

MESO–TETRAFERROCENYL–TETRAMETHYLCALIX[4]PYRROLE-MODIFIED GRAPHITE ELECTRODE WITH ANION RECOGNITION PROPERTIES

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The electrochemical behavior of meso–tetraferrocenyl–tetramethylcalix[4]pyrrole-modified graphite electrode (**G/TFCP**), was investigated in order to evaluate its anion recognition properties. Cyclic voltammetry measurements were used to investigate the **G/TFCP** electrochemical response in different experimental conditions (electrode materials, anion concentrations, pHs and potential scan rates), and in the presence of various anions (F^- , Cl^- , Br^- , SO_4^{2-} , $H_2PO_4^-$, ClO_4^- and NO_3^-). The voltammetric response of **TFCP** adsorbed on graphite presents only one wave, the value of the anodic peak potential allowing to range the binding strength between **TFCP** and the investigated anions in the following sequence: ($Br^- \cong H_2PO_4^- \cong SO_4^{2-}$) > F^- > Cl^- > NO_3^- > ClO_4^- .

INTRODUCTION

In the last years, much interest has been paid to the development of new receptors and sensors for anions.^{1–9} In this context, electrochemical recognition, based on the ability of redox responsive molecules to selectively bind and recognize guest species through the perturbations of the redox system, was proved to be a powerful tool in sensors design.^{1,9–14}

Among the compounds containing electrochemically active groups, which are promising candidates for fabrication of new amperometric or potentiometric sensory devices for anions, those based on ferrocene moiety are very attractive. Thus, besides the convenient value of the ferrocene formal potential and its good chemical stability,^{9,14,15} the oxidation of ferrocene to ferricinium “switches on” electrostatic interactions between the receptor and the detected anions.¹⁵ Incorporating this signaling moiety into various host framework such as calixarenes,^{1,9,16,17} pyrrole derivatives,^{18,19} urea derivatives,²⁰ amides,^{1,9,21–23} amines,^{5,9,24} aza-macrocycles,^{1,4,6} silicon and tin containing macrocycles⁶ etc. led to valuable approaches to obtain new and effective receptors for anion detection.

The strategy of combining a pyrrole binding entity with ferrocene²⁵ was recently developed by attaching one ferrocene unit to a calix[4]pyrrole ring.^{26,27} It was put on evidence that the resulting structure exhibits good anion recognition properties due to both ferrocene and calix[4]pyrrole interactions with the guest anion.

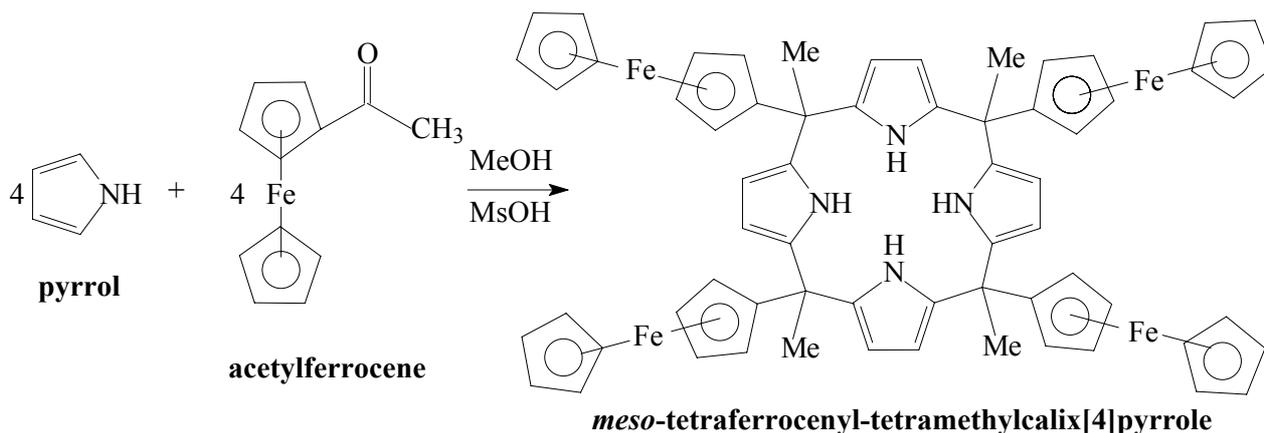
In this context, the electrochemical behavior of meso–tetraferrocenyl–tetramethylcalix[4]pyrrole-modified graphite electrode (**G/TFCP**) was investigated. Cyclic voltammetry measurements were performed in order to examine the **TFCP** electrochemical response in various experimental conditions (different electrode materials, anion concentrations, pH and potential scan rates), and in the presence of the following anions: ClO_4^- , NO_3^- , F^- , Cl^- , Br^- , SO_4^{2-} , $H_2PO_4^-$.

