# Lecture 8:
# Ch.7: Exciton dissociation and charge photogeneration in pristine and doped conjugated polymers

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

2009. 4. 16 & 21.

Changhee Lee
School of Electrical Engineering and Computer Science
Seoul National Univ.
chlee7@snu.ac.kr





## Large exciton binding energy?

- Organic semiconductor: small band width, low dielectric constant (3~4).

Photoexcitation → formation of excitons with strong Coulomb energy
e.d. poly-diacetylene (PDA), Eg~0.5 eV.

## Mechanism of the carrier generation upon photoexcitation.

- The applied electric field appears to enhance the carrier generation efficiency upon photoexcitation.

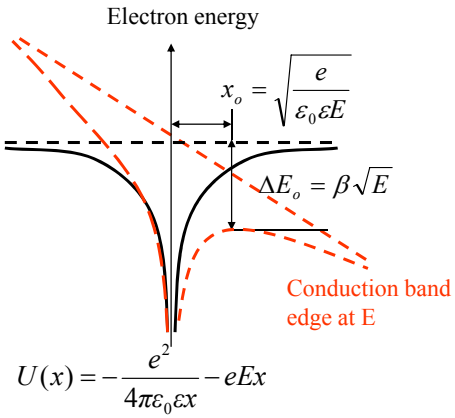
→ Reduction of the thermal ionization energy for the separation of two charges under their mutual Coulomb attraction.

(1) Poole-Frenkel mechanism

(2) Onsager mechanism

## Poole-Frenkel mechanism of carrier generation






Energy barrier in the presense of the field

$$E_b = E_0 - \Delta E_0 = E_0 - (\frac{e^2}{4\pi\varepsilon_0\varepsilon x_0} + eEx_0) = E_0 - \beta\sqrt{E},$$

where $\beta = \sqrt{\frac{e^3}{\pi\varepsilon_0\varepsilon}}$ and $x_0$ is obtained from

$$\frac{d}{dx}(-\frac{e^2}{4\pi\varepsilon_0\varepsilon x} - eEx)\Big|_{x_0} = 0.$$

Probability of electron escape due to thermal excitation in the presense of field :

$$e^{-E_0/kT} e^{\beta\sqrt{E}/kT} = e^{-E_0/kT}[1 + \frac{\beta\sqrt{E}}{kT} + \frac{1}{2!}(\frac{\beta\sqrt{E}}{kT})^2 + \cdots].$$

Steady-state rate equation

$$\frac{dN}{dt} = I_{ph} - \frac{N}{\tau_r} - \frac{N}{\tau_i} = 0.$$

Geminate recombination rate ← → Exciton dissociation rate

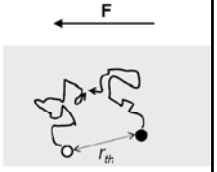
The efficiency of dissociation : $\eta = \frac{N/\tau_i}{I_{ph}} = \frac{1}{1 + \frac{\tau_i}{\tau_r}} = \frac{1}{1 + \frac{1}{\nu\tau_r} e^{E_0/kT} e^{-\beta\sqrt{E}/kT}}.$



## Onsager theory of geminate recombination



Equation of Brownian motion : $\frac{\partial f}{\partial t} = \frac{kT}{e}(\mu_1 + \mu_2)\nabla\cdot(e^{-\frac{U}{kT}}\nabla f e^{\frac{U}{kT}})$




Probability that two oppositely charged carriers are separated by an external electric field, E, as a function of the initial separation of the carriers, $r_0$, and orientation of the field, assuming that the carrier motion is described by hopping transport.

$$p(r,\theta,E) = e^{-A}e^{-B}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{A^m}{m!}\frac{B^{m+n}}{(m+n)!} \qquad A = \frac{e^2}{4\pi\varepsilon_0\varepsilon rkT}, \quad B = \frac{eEr}{2kT}(1+\cos\theta)$$

