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第一原理分子動力学計算による有機/金属界面のシミュレーション

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STATE-Senri
(Simulation Tool for Atom TEchnology)

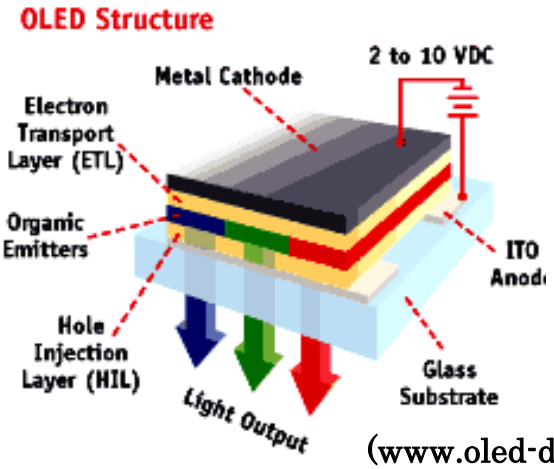
- First-principles electronic structure calculation with the Density Functional Theory (DFT)
  LDA, GGA, LDA+U,...
- Ultrasoft pseudopotential
- Plane wave basis set
- Iterative diagonalization
  Davidson method、RMM-DIIS method
- Broyden charge density mixing

→ Applied to wide range of materials
Powerful for metallic systems, surfaces and interfaces

- Tutorial course in "Computational Materials Design (CMD) Workshop"
  http://www.dyn.ap.eng.osaka-u.ac.jp/CMD13 (Sep 6-10, 2008)
- Twice a year (next is CMD14, Mar 2-6, 2009@CMC, Toyonaka Campus)
- Open to both theoretical and experimental researchers
- Open to Asian researchers and students

Organic-Metal Interfaces

- Important in applications of organic based devices such as organic light-emitting diodes (OLED), organic photovoltaic cells, organic field effect transistors.
- The performance and efficiency of those organic-based devices critically depend on the electronic structures at organic/metal interfaces.



(www.oled-display.net)

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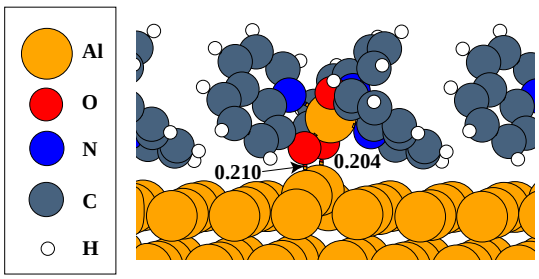
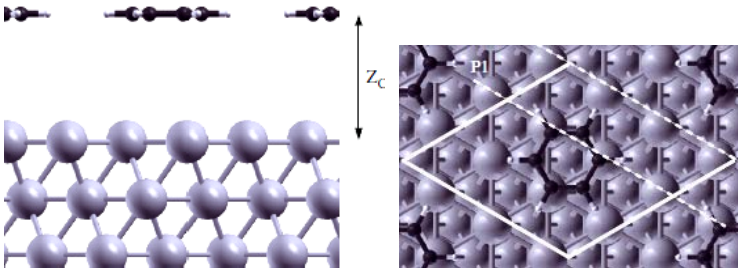
Organic-Metal Interfaces

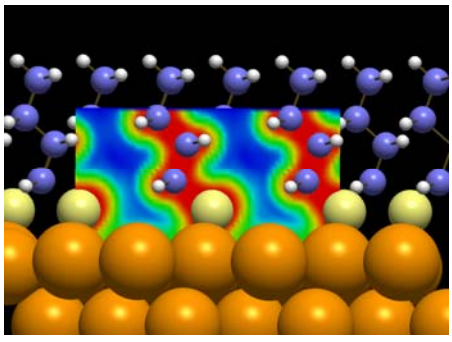


Alq_3 on metal surfaces

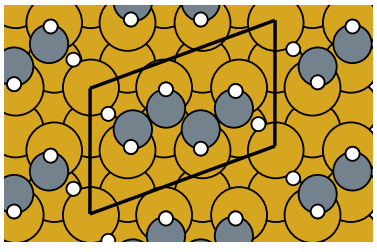


(side view) (top view)

