

Supporting Information for

**Assemblies of silver nanocubes for highly sensitive SERS
chemical vapor detection**

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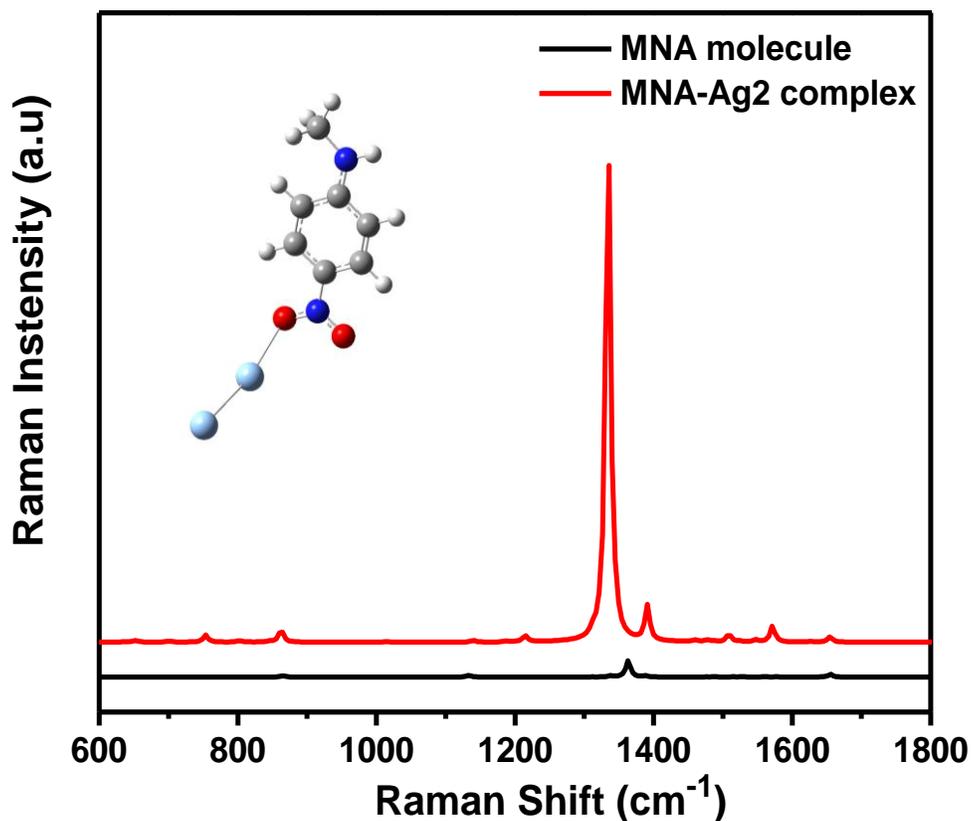


Figure S1. DFT simulation of the (black curve) MNA molecule using the quantum chemistry package Gaussian 03 by optimization at the B3LYP/6-31++G** level of theory, and (red curve) from MNA with a two atom Ag cluster (optimized at the B3LYP/LANL2DZ level of theory for the Ag atoms). The presence of Ag atoms leads to enhancement of the 865 and 1365 cm⁻¹ modes. The inset represents the MNA-Ag atom cluster used to determine the SERS response of MNA.

