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SUPPORTING INFORMATION

An Improved Method for Site-Specific End Modification of Zeolite L for the Formation of Zeolite L and Gold Nanoparticle Self-assembled Structures
John M. Beierle, Robby Roswanda, Petra M. Erne, Anthony C. Coleman, Wesley R. Browne*, Ben L. Feringa*

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1. Materials and Methods

Chemicals were purchased from Acros, Aldrich, Fluka or Merck. Solvents for extraction and chromatography were of technical grade. Analytical TLC was performed with Merck silica gel 60 F254 plates and visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM). Components were visualized by staining with a solution of a mixture of phosphomolybdic acid (4 g) in EtOH (80 mL).

NMR spectra were obtained using a Varian Mercury Plus and a Varian Unity Plus Varian-500, operating at 199.97, 299.97, and 399.93 MHz, respectively, for the $^1$H nucleus or at 50.29, 75.5, 100.57 and 125.70 MHz, respectively, for the $^{13}$C nucleus. Chemical shifts are reported in $\delta = \text{units (ppm)}$ relative to the residual protonated solvent signals of CDCl$_3$ ($^1$H NMR: $\delta = 7.26$ ppm) and DMSO-d$_6$ ($^1$H NMR: $\delta = 2.49$ ppm), or at the carbon absorption in CDCl$_3$ ($^{13}$C NMR: $\delta = 77.0$ ppm) and DMSO-d$_6$ ($^{13}$C NMR: $\delta = 39.5$ ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. MS (EI) spectra were obtained with a Jeol JMS-600 spectrometer.

UV–Vis and IR spectra were recorded using a Jasco V-630 spectrophotometer in Uvasol grade solvents (Merck). Infrared spectra were measured using a Perkin Elmer Spectrum 400 spectrophotometer complete with an ATR attachment. AuNPs were measured as a solid applied directly to the ATR crystal.

Microscopy studies of zeolite L were carried out with an Andor DSD Confocal microscope system. Filters used in the experiments described were median wavelength = 494 nm, bandwidth = 20 nm. Epifluorescence analysis was carried out using a Nikon Illuminator CoolLED system with Semrock Filters: LF488-A-NTE (median wavelength 482 nm, bandwidth = 18 nm).

Samples for TEM were prepared by depositing a few µL of solution on plain carbon coated grids. After blotting the excess liquid, the grids were air dried and transferred to a Philips CM 12 electron microscope operating at 120 kV. Micrographs were recorded on a slow scan CCD camera.

General Synthesis for silyl ether 1 and silanol 2. Fluorenylmethylocarbonyl (Fmoc) succinimide (526 mg, 1.6 mmol) was added batchwise to a stirring solution of aminopropyldimethylmethoxysilane (5, 182 mg, 1.3 mmol), triethylamine (347 µL, 2.5 mmol), and CH₂Cl₂ (5 mL) in a teflon tube. After 16 h the reaction mixture was worked up according to two different protocols for the isolation of 1 or 2:

Work up for isolation of Fmoc-bis-(aminopropyldimethylsilyl) ether (1). The reaction mixture from “General Synthesis for Silyl Ether 1 and Silanol 2” was transferred to a round bottom flask and the solvent removed in vacuo. A minimal amount of MeOH (1 mL) was added. While stirring 1M HCl (50 mL, aq) was added in one portion and a white precipitate formed. After one hour, the solution was extracted with CH₂Cl₂ (3×, 20 mL each). The organics were combined, dried with MgSO₄, filtered and evaporated. The resulting white residue was purified by column chromatography (SiO₂, flash, 50% Et₂O in pentane) to yield 1 (405 mg, 44% yield where 50% is quantitative). ¹H NMR (400 MHz, CDCl₃) δ: 7.75 (d, J = 7.5 Hz, 4H), 7.57 (d, J = 7.3 Hz, 4H), 7.38 (t, J = 7.5 Hz, 4H), 7.28 (t, J = 7.5 Hz, 4H), 5.00 (bs, 2H), 4.37 (d, J = 6.6 Hz, 4H), 4.18 (m, 2H), 3.17 (dd, J = 13.6, 6.7 Hz, 4H), 0.55 – 0.46 (m, 4H), 0.06 (s, 12H) ppm. ¹³C NMR (50 MHz, CDCl₃) δ: 156.5, 144.0, 141.3, 127.6, 127.0, 125.0, 119.9, 57.7, 47.3, 45.8, 33.9, 22.0, 0.30, -1.7 ppm. HRMS (ESI-TOF m/z): 715.2995; calculated [M+Na⁺]: 715.2999.

