Electronic Supplementary Material (ESI) for Polymer Chemistry.

Conductive Polythiophene-based Brushes Grafted from ITO Surface via Self-Templating Approach

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Supplementary Information

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1. Topography mapping of PMTM215 brushes at various stages of synthesis.

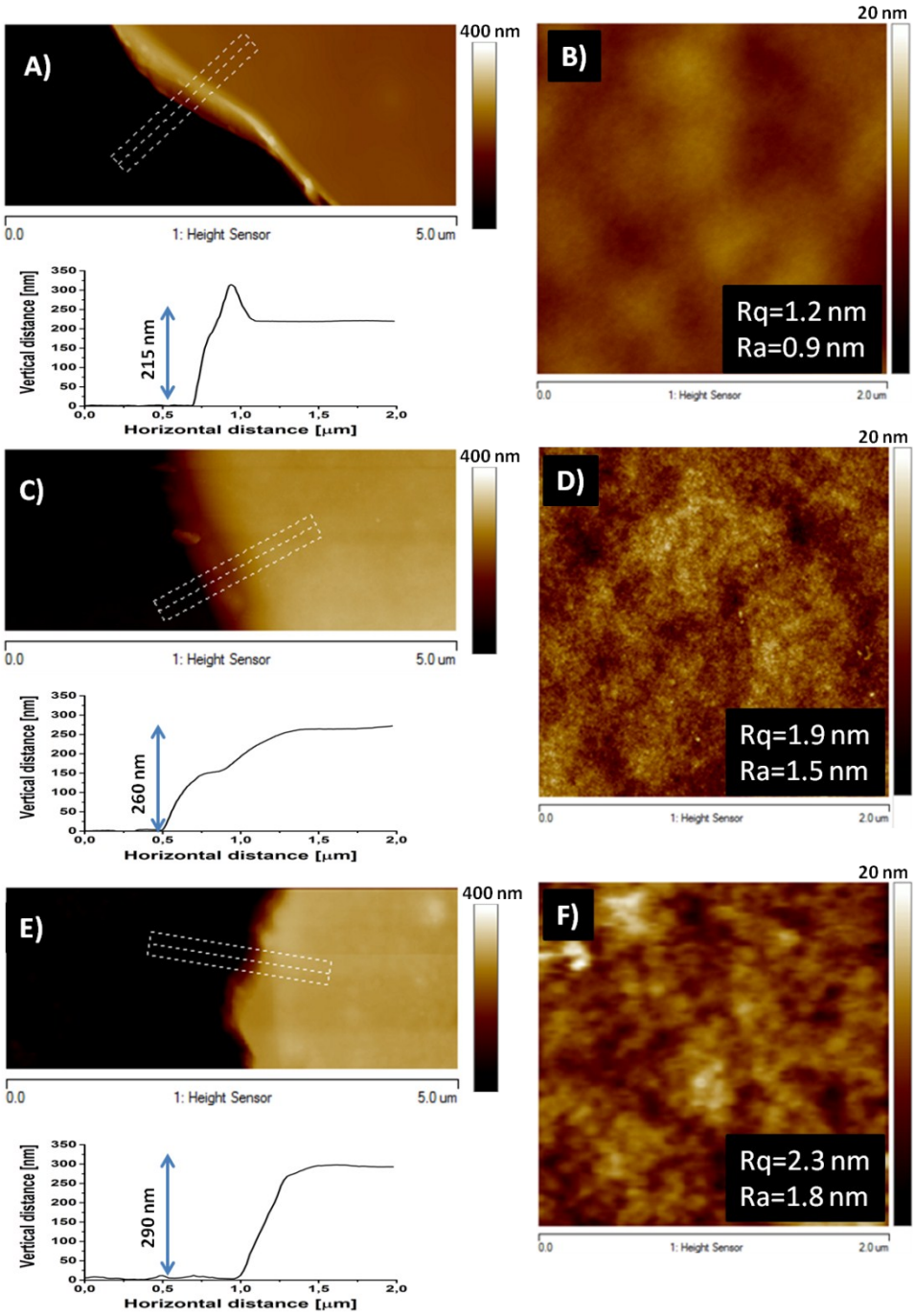

Fig. S1 AFM images of PMTM215 brush: A) height and B) topography after SI-PMP, C) height and D) topography after template polymerization, E) height and F) topography after iodine doping.

