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Electro- and Spectroscopic Studies of 2(3*H*)-Thiazolone Azine as Precursors to Air-Stable Radical Cations

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The electrochemical and spectroscopic properties of a new family of stable radical cations based on 2(3*H*)-thiazolone azine were investigated. All of the studied compounds display two redox processes, leading to a radical cation, and then to a dication, the radical mono-cation being intensely blue-colored. These properties suggest that this new family of dyes provides excellent candidates for electrochromic devices, such as electrochromic windows, or as redox indicators or mediators.

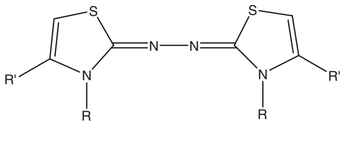
The 2(3*H*)-thiazolone azine, previously described in the literature, are colored compounds, resembling in this respect azopyridines.[1–3] The presence of electron-attracting groups, such as perfluoroalkyls, lowers the electron density of the azine π-electron system. As a direct consequence, a hypsochromic shift of the absorption maxima is observed, leading to colorless compounds. The fluoroalkylthiazolone azines are readily available through straightforward synthesis and commercial availability of the starting materials.[4] The variety of isothiocyanates allows one to control the lipophilic character of the resulting azines, and introduces various functionalities. While only two fluorinated bromoketones ($R = CF_3$, C_2F_5) precursors are commercially available, higher homologues are accessible from perfluoroalkanoic acids.

The redox potential values for the unsubstituted 2(3*H*)-thiazolone azines is too low to prevent air oxidation to occur readily (170 mV vs Ag/AgCl),[1,2] yielding highly colored radicals. Moreover, the neutral (unoxidized) material is already strongly colored due to the chromogenic azo functionality.[3]

In this work, we report on a new family of perfluoroalkyl-bearing 2(3*H*)-thiazolone azines, possessing interesting properties for applications in electrochromic devices. Improved redox potentials and spectroscopic properties were successfully obtained by the manipulating electron density through the influence of perfluoroalkyl groups (Scheme 1).

Experimental

The syntheses of five compounds have been described in a previous paper.[4] Electrochemical measurements were carried out under anhydrous conditions and argon atmosphere at room temperature. A platinum electrode was used as a working electrode ($S = 0.364$ cm^2), with an Ag/AgCl in KCl-saturated methanol as a reference electrode and a stainless-steel 305 wire as an auxiliary electrode. The working electrode was polished (alumina 0.1 µm) and then cleaned by a chemical treatment (a 1:1 solution of H_2SO_4/HNO_3 at 60 °C over 15 min) prior to each measurement.



1: R= Me, R'= CF_3; **2**: R= *n*-Bu, R'= CF_3; **3**: R= *n*-Hexyl, R'= CF_3;
4: R= Me, R'= C_2F_5; **5**: R= *n*-Hexyl, R'= C_2F_5

Scheme 1. The 2(3*H*)-thiazolone azine molecule containing a perfluoroalkyl substituent R′.

The chosen electrolyte[5–10] was 0.1 M (1 M = 1 mol dm^{-3}) lithium bis(trifluoromethane)sulfonimide salt $LiN(SO_2CF_3)_2$ (LiTFSI) in freshly distilled acetonitrile. The reference potential and the surface of the working electrode were measured with a 2.5 mM ferrocene solution in acetonitrile; the redox couple (Ferrocene/Ferricinium ($E_0 = 0.400$ V vs NHE)) is known for being almost solvent-independent due to its charge delocalization.

Cyclic voltammetry was performed using a Versastat 263A potentiostat–galvanostat from EG&G, monitored by a computer using the M270 software version 4.23.

Spectrophotometry measurements were carried out with a Varian Cary 100 spectrometer between 330 and 900 nm.

Results and Discussion

Electrochemical Study. The thiazolone azine prepared compounds exist in three oxidation states: a neutral one, (A^0), a singly oxidized state, which is thus a radical cation ($A^{\bullet +}$), and a second oxidized state, the dication (A^{2+}). The compound in the neutral state is colorless, which allows its use in electrochromic devices applications, in opposition to the already described thiazolone azines. The radical cation presents a blue color and the dication is pale green. The different states are summarized in Scheme 2.

