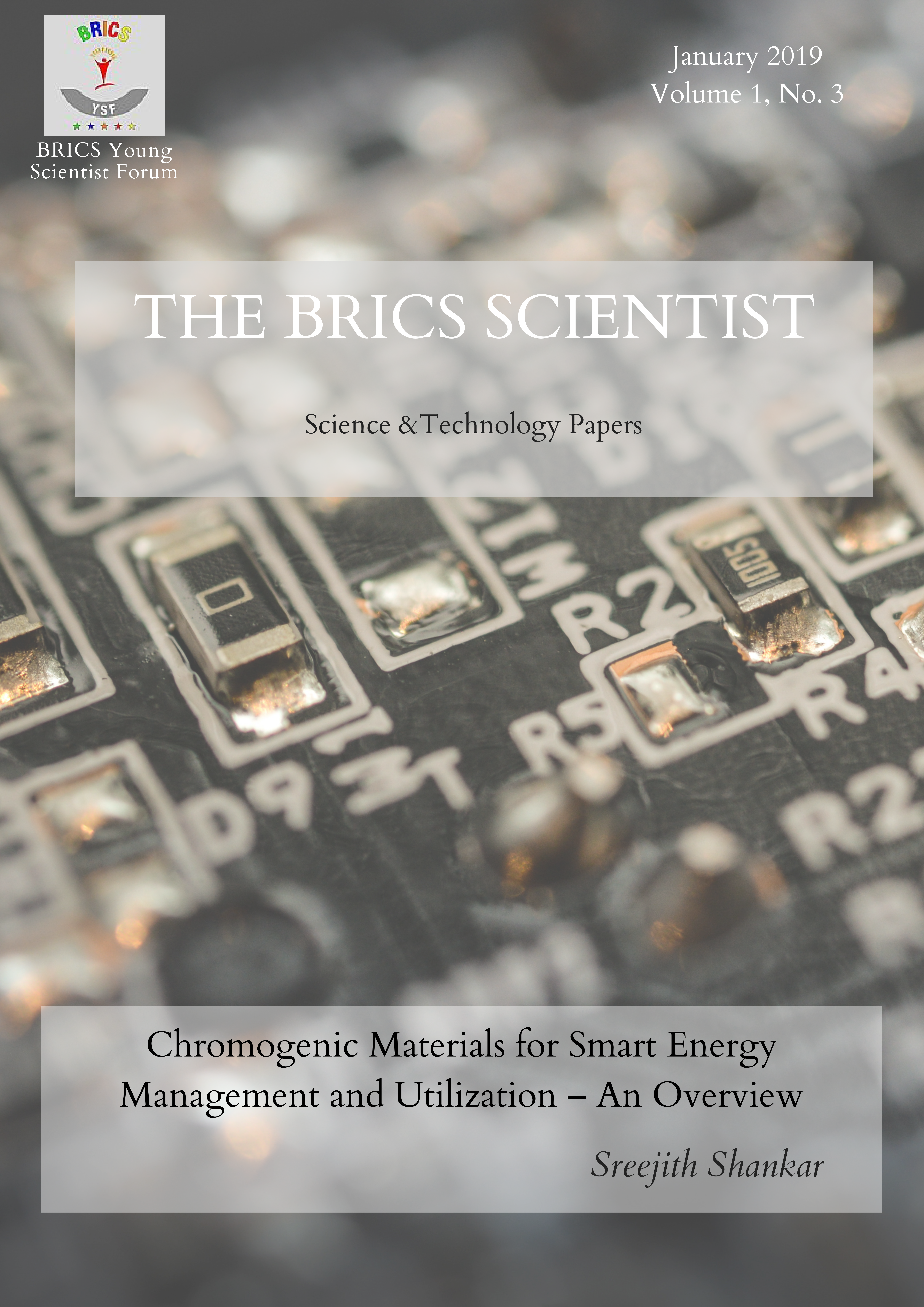

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Chromogenic Materials for Smart Energy Management and Utilization – An Overview

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Introduction

Stimuli-induced control and modulation of the functional properties of molecules and molecular assemblies has, to a great extent, revolutionized the area of supramolecular chemistry. Hence the development of stimuli-responsive materials has been a thrust area of research in various interdisciplinary approaches towards the realization of smart materials [1-4]. The unprecedented possibilities for modulating the optical properties of chemical systems from nano to macroscopic level under electrically stimulated conditions has led to a watershed moment in the area of optoelectronic materials and devices [5-9]. The active research in this field over the past couple of decades has largely been due to the increasing demand for smart technology applications such as smart windows, optical memory devices, improved display technologies and sensors. Chromogenic materials are a family of 'smart materials' that can change their optical properties in terms of absorbance, reflectance or emission via the application of an electric voltage, temperature, light, etc.

