UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

SMR/917 - 13

SECOND WORKSHOP ON SCIENCE AND TECHNOLOGY OF THIN FILMS

(11 - 29 March 1996)

" Electronic properties of organic films "

presented by:

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INTERNATIONAL CENTER FOR THEORETICAL PHYSICS
Trieste

Second Workshop on Science and Technology of Thin Films
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Electronic Properties of Organic Films

Roberto Zamboni, *Istituto di Spettroscopia Molecolare, CNR, via P. Gobetti, 101 40129 - Bologna, Italy*

Basic definitions of organic molecular systems

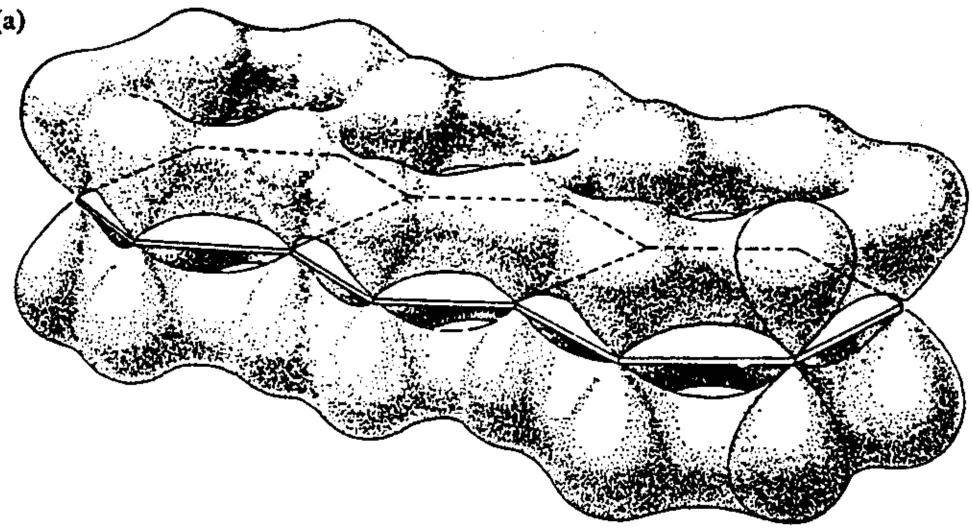
Basic definitions of fundamental electronic excitations in organic systems

Electronic levels ordering and energy transfer in a prototypical molecular sistem: the α-sexithiophene

Organic electroactive materials for devices: control of energy transfer in thin films and optoelectronic properties of organic light emitting diodes

Organic molecular beam deposition in ultra high vacuum of organic molecules: heteromultilayers, interfaces control and new electronic excitations

(a)



(b)

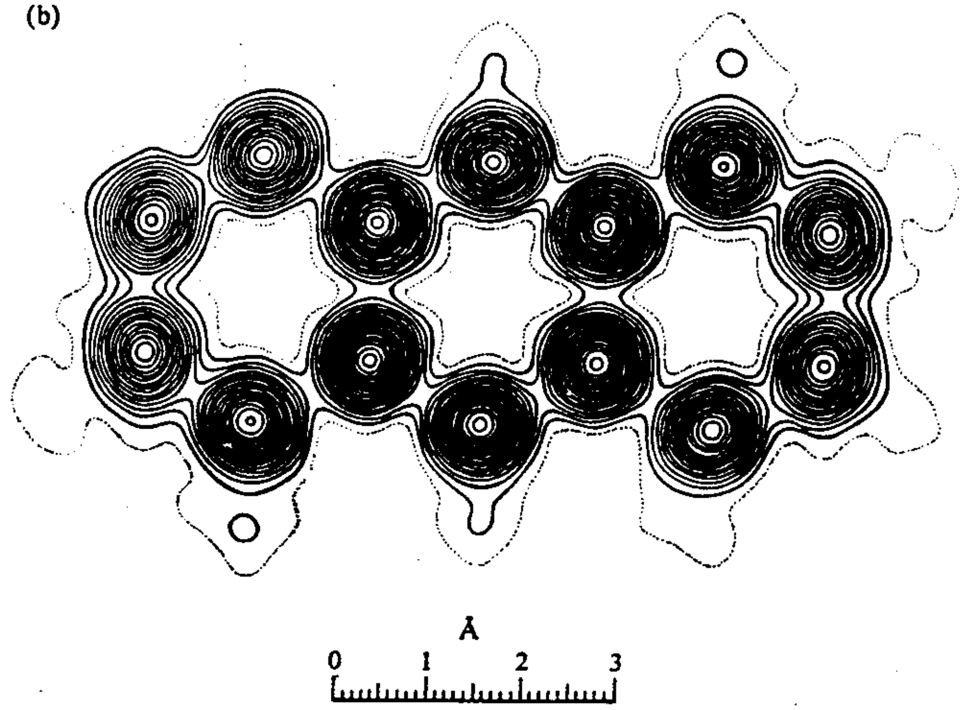
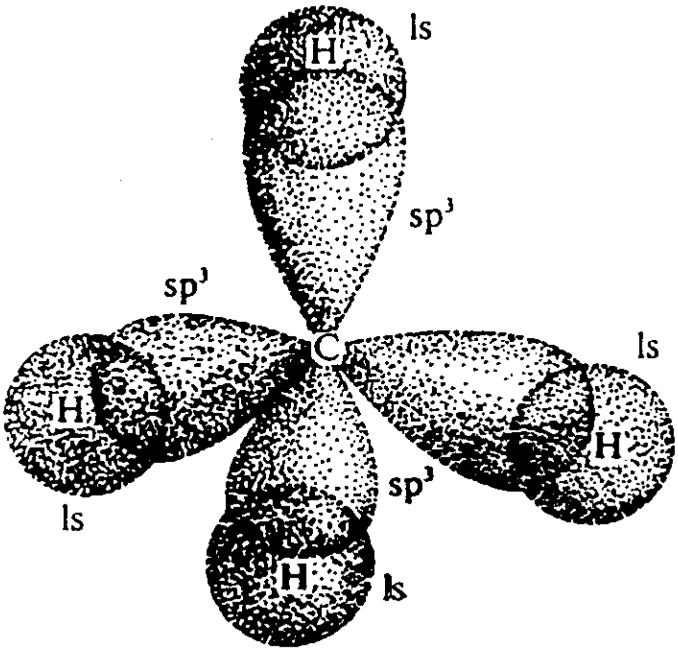


Fig. I.A.4. (a) Schematic view of the lowest bonding orbital π-electron cloud above and below the plane of the anthracene molecule. The H atoms are not shown. (Pope 1967) (b) Electron density sections through the central molecular planes in the anthracene crystal. Each contour line represents an increase in electron density of about 0.5 electrons $Å^{-3}$ moving in toward the carbon atoms. (From Robertson 1958)

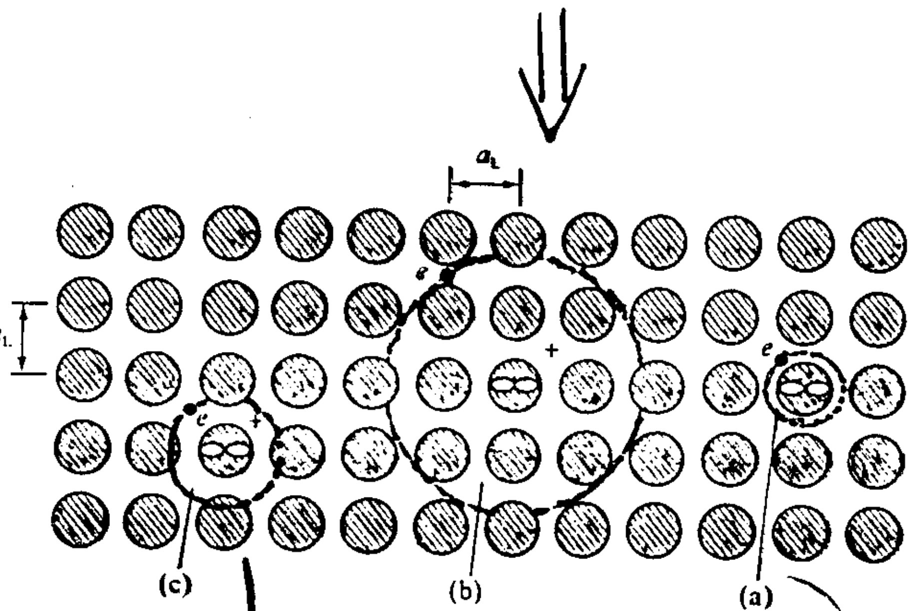
- Conjugated systems

alternation of single & double bonds

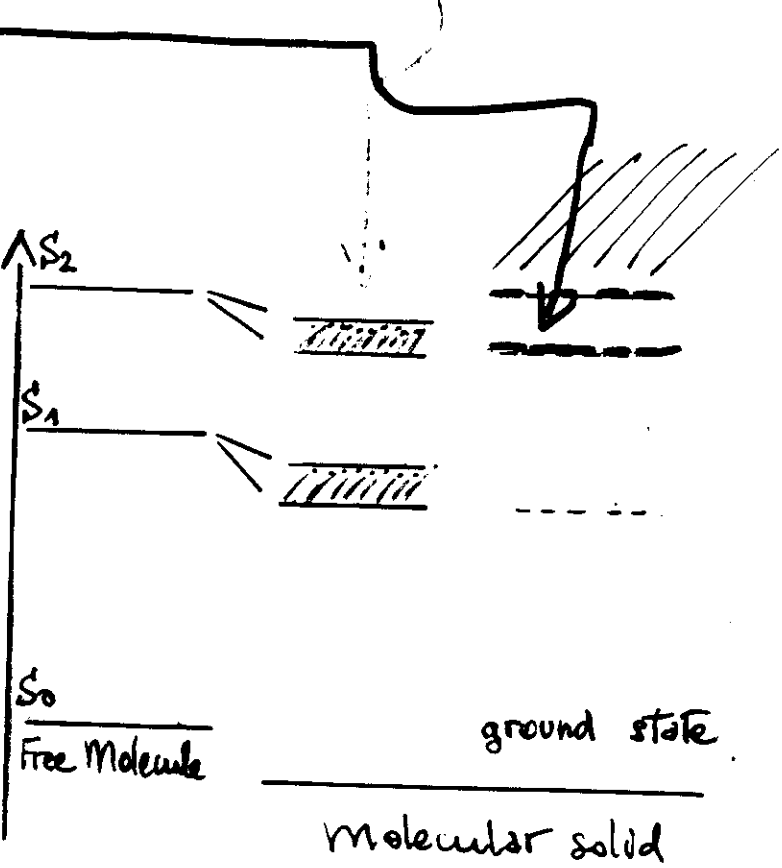


CH_4, methane

Fig. I.A.2. Molecular orbitals of methane. The four sp^3 orbitals are directed toward four hydrogen atoms, each with an electron in a 1s orbital. Each sp^3 orbital combines with one hydrogen 1s orbital to form a bonding molecular orbital. The four σ-bonds are tetrahedrally oriented. The surfaces represent the boundary enclosing 90 per cent of the electron density. (Modified from Moore, Davies, and Collins 1979, p. 215) inorganic semicond.



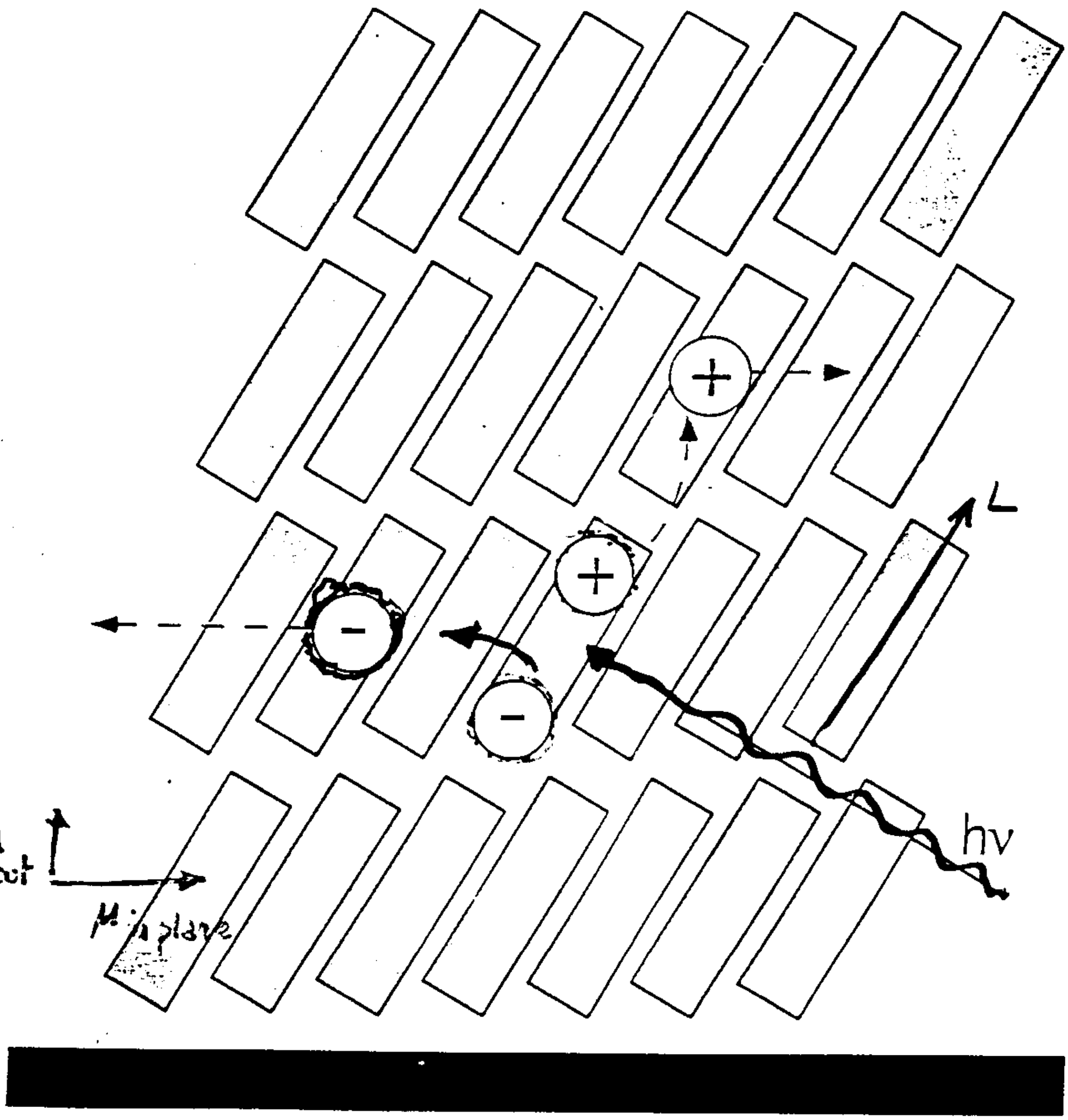
a) Frenkel exciton
b) Wannier-Mott exciton
c) Charge-Transfer exciton



