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Electroswitchable self-assembly of tetraferrocene-resorcinarene

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A new dynamic electroswitchable supramolecular system consisting of tetraferrocene-resorcinarene and viologen has been developed.

The development of dynamic systems with electroswitchable properties is of considerable current interest.[1] Dynamic supramolecular systems are noncovalently organized supramolecular systems that change their organization and properties as a result of an appropriate external stimulation. The dynamic supramolecular systems can be formed by hydrogen bonds,[2] hydrophobic interactions[3] and metal–ligand coordination.[4] Resorcinarenes[5] with their relatively rigid three-dimensional structure and the possibility of the modification of the upper and lower rims are attractive building blocks for the creation of dynamic systems. The dimeric and hexameric ensembles formed by resorcinarenes are well known.[6] Electrochemically driven formation of a molecular capsule around the ferrocenium ion was described.[7]

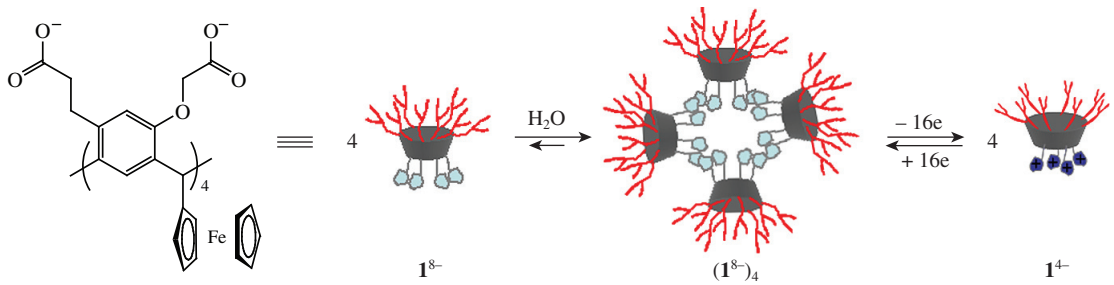
To create a redox-switchable dynamic system, we have designed a new water-soluble resorcinarene derivative with a hydrophobic electroactive lower rim and a hydrophilic upper rim. We assumed that the presence of nonpolar fragments on the lower rim and polar groups on the upper rim should lead to the self-assembly of resorcinarene into micelle structures. A change in the hydrophobicity of the lower rim by electrochemical stimuli should reorganize or dissociate the supramolecular assemblies. Ferrocene groups were selected as electroactive hydrophobic fragments. The polarity of ferrocene can be easily modified by its electrochemical oxidation to the ferrocenium ion. We intended to introduce carboxyl groups by the modification of hydroxyl groups of the resorcinarene platform to increase the hydrophilicity of the upper rim. Here, we report a new derivative of resorcinarene with ferrocene fragments at the lower rim and the carboxyl groups on the upper rim, as well as the investigation of its electro-driven assembly in aqueous media and the influence of its host-guest properties on the association.

Tetraferrocene-resorcinarene octaacetate **1** was obtained by the hydrolysis of tetraferrocene-resorcinarene with eight ester groups on the upper rim[8] (see Online Supplementary Materials). The self-assembly of **1** in aqueous media (Scheme 1) was characterized by various spectroscopic methods and cyclic voltammetry (CV). In the NMR diffusion experiment, an increase in the concentration of **1** results in a decrease in its self-diffusion coefficient (Table 1). At a 10 mM concentration, the self-diffusion coefficient is almost 1.6 times lower than that at 0.5 mM, suggesting the formation of tetrameric aggregates $\mathbf{1}_4$. The data of MALDI-TOF spectroscopy also confirms the formation of the supramolecular aggregates of **1**. Ion peaks in the regions of 1400–1700, 2800–3400, 4300–5000 and 5800–6800 correspond to the weight of monomer **1**, dimer $\mathbf{1}_2$, trimer $\mathbf{1}_3$ and tetramer $\mathbf{1}_4$, respectively (Figure S1, Online Supplementary Materials). Ferrocene is relatively low to none in polarity and insoluble in water; thus, the tail to tail aggregation is preferred for the arrangement of the ferrocene units of **1** in aqueous media.

Table 1 Self-diffusion coefficients for **1**, V^{2+} and their combinations (D_2O, 298 K).