Type	Stimulus	Type	Stimulus
Gasochromism	Gas-hydrogen/oxygen redox	Piezochromism	Mechanical pressure
Solvatochromism	Solvent polarity	Cathodochromism	e-beam irradiation
Vapochromism	Vapor chemical polarity	Radiochromism	Ionising radiation
Photochromism	Light	Magnetochromism	Magnetic field
Thermochromism	Heat	Biochromism	Biological entity
Ionochromism	Ions	Chronochromism	Passage of time
Halochromism	pH	Aggregachromism	Dimerisation/aggregation
Mechanochromism	Mechanical actions	Crystallochromism	Changes in crystal structure
Tribochromism	Friction	Electrochromism	Electric current

Table 1. Types of chromism and the respective external stimuli

Electrochromic (EC) materials are a family of 'smart materials' that can change their optical properties in terms of absorbance, reflectance or emission via an electrochemical redox process under the application of an electric voltage [10-11]. The tunable optical properties of these materials directly reflect in the light and heat transmission properties of the surface on which they are immobilized. This leads to efficient energy management and utilization scheme, especially for glare reduction and indoor lighting/cooling reduction. For instance, the dynamic modulation of heat and light transmission through these smart windows could be directly correlated to the energy consumption in maintaining the indoor temperature and visibility; thus a magnanimous portion of domestic and industrial energy consumption could be reduced. Further, the energy released during the switching process may be utilized for lighting or storage applications. Despite being an actively researched arena, significant efforts are still needed to develop such efficient materials, and to take these interactive smart systems beyond academic interest. According to "Electrochromic Glass Market by Material (Polymers, Nanocrystals, Viologens), Device (Windows, Mirror, Display, Application (Commercial, Residential, Transportation, Retail, Hospitality), and Geography - Global Forecast to 2020", the total electrochromic glass market was valued at $1.17 Billion in 2013 and is expected to reach $2.59 Billion by 2020, at an estimated CAGR of 12.27% between 2014 and 2020.

Generally, the change in optical properties of EC materials leads to reversible transition between colored to transparent (bleached) or between two or more colored states. The choice of commercially acceptable EC materials is limited by the following demands: high thermal and photochemical stabilities, high contrast ratio, fast and reversible switching, high coloration efficiency, low voltage of operation and easy processability. Several classes of electrochromic materials - transition metal oxides, viologens, conjugated conducting polymers, metal coordination complexes - are reported in the literature [8,12]. Most majority of these reports qualify as EC materials for their academic impact, but practically suffer from low to moderate efficiency, inferior redox, photochemical and cycling stability, write-erase inefficiency and laborious processability. Hence the current research in this field is actively driven by the quest for new generation EC materials with uncompromising performance. However, the potentials of molecule-based nanoscale metal-organic assemblies as homogeneous thin film electrochromic materials and their fabrication into solid state electrochromic devices (ECDs), though highly promising, are yet underexplored [13-17]. The applications of electrochromism includes smart mirrors (Figure 1), windows and displays, electronic papers, e-skins, strips as battery state-of-charge indicators, sunglasses, reusable price labels, protective eyewear, controllable aircraft canopies, glare-reduction systems for offices, devices for frozen-food monitoring, camouflage materials, chameleonic fabrics, spacecraft thermal control, optical iris for camera lens, optical information and storage, etc.

Figure 1. The electrochromic windows in a Boeing 787 Dreamliner that allows the passengers to adjust 5 levels of visibility. Image credit: Quora.com©

Discussion

Polymeric thin film based devices have been of tremendous interest to the material scientists due to their applications in solar cells, optoelectronic devices, sensors, display devices, etc. The unprecedented demand for smart technologies is driving the market for stimuli-responsive materials, especially electrochromic materials [6,8-9,18]. In conjugated polymers, low to high oxidation states can be achieved and have characteristically low band gaps [19-20]. A large number of the already reported EC materials suffer from low performance, efficiency, stability and processability. Hence the demand for new high performing, stable and easily processable EC materials has attracted much attention over the past few years. In contrast to the deeply investigated and well documented polymer chemistry, metal-organic coordination-based EC materials are yet partially exploited for their huge potential towards smart applications. In fact, only a very few examples of metal-organic molecular EC systems are reported [13-17].

