Mixed-Valence Compounds as a New Route for Electrochromic Devices with High Coloration Efficiency in the Whole Vis-NIR Region

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Abstract: Electrochromic devices (ECDs) that allow the modulation of light transmission are very attractive in the research field of energy saving. Here all-in-one gel switchable ECDs based on mixed-valence electroactive compounds were developed. The use of the thienoviologen/ferrocene couple as cathode and anode, respectively, leads to a significant electrochromic band in the visible range (550–800 nm), with a color change from yellow to green, and to a lower band in the NIR region (1000–1700 nm), due to the presence of one electroactive-chromic species. Replacement of the electroactive ferrocene with a fluorene-diarylamine electroactive-chromic species, allows to extend and intensify the absorption in the NIR region, thus affording modulation of the solar radiation from 500 up to 2200 nm. High optical contrast, fast coloration and bleaching times and outstanding coloration efficiencies were measured for all observed absorption bands upon the application of small potential differences (1.4 V < ΔV < 2 V).

Keywords: electrochromism; devices; Vis-NIR absorption; thienoviologens; diarylamines; mixed-valence; electrochemical properties

1. Introduction

Limiting climate change and fostering sustainable growth are two of the main diktats of modern life. The last report on global warming, called “GLOBAL WARMING OF 1.5 °C”, reported by the ONU Climate Committee, predicted that, already in 2030, the global warming could exceed the threshold of 1.5 degrees from the pre-industrial levels [1]. The scientists’ proposal provides different possible paths with a mix of different tools such as: (i) cutting emissions that can be actuated by switching to renewable energies and electric vehicles, energy efficiency and recycling of waste and (ii) “removal” of CO₂ in terms of reforestation, carbon capture and storage. The way indicated by the ONU is the “greenest” and focuses on energy saving and reforestation. Environmental challenges on energy saving provide the driving force for many studies in the field of electronic devices for energy, including the electrochromic (EC) one that can be exploited for smart windows. The latter technology can afford, simultaneously, energy efficiency in buildings and good indoor comfort [2–6], since it is able to cut and/or modulate a variable transmission percentage of solar radiation both in the near-infrared region, which is responsible of thermal contribution (heating and cooling) and in the visible one, which is responsible of lighting [4,7]. In fact, the electrochromism is defined as the reversible variation of chemical species between two redox states with distinguishable absorption spectra as effect of a stimulus of electrical nature [8,9].
It is particularly interesting for building application since a significant portion of consumed energy is for lighting, heating and cooling. Switchable windows and mirrors did not represent the only area of interest, indeed, many others can be added such as: controllable light-reflective or light-transmissive devices for optical information and storage, electromagnetic shutter, controllable aircraft canopies, protective eyewear for the military, glare reduction system for automotive and transport [10–12]. To date, open issues for successful EC products are low-cost manufacturing and long-term durability and these pave the way for the research of the most suitable materials. Vis-NIR EC materials include several transition metal oxides [13–15], inorganic coordination complexes [16,17], conjugated polymers [18–20] and small organic molecules [21–26]. Viologens and arylamine-based compounds are among the most studied cathodic and anodic materials in the class of small organic molecules. These compounds allow an easy structural functionalization, thus offering a wide modulation of the absorption properties as a function of the inserted functional units, all over the Vis-NIR spectrum. Viologens are generally transparent in the dicationic state but, upon reduction, a highly colored and exceptionally stable radical cation is formed [8,9,27–30]. The radical-cationic form of viologens exhibits different coloration depending on the nature of the substituents on the nitrogen atoms as well as of the π-system that can be inserted between the pyridinium rings [30–33]. Arylamine derivatives are well known for their photoactive and electroactive properties, which usually have many advantageous such as good solubility, thermal stability, strong electro-donating and excellent hole-transmission capability [34–37]. During the oxidation-reduction process, arylamines always switch their colors and thus were developed as a new family of electrochromic materials [38–40]. Both, viologens and arylamines radical cations belong to the class of mixed valence compounds (MVs), resulting particularly interesting since they may offer NIR Electrochromism [41–45]. Actually, the arylamines NIR EC is extremely widespread rather than that of viologens. Organic MVs are donor–acceptor compounds that possess an open shell ground state [41]. The donor and acceptor moieties, i.e., the redox centers, are chemically identical units but in different oxidation states. They are connected by a π-conjugated bridging unit, which plays a crucial role for exploiting intramolecular electron transfer (ET) processes [41]. Indeed, when the redox centers are electronically coupled, an electron transfer process from the reduced to the oxidized center may be thermally or optically induced. In the latter case, the process gives rise to the so-called Intervalance Charge Transfer Transition (IVCT), which generally has an energy falling in the NIR region.

