



Tetrahedron

Tetrahedron 62 (2006) 2050-2059

Hierarchical self-assembly of all-organic photovoltaic devices

Chih-Hao Huang,^a Nathan D. McClenaghan,^a Alexander Kuhn,^b Georges Bravic^c and Dario M. Bassani^{a,*}

^aLCOO/CNRS UMR 5802, Centre de Recherche en Chimie Moléculaire, Université Bordeaux 1, 33405 Talence, France

^bLACReM, ENSCPB Université Bordeaux 1, 33607 Pessac, France

^cInstitut de Chimie de la Matiére Condenseé de Bordeaux-CNRS, Université Bordeaux 1,

87 Avenue du Dr. Schweitzer, F-33608 Pessac, France

Received 14 June 2005; revised 22 September 2005; accepted 24 September 2005

Available online 16 November 2005

Abstract—Photovoltaic devices built by a hierarchical self-assembly process using hydrogen-bonding terminated self-assembled monolayers (SAMs) on gold and the combination of a hydrogen-bonding barbituric acid appended fullerene and a complementary melamine terminated π -conjugated thiophene-based oligomer are presented. The incorporation of these electron donor (oligomer) and electron acceptor (methanofullerene) assemblies into simple photovoltaic (PV) devices as thin films leads to a 2.5 fold-enhancement in photocurrent compared to analogous systems comprising non-hydrogen-bonding C₆₀–oligomer systems, which is ascribed to higher molecular-level ordering. The modification of the gold electrode surface with self-assembled monolayers bearing hydrogen-bonding molecular recognition endgroups was seen to further enhance the PV response of the corresponding functional supramolecular device. This superposition of two types of self-assembly facilitates the generation of binary supramolecular fullerene-containing architectures. Importantly, all functional materials are accessible in a direct fashion.

© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

Silicon-based photovoltaic devices have played a major role in the development of light energy-to-electrical energy conversion, and multi-junction solar cells have been reported with efficiencies of 31%.¹ Portability, durability (lack of moving parts), and zero emission during operation are attractive features that are countered only by their relatively high manufacturing costs and fragility. For these reasons, as well as concerns about the use of rare-earth heavy metals in the active layers, hybrid inorganic/organic and all-organic polymer alternatives have been actively pursued in recent years as viable alternatives amenable to large-scale deployment.² Based on current organic polymer technology and of additional interest for the construction of o-LED and o-FET devices, the polymer approach has benefited from increased interest since the report by Sariciftci and co-workers demonstrating that a substantial improvement in the photovoltaic properties of such materials could be obtained by blending a small amount of C₆₀ into the polymer mixture.³ In such composite devices, it has been

proposed that the fullerence component acts as the electron transport material, increasing the efficiency of charge separation and transport. However, the introduction of high proportions of C_{60} results in phase separation, creating unwanted heterogeneous domains, which adversely affect the photovoltaic response.⁴ A successful strategy to enhance compatibility between the organic polymer and fullerene components involves appending solubilizing groups to the latter. This allows a higher fullerene loading to be used, which results in improved performance (up to 3%) and increased device stability.⁵ At the same time, the synthesis and photophysical investigation of covalently-linked fullerene π -conjugated oligomer dyads, triads, and more complex dendritic assemblies has led to important breakthroughs in the comprehension of the fundamental energy and electron transfer processes leading to the generation of long-lived charge separated states. Thus, through covalent modification of C₆₀, introduction of a plethora of electron-rich oligomers, including oligo(p-phenylene vinylene)s,⁶ oligo $(thiophenes)^7$ and others⁸ has been achieved and used to construct increasingly complex covalent architectures, including several doubly fullerene-terminated oligomer 'dumbbells'.9 The construction of solidstate devices based on these covalent adducts is underway and bodes well for future applications.¹⁰

Keywords: Oligomer; Fullerene; Electron donor; Hydrogen-bonding; Photovoltaic; Self-assembly.

^{*} Corresponding author. Tel.: +335 4000 2827; fax: +335 4000 6158; e-mail: d.bassani@lcoo.u-bordeaux1.fr

Photoinduced charge separation in composite devices takes place at a heterojunction between the electron donor and electron acceptor materials. However, highly ordered materials are required for efficient charge transport, and the conciliation of these apparently contradictory requirements is a major challenge.¹¹ The effect of ordering on charge mobility was recently illustrated with sexithiophene whose charge carrier mobility increases on passing from an amorphous film $(10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ to a partially organized film $(2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ to the single crystal $(10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$.¹² Although covalent tethering surmounts the phase separation problem, a high degree of long-range ordering conducive to charge transport is more difficult to obtain. For these reasons, the induction of longrange ordering through self-assembly, using non-covalent supramolecular interactions, is particularly appealing. Hydrogen-bonding systems offer the possibility to generate preordained structures in which the binding strength can be modulated and the relative geometry between active units controlled.¹³ Additionally, in certain cases hydrogen-bonding has been shown to promote photoinduced electron transfer processes.14

Several examples of hydrogen-bonding systems combining fullerenes and π -conjugated oligomers have recently appeared in the literature, for example using ammonium groups and crown ethers,¹⁵ or self-complementary ureidopyr-imidinone units.¹⁶ However, the recently described fullerene–barbituric acid dyad **6**¹⁷ (see Scheme 1) presents a unique

combination of features compatible with the construction of functional self-assembled devices: (i) the hydrogen-bonding motif, capable of forming up to six hydrogen bonds, is nonself-complementary and can be introduced in a single synthetic step; (ii) the symmetry of **6**, which presents two identical edges, is conducive with the formation of extended arrays in the presence of conjugated oligomers bearing complementary hydrogen-bonding units; (iii) its compact nature is adapted to promote close inter-fullerene approach in a binary system where the other component is a melamine-like unit. The first two features are important to assure programmed extended bicontinuous photo-/electroactive molecular tapes and efficient photoinduced electron transfer, while the latter two points are prerequisites for charge movement following the primary electron transfer act.