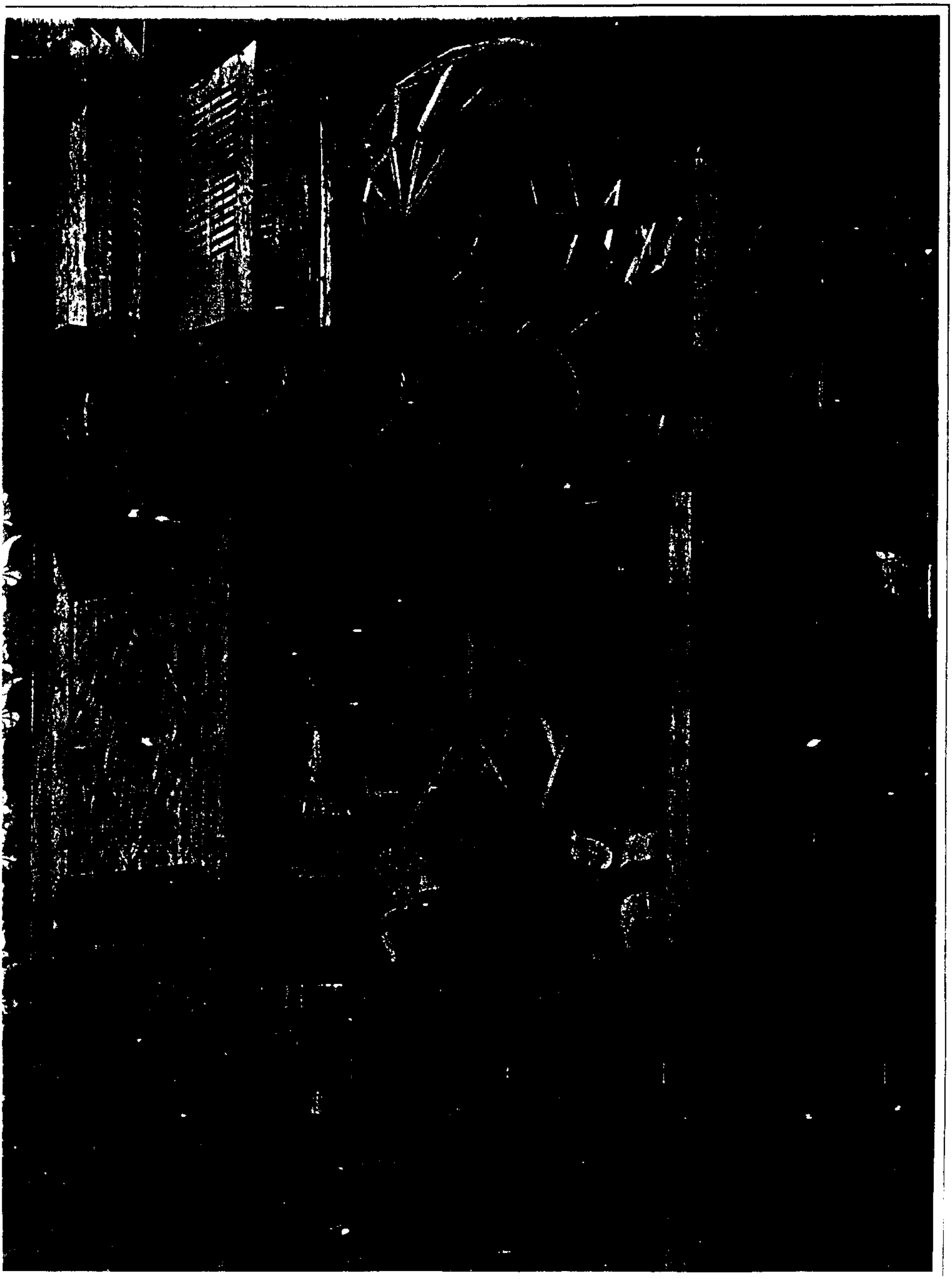
$R_{Bin} \gg R_{Bag.}$

Ref: M. Pope & C.E. Swenberg
"Electronic processes in Organic Xstals"
Oxford Univ. Press - N.Y (82)

A.S. Davydov
"Theory of Molecular Excitons" - Plenum Press
N.Y ('71)

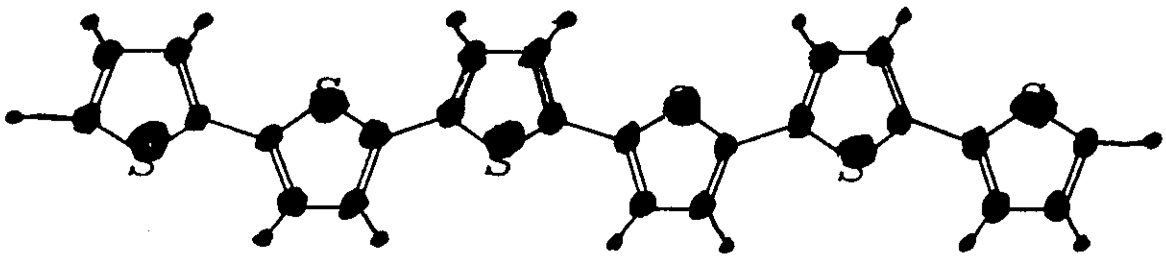


Substrate

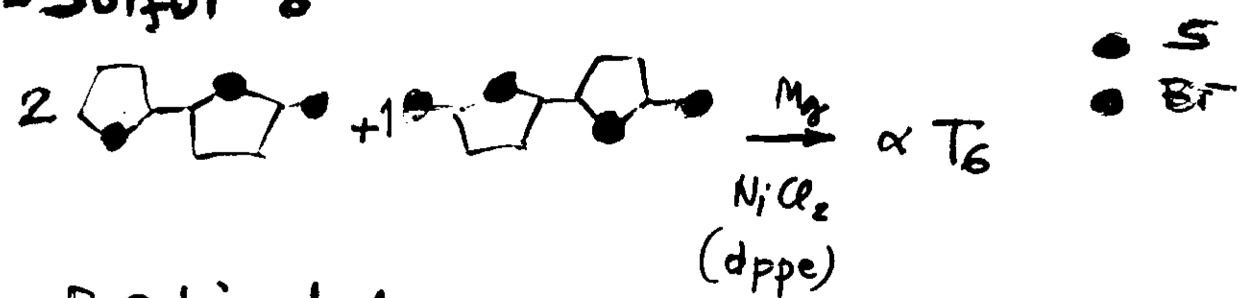


...APERTA ...ON POLIEDRI E LIBRI. SAGRESTIA. SPALLIERA DEGLI ARMADI.

Synthesis of α sexithienyle (αT$_6$)



• – Hydrogen 14
• – Carbon 24
• – **Sulfur** 6



P. Ostoja et. al.
Adv. Mat. for Opt. & Electr. 1, 127 (1992)

Horowitz - Garnier

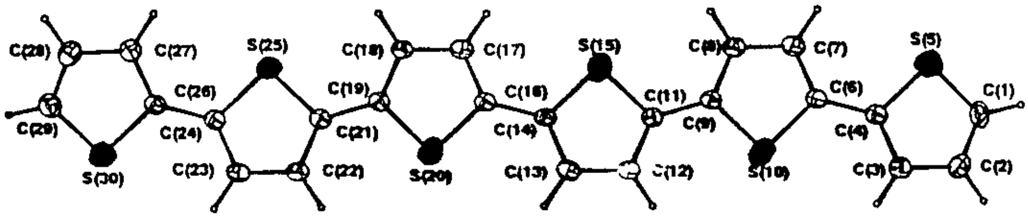
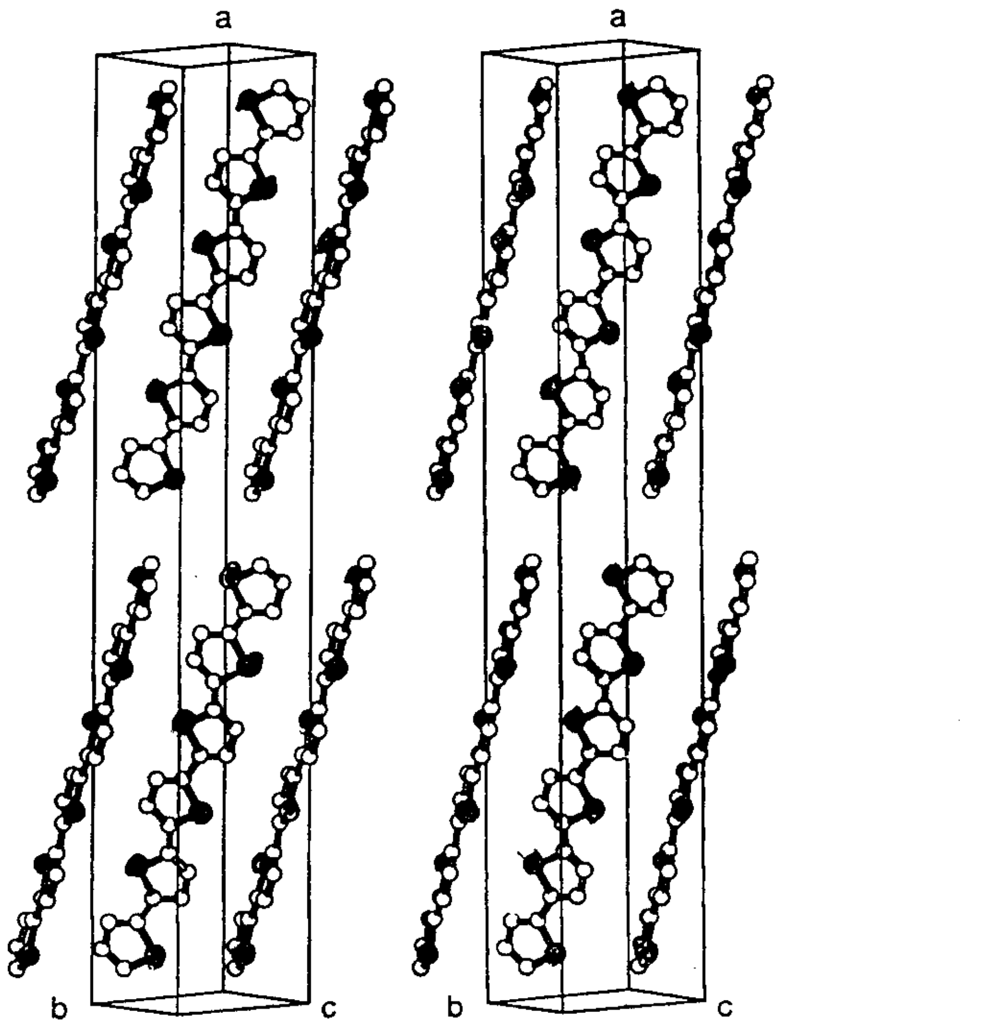
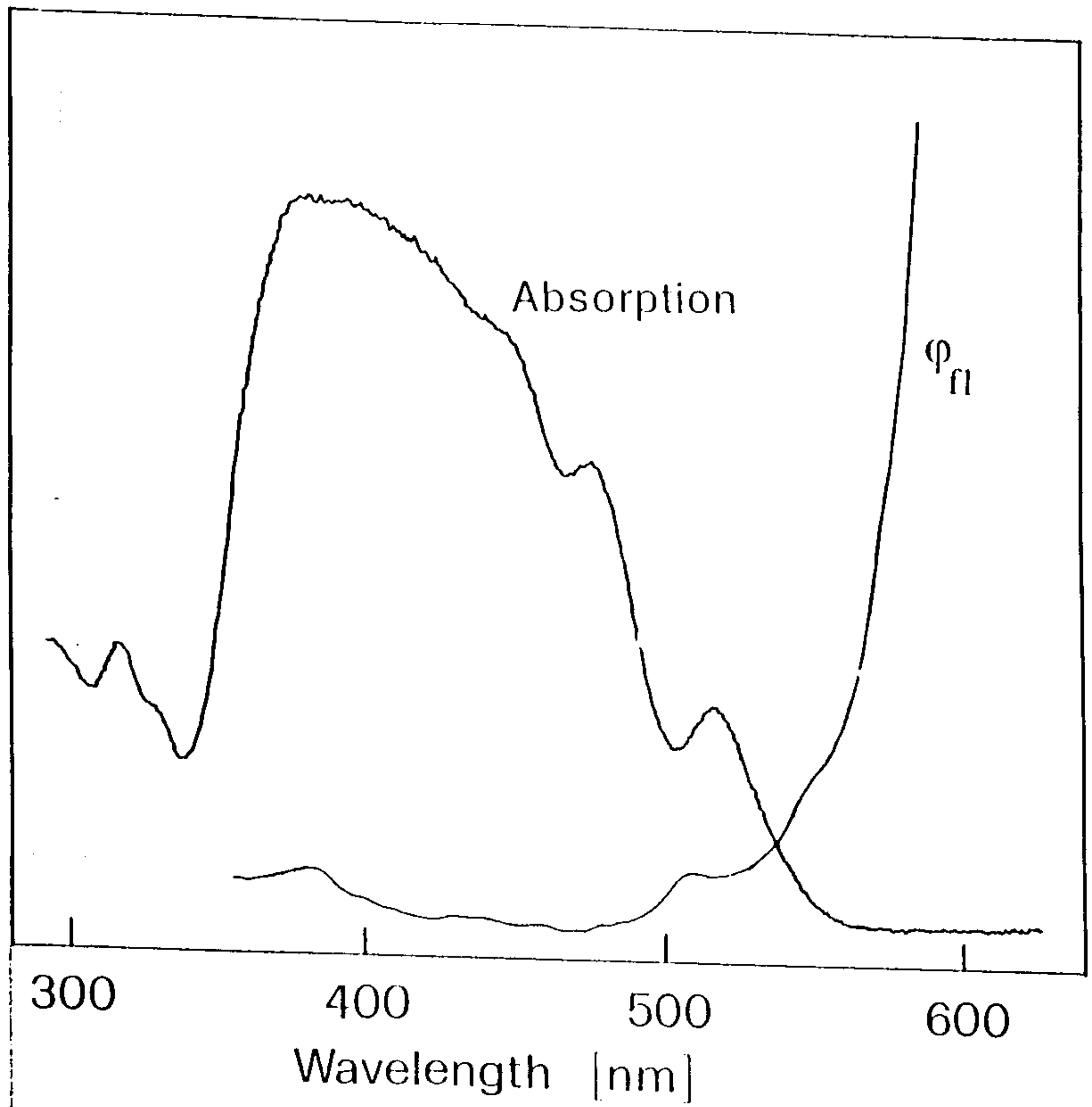


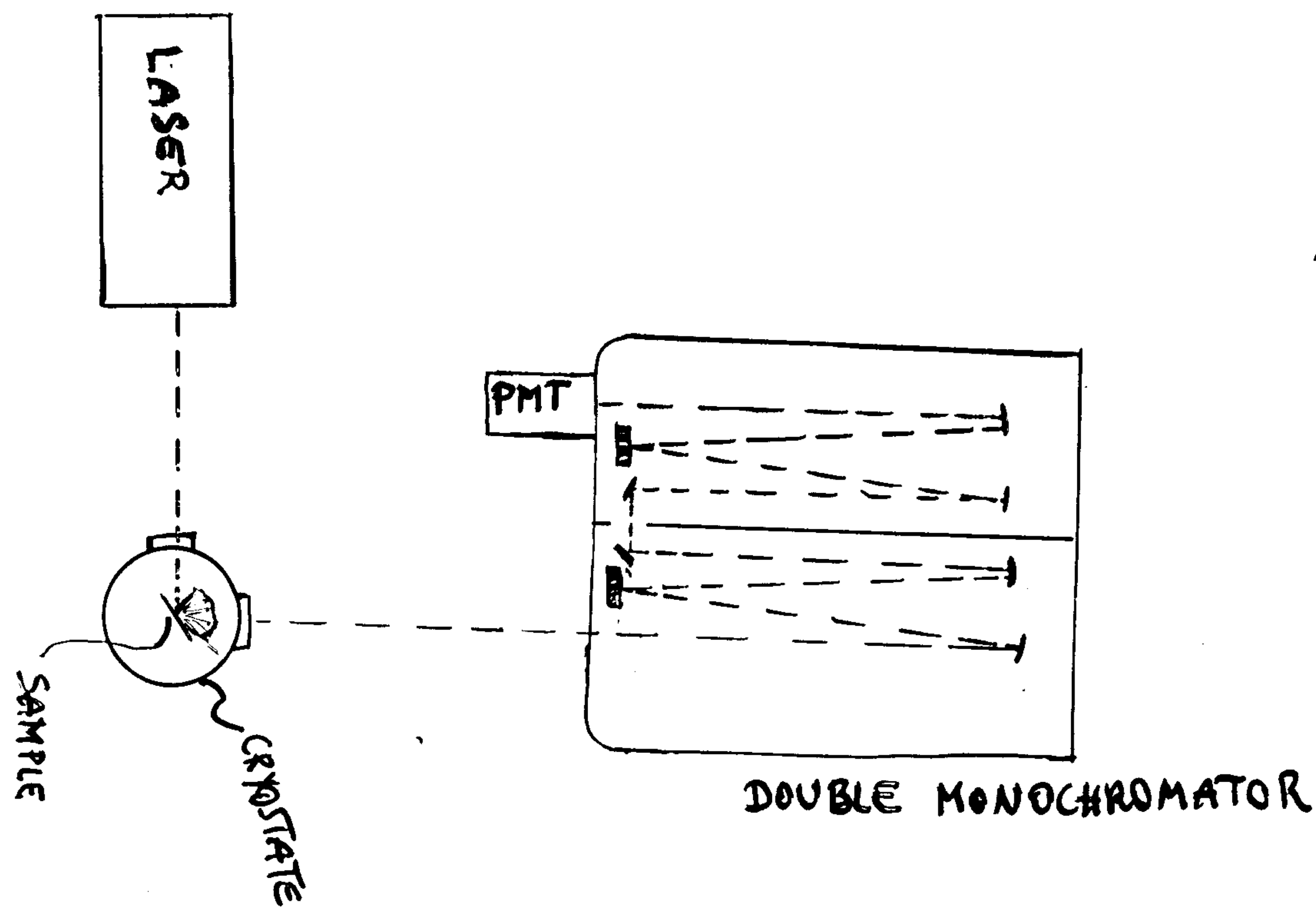
Figure 1. Molecular structure and numbering of sexithiophene (6T).