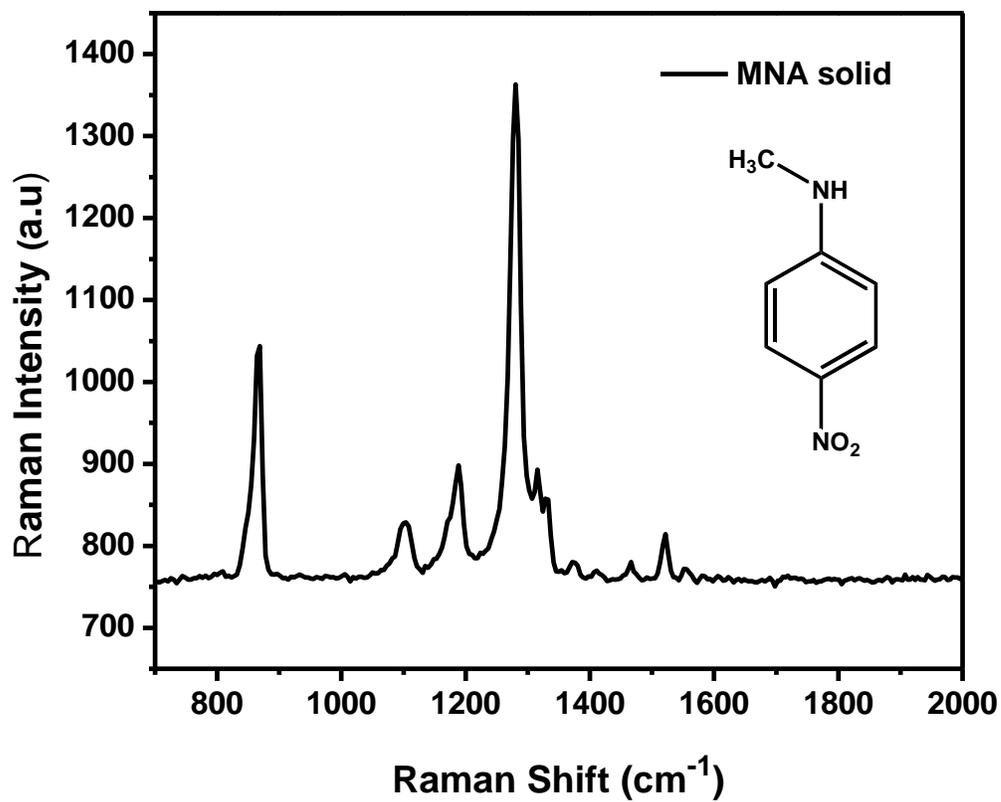


Figure S2. Raman spectrum of solid n-methyl-4-nitroaniline (MNA) and (inset) chemical structure of MNA.

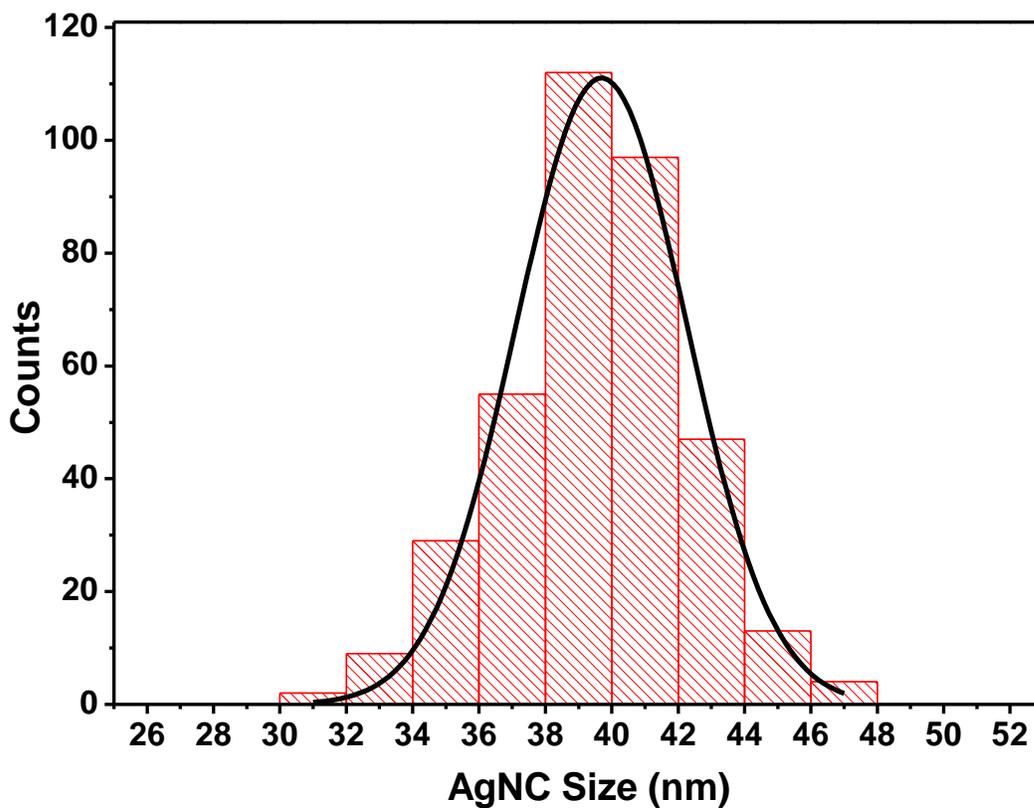


Figure S3. Size distribution of 40nm AgNC, synthesized using the polyol method, determined by TEM (more than 350 AgNC were measured). A Gaussian fit was applied in order to determine the average value and the standard deviation.