Molecule **6** was recently reported to form supramolecular assemblies in solution¹⁷ with simple melamine units, in a manner related to unfunctionalized barbituric acid,¹⁸ and to play the role of an electron acceptor in ultra-fast photoinduced electron transfer processes with oligothieny-lenevinylene electron donors in discrete 1:1 supramolecular complexes.¹⁹ Clearly, the presence of barbituric acid does not adversely affect the electronic properties of the fullerene cage, and the fullerene–grafted barbiturate is capable of forming hydrogen-bonded structures, even if a degree of distortion appears to be present on the barbiturate unit due to non-bonding interactions between the carbonyl groups and the fullerene cage.^{16,20} Molecule **6** was therefore deemed a



Scheme 1. Synthesis and structural formulae of 1-6.

good candidate for the pursuit of functional supramolecular devices.

2. Results and discussion

To be of interest for future development, the electron donor (oligomer) and acceptor (fullerene) components should be easily accessible in high yields with direct synthetic approaches (Scheme 1). The functionalized fullerene is obtained in one step,¹⁷ while the oligomer can be functionalized with hydrogen-bonding molecular recognition units, either melamine or barbituric acid, starting from the same dialdehyde also in one step.²¹ These strategies in themselves constitute a widely applicable methodology to introduce complementary molecular recognition motifs, which is currently lacking. Thus the possibility to incorporate complementary, yet non-self-complementary hydrogenbonding motifs onto conjugated oligomers (potentially different oligomers) opens the door to the construction of molecular fabrics and libraries of mixed chromophore layers, where the judicious choice of suitably-decorated chromophores assures a better matching of absorption properties with the solar spectrum.

In the current study, the focus is directed at the combination of a melamine-appended oligothiophene 5 with the complementary barbiturate-appended fullerene 6, and the development of self-assembled optoelectronic devices based on the resulting assemblies. Different microscopic hydrogen-bonding structures may be anticipated using these molecular building blocks bearing complementary units, in line with findings on simpler binary melamine:barbiturate structures described previously, which are shown schematically in Figure 1.¹⁸ Although rosettes, crinkled tapes, and linear tapes are possible, only the linear tape architectures can satisfy all the hydrogen-bonding sites present in the complementary components and their formation is expected to be thermo-dynamically favored.¹⁸ Preliminary photovoltaic measure-ments have been reported,²¹ and we now report the effect of elaborating the gold electrode surface with the appropriate bifunctional hydrogen-bonding motif and thiol-terminated species. The terminal thiol-group interacts with the gold surface resulting in the formation of self-assembled monolayers (SAMs) that are proposed to better accommodate the subsequent formation of the photo-/electroactive fullerenecontaining thin films due to complementary hydrogenbonding interactions. Several interesting all-organic systems have been recently reported in the context of photovoltaic devices, including examples based on photoactive SAMs²² and chromophore-appended nanotubes,²³ as well as fullerene–oligomer dyads/triads.¹⁰ The incorporation of hydrogen-bonding motifs giving photo-/electroactive molecules programmed to assemble into hierarchical extended photovoltaic arrays has received less attention.



Figure 1. Possible hydrogen-bonding architectures formed with compounds 5 (red) and 6 (green). Compared to the crinkled tape (II) and rosette (III), only the hydrogen-bonded tape structure (I) satisfies all the hydrogen-bonding requirements of both components.

2.1. Synthesis

Pertinent synthetic procedures and structural formulae of the molecules used in this study are shown in Scheme 1. Fullerene–barbituric acid dyad **6** was prepared by a Bingel reaction between 5-bromobarbituric and C_{60} in a toluene:DMSO mixture.^{17,24} The synthesis of the oligomers and introduction of molecular recognition motifs was recently reported.²¹ Briefly, the 5T chromophore (**3**; a symmetric linear pentathiophene oligomer with a central EDOT unit) was obtained via Suzuki cross-coupling reaction between the boron ester of dithiophene and 2,5-dibromo-EDOT. This parent unit was subsequently functionalized by a double Vilsmeier-Haack formylation giving dialdehyde **4**, which can be considered as a versatile starting point for the introduction of terminal molecular recognition motifs.

Introduction of the melamine unit was achieved using a Schiff base reaction to give 5. As Schiff base formation is an equilibrium process, good yields of the most stable adduct can be obtained on reaction with an excess of 2,4,5,6tetraaminopyrimidine. Equally, the symmetric complementary barbituric acid-terminated oligomer (not shown) could be prepared in one step in similarly high yield by a Knoevenagel reaction with barbituric acid. The alkylthioacetate terminated barbituric acid or cyanurate were prepared by adapting the above methodologies.²⁵ Structurally-related barbiturate species were previously reported by Ringsdorf, albeit in lower yields.²⁶ 4-Hydroxybenzaldehyde was alkylated with the appropriate α, ω -dibromoalkane² followed by condensation with potassium thioacetate28 giving an intermediate, which could be subsequently condensed with either barbituric acid or tetraminopyrimidine to give 1 or 2, respectively.

2.2. X-ray crystal structure of 3

Conjugation-and hence electron-hole pair delocalizationover adjacent heterocycles in oligo- and polythiophene derivatives is highest when the structure adopts a planar geometry maximizing π -overlap. This is indeed the case in most oligothiophenes (with the exception of some 3, 4-disubsitituted thiophene-containing derivatives), for which a large number of solid-state structures have been reported.¹² Substitution in the thiophene C-3 and C-4 position generally introduces sufficient steric repulsion to induce a deviation from planarity. Although only a few crystal structures of EDOT-containing oligothiophenes have been reported, these do not indicate that the EDOT moiety introduces a substantial deviation from planarity. To investigate whether this is the case in 3, its solid-state structure was determined by X-ray diffraction. Single crystals were grown from THF solution, crystallizing in a monoclinic p21/n unit cell.[†] The structure of **3**, shown in

[†] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 275009. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Figure 2, indicates that the planarity of the pentameric oligomer is indeed retained even upon introduction of the functionalized central unit, although one of the terminal thiophenes shows a torsion angle of 24.7° in the S(11)–C(15)–C(22)–(S21) plane, presumably due to crystal packing forces. The extended crystal packing structure is a herringbone type as observed with related oligothiophene species.¹²



Figure 2. X-ray crystal structure of 3 and crystal packing.