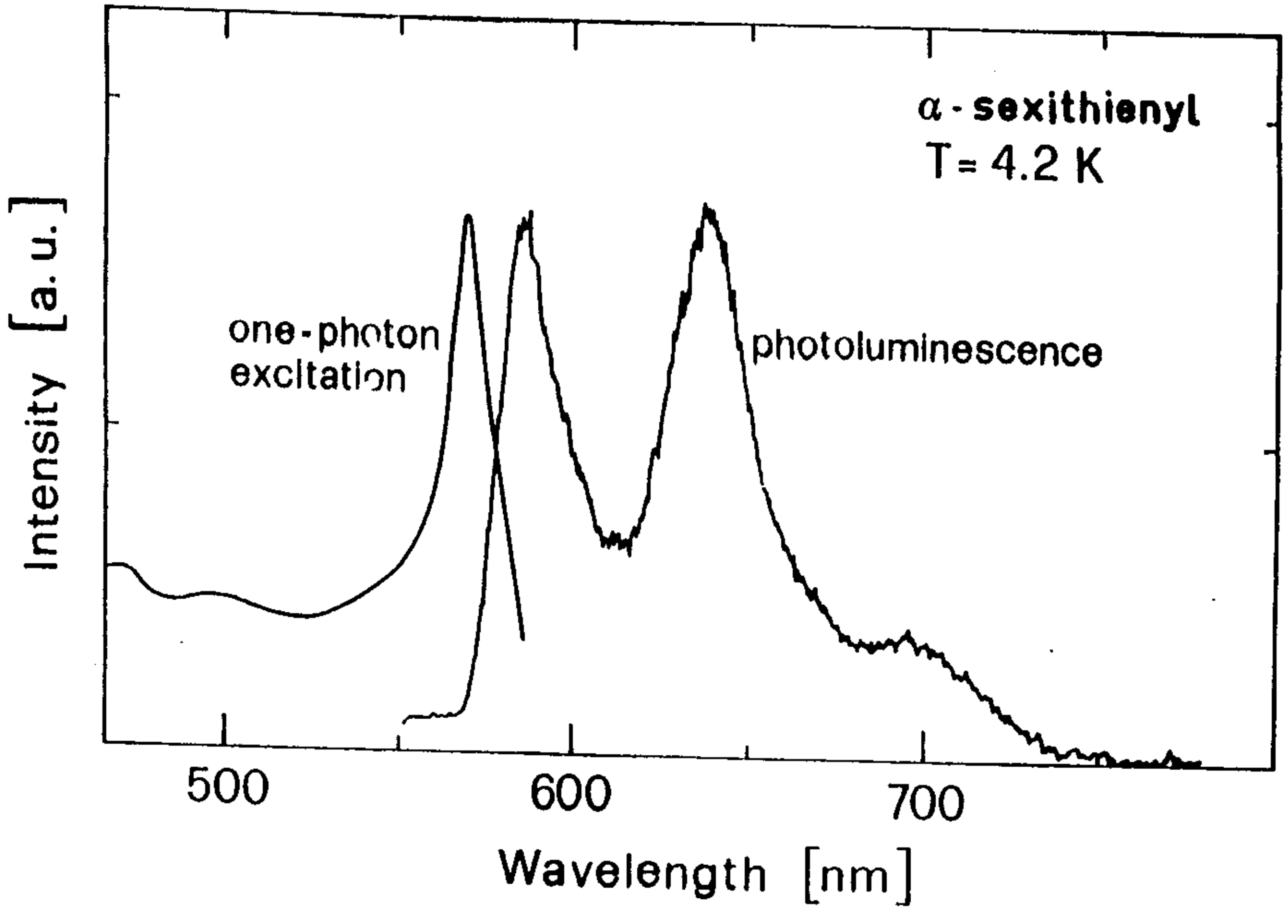


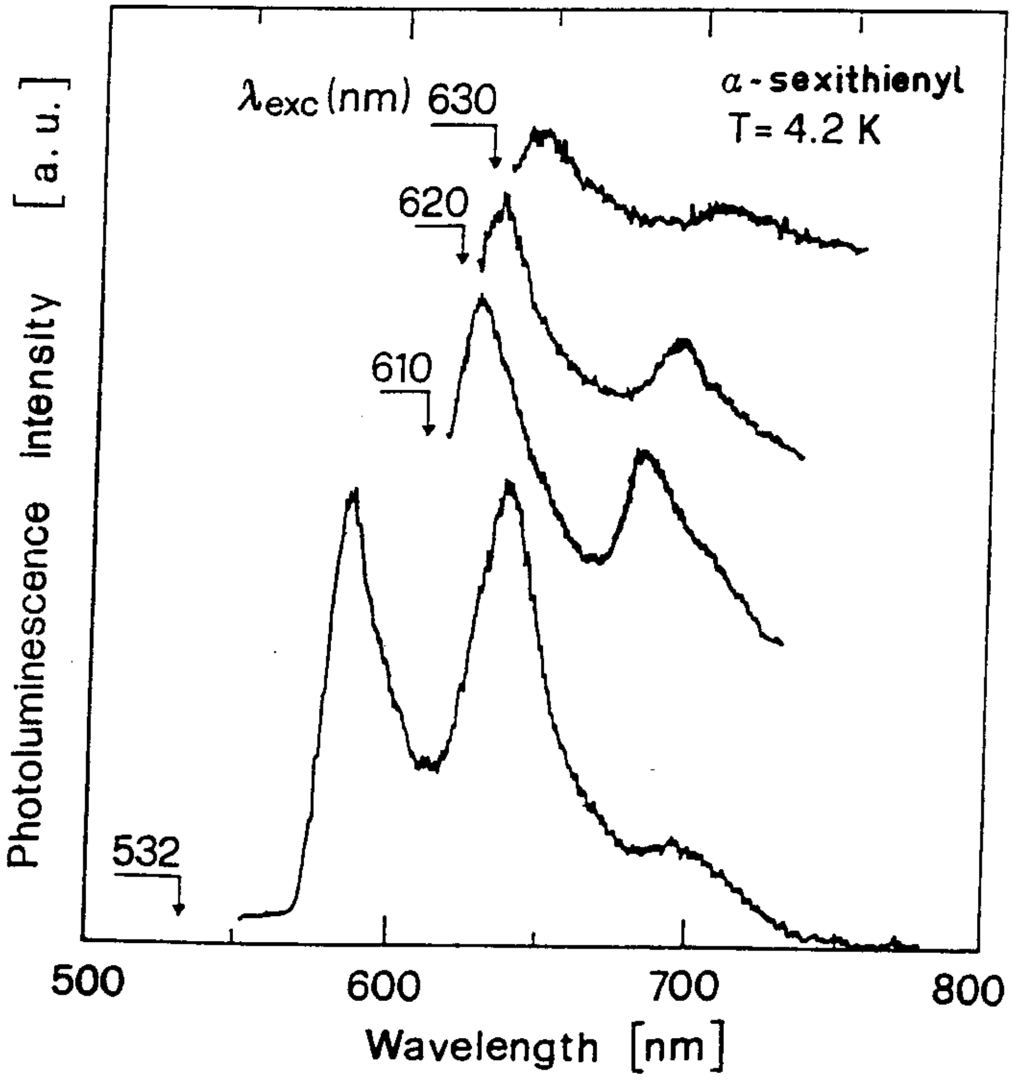


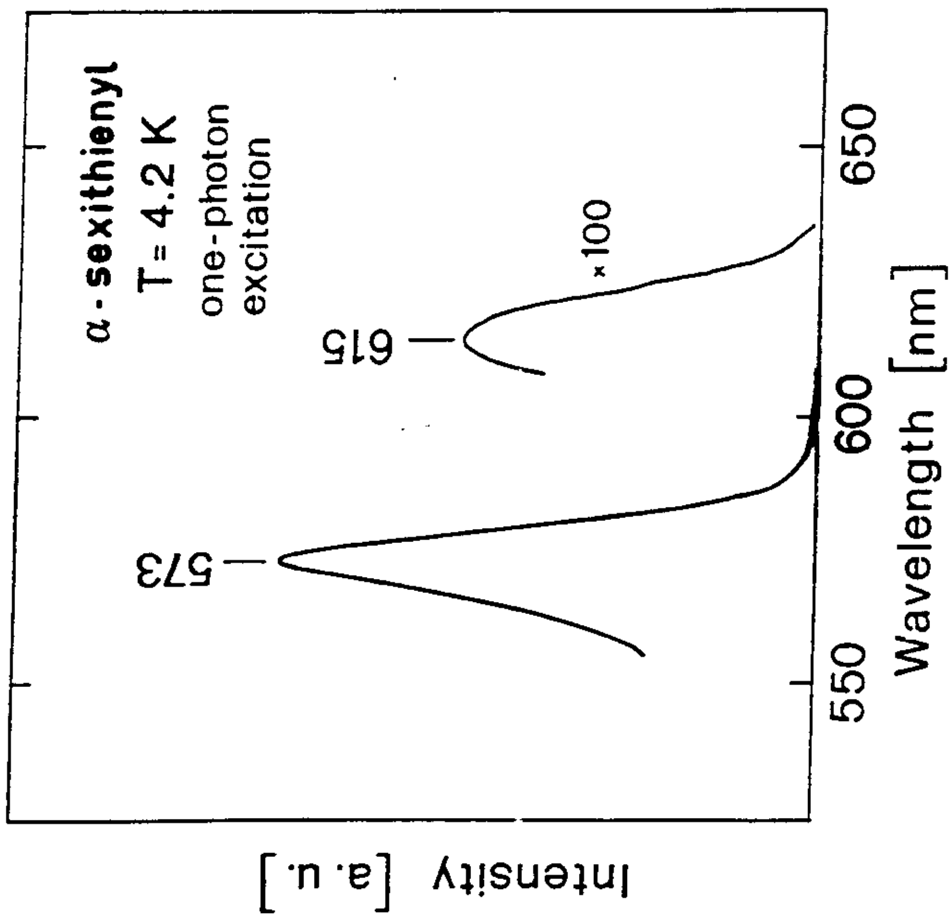
Absorption
φ_{fl}
300
400
500
600
Wavelength [nm]

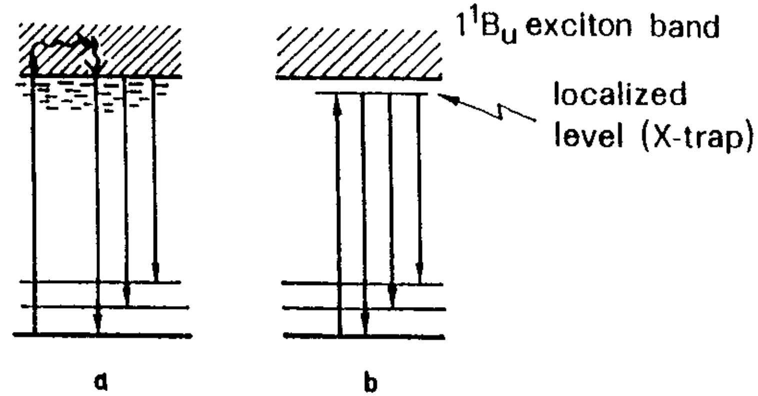
FLUORESCENCE EXP. SET-UP

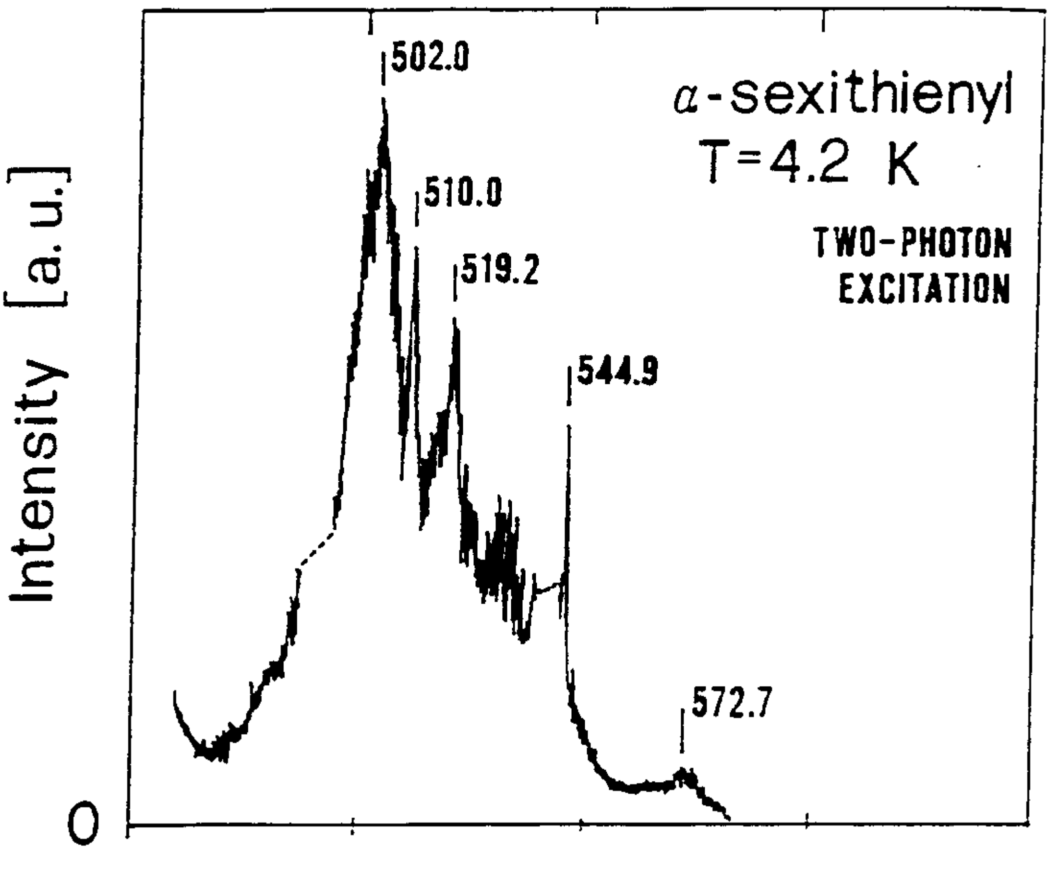



α - sexithienyl
T= 4.2 K
one-photon
excitation
photoluminescence
Intensity [a. u.]
500
600
700
Wavelength [nm]

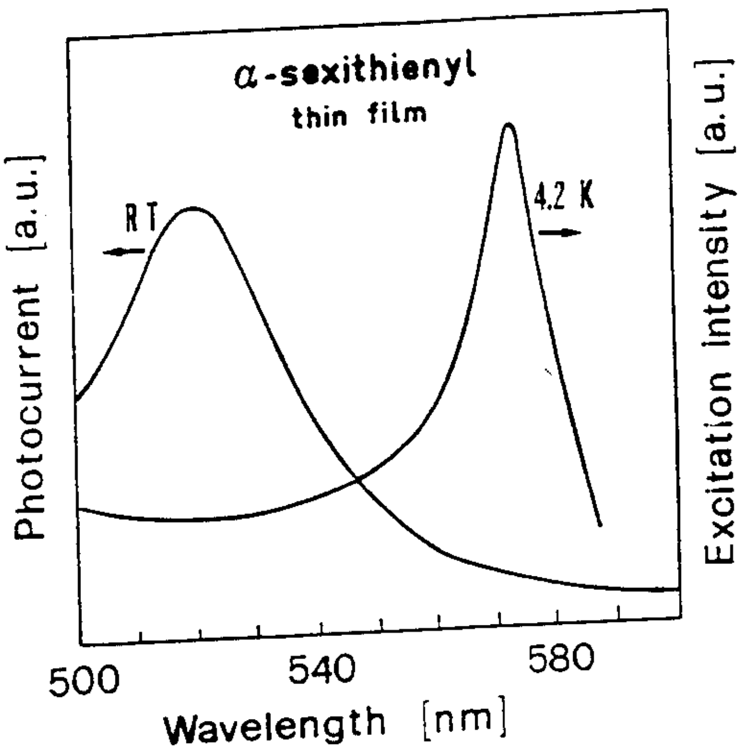

λexc (nm) 630
620
610
532
α-sexithienyl
T= 4.2 K
Photoluminescence Intensity [a. u.]
500
600
700
800
Wavelength [nm]

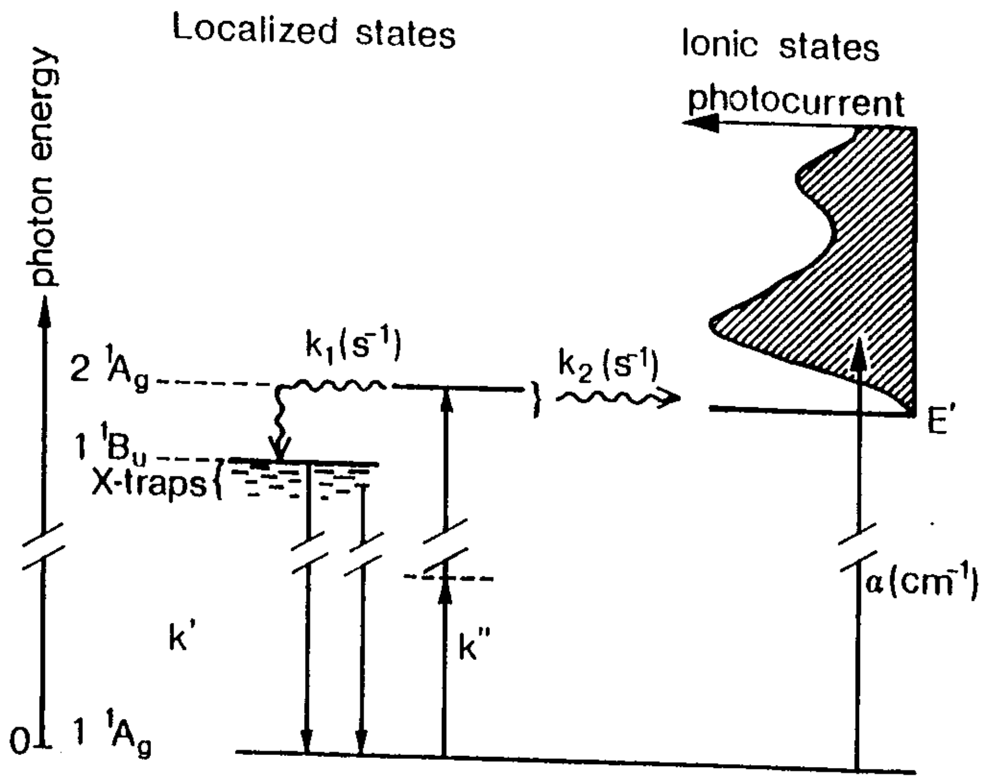

α - sexithienyl
T = 4.2 K
one-photon
excitation
573
615
×100
550
600
650
Wavelength [nm]
Intensity [a. u.]


