Chem. Mater. **2004,** *16,* 2852−2856

Electrochemical Patterning of a Polyfluorene Precursor Polymer from a Microcontact Printed (*μ*CP) Monolayer

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Received March 17, 2004. Revised Manuscript Received May 21, 2004

Selective area electropolymerization of a precursor polymer in a microcontact printed pattern was used to generate a patterned conjugated and fluorescent polymer thin film. The precursor polyfluorene polymer, which has photoluminescent properties defined by the polymer main chain and electropolymerizability from the pendant carbazole units, was synthesized using a Yamamoto coupling route. The polymer was then electrochemically deposited and cross-linked selectively on the alkyl SAM defined regions to form patterns (<50 nm height) with high fidelity. The patterns were characterized by atomic force microscopy and optical fluorescence microscopy. The fluorescence micrograph confirmed that the polymer main chain was largely unaffected by redox electrochemistry and showed highly regular patterning characteristics in a large area. This new combination of site-selective electropolymerization and the precursor approach should provide a unique way to make patterned conjugated polymer systems.

Introduction

π-Conjugated polymers have attracted a lot of attention during the past few decades because of their applications in organic electronic displays and semiconductor devices. Depositing conjugated polymers in a dimensionally controlled fashion is desirable. Microelectronics devices are inherently dependent on the construction of circuitry from micrometer and even nanometer size features.[1] In fabricating micropatterned conjugated thin films, a number of methods have been developed including area-selective electropolymerization,[2] photochemical patterning,[3] micromolding in capillaries,[4] microcontact printing,[5] and ink-jet printing.[6]

Under certain conditions, densely packed self-assembled monolayers (SAM) of alkylthiols can block interfacial electron transfer between solution and electrode. For example, a long-chain alkyl mercaptan monolayer is effective at blocking the access of a variety of redox molecules to the electrode in water. On the other hand, acetonitrile solutions appear to render the monolayer permeable to redox reactions.[7] This behavior can have important implications in selective deposition or patterning approaches in a electrochemical processes. In principle, by choosing the appropriate electrochemical conditions, SAMs can be used to allow or block the electrochemical deposition of electropolymerizable monomers. Therefore, by carrying out the electropolymerization using a patterned SAM on a Au working electrode, monomers can be electropolymerized only in the selective exposed regions of the electrode, generating patterned conjugated polymer thin films. This concept was previously demonstrated with polypyrrole thin films.[8] In this case, polypyrrole was electropolymerized on the exposed regions of a patterned Au electrode. The self-assembled monolayer was fabricated by microcontact printing (soft-lithography) or μCP. Besides microcontact printing, selective irradiation with UV light (photolithographic) has been used to fabricate SAMs and perform electrodeposition.[9]

Recently, we have developed a “precursor polymer” route to fabricating ultrathin network conjugated polymer films. We have demonstrated the method with a series of precursor polymers such as polyfluorenes,[10] polythiophene,[11] and polypyrrole.[12] The polyfluorene system in particular was interesting because the blue

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10.1021/cm049544g CCC: $27.50

light emitting properties of the polyfuorene polymer were maintained after electrodeposition. Electropolymerization occurred through the attached pendant carbazole groups on the main chain polyfluorene, which both cross-linked the polymer and grafted it to the indium tin oxide (ITO) electrode surface. In this report, we wish to present our results on the soft-lithographic electrochemical patterning of a polyfluorene precursor polymer, which has potential applications in micropatterned polymeric electroluminescent devices.[13]

Experimental Section

Materials. The synthesis procedure for the precursor polyfluorene, P4F4C2E, was done according to previous publications.[10,14] Tetrabutylammonium hexafluorophosphate, octadecane thiol, and anhydrous methylene chloride were purchased from Aldrich and used as received. Absolute ethanol was purchased from Fisher and used as received.

Monolayer Deposition. Freshly evaporated gold films (50−100 nm) on BK7 glass substrates (with ~2 nm Cr as adhesion layer) were immersed in a solution of the octadecane thiol (10 mM) in ethanol overnight followed by rinsing with copious amounts of ethanol and blow-dried with dry nitrogen. The thickness of a monolayer was monitored by surface plasmon spectroscopy and was of the order of 1.8 nm. This verified the cleanliness and the viability of the gold substrates for a SAM procedure.