EXPERIMENTAL

Chemicals

TFCP was synthesized in acidic catalysis at room temperature, starting from pyrrole and acetylferrocene (Scheme 1), following a strategy described elsewhere.²⁸ The overall yield was 65%.

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Scheme 1. Overall reaction corresponding to **TFCP** synthesis.

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use.

NMR spectra were recorded on a DPX-400 Bruker Advance instrument. IR spectra were recorded with a FTIR 600 spectrophotometer (Jasco, USA). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ_{H} 7.16 ppm (s, NH); 5.52 ppm (d, $\text{CH}_{\text{pyrrole}}$); 5.58 ppm (d, $\text{CH}_{\text{pyrrole}}$); 5.80-5.90 ppm (m, $\text{CH}_{\text{pyrrole}}$); 3.97-4.21 ppm (m, ferrocenyl); 2.36 ppm (s, CH_3); 1.82-1.98 ppm (s, CH_3); 1.25 ppm (s, CH_3); δ_{C} (CDCl_3) 1.01, 28.90, 39.39, 68.15, 77.01, 97.55, 104.75, 125.29, 129.03, 137.03 ppm; ν_{max} (KBr)/ cm^{-1} 3433, 3095, 2973, 2927, 1710, 1648, 1570, 1461, 1414, 1361, 1230, 1180, 1107, 1038, 1001, 818, 762, 505. NMR and IR spectra of the **TFCP** confirmed the structure presented in scheme 1.

DMSO (Merck, Darmstadt, Germany) was used as appropriate solvent for **TFCP**. The potassium salts of the investigated anions (NO_3^- , F^- , Cl^- , Br^- , SO_4^{2-} and H_2PO_4^-) and NaClO_4 were purchased from Merck (Darmstadt, Germany). All reagents were of analytical grade and used as received.

Electrochemical measurements

Electrochemical measurements were performed in a conventional single-compartment three-electrode cell using a computer-controlled voltammetric analyzer (AutoLab-PGSTAT 10, Eco Chemie, Utrecht, The Netherlands). The reference electrode was a saturated calomel electrode (SCE), to which all the electrode potentials were referred. A coiled platinum wire served as counter electrode.

The graphite (G; Ringsdorf-Werke, GmbH, Bonn-Bad Godesberg, Germany) working disc electrode ($\text{Ø} = 3$ mm) and the glassy carbon (GC; BAS, West Lafayette, USA) disc electrode ($\text{Ø} = 5$ mm) were wet polished on fine (grit 400 and 600) emery paper (Buehler, Lake Bluff, IL, USA) and, before surface modification, they were rinsed thoroughly with doubly distilled water. The gold (BAS, West Lafayette, USA) disc electrode ($\text{Ø} = 3$ mm) was cleaned using the conventional procedure recommended for gold electrodes.²⁹ Afterwards, the electrode was rinsed thoroughly with doubly distilled water. The platinum (BAS, West Lafayette, USA) disc electrode ($\text{Ø} = 3$ mm) was wet polished with alumina and then sonicated in distilled water.

The **TFCP**-modified electrodes were prepared by spreading 5 μL from a 1 mM solution of **TFCP** in DMSO onto

the electrode surface, followed by solvent evaporation. Before use, all modified electrodes were thoroughly rinsed with doubly distilled water.

RESULTS AND DISCUSSION

Adsorbed **TFCP** exhibits only one pair of peaks attributed to a quasi-reversible redox couple (Fig. 1). The anion nature affects this behavior, proving that even adsorbed **TFCP** maintains its ability to bind anions.²⁸ Thus, the $E_{\text{p,a}}$ value of adsorbed **TFCP**, recorded in the presence of NO_3^- , is shifted towards more negative potentials as compared to ClO_4^- (Fig. 1).

