



Spectroelectrochemical studies of electrochromic diarylethene ionic Liquids: From solution to ionogel based devices

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ABSTRACT

This study establishes the photoelectrochromic properties of four diarylethene ionic liquids (DAE-ILs) composed of a diarylethene dicarboxylate (DAE) moiety, as counter-anion, and different organic cations ($[\text{C}_{10}\text{mim}]^+$, $[\text{C}_{16}\text{Pyr}]^+$, $[\text{N}_{8,8,8,1}]^+$, $[\text{P}_{6,6,6,14}]^+$). The synthesized ILs viscous fluids maintain the photochemical and electrochemical properties of this well-known family of photoswitches, as well as the typical features of ILs (e.g., low melting point, and high thermal and electrochemical stability). Our strategy of making multi-stimuli-responsive ionic liquids by ionic exchange opens the door to easily tune the physicochemical properties of smart DAE-ILs in function of the selected cation. Finally, those DAE-ILs are used to formulate smart ionogels (IGs), a type of materials that, by showing good conductive properties and retaining the stimuli-responsive behavior of the embedded DAE molecules, allow the fabrication of photoelectrochemical devices.

1. Introduction

In the last decades, ionic liquids (ILs), which are organic salts with low melting points below 100 °C, have been explored to be applied in different academic and industrial fields, including material science [1,2]. Indeed, ILs have been reported as potential candidates to be used as a clean, efficient and eco-friendly alternative to conventional organic solvents, mainly due to their tunable physical, chemical, and thermal properties [3]. Besides these characteristics, other peculiar properties such as high ionic conductivities, large electrochemical windows, as well as excellent dissolution of organic, inorganic and polymeric materials [4–6], have contributed to an extensive range of applications from energy storage and conversion processes [7] to pharmaceutical ingredients [8–10].

Further uses can be envisaged for ILs if additional, stimuli-responsive functionalities are incorporated into their anion and/or cation structures, which can be exploited for the preparation of smart functional materials [11–13]. Indeed, “smart” ILs exhibiting photochromic [9,14], electrochromic [15–21] luminescent [22–26], magnetic [16,27] and rheological properties [28] have been explored by different research

groups, including our team. In this research area, diarylethene derivatives (DAEs) are excellent candidates to develop IL-based photoelectrochromic devices, since they are organic P-type, high fatigue-resistant photochromic molecules whose isomerization between their open and closed isomers can also be electro-induced [1,3]. Most of the previous studies on DAE-containing ILs (DAE-ILs) relied on the introduction of cationic groups to diarylethene scaffolds - e.g., by appending *N*-methyl pyridinium moieties to one or both of the lateral aryl rings [27] or replacing one of them by an imidazolium ion [29]. As expected, these DAE-ILs did not only show photochromic properties upon irradiation, but also demonstrated a rich electrochemical behavior, as they could undertake dimerization, ring closure and/or ring opening processes upon application of electric currents. Since these compounds often present an electron-rich nature, most of their electrochemical transformations were fulfilled upon oxidation. [30,31].

In our research group we have recently developed a different approach towards DAE-ILs that does not require the tedious synthesis of complex diarylethene ionic derivatives. Instead, they are composed of (i) an anionic diarylethene scaffold obtained from the deprotonation of a dicarboxylated DAE that can be produced in a large scale through a

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rather simple route [32–34], and (ii) conventional IL ammonium and phosphonium cations [35]. The two DAE-ILs that we reported based on this approach showed good photochromic properties, which were somewhat influenced by the type of the selected cation (e.g. the colors of their closed states) [35]. However, their electrochemical properties were scarcely investigated, and the use of spectroelectrochemical techniques to characterize their redox-induced behavior was totally neglected.

Spectroelectrochemical measurements, which allow monitoring the light absorbance or transmittance of a sample while applying electrical currents, have become the most suitable tools for the characterization of electrochromic compounds [34,36–38]. These techniques allow the massive oxidation or reduction of the electroactive compounds present in a sample, while the spectroscopic changes caused by the application of the electrical potential can be measured in real time. This enables to establish the electro-induced reaction mechanisms, their kinetics, as well as electrochromic parameters such as response times, color contrast and efficiencies. In addition, the experimental system can be easily adapted to perform measurements in liquid, solid or gel samples. This is especially relevant given the evolution of new electrochromic systems towards the formulation of solid materials, while maintaining the unaltered electrochromic properties. This is the case of the smart (photo) electrochromic ionogels based on a polymeric solid matrix and an IL phase doped with the (photo)electrochromic compounds of interest [39,40].