Microcontact Printing. The poly(dimethylsiloxane) (PDMS) elastomeric stamp (fabricated from a photolithographed master stamp) was cleaned with ethanol in an ultrasonic bath prior to use. The stamp was soaked in a 10 mM solution of octadecylthiol (Aldrich) in ethanol, blown dry with a dry nitrogen flow, and then pressed gently on the gold electrode for 30 s. The electrode was then rinsed with solvent and dried by continuous nitrogen flow. The electrode was used immediately for the electrochemistry procedure.

Electrochemistry. All potentiostatic and cyclic voltammety (CV) experiments were performed using a one-compartment, three-electrode electrochemical cell driven by an EG&G PAR system (Model 263A). Vacuum evaporated gold films (45 nm) on BK-7 glass substrates (~2 nm chromium layer was evaporated as an adhesive layer) were used as working electrode; the counter electrode was a platinum wire, and an Ag/Ag^+ nonaqueous electrode was used as reference. All the potentials referred in this paper are according to this reference. All solutions were carefully purged by dry nitrogen prior to the electrochemical measurements.

Instrumentation. NMR spectra were collected on a Bruker ARX 300 spectrometer using chloroform-*d* as the solvent and TMS as the internal standard. The UV−vis spectra were obtained on a Perkin-Elmer spectrophotometer (Lambda 20) with a quartz cuvette. Photoluminescence spectra were recorded on a Perkin-Elmer spectrofluorometer (LS50B) equipped with a Xe lamp and a quartz cell. Size-exclusion chromatography (SEC) data were measured using a Waters Chromatography setup and polystyrene calibration standards. Six columns with different pore sizes were connected serially to achieve the best resolution for different molecular weights of polymers. Fluorescence microscopy was done using an inverted Olympus IX70 fluorescence microscope. Atomic force microscopic (AFM) images were taken by tapping mode in air and ambient conditions using a Nanoscope II scanning probe microscopy (Digital Instruments) system equipped with a 150 × 150 μm scanner and Si_3N_4 cantilever.

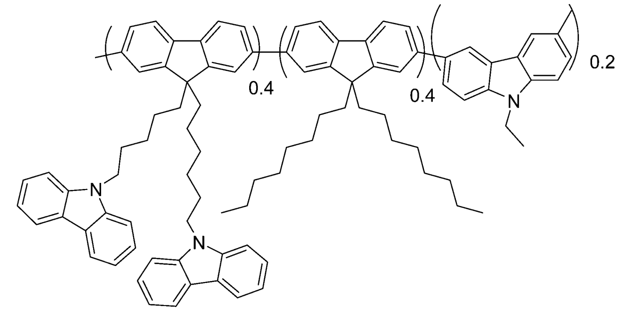

Figure 1. Chemical structure of P4F4C2E showing a statistical copolymer composition between fluorene and carbazole units.

Figure 2. Proton NMR peak assignment of the P4F4C2E copolymer. Between 7 ppm and 9 ppm are the aromatic proton assignments, and 4.0 and 4.4 ppm are from the aliphatic protons directly linked to the nitrogen in the carbazole units. The peak at 4.4 ppm is related to the carbazole units present in the main chain.

Results and Discussion

The electropolymerizable precursor polymer, P4F4C2E, has a chemical structure as shown in Figure 1. This polymer was synthesized by a nickel mediated coupling reaction, the so-called Yamamoto coupling reaction. The feed ratio of the three monomers is 4:4:2 for fluorene-carbazole:fluorene alkyl:carbazole, respectively. The polymer synthesis was done according to our previously published procedures.[10,14] The pendant carbazole groups are introduced to provide electrochemically cross-linkable units. Chemical coupling occurs when the carbazole monomers are oxidized either by electropolymerization or chemical oxidation. The other reasons for introducing carbazole units to the main chain are 2-fold. First, the introduction of carbazole into the polyfluorene backbone can increase the hole transport ability for a semiconductor device. Second, the kink linkage caused by the carbazole units can diminish the aggregation of the polymer. Figure 2 shows the proton NMR of this copolymer. The broad peaks of resonance indicate a polymeric structure. The peaks between 7 ppm and 9 ppm are in accordance with the aromatic proton assignments. Two broad peaks at around 4.0 and 4.4 ppm are from the aliphatic protons directly linked to the nitrogen in the carbazole units. Among these resonances, the peak at 4.4 ppm is related to the carbazole units present in the main chain. By comparing the integrated area under each peak, we are able to obtain a ratio between the two monomers (carbazole main chain and as fluorene side groups) at about 1:4. This result is consistent with the feed ratio of the polymerization. In addition, the results from the elemental analysis, which shows a composition of C: 87.88; H: 8.07; and N: 3.02, agree with the calculated values (C: 88.92; H: 8.03; N: 3.05). The molecular weight of the polymer was characterized by size exclusion chromatography against polystyrene standard. The number-average molecular weight, Mn,

