

Near-infrared absorbing organic materials*

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Abstract: Organic solids and polymers that absorb in the near-infrared (NIR) region (1000–2000 nm) represent a class of emerging materials and show a great potential for use in photonics and telecommunications. The radical anions of stacked aromatic imides, fused porphyrin arrays, polythiophenes, sandwich-type lanthanide bisphthalocyanines, semi-quinones, and mixed-valence dinuclear metal complexes are a few known examples of NIR-absorbing organic materials. Most of these NIR-absorbing materials are also electrochemically active or electrochromic (EC). This brief review covers several types of NIR-absorbing organic materials and discusses their potentials for applications in EC variable optical attenuators (VOAs).

INTRODUCTION

Most organic materials that are either being used or explored in optoelectronic devices (e.g., organic light-emitting diode display, liquid-crystal display, electrochromic (EC) display, and photovoltaic device) interact with or emit the light in the ultraviolet and visible region (ca. 250–800 nm). Typical materials include small molecules such as dyes, pentacene, and fused aromatics [1], conjugated oligomers and polymers [2], and transition metal-containing polymers [3]. On the other hand, organic materials that are optically responsive at the wavelengths in the near-infrared (NIR) region (e.g., 1000–2000 nm) are becoming an emerging material, mainly because of their interesting but less studied electrical/optical properties and foreseeable applications in photonics and telecommunications (e.g., for fiber optic communications at the wavelengths of 1310 and 1550 nm). NIR-absorbing organic materials are low bandgap materials (e.g., 0.75 eV or 1550 nm) and thus must contain an extended conjugation or mixed-valence system. For applications in photonics and telecommunications, there are still no photovoltaic, EC, optical switching, and other optoelectronic devices that are operated at the 1310- or 1550-nm wavelength and constructed with organic materials.

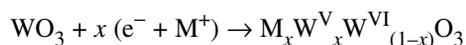
Organic materials that are electrically, optically, or thermally active in the NIR region, specifically at the telecommunication wavelengths (e.g., 1310 and 1550 nm) can in principle be used in a device for optical attenuation and absorption or antireflection, owing to their unique electrical and optical properties, low-cost fabrication, and feasibility for use in a monolithically integrated optical device. For a switching device such as electrically controlled variable optical attenuator (VOA), both anodically and cathodically NIR-coloring materials are ideally needed. In a device for NIR light absorption, a stable, NIR-absorbing material with high absorption coefficient at the wavelength of interest is desired.

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NIR-ABSORBING INORGANIC MATERIALS

Metal oxides such as tungsten oxide (WO_3), IrO_x , and Ta_2O_5 have been known for many years to be EC in the visible region and have been extensively investigated as an EC thin film [4]. The application has been realized in smart windows and antireflection rear mirrors in cars. The film of tungsten oxide deposited on an electrode can be electrochemically reduced in the presence of an electrolyte according to the following electrochemical reaction:



where M^+ is H^+ or Li^+ , x is the so-called ion insertion coefficient. Reduction of tungsten oxide involves entry of electrons into the tungsten oxide film from the electrode and of proton or lithium ion from other (electrolyte-facing) side. The reduced tungsten oxide is typically deep blue in color and also absorbs broadly in the NIR region. The absorbance in the vis–NIR region depends on the degree of reduction or ion insertion coefficient and as well WO_3 film morphology. Figure 1 shows the vis–NIR absorption spectra of tungsten oxide as sputtered on ITO electrode under different reduction potentials.

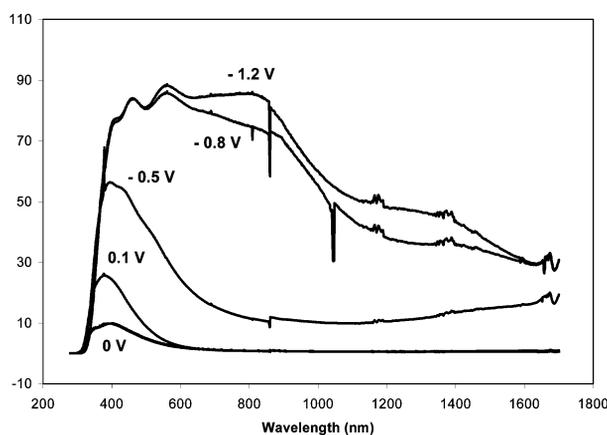


Fig. 1 Vis–NIR absorption spectra of WO_3 film on ITO under different reduction potentials in acetonitrile containing 0.1 M LiClO_4 .

