Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

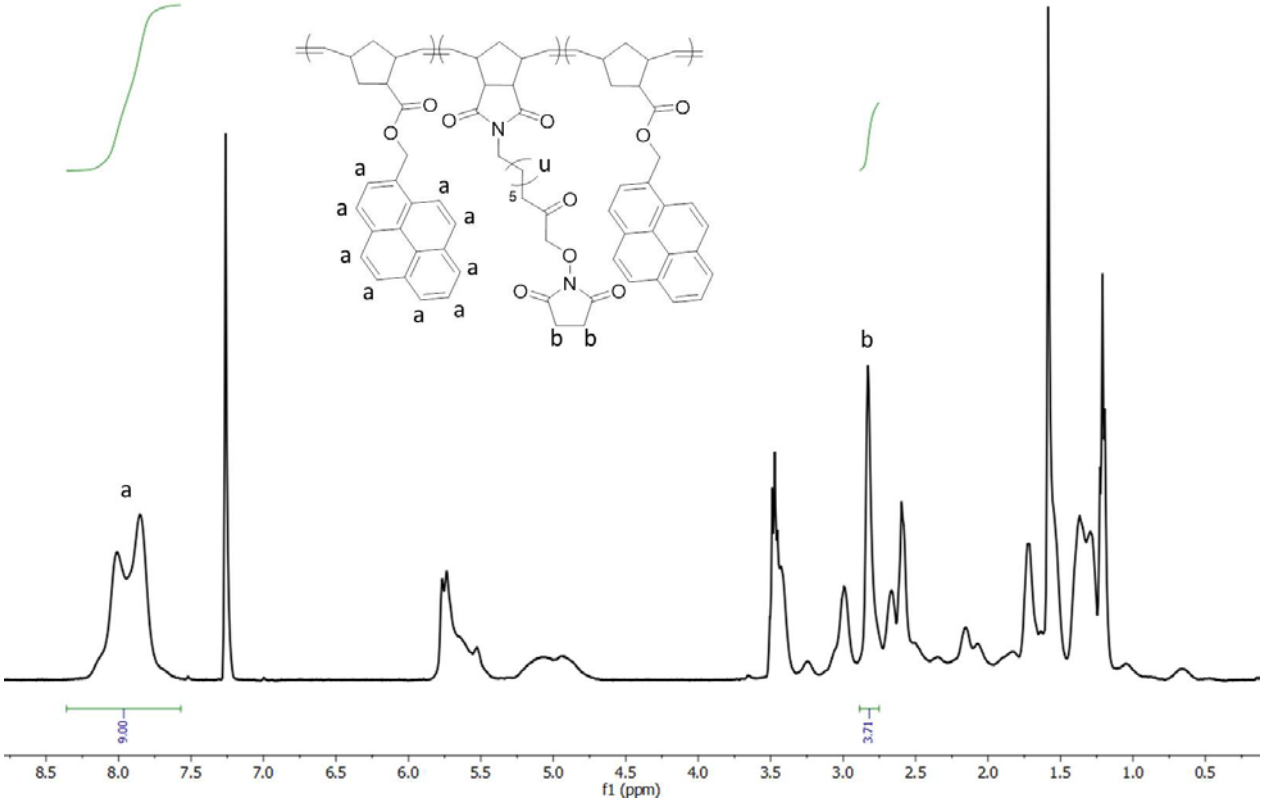

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the P(Py_{33}-b-NHS_{66}-b-Py_{33}) block copolymer showing a pyrene/NHS ratio of 1:0.93.

