Azulenyl-Pyryanium Salts For Anion Recognition

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The design of receptors for anions coordination is an important task in order to get a good electrochemical signal. 2,6-di(thien-2-yl)-4-(3,8-dimethyl-5-isopropyl-azulen-1-yl)pyrylum perchlorate has been characterized and tested for the anion electrochemical recognition using cyclic voltammetry and differential pulse voltammetry. It presents modified electrochemical properties in the presence of H2PO4\(_-\) and F\(-\).

Keywords: anion electrochemical recognition, 2,6-di(thien-2-yl)-4-(3,8-dimethyl-5-isopropyl-azulen-1-yl)pyrylum perchlorate, cyclic voltammetry, differential pulse

The anion recognition chemistry has its beginnings in the late '60s, in the period when Pedersen reported the coordination chemistry of metals from groups 1 and 2, and only in the last decades some exceptions. Contrary, anion recognition received none but little attention in view of illustrating the principles of molecular recognition [2-4].

Anions are sensitive to pH modifications (they are protonated at low pH values, loosing their negative charge), therefore the receptors must function in the target pH domain of the anion. Anion ligands design is a challenge for science because anions are bigger in volume than the isoelectronic cations, their radius, \( r_+ \) being in the order: \( r_{Na^+} < r_{K^+} < r_{Rb^+} < r_{Cs^+} \) [2]. Solvents could play a very important role in the anion binding force and in the anion selectivity. Electrostatic interactions are generally dominant in the anion dissolution and, particularly, the hydroxyclic solvents could form strong bonds with the anions. Therefore, a potential anion receptor has to compete with the solvation media in which the anion recognition occurs.

The investigated anions have a wide domain of shapes: spherical (F\(-\), Cl\(-\), Br\(-\), I\(-\)), trigonal planar (NO3\(^-\)), tetrahedrical (H\(_2\)PO\(_4\)\(^-\), HSO\(_4\)\(^-\)). The electrochemical molecular recognition of anions is a growing research domain situated at the confluence between electrochemistry and supramolecular chemistry [3, 4]. Three strategies could be used for the electrochemical detection of formation of receptor-anion complexes: 1) extraction of the singularly-charged target species in a membrane with the help of a non-electroactive host and the detection of the membrane potential (ion-selective electrode, potentiometric receptor), 2) detection of a current/potential modification of a redox property of host for the complex formation and 3) design of a modified electrode based on an active redox matrix and containing a site for selectively binding anions [5]. The present electrochemical study follows the second of the mentioned strategies. It can be correlated with the spectral investigation of the effect of the corresponding anions on similar ligands [6].

Our group has been involved in the study of azulene derivatives [7-11]. A series of azulene compounds has been synthesized [11] in order to be tested for molecular recognition. In this paper we present the electrochemical study of a ligand, derived from 4-azulen-pyridinium: 4-(3,8-dimethyl-5-isopropyl-azulen-1-yl)-2,6-bis(2-thienyl)pyridinium perchlorate (L). It contains a complexing unit (thiophene-pyridinium-thiophene) connected to a polymerizable unit (azulene). The purpose of this study was to investigate the complexation effect of this azulenic ligand toward anions in view of illustrating the principles of molecular recognition [2-4].

Experimental part

Acetonitrile (Rathburn, HPLC grade), and tetra-nbutylammonium perchlorate (TBAP) from Fluka were used as received for solvents and supporting electrolytes. 2,6-di(thien-2-yl)-4-(3,8-dimethyl-5-isopropyl-azulen-1-yl)pyrylum perchlorate, was obtained by specific condensation reactions and it was characterized by elemental and spectral (\(^1\)H-NMR, \(^13\)C-NMR, UV-Vis) analyses [8].

The anion electrochemical recognition with this ligand was performed in acetonitrile (CH\(_3\)CN) solutions containing 0.1M TBAP. The tested anions were: acid sulphate (H\(_2\)PO\(_4\)\(^-\)), nitrate (NO\(_3\)\(^-\)), diacid phosphate (H\(_2\)PO\(_4\)\(^-\), HSO\(_4\)\(^-\)), floride (F\(-\)), chloride (Cl\(-\)), bromide (Br\(-\)) and iodide (I\(-\)) which were used as tetrabutilammonium salts in a solution of azulenic compound (0.06mM) in CH\(_3\)CN. Their sources were the anhydrous tetrabutilammonium salts: tetraethylammonium iodide (TEAI), tetrabutilammonium bromide (TBA Br), tetrabutilammonium acid sulphate (TBAH\(_2\)SO\(_4\)), tetrabutilammonium diacid phosphate (TBAH\(_2\)PO\(_4\)), tetrabutilammonium nitrate (TBA\(_2\)NO\(_3\)) purchased from Fluka and they were used as received.