If the efficiency of production of thermalized ion pairs per absorbed photon is $\phi_0$ and the initial spatial distribution of separation between ions of each ion pair is g(r,θ), the overall generation efficiency is given by

$$\phi(E) = \phi_0\int p(r,\theta,E)g(r,\theta)d^3r \qquad g(r) = \frac{1}{4\pi r_0^2}\delta(r-r_0)$$

$$\phi(r_0,E) = \phi_0\frac{kT}{eEr_0}e^{-A}\sum_{m=0}^{\infty}\frac{A^m}{m!}\sum_{n=0}^{\infty}[1 - e^{-\frac{eEr_0}{kT}}\sum_{l=0}^{m+n}(\frac{eEr_0}{kT})^l\frac{1}{l!}] = \phi_0\frac{kT}{eEr_0}e^{-A}e^{-\frac{eEr_0}{kT}}\sum_{m=0}^{\infty}\frac{A^m}{m!}\sum_{n=0}^{\infty}\sum_{m+n+1}^{\infty}(\frac{eEr_0}{kT})^l\frac{1}{l!}$$

$$= \phi_0 e^{-\frac{r_c(T)}{r_0}}[1 + \frac{1}{2!}(\frac{e}{kT})r_cE + \frac{1}{3!}(\frac{e}{kT})^2 r_c(\frac{1}{2}r_c - r_0)E^2 + \frac{1}{4!}(\frac{e}{kT})^3 r_c(r_0^2 - r_0r_c + \frac{1}{6}r_c^2)E^3 + \ldots]$$

where $r_c(T) = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT}$ : critical Onsager distance

D. M. Pai and R. L. Enck, Phys. Rev. B 11, 5163 (1975)

# Onsager theory of geminate recombination

Onsager model:
Geminate recombination of a localized charge-carrier pair is the primary process responsible for limiting the efficiency of charge photogeneration in a wide class of condensed phases such as amorphous semiconductors, molecularly-doped polymers and molecular crystals.

The parameters used in the fitting are the initial yield ($\phi_0$) and separation of thermalized ion pairs ($r_0$). The final rate-determining step in photogeneration is the overcoming of a field-modulated Coulomb barrier with the aid of thermal fluctuations.

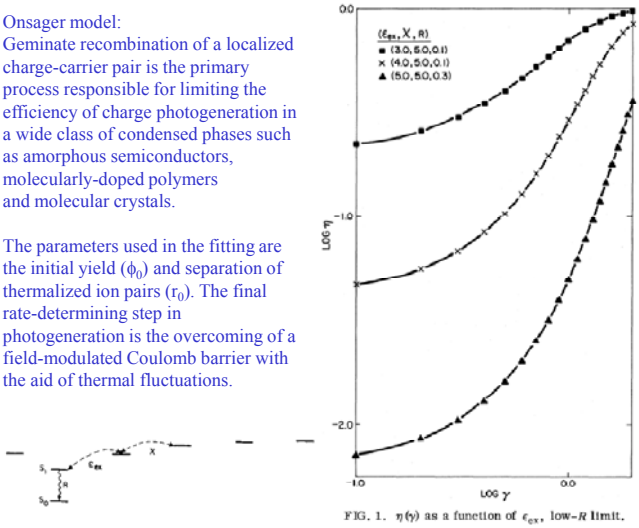
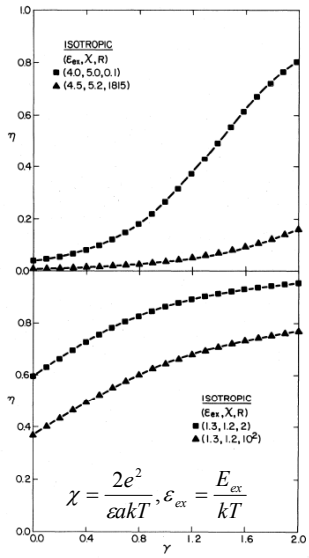



FIG. 1. $\eta(\gamma)$ as a function of $\epsilon_{ex}$, low-$R$ limit.




