Electronic Supplementary Information (ESI)

Instrumentation

NMR ^{1}H. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on a 300 MHz Bruker Avance II.

Infrared (FT-IR). Spectra were recorded with a Shimadzu FTIR-8400S spectrometer from thin films deposited onto a ZnS crystal plate.

UV-Visible. The samples were prepared in quartz cuvettes. The studies were carried out with a Varian Cary 50 UV-Vis Spectrophotometer with absorption spectra recorded from 250 to 1000 nm.

GPC. Average molar masses (M_n and M_w) and dispersity ($Đ$) were measured on an Agilent size exclusion chromatography (SEC) system equipped with an Agilent 1100/1200 pump (25°C; eluent: Chloroform/triethylamine/isopropanol, 94:4:2 v/v/v; flow rate: 1 mL/min), an Agilent differential refractometer and two PSS SDV columns (Beads 10 μm; porosity of column 1, 10000 Å; porosity of column 2, 1000 Å). The calibration was performed using polystyrene standards.

Thermogravimetric analysis. Thermograms are recorded on a TGA/SDTA 851e instrument from METTLER TOLEDO. These analyses are carried out with a heating ramp of 10°C min^{-1} and under a N$_2$ flow (100 ml min^{-1}) with the samples (3–5 mg) placed into 70 mL alumina containers.

X-ray photoelectron spectroscopy. The analyses were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray source (powered at 20 mA and 10 kV). Samples are stuck onto sample holders with a double-face adhesive tape and then placed on an insulating home-made ceramic carousel (Macor, Switzerland). The spot size for irradiation is set at 800 μm x 1200 μm. The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. In these conditions, the full width at half maximum (FWHM) of the Au 4f$_{7/2}$ peak of a clean gold standard sample was about 1.6 eV. A flood gun set at 8 eV and a Ni grid placed 1 mm above the sample surface were used for charge stabilization. The C-(C,H) component of the C1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK), some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a nonlinear baseline. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

Untethered PTMA-based control electrodes

A physical blend of untethered PTMA and pristine MWCNTs has been prepared in order to conduct electrochemical measurements as control data. For this purpose, a linear PTMA homopolymer (degree of polymerization = 69) was synthetized through ATRP. The control composite measurements are compared to the results obtained for the MWCNT-*g*-PTMA$_{60}$ electrodes.

The cathodes were prepared by blending the active material PTMA$_{69}$, MWCNTs (Nanocyl NC7000) and poly(vinylidene fluoride) (PVDF) binder. The blend has the following composition, 30 wt.% of PTMA$_{69}$, 60 wt.% of MWCNTs and 10 wt.% of PVDF binder. 12 mL of N-methylpyrorolidone were added per 1 g of solid materials. The ingredients were mixed uniformly in a ball-mill apparatus at room temperature for 30 min to yield the slurry. The slurry was cast on an aluminum foil using the doctor blade method (the thickness of the wet film was controlled to be 200 μm) and dried at 60°C for 24 h. Circular discs of diameter 1.25 cm were cut and used as cathodes for evaluating the electrochemical properties. The electrodes were assembled following the same protocol as for the MWCNT-*g*-PTMA$_{60}$ cathodes. All electrochemical measurements on the control composite were conducted with

the same devices, apparatus and parameters as for the MWCNT-*g*-PTMA$_{60}$ cathodes. 4 points conductivity measurements were obtained with the control composite coated on an insulate substrate. This coating was prepared with the same doctor blade protocol as for the control electrode but casted on a glass slide. The thickness of the coated material was found to be 30 µm (measured with a Draper Expert digital micrometer).
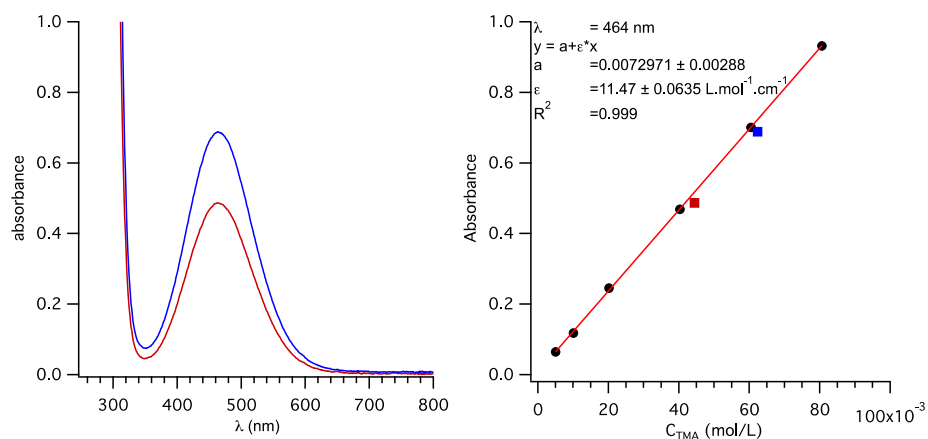

