Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

3D printed recyclable and self-poled polymer piezoelectric generators through single-walled carbon nanotube templating

Nick A. Shepelin,[a] Peter C. Sherrell,[a] Eirini Goudeli,[a] Emmanuel N. Skountzos,[bc] Vanessa C. Lussini,[d] Greg W. Dicinoski,[d] Joseph G. Shapter [e] and Amanda V. Ellis *[a]

[a] Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia

[b] Department of Chemical Engineering, University of Patras, Greece

[c] FORTH/ICE-HT, Patras, GR 26504, Greece

[d] Note Issue Department, Reserve Bank of Australia, Craigieburn, Victoria 3062, Australia

[e] Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland 4072, Australia

** Corresponding author*
Email address: amanda.ellis@unimelb.edu.au

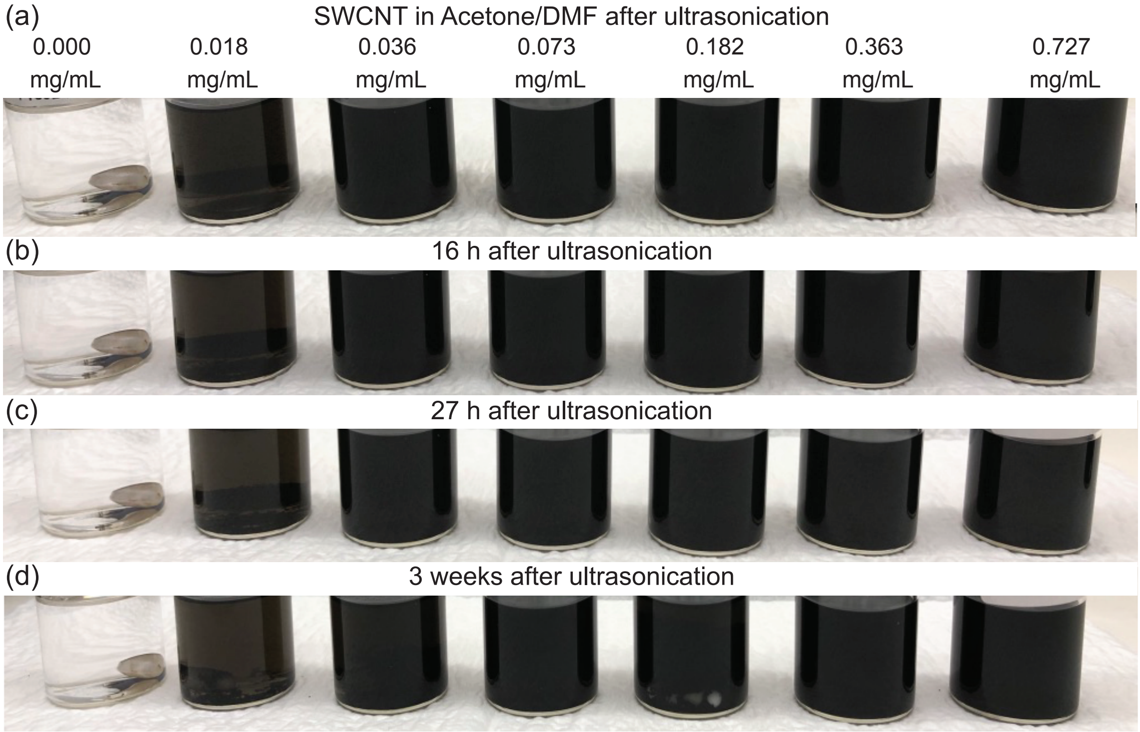

Figure S1: Images showing the SWCNTs dispersed in acetone (60 vol%) and DMF (40 vol%) after 30 min bath ultrasonication, showing concentrations between 0.000 mg mL^{-1} and 0.727 mg mL^{-1}, corresponding to SWCNT concentrations of between 0.000 wt% and 0.200 wt% relative to PVDF-TrFE. (a) Directly after ultrasonication in a bath sonicator. (b) 16 hours after ultrasonication. (c) 27 hours after ultrasonication. (d) 3 weeks after ultrasonication.

