Spray-coated PEDOT:OTf films: Thermoelectric properties and integration into a printed thermoelectric generator

Etienne YVENOU[a], Martina SANDRONI[a,b], Alexandre CARELLA[a,], Magatte N. GUEYE [a,b], Jérôme FAURE-VINCENT[b], Stéphanie POUGET[c], Renaud DEMADRILLE[b], and Jean-Pierre SIMONATO[a,d,*]*

[a] Univ. Grenoble Alpes, CEA, LITEN, DTNM, F-38000 Grenoble, France

[b] Univ. Grenoble Alpes, CEA, CNRS, IRIG, SYMMES, F-38000 Grenoble, France

[c] Univ. Grenoble Alpes, CEA, CNRS, IRIG, MEM, F-38000 Grenoble, France

[d] Duke University, Department of Chemistry, Durham, NC 27708, USA

E-mail addresses: alexandre.carella@cea.fr; jean-pierre.simonato@cea.fr

* Corresponding authors

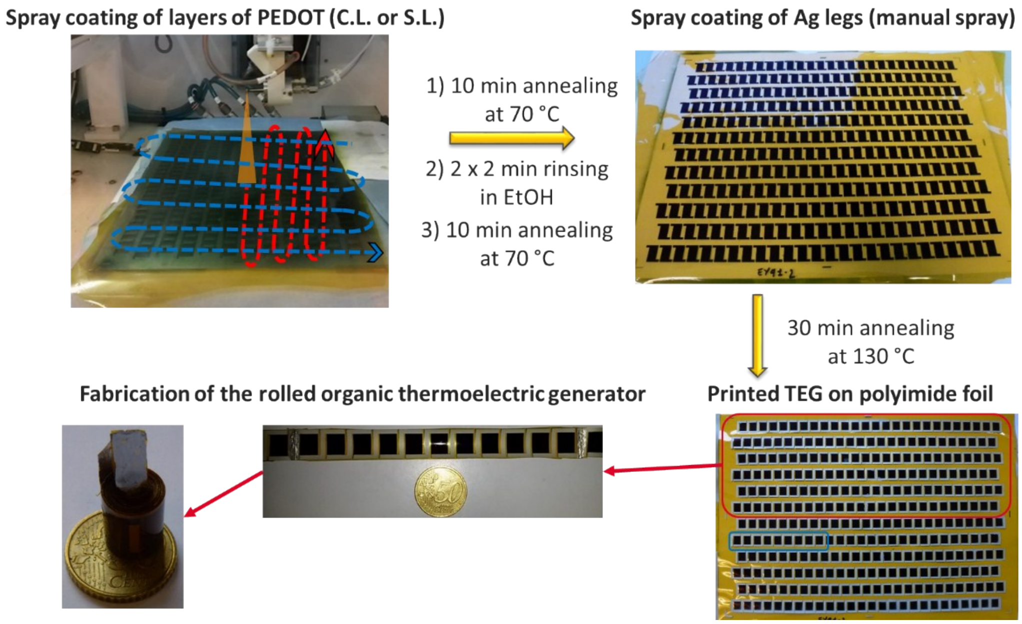

Figure S1. Description of PEDOT films and organic thermoelectric generators preparation

