Semiconducting Polymer Nanospheres in Aqueous Dispersion Prepared by a Miniemulsion Process**

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Solid layers of conjugated polymers have been successfully included as active layers into various electrical and electrooptical devices such as light-emitting diodes,[1] solar cells,[2] and field-effect transistors.[3] In the majority of cases, these layers have been deposited from solutions of the polymers in organic solvents. However, deposition from those solvents brings about several problems, particularly when dealing with large-area or multilayer devices. For example, large-area light-emitting diodes or large-area photodiodes require uniform coverage over large surface areas. Ink-jet printing and screen printing offer the ability to deposit a pattern of the active species in a well-controlled fashion on large substrates. In the last few years, ink-jet printing[4–7] and screen printing[8,9] have been reported for the fabrication of organic light-emitting diodes and high-performance plastic transistors. While in most of these cases printing has been performed from solutions of the active components in organic solvents such as chloroform, the deposition from aqueous or liquid components would be most desirable. One major problem in constructing multilayer assemblies with polymers is that most polymers used as charge transport, emission layers, or gate dielectrics are soluble in the same organic solvents, and coating of several layers on top of each other will lead to interdiffusion and undefined interfaces. One major approach used to avoid interdiffusion is to deposit a first layer from a common solvent and then to either crosslink (by thermal treatment or illumination with light) or chemically convert the polymer, resulting in an insoluble layer, which can subsequently be overcoated by the next layer.[10,11] However, these processes often are accompanied by chemical reactions, and reaction side products might affect the device performance. Recently, polymeric conductors such as polyethylenedioxythiophene (PEDOT) doped with poly(styrene sulfonate) (PSS) have been deposited from water-based dispersions,[12] but this approach is focused on the deposition of electrically conducting polyelectrolytes (PEDOT, or polyaniline (PANI)). Here we demonstrate, for the first time, film formation from semiconducting, preferably fluorescent, polymer nanospheres (SPNs), deposited onto solid substrates from aqueous dispersions. This approach can universally be used for many polymers.

Nanoparticles have been produced from a semiconducting polymer in aqueous phase via the miniemulsion process. Miniemulsions are understood as stable emulsions consisting of stable droplets with a size of 50–500 nm created by shearing a system containing oil, water, a surfactant, and a highly water insoluble compound, the so-called hydrophobe.[13,14] The surfactant stabilizes the droplets against collisions, mass exchange (Ostwald ripening) between the droplets is suppressed by the use of the hydrophobe. In order to obtain polymer dispersions, one can start from a miniemulsion where the monomeric droplets are polymerized to give polymer particles without changing the droplet identity. Another possibility is the formation of artificial latexes from the droplets consisting of a solution of the preformed polymer. After evaporation of the solvent, a polymer dispersion is obtained. For excellent electronic properties, high purity of the semiconducting polymers as used in this paper, namely poly(*p*-phenylene)s or polyfluorenes, is required, this can be best ensured by using the second approach.

Solutions of different conjugated semiconducting polymers in chloroform (with concentrations between 1.5 and 5.4 %) were successfully miniemulsified in water by using sodium dodecyl sulfate (SDS) as surfactant. Methyl substituted ladder-type poly(*para*-phenylene) (Me-LPPP) is a solution processable polymer that has been widely used as active semiconducting material in electronic devices (light-emitting diodes (LEDs), solid-state lasers, and photodiodes).[15] Polyfluorene (PF) derivatives are characterized by an unique combination of semiconducting and liquid crystalline (LC) properties, and have been applied as high-performance blue emitters in LEDs based on organic semiconducting polymers.[16] Polycyclopentadithiophenes (PCPDTs) as heteroaromatic PF analogues are characterized by a reduced bandgap (HOMO/LUMO) energy in relation to PF, and are promising materials for potential use in organic field-effect transistors (FETs) and solar cells.[17] The structure formula of these semiconducting polymers are given in Scheme 1, characteristics of the aqueous dispersions are summarized in Table 1. Using Me-LPPP as polymer, SDS concentrations of as low as 0.71 % of the polymer solution (RM114, 5.4 % polymer in chloroform) were sufficient in order to obtain miniemulsions with stable droplets in which the polymer itself, as an absolutely water-insoluble material, acts as a perfect ultrahydrophobe and therefore suppresses efficiently Ostwald ripening between the formed droplets. Due to the high stability of each droplet, evaporation of the solvent does not lead to any change of the droplet number. After evaporation of the chloroform, a stable polymer dispersion with a solid content of 5.6 % and a polymer particle size of about 150 nm was obtained. It is well known for the formation of a miniemulsion that the droplet size can easily be decreased by increasing the amount of SDS in the dispersed phase. The final particle size of the polymer parti-