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Stock solutions (concentration of 0.06M for TEAI and 0.6M for the other salts) were obtained from the anhydrous TBAF, TBACl, TBABr, TBAI, TBAHSO$_4$, TBAH$_2$PO$_4$, and TBAONO$_3$ salts in CH$_3$CN.

Electrochemical experiments were conducted in conventional three-electrode cells under argon atmosphere at 20°C using a PGSTAT 12 AUTOLAB potentiostat. The working electrode was a glassy carbon disk (3 mm diameter) polished with 200μm diamond paste. An Ag/10 mM AgNO$_3$ in CH$_3$CN + 0.1 M TBAP system was used as reference electrode. The counter electrode was a platinum netz in a separate compartment containing CH$_3$CN + 0.1 M TBAP for the synthesis cell, and a platinum wire for the transfer and redox probe cells. All potentials were referred to the potential of ferrocene/ferricinium (Fe/Fc+) couple, which was 0.07 V in our experimental conditions. CV experiments were usually performed at 0.1 V/s, and with different scan rates (0.1–1V/s), for investigation of the scan rate influence. DPV curves were recorded using differential pulse mode with 25 mV pulse amplitude.

Solutions were degassed with a stream of Ar for 20 min before each measurement and kept under Ar atmosphere during the entire experiment, conducted at 25°C. CV experiments were usually performed at 0.1V/s.

The additions (of the order of few μL) corresponding to increasing numbers of anion equivalents have been made directly in the electrochemical cell containing 3mL solution of the ligand in CH$_3$CN + 0.1 M TBAP under stirring, using a Hamilton microsyringe. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) curves have been recorded after each anion addition in the electrochemical cell.

Results and discussions
Ligand characterization

The electrochemical behaviour of the ligand has been investigated initially in order to find the characteristic signals in view of the anion recognition. The studies have been done by two complementary methods: cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in millimolar solutions of the ligand at different concentrations in CH$_3$CN + 0.1 M TBAP. The CV studies have been also performed at different scan rates and potential ranges, in order to establish the reversible character of each electrochemical process.

Figure 1 shows the DPV curves obtained for the azulene derivative L at different concentrations. Both anodic and cathodic curves are shown. One main anodic peak can be observed at: 0.701V (a1) and 1.641V (a2). Six reduction peaks can be seen in the cathodic region at: -0.945V (1c), -1.824V (2c), -2.115 (3c), -2.345V (4c), -2.507V (5c), and -2.673 (6c). The same processes are identified from the CV curves (fig. 2), but the peaks are less defined, with the exception of the first cathodic peak 1c. They appear at: 0.701V (a1) and 1.641V (a2). Six reduction cathodic curves are shown. One main anodic peak can be directly observed at 1.641V, with a slope of 24 μA/(V/s)-1/2 (mM)-1 of the peak currents for 1c and 1c'. The first oxidation peak obtained in DPV and CV for L could be attributed to the formation of the relatively-stable azulene radical cation. The inset from figure 1 shows the linear dependences of all the peak currents on L concentration, in the DPV experiments. Their equations are given in table 1. Figure 3 shows the CV curves for L on different scan ranges. It can be seen that most of the processes are not reversible. The reversibility of the first anodic and cathodic processes has been carefully evaluated from the CV curves obtained at different scan rates (fig. 4). The peaks 1c, 1c', and 1a have potentials with absolute slopes of about 20, 32, and 32mV/decade (table 2), and linear dependences of the peak currents on the square root of the scan rate (fig. 4, inset) showing diffusion controlled processes. The peak currents for 1c and 1c' have small slopes of around 14.3 and 2.74μA(V/s)$^{1/2}$ (mM)$^{-1}$, respectively, while the peak current for 1a has a slope of about 24μA(V/s)$^{1/2}$ (mM)$^{-1}$ (table 2). In the range of investigated scan rates the process 1c is irreversible. The first reduction potential 1c of L obtained in DPV and CV could be attributed to the reduction of pyrrolidinoyl moiety from the starting azulene to a rather stable radical. A diffusion coefficient of ~0.5*10$^{-5}$cm$^2$s$^{-1}$ has been calculated for L from 1c slopes using Randless-Sevcik equation for 1e transfers. This value for the diffusion coefficient of 2,6-di(thien-2-yl)-4-(3,8-dimethyl-5-isopropyl-azulen-1-yl)-pyrrole perchlorate is smaller than those for another azulene derivative, 4-azulen-1-yl-2,6-bis(2-thienyl)pyridine (having D = 10$^{-2}$ cm$^2$s$^{-1}$) [14], but it could be explained by their different charges and also by their number of substituents (L being more substituted). Figure 1-4 shows also the appearance of other cathodic peaks
which could be attributed to further reduction of the radical anion.