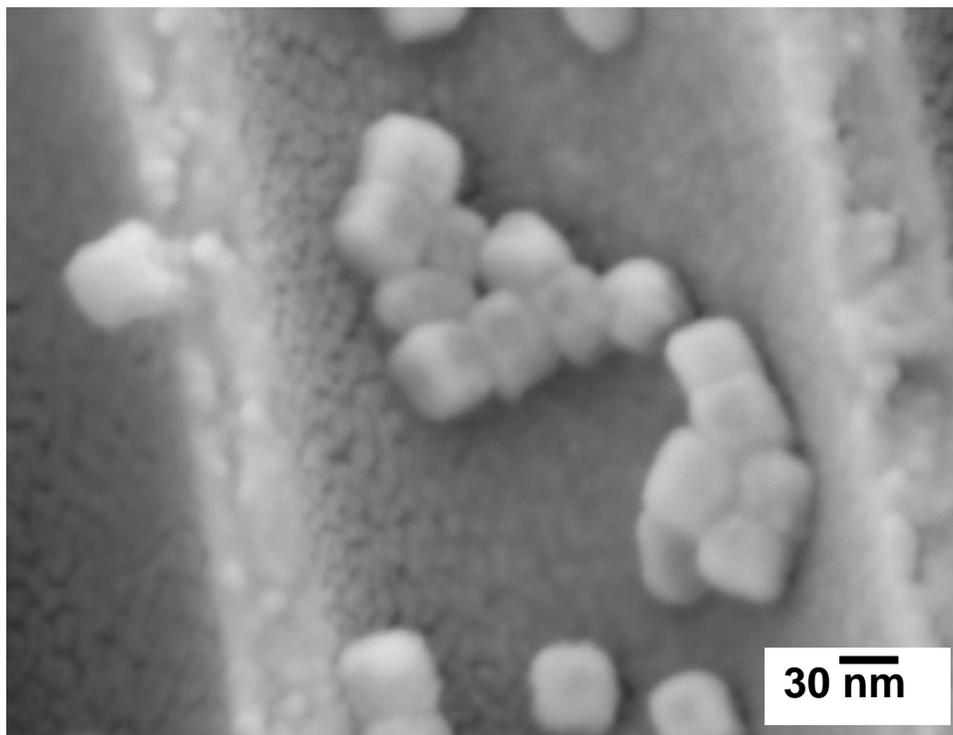


Figure S4. Magnified SEM micrograph of AgNC aggregate in an AgNC-PAH substrate, showing that the majority of AgNC in the aggregate take a face-face orientation to adjacent cubes.

