Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

High performance all-organic flexural piezo-FET and nanogenerator via nanoscale soft-interface strain modulation

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Supplementary Information SI-I: Experimental

Figure 1 shows the schematic of the process used for the formation of Polyaniline film on the flexible PET substrate and subsequent electrospinning of P(VDF-TrFE) fibers thereupon. Briefly, the PET substrate was first sonicated in soap solution, then in DI water, followed by oven-drying at 60^0C overnight. The starting monomer used i.e. aniline was distilled before use. Polyaniline emeraldine salt, was grown *in situ* on the PET substrate by simple slide-drop method as shown in the schematic. In this method 100 µl acidic aniline solution (HCl: Aniline = 1:1) was spread on the active area of the device. The ratio of aniline to oxidizing agent ammonium persulphate (APS) was kept as 4:1. The same volume of acidic ammonium persulphate solution HCl:ANI 1:1was poured on the aniline drop. Immediately a cleaned glass slide was tenderly placed on this mixture, with the drop spreading over the entire active area forming a thin uniform polymerized aniline layer on PET. The glass slide was kept for five minutes and then removed. The as-synthesized PANI film on PET was washed with DI water and rinsed in 1M HCl. Such films were then dried for 48 hours at 60°C. For the electrospinning of fibers, a 20 wt.% solution of P(VDF-TrFE) was prepared in DMF and acetone solvent mixture (ratio 3:2) and stirred continuously until a transparent and homogeneous solution was formed. This solution was then transferred to a plastic syringe hold. Electrospinning of this solution onto PANI film surface (which acts as the conducting bottom electrode) was carried out under an applied electric field of 10 kV, at a flow rate of 0.5 ml/hr and with collector to needle distance of 10 cm. The electrospinning was performed for 30 minutes. Conductive copper tapes were used as electrodes for making contact to the PANI film. These tapes of dimensions (0.5 cm x 3.0 cm) were pasted at the two sides of the PANI film defining the active device area as 1 cm^2. The use of PANI film itself as a bottom

electrode for electrospinning of fibers ensured a good interface between the channel and the modulator, which is important for the realization of strong strain field modulation effects. Mechanical pressing a pre-spun fiber mat does not yield similar levels of modulation. During measurements, first the strain response was recorded only for the PANI film with the electrical measurements performed using Keithley 2400 source meter. This was followed by the measurements of the PANI/P(VDF TrFE) heterostruture strain-FET device. For electromechanical measurements, Dynamic mechanical analyser (DMA) was used.

Supplementary Information SI-II

WAXS pattern was recorded by making the PANI film thicker by multiple coating on same substrate. According to the literature, the XRD pattern matches well with the emeraldine salt conducting phase having 50% doping. [1]

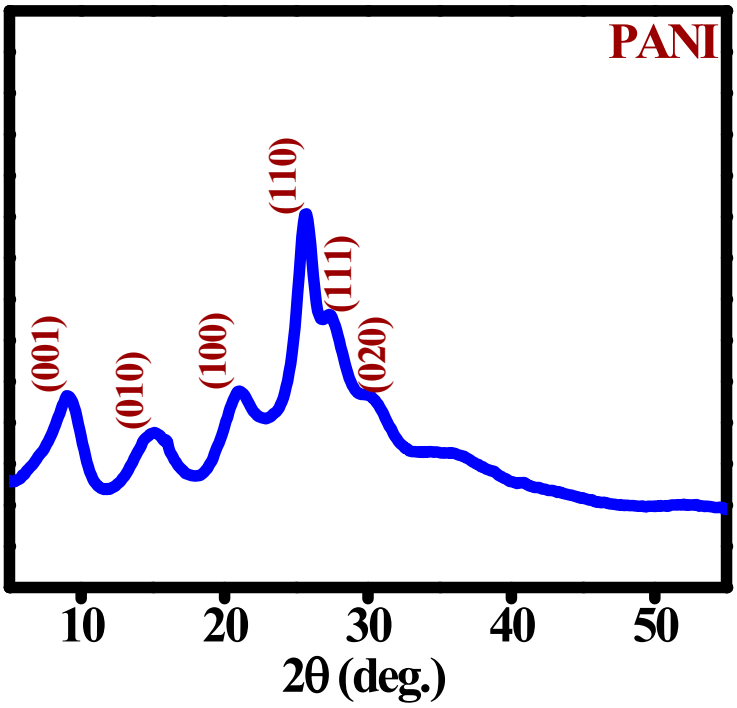


Figure SI-II: WAXS of Polyaniline film

Supplementary Information SI-III:

FTIR was recorded by making the PANI film thicker by multiple coating on same substrate. It confirms the emeraldine salt conducting phase. [2]

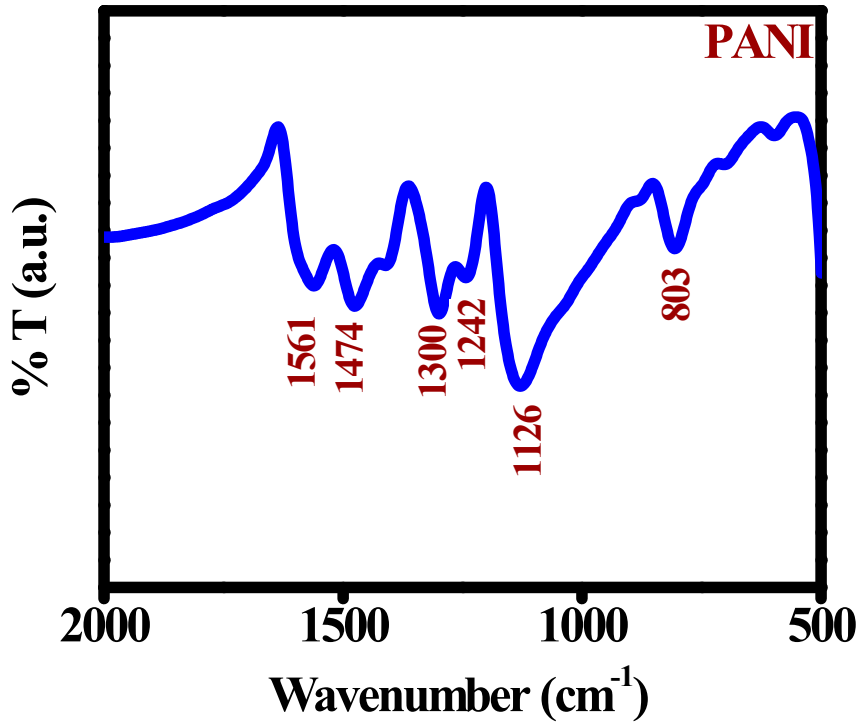


Figure SI-III: FTIR of Polyaniline film

Supplementary Information SI-IV:

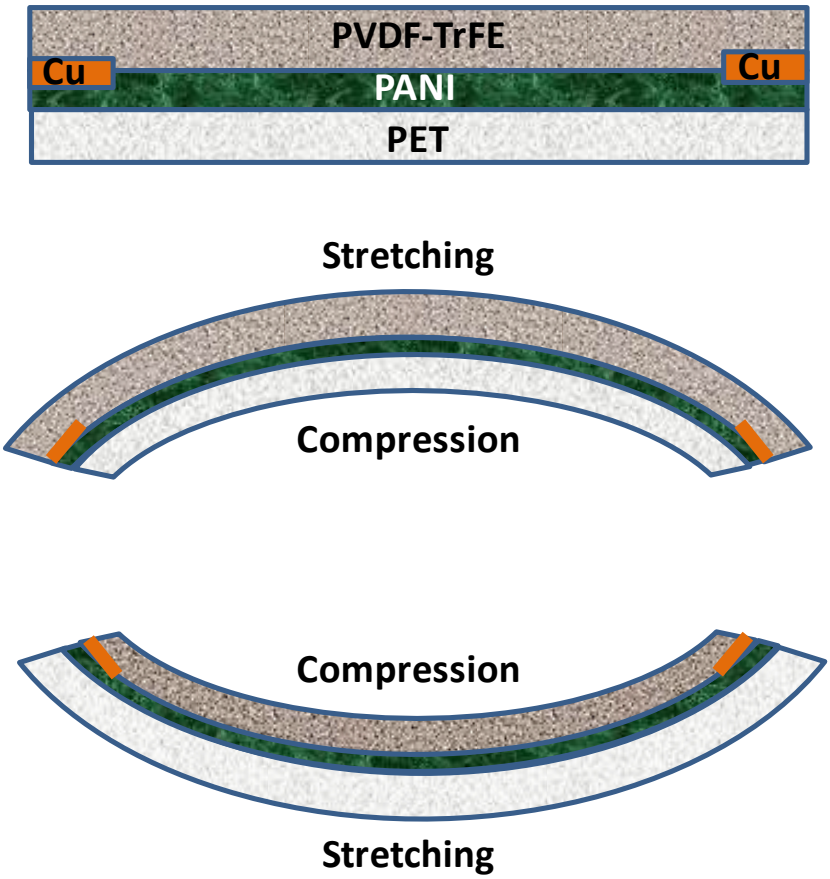


Figure SI-IV: PANI/ P(VDF-TrFE) ES device under complimentary flexural modes

Supplementary Information SI-V:

I-V characteristics for spin coated P(VDF-TrFE) film based devices measured under the same applied flexural strain for comparison.

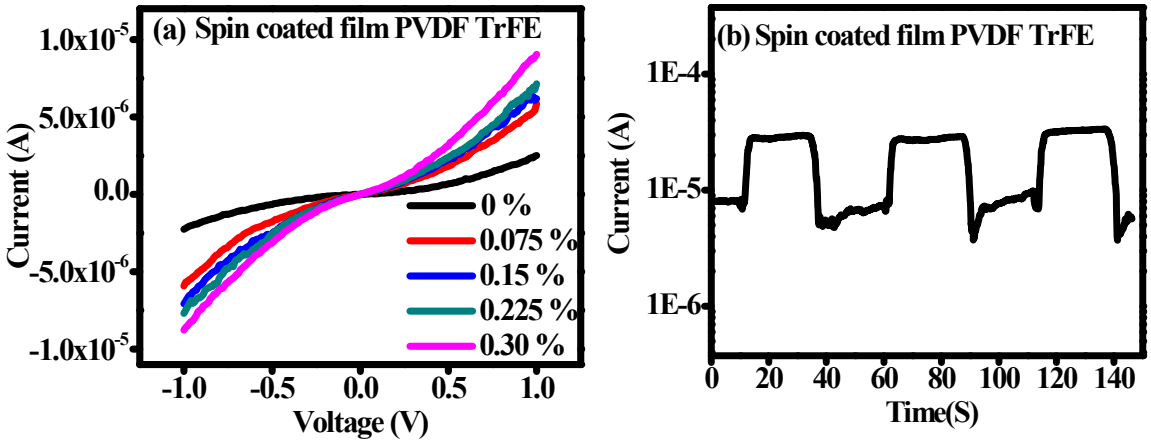


Figure SI-V: I-V for (a) I-Vs for Spin coated P(VDF-TrFE) film on PANI (b) Current-time response for Spin coated P(VDF-TrFE) film on PANI

Supplementary Information SI-VI:

I-V characteristics for non-Piezo, non-ferroelectric electrospun PVP based devices show marginal change under the flexural strain.

