

Supporting Information

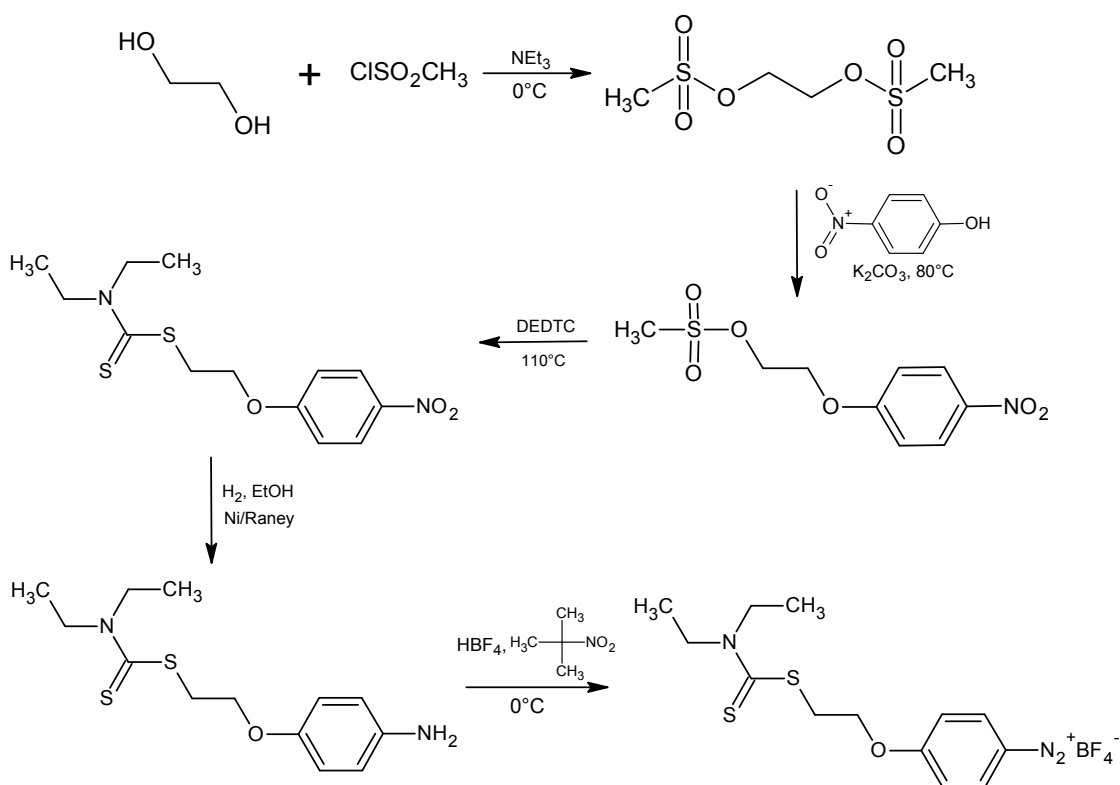
Micro-patterned anti-icing coatings with dual hydrophobic/hydrophilic properties

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Materials

2 mm thick copper disks were cut in a commercial copper bar. Acrylic acid (AA), N,N'-methylbisacrylamide (MBAm), perfluorooctyl methacrylate were purchased from Aldrich and used without purification.. Diethyldithiocarbamate (DEDTC), ethylene glycol, 4-nitrophenol, triethylamine methylsulfonyl chloride, sodium nitrite (NaNO₂), tertbutylnitrite, thionyl chloride (SOCl₂), 2-(4-aminophenyl), tetrafluoroboric acid (HBF₄), and tri-sodium citrate were purchased from Sigma-Aldrich and used as received. All the solvents were obtained from Acros organic and used as received. Water was deionized using a Millipore purification system.

Synthesis of Cl⁻, ⁺₂N-C₆H₄-(O-CH₂-CH₂)_{n= [1-3]}-DEDTC. To synthesize the diazonium salt, we followed the experimental protocol proposed by R. Ahmad et al¹. A summary of the procedure is given in Scheme S1.



