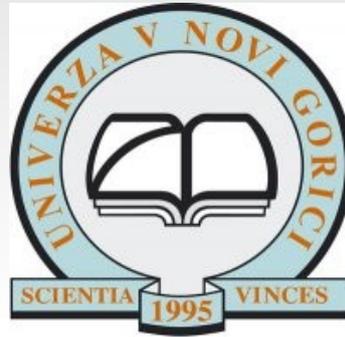


# Characterization of electric charge carrier transport in organic semiconductors by time-of-flight technique



**Raveendra Babu Penumala**

**Mentor: Prof. dr. Gvido Bratina**

**Laboratory of Organic Matter Physics**

**University of Nova Gorica**

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University of Nova Gorica

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## Electrical conductivity

Electrical conductivity is a measure of the transport of electric charge.

$$\sigma = J/E$$

$$\sigma = ne\mu_e \text{ for electrons,}$$

$$\sigma = pe\mu_h \text{ for holes.}$$

Total electric charge **conductivity** is

$$\sigma = (ne\mu_e + pe\mu_h)$$

n and p = density of charge carriers (n for electrons and p for holes) in  $\text{cm}^{-3}$

e = unit charge (C)

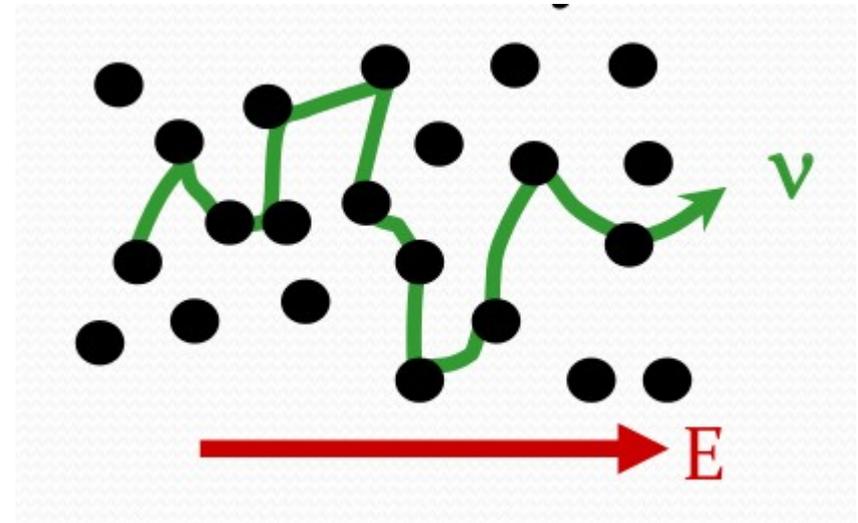
## Mobility of the charge carrier

- Mobility strongly depends on the nature, structure and purity of the material.
- The charge-carrier mobility is the major determining factor for the speed of electronic devices.

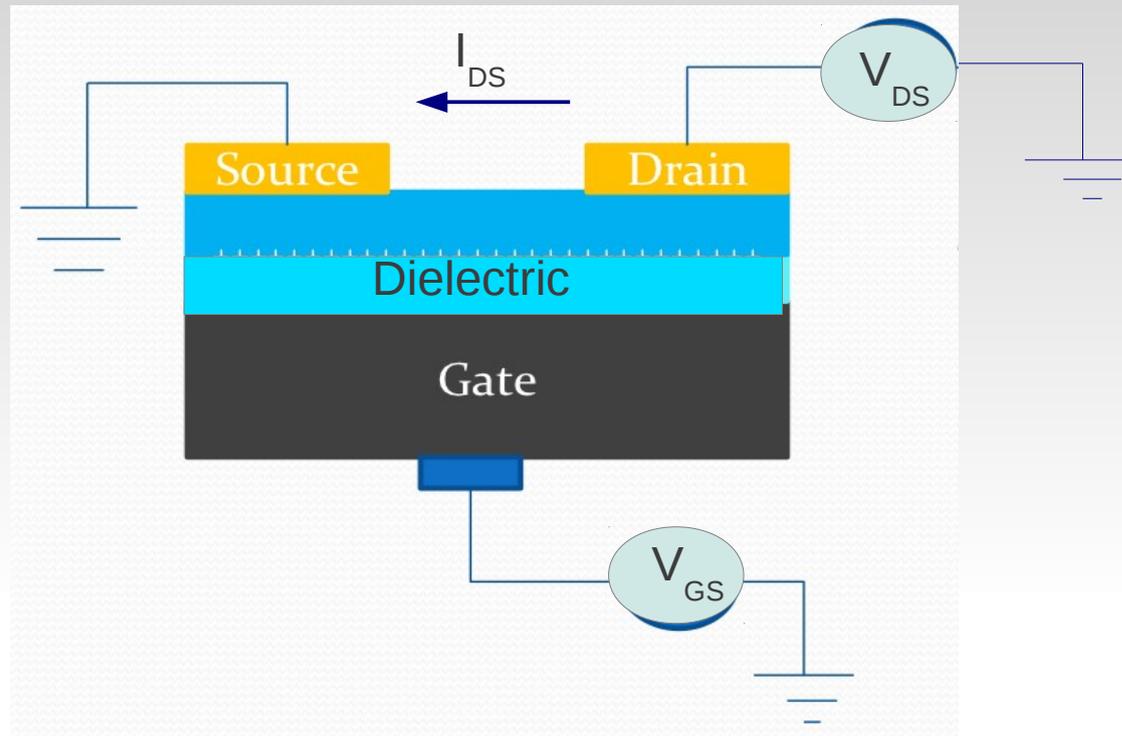
Charge carriers in a piece of material move with an average velocity in the presence of an electric field - **drift velocity**.