2.3. Thin films comprising photo-/electroactive oligomer and fullerene units

2.3.1. Fluorescence microscopy of thin films. Blends of π -conjugated oligomers and fullerenes have the tendency to undergo phase separation, and high-speed spin-coating of these species onto the appropriate substrate from volatile solvents is often used to overcome this process. In the current study, drop-casting of thin films from solution (0.5 mM 5 in DMSO or DMSO/THF solutions) onto a solid substrate followed by slow evaporation of the solvent is anticipated to favor the formation of thermodynamically equilibrated non-covalent architectures (see Fig. 1). As a preliminary test to see if homogeneous films would result from this drop-casting technique, mixtures of the pertinent species were separately deposited on microscope slides in order to visualize the residual fluorescence from the films. Bearing in mind that the oligomer fluorescence will be quenched in the presence of fullerene (either via energy or electron transfer), an estimation of bulk homogeneity can be made by examining the intensity and distribution of the residual fluorescent areas. The fluorescence microscopy images of three different thin films are shown in Figure 3. In the first case, the intense fluorescence of oligomer 5 can be clearly seen. In the second case (b), 5 and C_{60} were co-deposited in a 1:2 stoichiometry from DMSO solution. Though a portion of the intrinsic oligomer fluorescence is quenched by the presence of C₆₀, localized regions of fluorescence are visible showing that the film exhibits considerable heterogeneity, presumably due to phase separation during the deposition process. In the third case (c), films of **5** and **6** (in a 1:2 stoichiometry) were deposited. Here, the oligomer fluorescence is comprehensively quenched, indicating that the fullerene and oligomer components are more homogeneously dispersed than in (b). While these results per se do not provide irrefutable evidence as to the formation of the hydrogen-bonding

architectures proposed above, they do indicate that the compatibility between inherently incompatible compounds such as oligothiophenes and C_{60} can be significantly enhanced by the presence of complementary molecular recognition groups. In practical terms, this implies that the electron-rich oligomers are mostly located in the vicinity of a fullerene moiety, which can translate into enhanced charge separation efficiency.



Figure 3. Representative fluorescence microscopy images of thin films of oligomer 5 (left); $5+C_{60}$, 1:2 equiv (center); and 5+6, 1:2 equiv (right).

2.3.2. Electrochemical and photoelectrochemical studies of thin films on a gold surface. Thin films analogous to those described above were subsequently deposited from solution onto a gold electrode and introduced into a standard three-electrode photoelectrochemical cell, with methylviologen in water acting as an electron carrier, sodium sulfate as the supporting electrolyte and a platinum wire counter electrode.²¹ Irradiation was performed using a high-pressure mercury lamp equipped with a band-pass filter $(400-500 \text{ nm}; \text{ intensity}=150 \text{ mW cm}^{-2})$.²⁹ In line with the idea of higher organization and better compatibility of the two different electron donor and acceptor materials giving the highest photocurrent, the best performance was measured for a mixture of 5 and 6, which was anticipated to be the most organized thin film comprising the hydrogenbonding fullerene and the complementary π -conjugated oligomer.²¹ This response was 2.5 times higher than that obtained on combining 5 with unsubstituted C_{60} , while the lowest conversion was obtained for the film of oligomer 5 alone with a value, which was half that obtained with $5:C_{60}$.

From the I/V graph of photocurrent generated versus applied potential, the open-circuit voltage conversion efficiency $\Phi(V_{oc})$, and short-circuit quantum conversion efficiency $\Phi(I_{sc})$ of the photovoltaic device could be estimated. Respectively, these values express the fraction of light energy that is converted into voltage, and the number of photoelectrons generated for every photon of light that is absorbed³⁰ (film thickness was estimated at ca. 200 nm using AFM, which also showed that the films were even and reproducible).

$$\Phi(V_{\rm oc}) = V_{\rm oc}/E_{\rm oo} \tag{1}$$

$$\Phi(I_{\rm sc}) = (\mathrm{d}n_{\rm e}/\mathrm{d}t)/(\mathrm{d}n_{\rm h\nu}/\mathrm{d}t) \tag{2}$$

where n_e and $n_{h\nu}$ are the number of photoelectrons and number of photons absorbed, respectively, while E_{oo} is the energy of the S₁ \leftarrow S₀ transition in eV. The incident light intensity of 150 mW cm⁻² corresponds to an average photon flux of 5.6 $\times 10^{-8}$ Einstein (at 450 nm). Considering the device comprising an oligomer film without fullerene, it is estimated that ca. 2.7% of incident light is absorbed (based on the measured thickness of the film). From Eqs. 1 and 2 above and values of $V_{\rm oc} = 0.39$ V and $I_{\rm sc} = 6.8$ µA, one can estimate the efficiency of open-circuit voltage conversion, $\Phi(V_{oc}) = 0.14$, and the quantum conversion efficiency, $\Phi(I_{sc}) = 0.05$. These values are comparable to other photovoltaic devices based on similar technology (although experimental error, associated mainly with the determination of film thickness, must be taken into consideration). Thus, comparing the relative photocurrents generated for the thin films, the quantum conversion efficiencies were estimated at 5% for 5 alone; 9% for $5:C_{60}$; 1:2 stoichiometry_i and ca. 25% for 5:6; 1:2 stoichiometry. This latter value compares favorably with recent photovoltaic devices based on the layer-by-layer construction of conjugated polymers and C_{60} and with IPCE values of 15%.³¹ In all cases it can be assumed that absorption of light is effected almost exclusively by the oligomer, as fullerene derivatives possesses low molar absorptivities above 400 nm. Therefore, despite uncertainties in the absolute values for the efficiency of these simple devices, these results show that the films comprising two complementary hydrogen-bonding electroactive units are more performant. An additional factor that became immediately apparent during this initial testing phase of the devices is their inherent stability towards air and moisture. Indeed, the photovoltaic cell set-up uses an aerated aqueous solution of methylviologen as the electron transport agent. The response of 5 alone is stable over time, whereas device B (5 + pristine C_{60}) exhibits a slow (ca. 10%) loss) of efficiency over a period of 1 h. During this same period, no measurable decrease in efficiency was detected for the device prepared with 5+6.