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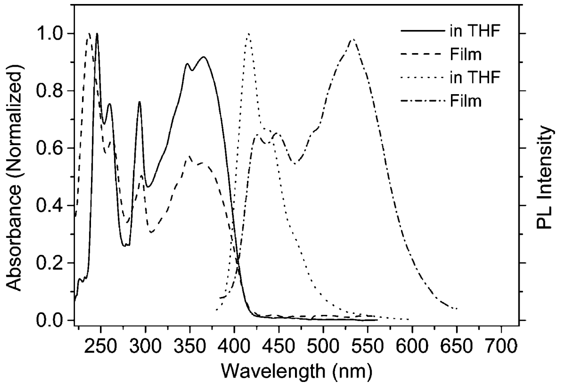

Figure 3. Absorption (— and - - -) and photoluminescence (.... and -.-.-) spectra of P4F4C2E in THF solution and solid-state film. Important photoluminescence peak observed at 532 nm due to excimer formation.

is 7200 with a polydispersity of 3.0. The polymer showed high thermal stability with only a 5% weight loss at above 400 °C. Figure 3 shows the spectroscopic properties of P4F4C2E in THF solution and film state. It exhibits similar properties as the polymers we reported previously. The peak positions of the absorption spectra in solution and film are almost identical. However, the intensity of each peak varies. The peak at around 364 nm is according to the $\pi-\pi^*$ transition of the polyfluorene polymer. The peaks at higher energies around 346, 294, 260, and 245 nm are from the carbazole unit and/or from other vibrational energy levels of the conjugated main chain. In the film state, the populations of the transitions are different from that of the solution. Therefore, the intensity of the peaks at different wavelength changes. On the contrary, the PL of the polymer in solution and film shows significant difference. It shows two vibronic peaks at 416 nm and 438 nm in solution, which is similar to other polyfluorene polymers. A peak at 532 nm appears in solid-state photoluminescence with the other two vibronic peaks shifting slightly to red at around 425 nm and 448 nm. As has been discussed by others, a featureless emission at around 530 nm can often be observed from polyfluorene films, and it is attributed to the emission of excimers or fluorenones.[15] Previously we have demonstrated that the introduction of the "kink" caused by carbazole in the main chain can avoid the excimer emission in the freshly prepared films. The bulky nature of the carbazole side chain should not allow good packing between different polyfluorene chains. Therefore, a possible explanation here is that the emission at 532 nm is attributed to the exciplex formed by the carbazole and the polyfluorene. The similarity of the absorption spectra in solution and solid state implies that the new emissive species is not directly accessible from the ground state. This is not without basis since the exciplex emission form polymer blends of poly(vinyl carbazole) and other conjugated polymers has been observed by others.[16]

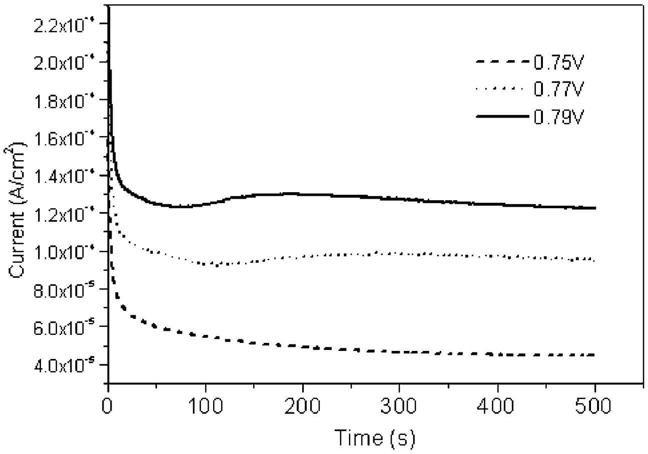

Figure 4. Electropolymerization of P4F4C2E under different potentiostatic conditions in methylene chloride using TBAH as supporting electrolyte.

