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Synthesis of Surface-Modified Nanoparticles *via* Cycloaddition-Reactions

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Summary. The surface modification of nanoparticles *via* azide/alkine-1,3-dipolar cycloaddition-reactions is described. Ligand exchange onto various nanoparticles was monitored by ^{1}H NMR spectroscopy and formed the basis for the attachment of ligands onto the nanoparticles and their subsequent modification by dipolar cycloaddition reactions. Nanoparticle-surfaces were monitored by binding onto self-assembled monolayers derivatized with matching supramolecular interactions after derivatization.

Keywords. Nanochemistry; 1,3-Dipolar cycloaddition-reactions; Hydrogen bonds; Atomic force microscopy.

Introduction

The stable incorporation of nanoparticles (NPs) [1] into matrices is an important prerequisite to develop their functional role in most applications such as solar cells, electronic circuits, optical detection systems, and magnetic storage devices. The important issues in this process concern (a) the choice of the appropriate location of the NP within the matrix (*i.e.*, at a specific position), (b) the embedding within the matrix with/without a designed interaction, and (c) the achievement of order within the NPs (*i.e.*, defined distances, defined "quasi"-crystalline arrays). Due to the small size of the NPs (usually starting from ~1 to ~50 nm) the embedding process is strongly influenced by surface/matrix interactions as well as the high entropy of the NPs resulting from their high mobility. Thus supramolecular ordering principles [2] are an important strategy to guide the self assembly-properties of NPs into matrices, putting the design of the interface between NP-surface and the surrounding matrix into the limelight of investigations (Fig. 1).

Presently we are following a supramolecular approach to organize polymers [3] and nanoparticles in bulk-materials [4] or surfaces [5] by use of multivalent hydrogen bonding systems. We have developed a general synthetic strategy to affix the

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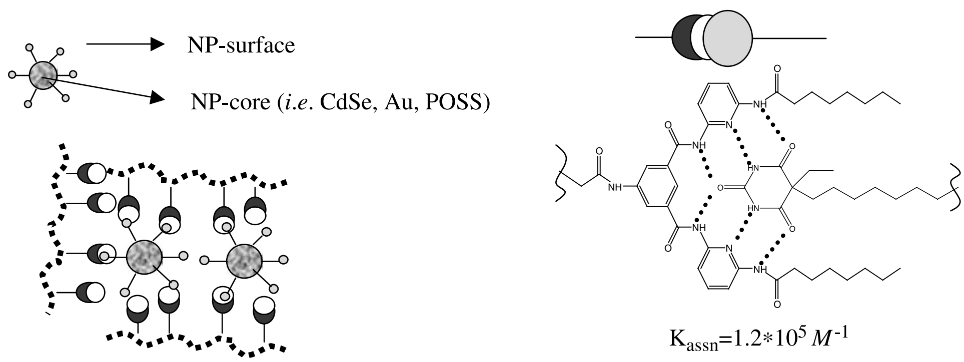

Fig. 1. Optimizing the interaction between nanoparticles (NP) and the matrix by use of supramolecular interactions

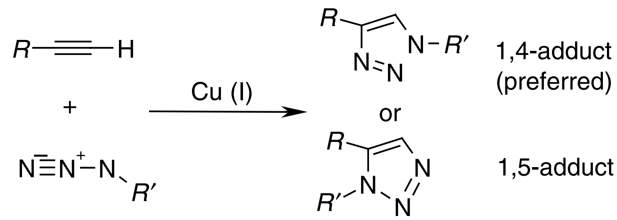

Fig. 2. Azide/alkine-"click"-reaction

hydrogen bonding systems onto homo- [6] and block-copolymers [7] by combining cationic polymerization strategies and ROMP with azide/alkine-"click"-reactions (also known as the *Sharpless/Huisgen* "click"-reactions) [8] (Fig. 2). The basic strategy of this coupling-reaction relies on a 1,3-dipolar cycloaddition process between a terminal alkine and a terminal azide under action of a Cu(I)-catalyst. The inherently broad substrate- and solvent tolerance of this reaction makes it an ideal tool for the functionalization of materials in general, and in particular of polymers and surfaces.