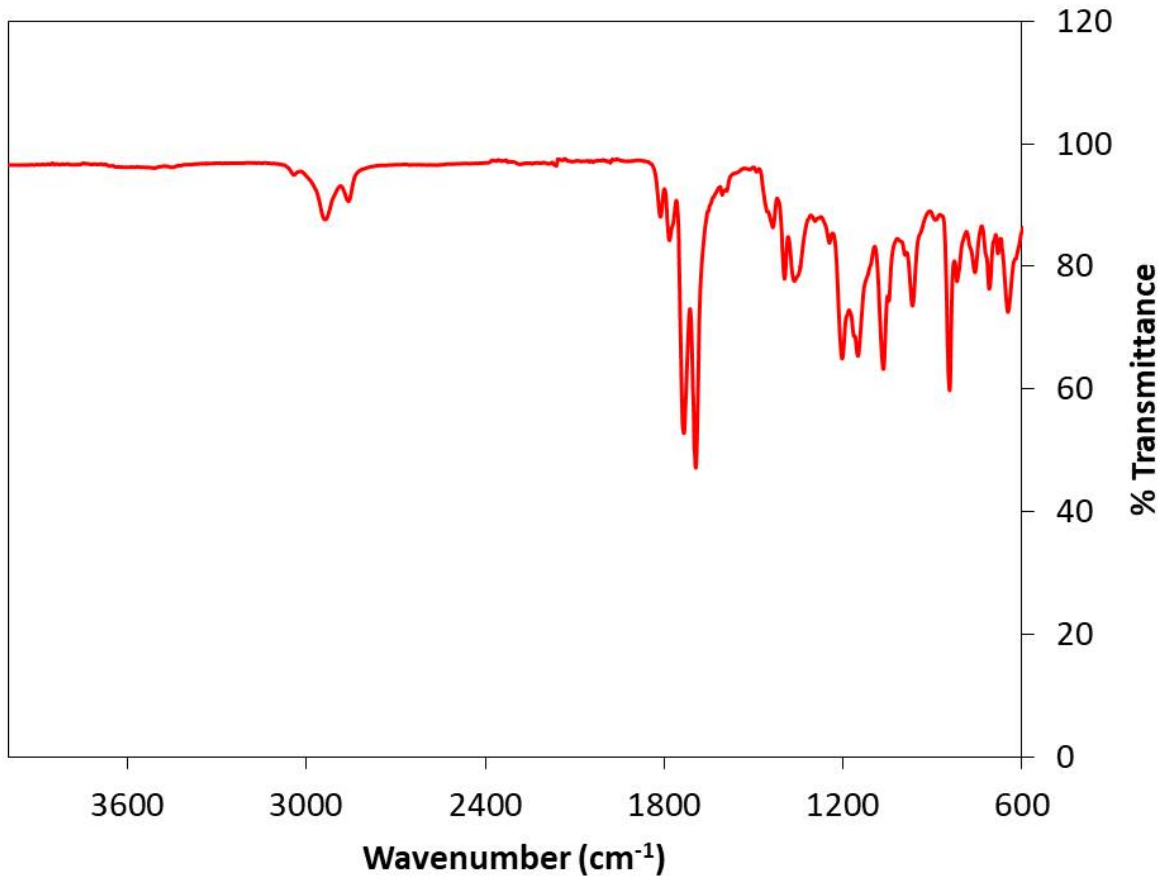

Figure S2. Infra-red spectrum of the P(Py_{33}-b-NHS_{66}-b-Py_{33}) block copolymer.

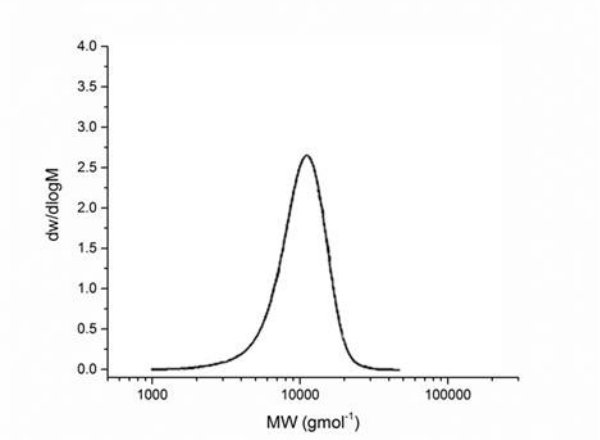

Figure S3. Molecular weight distribution for the P(Py_{33}-b-NHS_{66}-b-Py_{33}) block copolymer obtained by size exclusion chromatography ($CHCl_3$ eluent, DRI detector, polystyrene calibration).

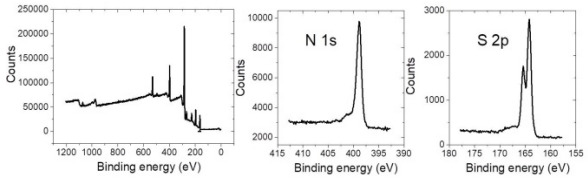

Figure S4. XPS survey spectra and XPS high resolution spectra at the S_{2p} and N1s core energy level for pyreneNHS-based BP with immobilized thionine

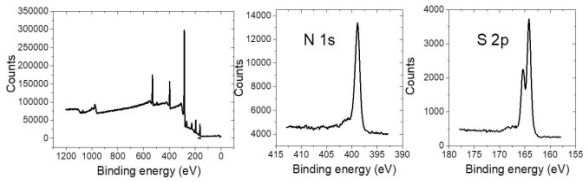

Figure S5. XPS survey spectra and XPS high resolution spectra at the S_{2p} and N1s core energy level for polynorbornene-based BP with immobilized thionine

