

Organic Soluble Antimicrobial Silver Nanoparticle-Polymer Composites in Gram Scale by One Pot Synthesis

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Supporting Information

Supporting Information-SI 1:

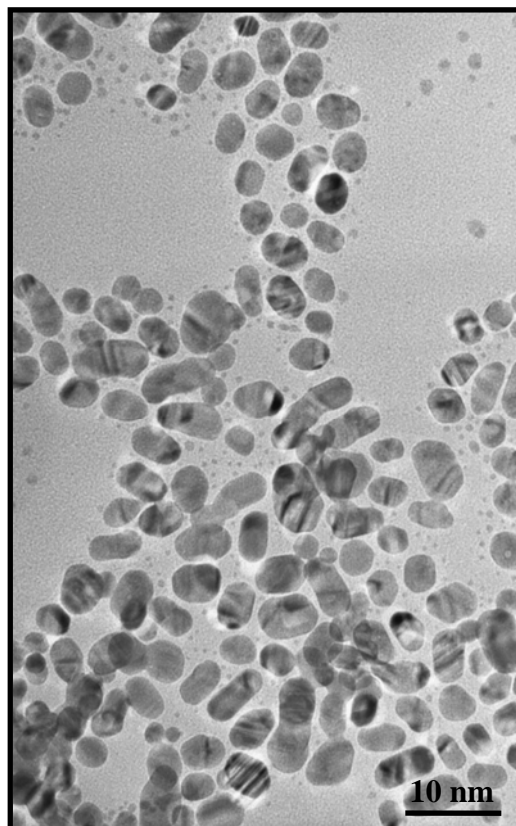


Figure S1. TEM image of ~ 4 nm Ag@citrate. Particles with spherical geometry are common. However, there are a few smaller particles and particles with elongated geometry. Due to the Ostwald ripening process,¹ the smaller particles disappeared over a period of time.

Supporting Information-SI 2

Time-dependent UV-visible spectra showing the adsorption of MeO-BzCl on the Ag nanoparticles' surfaces during the course of the polycondensation reaction

