Supporting Information

Electrochemically-deposited benzophenone moieties: Precursors for dual mode patterning of polymer brushes on conducting surfaces

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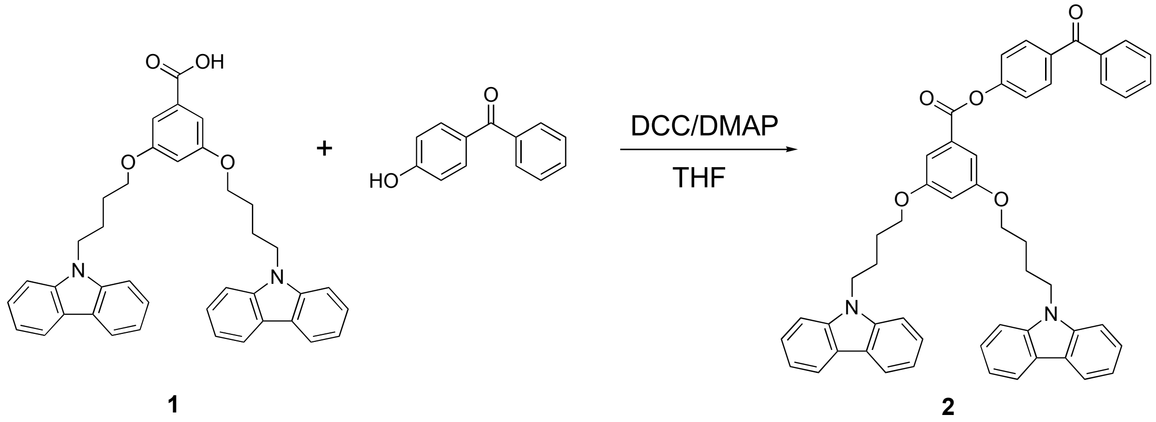
Materials. Reagent chemicals for the synthesis of the electro-active benzophenone photo-crosslinker were purchased from Aldrich and were used without further purification. Tetrahydrofuran (THF) used in the synthesis and polymerization reactions was distilled from sodium/benzophenone ketyl. Polystyrene (250 K) for photo-grafting was obtained from Acros Organics. Patterned ITOs were prepared by taping a transmission electron microscope (TEM) grid on the ITO surface and subsequent exposure with the hydrochloric acid (HCl) vapor. Areas exposed in the HCl vapor were etched, leaving the covered areas unaltered.

Synthesis of 4-benzoylphenyl-3,5-bis(4-(9*H*-carbazol-9-yl)butoxy)benzoate (CbzBP) (2). Hydroxybenzophenone (332 mg, 1.68 mmol), CBz acid (**1**)[1] (1000 mg, 1.68 mmol), 4-dimethylaminopyridine (DMAP) (30.7 mg, 0.252 mmol) and THF were placed in a round bottom flask equipped with a stir bar. The contents were stirred under nitrogen. The reaction flask was then placed in a cold ice-bath. Dicyclohexylcarbodiimide (DCC) (484.1 mg, 2.35 mmol) dissolved in THF was added drop wise into the reaction mixture with vigorous stirring. The reaction was stirred for 5 minutes while in the ice bath and continued stirring at room temperature overnight. The precipitate formed (dicyclohexyl urea (DCU)) was filtered off from the solution. THF was removed under reduced pressure and the residue was then dissolved in dichloromethane (DCM). The DCM layer was washed with dilute $NaHCO_3$ and the resulting DCM layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to obtain the crude product, which was purified by column chromatography (4:1 dichloromethane and hexane) to afford the CBzBP product (**2**) as a white powder (874 mg, 1.12 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$: δ 8.09 (d, J = 7.76 Hz, 4H), 7.82-7.97 (m, 2H), 7.79-7.84 (m, 2H), 7.57-7.63 (m, 1 H), 7.39-7.53 (m, 10H), 7.29-7.34 (m, 8H), 6.61 (t, J = 2.28 Hz, 1H), 4.41 (t, J = 6.88 Hz, 4H), 3.97 (t, J = 6.44 Hz, 4H), 2.04-2.16 (m, 4H), 1.81-1.90 (m, 4H).

