Supplementary Information for

Vapor Discrimination by Dual-Laser Reflectance Sensing of a Single Functionalized Nanoparticle Film

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Loss of LSPR absorbance peak upon exposure to saturated toluene. During preliminary testing, a C8-MPN coated glass slide was exposed to a saturated test atmosphere of toluene, created by injecting ~5 µL of neat liquid toluene into the cuvette that housed the C8-MPN coated glass substrate, and replacing the lid of the cuvette. Initially, the absorbance spectrum exhibited the blue shift in λ_{max} as described in the text of the article. However, over the course of several minutes the total absorbance decreased significantly, λ_{max} red shifted, and then the LSPR band diminished almost completely. Figure S1 displays the spectra prior to and after this change. Even after removing the sample from the cuvette and allowing it to stand unexposed for 24 hrs, the LSPR band did not reappear. Re-exposure to toluene vapor also had no effect. The sample was then removed from the cuvette and the MPN film was treated with a few drops of liquid toluene to redissolve the MPNs. The solvent was allowed to evaporate, leaving a recast film, the uniformity of which was visually degraded; a 'coffee-ring' pattern was evident in which the thickness at the periphery of the film patch was obviously much greater than in the central region. Upon replacement of the sample in the cuvette and collection of the absorbance spectrum, the LSPR peak returned, though at reduced intensity.

We cannot explain the loss of the LSPR peak upon initial exposure to this high concentration of toluene, but it obviously causes massive changes in film morphology, perhaps involving widespread agglomeration. We have observed analogous drastic increases in MPN film resistance upon exposure to high toluene vapor concentrations with CR sensors (unpublished results), and we note that Garcia-Berrios, et al. reported a similar permanent loss of film conductivity upon exposure of a C8 MPN film on a CR device to saturated atmosphere of ethanol.^{S1}



Figure S1. Visible absorbance spectrum of a C8-MPN coated glass slide before (solid line) and after (dashed line) several minutes of static exposure to vapors generated by injecting 5 μ L of liquid toluene into the cuvette and sealing the lid.

References

S1. E. Garcia-Berrios, T. Gao, M. Woodka, S. Maldonado, B. Brunschwig, M. Ellsworth and N. Lewis, J. Phys. Chem. C, 2010, 114, 21914- 21920.