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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,* and Ben L. Feringa*

The ability to site-selectively modify micro- and nanosized particles has allowed for directed self-assembly in two and three dimensions. Site-selective modification of particles can be a complicated task requiring the pre-organization of particles or enhanced particle fabrication methods. The aluminum silicate, zeolite L has been reported to undergo site-specific modification at the zeolite channel entrances, post-fabrication in a solution-based method. The process by which the channel entrances are site selectively modified is explored here. The preliminary step of charging the zeolite channels with aqueous acid allows for catalysis of covalent bond formation at the channel entrances. Three new end-specific modification reagents are described based on silanol and silyl ether functional groups. These reagents are purified by column chromatography and characterized by ^1H NMR spectroscopy and high resolution mass spectrometry (HRMS); they provide for reliable end modification of zeolites L. Preferential reactivity at the channel entrances is also observed. The utility of the approach is demonstrated by modifying zeolite L with adamantane at the channel entrances. Site-specific self-assembly with β -cyclodextrin coated gold nanoparticles can be triggered with a chemical stimulus. The resulting multivalent host-guest interactions give gold clustered nanoparticles at the ends of the micrometer-sized zeolites.

particle modification has allowed groups to develop directed self-assembly in a site-specific fashion allowing for the observation of highly organized particle systems in two and three dimensions.^[2,5]

To modify a certain region of a micro- or nanoparticle, advanced techniques can often be employed. For instance, pre-organized particles are frequently used to enable modification of one side and not the other.^[9,10] Zeolite L represents a special case where a particle can be site-selectively modified post-fabrication without preorganization.^[11] The process is performed in solution and the resulting covalent bond formation takes place at the channel entrances, or the “ends”, of the crystalline hexagonal prism (Figure 1a).^[12] The resulting functionalization results in an anchored amino group that can then be further derivatized to incorporate other functional groups. This study helps clarify the mechanism by which this process takes place and introduces new end-specific modification reagents 1, 2, and 3, which are capable of enhanced

selectivity and reproducibility (Figure 2). We demonstrate how this process can be exploited for site-specific self-assembly of zeolite-gold nanoparticle composites in response to a chemical stimulus (Figure 1b).

Zeolite L has been shown to be a useful particle for photochemical and functionalization studies.^[13,14] Facile fabrication techniques allow access to a range of specific sizes (micro- to nanosized) and shapes (disk and hexagonal prism) from inexpensive starting materials.^[15,16] Loading of the crystal channels with chromophores allows for easy detection via fluorescence microscopy without the need for external modification.^[11] Functionalization of the outside of the aluminosilicate is accomplished using any of a number of commercially available silanes, similar to glass surface modification procedures.^[17] The versatility of functionalization of zeolites has resulted in reports of self-assembly^[11,18–24] and biological applications using zeolite L.^[18,20,21,25] The potential to functionalize zeolite L in a highly specific manner at the channel entrances, i.e., only the ends of a hexagonal zeolite cylinder, offers a method for control in specific dimensions. This additional quality of zeolite L has been shown

1. Introduction

Directed and stimuli-responsive self-assembly of particles has been a burgeoning field of science in recent years.^[1–6] The modification of particles enabling them to undergo self-assembly has allowed the observation of new phenomena on the micro- and nanoscale such as enhanced surface plasmon effects,^[7] as well as the elucidation of new functions. For instance, the principle of self-assembly of microparticles is a fundamental process in current approaches in modern array technology.^[8] Site-specific

Dr. J. M. Beierle, Dr. R. Roswanda, P. M. Erne,
Dr. A. C. Coleman, Dr. W. R. Browne, Prof. B. L. Feringa
Center for Systems Chemistry,
Stratingh Institute for Chemistry
University of Groningen
Nijenborgh 4, 9747, AG, Groningen, The Netherlands
E-mail: w.r.browne@rug.nl; b.l.feringa@rug.nl

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a) Improved End Specific Functionalization

b) Particle-Particle Association Controlled by Supramolecular Interactions

Figure 1. a) End specific modification of zeolite L (hexagonal prism) has been improved by clarifying the role of acid in the channel functionalization step. Charging of the aqueous acid at the channel entrances allows for an enhancement of reactivity at the faces of the zeolite crystal (colored blue then pink). Deprotection of the amine using organic base allows for facile functionalization with electrophiles. Fmoc = Fluorenylmethoxycarbonyl. b) Adamantane and β -cyclodextrin interactions serve as the intermolecular adhesive between zeolite L and gold nanoparticles.

to be useful in applications such as the photochemical destruction of bacteria cells^[25] and end-to-end specific self-assembly of microsized particles.^[24] Although successful, the procedures available are not sufficiently robust for general application. This has prompted us to explore potential modes of reactivity at the channel entrances of zeolite L to understand the actual mechanism that leads to such site-specific modification and ultimately to describe reliable methods for such modifications.

