mechanism of a surface plasmon resonance, this work of Chen and co-workers might provide new strategies for, and an understanding of, the transfer of photogenerated electrons.

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The Size Does Matter!

This report features the work of Shu-Jung Tang and his co-workers published in Nat. Commun. ***4****, 2925 (2013).*

Varying the electronic structures at organic-metal interfaces to engineer an organic-based electronic device has always been a main topic in organic-optoelectronic technology. Shu-Jung Tang and collaborators introduced the physical concept of quantum-size effects (QSE) to manipulate the alignment of energy levels (ELA) at interfaces between organic molecules and thin metal films.[1]

They created a novel model to explain the uniform thin metal films of Ag sandwiched between top organic films and a bottom substrate. They then systematically studied, with photoemission, the QSE on the organic-metal interface on varying three factors – the thickness of the Ag films, the types of substrates for the Ag films, and the types of adsorbates; the latter are mainly phthalocyanine-family molecules, such as copper phthalocyanine (CuPc), phthalocyanine (H_2Pc) and tetra-*t*-butyl H_2Pc (TTB-H_2Pc). These molecules are generally considered to be *p*-type electron donors. A nontrivial interfacial electronic structure is thus expected with respect to the charge transfer as a result of the interaction between the molecular-orbital state and the Ag quantum-well states (QWS) in the context of chemisorption. It was discovered also that QWS carried the influence of the Ge substrate under the Ag films to the top organic-metal interface, as manifested by the QSE.

Figures 1(a) and 1(b) show 2D photoemission

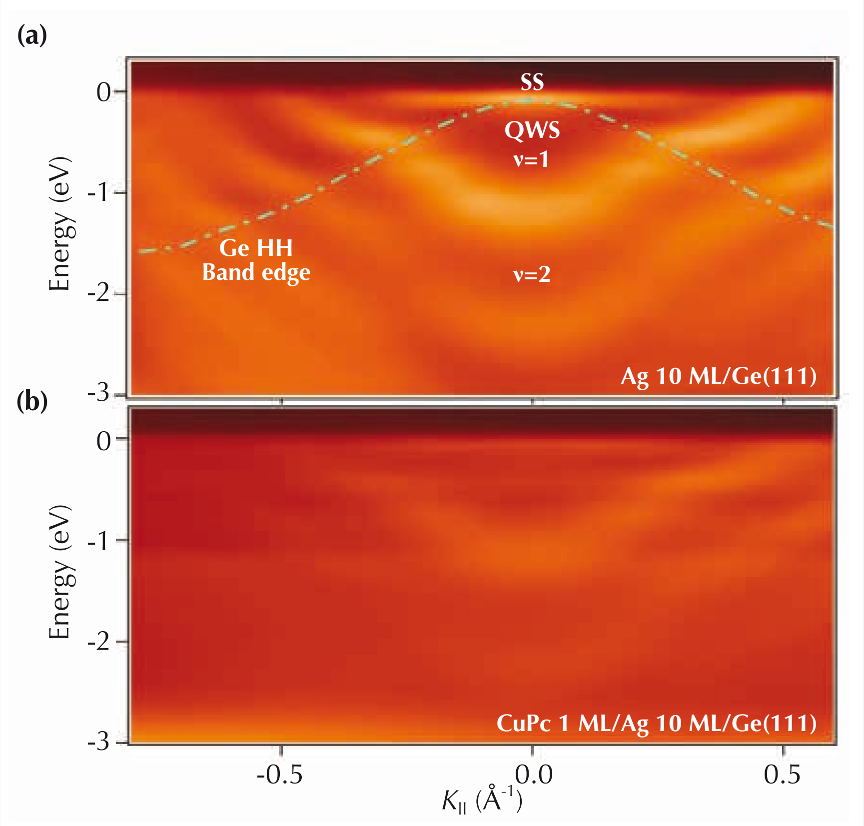

Fig. 1: Angle-resolved photoemission result along $\overline{\Gamma M}$ for (a) a 10-ML Ag thin film on Ge(111) and (b) for a 1-ML CuPc on a 10-ML Ag thin film on Ge(111).

spectra as a function of energy and wave vector, $k_{||}$, parallel to the interface for CuPc/ 10-ML Ag films/Ge(111) and CuPc/ 12-ML Ag films/Ge(111), respectively, in the symmetry direction from $\overline{\Gamma}$ to $\overline{M}$. According to preceding work on QWS electronic structures of uniform Ag films grown on Ge(111),[2] the bulk band edges of Ge, namely, heavy hole (HH), light hole and split-off, would have Anderson-type electron-electron interaction with the Ag QWS, causing a distortion or kink of QWS dispersion at the point of intersection with the Ge band edges, among which the HH band edge, depicted with the dashed-dotted curve in Fig. 1(a), shows the strongest effect. A flat band at energy position -0.43 eV corresponding to the top edge of the kink is visible at which the QWS band (v = 1) and the Ge HH band cross each other, as shown in Fig. 1(b) that represents an interfacial gap state. This gap state is implied to be related to the Ge substrate under the Ag films.

