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Mesoscopic Donor-Acceptor Multilayer by Ultra-High-Vacuum Deposition of Zn-Tetraphenyl-Porphyrin and C70

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Zn-porphyrin/C$_{70}$ complexes for solar cells: Molecular orientations, electronic properties and charge transfer time

Mesoscopic Donor-Acceptor Multilayer by Ultra-High-Vacuum deposition of Zn-Tetraphenyl-Porphyrin and C$_{70}$

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Short introduction on organic photovoltaic cells then…

1) Growth and orientation of Zn-TPP/C$_{70}$ films
   * Zn-TPP thick-layers on Si(111)
   * Double layer Zn-TPP/C$_{70}$/Si(111)
   * Multilayer co-deposited Zn-TPP/C$_{70}$

2) Electronic structure via NEXAFS and photoemission
   * Same systems as above
   * Evidence for interaction between C$_{70}$ and Zn-TPP

3) Charge-transfer time scale with resonant photoemission
   * Same systems as above
   * In mixed systems the excited electrons are delocalized more efficiently
Photovoltaic principles

- Photovoltaic energy conversion needs:
  - photon absorption across an energy gap
  - charge separation
  - Charge (electrons & holes) transport

\[
\text{Incident solar energy} = \text{Electricity} + \text{Heat}
\]
Reasons for the use of organics in solar cell applications

1) Easy processing, e.g. spin coating, sublimation.
2) Relatively small amount of organic molecules per device (100 nm of film thickness for 100% light absorption).
3) Large scale production easier than for inorganic materials.
4) Chemical tuning of band gap, charge transport and electronic properties, as well as structural properties and solubility.
5) Self assembled monolayers, layer by layer deposited films, Langmuir Blodgett films can allow the control of molecular order.
6) Can sensitize semiconductor for efficient electron-hole extraction.
7) Vast variety of materials (fullerenes, polymers, oligomers, dyes, pigments, liquid crystals, …) and structural combinations.
8) Every kind of transparent & conducting substrate (even plastic).
Photovoltaic inspired to natural processes

Bio-mimetic systems
**GOOD:**
Absorption spectrum of porphyrins covers almost the whole visible range (Donors)
Hole-transport (p-type)

**BAD:**
No triplet state $T_1$ reachable (long lived excitons) in a short time: $S_1$-$S_0$ luminescence decay dominates

Absorption Spectrum

**SOLUTION: DONOR-ACCEPTOR complexes**

Fulleranes (A) covalently linked to porphyrins (D) shows the formation of relatively long lived charge separated states: promising as photoactive materials for energy conversion.

\[ S_0 \to A^* \to S_0 \]

\[ k_{et} = \text{charge transfer time} \sim 100-500 \text{ fs} \]

On the other hand….

Marcus equation for charge transfer rate constant:
\[ k_{et} = \sqrt{\frac{\pi}{\hbar^2 \lambda k_B T}} |V|^2 \exp\left[-\left(\Delta G^\circ + \lambda\right)^2 / 4\lambda k_B T\right] \]

- Depends on D-A orbital overlap \(|V|^2 \propto e^{-d}\): minimize the distance between \(\pi\) orbitals

Close proximity between \(C_{60}\) and \(C_{70}\) and several kinds of porphyrins observed in cocrystals and in solution: the luminescence decay of porphyrin is strongly quenched.

GOOD COMPROMISE: The two molecules are close, good conjunction, but the molecular orbitals are well localized (HOMO on Zn-porphyrin macrocycle and LUMO on fullerene), so the charge transfer should be facilitated.
Basic structure is the porphine macrocycle, which consists of a 16-atoms ring containing four nitrogen atoms, obtained by linking four tetrapyrrolic subunits with four methine bridges. The macrocycle is an aromatic system containing 22 \( \pi \)-electrons, but only 18 of them are delocalized according to the Hückel's rule of aromaticity (4n+2 delocalized \( \pi \)-electrons, where n=4). The size of the macrocycle is perfect to bind almost all metal ions (e.g. Fe, Zn, Cu, Ni, and Co) which can be inserted in the center forming metal-porphyrins.