1^1B_u exciton band
localized
level (X-trap)
a
b

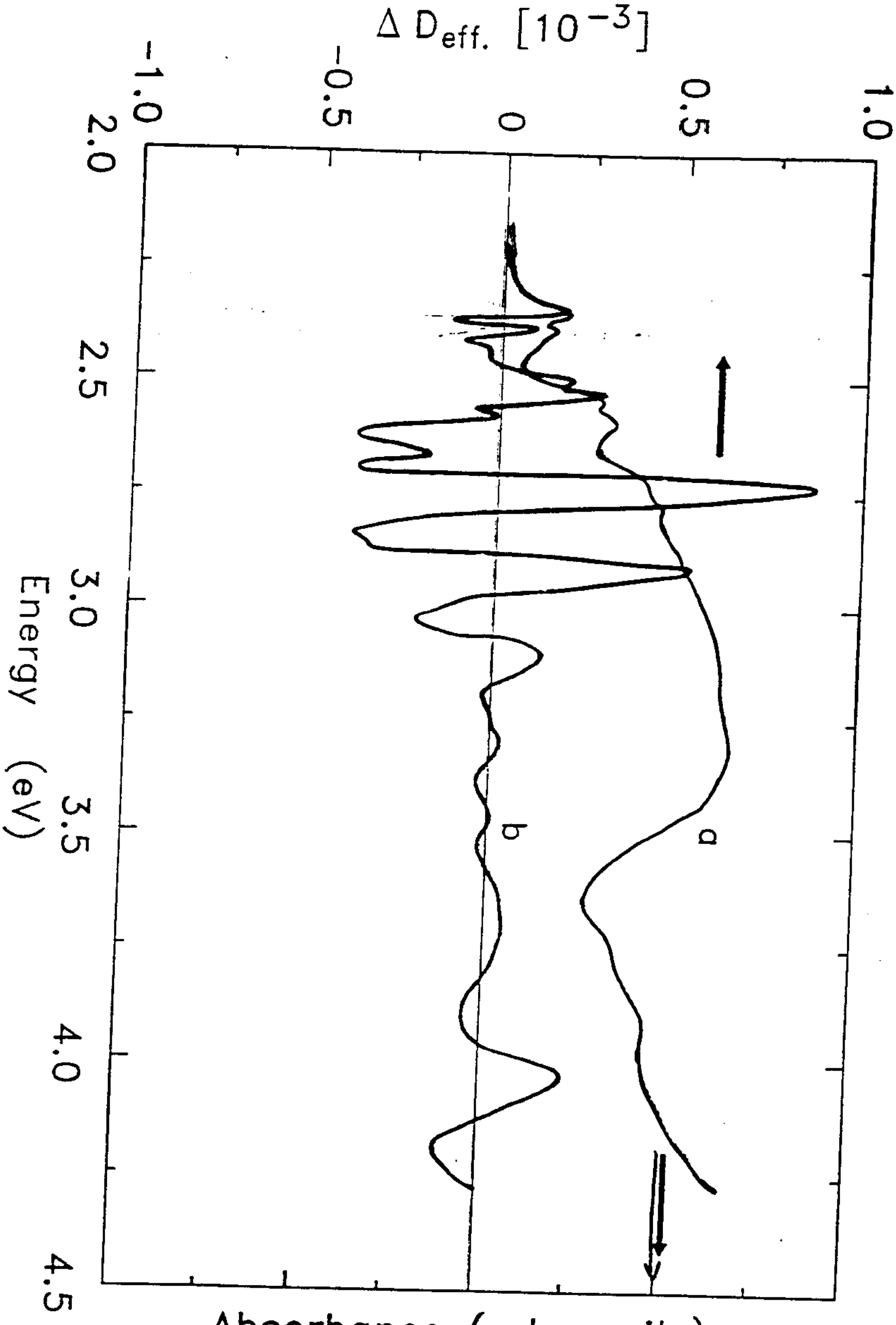

Intensity [a.u.]
0
502.0
510.0
519.2
544.9
572.7
α-sexithienyl
T=4.2 K
TWO-PHOTON
EXCITATION

15

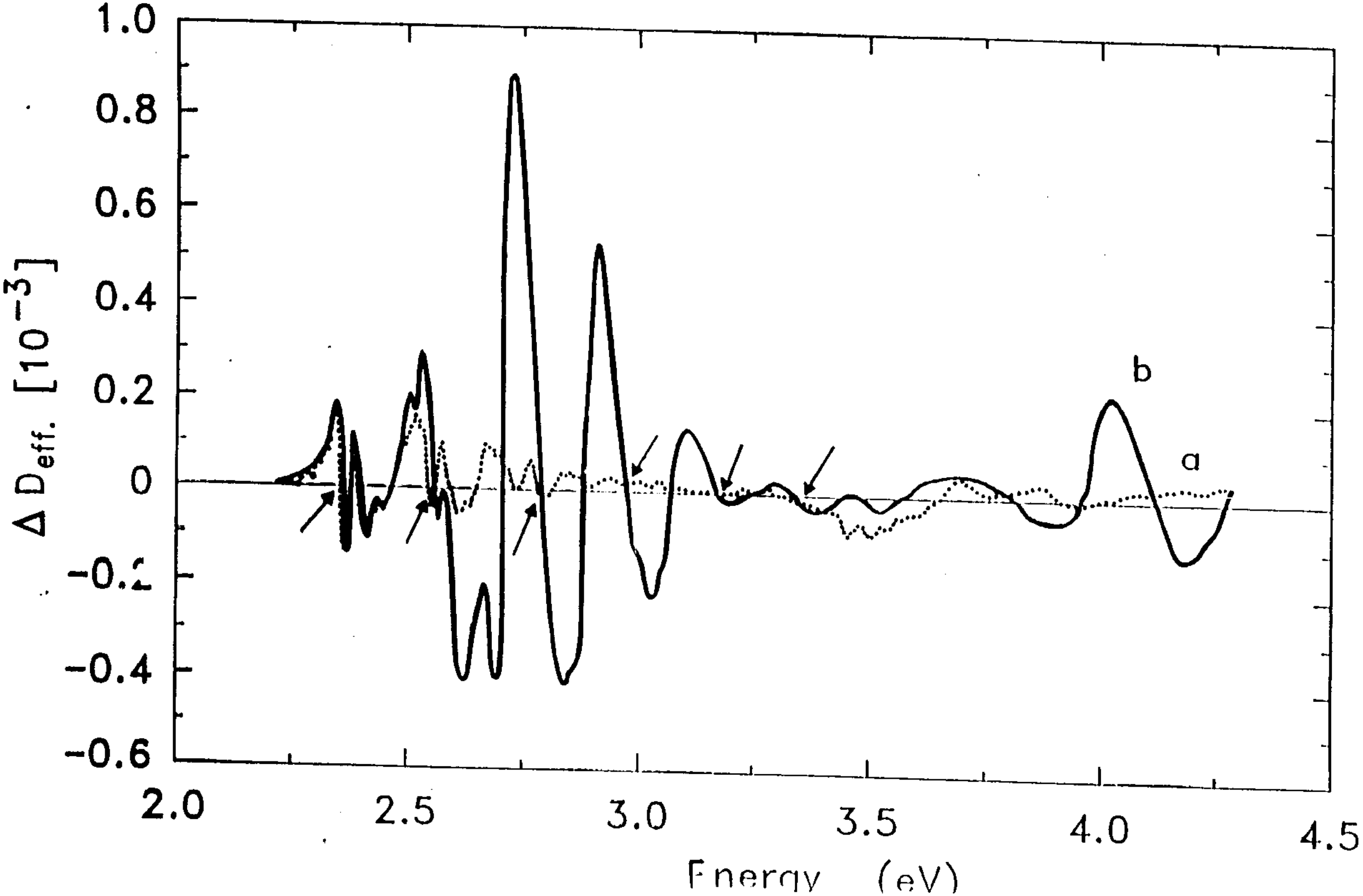

α-sexithienyl
thin film
RT
4.2 K
Photocurrent [a.u.]
Excitation Intensity [a.u.]
500
540
580
Wavelength [nm]



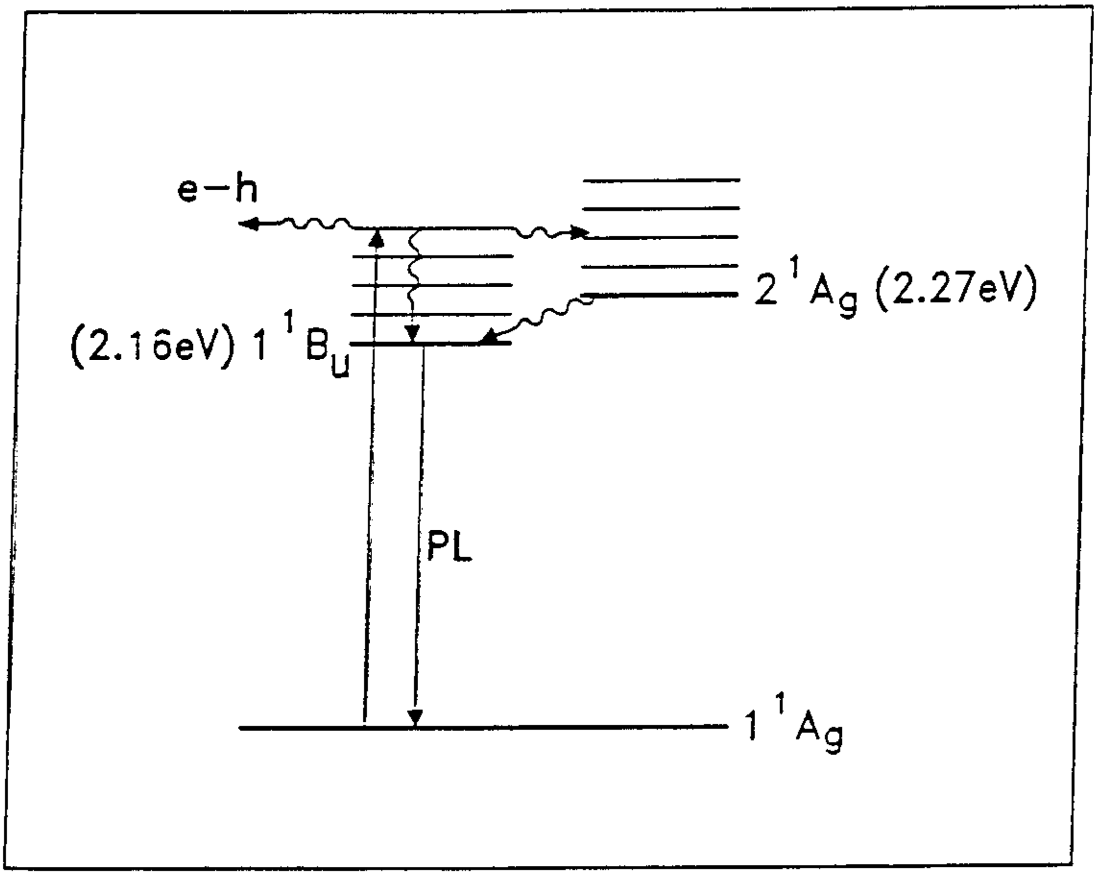
Localized states
Ionic states
photocurrent
photon energy
2 ^1A_g
$k_1(s^{-1})$
$k_2(s^{-1})$
1 ^1B_u
X-traps
E'
$\alpha(cm^{-1})$
k'
k''
0
1 ^1A_g



<u>Absorbance</u> (arb. units)

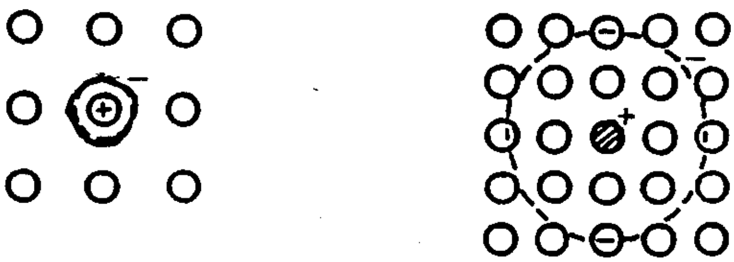


1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
Δ D eff. [10⁻³]
b
a
2.0
2.5
3.0
3.5
4.0
4.5
Energy (eV)