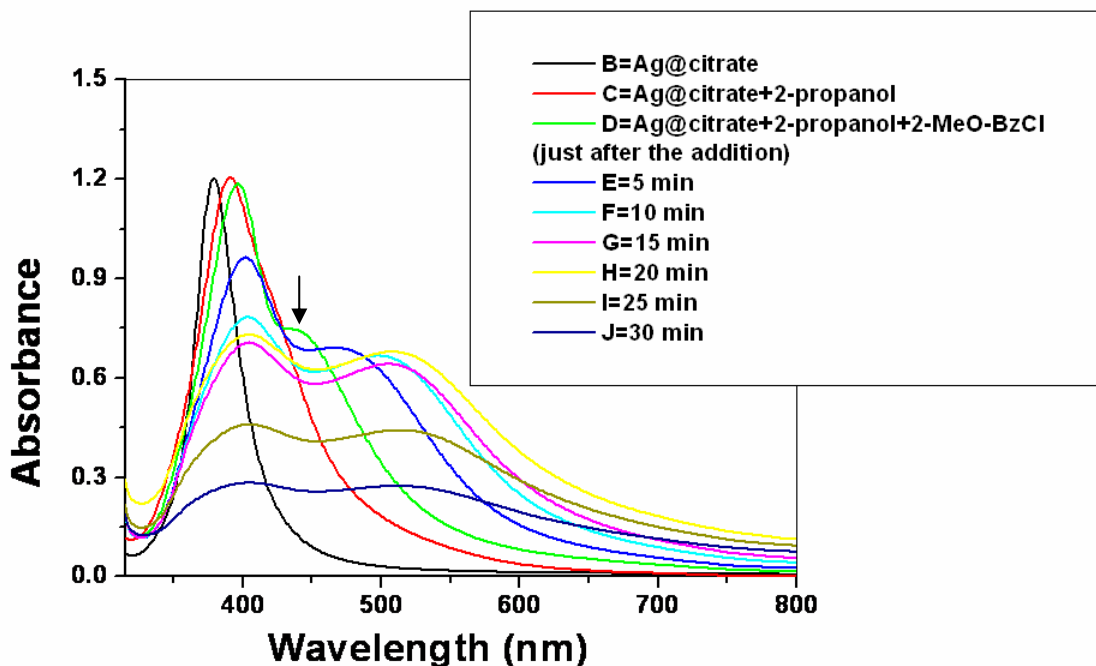


Figure S2. Time-dependent UV-visible spectra of the interaction of 2-MeO-BzCl with the Ag nanoparticles. Trace B is the UV-visible spectrum of the $\sim 4\text{m}$ Ag@citrate showing the surface plasmon resonance peak at 382 nm. Trace C is the UV-visible spectrum after the addition of 2-propanol (absorbance of the trace B was normalized to that of C for comparison). Trace D was taken immediately after the addition of 2-MeO-BzCl to the Ag nanoparticles. Note the emergence of a small peak (shown with an arrow) at longer wavelength in trace D just after the addition of MeO-BzCl due to its binding on the nanosurfaces. Traces E-J were taken at 5 min intervals thereafter. The binding of MeO-BzCl on the nanosurfaces results in partial adsorbate-induced aggregation of the Ag nanoparticles. This is characterized by a decrease in the intensity of the original surface plasmon peak and the emergence of another broad plasmon at longer wavelengths,²⁻⁴ which red-shifts in a time-dependent manner. These changes are evident in the traces D-F.

Supporting Information-SI 3

Infrared spectra

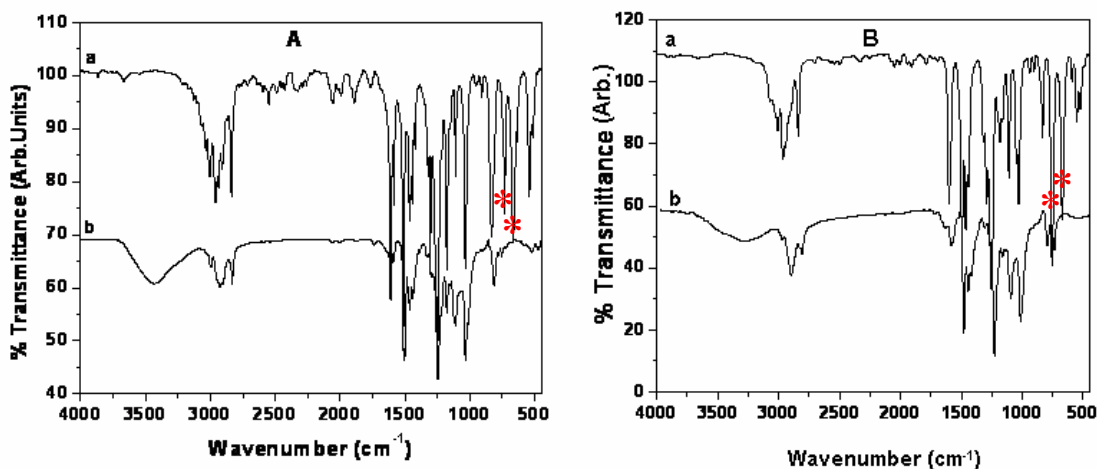


Figure S3. (A) IR spectra of pure 4-MeO-BzCl and the Ag-PNC formed from the same, respectively. The major peaks of pure 4-MeO-BzCl could be assigned⁵ as follows: ν/cm^{-1} 541 (in plane ring def vib), 657 (sym C-Cl stretch), 724 (asym C-Cl stretch), 832 (=C-H out of plane def), 1031 (-CH₂ def vib of O-CH₃), 1173 (=C-H in plane def vib), 1513 (-C-H asym def vib of -CH₂Cl), 1605 (-C=C of -Ph), 2836-2960 (asym and sym stretch of Ph-C-H), and 3005 (C-H str of CH₂Cl). (B) IR spectra of pure 2-MeO-BzCl and the Ag-PNC formed from it, respectively. The IR assignments here are the same as given above. Note the disappearance of the C-Cl bonds (starred peaks) of MeO-BzCl at ν/cm^{-1} 657 and 724 in the Ag-PNCs as a result of the polycondensation. Slight shifts in the IR signatures of the polymers in the Ag-PNCs in comparison to those of pure MeO-BzCl could be attributed to their proximity to the nanosurfaces. The broad peak seen at ν/cm^{-1} 3500 in traces b is due to the -OH stretch from the small amount of water impurity in the KBr matrix.