Scheme S1. Schematic illustration of the synthesis of the iniferter-derived diazonium salt.

a) ethane-1,2-diyl dimethanesulfonate

Ethylene glycol (18g, 0.29 mol) and triethylamine (105 mL, 0.75 mol) were dissolved in dichloromethane (360 mL). The mixture was cooled in an ice bath and a solution of methylsulfonyl chloride (49 mL, 0.64 mol) was added drop wise. The solution was stirred during 4 hours at room temperature. The mixture was filtered and washed with ether and sodium carbonate. Finally, the solution was dried with magnesium sulphate yielding a yellow oil after solvent removal. This oil was crystallized with methanol yielding 35.5g of white powder (74%).

IR ν (cm^{-1}): 1353, 1167 S=O

^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.47 (4H, s), 3.08 (6H, s)

b) 2-(4-nitrophenoxy)ethylmethanesulfonate

Ethane-1,2-diyl dimethanesulfonate (20g, 0.0957 mol), potassium carbonate (18g, 0.13 mol) and 4-nitrophenol (8.8g, 0.063 mol) were dissolved in 100 mL of acetonitrile. The solution was stirred at 80°C for 5 hours. The mixture was filtered and washed with dichloromethane. The organic layers were washed two times with water, dried over magnesium sulphate and filtered. The solvent was removed. Chromatography on silica gel using dichloromethane as solvent gave 8.74g of pure product as a yellow powder (66%).

IR ν (cm^{-1}): 1592 C=C aromatic, 1339 S=O

^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.2 (2H, d), 7.1 (2H, d), 4.6 (2H, t), 4.3 (2H, t), 3.1 (3H, s).

c) 2-(4-nitrophenoxy)ethyldiethylcarbamadithionate

To 8.74g (0.032 mol) of 2-(4-nitrophenoxy)ethylmethanesulfonate in 40 mL of acetonitrile was added 7.3g (0.032 mol) of sodium diethyldithiocarbamate (DEDTC^- , Na^+). The solution was stirred at reflux temperature during 3 hours. In the end of reaction, the solution was washed with dichloromethane and water leading to yellow oil. Crystallization in ether gave 7.1g of product (71%).

IR ν (cm^{-1}): 1593 C=C aromatic, 1258 C=S, 985 C-S, 875 SCS

^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.21 (2H, d), 7.41 (2H, d), 4.38 (3H, d), 4.09 (3H, d), 3.8 (4H, q), 1.33 (6H, t).

d) 2-(4-aminophenoxy)ethyldiethylcarbamadithionate

(7.1g, 22.59 mmol) of 2-(4-nitrophenoxy)ethyldiethylcarbamadithionate was dissolved in 30 mL of ethanol and a catalytic amount of Ni/Raney was added. The solution was hydrogenated under pressure (42 psi) for 1h. In the end of reaction, the solution was filtered and washed with ethanol and water. The removing of the solvent gave 6g (94%) of green oil, which was protecting against light.

IR ν (cm^{-1}): 1507 C=C aromatic, 1268 C=S, 979 C-S, 869 SCS

^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.78 (2H, d), 6.61 (2H, d), 4.17 (3H, d), 4.02 (3H, d), 3.71 (4H, q), 3.41 (2H, m), 1.28 (6H, t).

e) 4-(2-((diethylcarbamothioyl)thio)ethoxy)benzenediazonium tetrafluoroborate salt

The aniline derivative was suspended in a 50/50 by volume tetrafluoroboric acid and tert-butyl nitrite in ether or acetone. The mixture was cooled to 0°C in an ice bath and stirred for 30 minutes. Evaporation of the solvent gave the salt in a quantitative yield.

IR ν (cm⁻¹): 1570 C=C aromatic, 2260 N₂⁺, 1265 C=S, 973 C-S, 863 SCS

¹H NMR (400 MHz, DMSO) δ (ppm): 8.6 (2H, d), 7.5 (2H, d), 4.6 (2H, t), 3.97 (2H, q), 3.78 (2H, q), 3.2 (2H, t), 1.28 (6H, t).

