(Table 1). Finally, iii) the cyclohexyl functionalization reduces the molecular flexibility of the branches. DFT and TD-DFT show in fact that, whereas BT1 and BT2 have several isomers and are quite flexible (several local minima with comparable total energy being present), for BT3 only one ground-state energy minimum is found due to the presence of the cyclohexyl groups that strongly stabilize the conformation, thus increasing the molecular rigidity.

In order to show effectively that the cyclohexyl groups suppress the non-radiative decay channels, we have calculated the radiative (τ_r) and non-radiative (τ_{nr}) decay times of BTs via the relations $\eta_{PL} = \tau_{PL}/\tau_r$, $\tau_{PL}^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$, where τ_{PL} is the PL decay time in the solid state measured by time-resolved (TR) PL experiments. A strong increase in the PL efficiency, from 2–4 % to 21 %, in fact occurs for BT3. The measured τ_{PL} (Table 2) increases by almost one order of magnitude going from 0.10 ns in BT1 to 0.86 ns in BT3. Consequently, the calculated τ_r is only weakly affected by both oxygen and cyclohexyl functionalization, the τ_{nr} increases by one order of magnitude going from the less efficient BT1 (0.10 ns) to the efficient compound BT3 (1.09 ns).

These results show the key role of cyclohexyl groups in changing the supramolecular structure, the molecular conformation, and the stiffness of these molecules—reducing the electronic de-excitation via non-radiative channels. Since the energetic barrier between the cathode and the emissive layer is not substantially changed from BT2 to BT3 (Table 3), the reduction of non-radiative pathways turns out to be the main cause of the EL performance increase.

In conclusion, we have realized very bright thiophene-based OLEDs by a new approach based on the replacement of the conventional linear structure of the oligothiophenes by a branched structure. Substitution of these compounds with oxygens and cyclohexyls allowed us to realize devices exhibiting a luminance as high as 10 500 cd m^{-2} and an EL efficiency up to 0.45 % in air, which are the best results to date obtained for oligothiophene-based OLEDs, making these materials excellent for display technology.

Experimental

Devices: The OLEDs were fabricated by spin-coating a 100 nm thick hole-transporting layer, namely PEDOT doped with PSS, onto a pre-cleaned and oxygen-plasma-treated ITO (120 nm, 15 Ω/□) coated glass substrate. The active layer was spin-cast from chloroform solution (10^{-2} M) onto the PEDOT layer and finally the cathode (Ca, 100 nm, followed by Al, 150 nm) was deposited on the active medium by thermal evaporation at a pressure of 10^{-6} mbar. The device characterizations were carried out in air at room temperature.

Instrumentation: PL and PL efficiency measurements were performed on thin films, cast from chloroform solution (10^{-2} M), by exciting the samples with a He–Cd laser (used also to measure the PL of the solutions; 325 nm) in an integrating sphere and detecting the homogeneous signal using a charge-coupled device (CCD) spectrograph. Absorption measurements were carried out using a UV-vis spectrophotometer. Time-resolved PL measurements were made using a Ti-Sapphire-mode locked laser delivering 2 ps pulses at 85 MHz repetition rate. The luminescence was dispersed by a 0.24 m single monochromator coupled with a streak camera equipped with a two-dimensional CCD. The overall time resolution was about 8 ps.

Computational Details: Ground-state geometries were computed with the hybrid B3 LYP exchange-correlation (XC) energy functional and a TZVP basis-set (for BT3 this means 1439 cartesian basis functions). For excitation energies and excited-state geometries an SV(P) basis set was used. Emission energies are obtained as excitation energies of the molecules in their first singlet excited-state geometry. The method was described by Furche and Ahlrichs [8]. We note that the use of a hybrid XC kernel is required for the correct treatment of charge-transfer contributions. All calculations were performed on a Compaq Alpha-Server SC, using the parallelized quantum-chemistry package TURBOMOLE [13]. We thank R. Ahlrichs for providing the TURBOMOLE program and G. Aloisio for his support.