$$v = \mu E \quad [\text{cm/s}]$$

$$\mu = |v|/E \quad [\text{cm}^2/\text{Vs}]$$



# Field-Effect-Transistor (FET) mobility



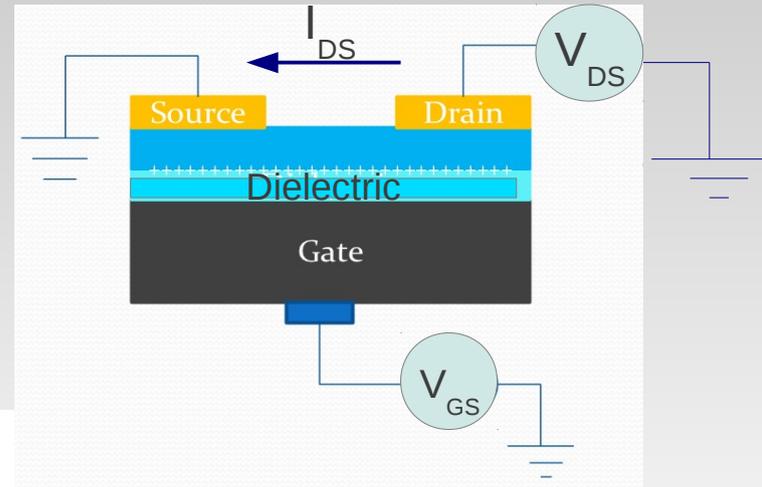
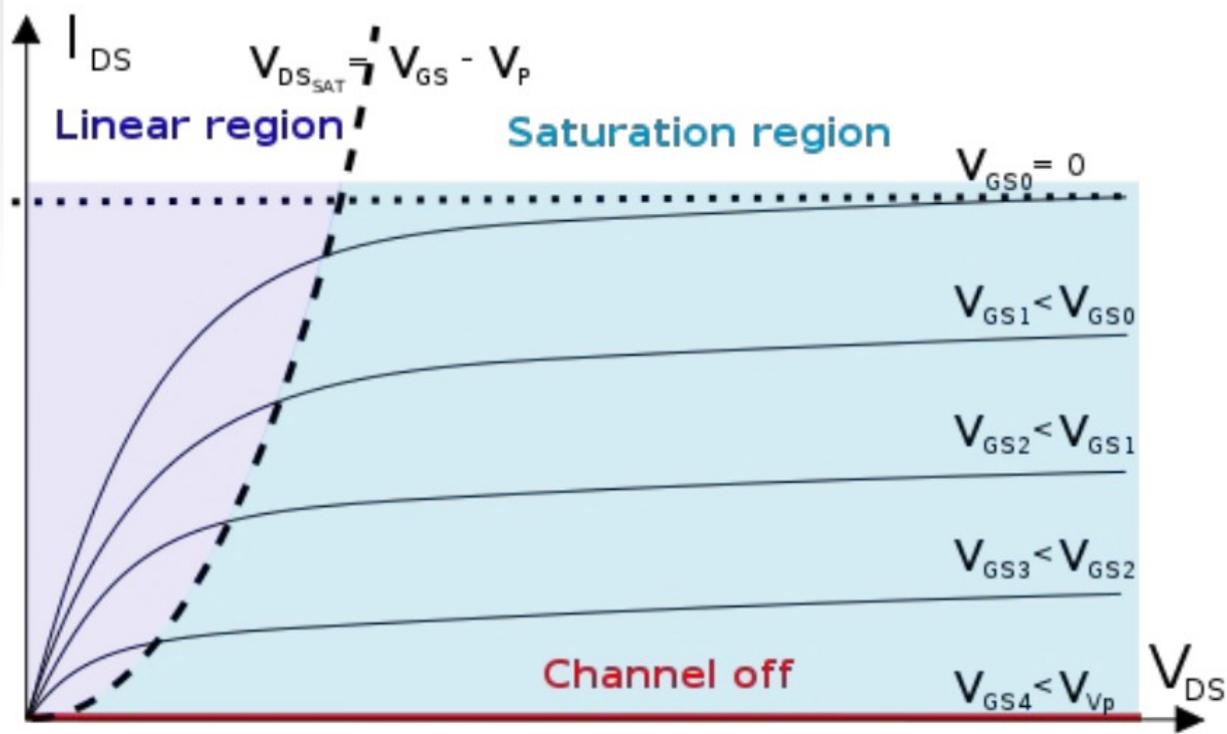
The measurement can work in two ways:

1. linear-region measurements

$$V_{GS} - V_{TH} > V_{DS}$$

2. saturation-mode measurements

$$V_{GS} - V_{TH} < V_{DS}$$



## For the linear region

$$\mu = \frac{I_{DS}}{C \frac{W}{L} \left( (V_{GS} - V_{TH}) V_{DS} - \frac{V_{GS}^2}{2} \right)}$$

## For the saturation region

$$\mu = \frac{I_{DS}}{C \frac{W}{2L} (V_{GS} - V_{TH})^2}$$

$W$  = width of the channel

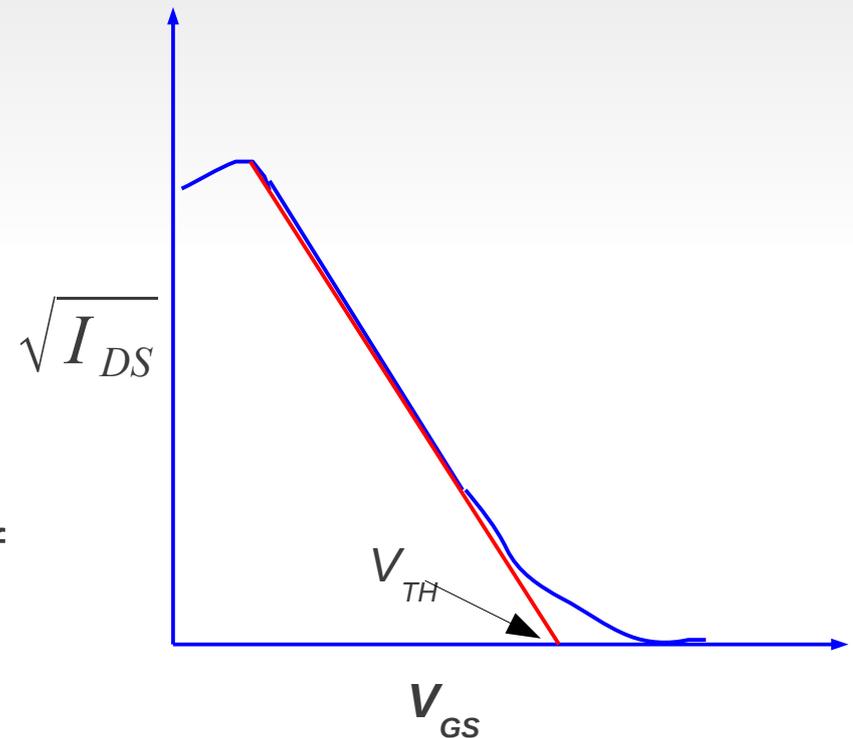
$L$  = length of the channel

$C$  = capacitance per unit area of the channel

$V_{GS}$  = gate-source voltage

$V_{DS}$  = drain-source voltage

$V_{TH}$  = threshold voltage



## Why Time-of-flight technique, why not FET

- For FET we need three electrodes
- Two voltage sources (one for gate-source, other one for drain-source).
- FET is time independent.
- We are not using any laser pulse to create photogenerated charge carriers in the FET operation.

## Time-of-flight Charge carrier mobility

Mobility is estimated from the time taken by the photoexcited carriers created at one electrode (photo injected) to reach the opposite (collecting) electrode.