The slope of the log-log dependence of peak current vs. potential scan rate, recorded for **G/TFCP** modified electrode immersed in 10^{-1} M NaClO_4 aqueous solution (0.78 ± 0.032 with $R/N = 0.997/5$ for the oxidation process; 0.93 ± 0.032 with $R/N = 0.998/5$ for the reduction process), proves that **TFCP** is relatively strongly immobilized on the electrode surface. Additionally, from the slope of the peak current dependence on the potential scan rate, for a surface-confined redox couple,³⁰ the number of electrons involved in voltammetric response of immobilized **TFCP** was found close to one (1.17).

A comparison of the voltammetric response for **TFCP** adsorbed on different electrode materials (Au, Pt, GC, G) shows that, irrespective of electrode material, the shape of the voltammogram remains invariant (results not shown). Within the experimental error, the peak potentials were not influenced by the electrode material but the highest current density was noticed for graphite (Table 1). Consequently, further results refer exclusively to **G/TFCP** modified electrode.

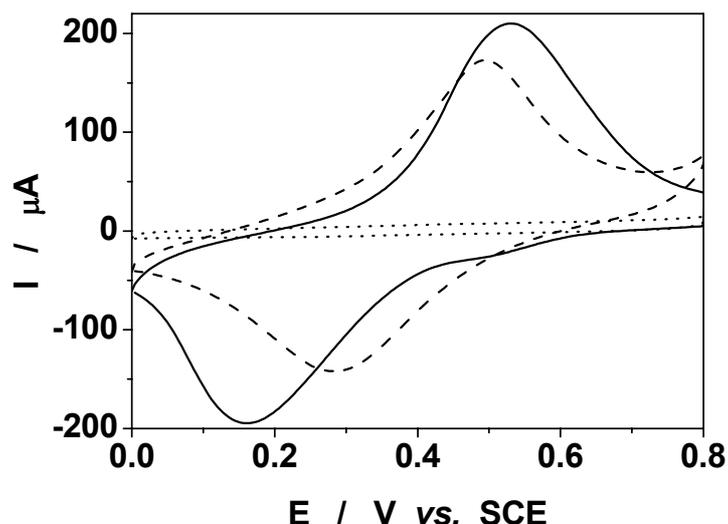


Fig. 1 – Cyclic voltammograms recorded at **G/TFCP** electrode in 0.1 M NaClO_4 (—) and 0.1 M NaNO_3 (- - -). The dotted line corresponds to the response of the bare graphite electrode. Experimental conditions: potential scan rate, 50 mV/s; starting potential, 0 V vs. SCE.

Table 1

Influence of electrode material on the electrochemical parameters for **TFCP**-modified electrodes. Experimental conditions: supporting electrolyte, 0.1 M NaClO_4 ; scan rate, 50 mV/s

Electrode material	$i_{p,a}$	$i_{p,c}$	$E_{p,a}$	$E_{p,c}$
	10^3 A/cm^2		V vs. SCE	
Au	0.15	0.28	0.455	0.248
Pt	0.09	0.29	0.442	0.274
GC	0.17	0.24	0.450	0.240
G	2.50	2.40	0.482	0.206

The analysis of the electrochemical parameters corresponding to the cyclic voltammograms, recorded at **G/TFCP** modified electrode in the presence of different anions (ClO_4^- , SO_4^{2-} , Br^- , F^- , NO_3^- , H_2PO_4^- , Cl^-) (Table 2) led to the following conclusions: (i) the redox process involved in the voltammetric response can be considered as a quasi-reversible one (see the values of ΔE_p and E_{FWHM}); (ii) strong repulsive interactions occur between the adsorbed **TFCP** molecules in its oxidized state ($E_{\text{FWHM}} > 90.6/n$);³¹ (iii) the increasing order of the anodic peak potentials allowed establishing the following sequence for the anion binding strength decrease: ($\text{H}_2\text{PO}_4^- \cong \text{SO}_4^{2-} \cong \text{Br}^-$) > F^- > Cl^- > NO_3^- > ClO_4^- . The selectivity sequence reported above, generally, corresponds to

that reported for monoferrocene calix[4]pyrrole ($\text{H}_2\text{PO}_4^- > \text{F}^- > \text{Cl}^- > \text{Br}^-$),^{26,27} excepting the case of bromide anion. In order to understand the reason of this discrepancy, further investigations are in progress.