2.3.3. Thin films on a hydrogen-bonding SAM modified gold surface. To obtain photoactive fullerene-containing architectures directed by a hierarchical combination of supramolecular self-assembly processes, gold-thiol interactions can be employed in addition to hydrogen-bonding. The self-assembly of different nanoparticles (gold and CdS) was recently demonstrated using nanoparticles whose surface was decorated with thiol-terminated melamines and barbiturates, respectively.²⁵ The gold electrode surface was first modified by reaction with a barbiturate or melamine unit bearing a thiol-terminated alkyl chain, thus generating a self-assembled monolayer with the capacity to bind electroactive units using non-covalent interactions. In the current case, the choice of hydrogen-bonding building blocks used to decorate the SAMs would be anticipated to dictate the chemical nature of the layer adjacent to the surface self-assembled monolayer. These anticipated second layers would be a π -conjugated melamine-bearing oligomer (5) with a barbiturate-decorated surface, and a barbituric acid bearing fullerene (6) with a melaminedecorated surface. In other words, the SAM may serve as a homogeneous starting point for subsequent deposition of the photoactive binary thin film.

Hydrogen-bonding SAMs were obtained by dipping the gold-substrate into a solution of the appropriate thiol 1-2, see Scheme 1 for structural formulae. The surface coverage was subsequently evaluated by electrochemical and surface

ellipsometry measurements. In the first case, the determination of surface coverage can be obtained by electrochemistry while the thickness of the monolayer can be determined by ellipsometry, and the surface coverage estimated by rastering the surface with the incident laser beam.

The surface coverage by self-assembled monolayers of the gold electrode can readily be evaluated by electrochemistry when the chemisorbed molecules serve as a barrier to block a redox process involving a species in solution at the electrode surface.³² In the current case the reduction of Fe^{3+} (as the potassium hexacyanoferrate (III) salt) to Fe^{2+} was employed to check for defects in the SAM. For the surface coated with 1a, a highly uniform close packing monolayer layer was formed. As shown in Figure 4, essentially no Fe^{III} reduction could be measured upon modification of the gold surface with the barbiturateterminated alkane-thiol, compared with the electrochemical response for bare gold. The situation was somewhat different when the experiment was repeated with the corresponding melamine-terminated alkane-thiol (Fig. 4). A much poorer blocking effect was observed with 2a suggesting a less ordered SAM. This result was rationalized by considering the experimentally determined 'odd-even' effect reported for simple alkanethiol SAMs where the number of repeat units (odd /or even) influences close-packing of the molecules.³³ The experiment was thus repeated with molecule 2b, which is identical with 2a except for the incorporation of an additional methylene repeat unit in the alkyl chain. This simple structural modification resulted in a much better passivation of the



Figure 4. Cyclic voltammograms of the reduction of aqueous $K_3[Fe(CN)_6]$ using gold electrodes whose surfaces were modified with 1a or 1b (top) and 2a or 2b (below).

electrode surface. This result is consistent with the formation of a better monolayer, as shown in Figure 4. A similar behavior was observed upon investigation of the *N*-methylated derivative of **1a**, for which compact SAMs took several days to form (data not shown). Again, incrementing the pentamethylene linker by one $-CH_2$ -unit (compound **1b**) significantly improved the self-assembly of compact monolayers, which were formed overnight.

Ellipsometry measurements of surfaces modified with **1a** and **2b** are shown in Figure 5, which correspond to the closest packing SAMs as estimated by electrochemistry, formed with thiol-terminated barbiturates and melamines, respectively. Rastering the modified surface gave infor-

mation on the coverage, and a homogeneous layer, in terms of height is obtained (Fig. 5a). Using this height profile (Fig. 5b), an estimation of the geometry adopted can be obtained and this is represented in Figure 5c for both **1a** and **2b**. The measured height corresponds well to the dimensions obtained using molecular modeling. In the case of **1a** the measured height was 1.50 nm while the calculated value was 1.42 nm. For **2b** the measured height was 1.83 nm with a calculated value of 1.90 nm.

7Photoelectronic devices similar to those reported in Section 2.3.2 were prepared using gold electrodes modified with SAMs prepared from compounds **1a**, **1b**, and **2b**. Comparison of the response obtained from electrodes modified with **2b** versus **1a** provides an indication as to the effect of the



Figure 5. Characterization of SAMs obtained for 1a (left) and 2b (right) modified gold surfaces using ellipsometry: (a) topology of surface; (b) height profile and (c) calculated height assuming close-packing of the molecules.

hydrogen-bonding endgroup, whereas the use of **1b** serves as a control in which hydrogen-bonding is blocked. Since it was shown that incorporating the barbiturate-appended fullerene **6** resulted in thin films giving greater photocurrent than pristine C_{60} , only devices based on **5** and **6** (in a 1:2 stoichiometry) are considered in this section. The different photocurrent response for each of the four different devices is shown in Figure 6, where device A is the film deposited on the bare gold; device B is the thin film deposited on the surface decorated with melamine **2b**; device C is the film deposited on the surface decorated with **1b**; and device D is the film deposited on the surface decorated with the alkanethiol–barbiturate **1a**. It was immediately clear that device A is the least performant device when compared to the devices incorporating SAM-decorated surfaces, all of which gave a higher photocurrent.



Figure 6. Top: Photocurrent generated with thin films of 5+6, 1:2 equiv deposited on: bare gold (device A); Au/2b (melamine endgroup, device B); Au/1b (N,N'-dimethylbarbiturate endgroup, device C); Au/1a (barbiturate endgroup, device D). Bottom: Effect of stirring on the photocurrent of devices A and D; with stirring off (I and V), slow stirring (II and IV) and fast stirring (III).

The behavior of device D is intriguing, displaying a rapid decrease in the photogenerated current upon each illumination cycle. We attribute this reproducible behavior to extension of the diffusion layer due to depletion of the MV^{2+} in the vicinity of the electrode. To confirm this, we proceeded to monitor the photovoltaic response of device D upon mechanical stirring of the solution. The results are presented in Figure 6, in which it is quite clear that the photovoltaic response of D increases substantially upon stirring, in a way that is proportional to the rate of stirring. Therefore, in the case of device D the observed performance is limited by the rate of diffusion of the electron-carrying species in solution rather than the charge carrier mobility in the material. This is not the case for the other devices, for which the effect of stirring the solution is much lower or absent, as in the case of device A. Device D also displayed exceptional stability, no deterioration in its response being observed after two week storage under ambient conditions.

