Angewandte Chemie

DOI: 10.1002/anie.200804596

Surface Assemblies

Free-Standing 3D Supramolecular Hybrid Particle Structures**

*Xing Yi Ling, In Yee Phang, Wouter Maijenburg, Holger Schönherr, David N. Reinhoudt, G. Julius Vancso, and Jurriaan Huskens**

The controlled fabrication of well-defined and stable colloidal particle crystals has received considerable attention in the field of nanotechnology owing to their potential application in optoelectronic devices,[1] biological sensors,[2] and photonic structures.[3] The order and packing symmetry within a particle crystal is of utmost importance for the development of materials with unique optical and electronic properties.[3–5] The assembly of nonfunctionalized particles by convective assembly or sedimentation can result in hexagonally close-packed (hcp) particle crystals.[6–8] Infiltration of the particle crystals with metals,[9] polymers,[10] and/or polyelectrolytes[11] has yielded inverse opals or capsules[12] with unique photonic properties.[9,13] However, these crystals generally lack stability and control over the geometry in both lateral and vertical directions. Hence, specific chemical interactions have been exploited to yield stable 2D or 3D particle crystals[14,15] and to direct the assembly of particles onto chemically or topographically patterned surfaces.[16] Careful manipulation of the specific chemical particle–surface and interparticle interactions are important to ensure sufficient affinity of particles on surfaces and organization of particles into highly ordered arrays.[17] Currently, most chemically directed particle assembly is focused on the formation of 2D particle arrays.[18–20] We have reported the formation of 3D supramolecular-functionalized particle lattices on a (patterned) β-cyclodextrin (CD) self-assembled monolayer (SAM) by supramolecular host–guest chemistry and layer-by-layer (LbL) assembly.[21–23] Cyclodextrin is a natural host molecule for organic guest molecules, such as adamantane (Ad), that forms specific and kinetically labile inclusion complexes in aqueous media owing to hydrophobic interactions. The binding constant (K_a) of a single CD–Ad interaction is approximately $1\times10^5\,\mathrm{M}^{-1}$.[37] In the case of particle assembly, the host- or guest-functionalized particles contain multiple binding sites that stoichiometrically increase the binding strength of the particles, as a result of multivalency. Hence, fine-tuning of the supramolecular binding strength is always needed to ensure the organization of the particles into an ordered particle array while maintaining the strong binding affinity between the particles and the CD-functionalized surface.[17]

Herein, we demonstrate a sequential process of assembly, infiltration, and transfer printing to form 3D particle structures with high order and stability. Our strategy exploits the combined advantages of convective assembly (in ordering particles) and supramolecular chemistry (in chemically bonding adjoining particles by infiltration with supramolecular glues into an integrated particle crystal). Patterned poly(dimethylsiloxane) (PDMS)[24–27] stamps were utilized as templates to provide spatial and geometrical confinement to the CD-functionalized polystyrene (PS–CD) particle crystal (Figure 1a). Controlled convective assembly directed the 500 nm particles to fill the predefined grooves on the template.[23,24] To facilitate the transfer of the particle structures, the depth of the grooves of the PDMS stamp (approximately 750 nm) was designed to be slightly lower than the height of two layers of PS–CD (approximately 770 nm). A fifth-generation adamantane-terminated poly(propylene imine) dendrimer (G5-PPI-(Ad)$_{64}$) was subsequently infiltrated into the particle crystal. The conformal contact of the supramolecular 3D Ad-dendrimer-infiltrated particle crystals with the target CD-functionalized surface yielded a transfer printing of highly ordered 3D PS–CD crystals in line structures, imposed by the geometry and dimension of the PDMS template. The particle lines remained hexagonally close packed and robustly attached to the surface even after sonication in water (Figure 1c).

In contrast to conventional direct assembly of particles onto surfaces by specific chemistry,[18–23] the sequential process allows the arrangement of particles into ordered structures within predefined patterned templates prior to the supramolecular bonding into an integrated building block. The transfer printing of the 3D supramolecular particle crystals highlights the importance of the infiltration of Ad dendrimers to form stable particle structures. The dendrimer functions as a supramolecular glue with multiple binding sites that connect neighboring PS–CD particles by host–guest interactions, and the supramolecular glue also binds the particle crystals to the CD SAM in the same manner (Figure 1a). Misalignments of particles sometimes occurred on the printed particles, probably resulting from drying after