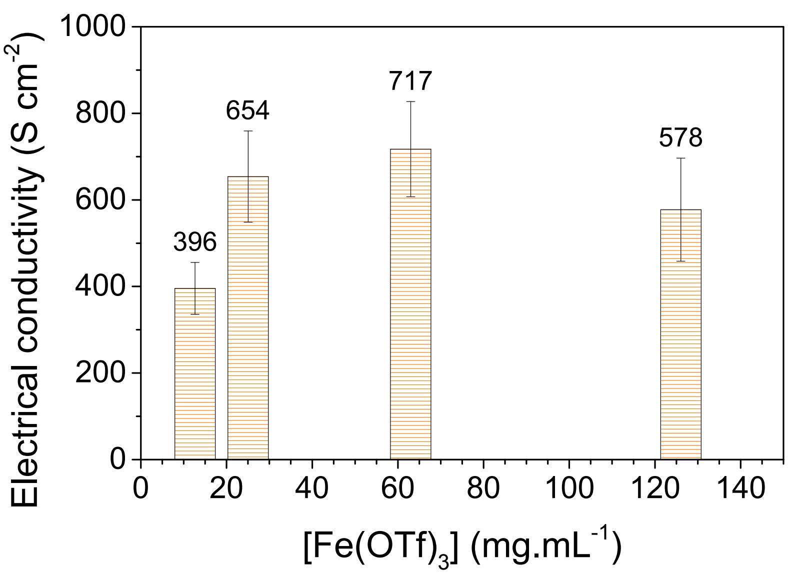

Figure S2. Electrical conductivity of PEDOT:OTf films spray-coated on glass at 12.6, 25.2, 63 and 126 g.L^{-1} of oxidant ($Fe(OTf)_3$) in ethanol containing 10% wt PEG-PPG-PEG.

Table S1. Experimental data on the thickness, the electrical conductivity, the Seebeck coefficient and the calculated power factor for PEDOT:OTf films deposited using different concentrations of NMP in the oxidizing solution. * The relative error for the determination of Seebeck coefficients is estimated at 10%.

[NMP] (%)	Thickness (nm)	σ (S cm^{-1})	Seebeck coefficient* (µV.K^{-1})	Power factor (µW.m^{-1}.K^{-2})
0	792 ± 190	805 ± 261	15.4	19 ± 6
0.5	565 ± 60	797 ± 109	16.9	23 ± 3
1	461 ± 116	821 ± 239	19.9	33 ± 10
2	540 ± 126	1090 ± 278	17.9	35 ± 9
3	538 ± 149	1246 ± 387	17.0	36 ± 11
4	280 ± 64	1422 ± 417	19.9	56 ± 16
5	149 ± 31	2278 ± 620	21.5	105 ± 28
6	61 ± 15	202 ± 64	16.5	5 ± 2

