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ORIGINAL ARTICLE

Redox-switchable binding of ferrocyanide with tetra(viologen)calix [4] resorcine

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Abstract A binding of ferrocyanide ($[Fe(CN)_6]^{4-}$) with octa-cationic tetra(viologen) calix [4] resorcine ($MVCA^{8+}$) and its "model" compound—dimethyl viologen (MV^{2+}) has been studied by cyclic voltammetry in DMSO-H_2O media (60 vol.% aqueous DMSO, 0.1 M $NaClO_4$). It was found that MV^{2+} does not interact with ferrocyanide. By contrast, a reversible redox-switchable interaction between $[Fe(CN)_6]^{4-}$ and $MVCA^{8+}$ has been observed. $MVCA^{8+}$ forms a 1:1 supramolecular complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ with ferrocyanide while its reduced forms ($MVCA^{4+\cdot}$ and $MVCA^0$) do not interact with the tetraanion. The switching of the ferrocyanide binding is also observed in the one electron oxidation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$. It has been shown, that the calix [4]resorcine in its partial and fully reduced forms and its complex with ferrocyanide form well-defined nanoscale multi-layer films on the electrode surface.

Keywords Supramolecular chemistry · Calixarenes · Ferrocyanide · Redox-switching · Adsorption

Introduction

Supramolecular systems [1] on the basis of macrocyclic compounds with electrochemically active fragments capable of reversible redox-transitions in the near-field potentials have lately attracted much attention for their using in creation of nanoscale molecular devices with redox-switchable properties. There are many examples of the construction of molecular machines of the catenane and rotaxane type containing electrochemically active building blocks [2–25]. The operation of these molecular mechanisms is based on the reversible redox-switchable interaction of their buildings blocks. The reversible electron transfer from a donor group or to an acceptor fragment involves a reversible molecular movement of components of the mechanisms due to the fundamental change in the donor–acceptor properties of the components [25].

Redox-active macrocycles are also widely used for the redox-switchable binding of different guest-molecules: inorganic cations [26–28], anions [29–31] or both of the ions [30]. Electrochemically inert macrocycles such as cyclodextrins and cucurbiturils are also applied for the creation of redox-switchable inclusion complexes which are generally operated on the electrochemical reduction or oxidation of guest-molecules (viologen derivatives, transition metal ions, iodide ion) [32–36].

(Thia)calix[n]arenas and calix [4] resorcines, as macrocyclic polyphenols, are electrochemically active compounds with a tendency for oxidation [37–43]. But these oxidation reactions are reversible only under specific conditions, and in most cases they are irreversible. Therefore, the most redox-switchable host–guest complexes of calixarenes [44–52] operate through redox-active guests. Exceptions are calixarenes with protected hydroxyl groups containing redox-active moieties, for example tetra(methylviologen) calix [4] resorcine ($MVCA^{8+}$). Previously [53], the redox-switchable interaction of $MVCA^{8+}$ with tetraanionic tetra(sulfonatomethylene)calix [4] resorcine (SCA^{4-}) was observed in the DMSO media. The viologen units of $MVCA^{8+}$ undergo a two-step electrochemical

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reduction with the formation of tetra(cation-radical) $MVCA^{4+\cdot}$ in the first step and neutral $MVCA^0$ in the second step. The switching interaction occurs at the second step of reduction, i.e. $MVCA^{8+}$ and $MVCA^{4+\cdot}$ bind SCA^{4-} with the formation of a supramolecular 1:1 capsule, while the full reduced neutral form of $MVCA^0$ does not interact with SCA^{4-}. In this paper, we report the results of our investigation of the complexation of $MVCA^{8+}$ with a smaller tetraanion—ferrocyanide $[Fe(CN)_6]^{4-}$.

Experimental

Cyclic voltammograms were recorded using potentiostat PI-50-1 interfaced to XY recorder H 307/2 at potential scan rate $\upsilon = 100$ mV·s^{-1} in DMSO-H_2O media (60 vol.% aqueous DMSO, 0.1 M $NaClO_4$) at 295 K. A glassy carbon working electrode ($\eth = 3.4$ mm) embedded in teflon and a saturated calomel electrode (SCE) as a reference electrode were used in electrochemical cell. Before each measurement the surface of the working electrode was mechanically polished. The diffusion nature of the peaks currents (i_p) was proved by the theoretical form of voltammograms and by a linear dependence of $i_p \sim \upsilon^{1/2}$ (υ–potential scan rate). The adsorption nature was established by the presence of an adsorption maximum and by a linear dependence of $i_p \sim \upsilon$ in the range of 10–200 mV·s^{-1} [54].

$MVCA^{8+}·8PF_6^-$ was synthesized as described previously [53]. $MV^{2+}·2Cl^-$, $K_4[Fe(CN)_6]$ and $NaClO_4$ were used as received from the manufacturers. The concentration of MV^{2+} in solution was $C = 0.8$ mM. The concentration of $MVCA^{8+}$ and $[Fe(CN)_6]^{4-}$ was $C = 0.2$ mM. DMSO was purified as described in [55]. Double distilled water was used throughout.