---

[*] Dr. X. Y. Ling, W. Maijenburg, Prof. D. N. Reinhoudt, Prof. J. Huskens
Molecular Nanofabrication Group
MESA+ Institute for Nanotechnology, University of Twente
7500 AE, Enschede (The Netherlands)
Fax: (+31) 53-489-4645
E-mail: j.huskens@utwente.nl
Homepage: http://mnf.tnw.utwente.nl

Dr. I. Y. Phang, Prof. H. Schönherr,[+] Prof. G. J. Vancso
Materials Science and Technology of Polymers Group
University of Twente (The Netherlands)

[+] Present address: Institut für Physikalische Chemie
Universität Siegen (Germany)

[**] X.Y.L and J.H. thank the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO-CW) for financial support (Vidi Vernieuwingsimpuls grant 700.52.423 to J.H.). I.Y.P and G.J.V thank the financial support from the Dutch Polymer Institute (grant DPI-510 to G.J.V.). D.N.R. and G.J.V thank the NWO Middelgroot grant.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804596.

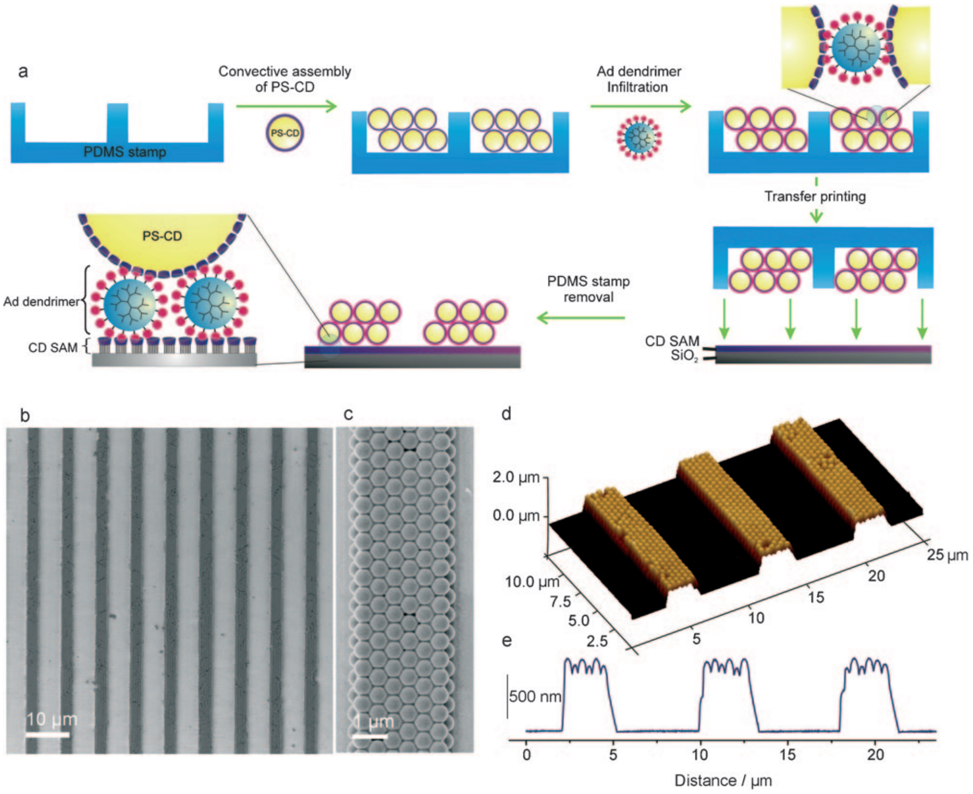

Figure 1. a) The formation of 3D supramolecular particle crystals by a combination of convective assembly, host–guest interactions, and transfer printing. b, c) SEM images of the transfer-printed 3D particle crystals (infiltrated with Ad dendrimers) on a CD SAM. d, e) 3D AFM image and AFM height profile of the printed particle structures.

the transfer printing process. The Ad-dendrimer-infiltrated particle crystals remained highly ordered and dense after sonication. The periodicity of the particle structure was analyzed by averaging the center-to-center distance between 30 particles. The average lattice constant was (501 ± 4) nm, as measured from the SEM image, which corresponds well to the particle size. The results highlight the strong cohesion among particles by supramolecular interactions. The success of the transfer printing was also facilitated by the similar heights of the particle structure and the PDMS template (Figure 1 d and e), which rendered an effective conformal contact between the particle crystals and the substrate. Hence, the layer thickness and lateral dimensions of the transferred crystal could be conveniently controlled by the design of the template. Moreover, the number of layers of the particle crystal can also be controlled by tuning of the individual particle diameter. Without infiltration with Ad dendrimers, the transfer printing of PS–CD onto a CD SAM resulted in the transfer of a disordered and incomplete single layer of particles (Figure S1 in the Supporting Information), while the remaining particles remained on the PDMS stamp.[25] Nearly all particles on the surface were removed by sonication in water, confirming the importance of the infiltration step in imparting stability to the particle crystals.

