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Electrochemical behaviour of a molecular capsule based on methylviologen–resorcinarene and sulfonatomethylene-resorcinarene

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ABSTRACT

A new molecular capsule based on viologen–resorcinarene and sulfonatomethylene-resorcinarene is synthesized and its redox-controlled stability is investigated.

Molecular capsules are of great interest in modern chemistry because of their potential applications for the isolation of molecular species,[1] and construction of new molecular materials.[2] A number of molecular capsules based on porphyrins,[3] cyclodextrins,[4] cucurbiturils,[5] cyclophanes[6] and metal-coordinated frameworks[7] have been reported. The most suitable macrocycles for constructing molecular capsules are derivatives of calixarenes[8] and resorcinarenes.[9] Their modification allows the production of macrocycles with different functional groups on the upper and lower rims preorganized rigidly by a cyclic aromatic skeleton.[10]

Here, we report the synthesis of a molecular capsule based on resorcinarene with four viologen units ($\mathbf{1}^{8+}$) and sulfonatomethylene-resorcinarene ($\mathbf{2}^{4-}$) (Scheme 1) and a study of its stability depending on the oxidation state of **1**. Resorcinarenes $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$ were synthesized according to literature procedures.[11,12] When an aqueous solution of $\mathbf{1}^{8+}$ was added to an aqueous solution of $\mathbf{2}^{4-}$ a light-red residue precipitated on stirring. The precipitate was isolated and identified as a 1:1 complex of $\mathbf{1}^{8+}$ with $\mathbf{2}^{4-}$ ($\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$).[†] Complex $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ was soluble in DMSO and DMF solutions and insoluble in aqueous media. According to NMR spectroscopy data, the driving force for formation of complex $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ was electrostatic interaction of the positively charged upper rim of $\mathbf{1}^{8+}$ with the negatively charged upper rim of $\mathbf{2}^{4-}$ by a 'head-to-head' arranged structure. In the DMSO-d_6 spectrum of the molecular capsule $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$, the proton signals of the resorcinarenes $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$ were not shifted significantly ($\Delta\delta \leqslant 0.02$ ppm) compared to free $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$ (Fig. 1), except for H_1, H_5 and H_4' (upfield shifts of 0.04–0.07 ppm) and H_6 (downfield shift of ca. 0.04 ppm). The cross-peaks in the 2D NOESY[13] spectrum between H_1' of $\mathbf{2}^{4-}$ and H_4, H_5 and H_6 of $\mathbf{1}^{8+}$ confirm the 'head-to-head' binding mode of the molecular capsule $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ (see Supplementary data). In order to obtain information on the stoichiometry of the capsule, a Job's experiment was carried out. However, the changes in the chemical shifts during the Job titration were very small (less than 0.07 ppm) and no conclusion could be derived in this case. Nevertheless, the curve obtained for the H_2 proton reached a maximum at 0.5 on the abscissa axis ($C_1/(C_1 + C_2)$) confirming 1:1 complex formation (see Supplementary data). Final proof of 1:1 complex formation between $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$ was obtained from diffusivity data analysis.[14] The strong $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ complex formation results in equality of the diffusion coefficients (D) of $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$ (see Table 1 and Supplementary data), the value of which is significantly different compared to free $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$ and correlates with the size of the 1:1 complex between $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$.

In resorcinarene $\mathbf{1}^{8+}\cdot 8I^-$ the I^- counter ions were exchanged for PF_6^- ions[11c] and the properties of $\mathbf{1}^{8+}\cdot 2PF_6^-$ towards sulfonatomethylene-resorcinarene $\mathbf{2}^{4-}\cdot 4Na^+$ were investigated. When a DMSO-d_6 solution of $\mathbf{1}^{8+}\cdot 2PF_6^-$ was added to a DMSO-d_6 solution