Repetitive cyclic voltammograms, performed in the potential range corresponding to the redox response of **TFCP**, allowed evaluating the stability of **G/TFCP** modified electrodes. Thus, in the presence of NO_3^- , **TFCP** is gradually removed from the graphite surface (Fig. 2A), while the presence of ClO_4^- anion, practically, does not affect the stability of **G/TFCP** electrode (Fig. 2B). This behavior is in agreement with the statements formulated above, referring to the stability of the **TFCP**-anion complex.

Table 2

Electrochemical parameters for the voltammetric response of G / TFCP modified electrodes in contact with different anions.
Experimental conditions: supporting electrolytes concentration 0.1 M; potential scan rate, 50 mV/s

Anion	Anodic peak		ΔE_p^{**} (V)	I_{pa}/I_{pc}	Γ (10^8 mole / cm^2)
	E_{pa} (V vs. SCE)	E_{FWHM} (V)*			
F ⁻	0.486	0.293	0.193	0.9	2.0
Cl ⁻	0.490	0.235	0.165	1.2	3.3
Br ⁻	0.474	0.210	0.177	0.9	3.9
H ₂ PO ₄ ⁻	0.474	0.222	0.161	1.2	3.4
NO ₃ ⁻	0.499	0.185	0.215	1.3	10.8
SO ₄ ²⁻	0.474	0.239	0.194	1.4	3.9
ClO ₄ ⁻	0.527	0.218	0.276	1.4	11.2

* E_{FWHM} stands for the peak width at half maximum

** ΔE_p stands for peaks split

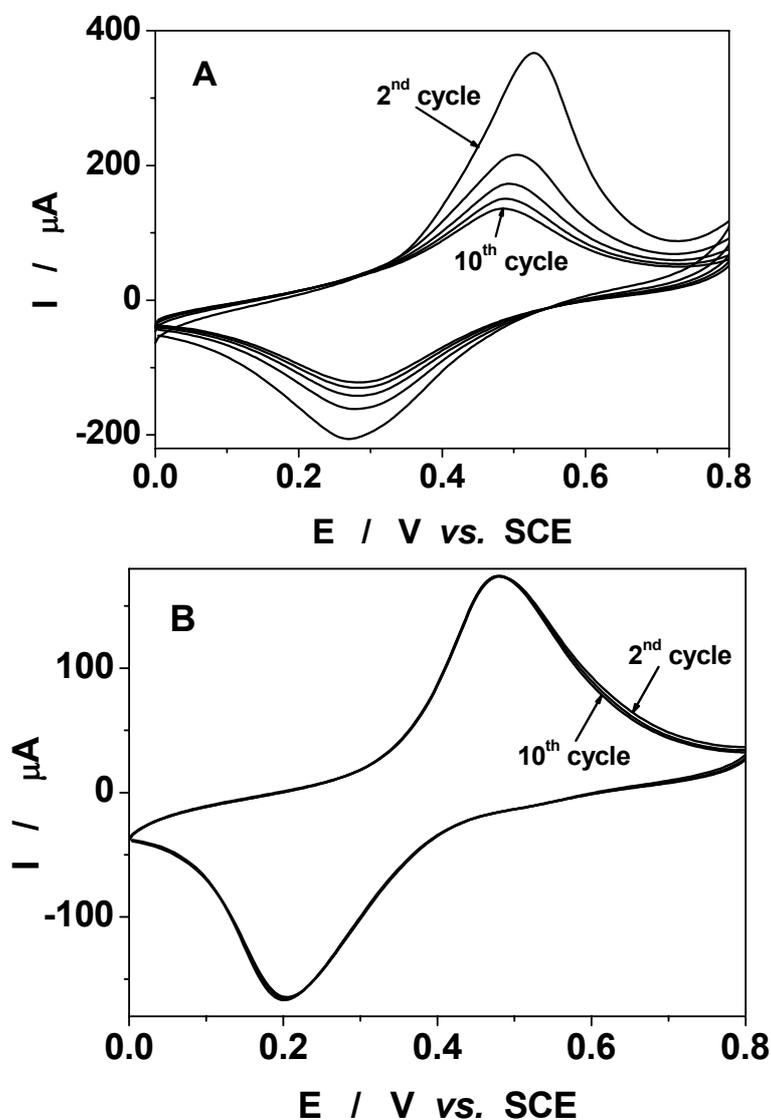


Fig. 2 – The stability of the voltammetric response for G / TFCP during repetitive electrode potential cycling in the presence of 0.1 M NaNO₃ (A) or 0.1 M NaClO₄ (B).
Experimental conditions: as in figure 3.

