

From Ligand-Stabilized Gold Nanoparticles to Hybrid Organic-Inorganic Superstructures

Jens Peter Hermes^{§a}, Fabian Sander^a, Torsten Peterle^{ab}, and Marcel Mayor^{*ac}

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Abstract: Gold nanoparticles (Au NPs) have many potential applications including nanoelectronics, catalysts and sensors. These future devices depend on stable and monodisperse NPs and their directed assembly. Herein we review our efforts to develop oligomeric thioether ligands able to direct the synthesis of Au NPs and their surface functionalization. A screening of different oligomeric thioethers indicates that the NPs become more stable and monodisperse with increasing length of the thioether oligomer. The heptameric benzylic thioether **4** stabilizes monodisperse NPs with a diameter of 1 nm and excellent long-term stability in solution. It is further monofunctionalized with a central protected acetylene. After NP formation in the presence of the ligands we utilize the peripheral functionality to interlink the NPs. A mild oxidative diacetylene coupling protocol is used to covalently bind these ‘artificial molecules’. This wet-chemical procedure leads to the formation of hybrid organic–inorganic superstructures.

Keywords: Gold nanoparticles · Hybrid materials · Organic–inorganic superstructures

Introduction

Gold is the most frequently used material for metal nanoparticles (NPs). This is due to the efficient synthesis of Au NPs, the advanced state of surface chemistry and their potential as model system for colloids and surfaces.^[1–3] Au NPs show size-dependent features, providing interesting physical properties, such as room temperature *Coulomb* blockade for small NPs.^[4–6] Stable and monodisperse NPs are essential for their use in many future technologies, including electronic devices,^[7–11] sensor applications^[12–17] and catalysis.^[18,19] The stabilizing agents in organic solvents are mainly based on thiols^[20] that show covalent interactions with the gold surface. In

general, thioethers form weak interactions to gold compared to thiols.^[21] There are however some examples where thioethers have been proven to be suitable ligands for the stabilization of Au NPs.^[22–26] Increased stability and monodispersity have been reported for multidentate ligands comprising more than one thioether unit.

Below we describe the screening of several multidentate thioether oligomers to find a suitable ligand that enables the formation of stable and monodisperse NPs. A large multidentate structure favors monodisperse NP sizes by enveloping the whole NP by a well-defined small number of ligands. This concept enables control of the number and nature of functional groups on the NPs’ surface simply by attaching the desired functional group to the ligand. To our knowledge only a few examples describe the realization of mono- and bifunctionalized NPs in organic solvents. The former was realized *via* ligand polymerization on the NPs’ surface^[27] and reaction on solid supports^[28,29] and the latter by profiting from the exposed pole positions of monodisperse NPs.^[30,31] Another major challenge for the integration of NPs in hybrid materials and future devices is their tailored spatial arrangement. Numerous studies geared towards the directed assembly of Au NPs have been reported and several review articles highlight the importance of the field.^[32–37]

Herein we summarize three recent publications on our research towards in-

terlinked Au NPs. In a first screening of thioether oligomers, a benzylic thioether heptamer was found to be a very promising ligand to stabilize Au NPs.^[38] It was further functionalized with a protected acetylene. This peripheral functionality was connected *via* an oligophenylene ethynylene (OPE) spacer of different lengths. The acetylene enabled the covalent interlinking of NPs by a mild oxidative diacetylene coupling. The NP size and the spatial arrangement of these hybrid organic–inorganic superstructures were investigated by transmission electron microscopy (TEM).^[39] In addition we investigated self-assembled monolayers of model compounds to study the sulfur–gold interactions. High-resolution X-ray photoelectron spectroscopy (HRXPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and scanning tunneling microscopy (STM) were used for this purpose.^[21]

Ligand-stabilized Gold Nanoparticles

The linear oligothioether ligands **1–4** (Fig. 1) were synthesized and their ability to stabilize and ensnare Au NPs was investigated.^[38] The goal of this series was to find a ligand that directs the size of small NPs leading to stable and monodisperse NPs. The thioether structure was intended to enable an evenly dispersed surface coverage with a low integer number of ligands.