C_6H_6 on metal surfaces



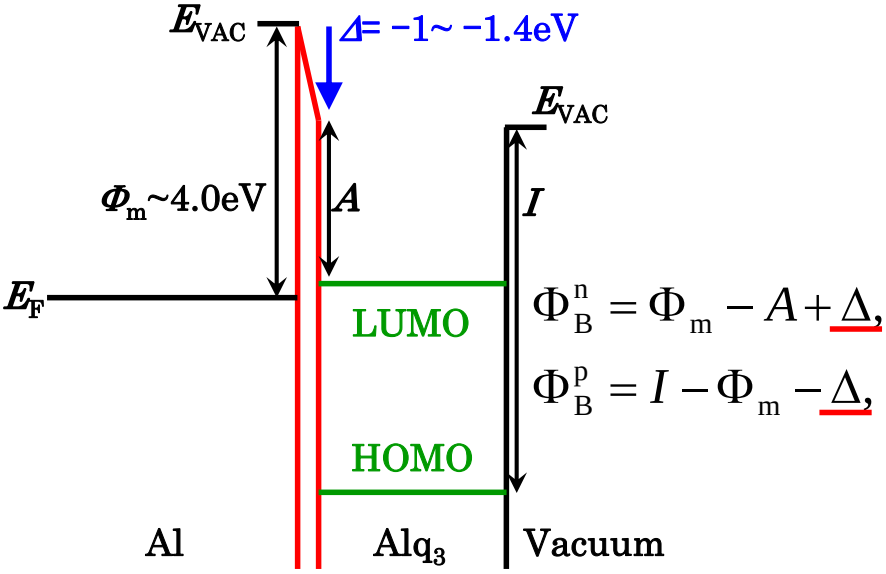
Self-Assembled Monolayers

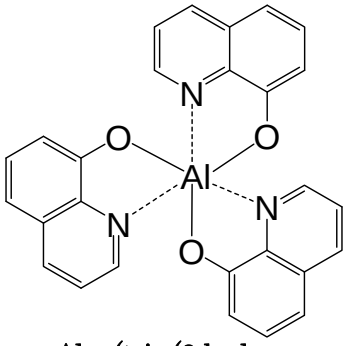


n-alkane on metal

Interfacial Dipole Layer

- Interfacial dipole layer and subsequent vacuum level shift Δ significantly alters the alignment between the organic levels (HOMO and LUMO) and the metal Fermi level E_F.
- In order to control and design the organic devices, it is necessary to understand the origin of interface dipole.

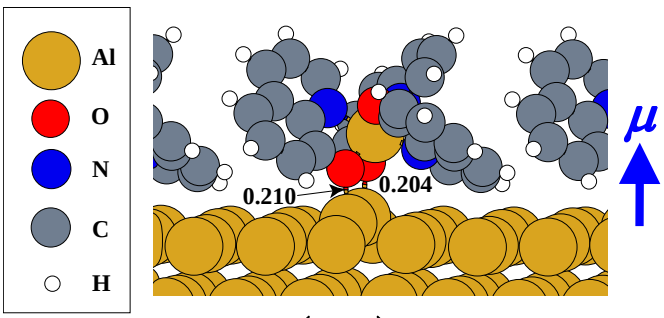




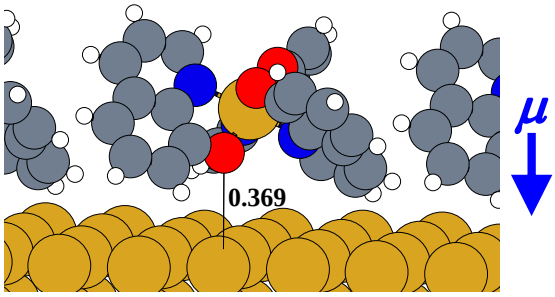
Alq_3 (tris-(8-hydroxy quinoline) aluminum) Most widely used electron-transport material in OLEDs.

H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater.* 11, 605 (1999).

Alq_3 on Al



Alq_3(*mer*)/up, stable



Alq_3(*mer*)/down, less stable

vacuum level shift Δ/eV

substrate	*mer*/up	*mer*/down
Al(111)	−1.2	+0.0
Al(332)	−1.0	+0.1
Al adatom /Al(111)	−1.4	−0.7

Vacuum level shift Δ is dominated by the molecular permanent dipole μ of Alq_3, and thus alters organic levels relative to the metal Fermi level E_F (see next page).