$$\chi = \frac{2e^2}{\varepsilon akT}, \varepsilon_{ex} = \frac{E_{ex}}{kT}$$

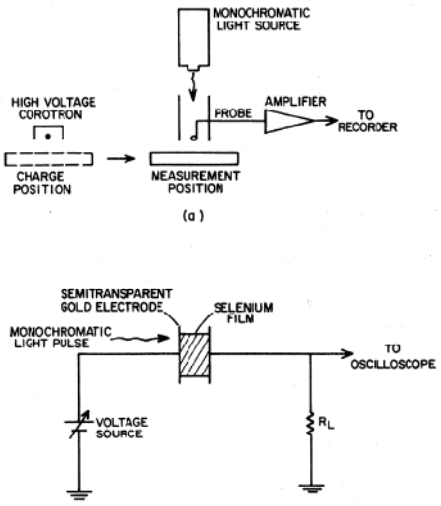
FIG. 2. $\eta(\gamma)$, comparison of low- and high-$R$ regimes

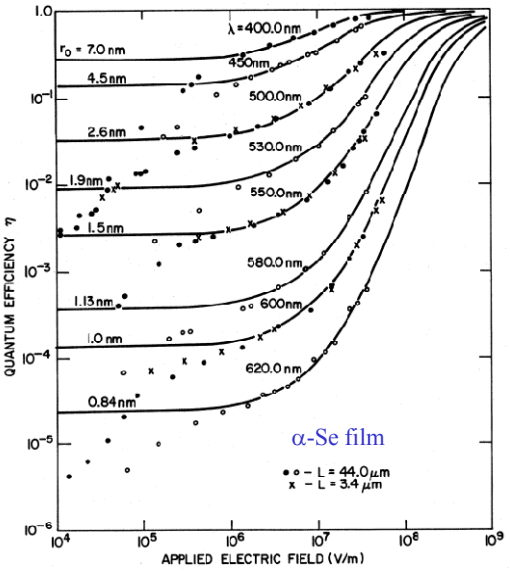
S. Rackovsky, H. Scher, Phys. Rev. Lett. 52, 453 (1984).
H. Scher, S. Rackovsky, J. Chem. Phys. 81, 1994 (1984).





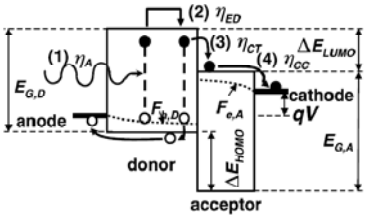
# Onsager mechanism of photogeneration in α-selenium