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† A 5 ml aqueous solution of $\mathbf{1}^{8+}I^{8-}$ (0.1 g, 0.039 mmol) was added to a 5 ml aqueous solution of $Na^{4+}\mathbf{2}^{4-}$ (0.04 g, 0.040 mmol) and the reaction stirred at room temperature for 10 min. The resulting red precipitate was filtered, washed with water and dried (0.1 g, 86%). ^{1}H NMR (DMSO-d_6) (600 MHz): δ 0.81 (t, 12H, J 7.2 Hz), 1.24–1.36 (m, 24H), 1.65 (d, 12H, J 5.2 Hz), 2.36 (m, 8H), 3.85 (s, 8H), 4.42 (m, 16H), 4.62 (s, 8H), 5.83 (s, 8H), 6.39 (s, 4H), 7.44 (s, 4H), 7.77 (s, 4H), 8.70 (d, 16H, J 6.3 Hz), 9.22 (d, 16H, J 6.3 Hz); elemental Anal. Calcd for $(C_{100}H_{112}N_8O_8)^{8+}\cdot(C_{36}H_{36}O_{20}S_4)^{4-}\cdot 4I^-\cdot 3H_2O$: C, 53.86; H, 5.12; N, 3.69; S, 4.23; I, 16.74. Found: C, 53.46; H, 5.06; N, 3.28; S, 3.89; I, 17.11.

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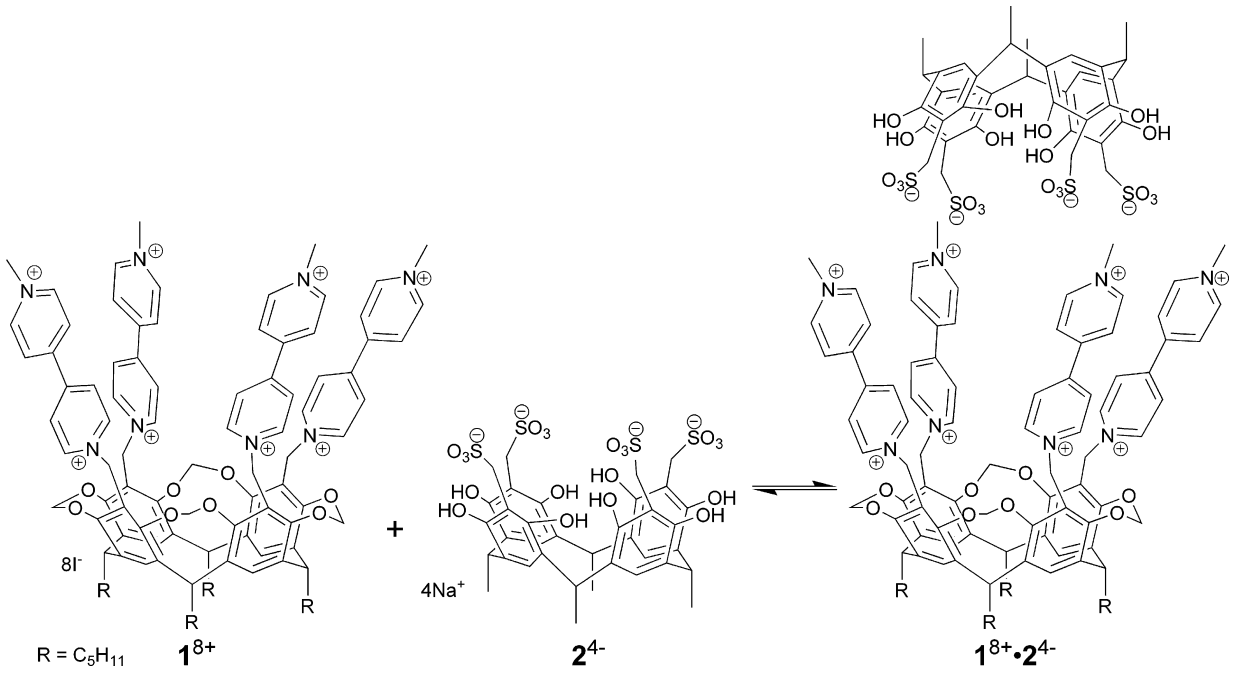


Scheme 1.