C\(_{70}\)-fullerene
The big brother of the most famous C\(_{60}\). Fullerenes are highly symmetric carbon cages with very good tendency of accepting electrons. Among the few organic materials that may behave as n-type conductors. Small reorganization energy \( \lambda \) and luminescence yield (optically forbidden lowest HOMO-LUMO transition)

Porphyrrins
from the Greek *porphura* = "purple"
Basic structure is the porphine macrocycle, which consists of a 16-atoms ring containing four nitrogen atoms, obtained by linking four tetrapyrrolic subunits with four methine bridges. The macrocycle is an aromatic system containing 22 \( \pi \)-electrons, but only 18 of them are delocalized according to the Hückel's rule of aromaticity (4n+2 delocalized \( \pi \)-electrons, where n=4). The size of the macrocycle is perfect to bind almost all metal ions (e.g. Fe, Zn, Cu, Ni, and Co) which can be inserted in the center forming metal-porphyrins.
OUR GOAL

Deposition of $C_{70}$ and Zn-TPP on substrates by UHV sublimation:

1) Formation of ordered compact films
2) Thickness control layer-by-layer
3) Sandwich structures with different molecular orientations
4) Self assembled mixed $C_{70}$/Zn-TPP thick films

Electronic structure, bonding formation and molecular orientations investigated using photoemission and x-ray absorption

D-A charge transfer time investigated by resonant photoemission

**Note:** order and molecular packing increase exciton and charges mobility by orders of magnitude (example: typical organic mobility $10^{-4} - 10^{-8}$ cm$^2$/V·s, while in $C_{60}$ single crystal $\sim$ 2 cm$^2$/V·s); Relative molecular orientations influence the charge transfer time and transport.
EXPERIMENTAL

Measurements performed at

SuperESCA: XPS, NEXAFS, UPS, RESPES
ALOISA: polariz. dependent NEXAFS, XPS

RESPES probes the charge transfer time of an excited state on the time scale of the core hole lifetime (core hole clock): pump & probe experiment in the energy domain ($\Delta E \cdot \Delta t \geq \hbar/2\pi$)

W. Wurth & D. Menzel, Chem. Phys. 251, 141 (2000);
ZnTPP multilayer

![Graphs and diagrams showing binding and photon energy distributions for Zn-octaethyl-porphyrin and C$_6$H$_6$]

- **N 1s**
  - $h\nu = 550$ eV
  - FWHM = 0.7 eV

- **C 1s**
  - $\pi^*$
  - $\sigma^*$
  - Zn-octaethyl-porphyrin

- **Zn 3d**
  - Valence states
  - Zn-TPP Multilayer 70° emission

- **C 2s**
  - $\sigma + \pi$ states

- **LUMO**
  - Intensity (arb. units)
  - Photon energy (eV)
  - $\phi = 85^\circ \pm 5^\circ$
  - LUMO Area %
  - Corrected $\theta$

- **Photon Energy (eV)**
  - 280 to 310

- **Binding Energy (eV)**
  - 394 to 406
Dihedral angle: angle $\theta$ between the phenyl plane and the macrocycle

The angle is big due to the steric interactions between the hydrogen atoms:
- Minimal $\pi$-overlap between macrocycle and phenyl-groups
- Small perturbation of the porphyrin electronic structure
The contribution from the different carbon atoms can be highlighted.
LUMO+2(3) feature is reduced. This indicates that when the electron is excited into the LUMO+2(3) states it remains localized on the molecule for a time bigger but comparable (competing) to the core-hole lifetime (~ 5 fs for the C 1s) and therefore this excited states contribute only partly to the core-hole decay as spectator state. On the contrary, in the LUMO and LUMO+1 states the electron remains localized for a time much bigger than the core-hole lifetime.
1 ML of ZnTPP/1ML C$_{70}$/Si(111): Double Layer Structure
Close packed $C_{70}$ ML are adsorbed on Si with the long axis perpendicular to the surface. ZnTpp single layer formed on top by depositing molecules with the substrate @200 °C.
The N equivalence is broken by the interaction with C\textsubscript{70}.