3. Conclusions

The formation of SAMs appended with suitable recognition motifs is shown to be advantageous in the construction of supramolecular all-organic photovoltaic devices. Based on the formation of hydrogen-bonded networks, the molecular constituents in these devices are programmed to selfassemble into molecular-level heterojunctions. Thus two levels of self-assembly can be employed to generate multicomponent functional fullerene-containing supramolecular architectures. Although direct measurement of the degree of order instilled by the presence of complementary hydrogenbonding donor-acceptor sites is difficult, considerable differences in efficiency and behavior are noted. The improvement of the photovoltaic response when using the SAM modified surfaces may in part originate from either the variations in the surface properties (the increased hydrophobicity of the SAM-covered surface results in lower contact angles when exposed to organic solvents) and/or inhibition of the phonon quenching of the excited states generated in close proximity of the gold surface.³ However, this reasoning alone is insufficient to explain the difference in behavior between devices B, C, and D. In the latter device, it can be anticipated that the presence of a barbituric acid-appended SAM may induce the preferential deposition of the complementary melamine-containing oligothiophene unit 5. In contrast, the use of the melamine-based SAM (device B) would lead to the selective deposition of fullerene derivative 6. Due to the electrical bias applied during the photovoltaic measurements, it is expected that the latter construction should be less efficient as the presence of the fullerene proximal to the gold electrode would induce an energy barrier to the transport of holes towards the cathode. Work is in progress to further elucidate the morphologies of these films and to test their photovoltaic response in solid-state devices.

4. Experimental

4.1. General

¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker DPS-200 FT, AC-250 FT or DPX-300 FT spectrometer using residual solvent proton peaks as internal references unless otherwise indicated. Chemical shifts are given in ppm (δ) with respect to tetramethylsilane. Abbreviations used are s=singlet, d= doublet, t=triplet, q=quartet, and br=broad. Mass spectra were recorded on a VG Autospec-Q by EI (70 eV); *m/z* (%). High resolution mass spectra were recorded on a FTICR mass spectrometer Bruker 4.7T BioApex II. The elemental analysis was carried out by the Service Centrale d'Analyse at Vernaison (CNRS-France). Merck silica gel 60 (70–230 mesh) was used for flash chromatography. Electronic absorption spectra were obtained using a Hitachi U-3300 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence microscopy images were taken on a Nikon Eclipse E600 FN instrument equipped with a 365 nm excitation filter.

4.1.1. Materials. Commercially available starting materials and anhydrous DMSO and DMF (Fluka) were used as received. The preparation of compound **5** was recently described.²¹ Tetrahydrofuran (THF) was distilled over sodium/benzophenone immediately before use. All reactions were carried out under a nitrogen atmosphere. The polycrystalline gold electrodes (nickel (80 Å), chromium (20 Å) and gold (3900 Å) on 1.0 mm glass) were purchased from ACM France. 4-(5-Bromopentyloxy)benzaldehyde and 4-(6-bromohexyloxy)benzaldehyde were prepared following a procedure described in the literature.²⁷

4.1.2. Cleaning of substrates and preparation of monolavers and devices. The gold electrodes were cut into slides (ca. $2.5 \text{ cm} \times 1.0 \text{ cm}$) and were cleaned by immersion in 'piranha' solution (H₂SO₄/30% H₂O₂, 7:3 (v/v); Caution: 'Piranha' is an extremely dangerous oxidizing agent and should be handled with care using appropriate shielding) for 30 min, and were then rinsed with deionized water and absolute ethanol and dried with a stream of argon. For SAM-based devices, the clean gold slides were immersed in anhydrous THF-ethanol (1/5) mixed-solutions of alkylthioacetate terminated 1a, 1b, 2a, or 2b (1 mM) overnight. To remove any solution-deposited material, the slides were then rinsed with ca. 5 mL of anhydrous ethanol, followed by immersing in an ethanol solution for 5 min, and dried with a stream of argon. In all devices, deposition was carried out by drop-casting 20 µL of 2.0×10^{-5} M DMSO solutions of 5 with 2.0 equiv of 6. The slow evaporation of the solvent under reduced pressure left a thin film of material on a well-defined area (2.50 cm^2) of the gold electrode. The modified slide was then dried with a stream of argon and before use in photoelectrochemical measurements.

4.1.3. Experimental conditions. All photoelectrochemical studies were performed as previously described.²¹ The cyclic voltammograms were recorded in 1 mM $K_3[Fe(CN)_6]$ aqueous solution with 0.1 M KNO₃ as the supporting electrolyte. The working electrode was a modified gold slide, the counter electrode was a platinum wire, and an Ag/AgCl (saturated KCl) reference electrode was used. The Fe^{3+}/Fe^{2+} redox potential was obtained with a scan speed of 50 mV s^{-1} . The ellipsometer (Ielli2000, Nanofilm Technologie GmbH, Germany) equipped with a frequency doubled Nd-Yag laser ($\lambda =$ 532 nm, $P_{\text{max}} = 50 \text{ mW}$), was used for the thickness measurements, and the obtained data were analyzed with the furnished software. The incident angle was set to 65°. A refractive index of 1.50 was assumed for all films in the calculation of the thickness.

4.2. Synthesis

4.2.1. 5-(4'-Formylphenoxy)pentyl thioacetate.²⁸ 4-(5-Bromopentyloxy)benzaldehyde (1.00 g, 3.68 mmol) and potassium thioacetate (0.43 g, 3.68 mmol) in acetone (20 mL) were stirred at room temperature overnight. The

resulting white precipitate was filtered off and the filtrate was concentrated under reduced pressure to give a white solid (0.97 g, yield=99%). ¹H NMR (200 MHz, CDCl₃) δ 9.87 (s, 1H, CHO), 7.82 (d, 2H, *J*=8.7 Hz, ArH), 6.98 (d, 2H, *J*=8.7 Hz, ArH), 4.03 (t, 2H, *J*=6.3 Hz, OCH₂), 2.90 (t, 2H, *J*=7.0 Hz, S–CH₂), 2.33 (s, 3H, CH₃), 1.87–1.77 (m, 2H), 1.67–1.50 (m, 4H); ¹³C NMR (50 MHz, CDCl₃) δ 195.2, 190.8, 164.1, 132.0, 129.8, 114.7, 104.5, 68.0, 30.6, 29.3, 28.9, 28.5, 25.2.

