Photochemistry

DOI: 10.1002/anie.201205540

Low-Threshold Photon Upconversion Capsules Obtained by Photoinduced Interfacial Polymerization**

*Ji-Hwan Kang and Elsa Reichmanis**

Photon upconversion (UC), that is, the emission of light at shorter wavelength than the excitation, is a promising optical process because of its potential application in photosensitive devices, including photovoltaics,[1] photocatalyst systems,[2] photochromic displays,[3] and biological imaging.[4] However, conventional UC systems based upon nonlinear phenomena such as two-photon absorption and second-harmonic generation require high excitation intensities (in the range of megawatts per square centimeter) and as a result may be undesirable.[5] An attractive alternative approach uses a triplet–triplet annihilation (TTA) based process which allows the use of low-power density (in the range of milliwatts per square centimeter) noncoherent continuous-wave excitation, for example, sunlight (100 $\mathrm{mW\,cm^{-2}}$, AM 1.5 G).[6] Recently, this UC method was integrated into a solar cell to overcome the theoretical power efficiency limit.[1d,7] The TTA approach typically uses an organometallic complex and an aromatic hydrocarbon as the sensitizer (donor) and emitter (acceptor), respectively. The metal-to-ligand charge-transfer characteristic of the sensitizer enables its long-lived triplet excited state by enhancing the intersystem crossing rate,[8] resulting in triplet–triplet energy transfer (TTET) to the acceptor. Two triplet excited acceptor molecules then undergo TTA through direct collision and subsequent generation of one singlet excited state, which produces the upconverted fluorescence upon decay to the ground state.

The overall efficiencies of TTA-assisted upconversion are determined by the diffusion length of the triplet excitons; spatial overlap between the donor and acceptor wave functions is required for exchange interaction through TTET and TTA.[6a,9] To maximize energy migration in multicomponent UC systems, molecular diffusivity of the chromophores within an inert medium is of paramount importance, especially in a solid-state matrix for practical operation. Therefore, many rubbery polymers with a low glass-transition temperature have been investigated.[6a,10] However, even within such matrices, molecular mobility is restricted in comparison to that of identical molecules in organic solvents resulting in much lower fluorescence efficiencies in the solid system. Dye-doped polymer nanoparticles have been studied as an alternative to achieve confinement at the nanoscale,[11] but stable upconverted emission is yet to be demonstrated in ambient air in the absence of surfactants.

We have developed an alternative UC system composed of uniform capsules fabricated through a microfluidic approach that uses a photocurable resin. The capsules comprise a core–shell structure consisting of a fluidic active core which allows for high translational mobility of the chromophores thus preventing the large decrease in efficiency observed in solids, and an elastomeric shell for mechanical integrity to allow facile integration into a device. To the best of our knowledge, this is the first report exploring control of diffusive energy-transfer-driven photoluminescence (PL) in a bimolecular UC system through controlled photopolymerization at the surface of a microdroplet and concomitant tuning of the properties of the capsules.

Microfluidics provides for microemulsions with desirable properties such as good sphericity and narrow size distribution.[12] The coaxial-flow microfluidic device composed of a T-junction system (Figure 1) effects shear-induced emulsification of the chromophore-dispersed prepolymer solution (see the Supporting Information for experimental procedure). The solution was injected through the inner needle, while an aqueous phase containing photoinitiator and surfactant was introduced through the outer glass tube. At the end of the needle, the continuous outer stream served to elongate the oil flow, eventually affording a stream of highly monodisperse spherical droplets. Upon UV irradiation, free radicals are produced in the aqueous phase based photoinitiator which diffuse into the oil phase. Polymerization then occurs at the inner surface of the emulsion. The degree of polymerization is easily controlled through the UV curing time, providing the ability to finely tune shell thickness and flexible robustness.

For a given device geometry, the size and production rate of the emulsion droplets are determined by the flow rate. Droplets were generated whenever the drag force was counterbalanced with the capillary force in the dripping regime. Increasing the flow rate of the continuous phase resulted in a decrease in droplet size. With an increase in flow rate of the dispersion phase, the droplet size enlarged, but it was rapidly saturated followed by a gradual decrease in production interval. Figure S1 in the Supporting Information shows fluorescence optical microscope images of monodisperse emulsions with several droplet sizes produced by

---

[*] J.-H. Kang, Prof. E. Reichmanis
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology, Atlanta, Georgia, 30332 (USA)
E-mail: ereichmanis@chbe.gatech.edu
Homepage: http://reichmanis.chbe.gatech.edu
Prof. E. Reichmanis
School of Chemistry and Biochemistry
School of Materials Science and Engineering
Georgia Institute of Technology, Atlanta, Georgia, 30332 (USA)

[**] This work was supported by the Georgia Institute of Technology. We thank Prof. Robert Dickson for useful discussions and J.-H.K. also thanks the Korea Institute for Advancement of Technology for fellowship support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205540.