2. XPS measurements

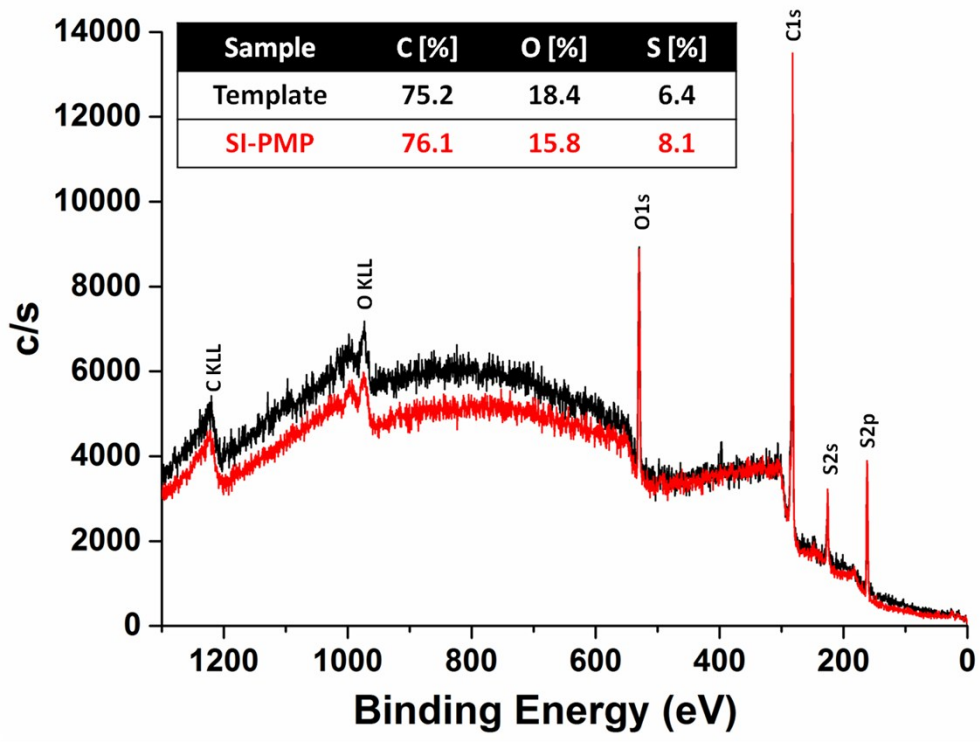

Fig. S2 XPS spectra of 20 nm thick PMTM brush after SI-PMP (red line) and oxidative template polymerization (black line).