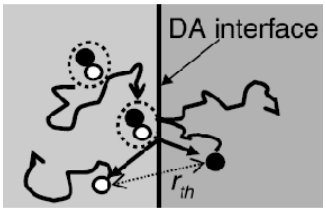


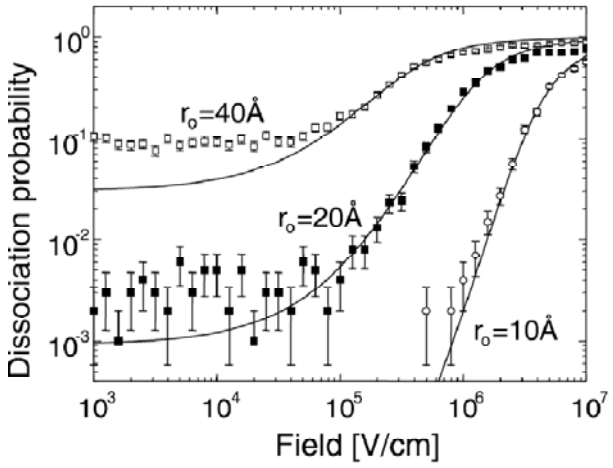




D. M. Pai and R. L. Enck, Phys. Rev. B 11, 5163 (1975)

## Probability of exciton dissociation at D/A heterojunction




P. Peumans and S. R. Forrest, Chem. Phys. Lett., 398, 27 (2004).





## Field-induced PL quenching

$$Q(F)=\frac{I(0)-I(F)}{I(0)}$$

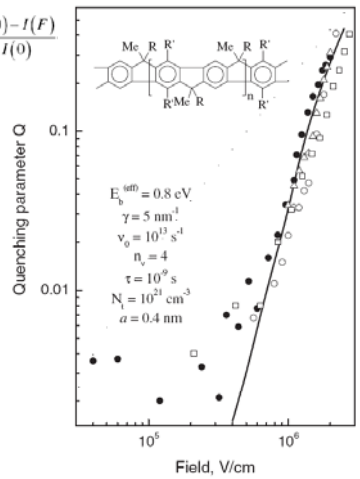
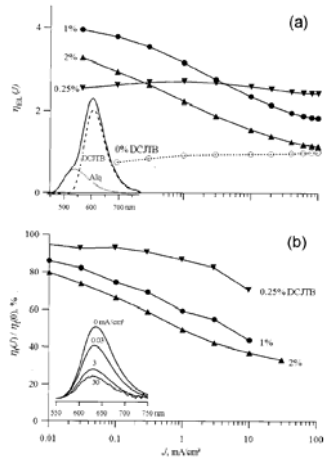



**Fig. 1** Field-induced PL quenching in MeLPPP (●) [33] and (○) [19], PPPV (□) [32], and PhPPV (△) [34]. The solid line is calculated from Eq. (10). The inset shows the chemical structure of MeLPPP.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

# Quantum efficiency roll-off at high current





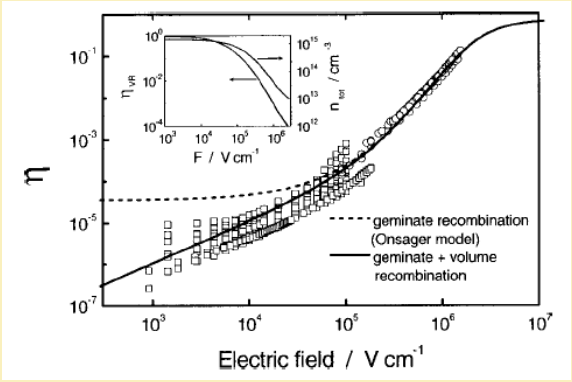

∗ Polaron - exciton quenching :

$$S_1, T_1 \xrightarrow{X^+ \text{ or } X^-} S_0$$

∗ Electric field dissociation of excitons :

$$S_1, T_1 \xrightarrow{\text{E-field}} X^+, X^-$$

J. Szmytkowski, W. Stampor, J. Kalinowski and Z. H. Kafafi, Appl. Phys. Lett. 80, 1465 (2002)

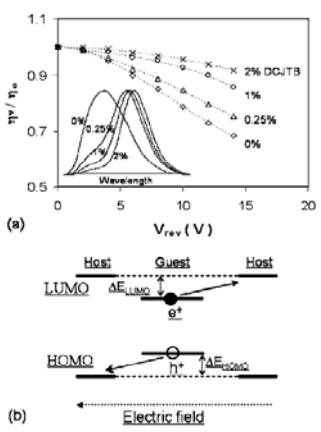


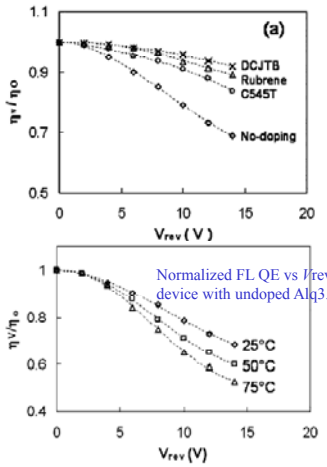

Ralph H. Young, Ching W. Tang, and Alfred P. Marchetti, Appl. Phys. Lett. 80, 874 (2002)



# Electric-field-induced fluorescence quenching






Normalized FL QE vs *V*rev for a device with undoped Alq3.

• Doped AlQ3 layers demonstrate smaller EFIFQ than undoped ones. → The narrower energy band gap of the guest molecule relative to that of the host material makes it less prone to electric-field-induced dissociation of the excited state.
• Results also show that increasing the concentration of the guest material or decreasing its band gap leads to a decrease in EFIFQ.