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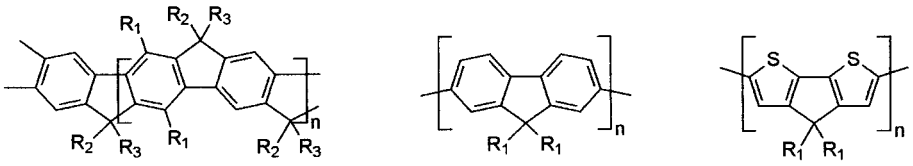

Scheme 1. Chemical structure of Me-LPPP ($-R_1$: hexyl, $-R_2$: methyl, $-R_3$: 4-decylphenyl), PF ($-R_1$: alkyl: 2-ethylhexyl—PF2/6, and 3,7,11-trimethyldodecyl—PF11112, respectively), and PCPDT ($-R_1$: 3,7-dimethyloctyl).

Table 1. Characteristics of the aqueous dispersions consisting of different conjugated semiconducting polymers in 10 g of water.

Sample	Polymer	Mass of polymer [mg] (% in $CHCl_3$)	$CHCl_3$ [g]	SDS [mg] (% compared to $CHCl_3$)	Solid content after evaporation [%]	Particle size [nm]
RM114	Me-LPPP	226 (5.4 %)	4.2	30 (0.71 %)	5.6	154
RM245	Me-LPPP	208 (4.2 %)	5	42 (0.84 %)	4.8	95
RM262	Me-LPPP	150 (5.0 %)	3.0	55 (1.83 %)	2.5	75
RM163	PF11112	222 (3.7 %)	6.0	30 (0.5 %)	9.3	120
RM116	PF11112	90 (3.0 %)	3.0	30 (1.0 %)	7.3	74
RM286	PF2/6	141 (2.1 %)	6.7	42 (0.62 %)	2.3	104
RM153	PCPDT	75 (1.5 %)	5.0	30 (0.6 %)	2.2	250

cles after evaporation of the chloroform also depends on the amount of polymer dissolved in the chloroform. By increasing the SDS amount to 1.83 %, the polymer particle size could be decreased to 75 nm. Particles were also obtained by miniemulsifying polyfluorene solutions in water. Concentrations as low as 0.5–0.62 % of SDS allowed the formation of stable miniemulsions and after evaporation stable dispersions of low T_g (RM163) or high T_g (RM286) polymer particles were obtained. Due to a lower polymer concentration the particle size after evaporation is less than in the case of RM114. In Figure 1, a droplet of a polyfluorene dispersion is shown, once taken in white light (Fig. 1a) and once where it was illuminated only with a UV lamp (λ_{max} = 365 nm) (Fig. 1b), which illustrates nicely the fluorescence behavior of the dispersion.

In Figure 2a, a TEM image of a dispersion with Me-LPPP particles (sample RM116) shows spherical particles which are hard due to their high T_g. It has to be mentioned that for this measurement, the dispersion is highly diluted leading to isolated clusters of particles.

Homogeneous layers could be prepared by spincoating the dispersion with the negatively charged particles at the concentration as listed in Table 1 onto a glass substrate. The resulting films consist of closely packed particles, as seen by AFM, but the images do not reveal any cracks within an area of 5 × 5 μm^2 (Fig. 2b). Because Me-LPPP has its glass-transition temperature well above the onset of decomposition (300–350 °C), the particulate structure also does not change during annealing at 200 °C for 2 h.

Large homogeneous layers of Me-LPPP could be prepared by taking advantage of the negative charge of the particles. It has recently been shown that well-defined layers of negatively charged CdS nanocrystals can be formed on polycationic films via spincoating.[18] Layers of Me-LPPP particles (sample RM245, particle size 95 nm) coated on poly(allylamine hydrochloride) (PAH) exhibit a homogeneous fluorescence over large areas as shown in Figure 3a. Further, the absorption and photoluminescence (PL) emission spectra recorded on these films (Fig. 3b) are identical to those reported for layers of Me-LPPP from organic solvents.[15] Since photoluminescence is very sensitive to defects, this result indicates that neither the preparation nor the deposition of the nanoparticles disturbs the principle electronic and optical properties of the conjugated polymers.

