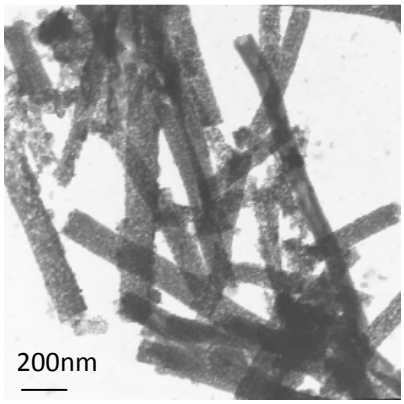
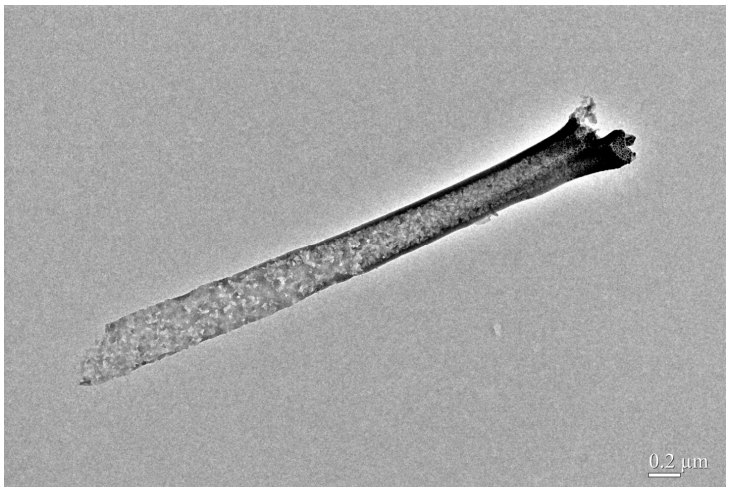
Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

SI 1: PVK nanotubes synthesized at 1.7V in 600mM PVK solution in 100mM $LiClO_4$ in ACN. No nanotubes were formed at 0.7V.