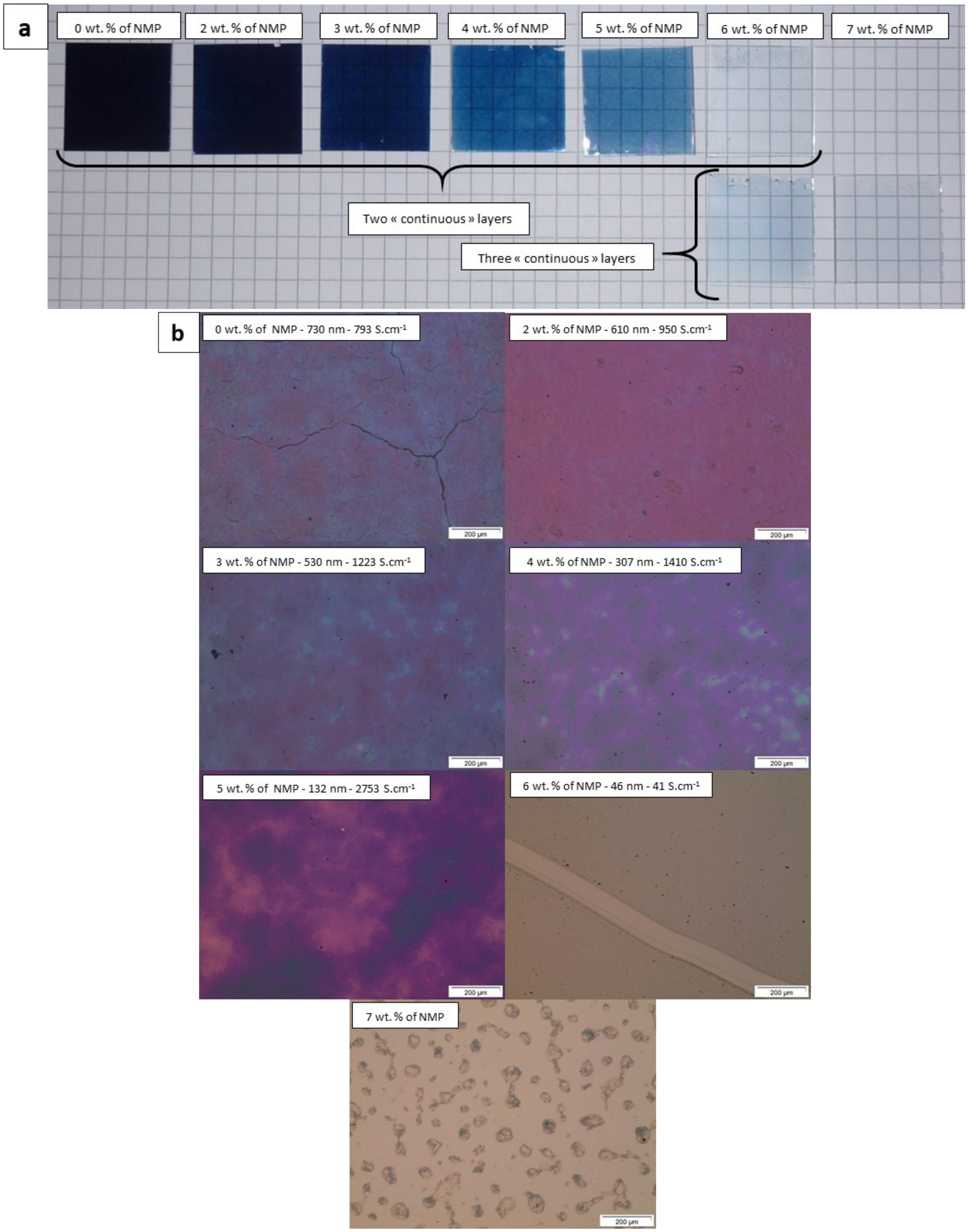

Figure S3. (a) Macroscopic aspect of spray-coated PEDOT:OTf films with increasing amounts of NMP and (b) Optical microscopic images of the same spray-coated films (insets indicate NMP amount, thickness and electrical conductivity).