**Anions recognition**

The studies have been done by two complementary methods: cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The first reduction peak from DPV and CV curves of the ligands in this series has been examined to put in evidence the influence of anions on the electrochemical behaviour of these ligands in view of molecular recognition by these substrates. The electrochemical behaviour of 4-(3,8-dimethyl-5-isopropyl)-azulen-1-yl-2,6-bis(2-thienyl)pyridinium perchlorate has been investigated in the presence of increased amounts of anions (HSO₄⁻, NO₃⁻, H₂PO₄⁻, F⁻, Cl⁻, Br⁻, and I⁻) in CH₃CN + 0.1 M TBAP in milimolar solutions of each ligand. A kinetic study was performed by CV at the beginning of the addition of each anion in order to check if there is any influence of time on the peak current or potential. Hence, CV curves were registered at specific moments (1, 3, 5, 10, 15, 20 min) after the first additions. It was shown that time has no influence. Some of the most representative curves are shown further for the ligand in the presence of each of the investigated anions, in order to show its influence on the peak 1c.

![Figure 3](image-url) CV curves on different anodic and cathodic scans at 0.1V/s on glassy carbon electrode (3mm in diameter) in 1 mM L, 0.1MTBAP, CH₃CN

![Figure 4](image-url) CV curves in anodic and cathodic scans at different scan rates on glassy carbon electrode (3mm in diameter) in 1 mM L, 0.1M TBAP, CH₃CN; upper inset: dependences of the recorded peak potentials (E1a, E1c, and E1c') on concentration logarithm (log c); lower inset: linear dependences of the recorded peak currents (i1a, i1c, and i1c') on concentration (c)

**Table 1**

| DATA CONCERNING THE DEPENDENCE OF PEAK CURRENTS AND POTENTIALS FROM DPV AND CV EXPERIMENTS ON CONCENTRATION OF L |
|---|---|
| Peak | \( i_{\text{p}} \), DPV | \( i_{\text{p}} \), CV |
| | \( i (\text{A}); c (\text{mM}) \) | \( i (\text{A}); c (\text{mM}) \) |
| a1 | \(-1.042E-6 + 7.907E-6\cdot c \) (\( R^2 = 0.919 \)) | \(-3.882E-7 + 1.701E-5\cdot c \) (\( R^2 = 0.993 \)) |
| a2 | \( 8.934E-6 + 3.732E-6\cdot c \) (\( R^2 = 0.646 \)) | \( 5.117E-5 + 9.189E-5\cdot c \) (\( R^2 = 0.963 \)) |
| 1c | \( 2.026E-6 - 8.504E-6\cdot c \) (\( R^2 = 0.927 \)) | \( 1.155E-6 - 1.565E-5\cdot c \) (\( R^2 = 0.954 \)) |
| 2c | \( 7.038E-7 - 3.824E-6\cdot c \) (\( R^2 = 0.951 \)) | \( -4.813E-6 - 1.128E-5\cdot c \) (\( R^2 = 0.482 \)) |
| 3c | \( 1.494E-6 - 7.051E-6\cdot c \) (\( R^2 = 0.953 \)) | \( -1.037E-7 - 2.493E-5\cdot c \) (\( R^2 = 0.947 \)) |
| 4c | \( 3.227E-6 - 1.361E-5\cdot c \) (\( R^2 = 0.969 \)) | \( 7.670E-6 - 5.753E-5\cdot c \) (\( R^2 = 0.999 \)) |
| 5c | \( 1.760E-6 - 8.975E-6\cdot c \) (\( R^2 = 0.964 \)) | \( 5.722E-6 - 6.049E-5\cdot c \) (\( R^2 = 0.999 \)) |
| 6c | \( 2.345E-6 - 1.227E-5\cdot c \) (\( R^2 = 0.966 \)) | \( 9.412E-6 - 8.655E-5\cdot c \) (\( R^2 = 0.997 \)) |