Transition metal coordination complexes exhibit electrochromic properties due to metal to ligand charge transfer, intervalence charge transfer, intra ligand excitation and visible region electronic transitions [8,12]. A few reports on bipyridyl complexes $[M(bipy)_3]^{2+}$ (M = Fe, Ru, Os), that are coloured in M^{II} (ground) state and colorless in the M^{III} (oxidized) state, clearly demonstrates the potential of these class of materials as candidates for practical EC systems [8,13-14]. Metallopthalocynines and Prussian blue are yet another class of metal coordination complexes with EC properties [8]. Most of these reported systems have delocalized π electron system, rigid network and stability. Metal-organic chromophores in general possess fast redox reactivity, stability and reversibility. The possibilities of polymerization, dip coating, spin coating, drop casting, spray coating, layer by layer deposition and printing make these class of materials highly favorable in terms of processability and film fabrication. Moreover, slight changes in the ligand design or choice of metal salts may lead to color tunability, leading to an almost complete span of the RGB color space [13-14].

The building and architectural sector uses Building sector accounts for >76% of the total electricity usage. Energy spent on cooling accounts for approx. 40% of the indoor energy utilization. Net Zero Energy Buildings is indeed the need of the day. Two possible ways to mitigate the current energy demands are: (i) use of renewable energy sources (Eg: Solar, smart grids, etc.) and (ii) smart management in energy utilization. Energy efficient buildings may be realized via deliberately designing (Eg: maximum use of natural light) them or integrating the components (Eg: energy saving) required. Smart Windows offer multifarious advantages including color tunalibility, aesthetics, dynamic modulation of light and heat transmission, etc. The control over light and heat entering the building will directly impact the energy required for indoor lighting and cooling. In fact, energy saved is energy produced.

There are four different classes of materials that are generally employed for electrochromic applications: (a) transition metal oxides, (b) viologens, (c) conjugated conducting polymers and (d) metal coordination complexes, phthalocyanines and prussian blue. The electrochromic color switching in these materials emanate via different mechanisms. While the electrochromic behavior of transition metal oxides originates from intervalence charge-transfer (IVCT) optical transitions, optical charge transfer between the +1 and 0 valent nitrogens is responsible for the redox color switching in viologens. Optical bandgap between the valence band and the conduction band determines the electrochromic properties of conducting conjugated polymers. The electrochromism in metal complexes and related coordination complexes involves several electron transfer processes including MLCT, IVCT, intraligand excitation, and related visible-region electronic transitions.

For a practical electrochromic device, the following parameters are highly desirable.

(a) High contrast ratio (defined as the difference in transmittance in the visible spectrum)
(b) Low response time (defined as the time for the color change to become 95% of the ultimate change in %T)
(c) High coloration efficiency (defined as the change in optical density per unit area of the electrode for a given wavelength)
(d) Write-erase efficiency (defined as the fraction of the originally formed colored state that can be electrochemically bleached)

(e) Good cycle life (defined as the number of write-erase cycles that can be performed before significant extent of degradation)

Use of electrochromic systems for efficient energy management has attained notable progress over the past few years. Many research groups have tried to explore and develop a knowledge base about material/component requirements and associated challenges [18-20]. Research in this field has been focused on developing electrochromic displays, wearable devices and smart windows with a variety of materials and with varying degree of success [5-9]. Efforts Were also made towards addressing systems that can offer engineering flexibilities [13-14,21-22]. Many inorganic and organic EC systems are proposed, however, much less hybrid materials have been in the lime light until recently [13-14,23-25]. As mentioned previously, several classes of electrochromic materials - transition metal oxides, viologens, conjugated conducting polymers, metal coordination complexes - are reported in the literature [8-9,12-14,21-25]. Many of these materials suffer from low to moderate efficiency, inferior redox, photochemical and cycling stability, write-erase inefficiency and laborious processability. However, the potentials of molecule-based nanoscale metal-organic assemblies as homogeneous thin film electrochromic materials and their fabrication into solid state electrochromic devices (ECDs), though highly promising, are yet underexplored and only a handful reports are available till date [13-17].