Results and discussion

At the beginning of the experiment a solvent was chosen for adequate solubility of all investigated compounds and their interaction products. $K_4[Fe(CN)_6]$ is soluble in water but not in DMSO. Dimethylviologen dichloride $MV^{2+}·2Cl^-$ is readily soluble in both solvents. $MVCA^{8+}·8PF_6^-$ is soluble in DMSO but not in water. An optimal ratio of water and DMSO was found as 60 vol.% DMSO when varying the composition of the solution. In this media all compounds are fully soluble at the concentration of $C = 0.2$ mM. The investigated salts, including $MVCA^{8+}·8PF_6^-$ readily dissociate in polar media, as do the salts, which can be formed in the presence of the background electrolyte $NaClO_4$ [53]. Thus, 60 vol.% aqueous DMSO media makes it possible to operate with individual ions: $[Fe(CN)_6]^{4-}$, MV^{2+} and $MVCA^{8+}$. All the studies were carried out in this mixed solvent.

$[Fe(CN)_6]^{4-}$ in aqueous DMSO is slowly oxidized to $[Fe(CN)_6]^{3-}$ during the time of recording of cyclic voltammograms (CV) (in ~30–40 min after dilution). For this reason both forms of the anion are present in solution. This is evidenced by the steady-state potential of glassy carbon electrode ($E_{st} = +0.45$ V), which is more positive than the potentials of the oxidation peak of $[Fe(CN)_6]^{4-}$ ($E_p = +0.35$ V) and the reduction peak of $[Fe(CN)_6]^{3-}$ ($E_p = +0.24$ V). We did not carry out specific experiments to determine the nature of oxidation of $[Fe(CN)_6]^{4-}$, assuming that ferrocyanide is oxidized by molecular oxygen dissolved in the DMSO media.

The binding of $[Fe(CN)_6]^{4-}$ with MV^{2+} and $MVCA^{8+}$ was assumed because of the influence of ferrocyanide anion on the characteristics of the two peaks of the reduction and re-oxidation of methylviologen and calix [4] resorcine. In addition, the control on the oxidation peak of tetraanion $[Fe(CN)_6]^{4-}$ was performed.

Two one-electron well-separated reduction peaks (E_p^1–$E_p^2 = 0.37$ V) and two re-oxidation peaks associated with them are presented on CV of MV^{2+} (Fig. 1). All peak currents are diffusion-controlled. Both reduction steps are completely reversible ($\Delta E_p = 56$ mV) [54]. Thus, MV^{2+} undergoes two reversible reductions with the formation of a stable cation-radical $MV^{+\cdot}$ and neutral diamine MV^0 respectively in the chosen media (60 vol.% aqueous DMSO) as described in the literature [53] (Scheme 1).

The addition of $[Fe(CN)_6]^{4-}$ to MV^{2+} solution in 1:4 ratio does not lead to any significant changes in the characteristics (diffusion nature, reversibility, current, and potentials) of the reduction peaks of MV^{2+} (Table 1, Fig. 1). Only

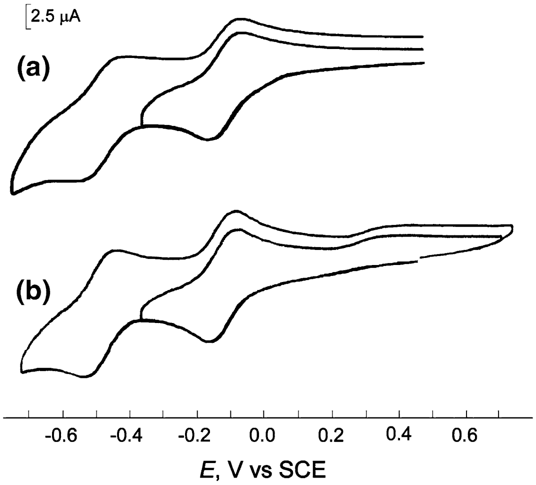
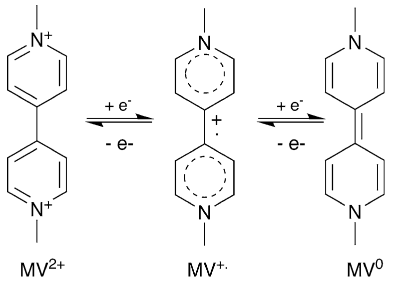


Fig. 1 Cyclic voltammograms of MV^{2+} ($C = 0.8$ mM) **a** in the absence and **b** in the presence of 0.25 equivalent of $[Fe(CN)_6]^{4-}$ (60 vol.% aqueous DMSO solution, 0.1 M $NaClO_4$, scan rate $\upsilon = 100$ mV·s^{-1})



Scheme 1 Reversible reduction of MV^{2+}

Table 1 Cyclic voltammograms data for MV^{2+} ($C = 0.8$ mM) in the presence and absence of 0.25 equivalent of $[Fe(CN)_6]^{4-}$ (60 vol.% aqueous DMSO solution, 0.1 M $NaClO_4$, scan rate $\upsilon = 100$ mV·s^{-1})

	$E^1_{p,red}$ [a]	$E^1_{p,ox}$ [a]	$E^2_{p,red}$ [b]	$E^2_{p,ox}$ [b]	$i^1_{p,red}$ [c]
MV^{2+}	−0.16	−0.08	−0.54	−0.45	5.0
MV^{2+}:$[Fe(CN)_6]^{4-}$ (4:1)	−0.16	−0.08	−0.54	−0.45	5.0

[a] Potentials (in V versus saturated calomel electrode (SCE)) for the first reduction process