In the present publication, we report on the modification of nanoparticle-surfaces by use of the azide/alkine-"click" reaction. The approach offers an excellent system to modify the surface of various NPs with many different receptors, starting from a few single-NP derivatives. Here we demonstrate the versatility of this approach on CdSe-NPs, polyhedral oligomeric silsesquioxanes (POSS), and gold-NPs.

Results and Discussion

Surface-Modification of Nanoparticles

The basic strategy for the surface modification is shown in Fig. 3, and relies on the generation of nanoparticles bearing azido-moieties on their surface and the subsequent "click"-process onto their surface. Thus CdSe-nanoparticles **1** ($r = 4$ nm) were prepared using the high-temperature method starting from cadmium acetate and tri-*n*-octylphosphine oxide as ligand (Fig. 3a) [9]. Subsequent exchange of the

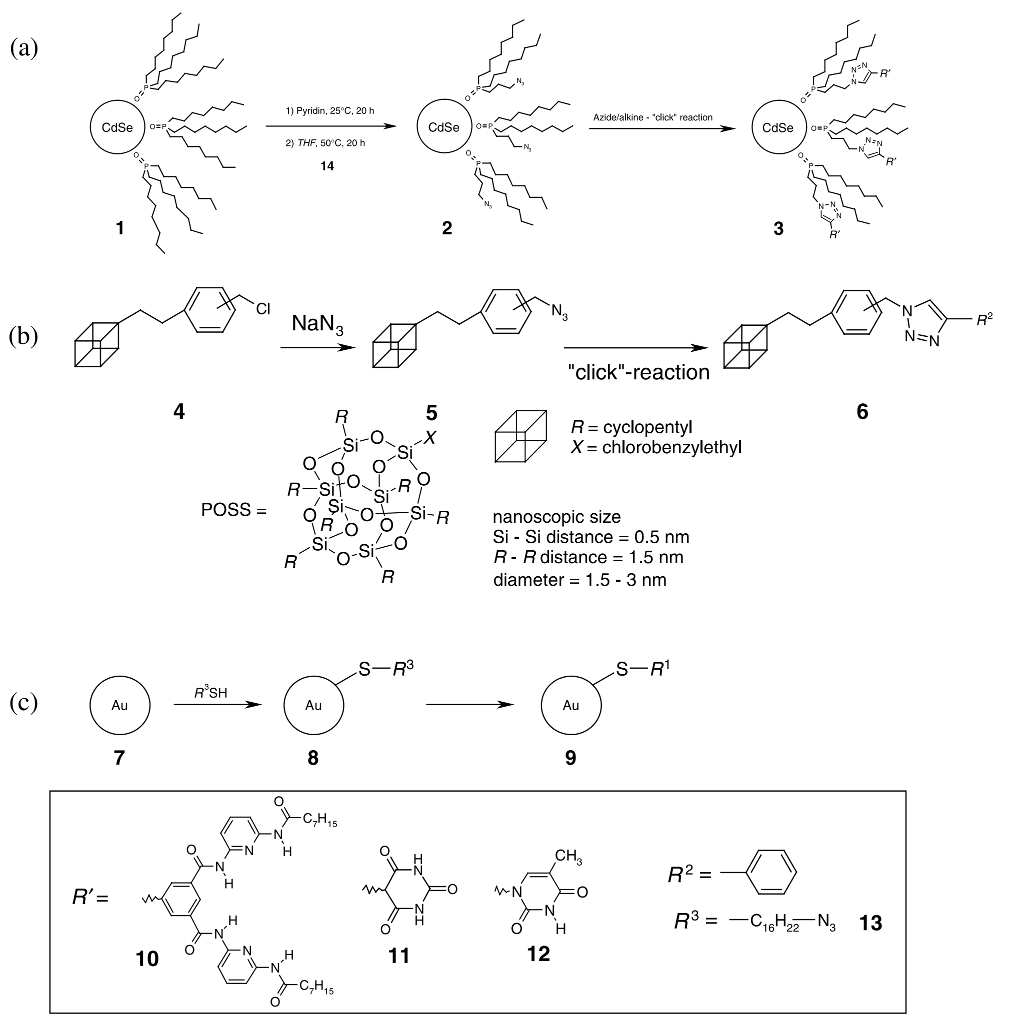

Fig. 3. (a) Ligand exchange and surface modification of CdSe-NPs; (b) "click"-reactions on POSS; (c) "click"-reactions on Au-NPs