2. Results and Discussion

2.1. Investigating Silane Reactivity at the Channel Entrance of Zeolite L

The original literature procedure for modification of zeolite L at the channel entrances details the use of dry solvents and

oven-dried zeolites.^[12] When we mixed oven-dried zeolite L in the presence of dry solvent and a stoichiometric amount of **4**, we obtained no evidence of zeolite modification by fluorescent labeling or the ninhydrin test described in the study. A modified procedure describing an initial step of stirring the zeolites in aqueous buffer^[26] and drying them with N_2 flow^[27] prior to mixing in the presence of **4** in a hydrophobic solvent was described in a later publication (see Supporting Information), and it was hypothesized that charging the channels with buffered water was mandatory for reactivity. Though this led to improved results in our hands, in that end-functionalized particles were obtained, the procedure was found to lack robustness, including the isolation of completely coated particles as well as no reaction. Attempts to improve the method were complicated by limited information available on the synthesis and characterization of **4**, most probably due to its high reactivity. Multiple attempts at the isolation of methoxysilane **4** showed

the isolation of pure compound could not be accomplished without contamination with hydrolysis products silyl ether **1** and silanol **2** (Figure 3a).

In an attempt to clarify the mechanism behind the end-specific modification procedure, the potential reactivity of **1** and **2** for channel modification of zeolite L was investigated under the new conditions. A priori it was unknown if the reactivity of **1** and **2** would be sufficient for zeolite modification. Characteristically, in surface modification

Figure 2. SEM image of cylindrical shaped zeolite L used in this study, measuring on average $4 \mu\text{m} \times 1.3 \mu\text{m}$. Scale bar is $1 \mu\text{m}$. Silylation reagents **1**, **2**, and **3** are used for end-specific channel modification of zeolite L reported here. Methoxy silane **4** has been previously reported.

Figure 3. Synthesis of silanes used for end-specific modification of zeolite L. a) Reported synthesis of **4** actually results in formation of three products following isolation. Conditions have been found to favor formation of both **1** and **2** based on modified acidic workups, which unlike **4** can be isolated and purified by column chromatography.

techniques, the formation of silanols and silyl ethers complicates modification due to a lack of reactivity. Following the procedure for the fluorenylmethyloxycarbonyl (Fmoc) protection of 3-amino propyldimethylmethoxysilane (**5**) with treatment of the crude reaction mixture with concentrated or dilute aqueous acid allowed for isolation of compounds **1** and **2** respectively (Figure 3b). We were surprised to find that the reactivities of **1** and **2** differed sufficiently from that of **4**, allowing for purification by column chromatography and characterization by NMR and HRMS (high resolution mass spectrometry).

This procedure was tried again by initially suspending zeolite L in citric acid buffer of pH = 5 followed by centrifugation and drying the particles under a N₂ flow.^[27] The zeolites were stirred in the presence of various concentrations of **1** or **2** at 65 °C. After an extended reaction time of 12 h, complete coating of

the zeolites in the presence of 100 fold excess of **2** was observed (relative to the channel entrances), while **1** did not react even after 24 h (see Supporting Information Figure S1,S2). The observation that the reaction required pre-mixing of the particles in aqueous buffer led us to hypothesize that the reactivity of **1** and **2** could be increased by lowering the pH of the solution. A new procedure was developed starting with suspending zeolite L in a citric acid solution at pH = 2.5 and subsequently drying the zeolites under N₂ flow. Deprotection and subsequent fluorescent labeling with FITC (fluorescein isothiocyanate) showed zeolite particles were obtained that were modified only at the channel entrances after mixing with reagent **1** (Figure 4) or reagent **2** (see Supporting Information, Figure S3). Furthermore, the reactivity of **1** and **2** was found to be highly selective for the channel entrances, showing a preference for channel

entrance modification even up to 100 fold excess of **1** relative to the number of channel entrances (Figure 4).