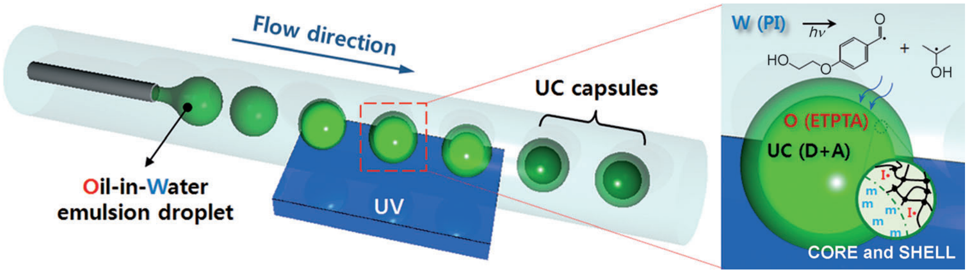

Figure 1. Fabrication of monodisperse capsules for photon upconversion (UC) through interfacial free-radical photopolymerization; UV = ultraviolet, W = water, O = oil, PI = photoinitiator, ETPTA = ethoxylated trimethylolpropane triacrylate, m = monomer, I• = photoinitiator radical, D = donor, and A = acceptor).

a change in flow rate; and the relationship of droplet size as a function of the continuous and dispersion phase flow rates.

To demonstrate the concept, platinum(II) tetraphenyltetrabenzoporphyrin (PtTPBP) and 9,10-bis(phenylethynyl)anthracene (BPEA) were used as the donor and acceptor, respectively. Figure S2 presents the normalized absorbance/PL spectra and corresponding energy level diagram for a pair of PtTPBP and BPEA dispersed in ethoxylated trimethylolpropane triacrylate (ETPTA) monomer solution. ETPTA was selected as the processable medium for the capsules showing UC emission because 1) it is readily polymerized with UV light to afford a moldable transparent resin, and 2) many alternative chromophores can be well-dispersed at high concentrations because of the high polarity, low viscosity, and non-volatility of ETPTA.[13]

According to Dexter energy transfer (by the Perrin approximation at the diffusion limit, $k_{ET} = 4\pi D\, C_A R_0$, where D is the overall diffusion coefficient, C_A is the acceptor concentration, and R_0 is the characteristic interaction dis-

