-purged Nexus 870 FTIR spectrometer (Nicolet) with a DTGS detector. In another method, the spectra of samples were recorded by a Bruker VERTEX 70 FTIR spectrometer equipped with a Harrick VideoMVP^{TM} diamond ATR accessory using liquid N_2 cooled MCT (broad-band) detector. The Raman spectra of the polymer or composite samples were recorded using visible laser excitation wavelength (λ_{exc}= 514 nm) and a Renishaw Ramascope (system 1000 B) equipped with a Leica DMLM microscope connected to a thermoelectrically cooled CCD detector. The scattering signal was collected at an angle of 180^0. For FTIR and Raman studies, comparative analysis was performed in order to track the structural changes and modifications in the materials.

XRD patterns of solid samples were measured using a Huber G670 image plate Guinier camera with copper $K_{\alpha 1}$ radiation (λ=1.5406 Å) and 2θ in the range of 4-100^0. Total 10 scans of the image plate were taken with data collection time of 30 min. For XPS measurements, the samples were placed on gold coated Si (100) wafers. A 100 nm thick gold layer was deposited on pre-cleaned Si (100) wafer using the Edwards E306A thermal coating system. XPS spectra were measured by a Perkin–Elmer PHI 5400 spectrometer using Mg Kα radiation (1253.6 eV) and the spectral analysis was performed with the Unifit2009 software (Unifit Scientific Software GmbH, Leipzig, Germany). XRD and XPS techniques were mainly employed for the analysis of PV-rGO composite materials. For SEM imaging, the thin electroactive films were deposited on ITO/glass electrodes. A Leo (Zeiss) 1530 Gemini FEG-SEM was used in order to obtain surface morphological features of the samples.

3.5 In situ spectroelectrochemical characterization

In situ UV-Visible spectroelectrochemistry

For spectroelectrochemical and electrochromic studies, the polymer or composite samples were electrosynthesized on FTO or ITO/glass electrode, with Pt wire as counter electrode and Ag/AgCl wire as reference electrode. The electrochemical set-up was assembled in a quartz cuvette (path length = 1 cm) with suitable electrolyte. For in situ measurements, HP 8453 or Agilent Cary 60 UV-Vis spectrometer was connected to an IviumStat potentiostat. The in situ UV-Vis spectra were recorded by stepwise changing of potential by 0.1 V between the recordings. In order to check the electrochromic performance of the films, two potential values are selected where the film showed bleaching and coloring state. The film was then switched between these two applied potentials and kinetics of switching at monochromatic wavelength was recorded using in situ UV-Vis measurements performing chronoamperometry.

In situ ESR/UV–Vis–NIR spectroelectrochemistry

Electrochemical techniques provide detailed understanding of charge transfer, transport and distribution, but very little is known about the structure, the intermediates, the electrode reaction mechanism and the magnetic features, which might be crucial for further potential applications. For this reason, in situ spectroelectrochemistry was introduced, performing time-dependent studies of electrode reactions simultaneously as the changes are recorded by spectroscopic techniques [168]. During an electrochemical reaction, an organic redox system initiate primary cathodic or anodic electron transfer which result in radical ion formation. Since the radicals are paramagnetic in nature, the spectroscopic method of choice would be ESR spectroscopy. A second electron transfer or the follow-up reaction of the radicals results in the dimer formation which is not detectable by ESR. For this purpose, an additional spectroscopic tool is required. Dunsch et al. developed an optical ESR cavity that significantly advances the era of spectroelectrochemistry, utilizing simultaneously both ESR and UV–vis-NIR spectroscopy in a single spectroelectrochemical cell [169]. Thus, both paramagnetic and diamagnetic features in the redox molecules can be followed at the same working electrode.

For in situ ESR/UV–vis–NIR spectroelectrochemical studies, a specially designed flat cell was employed (**Fig. 8**) which fits the optical electron spin resonance (ESR) cavity (ER 4104OR, Bruker Germany). ESR spectra were recorded by the EMX Micro X-band CW spectrometer (Bruker, Germany). UV–Vis–NIR spectra were measured by Avantes spectrometer AvaSpec-2048x14-USB2 equipped with a CCD detector and AvaSpec-NIR256-2.2 equipped with the InGaAs detector using the AvaSoft 7.5 software. A HEKA potentiostat PG 390 was connected to both the

ESR and the UV–Vis–NIR spectrometer for in situ measurements and triggering was performed by the software package PotMaster v2x40 (HEKA Electronic, Germany). A three electrode system consisted of a laminated working electrode, a Pt wire as a counter electrode and an Ag wire as pseudo reference electrode were positioned in a flat spectroelectrochemical cell. An ITO electrode or a Au microgrid (1024 meshes/cm^2) was positioned between two pieces of chemically inert polyester based lamination foils (DocuSeal, USA). A small, well defined electrochemically active surface area was obtained, with circular holes giving 0.1 cm^2 of free active electrode surface.