Work-up for isolation of Fmoc-aminopropyldimethylsilanol (2). The reaction mixture from “General Synthesis for Silyl Ether 1 and Silanol 2” was taken up in a separating funnel, additional CH₂Cl₂ (10 mL) was added, and the solution was washed with 0.1M HCl (1x, 10 mL), H₂O (1x, 10mL), and brine (1x, 10 mL). The organic solution was then dried with MgSO₄, filtered, and the solvent removed in vacuo. The resulting white residue was purified by column chromatography (SiO₂, flash, 50%-75% Et₂O in pentane) to yield 2 (251 mg, 51%). ¹H NMR (400 MHz, DMSO-d₆) δ: 7.87 (d, J = 7.7 Hz, 2H), 7.67 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.25 (bs, 1H), 4.24 (m, J = 14.1 Hz, 3H), 2.93 (m, 2H), 1.39 (m, 2H), 0.40 (m, 2H), 0.03 (s, 6H) ppm. ¹³C NMR (50 MHz, DMSO-d₆) δ: 156.1, 142.6, 139.4, 128.9, 127.3, 121.4, 120.1, 46.8, 43.3, 23.8, 14.9, 0.3, 0.1 ppm. HRMS (ESI-TOF m/z): 378.1748; calc’d [M+Na⁺]: 378.1501.
Bis-[Fmoc-PEG9-(aminopropylmethysilyl)] ether (3). Fmoc-PEG (9 atoms)-OH (100 mg, 0.26 mmol), obtained from Novabiochem, was dissolved in CH₂Cl₂ (5 mL) and TEA (73 µL, 0.52 mmol) in a polypropylene centrifuge tube. DIC (109 µL, 1.04 mmol) was added dropwise and the solution was left for 5 min with stirring. Finally, aminopropylmethoxysilane (5, 88 µL, 0.52 mmol) was added to the mixture dropwise and the reaction mixture was left stirring at rt for 16 h. The mixture was put directly onto a pad of silica where the hydrophobic products were removed (0-5% MeOH in EtOAc). The polar mixture of silane products were isolated and the organics evaporated leaving a white residue. The white residue was dissolved in MeOH (1 mL) and 1 M HCl (1 mL, aq) was added with stirring. The reaction was left for 30 min. The mixture was subject to rotary evaporation to yield a pale white oil that was then dissolved in DCM:MeOH:TEA (95:5:1) and purified by column chromatography (SiO₂, flash, DCM:MeOH:TEA [95:5:1]) to provide 79 mg of 3, 33% yield. 

\[ \begin{align*}
\text{Ph}_3\text{P} & \quad \text{DMF} \\
\text{MeOH} & \quad \text{N}_2 \\
\beta\text{-CD} & \quad \text{P}_2\text{O}_5
\end{align*} \]