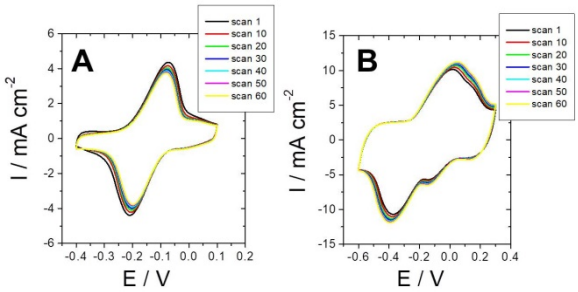

Figure S6. CV scans (1 to 60) for (A) pyreneNHS-based BP and (B) polynorbornene-based BP (20 mV s^{-1}) with immobilized thionine in 0.1 mol L^{-1} PB pH 7, 25 °C

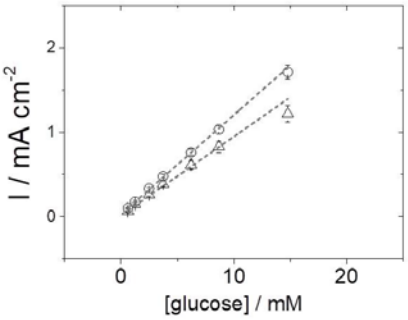

Figure S7. Evolution of the current density with the glucose concentration in the linear region between 0 and 15 mM glucose accompanied with a linear fitting curve for (△) pyreneNHS-based BP and (○) polynorbornene-based BP with immobilized thionine and FAD-GDH after addition of successive amounts of glucose with stirring in 0.1 mol L^{-1} PB pH 7, 25 °C. Error bars correspond to one standard deviation from at least two electrodes.

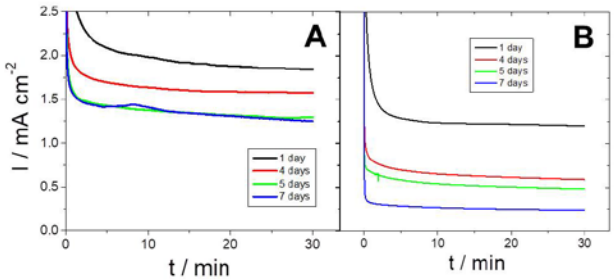

Figure S8. Chronoamperometric measurements performed at E_p = 0.2 V for (A) polynorbornene-based BP and (B) pyreneNHS-based BP with immobilized thionine and FAD-GDH in the presence of 150 mmol L^{-1} glucose after 1, 4, 5 and 7 days in 0.1 mol L^{-1} PB pH 7, 25 °C

Materials and Methods

1-methyl-2-pyrrolidinone (NMP), acetonitrile (MeCN), N,N-dimethylformamide (DMF), sodium phosphate dibasic, sodium phosphate monobasic, 1-pyrenebutyric acid N-hydroxysuccinimide ester (pyreneNHS), and thionine acetate (purity > 95%) were purchased from Sigma Aldrich and were used without further purification. Flavin adenine dinucleotide-dependent glucose dehydrogenase (FAD-GDH, 1150 U mg^{-1} solid) was purchased from Sekisui Diagnostics (UK). Commercial grade thin multi-walled carbon nanotubes (MWCNTs, 9.5 nm diameter, purity > 95%, 1.5 µm length) were obtained from Nanocyl. Commercial MWCNT proprietary blend buckypaper (NTL-12218, 60 gsm) was obtained from NanoTechLabs, Inc (Buckeye Composites). Carbon nanomaterials were used as received without any purification. When not used, the enzyme was stored at -20°C. All solvents were of analytical grade. Distilled water was passed through a Milli-Q water purification system to obtain ultrapure water at 18.2 MΩ cm^{-1}. Glucose solutions were left to mutarotate overnight to β-D-glucose prior to use. Three-dimensional and profile optical laser images were taken using a Keyence VK-X200 laser scanning confocal microscope. Phosphate buffer solution (PB) solution was prepared from Milli-Q water. XPS data was obtained using an ESCALAB 250 from Thermo Scientific with a monochromated Al Kα band (1486.6 eV) as the excitation source. The diameter of the surface spot analysed was 500 µm. The spectra obtained were calibrated according to the sp^2 carbon energy contribution (C=C) C1s at 284.4 eV. Conductivity measurements were performed on pyreneNHS and polynorbornene-based BP using a Keithley 2450 sourcemeter with an S-302-4 mounting stand and SP4 four-point probe head, taking into account the thickness of each sample.
Infrared spectra were recorded (neat) on a Perkin Elmer, Spectrum 100 FT-IR Spectrometer. ^{1}HNMR spectra were recorded on a Bruker DRX-400 spectrometer in $CDCl_3$ unless otherwise stated. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane. Size exclusion chromatography (SEC) measurements were conducted using a Varian 390-LCMulti detector suite fitted with differential refractive index (DRI), and UV/Vis detectors. A guard column (Varian Polymer Laboratories PLGel 5 mm, 50 \u0005 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 mm, 300 \u0005 7.5 mm) were used. The mobile phase was chloroform with 2% trimethylamine eluent at a flow rate of 1.0 mL min\u00031. SEC data was analysed using Cirrus v3.3.