Herein we assembled highly transmissive all-in-one gel devices based on the thienoviologens/ferrocene (TV/Fc) and thienoviologens/fluorene-diarylamine (TV/FD) systems, that were characterized by extensive electrochemical and spectroelectrochemical studies in order to disclose their potential applicability. Particularly, we studied the devices at different operating voltage highlighting an interesting tuning of the electroptical properties of device components. The voltage-induced switching studies highlight that the reduction and oxidation processes occurring in the devices, generate high optical contrast (Δ%T up to 82%) within fast response time (τON ≈ 2 s; τOFF ≈ 5 s) and with low surface charge injection, as revealed by the measurements of the coloration efficiency (CE) both in the visible and near-infrared region.

2. Materials and Methods

4,4′-(2,2′-bithiophene-5,5′-diyl) bis(1-nonylpyridinium) triflimide (TV(NTf2)) and 9,9-bis(2-(2-methoxyethoxy) ethyl)-N2, N2′, N7, N7′-tetrais(4-methoxyphenyl)-9H-fluorene-2,7-diamine were synthesized freshly before use, as previously reported [46,47] (Figure S1). Poly (vinyl formal) (PVF) was purchased from Sigma Aldrich and was not further purified before use. N-methyl-2-pyrrolidinone, NMP, Pancreac) was used as solvent.

The TV/Fc EC polymer gels were prepared with 2% (w/w) of the ferrocene, the 2% (w/w) of thienoviologens, the 44% (w/w) of PVF, and 52% (w/w) of NMP. The TV/FD EC polymer gels were prepared with 10% (w/w) of the anodic, electroactive MV compounds, the 2.5% (w/w) of thienoviologens, the 35% (w/w) of PVF and 52.5% (w/w) of NMP. The two electrochromic active species were first
dissolved in NMP at room temperature and then mixed with the polymer under continuous stirring at 120 °C for 30 min.

ITO (indium tin oxide)/EC gel/ITO devices were assembled by drop casting of the hot EC mixture onto a ITO-coated glass support (Visiontek Systems Ltd. (Upton Chester Cheshire CH2 1JL United Kingdom) with a sheet resistance of 25 Ω sq−1 and a thickness of 1 mm) with a second ITO electrode used to create a sandwich with active area of about 1.5 × 3 cm². The cell gap was controlled by inserting cylindrical spacers with mean base diameter of 30 × 10⁻⁶ m. The final cell gap was calculated by the interference fringes in its absorption spectrum in the NIR spectroscopy range (900–1500 nm).

Standard cyclic voltammetry of the electrochromic polymer gel (EC gel) was performed with an Amel Instruments 7050 model potentiostat on the ITO/EC gel/ITO cell in which the two ITO plates worked as working and counter electrodes. Spectroelectrochemical experiments were performed, on the two-electrode device, with the Vertex 80 (Bruker) spectrophotometer. The potential was supplied by means of an Amel 2049 model potentiostat. Measurements were performed at 25 °C.

Coloration efficiency measurements were performed by coupling to the above describe spectrophotometer a current source measure, Keithley 6517A Electrometer [48].

3. Results

3.1. Spectroelectrochemistry of the Devices

The electrochemical properties of the thienoviologen as well as that of the fluorene-diarylamine derivative in solution have been previously studied and reported by our group [33,47–49]. Cyclic voltammetry (CV) of the polymer gel (EC gel) was performed on a ITO/EC gel/ITO sandwich cell without a reference electrode, in which two ITO coated glass plates served as working and counter electrodes (Figure S1). The CV of the device with the TV/Fc complementary components shows two redox processes in the negative scan, at potential biases (the potential difference between the two ITO electrodes) of 1.10 V and 1.30 V. The first one is relative to the reduction of the thienoviologen dication (TV⁺⁺) into the radical-cation (TV⁺⁺⁺) while the second is due to the formation of the neutral species (TV). The CV of the device containing the TV/FD system is more complex and this is mainly due to: (i) the higher numbers of processes involved and (ii) the overlap of the redox processes of the TV⁺⁺⁺ and FD⁺⁺⁺ species within the same range of potential bias (0.75 V < ΔV < 2.0 V). In both devices therefore, the redox processes start at potential biases higher than about 0.75 V, above which huge spectral changes (electrochromism) should be expected.