The printed particle structures can be addressed as functional building blocks for further assembly of molecules or nanostructures. Lissamine rhodamine-labeled divalent adamantyl guest molecules (Figure 2 a) were printed perpendicularly to the particle lines. A fluorescence microscopy image of the particle structure printed with these guests showed that only squares, equivalent to the size of the contact areas between the particle structures and the PDMS stamp, had become fluorescent (Figure 2 b). After intense rinsing with CD solution, virtually homogeneous fluorescence emission was detected along the particle lines (Figure 2 c). The integrated fluorescence intensity along the particle lines remained constant, indicating the diffusion of **1** along the particle lines, with negligible

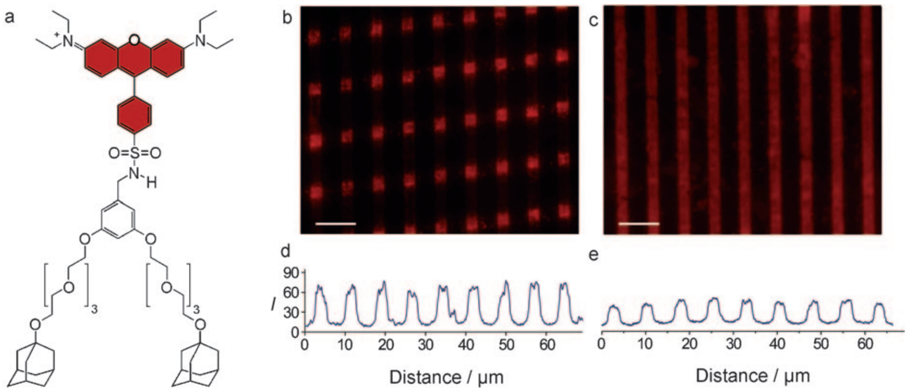

Figure 2. a) The molecular structure of a lissamine rhodamine-labeled divalent adamantyl guest. b, d) Fluorescence microscopy image and intensity profile of the particle structure after printing of lissamine rhodamine-labeled divalent adamantyl guest. c, e) Fluorescence microscopy image and intensity profile of the same particle structure after subsequent rinsing with CD solution. Scale bars indicate 10 µm.

desorption (Figure 2 d,e). The printing and diffusion of adamantyl guests on top of the particle crystal indicate that the supramolecular host property of the individual particles remains intact after the transfer printing process. Such supramolecular particle structures can thus potentially act as a "pathway" for the transportation of molecular information.

Most freely suspended and free-standing nanostructures with controlled composition and macroscopic robustness are free-standing polymer multilayer thin films,[28], with added metallic[29,30] or inorganic[31] fillers to enhance the mechanical stability. We have examined the transfer printing of supramolecular particle crystals onto a 3D patterned CD SAM. To fabricate free-standing particle structures, the bonding between the particles had to be further strengthened. Hence, Ad dendrimers and CD-functionalized Au nanoparticles (Au–CD, $d \approx 3$ nm) serve as the respective host- and guest-functionalized glues to be assembled within the PS–CD crystal in a supramolecular LbL manner to yield a particle composite on the PDMS stamp. A total of 30 LbL cycles of, alternately, Ad dendrimers and Au–CD resulted in interconnecting particles, thus forming a particle composite (Figure 3 b). The presence of Au–CD at the interface between adjacent PS–CD particles can be clearly observed by TEM (Figure 3 c). The PS–CD particle surface became rougher after 30 LbL cycles, indicating the mixing of Ad dendrimers and Au–CD during the adsorption steps.[21]