Increasing ClO_4^- concentrations shift the anodic peak potential of adsorbed **TFCP** towards more negative potentials (Fig. 3A), increase both anodic and cathodic peak currents (inset 2) and decrease drastically the peak width at half height (inset 1). The change of the voltammogram shape and the variation of anodic peak potential could be attributed to specific interactions arising between the ferricinium sites and ClO_4^- anion. This kind of interactions, leading to complexes or ion-pairs, was already put on evidence when ferrocene unit has been incorporated in anthracene-ferrocene ester³² and poly(vinylferrocene).³³

It is interesting to note that a behavior similar to that presented above was observed for **G/TFCP** modified electrode, when its voltammetric response was recorded in solutions containing NaClO_4 and HClO_4 with different pH values (Fig. 3B). The slight increase of the anodic peak current observed when pH decreases, simultaneously with the negative shift of the anodic peak potential should be due to the beneficial effect of H^+ concentration increase on the stability of the **TFCP**- ClO_4^- complex *via* calix[4]pyrrole macrocycle protonation.^{6,9}

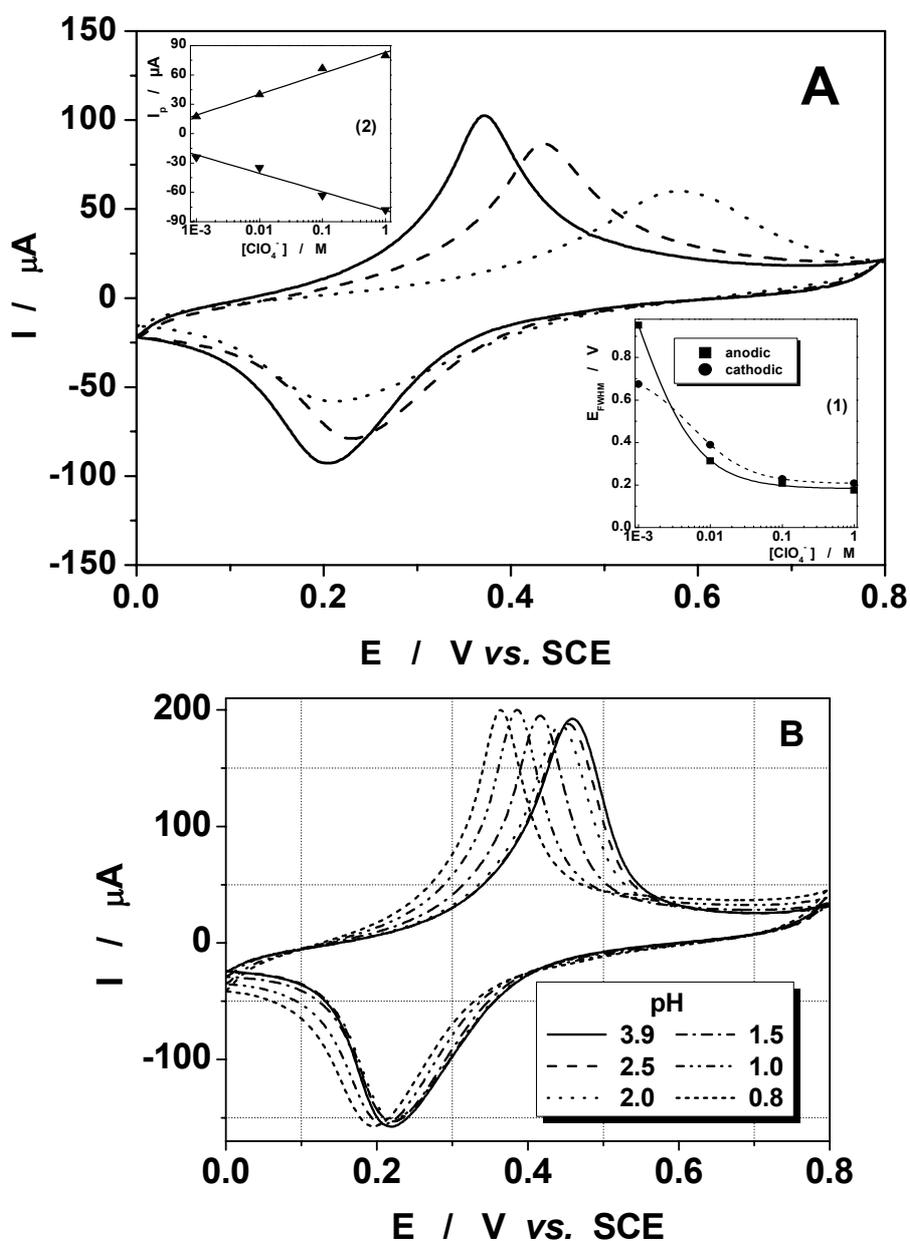


Fig. 3 – Influence of ClO_4^- concentration (A) and pH (B) on the voltammetric response of **G/TFCP** electrode: (A) (—) 1 M ClO_4^- ; (- - -) 0.1 M ClO_4^- ; (·····) 0.01 M ClO_4^- . Experimental conditions: potential scan rate, 50 mV/s; starting potential, 0 V vs. SCE. Inset (1) illustrates the peak current increase with ClO_4^- concentration, and inset (2) shows the dependence on ClO_4^- concentration of peak width at half height.

