Electronic Supplementary Material (ESI) for Analyst
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*Supplementary Information*

# In situ Raman Spectroscopy of Surfaces Modified by Ion Soft Landing

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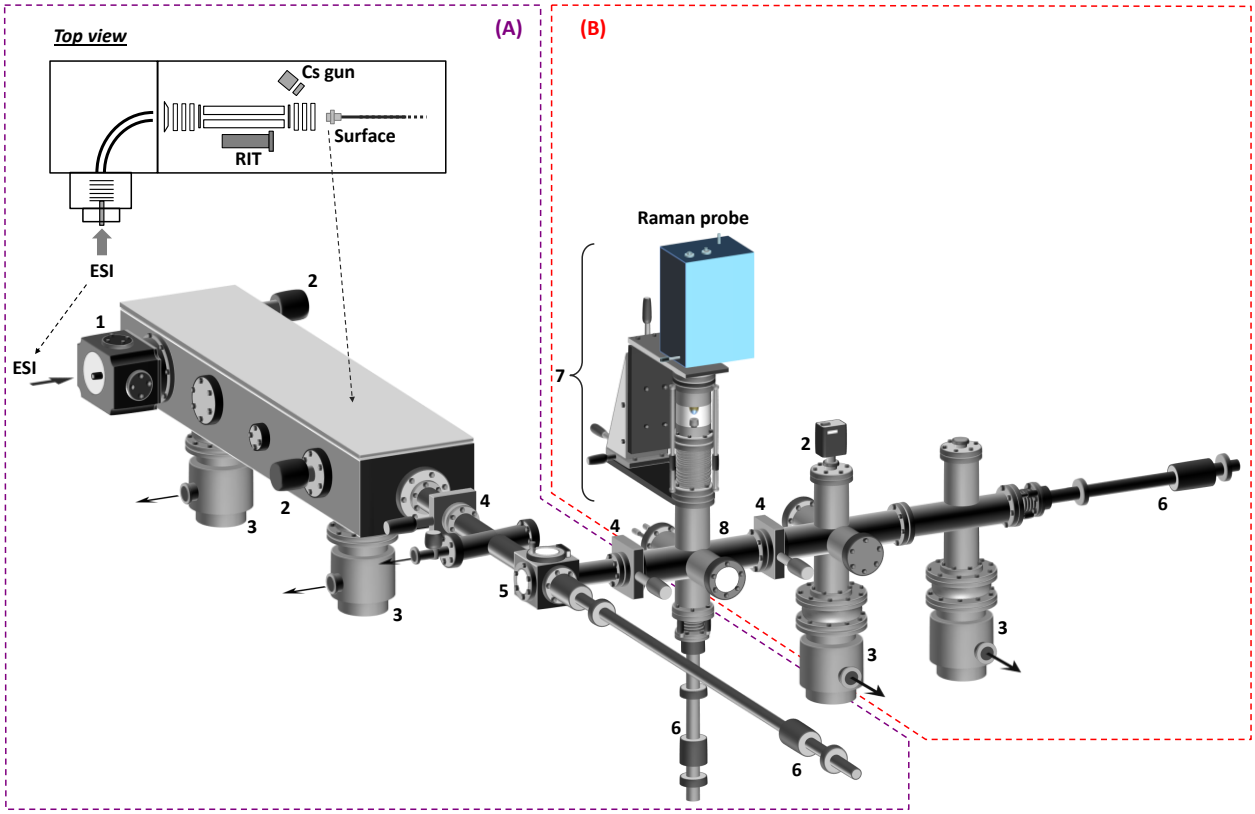


Figure S1. Schematic of the soft landing instrument (A) with attached vacuum chamber (B) designed to incorporate an in situ Raman measurement system: (**1**) ion funnel, (**2**) vacuum gauges (**3**) turbomolecular pumps (**4**) gate valves, (**5**) fast entry chamber, (**6**) linear/rotary drive, (**7**) in situ Raman assembly, (**8**) six ways cross.

