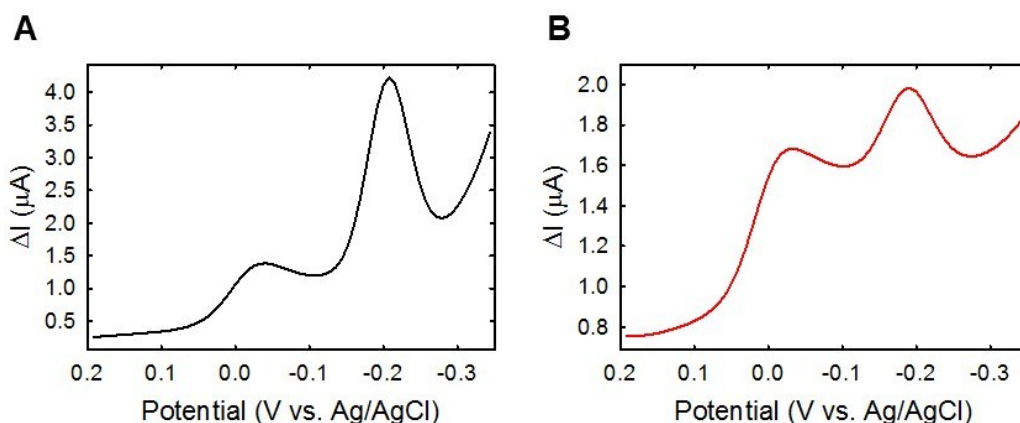


## Supporting Information

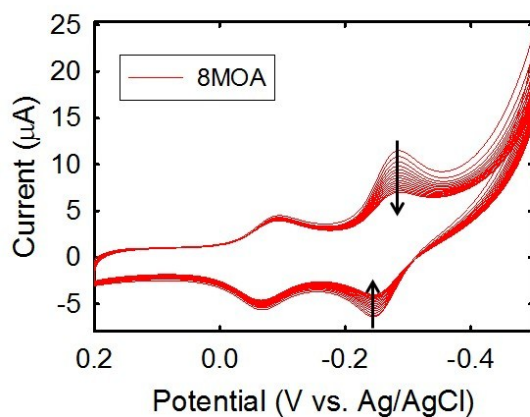
# Unforeseen distance-dependent SERS spectroelectrochemistry from surface-tethered Nile Blue: the role of molecular orientation

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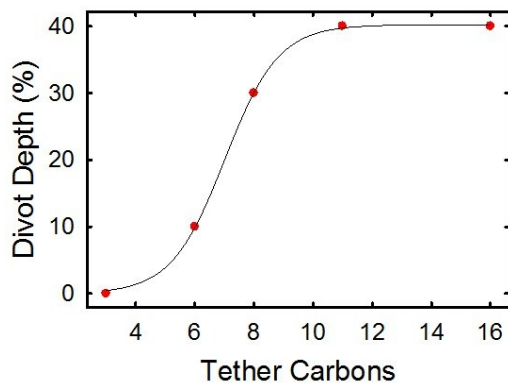
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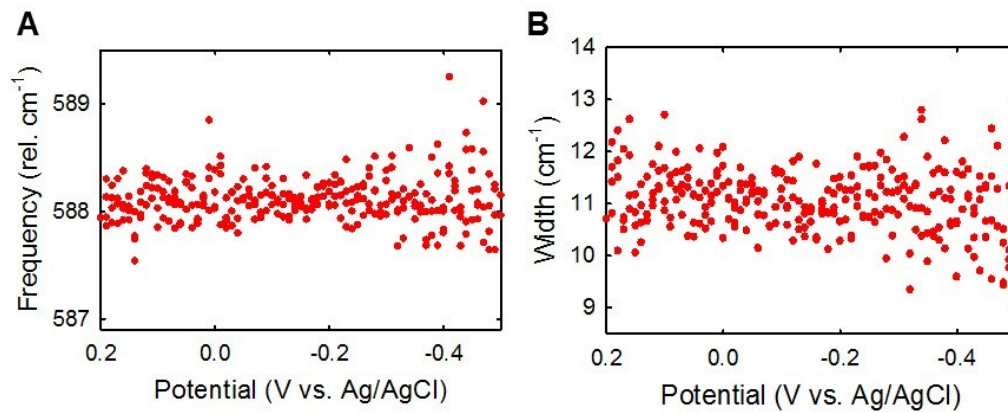
**Figure S1.** (A) Initial DPV of 8MOA functionalized AuIF acquired after electrode functionalization of Nile Blue. (B) DPV of the electrode in (A) after stabilizing the current response by potential cycling across the Nile Blue redox window.



**Figure S2.** Cyclic voltammograms of Nile Blue tethered to a 100 nm Au film by 8MOA and EDC coupling showing the initial decrease in the phenoxazine redox peak. This peak overlaps with the solution-phase NB redox chemistry, suggesting the initial presence and ultimate loss of the untethered version of the molecule.



**Figure S3.** Estimated 588  $\text{cm}^{-1}$  SERS divot depth relative to the maximum intensity ( $I_{\text{divot}}/I_{\text{max}}$ ) as the linker length is increased.



**Figure S4.** SERS spectral fits from 16MDHA which exhibits a strong intensity divot at oxidizing potentials. (A) CNC phenoxazine vibration frequency. (B) Spectral width of the 588 cm<sup>-1</sup> mode.