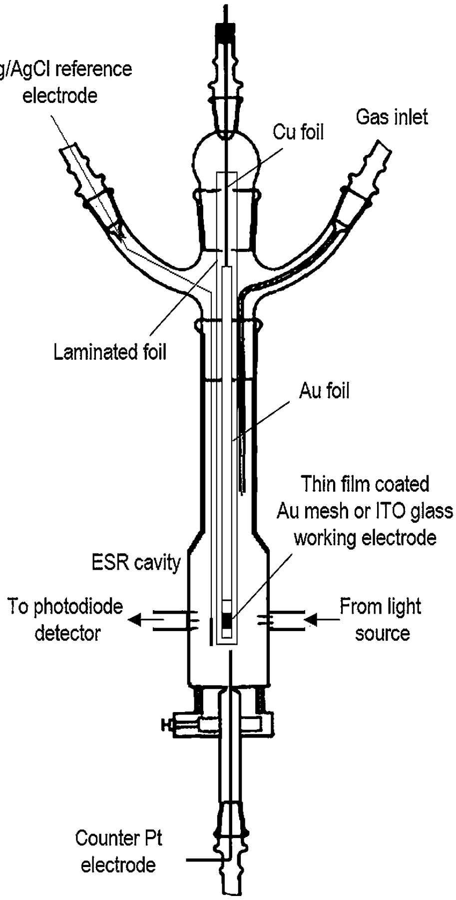


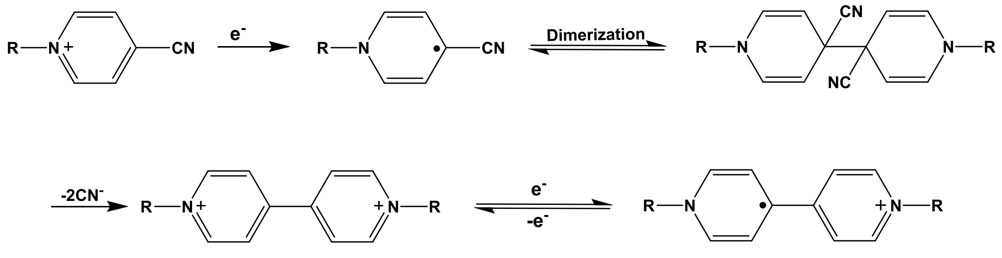
Fig. 8. Experimental design of in situ ESR/UV-Vis-NIR spectroelectrochemical flat cell [169].

4. RESULTS AND DISCUSSIONS

Following sections summarizes some of the key findings published in papers **I-IV** along with some additional details. More detailed information can be found in each publication.

4.1. Polyviologen from cyanopyridinium based monomer

Due to its significant electrochemical properties, viologen and polyviologen modified electrodes are commonly employed for several applications like electrochromics [170], electro-catalysis [171] and organic electronic devices [172]. There are several ways to develop viologen modified electrodes. It goes back to 1960's when Kosower et al. showed a unique synthesis of stable free radicals of viologen starting from 1-alkyl-4-cyanopyridinium iodide [173,174]. A chemical reducing agent, sodium dithionite ($Na_2S_2O_4$) was used for this purpose. Alternatively, viologen cation radicals can be deposited by electrochemical reduction of 4-cyanopyridinium species. Kitamura et al. showed both chemical and electrochemical ways of producing polymeric membrane cross-linked by viologen units via reduction of the homopolymer containing a pendant cyanopyridinium structure, poly (l-vinylbenzyl-4-cyanopyridinium perchlorate). Following this work, there are several reports on utilizing the cyanopyridinium structures for viologen formation directly on the electrode [135,138,139]. In publication **I**, a new monomer structure based on cyanopyridinium ion CNP (**XIII**) was synthesized, that is reductively polymerizable by both chemical [171] and electrochemical methods [140,175]. The mechanism for the reduction processes is illustrated in **Scheme 3**. 1-alkyl-4-cyanopyridinium ion gets reduced to its neutral radical, which can be equilibrated to its dimer. A part of this neutral dimer loses two of its cross-connected –CN groups, yielding a viologen dication. A successive reductive coupling reaction of 4-cyanopyridyl radicals gives a highly cross-linked viologen skeleton.



Scheme 3. Mechanism of the reductive coupling reaction of 4-cyanopyridinium to viologen.