Y. Luo, H. Aziz, Z. D. Popovic, and G. Xu, Appl. Phys. Lett. 89, 103505 (2006).

## Spectral dependence of relative fluorescence quenching

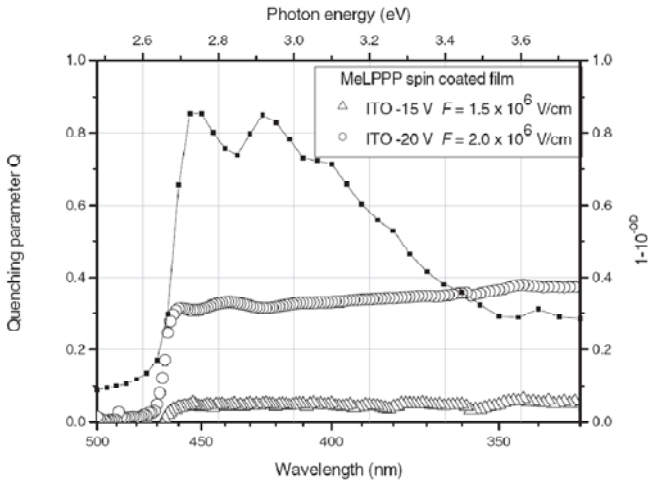


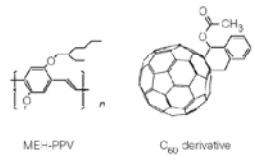

**Fig. 2** Spectral dependence of relative fluorescence quenching and optical density in a MeLPPP film at different applied voltages. The film thickness was 100 nm. (C. Im, unpublished results.)

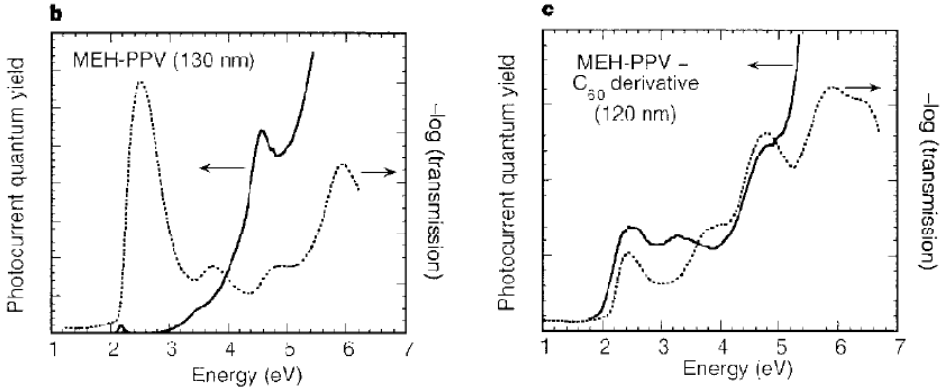
V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)





