Supplementary Materials

1. Experimental SERS spectra of AFs at different concentrations

Fig. S1 illustrates the SERS spectra of the negative control (methanol sample), AFB_1, AFB_2, AFG_1, and AFG_2 at selective concentrations (*C*): 1×10^{-3}, 5×10^{-4}, 1×10^{-4}, 5×10^{-5}, and 1×10^{-5} mol L^{-1} for AFB_1; 1×10^{-3}, 5×10^{-4}, 1×10^{-4}, and 5×10^{-5} mol L^{-1} for AFB_2; 1×10^{-3}, 5×10^{-4}, 1×10^{-4}, 5×10^{-5}, 1×10^{-5}, 5×10^{-6}, and 1×10^{-6} mol L^{-1} for both AFG_1 and AFG_2, respectively. The negative control spectrum shows a "flat" background with no obvious Raman peak, while the SERS spectra of AFs at different concentrations all show similar spectral features with elevated intensity when the concentration increases. Thus, we believe that our results reveal the true SERS spectra of the AFs without the interference of the background noise.

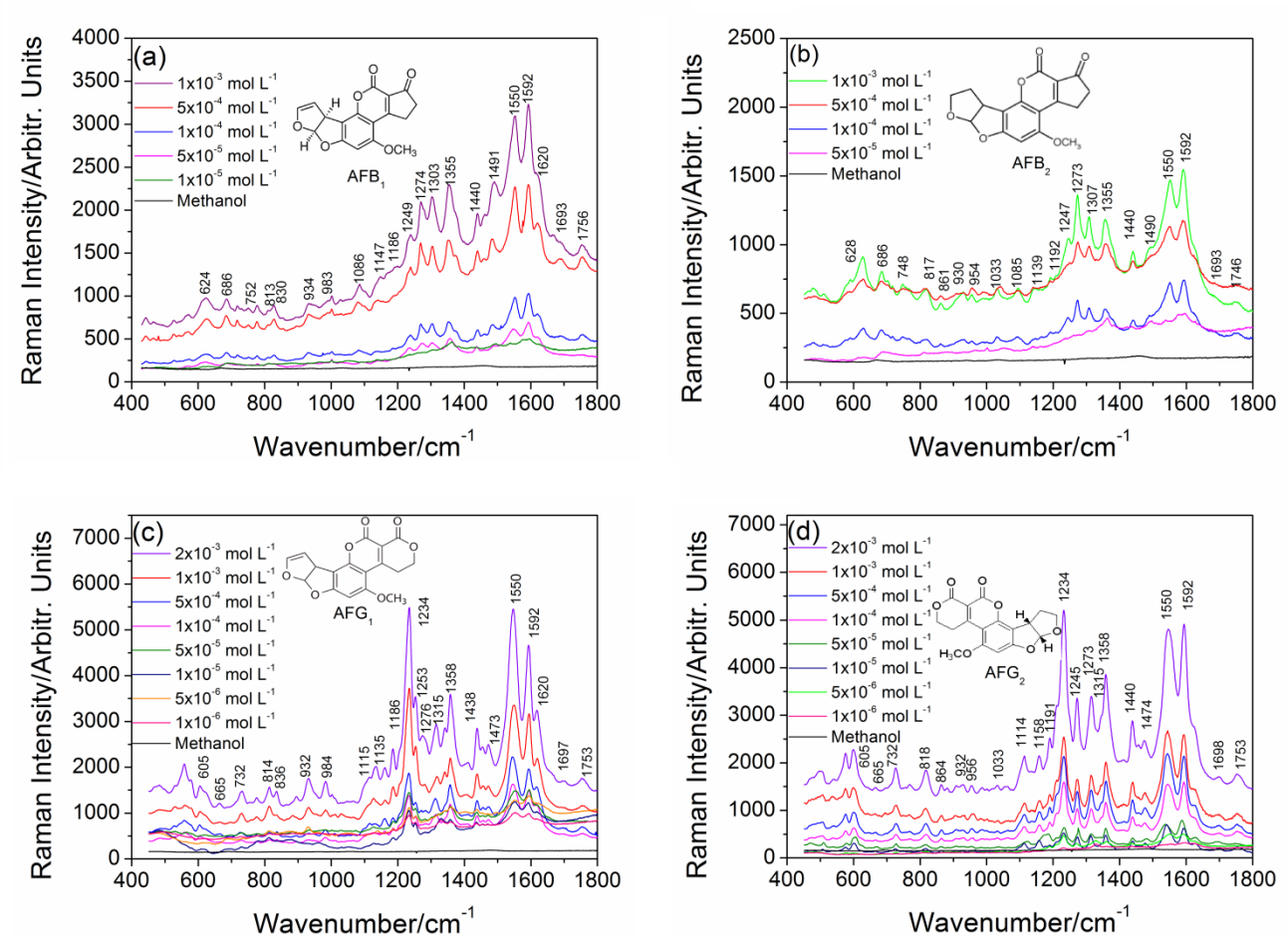

Fig. S1 Experimentally obtained SERS spectra of AFs at selective concentrations. The Raman shifts of significant peaks in each AF spectrum are indicated. (a) AFB_1, (b) AFB_2, (c) AFG_1, (d) AFG_2.

2. Using PCA to determine LODs of AF

When using PCA method to differentiate four types of AFs, the concentrations used in Fig. 5 (main article) are concentrations all above their LODs determined by the peak fitting method, and they all generate SERS spectra with good