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Surface-Initiated, Enzymatic Polymerization of Biodegradable Polyesters**

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Surface-initiated polymerization has intensively been studied as a new method for grafting polymers onto surfaces because of the possibility of achieving high polymer-grafting density and controlling physicochemical properties of surfaces

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vertically and laterally.[1–5] Among the polymers studied, thin films of a biocompatible and/or biodegradable polymer would find their applications in the biomedical areas, such as passivation of drug-delivery devices and implants, generation of microenvironments for tissue engineering, and formation of biologically responsive surfaces.[6] Many polymerization methods have been applied to surface-initiated polymerization, including radical,[1] cationic,[2] anionic,[3] ring-opening metathesis,[4] and ring-opening polymerization.[5] Biocompatible polymers, such as poly(methylmethacrylate) and poly(*N*-isopropylacrylamide), have been grown from surfaces by radical polymerization[1a–h] and biodegradable aliphatic polyesters, such as poly(ε-caprolactone) (PCL), poly(lactic acid) (PLA), and poly(*p*-dioxanone) (PPDX), by metal-catalyzed, ring-opening polymerization.[5a–f] The catalysts used so far for growing polyesters from surfaces are $Sn(Oct)_2$, $Sn(OTf)_2$, and $AlEt_3$. Stannous(II) 2-ethylhexanoate ($Sn(Oct)_2$) is preferably employed as a catalyst for ring-opening polymerization of biodegradable aliphatic polyesters because of its approval from the Food and Drug Administration (FDA).[7] It is, however, desirable to use more environmentally friendly and less hazardous catalysts than metal catalysts for wider clinical use of aliphatic polyesters, and in this respect an enzyme has been studied as a catalyst for solution or bulk polymerization of lactones and cyclic carbonates, including PCL and PPDX.[8] In this paper, we report the first example of enzyme-catalyzed, surface-initiated polymerization of biodegradable polyesters, PCL and PPDX, on a gold surface. Figure 1 outlines the procedure: 1) the formation of self-assembled monolayers (SAMs) of 1-mercaptoundec-11-yl-tri(ethylene glycol) on a gold substrate to introduce hydroxyl groups and 2) the polymerization of the monomer, ε-caprolactone (ε-CL) and *p*-dioxanone (PDX), from the surface catalyzed by an enzyme.

The enzyme used in this study was lipase B (Novozym-435 from *Candida antarctica*).[9] Figure 2 shows a proposed mechanism of enzymatic, ring-opening polymerization of PCL (and other lactones and cyclic carbonates) from surfaces.[8] The initiation step involves a ring opening of ε-CL by a serine residue

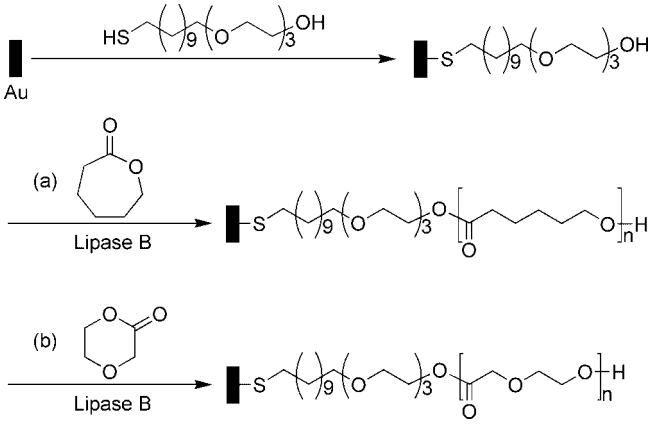

Fig. 1. Schematic description of the procedure. a) Polymerization of ε-caprolactone and b) polymerization of *p*-dioxanone.

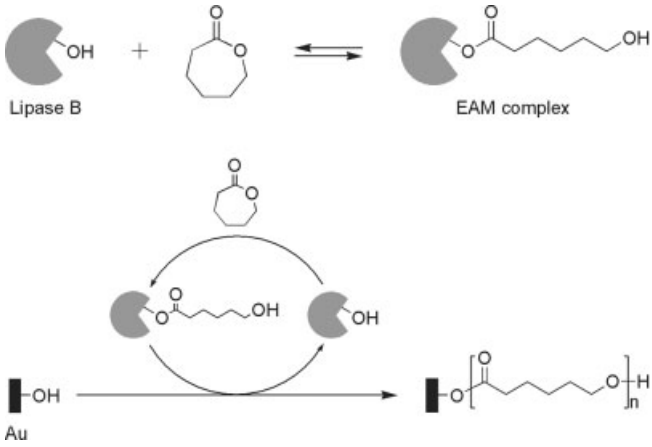

Fig. 2. Proposed mechanism for enzymatic polymerization of PCL (and other aliphatic polyesters) from surfaces.