Scheme S1. Synthetic route for the preparation of the CBzBP



Electro-deposition of the CBzBP on conducting surfaces. Electrochemical deposition of the CBzBP was carried out using the Parstat 2263 (Princeton Applied Research) instrument equipped with a PowerSuite software. All experiments were done using a three-electrode set-up where Au or ITO substrate was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. A solution of the CBzBP (1 mM) and the supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH) (0.1 M) in dichloromethane was used for preparing the electro-generated CBzBP film. A scan rate of 50 mV/s was employed for the 20-cycle run in a potential window of 0-1.3 V.

Surface Characterization. Null ellipsometry was used to determine the thickness of the films after each surface functionalization. All measurements were conducted using a null ellipsometer (Multiskop, Optrel Berlin) with a He-Ne laser ($\lambda = 632.8$ nm) as a light source. The angle of incidence was set to 60° on all measurements. A multilayer flat film model was used to calculate the thicknesses from the experimentally measured ellipsometric values Δ and ψ, assuming a refractive index of 1.6 for the electrochemically deposited CbzBP film[2] and 1.59 for the PS film.[3] The film thickness was calculated using a fitting program (Elli, Optrel).

All atomic force microscopy (AFM) images were recorded in air under ambient conditions on PicoScan 2500 (Agilent Technologies formerly Molecular Imaging, Corp.) equipped with an 100 × 100 μm scanner. Intermittent contact mode was used for all imaging. The AFM tip used was a silicon-nitride AFM probe from Ted Pella Inc.

A PHI 5700 X-ray photoelectron spectrometer was equipped with a monochromatic Al Kα X-ray source ($h\nu$=1486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. The spectrometer was operated both at high and low resolutions with pass energies of 23.5 eV and 187.85 eV, respectively, a photoelectron take off angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. The survey spectra were collected from 0 to 1400 eV, and the high-resolution spectra were obtained for photoelectrons emitted from C 1s and N 1s. All spectra were collected at room temperature with a base pressure of 1 $\times 10^{-8}$. Electron binding energies were calibrated with respect to the C 1s line at 284.8 eV. A PHI Multipak software (version 5.0A) was used for all data processing.

ATR-IR measurements of the PS film were done using Bio-RAD Digilab FTS700 series spectrometer (Varian). Spectrum (4000-750 cm^{-1}) was collected at 4 cm^{-1} resolution for 16 scans using the UMA 600 detector. Data processing was done using the Win-IR Pro 3.4 software package.

IR-imaging of the patterned brushes were obtained using the Digilab Stingray imaging system consisting of a Digilab FTS 7000 spectrometer, a UMA 600 microscope, and a 32 x 32 mercury-cadmium-telluride IR imaging focal plane array (MCT-FPA) image detector with an average spatial area of 176 μm x 176 μm in transmission mode. Four tiles were used during the imaging employing 16 scans each. All images were processed using the Win-IR Pro 3.4 software package.

Other Supporting Data

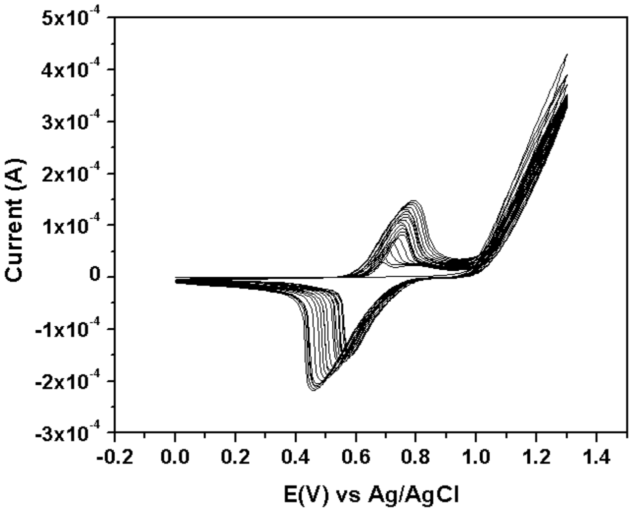


Fig. S1. Cyclic voltammogram during the electro-deposition of the CBzBP.