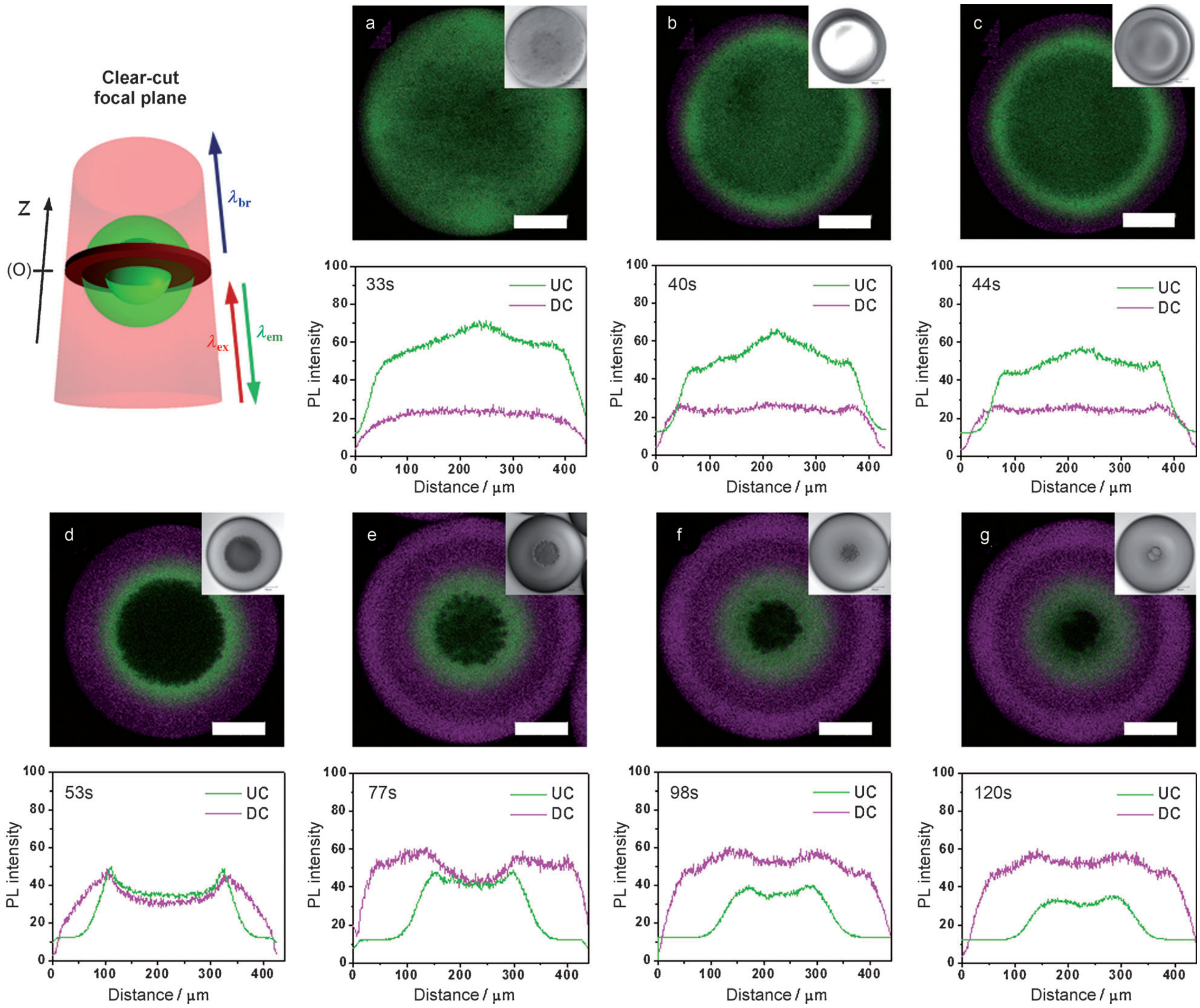

Figure 2. Confocal microscope images and the corresponding upconverted (UC) and downconverted (DC) photoluminescene profiles at clear-cut focal plane of capsules with variable UV curing times. Each inset shows a monochromic transmitted bright-field image. All scale bars are 100 µm.

tance),[9c,14] the fluorescence derived through TTET and TTA is significantly affected by molecular diffusivity within a given medium. The quantum yield (Φ) of the upconverted fluorescence for the PtTPBP–BPEA system as a function of the BPEA concentration is shown in Figure S3. Methylene blue in ethanol was used as a standard ($\Phi = 0.04$).[15] At a fixed PtTPBP concentration (about 1.01 μM), the quantum yield was saturated with increasing BPEA concentration. Although the more viscous ETPTA liquid solution (60 cP) versus dimethylformamide (DMF, 0.92 cP) initially exhibits a relatively low quantum efficiency because of reduced diffusional interactions, ETPTA retards the penetration of oxygen which rapidly quenches the excitons. Notably, the efficiency in bulk ETPTA remains almost constant even after 5 days in air. Further, within a freestanding film, the UC efficiency using a UV-cured ETPTA control matrix is higher than that observed from a commercial rubbery polyurethane film. Thus, the ETPTA encapsulation method described here can facilitate vital collisional energy transfer, especially within a liquid-phase core providing for highly efficient UC emission with enhanced stability.

