Combined near-infrared excited SEHRS and SERS spectra for pH sensors using silver nanostructures

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Electronic Supplementary Information
**Fig. S1.** Absorbance spectra of citrate reduced/stabilized (a) and hydroxylamine reduced (b) Ag nanoparticles with pMBA at different pH values.

**Fig. S2.** SERS spectra of pMBA excited at 532 nm with citrate reduced/stabilized (a), hydroxylamine reduced (b), NaBH₄ reduced, citrate stabilized I (c) and II (d) Ag nanoparticles. Excitation intensity: 3 x 10⁵ W/cm², acquisition time: 1 s (a,b,d), 2 s (c), pMBA concentration: 9 x 10⁻⁷ M, averages of 30 spectra.
Fig. S3. Extracts of SEHRS (a) and SERS spectra (b) of pMBA with Ag (citrate) nanoparticles at an excitation wavelength of 1064 nm and 532 nm, respectively. Experimental conditions as described in Fig. 2 and S2, respectively.
Table S1. Band positions (cm\(^{-1}\)) in SEHRS and SERS spectra of \(p\)MBA with Ag (citrate) at pH 7 and band assignments.

| SEHRS (1064 nm) | SERS (1064 nm) | SERS (532 nm) | Assignment | References |
|----------------|----------------|---------------|------------|------------|
| 363            |                |               | phenyl deformation + C-S-stretching | 1, 2        |
| 520            | 523            |               | in-plane ring deformation | 2, 3        |
| 684            |                |               | C-H out-of-plane deformation | 4          |
| 695*           | 697*           |               | C-H out-of-plane deformation + out-of-plane \(\gamma(\text{CCC})\) |           |
| 710            | 716            | 714           | out-of-plane \(\gamma(\text{CCC})\) | 1, 4, 5     |
| 800*           |                | 842           | COO\(^-\) deformation | 1, 5, 6     |
| 836            | 839            | 842           | COO\(^-\) deformation | 1, 5, 6     |
| 1009           | 1012           | 1013          | ring deformation | 7          |
| 1069           | 1075           | 1077          | ring breathing | 7          |
|                | 1138           | 1139          | C-COO\(^-\) stretching | 7          |
| 1178           | 1182           | 1185          | C-H-in-plane-bending | 7          |
| 1365           |                | 1368 (shoulder) | COO\(^-\) stretching (COO\(^-\) surface-bound) | 5, 8        |
|                | 1375           | 1381          | COO\(^-\) stretching (COO\(^-\) non-surface-bound) | 5          |
| 1479           |                | 1485          | C-H in-plane-bending | 7          |
| 1576           | 1583           | 1585          | ring stretching | 7          |
| 1685*          |                | 1703*         | C=O stretching of protonated carboxyl group | 5          |

\*band only observed at acidic pH

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