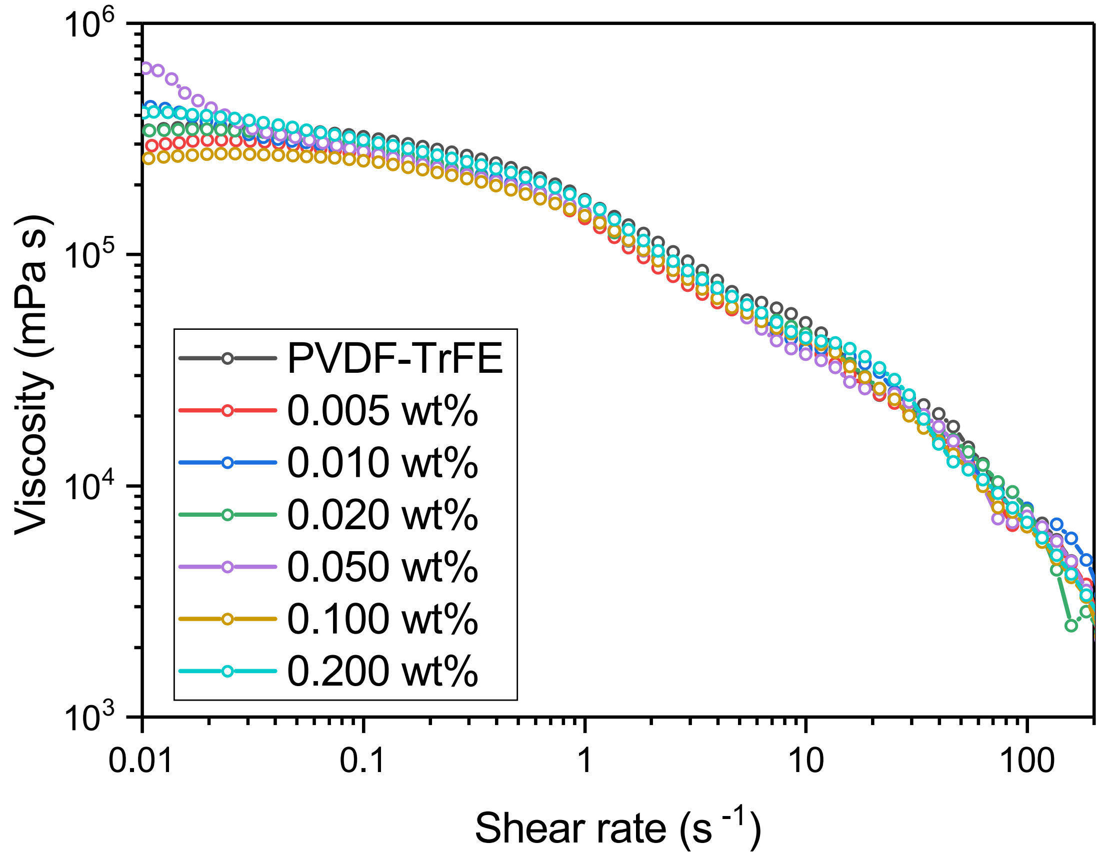

Figure S2: The viscosity of SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) inks as a function of shear rate.

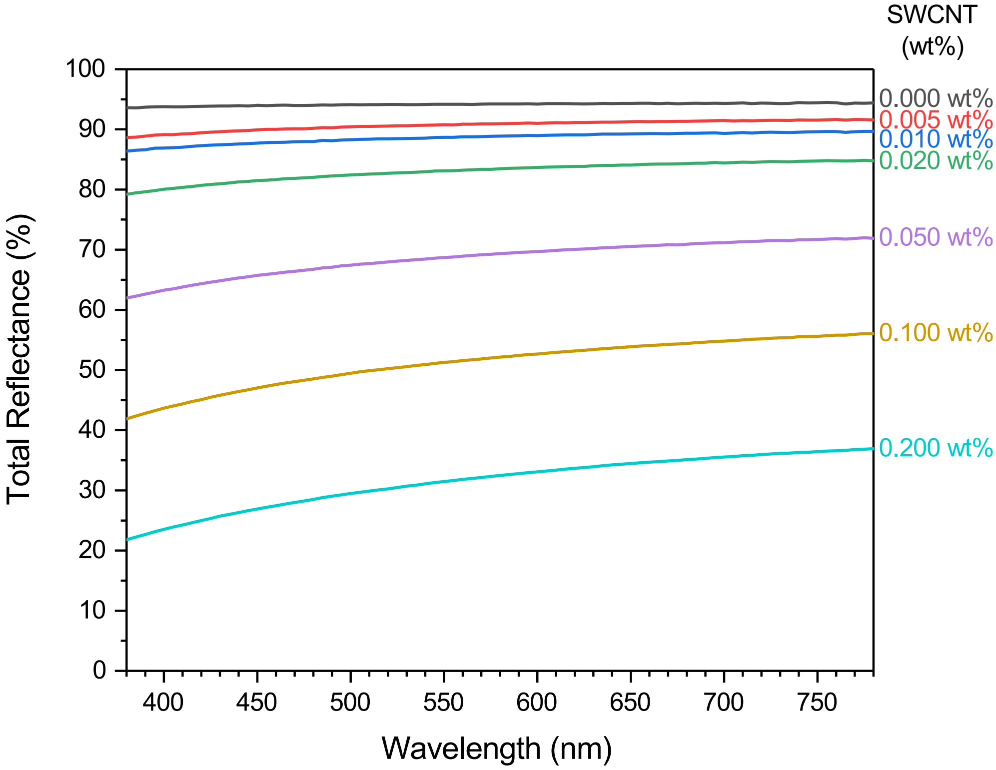

Figure S3: The visible wavelength (380 nm<λ<780 nm) transmittance of the SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films, shown as the total reflectance within the integrating sphere.

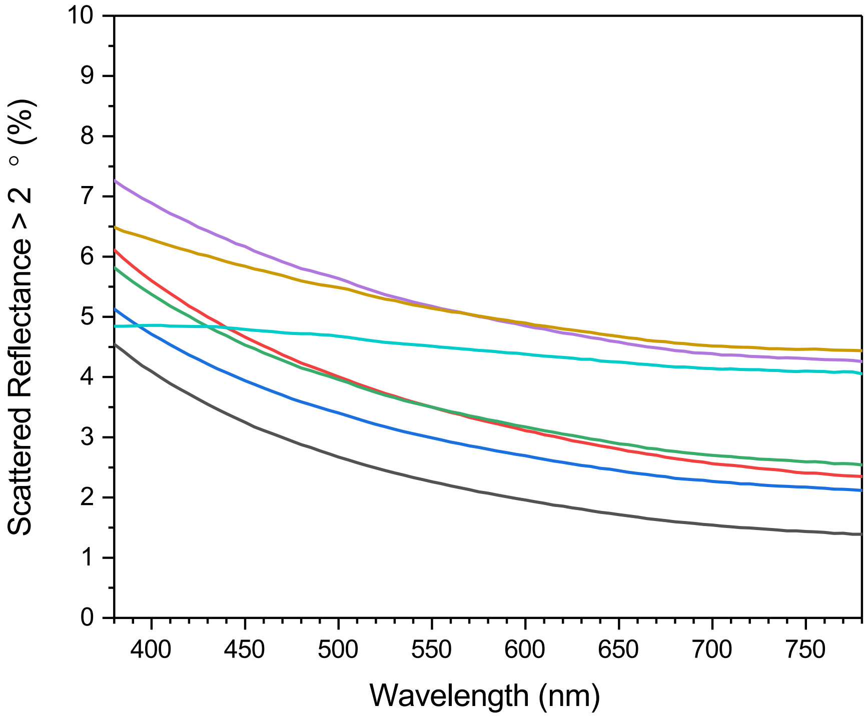

Figure S4: The visible wavelength (380 nm<λ<780 nm) transmittance at angles >2° of the SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films, shown as the scattered reflectance within the integrating sphere.