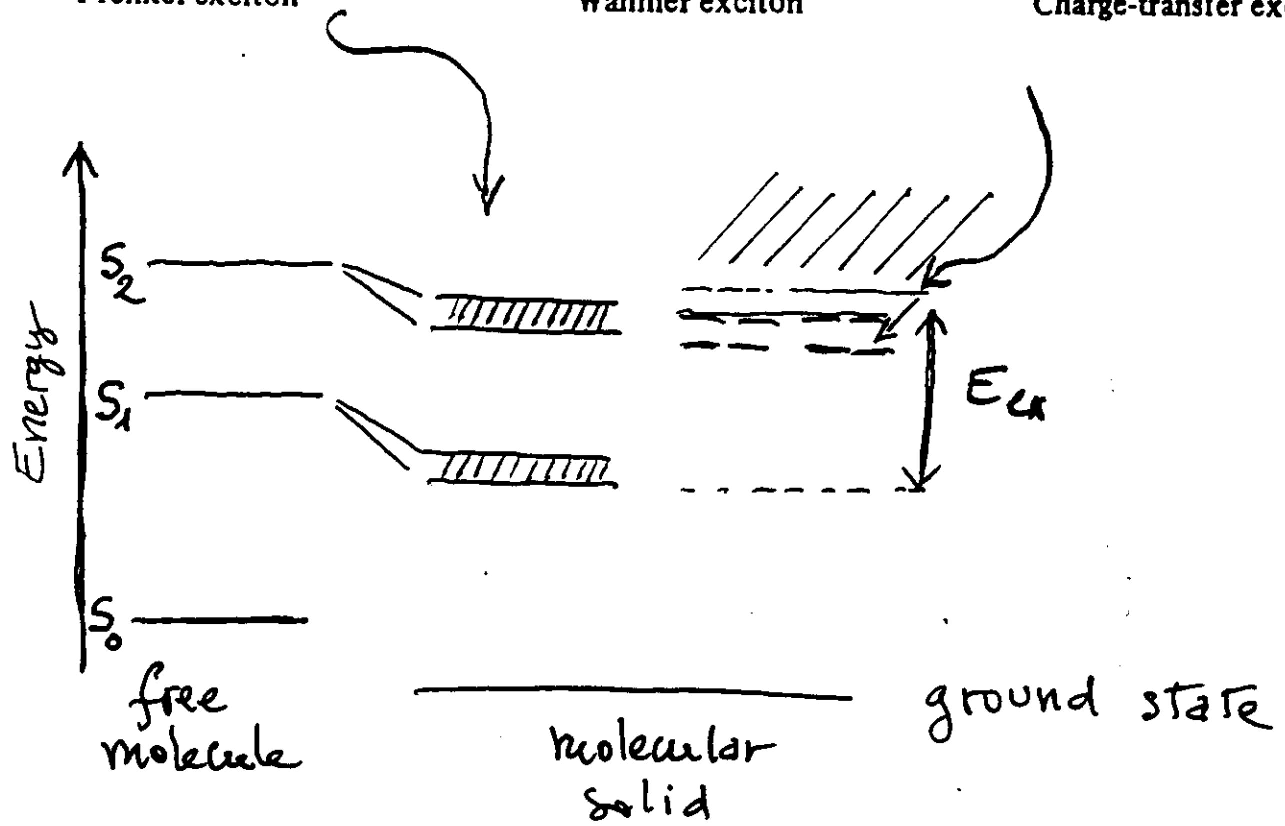

e−h
2 1 Ag (2.27eV)
(2.16eV) 1 1 Bu
PL
1 1 Ag

Inorganic semiconductors

⇓

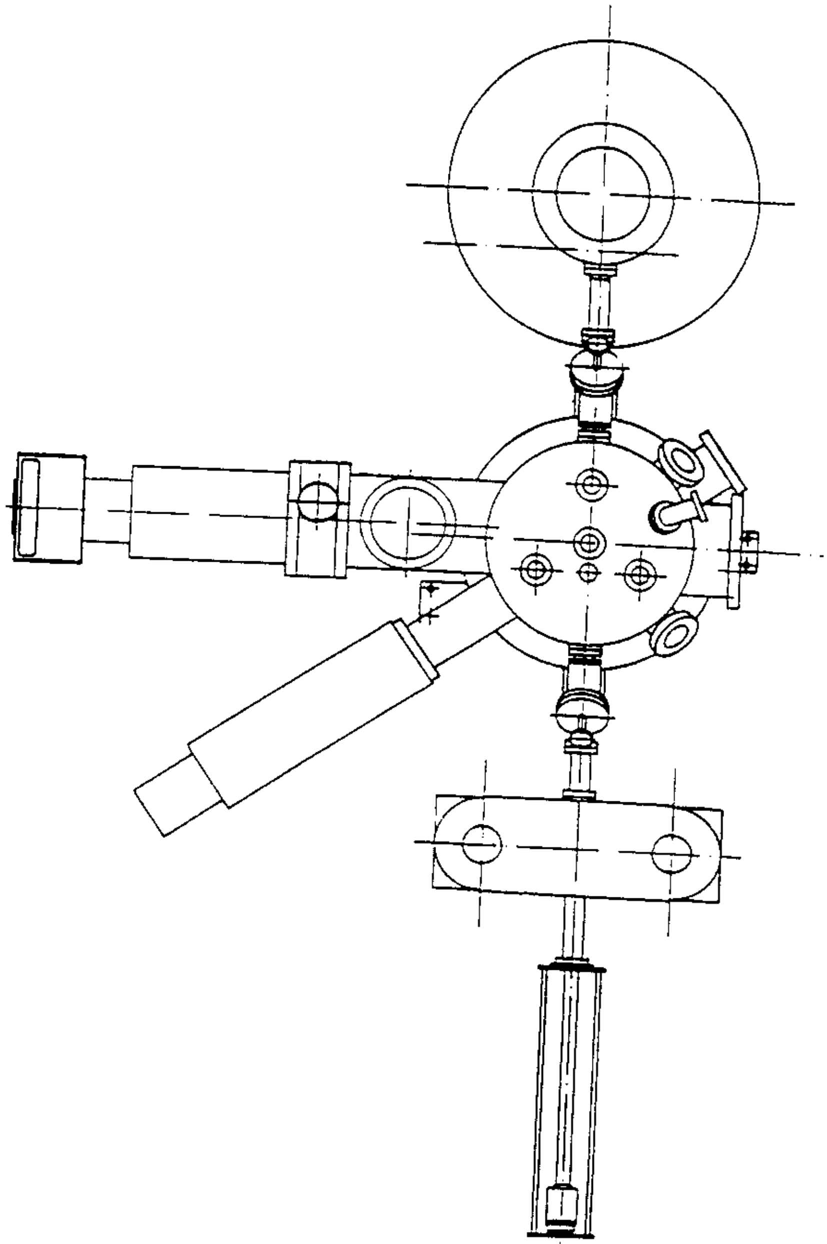


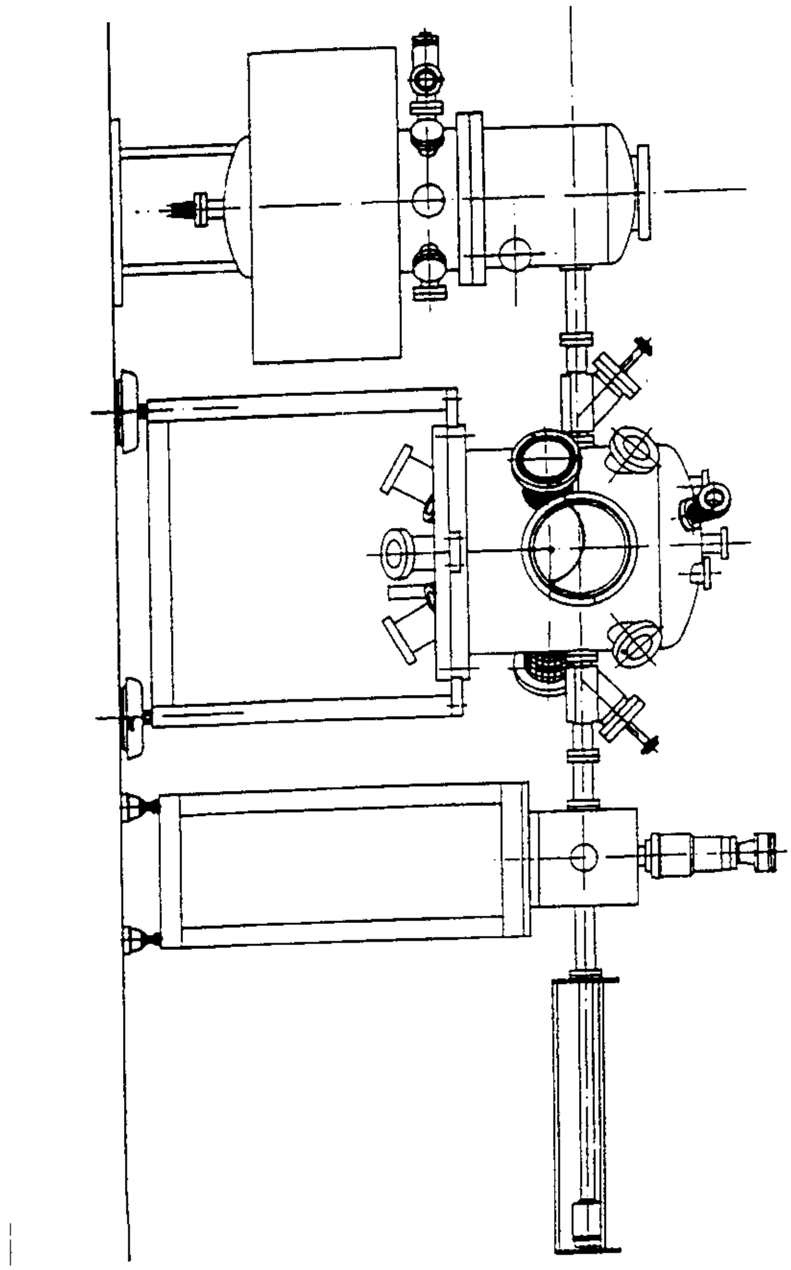
Frenkel exciton — Wannier exciton — Charge-transfer exciton



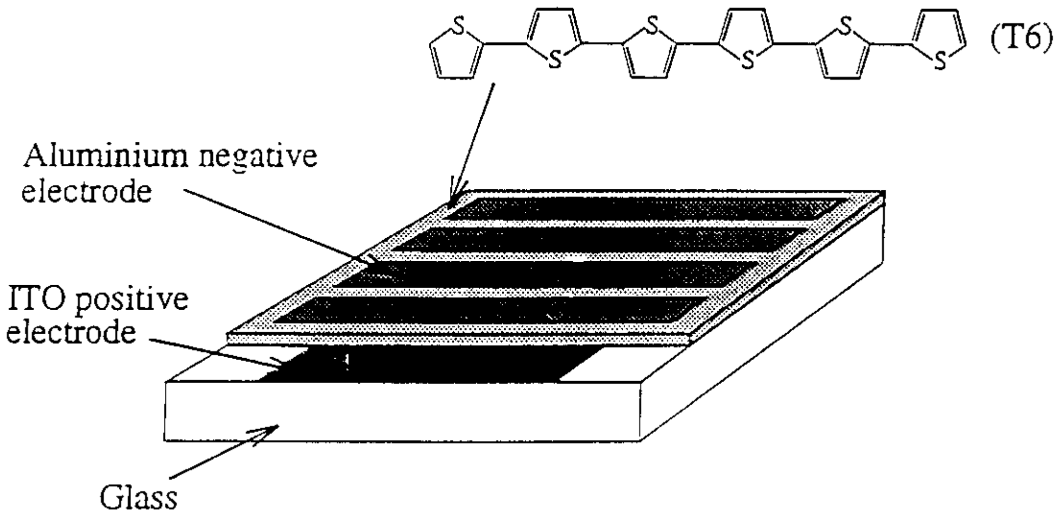
Exciton binding Energy (E_{ex})

- → small (few meV) — Wannier Exc
- → large (up to 2eV or more) — Frenkel Exc





Device structure...



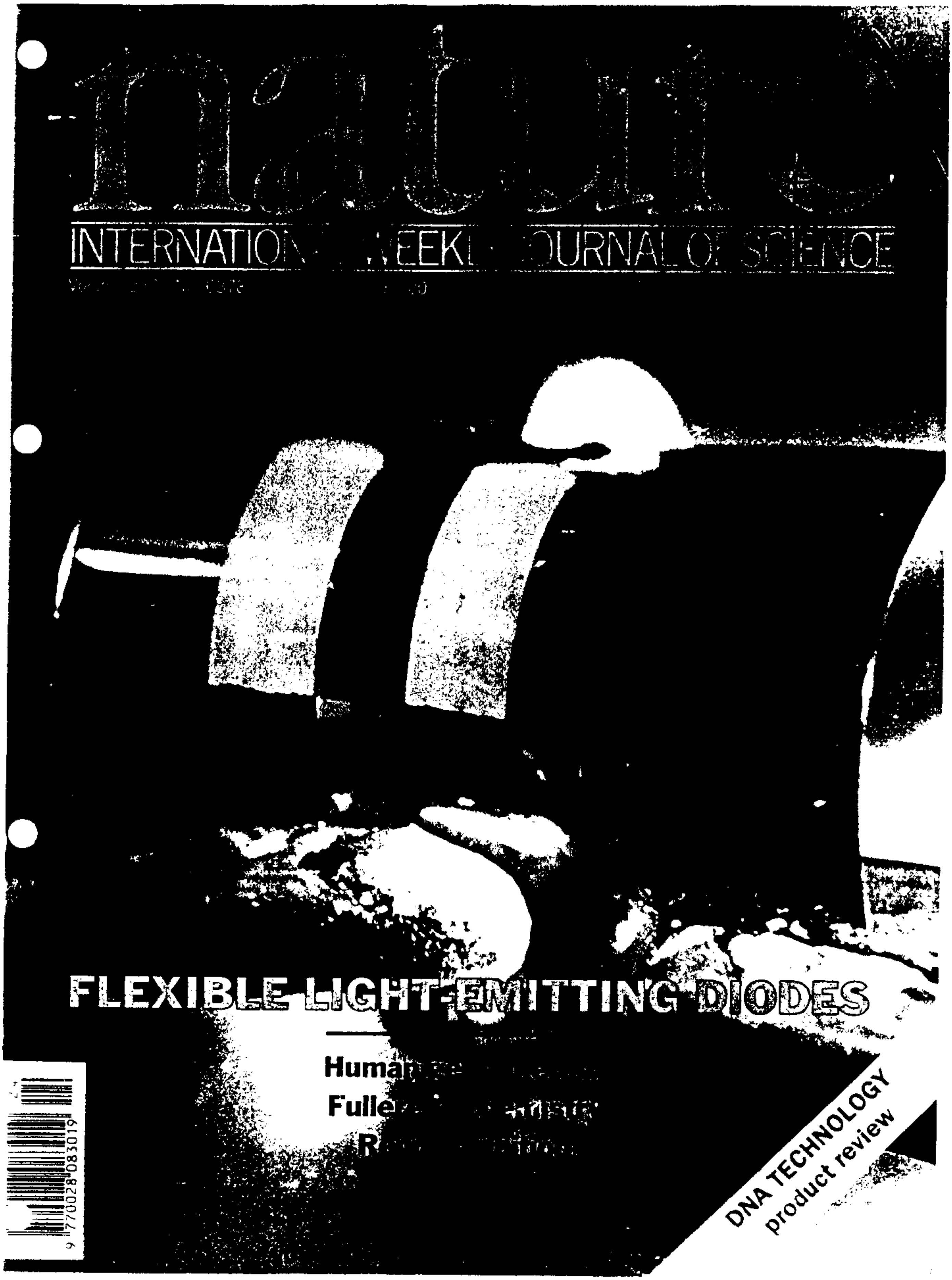
- T6 is insoluble

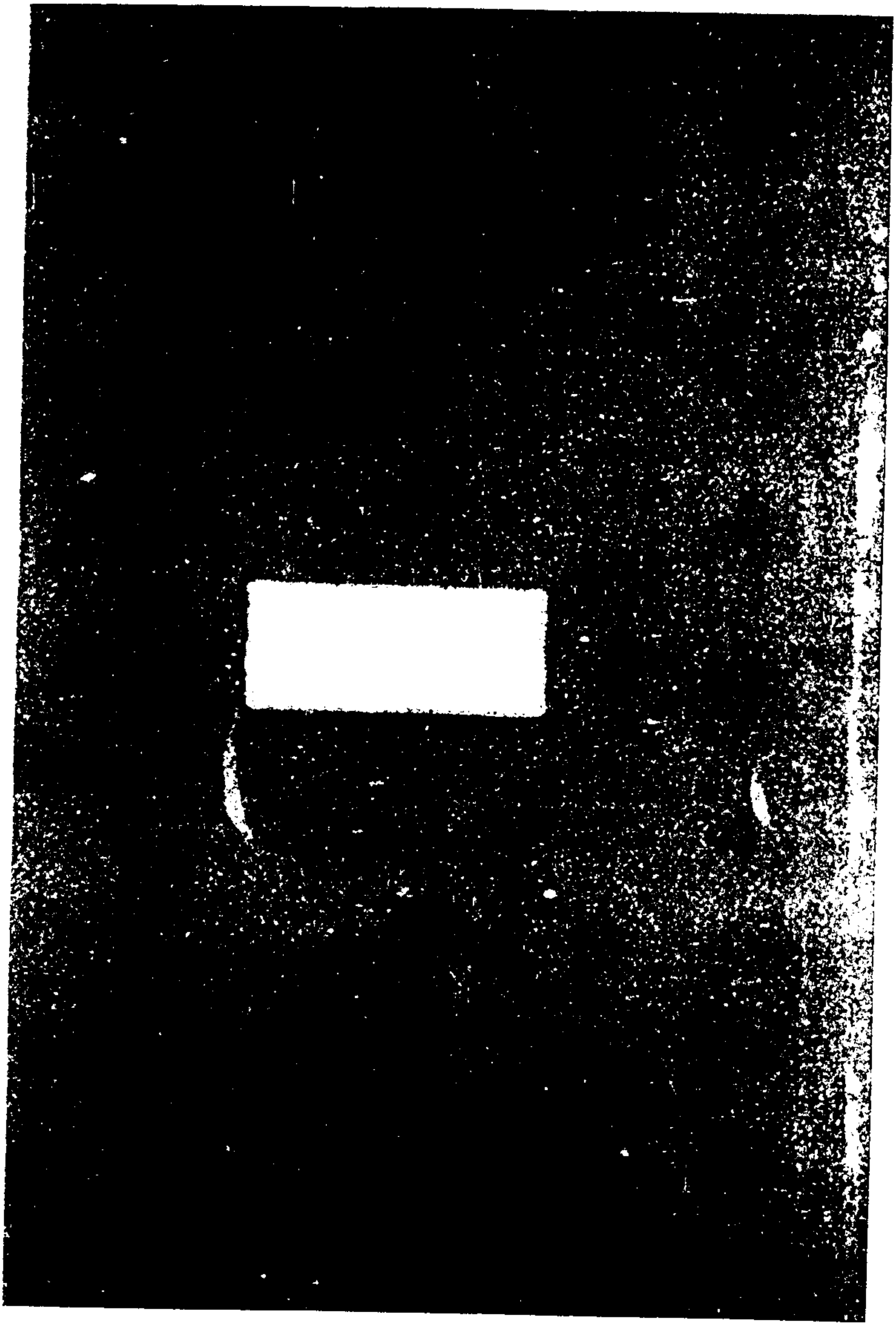
  Sublimed in high vacuum ($\sim 10^{-6}$mbar) → UHV

