# ORGANIC SEMICONDUCTOR 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA)

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**Abstract**

In the last decade organic molecular semiconductor has been the subject of many studies. The structural,electrical , optical and the application of such an organic semiconductor 3,4,9,10-perylenetetracarboxylic dianhydride has been presented in this paper.

# 1 Introduction

Made from natures building blocks of carbon, oxygen and hydrogen, organic semiconductors are a new class of materials for the opt electronics. Organic semiconductors provide significant advantages over their better known inorganic counterparts: namely the almost unlimited chemical synthesis and variability of organic molecules, as well as potentially lower fabrication costs of all-optical and opt electronic devices. One of the functional organic material 3,4,9,10 pereylenetetracarboxylic dianhydride (PTCDA) is potentially applicable to such optical electronic devices. The present paper gives the structure and some properties and application of PTCDA.

# 2 Structure

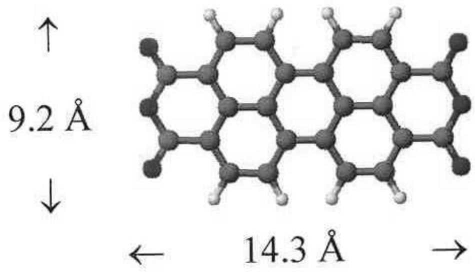


Figure 1: molecular structure of PTCDA ( Ref 4)

The aromatic compound 3,4,9,10-pereylenetetracarboxylic dianhydride (PTCDA) is a flat rectangular molecule, fig (1). The planar PTCDA molecule with symmetry point group $D_{2h}$ crystallizes in the monoclinic Centro-symmetric space group $\frac{P2_1}{c}(C^5_{2h})$ with two nearly co-planar molecules in the unit cell. Molecules of consecutive planes arrange in tilted stacks, with a smaller inter-planar distance than in non-polar materials like graphite or perylene due to the electrostatic interactions of the partly charged carboxyl and anhydride groups. The intermolecular distance of the ordered molecular stacks is nearly 0.321nm.

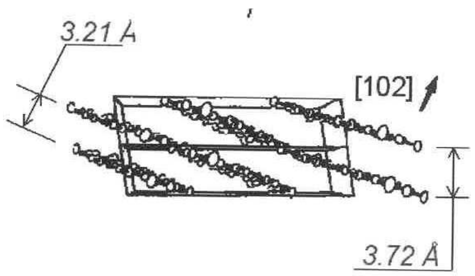


Figure 2: monoclinic structure of PTCDA on Si(ref 4)

It is known from transmission electron microscopy that PTCDA can grow into two existing polymorphs called $\alpha$-PTCDA and $\beta$-PTCDA . Both modifications have a monoclinic structure with slightly different lattice constants a, b, c and lattice angles $\beta$.Fig(3) (ref.1)

**Table 2. Unit Cell Parameters of PTCDA**

| parameter | α-PTCDA[a] | β-PTCDA[b] |
|---|---|---|
| space group | $P2_1/c(C_{2h}^5)$ | $P2_1/c(C_{2h}^5)$ |
| $a$ (Å) | 3.72 | 3.78 |
| $b$ (Å) | 11.96 | 19.30 |
| $c$ (Å) | 17.34 | 10.77 |
| $\beta$ | 98.8° | 83.6° |

Figure 3: Unit cell parameters of PTCDA, Ref(1)

# 3 Energy Levels

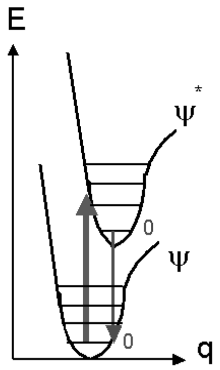


Figure 4: *Energy levels of PTCDA molecule* .

In organic solids the carbon atom forms a tetrahedral $SP^3$ hybridized single bond configurations but in double bond it has the configurations of $SP^2 - P_z$ and in triple bond it has $SP - P_z - P_y$ configurations. The intra-molecular interactions between the atoms lead to a splitting of the initially degenerate $2P_z$ energy levels into a bonding and an anti-bonding molecular $\pi$ orbital. The resulting bonding orbital takes the electrons while the anti-bonding orbital remains empty. On a downward positive electron binding energy scale there is a highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO) with an energy gap in between.For larger conjugated carbon-carbon double bonds system further splitting occurs and also intermolecular interactions in the solid lead to further splitting of these molecular levels under formation of narrow bands and the energy gap decreases as well. The energy gap in PTCDA is found to be 2.2eV.
The fig(4) is the energy diagram againast the generalised space co-ordinate q. The curve represents the electronic vibrational and rotational(libronic) energy of PTCDA molecule.It also shows the transitions for absorption and emission of light .

# 4 Properties

Due to the crystal geometry PTCDA shows distinct anisotropy behaviors in electrical and optical properties.

### 4.1 Conductivity

Carrier transport in aromatic compounds is based on the free electron gas of the $\pi$-electron system in the carbon net. In the molecular plane carrier transport is impeded by the distance between adjacent molecules and by the polar bonding of the oxygen and hydrogen atoms. In contrast carrier transport is very efficient perpendicular to the surface along the molecular stacks due to the low intermolecular distance. The $\pi$-electron systems of the carbon double bonds, bondings are in direct contact and carriers can easily be transmitted between adjacent molecules. Experimentally the conductivity $\frac{\sigma_\perp}{\sigma_\parallel}= 10^2$or $10^3$ was observed. Pioneering work by SR Forrest and his co-workers on contact barrier diodes and the light emitting diodes have clearly shown that PTCDA transports hole normal to the molecular planes. So PTCDA is predominantly a hole conducting material.