The capsule shell thickness can be controlled through UV exposure time. Here, the range from 33 to 120 seconds under illumination of 3.7 mW cm^{-2} at 365 nm was used, and the impact of shell thickness on capsule PL was investigated. Figure 2 depicts confocal microscope images at the clear-cut focal plane of the capsules. Two distinctly different emission bands were observed, one associated with the core and another from the shell. The intensities of these bands are dependent upon the respective diffusivities of the chromophores and required molecular energy transfer; upon excitation at 633 nm, annihilation fluorescence induced green emission emanates from the core, whereas the magenta signal derives from emission associated with phosphorescence of the sensitizer through the crosslinked shell (The confocal microscopy shows merged monochromic pseudocolors.). Increasing the UV curing time leads to a thicker downconverted PL region, which indirectly indicates the shell thickness. However, these results do not imply that the crosslinked shell is unable to produce detectable upconverted emission. Because TTA-assisted UC is a nonlinear process, the shell was also observed to release delayed fluorescence when stimulated with a high-power excitation source. The corresponding profiles display the relative intensities of upconverted and downconverted emissions. Their onset positions coupled with the PL signals define the interfaces between the core and shell of the capsules, confirmed by both the transmitted images displayed in the insets and scanning electron microscope images shown in Figure S5. If the shell layer was too thin, the capsules did not have sufficient mechanical strength and the core resin easily leaked out upon washing and drying. An overly thick shell layer reduces the volume of the core leading to a reduction in the upconverted emission. With controlled UV exposure, the solid capsule shell has reversible elastic properties and no leakage of core contents was detected (see Figure S6 in the Supporting Information).

Since each capsule behaves as a single, isolated photon upconverting unit, it can be used as a building block for a multidimensional optical system. Uniformly sized capsules enable self-assembly of the structures into a hexagonal close-packed monolayer array so that the relative PL yield is determined by the number of capsules per unit area. As illustrated in Figure 3 a, bluish green emission from the array was generated at the region of excitation in Figure 3 b. Although a portion of red excitation light was scattered at

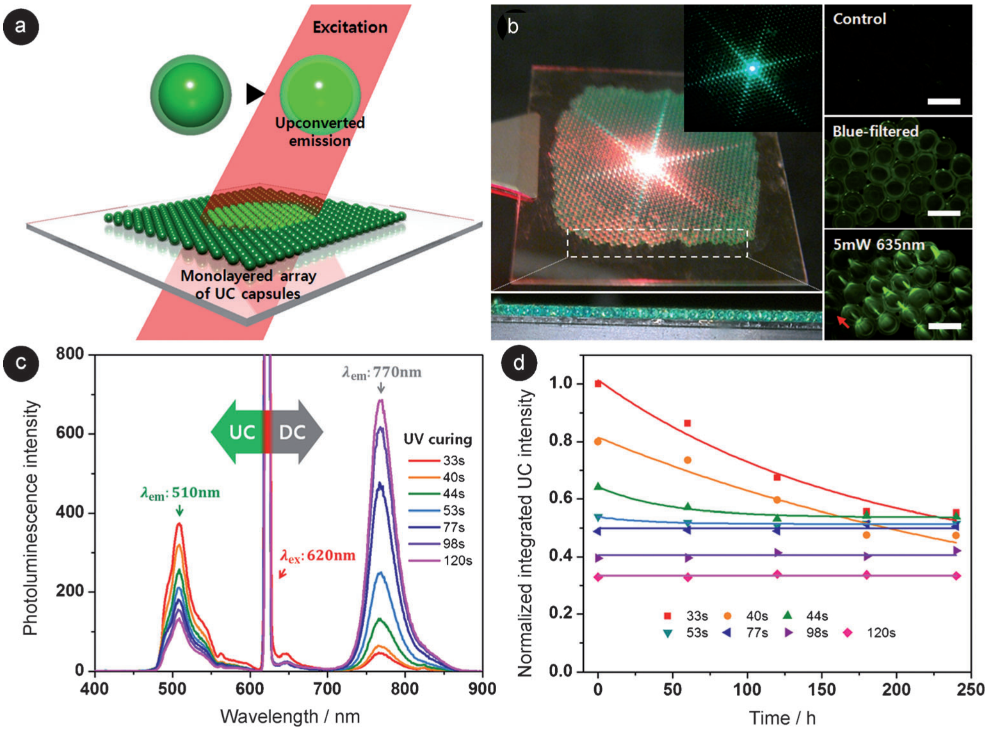

Figure 3. a) Upconverted emission from monolayered array of capsules, b) Digital image of photoluminescence of the array under a focusable laser of 5 mW at 633 nm (the inset shows a bandpass (full width at half maximum, FWHM, of 10 ± 2 nm) filtered emission at 520 nm), and optical microscopic images; Top panel: without excitation for control, middle panel: under blue-filtered light, and bottom panel: excited by a laser pointer of 5 mW at 635 nm (The red arrow indicates the direction of the lasing light.). All scale bars are 500 μm. c) Photoluminescence spectra of the monolayered arrays with variable UV curing times at room temperature. The intense signal at 620 nm comes from the scattered reflection of the spectrofluorophotometer excitation light. d) Normalized integrated upconverted emission intensities of the arrays shown in (c) as a function of time under ambient condition.