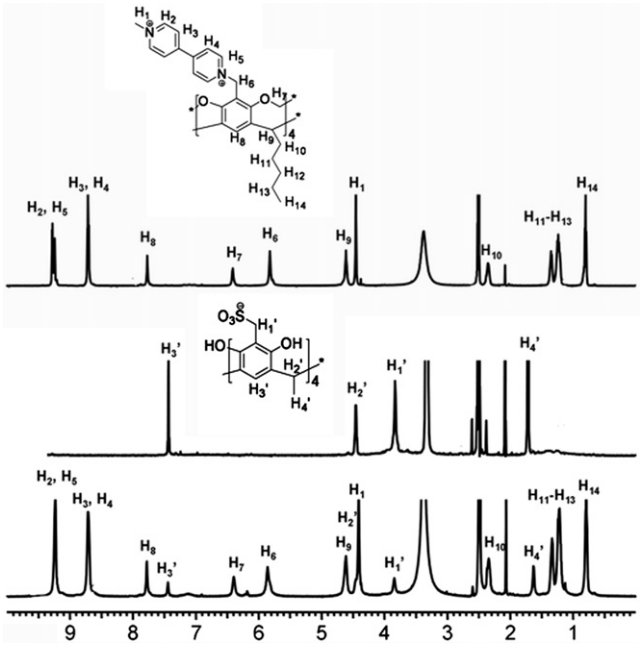


Figure 1. ^{1}H NMR spectra of (a) $\mathbf{1}^{8+}$, (b) $\mathbf{2}^{4-}$ and (c) $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ in DMSO-d_6 (1 mM, 303 K).

Table 1
Diffusion coefficients for $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$ and their combinations (DMSO-d_6, 1 mM, 298 K), $\times 10^{-10}$ m^2/s^{-1}

	D_1 (m^2 s^{-1})	D_2 (m^2 s^{-1})
Free compounds	0.85 ± 0.01	1.34 ± 0.01
$\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$	0.79 ± 0.01	0.79 ± 0.01
$\mathbf{1}^{0}$	0.9 ± 0.1	—
$\mathbf{1}^{0}$ + $\mathbf{2}^{4-}$	1.1 ± 0.1	n/a[a]

The results are average values of multiple data points.
[a] Not available due to the low signal-to-noise ratio.

of $\mathbf{2}^{4-}\cdot 4Na^+$, a similar ^{1}H NMR spectrum (Fig. 1c) was observed confirming complex formation between $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$. According to 2D DOSY data, the diffusion coefficients of the capsules $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ obtained from $\mathbf{1}^{8+}\cdot 8I^-$ and from $\mathbf{1}^{8+}\cdot 8PF_6^-$ had the same value indicating the absence of counter ion influence on the molecular capsule in DMSO solution.[‡]

The electrochemical behaviour of $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ was investigated in DMSO/0.1 M $Bu_4N^+BF_4^-$ at a glassy carbon electrode.[§] Resorcinarene $\mathbf{1}^{8+}$ undergoes two consecutive reduction processes with identical voltammetric peak heights, being quite similar to dimethyl-viologen ($\mathbf{MV}^{2+}$) (Fig. 2). The currents of the peaks are diffusively controlled due to the linear proportionality of the redox peak currents to the square root of the scan rate ($i_p \sim \upsilon^{1/2}$) being indicative of the stepwise reduction of all the viologen units of $\mathbf{1}^{8+}$ at the same potentials. Each viologen unit is reduced to a cation-radical during the first step with formation of tetra(cation-radical)resorcinarene $\mathbf{1}^{4+\cdot}$ and to a quinoid during the second step with generation of a neutral resorcinarene $\mathbf{1}^0$. Compared to $\mathbf{MV}^{2+}$, however, the first and second reduction potentials of $\mathbf{1}^{8+}$ are shifted positively to 110 mV and 40 mV, respectively, indicating easier reduction of $\mathbf{1}^{8+}$. This phenomenon can be explained by the close location of the positively charged viologen units on the calixarene platform, which resulted in their electrostatic repulsion. The cyclic voltammogram of the $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ molecular capsule shows two reduction processes at essentially the same potential as $\mathbf{1}^{8+}$ (Fig. 3).