Preparation of copper surfaces

The copper surfaces were mechanically polished with 0.3 μ m Al₂O₃ and rinsed three times under sonication in water. Afterwards, nano-structuration of the copper surfaces was achieved following ref². Basically, the surfaces were first dipped in a hydrochloric acid solution for 10 min to remove the native oxide film surface, rinsed with MilliQ water and then immersed into a hot alkaline solution composed of NaClO₂, NaOH, Na₃PO₄·12H₂O and DI water (3.75:5:10:100 wt %) during 5 min at 98 \pm 3 °C to form nanostructured CuO. The Cu disks were then rinsed again with deionized water and dried under argon.

Surface-initiated polymerization from iniferters grafted on Nano Cu

The nanostructured copper surfaces were first functionalized by the iniferter aryl diazonium salt in water. For this, the copper disks were immersed in a water solution containing 5mM of diethyldithiocarbamyl phenyldiazonium tetrafluoroborate. After 5 hours, the modified surfaces were rinsed with copious amounts of water and sonicated in acetone for 5 min. The Nano Cu surfaces modified with DEDTC groups were immersed in a polymerization solution containing 5mM of AA as the functional monomer and water as the solvent. The glass vessel was degassed by bubbling argon for 10 min. The slides were then exposed to UV light at 365 nm at room temperature for 2h. The modified slides (Cu-PAA) were rinsed with copious amounts of water and ethanol to remove the un-reacted monomers, and dried in a nitrogen stream. The final step consisted to grow patterned polymer brushes of perfluorooctyl methacrylate (PF) from Cu-PAA surfaces, using a photomask (see scheme of the procedure in Fig. S1). For this, the Cu-PAA slides were dipped in a homogeneous solution of perfluorooctyl methacrylate (5 mmol) in ACN. The glassy vessel containing the Cu-PAA was degassed by bubbling with argon for 5 min. Then, the photomask was placed in contact with the surface. The sandwich structure, including the slide and the photomask, in the monomer solution, was then exposed to UV light at 365 nm for 2h. After irradiation, the slides were taken out, thoroughly sonicated in ACN for 4 min to remove the unreacted monomer and then washed with ethanol to remove organic species. The polymer-coated slides were dried and stored under argon.

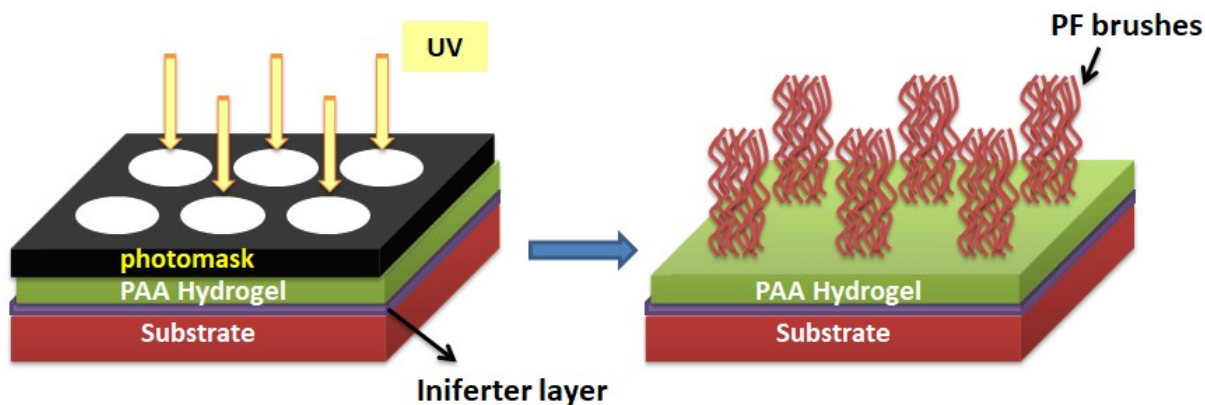


Figure S1. Illustration of the functionalization of Nano Cu surfaces from iniferter-grafted layers and photo-polymerization using a photo-mask, resulting in the formation of micropatterned block copolymers of PAA-PF.

