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Interaction between metals and organic semiconductors studied by Raman spectroscopy

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Silver and indium were deposited onto molecular layers of two perylene derivatives, viz. 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and N,N′-dimethylperylene 3,4,9,10-dicarboximide (DiMe–PTCDI). The interaction between the metals and the organic semiconductors was probed *in situ* by Raman spectroscopy. The molecular structure is found to be preserved when Ag or In are deposited onto PTCDA and DiMe–PTCDI layers. For In, this is in contrast to previous suggestions of strong reactivity with PTCDA and covalent bond formation between In and O atoms in PTCDA. However, the molecules having direct contact with the metal are involved in a ground state dynamical charge transfer with different strength for Ag and In, resulting in a breakdown of vibrational selection rules. A significant enhancement of Raman internal vibrational modes is observed both for Ag and In deposition as a result of metal-induced surface enhanced Raman scattering (SERS). The enhancement factors observed for the internal modes reflect a rough morphology of the metal films which is influenced by the morphology of the underlying organic film. Moreover, conclusions regarding the indiffusion of the two metals can be drawn from the comparison of the breakdown of the selection rules for the internal modes and the spectral evolution of the external molecular modes.

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