The results indicate that either the negatively charged channels of zeolite L serve as a host for protic solvents, or that the rougher (higher surface area) of the faces of the zeolite crystal serve to anchor a higher concentration of protic solvents as compared to the flatter outer body of the zeolite crystal. Following drying under an N₂ flow, the excess aqueous acid dries, and the faces and the interior of the zeolite crystal remain charged with acid. The use of hydrophobic solvents such as DCE and heptane ensure that the aqueous acid remains predominantly at the channel faces and in the entrances. This hypothesis is supported by the necessity for pre-saturating the zeolites for reactivity, an increase in the reactivity of **1** and **2** with the lowering of the pH of the buffer, and the preference for reactivity of **1** and **2** for the hexagonal faces and channel entrances of zeolite L (i.e., not the entire external surface of the particle) even in 100 fold excess relative to the channel entrances.

Figure 4. a) End specific modification with **1** begins 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 a hydrophobic solution in the presence of **1**. 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 amines with FITC in DMF. The pictures are labeled according to the molar equivalents of **1** used.

2.2. Site-Specific Self-Assembly of Gold Nanoparticles onto Zeolite L

We next sought to apply the methodology here toward site-specific self-assembly of gold nanoparticles onto zeolite L.^[28–30] Cases

Figure 5. β -Cyclodextrin functionalized gold nanoparticles aggregate in response to a chemical stimulus. a) Diadamantane species **7** causes the nanoparticles to aggregate over time via host-guest interactions between adamantane and per-thio- β -cyclodextrin. b) An initial increase followed by a large decrease over time is observed. The large drop in absorption due to aggregation occurs after 2 h. Aggregation is not observed when **7** is added to unmodified AuNPs, nor do AuNPs modified with **6** aggregate in response to fragments of **7** (see Supporting Information, Figure S8).

where the surface chemistry of gold surfaces and silyl surfaces can be manipulated to enable self-assembly between the two species are limited as are methods to analyze the self-assembled mixed species. The supramolecular host-guest interactions of hydrophobic functional groups such as adamantane with β -cyclodextrin (β CD) are well documented in the literature.^[31,32] However to date, this host-guest interaction has not been applied to zeolites. The gram scale preparation of β CD intermediates and the range of functionalized adamantane groups commercially available have made this versatile and reproducible Ad- β CD supramolecular interaction a general adhesive for a range of materials. Recently, groups have expanded the scope of this interaction to develop self-assembling macroscale phenomena such as polymer gels.^[33] The extent to which β CD-adamantane interactions can be manipulated toward assembling phenomena on the micro- and nanoscale has been the topic of recent reviews and remains an important question in the self-assembly of particles.^[31]

2.2.1. β -Cyclodextrin Coated Gold Nanoparticles Aggregate in Response to a Di-Adamantane Species

Work by Kaifer and coworkers has shown that perthio-septa-deoxy β -cyclodextrin (HS β CD, **6**) modified gold nanoparticles (AuNPs) spontaneously aggregated in response to a di-ferrocene species.^[34] This observation was applied to our own study using adamantane with a PEG linker (**7**) instead of ferrocene. We felt the greater abundance of commercially available adamantane derivatives and PEG linkers could allow for broader scope of the investigation. The effect reported by Kaifer and coworkers was observed in the present study also with PEG-linked diadamantane stimulus (**Figure 5**). AuNPs modified with HS β CD (**6**) spontaneously aggregated in response to the diadamantane-PEG species (**7**) as evidenced by a decrease in absorption of the AuNP over 24 h, as was reported by Kaifer and co-workers (**Figure 5b**). This stimuli-responsive self-assembly was specific for the diadamantane species **7**, as control reactions with the PEG linker and adamantane carboxylic acid resulted in no significant change in absorbance (see Supporting Information, Figure S8). Similarly, AuNPs that were not modified with HS β CD (**6**) did not aggregate in response to the diadamantane **7** (**Figure S8**), supporting the hypothesis that the aggregation process was specific for the β CD-adamantane host-guest interaction.

Figure 6. Zeolite L with linker modified, silyl ether precursor **5** (blue ended zeolite) allows for site specific adamantane modification following Fmoc deprotection (red ended zeolite).

