Patterned Nitroxide Polymer Brushes for Thin-Film Cathodes in Organic Radical Batteries†

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Contents

1. Materials.

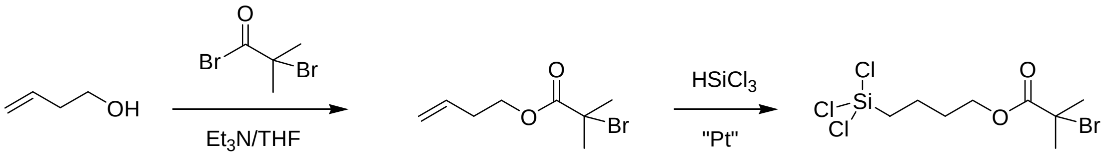
3-Buten-1-ol (98 %), 2,2,6,6-tetramethylpiperinyl methacrylate (TMPM, 98%), tetra-*n*-butylammonium perchlorate (98%) were obtained from TCI. 2-Bromo-2-methylpropionyl bromide (98%), copper (I) bromide (CuBr, 99.999%), Karstedt's catalyst (~ 2% Pt), and 1,1,4,10,10-hexamethyltriethylenetriamine (HMTETA, 99+%), and ITO/PET film (surface resistivity: 35 ohm/sq) were purchased from Aldrich. ITO/glass (surface resistivity: 10 ohm/sq) was purchased from UniRegion Bio-Tech. Trichlorosilane (>98%), sulfuric acid (97%), and hydrogen peroxide (35%) were obtained from Showa. Poly(dimethylsiloxane) (PDMS, Sylgard 184A) and its crosslinker (Sylgard 184B) were obtained from Gelest. *n*-Octadecyltrichlorosilane (OTS, 85%) and 3-chloroperoxybenzoic acid (*m*CPBA, 70~75%) were obtained from Alfa Aesar and Acros, respectively. Except for *m*CPBA, all chemicals were used as received. *m*CPBA was recrystallized in methanol.

2. Instruments.

An X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI Quantera SXM) with a focused monochromatic Al K_{α} radiation (1486.6 eV) was used to analyze the composition of the polymer brushes/ITO. ^{1}H- and ^{13}C-NMR spectra were acquired using a 500 MHz and a 125 MHz NMR Bruker spectrometer, respectively. Gel permeation chromatography (GPC) measurements were determined on a Shimadzu system in DMF using a Waters' column at 45°C, the calibration was performed using a series of polystyrene standards. The surface morphology and root mean squares (rms) of the polymer brushes ITO/glass were observed using an atomic force microscope (AFM, Nano-Man NS4+D3100). Electrochemical properties were obtained on a CHI model 6081 electrochemical analytical instrument.

3. Synthesis of the surface initiator

The surface initiator, (4-(2-bromo-2-methyl)propionyloxy)butyltrichlorosilane (BMPBTS), was synthesized according to the method of Matyjaszewski et al, as shown in Scheme S1.