The electro-optical properties of these devices were investigated by spectroelectrochemical measurement (Figure 1). The spectroelectrochemistry of the TV/Fc EC gel shows that in absence of applied potential a strong absorption band is found at wavelength values < 500 nm, due to the π-π* transition of the TV⁺⁺⁺ species [50]. Reduction to the radical cation species leads to the growing of a new broad band in the region 530–880 nm, and another in the range 1150–1700 nm (NIR region). Both these bands increase with the increase of the applied potential (Figure 1a). At about 1.7 V a partial bleaching of the NIR band at ~1457 nm occurs (see the isosbestic point at 1370 nm) with the increase of a new absorption between ~900–1300 nm. The application of a very small potential bias (≥1.1 V) enables the device to absorb almost all the visible region being accompanied by a color change of the gel from yellow to black-green (Figure 1b). Replacement of the Fc⁺⁺⁺/Fc redox couple with the anodic FD, allows to broad the absorption range fully covering the near infrared region (NIR) up to 2000 nm (Figure 1c). This NIR band, starts to grow up for potential bias of 1.3 V, where oxidation to the MV radical cation (FD⁺⁺⁺) and reduction to the thienoviologen radical cation (TV⁺⁺⁺) take place (Scheme 1). Therefore, the NIR absorption band extending from about 800 nm up to 2000 nm, is the result of the superposition of the NIR bands of the two radical cations above, which are attributed to inter-valence charge-transfer (IVCT) transitions typical for MV compounds [47]. At this potential, there is the concomitant rising up of another absorption band (confirmed by the absence of the isosbestic point)
in the range 550–800 nm, due to the formation of the TV radical cation (TV\(^{**}\)) on the ITO slide opposite to that where the FD oxidation occurs.

**Figure 1.** Spectroelectrochemistry of the ITO/EC/ITO device containing (a) the TV/Fc system and (c) the TV/FD as anode and cathode, respectively. Film thickness = 5 \(\mu\)m. Color code according to the longer-wavelength NIR band. Gray lines: spectral growth as a function of the potential up to 2 V bias, where the maximum absorption in the NIR band at 1450 nm is observed (red line); from blue to light blue lines: bleaching of the NIR band at 1450 nm above 2 V. Photographs of (b) the TV/Fc device in the off state (0 V), and in the intermediate (1.2 V) and fully colored states (1.7 V) and of (d) the TV/FD device at 0 V and 1.7 V.

![Spectroelectrochemistry of the ITO/EC/ITO device containing (a) the TV/Fc system and (c) the TV/FD as anode and cathode, respectively.](image)

**Scheme 1.** Schematization of the formation of the radical cation species in the FD (a) and TV (b) mixed valence species.
As the potential applied to the device is increased up to 2 V, a new intense band occurs in the range 840–980 nm. This band is typical of the dication FD$^{++}$ species. Actually, at this potential bias, the fluorene derivative should be fully oxidized to the dication species (FD$^{++}$) and the thienoviologen should be fully reduced to the neutral species (TV). Therefore, the corresponding radical cation bands should be bleached. In contrast, they are still present in the spectrum, though their intensity begins to decrease. The persistence of the radical cation bands at such potential value, can be explained by the invoking the following comproportionation reactions in the bulk of the EC film:

\[
\text{FD} + \text{FD}^{++} \rightarrow 2 \text{FD}^{+}
\]

\[
\text{TV}^{++} + \text{TV} \rightarrow 2 \text{TV}^{+}
\]

Reactions (1) and (2) have rather high comproportionation constants ($K_{CO} \approx 10^3$, $10^4$) \[33,47\].

In addition, the reaction between the fully oxidized FD$^{++}$ and the fully reduced neutral TV, which is a strong reducing agent \[30\], easily occurs:

\[
\text{FD}^{++} + \text{TV} \rightarrow \text{FD}^{+} + \text{TV}^{+}
\]

This device switches from a transmissive off state (pale yellow) to different opaque on states, depending on the applied voltage pulse sequence, leading to an almost black colored device (Figure 1d).

3.2. Device Performance Metrics

The electrochromic performances of these all-in-one gel based devices were further evaluated by switching them between alternating ON and OFF pulses with different voltages and times (Figure 2, Table S1). The transmittance contrast ($\Delta$T), defined as the difference between the transmittance in the ON and OFF states, and the switching times, defined as the time required for reaching 90% of the full change in transmittance in a single switching time, are reported in Table S1. It is important to note that the voltage windows used correspond to the ranges where the monocations species are generated and reach their maximum intensity ($\sim$1430 and $\sim$670 nm, respectively), according to the spectroelectrochemistry of the devices. Figure 2 and Table S1 show that the TV/Fc system can reach, at $\lambda = 670$ nm, transmittance changes ranging from 74% to 82%. Analogous values, for the same absorption band, were found switching the TV/FD device. In this last, $\Delta$T values ranging from 58% to 80% were found for the absorption band at $\lambda = 1430$ nm, depending on the $V_{ON}$ and its time of application (Figure 2, Table S1). For all the devices and for all absorption bands coloration times of few seconds (from 1.5 s to 5 s) and a little bit slower bleaching times (from 5 s to 8.5 s) were recorded.