*Correspondence: Prof. Dr. M. Mayor^{ac}

Tel.: + 41 61 267 71006

Fax: + 41 61 267 71016

E-mail: marcel.mayor@unibas.ch

^aDepartment of Chemistry

University of Basel

St. Johannisring 19

CH-4056 Basel

^bCreavis Technologies & Innovation

Evonik Degussa GmbH

Paul-Baumann-Str. 1

D-45772 Marl, Germany

^cKarlsruhe Institute of Technology (KIT)

Institute of Nanotechnology

P.O. Box 3640, D-76021 Karlsruhe, Germany

The number of ligands should be transferable to the number of functionalities that could be introduced with the ligand. Au NPs were formed following a protocol developed by Brust *et al.*^[20] In a two-phase system of water and dichloromethane with tetra-*n*-octylammoniumbromid (TOAB) as phase transfer agent, chloroauric acid was reduced by sodium borohydride in the presence of oligomers **1–4**. Monomer **1** could not prevent the bulk precipitation of gold but also stabilized some NPs. UV/vis spectroscopy showed the presence of a plasmon resonance band in the UV spectrum of Au-**1** indicating NPs larger than 3 nm.^[40] After several hours these NPs further coagulate and precipitate. Oligomers **2, 3** and **4** led to the formation of soluble NPs without precipitation. As the ligand-stabilized NPs Au-**2** precipitated within days upon storage in dispersion, we only determined the diameter of NPs Au-**3** and Au-**4** using transmission electron microscopy (TEM). While NPs Au-**3** range from 1 nm to 5 nm, NPs Au-**4** showed a narrow size distribution with a mean diameter of 1 nm (see below). UV/vis spectroscopy proved the excellent long-term stability, as the spectrum of NPs Au-**4** did not change upon storage in dichloromethane over several months. TEM, elemental analysis and thermogravimetry revealed a particle-to ligand ratio of 1:2. Upon ligand functionalization NPs with two peripheral groups should become available. Interestingly, these NPs might be exposed subsequently to wet chemical procedures acting as ‘artificial molecules’.

Self-assembled Monolayers of Thiol/Thioether Ligands

Self-assembled monolayers (SAMs) of model compounds **5–8** (Fig. 1) were formed on Au(111) to study the gold–li-

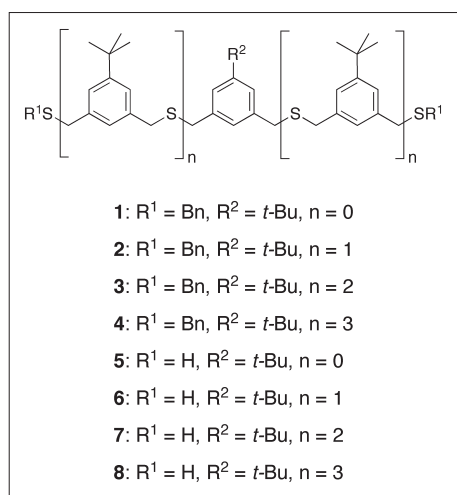


Fig. 1. Model compounds **1–8** used to investigate nanoparticle stabilizing features as well as binding behaviors on gold surfaces.

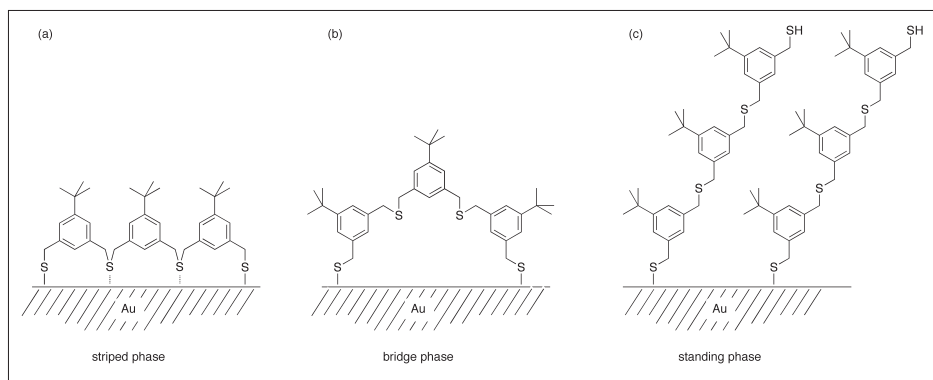


Fig. 2. Schematic representation of possible binding modes of the thiol-thioether oligomer **6** to the gold substrate.

gand interactions.^[21] These assemblies were investigated by high-resolution X-ray photoelectron spectroscopy (HRXPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and, in the case of molecules **5** and **6**, also by scanning tunneling microscopy (STM).