Fig. 9A shows continuous cyclic voltammogramms of CNP derivative dissolved in aqueous electrolyte containing 0.1 M KCl at GC electrode. On the first scan, a very steep reduction peak can be seen at -0.8 V with its corresponding oxidation peak at -0.6 V. These redox peaks are assigned to the –CN group reduction. As the electroreduction continues, these peaks decreased, and eventually diminished after nearly 5-6 cycles. With further scanning, new reduction peaks start to appear at -0.5 and -1.0 V, with their respective oxidation peaks observed at -0.4 and -0.8 V, respectively and then increased with repetition of scans. During the process, one can observe an insoluble, obscure purple colored layer being deposited at GC surface. The color can be more clearly visualized when using ITO as working electrode. The as-deposited film is insoluble in aqueous and most common organic solvents like ethanol, methanol, acetone, ACN, $CHCl_3$, propylene carbonate or THF. The CV response of PV deposited GC electrode comprises well resolved, two step redox process at -0.5 and -1.0 V (inset of **Fig. 9**). The CV peak positions are analogous to viologen species. FTIR analysis revealed vanishing of the -C≡N stretching band (at 2244 cm^{-1}) in PV, suggesting effective electroreduction of CNP moieties (**Fig. 9B**). Typical viologen UV-Vis absorption can be seen, at λ_{max}= 400, 550 and 900 nm, when the PV film undergoes one electron transfer at -0.6 V (**Fig. 9C**). Thus, the electrochemical tests as well as spectral analysis proves successful reductive coupling of cyanopyridyl structure to viologen/polyviologen skeleton via elimination of cyano groups.

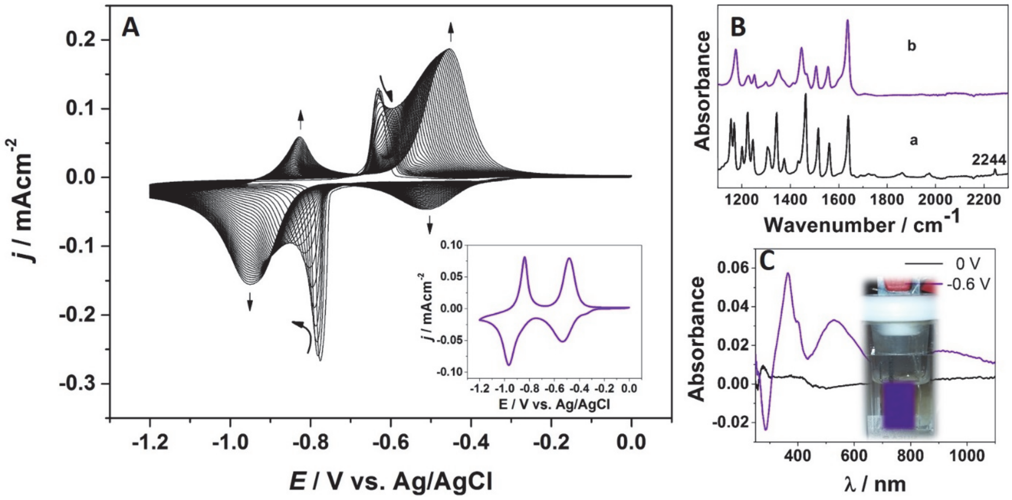


Fig. 9. A) Successive CVs of derivative XIII in 0.1 M KCl aq. electrolyte at GC electrode (Inset: CV response for a PV modified electrode after electrosynthesis). **B)** FTIR spectra of a) CNP and b) PV. **C)** In situ UV-Vis spectra of PV modified ITO electrode at 0 and -0.6 V and corresponding EC film.

4.2. Polyviologen-reduced graphene oxide (PV-rGO) electrochromic films

In recent years, there has been enormous interest in producing electroactive composite materials in order to enhance the electrochemical performance of an individual material in the hybrid assembly [176]. There are several methods of combining two or more materials for composite formation. The electrolytic co-deposition is best suitable method for different electrochemical applications like electro-catalysis, supercapacitors, photoactive materials and several other energy storage applications. Such electrodeposition processes consists of different electroactive precursors suspended in an electrolyte solution; and variable amounts of these materials can be embedded in the electrochemically produced solid phase. The material imparts special properties that are significantly improved compared to those of the individual components. Lately, graphene oxide has been utilized for this purpose owing to its surface oxygenating groups suitable for binding, extended π conjugation network and electrostatic forces [177]. Conjugated polymers and materials have been widely employed together with GO for several purposes [178]. Lindfors et al. showed that GO can be utilized as counter ion during the electropolymerization of conducting polymers [179,180]. The resulting polymer-graphene composites exhibit excellent electrochemical properties compared to pristine polymer.