**Table 2**

LINEAR CV PEAK CURRENTS AND POTENTIALS DEPENDENCES ON SCAN RATE FOR L (1mM)

<table>
<thead>
<tr>
<th>Peak</th>
<th>( i_{\text{p}} ), CV</th>
<th>( E_{\text{p}} ), CV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Y (i, A); X (V^{12}, \text{V}/\text{s}^{12}) )</td>
<td>( Y (E, V); X (\log (v, \text{V/s})) )</td>
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<tr>
<td>1a</td>
<td>( 7.416E-7 + 7.122E-5\cdot X ) (( R^2 = 0.985 ))</td>
<td>( 0.759 + 0.032 \cdot X ) (( R^2 = 0.938 ))</td>
</tr>
<tr>
<td>1c</td>
<td>(-2.459E-6 - 4.294E-5\cdot X ) (( R^2 = 0.999 ))</td>
<td>(-0.999 - 0.020 \cdot X ) (( R^2 = 0.858 ))</td>
</tr>
<tr>
<td>1c'</td>
<td>(-3.360E-7 - 8.107E-6\cdot X ) (( R^2 = 0.949 ))</td>
<td>(-0.901 + 0.032 \cdot X ) (( R^2 = 0.990 ))</td>
</tr>
</tbody>
</table>
Fig. 5. DPV (A) and CV (B) curves in the presence of increasing amounts of anions: $\text{H}_2\text{PO}_4^-$ in solutions of L (1mM) in 0.1M TBAP, CH$_3$CN; upper inset: dependences of the DPV ($i_{1c_f}$, $i_{1c_c}$) and CV ($i_{pc\text{CV}}$) peak potentials for the peak 1c on the number of $\text{H}_2\text{PO}_4^-$ equivalents (eq); lower inset: variation of the recorded peak currents ($i$) in CV on the number of $\text{H}_2\text{PO}_4^-$ equivalents (eq)

denoted 1c$^c$ linearly decreases (to extinction at 1eq) at the expense of a new peak 1c$^c$, which increases to a plateau value (after 1eq), as shown in the upper inset of figure 5. 1c$^c$ is situated at a more negative potential, and it is due to the reduction of the complexed ligand. After 1eq, the peak 1c$^c$ disappears, being replaced by 1c$^c$. The CV curves present a similar evolution, the reversible couple for 1c$^c$ (with a formal potential $E^\prime$ of -0.937V), being replaced by another reversible couple for 1c$^c$ (with $E^\prime = -1.08V$). The potential for 1c$^c$ is shifted in respect to 1c$^c$ with 0.143V to more negative values. The gradual increase of a negative current at the beginning of scanning during the anion addition could be an evidence of the formation of secondary degradation products. The inset in Fig 5A allows the evaluation of a 1:1 L: stoichiometry of the complex of L with $\text{H}_2\text{PO}_4^-$.

In the presence of F$^-$ (fig.6A) the peak current for 1c linearly decreases in absolute value till extinction (at 1eq) at the expense of a new peak 1c$^c$ which shows a plateau at higher amount of F$^-$ than 1eq. The CV curves for the free (0eq in fig. 6B) and complexed ligand (1.6eq in fig. 6B) are quite different in shape and current values, the complexed ligand reduction being more irreversible and with lower currents than the free ligand (the potential is shifted with about 0.13V towards negative potentials and the peak current is about half the value for the free ligand). The new couple for the complexed ligand has a smaller peak current than the free ligand both in DPV and CV. This two-wave behaviour is similar to that observed in the presence of $\text{H}_2\text{PO}_4^-$ ions, but the second couple is less reversible for the complex with F$^-$. Table 3 shows that the number of evidenced peaks is 2 for $\text{H}_2\text{PO}_4^-$ and F$^-$ (two-wave behaviour), and the shift of the signal for the complexed ligand is lower for F$^-$ (125mV) than in the case of $\text{H}_2\text{PO}_4^-$ (143mV). At the beginning of scanning during the anion addition there is also an increase of the cathodic current, as a result of formation of secondary degradation products.