4.2.2. 6-(4'-Formylphenoxy)hexyl thioacetate.²⁸ 4-(6-Bromohexyloxy)-benzaldehyde (7.78 g, 27.28 mmol) and potassium thioacetate (3.18 g, 27.28 mmol) in acetone (20 mL) were stirred at room temperature overnight. The resulting white precipitate was filtered off and the filtrate was concentrated under reduced pressure to give a white solid (6.98 g, yield=91%). ¹H NMR (200 MHz, CDCl₃) δ 9.87 (s, 1H, CHO), 7.82 (d, 2H, *J*=8.7 Hz, ArH), 6.98 (d, 2H, *J*=8.7 Hz, ArH), 4.03 (t, 2H, *J*=6.3 Hz, OCH₂), 2.87 (t, 2H, *J*=7.1 Hz, S–CH₂), 2.32 (s, 3H, CH₃), 1.82–1.76 (m, 2H), 1.67–1.55 (m, 2H), 1.54–1.43 (m, 4H); ¹³C NMR (50 MHz, CDCl₃) δ 195.5, 190.4, 163.9, 131.7, 129.5, 114.4, 104.5, 67.9, 30.3, 29.2, 28.7, 28.6, 28.1, 25.2.

4.2.3. 5-{4-[(Tetrahydro-2,4,6-trioxo-5(2H)-pyrimidinyliene)methyl]phenoxy}pentyl thioacetate (1a). 5-(4'-Formylphenoxy)pentyl thioacetate (0.67 g, 2.52 mmol), and barbituric acid (0.33 g, 2.52 mmol) in ethanol:water (14 mL, 5:2; v/v), was stirred under reflux for 10 min, and then at room temperature overnight. The resulting yellow suspension was filtered, washed with EtOH (10 mL) and dried under reduced pressure to give a yellow solid (0.87 g, yield = 92%). ¹H NMR (200 MHz, d_6 -DMSO) δ 11.29 (s, 1H, NH), 11.18 (s, 1H, NH), 8.36 (d, 2H, J=9.0 Hz, ArH), 8.24 (s, 1H, CH=C), 7.05 (d, 2H, J=9.0 Hz, ArH), 4.09 (t, 2H, J=6.4 Hz, OCH₂), 2.86 (t, 2H, J=6.9 Hz, S-CH₂), 2.31 (s, 3H, CH₃), 1.80–1.70 (m, 2H), 1.61–1.43 (m, 4H); ¹³C NMR (50 MHz, d_6 -DMSO) δ 195.3, 163.9, 162.9, 162.2, 154.9, 150.2, 137.5, 125.0, 115.4, 114.3, 67.8, 30.6, 28.9, 28.2, 27.9, 24.6. APCI-MS m/z (%) 377 (M+1, 100); 376 (M, 75). HRMS 376.1088, M⁺; Calcd 376.1093. Anal. Calcd for C18H20N2O5S: C 57.43, H 5.36, N 7.44. Found: C 57.28, H 5.40, N 7.43.

4.2.4. 6-{4-[(1,3-Dimethyl-tetrahydro-2,4,6-trioxo-5-(2H)-pyrimidinyliene)methyl]phenoxy}hexyl thioacetate (1b). 6-(4'-Formylphenoxy)hexyl thioacetate (1.55 g, 5.54 mmol), and N,N'-dimethylbarbituric acid (0.88 g, 5.54 mmol) in benzene (100 mL) were stirred under reflux for 4 h using Dean-Stark apparatus. After cooling to room temperature, the solvent was removed, and the residue was dissolved in CHCl₃ (100 mL), extracted with saturated aqueous NaHCO3 solution (50 mL), dried over MgSO4, and concentrated under reduced pressure to give a yellow solid (1.65 g, yield = 71%). ¹H NMR (200 MHz, CDCl₃) δ 8.51 (s, 1H, CH=C), 8.32 (d, 2H, J=9.0 Hz, ArH), 6.95 (d, 2H, J=9.0 Hz, ArH), 4.06 (t, 2H, J=6.4 Hz, OCH₂), 3.41 (s, 3H, N–CH₃), 3.39 (s, 3H, N–CH₃), 2.88 (t, 2H, J=7.1 Hz, S-CH₂), 2.33 (s, 3H, CH₃), 1.87-1.77 (m, 2H), 1.65-1.42 (m, 6H); 13 C NMR (50 MHz, CDCl₃) δ 196.0, 164.0, 163.2, 161.0, 159.0, 151.4, 138.1, 125.3, 114.1, 114.0, 68.2, 30.6, 29.4, 29.0, 28.9, 28.8, 28.4, 28.3, 25.5. HRMS 419.1634, M⁺; Calcd 419.1640.

4.2.5. 5-{4-[(2,4,6-Triamino-N5-pyrimidinyliene)methyl]phenoxy}pentyl thioacetate (2a). 2,4,5,6-Tetraaminopyrimidine sulfate (3.21 g, 13.06 mmol), potassium carbonate (1.79 g, 13.06 mmol), and 5-(4'-formylphenoxy)pentyl thioacetate (0.87 g, 3.27 mmol) in 2-propanol (15 mL) were stirred under reflux overnight. After cooling to room temperature, water (30 mL) was added to the reaction. The brown suspension solution was filtered, washed with water (10 mL), EtOH (10 mL), and diethyl ether (10 mL), then dried under reduced pressure to give a deep-yellow solid (1.31 g, yield = 90%). ¹H NMR (200 MHz, d₆-DMSO) δ 8.49 (s, 1H, N=CH), 7.79 (d, 2H, J=8.6 Hz, ArH), 6.97 (d, 2H, J=8.7 Hz, ArH), 5.95 (s, 4H, NH₂), 5.65 (s, 2H, NH₂), 4.00 (t, 2H, *J*=6.3 Hz, OCH₂), 2.86 (t, 2H, J=6.9 Hz, S-CH₂), 2.32 (s, 3H, CH₃), 1.80–1.67 (m, 2H), 1.65–1.43 (m, 4H); ¹³C NMR (50 MHz, d₆-DMSO) δ 195.4, 160.0, 159.2, 157.1, 152.9, 130.8, 129.0, 114.3, 102.0, 67.4, 30.6, 28.9, 28.3, 28.1, 24.7. ESI-MS *m*/*z* (M⁺, 387.7). HRMS 388.1680, M⁺; Calcd 388.1681.