In publication **II**, electrochromic composite films were prepared composed of polyviologen (PV) and reduced graphene oxide (rGO) [150]. Previously synthesized cyanopyridinium precursor monomer CNP is dispersed in GO suspension using ultra sonication. The ultrasonic forces separate clustered graphene sheets into their individual state, assisting the proper dispersion of both monomer and GO. Due to its anionic character, GO has been previously employed as counter ion/dopant during electropolymerization process, thereby hindering the use of any additional dopants or surfactants. This phenomenon is not applicable for electrodeposition of PV-rGO composite films, mainly due to the lack of sufficient electrical conductivity of the polymeric viologen as well of GO. Hence, 0.1 M KCl aqueous supporting electrolyte was employed during composite film formation. A cathodic potential window between 0 and -1.2 V has been used during electropolymerization of PV. And coincidently, the same potential window is desired for reducing GO to rGO. Therefore, we envisaged electrodeposition of PV-rGO films would not only form to PV from CNP moieties but also ensures the reduction of GO to rGO during the same process. We thus utilized the one step cathodic electrocodeposition of CNP-GO dispersion in 0.1 M KCl aqueous electrolyte using cyclic voltammetry. The three electrode system comprising FTO working electrode, Pt wire counter electrode and Ag/AgCl pseudo reference electrode was used. There is a small shift in all CV peaks to more negative applied potentials and the shape of all the peaks is broader, during electrodeposition of PV-rGO films in comparison to those of pristine PV. The as-obtained films possess tiny blackish colored material together with the highly colored PV, indicating the presence of rGO species in the composite. Since the GO dispersion is brown colored, the blackish spots suggests effective electroreduction of GO to rGO. The composite was thoroughly characterized by using several instrumental methods mentioned in the 'Materials and Methods' section. Cyclic voltammetry comprises two redox waves characteristics of viologen, at their respective, well documented potentials (**Fig. 10**). The FTIR, Raman, XRD and XPS and morphological analysis confirms the involvement of both PV and rGO components within the composite matrix. Moreover, GO was reduced efficiently to rGO during reductive electrodeposition, as evident by removal of most of the oxygen containing bands from PV-RGO spectra. For comparison, pristine PV, graphite, GO and rGO films were prepared beforehand. The possible interactions between PV and rGO are illustrated (**Fig. 10**), and confirmed by carrying out some simple measurements, as explained in Publication **II**. A negative zeta potential value of rGO (-25.2 mV) and positive value of PV (53.7 mV) was compensated in the composite which possesses a zeta potential value (25.1) in between the two, indicative of possible intermolecular non-covalent interactions. The fluorescence intensity of PV was quenched with the stepwise addition of rGO, due to the electrostatic interactions. Furthermore, viologen materials possess π- bipyridinium core, which is multiplied in the polymeric viologens while graphene sheets also contain π- conjugated network in their structure. Therefore, there might be π-π stacking of both rings in the composite assembly. The above experiments proved that the non-covalent interactions like π-π stacking, electrostatic (viologen cation and negative GO) and viologen cation-graphene π interactions might have stabilized the hybrid composite matrix and also facilitated the electrocodeposition process. The composite films showed improved electron transfer properties towards a redox mediator and better electrical conductivity verified by impedance measurements.

It was previously observed that the PV films exhibit explicit electrochromism between bleached and intense purple colored state when switched between 0 V and -0.6 V, respectively (**Fig. 9**). Owing to its effective and highly stabilized composite formation with rGO, the PV-rGO films deposited on FTO were further exploited to electrochromic switching's over long scan period (8000 s) at a monochromatic wavelength of 525 nm. In comparison to pristine PV/FTO, the composite PV-rGO/FTO films showed very high optical stability in terms of transmittance change (Δ%T), during continuous switching. PV/FTO films, on the other hand, decayed significantly during the switch cycles, showing continual decrease in Δ%T from ~60% to ~10% at the end of the scan. Especially, the transmittance at the coloring state has dropped dramatically by 43% in comparison to that of the bleaching state showing negligible %T decay (3.5%). A high optical stability of PV-rGO/FTO system suggests that the color bearing radical cation species are stabilized by intermolecular forces in the composite matrix with graphene. The response times and coloration efficiency values of composite films were also superior compared to those of the pure polymer. Similar improvement in the graphene based viologen electrochromic systems has also been reported [148,149,181]. The synergetic mechanism, high surface area and conductivity provided by graphene sheets, together with experimentally proven non-covalent interactions might have played a key role in enhancing the electrochromic properties of PV-rGO films. This particular study opens up an era of using nanostructured graphene materials in combination with electrochromes for improving the electrochromic performance parameters, especially the cycle life.

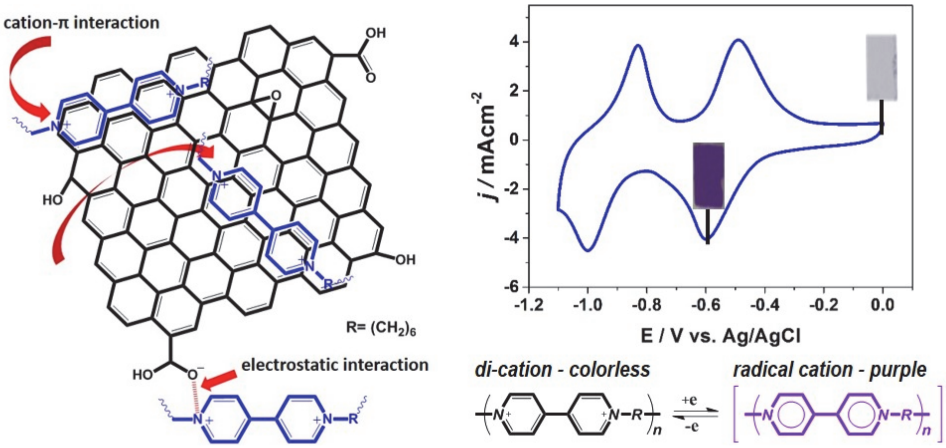
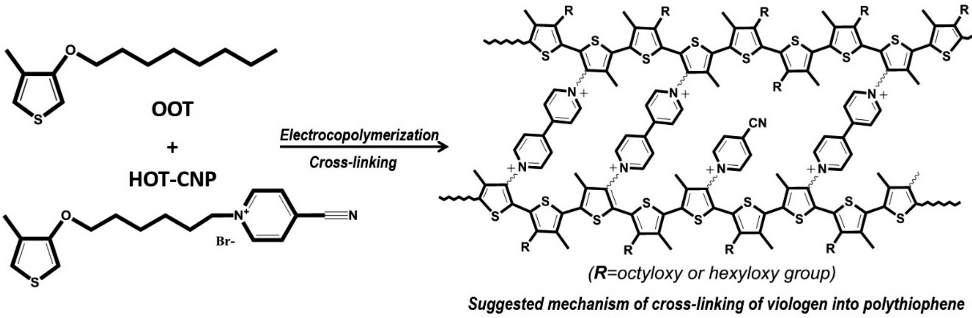


