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Electroswitchable self-assembly of tetraferrocene-resorcinarene

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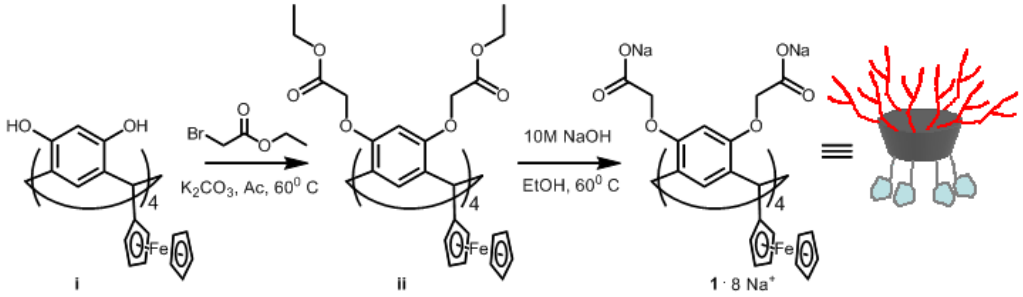
Experimental

Cyclic voltammograms were recorded using potentiostat PI-50-1 interfaced to XY recorder H 307/2 at potential scan rate υ = 10÷200 mV/s in H_2O/0.1 M NaCl at 295 K. A glassy carbon working electrode (δ = 3.4 mm) embedded in Teflon was 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. NMR spectra are recorded on the AVANCE-400 (^{1}H, 400 MHz) spectrometer.

Ferrocene, resorcinol, salts $V^{2+}\cdot 2Cl^-$ and NaCl were commercially available and used without purification. Resorcinarene **1** was synthesized in three steps as shown in Scheme S1. Ferrocene-aldehyde, resorcinarenes **i** and **ii** (Scheme S1) were synthesized according to literature procedure.[2-4]