The question addressed within these investigations is the contribution and quality of the different binding sites. Thus, we were wondering if such oligomers are binding with all binding sites (striped phase, Fig. 2a) or only with the two terminal thiols forming bridge phase arrangements (Fig. 2b). A standing phase (Fig. 2c) would result if only one terminal thiol group were bound to the surface.

The relation of SAM thickness to oligomer size, found by HRXPS, favors the bridge phase assembly displayed in Fig. 2 for these ligands. The monolayer thickness increased with oligomer size showing heights which matched the calculated values for bridge phase arrangements. This hypothesis is further supported by the analysis of the sulfur signals of the HRXPS spectra. In particular the expected ratios of strongly bound and uncoordinated sulfurs were found for the model compounds.

While additional NEXAFS spectra also confirmed the bridge phase model, STM investigations of shorter oligomers **5** and **6** revealed a further insight. The monomer **5** formed a dense packed SAM that was in excellent agreement with the bridge phase model. However the trimer **6** showed a few features with heights indicating unfolded upright standing molecules. This led to the estimation that about 10–20% of the molecules bind only with one thiol group to the substrate (Fig. 2b).

We propose that the observed bridged geometry is driven by the strong thiol–gold interaction. The strongly binding terminal thiols push the weakly coordinating thioether binding sites away from the surface, reducing the ligands’ multidenticity. As the multidentate coordination is desired, a homogeneously balanced sulfur–gold interaction over all binding sites is fundamental.

Therefore we omitted the use of free thiols in our future ligand design.

Hybrid Organic–Inorganic Superstructures

Based on the ligand investigations described above we choose heptamer **4** for addition of a peripheral functional group. A rigid OPE of different lengths was introduced with a terminal silyl-protected acetylene to obtain ligands **9–11** (Fig. 3).^[39]

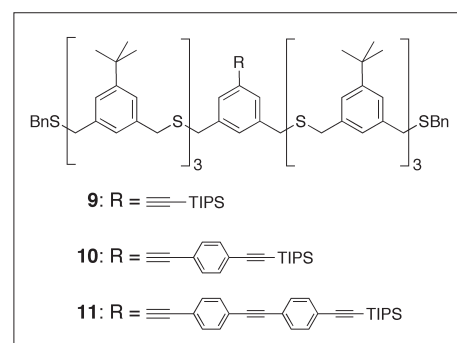


Fig. 3. Ligands **9–11** comprising a protected acetylene as an additional peripheral functional group for interlinking nanoparticles to organic–inorganic superstructures.

NPs were formed in the presence of these monofunctionalized ligands following the same protocol as for Au-(**1–4**). After removal of excess ligand the samples only contained ligand-stabilized NPs Au-**9**, Au-**10** and Au-**11**. The obtained UV/vis spectra were very similar to the spectrum of heptamer-stabilized NPs Au-**4** with differences between 300 nm and 400 nm, due to the elongation of the functional OPE unit in the ligands center. As this feature was clearly visible we confirmed that we obtained functional NPs with the OPE structure at their periphery. The ligand-stabilized NPs were further investigated by TEM. The analysis of micrographs indicated the same narrow NP size distributions of 1 nm as the unfunctionalized heptamer **4** (see below). This indicates that the

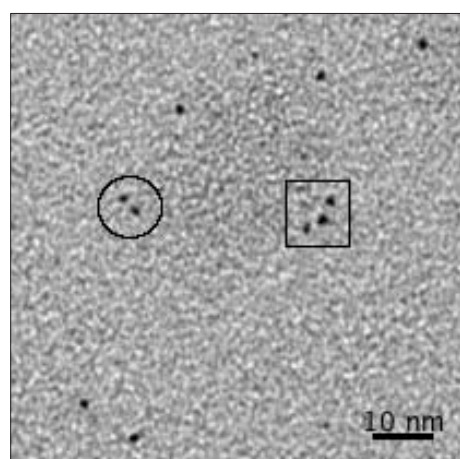


Fig. 4. Representative TEM micrograph of gold nanoparticle oligomers (Au-10_n), a dimer (circle) and a trimer (rectangle) are present as well as monomeric nanoparticles.

thioether oligomer stabilizes the NPs and is not affected by the new functionality. Thus, we assume that again two ligands are needed to stabilize one NP, which was corroborated by combining TEM results with thermogravimetric analysis data.