$$\mu = \frac{v}{E} = \frac{L}{t_{tr}} \frac{L}{V} = \frac{L^2}{V t_{tr}}$$

$\mu$  = Mobility of the carriers

$v$  = Drift velocity of the carriers

$L$  = Separation between the electrodes

$E$  = Electric field strength

$V$  = Voltage applied

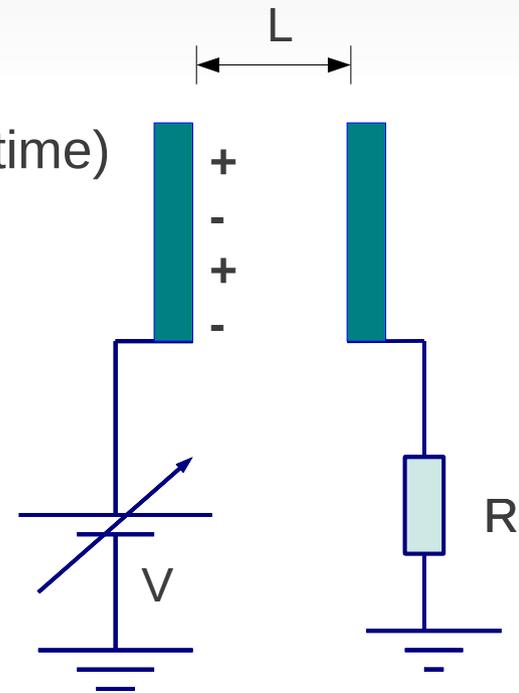
$t_{tr}$  = Transit time

## Time-of-flight characteristics

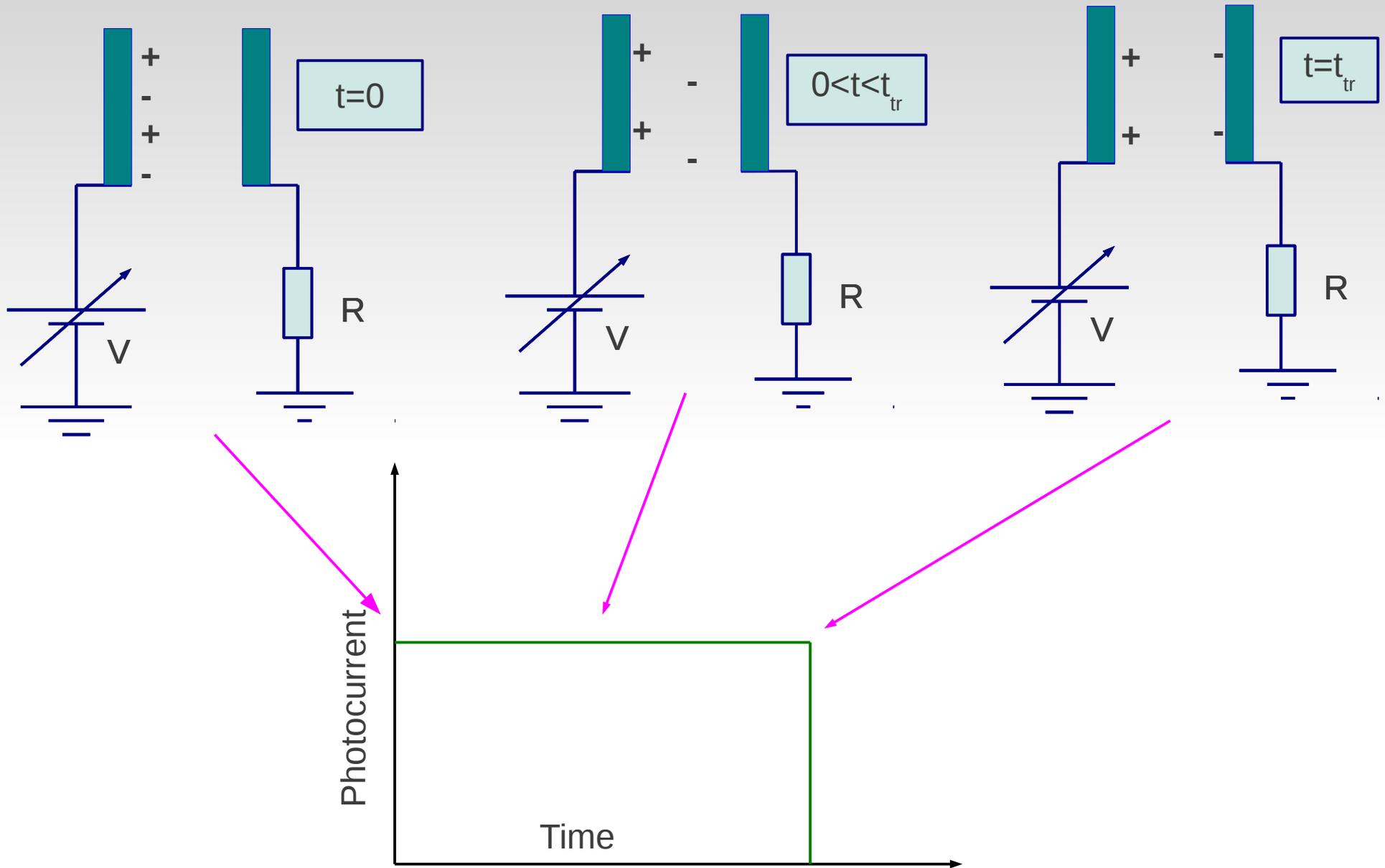
- TOF is used to study the charge carrier transport in low conductivity organic semiconductors.
- Also used to measure electron and hole mobility in organic semiconductors and other  $\pi$ -conjugated polymers theoretically and experimentally.
- Large availability of substrates (glass, sapphire, silicon).
- Variable channel length.
- Semiconductor deposition with different methods (spin-coat, drop-cast, dip-coat).
- Top-contact or bottom-contact electrodes.
- Charge injection and charge blocking electrodes needed.

## Experimental requirements:

1. Total photoinjected charge  $\ll CV$  (capacitor charge)
2. Electrodes – blocking contacts- non injecting electrodes
3. One electrode must be semitransparent
4. Excitation laser pulse width  $\ll t_{tr}$  (transit time)
5. Charge carrier recombination time  $\gg t_{tr}$  (transit time)
6. Dielectric relaxation time  $\gg t_{tr}$  (transit time)
7. Circuit response time  $RC \ll t_{tr}$  (transit time)



# Time-of-Flight mobility measurement



## Dispersive and non-dispersive transport of charge carriers

- The charge carrier transport in organic semiconductors is described by carrier **hopping** between localized states.
- Photo generated charge carriers are thermalizes. If time after that the charge thermalize is shorter than the transit time, then the photocurrent exhibits region of constant current.
- Tails represents the broadening of the photogenerated charge packet.
- Dispersive transport occurs when the thermodynamic equilibrium is not reached because the transit time is shorter than the time after the charge is thermalized.
- The dispersive character of the transport is evident in the continuous decay of the photocurrent.

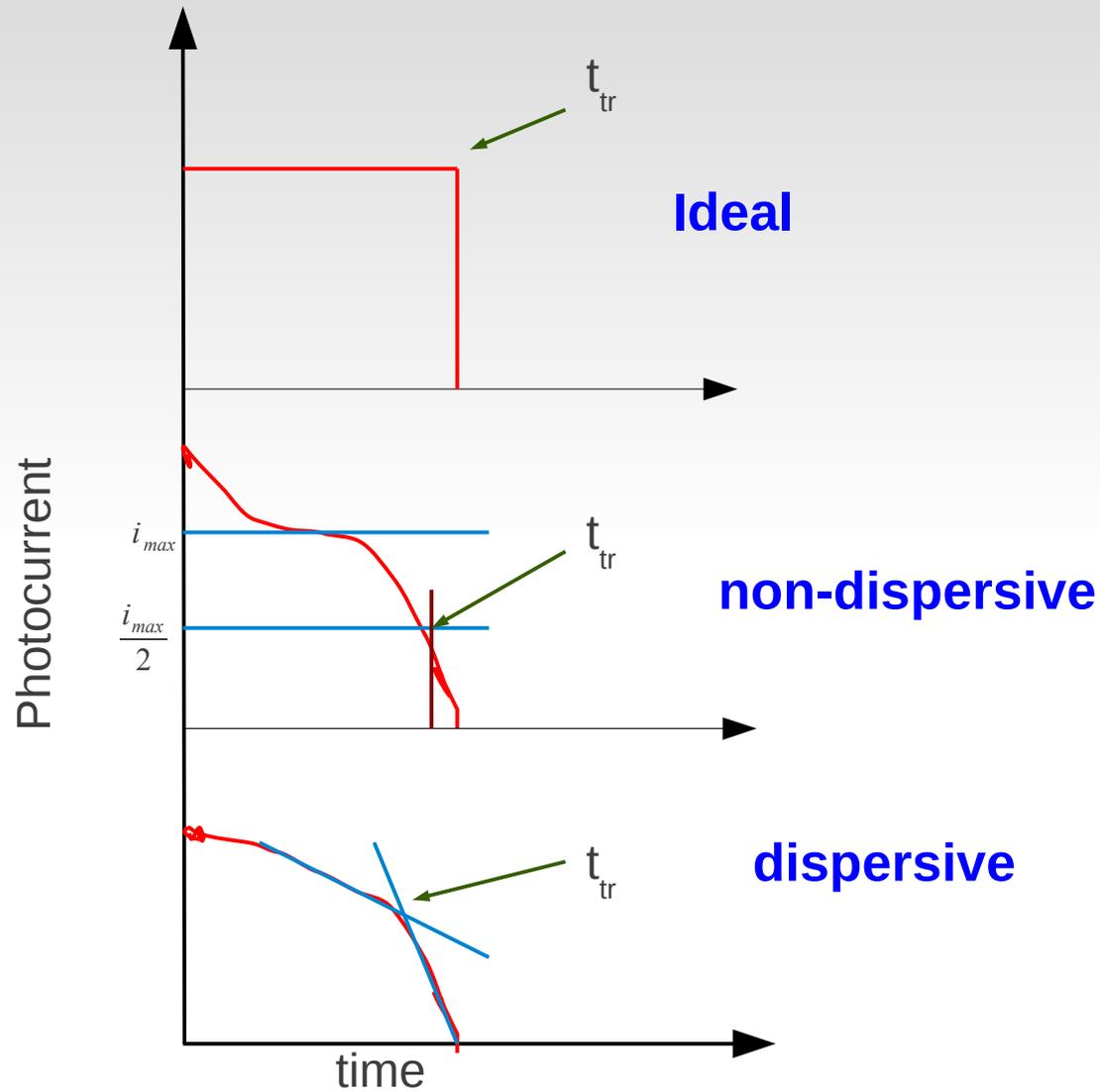
## Determination of the transit time:

The **time required** for the photoinjected carriers to traverse from one electrode to the other (collecting) electrode in the presence of electric field.

In the TOF technique charge carrier mobility can be measured in two ways.

- By using time when the fastest carriers reach the opposite contact (kink in the current).
- By measuring **average charge carrier mobility** from the time when the photocurrent has decayed to half of its plateau value.

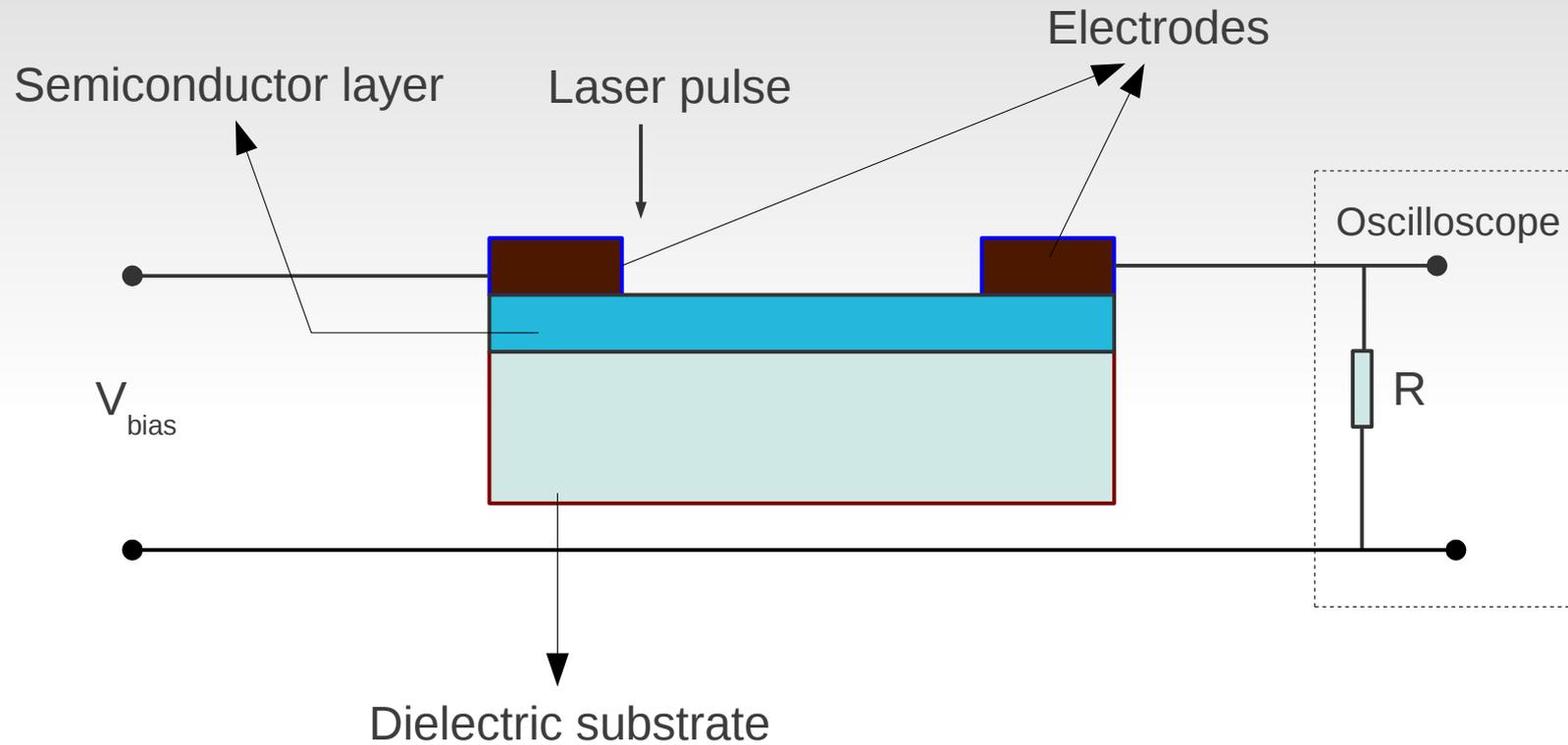
# Determination of the transit time:



## Typical TOF methods

1. Coplanar electrode structure
  2. Sandwich sample structure
- Coplanar electrode structure is used to measure the charge carrier transport of **thin** film organic semiconductors of only a few **nm** thickness.
  - Sandwich sample structure is used to measure the charge carrier transport of **thick** film organic semiconductors of tens of  **$\mu\text{m}$**  thickness.