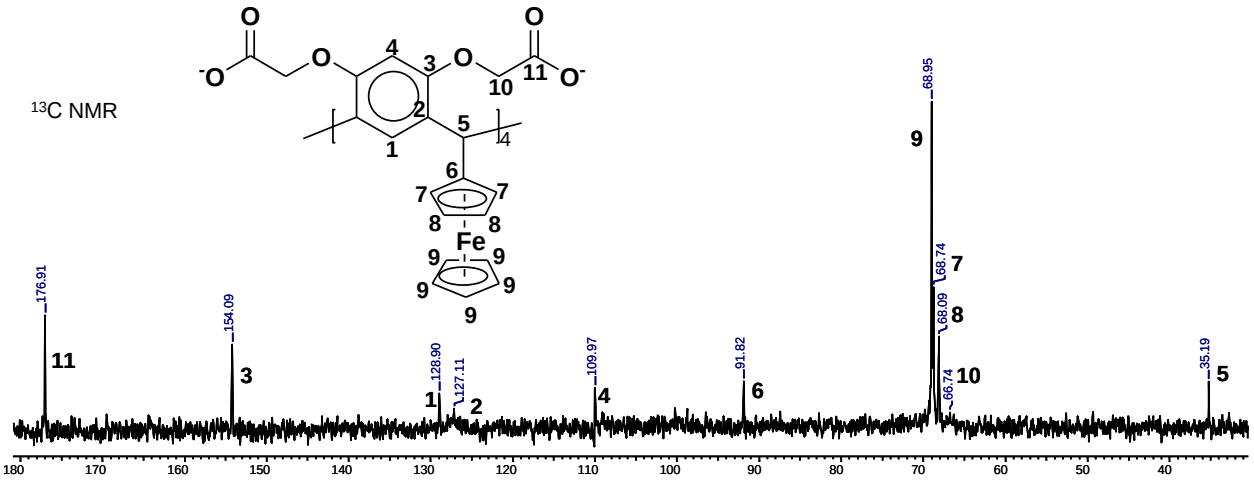


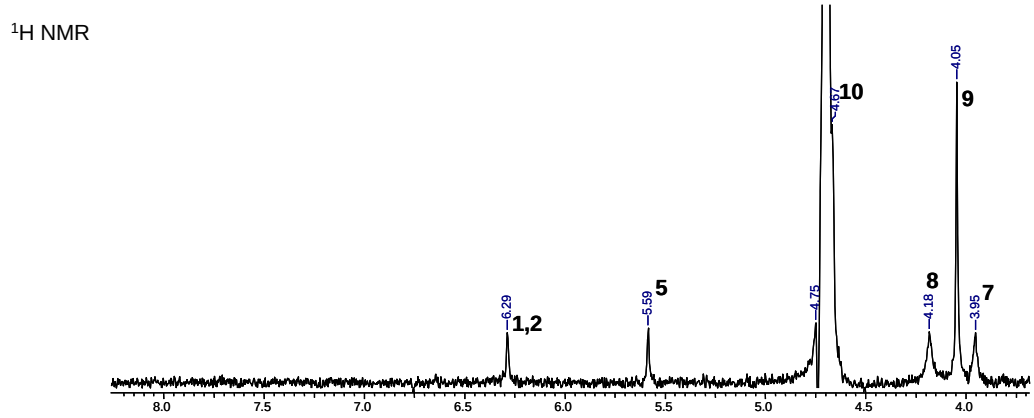
Scheme S1 Synthesis of **1**.

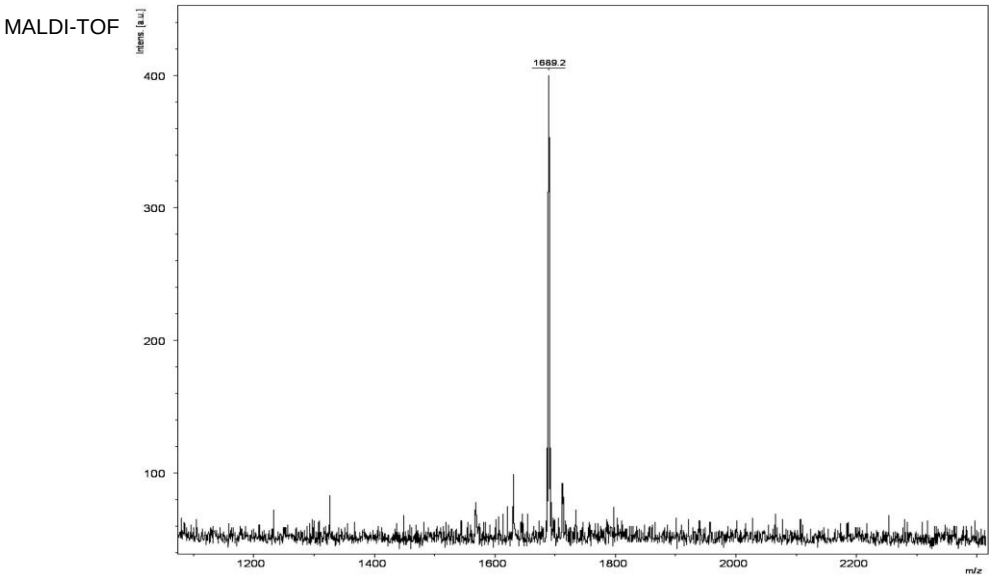
Resorcinarene 1. To a solution of **ii** (1g, 0.523 mM) in 25 ml ethanol was added 1 ml of the 10M solution of sodium hydroxide. The reaction mixture was stirred at 60 ^{0}C for 5 h. The white precipitate was filtrated, washed with ethanol, acetone and dried. Yield 90%. T.m. > 350 ^{0}C. ^{1}H NMR spectrum (D_2O, ppm): 6.29 (8H m); 5.59 (4H c); 4.18 (8H m); 4.05 (20H s); 3.95 (8H m).

Elemental analysis calcd for $C_{64}H_{48}Fe_4Na_8O_{24}$, (%):C, 47.79; H, 3.01; Fe, 13.89; found: C, 47.3; H, 2.9; Fe, 13.45. MALDI-TOF mass-spectrum: 1689.2 ($\mathbf{1}^{8-}$ + $8H^+$).

NMR and MALDI-TOF spectra of 1







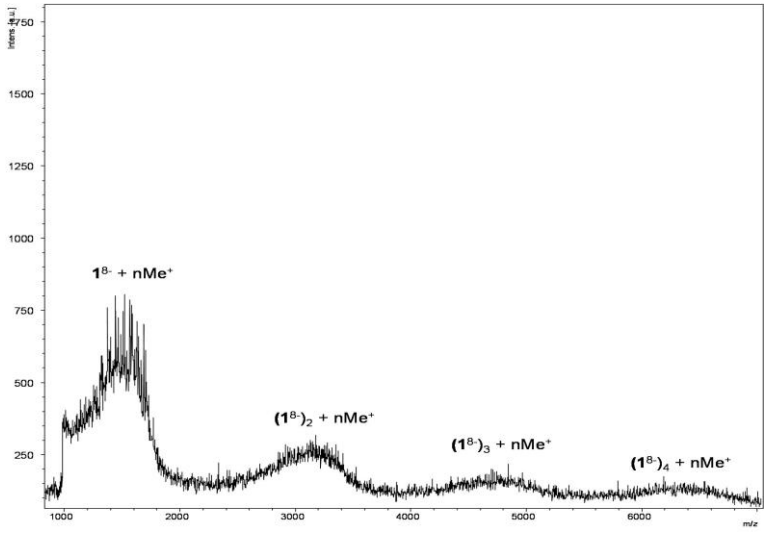


Figure S1 MALDI-TOF mass-spectrum of **1** in (a) DMSO.