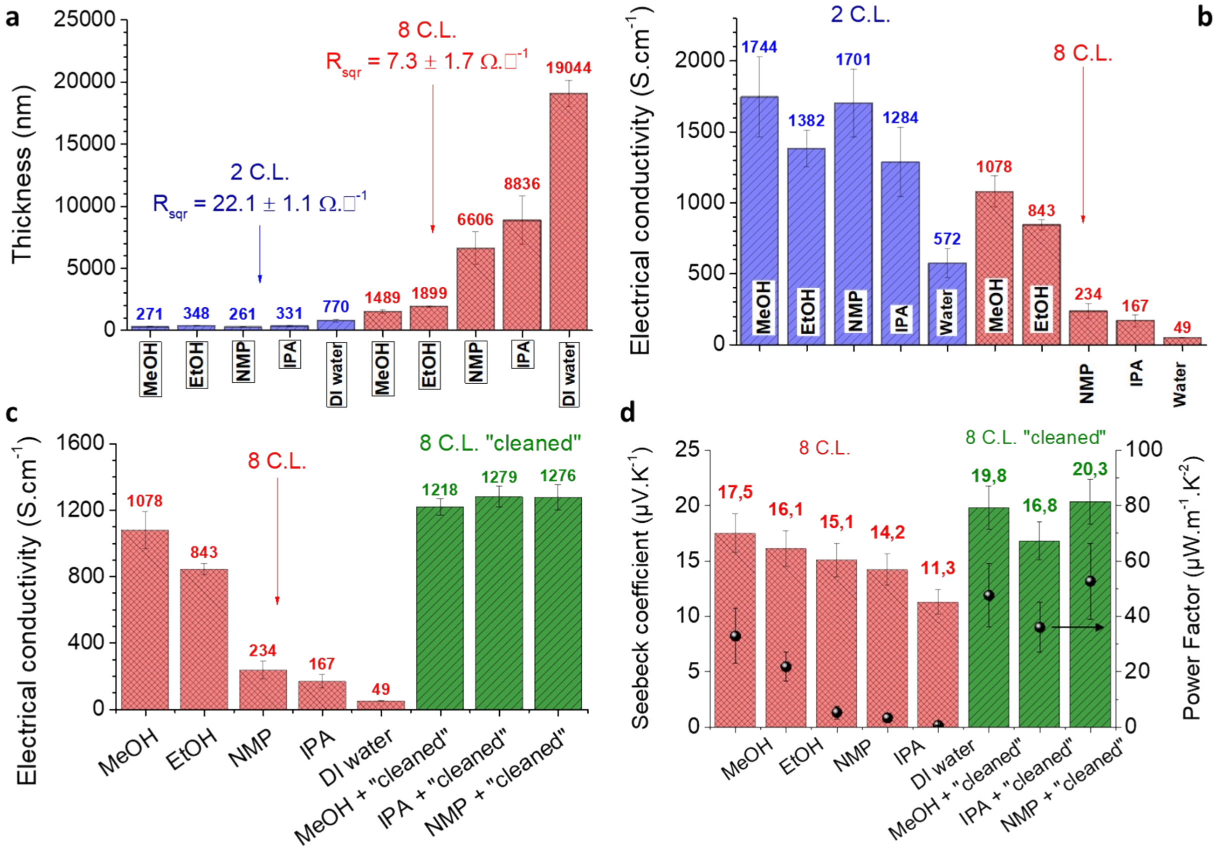

Figure S4. (a) Thickness and (b) electrical conductivity for two groups of samples. One of PEDOT:OTf thin (2 C.L.) films and one of thick (8 C.L.) films cleaned with various solvents (methanol, ethanol, N-methylpyrrolidone, isopropanol and deionized water). (c) Electrical conductivity, (d) Seebeck coefficient and power factor of samples post-treated 10 minutes in MeOH and labelled "cleaned" (green histograms).

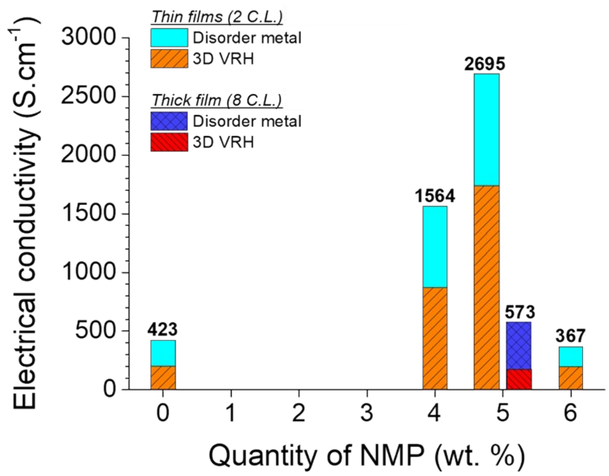

Figure S5. Electrical conductivity contribution at T = 300 K in the amorphous phase for thin films (2 C.L.) with various quantity of NMP and one thick film (8 C.L.) with residual PEG-PPG-PEG. Each contribution was calculated thanks to equation (1) with fitting parameters from Table S4.

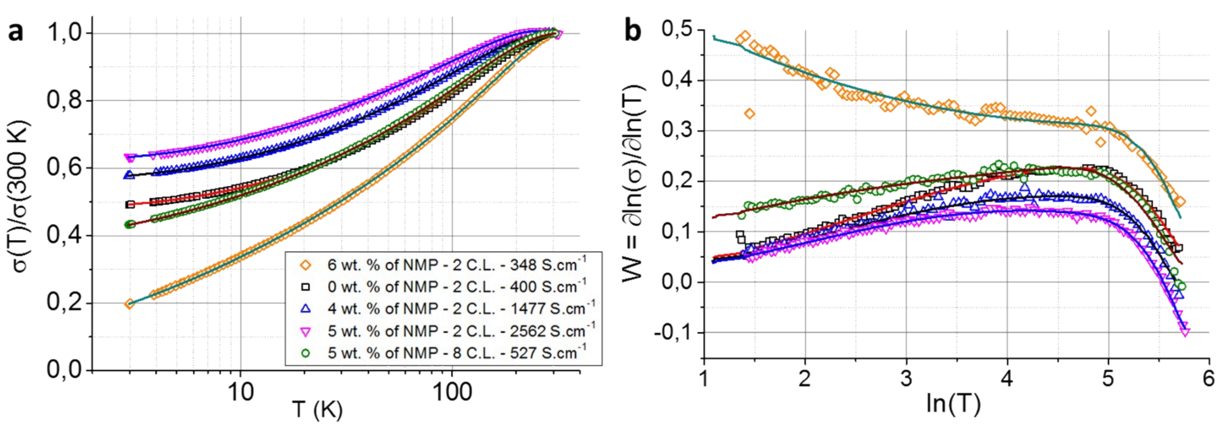

Figure S6. (a) Normalized conductivity temperature dependence of two continuous layers films of spray-coated PEDOT:OTf and synthesized with 0, 4, 5 and 6 wt. % of NMP and one thick film (empty red circle) of 8 continuous layers cleaned (symbols) and heterogeneous model of conduction (solid lines). (b) Evolution of the reduced activation energy of the same samples with ln(T).