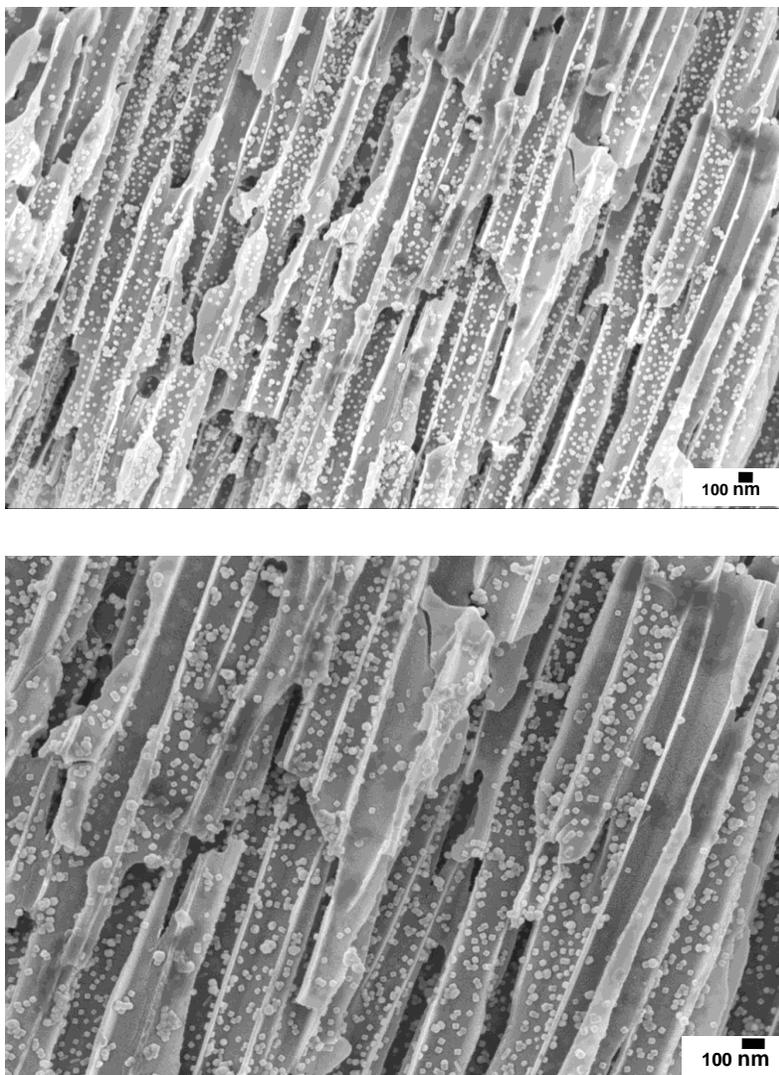


Figure S5. The more dispersed AgNC adsorption behavior that occurs when 2.5 (PAH-PSS) bilayers are spin-coated onto the PAM (instead of the single PAH or PEI used in the other AgNC substrates). There are a large number of AgNC present within the pores, primarily present as individual or small aggregates (on the average). The majority of the particles are located within 5-6 microns from the PAM surface.