at the active site (Ser105-His224-Asp187, where Ser: serine, His: histidine, and Asp: aspartic acid) of lipase B.[10] The ring-opening reaction generates an enzyme-activated monomer (EAM) complex, which would contain a highly reactive ester functionality. The EAM complex is then either hydrolyzed by residual water or attacked by hydroxyl-containing molecules. In solution polymerization the hydrolysis usually generates the initiator of polymerization in the absence of other hydroxyl-containing molecules. The mechanism therefore implies that PCL (and other aliphatic polyesters) could be grown from surfaces presenting hydroxyl groups by lipases: the surface-bound hydroxyl group competes with the initiator generated in solution if any. Lipase acts as a carrier of the activated monomer and the polymer chain is grown from the surface.

After a formation of SAMs terminating in hydroxyl group on gold, we mixed lipase B (0.25 g) and ε-CL (10 mmol) in anhydrous toluene (20 mL) containing the SAM-coated substrate, and heated the mixture at 55 °C for 24 h. The infrared (IR) spectrum of the film (93 nm thick, based on ellipsometric measurement) showed peaks characteristic of PCL at 2944 cm^{-1} (C–H stretching), at 1736 cm^{-1} (CO ester), and at 1165 and 1236 cm^{-1} (C–O–C stretching) (Fig. 3b). Water contact angles changed from 32° to 73° after the polymerization, showing the hydrophobic nature of PCL. Gel permeation chromatography (GPC) was used to characterize polymers grown in solution, which would give an insight into the polymers grown from the surface.[5c–e] The weight-average molecular weight (M_w) was 33 600 and M_w/M_n (M_n: number-average molecular weight) was 1.93. The M_w/M_n value is in agreement with the reported value (1.4–1.9) and a number of factors were suggested as the origin of the high M_w/M_n value, including random degradation between water and polymer chains, alcoholysis, and enzyme-catalyzed transesterification.[8] The morphology of the PCL films was characterized by atomic force microscopy (AFM; Fig. 4a). The PCL film was quite uniform: the root-mean-square (RMS) was about 1 nm for the 93 nm thick film. Although the M_w/M_n value of the polymers grown in solution is not directly related to the M_w/M_n value of the polymers grown from the surface, it would be

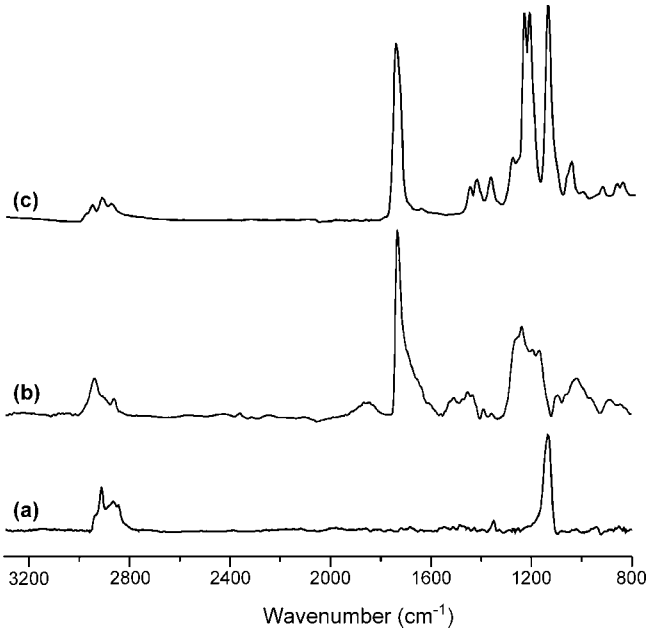

Fig. 3. PIERS spectra of a) SAMs of 1-mercaptoundec-11-yl-tri(ethylene glycol), b) the PCL film, and c) the PPDX film.