NIR-ABSORBING ORGANIC MATERIALS

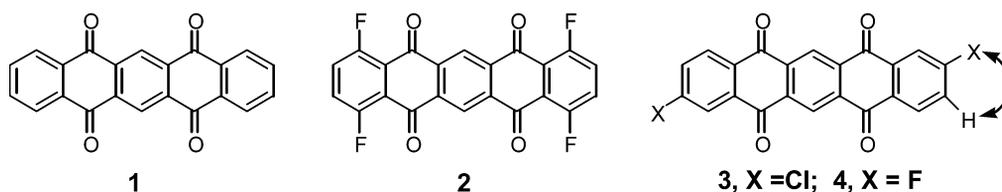
Several types of NIR-absorbing organic materials are reported in literature, including (1) stacked naphthalimide anion radicals [5], (2) fused porphyrin arrays [6], (3) doped polythiophenes and other related conducting polymers [7], (4) sandwich-type lanthanide bis-phthalocyanines [8], (5) radical anions of conjugated diquinones (also called semiquinones) [9], and (6) mixed-valence dinuclear metal complexes [10]. Considering the scope of this review, the last two types of NIR-absorbing materials are to be discussed in detail.

NIR-absorbing semiquinones

For a long time, quinones have been known as disperse dyes and also as electron acceptors. Although monoquinones and their corresponding radical anions have been thoroughly investigated, the radical anions of aromatic diquinones or semiquinones, have only recently received some attention, due to their unique NIR absorbing and semiconducting properties [11]. Although a variety of diquinones were prepared and studied by Miller and his coworkers more than 10 years ago, there is still a need to system-

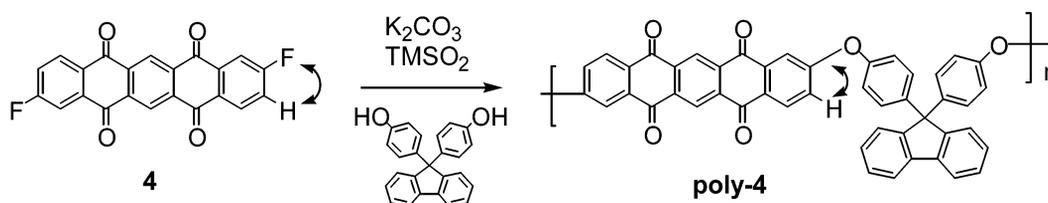
atically probe the NIR properties of aromatic diquinones and derivatives and explore the potential of this class of NIR-absorbing materials for device applications.

Since pentacenediquinone is known for its NIR electrochromism, a series of substituted pentacenediquinone analogs can be envisioned and prepared for investigating the substitution effect on the electrochemical and NIR EC properties. The positions of the substituents on pentacenediquinone may also affect the EC property. Pentacenediquinone (**1**) was prepared in two steps, by reaction of pyromellitic dianhydride and benzene and subsequent intramolecular acylation/cyclization of the keto-acid intermediate in concentrated sulfuric acid [12]. Thus, starting from the substituted benzenes, the functional groups were introduced onto the two external aromatic rings of pentacenediquinone to afford substituted pentacenediquinones **2–4**. The keto-acids mixtures were best cyclized in a melt of AlCl_3 and NaCl to form the corresponding pentacenediquinones.



The radical anion or semiquinone of compound **1** absorbs at 1335 nm. Substitution with the electron-withdrawing substituents like F and Cl causes a red shift in absorption toward 1500 nm for the corresponding semiquinones. In the case of dichloropentacenediquinone **3** and difluoropentacenediquinone **4**, their semiquinones absorb at 1372 nm and 1360 nm, respectively. The number of substituents and the substitution position on the external aromatic rings seem to be also of influence, since the semiquinone of tetrafluoropentacenediquinone **2** shows a maximum of absorption at 1508 nm.

Considering the device applications, these pentacenediquinones must be evaporated onto a substrate (e.g., ITO electrode) to form a thin film or incorporated into a polymer which can be cast or spin-coated on the electrode. To obtain a polymer containing the NIR-absorbing semiquinone moiety, the pentacenediquinone moiety can be introduced into the polymer backbone, as an example, via nucleophilic displacement polymerization of a functionalized pentacenediquinone (ca. difluoride **4**) and a bisphenol such as 9,9-bis(4-hydroxyphenyl)fluorene (Scheme 1). A regioisomeric mixture of difluoride **4** was used in polymerization, which afforded the corresponding polyether (**poly-4**). The **poly-4** was soluble in NMP and could be cast into a tough film on substrates (e.g., ITO).