Per-iodo-septadeoxy-β-cyclodextrin. The following procedure follows that of Defaye and Gadelle \[^1\] with the modified workup of Stoddart and coworkers \[^2\]. Iodine (56 g, 220 mmol) was added in batches to a stirring solution of Ph₃P (58 g, 220 mmol) in dry DMF (140 mL) in a 250 mL round bottomed flask under N₂. The reaction mixture became warm during the addition and turned dark brown. β-Cyclodextrin (βCD, 12 g, 11 mmol) that had been dried under vacuum over P₂O₅ for a minimum of 5 h was then added in one portion. The reaction vessel was heated with stirring to an oil bath temperature of 85 °C for 16 h. The reaction vessel was cooled to rt and the mixture was then reduced to approximately half its volume via rotary evaporation (~65 °C bath temperature). Na (4.2 g) was dissolved in MeOH (75 mL) with stirring in a rb flask (100 mL) while cooling in an ice bath. Following complete dissolution, the NaOMe in MeOH (~3M) mixture was carefully added to the reaction mixture on ice and stirred at ambient temperature and pressure for 1 h. The resulting brown solution was then poured into 1 L of MeOH and mixed. The flask was left for 1 h at rt. The resulting precipitate was isolated via vacuum filtration over a sintered glass funnel (porosity #3), washed with MeOH, and allowed to air dry. The solid was then purified by Soxhlet extraction with MeOH for 2d. Characterization data for the resulting pale white solid (10.1 g, 55 % yield) matched that reported in the literature.\[^{[1,2]}\]
Per-thio-septadecoxy-β-cyclodextrin (HSβCD, 6). [2] Per-iodo-septadecoxy-β-cyclodextrin (2.1 g, 1.1 mmol) was dissolved in dry DMF (25 mL) in a 100 mL round bottomed flask and thiourea (672 mg, 8.8 mmol) was added in one portion under N₂. The resulting solution was heated at an oil bath temperature of 80 °C for 20 h. The DMF was then removed by rotary evaporation (bath temperature ~65 °C) leaving a yellow residue. Water (80 mL) was added to the residue with stirring followed by NaOH (558 mg) and the solution was gently refluxed under N₂ for 2 h. Following reflux the cloudy white reaction was cooled to room temperature, acidified with KHSO₄ (aq, sat’d), and filtered over a sintered glass funnel (porosity #4). The resulting white solid was washed with water, air dried, then dried under vacuum over P₂O₅. Characterization data for the resulting fine white solid (1.2 g, 86% yield) matched that reported in the literature. [2]

Diadamantyloctathyleneglycol (7). Octaethylene glycol (100 mg, 0.27 mmol) was dissolved in CH₂Cl₂ and DMF (1:1, 5 mL). Adamantane carbonyl chloride (161 mg, 0.81 mmol) was added in one portion followed by the addition of pyridine (41 µL, 0.59 mmol). The solution was left at ambient temperature and pressure overnight. After 16 h the solvent was evaporated in vacuo and the crude residue purified by column chromatography [SiO₂, flash; EtOAc:MeOH (95:50)] to yield 7 (120 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ: 4.20 (t, J = 12, 8 Hz, 4H), 3.68 (t, J = 8, 4 Hz, 4H), 3.64 (bs, 24 H), 2.01 (bs, 6H), 1.89 (d, J = 4 Hz, 12H), 1.71 (bs, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 177.6, 70.6, 69.2, 63.3, 40.7, 38.8, 36.5, 27.9 ppm. HRMS (ESI-TOF m/z): 717.4195; calc’d [M+Na⁺]: 717.4190.
3. Zeolite L Synthesis, Modification, and Characterization

Synthesis of Large Hexagonal Cylinder Zeolites (4-6 µm x 1.5-2.0 µm). The synthesis of large zeolites follows Calzaferri and coworkers with a modified workup. [3,4] Potassium hydroxide (>86% purity, 3.11 g, 55.3 mmol) was dissolved in doubly distilled H₂O (ddH₂O) and stirred on ice for 5 min. Aluminium powder (>99% purity, 0.58 g, 22 mmol) was added under N₂ flow. The reaction mixture was left on ice for 15 min, after which the mixture was allowed to warm to rt. The mixture was then left at room temperature for 1.5 h, followed by filtration under gravity to leave a clear solution. This solution was then added to Ludox HS-40 (40 wt. % SiO₂, 14.3 g) that had been stirring for 5 min. The mixture should thicken to an opaque gel. After 5 min the mixture was transferred to a PTFE pressure vessel, sealed, and placed in an oven at 175 °C for 72 h.

After 72 h, the PTFE vessel was placed in ice for 30 min to cool the vessel. The mixture was then filtered over a sintered glass funnel (#4) and filter paper and washed with hot doubly distilled H₂O until the filtrate was at a neutral pH. The large zeolites were allowed to air dry on the filter overnight. The resulting material was added to 4.0 g of KNO₃ in 70 mL of doubly distilled H₂O for ion exchange, sonicated for 5 min, and stirred at 50 °C for 5 h. The solution was then filtered over a sintered glass funnel (#4) and filter paper and washed with doubly distilled H₂O until the filtrate pH was neutral. The zeolites were then dried overnight in an oven at 100 °C. The resulting large zeolite particles were measured and checked for uniformity by SEM.