In light of this, the aim of this work is to exploit spectroelectrochemical measurements to fully determine the electrochromic properties of several DAE-ILs based on a dicarboxylated anionic derivative of diarylethenes (Fig. 1): two new DAE-ILs systems bearing 1-decyl-3-methylimidazolium (**1-DAE**; *imidazolium*) and 1-hexadecylpyridinium (**2-DAE**; *pyridinium*) counter-cations and the two previously described by us with trioctylammonium (**3-DAE**; *ammonium*) and trihexyltetradecylphosphonium (**4-DAE**; *phosphonium*) counter-cations [35]. Once their electrochromic behavior is fully disclosed in solution, it is investigated in the solid state by synthesizing new smart photoelectrochromic DAE-IL-based ionogels. Finally, a proof of concept photoelectrochromic flexible device based on this material has been fabricated and investigated.

2. Material and methods

2.1. Reagents and chemicals

Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP), $M_w \sim 400000$ and $M_n \sim 130000$) and tetrabutylammonium hexafluorophosphate (TBAPF₆) (>99.5 % pur.) were purchased from Merck.

N-Trimethyl-*N*-butylammonium bis(trifluoromethanesulfonyl)imide ionic liquid ([N₁₁₁₄][TFSI]) was acquired from Solvionic and dried with molecular sieves under vacuum prior to use. Extra dry and high purity (≥ 99.5 % pur) acetone and acetonitrile (ACN) were purchased from Acros. The basic anion-exchange resin Amberlyst A26-(OH) (ion-exchange capacity 1.4 eq. mL⁻¹, Alfa Aesar) and the silica gel for flash column chromatography (230–400 mesh, Sigma-Aldrich) were used as received. Trihexyltetradecylphosphonium chloride ([P_{6,6,6,14}][Cl]) (Cytec, > 98 %), hexadecylpyridinium chloride ([C₁₆Pyr][Cl]), 1-decyl-3-methylimidazolium bromide ([C₁₀mim][Br]) and trioctylmethylammonium bromide ([N_{8,8,8,1}][Br]) were purchased from Solchemar and used without further purification.

2.2. Ionogel membranes preparation

P(VDF-co-HFP), [N₁₁₁₄][TFSI] ionic liquid and acetone were mixed in a 1:5:18 wt ratio, respectively. The synthesized DAE-ILs were added to this solution to obtain a concentration of 5 mM for the case of cyclic voltammetry experiments, or 0.5 mM for optical measurements. The resulting mixture was stirred overnight until a clear solution was obtained. 160 μ L of this solution was casted onto a circle-shaped mold with of 1 cm in diameter and, after acetone evaporation for 1 h at ambient conditions, a flexible and transparent membrane was obtained.

2.3. Techniques

A spectrophotometer Hamatsu L10290 for absorbance UV–vis measurements and spectroelectrochemical experiments was used. The equipment was controlled by the Bio-Kine32 V4.16 software. For electrochemical and spectroelectrochemical studies, a VSP100 potentiostat was used. In the case of spectroelectrochemical measurements, the equipment was synchronized with the UV–vis spectrometer and controlled with the EC-Lab V9.51 software. Cyclic voltammetry (CV) measurements in solution were done with a conical glass cell using a 1 mm-in-diameter glassy carbon working electrode (WE), a Pt wire as counterelectrode (CE) and a reference Ag/AgCl electrode. The solutions were prepared in acetonitrile (ACN) and adding 0.1 M concentration of the supporting electrolyte TBAPF₆. For **4-DAE**, 5–10 % of methanol was added to improve solubility. The number of electrons related to electron transfer is determined by comparison with known one electron redox probes under the same electrochemical conditions. For spectroelectrochemical measurements in solution, a quartz cell of 0.1 cm in optical path length was used along with a Pt mesh as WE, a Pt wire as CE and a reference Ag/AgCl electrode (Ref). (Spectro)electrochemical measurements of IG membranes were performed using screen printed electrodes purchased from DropSens, where: (i) ITO working electrodes (ref.

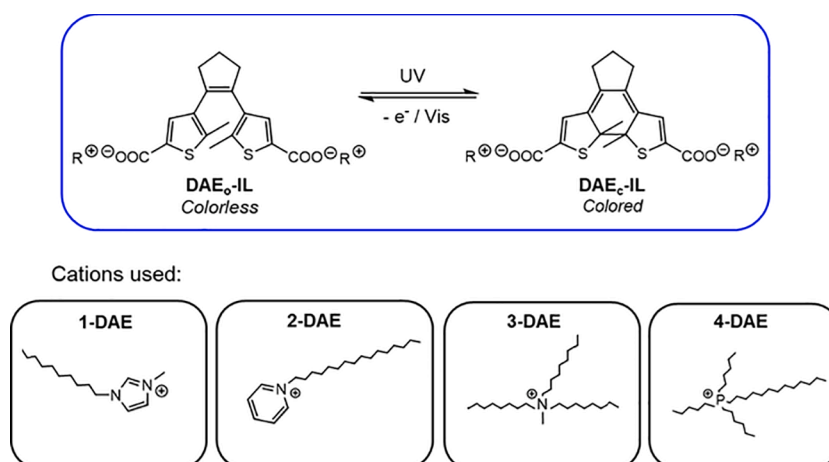


Fig. 1. Chemical structures and photoelectrochemical conversion between the open and closed isomers of all the DAE-ILs investigated in this work.