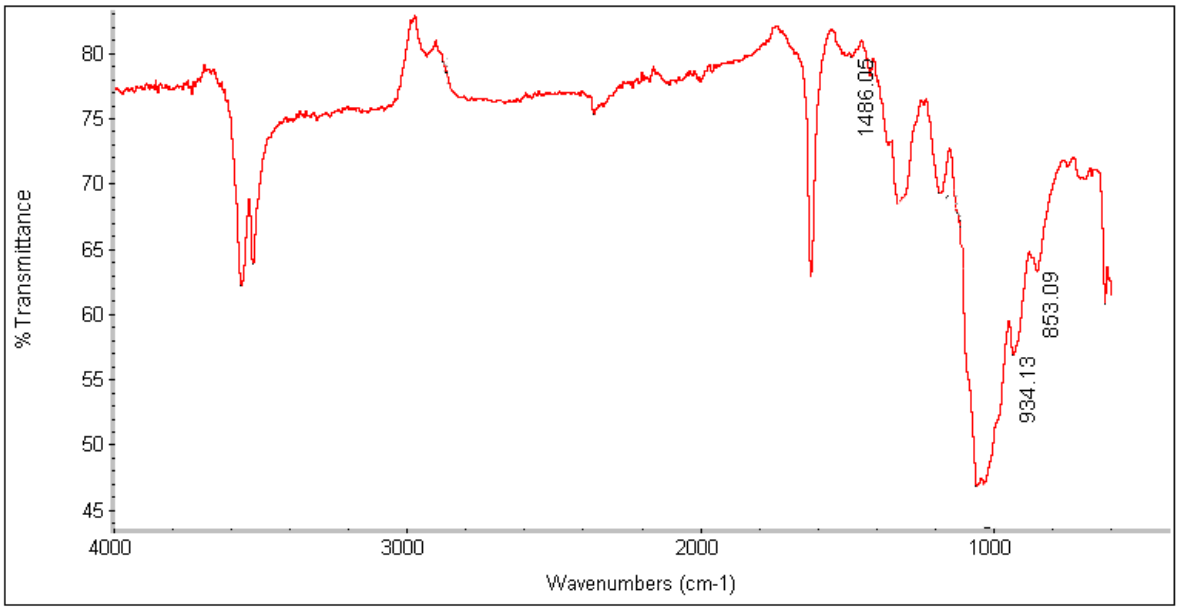


SI 2: PNT modified with PVK

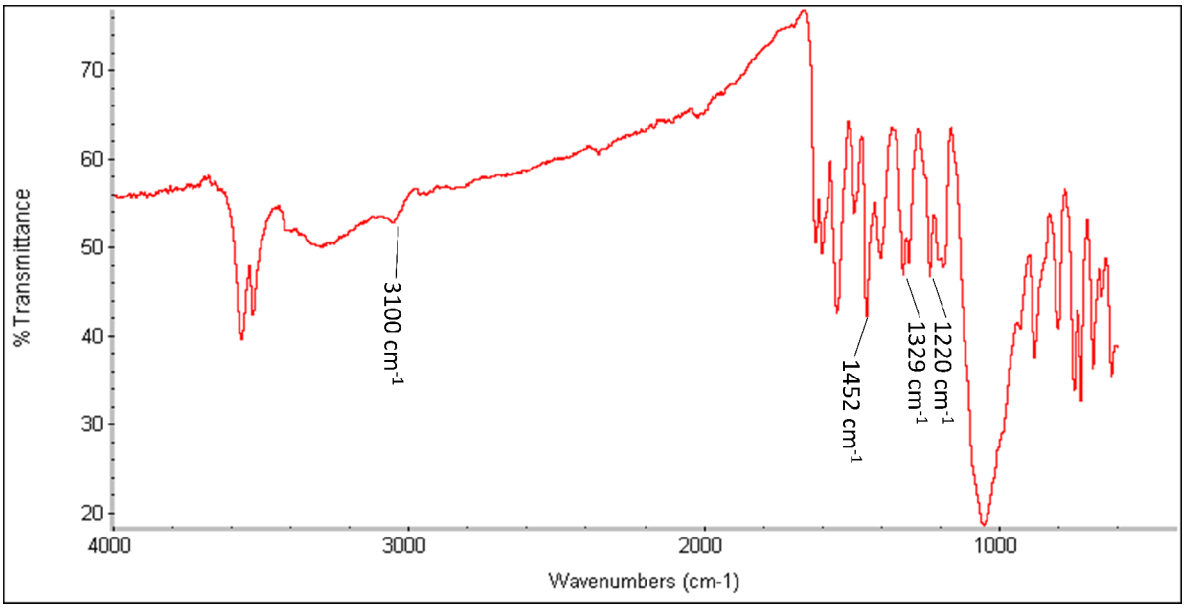


SI 3: IR spectra of PMProDot, PVK and PMProdot modified with PVK

SI 3a) PMProDot only

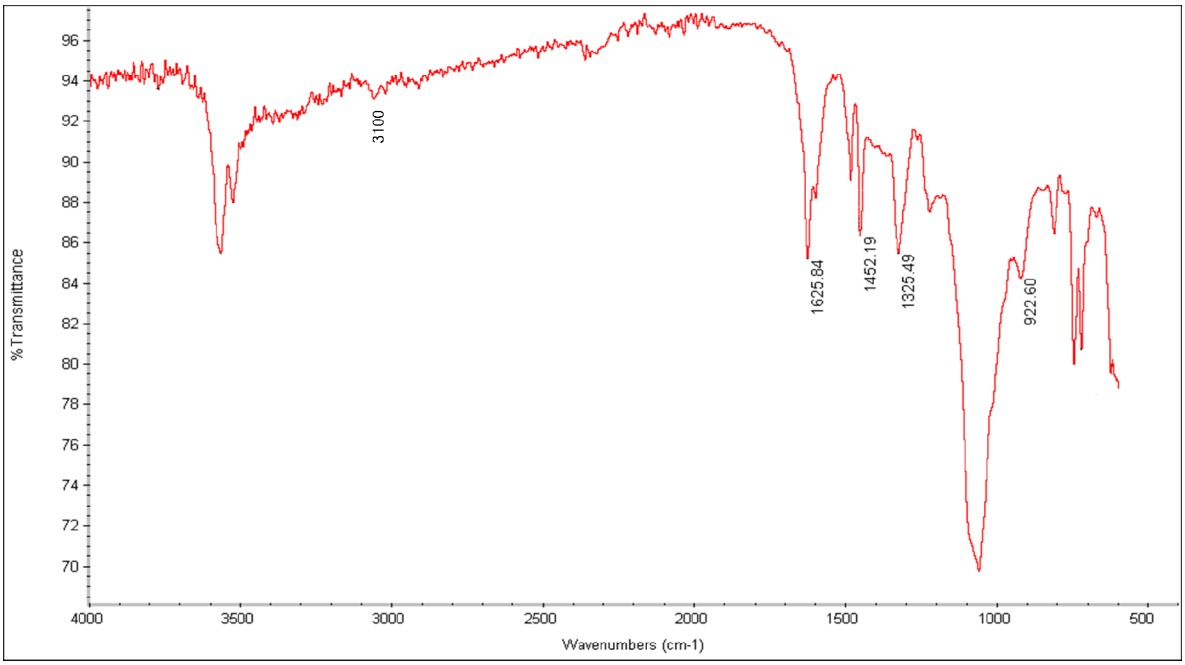


SI 3b) PVK only: 3100cm-1 is characteristic of C-H aromatic stretching of the ring, 1452 cm-1 is the ring vibration PVK, 1329 is C-H plane deformation of vinylidene group, and 1220 cm-1 is indicative of C-H plane deformation of aromatic ring.[12]



[1] Ballav, N. *Synthetic Met.*, 2003, **132**, 213;
[2] Ballav, N. *Mater. Chem. Phys.*, 2004, **87**, 120.

SI 3c) PMProdot modified with PVK