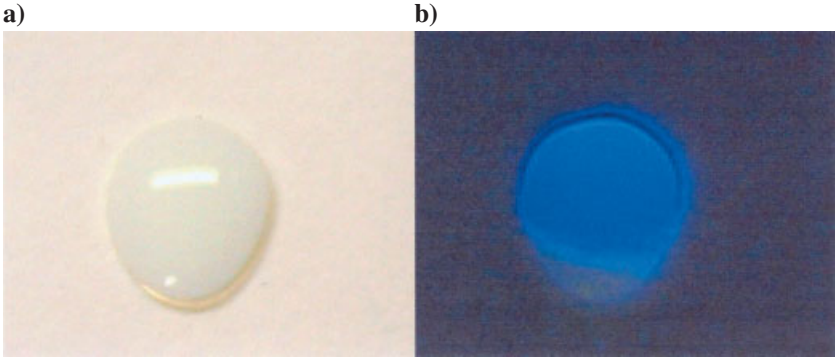

Fig. 1. Photographs of a droplet of a dispersion of polyfluorene nanospheres, taken either in white light (a) or when illuminated only with an UV lamp (b) (λ_{max}=365 nm).

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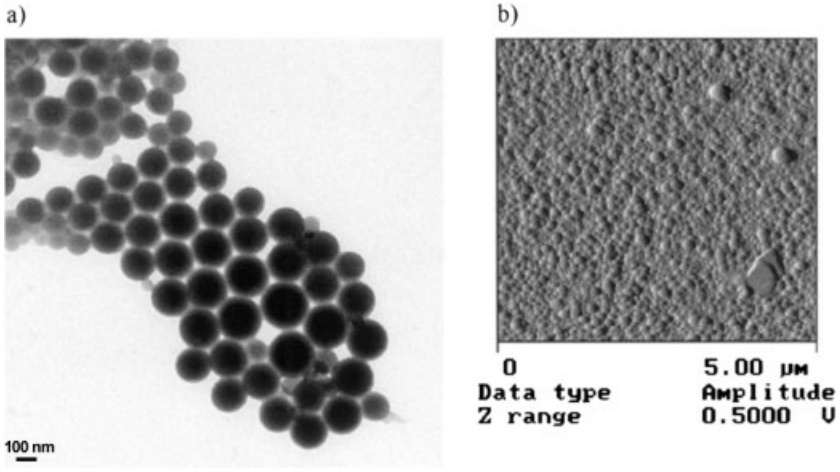

Fig. 2. a) TEM image of Me-LPPP particles. b) AFM image of a film formed by spincoating from a Me-LPPP dispersion.

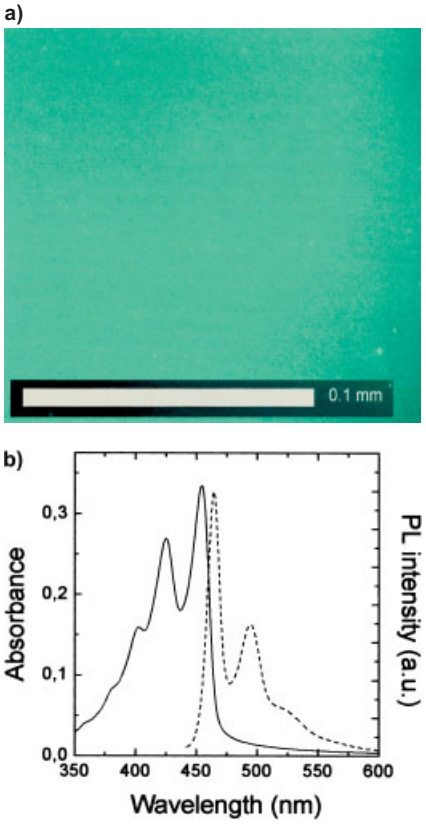

Fig. 3. a) Photoluminescence image of a Me-LPPP layer deposited from a nanoparticle dispersion on a thin polycationic PAH layer. b) Absorption (solid line) and photoluminescence (dashed line) spectra of the layer in (a).