Supporting Information-SI 4

Raman Spectra

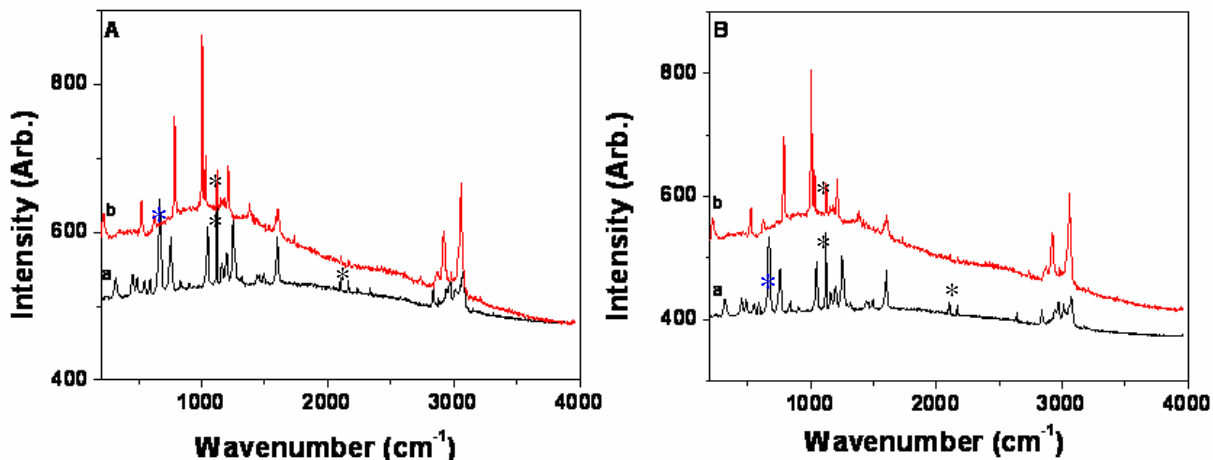


Figure S4. (A) Raman spectra of pure 4-MeO-BzCl and the Ag-PNC formed from the same. The assignments of major peaks are the same as that in the IR discussed above. Note the disappearance of the C-Cl features of MeO-BzCl (indicated with blue stars) in the Ag-PNCs (trace b) as a result of the polycondensation reaction. (B) Raman spectra of pure 2-MeO-BzCl and the Ag-PNC formed from it. The peaks labeled with black stars come from the cover glass slides on which the samples were drop-casted. The SERS effect in the Raman signatures of the polymers (Ag-PNCs) is evident in the traces b. The slight shift in the Raman frequencies of the polymers in the Ag-PNCs is due to their proximity to the nanosurfaces.