Table S2. Results of the adjustment of an asymmetrical pseudo-Voigt profile function to the first and second order diffraction peaks associated to the lamellar stacking.

		Bragg position (Å^{-1})	***FWHM(Å^{-1})***
2 CL	*1st order*	0.467(2)	0.081(5)
	2nd order	0.919(4)	0.114 (8)
8 SL	*1st order*	0.458(2)	0.118(5)
	2nd order	0.914(4)	0.146(8)
8 CL	*1st order*	0.458(4)	0.090(8)
	2nd order	0.914(4)	0.109(8)

Table S3. Fitting parameters from equation 1 in the main article and used to fit experimental data on Figure S5. "# C.L." is the number of continuous spray-coated layers.

General properties			***1D-metal***		***Disordered metal***		***3D VRH***	
NMP	***# C.L.***	***σ(300 K)***	***$\sigma_{1D\text{-}metal}$***	***T_m***	***σ_{DM}***	***m***	***σ_0 (3D)***	***T_0***
wt. %	***-***	***S.cm^{-1}***	***S.cm^{-1}***	***K***	***S.cm^{-1}***	***S.cm^{-1} K$^{-1/2}$***	***S.cm^{-1}***	***K***
0	2	400	460	813	186	2,1	1020	2092
4	2	1477	1327	905	829	-7,8	3697	1314
5	2	2562	1564	1056	1599	-37,2	6964	1106
6	2	348	219	1039	0	10	359	42
5	8	527	585	715	179	12,6	422	175

Figure S7. (a) Details of 2D PEDOT:OTf and silver thermocouples before rolling. (b) 156 rolled thermocouples used in real conditions on a hotplate. Here, R_i = 2,9 kΩ and due to poor thermal resistance between the hotplate and the TEG, the measured power on the picture is P_{OC} = 20 nW.

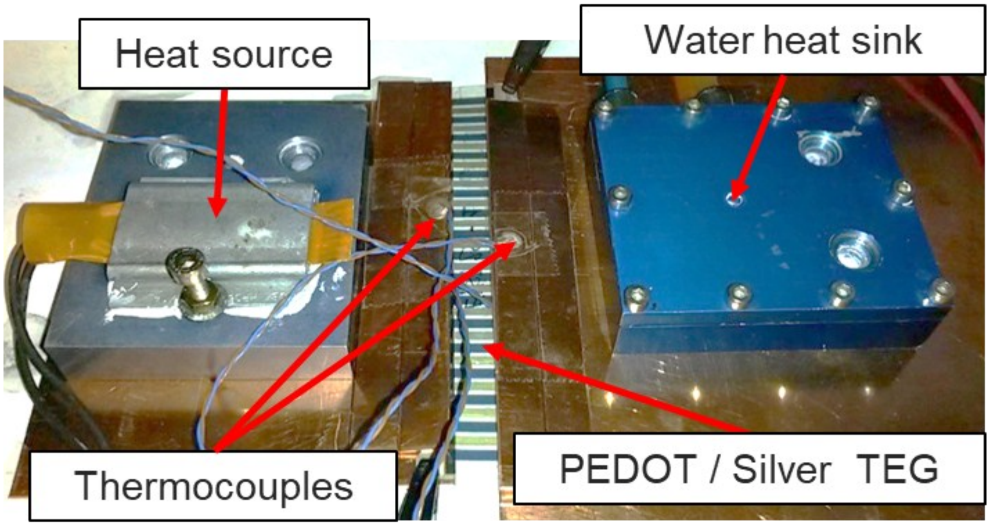

Figure S8. Thermoelectric generator power measurement bench. 2D TEG is thermalized with copper plate and a thermal gradient is applied between the heat source and the heat sink. Three thermocouples on the hot side are located under copper plate as close as possible of PEDOT-silver junctions. Two other thermocouples are located on the cold side which temperature remains at 23 °C maximum. A multimeter measures the open-circuit voltage (V_{OC}) and by knowing the internal resistance (R_i), the maximal theoretical power output can be estimated ($P_{OC} = \frac{V_{OC}^2}{4R_i}$).