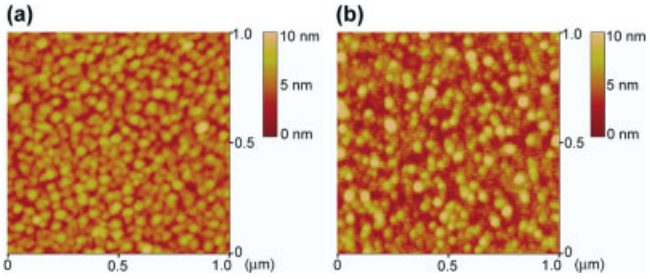

Fig. 4. Tapping-mode AFM images of a) the PCL film and b) the PPDX film.

generally acceptable to assume that the latter would be at most the same as the former. Therefore, the uniformity of the film is noteworthy, but we cannot exclude the possibility that the surface-grown PCL chains collapsed to generate the apparent uniformity although the surface-grown PCL had a high value of polydispersity and/or the polymerization did not occur at every potential initiation sites.

Several control experiments were performed to make sure that the PCL film was grown from the surface. The same polymerization conditions (0.25 g of lipase B and 10 mmol of ε-CL; heating at 55 °C for 24 h) were applied to a gold substrate presenting methyl groups, which was formed as a SAM of hexadecanethiol. The IR spectrum of the resulting surface did not show any peaks from PCL. Lipase B was also required for the polymerization: in the absence of lipase B, we did not observe any formation of polymers. PCL (grown in solution) might be grafted to the hydroxyl-terminated surface by a "grafting-onto" pathway, and this possibility was tested. We polymerized ε-CL (10 mmol) in the absence of the substrate at 55 °C for 24 h, placed the hydroxyl-terminated gold substrate in the reaction vessel, and heated the mixture at 55 °C for additional 24 h. A PCL film was formed on the gold substrate and the thickness of the film was 53 nm. This result suggests either lipase B remained active after 24 h and ε-CL was still present in the reaction mixture, or the solution-grown polymer was grafted to the surface. To decide the possibility of the "grafting-onto" pathway directly, we mixed lipase B (0.25 g) and PCL (1 g), which had been polymerized in solution and been purified, in anhydrous toluene (20 mL) containing the hydroxyl-terminated gold substrate, and heated the mixture at 55 °C for 24 h. No polymeric film was formed by this procedure, which clearly confirms that the PCL film was formed via the "grafting-from" pathway, not the "grafting-onto" pathway.

The PPDX film was also grown on the gold surface by heating a mixture of lipase B (0.25 g) and PDX (24 mmol) in anhydrous toluene (20 mL) containing the SAM-coated substrate at 55 °C for 24 h. The characteristic IR peaks of PPDX appeared at 2923 cm^{-1} (C–H stretching), at 1741 cm^{-1} (CO ester), and at 1138 and 1214 cm^{-1} (C–O–C stretching) (Fig. 3c).[11] A negative-ion secondary-ion mass spectrometry (SIMS) showed peaks at m/z 58 ($C_2H_2O_2^-$), 59 ($C_2H_3O_2^-$), 71 ($C_3H_3O_2^-$), 73 ($C_3H_5O_2^-$), and 89 ($C_3H_5O_3^-$), and X-ray photoelectron spectroscopy (XPS) analysis showed peaks at 289 eV (C 1s, C–O–C=O) and 533 eV (O 1s, C–O). Figure 4b shows an AFM image of the PPDX film, where the RMS was approximately 1 nm with 11 nm thick PPDX films. Control experiments confirmed that PPDX was grown from the surface by the "grafting-from" pathway: no PPDX film was formed by heating a mixture of lipase B and PPDX in anhydrous toluene containing the hydroxyl-terminated gold substrate.

In summary, we demonstrated the first surface-initiated, enzymatic polymerization of aliphatic polyesters, poly(ε-caprolactone) and poly(p-dioxanone). Biocompatible/biodegradable polymers have been used as coating materials in biomedical areas, such as passive or active coating of stents. The method reported in this paper would be beneficial in the applications where minimization of harmful species is critical, considering a growing interest in enzyme-catalyzed polymerization. We used an immobilized lipase B (Novozym-435) and the steric crowding might preclude a uniform growth of polymers from surfaces. Polymerization of polyesters catalyzed by other enzymes, including unbound lipases, is under investigation.