The electropolymerization processes of the polymer were then investigated under both potentiostatic conditions and cyclic voltammetry. Figure 4 shows the current response of the electropolymerization under potentiostatic conditions. Unlike electropolymerization of monomers,[17] which shows typical nucleation and propagation processes, the current did not show much increase even at high potentials. The current first decreased rapidly at different potentials. At 0.75 V, the current kept decreasing slowly and remained at a very low level. This indicated that a cross-linked polymer film was deposited at this potential. When the potential increased, the nucleation process became fast, but film growth was much slower compared with simple electropolymerization of electroactive monomers. AFM images of the polymer films showed smooth surface morphologies similar to our previous results.[10−12] The electrodeposition rate is likely determined by the conductivity of the deposited film. When the cross-linked network polymer was deposited on the electrode, it attenuated the electron-transfer rate between the electrode and the solution, which resulted in a passivated film with low conductivity.

Thin films can also be deposited by cyclic voltammetry. The carbazole units were oxidized when the potential was swept toward the positive direction (cathodic). The increase of the oxidation wave and the corresponding reduction wave indicated that network electropolymerization occurred. The oxidation potential of the coupled species remained almost at the same potential, at around 0.6 V, while the corresponding reduction wave showed peaks at 0.5 V initially but shifted toward lower potential with increasing number of cycles.

There was a need to examine the electrochemical deposition processes on different conditions and surfaces before the site selective electropolymerization method can be applied to fabricate patterned conjugated polymer thin films. Interestingly, the alkyl SAM did not provide any blocking behavior when the electropolymerization was done in methylene chloride with TBAH

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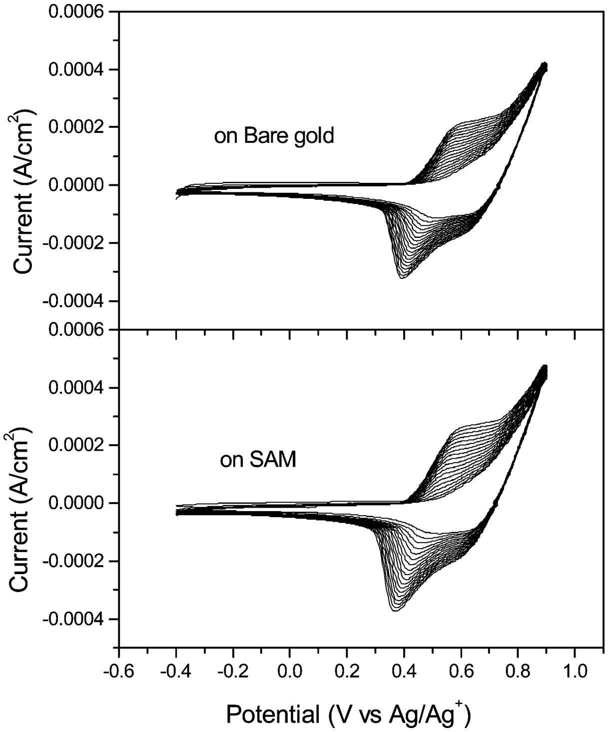

Figure 5. Cyclic voltammogram of P4F4C2E on bare gold (above) and SAM patterned gold electrode (below).

as the supporting electrolyte. Figure 5 shows the CV of the polymer using bare gold and SAM gold as the working electrode. Surprisingly, a small current enhancement was observed for the CV on the SAM. This observation is not necessarily unusual. Collard et al. have previously investigated the electrooxidative polymerization of aniline on electrode modified with SAMs. They found that simple alkanethiol monolayers could not attenuate the electron transfer sufficiently to produce well-defined polyaniline patterns.[18] By examining a number of different terminal groups, they were able to produce patterned polyaniline films. In our case, the hydrophobic interaction may play an important role during the electrochemical deposition process. The fresh gold surface is hydrophilic, and the SAM surface is very hydrophobic. Again, the polymerization solvent used, methylene chloride, was a relatively nonpolar solvent and has no strong affinity toward hydrophilic gold surfaces. On the other hand, the solvent can wet the hydrophobic SAM easily. The polymer itself is also hydrophobic, rendering good adhesion to the hydrophobic SAM. Therefore, the alkyl SAM in this case will serve as an adhesion element rather than an electron-blocking layer. In fact, this affinity difference was used by us to effectively fabricate patterned polymer films.

