

Supplementary Information

Self-assembly of Aminoalkylated Resorcinarene in Aqueous Media. Host-Guest Properties

Ruslan R. Kashapov, Dmitry E. Korshin, Leisan I. Murtazina, Rezeda K. Mukhitova, Sergey V. Kharlamov, Shamil K. Latypov, Irina S. Ryzhkina, Albina Y. Ziganshina and Alexandr I. Konovalov

*A.E. Arbuzov Institute of Organic & Physical Chemistry KazSC RAS, Arbuzov str. 8, 420088
Kazan, RUSSIA*

az@iopc.knc.ru

General Methods

All reagents were purchased from a commercial supplier and were used without further purification.

NMR (500 MHz) spectra were recorded by using a Bruker AVANCE-600 spectrometer with a 5 mm diameter inverse probe head with Z-active shielded gradients working at 600.013 MHz in ^1H . The 2D DOSY experiments were performed by BPP-STE-LED sequence.¹ Data were obtained with a 50 ms diffusion delay in all experiments. Bipolar gradient pulse duration was from 1.8 to 3.5 ms (depending on the system under investigation), spoil gradient pulse was 1.1 ms (30%) and an eddy current delay was 5 ms. The bipolar pulse gradient strength was varied incrementally from 0.01 to 0.32 T/m. The experimentally observed diffusion coefficients were then determined from 2D DOSY plots obtained by Bruker XWinNmr software package. Several measures of D were obtained at more than one place in the spectrum and all experiments were carried out in duplicate or triplicate. The reported results are the mean value of multiple data points and the standard deviations are less than $0.1 \times 10^{-10} \text{ m}^2/\text{s}$ in all cases. The temperature was set and controlled at 298 K with a 535 l/h airflow rate in order to avoid any temperature fluctuations owing to sample heating with the magnetic field pulse gradients.

The molecular weight and size distribution of assemblies were measured by static light scattering (SLS) and dynamic light scattering (DLS) carried out on a Malvern Zetasizer Nano instrument. The DLS and SLS data were analyzed by Malvern Dispersion Technology Software 5.10.

UV-vis spectroscopic measurements were carried out using a Perkin-Elmer Lambda 25 UV/vis spectrometer.

Measurements of pH and pD were made with I-130 ionomer with standardization of the glass electrode by aqueous buffer solutions. When D₂O was used as a solvent the measurements were made with the same glass electrodes and the pD was calculated by adding 0.4 units to the observed meter readings.

For all experiments, except the measurement of dissociation constants, fine-tuning of solution pH was carried out by adding concentrated aqueous HCl or NaOH. Changes in volume and concentration of the sample solutions after addition of HCl and NaOH were taken into account for the mathematical treatment of results.

Determination of pK_a values

Spectrophotometric and pH metric titrations were used for the determination of the pK_a values of **1**. For measurements calixarene **1** was dissolved in 2 mL of universal buffer (mixture of acetic acid, boric acid and phosphoric acid in water ($C(\text{universal buffer}) = 0.04 \text{ M}$, pH 1.8)) ($C(\mathbf{1}) = 0.1 \text{ mM}$ and 0.25 mM) and was titrated with a solution of sodium hydroxide ($C(\text{NaOH}) = 0.235 \text{ M}$). After stepwise addition of 0.05 mL of the sodium hydroxide solution, the pH value was measured using the pH meter and then the absorption spectra were measured with the UV-vis spectrometer.

Synthesis of **1**

A mixture of sodium sulfonatoethylene resorcinarene² (1 g, 1 mmol), *N,N,N',N'*-tetramethyldiaminomethane (0.51 g, 5 mmol) in water (10 mL) was stirred at 80°C for two days. The solvent was removed *in vacuum*. The ethanol was added to residue. The precipitate was filtrated, washed with ethanol (3 times) and dried (1.09 g, 89 %). ¹H NMR (D₂O) (600 MHz): δ 2.54 - 2.91 (m, 40H), 4.05 (s, 8H), 4.55 (t, 4H), 7.21 (s, 4H); MALDI-TOF/MS: 1277 ($[\text{M}+\text{K}+2\text{H}]^+$); elemental analysis calcd (%) for C₄₈H₆₄N₄Na₄O₂₀S₄·1.5 NaCl: C 43.51, H 4.87, N 4.23; found: C 43.07, H 4.66, N 4.38.

