

The Frontier Electronic Structure of Lutetium Bisphthalocyanine Thin Films

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【Introduction】

Lutetium bisphthalocyanine (LuPc₂) complex exhibits several interesting characteristics: It is a neutral radical with the unpaired electron spin residing on the organic macrocycles. It is easily oxidized and reduced, with five highly colored redox states identified over an applied electrochemical potential of ± 1.5 V.¹ Finally, the neutral, undoped material is semiconducting, with room temperature conductivities about 10^{-5} S Ω^{-1} cm⁻¹, comparable with amorphous silicon.² The structure is shown in Fig 1.

As the conductivity and visible absorption changes dramatically with the redox state, LuPc₂ thin films make efficient chemical sensors.³ In the present work we look at the effect of the unpaired, highly delocalized electron on the frontier energy levels in order to better understand the charge transport mechanism in radical organic systems. Inverse and ultraviolet photoemission spectroscopy is combined to determine the electrical transport gap, a quantity of fundamental importance pertaining to the conductivity. Density functional theory is employed to help further understand the organization and composition of the frontier π -states responsible for the charge transport.

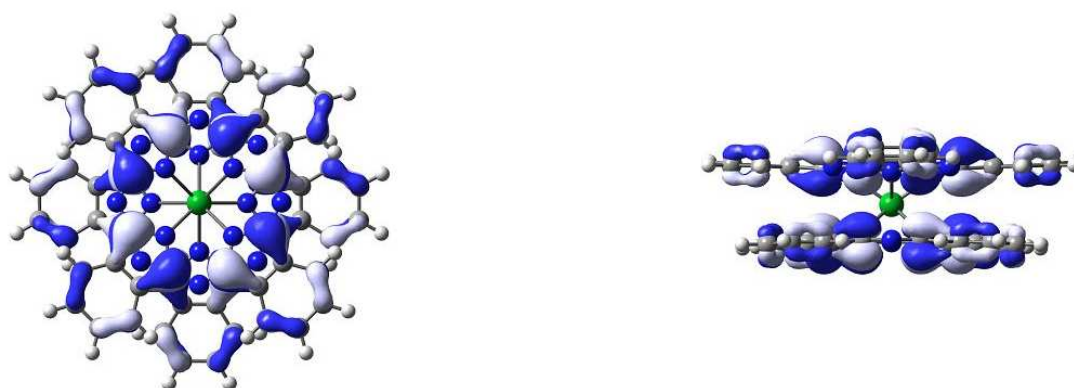


Fig. 1. Lithium bisphthalocyanine, from the crystal structure of de Cian. The spatial distribution of the highly delocalized single occupied molecular orbital (SOMO) is also shown, calculated by DFT methods. (UB3LYP/cc-pVDZ)

【Experimental】

LuPc₂ was provided by M. Bouvet and used as received. 25 nm films on were prepared on polycrystalline gold by thermal evaporation under ultrahigh vacuum (base pressure 1×10^{-6} Pa). Inverse photoemission (IPES) measurements were made with a custom apparatus with a variable energy electron gun and bandpass UV detector. The instrument resolution is 0.6 eV. Ultraviolet photoemission measurements were made with a commercial Specs Phoibos 150 electron spectrometer and non-monochromatized He(I) UV source. The resolution is 150 meV. All measurements were made in situ and at room temperature.

In the DFT calculations the unrestricted B3LYP density functional method was used with the cc-pVDZ basis set while the Stuttgart/Dresden (SDD form) effective core potentials were invoked for the Lu center. Ionization potentials and electron affinities were estimated from the total system energies of the fully geometry optimized molecule (UB3LYP/6-31G(d) SDD). Energy level diagrams were generated based on the molecular geometry of the published X-ray data by de Cian.⁴

【Results and Discussion】

The combined UPS-IPES data is shown in Fig. 2. A rigid energy shift of the calculated states was used to align the results with the experimental data, but no scaling was employed.

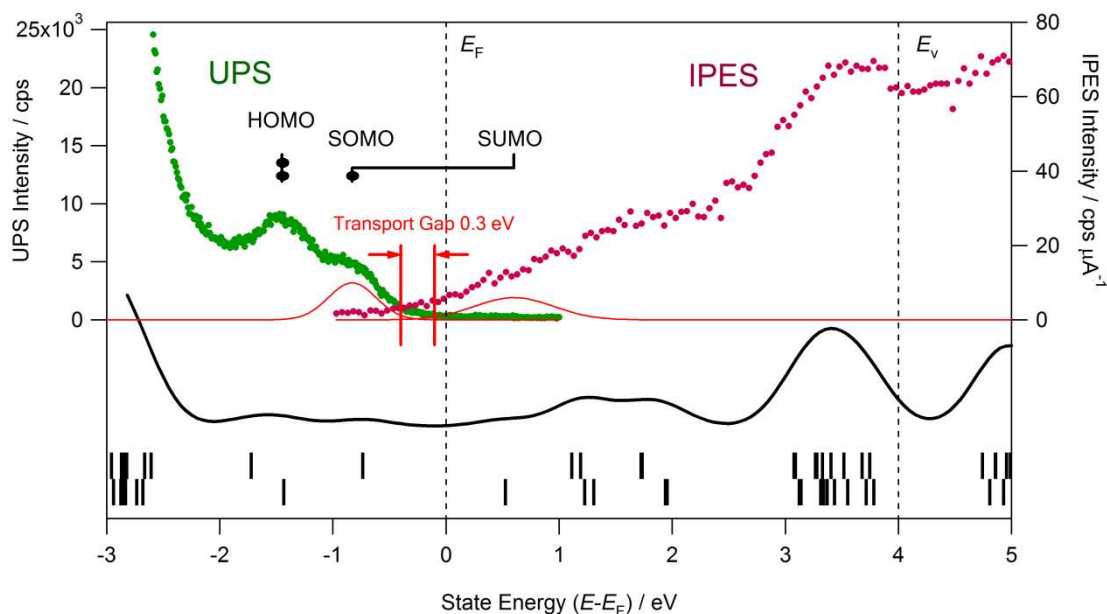


Fig. 2. IPES and UPS spectra for a 25 nm LuPc₂ film. The DFT results are shown at the bottom (single electron alpha and beta orbitals) with the simulated spectra based on a Gaussian broadening of 0.5 eV. The transport gap is estimated at 0.3 ± 0.2 eV.

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