Honeycomb-Patterned Photoluminescent Films Fabricated by Self-assembly of Hyperbranched Polymers

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SM1. Experiment Details

a) Synthesis of amphiphilic hyperbranched poly(amidoamine)s [1,2]. The palmitoyl chloride modified hyperbranched poly(amidoamine) (HPAMAM10K-C16) was synthesized by polycondensation of methylacrylate (MA) and diethylenetriamine (DETA) (1.2/1 mole ratio) followed by reaction with palmitoyl chloride (ca. 61% amino groups of the HPAMAM molecule were modified) in our lab according to the procedures published before.[1] The molecular weight ($M_n$) of the HPAMAM10K-C16 is ca. 10780 and the polydispersity index (PDI) is ca. 2.39 according to size exclusion chromatography (SEC).

Other amphiphilic HPAMAMs, HP(EDA-MA)8K-C16 ($M_n = 8310$, PDI = 1.90), HPAMAM8K-C16 ($M_n = 8220$, PDI = 1.86) and HP(TETA-MA)7K-C16 ($M_n = 7270$, PDI = 1.82), were prepared by polycondensation of methyl acrylate (MA) and ethylenediamine (EDA), diethylenetriamine (DETA), or
triethylenetetramine (TETA) with 1/1 feed mole ratio, respectively, followed by modification with palmitoyl chloride by the same protocol as that of HPAMAM10K-C16.

**b) Preparation of dye-loaded HPAMAM10K-C16 CHCl₃ solution** \[1\] The 0.5 g/L chloroform solution of HPAMAM10K-C16 was mixed with equal volume of aqueous solution of dye in a glass bottle. The mixture was shaken by hands for 10 minutes to ensure the two phases mixed adequately. The bottom layer of chloroform solution was used to fabricate the films after the two phases separated completely.

The following figure shows the scheme of dye-loaded HPAMAM10K-C16 (a), photographs of HPAMAM10K-C16 loaded with fluorescein sodium (b), Phloxine B (c), rose Bengal (d) and Congo red (e) in chloroform solution (bottom layer), and UV/Vis spectra (f) of HPAMAM10K-C16 (line 1), FSS-loaded HPAMAM10K-C16 (line 2) and PB-loaded HPAMAM10K-C16 (line 3) in chloroform.
c) Preparation of films. Typically, a solution of 0.5 g/L HPAMAM10K-C16 or dye-loaded HPAMAM10K-C16 in chloroform was dropped on a cleaned substrate (e.g., silicon wafer, quartz, glass slide, freshly cleaved mica, etc.) in a hood. The dropped solution amount is approximate 0.11-0.14 mL/cm². The film was obtained after the solvent evaporation.

The same protocol was used to prepare films from other amphiphilic HPAMAMs including HP(EDA-MA)8K-C16, HPAMAM8K-C16, and HP(TETA-MA)7K-C16 on substrates.

d) Instruments. SEM images were recorded using a field emission scanning electron microscope (SEM, Sirion 200, Philips, 5 kV, 20kV or 30kV). Prior to imaging by SEM, the samples were sputtered with a thin layer of gold. AFM images were recorded with a Digital Instrument (DI) Nanoscope IIIa scanning probe microscope, mounted with Si₃N₄ tips, in contact mode or tapping mode. TEM images were recorded with a JEOL JEM-100 CX II Electron Microscope. First, 35% poly(acrylic acid) solution in water was dropped onto the film. The honeycomb-patterned film was tore off from the substrate automatically after the water evaporated and was put into water carefully to remove the poly(acrylic acid) completely. Then, the film was transferred to the copper grid to conduct TEM measurements. Fluorescence microscopy was performed on a Nikon Eclipse E600 optical microscope equipped with a camera, which was connected to a personal computer for image processing. Three kinds of filters (UV-2A, B-2A, and G-2A) were used. Fluorescence and UV/Vis spectra were recorded on a Perkin Elmer LS 50B luminescence spectrometer and Perkin Elmer Lambda 20/2.0 UV/Vis spectrometer, respectively.
SM2. AFM images of the films prepared from 0.5 g/L HPAMAM10K-16C solutions on mica under different relative humidity (RH) and temperature: (a) 25 °C, 20%, (b) 25 °C, 30%, (c) 25 °C, 32%, (d) 25 °C, 75%, (e) 25 °C, 81%, (f) 21 °C, 40%. It is found that no honeycomb morphology is observed on the formed films below RH 20% (image a), and only irregular holes are found above RH 75% (images d and e). We investigated the effect factor of temperature in a range of 20-32 °C, and found that the temperature has less effect on the morphology of the patterned films at a suitable RH (image f).
SM3. AFM analysis of the films prepared from the HPAMAM10K-16C solutions with different concentrations on mica at 25°C and RH 40-42%: (a) 0.05 g/L, (b) 0.1 g/L, (c) 0.25 g/L, (d) 2.0 g/L.
SM4. AFM images of the films prepared from 0.5 g/L HPAMAM10K-16C solutions in different solvents on mica at 25 °C and RH 32%: (a) CH$_2$Cl$_2$, (b) CS$_2$, (c) mixture of CHCl$_3$ and toluene (1:1 in volume).
SM5. AFM images of the films prepared from 0.5 g/L solutions of different amphiphilic poly(amide amine)s in chloroform on mica: (a) HP(EDA-MA)8K-C16 (25 °C, RH 32%), (b) HPAMAM8K-C16 (25 °C, RH 32%), (c) HP(TETA-MA)7K-C16 (25 °C, RH 40%).
SM6. AFM images of the film prepared from Congo red-loaded HPAMAM10K-16C on quartz: surface plot (a), top view (b, 50 μm × 50 μm) and section analysis (c).
SM7. Photographs caught during the self-assembly course of the film: 1 min 14 sec (a), 2 min. 52 sec. (b), 3 min. (c), 3 min. 1 sec. (d), 3 min. 2 sec. (e), 3 min. 3 sec. (f), 3 min. 8 sec. (g), 3 min. 41 sec. (h) at 100 times magnification and 1 hour (i) at 400 times magnification.

References