Most of the reports in electrochromic materials have emerged out of curiosity driven intensive fundamental research. The electrochemical and photochemical properties of metal-organic materials have already been studied in detail [26-28]. Several research groups (Nishihara, Zharnikov, Gulino, van der Boom) have reported on the electron transport properties of metal-organic systems on surfaces [15-17,29-34]. Electrochromic coatings of metal-organic assembles on transparent conducting oxides have been achieved via several techniques: (a) layer-by-layer (spin or dip coating) [13-14,16,34-35], (b) supramolecular polymerization [17,36-37] and (c) organic functionalization (electropolymerization) [38-40]. Meyer, Elliot and co-workers have demonstrated the applicability of metal-pyridine complexes as electrochromic materials [39,41-43]. Later, van der Boom and co-workers have reported excellent electrochromic properties of metal-bipyridine complexes on rigid and flexible substrates [13-14,34]. Terpyridine complexes of iron and ruthenium are also studied for their electrochromic behavior by Zenkina *et al.* [44]. Kurth and Higuchi have recently demonstrated a modular approach towards electrochromic supramolecular metallopolymers as candidates in solid state devices leading to color to colorless and color to color electrochromism [17,36-37]. Reversible electrochemical photoluminescence switching has also been studied using iron-based supramolecular polymers [38]. Binuclear ruthenium complexes covalently connected with a redox active amine was shown by Zhong and co-workers to undergo several color to color transitions due to multiple redox states available in the system [40].

Subrahmanyam's group has published numerous important papers on electrochromics and transparent conducting oxide deposition [45-46]. Pahal *et al.* have explored electrochromism and redox switching of cobalt hexacyanoferrate–polyaniline hybrid films with comparably high coloration efficiency of 262 cm^2/C at 687 nm [47]. The same group has fabricated ECDs on flexible substrates using organic EC materials like zwitterionic viologens and PEDOT [48]. Tungsten oxide and molybdenum oxide based electrochromic coatings on glass have also been studied [49-51]. Fabrication of a large area, high-performance, transparent conducting electrodes using a spontaneously formed crackle network as template has also been reported [52]. This novel approach is particularly important as it is compatible with flexible substrates that enable fabrication of flexible ITO free ECDs. Sindhu and co-workers have several articles to their credit on polymer-based organic electrochromic materials [53-55]. Studies were also directed towards ITO-free solution-processed flexible electrochromic devices based on PEDOT:PSS with good conductivity and figure of merit [56]. The electrochromic properties of polycarbazole films to delineate the mechanism of switching reaction in semiconducting films was reported already in the late 90s [57]. The electrochromic performance of nickel oxide thin films formed via electrodeposition has also been investigated in detail and low response times (less than 6 s) and good reversibility were achieved [58]. Fast electrochromic displays using as facilitating materials (tetrathiafulvalene-graphene nanoflakes) have also been reported very recently. A switching time less than a second was achieved with coloration efficiencies >200 cm^2/C. [59]. Deb and Joseph have also published several reports on transition metal oxide (inorganic) and polymeric (organic) electrochromic materials and devices over the past few years [60-63].

The significance of using metal complexes as electrochromic materials lies in the vast coloration possibilities on offer and are potential candidates for practical EC systems. These materials possess well defined and reversible metal redox reactions. The structural identity of metal coordination complexes offers a delocalized π-electron system leading to rigid networks and better stability. Highly favorable electrochromic switching is guaranteed by fast redox reactivity, high electron conductivity and coloration efficiency and reversibility, apart from offering facile processability and film/device fabrication possibilities (polymerization, dip coating, spin coating, drop casting, spray coating, layer by layer deposition and printing). Color tunability in the whole of the RGB color space may be achieved via the rational choice of ligand, metal or ligand-metal combination as well as ligand structure modifications. Moreover, this class of materials represents one of the least investigated family of electrochromic materials.

Highly efficient and fast electrochromic switching using bipyridine based metal complexes has been demonstrated by Shankar, van der Boom and co-workers [13-14]. The electrochromic assemblies were fabricated via a layer-by-layer assembly (dip and spin coating) using a Palladium (II) based cross-linker. These assemblies showed high contrast ratio (up to 65%), low response times (<500 ms) and excellent coloration efficiencies (>1400 cm^2/C). High thermal (>5 months at 70 ^oC) and electrochemical (>1.2 × 10^5 cycles) stabilities were also achieved. Slight changes in the ligand structure has led to drastic changes in the color profile of the electrochromic assemblies and a large area of the RGB color space was covered using four metal complexes. Electrochromic thin films were realized on rigid (glass) and flexible (PET) substrates. Single electrochrome laminated devices (SELDs) were fabricated and efficient color switching under the application of comparably low potentials was observed. Similar LbL assemblies were also used to demonstrate the control over electron transfer in surface confined molecular architecture.