Scheme S1. Synthesis of (4-(2-bromo-2-methyl)propionyloxy)butyltrichlorosilane

Synthesis of but-3-enyl-2-bromo-2-methylpropanate

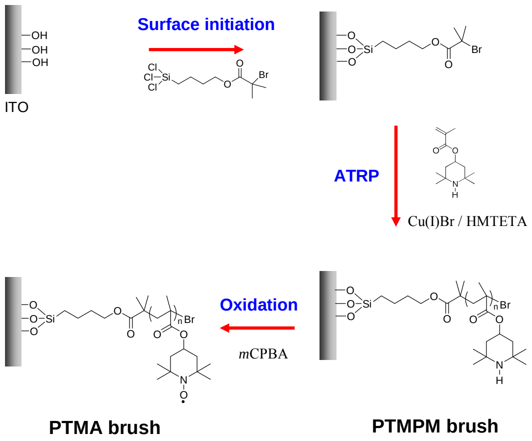
3-Buten-1-ol (2.47 mL, 0.02 mol) and triethylamine (2.79 mL, 0.02 mol) were dissolved in 25.0 mL of tetrahydrofuran. 2-Bromo-2-methylpropionyl bromide (1.76 mL, 0.02 mol) was slowly added to the above solution at room temperature under a nitrogen atmosphere. After stirring for three hours, the reaction was terminated. The solution was filtered by a short aluminum oxide column to remove the salt. Finally, the solvent was removed by a rotavapor to yield but-3-enyl-2-bromo-2-methylpropanate (2.68 g, 0.13 mol). Yield: 66%. ^{1}H-NMR (500 MHz, $CDCl_3$, TMS as standard): δ 5.81 (1H, ddt, J = 17.0, 10.0, 6.5 Hz, $CH_2C\mathit{H}CH_2$), 5.14 (1H, dd, J = 10.0, 7.0 Hz, $C\mathit{H}_2CHCH_2$), 5.10 (1H, dd, J = 17 , 1.5 Hz, $C\mathit{H}_2CHCH_2$), 4.23 (2H, t, J = 6.5 Hz, $CH_2C\mathit{H}_2O$), 2.45 (2H, q, J = 6.5 Hz, $C\mathit{H}_2CH_2O$), 1.93 (6H, s, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.6 ($CH_2O\mathit{C}O$), 133.6 ($CH_2\mathit{C}HCH_2$), 117.5 ($\mathit{C}H_2CHCH_2$), 64.9 ($CH_2\mathit{C}H_2O$), 55.8 ($CO\mathit{C}Br$), 32.8 ($CH\mathit{C}H_2CH_2O$), 30.8 ($C(\mathit{C}H_3)_2Br$). MS (ESI): calculated for $C_8H_{12}O_2Br$: $[M+Na]^+$, 242.9997 $[M+Na]^+$, found $[M+Na]^+$, 242.9999).

Synthesis of BMPBTS

But-3-enyl 2-bromo-2-methylpropanate (0.23 g, 1.02 mmol) was dissolved in 1.0 mL of trichlorosilane under a nitrogen atmosphere. A Karstedt's catalyst (30 μL) was added into the above solution. After stirring for five hours, the excess trichlorosilane was removed under reduced pressure to get BMPBTS (0.32 g, 0.91 mmol). Yield: 89%. ^{1}H-NMR. (500 MHz, $CDCl_3$, TMS as standard): δ 4.22 (2H, t, *J* = 6 Hz, $CH_2\mathit{CH_2}O$), 1.93 (6H, s, CH_3), 1.83 (2H, p, *J* = 6 Hz, $SiCH_2\mathit{CH_2}$), 1.73 (2H, m, $\mathit{CH_2}CH_2O$), 1.46 (2H, t, $Cl_3Si\mathit{CH_2}$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.7 ($CH_2O\mathit{C}O$), 64.9 ($CH_2\mathit{C}H_2O$), 55.7 ($CO\mathit{C}Br$), 30.7 ($C(\mathit{C}H_3)_2Br$), 30.3 ($CH_2\mathit{C}H_2CH_2O$), 23.7 ($Cl_3SiCH_2\mathit{C}H_2$), 18.8 ($Cl_3Si\mathit{C}H_2$).

4. Synthesis of PTMA Brushes

The attachment of surface initiator and the subsequent surface-initiated polymerization of 2,2,6,6-tetramethyl-piperinyl methacrylate on a ITO glass were carried out by ATRP. Poly(2,2,6,6-tetramethylpiperinyl-4-yl methacrylate), PTMPM, brushes were oxidized by *m*-chloroperoxybenzoic acid (*m*CPBA) in dichloromethane to give nitroxide polymer brush/ITO substrates.



Scheme S2. Synthesis of PTMA Brushes

Attachment of surface initiator

An ITO substrate was cleaned by RCA method (DI water : ammonia : hydrogen peroxide = 5:1:1 in volume).[1] The cleaned ITO substrate was immersed in a 10 mM surface-initiator, BMPBTS, toluene solution at 80°C for 30 minutes. Then, the initiator-attached ITO substrate was ultrasonicated in toluene for 10 minutes. Finally, the ITO substrate was dried by a nitrogen stream.