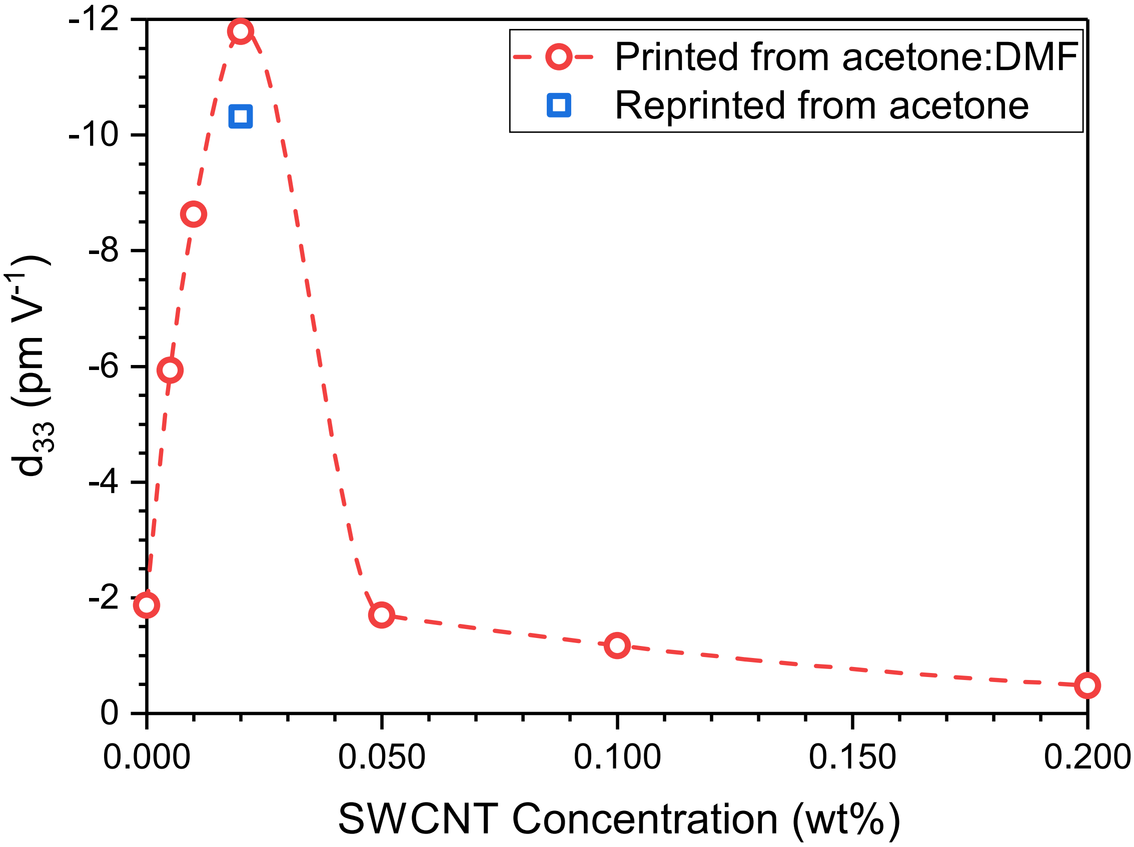

Figure S5: The d_{33} values calculated using PFM at +10 V for the initial 3D printed SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films (shown in red) and the SWCNT/PVDF-TrFE (0.020 wt%) film recycled and reprinted from acetone (shown in blue).

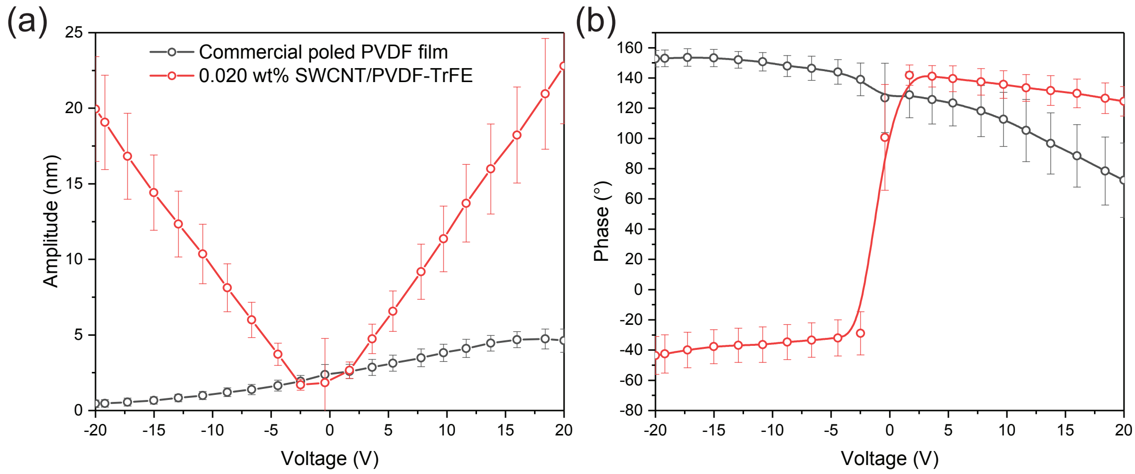

Figure S6: PFM lithography (a) amplitude and (b) phase plots showing the data obtained for the extrusion printed 0.020 wt% SWCNT/PVDF-TrFE film (red) and the commercially available poled PVDF film (grey) (Measurement Specialities).

