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Hierarchical Host-Guest Assemblies Formed on Dodecaborate-Coated Gold Nanoparticles

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1. Materials and Methods

Chemicals were purchased from Sigma-Aldrich (Germany) and used without further purification. CX4Ach was synthesized according to the published procedure.¹ Di-sodium undecahydro-mercapto-*closo*-dodecaborate (BSH) was purchased from Boron Biologicals, Inc. UV-vis measurements were performed on a Varian Cary 4000 UV-Visible spectrophotometer and fluorescence measurements were done on a Varian Cary Eclipse fluorimeter. DLS and zeta potential measurements were performed on a Malvern Zetasizer Nano ZS instrument. IR spectra were recorded on a Nicolet 170SX-FT/IR spectrometer using KBr pellets.

2. Synthesis of BSH-AuNPs

A 250-mL aqueous solution of 1 mM HAuCl₄ was boiled vigorously under stirring in a roundbottomed flask and 38.8 mM trisodium citrate (25 mL) were added. The solution was refluxed for 15 minutes resulting in a color change from pale yellow to deep red. The solution was cooled to room temperature while stirring continuously. The capping with disodium undecahydro-mercapto-*closo*-dodecarborate (BSH) was achieved by adding 3.4 mM BSH (175 μ L) to the pre-formed citrate-AuNPs (275 mL) under stirring for 2 days at room temperature. The BSH-AuNPs were subsequently concentrated to 2 ml final volume (ca. 0.3 μ M) and washed several times with water to remove citrate and excess BSH by centrifugation. Gold nanoparticle concentrations were determined by using an extinction coefficient of 8.78 x 10⁸ L mol⁻¹ cm⁻¹.²

3. Characterization of BSH-AuNPs



Figure S1. Size distribution of BSH-AuNPs measured by DLS.



Figure S2. FT-IR spectra: a) BSH and b) BSH-AuNPs. The presence of the distinct B-H infrared stretching band at ca. 2490 cm⁻¹ in the FT-IR spectrum of the BSH-NPs indicates that the BSH molecules are bound to the AuNPs.



Figure S3. Dependence of the ratio of the absorbance values at 520 and 650 nm of BSH-AuNPs with 1 mM of different monovalent and divalent cations (as chloride salts).



Figure S4. Absorption spectral changes of AuNPs (0.5 nM) at different NaCl concentrations: a) citrate-stabilized AuNPs and b) BSH-AuNPs.

4. Polycationic Calixarene-Induced AuNP Aggregation



Figure S5. a) Absorption spectral changes of 0.6 nM BSH-AuNPs with varying $CX4NH_3^+$ concentrations in water. The inset shows the respective visual color changes. b) Dependence of the ratio of the absorbance values at 520 and 650 nm. The inset shows the chemical structure of $CX4NH_3^+$ (as chloride salt). Upon addition of excess $CX4NH_3^+$ the SPR band retained its original position indicating the formation of a higher-generation supramolecular structure, which we assign to the bi-layer assembly.



Figure S6. a) Absorption spectral changes of 0.6 nM BSH-AuNPs with varying CX4NMe₂ concentrations in water. The inset shows the respective visual color changes. b) Dependence of the ratio of the absorbance values at 520 and 650 nm. The inset shows the chemical structure of CX4NMe₂, which is protonated in aqueous solution. Upon addition of excess CX4NMe₂ the SPR band retained its original position indicating the formation of a higher-generation supramolecular structure, which we assign to the bi-layer assembly.

5. Host-Guest Complexation of BSH and CX4Ach



Figure S7. a) Fluorescence displacement titration of 1,8-ANS (1 μ M) complexed to CX4Ach (4 μ M) by addition of free BSH as a competitive guest. b) Fitted data by assuming a 1:1 binding model from which the association constant was derived. The initial increase in the fluorescence intensity at low BSH concentration (> 2 μ M) might be attributed to a ternary complex formation (CX4AcH•1,8-ANS•BSH).

6. Characterization of the CX4Ach Assembly on BSH-AuNPs

Table S1. Absorption peak position (λ), average diameter (*d*), and zeta potential (ζ) of BSH-AuNPs^a at different CX4Ach concentrations.

[CX4Ach]/µM	λ_{\max} / nm	<i>d/</i> nm	<i>ζ</i> / mV
0.00	523	30.8	-33.6
0.05	524	100.3	-24.3
0.17	530	153.4	-18.6
0.37	592	198.9	-15.7
0.62	620	1330.0	+32.6
1.50	575	102.7	+36.1
37.5	531	201.9	+47.1
50.0 ^b		268.3	+55.5

^a Measurements were done at 25° C with 0.5 nM BSH-AuNP solutions. ^b Measured for free CX4Ach, without AuNP.

7. Critical Aggregation Concentration (CAC) of CX4ACh in the absence and presence of BSH-AuNPs

The CAC value for the CXAch was determined for CX4Ach in the presence and absence of the NPs by using pyrene as a probe. Figure S8 shows that, without NPs, CX4Ach exhibits a CAC of 3.5 μ M. With NPs, two steps of aggregation were observed, the first is assigned to the formation of a bilayer on the BSH-AuNP surface at ca. 1.5 μ M CX4Ach and the second to the formation of CX4Ach micelles/vesicles at ca. 13 μ M.



Figure S8. Determination of the CAC values of CX4ACh a) in the absence and b) in the presence of 0.5 nM BSH-AuNPs by using pyrene (0.4 μ M) as a probe in water at pH 7.0, λ_{exc} = 334 nm. Different emission slits were used in the two measurements leading to different initial values of I_1/I_3 for instrumental reasons.



Figure S9. Size distribution and zeta potential of the BSH-AuNPs-CX4Ach assembly (0.5 nM BSH-AuNPs and 1.5 μ M CX4ACh): a) without AchE and b) with AchE (0.5 U ml⁻¹) after 2 hours reaction time.

9. References

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