Fig. 10. Illustration of the possible non-covalent interactions in PV-rGO composite structure (left). A CV of PV-rGO coated FTO-glass electrode with inserted photographs of the bleached and colored state films at their respective applied potentials and the equation showing the coloration mechanism (right).

4.3. Electrosynthesis of viologen cross-linked thiophene copolymer

When two or more dissimilar monomers couple and polymerize, the resulting material is termed as copolymer and the process is called copolymerization. The copolymers offer several advantages not normally seen in the homopolymers. An enhancement in terms of electrical conductivity, electrochemical activity, solubility, thermal stability etc. can be observed in copolymers [182]. The copolymer thus possesses improvement in the desired electrochemical properties that are intermediate between the individual polymers.

Among the conjugated polymers, polythiophenes (PTh) family has been extensively studied due to their great synthetic flexibility, good electrical conductivity and chemical stability in both the neutral and doped states, satisfying operational and environmental stability, good optical properties etc. Especially, for improving the optoelectronic related properties, chemical modifications of monomers/polymers is desired. An introduction of substituent functionality to PTh is a well-established approach for tuning and enhancing several properties, that a pure polymer does not offer.



Scheme 4. Schematic representation of electrocopolymerization of OOT and HOT-CNP monomer and suggested mechanism for cross-linking of viologen into polythiophene backbone.

In publication **III**, a monomer precursor of a thiophene derivative containing a cyanopyridinium moiety in its side chain (HOT-CNP) is synthesized. The anticipation was that electrochemical oxidation of HOT-CNP would yield a stable PTh film. Subsequently, the attached CNP functionality can be electrochemically reduced to viologen by coupling the two cross-connected cyano groups. The final PTh backbone can thus be cross-linked by viologen units and might offer improved electrochromic properties. Accordingly, the electropolymerization was carried out in a three electrode setup using the CV technique. The resulting film started to drop off from the electrode during successive CV scans in organic supporting electrolyte. This might be due to the bulky structure of HOT-CNP. Similarly, a poor adhesion of conjugated PTh films containing viologen functionality has been reported previously [120,121]. Due to the solubility problem of the resultant film, we introduced another analogous thiophene monomer without any functionality OOT, for copolymerization with HOT-CNP. OOT was easy to polymerize and could produce a very firm thin film deposited on the electrode during electropolymerization. The anodic copolymerization of these two monomers was thus performed, which generated a well adhered insoluble copolymer film at the surface of an electrode. After polymerization, the films were subjected to cathodic potential sweep where the attached cyanopyridinium moiety could be reduced to viologen units. In order to ensure optimum structural composition, different feed ratios of monomers were employed. The copolymer films with feed ratio of 1:4 (HOT-CNP:OOT) yielded the best possible PTh copolymer, evident by different characterization techniques. The CV response of the copolymer shows typical PTh and also characteristic viologen voltammogramms. The FTIR spectra of the copolymer in comparison to the individual monomers, showed successful viologen formation marked by disappearance of -C≡N stretching band at 2246 cm^{-1}. An intense broad band at 1633 cm^{-1} assigned to the C=N ring stretching vibration in viologen can also be observed in the copolymer FTIR spectra. A speculated mechanism of viologen crosslinking into the polythiophene backbone is given in **Scheme 4**. In situ UV-Vis spectroscopy of homopolymer derived from OOT and copolymer showed an absorbance doublet at 530 and 590 nm during initial anodic scans and polaronic absorption at 830 nm after the oxidation state of PTh is achieved. Additionally, a band at 400 nm analogous to the viologen dimer absorption can also be seen in the copolymer absorption spectra already during the anodic scanning. When the copolymer was scanned to the cathodic side, representative viologen absorption bands can be seen at 400, 550 and 700 nm (tiny band) and are increasing successively with increase of applied potential. The results indicate successful cross-linking of viologen from the cyanopyridinium ion into the polythiophene backbone. The copolymer exhibits electrochromism with striking color changes between purple and greenish blue at fully reduced and oxidized state, respectively (**Fig. 11**). The copolymerization concept turned out to be a successful approach for improving the adherence of the electropolymerized films and modifying the polymer backbone properties by introducing another redox functionality with improved stability and electrochromism.