Conclusions and Outlook

Sustainable energy solutions and better energy efficiencies are indeed the demands of an ever growing society. Recent developments in electrochromic research has bestowed an unprecedented promise towards meeting this challenging demand by implementing smart management in indoor energy utilization. An affordable smart glass technology with high performance is expected to revolutionize the coating sector. However, the industrial scale production of electrochromic materials, coatings and device fabrication is still a big challenge. Development of multifunctional and efficient electrochromic materials with high stability, better coating techniques, device components and engineering will undoubtedly lead to an electrochromic revolution that is already shaping behind the stage. With the current pace and intensity of R&D happening in this field, the large scale production of electrochromic smart windows capable of managing the utilization of energy, especially for indoor applications, and its commercialization may be accomplished in the near foreseeable future.

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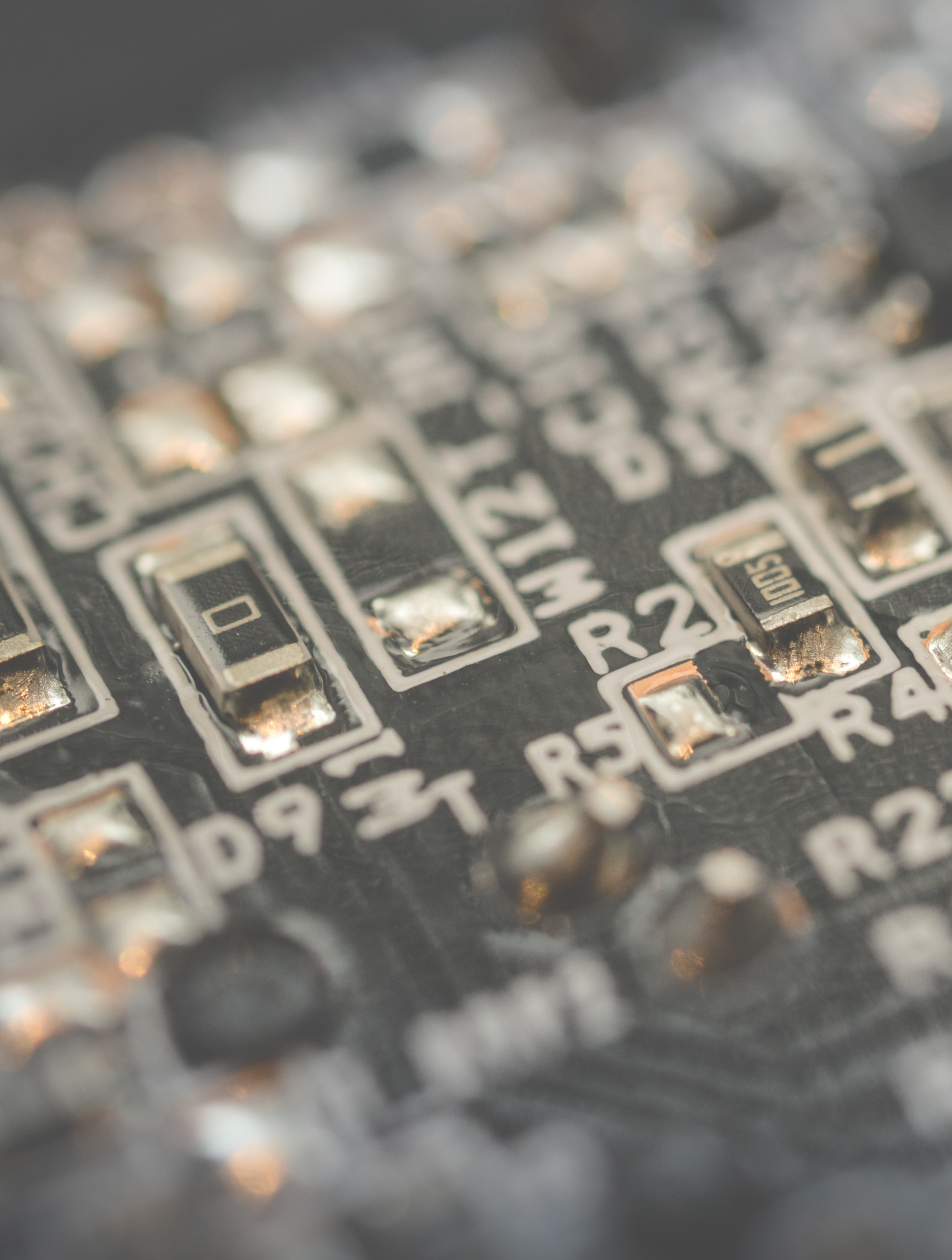
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