[b] For the second reduction process

[c] Current (in μA) of the first reduction peak

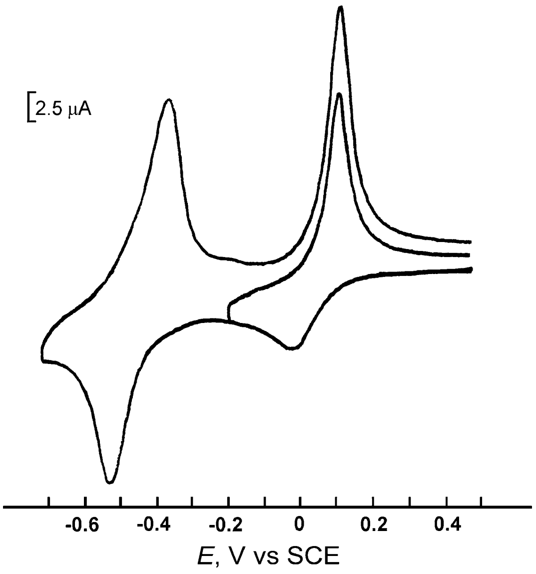


Fig. 2 Cyclic voltammograms of $MVCA^{8+}$ ($C = 0.2$ mM) (60 vol.% aqueous DMSO solution, 0.1 M $NaClO_4$, scan rate $\upsilon = 100$ mV·s^{-1})

the additional wide peaks of the reduction of $[Fe(CN)_6]^{3-}$ and the oxidation (re-oxidation) of $[Fe(CN)_6]^{4-}$ appears in CV. This result reveals that $[Fe(CN)_6]^{4-}$ and MV^{2+} do not interact with each other.

The CV of $MVCA^{8+}$ (Fig. 2) is similar to the CV of MV^{2+}. Two reduction peaks and two re-oxidation peaks are also observed in 60 vol.% aqueous DMSO solution. Although, as compared with MV^{2+}, only the first peak of the reduction of $MVCA^{8+}$ is diffusion-controlled. All the other peaks are by nature adsorption peaks. The peak potentials (except the second reduction peak) are shifted to the positive side. The current of the first diffusion-controlled reduction peak is 3.84 times larger than that of MV^{2+}. Previously [53], the reduction of $MVCA^{8+}$ was studied in DMSO. It was shown that $MVCA^{8+}$ undergoes two diffusion-controlled four-electron (one electron per one viologen unit) reduction with the formation of the tetra(cation-radical) $MVCA^{4+\cdot}$ in the first step and the fully reduced neutral compounds $MVCA^0$ in the second step (Scheme 2). The reduction in the first step occurs more readily than for MV^{2+}, which is due to the influence of the calixarene platform. Evidently the reduction of $MVCA^{8+}$ in 60 vol.% aqueous DMSO solution occurs in a similar way. At the potential of the first reduction peak $MVCA^{8+}$ is reduced to tetra(cation-radical) $MVCA^{4+\cdot}$ which is transferred to the neutral molecule $MVCA^0$ at the potential of the second reduction peak. However, as compared to DMSO, only the starting compound $MVCA^{8+}$ in 60 vol.% aqueous DMSO solution does not adsorb on the electrode surface. The electrode surface is covered with a film by the partial and fully reduced forms of $MVCA^{4+\cdot}$ and $MVCA^0$.

The different behaviour of $MVCA^{8+}$ in DMSO and in 60 vol.% aqueous DMSO solution can be due to the influence of water on MVCA. The decrease in the solubility of MVCA is the result of the increase of water in the solution and the decrease in the charge of the MVCA forms. The calixarene in its reduced forms of $MVCA^{4+\cdot}$ and $MVCA^0$ with a lesser charge "salts out" from the solution and adsorbs on the electrode surface.

The addition of an equimolar amount of $[Fe(CN)_6]^{4-}$ to the solution of $MVCA^{8+}$ produced a pronounced effect on CV of $MVCA^{8+}$ (Fig. 3). Peaks of the reduction and re-oxidation of $MVCA^{8+}$ with the same potentials and of the same nature as that in the absence of $[Fe(CN)_6]^{4-}$ are observed in the CV curve. There also appears an additional reduction peak shifted to −100 mV relative to the first reduction peak of $MVCA^{8+}$ (Table 2). On the second cycle of bicyclic voltammograms the current of the additional peak that appeared significantly decreases if the second potential scan starts from + 200 mV—from the bottom of the first reduction peak of $MVCA^{8+}$.

Besides, only the diffusion-controlled reduction peak of the free unbound $[Fe(CN)_6]^{3-}$ exists in the CV curve, while the peak of the oxidation of $[Fe(CN)_6]^{4-}$ does not appear. This oxidation peak appears as a re-oxidation peak only on the reversed CV curve, i.e. only after the electrochemical reduction of $[Fe(CN)_6]^{3-}$ (Fig. 3). These results clearly show that (i) tetraanion $[Fe(CN)_6]^{4-}$ is fully oxidized to $[Fe(CN)_6]^{3-}$ while preparing the solutions and recording the CV; (ii) $MVCA^{8+}$ does not bind $[Fe(CN)_6]^{3-}$ in the 60 vol.% aqueous DMSO solution.