2.2.2. Functionalization of Zeolite L followed by Self-Assembly with Gold Nanoparticles

To initiate focused aggregation of gold nanoparticles onto zeolite L in site-specific manner, the methodology developed herein was applied to end-functionalize zeolite L with modified silyl derivative **3**. Compound **3** differs from **1** and **2** by inclusion of a glycol linker. This modification was made to increase the accessibility of the adamantyl species at the zeolite channel entrance. End-specific modification of zeolite L was confirmed by deprotection of the Fmoc group with 20% piperidine in DMF followed by treatment of the free amine with FITC. The results were analogous to those in **Figure 4** (see Supporting Information, Figure S4). Reacting the deprotected amine with commercially available adamantane carboxyl chloride resulted in zeolite L functionalized with adamantane specifically at the channel entrances (**Figure 6**).^[35]

The site-specific aggregation of HS β CD (**6**) modified AuNPs onto end-modified zeolite L was investigated by simply mixing the two modified particles together. Following mixing of adamantane modified zeolite L with AuNPs modified with **6**, no AuNPs were anchored on the zeolites as observed by TEM. When we added diadamantyl species **7** to the same mixture, however, aggregates of AuNP were seen anchored specifically to the zeolite ends (**Figure 7**). This effect can be rationalized by the necessity for a multivalent interaction between the AuNP clusters and zeolite L in order to overcome the repulsion between the negatively charged particles. The result is a site-specific, stimuli-responsive

Figure 7. Zeolite L can be modified at the channel entrances in a site specific fashion with adamantane. When these particles are added to a dispersion of HS β CD (**6**) functionalized AuNPs and a chemical stimulus in the form of a diadamantane (**7**) species is added, the AuNPs aggregate to the ends of the hexagonal prism, zeolite L crystal. a) Scheme of addition. b-d) Examples of zeolite L-AuNP composites. Note the AuNPs have aggregated specifically at the ends of zeolite L. Scale bars are 1 μ m.

aggregation that only takes place when the stimulus **7** is present. Importantly, when we functionalized zeolite L entirely with adamantane in a non-site specific fashion, and we added both **7** and AuNPs modified with **6**, we saw aggregates of AuNP all over the zeolite L crystals as well as zeolites linked to one another at random (see Supporting Information, Figure S9).

3. Conclusions

We have clarified the mechanism for the end specific functionalization of zeolite L, a process that has been shown to be catalyzed by protic solvent localized at high concentration at the rough hexagonal faces and at the channel entrances of the aluminum silicate crystal. The results show that both water and pH are important to catalyze the site-specific reaction. Zeolite L end-functionalization reagents **1**, **2**, and **3** have been developed using the methodology discussed herein. The new functionalization reagents described not only served to clarify the mechanism for end-specific modification, but these reagents can also be isolated, purified, and fully characterized.

Further modification to zeolite L functionalization were also performed toward the development of zeolite-gold nanoparticle self-assembled nanostructures based on adamantane and β -cyclodextrin host-guest interactions. Our studies show the end-modification of zeolite L with adamantane provides an anchoring point for the aggregation of gold nanoparticles in the presence of diadamantane linker species **7**. This shows an example of the level of differentiation the reactivity shows between the smooth outer surface of the zeolite crystal and the rougher face of the channel entrances at the ends of the zeolites. This approach further shows how the site-specific modification of zeolite L can

be used to develop novel self-assembled particle composites between gold and silyl species in response to a chemical stimulus. As zeolite L is readily synthesized from inexpensive starting materials, these new reagents coupled with the methodology developed herein should allow for the expanded role of these aluminum silicates in site-specific self-assembly approaches.