Figure S1. Determination of the oxidation degree by UV-Vis analyses thanks to a TEMPO-*tert*-butyrate calibration in CH$_2$Cl$_2$. The UV-Vis spectra of solutions of PTMA$_{37}$-*b*-PAzPMA$_{2.5}$ in CH$_2$Cl$_2$ are depicted on the left inset (red and blue curves, 11.25 g/L and 16.25 g/L respectively). The maximum of absorbance (λmax = 464 nm) was measured for the two different concentrations and compared to a TEMPO-*tert*-butyrate calibration (red line in the right inset).

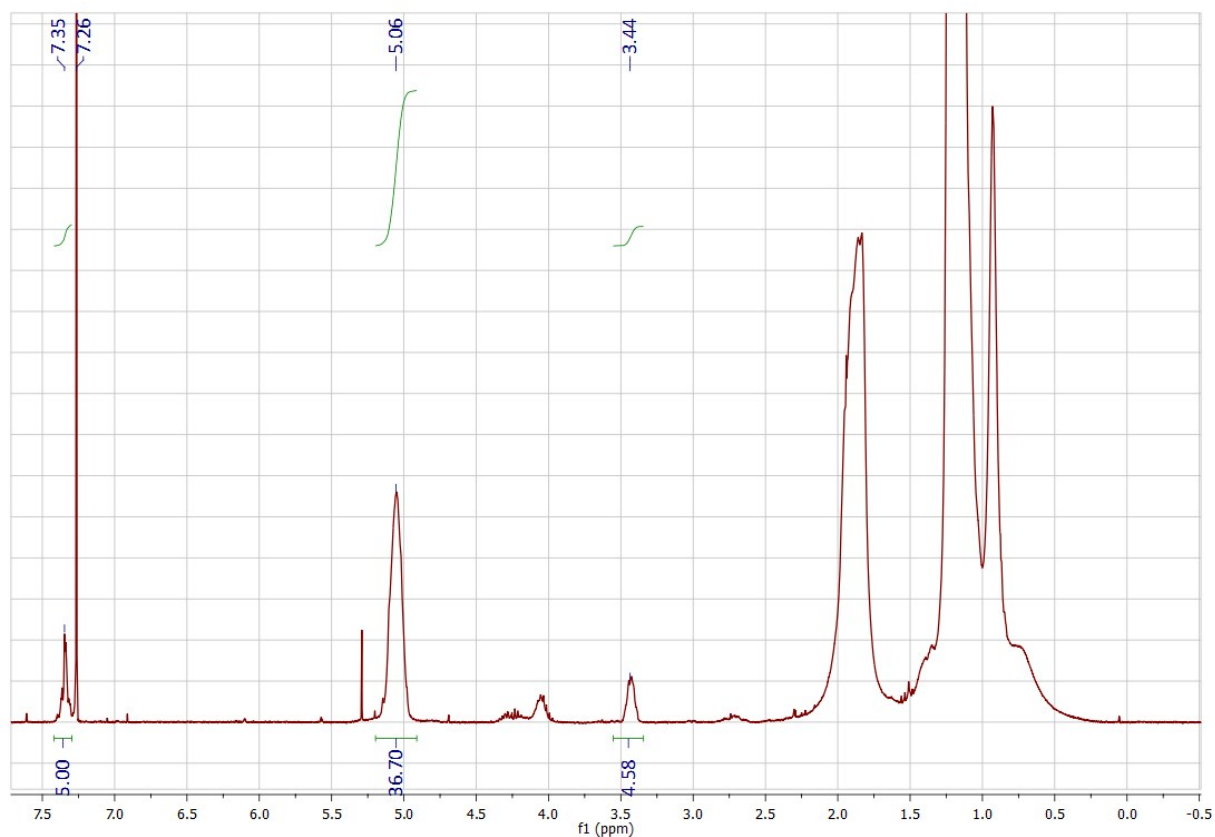**Figure S2.** ^{1}H NMR Spectrum of the purified PTMPM$_{37}$-*b*-PAzPMA$_{2.5}$.
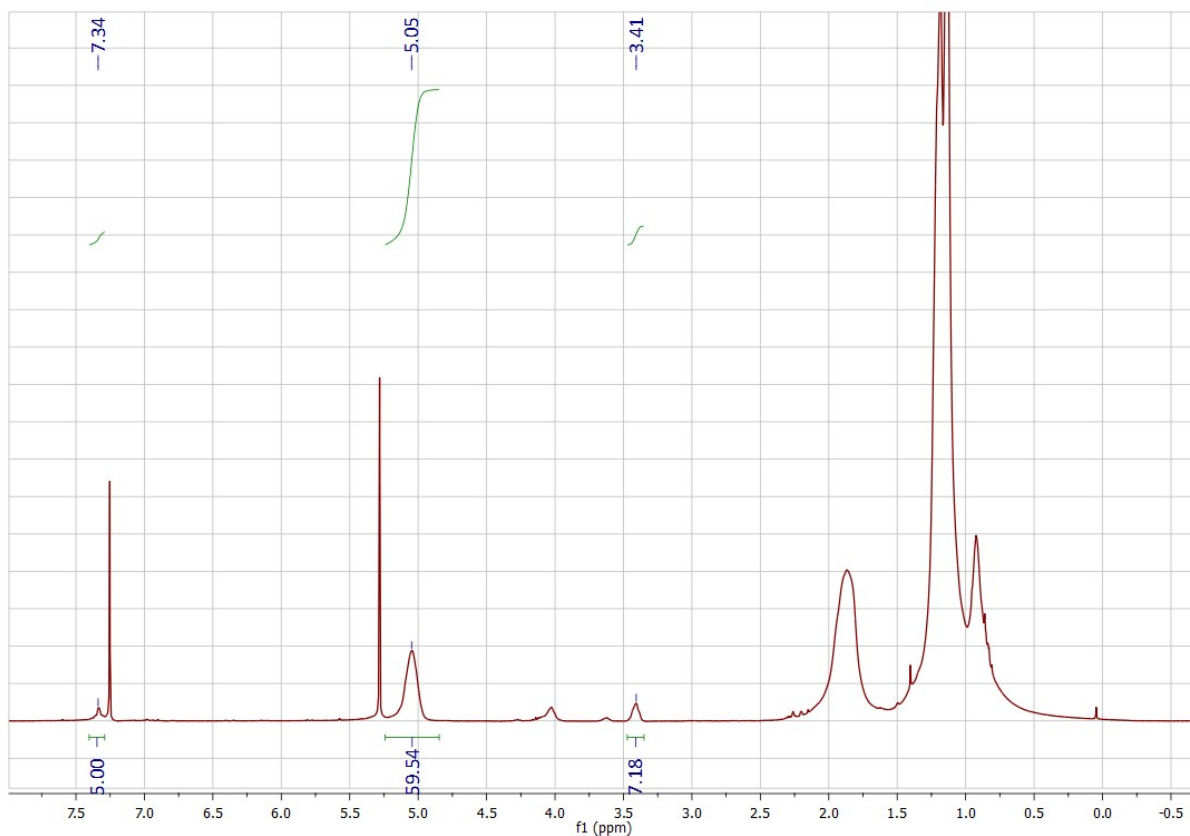
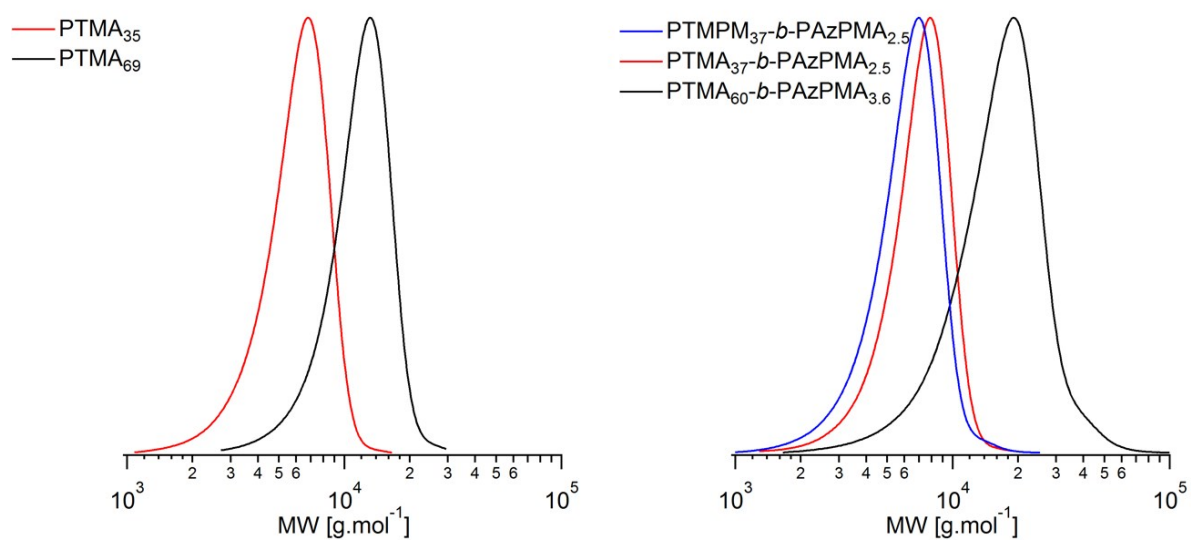**Figure S3.** ^{1}H NMR Spectrum of the purified PTMPM$_{60}$-*b*-PAzPMA$_{3.6}$.