The electrochemical behavior of compounds **1–5** has been investigated using cyclic voltammetry at a 50 mV s^{-1} scan rate. The voltammograms obtained for each compound are given in Fig. 1. It was possible to observe two oxidized states. The first one was highly reversible, and appeared at around 0.7 V vs Ag/AgCl, and the second one at around 1.25 V vs Ag/AgCl. However, the second oxidation for the peak for com-

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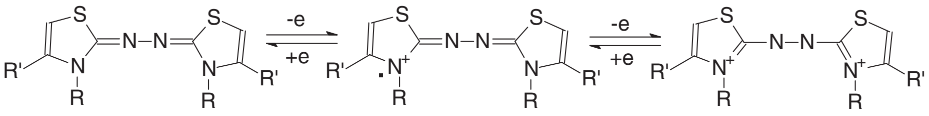
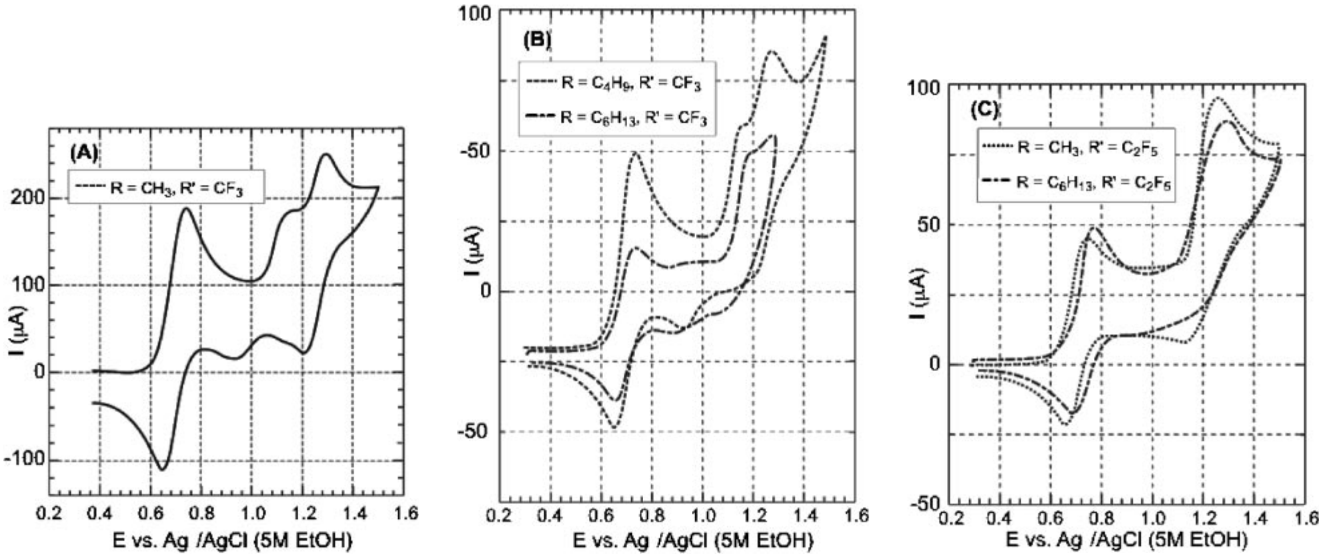


Neutral state
colorless

First oxidized state
blue, radical cation

Second oxidized state
pale green, dication

Scheme 2. Oxidation states of the 2(3*H*)-thiazolone azine family compounds.



(a) (b) (c)

Fig. 1. Cyclic voltammetry of compounds **1**–**5** at 1.4 mM concentration in 0.1 M LiTFSI/CH_3CN electrolyte. The sweep rate is 50 mV s^{-1}. Fig. 1A, compound **1**; 1B, compounds **2** and **3**; 1C, compounds **4** and **5**.

Table 1. Potential Values in Volts for Compounds **1**–**5** for the Two Redox Processes

Compounds	First peak E/V		Second peak E/V	
	vs Ag/AgCl 5 M LiCl/EtOH	vs NHE	vs Ag/AgCl 5 M LiCl/EtOH	vs NHE
1	0.687	0.541	1.244	1.098
2	0.677	0.531	1.237	1.091
3	0.680	0.534	1.155	1.009
4	0.693	0.547	1.193	1.047
5	0.715	0.569	1.207	1.061

pound **1** ($R = CH_3$, $R' = CF_3$) was cleary reversible (Fig. 1A). The potential difference between the anodic and cathodic peaks for each process was around 80 mV indicating a good reversibility of the two electrochemical reactions. Longer R or R′ moieties (compounds **2** to **5**) result in progressively blurred reduction peaks after the ultimate oxidation (Fig. 1B and C), which can no longer be considered to be fully reversible. In this potential region, electrolyte oxidation has to be considered. The redox couples potentials are given in Table 1.

