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Calixresorcinarene-capped silver nanoparticles as new supramolecular hybrid nanocontainers

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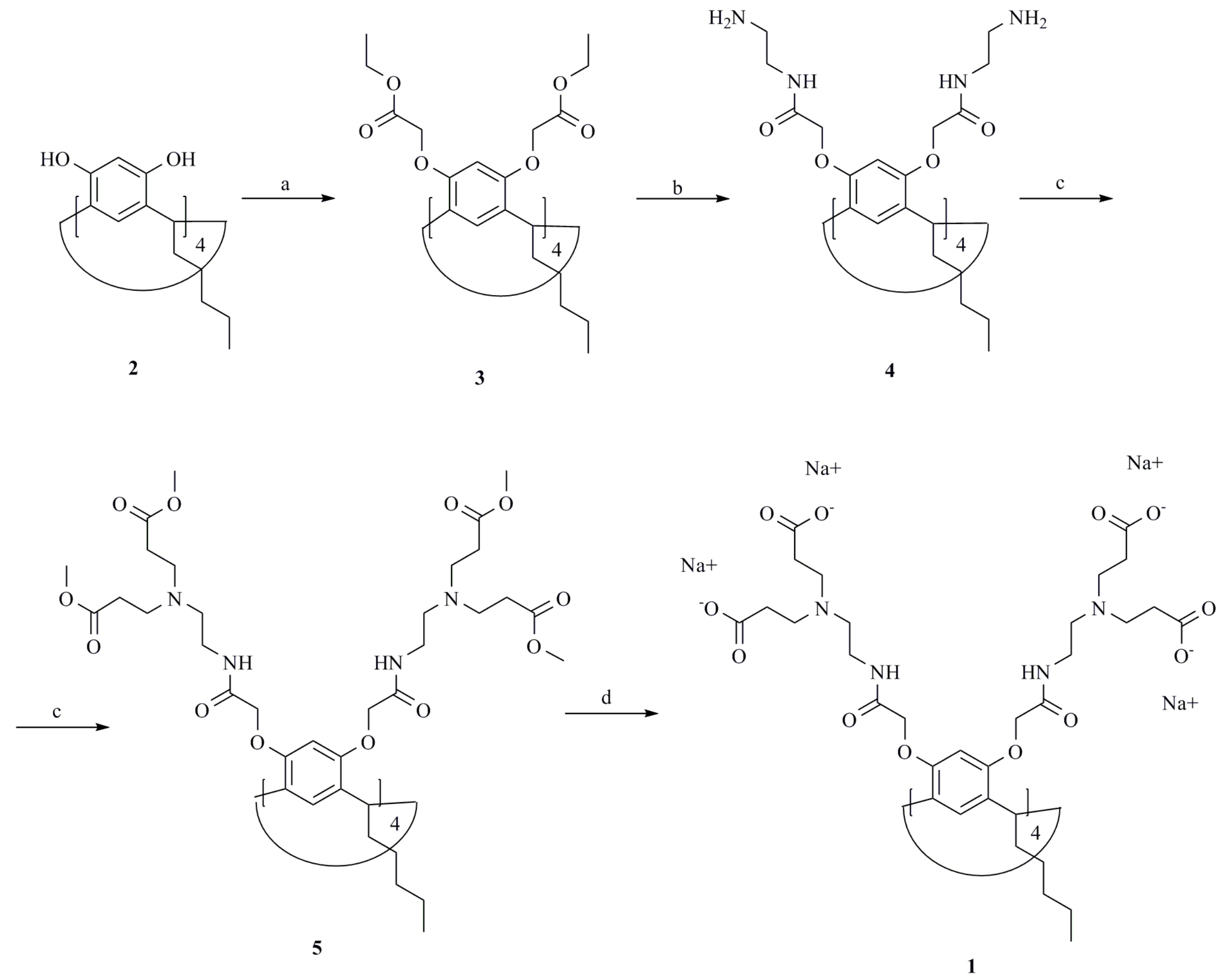

Figure S1 Scheme of macrocycle **1** synthesis: (a) –$BrCH_2COOCH_2CH_3$, K_2CO_3, AN, $t_{bath}=60^0C$, 60h; (b) –$NH_2CH_2CH_2NH_2$, 60^0C, 40h; (c) –$CH_2CHCOOCH_3$, MeOH, $t_{bath}=50^0C$, 170h; (d) – NaOH, EtOH, $t_{bath}=60^0C$, 8h.