Compared to $\mathbf{1}^{8+}$, however, $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ exhibits a 15% lower first voltammeric reduction peak and a sharp second peak owing to adsorption of the fully reduced species on the electrode surface.

The shape of the oxidation process depends on the reverse potential. If oxidation is started after the first reduction potential

[‡] According to the ^{31}P DOSY experiment, the D values of PF_6^- (ca. $5.0 \pm 0.6 \times 10^{-10}$ m^2/s) of $\mathbf{1}^{8+}\cdot 8PF_6^-$ and molecular capsule $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}\cdot 2PF_6^-$ are larger than the value of $\mathbf{1}^{8+}$ (ca. 0.85×10^{-10} m^2/s) and $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ (ca. 0.85×10^{-10} m^2/s) indicating the absence of PF_6^- association with $\mathbf{1}^{8+}$ and $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ in solution.

[§] The electrochemical experiment was carried out in the presence of I^- and PF_6^- counter ions. Any differences in electrochemical behaviour of the viologen units in the presence of I^- and PF_6^- were not observed indicating the absence of any influence from I^- and PF_6^- on the reduction of $\mathbf{1}^{8+}$ and $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ in DMSO.

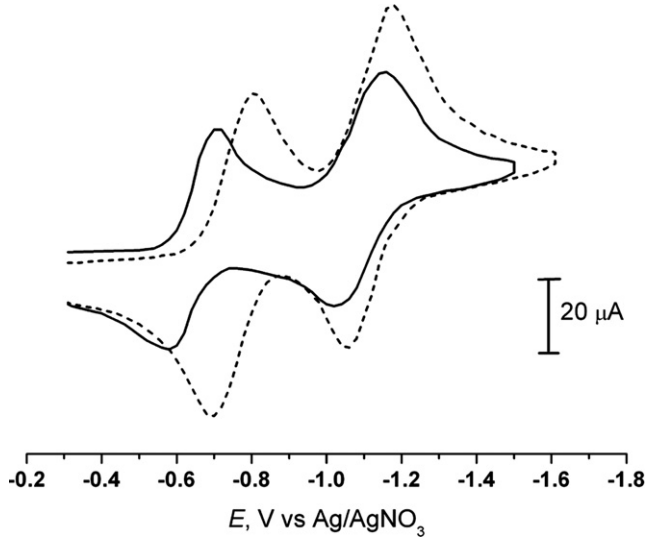


Figure 2. Cyclic voltammograms (1 mM DMSO solutions, 0.1 M Bu_4NBF_4, scan rate 100 mV s^{-1}) for $\mathbf{MV}^{2+}$ (dashed line) and $\mathbf{1}^{8+}$ (solid line).