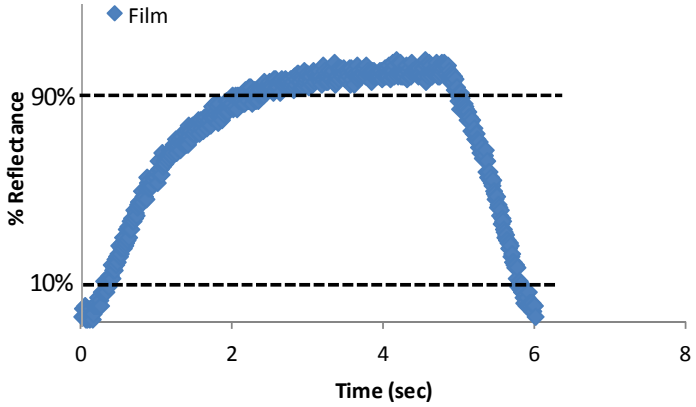
SI 4: Electrochromic response

The effect of electrochromism has been known for many years and it is based on the fact that certain materials change color by depending on their redox state[34]. The electrochromic behavior is due to an electron transfer reaction that takes place during the electrochemical oxidation and reduction of the polymer. The speed in which the electron transfer occurs can be referred to as the "response time", and the measurement of the response time is a fast and easy method of determining electrochemical changes to the conductive polymer.

