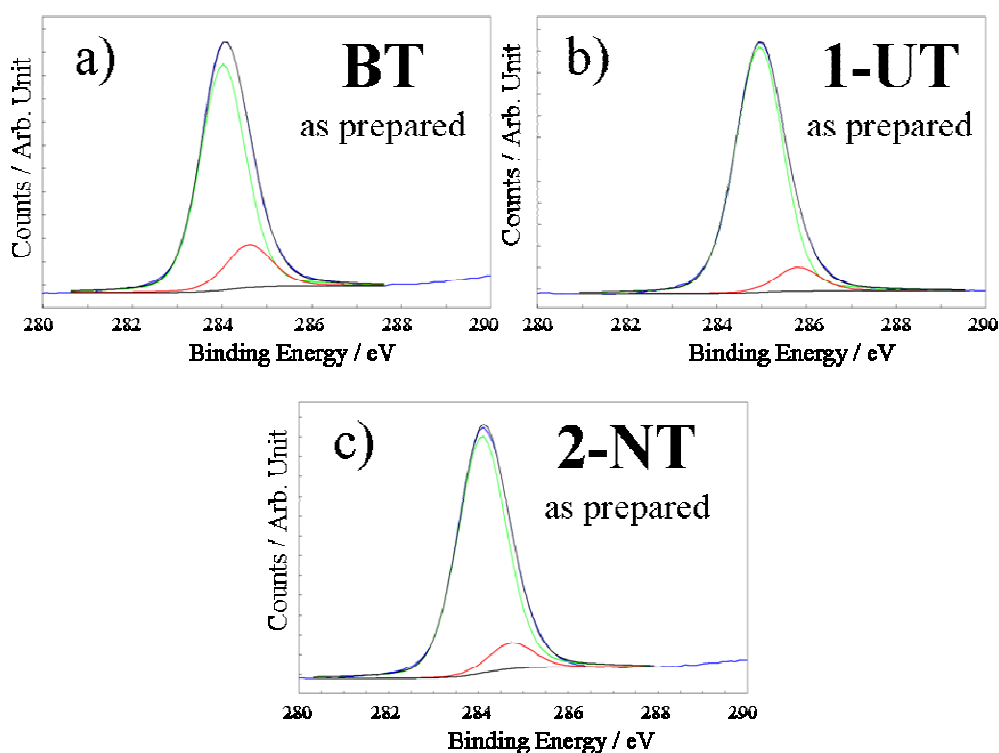


Supporting information for:

Enhanced protective properties and structural order of Self-Assembled Monolayers of aromatic thiols on copper in contact with acidic aqueous solution