Scheme 2 Reversible reduction of $MVCA^{8+}$

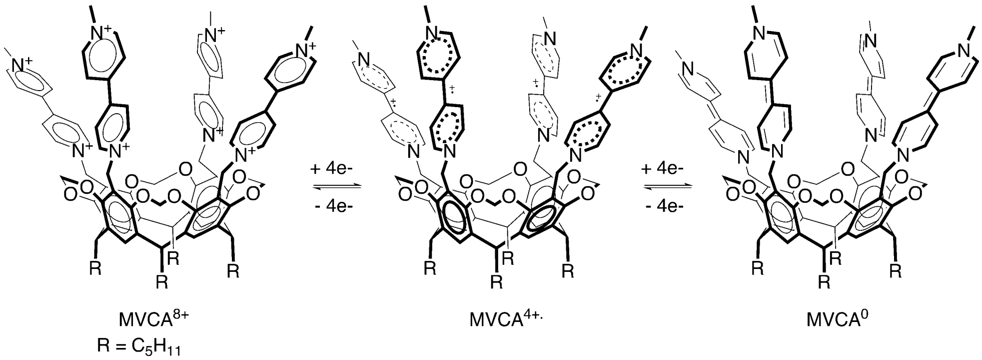


Fig. 3 Bicyclic (**a**) and monocyclic (**b**) voltammograms of $MVCA^{8+}$ ($C = 0.2$ mM) in the presence of one equivalent of $[Fe(CN)_6]^{4-}$ (60 vol.% aqueous DMSO solution, 0.1 M $NaClO_4$, scan rate $\upsilon = 100$ mV·s^{-1})

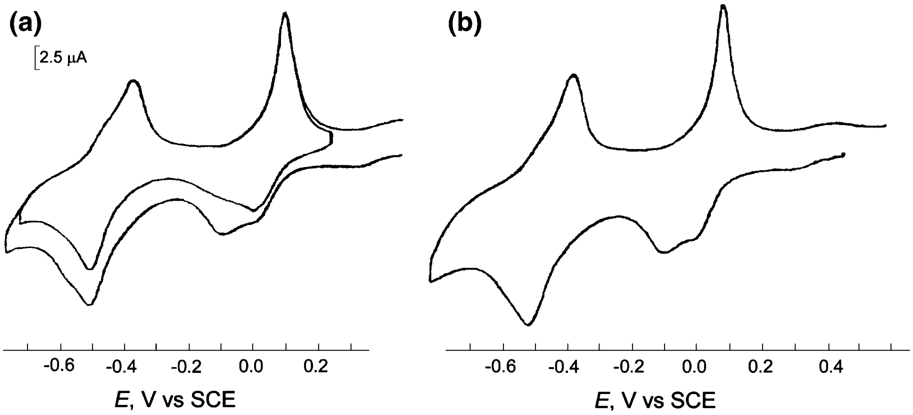


Table 2 Cyclic voltammograms data for $MVCA^{8+}$ and $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ (60 vol.% aqueous DMSO solution, 0.1 M $NaClO_4$, scan rate $\upsilon = 100$ mV·s^{-1}, concentration $C = 0.2$ mM)

	Electrolysis		$E^1_{p,red}$ [c]	$i^1_{p,red}$ [c]	$E^{1,ads}_{p,red}$ [d]	$i^{1,ads}_{p,red}$ [d]	$E^1_{p,ox}$ [e]	$i^1_{p,ox}$ [e]	$E^2_{p,red}$ [f]	$i^2_{p,red}$ [f]	$E^2_{p,ox}$ [g]	$i^2_{p,ox}$ [g]
	E[a]	τ[b]										
$MVCA^{8+}$	–	–	−0.03	4.8	–	–	+0.10	17.5	−0.54	13.5	−0.39	12.8
$MVCA^{8+}$:$[Fe(CN)_6]^{4-}$	–	–	0.00	3.5	−0.10	6.0	+0.10	12.3	−0.50	12.3	−0.38	8.3
	+0.20	1	–	–	−0.16	20.0	+0.12	21.5	−0.55	20.3	−0.37	24.0
		2	–	–	−0.16	18.8	+0.12	18.0	−0.56	20.0	−0.37	22.0
	−0.33	1	0.00	4.8	–	–	+0.10	21.5	−0.51	21.5	−0.38	19.5
		2	−0.02	9.5	–	–	+0.12	37.5	−0.55	43.5	−0.36	42.5
	−0.75	1	0.00	6.3	–	–	+0.09	13.5	−0.51	15.0	−0.34	11.3
		2	−0.02	7.5	–	–	+0.09	17.0	−0.52	17.3	−0.33	11.5

[a] Applied potential (in V vs. SCE) of the previous electrolysis

[b] Time (in min) of the previous electrolysis

[c] Potential (in V vs. SCE) and current (in μA) of the first diffusion reduction peak

[d] Potential (in V vs. SCE) and current (in μA) of the first adsorption reduction peak

[e] Potential (in V vs. SCE) and current (in μA) of the first re-oxidation peak

[f] Potential (in V vs. SCE) and current (in μA) of the second reduction peak

[g] Potential (in V vs. SCE) and current (in μA) of the second re-oxidation peak

Due to the fact, that the chemical oxidation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ occurs quite slowly by dissolved oxygen in 60 vol.% aqueous DMSO solution it is possible to study the binding of $[Fe(CN)_6]^{4-}$ with $MVCA^{8+}$ after the electrochemical reduction of $[Fe(CN)_6]^{3-}$ in situ in an inert atmosphere. After the electrochemical generation of $[Fe(CN)_6]^{4-}$ at the potential of $E = 0.2$ V for one minute, two adsorption peaks of the reduction and the two adsorption peaks of the re-oxidation of $MVCA^{8+}$ appear on the CV curve (Fig. 4). The potential