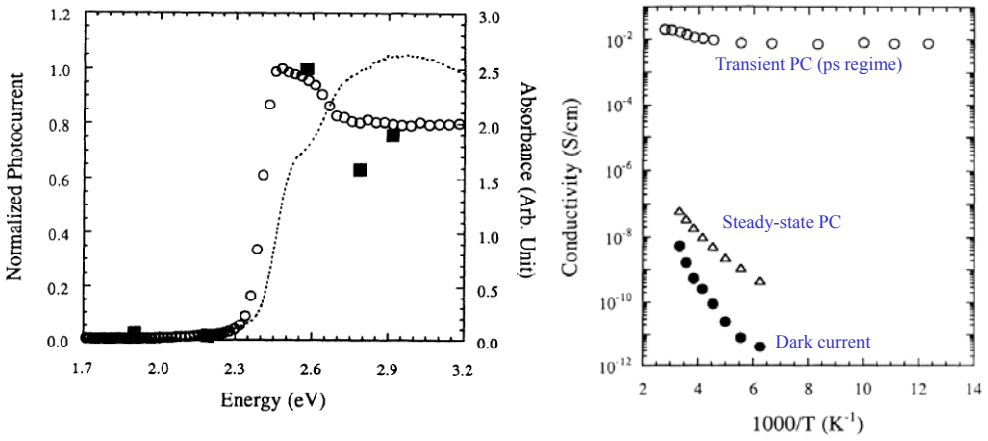
## Photo-generation of charge carriers




A. Kohler et al., Nature 392, 903 (1998).

## Photo-generation of charge carriers in PPV



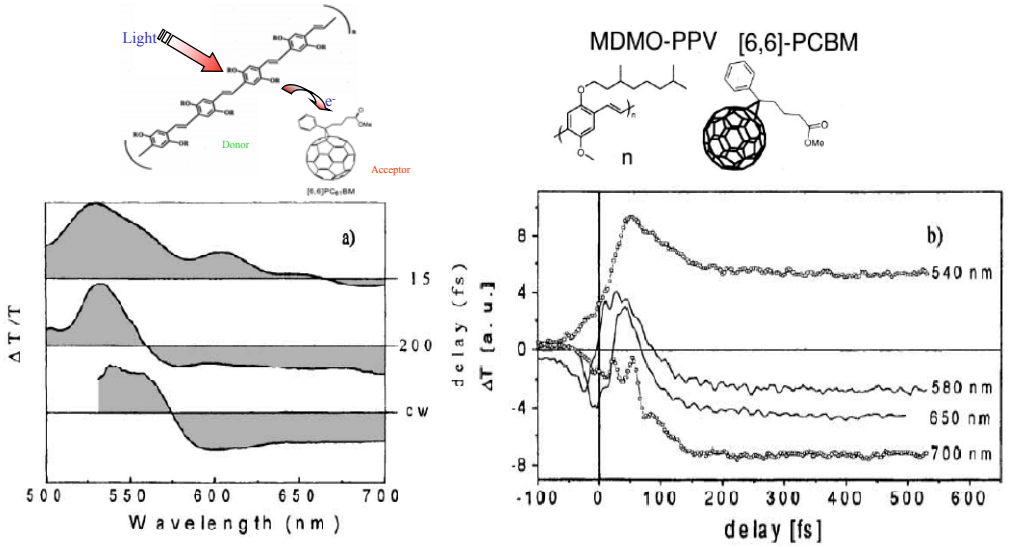

C. H. Lee et al., Phys. Rev. B 49, 2396 (1994).





## Ultrafast Photo-generation of charge carriers in PPV

Ultrafast process (~100fs) & Very efficient PICT in MDMO-PPV/PCBM




G. Zerza, C. J. Brabec, G. Cerullo, S. De Silvestri, and N. S. Sariciftci, *Synth. Metals* 119, 637 (2001)

## Electromodulated differential absorption spectra of MeLPPP



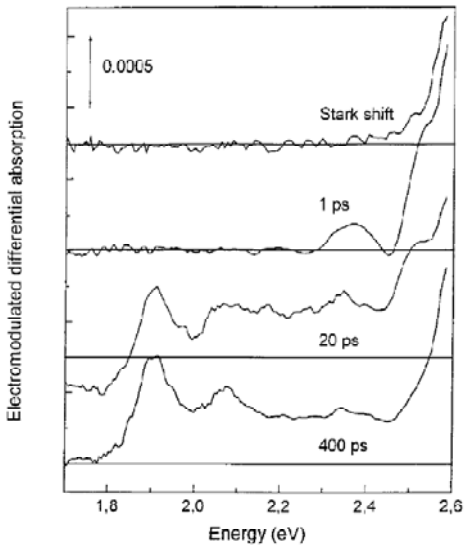



**Fig. 3** Electromodulated differential absorption spectra of MeLPPP obtained at different delay times after excitation. The upper curve shows the electric field induced differential absorption, measured without excitation. The dashed line is EDA spectrum corrected for the Stark effect.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)