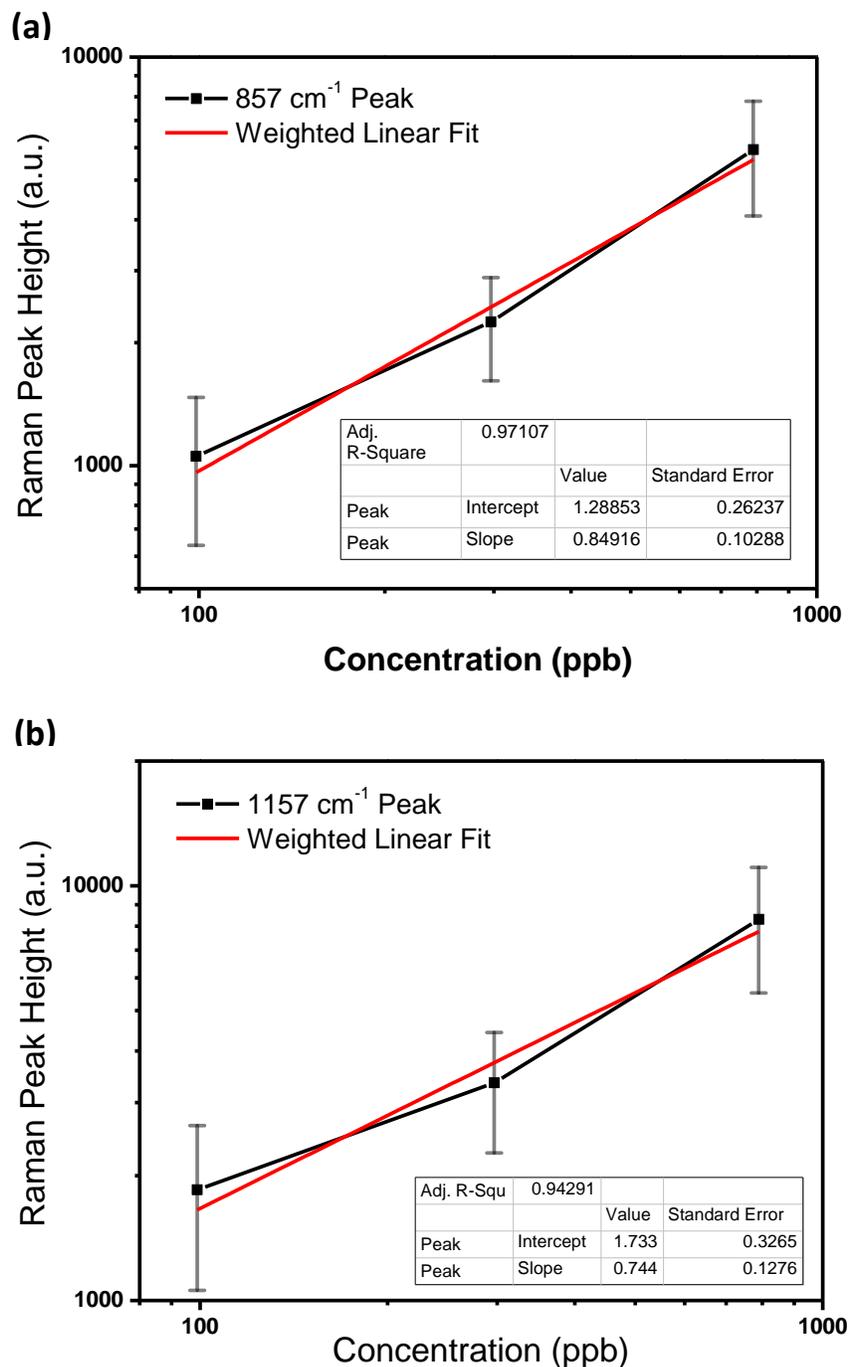


Figure S6. The instrumental error weighted linear fit for the (a) 857 cm^{-1} and (b) 1157 cm^{-1} MNA peak using the AgNC-(PAH-PSS) substrate, demonstrating the linear response of the substrate at higher ppb concentrations. The weighting (w_i) is inversely proportional to the standard deviation (σ_i) of the data point ($w_i=1/(\sigma_i)^2$).