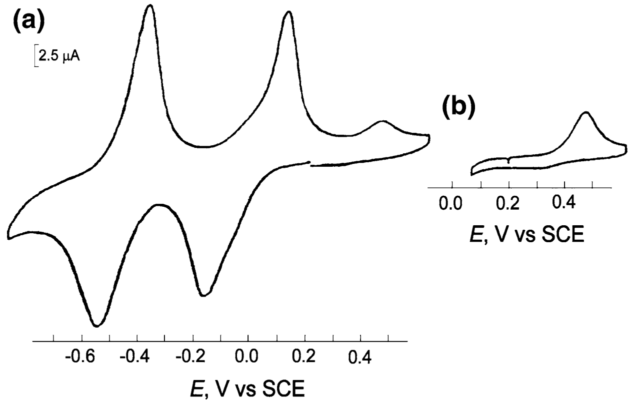


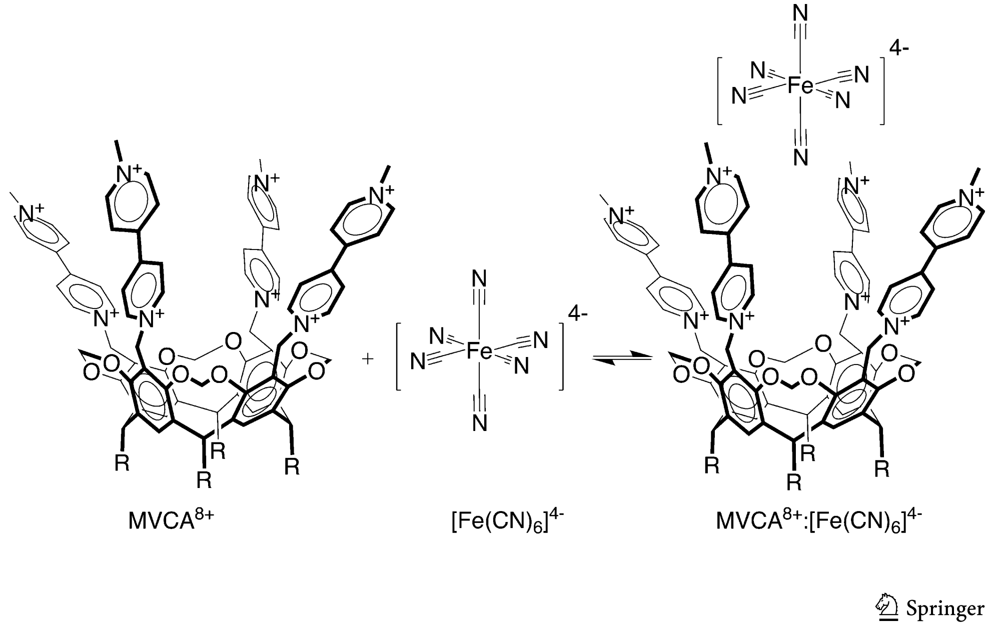
Fig. 4 Cyclic voltammograms of $MVCA^{8+}$ ($C = 0.2$ mM) in the presence of one equivalent of $[Fe(CN)_6]^{4-}$ after the applying potential $E = +0.2$ V for one minute with the potential scan in **a** negative and **b** positive directions (60 vol.% aqueous DMSO solution, 0.1 M $NaClO_4$, scan rate $\upsilon = 100$ mV·s^{-1})

of the first reduction peak is of the same value as the potential of the additional peak obtained in CV without previous electrolysis. The second reduction and two re-oxidation processes occur at essentially the same potential as free $MVCA^{8+}$. The current of all peaks is significantly larger than that of peaks without previous electrolysis. An intensive adsorption peak of the oxidation of $[Fe(CN)_6]^{4-}$ also appears, and its intensity is reduced if the reverse scan occurs after the reduction of $MVCA^{8+}$. The increase of the electrolysis time up to 2 min does not lead to significant changes in the CV curve. Thus, the results demonstrate that: (i) the octacation $MVCA^{8+}$ effectively binds tetra-anion $[Fe(CN)_6]^{4-}$ with the formation of the supramolecular complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ (Scheme 3); (ii) the complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ adsorbs on the surface of the glassy electrode; (iii) the limiting value of the adsorbed complex is reached within 1 min of the electrolysis at the potential $E = 0.2$ V. Further increase of the electrolysis time does not lead to an increase in the amount of the adsorbed complex because of the adsorption saturation of the electrode surface. The complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ blocks the electrode surface inhibiting the next reduction of $[Fe(CN)_6]^{3-}$ in the solution and the generation of the following amount of the complex $MVCA^{8\ +}$:$[Fe(CN)_6]^{4-}$.

It is possible to determine the stoichiometry of the supramolecular complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ with using the ratio of the adsorbed amount of $MVCA^{8+}$ and $[Fe(CN)_6]^{4-}$ because only the complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ adsorbs on the electrode surface while its individual compounds $MVCA^{8+}$ and $[Fe(CN)_6]^{4-}$ do not cover the electrode surface. The experimentally observed dependence *i–E* at $\upsilon = 100$ mV·s^{-1} obtained after applying the fixed potential $E = 0.2$ V for a minute was converted into a relationship *i–τ* (where τ is the time). The electrical charge Q was determined with using the area of the first four-electron adsorption peak of the reduction of $MVCA^{8+}$ and the one-electron adsorption oxidation peak of $[Fe(CN)_6]^{4-}$. The amount of the adsorbed ions was calculated using Faraday's law. It was found that the ratio of $MVCA^{8+}$ and $[Fe(CN)_6]^{4-}$ in the complex adsorbed on the electrode surface is 1.25:1, i.e. $MVCA^{8+}$ and $[Fe(CN)_6]^{4-}$ form mostly the 1:1 complex (75%) and partly the 2:1 complex (25%). Thus, the calixarene $MVCA^{8+}$ binds only one molecule of tetraanion $[Fe(CN)_6]^{4-}$. Apparently, a small amount of the supramolecular complex of capsular type is formed where $[Fe(CN)_6]^{4-}$ is bonded with two calixarenes $MVCA^{8+}$.