# Coplanar electrode configuration



Laser used = Nd:YAG

Wavelength  $\lambda$  = 530 nm

Voltage source = Keithley 2400

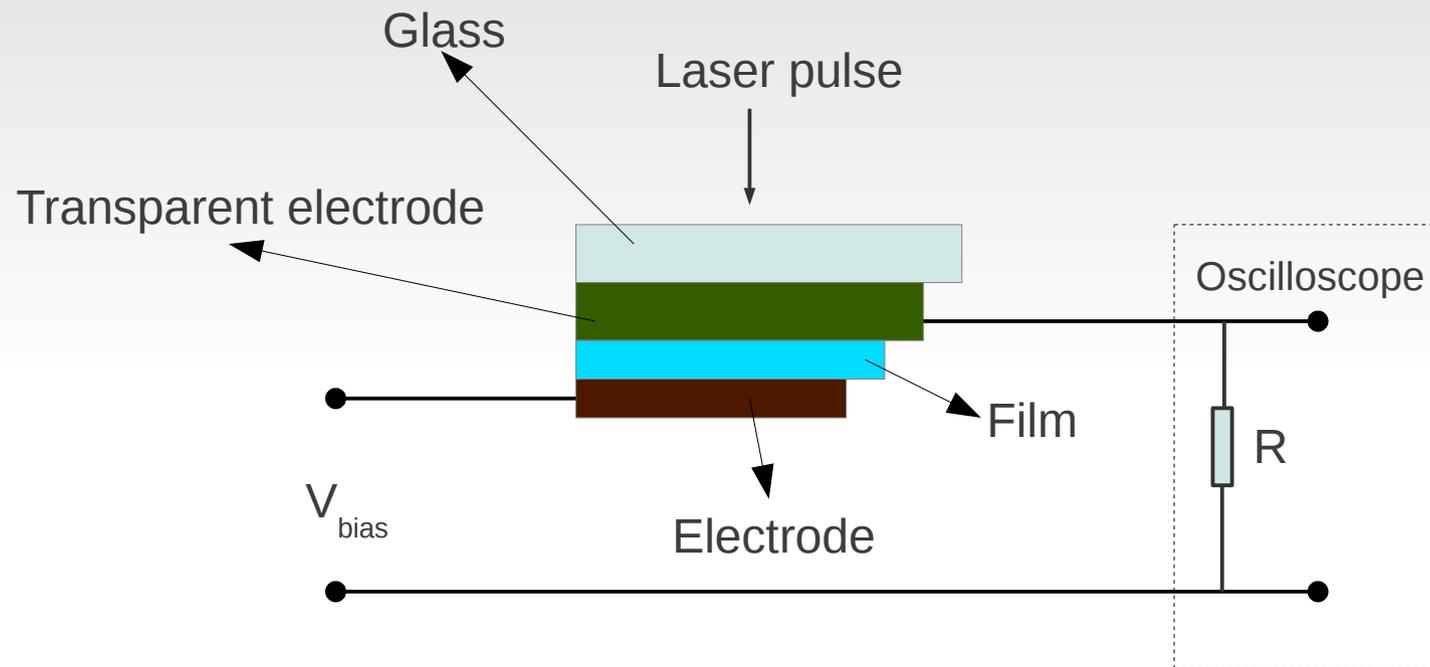
Oscilloscope = LeCroy @ 2.5 G Hz

Capacitance = 16 PF

Resistance = 1 M $\Omega$

Circuit response time  $\tau_{RC} = \mu \text{ sec}$

## Sandwich sample configuration



## TOF modes

The TOF can be used in two modes depending on the relation between The charge carrier transit time  $t_{tr}$  and external circuit time constant  $\tau_{RC}$

1. Differential (current) j-TOF:  $t_{tr} \gg \tau_{RC}$
2. Integral (charge) Q-TOF:  $t_{tr} \ll \tau_{RC}$

Depending on the film thickness  $d$  and material light absorption coefficient  $\alpha$ , the charge carriers can be photogenerated either at the surface or in the volume.

1. Surface photogeneration, when  $\alpha d \gg 1$
2. Volume photogeneration, when  $\alpha d \ll 1$

when  $\alpha d \approx 1$  , the effective film thickness  $d_{\text{eff}}$  should be used instead of real sample thickness  $d$  to calculate the charge carrier mobility:  $d_{\text{eff}} = d - d_L$

Where

$d$  = sample thickness

$d_L$  = reservoir thickness

$$d_L = \ln(Q_0/CV+1)/\alpha$$

$d_L = d$  (for volume photogeneration)

$C$  = capacitance

$V$  = external applied voltage

$Q_0$  = photogenerated charge carrier

- In the charge (Q-TOF) mode the carrier transit time is not clearly seen in the transients even in the ideal case, especially when the dispersive carrier transport is present.
- So experimentally it is convenient to estimate the time when the current equals half of its maximum value.