quality. A question raised here is whether the SERS spectra of AFs will also be grouped similarly if the concentrations lower than the determined LODs are used. Adding AFB_1 at 1×10^{-5} mol L^{-1}, AFB_2 at 1×10^{-4} mol L^{-1}, and both AFG_1 and AFG_2 at 1×10^{-6} mol L^{-1} to the data set used in Fig. 5, the resulting new PCA plot of PC1 vs. PC2 is shown in Fig. S2. It shows a group pattern similar to that in Fig. 5. Each type of AFs forms a close group in Fig. S2, but they are more scattered than the groups shown in Fig 5. At the lowest concentration of each AF, some of the data points indicated by yellow dots in Fig. S2 are far away from the rest of their groups. These points become hard to distinguish and category. This result suggests that for concentration level of 1×10^{-5} M for AFB_1, 1×10^{-4} M for AFB_2, and 1×10^{-6} M for both AFG_1 and AFG_2, the spectral data are not discriminated enough to separate one type of AFs from the other. This confirmed that the LODs necessary to distinguish these four AFs from each other are 5×10^{-5} M for AFB_1, 1×10^{-4} M for AFB_2, and 1×10^{-6} M for both AFG_1 and AFG_2. These LODs match the results obtained by using the peak fitting methods, as demonstrated in the main article.

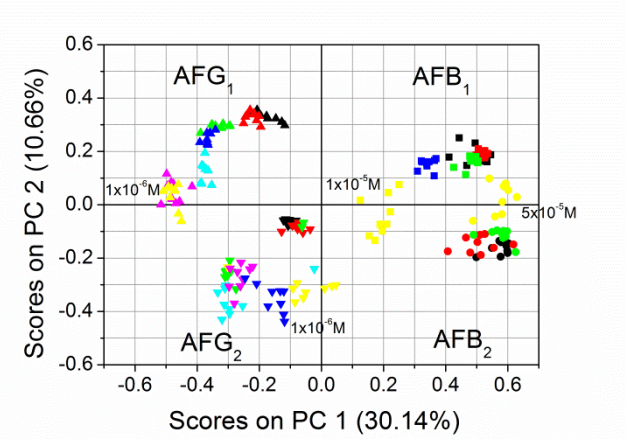

Fig S2. PCA plot of four different types of AFs at concentrations above and below their LODs.