Scheme 1 Synthesis of polyether **poly-4**.

Cyclic voltammogram of compound **4** showed two reversible couples (first $E_{1/2}$ at 200 mV and second $E_{1/2}$ at 642 mV vs. NHE) attributable to the two one-electron couples for its radical anion and dianion intermediates. Accordingly, the radical anion species showed a strong absorption at 1360 nm and the dianion species had a peak at 890 nm. The **poly-4** had similar electrochemical behavior as compound **4**. The radical anion of the polymer film (**poly-4**) on ITO was prepared electrochemically in a solution of 0.1 M LiClO_4 as the supporting electrolyte, which also showed a broad NIR band (Fig. 2). Interestingly enough, this semiquinone polymer alone on ITO was found to be stable in air over months.

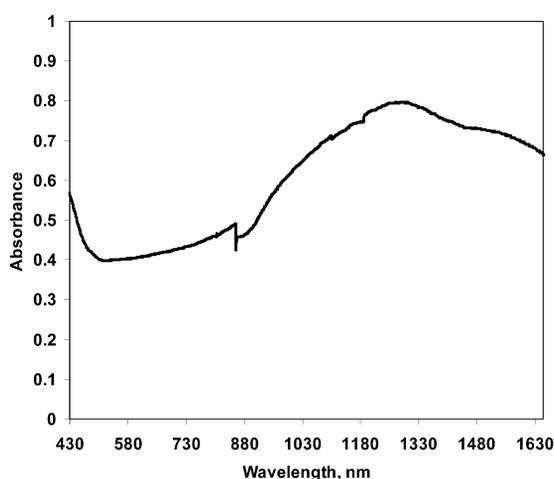
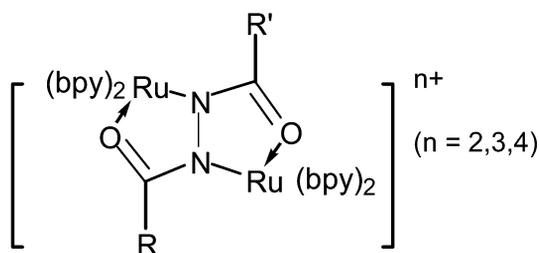


Fig. 2 Absorption of the radical anion of poly-4 on ITO electrode.

NIR-absorbing dinuclear mixed-valence ruthenium complexes

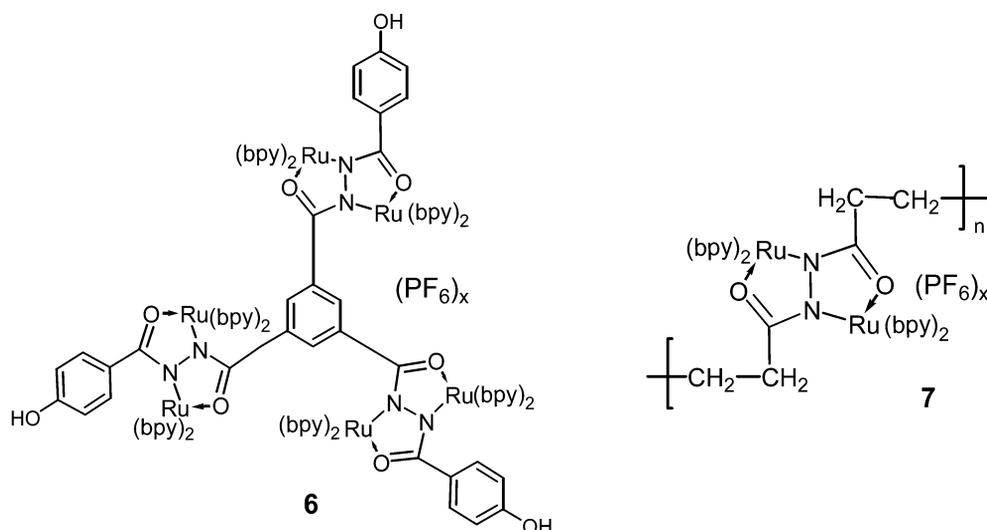
The study of symmetric d^5/d^6 mixed-valence dinuclear ruthenium(II/III) species has contributed significantly to the understanding of bonding and electron transfer in and between metal complexes such as a classical example of the molecule-bridged Creutz–Taube ion [13]. The dinuclear mixed-valence ruthenium complexes are known to be EC and NIR absorbing [14]. We have prepared a series of dicarbonylhydrazido ruthenium complexes (DCH-Ru) **5** (Fig. 3) [15]. When the dinuclear metal center is oxidized from the Ru^{2+}/Ru^{2+} to Ru^{2+}/Ru^{3+} states, the complexes **5** display an intense absorption (e.g., $\epsilon \sim 10^4 M^{-1} cm^{-1}$) centered at 1550 nm. At the Ru^{2+}/Ru^{2+} state, it shows no absorption within 1000–2000 nm. Other unique features of this type of ruthenium complexes include the stability toward water, air, and strong base (e.g., NaOH) and high thermal stability ($>300\text{ }^\circ C$). In addition, these materials have been demonstrated to be a promising material for optical attenuation at the telecommunication wavelength of 1550 nm [16].