Surface-initiated ATRP of TMPM

CuBr (21.6 mg, 0.15 mmol) and HMTETA (42 μL, 0.15 mmol) were dissolved in 15 mL of acetone and degassed by four freeze-pump-thaw cycles.[2] The above solution was transferred *via* a cannula into a degassed flask containing TMPM (0.94 g, 15.0 mmol) as a monomer. Finally, the above solution of the monomer and the catalyst was transferred by a cannula into a degassed container containing the initiator-attached ITO substrate. The polymerization was carried out at reflux under a nitrogen atmosphere for a predetermined time to give a PTMPM brush. The PTMPM brush/ITO substrates were rinsed and ultrasonicated with acetone. Finally, they were dried in a nitrogen stream.

PTMA brush on ITO: Oxidation of the TMPM brush

A TMPM brush on ITO was immersed in a 5 mL dichloromethane solution of *m*CPBA (8.7 mg) at room temperature for 10 minutes. The oxidized TMPM brush on ITO was ultrasonicated with several solvents, such as dichloromethane, hexane, and acetone and then dried in a nitrogen stream.

5. Electrochemical measurements of PTMA brushes

For the electrochemical cell, a PTMA brush/ITO electrode was used as a working electrode; platinum wire was used for the counter electrode. The reference electrode was Ag/$AgNO_3$ (0.01 $AgNO_3$ and 0.1 M tetra-*n*-butylammonium perchlorate, $(C_4H_9)_4NClO_4$, in acetonitrile); the electrolyte was 0.1 M $(C_4H_9)_4NClO_4$ in acetonitrile. For the cyclic voltammogram (CV), the cells were observed between 0.0 to 0.6 V at a scan rate of 5.0 mV/s. The half cells were cycled at a constant current at the 10 C rate between 0.3 and 0.55 V.

In the lithium-ion battery, a PTMA brush ITO/PET electrode was used as a working electrodes; a lithium metal foil was used for the counter and reference electrodes. A separator (Celgard 2320) was placed between the PTMA brush/ITO electrode and the lithium counter electrode. The electrolyte was 1.0 M $LiPF_6$ in EC/PC/DEC (= 3/2/5 in volume). For the cyclic voltammogram (CV), the cell was observed between 3.2 to 4.0 V at a slow scan rate of 0.1 mV/s.

6. Optical microscope images of patterned PTMA brushes

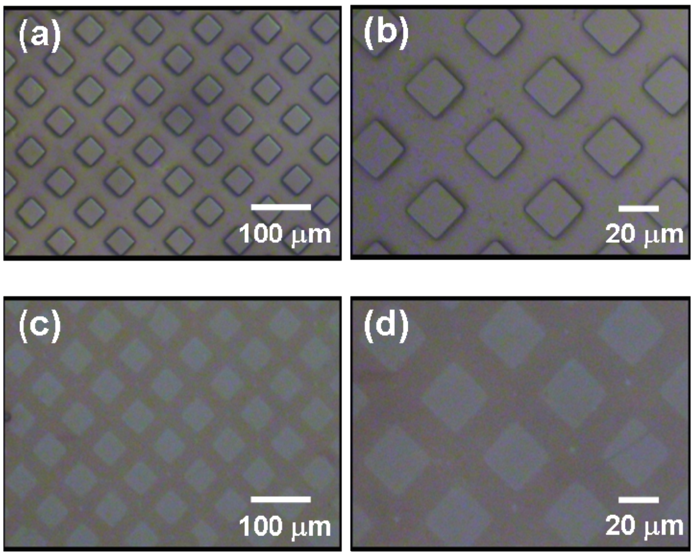


Fig. S1 Optical microscope images for (a) and (b) a grid-patterned PDMS stamp; (c) and (d) a grid-patterned PTMA brush (dark regions) on ITO.

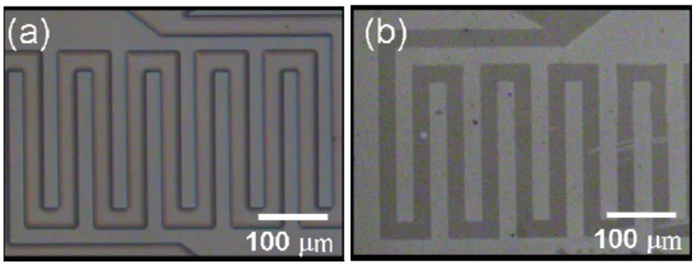


Fig. S2 Optical microscope images for (a) a patterned PDMS stamp; (b) a patterned PTMA brush (dark regions) on a Si substrate.