phosphinoxide-ligand was effected *via* ligand-desorption using pyridine, and subsequent second ligand exchange using the azido-modified phosphinoxide-ligand **16** to yield the azido-bearing CdSe-nanoparticles **2**. The ligand exchange was followed *via* NMR-spectroscopy in solution (see Fig. 4). The resonances of the initial pyridine-exchange and the subsequent phosphinoxide **14** are clearly visible.

In a similar manner (see Fig. 3b) POSS-nanoparticles with an azido-moiety **5** were prepared from the corresponding POSS-oxirane **4** using sodium azide under action of a *Lewis* acid to achieve the controlled ring opening of the oxirane moiety. The presence of the azido-moiety was proven by IR-spectroscopy, the integrity of the POSS-derivative by ^{29}Si NMR-spectroscopy.

Au-nanoparticles ($d = 20$ nm) with an azido-surface **8** were prepared by exchange with an ω-azido-thiol to freshly prepared Au-NPs *via* the citrate-reduction method.

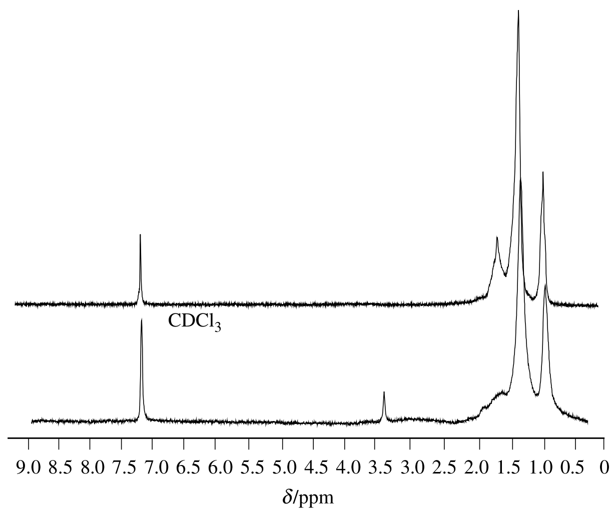

Fig. 4. [1]H NMR spectra of the ligand exchange in CdSe-NP using azidophosphinoxide-ligand **14**; upper trace: before ligand exchange, lower trace: after ligand exchange

The subsequent ''click'' reaction of the azido-NPs **2**, **5**, and **8** with the ligands **10**, **11**, **12**, and **13** was performed under classical *Sharpless*-conditions using Cu(I)-salts as coupling agents. As has been demonstrated in the case of planar surfaces [5], the reactions using this method proceed quantitatively. Thus the reaction can be assumed to proceed in accordance with the results obtained in solution and on SAM-surfaces [5]. A large variety of different NPs can thus be obtained from a few single NP precursors.

Probing the Attachment of the Surface-Modifed NPs

The surface modification of the NPs was studied using a matching receptor-interaction with a binding constant of $\sim 1.2 \cdot 10^5 M^{-1}$ (in $CDCl_3$) between the *Hamilton* receptor and barbituric acid-modified NP **9** (*i.e.*, Au-NPs derivatized with the barbituric acid **12**). Previous studies (see Ref. [5]) have shown that a SAM-surface

