Doping of Single Polymeric Nanoparticles**

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Supporting Information

Experimental Section

Poly (N-vinylcarbazole) (PVK, molecular weight M = 40,000) was purchased from Polysciences (Warrington, PA, USA). Unless stated otherwise, all chemicals in this work were acquired from Sigma–Aldrich at the highest purity available. All solutions were made up using ultrapure water of resistivity 18.2 MΩ cm (Millipore) at 25°C and degassed thoroughly with nitrogen (oxygen-free, BOC Gases plc) before use. PVK nanoparticles were synthesised by the re-precipitation method \[1\]. Briefly, 0.0380 g PVK powder was dissolved in 20 mL tetrahydrofuran (THF, 99.9%, anhydrous) solution. Then 100 μL PVK/THF solution was injected into 25 mL de-ionized water under vigorously stirring by magnetic vortexing at 800 rpm for 5 minutes. The nanoparticles suspension was subjected to sonication for 30 minutes at room temperature. The size distributions of the synthesised PVK nanoparticles were measured by dynamic light scattering (Malvern Instruments Ltd, UK).

Electrochemical experiments were conducted at room temperature inside a double Faraday cage with a three electrode system using an Autolab II potentiostat (Metrohm-Autolab BV, Netherlands). For drop-casting and voltammetric measurements experiment, a glassy carbon macroelectrode (3 mm diameter) was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode (Radiometer, Copenhagen) and a large platinum mesh as the counter electrode. Varying amounts of the PVK NPs suspension were drop-casted on the glassy carbon macroelectrode to modify the electrode, and left to dry under a N\(_2\) atmosphere. Cyclic voltammetry (CV) was conducted at scan rate of 50 mV/s in 1.0 M NaClO\(_4\). Before each voltammetric scan the glassy carbon macroelectrode was polished using three grades of diamond spray (3, 1 and 0.1 microns) before sonication in water and drying with nitrogen.

For nano-impact and chronoamperometry, a carbon microelectrode (diameter = 11 μm) was used as working electrode with the same reference and counter electrodes as above. The carbon micro-electrode diameter was calibrated electrochemically by analysing the steady state voltammetry of a 2.0 mM ferrocene in acetonitrile containing 0.1 M tetrabutylammonium perchlorate, using a diffusion coefficient for ferrocene of 2.30 ×10\(^{-9}\) m\(^2\)s\(^{-1}\) at 298 K\[2\]. The program “Signal Counter” (developed by Dr. D Omanovic’ at Center for Marine and Environmental Research Zagreb, Croatia) was used for impact spike identification and individual spike area determination. OriginPro8.5.1 was applied for electrochemical data analysis.
Figure S1 Cyclic voltammetric response of a glassy carbon macroelectrode modified with PVK nanoparticles (10^{-10} mol carbazole moieties) in 1.0 M NaClO₄ at a scan rate of 50 mV/s. (black: first scan; red: second scan).

Figure S2 (a) Cyclic voltammograms recorded for a glassy carbon macroelectrode modified with PVK nanoparticles of various amount (moles) of carbazole moieties: 5\times10^{-11} mol (black), 1\times10^{-10} mol (red), 2\times10^{-10} mol (blue), 3\times10^{-10} mol (magenta) and 4\times10^{-10} mol (green) in 1.0 M NaClO₄ at a scan rate of 50 mV/s; (b) Linear relation between the anodic peak charge (obtained from the integration of the peak area from Figure S2(a)) and the PVK nanoparticle loadings on the electrode surface.
Figure S3 The charge resulting from the oxidative doping of single individual PVK nanoparticles of a total number of 249.

Figure S4 Size distribution of PVK NPs by DLS measurement
Normal distribution:

The following function for a normal distribution was fitted to the charge distribution from the oxidative doping by nano-impact method for all 249 single polymeric PVK nanoparticles.

\[ f(x) = \alpha \exp\left[ \frac{-(x - \mu)^2}{2\sigma^2} \right] + d \]

Thus gave value of \( \mu \) (mean) of -11.97 and -12.03 respectively, and variance (standard deviation) \( \sigma \) of -0.41 and -0.49 for the theoretical estimation and experimental data respectively.