Instrumentation

Photopolymerization was performed using the commercial ultraviolet processor Spectrolinker XL 1500 UV (Spectronics Corp.). This processor was equipped with 6 tubes (8 W) with a wavelength range of 365 nm and intensity of 17.6 mW cm^{-2} . Scanning Electron Microscope (SEM) images of the different samples were obtained with a Cambridge Supra 40 ZEISS apparatus. The acceleration voltage was set at 5 kV. XPS measurements were performed using a K-Alpha⁺ system (ThermoFisher Scientific, East-Grinstead, UK) fitted with a micro-focused and monochromatic Al K α X-ray source (1486.6 eV, spot size: 400 μm). The pass energy was set to 150 and 40 eV for the survey and the high resolution spectra, respectively. The spectra were calibrated against the C—C/C—H C1s component set at 285 eV. The chemical composition was determined by using the manufacturer sensitivity factors using Avantage software, version 5.977. The water contact angles were measured with a Kruss DSA3 instrument. A drop (20 μL) of Milli-Q water was deposited on the top on the sample placed in a horizontal position on the instrument stage. At least, five measurements were made for each sample. The values of the contact angles were calculated by the tangent method using Drop Shape Analysis software.

Complementary results

Characterization of the hierarchical structure of the binary coating

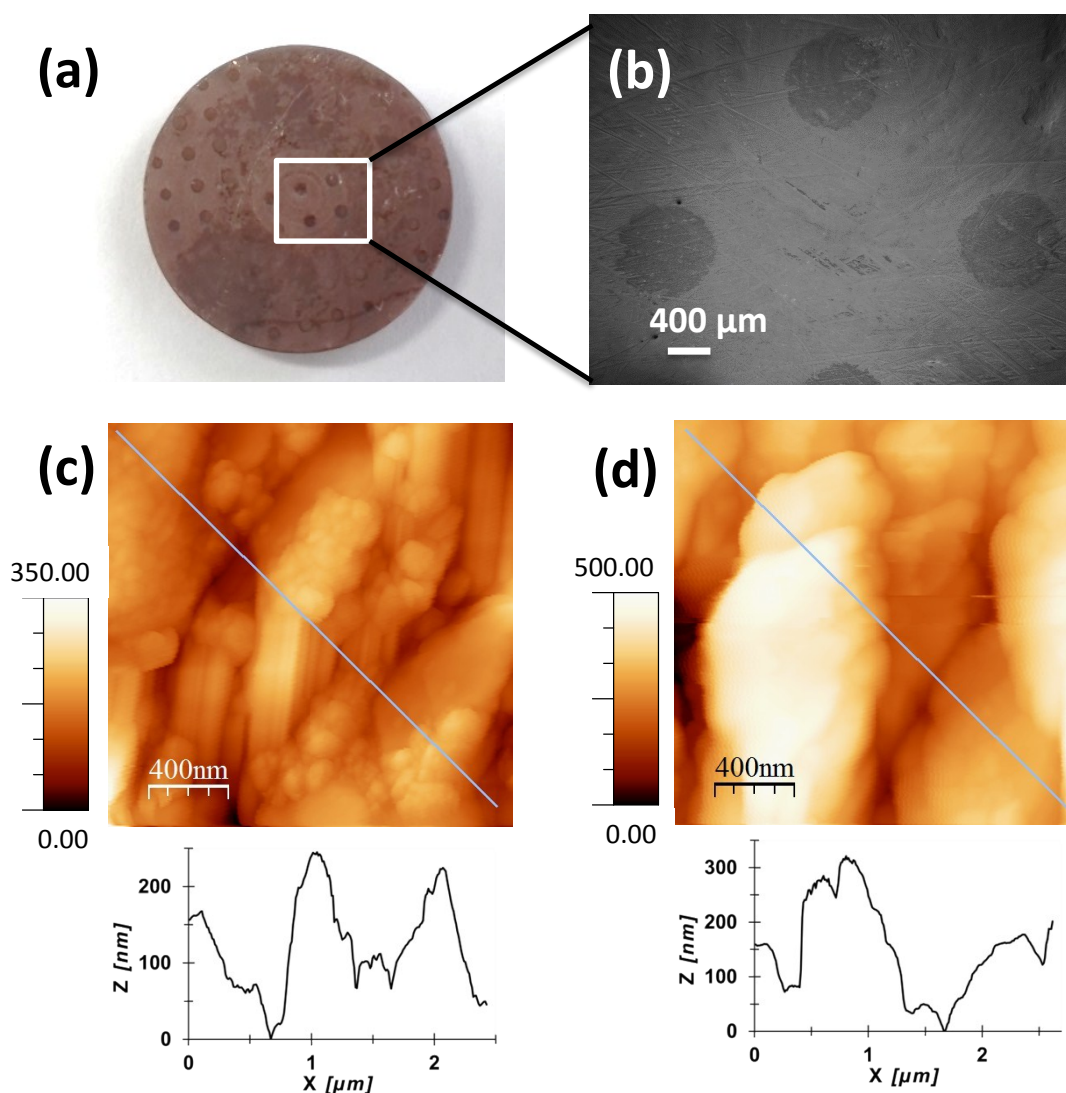