ITO10) were used for spectroelectrochemical measurements, and (i) carbon WEs were employed for electrochemical measurements (ref. DRP-110).

NMR spectra were recorded at 25 °C on a Bruker AMX 400 spectrometer operating at 400.13 MHz (^1H) and 100.61 MHz (^{13}C) and using TMS as internal standard.

2.4. Synthesis of DAE-ILs

1,2-Bis(5'-carboxy-2'-methylthien-3'-yl)-cyclopentene (DAE): This compound was prepared according to a previous synthetic procedure developed in our group [36].

1-DAE: Amberlyst A26 (OH) (~1.5 mL; 0.80 equivalents) was added to $[\text{C}_{10}\text{mim}]\text{Br}$ (0.1214 g, 0.40 mmol) in methanol solution (15 mL) and the suspension was stirred at room temperature during 1 h. The resin was removed by filtration and $[\text{C}_{10}\text{mim}]\text{OH}$ was slowly added to DAE (0.07 g, 0.20 mmol) in methanol solution (10 mL) and stirred at room temperature during ca. 21 h in the dark. The solvent was removed and the desired product was dried at 40 °C in vacuum to give a yellow liquid (0.1958 g, 99 %).

^1H NMR (400.13 MHz, MeOD, 25 °C) δ = 8.98 (s, 2H), 7.64 (d, J = 4.0 Hz, 2H), 7.58 (d, J = 4.0 Hz, 2H), 7.35 (s, 2H), 4.21 (t, J = 8.0 Hz, 4H), 3.94 (s, 6H), 2.81 (t, J = 8.0 Hz, 4H), 2.06 (m, 2H), 1.89 (m, 4H), 1.84 (s, 6H), 1.37–1.31 (m, 28H), 0.91 (t, J = 8.0 Hz, 6H).

^{13}C NMR (100.61 MHz, MeOD, 25 °C) = 168.57, 138.98, 138.29, 136.06, 134.39, 130.52, 123.53, 122.22, 49.44, 38.39, 35.03, 31.63, 29.75, 29.21, 29.14, 29.03, 28.71, 25.88, 22.42, 22.32, 13.36, 13.03.

2-DAE: Amberlyst A26 (OH) (~1 mL; 0.79 equivalents) was added to $[\text{C}_{16}\text{Pyr}]\text{Cl}$ (0.1059 g, 0.29 mmol) in methanol solution (12 mL) and the suspension was stirred at room temperature during 1 h. The resin was removed by filtration and $[\text{C}_{16}\text{Pyr}]\text{OH}$ was slowly added to DAE (0.05 g, 0.143 mmol) in methanol solution (10 mL) and stirred at room temperature during ca. 21 h in the dark. The solvent was removed and the desired product was dried at 40 °C in vacuum to give a brown liquid (0.1742 g, 84 %).

^1H NMR (400.13 MHz, MeOD, 25 °C) 9.03 (d, 3J = 4.0 Hz, 4H), 8.61 (t, J = 8.0 Hz, 2H), 8.14 (t, J = 4.0 Hz, 4H), 7.43 (s, 2H), 4.64 (t, J = 8.0 Hz, 4H), 2.83 (t, J = 8.0 Hz, 4H), 2.10 (m, 2H), 2.03 (m, 4H), 1.90 (s, 6H), 1.39–1.30 (m, 52H), 0.92 (t, J = 8.0 Hz, 6H).

^{13}C NMR (100.61 MHz, MeOD, 25 °C) = 166.86, 145.44, 144.53, 140.06, 136.30, 135.48, 134.59, 132.01, 128.11, 61.73, 38.19, 31.70, 31.16, 29.41, 29.39, 29.35, 29.26, 29.14, 29.11, 28.75, 25.81, 22.43, 22.37, 13.41, 13.10.

3-DAE and 4-DAE: they were prepared according to a synthetic procedure previously reported by the team [35].