In order to compare the performance of the EC devices it is of noteworthy importance the correlation between the measurement of the charge passed during the oxidation and reduction processes and the transmittance change at a specific wavelength. This correlation parameter is known as coloration efficiency (CE, $\eta$). The $\eta$ is given by the equation:

\[
\eta = \frac{\Delta OD}{Q_i} = \log \left[ \frac{T_b}{T_c} \right] / Q_i
\]

This also determines the amount of optical density change ($\Delta OD$) as a function of the injected/ejected electronic charge ($Q_i$) per unit area. $T_b$ and $T_c$ are, respectively, the transmittance in the bleached and colored states. Figure 3 shows the change in optical density at three wavelengths (670, 890 and 1430 nm) as a function of the surface charge density. The CE value, extracted as the slope of the linear fitting of the reported curves, for both systems (TV/Fc and TV/FD), at 670 nm, is as high as 500 cm$^2$/C, which is an outstanding result compared with analogous systems \[51–53\]. The CEs registered for the NIR bands in the TV/FD system, due to the electrogeneration of the TV$^{++}$/FD$^{++}$ and TV$^{++}$/FD$^{++}$ species, respectively, are 180 cm$^2$/C and 170 cm$^2$/C, thus, approximately three times smaller.
than that of the calculated at 670 nm and due to the formation of TV+++. Furthermore, the coloration efficiency of the band at 670 nm calculated for the TV/FD devices, is only slightly smaller than that calculated for the TV/Fc devices (490 cm²/C vs. 500 cm²/C), thus suggesting that the replacement of the ferrocene anodic component with the FD one, does not affect significantly the EC performances of the device in the visible wavelength range. Importantly, the coloration efficiency calculated at 1430 nm in the TV/Fc device is almost half that found in the TV/FD one (105 cm²/C vs. 180 cm²/C).

Figure 2. Representative Vis and NIR switching cycles of the devices showing the Δ%T as a function of the potential difference applied. The wavelengths at which the transmittance was measured and the switching pulse sequence are labeled on each panel.

Figure 3. Optical density versus charge density of the EC devices containing the Fc-TV (electroactive area of 2.3 cm²) and MV-TV systems (electroactive area of 4 cm²).

Let’s try to explain the above differences in the CE of the three bands. The infinitesimal change of absorbance dA at the wavelength of maximum absorption, at time t, is given by the Equation (5):

$$dA(t) = l \varepsilon_c d[+]_c(t)$$ (5)
where, \( l \) is the sample optical depth (cm), \( \varepsilon_+ \), and \( dc_+(t) \) are the molar extinction coefficient (\( \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} \)) and the infinitesimal change in the concentration of the radical cation species. Integration of Equation (2) gives the change in the optical density of the sample at time \( t \):

\[
\Delta OD(t) = l \varepsilon_+ [c_+(t) - c_+(0)] = l \varepsilon_+ c_+(t)
\]  

(6)

being \( c_+(0) = 0 \).

It follows that:

\[
\Delta OD(t) = l \varepsilon_+ c_+(t) = \eta_+ Q_l
\]

(7)

Equation (7) tells us that the coloration efficiency is a function of the molar extinction coefficient of the active electrochromic species (the radical cation in our case) and of its concentration at time \( t \). The molar extinction coefficient of the two species are \( 1.9 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \) and \( 1.2 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \) respectively for the TV**+ and FD**+. In order to estimate the concentration of the radical cation at time \( t \) in the device, we can assume that the heterogeneous electron transfer reactions at the ITO electrode are of first order with rate coefficients \( k_c \). The rate of change of \( c_+(t) \) is therefore expressed as

\[
\frac{d}{dt}c_+(t) = k_c c_p(t) = k_c [c_p(0) - c_+(t)]
\]

(8)

where, \( c_p(t) \) is the concentration of the precursor species (the dication state for TV and the neutral state for FD) at time \( t \).

Integration of the differential Equation (8) leads to the desired equation that expresses the concentration of the radical cation species as a function of time:

\[
c_+(t) = c_p(0) \left[ 1 - e^{k_c t} \right]
\]

(9)

Equation (9) shows that the concentration of the monocation species is an exponential growing function of time with characteristic time \( k_c^{-1}(s) \) and depends on the initial concentration of the precursor species \( c_p(0) \). The higher is the kinetic constant of the heterogeneous electron transfer process, the faster is the coloration kinetics.

Figure 4 displays the optical density change of the devices at the two wavelengths investigated, as a function of time. It clearly shows the exponential growth of the OD with time that can be very well fitted by the Equations (6) and (9) (\( R^2 > 0.99 \)). The fitting results are summarized in Table 1.