7. NMR Spectra

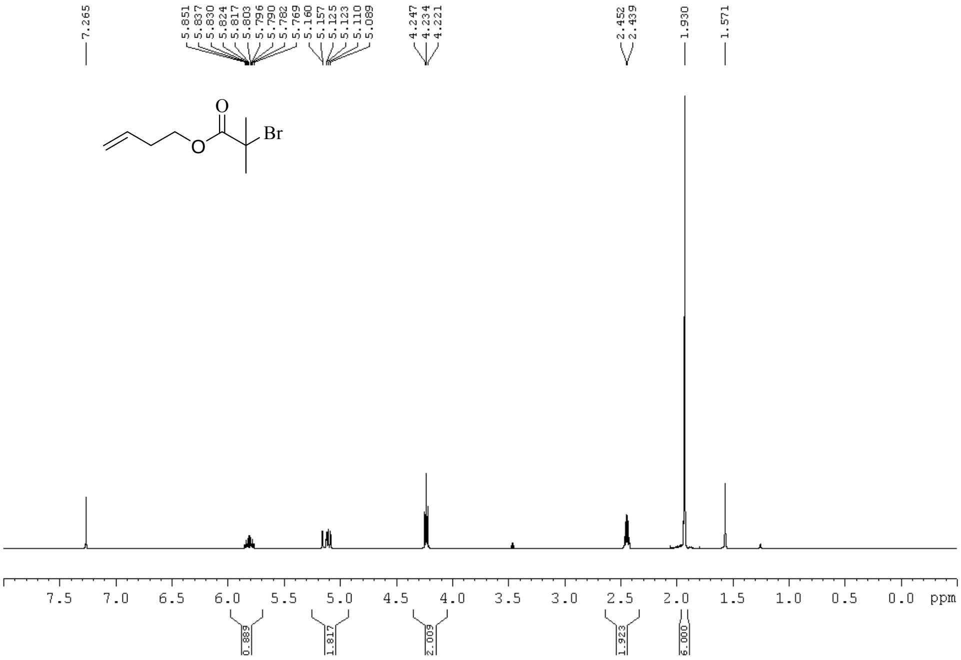


Fig. S3 ^{1}H-NMR spectrum for but-3-enyl-2-bromo-2-methylpropanate.

