# Supporting Information

# Integrated Microstructured Photonic Fiber as Bifunctional Robust Frit and Efficient Electrospray Emitter of Packed Column for capillary liquid chromatography-tandem mass spectrometry Analysis of Complex Biological Samples

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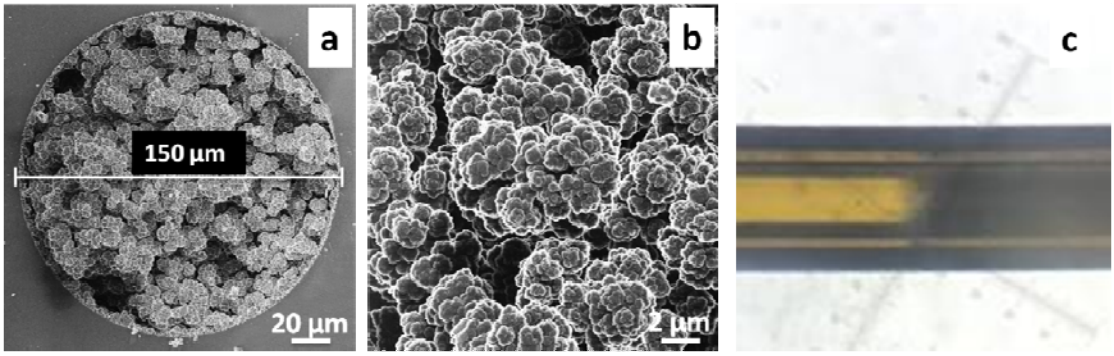


**Figure S1.** Images of PPM as frit in the fused-silica capillary. (a, b) SEM images and (c) optical microscope image (150 µm i.d. × 360 µm o.d.).

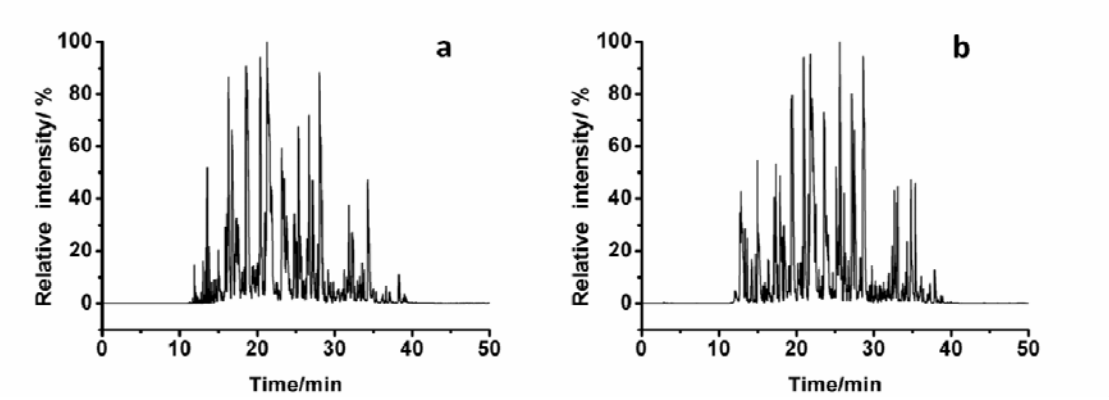


**Figure S2.** Separation chromatograms of tryptic digest of BSA on packed capillary columns integrated with (a) MPF-1 and (b) tapered tip emitter by cLC-MS/MS. Experimental conditions: column dimension, (a) 24 cm × 150 μm i.d. (including 1.0-cm-long frit at inlet and 3.0-cm-long frit-emitter at outlet of the packed column), (b) 22 cm × 150 μm i.d.; packing material, 3 μm ODS beads; mobile phase A, 0.1% aqueous FA, B, 0.1% FA in ACN, gradient 0-5% B in 2 min, 5-35% B in 30 min, 35-80% B in 3 min and retained 80% B for 10 min; flow rate, 900 nL/min; spray voltage, 2.0 kV.