6-{4-[(2,4,6-Triamino-N5-pyrimidinyliene)-4.2.6. methyl]phenoxy}hexyl thioacetate (2b). 2,4,5,6-Tetraaminopyrimidine sulfate (8.51 g, 34.65 mmol), potassium carbonate (4.78 g, 34.65 mmol), and 6-(4'-formylphenoxy)hexyl thioacetate (2.43 g, 8.66 mmol) in 2-propanol (25 mL) was stirred under reflux overnight. After cooling to room temperature, water (150 mL) was added to the reaction. The brown suspension solution was filtered, washed with water (100 mL), and CH₂Cl₂ (20 mL), then dried under reduced pressure to give a deep-yellow solid (0.92 g, yield = 27%). ¹H NMR (200 MHz, d_6 -DMSO) δ 8.49 (s, 1H, N=CH), 7.78 (d, 2H, J=8.6 Hz, ArH), 6.96 (d, 2H, J=8.6 Hz, ArH), 5.90 (s, 4H, NH₂), 5.57 (s, 2H, NH₂), 4.00 (t, 2H, J=6.4 Hz, OCH₂), 2.84 (t, 2H, J=7.0 Hz, S–CH₂), 2.32 (s, 3H, CH₃), 1.80–1.60 (m, 2H), 1.60–1.30 (m, 6H); ¹³C NMR (50 MHz, d_6 -DMSO) δ 195.3, 159.9, 159.8, 157.4, 152.4, 130.9, 128.9, 114.3, 102.2, 67.4, 30.6, 29.1, 28.5, 28.3, 27.9, 25.0. APCI-MS m/z (%) 404 (M+1, 100); 403 (M, 30). HRMS 403.1904, M⁺; Calcd 403.1916.

Acknowledgements

We thank Dr. B. Desbats for assistance with ellipsometry measurements and Dr. R. Oda for access to fluore scence microscope instrumentation. Financial support from the CNRS and French Ministry of Research (AC Nanosciences-Nanotechnologies) is gratefully acknowledged.

References and notes

- 1. Takamoto, T.; Agui, T.; Ikeda, E.; Kurita, H. Proc. of the 28th IEEE Photovoltaic Specialists Conf., 2000, p 976.
- Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. Adv. Funct. Mater. 2001, 11, 15–26. Brabec, C. J. Sol. Energy Mater. Sol. Cells 2004, 83, 273–292.
- Shaheen, S.; Brabec, C.; Fromherz, T.; Padinger, F.; Sacariftci, S.; Gloetzl, E. Patent WO0184645, Nov 8, 2001, published.

- Yu, G.t; Gao, Y.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science 1995, 270, 1789–1791. Matsumoto, K.; Fujitsuka, M.; Sato, T.; Onodera, S.; Ito, O. J. Phys. Chem. B 2000, 104, 11632–11638.
- Al-Ibrahim, M.; Ambacher, O.; Sensfuss, S.; Gobsch, G. Appl. Phys. Lett. 2005, 86, 201120/1–201120/3.
- Nierengarten, J.-F.; Eckert, J.-F.; Nicoud, J.-F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617–618. Peeters, E.; van Hal, P. A.; Knol, J.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174–10190. Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Armaroli, N.; Barigeletti, F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479.
- Yamashiro, T.; Aso, Y.; Otsubo, T.; Tang, H.; Harima, Y.; Yamashita, K. *Chem. Lett.* **1999**, 443–444. Hirayama, D.; Yamashiro, T.; Takimiya, K.; Aso, Y.; Otsubo, T.; Norieda, H.; Imahori, H.; Sakata, Y. *Chem. Lett.* **2000**, 570–571. Sànchez, L.; Rispens, M. T.; Hummelen, J. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 838–840.
- Gu, T.; Nierengarten, J.-F. *Tetrahedron Lett.* 2001, 42, 3175–3178. Martineau, C.; Blanchard, P.; Rondeau, D.; Delaunay, J.; Roncali, J. *Adv. Mater.* 2002, *14*, 283–287. Apperloo, J. J.; Martineau, C.; van Hal, P. A.; Roncali, J.; Janssen, R. A. J. *J. Phys. Chem. A* 2002, *106*, 21–31. Obara, Y.; Takimiya, K.; Aso, Y.; Otsubo, T. *Tetrahedron Lett.* 2001, *42*, 6877–6881.
- See examples: van Hal, P. A.; Knol, J.; Lamgeveld-Voss, B. H. W.; Meskers, S. C. J.; Hummelen, J. C.; Janssen, R. A. J. J. Phys. Chem. A 2000, 104, 5974–5988. Segura, J. L.; Martín, N. Tetrahedron Lett. 1999, 40, 3239–3242. Guldi, D. M.; Luo, C.; Swartz, A.; Gomez, R.; Segura, J. L.; Martín, N. J. Phys. Chem. A 2004, 108, 455–467. van Hal, P. A.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J.; Jousselme, B.; Blanchard, P.; Roncali, J. Chem. Eur. J. 2002, 8, 5415–5429. Dhanabalen, A.; Knol, J.; Hummelen, J. C.; Janssen, R. A. J. Synth. Met. 2001, 119, 519–522.
- Guldi, D. M.; Luo, C.; Swartz, A.; Gómez, R.; Segura, J. L.; Martìn, N.; Brabec, C.; Sariciftci, N. S. *J. Org. Chem.* 2002, 67, 1141–1152. Negishi, N.; Takimiya, K.; Otsubo, T.; Harima, Y.; Aso, Y. *Chem. Lett.* 2004, *33*, 654–655.
- Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. Chem. Rev. 2004, 104, 4971–5003. Fox, M. A. Acc. Chem. Res. 1999, 32, 201–207.
- Servet, B.; Horowitz, G.; Ries, S.; Lagorse, O.; Alnot, P.; Yassar, A.; Deloffre, F.; Srivastava, P.; Hajlaoui, R.; Lang, P.; Garnier, F. *Chem. Mater.* **1994**, *6*, 1809–1815. Horowitz, G.; Garnier, F.; Yassar, A.; Hajlaoui, R.; Kouki, F. Adv. Mater. **1996**, *8*, 52–54. Garnier, F. *Philos. Trans. R. Soc. London, Ser. A: Math. Phys. Eng. Sci.* **1997**, *355*, 815–827.
- For a recent review on hydrogen-bonding fullerenes, see: Sánchez, L.; Martín, N.; Guldi, D. M. Angew. Chem., Int. Ed. 2005, 44, 5374–5382.
- De Rege, P. J. F.; Williams, S. A.; Therien, M. J. Science 1995, 269, 1409–1413.
- Guttierrez-Nava, M.; Nierengarten, H.; Masson, P.; Van Dorsselaer, A.; Nierengarten, J.-F. *Tetrahedron Lett.* 2003, 44, 3043–3046.
- Beckers, E. H. A.; Schenning, A. P. H. J.; Van Hal, P. A.; El-Ghayoury, A.; Sanchez, L.; Hummelen, J. C.; Meijer, E. W.; Janssen, R. A. J. *Chem. Commun.* 2002, 2888–2889.