Compound	C/mmol dm^{-3}	$D_1/10^{-10}$ m^2 s^{-1}	$D_V/10^{-10}$ m^2 s^{-1}
1	0.5	2.11	—
	1	2.10	—
	6	1.53	—
	10	1.35	—
V^{2+}	1	—	7.25
1:V^{2+}	1:1	1.5	1.5
	10:1	1.35	1.35
	10:10	1.30	1.30

The CV data showed that **1** does not undergo reduction in an accessible range of potentials in H_2O/0.1 M NaCl media on a glassy-carbon electrode in an inert atmosphere. Regardless of concentration (0.2, 1 or 10 mM) in anodic area, a diffusion peak of the oxidation of ferrocene units to ferrocenium ions and a peak of back reduction are observed. The peak potentials depend on concentration (Figure 1, see also Table S1, Online Supplementary Materials). At a concentration of 1 mmol dm^{-3}, the



Scheme 1 Redox-driven self-assembly of resorcinarene **1** in aqueous media.

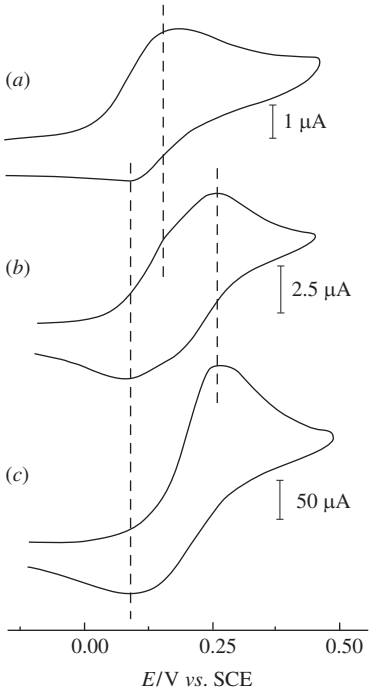


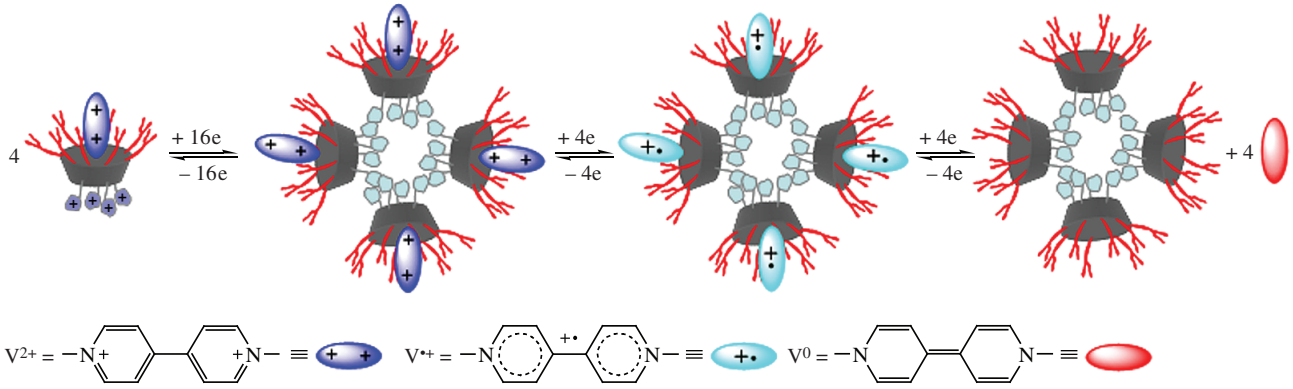
Figure 1 Cyclic voltammograms of **1** for (*a*) C_1 = 0.2 mM, v = 20 mV s^{-1}; (*b*) C_1 = 1 mM, v = 10 mV s^{-1}; (*c*) C_1 = 10 mM, v = 100 mV s^{-1} at glassy-carbon electrode (H_2O/0.1 M NaCl).

oxidation and back reduction peaks are bifurcated. The potential differences between the oxidation peaks $E'_{p,ox}$ and $E''_{p,ox}$ and the corresponding back reduction peaks $E'_{p,rered}$ and $E''_{p,rered}$ almost match theoretical values for reversible one-electron processes. The first pair of the peaks ($E'_{p,ox}$ and $E'_{p,rered}$) occurs at the same potential as in a concentration of 0.2 mM and corresponds to the oxidation and back reduction of the ferrocene units in individual molecules of **1**. The second pair of the peaks ($E''_{p,ox}$ and $E''_{p,rered}$) corresponds to the same processes in the aggregates of **1**. At a concentration of 10 mM, one oxidation peak at $E''_{p,ox}$ and one back reduction peak with a potential between $E'_{p,rered}$ and $E''_{p,rered}$ are observed independently of scan rate. The shape and height of the peaks at all concentrations do not change after repeated cycling (10 cycles) in a potential range from –0.1 to +0.5 V and after keeping the electrode at +0.5 V for 1 and 3 min. The reproducibility of voltammograms after repeated cycling indicates the quantitative back reduction of ferrocenium ions to ferrocene with returning **1** to its original state, *i.e.* the chemical reversibility of the oxidation processes. The peak height and shape are in agreement with the four-electron reversible oxidation of resorcinarene **1**.