Supporting Information-SI 5

X-Ray Diffraction

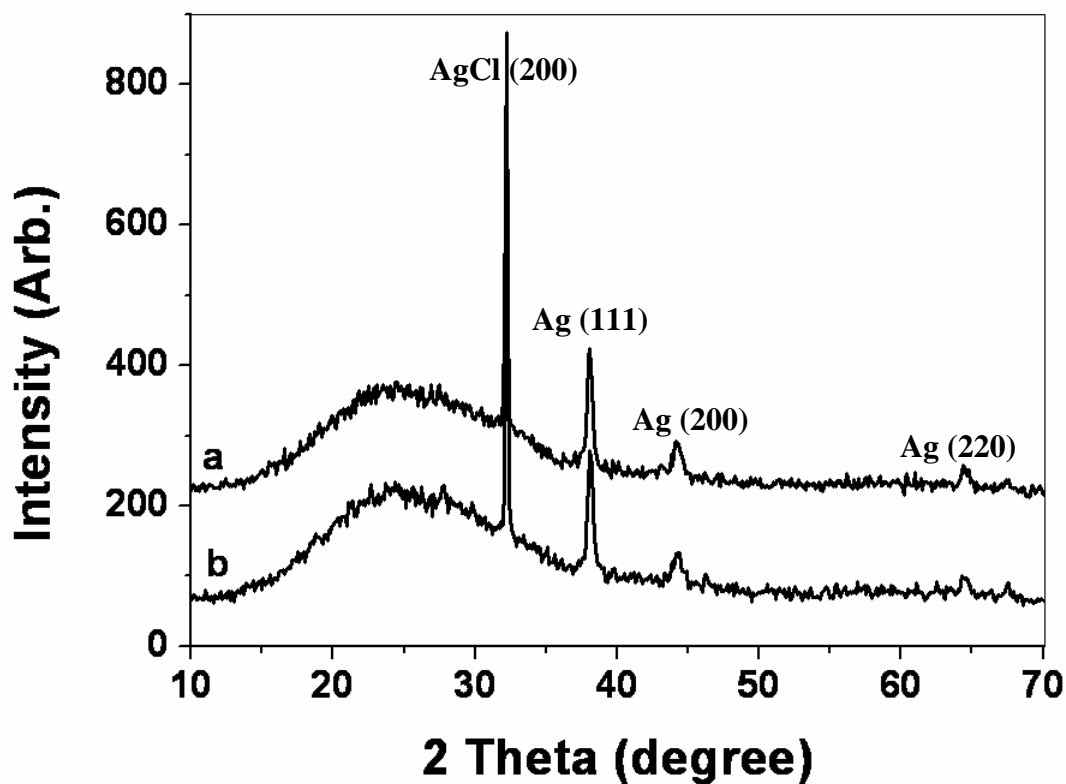


Figure S5. Traces a and b show the XRD patterns of the Ag-PNCs formed from 4-MeO-BzCl and 2-MeO-BzCl, respectively. Major peaks are assigned. A part of the Ag gets converted to AgCl during the polycondensation reaction and lies attached with the polymer. The peak corresponding to AgCl disappeared in the XRD of the NH₃ washed sample.

Supporting Information-SI 6

^1H NMR Spectrum

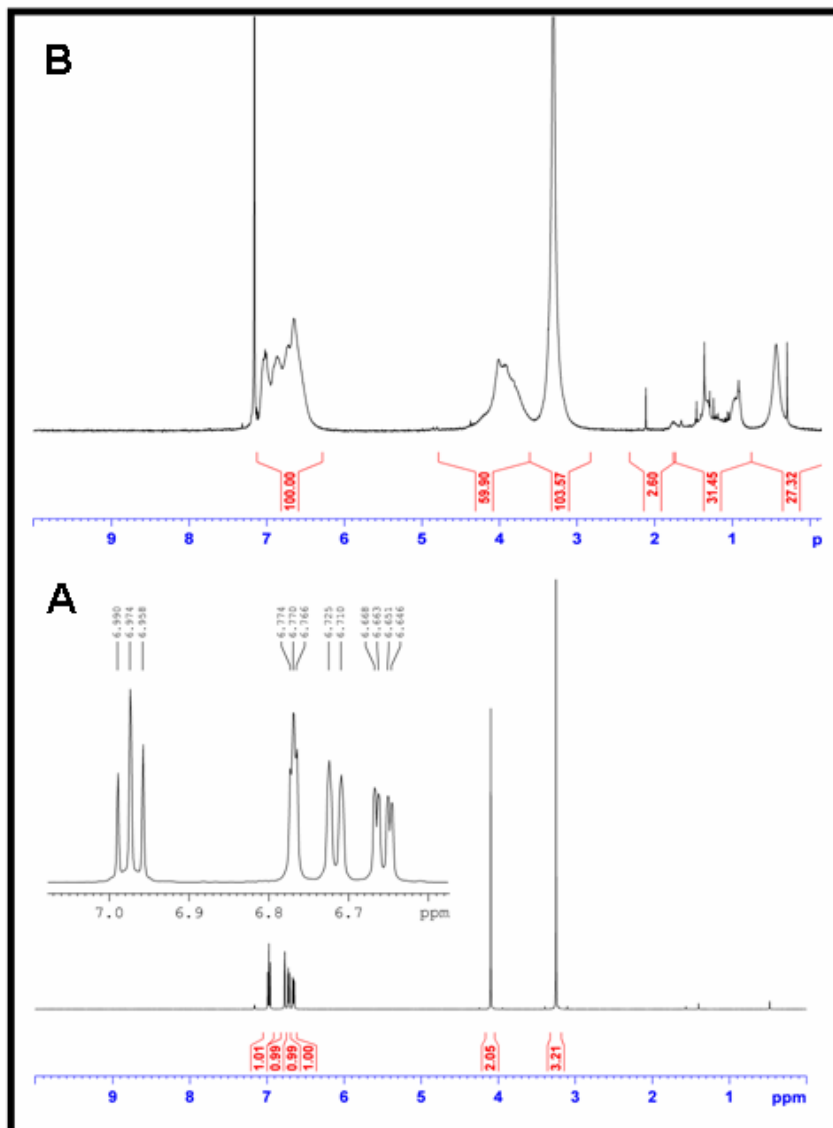


Figure S6. Comparison of the ^1H -NMR spectra of the 2-MeO BzCl (trace A) and the Ag-PNC formed from 2-MeO-BzCl (trace B) in C_6D_6 . The relatively broad peaks in the polymer could be assigned as follows: δ_{H} (600 MHz, C_6D_6 , Me_4Si), 7.1-6.5 (m, -Ph), 3.2 (-O- CH_3), and 4.1 (-C(6) CH_2). The low intense peaks below 2 ppm are due to possible impurities in C_6D_6 .⁶