The protected acetylene of these ‘artificial molecules’ enabled the covalent coupling of NPs with a mild oxidative diacetylene coupling protocol developed by Hay.^[41] This copper-catalyzed wet-chemical process was performed after deprotection of the acetylene and led to hybrid organic–inorganic superstructures (Au-9_n), (Au-10_n) and (Au-11_n). Fig. 4 depicts a representative TEM micrograph showing a dimer ($n = 2$), trimer ($n = 3$) and monomeric NPs. Besides dimers and trimers tetramers ($n = 4$) were also obtained. These three different oligomers were used for further analysis. Higher oligomers precipitated from solution due to their low solubility. The reaction time was thus reduced to

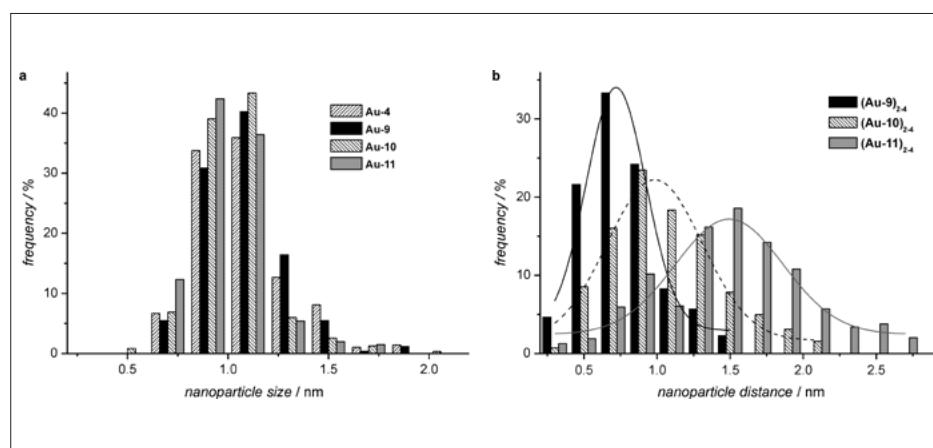


Fig. 5. a) Size distribution of ligand-stabilized particles, b) distance distribution of superstructures reflecting the various spacer lengths.

15 minutes to favor short oligomers instead of long insoluble polymers. The success of the coupling was preliminary detected by UV/vis. The elongation of OPE due to diacetylene formation was clearly shown by a bathochromic shift. Investigations of the interparticle spacings of these superstructures *via* TEM revealed that the different lengths of rigid-rod linkers were reflected in the interparticle distances (Fig. 5).

We obtained Gaussian-like distance distributions with increasing maxima for larger spacer lengths. The shape of the Gaussian-like fit broadens with each extension of the OPE linker and the maxima are at shorter values than the calculated distances for the outstretched rods. These two aspects lead to the assumption that the ligands arrange with various possible angles on the NP’s surface. A tangential alignment is favored over a perpendicular arrangement probably due to the steric repulsion of the aromatic hydrogen, which

anchors the central functionality. This hypothesis was further corroborated by recent studies with model ligands comprising a central pyridine unit.^[42] The coordination of the pyridine’s nitrogen to the Au NP resulted in a perpendicular arrangement of the rod at the NP’s surface. Thus the calculated length of the rod and the observed interparticle spacings perfectly matched.

Summary and Conclusion

Our efforts towards the realization of covalently bound NPs are presented. After two ‘casting’ series we choose a ligand design that is able to stabilize Au NPs with a narrow size distribution and controlled thioether gold interactions. It was found that two ligands stabilize one NP. The ligand structure was further functionalized with a peripheral protected acetylene providing bifunctional NPs (see Fig. 6).