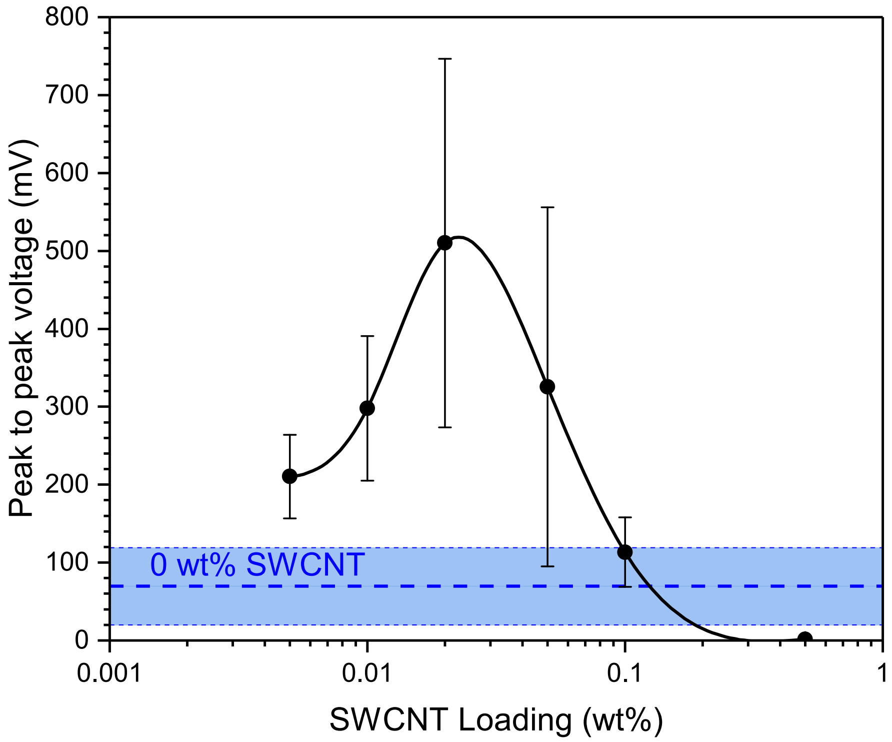

Figure S7: Peak to peak voltage (V_{pp}) of SWCNT/PVDF-TrFE (0.000 wt% to 0.500 wt%) PEGs, with error presented for three separate samples at each data point.

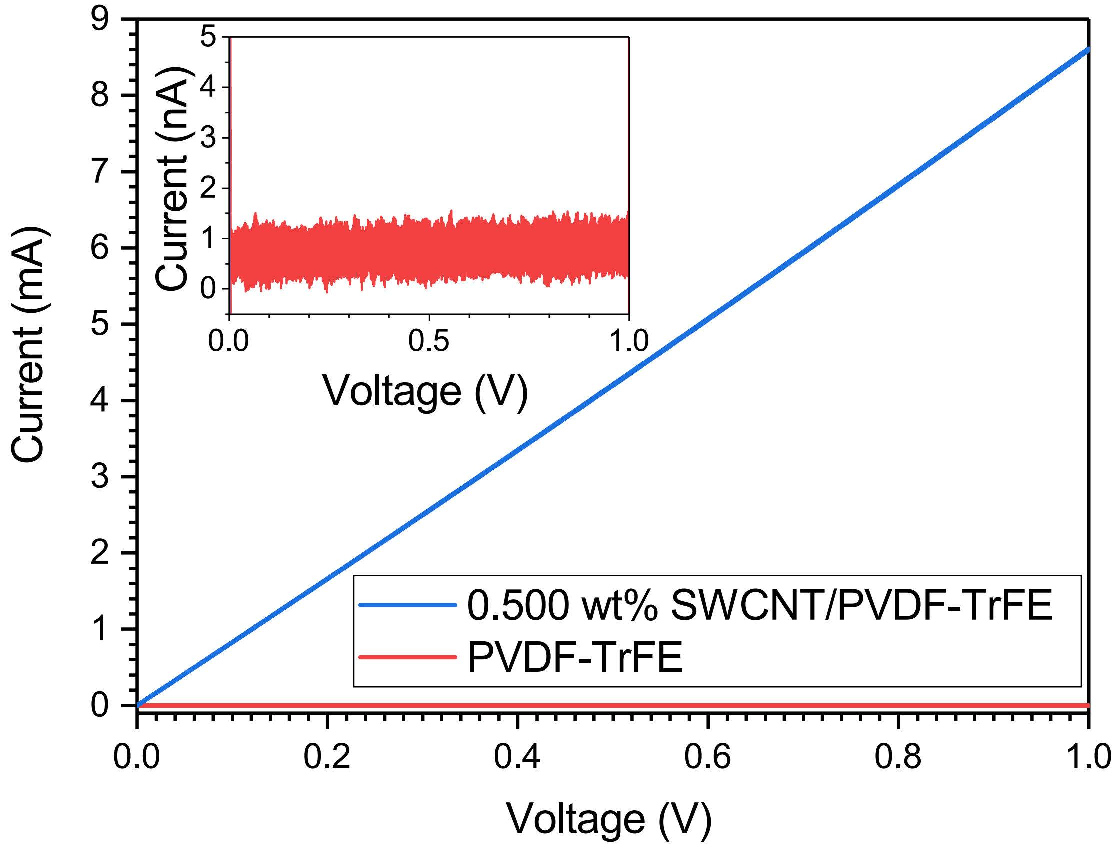

Figure S8: Cyclic voltammetry (CV) for 3D printed SWCNT/PVDF-TrFE (0.000 wt% and 0.500 wt%) films. Inset shows the y-axis expanded to a maximum of 5×10^{-6} mA.