The N 1s XPS spectrum of the ZnTpp/C\textsubscript{70} double layer can be reproduced by the superposition of two N 1s spectra of the ZnTpp multilayer (1:1).
Figure S4. Molecular electrostatic potentials of 5,10,15,20-tetraphenylporphyrinato-zinc, mapped from -0.02 to +0.10 e/4πε₀a₀, onto 0.02 e Å⁻³ isosurface of the electron density at the PBE/6-31G(d,p) level.

Figure S2. Molecular electrostatic potentials of C₇₀ from difference perspective projections, mapped from -0.0004 to +0.007 e/4πε₀a₀, onto 0.001 e Å⁻³ isosurface of the electron density at the PBE/6-31G(d,p) level.
Counts

Photon Energy (eV)

1ML-ZnTPP/1ML-C\textsubscript{70}/Si
Multilayer ZnTPP
1ML-C\textsubscript{70}/Si(111)

Normal Incidence
Full core hole calculations.
Contribution of the 5 different atoms to the C$_{70}$ NEXAFS spectrum
Already from a first sight in comparison with the ZnTPP multilayer there is a general reduction of the intensity enhancement at resonance (a factor of 1.5).
This global reduction of the resonant intensity indicates that in the ZnTPP/C$_{70}$ double layer system the electron excited on a ZnTPP molecule is transferred away on a time scale of $\sim$ 7 fs.

The transition to the LUMO+2(3) is completely quenched: the charge transfer from these states is much faster than the core-hole lifetime (5 fs).
Co-deposition of $C_{70}$ and ZnTPP
Small charge transfer from porphyrin to C$_{70}$ $\sim 0.013$ el/molecule

The ground state electronic spectra are a simple summation of ZnTPP and C$_{70}$ properties
Orientation of ZnTPP and $C_{70}$

$\gamma = 47.8$

N 1s NEXAFS
Co-deposited system

$\theta = 80^\circ$

$\theta = 50^\circ$

$\theta = 0^\circ$

$\pi_1^*$

$\pi_2^*$

$\pi_3^*$

Photon Energy (eV)
Substantial disorder, but tendency of the $\pi^*$ of porphyrins to stay at $\sim 47^\circ$.

It turns out that $C_{70}$ long axis is almost parallel to the ZnTPP macrocycle.

Maximization of the electrostatic interactions
Similar molecular arrangements observed in CuTpp-C$_{70}$, ZnTpp-C$_{70}$ and H$_2$TPP-C$_{70}$ cocrystals precipitated from solutions

P.D.W. Boyd et al, JACS 121, 10487 (1999)

and predicted for ZnTpp-C$_{70}$

HOMO and HOMO-1 on the porphyrin

LUMO and LUMO-1 on the C$_{70}$
Excited state interactions in the contiguous chromophores

There are many resonances which, more or less, follow the NEXAFS peaks, but …
Excited state interactions are present in the contiguous chromophores and this system acts as a donor/acceptor junction where the excited charges at the porphyrin macrocycle can fast delocalize to the fullerene. The time scale of the ultra-fast charge transfer is smaller than 1-2 fs.
CONCLUSIONS

• The attraction of C$_{70}$ and ZnTPP allows the engineering of supramolecular solids on a mesoscopic scale.

• We were able to grow in ultra-high vacuum molecular complexes of ZnTPP and C$_{70}$ deposited on a semiconductor surface, where the two molecules assume a preferential reciprocal orientation.

• The double-layer system can fast delocalize (5-7 fs) the excited charge and could act as a dye in Gratzel cell.

B. O’Regan, M. Grätzel Nature 1991, 353, 737
• The ground state electronic spectra of our co-deposited material reflect a simple summation of components, so the ground state perturbation is weak.

• However, the excited state interactions are present in the contiguous chromophores and this system acts as a donor/acceptor junction where the excited charges at the porphyrin macrocycle can fast delocalize to the fullerene. The time scale of the ultra-fast charge transfer is smaller than 1-2 fs.