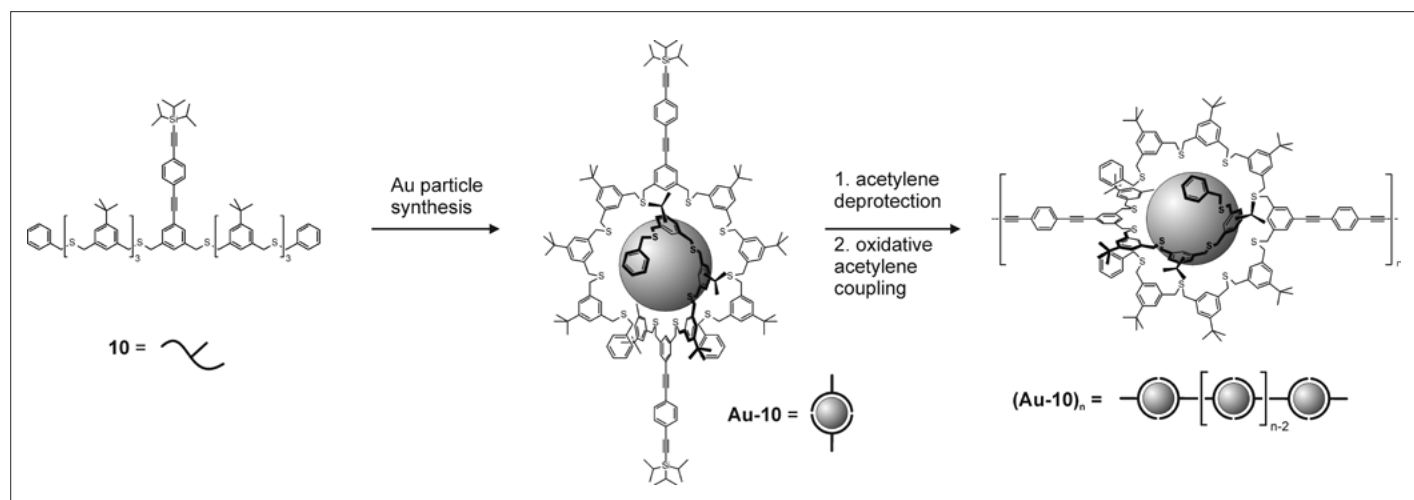


Fig. 6. The concept of using ligand-functionalized nanoparticles as ‘artificial molecules’. The oligomeric ligand **10** stabilizes particles with diameters of about 1 nm by covering its surface. As two ligands are required to cover the particles surface, exactly two triisopropylsilyl (TIPS) protected acetylenes are available as functional group on the periphery of the particle allowing their interlinking to form hybrid organic–inorganic oligomers or polymers by wet chemistry.

These 'artificial molecules' enabled the formation of organic-inorganic architectures *via* diacetylene coupling. In a series of interlinked NPs the spacer length was reflected in the spatial arrangement of the NPs in these hybrid superstructures.

Currently we are working on a greater control over the arrangement of the spacer group at the NP's surface, the realization of increased NP sizes, other metal NPs and hybrid materials consisting of periodically arranged subunits.