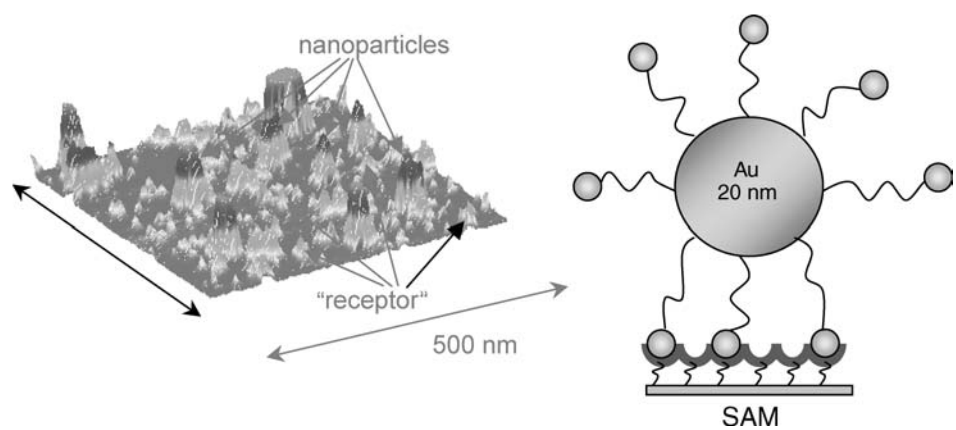

Fig. 5. Binding of Au-NPs to SAM consisting of matching receptor-interactions

covered with 100 mol% of the *Hamilton* receptor is highly effective in binding NPs derivatized with the matching barbituric acid receptor. Thus the binding of NPs **9** to SAM-surfaces bearing the complementing *Hamilton* receptor (see Ref. [5]) was studied by AFM. A picture of the binding structure is shown in Fig. 5, demonstrating the bound NPs together with the bound receptor. As counted statistically over an area of 1 μm^2 a nearly full coverage with NPs was obtained, whereas NP devoid of the *Hamilton* receptor (*i.e.*, NP **9** with the surface-molecule **13**) did not show binding onto the SAM-surface. Thus the chemical modification of the NP-surface can be translated and probed into a selective binding process on planar surfaces as visualized by AFM.

Conclusion

We have demonstrated a general approach for the derivatization of NPs by use of the azide/alkine-"click" reaction. The present approach allows the modification of CdSe-, Au-, and POSS nanoparticles in an easy mode. The surface modification of the NPs was proven *via* the attachment of supramolecular ligands and the subsequent selective binding onto SAM-surfaces.

Experimental

Self assembled monolayers were prepared as described in literature [5]. The precursor **14** was prepared starting from 1-[3-bromopropyl)octyl-phosphinoyl]octan [12] in one step. Azide-/alkine-"click" reactions were conducted as described in previous publications [6–8]. Au-nanoparticles were prepared by ligand exchange as described in Ref. [5]. All other materials were of highest purity and commercially available from Sigma-Aldrich.

AFM was measured on a Nanoscope III in the tapping mode. NMR-spectra were acquired on a Bruker DRX-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C). IR-spectra were done as KBr-mixtures after pressing on a conventional FT-IR spectrometer from Bruker.

TOPO-Covered CdSe Nanoparticles (**1**) [9]

Preparation of the selenium stock solution under Ar atmosphere was achieved by mixing 0.3 g selenium (3.8 mmol), 7.5 g TOP (18.1 mmol) and 0.135 g anydrous toluene in a sealed glass vial. 0.195 g cadmium acetate (0.73 mmol) and 15 g TOPO (35 mmol) were weighed in a reaction vessel and heated to 330°C under Ar flow. The selenium stock solution was swiftly injected into the vessel in a single step. After injection the temperature was immediately adjusted to 270°C to continue particle growth for 5 min. After stopping the reaction by cooling to 30–50°C the nanocrystals were precipitated by adding methanol/acetone = 1:1 (vol%). The CdSe nanocrystals were centrifuged and stored under exclusion of light in the refrigerator.

Determination of the particle size was done by UV-VIS spectrography showing the first excition peak at 545 nm corresponding to a radius of 4 nm.

Preparation of **14**-*Covered CdSe Nanoparticles* (**3**) [10]

TOPO-covered nanocrystals were dissolved in pyridine and stirred at room temperature for 20 h. Most of the pyridine was evaporated to give a viscous solution. Pyridine-covered nanocrystals were precipitated in *n*-hexane, centrifuged and dissolved in freshly distilled anhydrous *THF*. After addition of **14** stirring was continued for 20 h. Most of the *THF* was removed by distillation and the **14**-covered nanocrystals were twice precipitated in anhydrous acetone. Ligand exchange was proven by ^{1}H NMR showing a broad signal of the CH_2N_3-group.