The length of the alkyl chains has no effect on the redox values, because their inductive effect is limited, but helps to enhance the solubility in organic solvents. On the other hand, the perfluoro moieties shift the redox potential to a more positive value by 223 mV vs Ag/AgCl, as compared to the simple 2(3*H*)-thiazolone azine,[3] and bring the redox couple into the air stability region (≥0.3 V vs Ag/AgCl).

A third electrochemical process can be observed, as a shoulder between the two main peaks, around 1.15 V vs Ag/AgCl. Its contribution is small compared, in terms of current, to the main peaks, and decreases in intensity from compound **1** to **5**. It could be attributed to the electrochemical activity of a possible dimer, A_2^{2+}, formed by the combination of two radical cations, $A^{\bullet +}$. This phenomenon has already been observed for the viologens.[11,12] As expected, longer alkyl/perfuoroalkyl chains, jutting out of the ring planes, hinder the "π" interaction responsible for dimer formation, explaining the decreased effect when going from compound **1** to **5**.

Kinetic of the First Redox Couple. We have focused further on the characterization of the radical monocation because of its intense blue color. In addition, the second oxidation wave near 1.2 V vs Ag/AgCl is close to the limit of the solvent stability, and the dication would oxidize water if present. The very good reversibility of the first redox couple is important for stable electrochromic devices, and the existence of a well-separated further oxidation step (>500 mV) avoids destruction of the dye upon the accidental application of an overvoltage.

In order to determine the kinetics of the reaction, cyclic voltammetry was performed using different scan rates from 10 to 500 mV s^{-1}. The case of compound **4** is shown in Fig. 2. As it can be seen in the Fig. 3, the plot of the anodic peak intensity

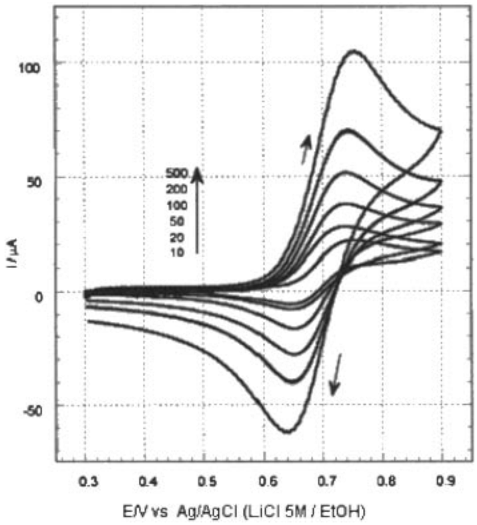


Fig. 2. Cyclic voltammetry of compound **4** at different scan rates.

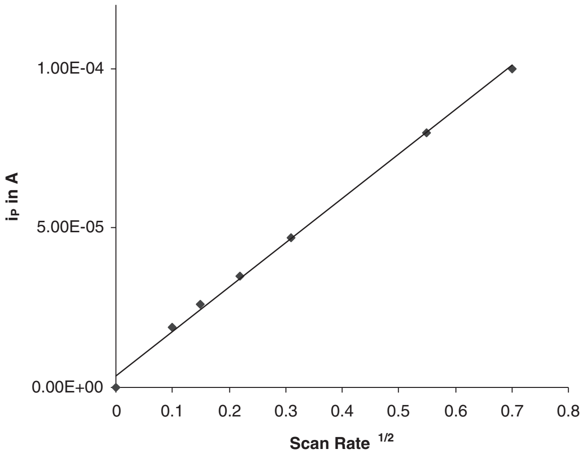


Fig. 3. Variation of anodic peak current as a function on the square root of the scan rate for the compound **4**.

peak versus the square root of the scan rate is perfectly linear.

This result indicates a system limited by diffusion, rather than the kinetics of the electrochemical oxidation, i.e., electronic charge transfer. The diffusion coefficient (D) of the active species in the solution is calculated from the slope of the curve using the following equation:

$$I_p = 2.67 \times 10^5 n^{3/2} S C D^{1/2} v^{1/2}, \tag{1}$$

where n is the electron number involved in the redox reaction, S the electrode surface area in cm^2, C the species concentration in mol cm^{-3} and v the scan rate in V s^{-1}.