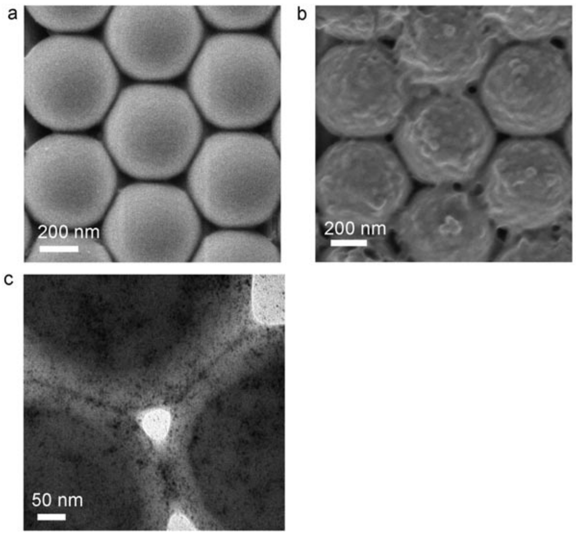

Figure 3. SEM images of a) as-prepared convectively assembled PS–CD particles, and b) particle composites built up from a supramolecular LbL assembly of Ad dendrimers and Au–CD nanoparticles. c) TEM image of the particle composites.

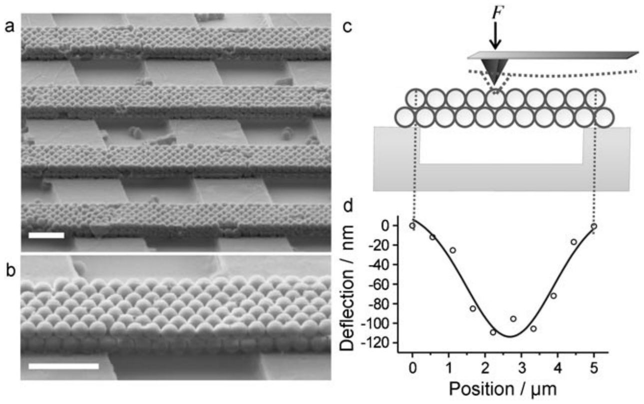

Figure 4. a, b) SEM images of the transfer-printed free-standing particle composite structures on topographically patterned CD substrates. Scale bars indicate 2 µm. c) AFM bending test. d) AFM force-deflection curve of the particle composite bridge when deflected at 8 µN point loads.

The particle composite on a PDMS stamp was perpendicularly printed onto a 3D line-featured CD-functionalized substrate to yield 3D free-standing and ordered composite lines (Figure 4). A few individual particles were randomly distributed over the substrate, which could originate from the convective assembly step. The free-standing particle composite structures were supported by the vertical posts of the substrate. The results suggest that the discrete particles bridge the micrometer distances between the posts to form single-span particle microbridges. The yield of these particle bridges was typically in the range 50–90 % across the entire substrate (Figure S2 in the Supporting Information). Compared to the particle crystal without LbL assembly, in which only sections of the particle crystals that were in direct contact with the substrate were transferred (Figure S3 in the Supporting Information), the mechanical stability of the particle composite was drastically reinforced, allowing the formation of several micrometer-long and continuous free-standing structures. The average lattice constant, measured from the SEM image, was (502 ± 4) nm. The negligible change in the dimensions of the particle crystals, before and after printing, suggest that the gluing and printing strategy could be employed in dimension-sensitive applications, such as photonic crystals and optoelectronic devices.

The mechanical properties of the particle composite bridges were examined by AFM. The deflection of each individual particle across the particle bridge was probed by AFM (Figure 4 c; for details, see the Supporting Information and Figure S4). A deflection-position graph of the particle bridge was obtained when it was loaded with a constant force of 8 µN across the microbridge (Figure 4 d). These results are attributed solely to the bending of the microbridge, as the graph was corrected for the indentation of particles on a flat substrate (at positions 0 and 5 µm, respectively, Figure 4 d) and slippage occurred only at higher forces. Maximum deflection occurred at the center of the particle composite bridge. The bending modulus of a nanomaterial can be estimated, according to classical beam theory, from the experimentally determined force–deformation relationships.[32–36] The classical beam theory is the most frequently used model to quantitatively describe the resistance of a material toward bending. It is derived from Hooke's law ($F = k\delta$; k = material spring constant). The relation of the maximum deflection (δ) of a rectangular beam to the midpoint applied load (F) can be calculated using Equation (1), where

$$F = \frac{48\,I\,E}{L^3}\,\delta \qquad (1)$$

E = bending modulus, $I = (w h^3)/12$, the moment of inertia (w and h are the width and thickness of the particle bridge, respectively), and L is the span length of the free-standing structure. Treating the particle bridge as a continuous material, the bending modulus was estimated to be (1.2 ± 0.4) GPa,[34] which is of the same order of magnitude as bulk polystyrene at room temperature, indicating that the infiltration procedure led to an increase in the internal cohesion of the material, likely to a similar strength as unfunctionalized PS.