1-[2-[(Azidomethyl)phenyl]ethyl]-3,5,7,9,11,13,15-heptacyclopentyl-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**5**, $C_{44}H_{59}N_3O_{12}Si_8$)
To 0.1 g of 1-[2-[(chloromethyl)phenyl]ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**4**, mixture of isomers, 0.095 mmol) dissolved in 9 cm^3 of a mixture of *DMF* and *THF* (5:4) 0.03 g sodium azide (0.48 mmol) were added. The mixture was stirred at 70°C under Ar for 24 h. The excess of solvents was removed *in vacuo* and the crude product was dissolved in chloroform. The organic phase was washed with H_2O (2 times) and dried over sodium sulfate. Removal of solvent in vacuum gave a white solid (0.098 g, 98%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.3$–7.0 (m, 4H), 2.73 (t, 2H), 1.76–1.51 (m, 58H), 1.0–0.96 (m, 7H) ppm; ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 154.40$, 135.30, 128.76–125.41, 54.87, 29.01, 27.28, 26.99, 22.19, 14.19 ppm; ^{29}Si NMR (400 MHz, $CDCl_3$): $\delta = -66.25$, -67.29 ppm; IR (KBr): $\bar{\nu} = 2800$–2900, 2100, 1000–1180 cm^{-1}.

1-[2-[4-Phenyl-1-H-[1,2,3]triazol-1-yl)methyl)phenyl]ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (**6**, $C_{52}H_{65}N_3O_{12}Si_8$)
To a solution of 1-[2-[(azidomethyl)phenyl]ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**5**, 0.053 g, 0.05 mmol) and 0.01 g phenyl acetylene (0.098 mmol) in dry toluene (5 cm^3) bis(benzyltriazolylmethyl)amine (*TBTA*, 0.002 g, 0.005 mmol) was added. In the last step the Cu(I)-catalyst (tetrakis(acetonitrile)copper(I) hexafluorophosphate, 0.002 g, 0.0048 mmol) was added and the mixture was stirred at 70°C for 48 h. The evaporated residue was chromatographed on silica gel (ethyl acetate/hexane 1/10) to yield 0.03 g (56%) **6**. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.83$–7.78 (d, 2H), 7.65 (s, 1H), 7.4–7.08 (m, 7H), 5.54 (s, 2H), 2.71 (t, 2H), 1.72–1.51 (m, 56H), 1.1–0.88 (m, 7H) ppm; ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 145.83$, 134.52, 130.52, 129.10–125.34, 54.35, 28.95, 27.31, 27.26, 14.13 ppm; ^{29}Si NMR (400 MHz, $CDCl_3$) $\delta = -66.25$, -67.44 ppm.

1-[3-Azidopropyl)octylphosphinoyl]octan (**14**, $C_{19}H_{40}O_1P_1N_3$)
A reaction mixture of 0.96 g *1-[3-bromo propyl)octylphosphinoyl]octan* [11] (2.43 mmol) and 0.5 g sodium azide (7.69 mmol) in 10 cm^3 dry *DMF* was stirred 24 h at 50°C. *DMF* was evaporated. The residue was diluted with dichloromethane and extracted with water. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The pure product was obtained by LC chromatography (silica gel, $CHCl_3$:$CH_3OH = 60:1$) yielding 0.81 g (93%) **14**. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.82$ (t, 6H, $J = 6.3$ Hz), 1.20–1.90 (m, 32H), 3.35 (t, 2H, $J = 6.3$ Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.98$ (2C), 21.57–31.65 (16C), 52.01 (CH_2N_3) ppm; ^{31}P NMR (162 MHz), $CDCl_3$): $\delta = 49.20$ ppm; IR (KBr): $\bar{\nu} = 2958$–2853 (CH_2, CH_3), 2100 (N_3), 1305–1247 (P=O) cm^{-1}.

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