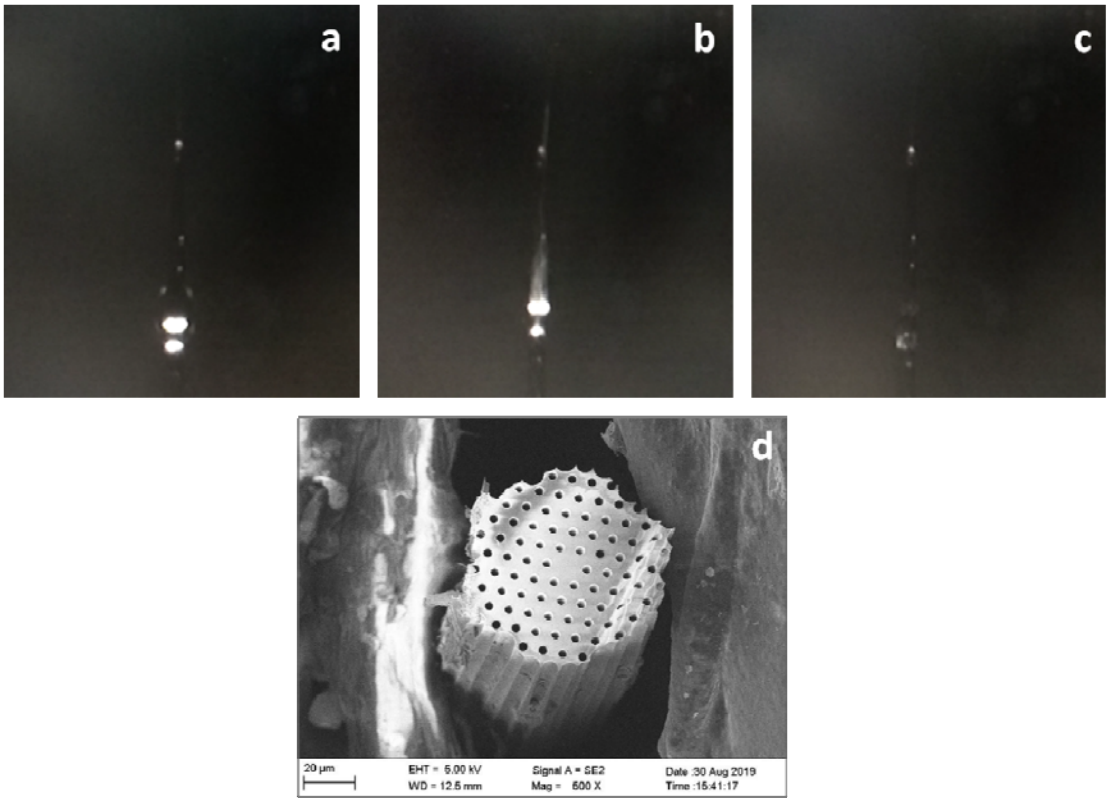


**Figure S3.** (a-c) Optical images of at a spray voltage of 2.0 kV and (d) SEM images of cross-section of an etched MPF-1 emitter. Experimental conditions: column dimension, 24 cm × 150 µm i.d. (including 1.0-cm-long frit at inlet and 3.0-cm-long frit-emitter at outlet of the packed column); packing material, 3 µm ODS beads; mobile phase, $H_2O$/FA (99.9/0.1, v/v); flow rate, 900 nL/min.

**Figure S4.** Optical images of tapered MPF-1 emitter at a spray voltage of 2.0 kV. Experimental conditions: column dimension, 24 cm × 150 μm i.d. (including 1.0-cm-long frit at inlet and 3.0-cm-long frit-emitter at outlet of the packed column); packing material, 3 μm ODS beads; flow rate, 900 nL/min; mobile phase, ACN/$H_2O$/FA (80/19.9/0.1, v/v/v) flow rate, 900 nL/min.