Electrochemical measurements

The electrochemical experiments were carried out in a three electrode electrochemical cell using an Autolab potentiostat (Eco Chemie, Utrecht, The Netherlands) using the GPES program. A Pt wire was used as the counter electrode and the Ag/AgCl (KCl sat.) served as the reference electrode. All experiments were conducted at room temperature. All current densities are normalized towards the geometrical surface of the BP electrode. All simulated curves were obtained via Origin Pro 9.0. Error bars were estimated from 6 measurements recorded per sample from a minimum of 2 independent samples.

Preparation of the homemade free-standing polynorbornene-based BP modified with thionine and FAD-GDH

The polynorbornene triblock copolymer (Py_{33}-b-NHS_{66}-b-Py_{33}, 50 kg mol^{-1}) was synthesized via ring opening metathesis polymerization (ROMP), as previously reported, from the pyrene monomer, (1-pyrenyl)methyl *exo*-5-norbornene-2-carboxylate, and the NHS monomer, N-(2,5-dioxopyrrolidin-1-yl octanoate)-cis-5-norbornene-exo-dicarboximide (NHSNb).[1] For preparation of the polynorbornene-based BP, first, 66 mg of MWCNTs was added into 66 mL of DMF and dispersed by 30 min sonication using a Bandelin sonorex RK100 ultrasonication bath. Next, 16.5 mg of polymer was added to the dispersion and the resulting mixture was sonicated for a further 30 minutes. The dispersion was subsequently passed through a Millipore PTFE filter (JHWP, 0.45 µM pore size, 47 mm diameter) under high vacuum using a MZ 2C NT

Vacuubrand GMBH membrane pump, rinsed with ultrapure water, then left under vacuum for a further 30-60 min. The BP coated filter papers were left overnight, peeled off the filter to obtain the free-standing BP, then cut into 6 mm diameter circular disk electrodes. For surface modification with thionine, BP electrodes were modified by drop-casting 40 µL of 10 mmol L^{-1} thionine in 0.1 mol L^{-1} PB pH 9 onto the smooth BP surface (the side that was in contact with the filter paper) then left to dry overnight at room temperature. For enzyme immobilization, 40 µL of 2.5 mg mL^{-1} FAD-GDH in 0.1 mol L^{-1} PB pH 7 was drop-casted onto the electrode then dried overnight in the fridge. All electrodes were rinsed thoroughly with 0.1 mol L^{-1} PB pH 7 before use. Electrical contact to the BP was obtained via a metal wire with carbon paste. The back and sides of the electrode were sealed with silicone paste.

Preparation of the commercial pyreneNHS-based BP modified with thionine and FAD-GDH

For preparation of the pyreneNHS-based BP, high conductivity MWCNT buckypaper from NanoTechLabs Inc was first cut into 6 mm diameter circular disk electrodes. Next, 40 µL of 2.5 mmol L^{-1} pyrene-NHS in DMF was drop-coated onto the electrode and left to dry for 10 hours at room temperature. For surface modification with thionine, buckypaper electrodes were modified by drop-casting 40 µL of 10 mmol L^{-1} thionine in 0.1 mol L^{-1} PB pH 9 onto the BP surface then left to dry overnight at room temperature. For enzyme immobilization, 40 µL of 2.5 mg mL^{-1} FAD-GDH in 0.1 mol L^{-1} PB pH 7 was drop-casted onto the electrode then dried overnight in the fridge. All electrodes were rinsed thoroughly with 0.1 mol L^{-1} PB pH 7 before use. Electrical contact to the BP was obtained via a metal wire with carbon paste. The back and sides of the electrode were sealed with silicone paste.