Supporting Information-SI 7

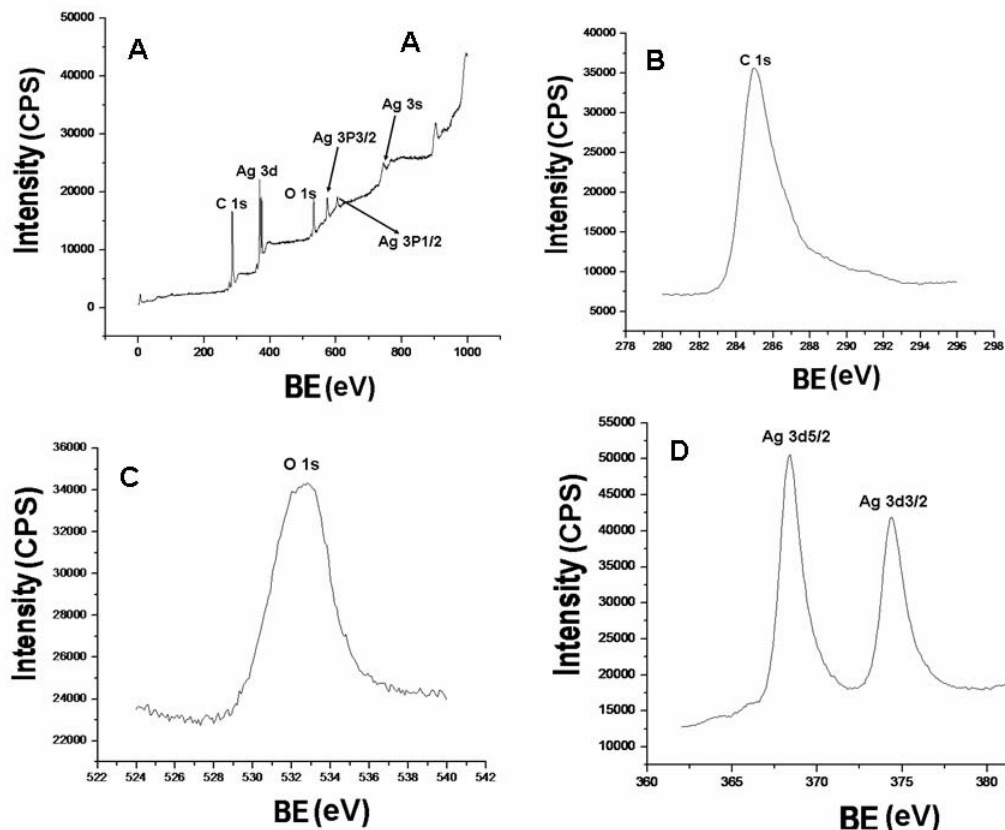


Figure S7. (A) XPS survey spectrum of the purified Ag-PNC (NH_3 washed) prepared from 2-MeOBzCl showing the elemental distribution. B, C and D are separate scans of the C1s, O1s and the Ag 3d regions. The Ag3d position suggests the existence of Ag as Ag (0).