3. Results and discussion

3.1. Electrochemical behavior and spectroelectrochemical study of DAE-ILs in solution

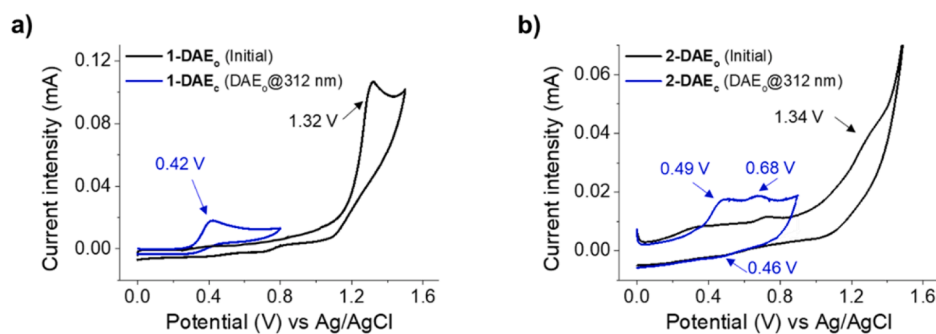
Initially, the electrochemical behavior of the open state of the ILs **1-DAE** and **2-DAE** was studied in acetonitrile solution by CV (Fig. 2). As shown in the voltammograms, an irreversible two-electron oxidation wave was registered at relatively high potentials for both compounds, whose peak lies at $E_{\text{pa}} \sim 1.35$ V vs Ag/AgCl (Table 1 and Fig. 2a and b). A comparison of the oxidation peak potential values of DAE-ILs open states in solution indicates no significant differences, which means that the chemical environment is very similar (Table 1). Once all these samples

Table 1

Photo and electrochemical parameters for DAE ILs in solution.

Compound	Solution	
	E_{pa} (V) vs Ag/AgCl	λ^{max} (nm)
1-DAE _o	1.32	350
1-DAE _c	0.42	510
2-DAE _o	1.34	352
2-DAE _c	0.49 and 0.68	508

Cyclic Voltammetry



Spectroelectrochemistry

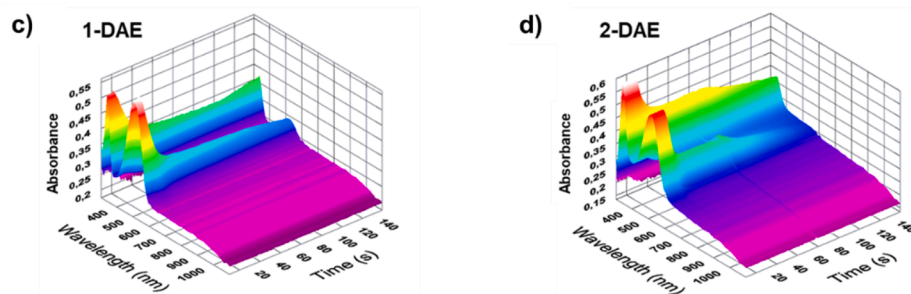


Fig. 2. a-b) Cyclic voltammograms recorded at 0.5 V/s of **1-DAE** and **2-DAE** in their open and closed form after UV irradiation. Experiments were performed in ACN 0.1 M TBAPF₆. The concentration values of **1-DAE** and **2-DAE** were 13 mM and 5.3 mM, respectively. c-d) 3D spectroelectrochemical measurements performed for 0.5 mM solutions of **1-DAE_c** and **2-DAE_c** using TBAPF₆ as supporting electrolyte. A constant potential of $E_{\text{app,ox}} = +1.00$ V vs Ag/AgCl was applied and, after 140 s, this led to a major decrement of the absorption band at ~510 nm, which indicates electroinduced isomerization towards their DAE_o isomer.

were irradiated at 312 nm, ring cyclization of the DAE counter-anion was evidenced by the appearance of strong reddish coloration associated to the formation of the corresponding DAE_c -containing ILs with $\lambda_{\text{abs,max}} \sim 510$ nm. As expected [36], the oxidation potential value of this new state was measured to be lower in comparison with the open isomer of **1-DAE** and **2-DAE**. In particular, when **1-DAE_o** and **2-DAE_o** solutions were irradiated, a new one-electron oxidation peak at $E_{\text{pa}} \sim 0.40$ V vs Ag/AgCl was registered. Table 1 summarizes the oxidation potentials for each compound, as well the photo-electrochemical parameters characteristic for each sample. However, a closer look to the Cvs of **1-DAE (1-DAE_c)** and **2-DAE (2-DAE_c)** ILs closed forms (Fig. 2a and b, blue line) reveals significant differences. In the case of **2-DAE_o**, the first electron transfer is slightly reversible, which indicates that the cation radical of **2-DAE_o** has a greater solvation effect when pyridinium is used as counterion. Whereas, in the case of the rest of DAE_c ILs possess one electron irreversible wave, which indicates that a chemical reaction is coupled to the electron transfer. Moreover, in this case it is possible to distinguish a second irreversible oxidation peak, which is related with the formation of the corresponding dication of **2-DAE_c**. The same general trend is observed for ILs **3-DAE_o** and **4-DAE_o**, as previously reported by our research group [35].