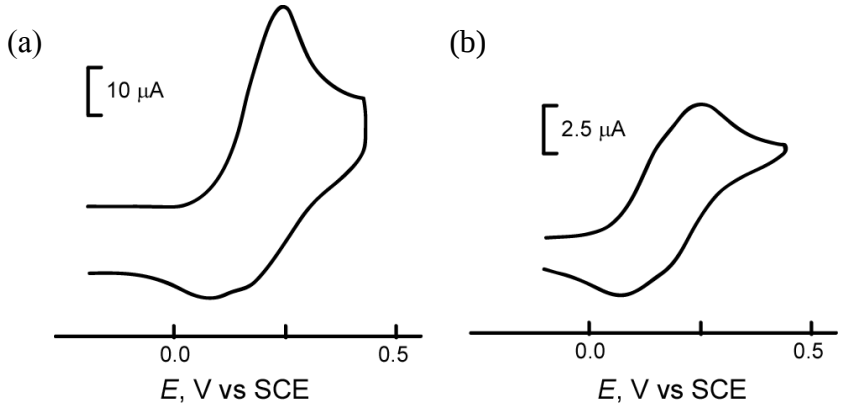


Figure S2 Cyclic voltammograms for **1** (C = 1mM) at a glassy-carbon electrode (H_2O/0.1 M NaCl) at (a) υ = 100 mV/s; (b) 10 mV/s.

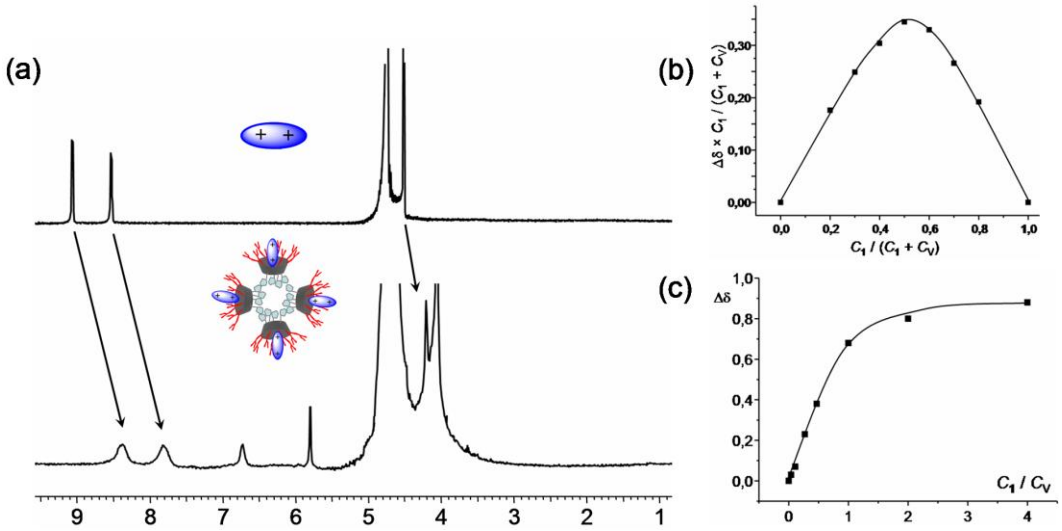


Figure S3 (a) ^{1}H NMR spectra of V^{2+} and **1**+V^{2+} (C = 1mM); (b) Job's plots for aromatic proton of V^{2+} ($C_\mathbf{1}$ + C_V = 1 mM); (c) Plot of the up-field shifts of the aromatic proton of V^{2+} as function of $C_\mathbf{1}/C_V$ (C_V = 1 mM, D_2O).