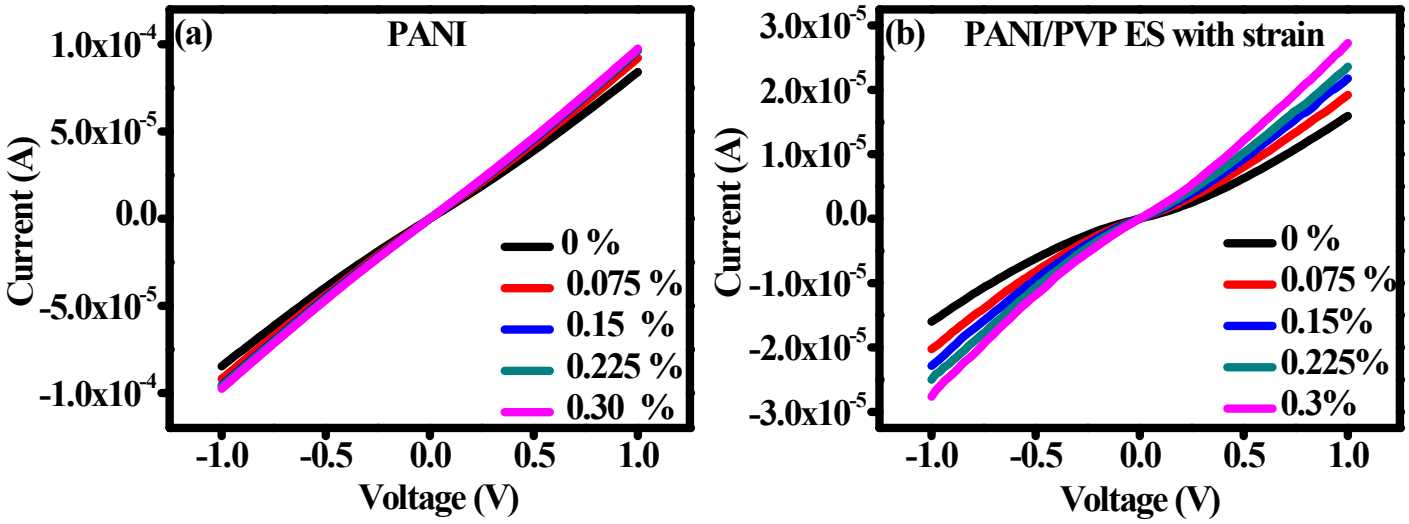
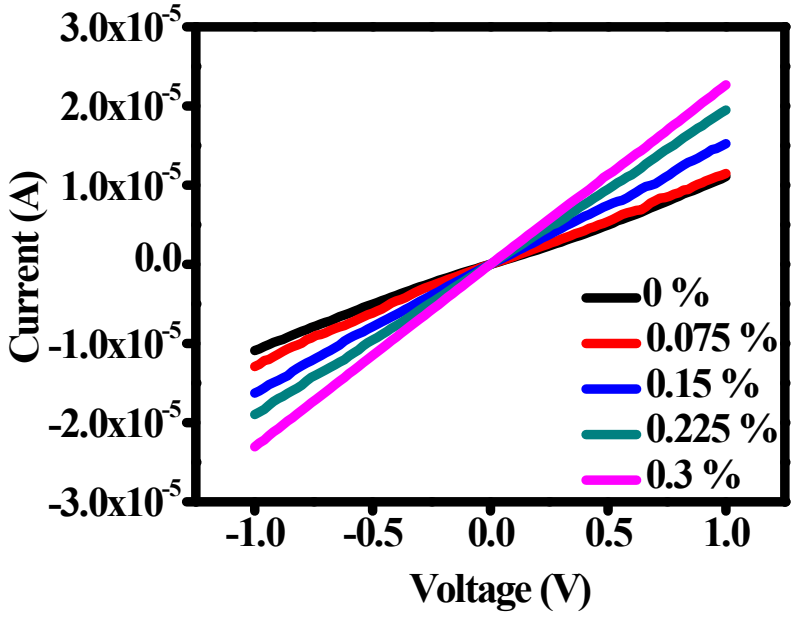


Figure SI-VI: I-V for (a) Only PANI Device (b) Only PANI/ PVP ES Device

Supplementary Information SI-VII:

(a)



(b)