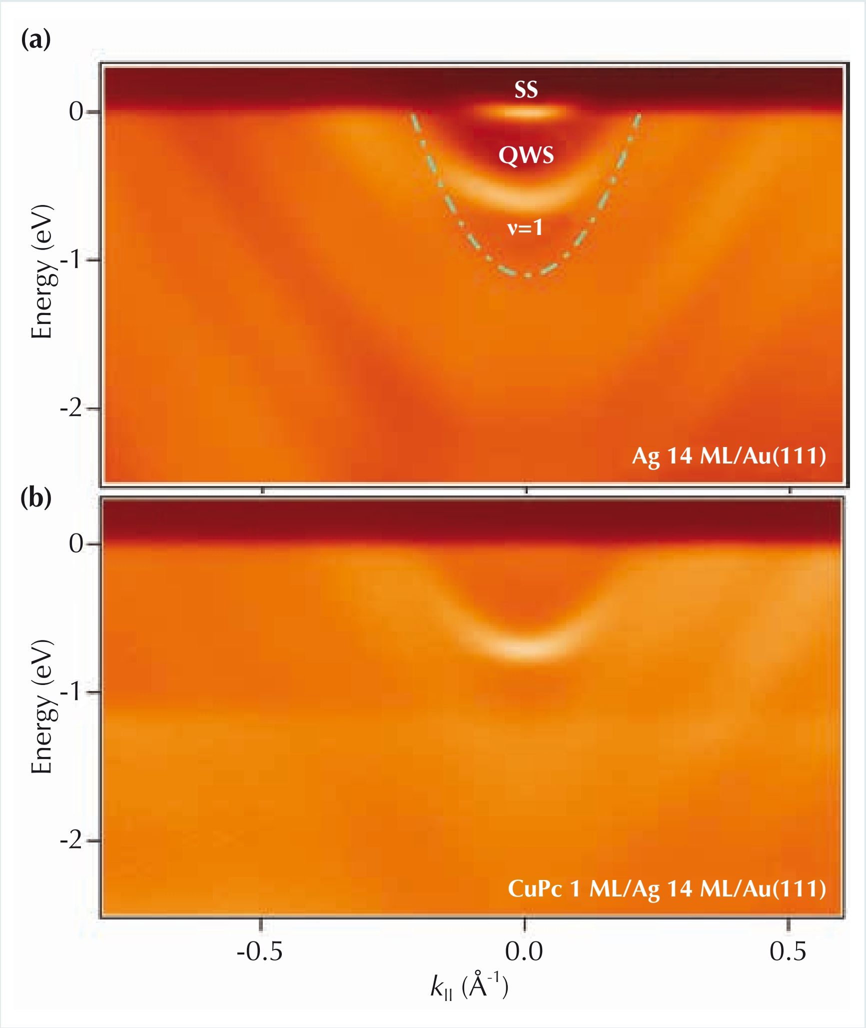

Fig. 2: Angle-resolved photoemission result along $\overline{\Gamma M}$ for (a) 10-ML Ag thin film on Au(111) and (b) for 1-ML CuPc on a 10-ML Ag thin film on Au(111).

Figures 2(a) and 2(b) show 2D photoemission spectra as a function of energy and wave vector, $k_{||}$, parallel to the interface for CuPc/ 10-ML Ag films/ Au(111) and CuPc/ 14-ML Ag films/Au(111), respectively, in the symmetry direction from $\overline{\Gamma}$ to $\overline{M}$. The dashed-dotted curve in Fig. 2(a) depicts the Au bulk band edge projected onto the (111) surface. The QWS observed in Fig. 2(a) exhibits a free-electron-like dispersion within the gap, entirely distinct from the case of Ag films on Ge(111) at which the Ag QWS dispersions are distorted because of an interaction with the Ge bulk band edges. The flat band of the gap state in the former case is consequently not observed in Fig. 2(b).

