Supporting Information to

The Pyroelectric Effect Enables Simple and Rapid Evaluation of biofilm formation

O. Gennari[1], V. Marchesano[1], R. Rega[1], L. Mecozzi[1], F. Nazzaro[2], F. Fratianni[2], R. Coppola[3] L. Masucci[4], E. Mazzon[5], A. Bramanti[1], P. Ferraro[1] and S. Grilli[1*]

[1]*Institute of Applied Sciences & Intelligent Systems, National Research Council (CNR-ISASI), Via Campi Flegrei 34, 80078 Pozzuoli (NA), Italy*
[2]*Institute of Food Sciences, National Research Council (CNR-ISA), Via Roma 64, 83100 Avellino, Italy*
[3]*DIAA – University of Molise, Via de Sanctis, snc 86100, Campobasso (Italy)*
[4]*Institute of Microbiology, Università Cattolica del Sacro Cuore, Policlinico "A. Gemelli", Rome, Italy*
[5]*IRCCS Centre for Neuroscience Bonino-Pulejo, Strada Statale 113, 98124 Messina, Italy*

*s.grilli@isasi.cnr.it

The preparation of the BET-carrier

The BET-carrier in the form of strip

Figure S1 shows the schematic view of the fabrication of the BET-carrier in the form of strip by the pyro-electrification technique.

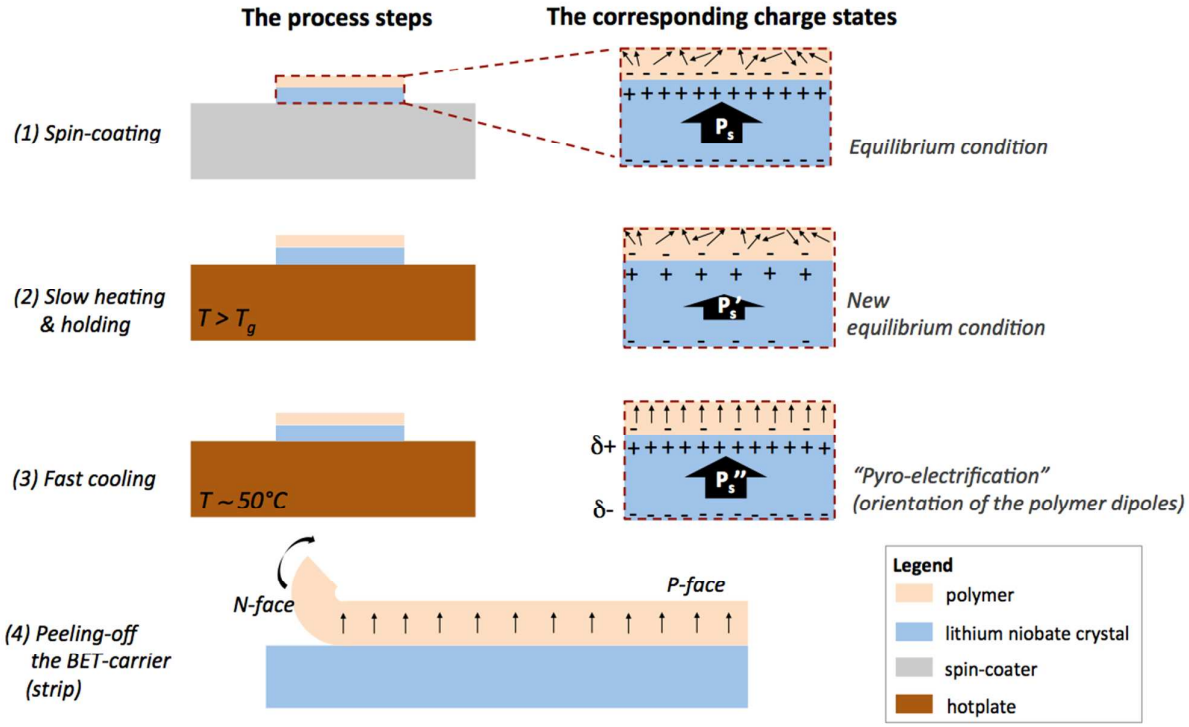

Figure S1. Schematic view of the fabrication of the BET-carrier in the form of srip by the pyro-electrification technique. The column on the left shows the view of the process steps, while the column on the right shows the view of the corresponding charge states in the polymer layer and lithium niobate crystal.

The polymer solution was first spread onto a sample of ferroelectric $LiNbO_3$ crystal by spin coating at 4000 RPM for 2 minutes, instead of the glass coverslip used for the bare strips, in order to exploit the pyroelectric effect. The LN crystals were bought from Crystal Technology in the form of *c*-cut wafers (4×4) cm^2 sized, 500 μm thick and optically polished on both sides. They were cut into (2×2) cm^2 crystal samples by a standard diamond saw. The polymer layer was then subjected to pyro-electrification as follows. We first heated the crystal slowly from the room temperature T_r up to the glass transition temperature T_g of the polymer by a conventional digital hotplate (HP RT2 basic, Thermo Scientific). The T_g was reached in about 3 h and hold for about 10 min. Afterwards,