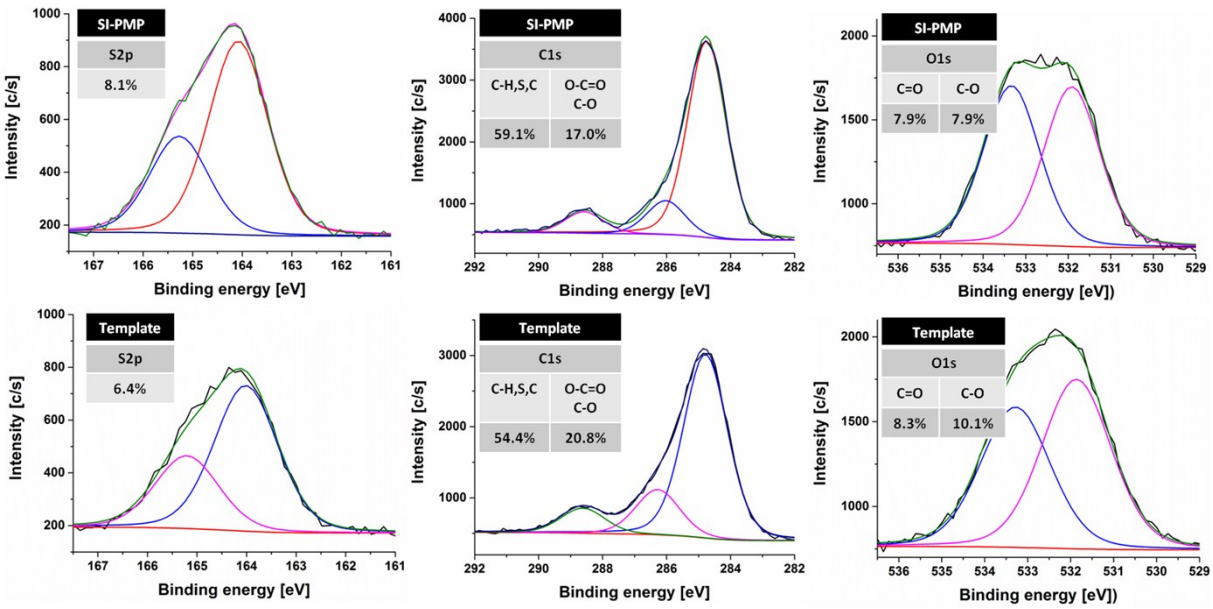

Fig. S3 XPS high resolution spectra of S2p, C1s and O1s for 20 nm thick PMTM brushes after surface-initiated photoiniferter-mediated polymerization (SI-PMP) and template oxidative polymerization (Template).