At this point, the use of spectroelectrochemical techniques is crucial to disclose the oxidation mechanism of the closed isomers of our DAE-ILs, to establish the nature of the chemical reaction linked to the electron transfer processes, as well as their electrochromic behavior. For this reason, spectroelectrochemical studies were performed for acetonitrile solutions of **1-DAE_c** and **2-DAE_c**, which were previously prepared by exposure of the **1-DAE_o** and **2-DAE_o** samples to 312 nm until a photo-stationary state was reached. As previously mentioned, this was confirmed by the emergence of a strong absorbance band at ca. 510 nm arising from the photogenerated closed isomer molecules. Fig. 2c and d show a 3-D plot where the optical response of the **1-DAE_c** and **2-DAE_c** solutions was monitored in time upon applying a constant oxidation potential value of $E_{\text{app,ox}} = +1.00$ V during 140 s - i.e., at a potential value that selectively oxidizes the closed state of these compounds. For both samples, a concomitant decrement of the absorbance band at $\lambda_{\text{abs,max}} \sim 512$ nm was observed.

As previously reported for similar DAEs [36], this result is consistent with a ring-opening electrochemically-induced process, where the electrogenerated cation radical of DAE_c follows a ring-opening reaction leading to the corresponding cation radical of DAE_o (Scheme 1, first

electron transfer). It is important to note that, because this latter specie is more oxidizing than DAE_c , the homogeneous electron transfer reaction between $[\text{DAE}_o]^+$ and DAE_c may also contribute to the ring-opening reaction and the discoloration of the samples, which would make this isomerization process electrocatalytic.

These results were also confirmed by conducting controlled potential electrolysis experiments on DAE_c solutions. When quantitatively electrolyzing these samples at $E_{\text{app,ox}} = 1.2$ V, the bleaching of the original characteristic red color of the closed isomers was observed for all compounds. Chemical analysis of the electrolyzed samples by UV-vis Absorbance spectroscopy, cyclic voltammetry and thin layer chromatography (TLC), confirmed that only DAE_o was recovered. This process, results in a permanent modification of the color, which is known as "electrochromism with memory".

Note that for **2-DAE_c** IL, the absorption peak at 512 nm disappears following two different reaction pathways. At an applied potential of 1.00 V, the oxidation of the **2-DAE_c** sample generates the corresponding dication (Scheme 1, 2nd electron transfer). In both cases, it seems that the chemical reaction linked to the electron transfer is a ring opening reaction. Hence, the corresponding cation radical and dication of the open isomer are generated. In the case of the electro generated **2-DAE_o** cation radical, it reacts with the starting material following the mechanism previously described for **1-DAE_c**. However, in the case of the **2-DAE_o** dication, it will involve a homogenous electron transfer with the starting material, leading to the open and closed **2-DAE** cation radical. As a consequence, a plateau between 20 and 80 s in the spectroelectrochemical plot is seen, indicating that the concentration of **2-DTAC** cation radical remains constant due to the competition between the homogeneous electron transfer and the ring opening reactions.

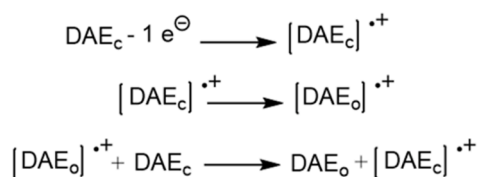
3.2. Electrochemical behavior and spectroelectrochemical study of DAE-IL-based ionogel membranes

Further studies were performed on DAE-ILs to investigate whether it is possible to transfer the photoelectrochemical results obtained in solution to solid state. To do so, IG membranes doped with **1-DAE**, **2-DAE**, **3-DAE** and **4-DAE** were prepared, and their photoelectrochemical behavior was disclosed. As expected, an oxidation wave at high potentials ($>+1.10$ V vs Ag/AgCl) was initially observed for all the resulting IGs in the dark - i.e., for the open isomer of the embedded IL molecules (Fig. 3a-d, Table 2). Relative to the solution measurements, the oxidation peaks registered were less well-defined, which we ascribe to the lower molecular diffusion within the semisolid ionogel matrix and the higher capacitive current shown by the membranes. In spite of this, the fact that the waves measured fairly reproduced the E_{pa} values previously in solution corroborates that the DAE-ILs did not suffer from any chemical variation by incorporation into the IG matrix.