Synthesis of 2,8,14,20-tetrakis(n-pentyl)-4,6,10,12,16,18,22,24-octakis(etoxycarbonyl-methoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene **3**.

Compound **2** (15.25 g; 0.0198 mol) was dissolved in dry acetonitrile with stirring at 60 ^0C. Then anhydrous K_2CO_3 (27 g) was added and the reaction mixture was stirred at 70 ^0C for 30 min. Then ethyl bromoacetate (17.56 ml; 0.1584 mol) was added. The mixture was stirred at 60 ^0C for 42 h. The non-organic precipitate was filtered, the filtrate was evaporated and washed with methanol (100 ml), then dried under reduced pressure at room temperature to obtain light yellow solid (17.53 g; 60.6% yield). MS (MALDI-TOF, m/z): 1480.98 (M^++Na^+), 1496.78 (M^++K^+). ^1H NMR ($CDCl_3$, 600 MHz, δ, ppm): 6.62 s. (ArH_{down}, 4H); 6.23 s. (ArH_{up}, 4H); 4.60 m. (CH, 4H), 4.26 s. ($(CH_2)_4$

$_{ethereal}$, 32H), 4.20 q. (O$\underline{CH_2}$CH$_3$, 16H, J$_{HH}$=12 MHz), 1,84 t. (CH$_2$$\underline{CH_2}$H), 24H, J$_{HH}$=18 MHz), 1.27 t. ((CH$_2$)$_3$, 24H, J$_{HH}$=18 MHz), 0.84 t. (CH$_3$, 4H, J$_{HH}$=18 MHz). IR (KBr tablets, ν, cm^{-1}): 1510, 1612, 1760, 2954, 2929, 2859.

Synthesis of 2,8,14,20-tetrakis(n-pentyl)-4,6,10,12,16,18,22,24-octakis[(N-aminoethyl)amido-methoxy]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene **4**.

The mixture of **3** (5 g; 0.00343 mol) and ethylenediamine (20 ml) was stirred at room temperature for 30 min, then at 60 ^{0}C for 40 h. The precipitate was filtered and washed with acetonitrile (20 ml). The white solid was dried under reduced pressure at 50 ^{0}C (4.66 g; 86.5% yield). MS (MALDI-TOF, m/z): 1570.1 (M$^+$+H$^+$), 1593.7 (M$^+$+Na$^+$). ^{1}H NMR (D$_2$O, 600 MHz, δ, ppm.): 7.15 br. s. (ArH$_{up}$, 4H); 6.38 br. s. (ArH$_{down}$, 4H); 4.70 m (CH, 4H), 1.70 br. s. (CH$_2$, 8H), 1.04 br. s. ((CH$_2$)$_3$, 24H), 0.57 t. (CH$_3$, 12H, J_{HH} 8 MHz), 4.24 m. (OCH$_2$, 16H), 3.35 m. (NHCH$_2$, 16H), 2.89 m. (NC$\underline{H}_2$CH$_2$NH, 16H).

Synthesis of 2,8,14,20-tetrakis(n-pentyl)-4,6,10,12,16,18,22,24-octakis([N-(2-(3,3'-azanedylbis(1-methylpropanoate)amino)ethyl]amidomethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene **5**.

Compound **4** (1,5 g; 0,0009 mol) was dissolved in methanol (30 ml) with stirring at 60 ^{0}C, then the solution was cooled in ice bath. The cold freshly distilled methyl acrylate was added to the solution. The mixture was stirred in ice bath for 30 min, then at 50 ^{0}C for 170 h. The solvent and excess of methyl acrylate were removed (in the presence of hydroquinone to prevent the unreacted methyl acrylate polymerization) to obtain a yellow oil. The product was purified by column chromatography with chloroform, then with methanol as eluents to give 1.59 g of the product (60.1% yield). MS (MALDI-TOF, m/z): 2947 (M$^+$).