Thus, the electrochemical oxidation of **1** leads to the quantitative oxidation of all of the four ferrocene units of **1** to ferrocenium ions. The aggregates in aqueous media are usually stabilized by hydrophobic interactions. The hydrophobic part of **1** is the ferrocene units attached to the resorcinarene platform. The oxidation of ferrocenes results in the appearance of a positive charge, which leads to a decrease in hydrophobicity and to the dissociation of the aggregates formed by **1**. At a concentration of 1 mM, the percentage of individual molecules is sufficiently high, and for this reason the signals of both individual molecules and aggregates can be detected. This was specifically observed at a slow scan rate (Figure S2, Online Supplementary Materials). The decrease in the scan rate, which is equivalent to the electrolysis prolongation, causes the increasing share of processes involving individual molecules due to the slow dissociation of the aggregates $(\mathbf{1}^{8-})_4$ into individual molecules. The dissociation of the aggregates at the timeline recording CV (seconds) occurs only partly. At high concentrations (10 mM), **1** exists in an aggregated state. For this reason, the oxidation peak of the individual molecules is not observed at any scan rates. The presence of the individual molecules in solution is noticeable only in the broadening of the oxidation peak. However, after the oxidation of ferrocene units to the ferrocenium ions, the aggregates are destroyed and we observe a single peak of back reduction of the individual and aggregated molecules of **1**. Thus, the CV results demonstrate the redox-driven reversible self-assembly of **1** in aqueous media. Compound **1** is aggregated at a concentration of 10 mM. The four-electron oxidation of ferrocene moieties to ferrocenium ions results in destroying the aggregates, and the reverse four electron transfer leads to the complete restoration of the aggregates (Scheme 1).

According to the NMR spectroscopy data, the aggregates formed by **1** bind dimethylviologen V^{2+} with the formation of two-component supramolecular assemblies (Scheme 2). The addition of **1** to an aqueous solution of V^{2+} leads to an upfield shift of the proton signals of V^{2+}, conforming to the binding of V^{2+} by the resorcinarene platform (Figure S3, Online Supplementary Materials). According to Job's experiment, the stoichiometry of the complex formed is 1:1, *i.e.*, each resorcinarene cavity in the aggregates formed by **1** binds V^{2+} with the arrangement of two-component supramolecular assemblies. The binding constant of the interaction of V^{2+} with the resorcinarene cavity is $\lg K$ = 4.3±0.6. Moreover, the mixing of **1** and V^{2+} solutions results in the decrease of the self-diffusion coefficient both in **1** and V^{2+}, as shown in Table 1.

The CV solution of the equimolar mixture of V^{2+} and **1** (1 mM) is almost equal to the sum of the cyclic voltammograms of the individual components with the exception of the second reduction peak of V^{2+}, which is shifted negatively by 10 mV (Figure 2; Figures S4–S7, Online Supplementary Materials). Raising the concentration of 1 up to 10 mM provides a larger shift of the second peak of the reduction of V^{2+} by 70 mV and



Scheme 2 Electroswitchable self-association and binding in the **1**:V^{2+} system.