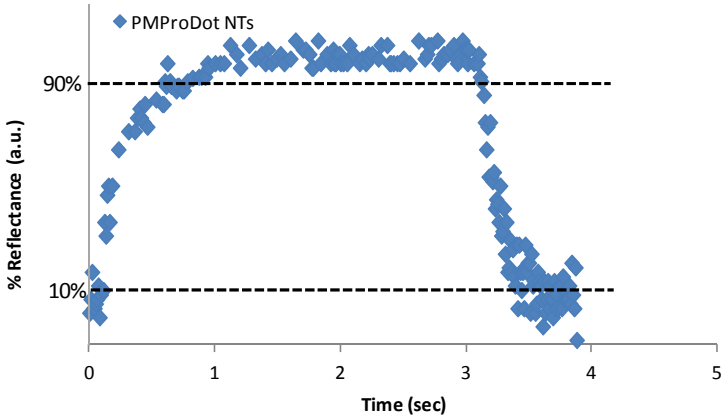
We measured the electrochromic response by applying a potential via a potentiostat (CH instrument 660 A). The color-switching rate of the electrochromic device was measured using a reflectance measurement system (Ocean optics Inc.), composed of a light source (LS-1), a standard reflection probe (R400-7), and a prove holder (R PH-1). The reflected light was detected with a photodiode and analyzed using an oscilloscope (Tektronics, TDS1012,

[3] J. R. Platt, J. Chem. Phys., 1961, 34, 826;
[4] P.M.S. Monk, R.J. Mortimer, D.R. Rosseinsky, Electrochromism, Fundamentals and Applications, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1995.

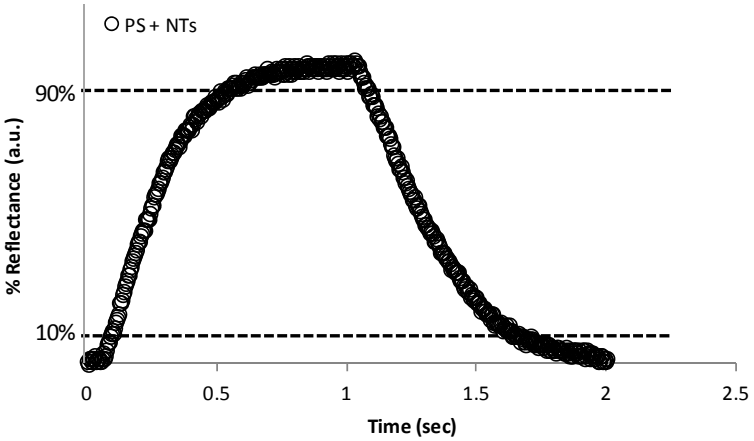
SI 4a: PMProDot Film (t = 2.25s)



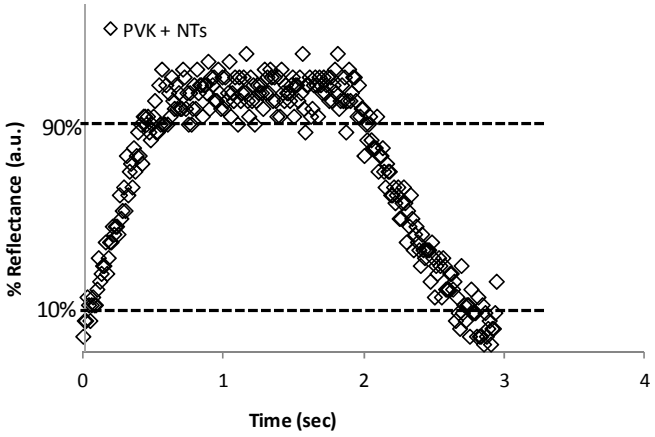
SI 4b: PMProDot NTs (t = 1.03s)



SI 4c: NTs + PS (t = 0.54s)



SI 4d: NTs + PVK (t = 0.41 s)



AFM nanoindentation

The mechanical properties of PMProDot and PVK-modified PMProDot film were tested by AFM nanoindentation technique. The PMProDot film was prepared by applying +1.1V. PVK was grafted on the PMProDot film by applying a potential of 0.75V. The force vs indentation curves were obtained using Atomic Force Microscope (MFP-3D AFM, Asylum Research) at 1 Hz rate. The silicon tip, CSR-10, (VISTA Probes, nanoScience Instruments) with spring constant of 34.53 nN/nm was used to indent the film locally. Inverse optical lever sensitivity (87.56 nm/V) was obtained using ITO substrate which was incompressible in the force range that we tested.