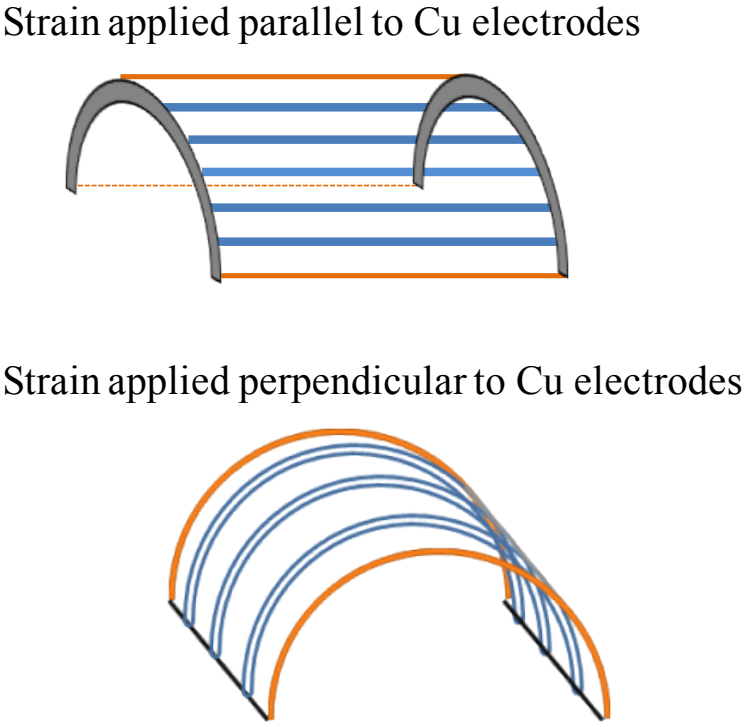


Figure SI-VII: I-V for a) tensile axial bending for PANI/P(VDF-TrFE) ES device b) strain applied perpendicular or parallel to the Cu electrodes

Supplementary Information SI-VIII:

Voltage generated for PANI/P(VDF-TrFE) device measured under the flexural strain of 0.7 % with zero bias.

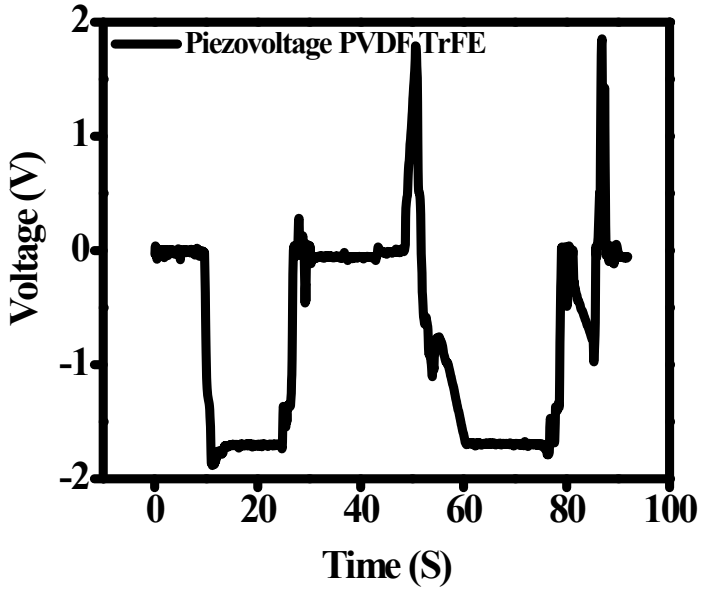


Figure SI-VIII: Voltage generated for P(VDF-TrFE) NF

Supplementary Information SI-IX:

a) The pictorial presentation below show, probable interactions at the heteromolecular interface of PANI-P(VDF-TrFE) without and with applied flexural strain.

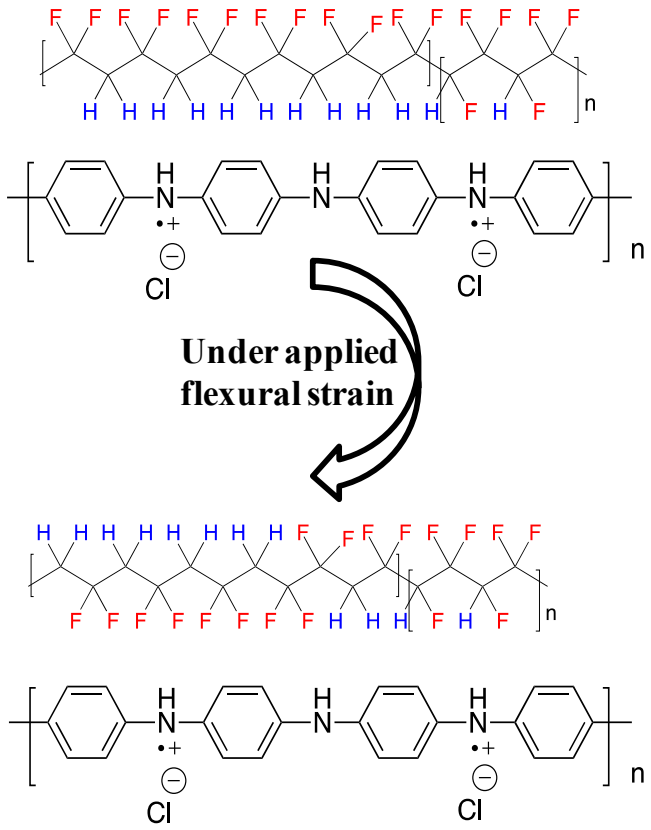


Figure SI-IX: (a) Molecular interface interactions without and with applied flexural strain for PANI/P(VDF-TrFE). Note that the figure suggests that under applied strain more number of F ions will get directed towards PANI by C-C bond re-orientation under strain.