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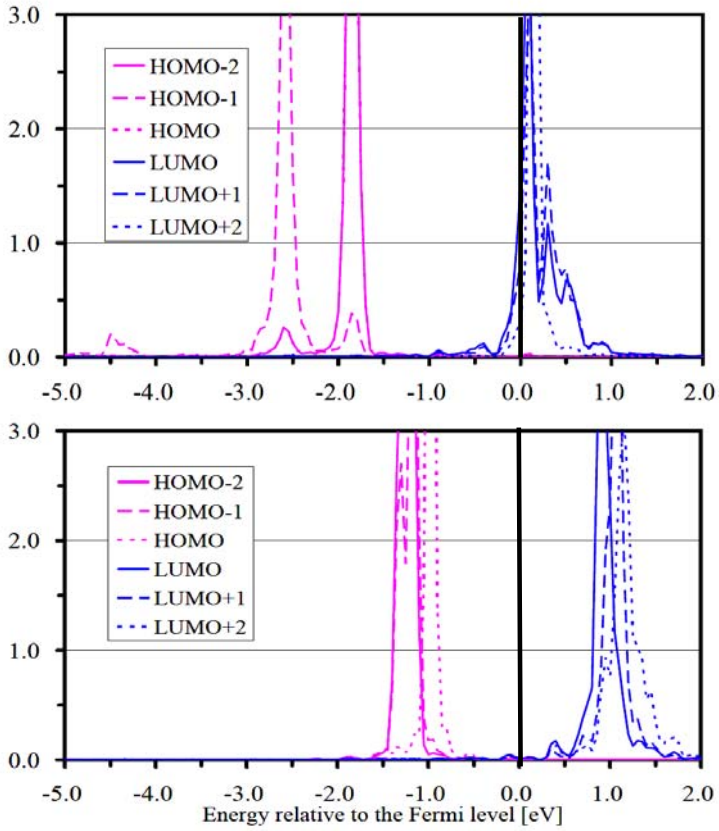
Projected Density of States of Alq_3/Al



Alq_3(mer/up)/Al(111)

Alq_3(mer/down)/Al(111)

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C_6H_6 on Al(111)

- C_6H_6-adsorbed metal is a typical physisorption system, and is regarded as a prototype of interfaces related to organic field-effect transistors.
- Even though the molecule-substrate interaction is weak, non-negligible work function shift has been experimentally reported.
- In addition to the first-principles calculations, we investigated the applicability of the recently proposed simple model for dipole layer (Induced Density of Interface States (IDIS) model).

IDIS model derives the vacuum level (VL) shift Δ as

$$\Delta_{IDIS} = Z_C \frac{\Delta N^A}{S\varepsilon_i}$$

Z_C: molecule-substrate distance, ΔN^A: amount of electronic charge transferred from substrate to adsorbate, S: area of molecule-substrate contact, ε_i: dielectric constant

In IDIS model, the VL shift Δ is assumed to be dominated by the amount of electronic charge transferred through the interface.

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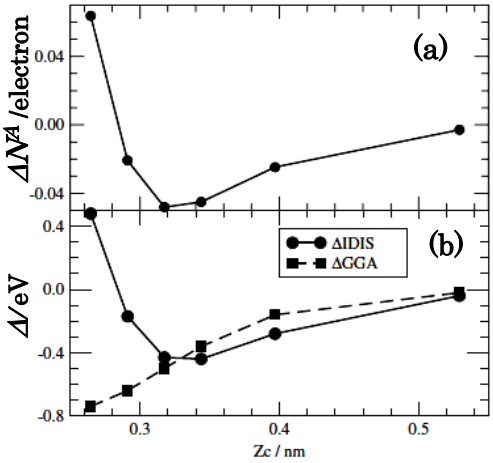
C_6H_6 on Al(111)

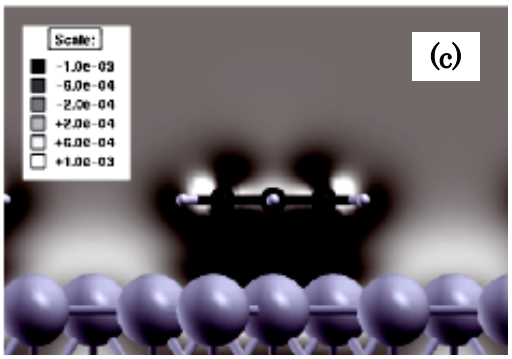
GGA vs IDIS



(a): number of electrons transferred from substrate to molecule

(b): VL shift Δ estimated with the first-principles calculation (GGA) and the model (IDIS)

Z_C = 0.26 nm



(c): Adsorption-induced electronic charge difference distribution with Z_C=0.26 nm on the cut plane normal to the substrate.

As the electronic charge donation from substrate to molecule begins (Z_C~0.32 nm in Figs. (a) and (b)), the deviation between ΔGGA and ΔIDIS becomes larger.

The result indicates that the adsorption-induced charge redistribution at the interface is more complicated than expected based on the simple charge transfer through the interface (also see Fig. (c)).

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