Homogeneous layers have also been prepared from dispersions of polyfluorene particles. In case of PF2/6 with a softening temperature at ca. 90 °C the particle structure can be well preserved and detected in the deposited layers (Fig. 4a). But in contrast to Me-LPPP, annealing of these layers above T_g at 200 °C for 2 h (transition into the birefringent fluid (nematic) liquid crystal (LC) phase at ca. 170 °C, isotropization at >280 °C[19]) results in coalescing of particles, and larger structures are formed (Fig. 4b). This film formation shows remarkable characteristics, which are untypical for usual latex film formation: a) the particle sizes grow, b) steps are built, and c) anisotropic structures can be detected resulting from the LC behavior of the polymer. When films are formed from the low T_g polyfluorene (PF11112),[20] T_g below room temperature) nanoparticles (RM116), the particles already coalesce during film formation at room temperature. Moreover, the sizes of the particles as found in the dispersion can not be detected, anisotropic structures are seen, and the film also exhibits a lower surface roughness (Fig. 4c). After annealing at 200 °C for 10 h, the surface roughness decreases even more.

In conclusion, we have shown that layers of conjugated semiconducting polymers can be deposited from aqueous dispersions prepared by the miniemulsion process. Dispersions of particles of different conjugated semiconducting polymers such as a ladder-type poly(*para*-phenylene) and several soluble derivatives of polyfluorene could be prepared with controllable particle sizes ranging between 70–250 nm. Layers of these particles formed by spincoating exhibit a particulate structure, revealing the shape of the individual polymer nanoparticles. Annealing above the polymer's glass transition temperature results in coalescing of the particles and larger domains of continuous structure are formed. We, therefore, propose that the concept of semiconducting polymer nanoparticles will allow multilayer structures to be formed by, e.g., depositing a first layer from a solution of a polymer and coating it by semiconducting polymer nanospheres of the second polymer from an aqueous phase, followed by annealing and film formation. Most important, this will allow the formation of a multilayer structure from polymers that are highly soluble in the same solvents, without introducing any additional chemical conversion steps.

Experimental

Synthesis of the Aqueous Polymer Dispersion: The polymer was dissolved in $CHCl_3$ (for the exact amounts see Table 1) and added to 10 g of an aqueous

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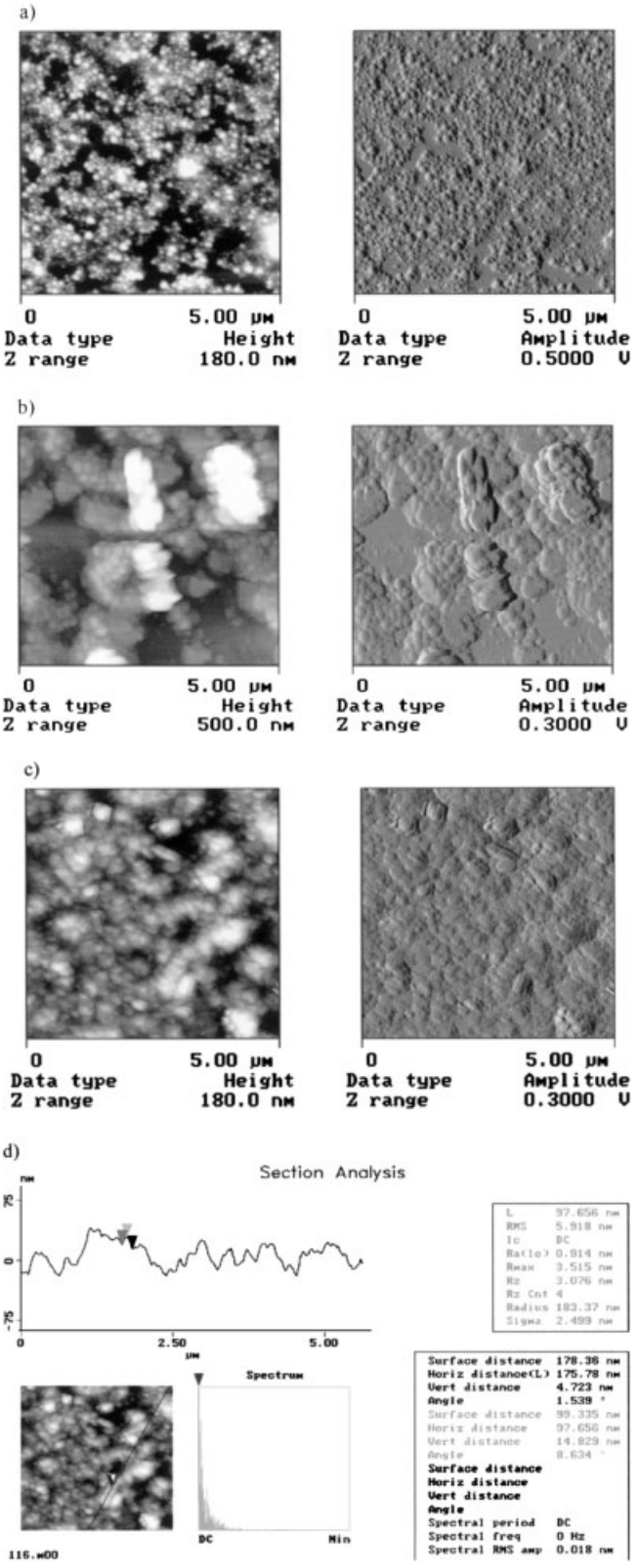