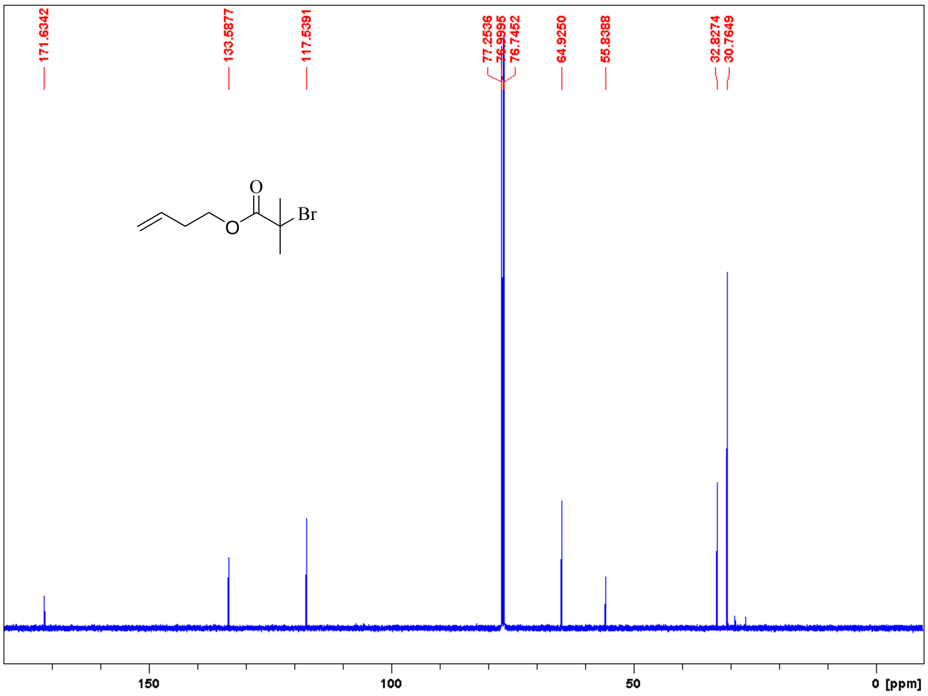


Fig. S4 ^{13}C-NMR spectrum for but-3-enyl-2-bromo-2-methylpropanate.

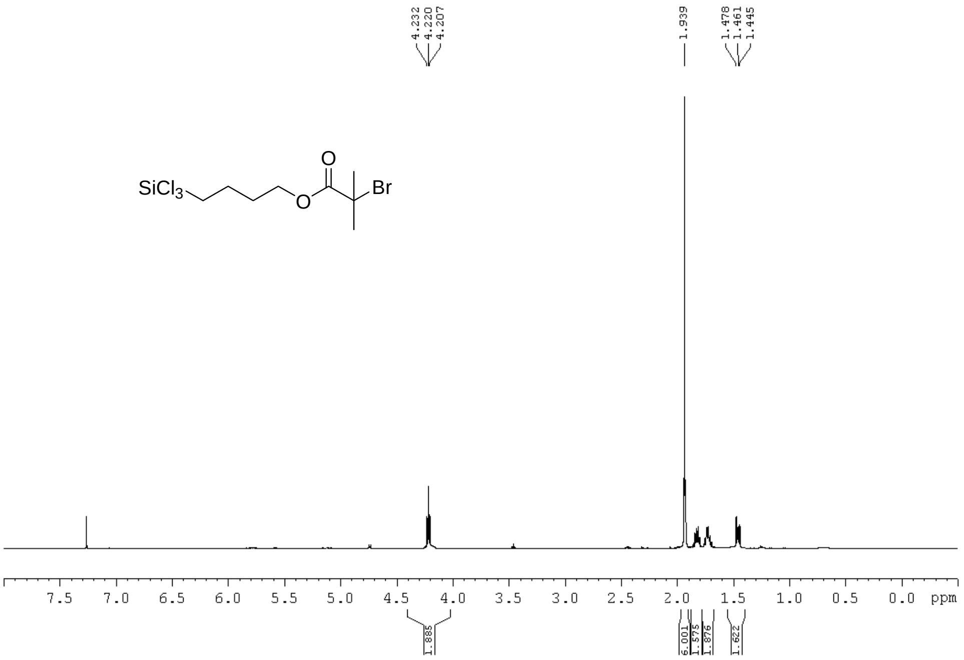


Fig. S5 ^{1}H-NMR spectrum for 4-(2-bromo-2-methyl)proionyloxy)butyltrichlorosilane.