**Figure 4.** Optical density changes vs. time at 670 nm and 1430 nm of the devices with TV/Fc and TV/FD, respectively. The continuous lines are the best fitting curves obtained by the Equation (6).
Table 1. Fitting parameters for the coloration kinetics at 670 nm and 1430 nm.

| Sample       | $\lambda_{\text{max}}$ | $k_e (s^{-1})$ | $l \cdot \varepsilon_p(t) | $ \cdot c_p(0)$ | $R^2$ | $\chi^2$ |
|--------------|-------------------------|----------------|--------------------------------|--------------------|-------|---------|
| TV/Fc-670 nm | 0.64 (0.02)              | 1.160 (0.007)  |                              | 0.9880             | 0.000888 |         |
| TV/FD-1240 nm| 0.08 (0.01)              | 0.39 (0.02)    |                              | 0.9612             | 0.000709 |         |

* This has been fitted as a unique parameter.

It is interesting to note that the rate coefficient $k_e$ for the reduction of the thienoviologen dication is almost 8 times larger than that for the oxidation of the neutral diarylamine species at the ITO electrode surface. This should be expected due to the charged nature of the first species which can migrate more rapidly toward the cathode surface upon application of the DC bias.

The difference in the CE observed for the two bands can then be rationalized on the basis of the Equation (4) rearranged as follows and the coloration kinetics data:

$$\eta_+ = \frac{l \cdot \varepsilon_p(t) | \cdot c_p(0)\cdot \Delta V}{Q_i}$$

It is clear from the Equation (10) that the faster is the kinetics of coloration and the higher is the extinction coefficient, the larger is the coloration efficiency, being the same the thickness of the absorbing layer (l) and the injected/ejected surface charge, as is the case for the thienoviologen compared to the arylamine.

4. Discussion

Herein, we presented all-in-one thermoplastic gel-based EC devices whose components are organic mixed valence compounds belonging to the class of small molecules. In the TV/Fc system we used the thienoviologen as the only electro-active/chromic species while, in the case of TV/FD system we incorporated two electro-active/chromic species as complementary cathodic (thienoviologen) and anodic (the fluorene-diarylamine derivative) components. Replacement of ferrocene with the MV fluorene-diarylamine allows a more efficient control of the solar radiation over a large part of the vis-NIR spectrum. Cyclic voltammetry and spectroelectrochemistry demonstrate the good electrochemical behavior of the anodic and cathodic compounds, highlighting that low operating voltages (potential difference as $1.4 \text{ V} < \Delta \text{V} < 2\text{ V}$) are enough to reach high optical contrasts both in the visible range and in the NIR region, low response times and outstanding coloration efficiencies. The dual EC response of the Vis-NIR absorbing system coupled with a fine tuning of the coloration at low voltages indicate a great potential for practical use of these systems in many technological fields such as smart windows, electronic displays, optical communication, information storage, and thermal control.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/10/23/8372/s1, materials: cyclic voltammetry of the ITO/EC/ITO devices containing the Fc/TV and the TV/FD systems (Figure S1), transmittance changes and switching times for the TV/FD and TV/Fc devices (Table S1).

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References

1. IPCC. Global Warming of 1.5 °C. An IPCC Special Report on the Impacts of Global Warming of 1.5 °C Above Pre-industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty; Masson-Delmotte, V.; Zhai, P.; Pörtner, H.-O.; Roberts, D.; Skea, J.; Shukla, P.R.; Pirani, A.; Moufouma-Okia, W.; Péan, C.; Pidcock, R., et al., Eds.; 2018; Available online: https://www.ipcc.ch/site/assets/uploads/sites/2/2019/06/SLR15_Full_Report_High_Res.pdf (accessed on 12 June 2020).

2. Loonen, R.C.G.M.; Trčka, M.; Cóstola, D.; Hensen, J.L.M. Climate adaptive building shells: State-of-the-art and future challenges. Renew. Sustain. Energy Rev. 2013, 25, 483–493.

3. Piccolo, A. Thermal performance of an electrochromic smart window tested in an environmental test cell. Energy Build. 2010, 42, 1409–1417. [CrossRef]

4. Baetens, R.; Jelle, B.P.; Gustavsen, A. Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: A state-of-the-art review. Sol. Energy Mater. Sol. Cells 2010, 94, 87–105. [CrossRef]

5. Byker, H.J. Variable Reflectance Motor Vehicle Mirror. U.S. Patent 5,128,799, 7 July 1992.

6. Varaprasad, D.V.; Habibi, H.; McCabe, I.A.; Lynam, N.R.; Zhao, M.; Dornan, C.A. Electrochromic Mirrors and Devices. U.S. Patent 5,724,187, 3 March 1995.