In this case, a SAM was formed using a microcontact-printing method on a freshly evaporated gold film on glass. This substrate was then used as the working electrode for the electrochemical deposition. Under both potentiostatic and CV conditions, well-defined patterns were produced as examined by atomic force microscopy.

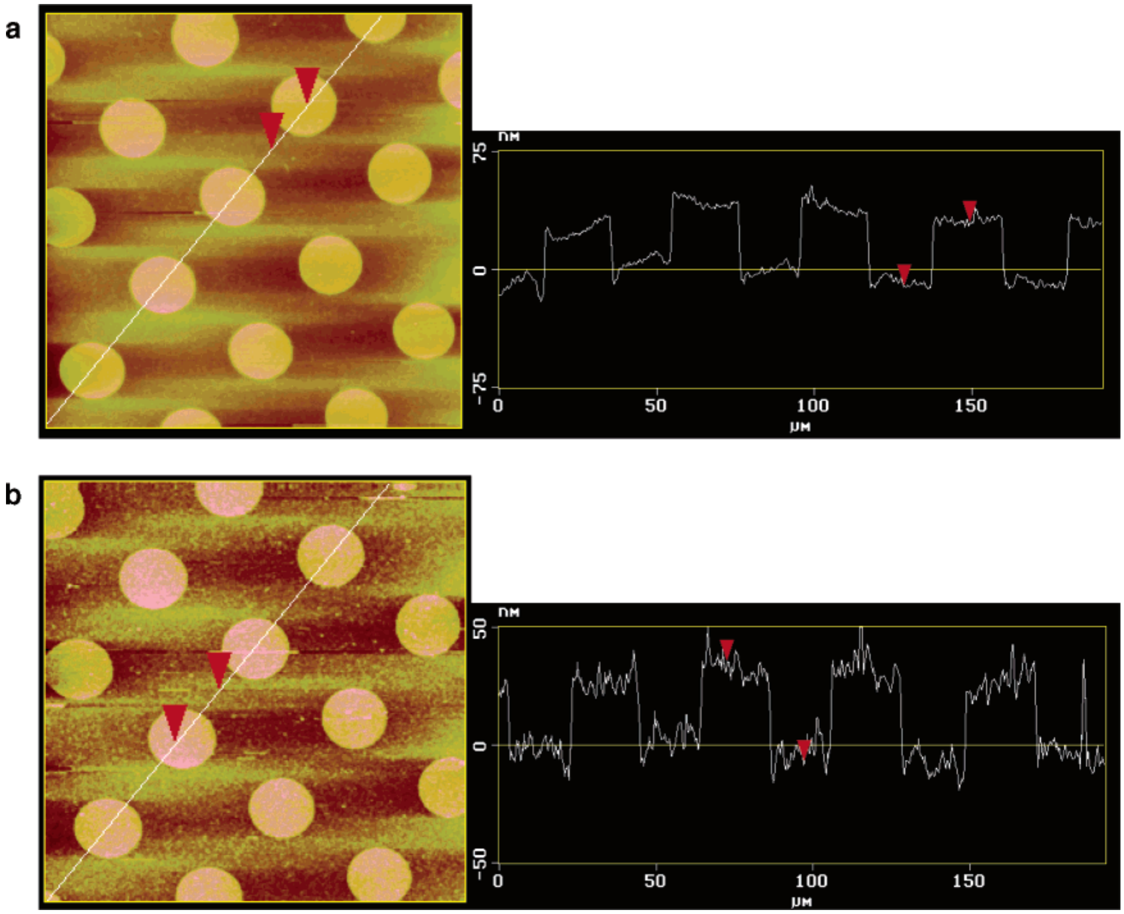

Figure 6. (a) AFM of the soft-lithographically patterned dots from the electrochemically cross-linked polymer. Potentiostatic deposition was used at 0.75 V for 200 s. (b) AFM of the soft-lithographically patterned dots made by sweeping the potential between −0.4 and 0.9 V under cyclic voltammetry conditions.