The absence of the influence of $[Fe(CN)_6]^{4-}$ on the potentials of the second reduction peak and the two re-oxidation peaks of $MVCA^{8+}$ assumes that the tetra(cation-

Scheme 3 Compexation of $MVCA^{8+}$ with $[Fe(CN)_6]^{4-}$



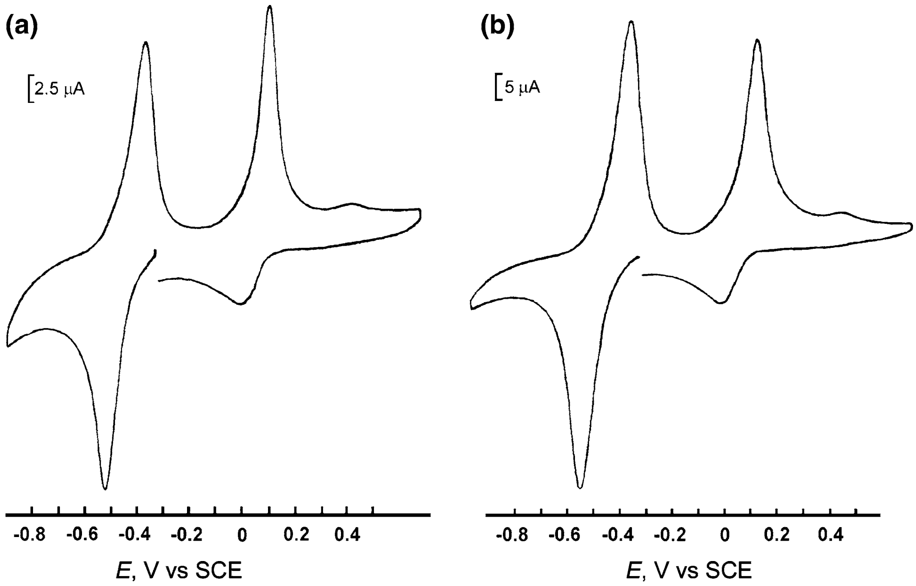


Fig. 5 Cyclic voltammograms of MVCA^{8+} ($C = 0.2$ mM) in the presence of one equivalent of $[\mathrm{Fe(CN)}_6]^{4-}$ after applying potential $E = -0.33$ V for **a** 1 min and **b** 2 min (60 vol.% aqueous DMSO solution, 0.1 M NaClO_4, scan rate $\upsilon = 100\ \mathrm{mV{\cdot}s^{-1}}$)

radical) $\mathrm{MVCA}^{4+\cdot}$ and the neutral MVCA^{0} do not bind $[\mathrm{Fe(CN)}_6]^{4-}$. For confirming this hypothesis, the electrode was maintained for one and for two minutes at the more negative potentials than the potentials of the reduction of MVCA^{8+} and $\mathrm{MVCA}^{4+\cdot}$ and then the CV were recorded beginning from the applied potentials. After applying the potential $E = -0.33$ V (i.e. the potential of the reduction of the free and complexed MVCA^{8+} to $\mathrm{MVCA}^{4+\cdot}$) for one minute the currents of the second reduction peak and two re-oxidation peaks increase. The peak of the re-oxidation of $[\mathrm{Fe(CN)}_6]^{4-}$ and the first peak of re-reduction of MVCA^{8+} become diffusion-controlled and are observed at the potentials of free unbound compounds (Fig. 5). These data clearly demonstrate that $\mathrm{MVCA}^{4+\cdot}$ adsorbs on the electrode surface and does not bind $[\mathrm{Fe(CN)}_6]^{4-}$. When the potential $E = -0.33$ V was applied for two minutes the heights of all peaks, except the re-oxidation peak of $[\mathrm{Fe(CN)}_6]^{4-}$, almost doubled and were significantly higher than after applying potential $E = +0.2$ V (Fig. 5, Table 2).

Thus, the tetra(cation-radical) $\mathrm{MVCA}^{4+\cdot}$ adsorbs on the electrode surface with the formation of a film. The increase of the time of applying the fixed potential leads to the increase in the thickness of the adsorbed film. The limit of this process is as yet unknown.

When the potential $E = -0.75$ V (i.e. the potential of the generation of the fully reduced form MVCA^{0}) was applied for a minute, the adsorption peak heights of the re-oxidation of the calixarene increased. The peak of $[\mathrm{Fe(CN)}_6]^{4-}$ and the first reduction peak of MVCA^{8+} are of a diffusion nature and are observed at potentials of the free unbound compounds, suggesting that MVCA^{0} does not bind $[\mathrm{Fe(CN)}_6]^{4-}$ (Fig. 6). The increase in the duration of the applied potential up to 2 min does not affect the height of the peaks. Obviously, the amount of the neutral calixarene MVCA^{0} adsorbed on the electrode surface is limited.