7. Granqvist, C.G. Electrochromics for smart windows: Oxide-based thin films and device. Thin Solid Films 2014, 564, 1–38. [CrossRef]

8. Monk, P.M.S.; Mortimer, R.J.; Rosseinsky, D.R. Electrochromism and Electrochromic Devices; Cambridge University Press: Cambridge, UK, 2007.

9. Mortimer, R.J.; Rosseinsky, D.R.; Monk, P.M.S. Electrochromic Materials and Devices; Wiley-VCH: Weinheim, Germany, 2015; p. 211.

10. Cai, G.; Wang, J.; Lee, P.S. Next-Generation Multifunctional Electrochromic Devices. Acc. Chem. Res. 2016, 49, 1469–1476. [CrossRef]

11. Beaujuge, P.M.; Reynolds, J.R. Color Control in π-Conjugated Organic Polymers for Use in Electrochromic Devices. Chem. Rev. 2010, 110, 268–320. [CrossRef]

12. Yan, S.M.; Dong, Y.J.; Li, W.J.; Chen, L.; Dai, Y.Y.; Ren, N.; Wu, Y.Z.; Zhang, Y.J.; Zhang, C. Electrochemical and electrochromic properties of bilayer polymer films prepared by electrochemical polymerization based on star-shaped thiophene derivatives. New J. Chem. 2019, 43, 9566–9573. [CrossRef]

13. Ding, J.J.; Liu, Z.; Wei, A.X.; Chen, T.P.; Zhang, H. Study of electrochromic characteristics in the near-infrared region of electrochromic devices based on solution-processed amorphous WO3 films. Mater. Sci. Semicond. Process. 2018, 88, 73–78. [CrossRef]

14. Zhou, J.; Chen, M.; Xie, J.; Diao, G. Synergistically Enhanced Electrochemical Response of Host–Guest Recognition Based on Ternary Nanocomposites: Reduced Graphene Oxide-Amphiphilic Pillar [5] arene-Gold Nanoparticles. ACS Appl. Mater. Interfaces 2013, 5, 11218–11224. [CrossRef]

15. Zhang, B.; Xu, C.; Xu, G.; Tan, S.; Zhang, J. Amorphous titanium dioxide film with improved electrochromism in nearinfrared region. Mater. Sci. 2019, 89, 191–196. [CrossRef]

16. Shankar, S.; Lahav, M.; Van der Boom, M.E. Coordination-Based Molecular Assemblies as Electrochromic Materials: Ultra-High Switching Stability and Coloration Efficiencies. J. Am. Chem. Soc. 2015, 137, 4050–4053. [CrossRef] [PubMed]

17. Zhong, Y.-W.; Wu, S.-H.; Burkhardt, S.E.; Yao, C.-J.; Abruña, H.D. Mononuclear and Dinuclear Ruthenium Complexes of 2,3-Di-2-pyridyl-5,6-diphenylpyrazine: Synthesis and Spectroscopic and Electrochemical Studies. Inorg. Chem. 2011, 50, 517–524. [CrossRef] [PubMed]

18. Zhang, Q.; Tsai, C.-Y.; Abidin, T.; Jiang, J.-C.; Shie, W.-R.; Li, L.-J.; Liaw, D.-J. Transmissive-to-black fast electrochromic switching from a long conjugated pendant group and a highly dispersed polymer/SWNT. Polym. Chem. 2018, 9, 619–626. [CrossRef]

19. Zhang, L.; Wang, B.; Li, X.; Xu, G.; Dou, S.; Zhang, X.; Chen, X.; Zhao, J.; Zhang, K.; Li, Y. Further understanding of the mechanisms of electrochromic devices with variable infrared emissivity based on polyaniline conducting polymers. J. Mater. Chem. C 2019, 7, 9878–9891. [CrossRef]
20. Teran, N.B.; Reynolds, J.R. Discrete Donor–Acceptor Conjugated Systems in Neutral and Oxidized States: Implications toward Molecular Design for High Contrast Electrochromics. Chem. Mater. 2017, 29, 1290–1301. [CrossRef]

21. Beneduci, A.; Corrente, G.A.; Chidichimo, G. Electrochromic and Electrofluorescence Liquid Crystals. In Electrochromic Smart Materials: Fabrication and Application; Xu, J.W., Chua, M.H., Shah, K.W., Eds.; Royal Society of Chemistry: Cambridge, UK, 2019; pp. 261–292.