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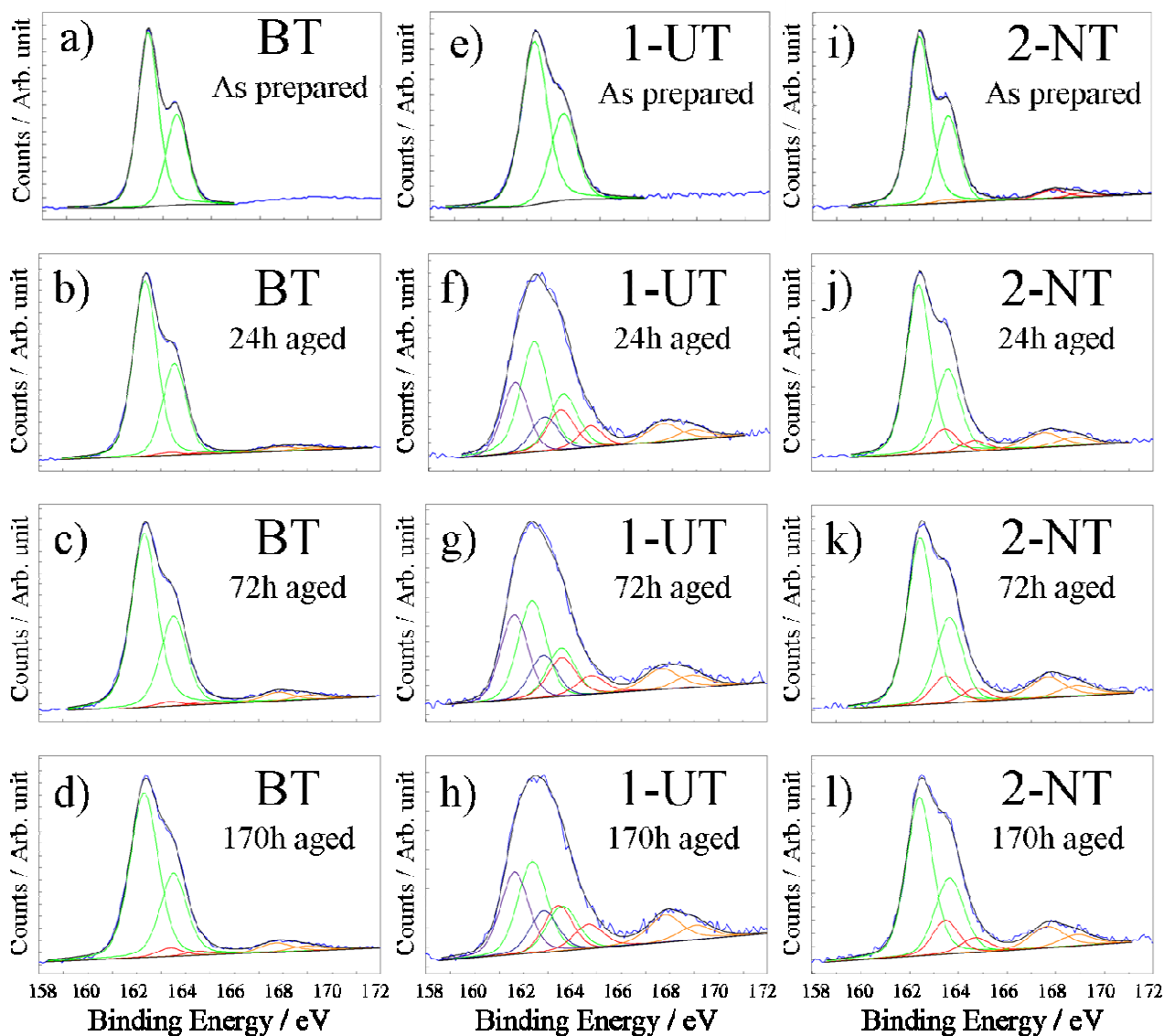


Best fit performed on C1s XP spectra relative to as prepared a) BT; b) 1-UT and c) 2-NT samples.

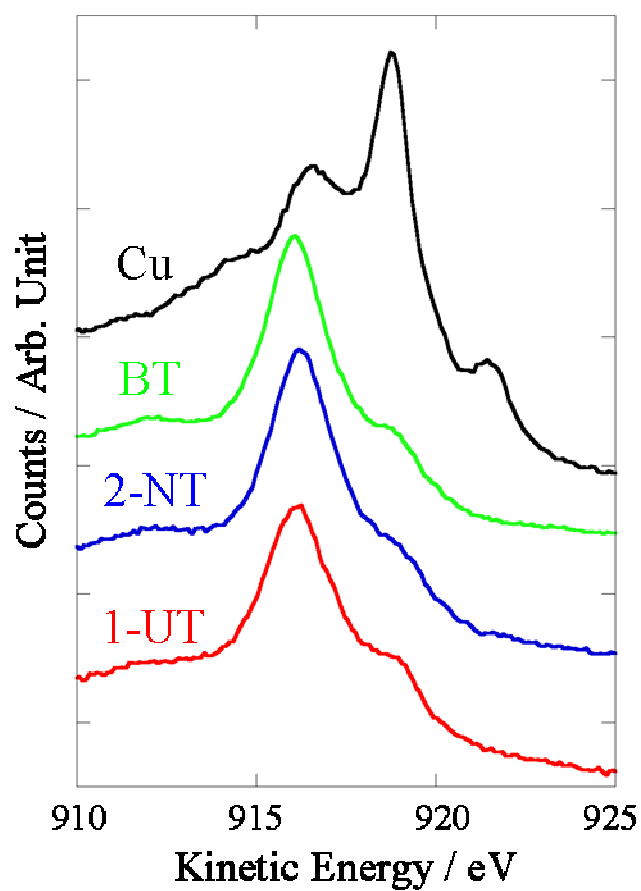
— : aromatic (for BT and 2-NT, 284.1 ± 0.1 eV) or alkylic (for 1-UT, 285.0 ± 0.1 eV) backbone

— : carbon atom bonded to the sulfur.