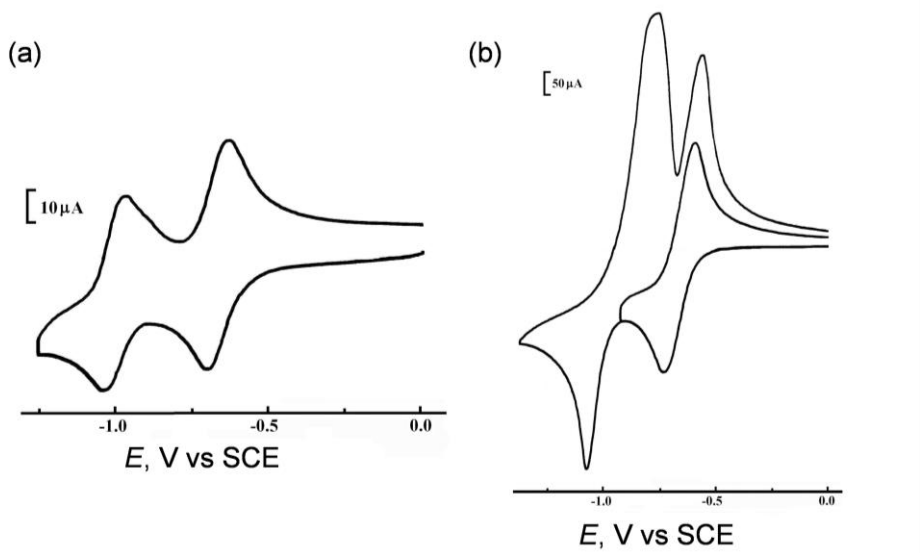


Figure S4 Cyclic voltammograms for V^{2+} ((a) C = 1 mM, (b) 10 mM) at a glassy-carbon electrode (H_2O/0.1 M NaCl, υ = 100 mV/s).

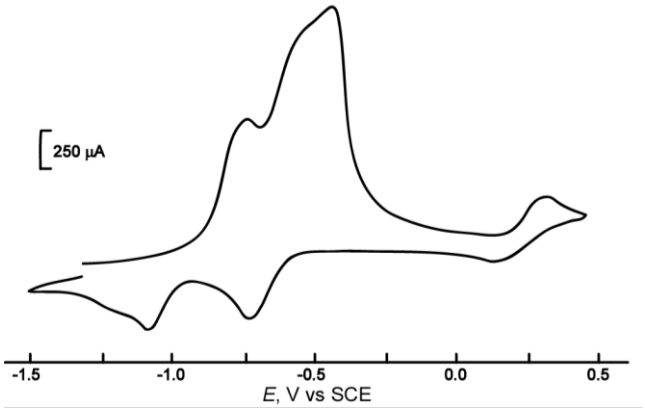
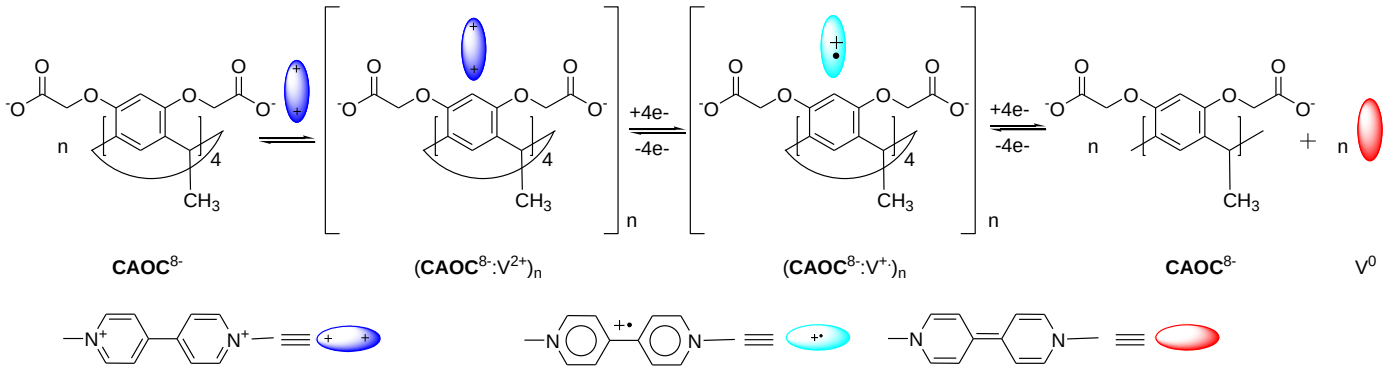


Figure S5 Cyclic voltammogram for **1** + V^{2+} (C = 10 mM) at a glassy-carbon electrode (H_2O/0.1 M NaCl) after the applying potential E = -1.3 V for one minute with the scan rate υ = 100 mV/s.