The diffusion coefficients obtained for the different compounds are summarized in Table 2. The high values for D indicate a very good diffusion of the species, which is an important factor for an electrochromic compound. This diffusion coefficient is the sum of two contributions: the chemical diffusion on the entities (D_{chem}) and that due to electron hopping between charged and neutral species (D_{hopping}). The contribution of D_{hopping} explains the high values found in Table 2. Indeed, in addition of the fast change of the color due to the fast electronic transfer, the solution is rapidly and homogeneously colored in a large volume. The composition of the substituents on the molecules has an effect on their diffusion. The longer are the alkyl chain and the perfluoroalkyl group, the higher is the coefficient. Although the size is in principle an unfavorable factor concerning the diffusion process, the free volume around the cation radical increases, especially for the perfluoroalkyl groups known for their high exclusion volume; also, and there is less solvation, influencing both D_{chem} and D_{hopping}. An optimum should exist between these two opposing factors, beyond, in chain length, those under the present study.

Table 2. Values of the Diffusion Coefficient and of the Comproportionation Constant for Compounds **1**–**5** Obtained at 25 °C

Compounds	D/cm^2 s^{-1}	K_{comp}
1	1.4×10^{-5}	2.8×10^9
2	2.1×10^{-5}	3.1×10^9
3	1.9×10^{-5}	1.1×10^8
4	2.0×10^{-5}	2.3×10^8
5	4.5×10^{-5}	2.2×10^8

Dis/Comproportionation Constant Calculations. The cation radical stability is crucial to maintain the color of the system. In the case of viologens, the reactions of comproportionation and disproportionation (K^{-1}) were demonstrated in the thirties.[13–15] To evaluate the facility of our compounds to undergo reactions of com/dis-proportionation, the constant of the reaction has been determined. The reaction can be illustrated by the following scheme:

$$A^0 + A^{2+} \underset{K_{\text{di}}}{\overset{K_{\text{comp}}}{\rightleftarrows}} 2\ A^{\bullet +}, \tag{2}$$

with

$$K_{\text{comp}} = \frac{[A^{\bullet +}]^2}{[A^0]\cdot[A^{2+}]} = K_{\text{di}}^{-1}. \tag{3}$$

The constant has been calculated using the Nernst equation for the two redox couples of the system:

$$A^0 \overset{E_1}{\rightleftarrows} A^{\bullet +} + e^-, \tag{4}$$

$$A^{\bullet +} \overset{E_2}{\rightleftarrows} A^{2+} + e^-, \tag{5}$$

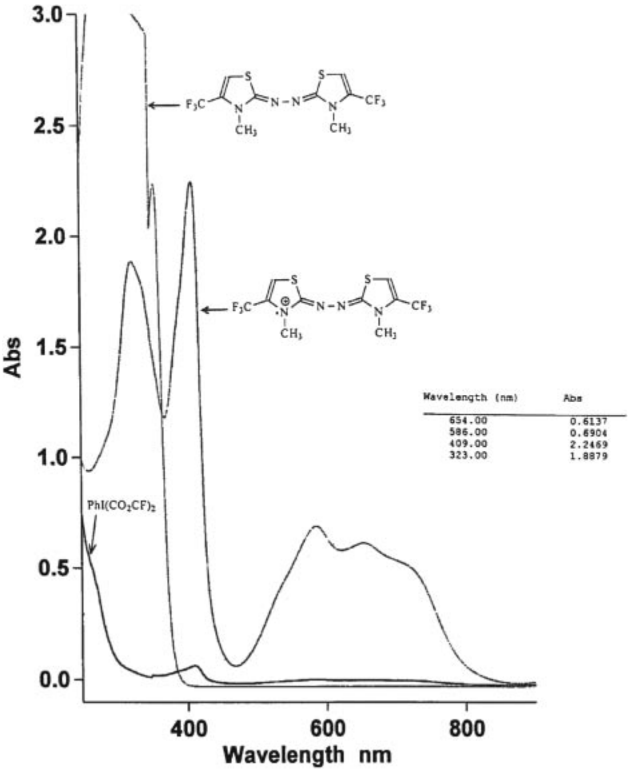
$$E_2 - E_1 = (RT/nF)\ln K_{\text{comp}} = 0.059 \log K_{\text{comp}}. \tag{6}$$

The calculated values for K_{comp}, given in Table 2, are very high, higher or equal to 1.1×10^8, indicating that the disproportionation reaction will be negligible. For a comparison, the comproportionation constant for the methyl viologen, an admittedly good electrochromic compound, is evaluated at around 10^6.[16]

Spectrophotometry. The blue cation radicals formed for compounds **1**–**5** absorb in the visible wavelengths; therefore, we have conducted spectrophotometric studies to determine the extinction coefficient ($\mathcal{E}$) using the Beer–Lambert law,

$$A = \mathcal{E} b C, \tag{7}$$

where A is the absorption, C the concentration in mol dm^{-3} and b the cell width (1 cm).