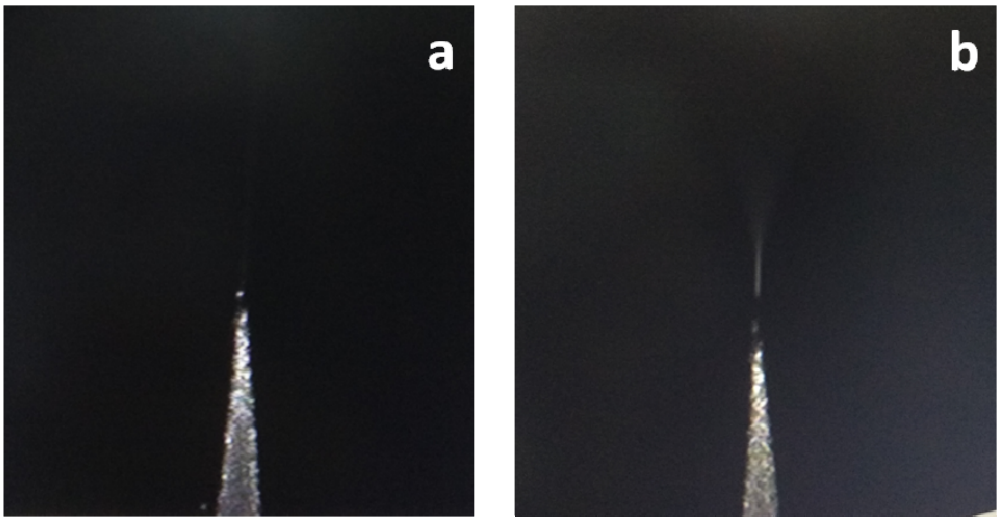


**Figure S5**. Optical images of tapered tip emitter at a spray voltage of 2.0 kV. Experimental conditions: column dimension, 22 cm × 150 μm i.d.; packing material, 3 μm ODS beads; mobile phases, (a) $H_2O$/FA (99.9/0.1, v/v) and (b) ACN/$H_2O$/FA (80/19.9/0.1, v/v/v); flow rate, 900 nL/min.

**Figure S6**. Optical images of MPF-2 emitter at a spray voltage of 2.0 kV. Experimental conditions: column dimension, 24 cm × 150 μm i.d. (including 1.0-cm-long frit in inlet and 3.0-cm-long frit-emitter in outlet of the packed column); packing material, 3 μm ODS beads; mobile phase, ACN/$H_2O$/FA (50/49.9/0.1, v/v/v); flow rate, 900 nL/min.