Then the transit time can be calculated as

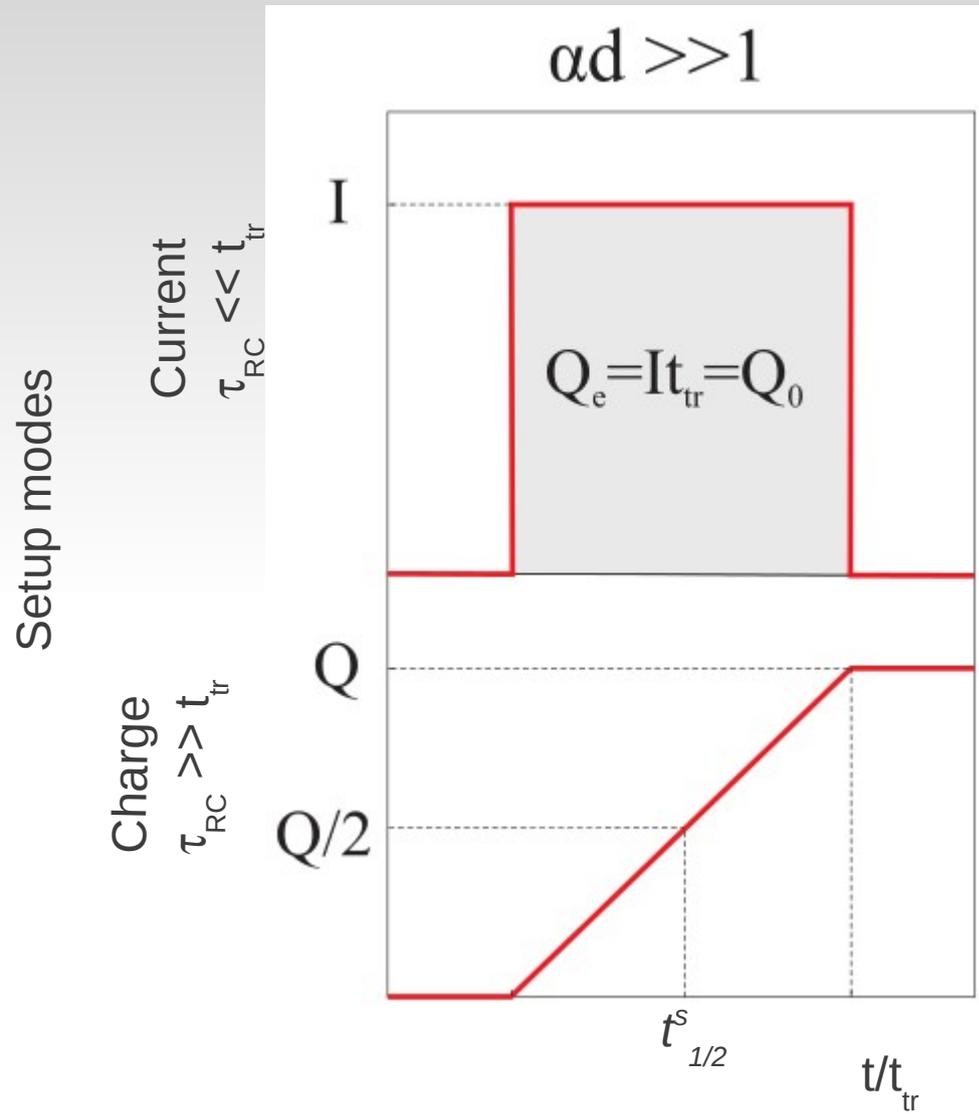
$$t_{tr}^s = 2 \times t_{1/2}^s$$

$t_{1/2}^s$  = current half-decay time for surface photogeneration

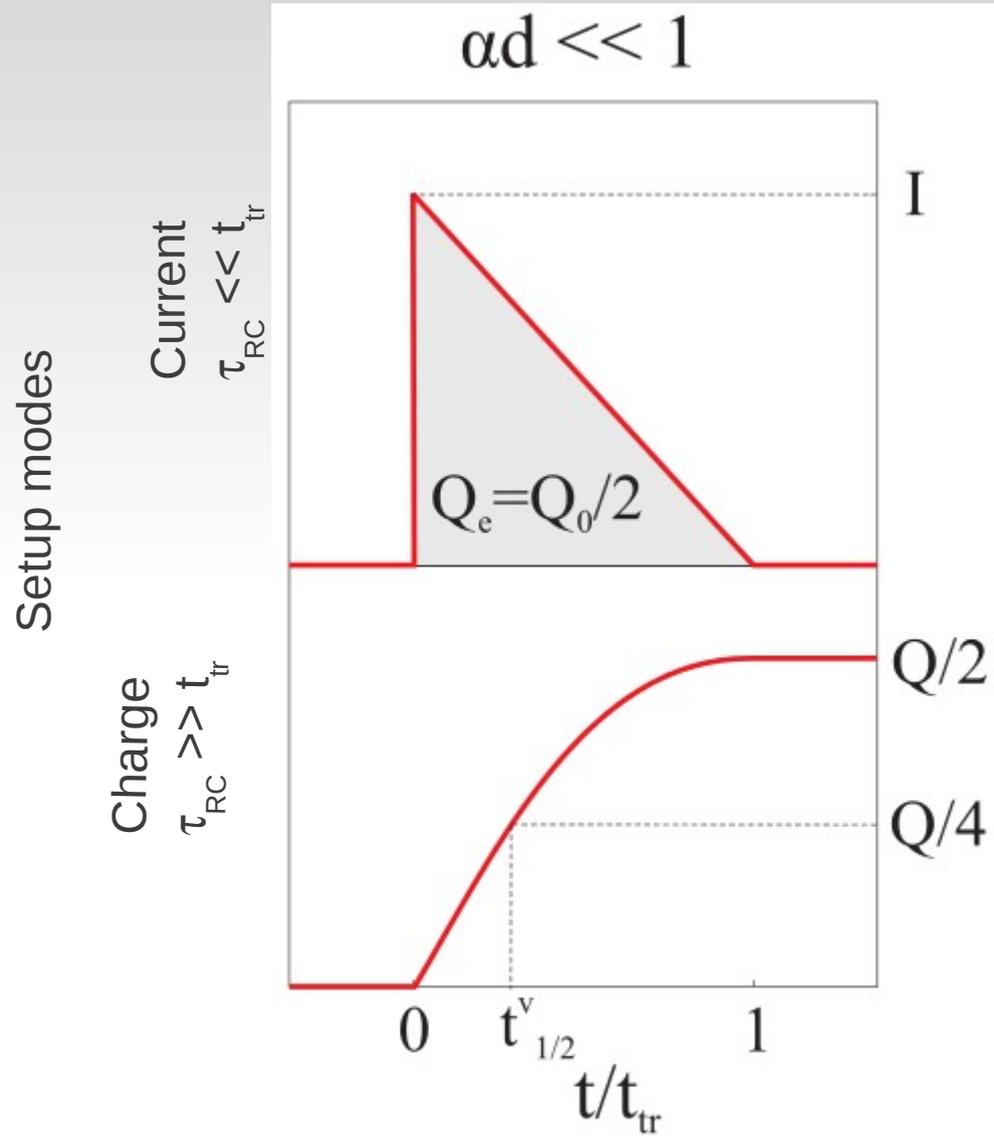
$$t_{tr}^v = \frac{\sqrt{2}}{(\sqrt{2}-1)} \times t_{1/2}^v$$

$t_{1/2}^v$  = current half-decay time for volume photogeneration

# Surface photogeneration

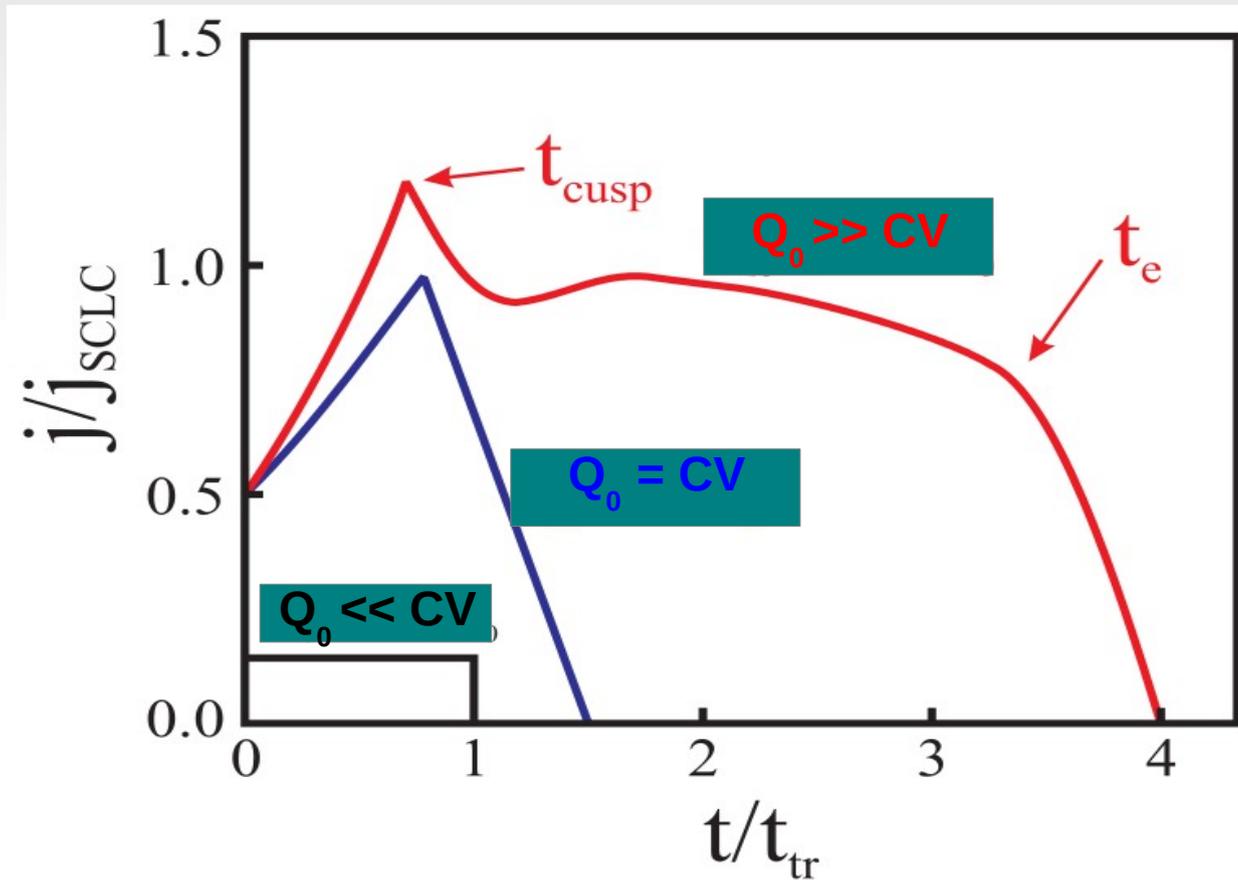


# Volume photogeneration



## High light intensity TOF

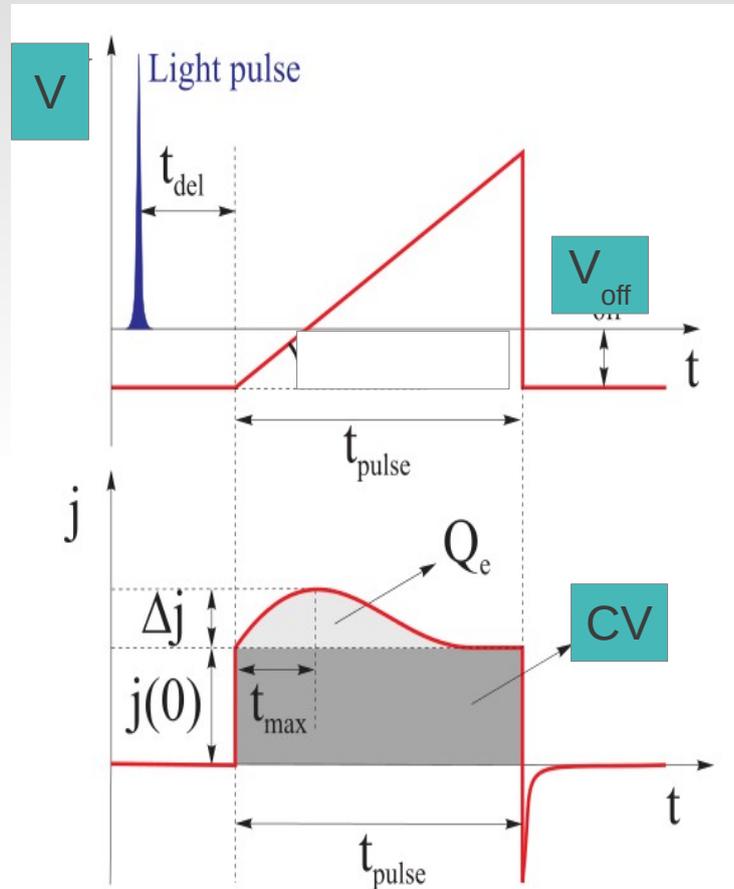
At high laser light intensity a charge carrier reservoir with more charge than  $CV$  is created in the film ( $Q_0 \gg CV$ )