In the presence of other anions: Br$^-$ (fig.7), Cl$^-$ (fig. 8), I$^-$ (fig. 9), NO$_3^-$ (fig. 10), HSO$_4^-$ (fig. 11), the properties of the ligand are not significantly altered.

Fig. 6. DPV (A) curves in the presence increasing amounts of anions: F$^-$ in solutions of L (1mM) in 0.1M TBAP;CH$_3$CN; CV curves of the free and complexed ligand (B); variation of $i_{c}/(i_{c})^0$ ratio with the number of F$^-$ equivalents (eq) added in the ligand solution (C)

Fig. 7. DPV (A) and CV (B) curves in the presence increasing amounts of Br$^-$ in solutions of L (1mM) in 0.1M TBAP;CH$_3$CN; variation of CV anodic (ipa) and cathodic (ipc) currents and DPV anodic current (idpv) with the number of Br$^-$ equivalents (eq) added in the ligand solution (C)
Fig. 8. DPV (A) and CV (B) curves in the presence increasing amounts of Cl\textsuperscript{-} in solutions of L (1mM) in 0.1M TBAP, CH\textsubscript{3}CN; variation of CV anodic (ipa) and cathodic (ipc) currents and DPV anodic current (idpv) with the number of Cl\textsuperscript{-} equivalents (eq) added in the ligand solution (C).

Fig. 9. DPV (A) and CV (B) curves in the presence increasing amounts of NO\textsubscript{3}\textsuperscript{-} in solutions of L (1mM) in 0.1M TBAP, CH\textsubscript{3}CN; variation of CV anodic (ipa) and cathodic (ipc) currents and DPV anodic current (idpv) with the number of NO\textsubscript{3}\textsuperscript{-} equivalents (eq) added in the ligand solution (C).

Fig. 10. DPV (A) and CV (B) curves in the presence increasing amounts of I\textsuperscript{-} in solutions of L (1mM) in 0.1M TBAP, CH\textsubscript{3}CN; variation of CV anodic (ipa) and cathodic (ipc) currents and DPV anodic current (idpv) with the number of I\textsuperscript{-} equivalents (eq) added in the ligand solution (C).

Fig. 11. DPV (A) and CV (B) curves in the presence increasing amounts of HSO\textsubscript{4}\textsuperscript{-} in solutions of L (1mM) in 0.1M TBAP, CH\textsubscript{3}CN; variation of CV anodic (ipa) and cathodic (ipc) currents and DPV anodic current (idpv) with the number of HSO\textsubscript{4}\textsuperscript{-} equivalents (eq) added in the ligand solution (C).

### Table 3

<table>
<thead>
<tr>
<th>Anion</th>
<th>F\textsuperscript{-}</th>
<th>Cl\textsuperscript{-}</th>
<th>Br\textsuperscript{-}</th>
<th>I\textsuperscript{-}</th>
<th>NO\textsubscript{3}\textsuperscript{-}</th>
<th>HSO\textsubscript{4}\textsuperscript{-}</th>
<th>H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}</th>
<th>(\Delta E) DPV (V)</th>
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<tr>
<td>Number of evidenced peaks</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>0,125</td>
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<tr>
<td>(\Delta E) DPV (V)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0,143</td>
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</table>
Conclusions

2,6-di(thien-2-yl)-4-(3,8-dimethyl-5-isopropyl-azulen-1-yl)-pyrilium perchlorate has been characterized by cycling voltammetry and differential pulse voltammetry. This ligand has been tested for anion recognition. It showed a modified electrochemical behaviour in the presence of $H_2PO_4^-$ and $F^-$. 1:1 complexes have been formed with these anions. No influence was noticed in the presence of other anions (Br, Cl, I, $NO_3^-$, $HSO_4^-$).

References


Manuscript received: 28.06.2011