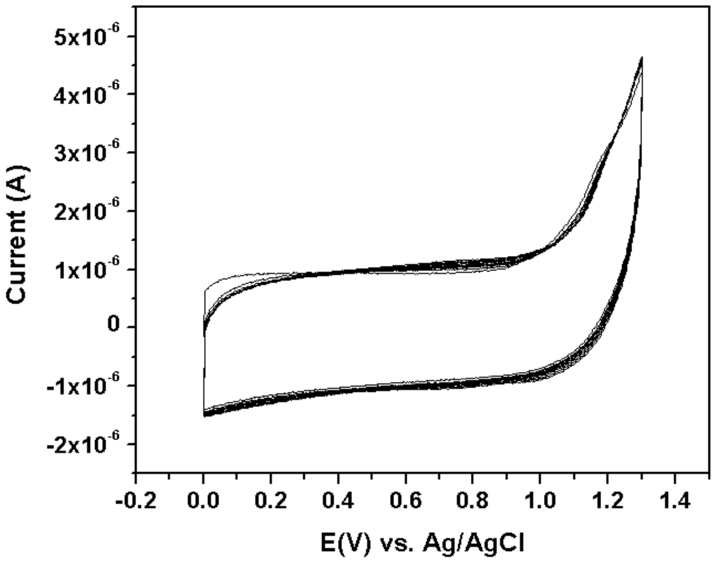


Fig. S2. Cyclic voltammogram of the 1 mM benzophenone in dichloromethane with 0.1M TBAH as supporting electrolyte. No redox peaks were observed at this potential window.

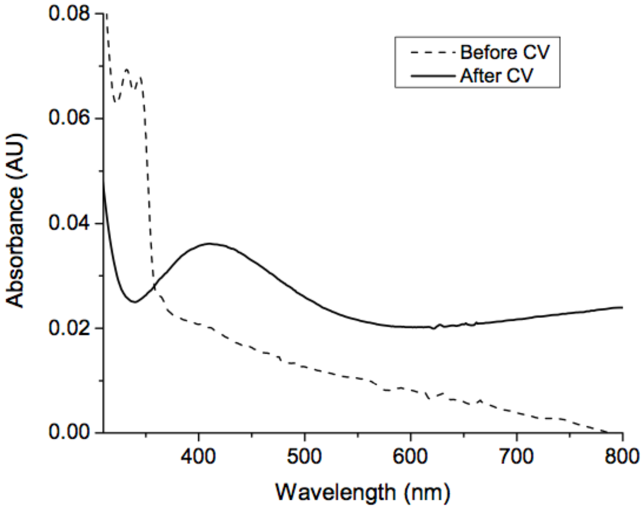


Fig. S3. UV-vis spectra of the electro-deposited CBzBP (solid line) after CV and the spin-coated CBzBP (broken line) on ITO.

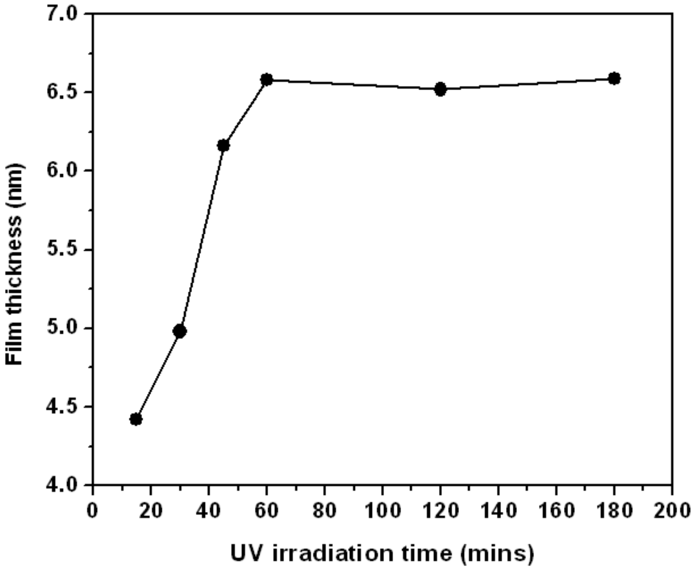


Fig. S4. Dependence of the photochemical attachment of PS on the UV illumination time. Saturation was achieved after one hour.