Table S1 Data of Cyclic voltammograms for the reduction of V^{2+} and the oxidation of **1** at a glassy-carbon electrode (H_2O, 0.1 M NaCl, υ = 100 mV/s, vs SCE

C_1, mM	C_V, mM	$E_{p,red}^1$, V	$E_{p/2,red}^1 - E_{p,red}^1$, mV	$i_{p,red}^1$, μA	$E_{p,reox}^1$, V	$E_{p,red}^2$, V	$E_{p,reox}^2$, V	$E_{p,ox}$, V	$E_{p,ox} - E_{p/2,ox}$, mV	$i_{p,ox}$, μA	$E_{p,rered}$, V
0.2	-							0.20	80	6.8	0.10
1	-							0.26	110	42	0.08, 0.16
10	-							0.27	100	240	0.10
-	1	-0.70	60	28	-0.63	-1.03	-0.96				
-	10	-0.71	70	270	-0.59*	-1.06*	-0.77*				
1	1	-0.69	60	27	-0.63	-1.04	-0.92	0.26	110		0.09, 0.17
10	1	-0.70	60	23	-0.64	-1.11	-1.00	0.27	100	245	0.10
10	10	-0.70	70	185	-0.60*	-1.09*	-0.81*	0.27	80	225	0.11

* Peaks contain an adsorption part



Scheme S2 The electrochemicaly driven interaction of **CAOC** with V^{2+}

Table S2 Data of Cyclic voltammograms for the reduction and re-oxidation of V^{2+} in the absence and presence of **CAOC** at a glassy-carbon electrode (H_2O, 0.1 M NaCl, υ = 100 mV/s, vs SCE

C_{CAOC}, mM	C_V, mM	$E_{p,red}^1$, V	$E_{p,red}^1 - E_{p/2,red}^1$, mV	$I_{p,red}^1$, μA	$E_{p,reox}^1$, V	$E_{p,red}^2$, V	$E_{p,reox}^2$, V
-	1	-0.70	70	28	-0.63	-1.02	-0.96
1	1	-0.70	70	28	-0.63	-1.05	-0.99
10	1	-0.70	70	22	-0.63	-1.14	-1.03
-	10	-0.71	70	220	-0.60	-1.05	-0.79
10	10	-0.71	80	165	-0.61	-1.09	-0.87

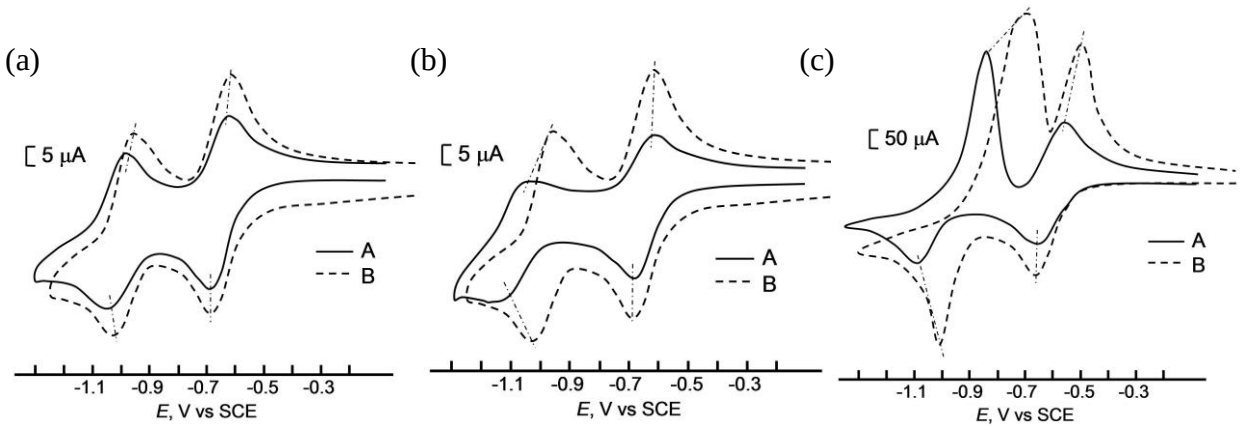


Figure S6 Cyclic voltammograms of (A) mixture **CAOC** + V^{2+}, (B) V^{2+} at the concentration of (a) $C_{\mathbf{CAOC}} = C_V$ = 1 мМ; (b) C_V = 1 мМ, $C_{\mathbf{CAOC}}$ = 10 мМ; (c) $C_{\mathbf{CAOC}} = C_V$ = 10 мМ at glassy-carbon electrode (H_2O/0.1 M NaCl, υ = 100 mVs^{-1}).

[1] Z. Galus, *Teoretycheskiye osnovy electrokhimicheskogo analiza (Theoretical Bases of Electrochemical Analysis)*, Moscow, Mir, 1974 (in Russian).

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