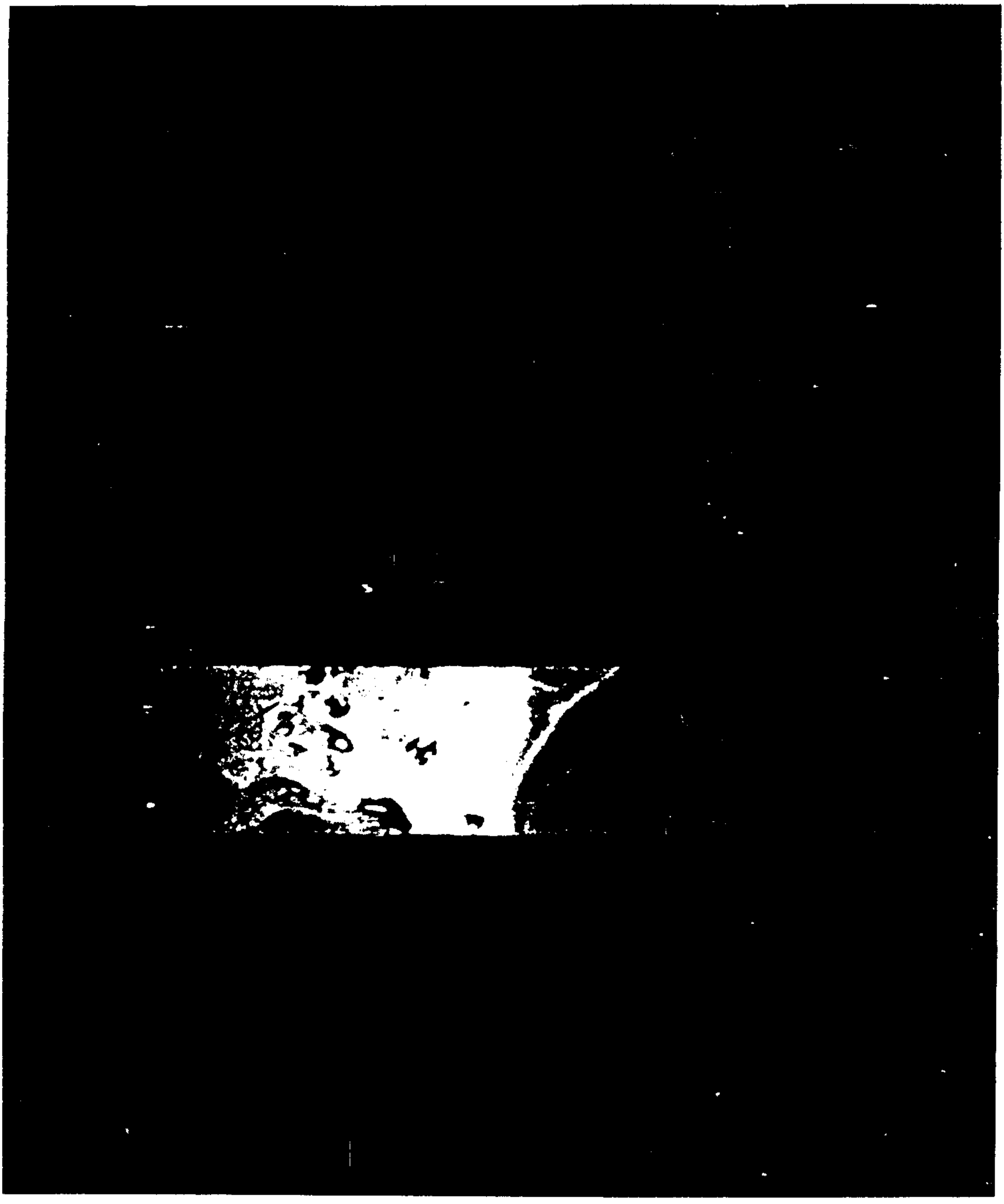
- Device thickness ~100nm
- Device area is $\sim 12mm^2$
- T6 forms well ordered films, with molecules aligned perpendicular to the substrate surface
- We can control the film morphology by varying the substrate temperature.

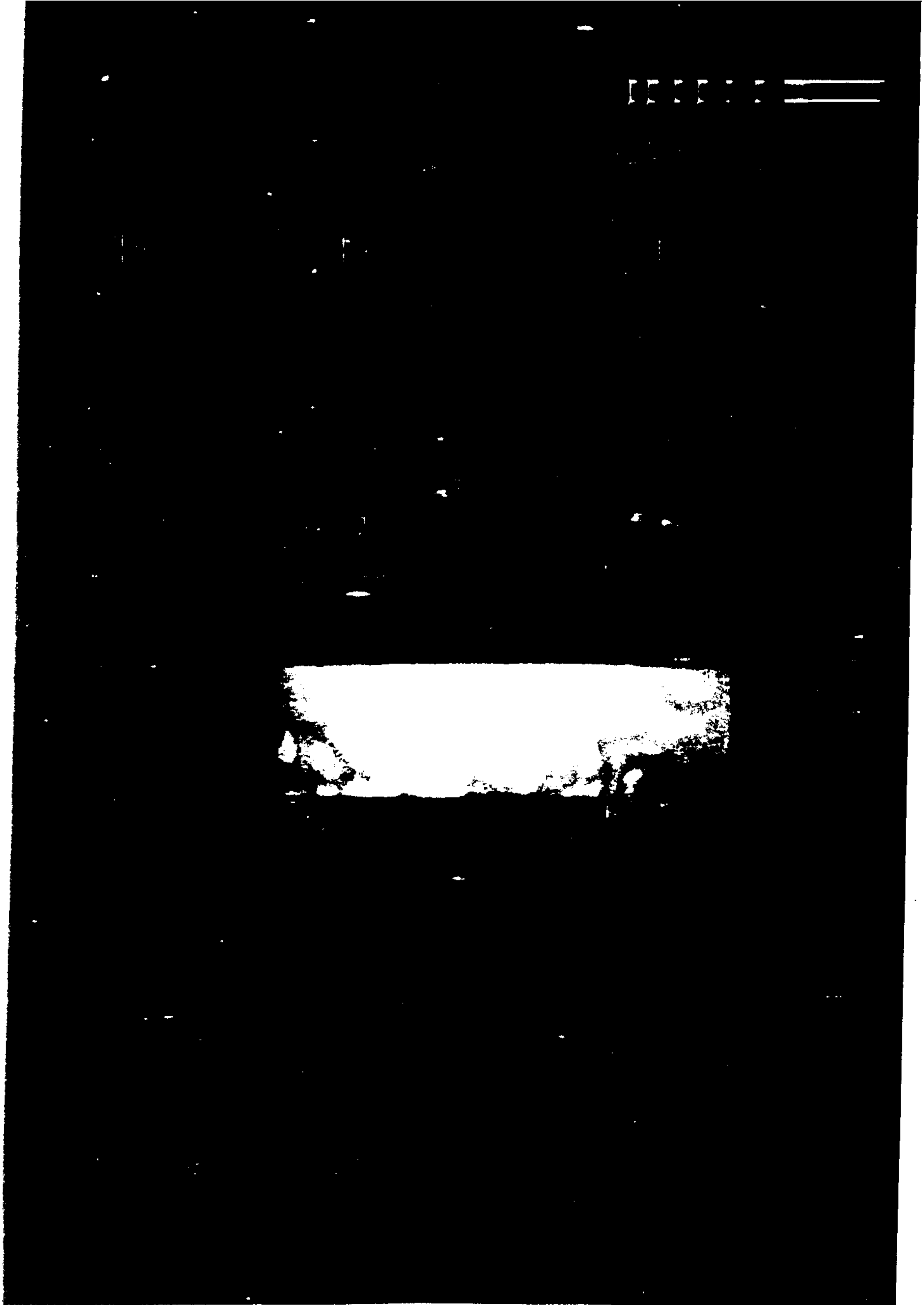
  At 22C, T6 grains have a radius of ~100nm

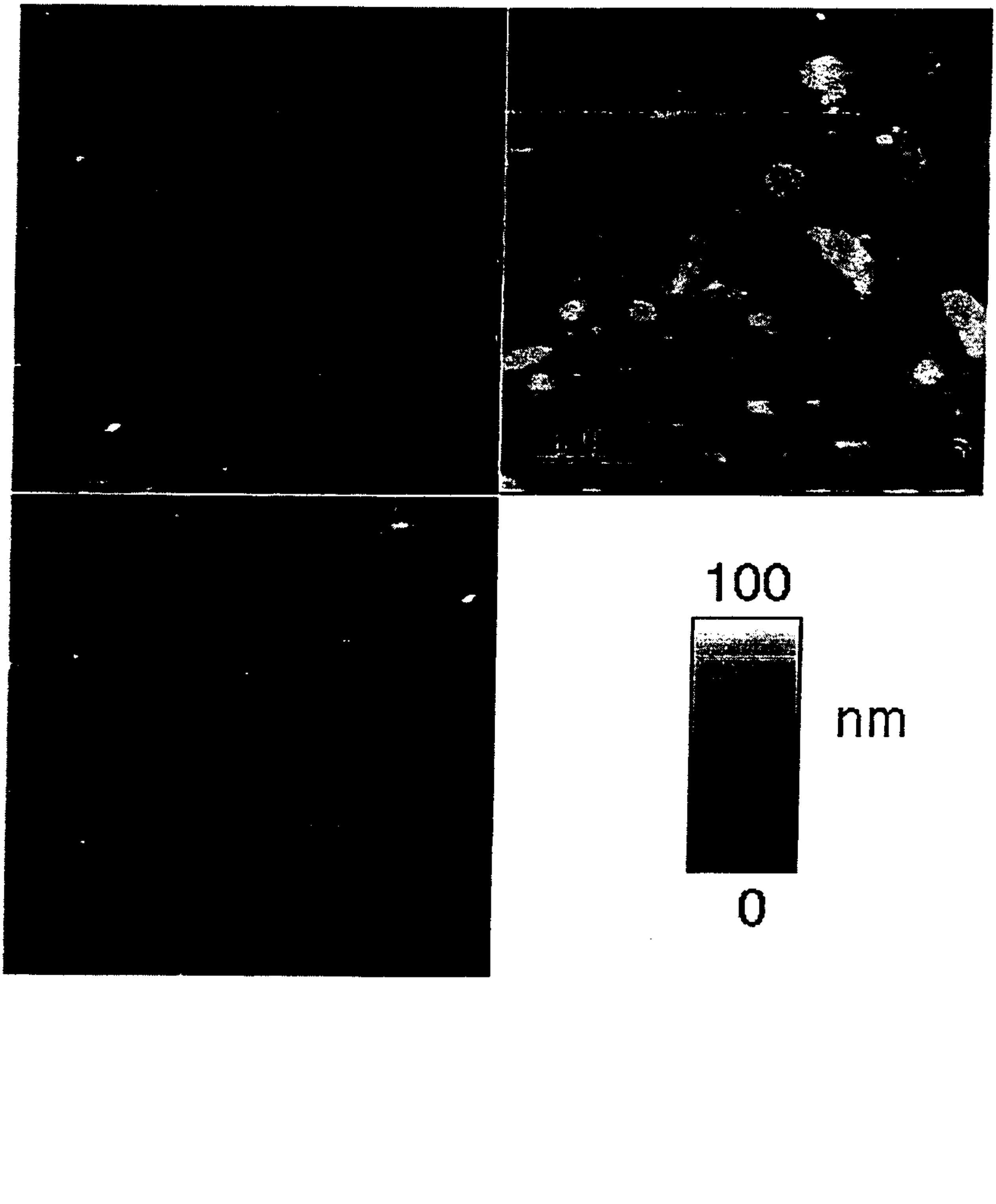
  At 150C, T6 grains have a radius of ~1000nm

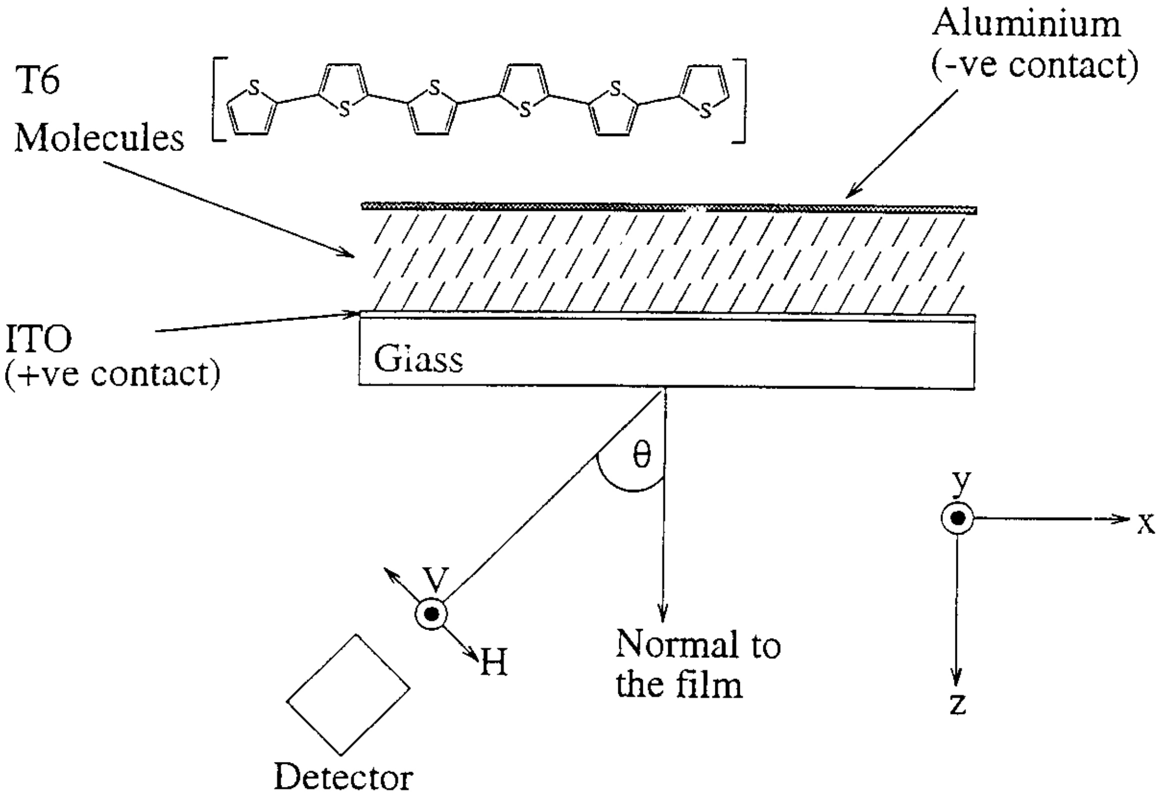

nature
FLEXIBLE LIGHT-EMITTING DIODES
DNA TECHNOLOGY
product review



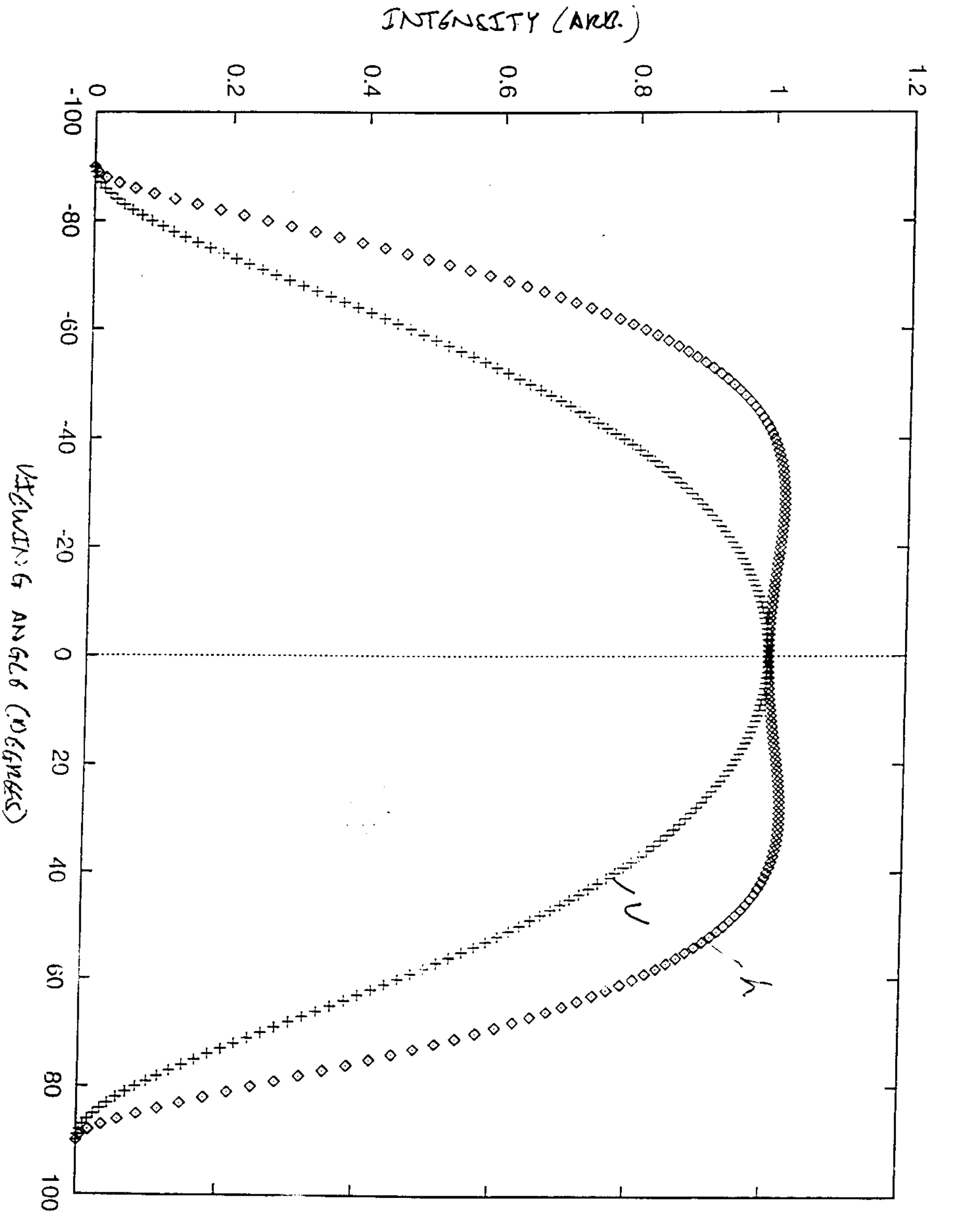





100
nm
0



Aluminium
(-ve contact)
T6
Molecules
ITO
(+ve contact)
Giass
θ
y
x
z
V
H
Normal to
the film
Detector