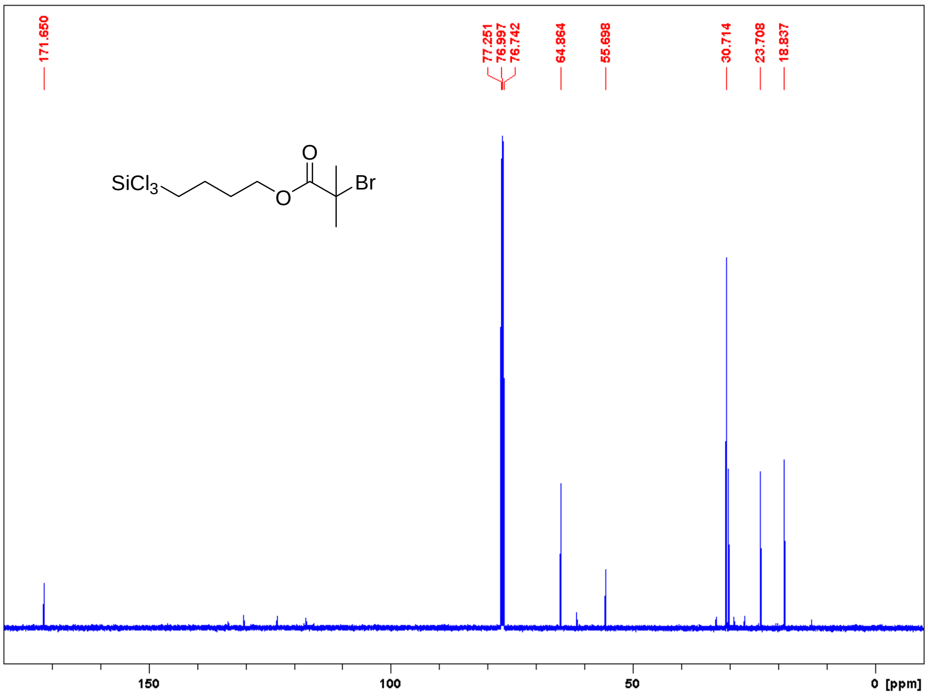


Fig. S6 ^{13}C-NMR spectrum for 4-(2-bromo-2-methyl)proionyloxy)butyltrichlorosilane.

8. AFM images

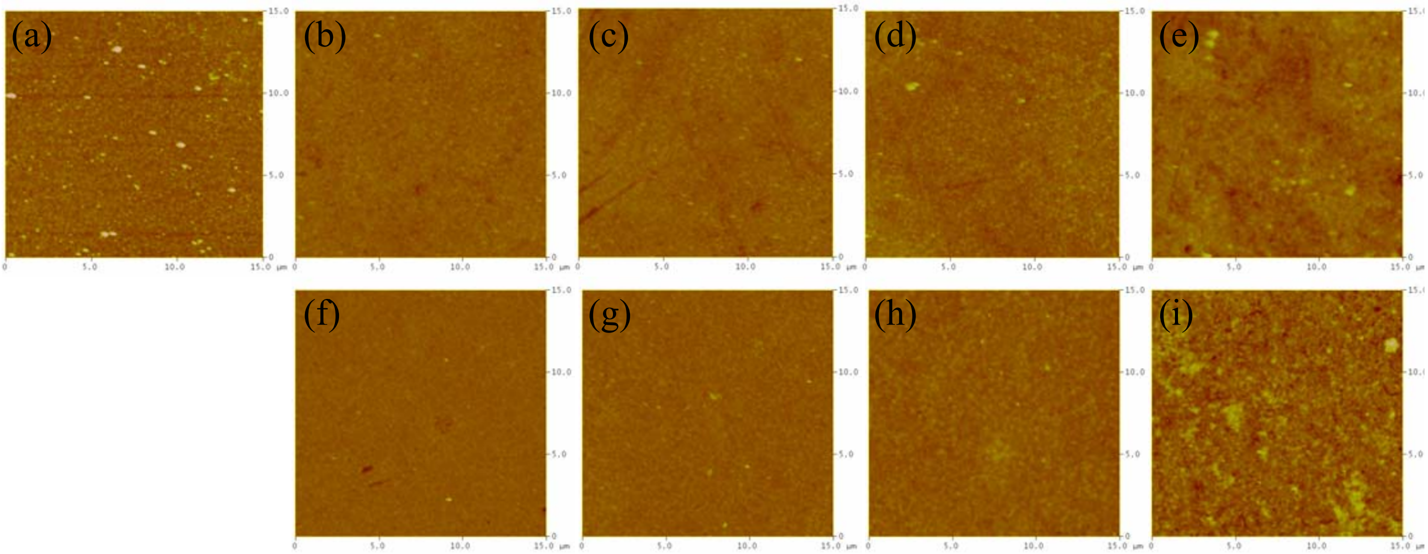


Fig. S7 AFM images for (a) blank ITO/ITO, (b-e) initiator-attached ITO substrates being polymerized with the PTMPM brush using ATRP for 2, 3, 4, and 5 hours, respectively, and (f-i) the specimens of (b-e) after the oxidation using *m*CPBA for 10 minutes, respectively.