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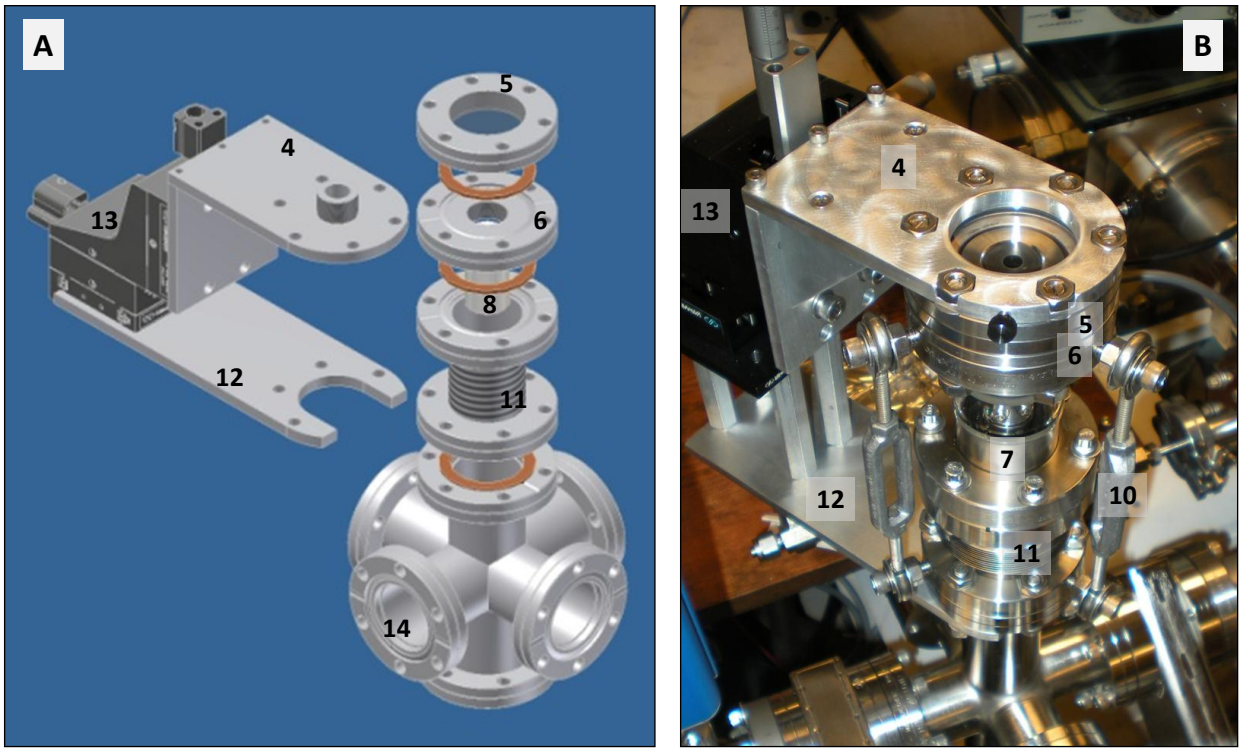


4. **Aluminum plate to hold Raman probe**
5. **Quartz view port**
6. **Custom made double side flange with threaded hole for mounting 40x microscope objective**
7. **Union coupling with glass window**
8. **Microscope objective 40x**
9. **Sample holder**
10. **Turnbuckle to adjust *z* motion**
11. **Flex metal bellow**
12. **Aluminum plate to fix xyz stage**
13. **xyz stage (Newport)**
14. **View port**

Figure S2. (A) CAD drawing of microscope assembly shown in Figure 1. (B) Shows the photograph of the microscope assembly. Parts numbers are listed as in Figure 1. In both figures the Raman probe is not shown for clarity.

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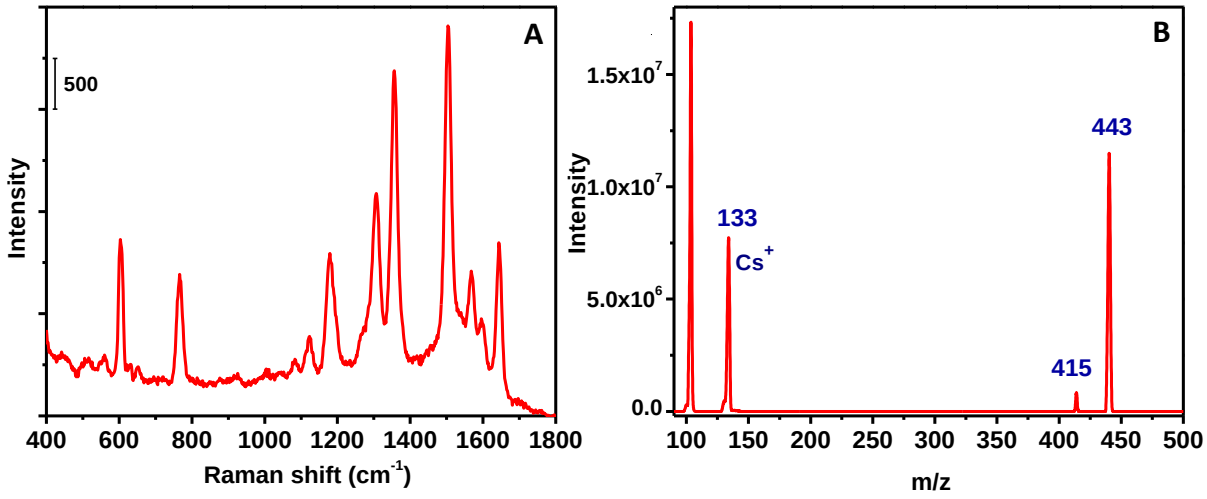