INTENSITY (ARB.)
VIEWING ANGLE (DEGREES)
0
0.2
0.4
0.6
0.8
1
1.2
-100
-80
-60
-40
-20
0
20
40
60
80
100
V
h

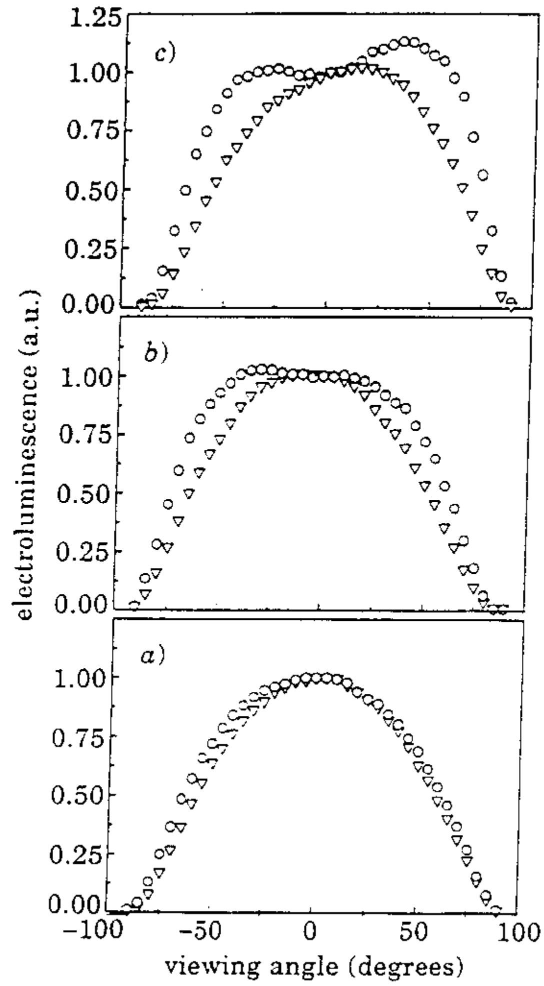


Fig. 3. – The angular dependence of emission from LEDs with αT6 deposited at the substrate temperatures indicated, for vertical (triangles) and horizontal (circles) polarisation. The data at different temperatures are offset for clarity. *a*) 155 °C, *b*) 104 °C, *c*) 22 °C. At each temperature the electroluminescence has been normalised to unity at the 0° viewing angle for the two polarisations.

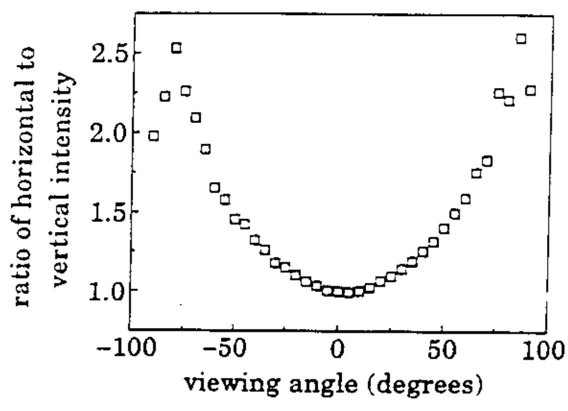
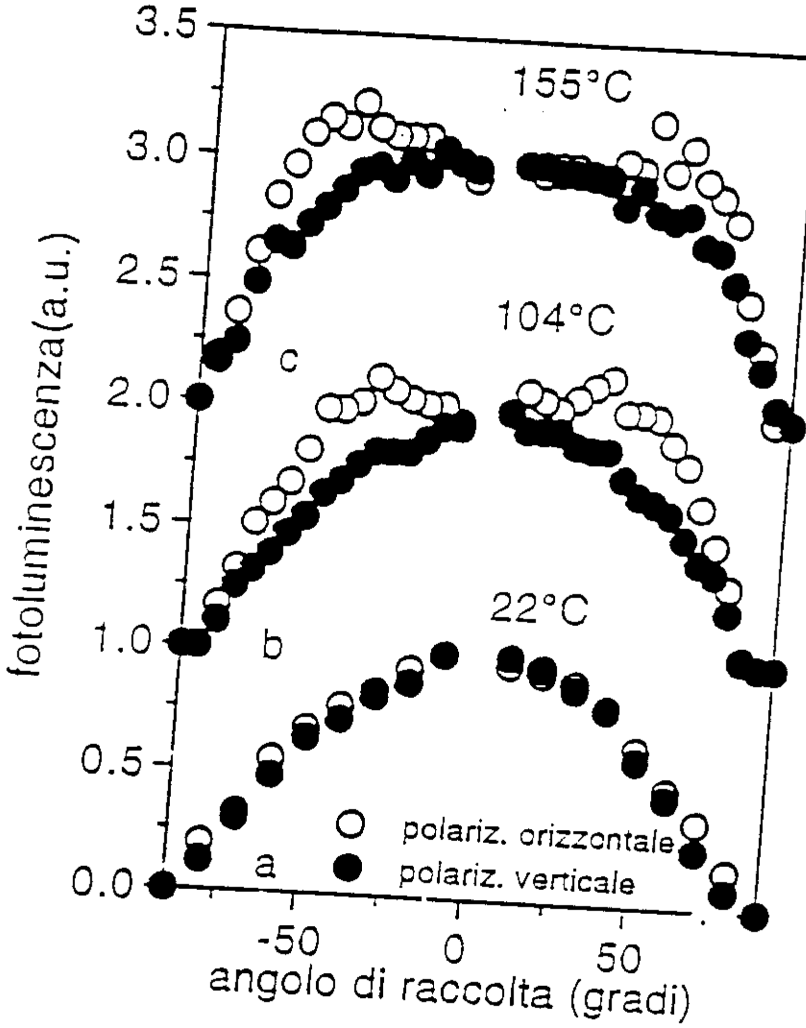
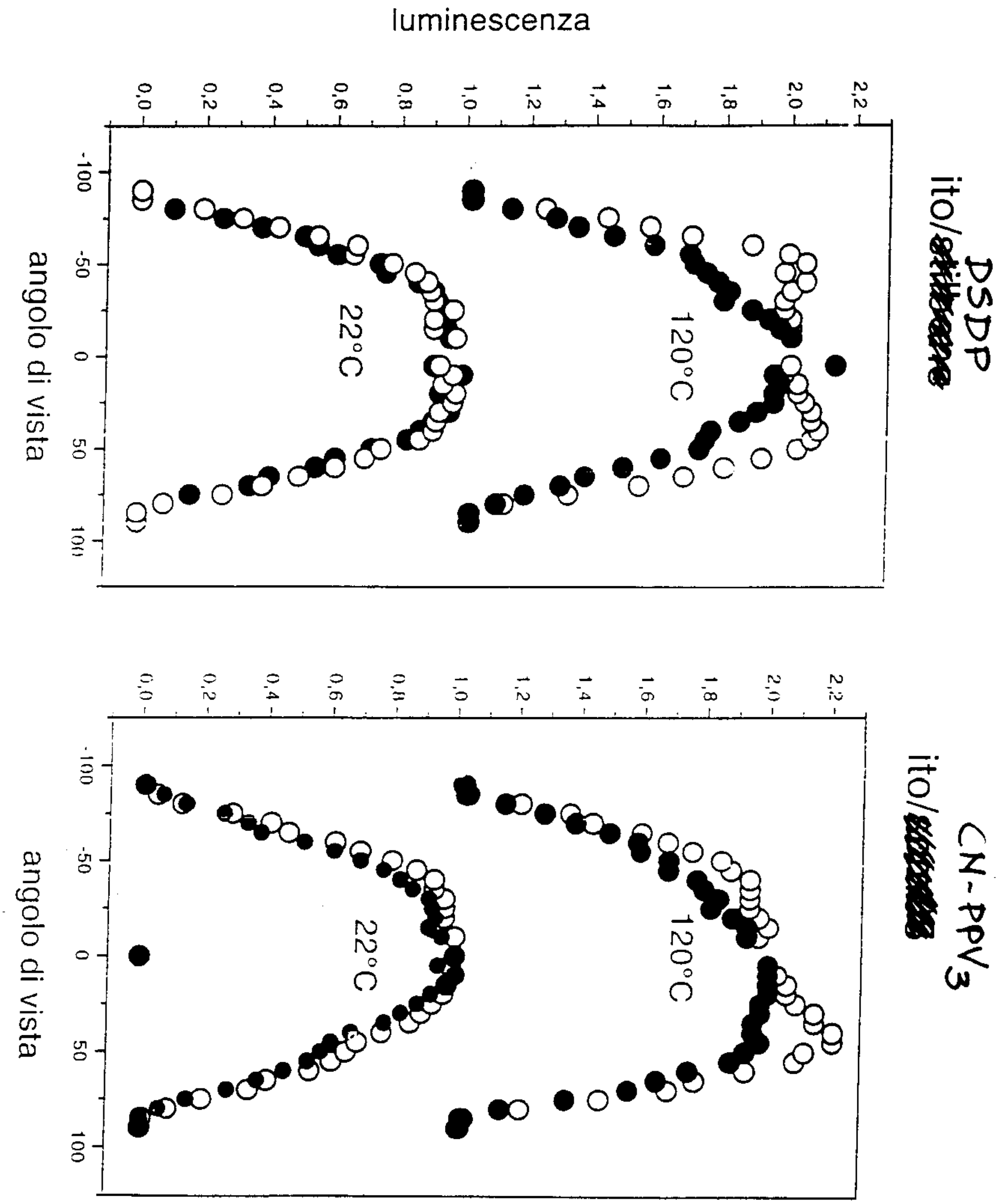
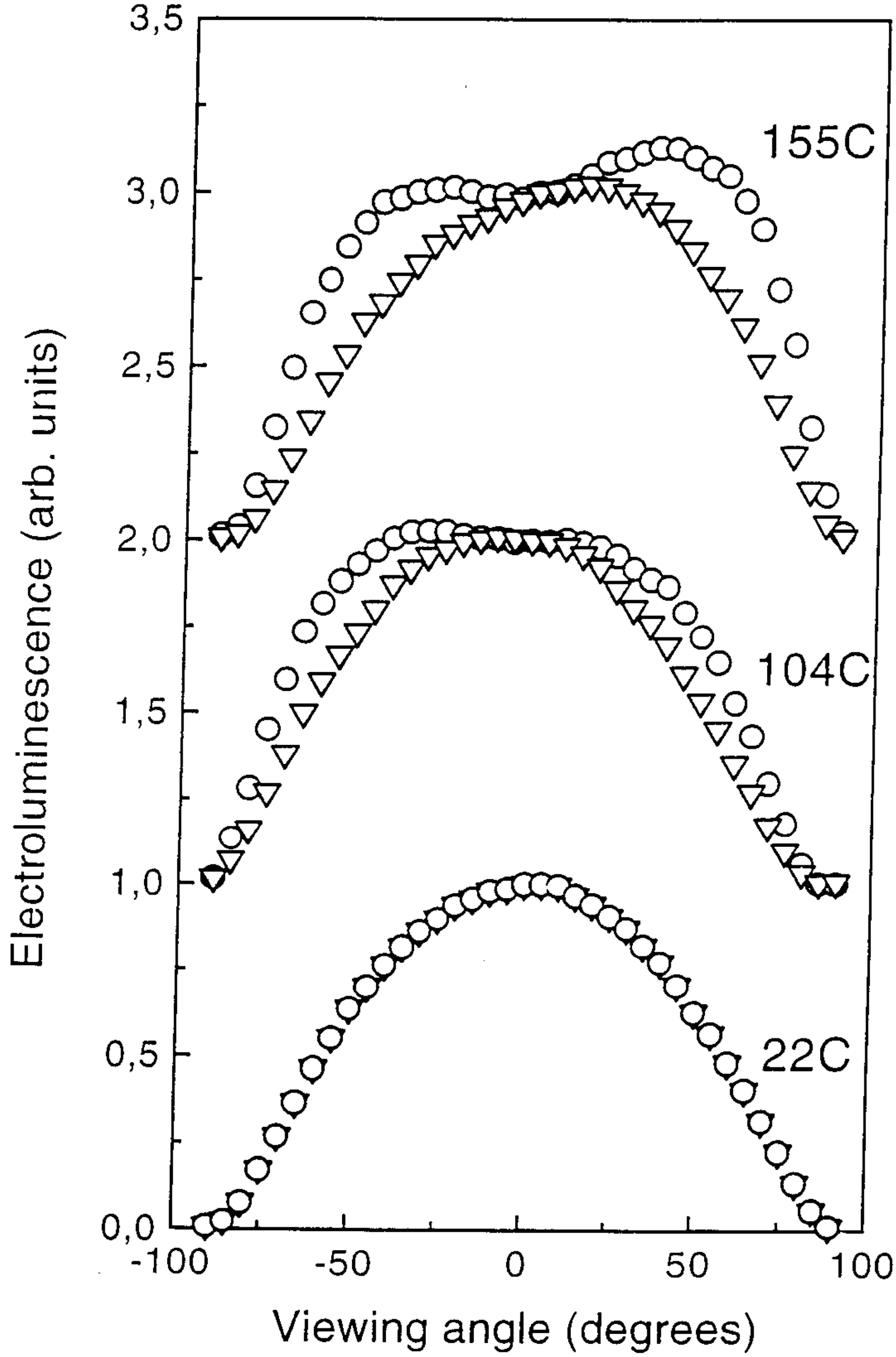


Fig. 4. – The ratio of horizontally-to-vertically polarised emission as a function of the viewing angle, for the device shown in fig. 3*c*) (155 °C film growth).