Synthesis of (2,8,14,20-tetrakis(n-pentyl)-4,6,10,12,16,18,22,24-octakis([N-(2-(3,3'-azanedyl-bispropanoate)amino)ethyl]amidomethoxy)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene octasodium salt **1**.

To the solution of **5** in methanol, NaOH (2 g; in 5 ml of H_2O) was added; the mixture was stirred at room temperature for 30 min, then at 60 ^{0}C for 8 h. The precipitate was filtered, washed with methanol (20 ml) and dried under reduced pressure. The product was purified by dialysis (Cellu Sep, 1000 kDa, 3×1000 ml, 3 h), the water was removed and the product was dried under reduced pressure at 60 ^{0}C to afford amorphous light substance (1.06 g; 95% yield). ^{13}C NMR (D_2O, 500 MHz, δ, ppm.): 180.2, 170.1, 152.8, 129.8, 125.9, 100.4, 67.6, 51.1, 49.5, 35.5, 33.7, 33.5, 33.5, 31.4, 26.6, 21.7, 13.3 (Fig. S3). ^{1}H NMR (D_2O, 600 MHz, δ, ppm): 6.38, 6.81 2 s. (ArH_{up}, 4H); 5.84, 7.23 2 s. (ArH_{down}, 4H); 4.65 m. (CH, 4H); 1.83 br. s. (CH_2, 8H); 1.21 br. s. ($(CH_2)_3$, 24H); 0.74 t. (CH_3, 12H, J_{HH} 8 MHz); 4.89-4.24 m. (OCH_2, 16H); 3.53 m. ($NHCH_2$, 16H); 2.69 m. ($NC\underline{H}_2CH_2NH$, 16H); 2.85 m. ($NC\underline{H}_2CH_2C(O)O^-$, 26H); 2.38 m. ($CH_2C(O)O^-$, 26H). IR (KBr tablets, ν, cm^{-1}): 1501 ($\delta_{(amide\ II)}$), 1575 (C=C arom.), 1670 ($\nu_{(amide\ I)}$), 2954, 2930, 2857 (CH), 3407 (NH/OH). Elemental analysis calculated for ($C_{128}H_{176}N_{16}Na_{16}O_{48}$) (%): C, 50.00; H, 5.77; N, 7.29; Na, 11.96. Found (%): C, 49.85; H, 5.70; N, 7.15; Na, 11.80.