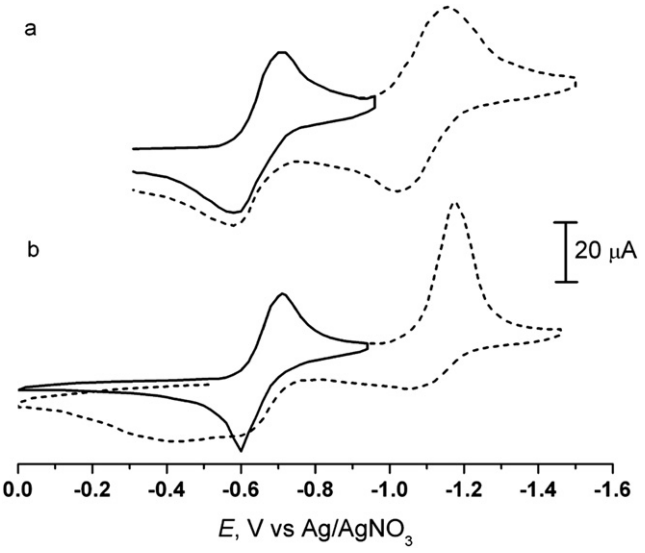
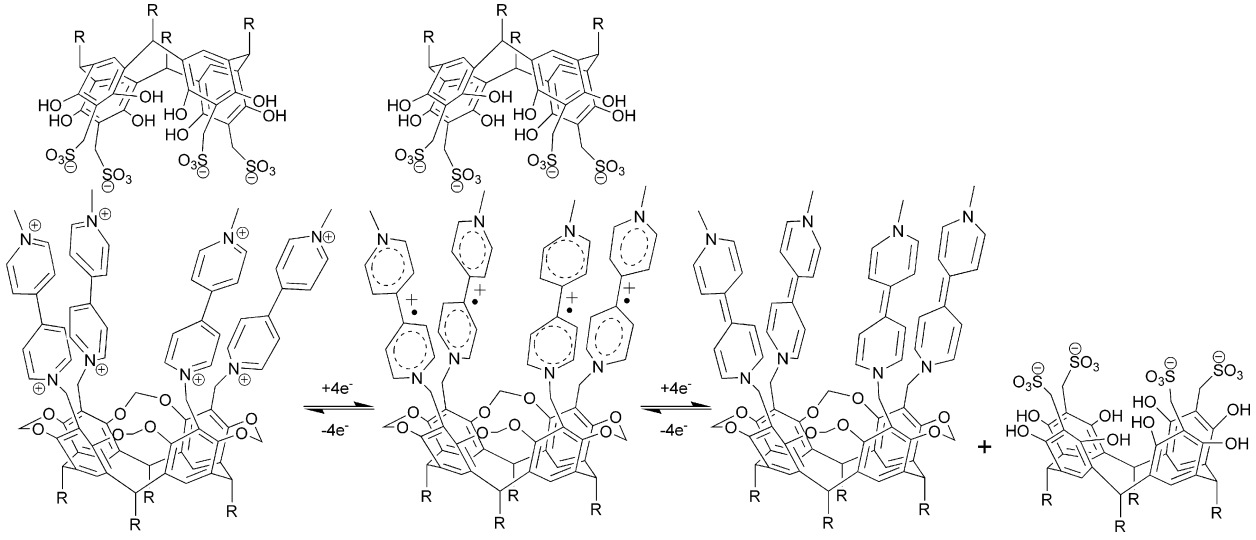


Figure 3. Cyclic voltammograms (1 mM DMSO solutions, 0.1 M Bu_4NBF_4, scan rate 100 mV s^{-1}) for (a) $\mathbf{1}^{8+}$ and (b) $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$.

then a sharp adsorption oxidation peak occurs at −0.6 V (Fig. 3b). If the reverse scan occurs after the second reduction potential, the oxidation processes exhibit poorly defined oxidation peaks. Moreover, compared to $\mathbf{1}^{8+}$, a new oxidation wave with a poor definite maximum appears at −0.4 V. The cyclic voltammogram confirms the existence of a molecular capsule between $\mathbf{1}^{8+}$ and $\mathbf{2}^{4-}$, which results in a decrease in the current of the first reduction peak of $\mathbf{1}^{8+}$. The half reduction of $\mathbf{1}^{8+}$ in the molecular capsule does not lead to destabilization of the capsule, moreover, the half-reduced molecular capsule $\mathbf{1}^{4+\cdot}\cdot\mathbf{2}^{4-}$ partly adsorbs on the electrode surface as was evident from the adsorption feature of the second reduction peak and of the oxidation peak after the first reduction process. It is well known that the adsorption of a species on an electrode surface affects the reverse processes, and therefore the next reduction of the adsorbed capsule $\mathbf{1}^{4+\cdot}\cdot\mathbf{2}^{4-}$ until $\mathbf{1}^{0}\cdot\mathbf{2}^{4-}$ results in essential modification. The absence of well-defined re-oxidation peaks during the reverse process after the second reduction peak is evidence of the formation of an inhibition layer with the $\mathbf{1}^{0}$ species on the electrode surface.