Figure S2. Microscopic characterization of the binary coating. **(a)** Optical image of the copper disk recorded after the whole treatment, exhibiting circular micropatterns of PF brushes, regularly arranged on top of the hydrophilic PAA layer. **(b)** SEM image of the copper disk, revealing the 800 μm diameter circular micropatterns on the surface, in agreement with the hole diameter of the photomask. **(c)** AFM image of the copper disk, recorded inside the PAA area (outside the circular micropatterns), providing the topographic nanoscale profile of the surface. The surface nanostructuration is clearly observed through the height profile below. **(d)** AFM image recorded inside the circular micropatterns of PAA-PF and corresponding height profile.

High resolution Cu2P spectra obtained by XPS.

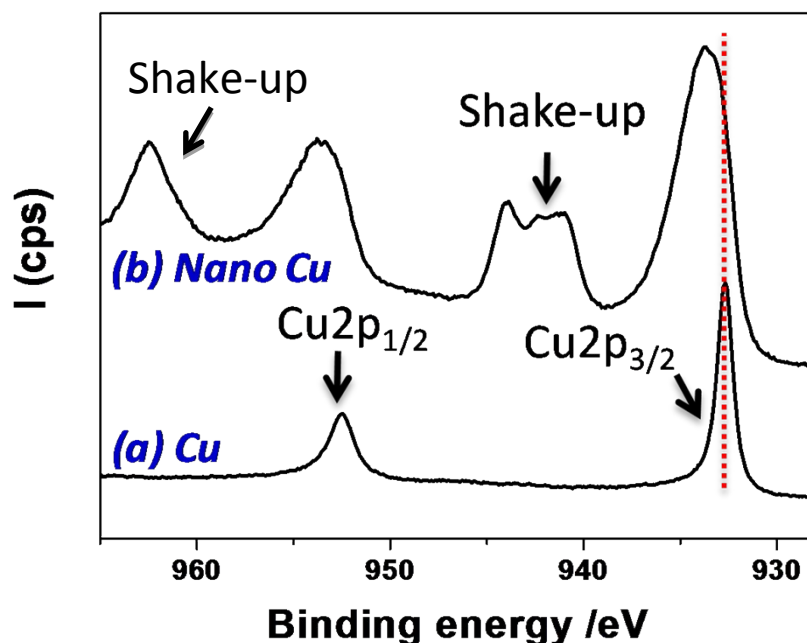


Figure S3. High resolution Cu2p XPS spectra of (a) bare Cu and (b) nano-structured Cu surfaces.

Instrument for icing control

The anti-icing properties of the copper surfaces were evaluated by measuring the freezing delay time of small droplets (100 μL) cooled down to -20°C starting from an ambient temperature (15°C) at a constant cooling rate of $1,2^\circ\text{C}/\text{min}$, using an experimental chamber maintained at controlled humidity ($H=30\%$) and temperature (see experimental setup in Fig. S3). The freezing process was recorded by an Infrared camera (placed on the top) and CCD (placed on the side). Twenty five measurements were made on each surface. Measurements of the droplet temperature were established by an FLIR A600-series thermographic camera (emissivity fixed at 0.98). The values were provided by the controller with an accuracy of $\pm 0.5^\circ\text{C}$.