Synthesis of Fmoc-aminopropyldimethylmethoxysilane (4) and End Specific Modification of Zeolite L adapted from the procedure of Huber and Calzaferri. [5-7]

The procedure described by Huber and Calzaferri is

“...In a teflon tube, 10 µl of (3-aminopropyl)dimethylmethoxysilane (APMS, 0.059 mmol) were diluted with 1 ml of CH₂Cl₂, and 30 mg of FMOC–N–hydroxysuccinimidylester (FMOC–NHS, Fluka, > 98 % HPLC; 0.089 mmol, 1.5 eq) dissolved in 1 ml CH₂Cl₂ were added dropwise. The reaction mixture was stirred at room temperature and followed by TLC. After stirring for 30 min, no more free amino groups could be detected with a ninhydrin test showing that FMOC–NHS had reacted with all free NH₂ groups to build FMOC–APMS. A weighted amount of zeolite L, typically 10–20 mg was dispersed in a puffer solution of pH 5 and stirred for 1 h. After washing the crystals once with bidest. water, they were blown dry with N₂ and kept at 22% rel. humidity for some hours to rehydrate. The zeolite L crystals were then transferred to a teflon tube and dispersed in 2 ml n–hexane. The amount of channel entrances was calculated using and exactly the corresponding amount of APMS–FMOCS solved in 10 µl CH₂Cl₂ was added. The dispersion was sonicated for 15 min to allow adsorption of the FMOC–APMS stopcock at the channel entrances. Afterwards, the dispersion was refluxed at 65°C for 3 h to covalently bind the stopcock molecules. After centrifuging, the FMOCS–APMS–zeolite L sample was dispersed in 2 ml of DMF and 0.2 ml of piperidine was added. The deprotection was complete after stirring the dispersion for 30 min at room temperature, giving H₂N–zeolite L. The modified zeolite L sample was washed two times with 2 ml acetonitrile to get rid of the remaining piperidine and dried in a oven for 2 h at 80 °C. The zeolite L crystals modified covalently with amino groups at the channel entrances can be used as a precursor and any amino reactive substance can be bound to the free amino groups.” [7]
Procedure for End Specific Zeolite Modification with Compounds 1-3. Dry, powdered Zeolite L (100 mg, 4 µm x 1.5 µm) was dispersed in citric acid buffer (25 mL, pH = 2.5, 1M, aq) in a centrifuge tube. The tube was sonicated for 20 min, then heated at 50 °C with vigorous stirring for 1 h. After cooling to room temperature, the tube was centrifuged (5000 rpm, 8 min) and the buffer decanted. The remaining zeolites were redispersed in doubly distilled H₂O, shaken briefly, centrifuged (5000 rpm, 8 min), and the supernatant thoroughly decanted. The remaining zeolites were then dried using a gentle flow of N₂ just until zeolites were again a dry powder (~15-30 min). The zeolites were then dispersed in heptane (25 mL), shaken, and a calculated amount of silane (see below for quantities and calculations) was added from a 1 mg/mL stock solution in DCE with vigorous stirring. The mixture in the centrifuge tube was sonicated for 30 min and then heated at 65 °C for 16 h with vigorous stirring. Once cooled to rt the stirring bar was removed and the tube centrifuged (5000 rpm, 8 min). The organic solution was decanted. The zeolites were then washed by suspending in CH₂Cl₂ (25 mL), shaken, sonicated briefly (~ 3 s), centrifuged (5000 rpm, 8 min), and decanted. The wash process was repeated two more times (three times total), and then the zeolites were allowed to air dry. The zeolites were deprotected and fluorescently labeled as is detailed below for analysis and characterization by fluorescent microscopy.

Calculation for Number of Channels of Zeolite L in Solution and Volume of Silane 1-3 to add. [8,9]

The number of channel entrances on a zeolite can be calculated by:

\[
\text{number of hexagonal faces} \times \text{fraction of channels/area of zeolite} \times \text{area of a hexagonal face} = 2(0.267)(1500^2) = 1.2 \times 10^6
\]

The weight of a single zeolite crystal (4 µm in length and 1.5 µm in hexagonal diameter) can be calculated by:

\[
\frac{\text{volume of a zeolite crystal} \times \text{weight of one unit cell}}{\text{volume of a unit cell}} = \frac{0.267(1500^2)(4000)(2880)}{(0.75)(6.023 \times 10^{23})} = 1.53 \times 10^{-11} \text{ g}
\]