Table S1 Surface roughness measured by AFM on PTMPM and PTMA brushes polymerized for 2, 3, 4, and 5 hours.

polymerization time (hours)	**rms roughness**	
	PTMPM brush (nm)	**PTMA brush (nm)**
2	1.17	2.00
3	1.29	2.23
4	1.82	3.12
5	2.50	3.74

* The rms roughness of blank ITO is 2.39 nm.

9. XPS spectra

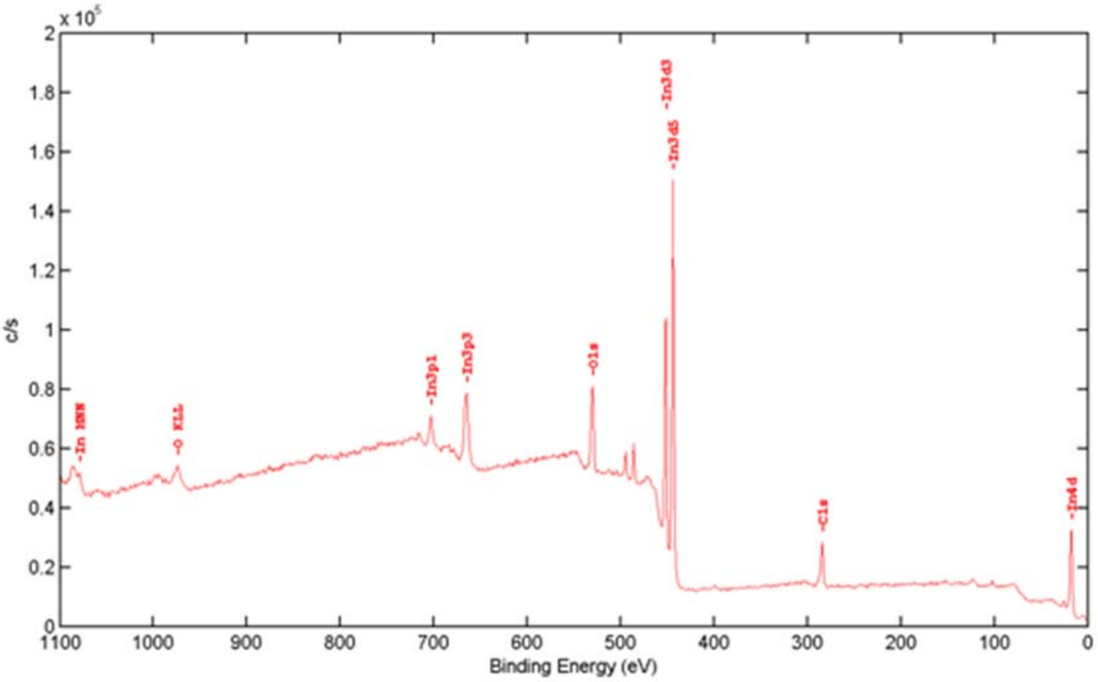


Fig. S8 XPS survey spectrum for 4-(2-bromo-2-methyl)proionyloxy)butyltrichlorosilane grafted on ITO.