Figure S3. (A) In situ Raman and (B) positive ion SIMS spectra of soft landed Rhodamine 6G. Soft landing duration was 2 h with 3 x $10^{-10}$ A ion current

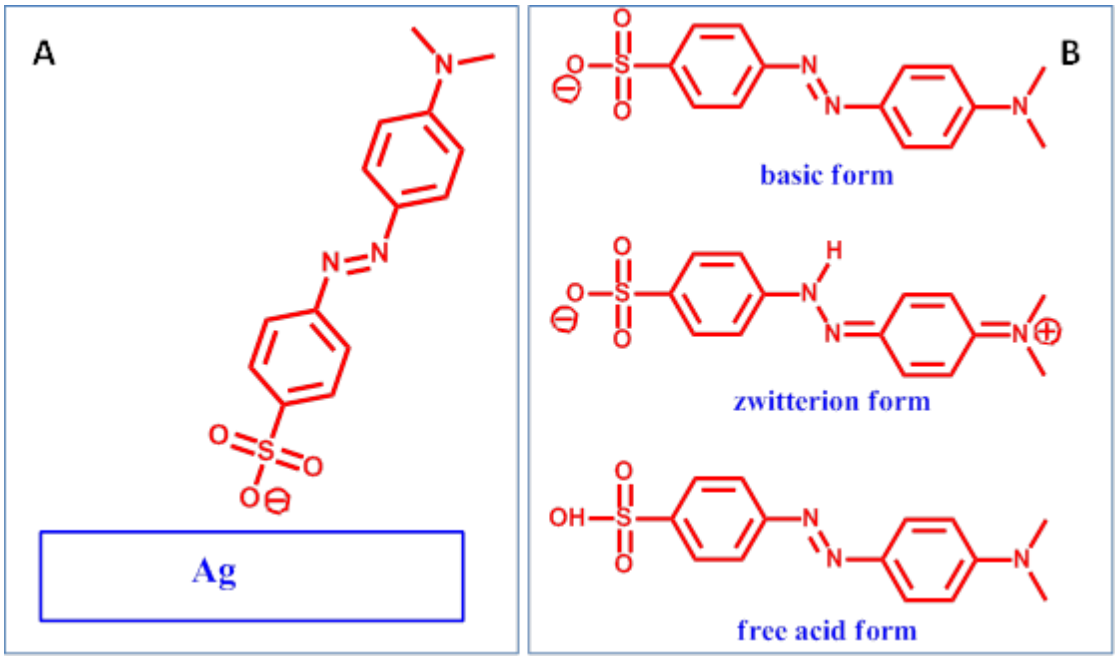


Figure S4. (A) Schematic of possible methyl orange adsorption orientation on Ag surface; (B) basic, zwitterionic and free acid forms of MO.

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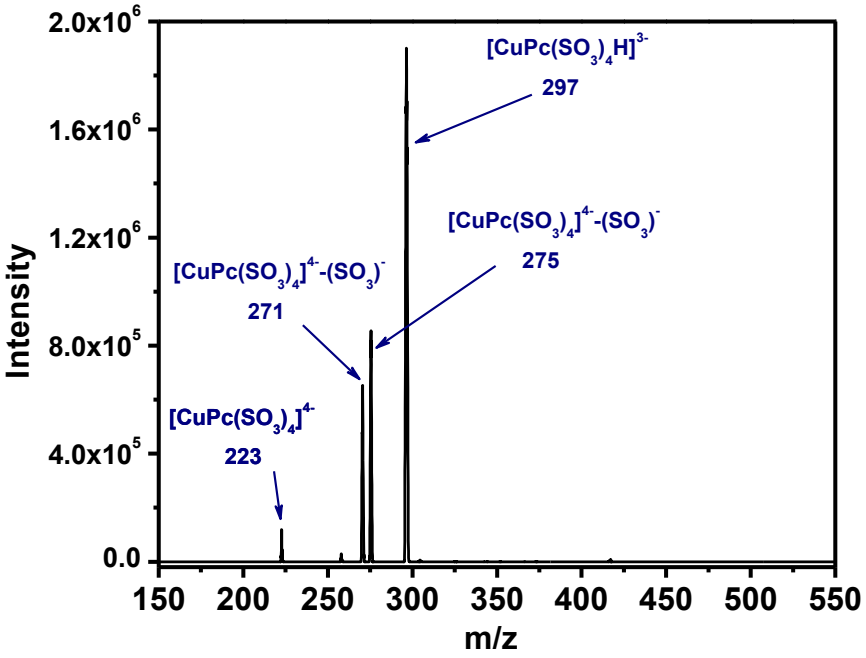