## Charge Extraction by Linearly Increasing Voltage (CELIV)

- CELIV is used to study the charge carrier drift mobility in high conductivity organic semiconductors.
- The experimental setup of CELIV is same as in TOF, expect that a linearly increasing voltage pulse is used.
- The most significant advantage of the CELIV technique is that *directly and simultaneously* measure the charge carrier mobility and concentration as a function of time, electric field and temperature.

# Charge Extraction by Linearly Increasing Voltage (CELIV)



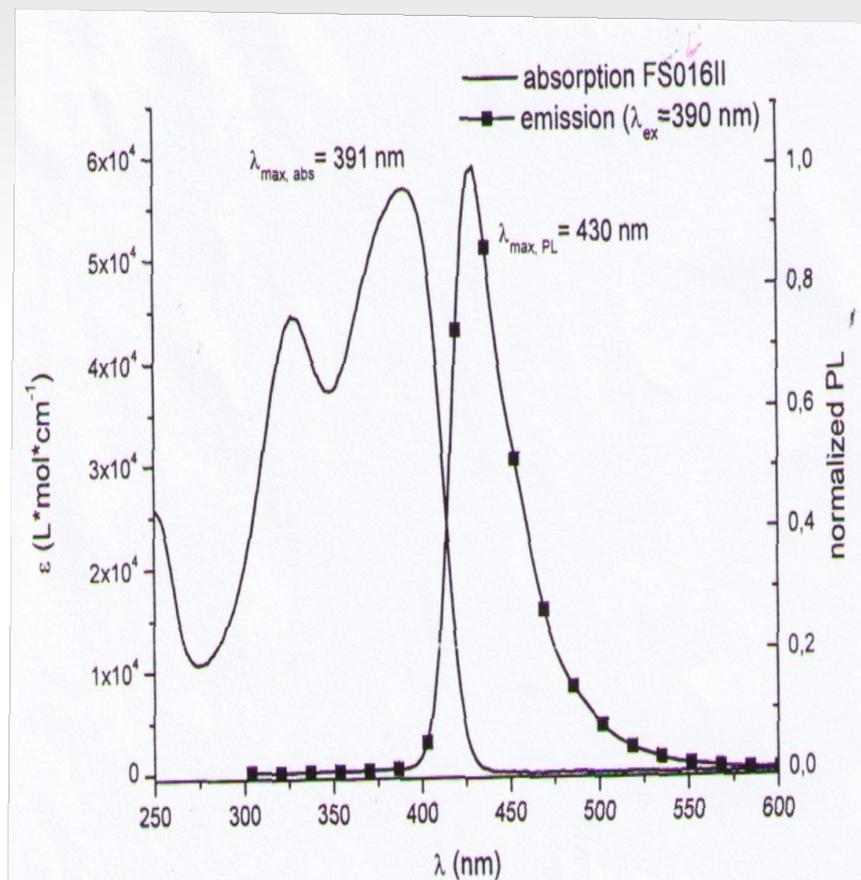
## Limitations of CELIV

- At least one blocking contact is required, otherwise the extraction current will overlap with the conductivity current and the characteristic extraction feature will be hidden.
- Electric field dependencies are inaccurate due to constantly increasing applied voltage.
- The  $V_{\text{off}}$  can significantly increase the dark current and disturb the measurements.

## Undergoing and future experiments

We are doing TOF measurements on P3HT and triangulene-polymer

Molecular weight of triangulane-polymer = 17.8 g/mol

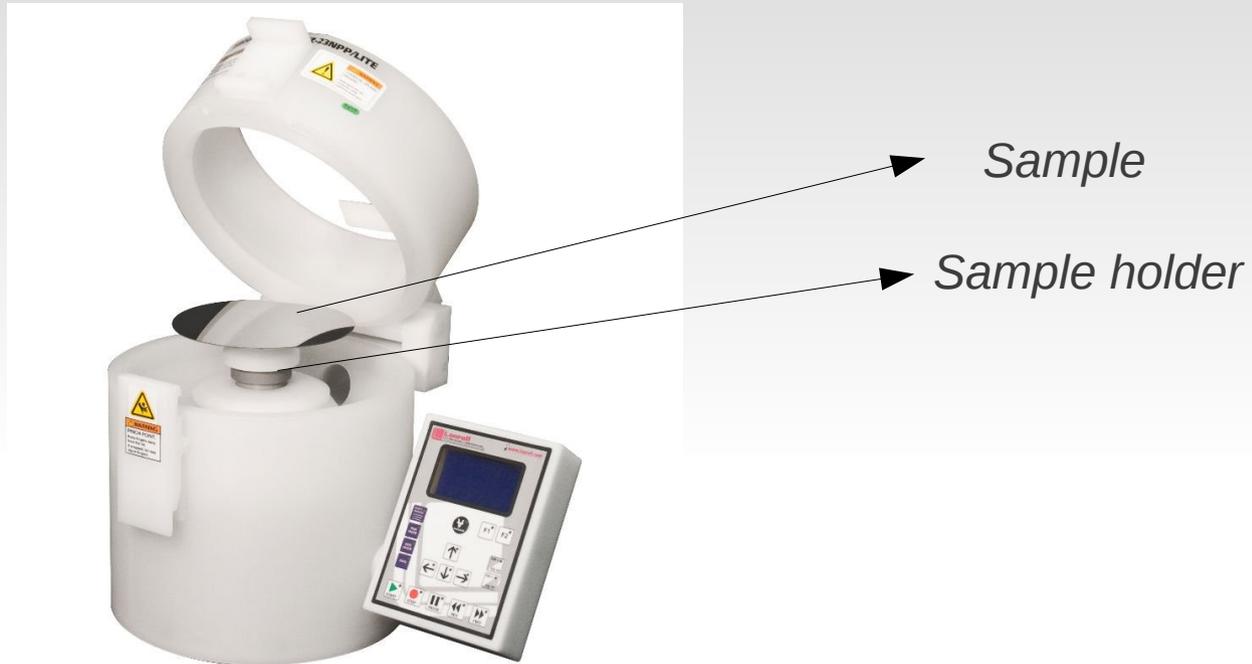


Absorption and emission spectra of triangulene-polymer

## Sample preparation

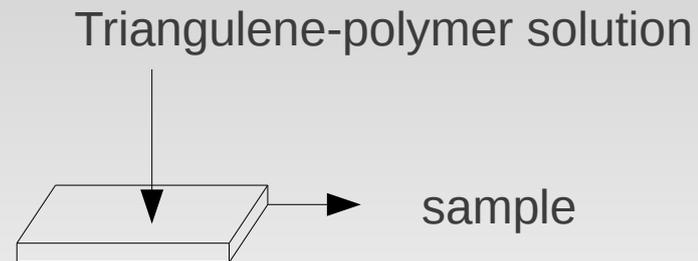
1. Spin coating
  2. Drop casting
  3. Dip coating
- The powdered shaped triangulane-polymer is rinsed with toluene solution (3 g/l).
  - Toluene is absolute solvent for organic materials.
  - Deposited Al electrodes on the sample.