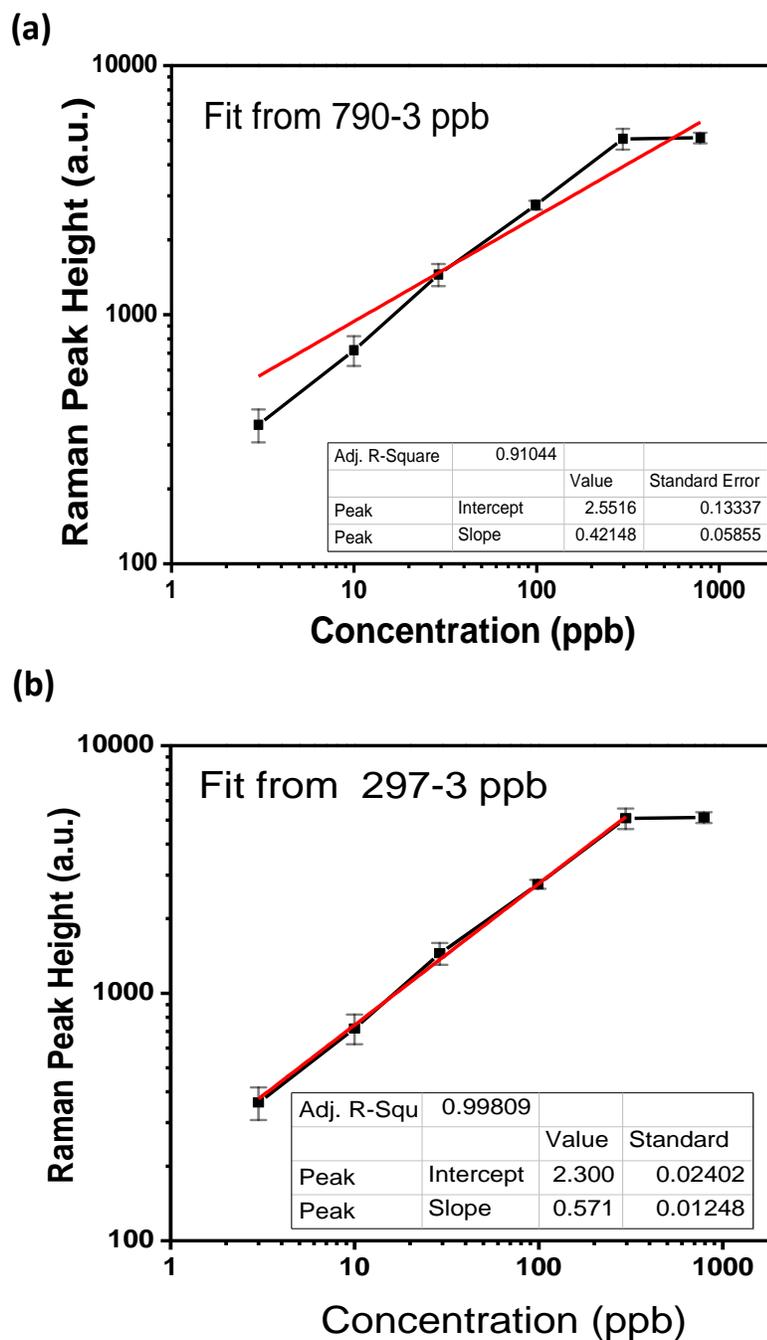


Figure S7. The instrumental error weighted linear fit for the 857 cm^{-1} MNA peak using the AgNC-PAH substrate, where the weighting (w_i) is inversely proportional to the standard deviation (σ_i) of the data point ($w_i=1/(\sigma_i)^2$). The R-squared value improves significantly when the fit is applied to the (a) 297-3 ppb range compared to the fit (b) from 790-3 ppb.