b)

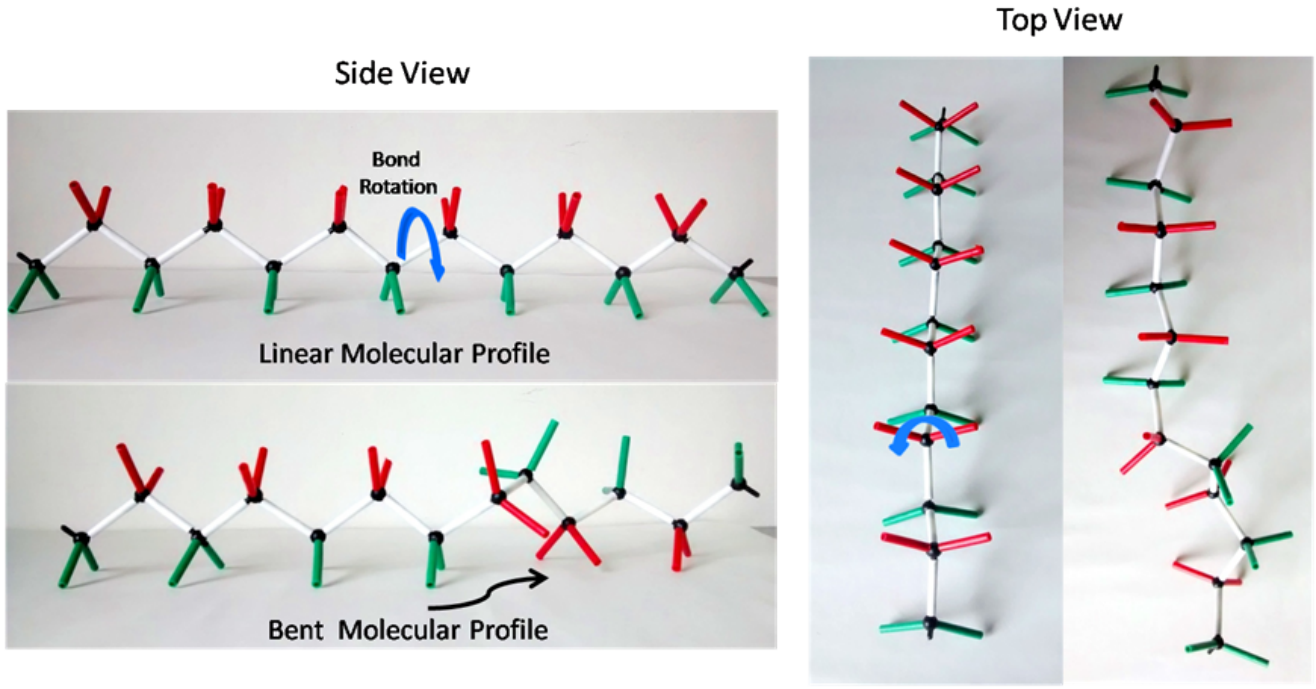


Figure SI-IX: (b) Model picture for molecular profile for the case of PVDF

Supplementary Information SI-X:

The results of nanogenerator measurements are shown in the figure 4 of the revised manuscript. We calculated the areal power density of our device by taking the product of peak V_{oc} and peak J_{sc} divided by the area. Prior to measurements we varied the load resistances from 100 Ω to 10 MΩ as the power density of the device does depend on load matching [3, 4, 5]. It was found to have maximum power density of 0.25μW/cm^2 at a load of 10 MΩ. All the further measurements were done under the same load of 10 MΩ.

For the capacitor charging, a simple bridge rectifier circuit was used as shown in the **figure 4**c in the revised manuscript. The cantilever beam set up was used for applying mechanical strain. The strain applied was 0.2 % at a frequency of 10 Hz with a excitation amplitude of 2V. The strain was applied to the free end of the scale which generated mechanical vibrations along the length of the scale.

References:

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