Supporting Information-SI 8

Thermogravimetric Analyses

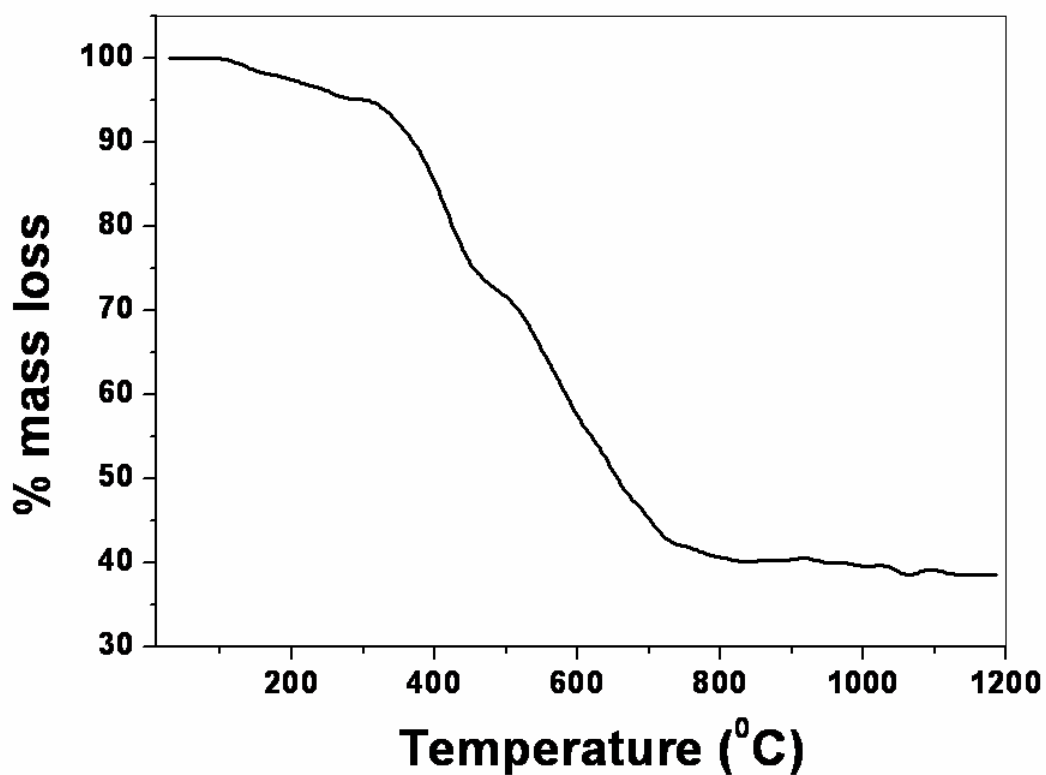


Figure S8. Thermogravimetry trace of Ag-PNC formed from 2-MeO-BzCl. In the Ag-PNC, the polymer was stable up to 320⁰C, and thereafter degradation of the polymer occurs. The initial loss of mass observed up to 300⁰C could be due to the loss of some trapped solvent. The composite retains ~38% of the weight even at 1200 ⁰C, corresponding to the metal.

Supporting Information-SI 9

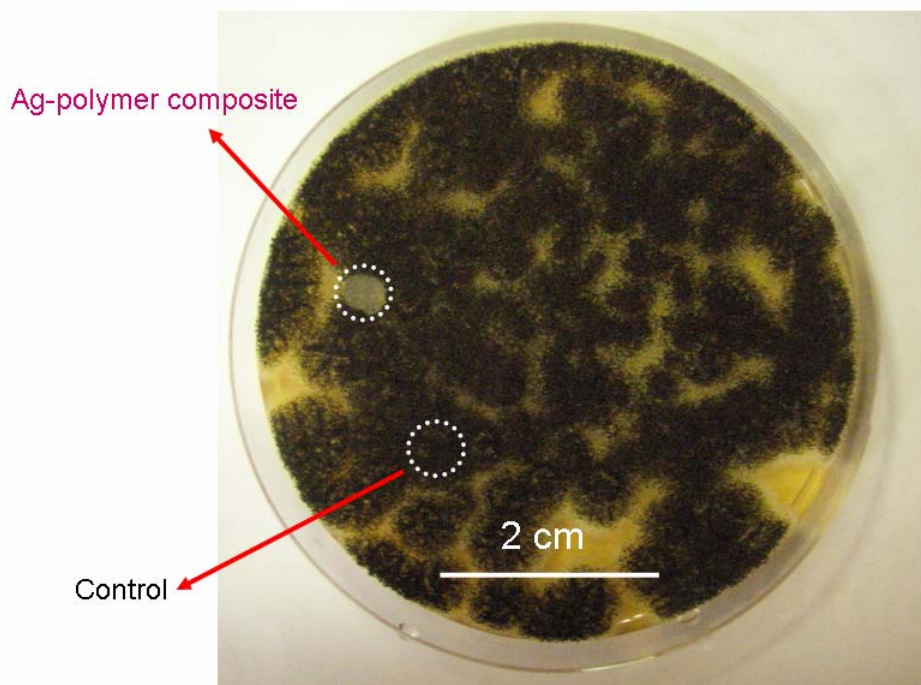


Figure S9. Result of an antifungal test with a mixture of fungi collected from a wall. The filter paper strip was loaded with the Ag-PNC prepared from 2-MeO BzCl.

References

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