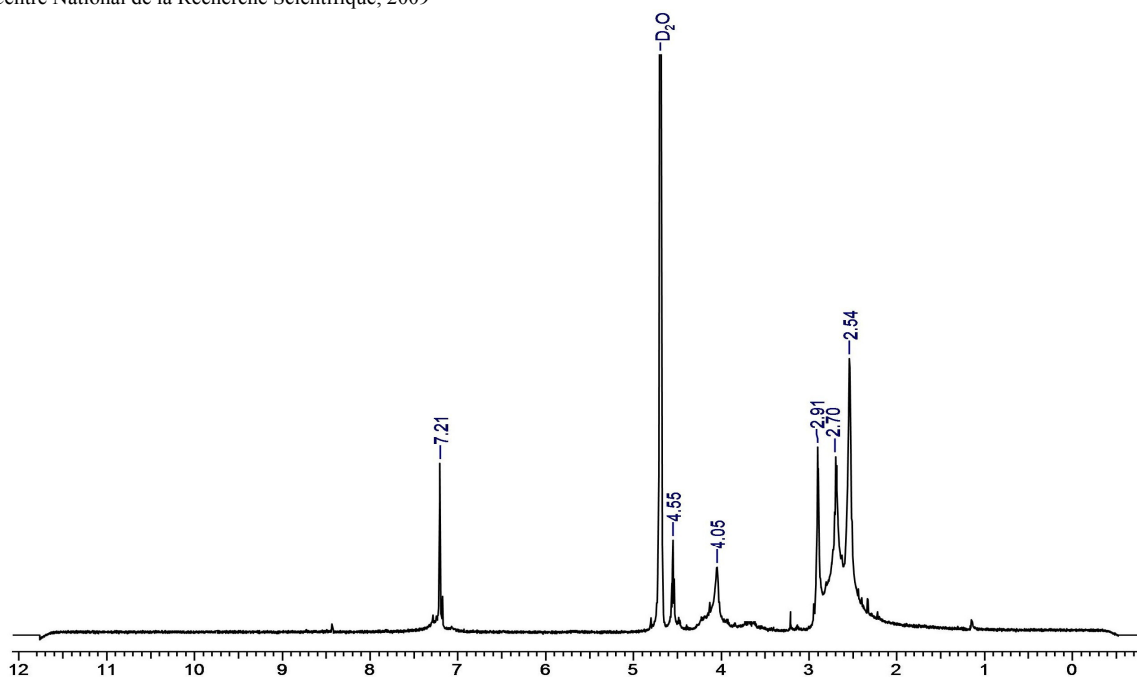


Figure S1. ^1H NMR spectrum of **1** in D_2O $C = 5 \text{ mM}$

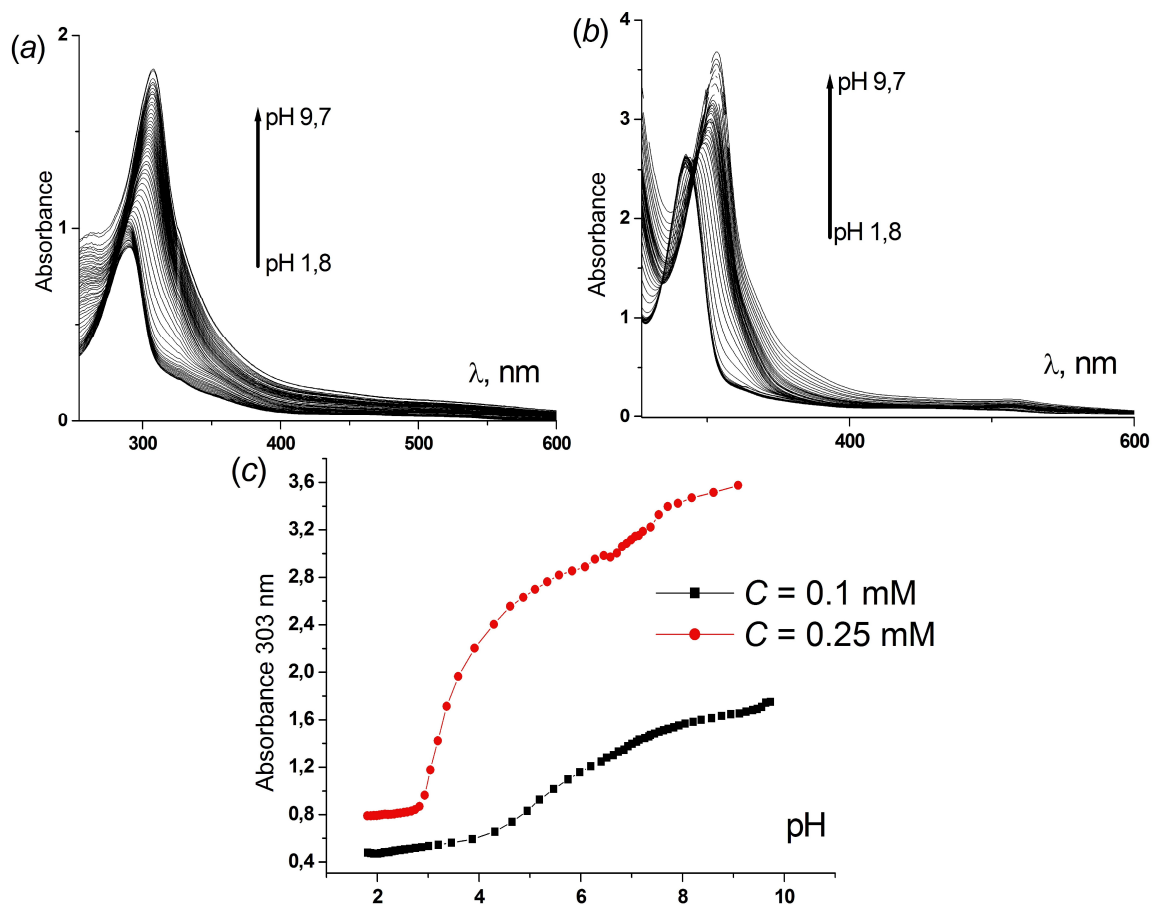


Figure S2. (a, b) UV spectral change of **1** at different pH values from 1.8 to 9.7 (a) 0.1 mM; (b) 0.25 mM; (c) Absorbance