Controlling the charge transfer between plasmonic PdAg nanoparticles and C_{60} molecules

Xingtong LI, Céline DABLEMONT, Aimeric OUVRARD

Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, 91405, Orsay, France
E-mail: aimeric.ouvrard@universite-paris-saclay.fr

Understanding the interaction of molecules with nanoparticles (NP) is crucial to control charge transfer in nanoscience for various applications in molecular electronics, sensing and energy harvesting. Using long-range ordered NP arrays is an efficient way to reduce the impact of size dispersion [1], access local information at nanoscale [2], drive molecular organization to form hybrid assemblies [3], assess precisely molecular adsorption sites, control optical, plasmonic and electronic properties [4-5]. We have investigated surface driven self-assemblies of ordered Pd-Ag core-shell plasmonic NP [5] in strong interaction with fullerene (C_{60}). We aim to understand the role of the NP surface plasmon resonance (SPR) on the photophysical properties of the molecule and follow in real-time the ultrafast photoinduced charge transfer dynamics. Their structural, photophysical, plasmonic and vibrational properties are monitored by scanning tunneling microscopy (STM), UV/Vis surface differential reflectance spectroscopy (SDRS) and vibrational sum frequency generation (SFG) spectroscopy techniques during and after the growth. Those investigations revealed a strong charge transfer between NP and C_{60} that hinders molecular optical response probably due to the overlapping between SPR and molecular orbitals.

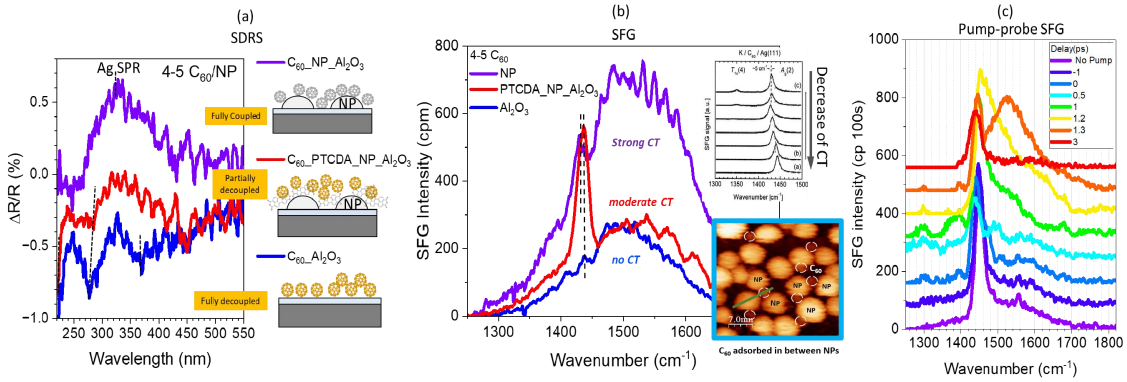

Fig. (a) SDRS and (b) SFG spectra of C_{60} deposit on different surfaces; (c) Pump-probe SFG: With 800 nm 100 mW pump, different delays of C_{60} on 1.5 ML Pd NP.

However, ultrafast charge transfer dynamics cannot be investigated if molecule is optically inactive. Thus, we have decoupled C_{60} from NPs and modify the charge transfer by intercalating perylenetetracarboxylic dianhydride (PTCDA) in between (Fig.a-b). Since Ag shell significantly affect NP array ordering and the molecular activity, we intend to study C_{60} on Pd NP (Fig.c) so that C_{60} form a molecular bridge between adjacent NP. Pump-probe SFG reveals a strong and rich vibrational dynamics through several relaxation steps. It opens the way to control charge and energy transfer processes more effectively.

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