- McClenaghan, N. D.; Absalon, C.; Bassani, D. M. J. Am. Chem. Soc. 2003, 125, 13004–13005. McClenaghan, N. D.; Bassani, D. M. Int. J. Photoenergy 2004, 6, 185–192.
- Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D.; Mammen, M.; Gordon, D. M. Acc. Chem. Res. 1995, 28, 37–44. Simanek, E. E.; Li, X.; Choi, I. S.; Whitesides, G. M. In Lehn, J. M., Ed.; Comprehensive Supramolecular Chemistry; Pergamon: New York, 1996; Vol. 9; Chapter 17.
- McClenaghan, N. D.; Grote, Z.; Darriet, K.; Zimine, M.; Williams, R. M.; De Cola, L.; Bassani, D. M. *Org. Lett.* **2005**, 7, 807–810.
- Robinson, A. P. G.; Palmer, R. E.; Tada, T.; Kanayama, T.; Preece, J. A.; Philp, D.; Jonas, U.; Diederich, F. *Chem. Phys. Lett.* **1998**, 289, 586–590. Lamparth, I.; Schick, G.; Hirsch, A. *Liebigs Ann. Recl.* **1997**, 253–258.
- Huang, C.-H.; McClenaghan, N. D.; Kuhn, A.; Hofstraat, J. W.; Bassani, D. M. Org. Lett. 2005, 7, 3409–3412.
- Cho, Y.-J.; Ahn, T. K.; Song, H.; Kim, K. S.; Lee, C. Y.; Se, W. S.; Lee, K.; Kwangyeol, K.; Seong, K.; Kim, D.; Park, J. T. J. Am. Chem. Soc. 2005, 127, 2380–2381. Kim, K.-S.; Kang, M. S.; Ma, H.; Jen, A. K.-Y. Chem. Mater. 2004, 16, 5058–5062.
- Guldi, D. M.; Rahman, G. M. A.; Prato, M.; Jux, N.; Qin, S.; Ford, W. Angew. Chem., Int. Ed. 2005, 44, 2015–2018.
- 24. Bingel, C. Chem. Ber. 1993, 126, 1957-1959.
- Baron, R.; Huang, C.-H.; Bassani, D. M.; Onopriyenko, A.; Zayats, M.; Willner, I. Angew. Chem., Int. Ed. 2005, 44, 4010–4015.
- 26. Steinbeck, M.; Ringsdorf, H. Chem. Commun. 1996, 1193–1194.

- Sudeep, P. K.; Ipe, B. I.; Thomas, K. G.; Gerore, M. V.; Barazzouk, S.; Hotchandani, S.; Kama, P. V. *Nano Lett.* 2002, 2, 29–35.
- Nicolaou, K. C.; Cho, S. Y.; Hughes, R.; Winssinger, N.; Smethurst, C.; Labischinski, H.; Endermann, R. *Chem. Eur. J.* 2001, *7*, 3798–3823.
- Compare with: Hirayama, D.; Takimiya, K.; Aso, Y.; Otsubo, T.; Hasobe, T.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Sakata, Y. *J. Am. Chem. Soc.* 2002, *124*, 532–533. Imahori, H.; Liu, J.-C.; Hosomizu, K.; Sato, T.; Mori, Y.; Hotta, H.; Matano, Y.; Araki, Y.; Ito, O.; Maruyama, N.; Fujita, S. *Chem. Commun.* 2004, 2066–2067.
- Lahav, M.; Heleg-Shabtai, V.; Wasserman, J.; Katz, E.; Willner, I.; Dürr, H.; Hu, Y.-Z.; Bossmann, S. H. *J. Am. Chem. Soc.* 2000, *122*, 11480–11487. Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* 2001, *123*, 100–110.
- Brabec, C. J.; Padinger, F.; Hummelen, J. C.; Janssen, R. A. J.; Sariciftci, N. S. Synth. Met. 1999, 102, 861–864.
- Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. J. Am. Chem. Soc. 1987, 109, 3559–3568.
- Ulman, A. Chem. Rev. 1996, 96, 1533–1554. Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Chem. Rev. 2005, 105, 1103–1169. Rong, H.-T.; Frey, S.; Yang, Y.-J.; Zharnikov, M.; Buck, M.; Wühn, M.; Wöll, C.; Helmchen, G. Langmuir 2001, 17, 1582–1593. Cyganik, P.; Buck, M. J. Am. Chem. Soc. 2004, 126, 5960–5961.
- Ekgasit, S.; Yu, F.; Knoll, W. Langmuir 2005, 21, 4077–4082.