155°C
104°C
22°C
c
b
a
polariz. orizzontale
polariz. verticale
fotoluminescenza(a.u.)
angolo di raccolta (gradi)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-50
0
50


luminescenza
DSDP
ito/
120°C
22°C
angolo di vista
CN-PPV3
ito/
120°C
22°C
angolo di vista


3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
-100
-50
0
50
100
155C
104C
22C
Electroluminescence (arb. units)
Viewing angle (degrees)

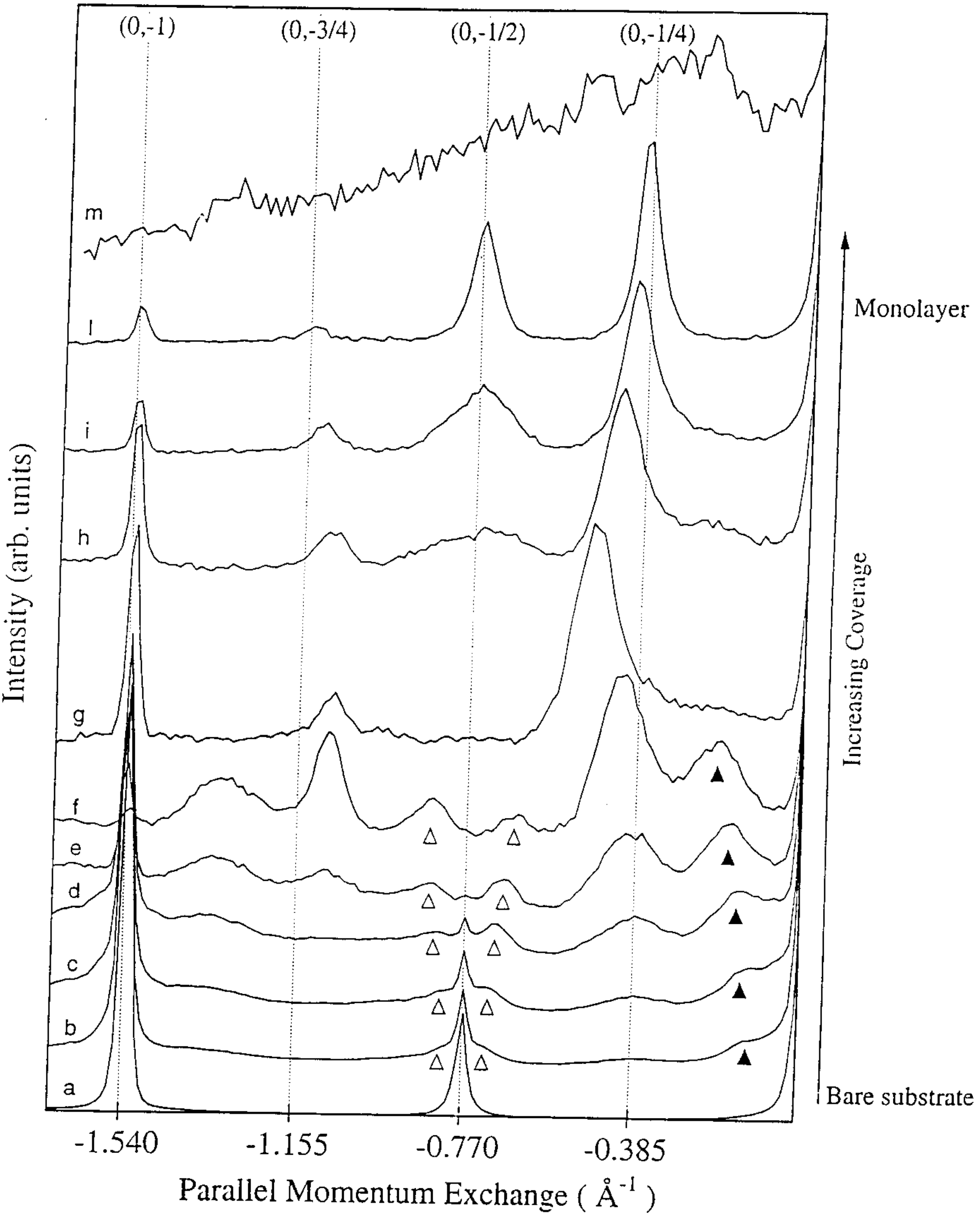


FIG. 1 by Buongiorno Nardelli et al.

Phys. Rev. B 53, no3 (1996)

a)

b)

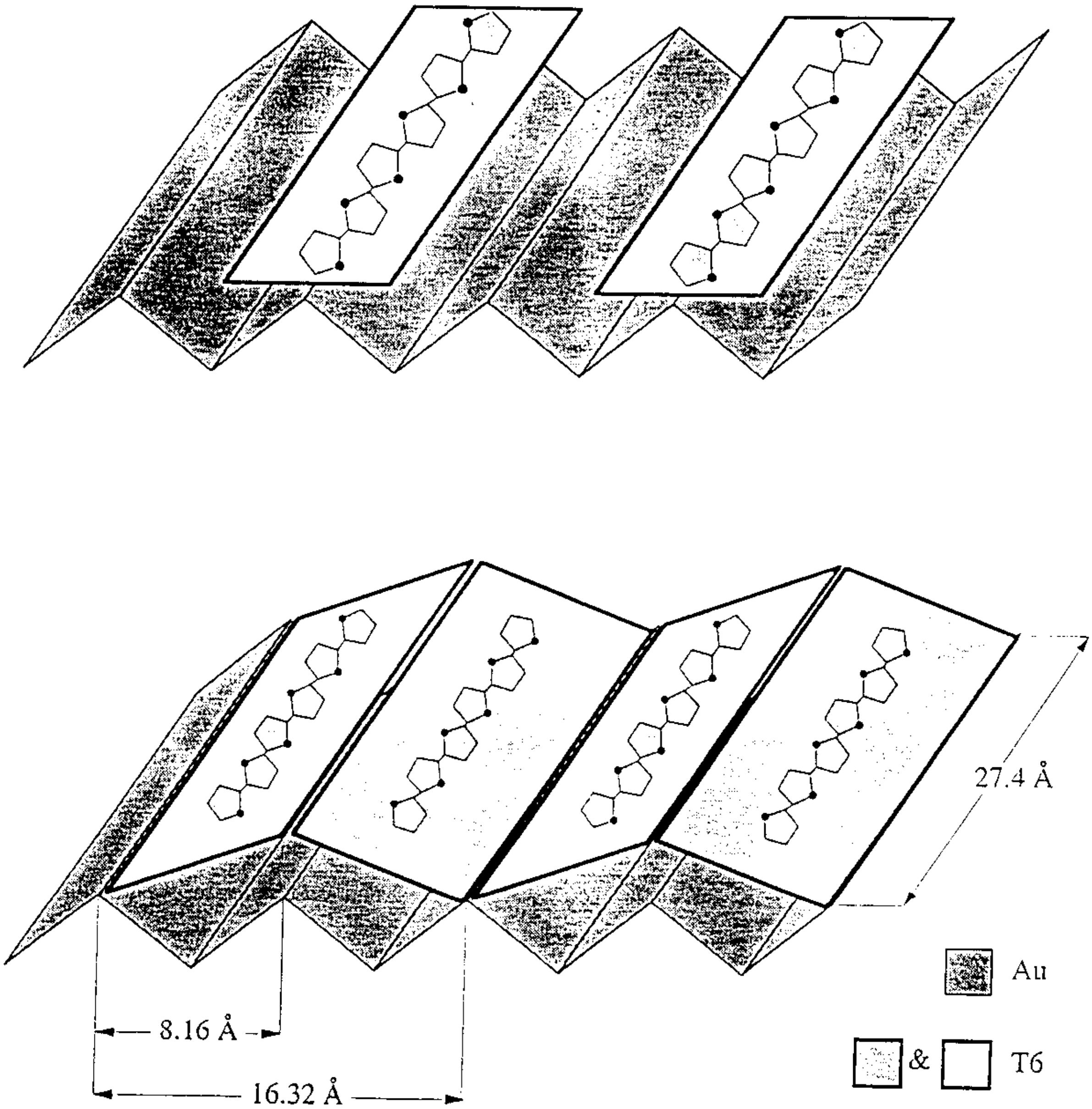


Fig. 2 by M. Buongiorno Nardelli et al. Phys. Rev. B, 53, 403 (1996)

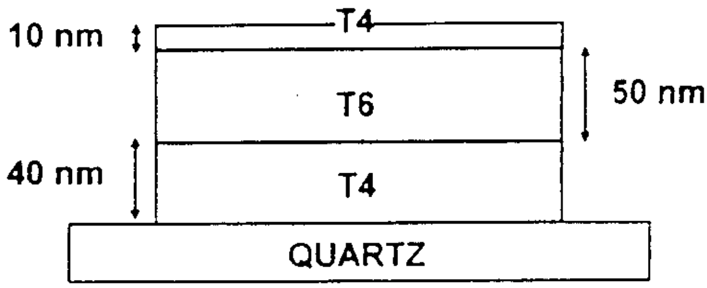


Fig. 1. Schematic representation of the three-layer structure of tetrathiophene (T4) and hexathiophene (T6) deposited on a quartz substrate by vacuum evaporation.

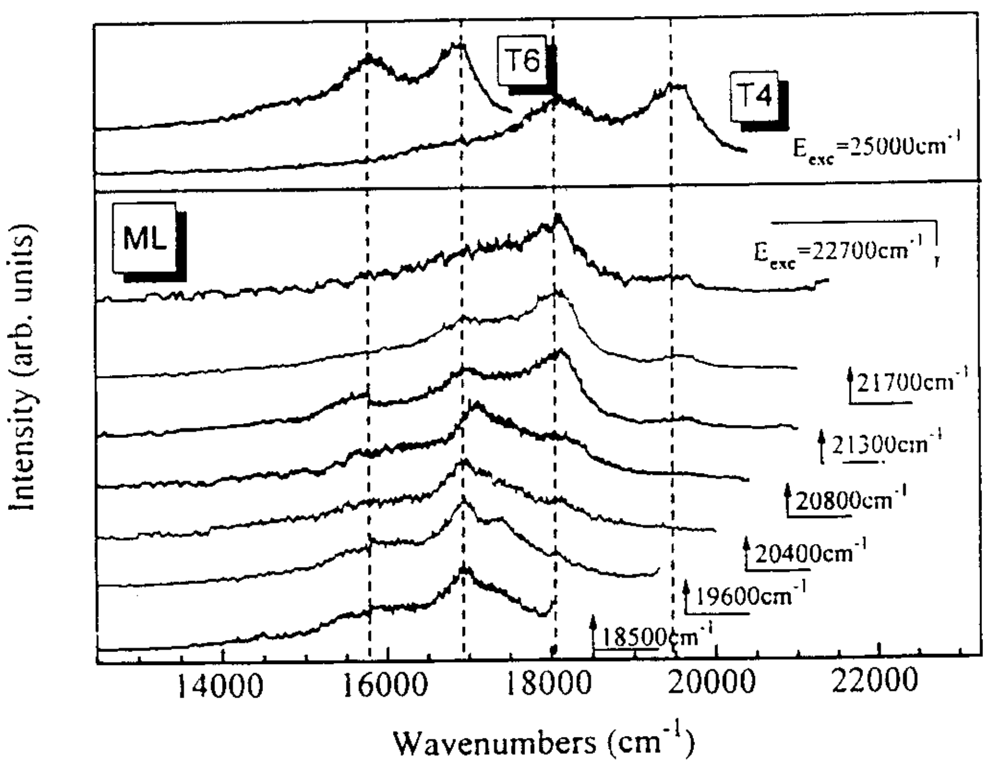


Fig. 2. Site-selective PL spectra of the multilayer (ML) structure and photoluminescence spectra of pure T4 and T6 films at $T = 10$ K. The excitation energy for each spectrum is indicated by arrows.

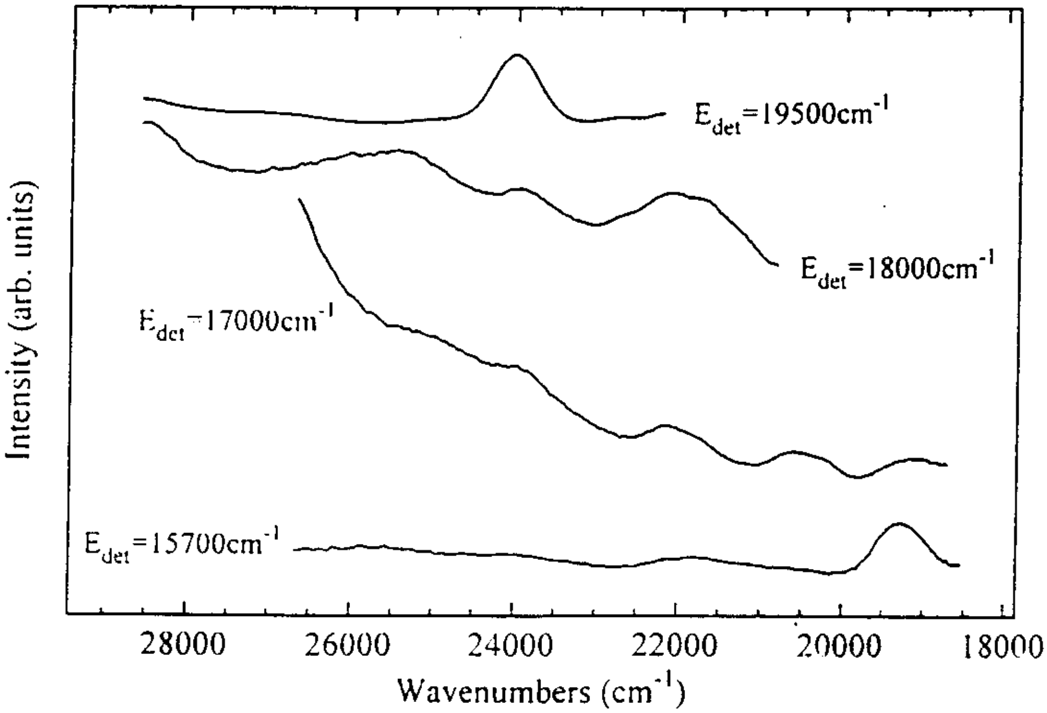


Fig. 3. Photoluminescence excitation spectra of the tetrathiophene/hexathiophene/tetrathiophene multilayer (ML) structure at $T = 10$ K. The spectra were measured by monitoring the ML emission bands at the spectral positions indicated by the dashed lines in Fig. 2.

M. Muccini et al. / Chemical Physics Letters 242 (1995) 207–211

4P

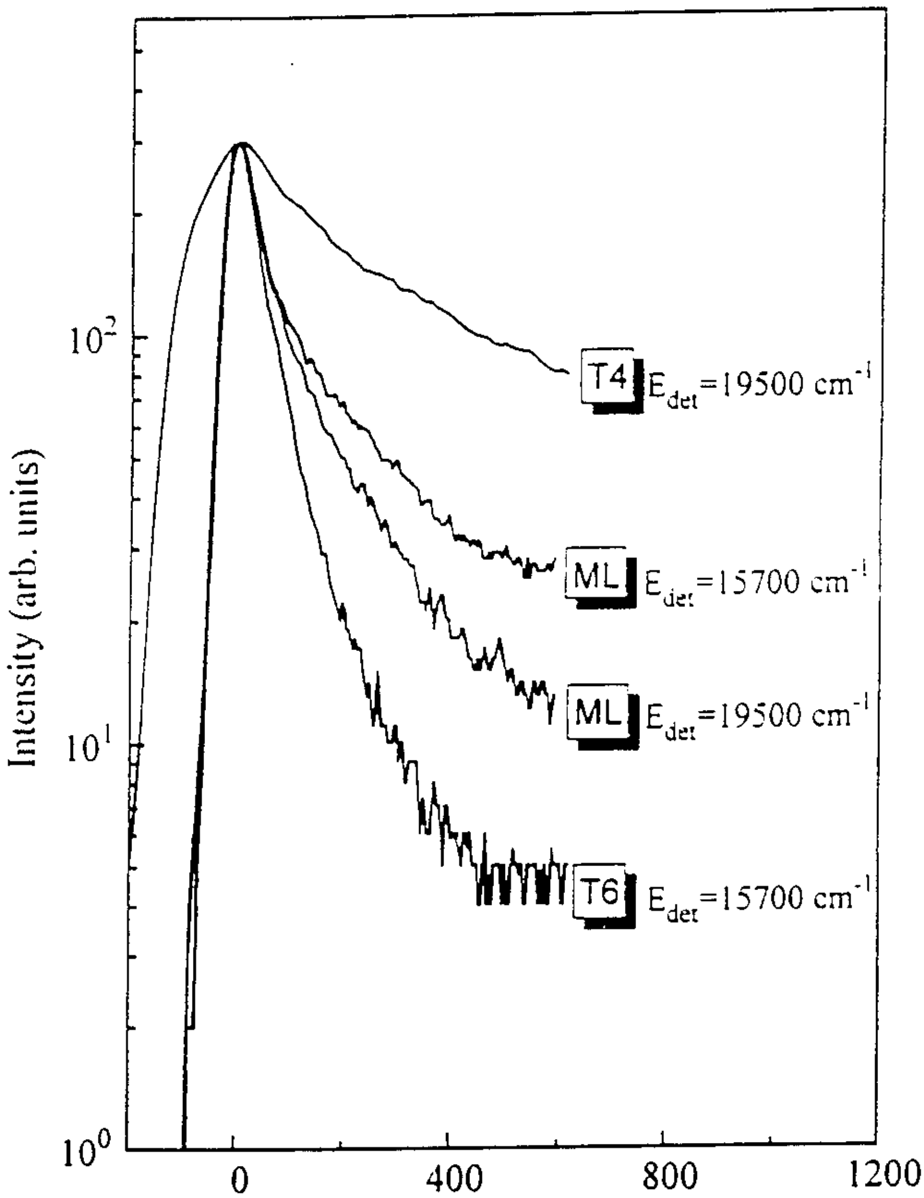


Fig. 4. Time-resolved photoluminescence spectra of the same emission peaks in the multilayer structure (ML) and in pure T4 and T6 films. All the measurements were performed by exciting with $E_{exc} = 25000$ cm^{-1} at $T = 10$ K. The detection energy for each spectrum is reported nearby.

M. Muccini et al. / Chemical Physics Letters 242 (1995) 207–211