| R, R' | R, R' |
|--------------------------------------|---|
| Ph, N(CH ₃) ₂ | CH ₃ OPh, N(CH ₃) ₂ |
| Ph, CH ₃ | CH ₃ OPh, CH ₃ |
| Ph, CH ₃ OPh | CH ₃ OPh, CH ₃ OPh |
| Ph, Ph | CH ₃ OPh, NO ₂ Ph |
| Ph, CF ₃ | CH ₃ OPh, CF ₃ |
| Ph, NO ₂ Ph | NO ₂ Ph, NO ₂ Ph |

Fig. 3 Dinuclear DCH-Ru complexes **5**.

There are a number of ways to incorporate the DCH-Ru moiety into processable polymers, oligomers, and dendrimers. A common method is to first synthesize the corresponding ligand polymer and then introduce the ruthenium metals through the exchange reaction with *cis*- $Ru(bpy)_2Cl_2 \cdot 2H_2O$ which is readily available [17]. A film-forming DCH-Ru [G]-1 dendrimer (**6**) was prepared by this ligand-exchange method [18].



A viable synthetic route was established for the synthesis of the linear DCH-Ru polymers, such as **7**, based on the use of the polymeric DCH ligand. The ligand polymer, as synthesized from equimolar amounts of each monomers in NMP using the method of Frazer et al. [19], was found to be sparingly soluble in DMF, acetonitrile, and DMSO. Its inherent viscosity was measured in DMSO and was found to be 0.26 dl/g, indicative of low molecular weight. The synthesis of polymer **7** was performed in the same manner as for the structurally similar DCH-Ru complexes. Polymer **7** was thus obtained as brilliantly purple-colored solids.

Polymer **7** showed no glass transition temperature by DSC and had the onset temperature for 5 % weight loss in nitrogen at 202 °C. Electrochemistry was performed on polymer **7** as a thin film on a Pt disk electrode in chloroform containing 0.1 M TBAH. The CV trace showed two quasi-reversible couples attributable to the two one-electron couples per dinuclear DCH-Ru fragment in the polymer. The first $E_{1/2}$ potential was found to be 310 mV (vs. silver pseudo-reference electrode at 10 mV/s scan rate), and the second one appeared at 920 mV. The peak-to-peak separations for both couples ranged between 75 and 272 mV. The magnitude of this separation was generally higher vs. the DCH-Ru complexes **5** and can be attributed to lower kinetics due to the uptake and expulsion of electrolyte from the film. The UV-vis-NIR spectra for polymer **7** in its reduced, mixed-valence, and oxidized form were taken in situ with the polymer on ITO (Fig. 4). In its mixed-valence state, an absorption peak was found to be centered on 1530 nm, which is consistent with the presence of isolated DCH-Ru fragments within a saturated polymer where no electronic interaction between the DCH-Ru fragments exists.

Similar to polymer **7**, many linear DCH-Ru polymers could be designed and prepared, as long as the ligand polymers could be made available. An interesting attempt was made in our group to connect the DCH-Ru monomeric units through a conjugated moiety such as the acetylene unit, in order to investigate a conceivable “metal–ligand–metal–ligand” type of the extended conjugation through a number of the DCH-Ru units.

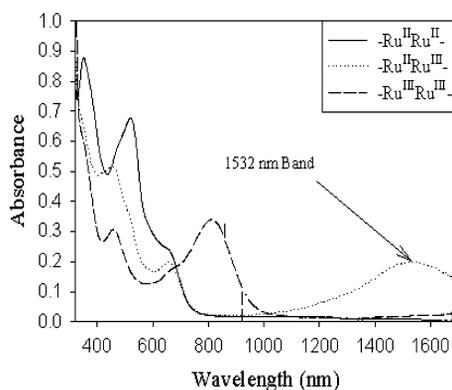


Fig. 4 Spectroelectrochemical spectra for the film of polymer **7** on ITO electrode in chloroform with 0.1 M TBAH.