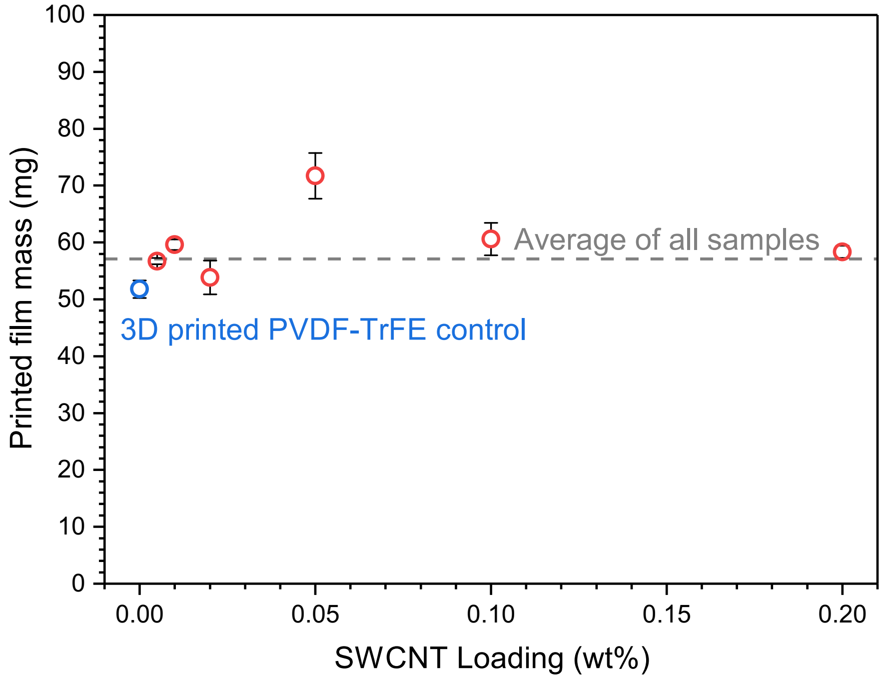

Figure S9: The measured mass for SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films.

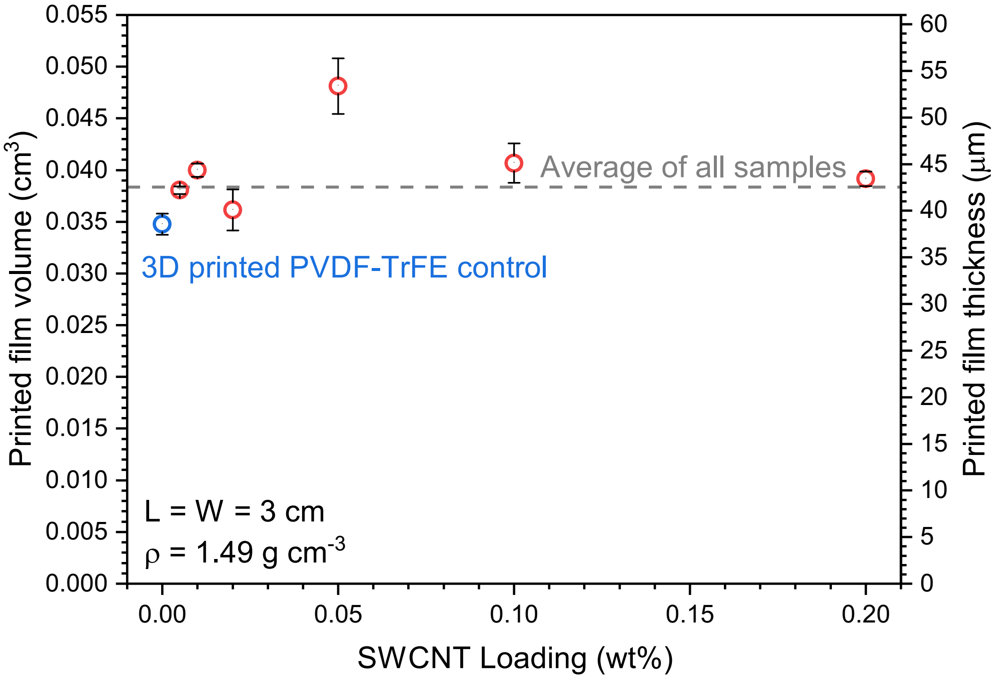

Figure S10: The volume and thickness calculated from Fig. S8 for SWCNT/PVDF-TrFE (0.000 wt% to 0.200 wt%) films. The length and width of the films was 3 cm and density was 1.49 g cm^{-3} (75 mol% VDF and 25 mol% TrFE, 420 kDa, Solvay).