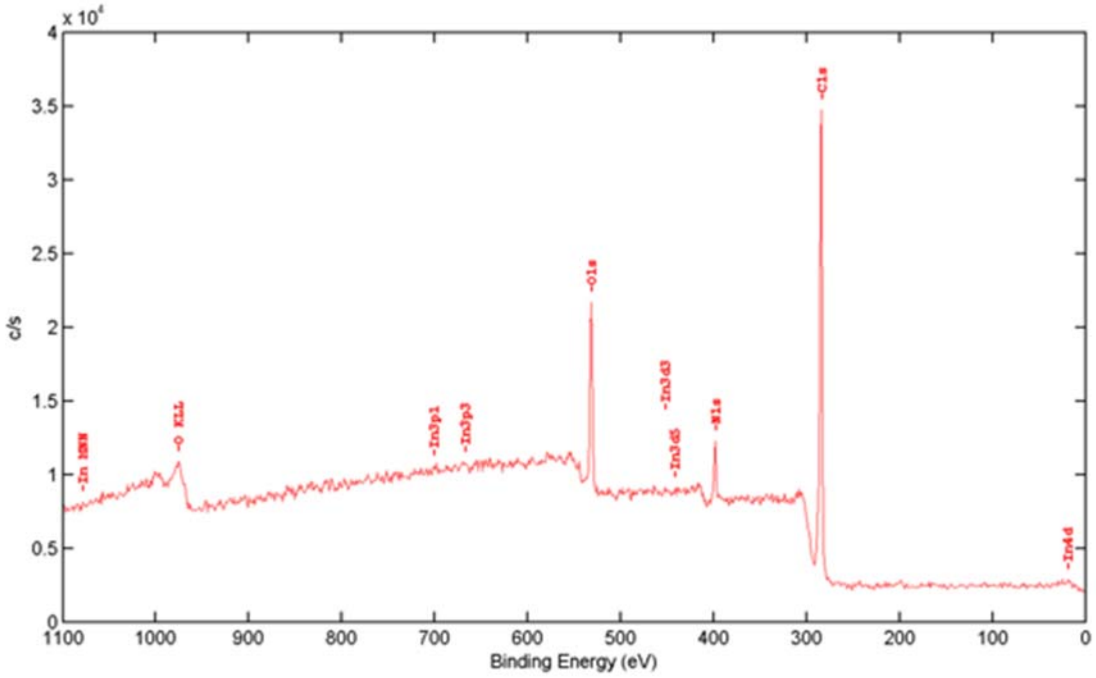


Fig. S9 XPS survey spectrum for the PTMPM brush on ITO.

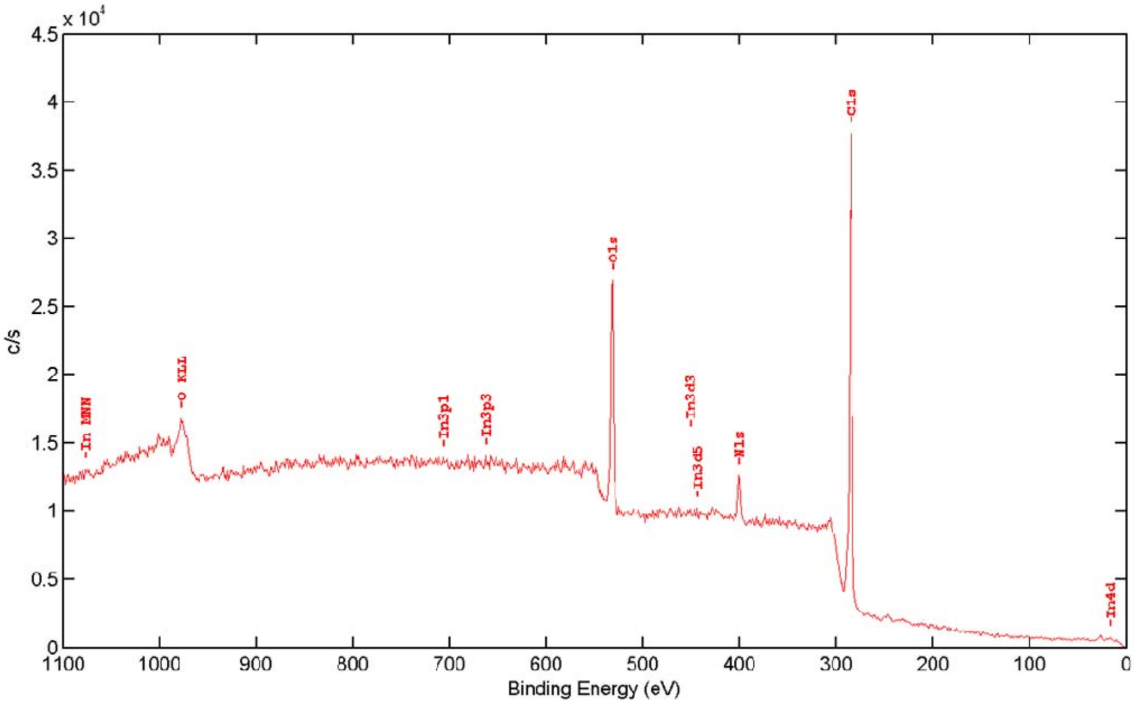


Fig. S10 XPS survey spectrum for the PTMA brush on ITO.