Thus, MV^{2+} and its reduced forms $\mathrm{MV}^{+\cdot}$ and MV^{0} do not bind $[\mathrm{Fe(CN)}_6]^{3-}$ and $[\mathrm{Fe(CN)}_6]^{4-}$ in 60 vol.% aqueous DMSO solution. The calixarene in all its forms MVCA^{8+}, $\mathrm{MVCA}^{4+\cdot}$ and MVCA^{0} does not complex with $[\mathrm{Fe(CN)}_6]^{3-}$ either. For the $[\mathrm{Fe(CN)}_6]^{4-}$ a reversible redox-switchable binding with the calixarene MVCA is observed. The octa-cation MVCA^{8+} mostly forms 1:1 complex with ferrocyanide while the tetra(cation-radical) $\mathrm{MVCA}^{4+\cdot}$ and the neutral MVCA^{0} do not bind the tetra-anion (Scheme 4). Obviously, the redox-switching of the binding metallocomplex occurs under reversible one electron oxidation of $[\mathrm{Fe(CN)}_6]^{4-}$ to $[\mathrm{Fe(CN)}_6]^{3-}$ as well. This type of the redox-switching process is typical for systems

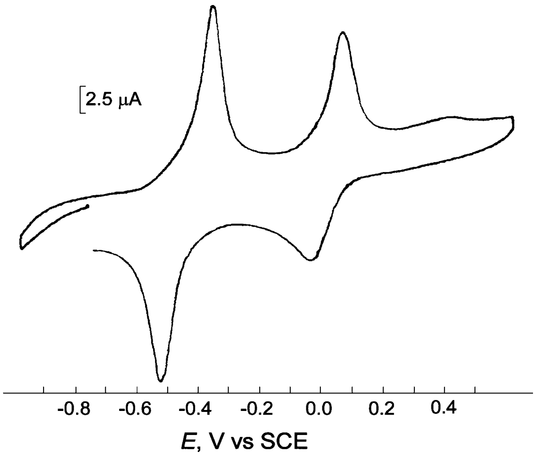
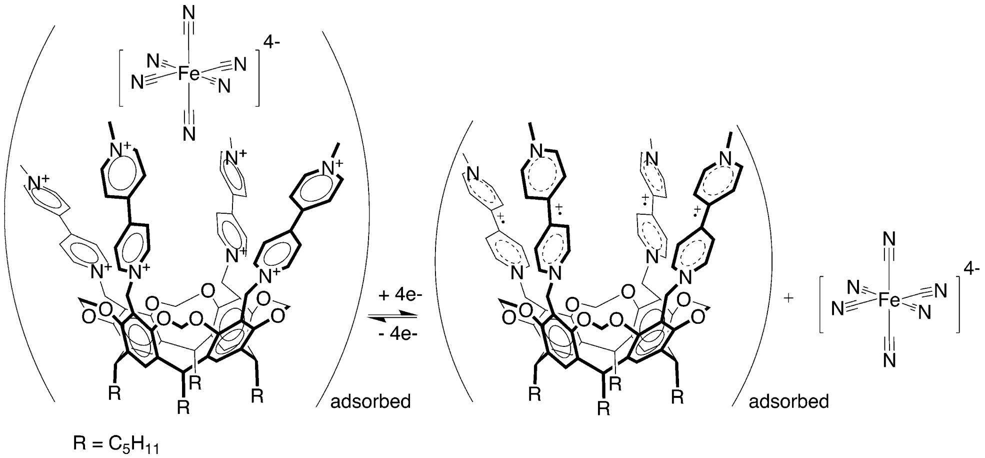


Fig. 6 Cyclic voltammograms of MVCA^{8+} ($C = 0.2$ mM) in the presence of one equivalent of $[\mathrm{Fe(CN)}_6]^{4-}$ after applying potential $E = -0.75$ V for one minute (60 vol.% aqueous DMSO solution, 0.1 M NaClO_4, scan rate $\upsilon = 100\ \mathrm{mV{\cdot}s^{-1}}$)



Scheme 4 Redox- switchable interaction of MVCA^{8+} with $[Fe(CN)_6]^{4-}$

in which the main binding force is electrostatic interaction. The more charged octa-cation MVCA^{8+} binds the more charged anion $[Fe(CN)_6]^{4-}$ while its less charged or uncharged forms do not interact with each other.

It is necessary to note that the pre-organization of four methyl viologen units on calixarene platform plays an important role in the binding processes. In the absence of this pre-organization four dimethyl viologen does not bind the ferrocyanide ion, while their organization on the calixarene platform results in their effective interaction with tetraanion. It is notable, that the calixarene MVCA^{8+} forms 1:1 complexes with tetraanions independently of the structure of these tetraanions, while the redox-switching process strongly depends on the structure of the tetraanion. If the redox-switching interaction of MVCA^{8+} with tetraanion SCA^{4-}occurs during the second reduction step of MVCA [53], the binding of the tetraanionic ferrocyanide switches onto the first reduction step. Probably, SVA^{4-} and MVCA are more complementary to each other, because the interacting units are located on a similar calixarene platform.

The octa-cation MVCA^{8+} does not adsorb on the surface of the glassy electrode, while its less-charged forms MVCA$^{4+\cdot}$ and MVCA^0 and its complex with ferrocyanide MVCA^{8+}:$[Fe(CN)_6]^{4-}$ cover the electrode surface. The amount of adsorbed substrates depends on the nature of the substrates. The limiting molar quantity for the adsorbed neutral molecule MVCA^0 is lower than that for the adsorbed complex MVCA^{8+}:$[Fe(CN)_6]^{4-}$. MVCA$^{4+\cdot}$ adsorbs in larger amounts and we have not reached the limiting value in the conditions of our experiments.