### 4.2 Optical

Because of the inherent asymmetries in the molecular crystal structure one would expect that the dielectric properties of ordered films would also be anisotropy along different crystal directions. The index of refraction of PTCDA thin films at a wavelength of $\lambda$=1.064$\mu$m in the direction perpendicular to the molecular plane is $\eta_\perp$=1.36 $\pm$ 0.01 where as parallel to the plane $\eta_\parallel$=2.017$\pm$ 0.0005 resulting in an index difference of $\Delta\eta$ = 0.66 . Furthermore the low frequency dielectric constant of the film is $\epsilon_\perp$=1.9$\pm$ 0.1 and $\epsilon_\parallel$= 4.5$\pm$0.2. (Ref. 2)

## 5 Application

### 5.1 Waveguides

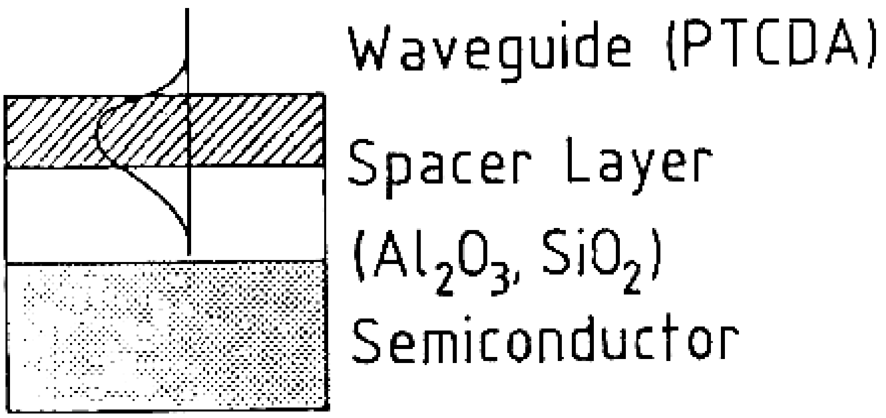


Figure 5: Structure of PTCDA wave guides

Due to low losses in the long wavelength region PTCDA layers grown under optimized conditions are well suited for wave-guide applications (Fig.4). So far losses of PTCDA-wave guides less than 2.5dB/cm have been published.To separate the PTCDA waveguide from the highly refractive III-V or silicon substrate a dielectric spacer layer is required, as indicated in fig.4.Based on this layer sequence common rib wave-guides can be defined by a lift-off technique.Due to the strong anisotropy of the refractive index. PTCDA wave-guides prepared on $SiO_2$ (n=1.44). SiO (n=1.87). $Al_2O_3$(n=1.63)or photoresist (n=1.6) spacer layers only guide optical waves polarized parallel to the substrate surface.(Ref.2) The strong anisotropy of the refractive index is promising for TE/TM filter and polarization splitters.

## 5.2 Organic light-emitting devices

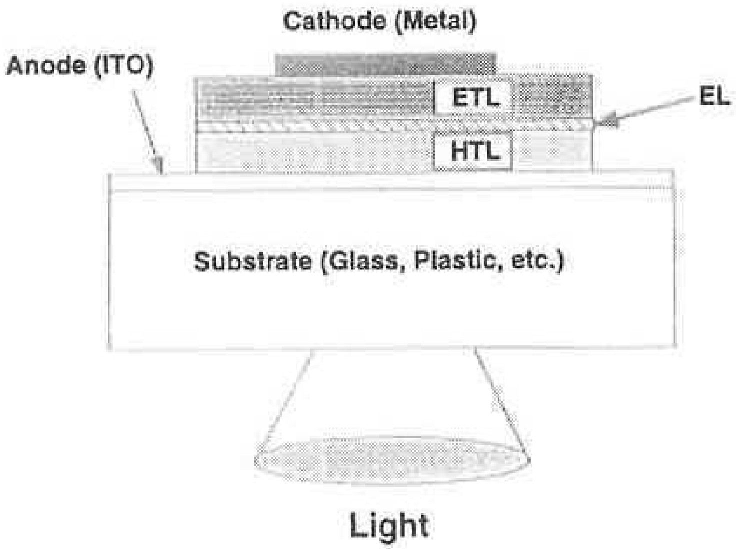


Figure 6: Conventional light emitting device(OLED) double hetero structure showing the contacts the lectron transport layer (ETL),light-emitting layer(EL),and hole transport layer(HTL), Ref. 1

A schematic cross section of a conventional light-emitting device with three organic layers (a double heterostructure) is shown in fig6. The top ohmic, electron-injecting electrode consists of a low work function metal alloy, typically Mg-Mg deposited by vacuum-evaporation. The bottom, hole injecting electrode is a typically a thin film of transparent semiconductor indium tin oxide (ITO), deposited on to the substrate by electron beam evaporation. Light is emitted through this electrode when the device is operated in forward bias. The next layer deposited is a hole-transporting layer (HTL). This is followed by light emitting layer (EL) consisting of material such as TAZ completes the double heterostructure.
Because PTCDA is an extremely robust molecule and it has high hole mobility, which improves the carrier injection, it canbe used in stacked organic light emitting devices (SOLED)

# 6 Conclusion

Organic materials are new class of materials which shows similar optical and electronic properties as classical semiconducots. How-ever since specific organic molecules may be synthesized for almost any purpose ,this class of materials has tremoundous potential for the growth of novel structures for opto-electronics. also it is expected with time that organic materials may eventually supplement or even replace conventional semiconductor devices.

# 7 Acknowledgements

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