The total number of zeolites in a 100 mg sample can be calculated by:

\[
\frac{\text{mass}}{\text{weight of a single crystal}} = \frac{0.100}{1.53 \times 10^{-11}} = 7.84 \times 10^{15}
\]

The molar quantity of channel entrances in a 100 mg sample of zeolites can be calculated by:

\[
\frac{\text{(number of channel entrances on a single zeolite) \times \text{total number of zeolites in a sample}}}{\text{Avogadro’s number}} = \frac{(1.2 \times 10^6)(7.84 \times 10^{15})}{(6.023 \times 10^{23})} = 1.30 \times 10^{-8} \text{ mol}
\]

Fmoc-Bis-(Aminopropyl)dimethylsilyl ether (1). For 100 mg of zeolite L measuring 4.0 µm x 1.5 µm a 1x solution was 9 µg of 1. It should be noted that the leaving group of this end functionalization reaction is 2. One could consider that this reaction is effectively 2x in this regard.

Fmoc-Aminopropydimethylsilanol (2). For 100 mg of zeolite L measuring 4.0 µm x 1.5 µm a 1x solution was 4.9 µg of 2.
Bis-[Fmoc-PEG (9 atoms)–(Aminopropyl(dimethyl)silyl)] ether (3). For 100 mg of zeolite L measuring 4.0 µm x 1.5 µm a 1x solution was 13 µg of 3.

Deprotection of Fmoc Protected Amines Fixed at the End of Zeolite Channels. Zeolite L (5 mg, 4 µm x 1.5 µm) was dispersed with a mixture of Piperidine and DMF (20% Piperidine) in an Eppendorf tube. The solution was sonicated briefly (~5 s) and was stirred vigorously for 20 min at rt. The contents of the tube was then centrifuged (5000 rpm, 8 min) and the supernatant decanted. This entire process was repeated a second time. The zeolites were then washed with DMF (1mL) with brief sonication (~ 1 s) followed by centrifugation (5000 rpm, 8 min) twice. The deprotected amino functionalized zeolites were then used in the following step immediately.

Procedure for FITC Modification of Amine Terminated Channel Modified Zeolites. Freshly deprotected amine terminated zeolite L (5 mgs, 4 µm x 1.5 µm) was dispersed in a solution of fluorescein isothiocyanate (FITC, 2mg/mL in DMF with 0.5% TEA) in an Eppendorf tube. The solution was sonicated briefly and stirred for 45 minutes at ambient temperature and pressure. The contents of the tube was then centrifuged (5000 rpm, 8 min) and decanted. The resulting yellow zeolite L was washed with DMF (1 mL), sonicated briefly (~1 s), centrifuged (5000 rpm, 8 min), and the supernatant decanted. The wash process was repeated two more times with MeOH and a final time with CH₂Cl₂. The zeolites were allowed to air dry before being analyzed by fluorescent microscopy.

No Fluorescence Detected.

Figure S1. a) End specific modification with 1 according to the method of Calzaferri and coworkers, [7] begins with stirring the large zeolites in citric acid buffer (pH = 5, 30 min) followed by drying with nitrogen flow. The zeolites were then heated in heptane/dichloroethene in the presence of 1. b) Following attempted deprotection of the amines with 20% piperidine in DMF and fluorescent labeling with FITC in DMF no fluorescence was detected, indicating that 1 did not react with the zeolites.
Figure S2. a) End specific modification with 2 according to the method of Calzaferri and coworkers, begins with stirring the large zeolites in citric acid buffer (pH = 5, 30 min) followed by drying with nitrogen flow. The zeolites were then heated in hydrophobic solution in the presence of 2. b) Following deprotection of the amines with 20% piperidine in DMF and fluorescent labeling with FITC in DMF. Fluorescence microscopy indicated that only in large excess did 2 react. Those batches that were reactive seemed to be completely nonspecific. The pictures are labeled according to the molar equivalents of 2 used. The zeolites in all of the examples measure an average of 4 µm x 1.5 µm.