22. Corrente, G.A.; Fabiano, E.; Manni, F.; Chidichimo, G.; Gigli, G.; Beneduci, A.; Capodilupo, A.-L. Colorless to All-Black Full-NIR High-Contrast Switching in Solid Electrochromic Films Prepared with Organic Mixed Valence Systems Based on Dibenzofulvene Derivatives. Chem. Mater. 2018, 30, 5610–5620. [CrossRef]

23. Pibiri, I.; Beneduci, A.; Carraro, M.; Causin, V.; Casella, G.; Corrente, G.A.; Chidichimo, G.; Pace, A.; Riccobono, A.; Saielli, G. Mesomorphic and electrooptical properties of viologens based on non-symmetric alkyl/polyfluoroalkyl functionalization and on an oxadiazolyl-extended bent core. J. Mater. Chem. C 2019, 7, 7974–7983. [CrossRef]

24. Veltri, L.; Cavallo, G.; Beneduci, A.; Metrangolo, P.; Corrente, G.A.; Ursini, M.; Romeo, R.; Terraneo, G.; Gabriele, B. Synthesis and thermotropic properties of new green electrochromic ionic liquid crystals. New J. Chem. 2019, 43, 18285–18293. [CrossRef]

25. Cospito, S.; De Simone, B.C.; Beneduci, A.; Imbardelli, D.; Chidichimo, G. Novel electrochromic gel with high optical contrast in the visible and near-infrared. Mater. Chem. Phys. 2013, 140, 431–434. [CrossRef]

26. Malteste, V.; Cospito, S.; Beneduci, A.; De Simone, B.C.; Russo, N.; Chidichimo, G.; Janssen, R.A.J. Electro-optical properties of neutral and radical ion thienosquaraines. Chem. Eur. J. 2016, 22, 10179–10186. [CrossRef]

27. Mortimer, R.J.; Dyer, A.L.; Reynolds, J.R. Electrochromic organic and polymeric materials for display applications. Displays 2006, 27, 2–18. [CrossRef]

28. Rosseinsky, D.R.; Mortimer, R.J. Electrochromic Systems and the Prospects for Devices. Adv. Mater. 2001, 13, 783–793. [CrossRef]

29. Mortimer, R.J. Electrochromic materials. Chem. Soc. Rev. 1997, 26, 147–156. [CrossRef]

30. Monk, P.M.S. The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4′-Bipyridine; Wiley-VCH: New York, NY, USA; Weinheim, Germany, 1998.

31. Yolanda, A.; Ana, V.; Javier, R.; Ramon, T.-Z. All-in-One Gel-Based Electrochromic Devices: Strengths and Recent Developments. Materials 2018, 11, 414. [CrossRef] [PubMed]

32. Beneduci, A.; Cospito, S.; La Deda, M.; Veltri, L.; Chidichimo, G. Electrofluorochromism in π-conjugated liquid crystals. Nat. Commun. 2014, 5, 3105. [CrossRef]

33. Cospito, S.; Beneduci, A.; Veltri, L.; Salamonczyk, M.; Chidichimo, G. Mesomorphic and electrochemistry of thienoviologen liquid crystals. Phys. Chem. Chem. Phys. 2015, 17, 17670–17678. [CrossRef]

34. Thelakkat, M. Star-shaped, dendrimeric and polymeric triarylamines as photoconductors and hole transport materials for electro-optical applications. Macromol. Mater. Eng. 2002, 287, 442–461. [CrossRef]

35. Kurosawa, T.; Higashihiara, T.; Ueda, M. Polyimide memory: A pithy guideline for future applications. Polym. Chem. 2013, 4, 16–30. [CrossRef]

36. Chang, C.-W.; Yen, H.-J.; Huang, K.-Y.; Yeh, J.-M.; Liou, G.-S. Novel organosoluble aromatic polyimides bearing pendant methoxy-substituted triphenylamine moieties: Synthesis, electrochemical, and gas separation properties. J. Polym. Sci. A Polym. Chem. 2008, 46, 7937–7949. [CrossRef]

37. Yen, H.-J.; Guo, S.-M.; Yeh, J.-M.; Liou, G.-S. Triphenylamine-based polyimides with trimethyl substituents for gas separation membrane and electrochromic applications. J. Polym. Sci. A Polym. Chem. 2011, 49, 3637–3646. [CrossRef]

38. Cai, J.W.; Niu, H.J.; Zhao, P.; Ji, Y.; Ma, L.; Wang, C.; Bai, X.; Wang, W. Multicolored near-infrared electrochromic polyimides: Synthesis, electrochemical, and electrochromic properties. Dyes Pigm. 2013, 99, 1124–1131. [CrossRef]

39. Ma, L.N.; Niu, H.J.; Cai, J.W.; Zhao, P.; Wang, C.; Bai, X.; Lian, Y.; Wang, W. Photoelectrochemical and electrochromic properties of polyimide/graphene oxide composites. Carbon 2014, 67, 488–499. [CrossRef]