Wavelength (nm)	Abs
654.00	0.6137
586.00	0.6904
409.00	2.2469
323.00	1.8879

Fig. 4. UV–visible scan spectrum of $PhI(CO_2CF_3)_2$, compound **1**, and its radical cation at 0.1 mM in CH_3CN.

It was not possible to produce simultaneous electro-oxidation of the compound with the spectrometer used. We thus oxidized the compound with a reagent that possesses a redox potential between both redox couples of the compounds. This oxidant must also have a low absorption in the visible region. The chemical oxidant chosen for its low absorption in the visible region is the [bis(trifluoroacetoxy)iodo]benzene PhI-$(CO_2CF_3)_2$. Figure 4 illustrates the absorption vs wavelength spectrum of the involved compounds before and after oxidation in the case of compound **1**. The starting 2(3*H*)-thiazolone azine and the [bis(trifluoroacetoxy)iodo]benzene have no absorbance in the visible region, whereas the radical cation shows an absorbance in the visible region at very low concentrations.

Two wavelengths have been selected for the study, $\lambda = 409$ nm and $\lambda = 586$ nm, corresponding to the maximum of the absorbance. The extinction coefficient is obtained after measuring of the absorbance for different concentrations. The extinction coefficient at 409 nm, calculated from the slope of the curve $A = f(C)$ (Fig. 5a), has a value of 18000 $M^{-1}\,cm^{-1}$, while that at 586 nm equals 6000 $M^{-1}\,cm^{-1}$ (Fig. 5b).

Compared with the simple 2(3*H*)-thiazolone azines and the viologens having a coefficient, between 15000 and 20000 $M^{-1}\,cm^{-1}$,[16–18] the very high value of the extinction coefficient ranks this compound as being among the most efficient dyes known. This is an excellent characteristic for an electrochromic device where the largest variation of the optical density vs charge is sought.

Though electrochemical experiments have been conducted in an aprotic solvent (CH_3CN), a similar behavior is expected in propylene carbonate or γ-butyrolactone having comparable electrochemical window. The stability of the carbocation is also excellent in water, when the counter-anion is hydrophilic (Cl^-, Br^-, $CF_3CO_2{}^-$). In the case of the bromide ion, the proximity of the redox couples Br^-/Br_2 and $A^0/A^{\bullet+}$ interestingly renders the dye photochromic: a brief exposure to laboratory light discharges the blue color, which returns in the dark. The other salts show extreme fastness, as several months expositions to day-light does not affect the intensity of the coloration.

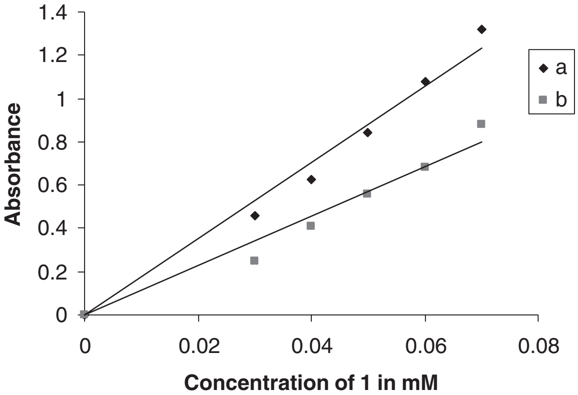


Fig. 5. Standard curve for the determination of the extinction coefficient of the radical cation **1**.

Conclusion

The new family of perfluoroalkyl-2(3*H*)-thiazolone azines displays very interesting electrochromic properties. The starting compounds are colorless, although the radical cations produced during their oxidation have a strong blue color, allowing high extinction coefficient values. The redox couple involved is reversible, and has a potential allowing air stability of the radical cation. The reaction has fast electronic charge transfer and the species have good diffusion. All of these features point to their usefulness in electrochromic applications.

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