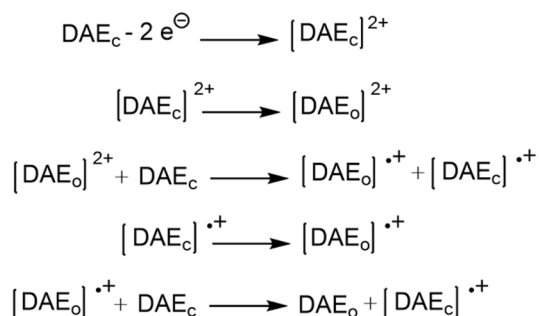
After 1 min of direct irradiation at 312 nm, the ionogels red-colored and a clear change in their cyclic voltammograms was detected. For all the DAE-IL@IGs, the oxidation peak registered in the dark at ca. 1.10–1.40 V vs Ag/AgCl shifted to lower potentials (~ 0.60 – 0.90 V vs Ag/AgCl), which is consistent with the ring-closing photoisomerization reaction of the embedded molecules (Table 2). Again, the oxidation potential values recorded upon irradiation were in good agreement with the values previously determined in solution.

A good match between the optical properties of DAE-ILs in solution and in the IGs was also observed. Initially, all the IGs were essentially colorless and only showed a defined absorption band in the UV region at 340–350 nm, as expected for the open isomer of their DAE-IL molecules (DAE_o -IL@IG, Fig. 3e-h, Table 2). Once irradiated at 312 nm, a very pronounced increase of absorption around $\lambda_{\text{abs,max}} \sim 515$ nm was observed due to DAE_c -IL formation (DAE_c -IL@IG, Fig. 3e-h, Table 2). A larger variability in $\lambda_{\text{abs,max}}$ for the photogenerated close isomer was observed in the IGs with respect to solution, which was attributed to the absence of solvent and to the distinctive stabilization effect of the DAE_c excited state by each of the counteranions. In spite of this, subsequent

1st Electron transfer

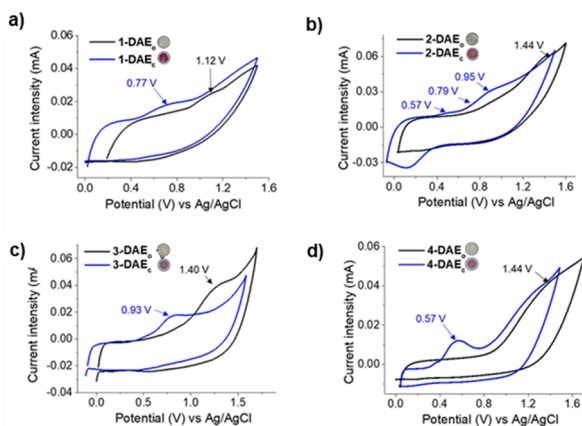


2nd Electron transfer

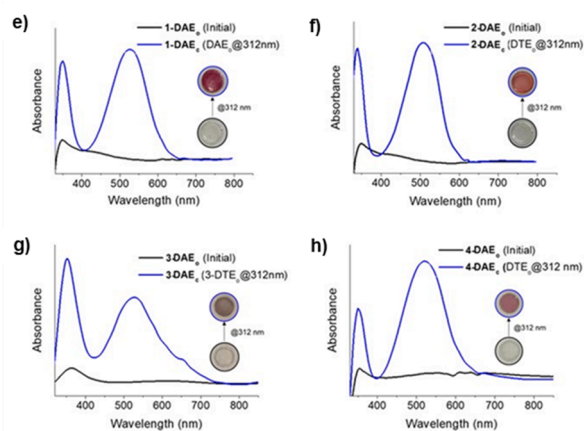


Scheme 1. Electrochemical oxidation mechanism of **1-DAE** ILs.

