Surface-enhanced Raman scattering and theoretical study of the bilichromes biliverdin and bilirubin

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 The surface-enhanced Raman scattering spectra of biliverdin and bilirubin were obtained and analyzed; a physical silver ligand interaction was inferred. The structural conformation of biliverdin is practically the same when passing from the dry to solution relative to that observed in Raman solid. However, the surface effect induces a different molecular orientation on the surface in dry and in solution. The conformational structure of bilirubin is modified when passing from dry to solution conditions; the orientation of the analyte on the surface is different in both media. The carboxylate groups interact with the surface more closely in bilirubin than in biliverdin. The unsaturated methine bridge in biliverdin confers an additional stability by delocalizing the ?-electronic cloud. Both sides of the molecule could be in the same plane. On contrary, bilirubin with a tetrahedric carbon (methylene bridge) confers the whole system a rather