4. Experimental Section

General Synthesis for Silyl Ether 1 and Silanol 2: Fmoc succinimide (526 mg, 1.6 mmol) was added batchwise to a stirring solution of aminopropyltrimethoxysilane (5, 182 mg, 1.3 mmol), triethylamine (347 μ L, 2.5 mmol), and CH_2Cl_2 (5 mL) in a teflon tube. After 16 h the reaction was worked up according to two different protocols for the isolation of **1** or **2**:

Work-Up for Isolation of Fmoc-bis-(aminopropyltrimethylsilyl) Ether (1):

The reaction media from “General Synthesis for Silyl Ether 1 and Silanol 2” was transferred to a round bottom flask and evaporate in vacuo. A minimal amount of MeOH (1 mL) was added. While stirring 1 M HCl (50 mL, aq) was added in one portion and a white precipitate formed. After 1 h, the solution was extracted with CH_2Cl_2 (3 $\times$, 20 mL each). The organics were combined, dried with Mg_2SO_4 , filtered and evaporated. The resulting white residue was purified by column chromatography (SiO_2 , flash, 50% Et_2O in pentane) to yield **1** (405 mg, 44% yield where 50% is quantitative). ^1H NMR (400 MHz, CDCl_3) 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. ^{13}C NMR (50 MHz, CDCl_3) 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; calcd [$\text{M}+\text{Na}^+$]: 715.2999.

Work-Up for Isolation of Fmoc-aminopropyltrimethylsilanol (2): The reaction media from “General Synthesis for Silyl Ether 1 and Silanol 2” was taken up in a separating funnel, additional CH_2Cl_2 (10 mL) was added, and the solution was washed with 0.1 M HCl (1 $\times$, 10 mL), H_2O (1 $\times$, 10 mL), and brine (1 $\times$, 10 mL). The organic solution was then dried with MgSO_4 , filtered, and the solvent evaporated. The resulting white residue was purified by column chromatography (SiO_2 , flash, 50%–75% Et_2O in pentane) to yield **2** (251 mg, 51%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) 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. ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) 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; calcd [$\text{M}+\text{Na}^+$]: 378.1501.

Bis-[Fmoc-PEG9-(aminopropyltrimethylsilyl)] Ether (3): Fmoc-PEG9-OH (100 mg, 0.26 mmol), obtained from Novabiochem, was dissolved in CH_2Cl_2 (5 mL) and TEA (73 μ L, 0.52 mmol) in a polypropylene centrifuge tube. DIC (109 μ L, 1.04 mmol) was added dropwise and the solution was left for 5 min with stirring. Finally, aminopropyltrimethoxysilane (5, 88 μ L, 0.52 mmol) was added to the mixture dropwise and the reaction was left stirring at rt for 16 h. The reaction 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 1M 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]). 79 mg, 33% yield. ¹H NMR (400 MHz, CDCl₃) δ: 7.76 (dJ = 7.5 Hz, 4H), 7.59 (dJ = 7.4 Hz, 4H), 7.39 (tJ = 7.3 Hz, 4H), 7.30 (tdJ = 7.4, 1.1 Hz, 4H), 6.84 (bs, 2H), 5.29 (bs, 2H), 4.40 (dJ = 6.8 Hz, 4H), 4.21 (tJ = 6.6 Hz, 2H), 3.99 (s, 4H), 3.60 (m, 12H), 3.40 (m, 4H), 3.25 (m, 4H), 1.58 – 1.45 (m, 4H), 0.55 – 0.38 (m, 4H), 0.03 (s, 12H) ppm. ¹³C NMR (50 MHz, CDCl₃) δ: 169.8, 156.4, 144.1, 141.5, 127.9, 127.3, 125.2, 120.2, 71.1, 70.9, 70.3, 66.9, 65.0, 53.1, 47.5, 42.1, 41.2, 29.0, 23.9, 17.4, 5.5 ppm. HRMS (ESI-TOFm/z): 983.4652; calcd [M+H⁺]: 983.4658.

Improved Procedure for End Specific Zeolite Modification with Compounds 1–3: Dry, powdered Zeolite L (100 mg, 4 μm × 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 double 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 Supporting Information for calculations) was added from a 1 mg/mL stock solution in DCE with vigorous stirring. 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.

Fmoc-bis-(aminopropyltrimethylsilyl) Ether (1): For 100 mg of zeolite L measuring 4.0 μm × 1.5 μm a 1× 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 2× in this regard.

Fmoc-aminopropyltrimethylsilyl alcohol (2): For 100 mg of zeolite L measuring 4.0 μm × 1.5 μm a 1× solution was 4.9 μg of **2**.

Bis-[Fmoc-PEG9-(Aminopropyltrimethylsilyl)] Ether (3): For 100 mg of zeolite L measuring 4.0 μm × 1.5 μm a 1× solution was 13 μg of **3**.

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.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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