An intriguing and novel picture hence appears such that the bottom Ge substrate under the Ag thin films can affect the interfacial electronic structures between the top CuPc molecules and the Ag thin films through the interactions mediated with the QWS. The mechanism of formation of this gap state must first be verified. H_2Pc lacks a centered metal atom, and TTB-H_2Pc has four TTB substituents at the periphery of H_2Pc, so that both the entire H_2Pc molecule and the aromatic rings become lifted slightly above the Ag surface. In Fig. 3, for comparison, we show energy-distribution curves at normal emission for 1 ML of CuPc, H_2Pc, TTB-H_2Pc and tetratetracontane (TTC) on a 12-ML Ag film/Ge(111). The gap states have clearly an intensity large for CuPc and H_2Pc but small for TTB-H_2Pc. TTC, which has mainly

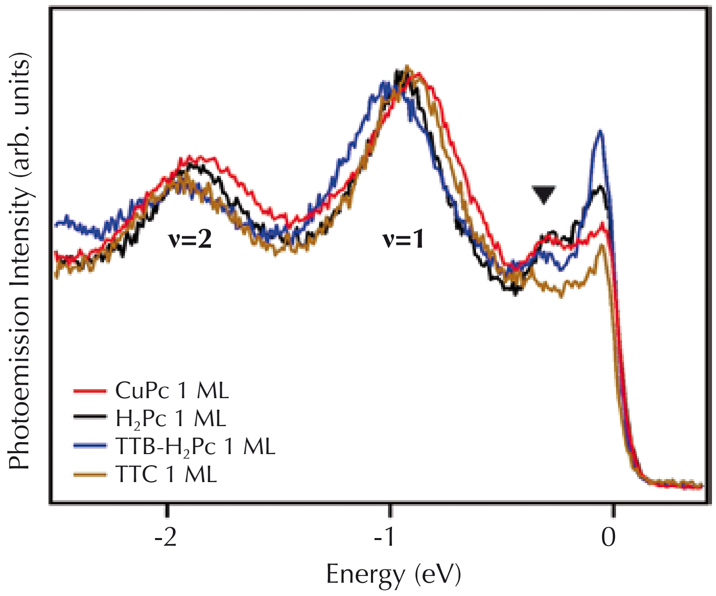

Fig. 3: Normal emission spectra for 1-ML CuPc, H_2Pc, TTB-H_2Pc, and TTC on 12-ML Ag thin films/Ge(111).

σ bonding characteristic of long-chain alkane molecules, exhibits a negligible intensity of the gap state. The crucial role of π-bond electrons in aromatic rings for the formation of the observed gap state is assured.

The dependence on Ag thickness of this gap state at CuPc coverage 1 ML was further examined; Fig. 4(a) shows that, with increasing thickness of Ag, the energy of the gap state shifted toward the Fermi level with increasing maximum intensity and decreasing linewidth. The energies of the gap state at Ag thicknesses 7 ML and 12 ML are -0.67 and -0.33 eV, respectively; the QSE of Ag films on the interfacial electronic structures of the CuPc-Ag interface is evident. The dependence of the gap state energy