we moved the polymer-coated crystal to a second hotplate set at a cooling temperature T_c of about 50 °C, in order to cool rapidly the crystal and, consequently, to induce the pyroelectric effect [1-5]. We devoted great attention to the T_c value that had to allow us to cool down the crystal enough to induce the pyroelectric effect but avoiding stress-related breakage. The thermal gradient ΔT induced a variation $\Delta P_s \propto \Delta T$ of the spontaneous polarization P_s of LN and therefore the onset of transient uncompensated charges on the surface of the crystal. Due to the relatively high pyroelectric coefficient of $LiNbO_3$ ($-8{,}3 \cdot 10^{-5}$ $C \cdot m^{-2} \cdot °C^{-1}$), the resulting polarization charge was able to polarize the polymer molecules during the glass transition state – namely when the polymer molecules were free to change their orientation – under the action of the electric field. The simultaneous cooling process allowed us to freeze the new well-oriented configuration of the polymer molecules. The crystal was then peeled off gently in order to get a freestanding pyro-electrified strip that we call here BET-carrier in the form of strip. It has a net dipole orientation exhibiting one surface with negative polarity (δ-) indicated by N-face in the scheme, and the other surface with positive polarity (δ+), indicated by P-face in the scheme. The BET experiments presented in this paper were carried out by putting the BET-carrier in the Petri dish with the P-face up in order to attract electrostatically the bacterial cells, as described in the Discussion section in the paper. The interaction of the bacterial cells with the N-face was similar to the control and the corresponding results are not reported in this paper for the sake of simplicity.

The BET-carrier in the form of fiber

Figure S2 shows the schematic view of the procedure used for producing the polymer fibers. Since the control on fiber size was not an issue at this stage, we used a simple and rapid manual procedure.

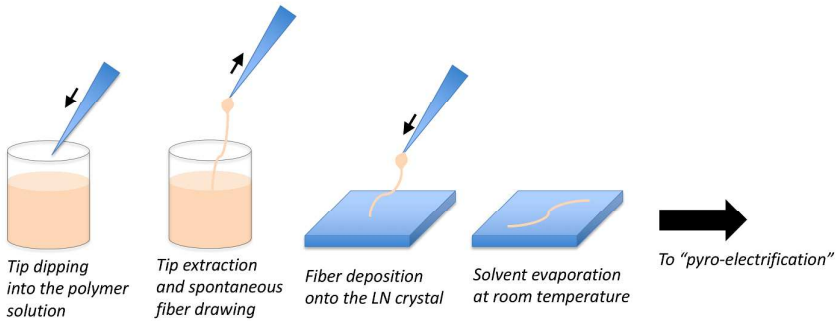

Figure S2. Schematic view of the procedure used for producing the polymer fibers.

A conventional pipette tip was first dipped into the vial containing the polymer solution and, successively, was extracted gently in order to induce the spontaneous fiber drawing and break, similar to that of melted cheese. The resulting fiber was deposited onto the LN crystal and let the solvent to evaporate at room temperature. Afterwards the fiber was used as it was for the experiments with bare fibers or was subjected to the pyro-electrification process following the steps (2) and (3) in Fig.S1 in order to produce the BET-carrier in the form of fiber. The fibers were around 60 μm thick but, when desired, thinner fibers can be produced by our μ–pyro-electrospinning (μPES) [6] or tethered PES [7]. The same LN crystal was re-used for numerous replications of the pyro-electrification process.

References

(1) Grilli, S.; Miccio, L.; Gennari, O.; Coppola, S.; Vespini, V.; Battista, L.; Ferraro, P., Active Accumulation of Very Diluted Biomolecules by Nano-Dispensing for Easy Detection Below the Femtomolar Range, *Nat. Commun.* **2014**, 5, 5314-5319.
(2) Ferraro, P.; Coppola, S.; Grilli, S.; Paturzo, M.; Vespini, V., Dispensing Nano-Pico Droplets and Liquid Patterning by Pyroelectrodynamic Shooting, *Nat. Nanotechnol.* **2010**, 5, 429-435.
(3) Rega, R.; Gennari, O.; Mecozzi, L.; Grilli, S.; Pagliarulo, V.; Ferraro, P., Bipolar Patterning of Polymer Membranes by Pyroelectrification, *Adv. Mater.* **2015**, 28, 454-459.
(4) Gennari, O.; Battista, L.; Silva, B.; Grilli, S.; Miccio, L.; Vespini, V.; Coppola, S.; Orlando, P.; Aprin, L.; Slangen, P.; Ferraro, P., Investigation on Cone Jetting Regimes of Liquid Droplets Subjected to Pyroelectric Fields Induced by Laser Blasts, *Appl. Phys. Lett.* **2015**, 106, 054103-5.
(5) Gennari, O.; Grilli, S.; Coppola, S.; Pagliarulo, V.; Vespini, V.; Coppola, G.; Bhowmick, S.; Gioffré, M.A.; Gentile, G.; Ambrogi, V.; Cerruti, P.; Carfagna, C.; Ferraro, P., Spontaneous Assembly of Carbon-Based Chains in Polymer Matrizes through Surface Charge Templates, *Langmuir* **2013**, 29, 15503-15510.
(6) Mecozzi, L.; Gennari, O.; Rega, R.; Grilli, S.; Bhowmick, S.; Gioffrè, M.A.; Coppola, G.; Ferraro, P., Spiral Formation at the Microscale by μ-Pyro-Electrospinning, *Soft Matter* **2016**, 12, 5542-5550.
(7) Coppola, S.; Vespini, V.; Nasti, G.; Gennari, O.; Grilli, S.; Ventre, M.; Iannone, M.; Netti, P.A.; Ferraro, P., Tethered Pyro-Electrohydrodynamic Spinning for Patterning Well-Ordered Structures at Micro- and Nanoscale, *Chem. Mater.* **2014**, 26, 3357-3360.