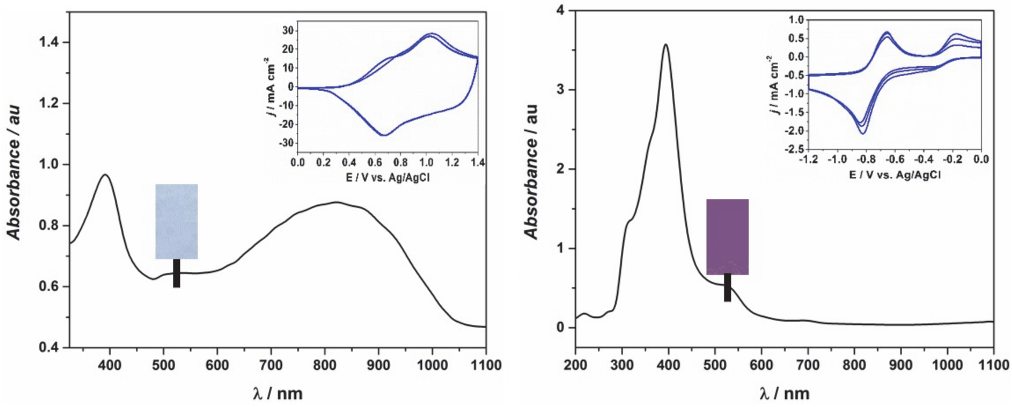


Fig. 11. In situ UV-Vis spectra of electrochromic copolymer film at 1.0 V (left) and -0.8 V (right), showing color changes at 525 nm. Inset: CV response of copolymer at anodic (left) and cathodic side (right).

4.4. Electrosynthesis of polythiophene derivative bearing a pendant viologen

Due to the difficulties in the electropolymerization of HOT-CNP, a thiophene dimeric derivative was synthesized bearing viologen moiety in its side chain, Th-V (**XVII**). The electropolymerization was carried out in mixed electrolyte comprising water and acetonitrile (v/v; 50:50) containing 0.1 M $LiClO_4$ as supporting salt. Since the viologens could be well studied in aqueous solutions while the polythiophenes in the organic electrolyte media, an electrolyte mixture was employed. Three electrode system using Au working electrode, Pt wire counter electrode and Ag/AgCl pseudo-reference electrode was employed for electropolymerization experiments using the cyclic voltammetry technique. As discussed in publication **IV**, the successive CV scanning was initiated in the cathodic direction in order to accumulate the viologen species, and thereafter continued in the anodic direction for polymerizing the thiophene moieties. This procedure was adapted from previous works on similar materials [122] and a potential window between -1.2 to +1.5 was selected for polymerization based on the initial trials. During the reductive scan, a sharp redox peak can be observed at ~-0.4 V, assigned to the viologen radical cation formation. A broad peak due to neutral viologen can be detected at -0.75 V. In the anodic direction, three peaks were seen between 0.8-1.2 V assigned to oxidation of thiophene. With continues scanning, constant increase in current could be observed indicating film growth. At the end of polymerization, an obscure layer could be noticed near the electrode surface. More importantly, the film did not drop off the electrode and could withstand 30 CV sweeps during polymerization, without any degradation.

The redox response of the PTh-V modified electrode in the monomer free electrolyte showed redox activity due to the viologen as well as PTh at their respective potentials. The in situ UV-Vis spectra of a PTh-V thin film deposited on ITO demonstrate the electrochromic behavior of the film, discussed in great details in publication **IV**. The absorption intensity is higher in the range where viologen absorbs, indicating the significance of adding extra redox active viologen moiety into the polymeric chain for enhancing electrochromic properties. An improved contrast of the PTh film bearing a pendant viologen could be spotted visually as well as by potential dependent absorbance changes (**Fig. 12**). Bleaching of the film is fixed at the PTh side, in its fully oxidized state (+1.0 V) while the coloring of the film occurred obviously at the cathodic side, due to the viologen cation radical, showing deep violet color at -0.6 V. The color/bleach characteristics of PTh-V showed reasonable optical contrast (Δ%T=39%) during switching. The film was found to be very stable over 1000 cycles, without any sign of significant degradation. Introducing some conducting properties of PTh into the colored viologen functionality seems to have improved the overall electrochrome durability. The thermal stability of PTh-V has also been enriched due to similar reasons. Although, a real ECD was not presented, these initial experiments showed that PTh-V film can be upgraded for device applications.