3. Chain extension experiment

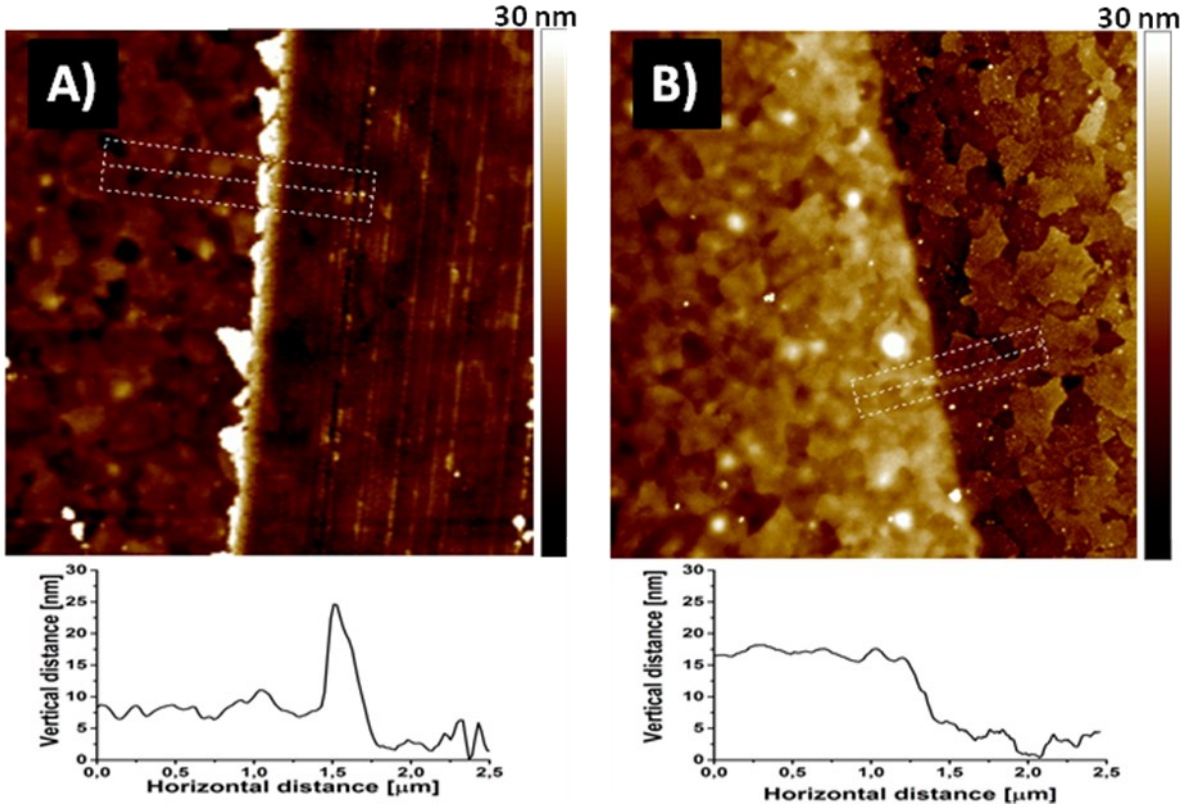

Fig. S4 Thickness of the PMTM12 brush: A) after 2h of SI-PMP and B) after 2+2 h of SI-PMP.

4. IR and UV-VIS characterization of PMTM brushes

Grazing angle FTIR spectra of PMTM brushes after oxidative polymerization with different thicknesses are presented in fig. S5.

UV-VIS spectra of PMTM215 brushes before and after purification procedure as well as after subsequent doping with iodine are presented in fig. S6. It is clearly shown that after purification the spectrum of the brushes changes (some bands are shifted and some, e.g. at 360 and 530 nm disappear) and returns to almost its original shape upon doping with iodine. It indicates the removal of $FeCl_3$ that leads to, at least partial, dedoping of the brushes that are subsequently redoped by iodine treatment. The results also indicate that the red-shift observed in the spectra after oxidative polymerization is most likely caused by increase of the conjugation length but not doping (some contribution of the doping effect cannot be excluded and the effect requires more detailed studies).

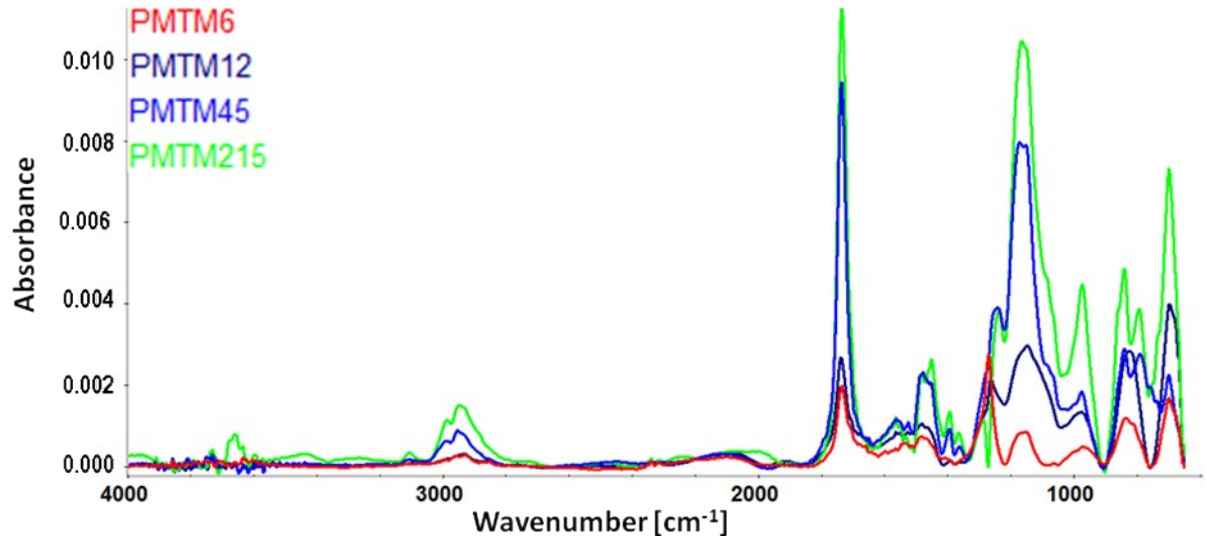

Fig. S5 FTIR spectra of PMTM brushes after template polymerization in original scale.