the surface of the capsules because of their spherical shape and refractive index difference between air and ETPTA (*n* is about 1.469), a bandpass filter allowed for distinguishing upconverted emission from the scattered light of the source. Fluorescence optical microscopic images also depict the dramatic emissive response of the capsules. While upconverted emission is barely discernible under conditions of no excitation (top) or filtered blue light (middle), the bottom image shows the intensively condensed emission from the capsule cores upon excitation with a conventional laser pointer. Figure 3c depicts the relevant PL intensities of monodisperse capsule arrays with different shell thicknesses (as described in Figure 2). Integrated spectra of upconversion at about 510 nm signal and downconversion at about 770 nm were obtained under exposure to radiation of approximately 0.165 $\mathrm{mW\,cm^{-2}}$ at (620 ± 1.5) nm. As the UV curing time increases, upconverted signals diminish while downconverted bands ascend dramatically. This phenomenon can be explained by both the formation of one excited singlet state obtained from two sensitizer triplet states through sequential energy transfer and a large volume change of the shell.

Meanwhile, the shield offered by encapsulation prolongs the natural lifetime of the process by retarding oxygen penetration which typically quenches the excited states in organic systems and represents a significant drawback for standard TTA-assisted upconverion processes.[14] For evaluation of capsule stability, integrated upconverted PL was measured as a function of time in ambient air, as shown in Figure 3d. Except for the first two samples receiving the shortest UV curing times (33 and 40 seconds), most of the core–shell-structured capsules appear stable, with no apparent reduction in PL intensity over 240 h. Thus, through appropriate control of the shell thickness, the active core is readily protected from the ambient.

In conclusion, we have designed an effective approach to provide for low-threshold TTA-based UC within a structure that could be readily incorporated into a photonic device using conventional processing methodologies. The fabrication of monodisperse core–shell microcapsules for photon UC using UV-initiated free-radical inverse polymerization through a microfluidic channel has been demonstrated. A photocurable resin served as both a medium for TTA-based UC and a shell for practical passive protection. By taking advantage of a structure composed of a liquid core and a solid shell, self-assembled capsule arrays were shown to offer outstanding optical emission under ultralow power excitation coupled with high mechanical integrity and strength. We believe that this two-phase structure has significance not only for enabling promising applications in photovoltaic devices and photochromic displays, but also for providing a useful platform for photocatalytic and photosensor units.

Received: July 13, 2012

Keywords: luminescence · microcapsules · photochemistry · triplet–triplet annihilation · upconversion

[1] a) J. de Wild, A. Meijerink, J. K. Rath, W. G. J. H. M. van Sark, R. E. I. Schropp, *Energy Environ. Sci.* **2011**, *4*, 4835–4848; b) A. C. Atre, J. A. Dionne, *J. Appl. Phys.* **2011**, *110*, 034505; c) G.-B. Shan, G. P. Demopoulos, *Adv. Mater.* **2010**, *22*, 4373–4377; d) Y. Y. Cheng, B. Fuckel, R. W. MacQueen, T. Khoury, R. G. C. R. Clady, T. F. Schulze, N. J. Ekins-Daukes, M. J. Crossley, B. Stannowski, K. Lips, T. W. Schmidt, *Energy Environ. Sci.* **2012**, *5*, 6953–6959.

[2] a) Z. Zhang, W. Wang, W. Yin, M. Shang, L. Wang, S. Sun, *Appl. Catal. B* **2010**, *101*, 68–73; b) W. Qin, D. Zhang, D. Zhao, L. Wang, K. Zheng, *Chem. Commun.* **2010**, *46*, 2304–2306; c) R. S. Khnayzer, J. Blumhoff, J. A. Harrington, A. Haefele, F. Deng, F. N. Castellano, *Chem. Commun.* **2012**, *48*, 209–211.

[3] a) F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, X. Liu, *Nature* **2010**, *463*, 1061–1065; b) T. Miteva, V. Yakutkin, G. Nelles, S. Baluschev, *New J. Phys.* **2008**, *10*, 103002.