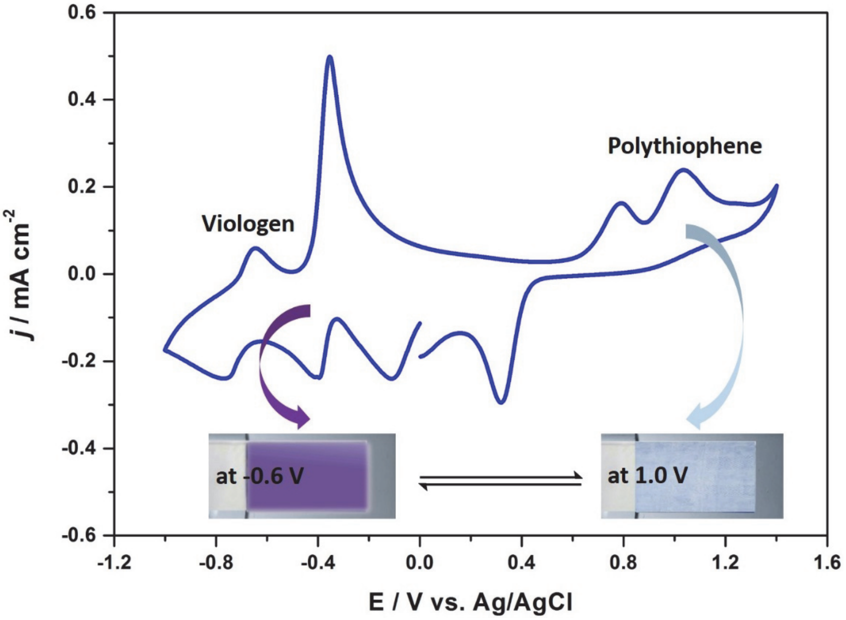


Fig. 12. A CV of PTh-V film with inserted photographs of the films showing its color/bleach characteristics.

4.5. In situ ESR-UV-Vis-NIR spectroelectrochemical studies

Due to its radical forming ability and the importance of radical cation in the electrochromic investigations, viologen/polyviologen system was studied by using multi in situ ESR/UV-Vis-NIR spectroelectrochemistry. Part of publication **I** and **IV** presents the in situ ESR/UV-Vis-NIR spectroelectrochemical studies of polyviologen (PV) and viologen functionalized polythiophenes (PTh-V), respectively.

At cathodic side (n-doping):

Polyviologen and viologen connecting polythiophene chain showed quite similar behavior in both ESR and UV-Vis-NIR spectroscopy during the cathodic scan, despite of its structural differences. At the beginning of the cathodic scan, both the ESR and UV-Vis spectra remain unchanged for the PV and PTh-V film modified electrode. Once the applied potential reached the viologen reduction onset, a sudden increase in the ESR signal as well as UV-Vis absorbance response could be observed. Interestingly, ESR only shows a single line in its spectrum (**Fig. 13**) instead of well documented hyperfine splitting generally reported for the molecular viologen cation radical. This is probably due to the presence of polymer structures in both PV and PTh-V, restricting viologen species within the polymer matrix. The UV-Vis spectra, on the other hand, show a very typical viologen absorption with three characteristic bands at 400, 550 and 900 nm assigned to the viologen cation radical (**Fig. 13**). Dedoping of materials eventually decreases the spin concentrations detected by a decrease in ESR and UV-Vis intensity. At the end of the scan, the trapped radical species gives rise to a higher ESR signal and absorption intensity compared to that observed at the beginning of the scan.

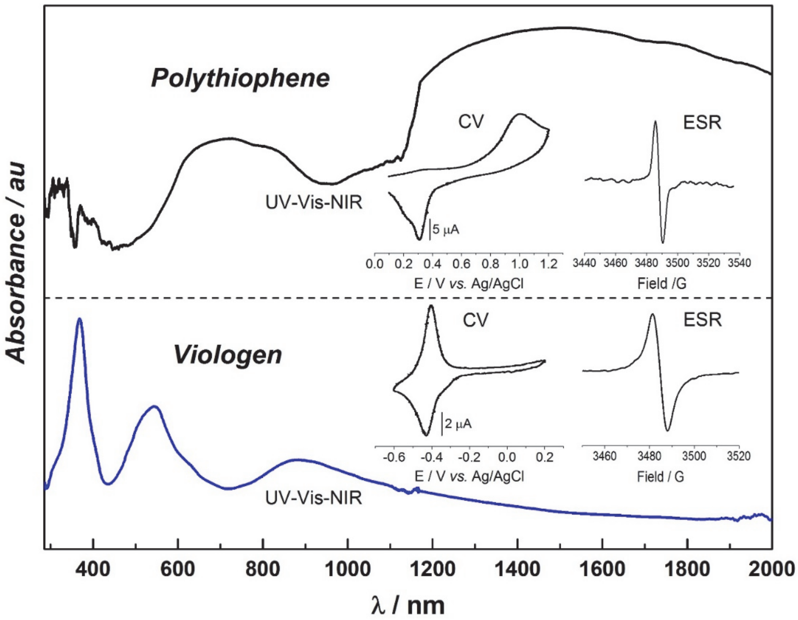


Fig. 13. A PTh-V film deposited on the Au mesh electrode during in situ ESR-UV-Vis-NIR spectroelectrochemical studies showing UV-Vis-NIR spectra at its fully oxidized (+1.0 V) and reduced (-0.6 V) state with their respective CV and ESR spectra as inset.