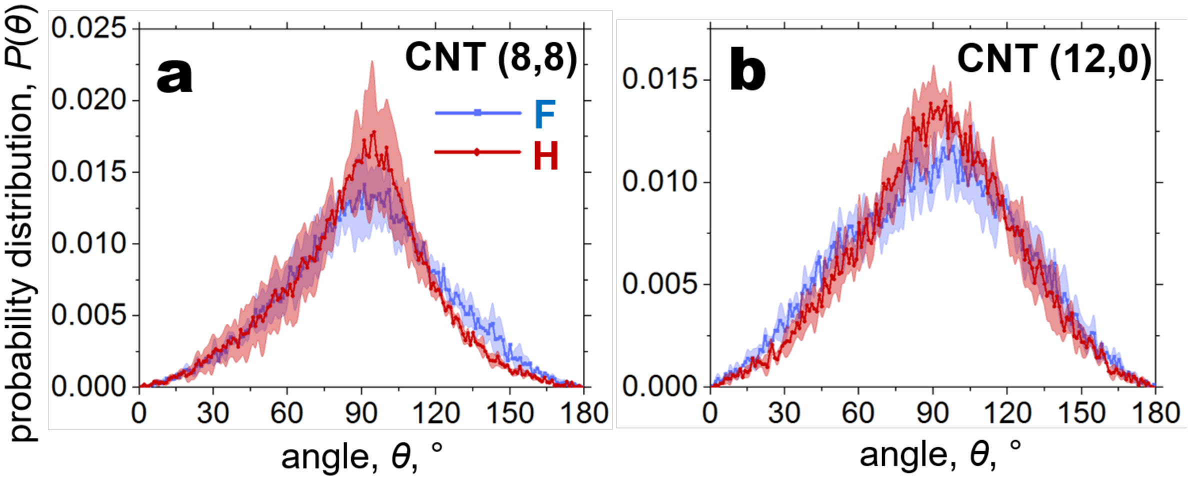

Figure S11: The probability distribution of the angle, θ, between the F – C (blue lines) or the C – H (red lines) of the TrFE units and the CNT axis of symmetry having (a) armchair (8,8) and (b) zig-zag (12,0) chirality. The F – C and the C – H branches are mostly perpendicular to the CNT surface. The shaded regions represent the error bar obtained from three different MD simulations.

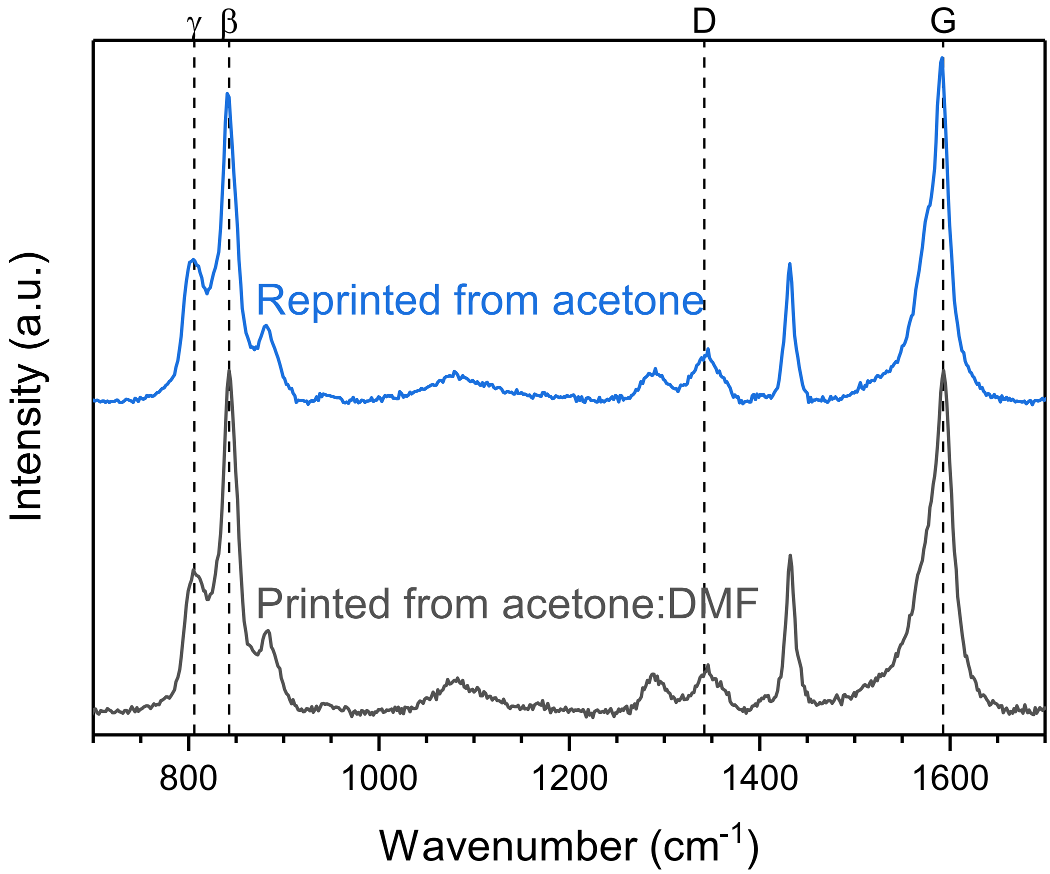

Figure S12: The Raman spectra for the initial 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film (shown in grey) and SWCNT/PVDF-TrFE (0.020 wt%) recycled and reprinted from acetone.