The layer hampers the oxidation/reduction processes of the reagents encapsulated in the layer as well as the reagents diffusing through the layer from the solution to the electrode. Presumably, the formation of the layer is initiated by $\mathbf{1}^{0}$, but not by $\mathbf{1}^{4+\cdot}$. The layer consists of species $\mathbf{1}^{0}$ as well as $\mathbf{2}^{4-}$. Thus, full reduction of the molecular capsule to $\mathbf{1}^{0}\cdot\mathbf{2}^{4-}$ results in destruction of the capsule and its dissociation to $\mathbf{1}^{0}$ and $\mathbf{2}^{4-}$ with aggregation of $\mathbf{1}^{0}$ and $\mathbf{2}^{4-}$ on the electrode surface (Scheme 2). The new oxidation peak at −0.4 V is evidently a response to the oxidation of $\mathbf{1}^{4+}$ being in the aggregates.

Direct indications of the redox behaviour of the $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ system were provided by the NMR diffusivity measurement. Although there is a high risk that the reduction of $\mathbf{1}^{8+}$ could lead to broadening of the NMR signals, we reasoned that it might only affect the polar viologen fragments whilst the lower rim aliphatic moieties could be used for monitoring of the complex mobility. In order to verify this hypothesis, an ab initio calculation of the charge distribution of $\mathbf{1}^{8+}$, $\mathbf{1}^{4+\cdot}$ and $\mathbf{1}^{0}$ was carried out (GIAO DFT RHF/STO-3G).[15] Indeed, the charges of the aliphatic fragments changed



Scheme 2.

slightly ($\Delta q < -0.01$) going from $\mathbf{1}^{8+}$ and $\mathbf{1}^{4+\cdot}$ to $\mathbf{1}^{0}$, whilst the charge changes in the viologen fragments were remarkable ($\Delta q = -0.01$ to -0.09). Moreover, the upfield shifts of the viologen proton signals during reduction were also expected. Thus, according to the calculations, the proton signals of the viologen moieties might be broadened whilst for the aliphatic protons, no changes should be expected. Indeed, the reduction of $\mathbf{1}^{8+}$ to $\mathbf{1}^{0}$[¶] resulted in the disappearance of the sharp proton signals of the viologen units at 5.5–9.5 ppm and the appearance of broadened upfield shifted proton signals of the reduced viologen moieties at 4–9 ppm. Shifts due to the aliphatic signals at 0.8–1.4 ppm were not observed (see Supplementary data).

Moreover, a 2D DOSY experiment was carried out successfully, and the *D* values of the aliphatic protons of reduced $\mathbf{1}^{0}$ were determined. The *D* value of $\mathbf{1}^{0}$ is very close to the *D* value for the initial $\mathbf{1}^{8+}$ (Table 1).[16] The *D* values of the broadened signals of the reduced viologen moieties of $\mathbf{1}^{0}$ have the same values as the aliphatic protons. Reduction of the molecular capsule $\mathbf{1}^{8+}\cdot\mathbf{2}^{4-}$ leads to reduction of the viologen moieties of **1** with destruction of the molecular capsule and precipitation of free $\mathbf{2}^{4-}$.[¶] The changes in the ^{1}H spectrum and the *D* value are similar to those for the free reduced resorcinarene $\mathbf{1}^{0}$ (Table 1), and the latter indicates destruction of the capsule.

In conclusion, a new molecular capsule based on viologen–resorcinarene and sulfonatomethylene-resorcinarene has been synthesized. The stability of the molecular capsule depends on the oxidation state of the viologen–resorcinarene. Its complete reduction leads to destruction of the capsule and its dissociation.

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Supplementary data

Supplementary data (^{1}H, 2D NOESY and 2D DOSY experimental data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.06.084.

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16. The slight increase in the *D* value of free $\mathbf{1}^{0}$ compared to free $\mathbf{1}^{8+}$ is caused by the different solvation of charged and reduced molecules.

[¶] The reduction was carried out using zinc in DMSO-d_6 under an argon atmosphere over 48 h at 80 °C.