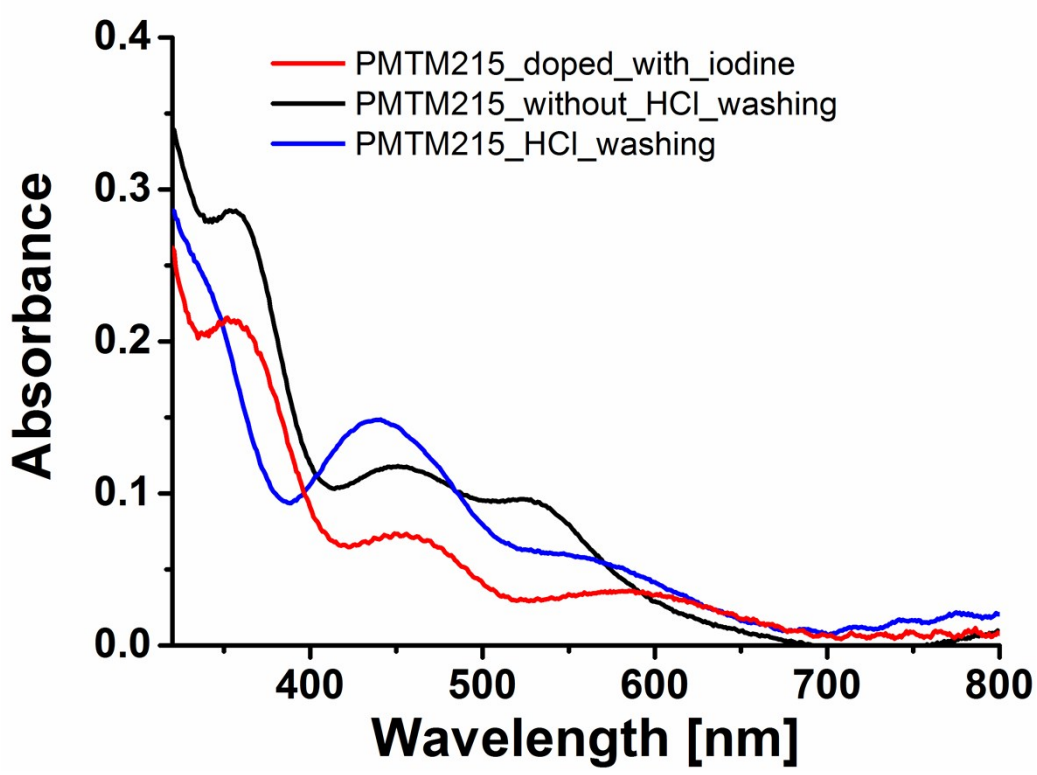

Fig. S6 UV-VIS spectra of PMTM215 brushes after template polymerization: without washing with HCl, washed with HCl and subsequently doped with iodine.