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- [1] M. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
- [2] R. Sardar, A. M. Funston, P. Mulvaney, R. W. Murray, *Langmuir* **2009**, *25*, 13840.
- [3] M. Homberger, U. Simon, *Phil. Trans. R. Soc. A* **2010**, *368*, 1405.
- [4] G. Schmid, *Adv. Eng. Mater.* **2001**, *3*, 737.
- [5] L. M. Liz-Marzán, *Langmuir* **2006**, *22*, 32.
- [6] A. J. Quinn, G. Redmond, *Surf. Sci.* **2007**, *601*, 2740.
- [7] R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney, R. G. Osifchin, *Science* **1996**, *273*, 1690.
- [8] G. Schmid, U. Simon, *Chem. Commun.* **2005**, 697.
- [9] J. Liao, L. Bernard, M. Langer, C. Schönenberger, M. Calame, *Adv. Mater.* **2006**, *18*, 2444.
- [10] S. W. Boettcher, N. C. Strandwitz, M. Schierhorn, N. Lock, M. C. Lonergan, G. D. Stucky, *Nat. Mater.* **2007**, *6*, 592.
- [11] S. Kim, J. Lee, *Nano Lett.* **2010**, *10*, 2884.
- [12] C. Zhong, R. C. Brush, J. Andereg, M. D. Porter, *Langmuir* **1999**, *15*, 518.
- [13] S. D. Evans, S. R. Johnson, Y. L. Cheng, T. Shen, *J. Mater. Chem.* **2000**, *10*, 183.
- [14] Y. Kim, R. C. Johnson, J. T. Hupp, *Nano Lett.* **2001**, *1*, 165.
- [15] M. Riskin, R. Tel-Vered, T. Bourenko, E. Granot, I. Willner, *J. Am. Chem. Soc.* **2008**, *130*, 9726.
- [16] Y. Zhou, S. Wang, K. Zhang, X. Jiang, *Angew. Chem. Int. Ed.* **2008**, *47*, 7454.
- [17] X. Zhang, Q. Guo, D. Cui, *Sensors* **2009**, *9*, 1033.
- [18] C. Della Pina, E. Falletta, L. Prati, M. Rossi, *Chem. Soc. Rev.* **2008**, *37*, 2077.
- [19] A. Corma, H. Garcia, *Chem. Soc. Rev.* **2008**, *37*, 2096.
- [20] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.* **1994**, 801.
- [21] F. Sander, T. Peterle, N. Ballav, F. V. Wrochem, M. Zharnikov, M. Mayor, *J. Phys. Chem. C* **2010**, *114*, 4118.
- [22] X. Li, M. R. D. Jong, K. Inoue, S. Shinkai, J. Huskens, D. N. Reinhoudt, *J. Mater. Chem.* **2001**, *11*, 1919.
- [23] E. J. Shelley, D. Ryan, S. R. Johnson, M. Couillard, D. Fitzmaurice, P. D. Nellist, Y. Chen, R. E. Palmer, J. A. Preece, *Langmuir* **2002**, *18*, 1791.
- [24] A. Taubert, U. Wiesler, K. Müllen, *J. Mater. Chem.* **2003**, *13*, 1090.
- [25] A. D'Aléo, R. M. Williams, F. Osswald, P. Edamana, U. Hahn, J. van Heyst, F. D. Tichelaar, F. Vögtle, L. De Cola, *Adv. Funct. Mater.* **2004**, *14*, 1167.
- [26] W. M. Pankau, S. Mönninghoff, G. von Kiedrowski, *Angew. Chem. Int. Ed.* **2006**, *45*, 1889.
- [27] C. Krüger, S. Agarwal, A. Greiner, *J. Am. Chem. Soc.* **2008**, *130*, 2710.
- [28] K. Sung, D. W. Mosley, B. R. Peelle, S. Zhang, J. M. Jacobson, *J. Am. Chem. Soc.* **2004**, *126*, 5064.
- [29] J. G. Worden, A. W. Shaffer, Q. Huo, *Chem. Commun.* **2004**, 518.
- [30] G. A. DeVries, M. Brunnbauer, Y. Hu, A. M. Jackson, B. Long, B. T. Neltner, O. Uzun, B. H. Wunsch, F. Stellacci, *Science* **2007**, *315*, 358.
- [31] D. F. Perepichka, F. Rosei, *Angew. Chem. Int. Ed.* **2007**, *46*, 6006.
- [32] Y. Min, M. Akbulut, K. Kristiansen, Y. Golan, J. Israelachvili, *Nat. Mater.* **2008**, *7*, 527.
- [33] F. Westerlund, T. Bjørnholm, *Curr. Opin. Colloid In.* **2009**, *14*, 126.
- [34] S. Srivastava, N. A. Kotov, *Soft Matter* **2009**, *5*, 1146.
- [35] K. J. M. Bishop, C. E. Wilmer, S. Soh, B. A. Grzybowski, *Small* **2009**, *5*, 1600.
- [36] C. L. Choi, A. P. Alivisatos, *Annu. Rev. Phys. Chem.* **2010**, *61*, 369.
- [37] P. K. Jain, M. A. El-Sayed, *Chem. Phys. Lett.* **2010**, *487*, 153.
- [38] T. Peterle, A. Leifert, J. Timper, A. Sologubenko, U. Simon, M. Mayor, *Chem. Commun.* **2008**, 3438.
- [39] T. Peterle, P. Ringler, M. Mayor, *Adv. Funct. Mater.* **2009**, *19*, 3497.
- [40] M. M. Alvarez, J. T. Houry, T. G. Schaaff, M. N. Shafiqullin, I. Vezmar, R. L. Whetten, *J. Phys. Chem. B* **1997**, *101*, 3706.
- [41] A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320.
- [42] J. P. Hermes, F. Sander, T. Peterle, C. Cioffi, P. Ringler, M. Mayor, *Small* **2011**, *7*, 920.