Electrochemistry



Photochemistry



Spectroelectrochemistry

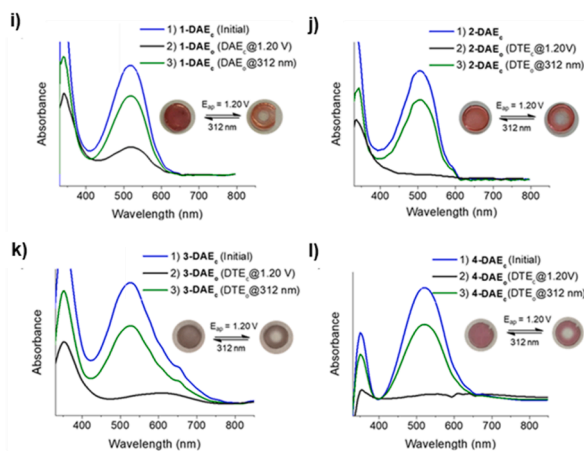


Fig. 3. Top: Cyclic voltammograms obtained for iongel membranes containing (a) 1-DAE, (b) 2-DAE, (c) 3-DAE and (d) 4-DAE. Carbon screen printed electrodes were used in this case to record the electrochemical response. Middle: Absorbance spectra of (e) 1-DAE, (f) 2-DAE, (g) 3-DAE and (h) 4-DAE in iongel membranes before (dark line) and after irradiation (blue line) at 312 nm for 1 min. The images in the insets show the color change achieved in this way for the IGs. Bottom: Spectroelectrochemical measurements of (i) 1-DAE, (j) 2-DAE, (k) 3-DAE and (l) 4-DAE in iongel membranes. Initially, these materials are colored because of pre-irradiation at 312 nm that generates the DAE_c-IL form. After the application an oxidation potential of $E_{ap} = +1.20$ V vs Ag/AgCl, the area in contact with the conductive electrode is bleached due to the formation of DAE_o-IL. This process can be reverted by further irradiation at 312 nm to obtain the DAE_c-IL form again.

Table 2

Photo and electrochemical parameters for DAE-IL in iongel membranes.

Compound	Longel membranes	
	E_{pa} (V) vs Ag/AgCl	λ^{max} (nm)
1-DAE _o	1.12	349
1-DAE _c	0.77	527
2-DAE _o	1.44	340
2-DAE _c	0.95	506
3-DAE _o	1.40	352
3-DAE _c	0.93	527
4-DAE _o	1.44	352
4-DAE _c	0.57	521

irradiation with green light (532 nm) resulted in color bleaching for all the samples, thus revealing the reversible photochromic behavior of the membranes prepared with our DAE-ILs.

Finally, the photoelectrochromic properties of the DAE-IL@IGs were fully determined. To do so, spectroelectrochemical experiments were conducted to demonstrate that the oxidation of DAE_c-IL@IGs leads to redox-induced conversion into DAE_o-IL@IG. Fig. 3 i-l shows the variation of the UV-vis absorbance spectra of all the IG membranes pre-irradiated at 312 nm when a potential of $E_{ap} = +1.20$ V was applied. The observed decrease in the visible absorption band of these samples was associated with the electrochemical ring-opening of the DAE_c-IL structure to generate the colorless form DAE_o-IL, as previously shown in solution. It is important to highlight that, by subsequently irradiating the membranes at 312 nm, we regenerated the DAE_c-IL state again. Hence, this demonstrated the reversible photoelectrochromic properties of DAE-based ionic liquids when those systems were transferred to solid materials.

3.3. DAE-IL-based membranes as smart materials for the fabrication of molecular logic gates

Given the good rheological properties shown by the fabricated membranes, they could be used for the fabrication of flexible multi-stimuli-responsive devices able to respond to both the application of electric potentials and irradiation with UV or visible light. As a probe of concept, 2-DAE was selected for preparing the IG membrane due to its excellent photoelectrochemical properties.

For this purpose, a device was made by cutting flexible pressure sensitive adhesive (PSA, 175 μ m thick, Sertek Global Technology, Barcelona, Spain) and polycarbonate (PC, 175 μ m thick, MicroPlanet Laboratorios S.L., Barcelona, Spain) layers with a CO₂ laser writer (Epilog Mini 24, Epilog Laser, United States). Two transparent PC layers (25 mm \times 25 mm) were sandwiched by using two white PSA layers. The bottom PSA layer defined a 10 mm \times 20 mm hold for positioning and aligning the electrode in the device. The top PSA layer was used to define the 8 – mm diameter electrochemical cell. Before closing the device with the top PC layer, the flexible iongel membrane of 2-DAE was adhered to the top of the electrode by placing it on the circle hole defined in the top PSA layer. Finally, the electrode was connected to a potentiostat to finish assembling the set up. The transparent circular aperture constructed in the device allowed one to observe the color change of the membrane with the naked eye, as well as exposing the sample to UV or visible light (Fig. 4a). The main electrochromic features of the devices were also assessed. It was determined a switching color contrast, which is defined as the ratio in transmittance of the material in it bleached and colored form, of 70 % measured at $\lambda^{max} = 506$ nm for 2-DAE. The switching time needed to obtain the 90 % of the total bleaching color was 108 s, while 41 s was required to observe the 50 % of color change. Despite of the times obtained to produce a color change are relatively higher compared to other electrochromes [41–43], it would be possible to improve them by optimizing the thickness of the IG films. The coloration efficiencies of the device were also calculated, obtaining 171.3 cm²·C⁻¹ at $\lambda^{max} = 506$ nm which. Those values are in