Figure S5. Negative ion ESI mass spectrum of CuPcS4. Solution (1 x $10^{-5}$ M) prepared in 1:1 water/acetonitrile and used for electrospray. All these ions are soft landed onto the substrate.

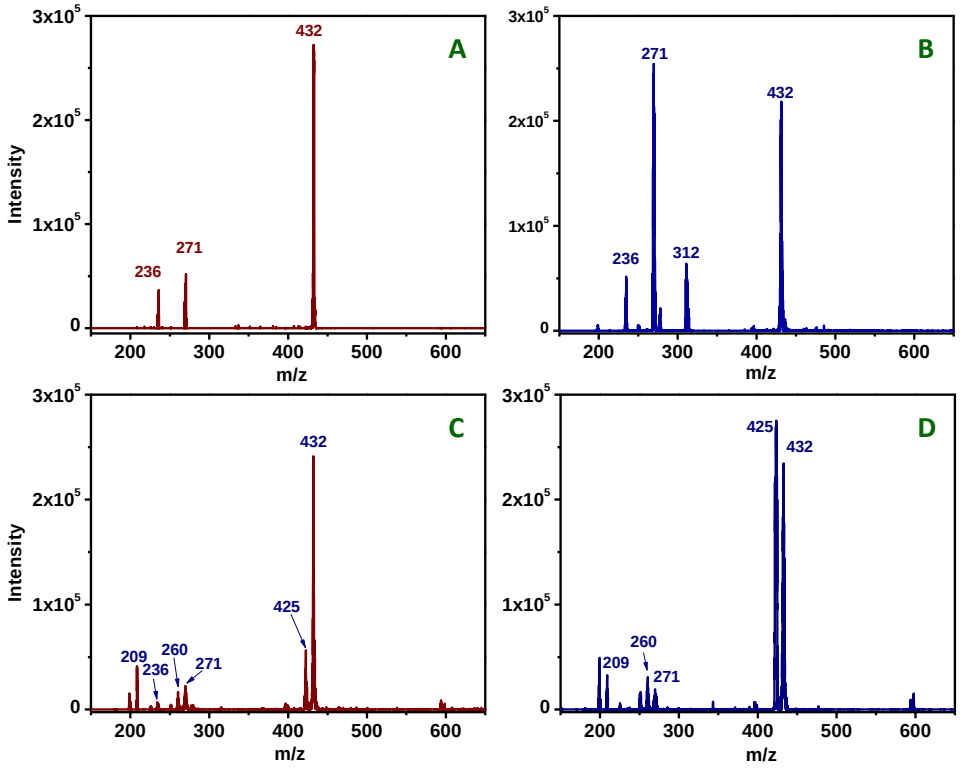

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Figure S6. Negative ion SIMS spectra of CuPcS4 from various experiments. (A) Soft landed onto bare Au substrate, (B) spin coated onto bare Au substrate, (C) soft landed onto Ag nanoparticle coated substrate, (D) reference sample (by mixing CuPcS4 and Ag nanoparticle) is spin coated onto bare Au substrate. Soft landing duration was 2 h at $1 \times 10^{-10}$ A ion current.

- m/z 425 = $[CuPc(SO_3)_3ONa]^{2\bullet-}$
- m/z 312, m/z 260, m/z 236 = Ring opening fragmentation in the phthalocyanine macrocycles results these ions. It involve the bond cleavage in the pyrrole ring as well. Possibility of bond cleavage in several position and abstractions of H make difficult to propose a particular pathway.
- m/z 199, 398, 597 = $Au_n^-$

Figure S7. Possible mass spectral fragments seen in SIMS spectra. Some other fragments are given at right

**Supplementary Information S8**. The nanoparticle coating on the bare gold substrate exists as 30 μm spots, and these are visible in confocal Raman imaging (Figure 5B). The intensity variation between the spots is due to differences in nanoparticle aggregation present in the spots rather than the presence of contamination for which there is no evidence. Spots that have larger enhancements contain more nanoparticles than spots with lower enhancement. The optical image (Figure 5A) is prepared from multiple images as the entire area could not be captured in one snapshot.