Figure S3. a) End specific modification with 2 is analogous to that of the procedure with 1, beginning with stirring the large zeolites in citric acid buffer (pH = 2.5, 30 min) followed by drying with nitrogen flow. End modification is completed by sonicating and heating the zeolites in hydrophobic solution in the presence of 2. b) Widefield (top) and epifluorescence (bottom, artificial coloring) microscopy images of end-modified zeolites following deprotection of the amines with 20% piperidine in DMF and fluorescent labeling of the amine.
with FITC in DMF. The samples shown in the pictures are labeled according to the molar equivalents of 2 used. The zeolites in all of the examples measure an average of 4 µm x 1.5 µm.

Figure S4. a) End specific modification with 3 is analogous to that of the procedure with 1, beginning with stirring the large zeolites in citric acid buffer (pH = 2.5, 30 min) followed by drying with nitrogen flow. End modification is completed by sonicating and heating the zeolites in hydrophobic solution in the presence of 3. b) Widefield and epifluorescence (c) microscopy images of end-modified zeolite L following deprotection of the amines with 20% piperidine in DMF and fluorescent labeling of the amine with FITC in DMF. The zeolites measured an average of 4 µm x 1.5 µm. [Linker] refers to HNCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CO.

Procedure for Adamantane Modification of Amine Terminated Channel Modified Zeolites. Freshly deprotected, amino end functionalized zeolite L (20 mg, 4 µm x 1.5 µm) was dispersed in a solution of adamantane carbonyl chloride (4 mL of 4 mg/mL solution in DMF with 0.5% TEA) in a centrifuge tube. The solution was sonicated for 5 min and stirred for 16 h at rt. The contents of the reaction vessel was then centrifuged (5000 rpm, 8 min) and the supernatant decanted. The zeolites were washed with DMF by shaking and brief sonication (~ 3 s), centrifuged (5000 rpm, 8 min), and the supernatant decanted. The process was repeated two more times with CH$_2$Cl$_2$, and the zeolites were air dried. Attempts to characterize adamantane functionalization by fluorescent labeled βCD were complicated by excessive aggregation of modified βCD derivatives tested.

Procedure for coating of Zeolite L with triethoxyaminopropylsilane. Zeolite L (20 mg) was dispersed in DMF (5 mL) and aminopropyltriethoxysilane (20 µL) was added while stirring. The resulting dispersion was sonicated for 15 min and subsequently stirred for 3 h at 60 ºC. After centrifuging (4000 rpm, 8 min) the supernatant was removed and the solid residue was washed twice with DMF, twice with DCM and once with methanol with centrifugation and decanting steps between. The zeolites were moved immediately to the following functionalization steps.

Procedure for FITC Modification of Amine Terminated Channel Modified Zeolites. Amino-functionalized zeolite L (4 mg) was added to a solution of DMF and 0.5%
triethylamine (1 mL) containing FITC (2 mg/mL). The resulting dispersion was sonicated quickly and stirred at room temperature for 45 min. After centrifuging (4000 rpm, 8 min) the supernatant was removed and the solid residue was washed twice with DMF, twice with DCM and once with methanol with centrifugation and decanting steps between. The zeolites were then air dried before analysis by fluorescence microscopy.

![Figure S5](image-url)

**Figure S5.** After coating the zeolites with triethoxyaminopropylsilane, the zeolites were treated with FITC in DMF. a) Widefield and b) epifluorescent images of FITC coated zeolites. Once can see the zeolites are completely fluorescent rather than just at the channel entrances. The zeolites measured an average of 4 µm x 1.5 µm. Coloring is artificial.

**Procedure for Adamantane Modification of Amine Modified Zeolites.** Amino-functionalized zeolite L (4 mg) was added to DMF containing adamantane carbonyl chloride (1 mL of a 4mg/mL solution). The resulting dispersion was sonicated briefly and stirred at rt for 45 min. After centrifuging (4000 rpm, 8 min) the supernatant was removed and the solid residue was washed twice with DMF, twice with DCM and once with methanol with centrifugation and decanting steps between.
4. Gold Nanoparticle (AuNP) Synthesis, Modification, and Characterization

Synthetic Procedure for Citric Acid Stabilized Gold Nanoparticles (18 ± 3 nm). All glasswares used in gold particle synthesis and gold particle modification were thoroughly cleaned in aqua regia (3 parts HCl, 1 part HNO₃), rinsed in triply distilled H₂O. The gold synthesis is based on Grabar[10] with minor modification. Gold particles modification with β-cyclodextrin was based on the method of Liu et al.[11] with minor modifications.