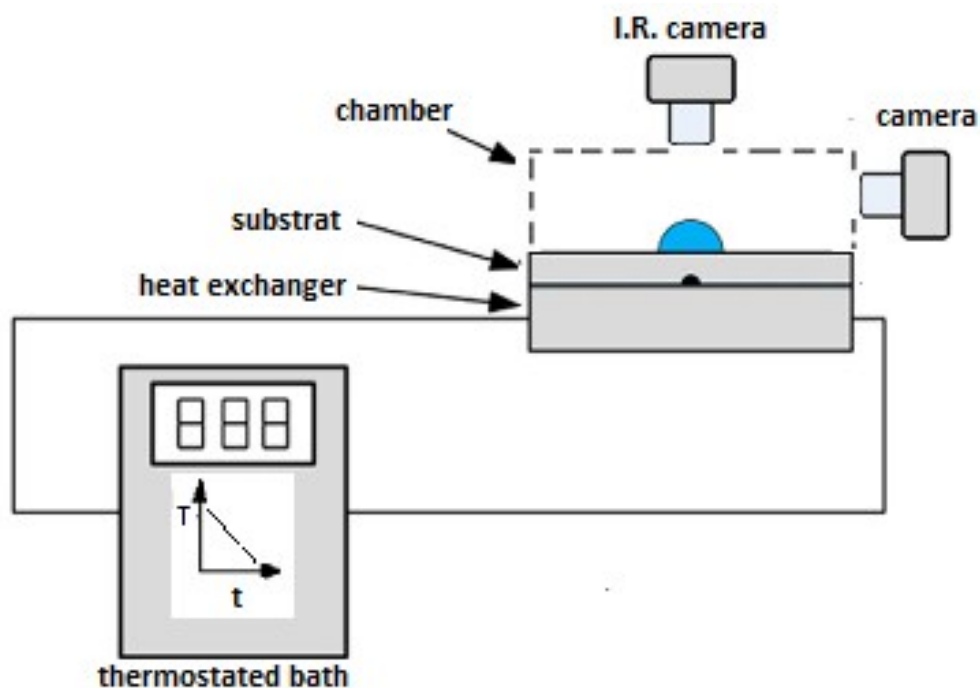


Figure S4. Sketch of the experimental device. A 100 μL drop is deposited onto the substrate at temperature $T=15^\circ\text{C}$. The substrate is cooled down to -20°C starting from $+15^\circ\text{C}$ at a constant rate of $1,2^\circ\text{C}/\text{min}$. IR camera (FLIR A600) and visible camera (Imaging Source) are used to view, on the top and on the side respectively, events and record the dynamics of freezing of the sessile drops. This process was repeated 25 times for each sample.