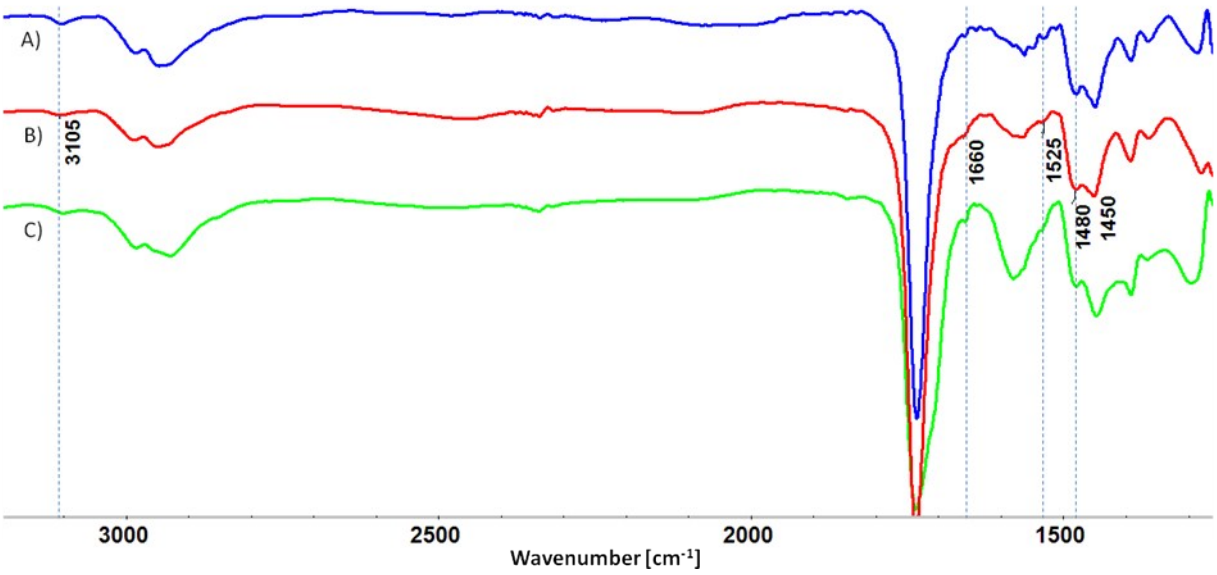

Fig. S7 FTIR spectra of PMTM brushes after template polymerization ($FeCl_3$ as oxidising agent): A) in CH_3NO_2 (with slow addition of $FeCl_3$) at 0°C for 6h and than at 25°C for 14 h (brush thickness 260 nm), B) in CH_3NO_2 at 0°C for 6h and than at 25°C for 14 h (140nm), C) in dry $CHCl_3$ at 0°C for 6h and than at 25°C for 14h (170 nm).