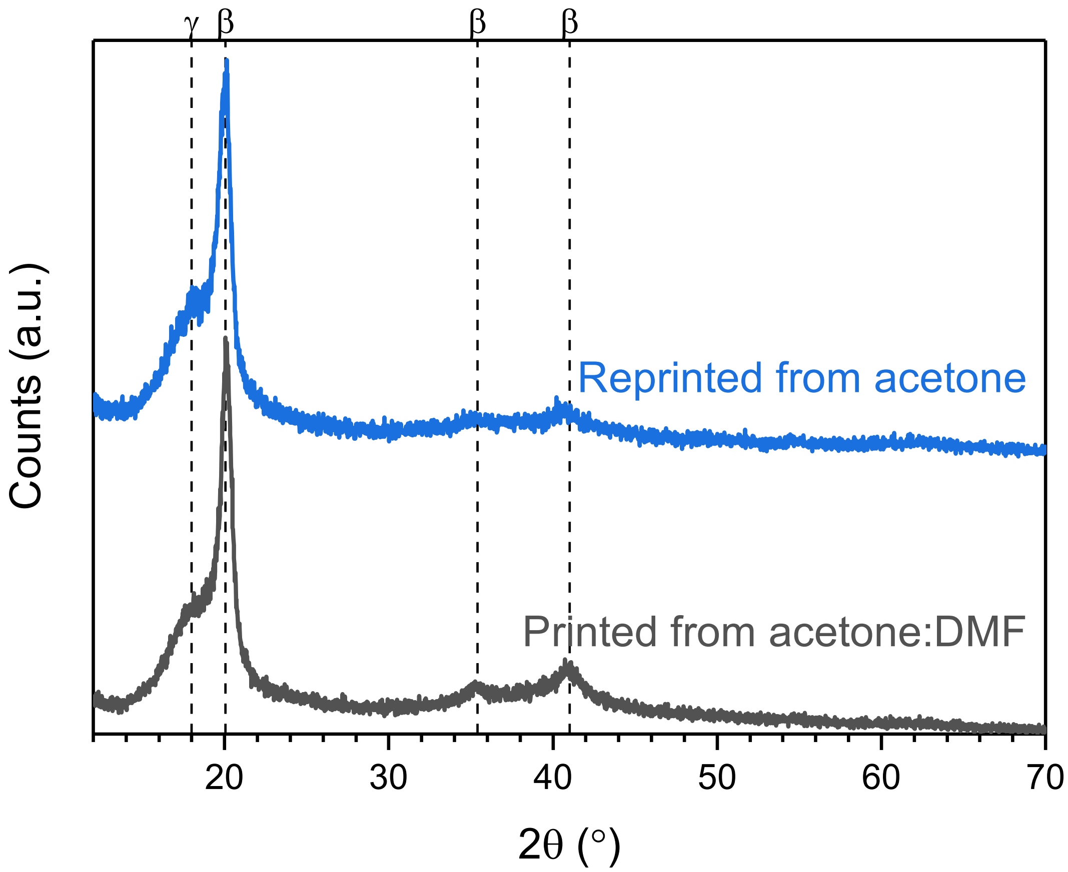

Figure S13: The XRD spectra for the initial 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film (shown in grey) and SWCNT/PVDF-TrFE (0.020 wt%) recycled and reprinted from acetone.

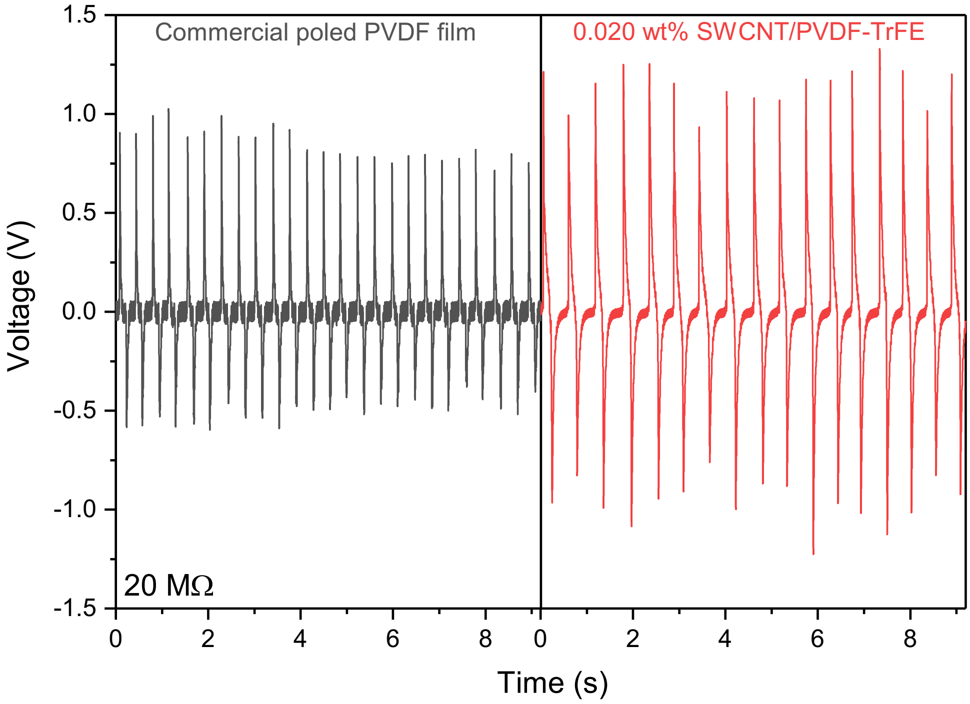

Figure S14: The voltage as a function of time for a PEG made from commercially available poled PVDF film (grey) and a PEG made using the extrusion printed 0.020 wt% SWCNT/PVDF-TrFE film. Low force cyclic compression using a finger pinch was used, with a load resistance of 20 MΩ.