Fig. 4. a) AFM images of a film of the high T_g polymer (PF2/6) particles before annealing (sample RM286). b) AFM images of the film in (a) after annealing. c) AFM images of a film of the low T_g polymer (PF11112) particles before annealing (RM116). d) Section analysis of the film in (c).

SDS solution (for SDS amounts see Table 1). After stirring 1 h for pre-emulsification, the miniemulsion was prepared by ultrasonicating the mixture for 5 min at 90 % amplitude (Branson sonifier W450 Digital, 1/2″ tip) in order to reach the steady state of droplet sizes. The steady state was confirmed by a constant turbidity of the miniemulsion (the turbidity measurements were carried out by a process turbidity meter FSC402 (Mettler Toledo, Switzerland) with a sensor for high turbidity values, which is sensitive to backscattered light). After sonication the sample was stirred in an oil bath at 62 °C for 3 h in order to evaporate the $CHCl_3$.

Analysis: The particle sizes were measured using a Nicomp particle sizer (Model 370, PSS Santa Barbara, USA) at a fixed scattering angle of 90°. Electron microscopy was performed with a Zeiss 912 Omega electron microscope operating at 100 kV. The diluted colloidal solutions were applied to a 400-mesh carbon-coated copper grid and left to dry; no further contrasting was applied.

Atomic force microscopy (AFM) was performed with a NanoScope IIIa microscope (Digital Instruments, Santa Barbara) operating in tapping mode. The instrument was equipped with a 10 × 10 µm E-scanner and commercial silicon tips (model TSEP, the force constant was 50 $N\,m^{-1}$, the resonance frequency was 300 kHz, and the tip radius was smaller than 20 nm).

Absorption spectra were measured with a Perkin Elmer Lambda 19 UV-vis spectrometer. The sample spectra were corrected for the transmission of an uncoated glass slide.

Fluorescence spectra were recorded with a Perkin Elmer LS 50 luminescence spectrometer. The excitation was incident at an angle of 60° onto the front face of the sample and the emission was recorded in reflection at an angle of 30° with respect to the surface normal.

Preparation of the Films: Glass substrates were cleaned with the standard procedure. After ultrasonication in a hot mixture of H_2SO_4/H_2O_2 (7:3) for 3 h, the substrates were heated in a mixture of $H_2O/H_2O_2/NH_3$ (5:1:1) at 80 °C for 1 h and dried under N_2 gas purging. For a first layer a few drops of cationic PAH (10 mM) were placed on the substrate. The substrate was rotated on a spinner for 10 s with 3000 rpm. After deposition of the PAH layer the substrates were rinsed twice with plenty of MilliQ water. After that, anionic LPPP (4.8 %) was deposited with the same method as described before.