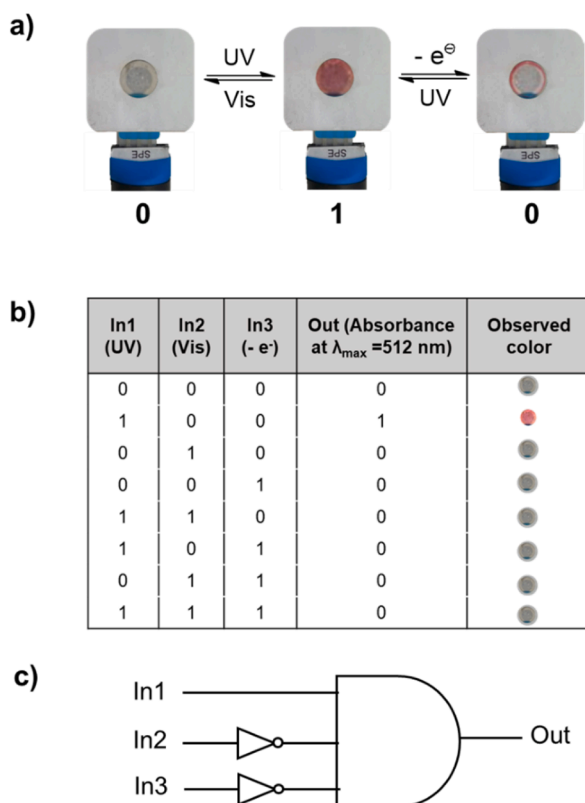


Fig. 4. a) Multistimuli device connected to a potentiostat. The center of the device contains the membranes formulated with 2-DAE. The configuration enabled the membrane to be exposed to the light source and also allowed its electrical contact with the transparent ITO electrode to apply the electric potential. b) Truth table and c) logic circuit corresponding to DAEs logic gate system.

good agreement with some coloration efficiencies reported in the literature for ionogel based electrochromic materials. [44,45].

Thanks to the dual-stability of DAE compounds and their ability to respond to three different inputs (In (UV light (In1), visible light (In2) and an oxidative electrical potential (In3)), the response obtained (Out) by the prepared device should be different depending on the presence (In = 1), absence (In = 0) or combination of stimuli (Fig. 4b). In this way, it could be possible to build a logic gate since the response of the material to the distinct input signals acted as a Boolean function (Out = 0 for colorless membranes absorbing at $\lambda_{\text{abs,max}} \sim 340 \text{ nm}$, and Out = 1 for red-colored ones absorbing at $\lambda_{\text{abs,max}} \sim 510 \text{ nm}$).

In the device (Fig. 4c), when only UV light was applied (In1 = 1, In2 = 0, In3 = 0), visible light absorbance was observed at ca. 510 nm (Out = 1). However, this effect was inhibited in absence of stimuli (In1 = 0, In2 = 0, In3 = 0), when no UV irradiation was used (In1 = 0, In2 = 1, In3 = 0; In1 = 0, In2 = 0, In3 = 1; and In1 = 0, In2 = 1, In3 = 1) or when visible light and/or an oxidative potential were applied subsequently after to UV irradiation (In1 = 1, In2 = 1, In3 = 0; In1 = 1, In2 = 0, In3 = 1; and In1 = 1, In2 = 1, In3 = 1).

4. Conclusions

Two new diarylethene ionic liquids (DAE-ILs) composed by a diarylethene dicarboxylate dianion and imidazolium and pyridinium counteranions were prepared using a simple ion exchange process. The photoelectrochemical properties of these systems together with two other analogous DAE-ILs previously prepared with ammonium and phosphonium counter-cations were determined in solution and in the solid state as ionogels. In both platforms, the DAE-ILs analyzed showed reversible photochromic and photoelectrochromic behavior, as their

closed isomer was generated with UV radiation, while back-isomerization to the initial open state was produced both with visible light and oxidative potentials. This suggests that it is possible to access a wide range of smart ILs by incorporation of appropriate ions, which allows combining the very advantageous properties that ionic liquids possess (eco-friendliness, low melting point, low volatility, high ionic conductivity...) with the advanced stimuli-responsive features of the functional units introduced (e.g., photo- and electrochromic responsiveness). In addition, we showed that DAE-ILs are also compatible with organic polymeric matrices, which allows the formation of solid-gel type membranes that can be applied for the fabrication of functional devices such as sensors, smart labels, panels or displays.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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