[4] a) Q. Liu, T. Yang, W. Feng, F. Li, *J. Am. Chem. Soc.* **2012**, *134*, 5390–5397; b) S. F. Lim, R. Riehn, W. S. Ryu, N. Khanarian, C.-k. Tung, D. Tank, R. H. Austin, *Nano Lett.* **2005**, *6*, 169–174; c) M. Haase, H. Schäfer, *Angew. Chem.* **2011**, *123*, 5928–5950; *Angew. Chem. Int. Ed.* **2011**, *50*, 5808–5829; d) C. Wohnhaas, A. Turshatov, V. Mailänder, S. Lorenz, S. Baluschev, T. Miteva, K. Landfester, *Macromol. Biosci.* **2011**, *11*, 772–778.

[5] S. Baluschev, V. Yakutkin, T. Miteva, Y. Avlasevich, S. Chernov, S. Aleshchenkov, G. Nelles, A. Cheprakov, A. Yasuda, K. Müllen, G. Wegner, *Angew. Chem.* **2007**, *119*, 7837–7840; *Angew. Chem. Int. Ed.* **2007**, *46*, 7693–7696.

[6] a) T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560–2573; b) A. Monguzzi, R. Tubino, S. Hoseinkhani, M. Campione, F. Meinardi, *Phys. Chem. Chem. Phys.* **2012**, *14*, 4322–4332; c) R. R. Islangulov, F. N. Castellano, *Angew. Chem.* **2006**, *118*, 6103–6105; *Angew. Chem. Int. Ed.* **2006**, *45*, 5957–5959; d) S. Ji, H. Guo, W. Wu, W. Wu, J. Zhao, *Angew. Chem.* **2011**, *123*, 8433–8436; *Angew. Chem. Int. Ed.* **2011**, *50*, 8283–8286; e) P. Ceroni, *Chem. Eur. J.* **2011**, *17*, 9560–9564; f) J. Zhao, S. Ji, H. Guo, *RSC Adv.* **2011**, *1*, 937–950.

[7] W. Shockley, H. J. Queisser, *J. Appl. Phys.* **1961**, *32*, 510–519.

[8] A. T. Yeh, C. V. Shank, J. K. McCusker, *Science* **2000**, *289*, 935–938.

[9] a) A. Monguzzi, R. Tubino, F. Meinardi, *J. Phys. Chem. A* **2009**, *113*, 1171–1174; b) J. Mezyk, R. Tubino, A. Monguzzi, A. Mech, F. Meinardi, *Phys. Rev. Lett.* **2009**, *102*, 087404; c) A. Monguzzi, R. Tubino, F. Meinardi, *Phys. Rev. B* **2008**, *77*, 155122.

[10] a) R. R. Islangulov, J. Lott, C. Weder, F. N. Castellano, *J. Am. Chem. Soc.* **2007**, *129*, 12652–12653; b) T. N. Singh-Rachford, J. Lott, C. Weder, F. N. Castellano, *J. Am. Chem. Soc.* **2009**, *131*, 12007–12014; c) J.-H. Kim, F. Deng, F. N. Castellano, J.-H. Kim, *Chem. Mater.* **2012**, *24*, 2250–2252; d) T. N. Singh-Rachford, F. N. Castellano, *J. Phys. Chem. Lett.* **2009**, *1*, 195–200.

[11] A. Monguzzi, M. Frigoli, C. Larpent, R. Tubino, F. Meinardi, *Adv. Funct. Mater.* **2012**, *22*, 139–143.

[12] P. B. Umbanhowar, V. Prasad, D. A. Weitz, *Langmuir* **1999**, *16*, 347–351.

[13] a) P. Jiang, M. J. McFarland, *J. Am. Chem. Soc.* **2004**, *126*, 13778–13786; b) S.-H. Kim, S.-J. Jeon, G.-R. Yi, C.-J. Heo, J. H. Choi, S.-M. Yang, *Adv. Mater.* **2008**, *20*, 1649–1655; c) S.-H. Kim, S.-H. Kim, W. C. Jeong, S.-M. Yang, *Chem. Mater.* **2009**, *21*, 4993–4999.

[14] A. Monguzzi, R. Tubino, M. M. Salamone, F. Meinardi, *Phys. Rev. B* **2010**, *82*, 125113.

[15] J. Olmsted, *J. Phys. Chem.* **1979**, *83*, 2581–2584.