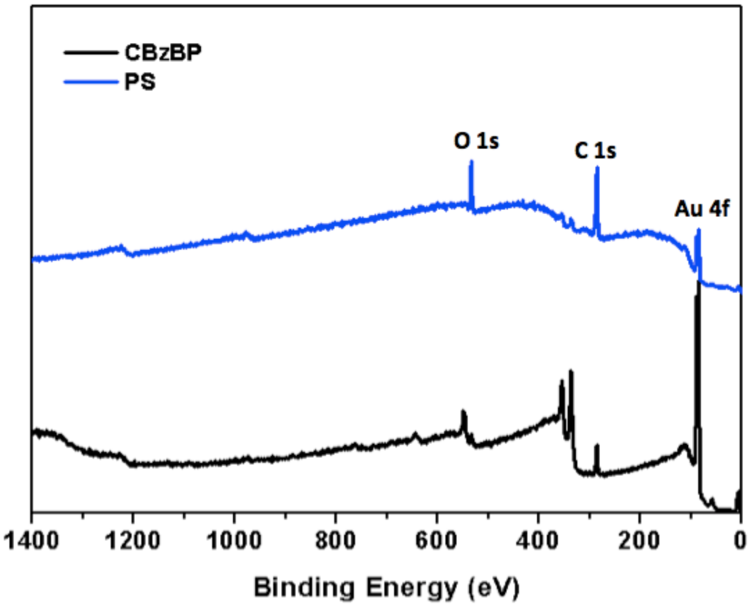


Fig. S5. Survey spectra of the electro-deposited CBzBP (black line) and the photo-grafted PS film after UV irradiation (blue line). *Note:* The signal for N 1s for both films are both small and could not be seen clearly in the survey scan. However, high-resolution scans (see main text) clearly showed the presence of the N 1s peak.

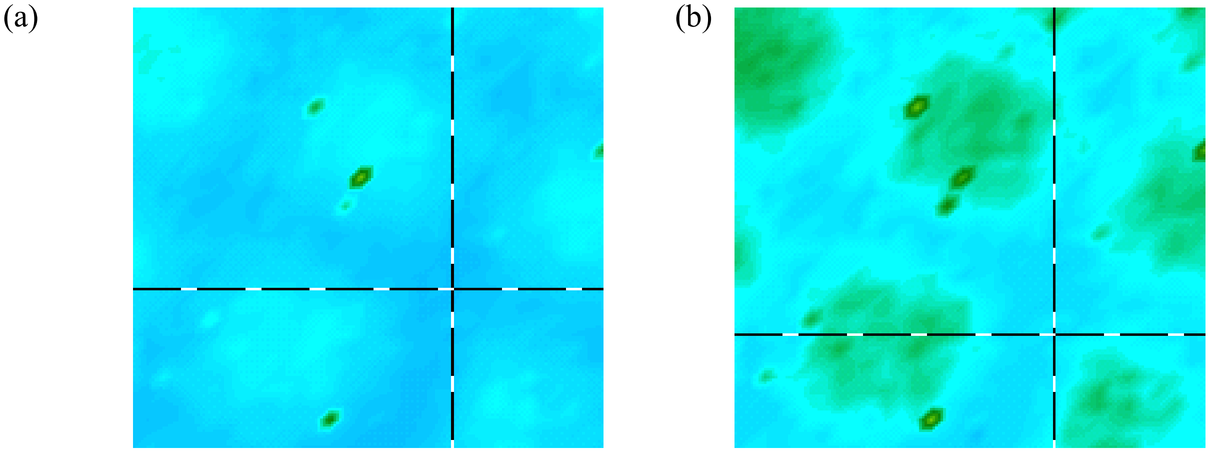


Fig. S6. Other representative images obtained from the IR-imaging analysis. Focused at (a) 1700 cm^{-1} and (b) 2900 cm^{-1}. The image focused at 1700 cm^{-1} did not show a distinct pattern since the PS has no C=O functional groups. The slight image seen may be due to the incomplete photo-crosslinking of the CBzBP, which contains the C=O functionality. The image focused at 2900 cm^{-1}, on the other hand also showed a distinct pattern, similar to the image focused at 3034 cm^{-1} (see main text) due to the presence of the aliphatic C-H stretches in the PS backbone.

References:

1 C. Kaewtong, G. Jiang, M.J. Felipe, B. Pulpoka and R. Advincula, *ACS Nano*, 2008, **2**, 1533-1542.

2 R. Ravindranath, P.K. Ajikumar, S. Bahulayan, N.B.M. Hanafiah, A. Baba, R. Advincula, W. Knoll and S. Valiyaveettil, *J. Phys. Chem. B.,* 2007, **111**, 6336-6343.

3 J. Feng, R. Haasch and D. Dyer, *Macromolecules,* 2004, **37**, 9525-9537.