At anodic side (p-doping):

There is no reaction for viologens on the anodic side. Therefore, the anodic sweep is applied only on the PTh modified electrode and presented in publication **IV**. ESR comprises a single line (**Fig. 13**) during oxidation of PTh that increases linearly with potential scan. The UV-Vis spectra follow a similar trend where the absorbance at around 700 and 1400 nm evolved and increased (**Fig. 13**). With increase in the oxidation potential, there was no sign of evolution of any new band which is very typical for many conjugated polymers. These additional bands are normally assigned to polaron pairs or bipolaron formation. Since there was no sign of these processes, the obtained ESR and UV-Vis-NIR signals can be associated to only polaronic bands. Such behavior can be due to the formation of short polymer chains due to the dimeric structure of the precursor. During dedoping, the spins decreases and eventually vanished at the end of the scan.

Both techniques follow a similar potential dependence trend, signifying the sensitivity and importance of multi in situ ESR/UV-Vis-NIR spectroelectrochemistry towards precise structural investigation.

5. CONCLUSIONS AND OUTLOOK

In conclusion, this thesis provides a detailed study on the structural and electrochromic properties of viologen/polyviologen based conjugated polymers and composite structures. Starting from the synthesis, the electrochemical fabrication of different electroactive thin films was assembled on the electrode surfaces for their electrochemical and spectroelectrochemical characterization. Finally, the different films were tested for their electrochromic properties and the effect of structural modifications on the electrochromic parameters was evaluated.

The main conclusions based on each publication are:

I. Since the reduction process of cyanopyridinium to viologen is well-established, a new cyanopyridinium based monomer was synthesized and reductively electropolymerized to yield polymeric viologen species at the electrode surface. The structural investigations proved a successful polyviologen formation via coupling of 4-cyanopyridyl radicals. Spectroelectrochemical investigations endorse single line ESR spectra and characteristic viologen absorption features.

II. The above mentioned monomer was mixed in a graphene oxide aqueous dispersion and utilized for electrodeposition of polyviologen-reduced graphene oxide composite films at the electrode in a cathodic potential window. The composite films were exclusively characterized by FTIR, Raman, XRD, XPS, SEM and in situ UV-Vis spectroelectrochemistry and structural changes were analyzed. Besides successful composite assemble, an enhancement in the electrochromic cycle life was observed in composite films compared to those of pristine polyviologens. High electrical conductivity and high surface area offered by graphene sheets together with non-covalent interactions between viologen cation and anionic graphene oxide is accounted for such improvement.

III. A thiophene monomer with cyanopyridinium functionality was synthesized and copolymerized with another thiophene monomer. A stable, insoluble copolymer film was obtained and characterized thoroughly by using cyclic voltammetry, FTIR, SEM and UV-Vis spectroelectrochemistry and structural differences between homopolymers and copolymer were studied. The copolymer film showed multi-electrochromic properties due to the involvement of viologen in the polythiophene structure.

IV. A thiophene monomer with pendant viologen moiety was synthesized and electropolymerized. The ESR/UV-Vis-NIR spectroelectrochemistry showed single line ESR and characteristic absorption bands for viologen and polythiophene derivative films during cathodic and anodic scanning, respectively. Addition of such pendant viologen into the polythiophene backbone was found to enhance the electrochromic contrast of the overall film and showed good thermal stability.

The thesis offers a novel approach towards the synthesis of polyviologens, via successive electroreduction of a unique cyanopyridinium based precursor, which is electrochemically stable and appropriate for EC applications. The polyviologen forms highly stable composite films with reduced graphene oxide showing enhanced long term durability of the viologen electrochrome, greatly desired for progressive field of ECDs. Although, viologen based polythiophene structures have also been proposed, their stability is a concern towards device applications. Nevertheless, polythiophenes with pendant viologen moiety synthesized in this work is more stable in comparison to the similar structures reported previously and found to sustain several EC switching cycles without any significant degradation. Moreover, these structures were thoroughly studied by using specialized multi in situ techniques, which provide detailed insights into the structural aspects necessary to understand the absolute properties of these materials. Future directions of this work could be towards utilizing polyviologen derivatives in the ECD assembly. Addition of nanostructured materials has been found to improve the EC performance of viologens. Therefore, fabrication of ECDs based on polyviologens and its composites with nanomaterials could also be tested aiming at durable ECD performance. A polythiophene derivative with pendant viologen could be more suitable for multicolored ECDs. I believe that the work presented in this thesis is very fundamental touching the basics of viologen/polyviologen EC materials and certainly valuable considering high demand for durable smart windows and displays. Though, some experiments could still be improved and some interpretations might be considered as intermediate, the study proposes strong guidelines for further work on polyviologen based ECDs.

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Turku, April 2016

Bhushan Gadgil

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