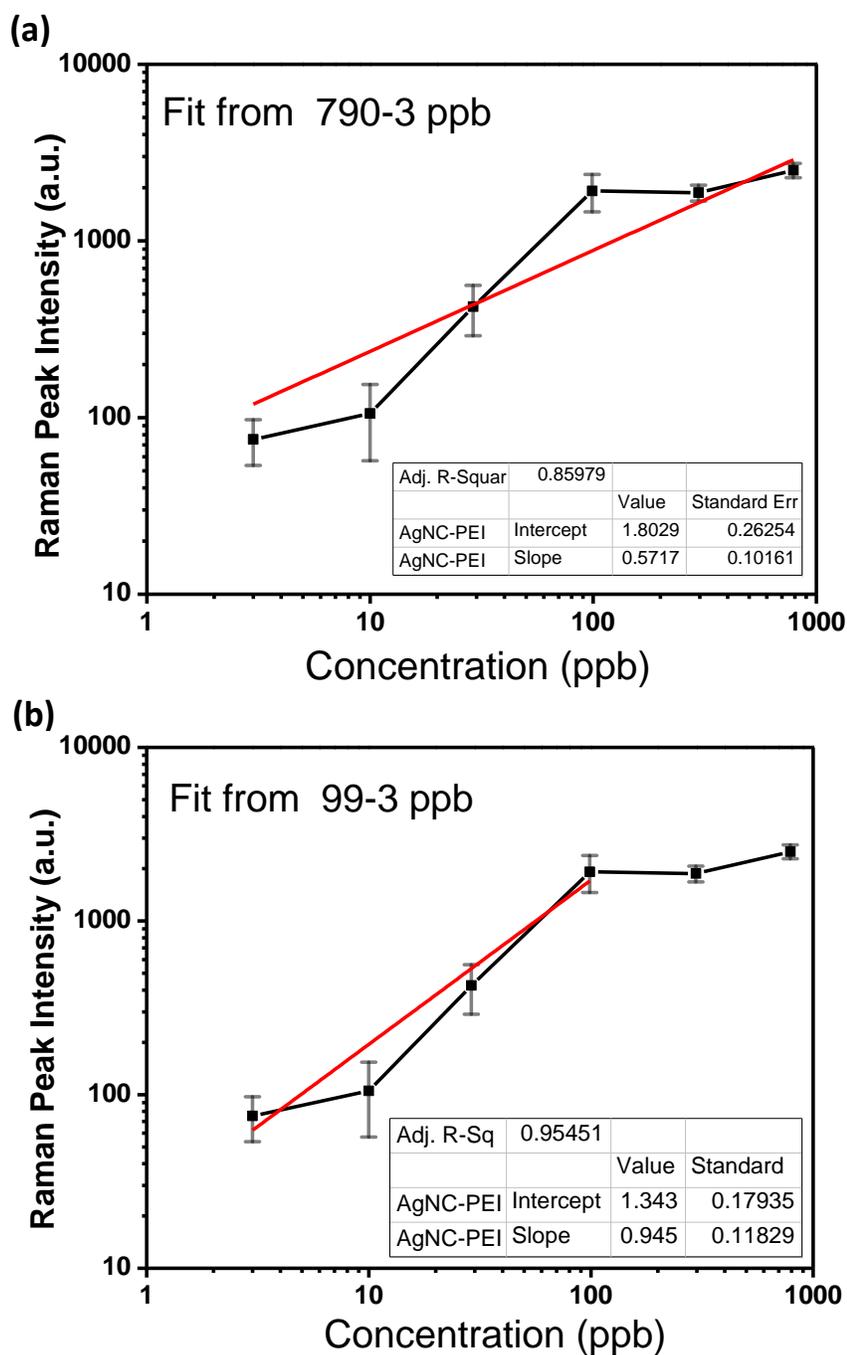


Figure S8. The instrumental error weighted linear fit for the 857 cm^{-1} MNA peak using the AgNC-PEI substrate, where the weighting (w_i) is inversely proportional to the standard deviation (σ_i) of the data point ($w_i=1/(\sigma_i)^2$). The R-squared value improves significantly when the fit is applied to the (a) 99-3 ppb range compared to the fit (b) from 790-3 ppb.

Calculation of MNA vapor concentration:

The vapor concentration of MNA (in ppb) was calculated using theoretical estimations of the vapor pressure of MNA over a temperature range of 270K to 400K (or -3°C to 127°C). The vapor pressure of MNA at various temperatures is approximately¹:

$$5.0^{\circ}\text{C} (278 \text{ K}): P \sim 0.0003$$

$$15^{\circ}\text{C} (288 \text{ K}): P \sim 0.001 \text{ Pa}$$

$$25^{\circ}\text{C} (298 \text{ K}): P \sim 0.003 \text{ Pa}$$

$$35^{\circ}\text{C} (308 \text{ K}): P \sim 0.01 \text{ Pa}$$

$$45^{\circ}\text{C} (318 \text{ K}): P \sim 0.03 \text{ Pa}$$

$$55^{\circ}\text{C} (328 \text{ K}): P \sim 0.08 \text{ Pa}$$

The vapor concentration (in ppb) was determined using the typical method found in the literature, shown below:

$$C (\text{ppb}) = \frac{P_{\text{MNA}}}{P_{\text{Tot}}} * 10^9$$

Where C (ppb) is the concentration in parts per billion, P_{MNA} is the partial pressure of MNA at a specific temperature, and P_{Tot} is the total pressure of the system. This calculation assumes ideal gas conditions so that a ratio between pressures can be related to a ratio between molar values

$$\left(\frac{P_i}{P_{\text{Tot}}} = \frac{n_i}{n_{\text{Tot}}} \right).$$

In reality the vapor pressures we are reporting are likely higher than those actually present because the theoretical estimations for vapor pressure have been found to be consistently higher than experimental values, so the MNA values reported are likely overestimating the vapor pressure of MNA (and hence its concentration). In some instances this can be found to overestimate the vapor pressure by two to three orders of magnitude.¹

The molar concentration can be obtained from the vapor pressure through the ideal gas law (appropriate given the low pressures and temperatures involved).

$$C = \frac{n_i}{V} = \frac{P_i}{RT} \quad (R = 8.31 \text{ J/K*mol})$$

5.0 °C (278 K), P ~ 0.0003	→	C = 1.38*10 ⁻⁷ moles/m ³ = 1.38*10 ⁻¹⁰ moles/L
15 °C (288 K), P ~ 0.001 Pa	→	C = 4.28*10 ⁻⁷ moles/m ³ = 4.28*10 ⁻¹⁰ moles/L
25 °C (298 K), P ~ 0.003 Pa	→	C = 1.21*10 ⁻⁶ moles/m ³ = 1.21*10 ⁻⁹ moles/L
35 °C (308 K), P ~ 0.01 Pa	→	C = 3.91*10 ⁻⁶ moles/m ³ = 3.91*10 ⁻⁹ moles/L
45 °C (318 K), P ~ 0.03 Pa	→	C = 1.14*10 ⁻⁵ moles/m ³ = 1.14*10 ⁻⁸ moles/L
55 °C (328 K), P ~ 0.08 Pa	→	C = 2.94*10 ⁻⁵ moles/m ³ = 2.94*10 ⁻⁸ moles/L

References

(1) Toghiani, R. K.; Toghiani, H.; Maloney, S. W.; Boddu, V.M. *Energetic Materials: Thermophysical Properties, Predictions, and Experimental Measurements. Research and Development*. Taylor and Francis Group, LLC. **2011**. Pages 171-195.