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Alignment of Liquid Crystals on Self-Assembled Monolayers Using Ultra-Thin Gold Films**

By *Hans T. A. Wilderbeek*,* *Frank J. A. van der Meer*, *Kirill Feldman*, *Dirk J. Broer*,* and *Cees W. M. Bastiaansen**

Liquid crystal displays (LCDs) have maintained their dominant position as a man–machine interface particularly for portable electronic devices despite the rapid developments in new flat panel displays such as polymeric light-emitting diodes,[1] electrochromic displays,[2] and electrophoretic displays.[3] Classical liquid crystal displays are notorious for their high-energy consumption, slow switching kinetics, and poor viewing angle. However, enormous technological advances have been made that reduce energy consumption with improved illumination schemes, polarizing films, and color filters. Displays based on the new switching principles were developed to improve switching voltages and switching kinetics (e.g., (super) twisted nematic,[4,5] vertically aligned,[6] ferroelectric[7] LCDs and π-cells[8]). In addition, the viewing angle was improved drastically; this is usually performed with external, out-of-cell compensation methods. Typically, birefringent polymeric films are used, which, in the ideal case, are exact inverse copies of the retardation of the liquid crystal display in the bright state. The completed device therefore behaves as a quasi-isotropic system, which results in displays with a wide viewing angle.[9,10]

More recently, new principles have been introduced for the improvement of the viewing angle in liquid crystal displays based on reducing in-cell anisotropy by the micro-patterning of orientation layers and liquid crystals.[11–14] For instance, special polymeric alignment layers were developed that are oriented using linearly polarized light and these alignment layers are micro-patterned using a photo-mask.[15–17] Also, self-assembled monolayers (SAMs) were investigated as orientation layers for liquid crystals and their micro-patterning was performed using micro-contact printing techniques. For instance, it was shown by Abbott et al. that the alignment of liquid crystals on SAMs can be tuned accurately by the appropriate choice of thiol and deposition conditions of the gold substrates.[18–21] At first sight, the use of these micro-patterned SAMs in displays seems attractive because both the azimuthal and polar orientation of the liquid crystals can be controlled accurately contrary to photo-aligned orientation layers.

However, the use of gold substrates in the production of the monolayers also imposes some rather serious limitations. For instance, twisted nematic electro-optical displays exhibit an extremely poor maximum transmission if SAMs on gold substrates are used as alignment layers, which originates from the poor transmission of the gold films.

Here, a different and rather straightforward approach was used to enhance the transparency of the alignment layers, i.e., the thickness of the gold substrate was reduced to decrease light absorption and to shift the absorption band towards the ultraviolet (UV) wavelength region.[22] Gold films with an average thickness ranging from 1–100 Å were sputtered onto glass substrates with an indium tin oxide layer, a non-rubbed polyimide planarization layer, and a chromium adhesion interlayer. Atomic force microscopy (AFM) illustrates that discontinuous gold structures with gold nuclei are obtained for gold layer thicknesses of 1 and 2 Å (Fig. 1a,b). This discontinuity agrees with an average gold film thickness smaller than the diameter of a single gold atom (2.88 Å). Gold films with an average thickness between 10 and 25 Å appear to be continuous with a grain structure, whereas 100 Å films exhibit crack-like structures (Fig. 1c). In Figure 2a, transmission spectra of the substrates are shown, which illustrate that light absorption losses in the gold layers are reduced significantly simply by using ultra-thin gold layers. In fact, the transparency of gold films with a thickness below 10 Å is virtually identical to a reference substrate without gold.

SAMs created from polar (e.g., 11-mercapto-1-undecanol) and apolar (e.g., *n*-dodecanethiol) thiols with odd and even numbers of carbon atoms in the aliphatic tail were deposited on the substrates and their alignment of liquid crystals was investigated. In Figure 2b, it is shown that a highly heterogeneous alignment is obtained on (ultra-)thin gold films in the case of thiols with a polar end-group. Such a heterogeneous LC alignment is also observed with apolar thiols on gold substrates with average thicknesses of 1 and 2 Å. Independent of the parity of the thiols, a monolithic homeotropic alignment is observed using aliphatic apolar thiols in combination with an average gold layer thickness of between 5 and 25 Å. Yet, a monolithic planar alignment is obtained for a large gold layer thickness (i.e., 100 Å). It is not yet understood where the planar alignment observed in these cells originates from, in view of the uncollimated isotropic deposition method used to de-

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