change at 303 nm plotted as a function of pH in aqueous solutions (1 cm cell).

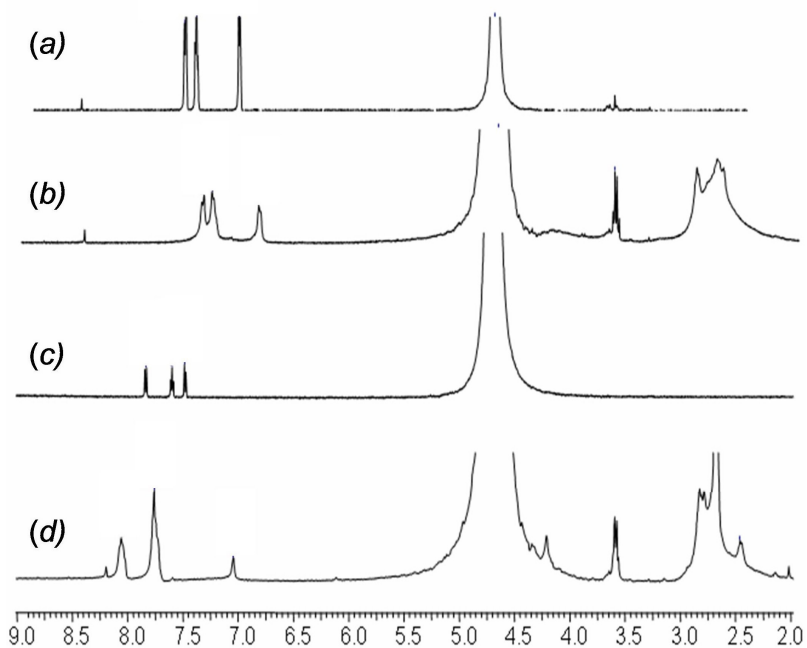


Figure S3. ^1H NMR spectra in D_2O of (a) DAN (5 mM, pH 8); (b) **1** + DAN (5 mM, pH 8); (c) DAN (2 mM, pH 2); (d) **1** + DAN (2 mM, pH 2).