Using the Laviron treatment,³⁴ from cyclic voltammetric measurements performed in 0.1 M perchlorate solutions at different potential scan rates (Figure 4), by using the equation:

$$E_{pc} - E^0 = \frac{RT}{\alpha nF} \cdot 2,3 \lg \frac{\alpha nF}{RTk_s} + \frac{2,3RT}{\alpha nF} \lg v$$

where k_s [s^{-1}] is the heterogeneous electron transfer rate constant, α the transfer coefficient and n the number of transferred electrons, the kinetic parameters for the heterogeneous electron transfer process at G / TFCP electrode were estimated: $\alpha = 0.17$; $k_s = 0.2 s^{-1}$.

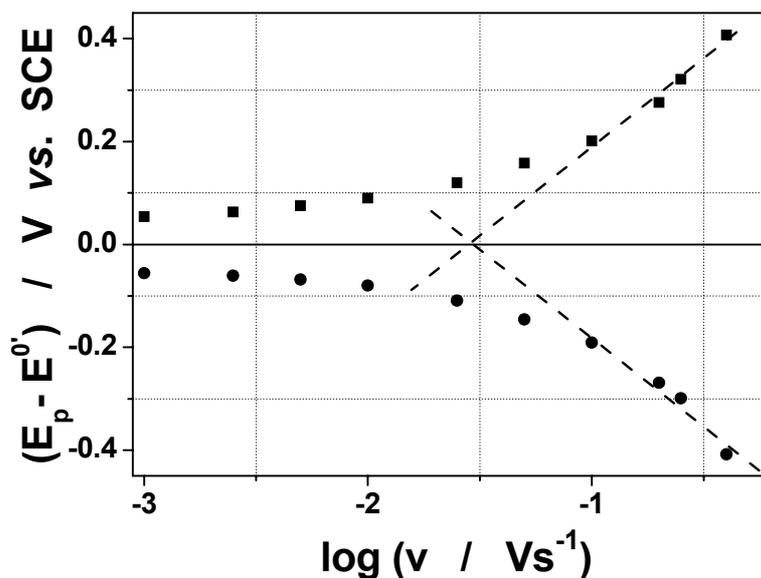


Fig. 4 – Influence of potential scan rate on the $(E_p - E^0)$ difference for G/TFCP electrode, in contact with 0.1 M $NaClO_4$ aqueous solution.

CONCLUSIONS

In this work, on our best knowledge, the first example of a modified electrode with a redox-switchable receptor for anions, containing four ferrocene subunits connected to calix[4]pyrrole macrocycle, is reported. The electrochemical parameters of the voltammetric response, estimated in different experimental conditions, point to a quasi-reversible redox process ($k = 0.2 s^{-1}$) involving one electron.

The repetitive potential cycling, as well as the influence of ClO_4^- and H^+ concentrations on the TFCP voltammetric response prove that, even immobilized, TFCP maintains its ability to selectively bind anions. The value of the anodic peak potentials allows ranging the binding strength between TFCP and the investigated anions in the following sequence: $(H_2PO_4^- \cong SO_4^{2-} \cong Br^-) > F^- > Cl^- > NO_3^- > ClO_4^-$.

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