In summary, a highly versatile approach to fabricating stable and highly ordered particle crystals has been demonstrated by serially combining convective assembly, supramolecular assembly, and transfer printing. To our knowledge, these results constitute the first report on 3D self-supported free-standing mesoscopic structures, assembled using a bottom-up strategy from discrete individual particles held together by intrinsically weak, dynamic, and reversible supramolecular host–guest interactions. The mechanical stability of the particle crystals was improved by supramolecular LbL assembly of guest- and host-functionalized supramolecular glues within the particle crystals. We have also demonstrated the fabrication of these 3D free-standing particle composites on topographically patterned substrates. These stable and ordered supramolecular particle structures could become materials for future sensing and photonic devices.

Experimental Section

Assembly of PS–CD particles: On an oxidized PDMS stamp with 3 μm lines, with a height of 750 nm, separated by 5 μm trenches, 500 nm CD-functionalized polystyrene (PS–CD) particles were convectively assembled into the grooves of the PDMS stamp by using a capillary-assisted deposition setup.[23] The preformed particle array was then dipped into a 1 mM aqueous solution of a fifth-generation adamantane-terminated poly(propylene imine) dendrimer (G5-PPI-(Ad)$_{64}$) for 30 minutes, rinsed with water, and dried with N_2.

Formation of particle composites: The particle composites were prepared by layer-by-layer (LbL) assembly of Au–CD nanoparticles ($d \approx 3$ nm) and G5-PPI-(Ad)$_{64}$ on the pre-assembled PS–CD particle layers, according to a published procedure.[21] A total of 30 LbL cycles were performed. After each adsorption step, the substrate was dried under a stream of N_2.

Transfer printing of particle arrays: Oxidized PDMS stamps, onto which PS–CD particles were deposited and infiltrated with G5-PPI-(Ad)$_{64}$ or by LbL assembly, were brought into conformal contact with a flat or micropatterned CD SAM. The printing was carried out in a humid environment. After removal of the stamp, the substrates were thoroughly rinsed with water and dried under a stream of N_2.

Printing of divalent adamantyl guest on printed particle structures: A hydrophilic PDMS stamp with 15 μm lines, with a height of 2 μm, separated by 5 μm trenches, was inked by soaking in a 10 μM aqueous solution of divalent adamantyl guest for 2 minutes. The stamp was dried under a stream of N_2 before printing. The stamp was brought into conformal contact with the printed particle-based microstructures for 2 minutes and then carefully removed. The printed particle-based microstructures were rinsed with a 10 mM aqueous solution of CD at pH 2 and 1M aqueous NaOH, respectively, for 30 minutes and dried under a stream of N_2.

Received: September 18, 2008

Keywords: atomic force microscopy · dendrimers · host–guest systems · monolayers · self-assembly

---

[1] U. Jeong, X. W. Teng, Y. Wang, H. Yang, Y. N. Xia, *Adv. Mater.* **2007**, *19*, 33–60.

[2] A. N. Shipway, E. Katz, I. Willner, *ChemPhysChem* **2000**, *1*, 18–52.

[3] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, H. M. van Driel, *Nature* **2000**, *405*, 437–440.

[4] N. V. Dziomkina, G. J. Vancso, *Soft Matter* **2005**, *1*, 265–279.

[5] S. H. Ko, I. Park, H. Pan, C. P. Grigoropoulos, A. P. Pisano, C. K. Luscombe, J. M. J. Frechet, *Nano Lett.* **2007**, *7*, 1869–1877.

[6] P. Jiang, G. N. Ostojic, R. Narat, D. M. Mittleman, V. L. Colvin, *Adv. Mater.* **2001**, *13*, 389–393.

[7] D. J. Norris, E. G. Arlinghaus, L. L. Meng, R. Heiny, L. E. Scriven, *Adv. Mater.* **2004**, *16*, 1393–1399.

[8] N. V. Dziomkina, M. A. Hempenius, G. J. Vancso, *Adv. Mater.* **2005**, *17*, 237–240.

[9] J. Wijnhoven, W. L. Vos, *Science* **1998**, *281*, 802–804.

[10] A. C. Arsenault, H. Miguez, V. Kitaev, G. A. Ozin, I. Manners, *Adv. Mater.* **2003**, *15*, 503–507.

[11] D. Y. Wang, R. A. Caruso, F. Caruso, *Chem. Mater.* **2001**, *13*, 364–371.