HAuCl₄•3H₂O (100 mg, 0.25 mmol) was dissolved in 250 mL doubly distilled H₂O. The yellow solution was then refluxed for 15 min. To this yellow solution, 0.285 mg of Sodium citrate dihydrate in 25 mL doubly distilled H₂O was added. The mixture immediately turned to violet and reflux was continued for 20 min. The mixture was then left cool to room temperature. The solution was filtered through a 0.45µm Whatman membrane. Analysis by UV-vis absorption show a maxima at 524 nm and TEM measurement showed that the average diameter of the particle is at 18 ± 3 nm.

![Figure S6. TEM image of citric acid stabilized AuNPs.](image)

Synthetic Procedure for Functionalization of Gold Nanoparticles (AuNP, 18 ± 3 nm) with perthio-septadeoxy-β-cyclodextrin (HSβCD). The following procedure is a modified from that reported by Katsfer and coworkers.[11] AuNPs (18 ± 3 nm, 100 mL of an approximately ~1mM solution of Au in doubly distilled H₂O) were additionally diluted with doubly distilled H₂O (80 mL). HSβCD (6, 100 mg) was dispersed in 20 mL doubly distilled H₂O with sonication and heating until a stable dispersion was achieved. This dispersion was then added to the AuNP solution and stirred for 24 h. The reaction was monitored by UV/Vis spectroscopy for aggregation. After 24 h, DMSO (100 mL) was added and the reaction was stirred for an additional 24h at ambient temperature and pressure. The water was then removed by rotary evaporation with heating (~45 °C) and under vacuum. Acetonitrile (100 mL) was added to the clear red/violet solution with mixing. The AuNP colloid was then centrifuged (5000 rpm, 45 min) and decanted. The resulting red-purple solid was redispersed in ACN:DMSO (1:1, 200 mL) and shaken and sonicated to resolubilize until no particulate matter could be observed. The colloid was then again centrifuged (5000 rpm, 45 min) and
decanted. The resulting red-purple solid was redispersed in doubly distilled H₂O (50 mL) with sonication until no particulate matter was observed. The resulting HSβCD coated AuNP were characterized by IR, UV/Vis, and TEM.

**Figure S7.** IR spectra of HSβCD (black) and AuNP modified with HSβCD (red).
5. Procedure for Self-Assembly Studies and Characterization

**Procedure for AuNP aggregation triggered by a chemical stimulus.** HSβCD (6)-functionalized gold colloid (1 mL, approximately 1 mM Au indoubly distilled H₂O) was treated with adamantane dimer 7 from a stock solution of 10 mg/mL in EtOH. Particle aggregation was monitored by UV-Vis, signified by a drop in absorbance at 550 nm. The observations are in agreement with that reported by Kaifer and coworkers, [11] for the stimulated aggregation of HSβCD (6)-functionalized AuNP with a di-ferrocene species.

**Figure S8.** Control reactions show that AuNPs modified with HSβCD (6) only aggregate in response to adamantane dimer 7 signifying the aggregation process is specific for the host-guest interaction. a) Unmodified AuNPs do not decrease in absorbance over time in response to 7. b) HSβCD (6) modified AuNPs do not decrease in absorbance over time in response to the linker unit of 7, octaethylene glycol. c) HSβCD (6) modified AuNPs do not decrease in absorbance over time in response to adamantane monomer, adamantane carboxylic acid.

**Procedure for Adamantane Modified Zeolite L and HSβCD-Modified AuNPs Supramolecular Conjugation.** To the HSβCD (6)-functionalized gold colloid (1 mL, ~1 mM Au indoubly distilled H₂O) was added 100 µL adamantane dimer 7 from a stock solution of 10 mg/mL in EtOH. This mixture was left stirring at room temperature for 24 h. Adamantane functionalized zeolite L (2 mg) was then added and stirring was continued for another 24 h. The mixture then checked for self-assembly by drawing aliquots and checking by TEM.
Figure S9. Examples of self-assembly of HSβCD (6)-modified AuNPs with the control: adamantane coated zeolite L. a) AuNP anchoring takes place all over zeolite L. b) Close-up of AuNP anchoring. c-d) Zeolite-AuNP-Zeolite aggregation is prevalent throughout and takes place at random positions around the zeolite.
6. References