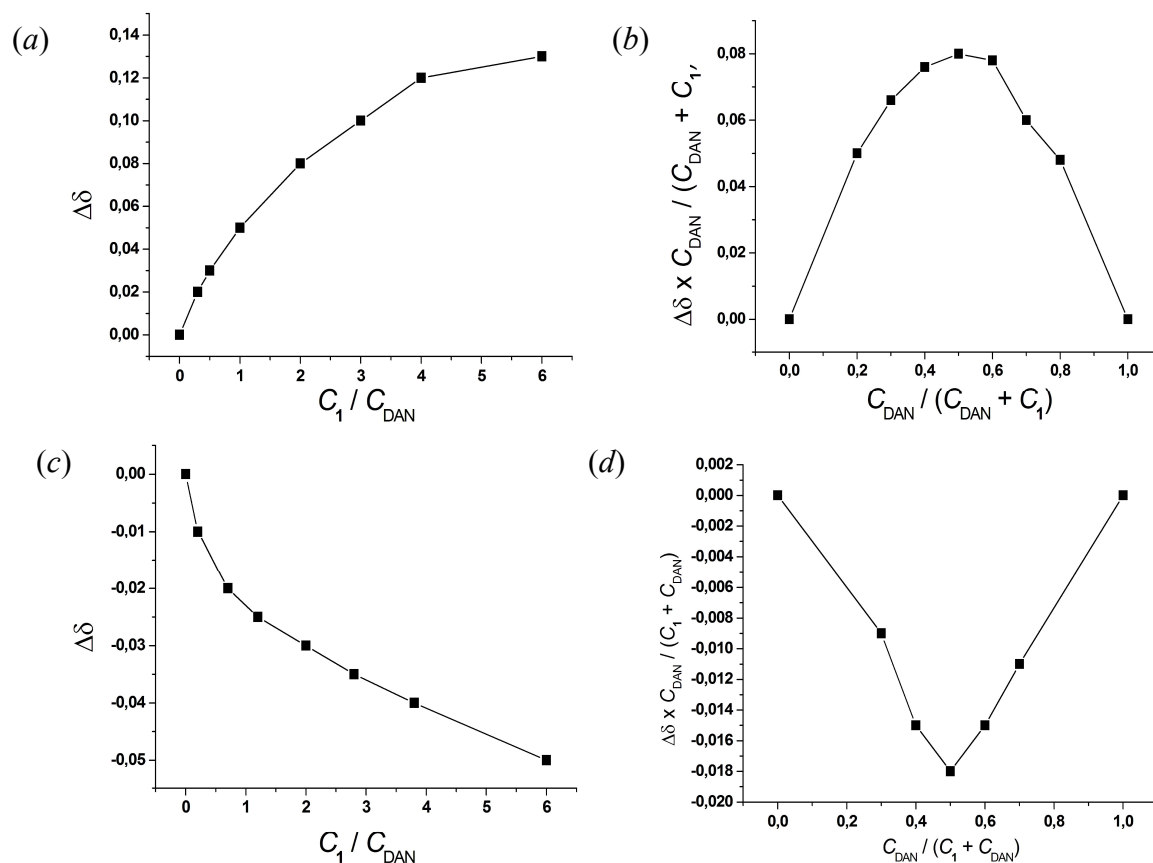


Figure S4. (a, c) Plots of complexation-induced shifts for the DAN proton (1 mM) as functions of C_1 / C_{DAN} ; (b, d) Job's plot for DAN proton ($C_1 + C_{\text{DAN}} = 1$ mM);

$$\Delta\delta = \delta_{\text{DAN}} - \delta_{\text{obs}}; \text{ (a, b) } \text{D}_2\text{O pH 7; (c, d) } \text{D}_2\text{O pH 2.}$$

(1) Wu, D.; Chen, A.; Johnson, C.S. *J. Magn. Reson. A*. **1995**, *115*, 260.

(2) Kobayashi, K.; Asakawa, Y.; Kato, Y.; Aoyama, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10307.