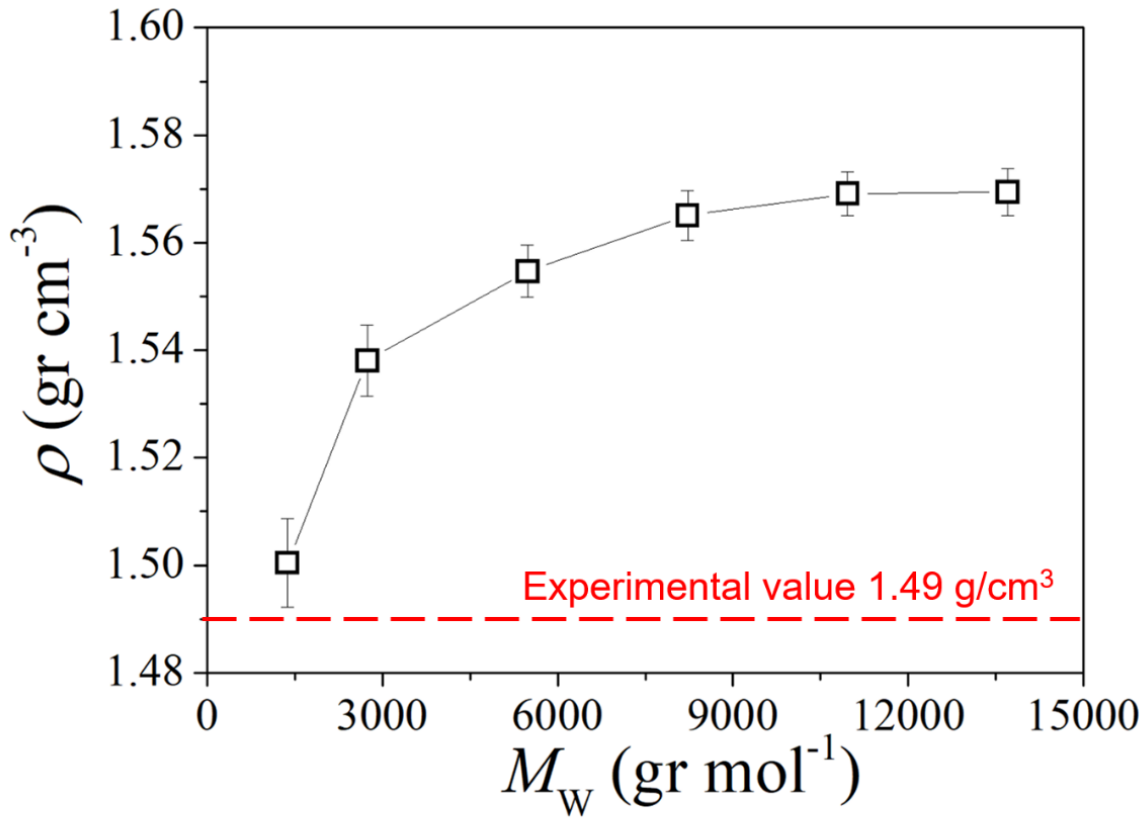

Figure S15: The density of the PVDF-TrFE melt at 230 °C as function of the co-polymer molecular weight obtained by MD simulations (symbols). Increasing the molecular weight leads to a slight increase in the co-polymer density with attains asymptotically a value of about 1.57 g cm^{-3} for molecular weights bigger than about 10,000 g mol^{-1}. The MD-obtained density is in excellent agreement with the experimental value provided by the PVDF-TrFE manufacturer (Solvay, horizontal broken line).

Table S1: The CNT/fluoropolymer energy harvesting figures of merit found in recent literature and the materials and processes used to fabricate the PEGs.

CNT type	Polymer type	CNT concentration (wt%)	Power density (μW/cm^3)	Deposition technique	Poling technique	Reference
MWCNT	PVDF	0.075	0.45	Spray coating	Unpoled	Lee *et al.*[1]
MWCNT	PVDF	0.050	59.4	Solvent casting	Drawing (60 °C) up to 400-500% and electrode poling up to 60 MV/m in silicone oil	Ning *et al.*[2]
SWCNT	PVDF-TrFE	0.100	1481.5	Solvent casting	Electrode poling 58 MV/m at 43 °C in silicone oil	Kim *et al.*[3]
MWCNT	PVDF	0.030	26.2	Electrospinning (1.5 MV/m)	Electrode poling 7 MV/m at 80 °C	Liu *et al.*[4]
MWCNT	PVDF-HFP	0.050	4.0	Solvent casting	Drawing (60 °C) up to 400-500% and electrode poling up to 60 MV/m in silicone oil	Wu *et al.*[5]
SWCNT	PVDF-TrFE	0.020	20.0	3D printing	Unpoled	This work
SWCNT	PVDF-TrFE (recycled from acetone)	0.020	70.6	3D printing in green solvent	Unpoled	This work

References

1 S. Lee and Y. Lim, *Macromol. Mater. Eng.*, 2018, **303**, 1700588.

2 H. M. Ning, N. Hu, T. Kamata, J. H. Qiu, X. Han, L. M. Zhou, C. Chang, Y. Liu, L. K. Wu, J. H. Qiu, H. L. Ji, W. X. Wang, Y. Zemba, S. Atobe, Y. Li, Alamusi and H. Fukunaga, *Smart Mater. Struct.*, 2013, **22**, 065011.

3 J. Kim, K. J. Loh and J. P. Lynch, in *Sensors and Smart Structures for Civil, Mechanical, and Aerospace Systems 2008*, Proc. SPIE 6932, San Diego, California, United States, 2008, p. 693232.

4 Z. H. Liu, C. T. Pan, L. W. Lin and H. W. Lai, *Sensors Actuators, A Phys.*, 2013, **193**, 13–24.

5 L. Wu, W. Yuan, T. Nakamura, S. Atobe, N. Hu, H. Fukunaga, C. Chang, Y. Zemba, Y. Li, T. Watanabe, Y. Liu, Alamusi, H. Ning, J. Li, H. Cui and Y. Zhang, *Adv. Compos. Mater.*, 2013, **22**, 49–63.

Supplementary videos

Video S1: Time evolution of the dipole moment vector for the adsorption of two PVDF-TrFE chains on SWCNTs with (8,8) chirality on top and (12,0) chirality on the bottom.

Video S2: The dissolution of PVDF and PVDF-TrFE in 5 mL acetone at 1/8 speed. 3D printed PVDF-TrFE film, 3D printed SWCNT/PVDF-TrFE (0.020 wt%) film, 3D printed SWCNT/PVDF-TrFE (0.200 wt%) film, melt-extruded and poled PVDF film, solvent-cast PVDF-TrFE film and PVDF-TrFE powder are shown.