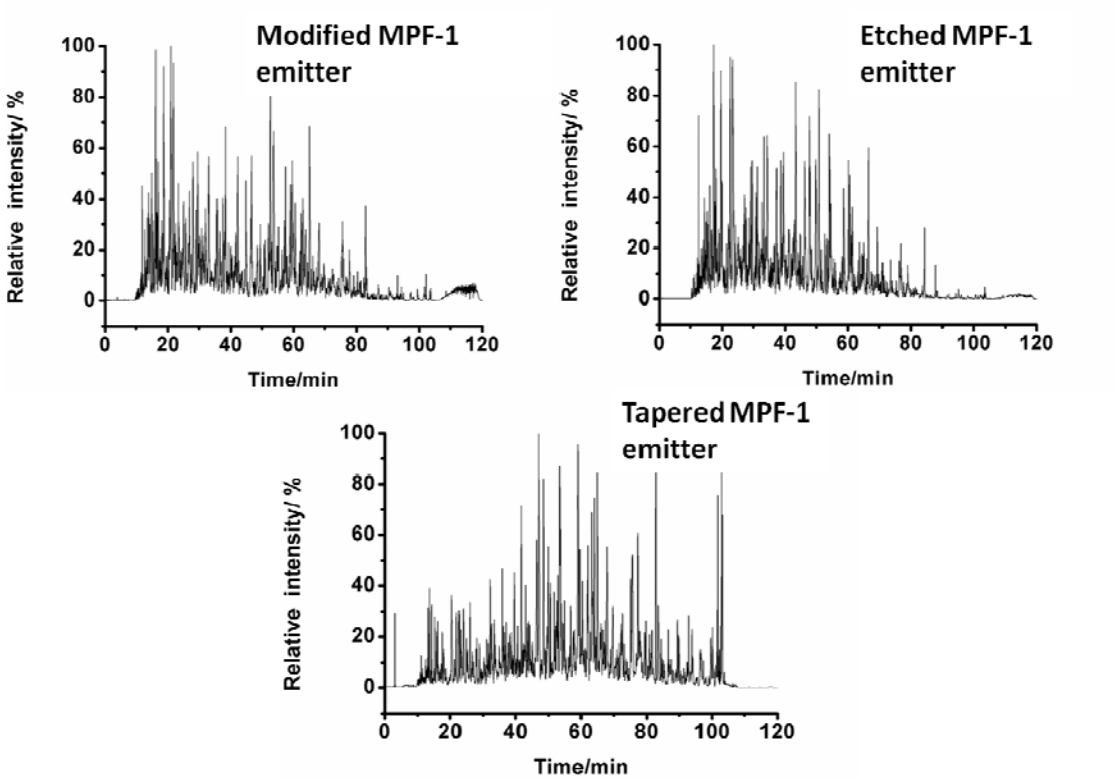


**Figure S7**. Separation chromatograms of tryptic digest of Hela cells on packed capillary columns integrated with different treated MPF-1 emitters by cLC-MS/MS. Experimental conditions: column dimension, 24 cm × 150 μm i.d. (including 1.0-cm-long frit at inlet and 3.0-cm-long frit-emitter at outlet of the packed column); packing material, 3 μm ODS beads; mobile phase A, 0.1% aqueous FA, B, 0.1% FA in ACN, gradient 0-5% B in 2 min, 5-35% B in 90 min, 35-80% B in 3 min and retained 80% B for 10 min; flow rate, 900 nL/min.

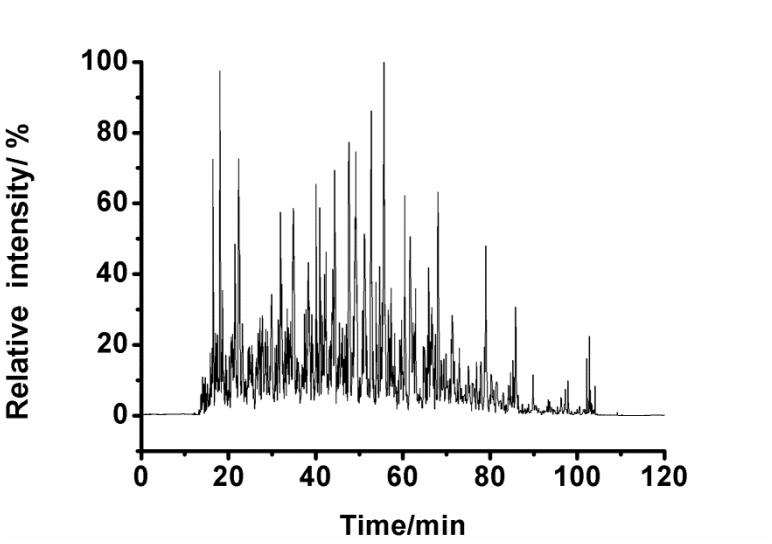


**Figure S8**. Separation chromatogram of tryptic digest of Hela cells on packed capillary column integrated with an MPF-2 emitter by cLC-MS/MS. Experimental conditions: column dimension, 24 cm × 150 μm i.d. (including 1.0-cm-long frit at inlet and 3.0-cm-long frit-emitter at outlet of the packed column); packing material, 3 μm ODS beads; mobile phase A, 0.1% aqueous FA, B, 0.1% FA in ACN, gradient 0-5% B in 2 min, 5-35% B in 90 min, 35-80% B in 3 min and retained 80% B for 10 min; flow rate, 900 nL/min.