40. Liaw, D.-J.; Hsu, P.-N.; Chen, W.-H.; Lin, S.-L. High glass transitions of new polyamides, polyimides, and poly(amide-imide) s containing a triphenylamine group: Synthesis and characterization. Macromolecules 2002, 35, 4669–4676. [CrossRef]
41. Heckmann, A.; Lambert, C. Organic Mixed-Valence Compounds: A Playground for Electrons and Holes. *Angew. Chem. Int. Ed.* 2012, 51, 326–392. [CrossRef] [PubMed]

42. Chuang, Y.-W.; Yen, H.-J.; Wu, J.-H.; Liou, G.-S. Colorless Triphenylamine-Based Aliphatic Thermoset Epoxy for Multicolored and Near-Infrared Electrochromic Applications. *ACS Appl. Mater. Interfaces* 2014, 6, 3594–3599. [CrossRef]

43. Barlow, S.; Risko, C.; Coropceanu, V.; Tucker, N.M.; Jones, S.C.; Levi, Z.; Khrustalev, V.N.; Antipin, M.Y.; Kinnibrugh, T.L.; Timofeeva, T.; et al. A mixed-valence bis(diarylamino)stilbene: Crystal structure and comparison of electronic coupling with biphenyl and tolane analogues. *Chem. Commun.* 2005, 6, 764–766. [CrossRef] [PubMed]

44. Beneduci, A.; Corrente, G.A.; Fabiano, E.; Maltese, V.; Cospito, S.; Ciccarella, G.; Chidichimo, G.; Gigli, G.; Capodilupo, A.-L. Orthogonal electronic coupling in multicentre arylamine mixed-valence compounds based on a dibenzofulvene-thiophene conjugated bridge. *Chem. Commun.* 2017, 53, 8960–8963. [CrossRef]

45. Takahashi, K.; Nihira, T.; Akiyama, K.; Ikegami, Y.; Fukuyo, E. Synthesis and Characterization of New Conjugation-extended Viologens Involving a Central Aromatic Linking Group. *J. Chem. Soc. Chem. Commun.* 1992, 8, 620–622. [CrossRef]

46. Beneduci, A.; Cospito, S.; Crispini, A.; Gabriele, B.; Nicoletta, F.P.; Velti, L.; Chidichimo, G. Switching from columnar to calamitic mesophases in a new class of rod-like thienoviologens. *J. Mater. Chem. C* 2013, 1, 2233–2240. [CrossRef]

47. Corrente, G.A.; Fabiano, E.; La Deda, M.; Manni, F.; Gigli, G.; Chidichimo, G.; Capodilupo, A.L.; Beneduci, A. High-Performance Electrofluorochromic Switching Devices Using a Novel Arylamine-Fluorene Redox-Active Fluorophore. *ACS Appl. Mater. Interfaces* 2019, 11, 12202–12208. [CrossRef]

48. Angiolini, L.; Giorgini, L.; Li, H.; Golemme, A.; Mauriello, F.; Termine, R. Synthesis, characterization and photoconductive properties of optically activemethacrylic polymers bearing side-chain 9-phenylcarbazole moieties. *Polymer* 2010, 51, 368–377. [CrossRef]

49. Beneduci, A.; Cospito, S.; Crispini, A.; Gabriele, B.; Nicoletta, F.P.; Velti, L.; Chidichimo, G. Highly fluorescent thienoviologen-based polymer gels for single layer electrofluorochromic devices. *Adv. Funct. Mater.* 2015, 25, 1240–1247. [CrossRef]

50. Alberto, M.E.; De Simone, B.C.; Cospito, S.; Imbardelli, D.; Velti, L.; Chidichimo, G.; Russo, N. Experimental and theoretical characterization of a new synthesized extended viologen. *Chem. Phys. Lett.* 2012, 552, 141–145. [CrossRef]

51. Zhao, S.; Huang, W.; Guan, Z.; Jin, B.; Xiao, D. A novel bis(dihydroxypropyl) viologen-based all-in-one electrochromic device with high cycling stability and coloration efficiency. *Electrochim. Acta* 2019, 298, 533–540. [CrossRef]

52. Fang, H.; Zheng, P.; Ma, R.; Xu, C.; Yang, G.; Wang, Q.; Wang, H. Multifunctional hydrogel enables extremely simplified electrochromic devices for smart windows and ionic writing boards. *Mater. Horiz.* 2018, 5, 1000–1007. [CrossRef]

53. Li, X.; Perera, K.; He, J.; Gumyusenge, A.; Mei, J. Solution-processable electrochromic materials and devices: Roadblocks and strategies towards large-scale applications. *J. Mater. Chem. C* 2019, 7, 12761–12789. [CrossRef]

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