Figure 6 shows the patterned conjugated polymer films. Figure 6(a) shows the pattern fabricated under potentiostatic conditions. The electrode was held at 0.75 V for 200 s. The electrode was then rinsed thoroughly using methylene chloride to wash away the soluble precursor polymer. The film shows a relatively smooth surface compared with that generated under CV conditions. The height difference is around < 50 nm. Figure 6(b) shows the pattern generated under CV conditions. Although the film is rougher than the potentiostatic film, sharp edges can also be clearly seen from the image. The film roughness clearly shows that under potentiostatic condition, a more compact and smooth film can be deposited. We also investigated the film morphologies deposited under higher potential. The results showed that as the potential increased, the deposition rate increased, and the film roughness also increased. However, even with thicker films, the pattern did not lose its definition. We would like to emphasize the shape edges of the pattern produced under both conditions, which implies a very different deposition rate on the bare region and the SAM modified region of the gold substrate. As has been previously investigated, the microcontact printed SAM is not as compact as those generated from immersing in solution for a long time.[19] Therefore, this loose packed SAM has less effect on blocking the electron transfer. On the other hand, the hydrophobicity, which provides the affinity to the polymer, remains. Thus, polymers are preferably deposited on the SAM pattern modified regions of the electrode.

As mentioned earlier, the electropolymerization occurred through the pendant carbazole units, and the polyfluorene backbone did not undergo any redox reactions in the electropolymerization potential. Therefore, upon dedoping, the fluorescence of the polymers remained. The fluorescence of the polymer films was studied by fluorescence microscopy. Figure 7 shows the fluorescence micrograph of the deposited film. As one can see, regular patterning of the fluorescent polyfluorene films has been produced even in a large area. The film shows uniformity in the whole area and homogeneity in their fluorescence intensity. Of special note is the *insolubility* of these patterns because of the electrochemical cross-linking reaction.

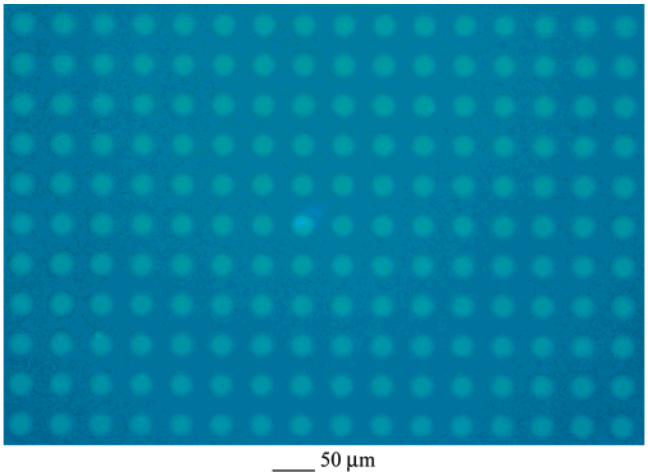

Figure 7. Fluorescence microscopy of the soft-lithographically patterned film made under potentiostatic electropolymerization conditions showing high pattern fidelity.

Conclusions

We have used selective area electropolymerization to generate patterned conjugated and fluorescent polymer thin films. Instead of using electroactive monomers, we have used a precursor polyfluorene polymer, which has fluorescent properties defined by the polymer main chain and electropolymerizability of pendant carbazole units. The polymer preferably deposited on the alkyl SAM defined regions to form sharp patterns. The patterns have been characterized by atomic force microscopy. The fluorescence micrograph confirmed that the polymer main chain was largely unaffected by the redox electrochemistry, and it also showed highly regular patterning characteristics in a large area. This new combination of site selective electropolymerization and the precursor approach should provide a new approach to making micropatterned polymer light-emitting diodes in the future.

Acknowledgment. The authors gratefully acknowledge partial funding from the Robert A. Welch Foundation (E-1551), NSF-CTS (0330127), NSF-DMR (99-82010), and the Max Planck Society.

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