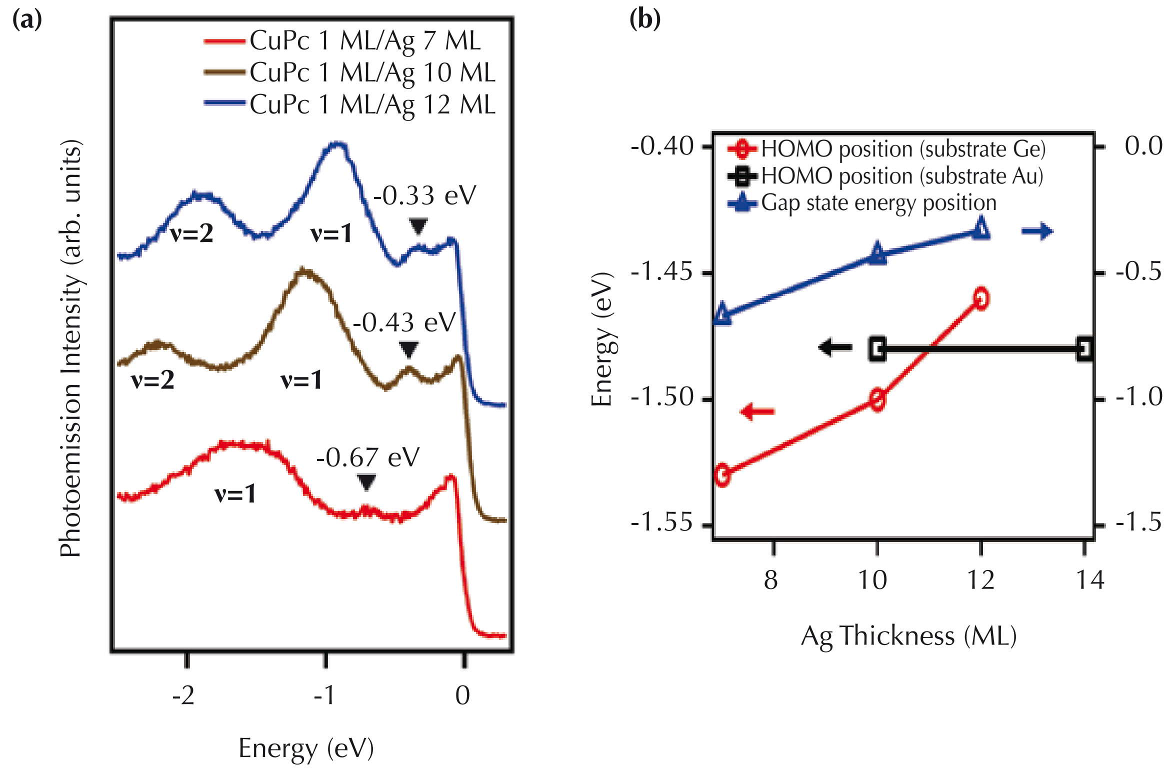

Fig. 4: (a) Normal emission spectra for 1-ML CuPc on 7-, 10-, and 12-ML Ag thin films. The black wedges indicate the energies of the gap states. (b) Dependence of the energies of the gap state and the second-layer HOMO on the thickness of Ag for thin Ag films on Ge(111) and Au(111).

on the thickness of the Ag film can be understood in that the gap state occurs at the intersection between the QWS band and the Ge band edge, which must vary as the entire QWS band shifts in energy with the thickness of Ag. Figure 4(b) displays the dependence of gap states and the second-layer, highest-occupied-molecular-orbital (HOMO) positions on the thickness of the Ag film for CuPc/Ag films/Ge(111) and CuPc/Ag films/Au(111). This dependence produces a possibility of tuning the Femi-level pinning position at the interface via altering the Ag thickness. As shown in Fig. 4(b), the measured second-layer HOMO position shifts to decreased energy with increasing Ag thickness, like the gap state, for Ag films on Ge(111), whereas that for Ag films on Au(111) remains constant. The reason is that the energy position of the gap state with respect to the Fermi level is directly related to the density of the gap state at the Fermi level, which is the key determining the ELA.

The research team performed the photoemission experiment at **BL08A1** in the TLS. For further information, please refer to the principal reference and related references.

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A New Way to Create Multifunctionality

*This report features the work of Heng-Jui Liu and his co-workers published in ACS Nano **6**, 6952 (2012) and Adv. Mater. **25**, 4753 (2013).*

Self-assembled vertical heteroepitaxial nanocomposites (VHN) become objects of fascination because of their large ratio of interface to volume, according to the scheme in Fig. 1. The couplings of spin, orbital, charge and lattice degrees of freedom at interfaces provide many possibilities to explore new condensed physics or multifunctionality. Of particular interest are self-assembled perovskite-spinel nanostructures, posing promising applications over a wide range. A famous case proposed by Zheng *et al*. has demonstrated an enhanced and controllable magnetoelectric effect, revealed in the ferroelectric $BaTiO_3$-ferrimagnetic $CoFe_2O_4$ VHN.[1] The multifunctionality of this magnetoelectric effect indicates that the magnetic properties can be altered with an electric field, and *vice versa*. The origin of such multifunctionality in nanostructures of this kind has been confirmed to correlate strongly with the intimate structural coupling between these two constituents. The research team from National Chiao Tung University in this report has demonstrated multifunctionality of a new kind, a photomagnetic effect and spectacularly large magnetoresistance, on fabricating VHN composed of $SrRuO_3$ (SRO) and $CoFe_2O_4$ (CFO). High-resolution

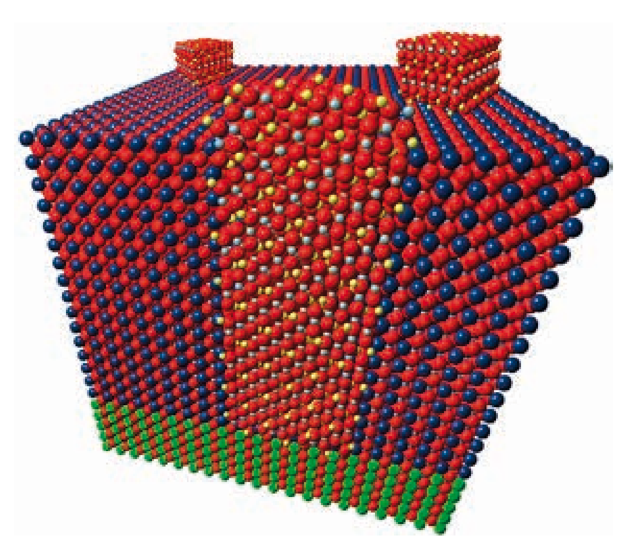

Fig. 1: Typical scheme of self-assembled vertical heteroepitaxial nanocomposites.