Supercooling temperature ΔT as a function of the number of cycles

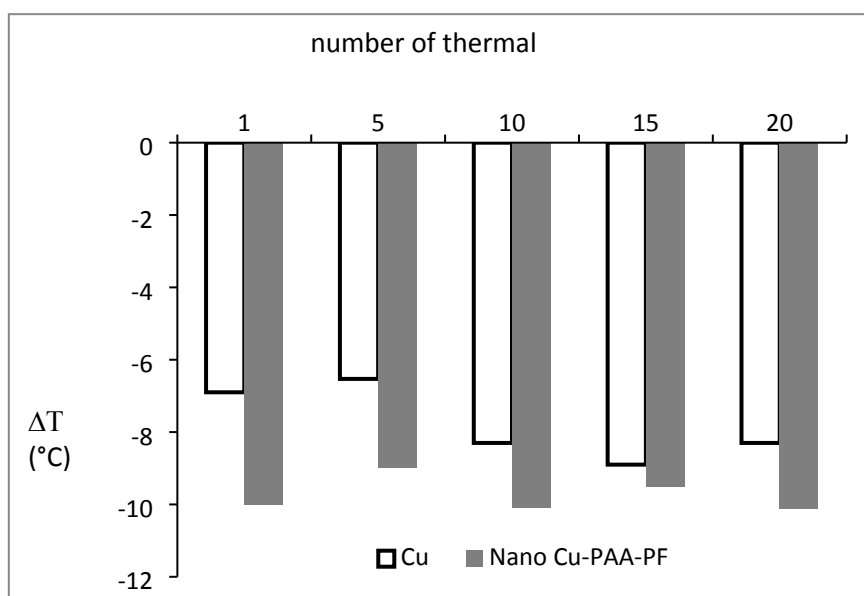


Figure S5. Supercooling temperature ΔT as a function of the number of cycles. The white columns report the values obtained for the reference bare Cu and the grey columns report the values recorded on Cu-PAA-PF surfaces.

Mean delay times Δt as a function of the number of thermal cycles

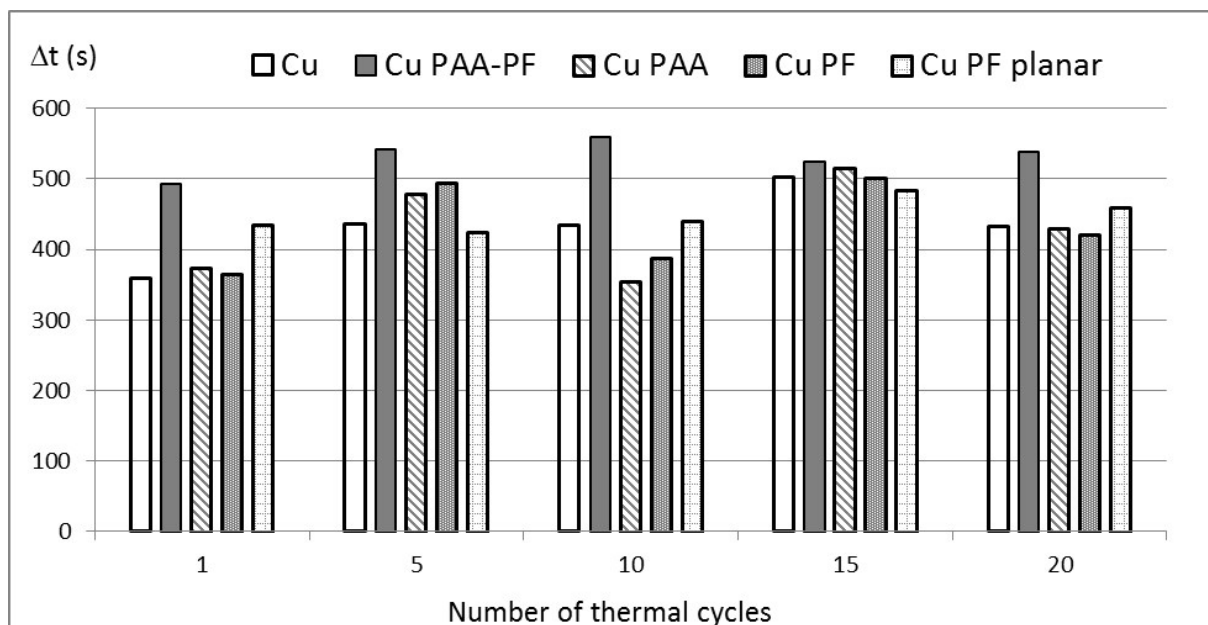


Figure S6. Delay times of freezing (Δt) as a function of the number of cycles. Each column corresponds to a different sample, indicated at the top of the graph.

¹ R. Ahmad, A. Mocaer, S. Gam-Derouich, A. Lamouri, H. Lecoq, P. Decorse, P. Brunet, C. Mangeney, Grafting of polymeric platforms on gold by combining the diazonium salt chemistry and the photoiniferter method, *Polymer*, **2015**, *57*, 12-20.

² N. Miljkovic, R. Enright, Y. Nam, K. Lopez, N. Dou, J. Sack, E.N. Wang, Jumping-Droplet-Enhanced Condensation on Scalable Superhydrophobic Nanostructured Surfaces, *Nano Lett.* **2013**, *13*, 179-187.