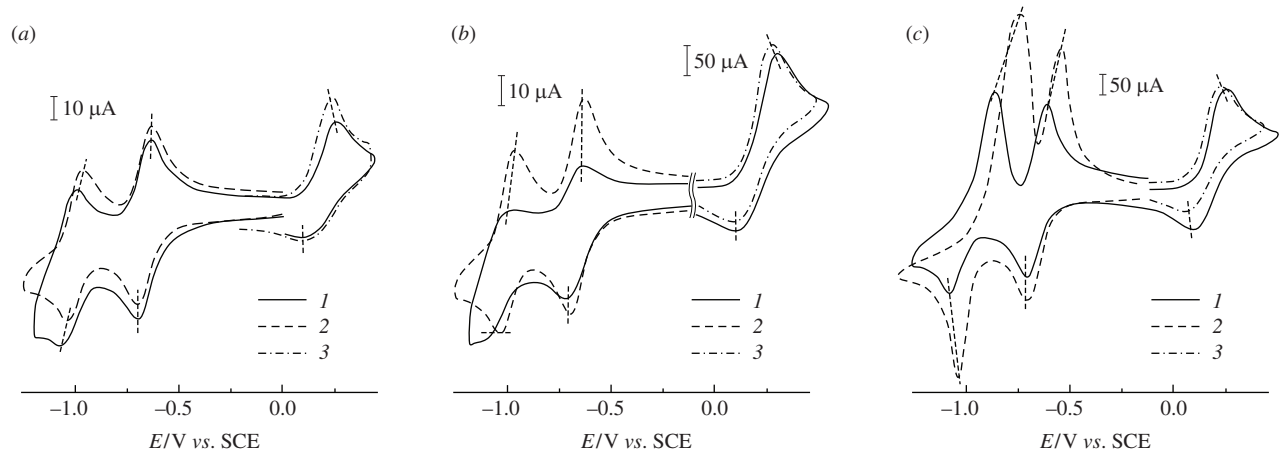


Figure 2 Cyclic voltammograms of (*1*) a mixture of **1** + V^{2+}, (*2*) V^{2+} and (*3*) **1** at the concentration of (*a*) $C_{\mathbf{1}} = C_V$ = 1 mM; (*b*) C_V = 1 mM, $C_{\mathbf{1}}$ = 10 mM; (*c*) $C_{\mathbf{1}} = C_V$ = 10 mM at a glassy-carbon electrode (H_2O/0.1 M NaCl, v = 100 mV s^{-1}).

a decrease in the height of the first peak by 15% without changing its potential. At the equimolar tenfold concentrations of the substrates (V^{2+}:**1** = 10:10 mM), the mutual influence of components in the mixture is displayed by decreasing the current of the reduction and oxidation peaks, a slight decrease in the slope of the oxidation peak of **1** and the negative shift of the second reduction peak of V^{2+} by 50 mV. The CVs of the mixtures of **1** + V^{2+} at various concentrations do not change after 10 times repeatedly cycling of the potential range from –1.3 to +0.5 V. The electrochemical generation of the neutral form of dimethylviologen V^0 for one minute at E = –1.2 V results in a significant growth of the height of the reoxidation peak of V^0, while the parameters of the oxidation peak of **1** remain unchanged (Figure S8, Online Supplementary Materials).

From the results of CV it may be concluded that resorcinarene binds the dication V^{2+} and the radical cation $V^{\bullet+}$ of dimethylviologen. The energy of the interaction of **1** with $V^{\bullet+}$ is approximately the same as that for V^{2+} ($\Delta G^0 = -2.3RT\lg K = -24\pm4$ kJ mol^{-1}). For this reason, the potential of the first reduction peak of V^{2+} is not sensitive to the addition of **1** in the viologen solution and to the change of its concentration. The fully reduced viologen V^0 does not interact with **1**. This is indicated by the dependence of the potential of the second reduction peak of viologen on the concentration of **1** and the accumulation of the neutral form V^0 on the electrode surface during electrolysis without any significant accumulation of **1**. The reverse oxidation of V^0 to $V^{\bullet+}$ and V^{2+} brings the complex back into the initial state, which is conformed by the complete reproducibility of the multicyclic voltammograms. Similar pictures are observed for the system consisting of V^{2+} and a resorcinarene with methyl groups at the lower rim (Scheme S2, Table S2, Figures S9–S11, Online Supplementary Materials), suggesting that the binding of V^{2+} occurs with carboxylate groups of the upper rim by the electrostatic interaction. For this reason, the V^{2+} is located at a sufficient distance from the ferrocene fragments of **1** and the oxidation potential of **1** does not exert a significant effect on V^{2+}. Nevertheless, the decrease in the slope of the oxidation peak of **1** in the presence of V^{2+} should be noted. Apparently, the binding of V^{2+} leads to the enhancement of the aggregation of **1** and the formation of more complex assemblies. The percentage of the unaggregated compounds decreases, which is reflected in a decrease in the slope of the oxidation peak of **1**. The aggregates formed by **1** or its complex with V^{2+} are electrochemically controlled. At 10 mM the **1**:V^{2+} complex is mainly in the aggregated state. The aggregates are destroyed after the four electron oxidations of ferrocene fragments to ferrocenium ions and then fully restored after the reverse electron transfer (Scheme 2).

Thus, the electro-driven association of **1** and its complex with V^{2+} is demonstrated in aqueous media. The reversible electro-driven switching of the aggregated state is reached after the oxidation/reduction of ferrocene fragments. The reversible electro-driven binding of viologen with the resorcinarene cavity is responsible for the switch of the binding of viologen at the step of $V^{\bullet+}/V^0$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.03.004.

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