Figure S4. SEC chromatograms of PTMA$_{35}$ and PTMA$_{69}$ homopolymers (left) and PTMPM$_{37}$-*b*-PAzPMA$_{2.5}$, PTMPA$_{37}$-*b*-PAzPMA$_{2.5}$ and PTMPA$_{60}$-*b*-PAzPMA$_{3.6}$ functional copolymers (right).
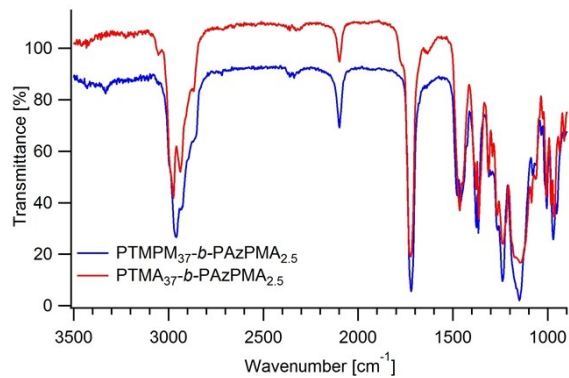
Figure S5. Overlay of the FTIR spectra of PTMPM$_{37}$-*b*-PAzPMA$_{2.5}$ (blue curve) and of PTMA$_{37}$-*b*-PAzMPA$_{2.5}$ (red curve).
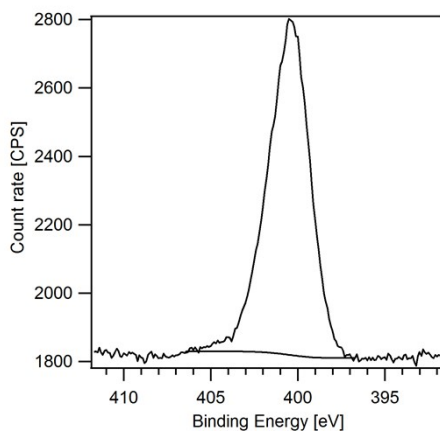

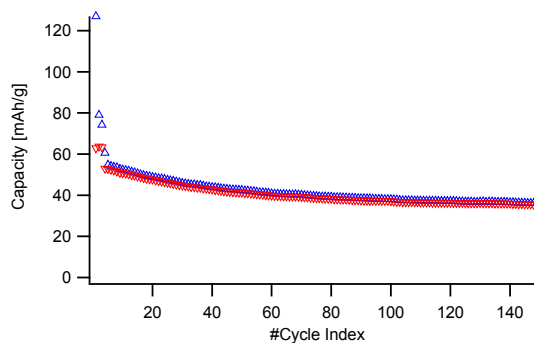**Figure S6.** XPS N$_{1s}$ peaks of MWCNT-*g*-PTMA$_{60}$.

Figure S7. Cycle stability of the PTMA$_{69}$-based control electrode at C/2 rate over 150 cycles (The 3 first cycles were recorded at C/10 rate).