DEVICE APPLICATIONS

NIR-absorbing organic materials are likely to find applications in the areas of photonics and telecommunications and in the devices that operate at the wavelengths within the NIR region. There is a need to find a niche market or application for organic thin film-based devices, rather than aiming at replacing the semiconductors and silica that are currently used in devices. VOA is an essential component for gaining control of optical signals in wavelength-division multiplexing networks and for dynamic channel power regulation and equalization in cross-connected nodes. Various types of VOA devices have been explored, such as microelectromechanical devices [20], sliding-block mechanical devices [21], side-polished fiber devices [22], and thermo-optic systems [23]. At present, a major challenge in the telecom industry is to develop inexpensive planar integrated VOA devices in response to the ever-increasing data transmission and processing rates, as well as lowering fabrication costs.

Electrochromic variable optical attenuator (ECVOA)

Considering their NIR EC property and feasibility of tuning the electrical and optical properties through structural modification, a new electrochromic VOA (ECVOA) can be realized using NIR EC materials—inorganic, organic, or both materials together. ECVOA works in the same principle as an EC device and employs EC materials that exhibit reversible and stable optical changes at the telecommunication wavelengths. If under one applied voltage the EC materials on the electrodes in ECVOA exit in a redox state that is NIR-absorbing, the materials should be in an opposite redox state at another voltage that is NIR-inactive. When the NIR light is directed through an ECVOA device, the light will either pass through or be absorbed at two distinct applied voltages and thus can be attenuated variably depending on the degree of the redox reaction or applied voltage. Accordingly, basic requirements for the materials to be used in ECVOA should include high EC efficiency, fast switching speed at low voltages, good film-forming property, and stability.

In principle, the anodically NIR-coloring DCH-Ru materials (e.g., **6** and **7**) and cathodically NIR-coloring materials such as WO_3 and **poly-4** can be used individually in a single-layer device or in pair in a double-layer device for optical attenuator at telecommunication wavelengths of 1300–1600 nm.

ECVOA device configurations

There are at least two types of ECVOA devices. One is a reflection device, such as device (a) in Fig. 5, and another is in a transmission device (Figs. 5b and 5c). For device (a), it consists of top and bottom electrical conductors sandwiching an EC material such as WO_3 , one being gold or aluminum and the other being highly transparent at the wavelengths of interest, such as doped single-crystal Si. To con-

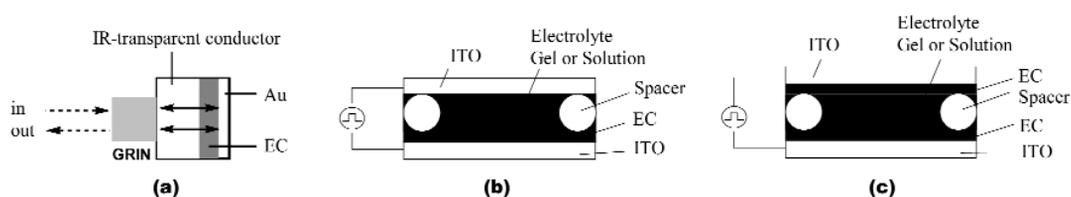


Fig. 5 Reflection and transmission ECVOA concept devices.

struct a fiber optic device, a GRIN lens is used and bonded to the EC device. A dynamic attenuation of 15 dB with a switching response of 5 dB/s at 1500–1600 nm has been demonstrated [24]. In the transmission device, either single EC layer (device b) or double EC layer (device c) can be employed. An electrolyte layer is used and could exist as a polymeric gel or a solution.

Single-layer ECVOA

A single-layer ECVOA based on thermally annealed WO_3 thin film in an electrolyte solution has been patented recently [xxv]. The device was demonstrated with an attenuation range from 0.26 to 40 dB at 1310 and 1550 nm and could achieve an attenuation of 30 dB in 10 s. However, the reverse process, from NIR colored to colorless, took 10–15 min to recover about 80 % of its transparency and up to 60 min for a full recovery.

Compared to metal oxides, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives show a much faster switching response (ca. in the ms range) [26]. However, for a single-layer EC device, its absorption coefficient is still low to allow for a VOA to operate in a transmission mode with a dynamic attenuation over 20 dB at the 1550-nm wavelength. Increasing the thickness of EC layer can improve the attenuation range, but significantly slows down the switching process or ion transport process.