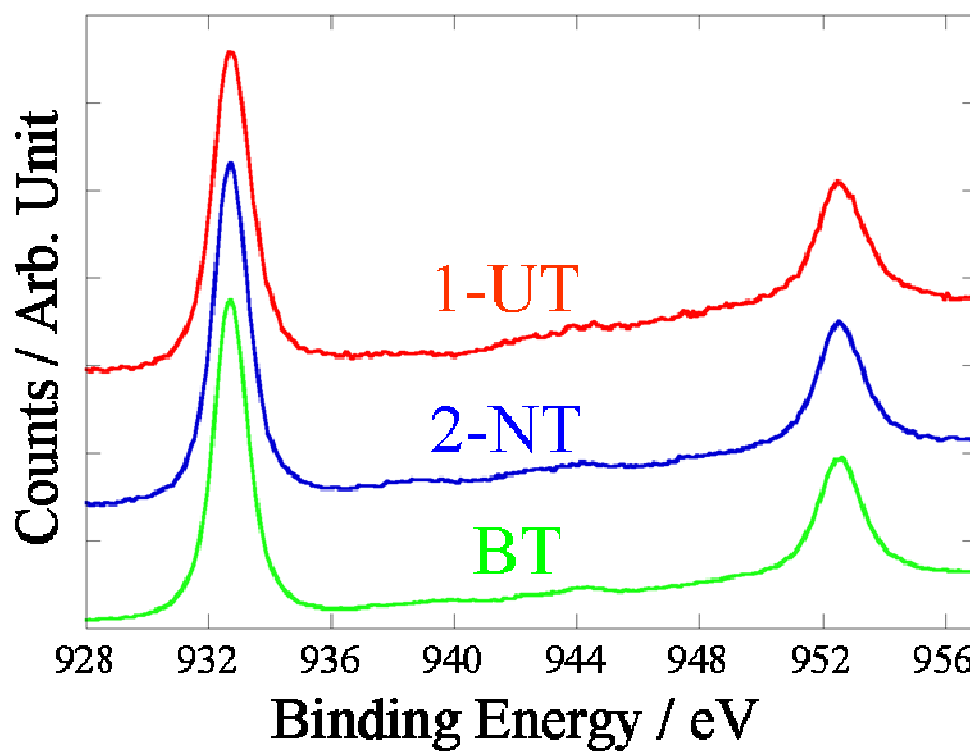
The ratio between the two components is perfectly in agreement with the molecular structure: 5:1 for BT, 9:1 for 2-NT, 10:1 for 1-UT