[12] C. López, *Adv. Mater.* **2003**, *15*, 1679–1704.

[13] W. Cheng, J. J. Wang, U. Jonas, G. Fytas, N. Stefanou, *Nat. Mater.* **2006**, *5*, 830–836.

[14] N. A. Kotov, I. Dekany, J. H. Fendler, *J. Phys. Chem.* **1995**, *99*, 13065–13069.

[15] R. Klajn, K. J. M. Bishop, M. Fialkowski, M. Paszewski, C. J. Campbell, T. P. Gray, B. A. Grzybowski, *Science* **2007**, *316*, 261–264.

[16] D. Qin, Y. N. Xia, B. Xu, H. Yang, C. Zhu, G. M. Whitesides, *Adv. Mater.* **1999**, *11*, 1433–1437.

[17] X. Y. Ling, L. Malaquin, D. N. Reinhoudt, H. Wolf, J. Huskens, *Langmuir* **2007**, *23*, 9990–9999.

[18] H. P. Zheng, I. Lee, M. F. Rubner, P. T. Hammond, *Adv. Mater.* **2002**, *14*, 569–572.

[19] V. Santhanam, R. P. Andres, *Nano Lett.* **2004**, *4*, 41–44.

[20] T. P. Bigioni, X. M. Lin, T. T. Nguyen, E. I. Corwin, T. A. Witten, H. M. Jaeger, *Nat. Mater.* **2006**, *5*, 265–270.

[21] O. Crespo-Biel, B. Dordi, D. N. Reinhoudt, J. Huskens, *J. Am. Chem. Soc.* **2005**, *127*, 7594–7600.

[22] X. Y. Ling, D. N. Reinhoudt, J. Huskens, *Langmuir* **2006**, *22*, 8777–8783.

[23] P. Maury, M. Peter, O. Crespo-Biel, X. Y. Ling, D. N. Reinhoudt, J. Huskens, *Nanotechnology* **2007**, *18*, 044007.

[24] T. Kraus, L. Malaquin, H. Schmid, W. Riess, N. D. Spencer, H. Wolf, *Nat. Nanotechnol.* **2007**, *2*, 570–576.

[25] M. A. Meitl, Z. T. Zhu, V. Kumar, K. J. Lee, X. Feng, Y. Y. Huang, I. Adesida, R. G. Nuzzo, J. A. Rogers, *Nat. Mater.* **2006**, *5*, 33–38.

[26] J. H. Liao, L. Bernard, M. Langer, C. Schönenberger, M. Calame, *Adv. Mater.* **2006**, *18*, 2444–2447.

[27] Z. Y. Zhong, B. Gates, Y. N. Xia, D. Qin, *Langmuir* **2000**, *16*, 10369–10375.

[28] W. T. S. Huck, A. D. Stroock, G. M. Whitesides, *Angew. Chem.* **2000**, *112*, 1100–1103; *Angew. Chem. Int. Ed.* **2000**, *39*, 1058–1061.

[29] C. H. Lu, I. Donch, M. Nolte, A. Fery, *Chem. Mater.* **2006**, *18*, 6204 – 6210.

[30] C. Y. Jiang, S. Markutsya, Y. Pikus, V. V. Tsukruk, *Nat. Mater.* **2004**, *3*, 721 – 728.

[31] P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, B. S. Shim, J. D. Xu, H. Nandivada, B. G. Pumplin, J. Lahann, A. Ramamoorthy, N. A. Kotov, *Science* **2007**, *318*, 80 – 83.

[32] H. Ni, X. D. Li, *Nanotechnology* **2006**, *17*, 3591 – 3597.

[33] M. Roerdink, M. A. Hempenius, U. Gunst, H. F. Arlinghaus, G. J. Vancso, *Small* **2007**, *3*, 1415 – 1423.

[34] Q. Xiong, N. Duarte, S. Tadigadapa, P. C. Eklund, *Nano Lett.* **2006**, *6*, 1904 – 1909.

[35] L. Yang, K. O. Van der Werf, C. F. C. Fitie, M. L. Bennink, P. J. Dijkstra, J. Feijen, *Biophys. J.* **2008**, *94*, 2204 – 2211.

[36] C. Mathioudakis, P. C. Kelires, Y. Panagiotatos, P. Patsalas, C. Charitidis, S. Logothetidis, *Phys. Rev. B* **2002**, *65*, 205203 – 205214.

[37] M. V. Rekharsky, Y. Inoue, *Chem. Rev.* **1998**, *98*, 1875 – 1917.