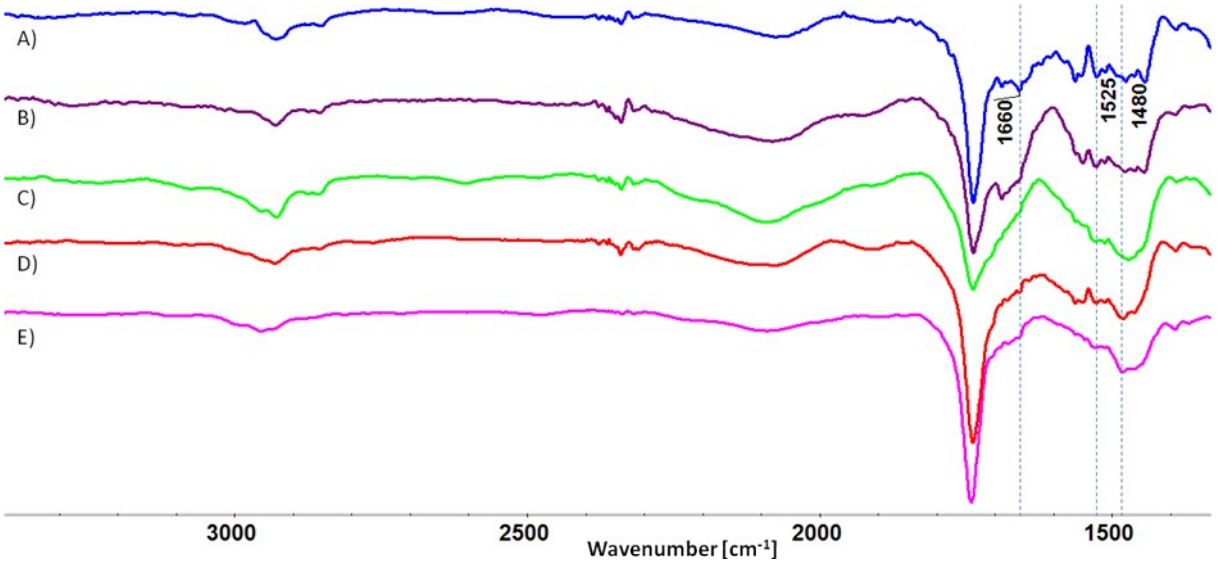

Fig. S8 FTIR spectra of PMTM brushes after template polymerization ($FeCl_3$ as oxidising agent): A) in CH_3NO_2 (with slow addition of $FeCl_3$) at 0°C for 6h and than at 25°C for 14 h (brush thickness 10 nm), B) in CH_3NO_2 at 25°C for 20 h (12 nm), C) in dry $CHCl_3$ at 0°C for 2h and than at 25°C for 18h (12nm), D) in CH_3NO_2 (with slow addition of $FeCl_3$) at 0°C for 6h and than at 25°C for 14 h (15 nm), E) in CH_3CN at 25°C for 20h (33 nm).

5. Estimation of the conductivity of the doped PMTM brushes

Electrical conductivity (σ) values for the doped PMTM brushes were calculated using a simple formula (eq. 1)

$$\sigma = l/RS \qquad (1)$$

where: S - the tip-surface contact area; l - the average length of the brush chains; R - the electrical resistance of the brushes that was taken as an average reciprocal slope of the curves obtained by fitting line equations to the linear parts of the I/U plots (see figure S9). For the plots ramped in the range of -5000 mV to 5000 mV, the linear range employed for calculations was typically -3000mV to 3000mV while for the plots ramped in the range from -500mV to 500mV it was typically -300 mV to 300mV.

Assuming small indentation of the tip (nominal tip radius 25 nm, low external load) into the brush the contact area (S) may be estimated on the level not larger than 10^{-17} m^2. The actual dry thicknesses of the brush were taken as chain lengths (depending on brush thickness, in the range between $10\text{-}290 \cdot 10^{-9}$ m).

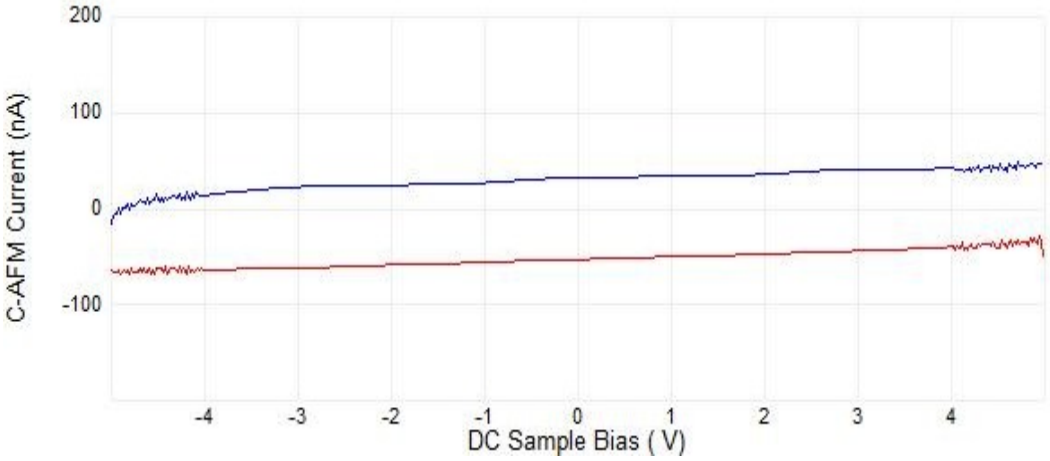

Fig. S9 Exemplary I/V plot captured for PMTM12 sample.