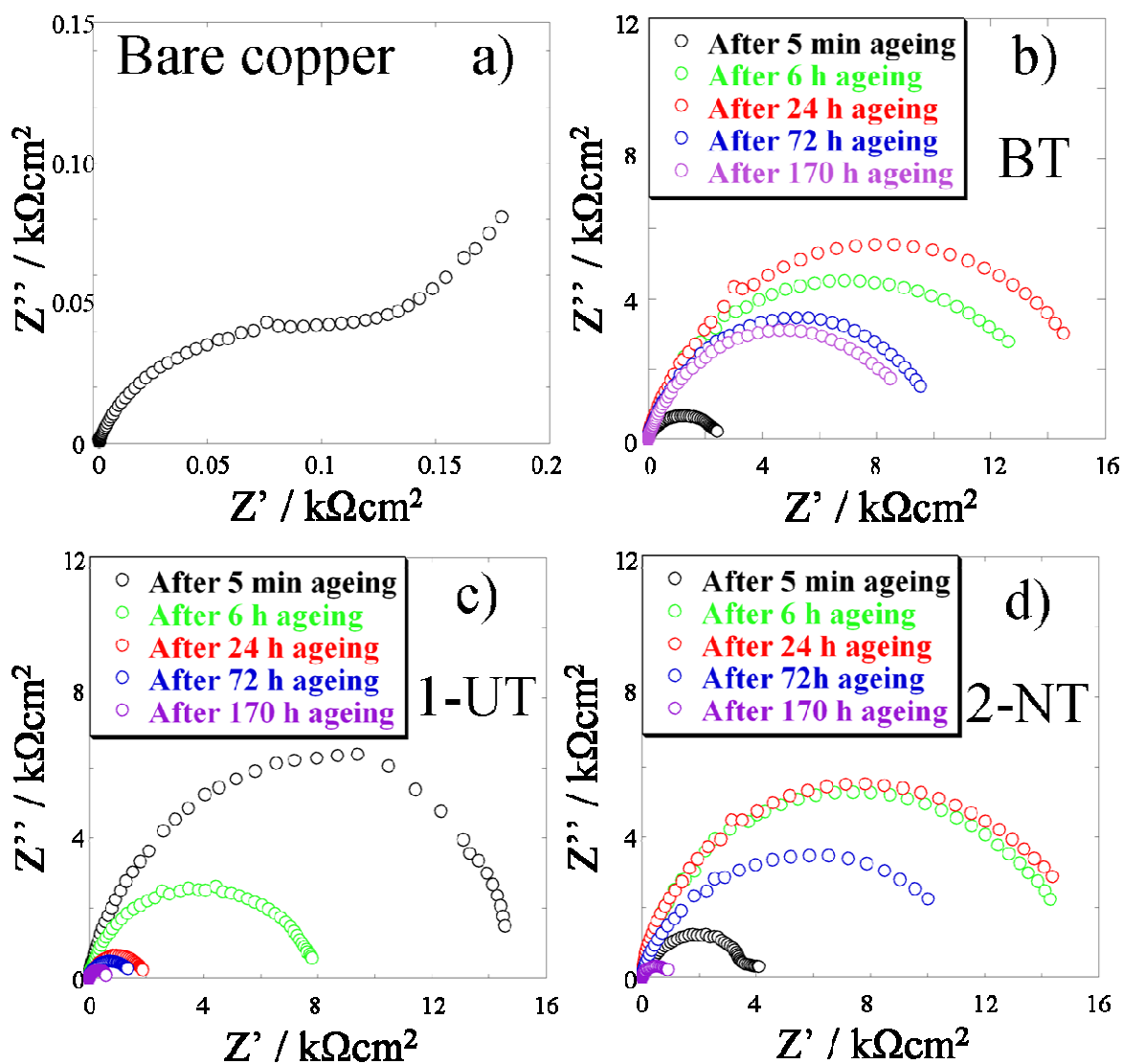
Best fit obtained by XP S2p spectra of different samples: a), b) and c) BT; d), e) and f) 2-NT; g), h) and i) 1.UT; at different ageing time: a), d) and g) as prepared samples; b), e) and h) after 24 h ageing in aerated H₂SO₄ 0.5 M; c), f) and i) after 170 h ageing in aerated H₂SO₄ 0.5 M. The fit component have been assigned to: — chemisorbed thiol (main peak maximum at 162.3 ± 0.1 eV); — disulphide and/or physisorbed material (main peak maximum at 163.4 ± 0.1 eV); — sulphonate (main peak maximum at 167.7 ± 0.2 eV); — Cu₂S (main peak maximum at 161.6 ± 0.1 eV)



CuLMM Auger spectra recorded on as prepared: — bare Cu; — BT; — 2-NT; — 1-UT. Peaks at 916.5 ± 0.1 eV (naked copper) and 916.1 ± 0.1 eV (coated copper) are ascribable to Cu(I) species, whereas the signals lying at 918.7 ± 0.1 eV are ascribable to bulk Cu atoms.



Cu₂p spectra recorded on as prepared: — BT; — 2-NT; — 1-UT. The symmetric shape of the peaks clearly indicate the absence of Cu(II) species. The position of the peak Cu₂p_{3/2} at 932.7 eV has been used as internal standard.



Nyquist plot relative to EIS measurements performed in aerated H_2SO_4 0.5 M on Cu electrodes coated by films of: a) BT; b) 1-UT and c) 2-NT after different ageing time: \circ 5 min; \circ 6 h; \circ 24 h; \circ 72 h and \circ 170 h.