We modelled (MM + force field, Hyperchem 7.0) the structure of the calixarene forms MVCA^{8+}, MVCA$^{4+\cdot}$ and MVCA^0 and the complex MVCA^{8+}:$[Fe(CN)_6]^{4-}$ for estimating their size (Fig. 7, Table 3). The amount of the compound adsorbed on the electrode surface was calculated using the area of the adsorption peaks as described above. We approximately calculated the number of adsorption layers formed on the electrode surface assuming that the substrates adsorb the electrode surface with hydrophobic tails with formation of the dense packing (Fig. 8).

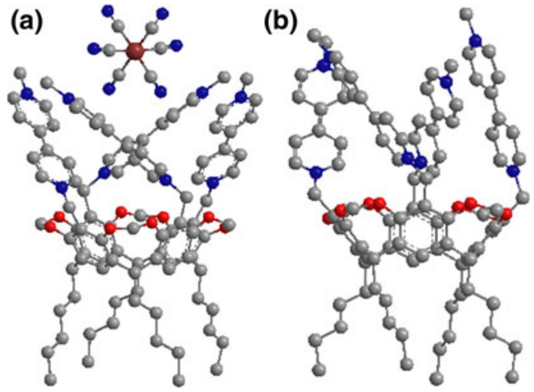


Fig. 7 MM + calculated ball and stick models of **a** MVCA^{8+}:$[Fe(CN)_6]^{4-}$ and **b** MVCA^0. Hydrogen atoms are not shown

It was found that all substrates form multi-layer films on the electrode surface. The neutral MVCA^0 forms less layers (~8) (Table 3). The complex MVCA^{8+}:$[Fe(CN)_6]^{4-}$ assembles 1.5 times more layers. In the case of MVCA$^{4+\cdot}$ the limiting number of adsorbed layers was not reached, but nevertheless the number of layers in this case is substantially greater. The thickness of the films formed on the electrode surface was also estimated. In all cases the films are of a nanoscale character. The thinnest film is formed from the neutral calixarene MVCA^0 (Table 3). It is necessary to note that the calculated characteristics have much smaller values than in reality. In reality the adsorption molecules are packed on the electrode surface with the formation of porous films containing counter ions and solvent shells along with the substrates.

These results lead to a clear understanding that the limiting adsorption of the complex MVCA^{8+}:$[Fe(CN)_6]^{4-}$ and the neutral MVCA^0 on the glassy electrode surface is not related to the formation of dense insulating mono-and

Table 3 Mode of formation and characteristics of the adsorption films of $MVCA^{0}$, $MVCA^{4+\cdot}$ and the complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ on the surface of the glassy electrode

Substrate	Mode		Q^c	Amount of substance, mol	Total number of molecules	The area of one molecule^d	Number of molecules in a single layer	Number of layers	Height of molecule^e	Film thickness^f
	E^a	τ^b								
$MVCA^{8+}$:$[Fe(CN)_6]^{4-}$	+0.20	1	37.77	0.98×10^{-10}	5.90×10^{13}	1.8×10^{-18}	5.05×10^{12}	~11–12	2.18	~23–26
		2	38.03	0.99×10^{-10}	5.96×10^{13}			~11–12		~23–26
$MVCA^{4+\cdot}$	−0.33	1	34.33	0.89×10^{-10}	5.36×10^{13}	1.74×10^{-18}	5.21×10^{12}	~10–11	2.01	~20–22
		2	69.96	1.81×10^{-10}	10.9×10^{13}			~20–21		~40–42
$MVCA^{0}$	−0.75	1	18.80	0.49×10^{-10}	2.95×10^{13}	1.85×10^{-18}	4.91×10^{12}	~6	1.8	~11
		2	20.72	0.59×10^{-10}	3.55×10^{13}			~7–8		~12–14

[a] Applied potential (in V vs. SCE) of the previous electrolysis

[b] Time (in min) of the previous electrolysis

[c] Electric charge (in μA·s)

[d] In m^2

[e] In nm

[f] In nm

Fig. 8 Schematic representation of the packing of $MVCA^{0}$, $MVCA^{4+\cdot}$ and the complex $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ on the surface of the glassy electrode

bilayered films of the Langmuir–Blodgett type. The films of $MVCA^{8+}$:$[Fe(CN)_6]^{4-}$ and $MVCA^{0}$ consist of multilayers with porous and conductive properties. The pores of the films are completely blocked with a covering of several layers and the films inhibit the further reduction of $MVCA^{8+}$ and $[Fe(CN)_6]^{3-}$ on the electrode surface, while the film assembled from $MVCA^{4+\cdot}$ proves more porous and/or conductive.

Conclusion

Calixarene electro-switchable host–guest systems described in literature [37–43] operate through the reversible redox switching of guests. Our results obtained previously [53] and in this investigation demonstrate the possibility of creating switchable systems with the redox-conversion of calixarene containing redox-active groups. In particular, the electro-switchable binding of tatraanions (SCA^{4-} and $[Fe(CN)_6]^{4-}$) with $MVCA^{8+}$ is based on the electrochemical conversion of viologen units of $MVCA^{8+}$. The main binding force in these systems is the electrostatic interaction. It is notable, that the stoichiometry (1:1) of the complexes formed with $MVCA^{8+}$ does not depend on the structure of the tetraanion, while the switching process strongly depends on the nature of the tetraanion. The switching of the binding of SCA^{4-} occurs only on the second step of the reduction of $MVCA^{8+}$ [53]. In the case of the tetraanion $[Fe(CN)_6]^{4-}$ the switching process is performed on the first reduction step.

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