Experimental

Lipase B-Catalyzed, Surface-Initiated Polymerization: 1-Mercaptoundec-11-yl-tri(ethylene glycol) ($HS(CH_2)_{11}(CH_2CH_2O)_3OH$) was synthesized by following the reported procedure [12]. The surface presenting hydroxyl groups was generated by immersing a gold substrate into an EtOH solution of 1-mercaptoundec-11-yl-tri(ethylene glycol) (2 mM) for 12 h. Lipase B used in this study contained a huge amount of water and we were not successful in polymerizing the monomer (ε-CL and PDX) from the surface without any pre-treatment. We placed the SAM-coated substrate and lipase B in a reaction vessel and dried

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them under vacuum at 55 °C for 24 h. After drying, anhydrous toluene and the monomer (ε-CL or PDX) were added sequentially using a syringe pump. The reaction mixture was stirred under an argon atmosphere at 55 °C for 24 h. To remove any physisorbed polymers that were polymerized from hydroxyl-terminated impurities in solution or water the substrate was thoroughly washed and sonicated for 5 min. The solvent was 1,2-dichloroethane for PCL and 1,1,1,3,3,3-hexafluoro-2-propanol for PPDX, respectively. Prior to analysis, the substrate was further dried under reduced pressure at room temperature for 24 h.

Instrumentation: Polarized IR external reflectance spectroscopy (PIERS) spectra were recorded on a Thermo Nicolet Nexus Fourier-transform infrared (FTIR) spectrometer in single reflection mode. The *p*-polarized light was incident at 80° relative to the surface normal of the substrate. A narrow band mercury–cadmium–telluride (MCT) detector was used. We averaged 1024 scans to yield the spectrum at a resolution of 4 cm^{-1}. The sample compartment was purged with dry and CO_2-free air. An ellipsometer (Gaertner L116 s) equipped with a He–Ne Laser (632.8 nm) was used to determine the thickness of the films. Contact angles were determined using a Phoenix 300 apparatus (Surface Electro optics Co. Ltd, Korea). Gel permeation chromatography (GPC) traces were obtained at room temperature by Waters 210 GPC. The concentration of polymer samples was 1.0 mg mL^{-1} with a flow rate of 1.00 mL min^{-1} and injection volume of 200 μL. XPS study was performed with a VG-Scientific ESCALAB 250 spectrometer with monochromatized Al Kα X-ray source. Secondary-ion mass spectra were recorded by a PHI 7200 time-of-flight secondary ion mass spectrometer. AFM images were recorded using a Nanoscope IIIa apparatus (Veeco). We used tapping-mode AFM to image the polymer films.

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Photosensitive Pentacene Precursor: Synthesis, Photothermal Patterning, and Application in Thin-Film Transistors

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Organic semiconductors have attracted considerable interest for use as active channels in electronic and photonic devices, such as organic thin-film transistors (OTFTs),[1] photovoltaic cells, and light modulators. These materials are compatible with plastic substrates and thus are advantageous for lightweight, large-area electronics applications that require structural flexibility. Thin-film transistors with organic semiconductors as active channel material have made significant progress in the past decade and their utility in active matrix displays[1a,2–4] and integrated circuits[5–8] has been demonstrated. The technology that is believed to have the highest potential for minimizing the manufacturing cost of large-area electronics requires the use of soluble organic semiconductors, which include polymers, oligomers, and other small molecules, for solution deposition. This approach, combined with direct patterning techniques, such as large-area stamping,[4] screen printing,[9] and inkjet printing,[10] are very attractive and suitable for relatively low-resolution patterning in the range 25–100 μm. While higher-resolution (10–20 μm) inkjet printing has been demonstrated[11] by patterning of conducting polymers, it involves an additional costly step of standard lithography for defining hydrophilic–hydrophobic regions on the substrate. In these techniques only the source and drain electrodes are patterned to define the channel length and the organic semiconductor is uniformly coated and its coverage is not limited to the channel area. These approaches might satis-

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