# 1. Spin coater

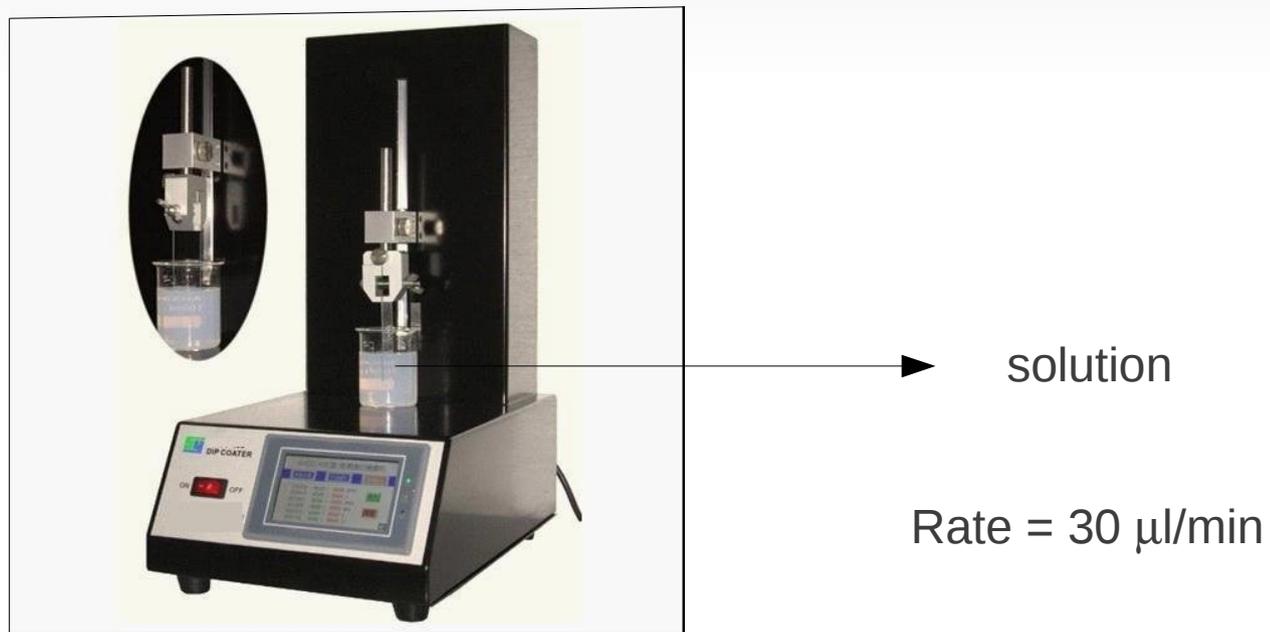


- Liquid shaped triangulene-polymer is spin coated on the sample (sapphire substrate) with 1500 rpm for 1 minute and transferred in to hot plate for 1 hour @ 60° C.

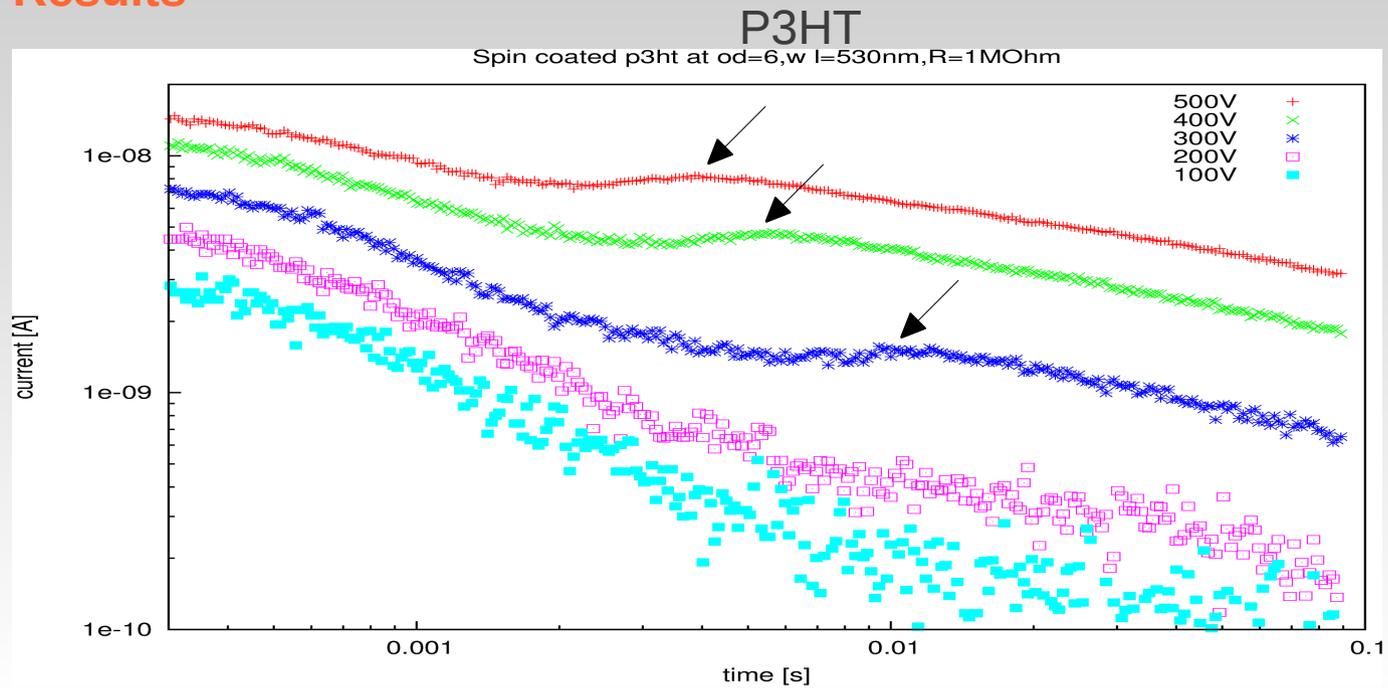
## 2. Drop casting



## 3. Dip coating



# Results



$$\mu = \frac{L^2}{V_{bias} \times t_{tr}} \quad L = 100 \mu\text{m}, R = 1\text{M}\Omega, \lambda = 530 \text{ nm}$$

$V_{bias}$ [V]	$t_{tr}$ [s]	$\mu = [\text{cm/Vs}]$
500	$3.77 \cdot 10^{-3}$	$5.30 \cdot 10^{-5}$
400	$5.72 \cdot 10^{-3}$	$4.37 \cdot 10^{-5}$
300	$10.74 \cdot 10^{-3}$	$3.10 \cdot 10^{-5}$

## Conclusions

- Electrical mobility of the organic materials can be estimated by TOF method.
- Coplanar electrode configuration is used to measure TOF mobility for **thin** films of organic semiconductors of few **nm** thickness.
- For Coplanar electrode configuration  $t_{tr} \ll \tau_{RC}$
- Sandwich sample structure is used to measure TOF mobility for **thick** films of organic semiconductors of tens of  **$\mu\text{m}$**  thickness.
- Solution require for preparing coplanar electrode configuration is less than the preparation of sandwich sample structure.

# Thank you