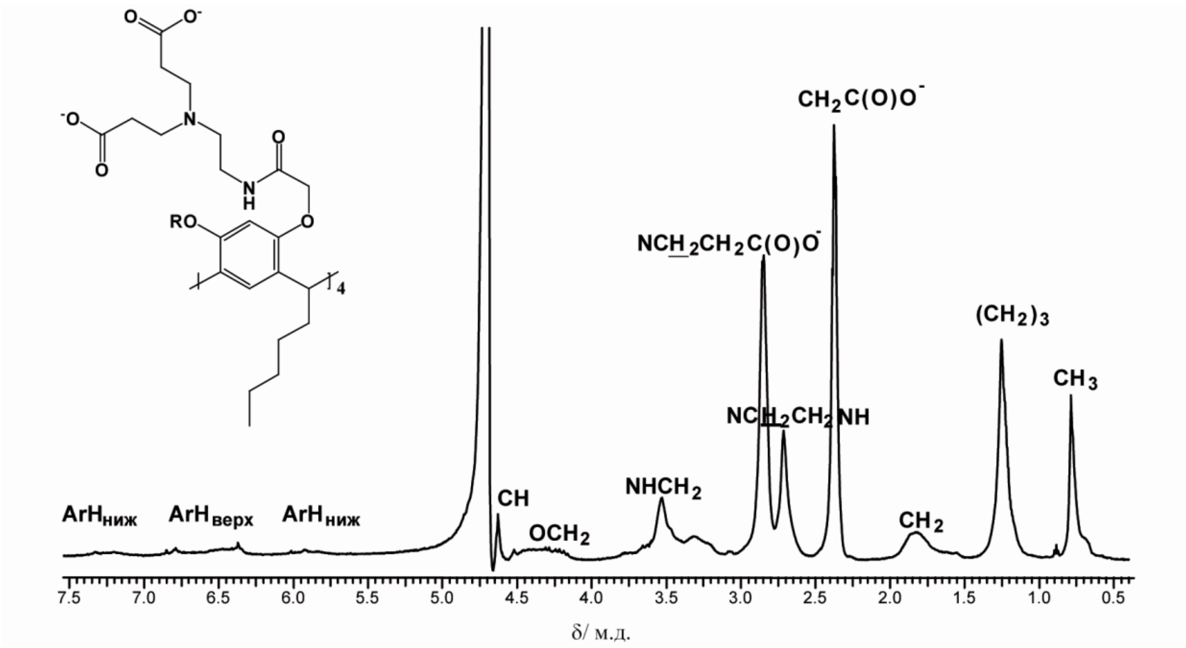

Figure S2 ^{1}H NMR spectrum of **1** in D_2O (5mM).