Calculation of the elastic modulus of the polymers (SI Fig. 4a-b)

The elastic modulus of the polymer films were obtained using the method developed by Guo et al.[5] The force as a function of indentation is expressed in the following equation;

$$F^{2/3} = \mathrm{C} + \left[\frac{4}{3}\frac{\mathrm{E}\cdot\mathrm{R}^{1/2}}{(1-\sigma^2)}\right]^{2/3} \cdot \Delta \qquad (1)$$

Where F is the loaded force, Δ is the indentation, R is the curvature of the tip, σ is the Poisson Ratio, E is the Young's modulus of the sample and C is the constant obtained from the fitting. Here, the nominal tip radius (20 nm) was used as specified by the manufacturer and the Poisson Ratio is approximated to be 0.3, which is a good estimate for conventional polymers. The force versus indentation profile near the contact point ($\Delta < 30nm$) is plotted and fitted with the above equation using Origin8 software (OriginLab, USA). In this small indentation region, the material is assumed to behave elastic without adhesion.

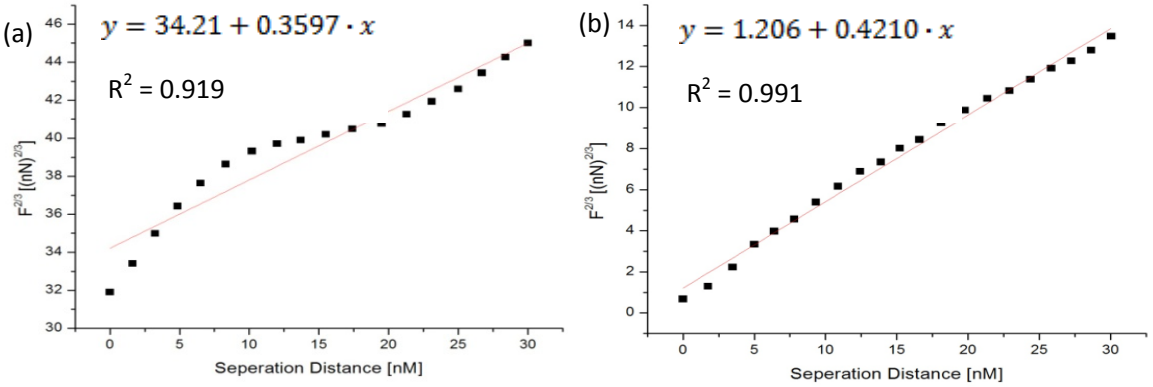
Observation

[5] Guo, S.; Akhremitchev, B. B. *Langmuir,* **2007**, *24*, 880.

ITO showed incompressible behavior in the force range that was tested (up to 1 µN) (SI Fig. 4c). From this measurement, we obtained inverse optical lever sensitivity and used it to calculate an indentation depth during the measurements. We examined the short indentation length (up to 30 nm) since we can only apply the model when the material behaves like an elastic material. The large indentation data (SI Fig. 5c-d) showed characteristic behaviors for each sample. As mentioned, ITO (SI Fig. 5c) was not compressed at all during the force range tested whereas PMProDot and PVK crosslinked PMProDot showed over 1 micrometer indentation. SI Fig. 5d clear show the initial slopes between the films were different, however as the tip indents deeper, the slope becomes similar. The indentation depth of homopolymer decreased when the same area was repeatedly indented. This suggests that the material is brittle and likely to be damaged during repeated tapping with the AFM tip. In a sharp contrast, PVK crosslinked PMProDot showed repeatable force vs indentation profile hysteresis, indicating that no permanent damage is caused during the large indentation. We hypothesize this behavior is likely due to the crosslinking provided by the grafting copolymerization of PVK in PMProDot. The hysteresis is likely due to the adhesion between the tip and substrate during the large indentation.

SI 5: AFM Nanoindentation data and analysis.

SI 5a-b) Force vs Distance fitting for (a) PMProDot and (b) PMProDot grafted with PVK



SI 5c-d) Force curve of (c) ITO (Control) and (d) PMProDot film, PMProDot grafted with PVK, and ITO