We have recently demonstrated a viable approach to improving the attenuation range at reasonably fast response time by using a relatively thick film of an electrolyte-doped EC polymer. PEDOT is EC and has a strong absorption in the NIR region. Figure 6 shows the vis–NIR absorption spectra of PEDOT film (140 nm thickness) on ITO in 0.1 M LiClO_4 solution of propylene carbonate under different applied potentials. PEDOT as received is in the oxidized state and has a strong absorption in the NIR region (1000–2000 nm) with a peak maximum at about 1800 nm and an absorption coefficient of $\epsilon_{\text{ox}} = 2.8 \times 10^4 \text{ cm}^{-1}$ at 1550 nm. When a negative potential is applied, PEDOT changes to its reduced state that has a weaker absorption in the NIR region. It was found that at the -2.0 V potential, PEDOT has nearly zero absorption (or $\epsilon_{\text{red}} \sim 0 \text{ cm}^{-1}$ within the experimental error) at 1550 nm. Thus, a maxi-

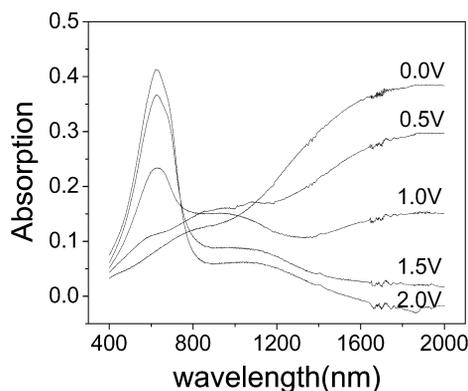


Fig. 6 Vis–NIR absorption spectra of PEDOT film (140 nm thickness) on ITO in 0.1 M LiClO_4 propylene carbonate solution under different applied potentials.

imum power of optical attenuation in the transmission mode that PEDOT could offer, relates to the difference between the absorption coefficients of the oxidized and reduced (or bleached) states, that is $\Delta\epsilon = \epsilon_{\text{ox}} - \epsilon_{\text{red}} = 2.8 \times 10^4 \text{ cm}^{-1}$. Accordingly, its attenuation per film thickness is calculated to be 27.7 dB/ μm at 1550 nm.

The ECVOA device (type b, Fig. 5) containing 400-nm-thick PEDOT film in solution of propylene carbonate containing ferrocene had the optical loss of 0.86 dB at the bleached state. It can achieve a dynamic attenuation range of 10.2 dB for 95 % recovery and with the switching time of 5 s (bleaching) and 7 s (coloring).

All-solid/gel double-layer ECVOA

To demonstrate the ECVOA device type (c), the DCH-Ru film was prepared by crosslinking of complex **6** and a triisocyanate and coated on ITO electrode and a thin layer of WO_3 electrochemically deposited on ITO as a complementary material [18]. A polymer electrolyte gel was used. The device showed only a small attenuation range of 5.4 dB at 1550 nm with a 5-s cycle, mainly due to slow ion conduction (Fig. 7).

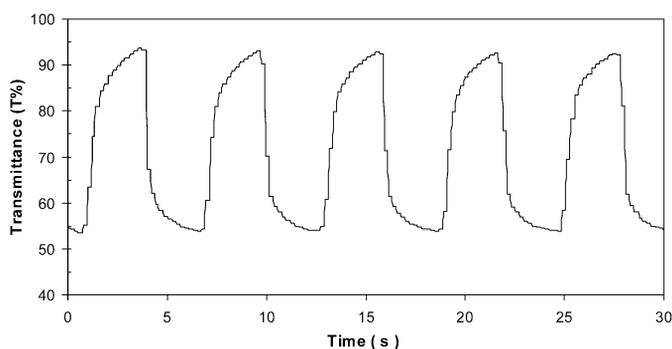


Fig. 7 Variation of transmittance for double-layer ECVOA containing **6** and WO_3 .

CONCLUDING REMARKS

The EC NIR materials only represent a fraction of a whole family of the emerging NIR organic materials. Although less known and studied, many others that are responsive in the NIR region, such as photochromic, thermochromic, optically active, photovoltaic, light-harvesting, and light-emitting organic materials, are both scientifically interesting and practically useful. New optoelectronic devices that are based on NIR organic and inorganic–organic hybrid materials and can operate at the wavelengths beyond human vision limit (ca. 800 nm) are becoming the targets for research and development, due to the needs of either intellectual curiosity or commercial applications.

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