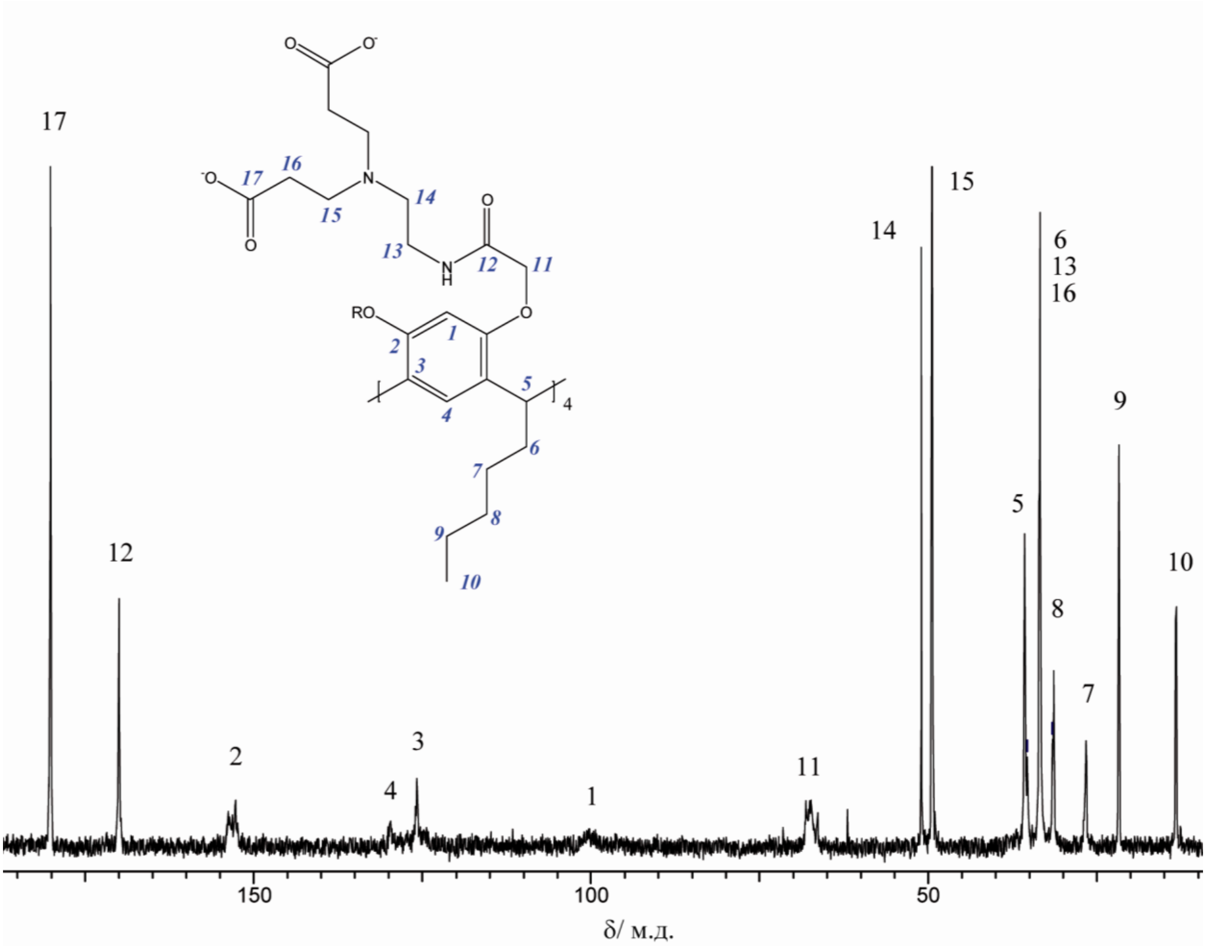

Figure S3 ^{13}C NMR spectrum of **1** in D_2O (30 mM).

The FT-PGSE NMR experiment.

All NMR experiments were performed on a Bruker AVANCE-500 spectrometer. The spectrometer was equipped with a Bruker multinuclear z-gradient inverse probe head capable of producing gradients with the strength of 50 G cm^{-1}. All experiments were carried out at 303±0.2 K. Chemical shifts (δ) were reported relative to HDO (4.7 ppm) as an internal standard. The standard deviations of the chemical shifts determination was ±0.002.

The Fourier transform pulsed-gradient spin-echo (FT-PGSE) experiments were performed by BPP-STE-LED (bipolar pulse pair–stimulated echo-longitudinal eddy current delay) sequence.[1-3] Data were acquired with a 50.0 ms diffusion delay, with bipolar gradient pulse duration from 2.2 to 4.8 ms (depending on the system under investigation), 1.1 ms spoil gradient pulse (30%) and a 5.0 ms eddy current delay. The bipolar pulse gradient strength was varied incrementally from 0.01 to 0.32 T/m in 16 steps. The temperature was set and maintained at 303K with a 535 l/h airflow rate in order to avoid any temperature fluctuations caused by sample heating during the magnetic field pulse gradients. After Fourier transformation and baseline correction, the diffusion dimension was processed with the Bruker Xwinnmr software package (version 3.5). The diffusion experiments were preformed at least three times and only the data with the correlation coefficients of a natural logarithm of the normalized signal attenuation (ln I/I0) as a function of the gradient amplitude, b, higher than 0.999 were included: $b = \gamma2\delta2g(\Delta - \delta)/3$, where γ is the gyromagnetic ratio, g is the pulsed gradient strength, Δ is the time separation between the pulsed-gradients, δ is the duration of the pulse. All separate peaks were analyzed and the average values were presented. The standard deviations of the self-diffusion coefficients determination did not exceed 5%. The pulse programs for all NMR experiments were taken from the Bruker software library.

The aggregation number N_{agr} were calculated as: $N_{agr}= (R_H^{agr}/R_H^{mon})^3$, where R_H^{agr} и R_H^{mon} are hydrodynamic radii of the molecules in aggregated and monomeric states. The values of R_H^{Mon} of calixresorcinarene was estimated with the help of HYDRONMR program.[4]

The TEM experiment.

The transmission electron microscopy (TEM) images were obtained with Hitachi HT7700, Japan. The images were acquired at an accelerating voltage of 100 kV. Samples were dispersed on 300 mesh copper grids with continuous carbon-formvar support films.

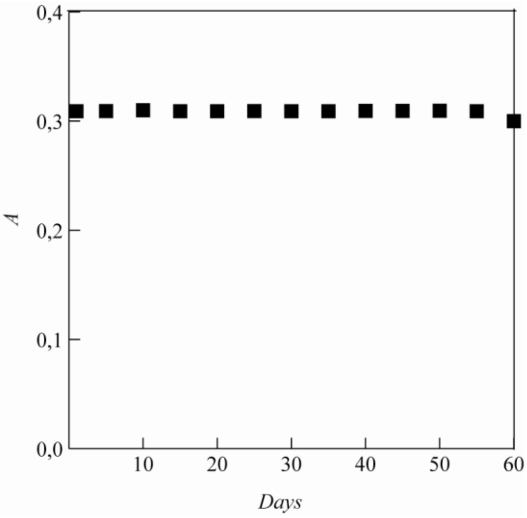

Figure S4 The time dependence of surface plasmon resonance band maximum intensity of **1**.

References

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