## Time resolved fluorescence quenching



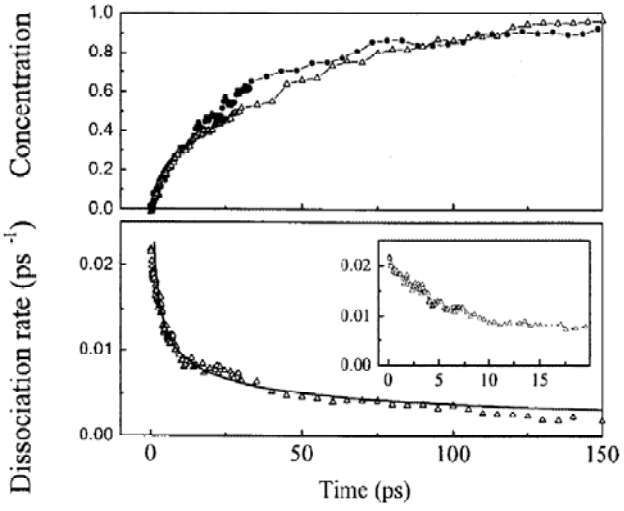



**Fig. 4** a) Normalized concentration of broken excitons (open triangles) and polarons (solid circles) in MeLPPP as a function of time; (b) the rate of exciton dissociation as a function of time (open triangles). The inset shows the signal at short times. The full curve is a fit based upon an algebraic $t^{-0.4}$ law.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

## A model of field-assisted dissociation of optical excitations

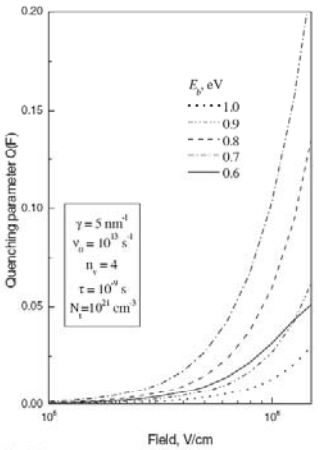



**Fig. 5** Field dependence of the PL quenching parameter calculated for different values of the exciton binding energy in a material with uncorrelated positions of neighbouring localized states.

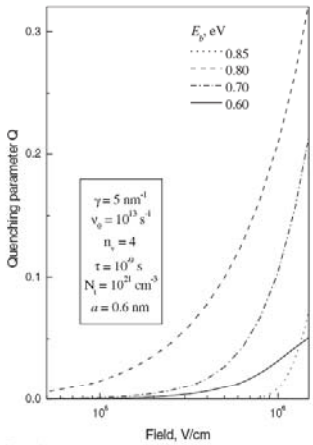



**Fig. 6** Field dependence of the PL quenching parameter calculated for different values of $E_b$ in a material with correlated positions of neighboring localized states.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)





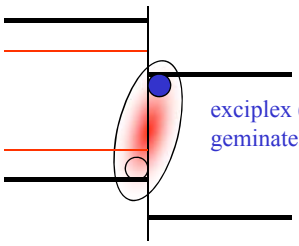
## Exciton dissociation in doped conjugated polymers

## Exciton dissociation in doped conjugated polymers

Exciton quenching can occur whenever the energy of an eh-pair, if coulombically bound, is less than that of its excitonic precursor.

Criterion of exciton quenching

$$E_{LUMO}^{(dopant)} - E_{HOMO}^{(host)} - E_b^{(\text{Geminate pair})} < E_{S_1}^{(host \text{ or } dopant)}$$



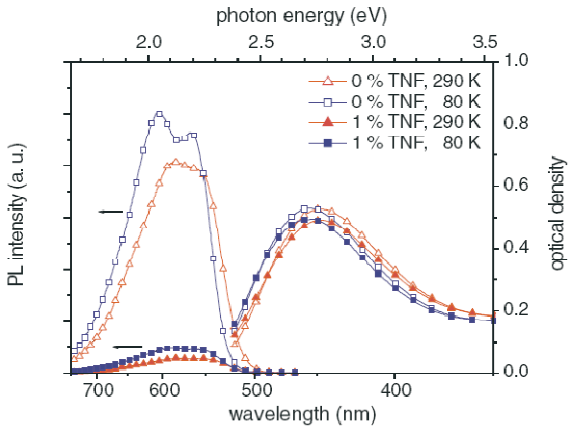
exciplex (charge transfer excited state or geminately bound eh pair )

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)





## Photoluminescence quenching in doped polymers




PhPPV: HOMO= –5.5 +/–0.5 eV
trinitrofluorene (TNF): LUMO= –3.9 eV,
a strong electron donor.

**Fig. 7** (online colour at: www.interscience.wiley.com) Steady state photoluminescence and absorption spectra of spin-coated PhPPV films with and without TNF at 290 and 80 K.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

## Photoluminescence quenching in doped polymers

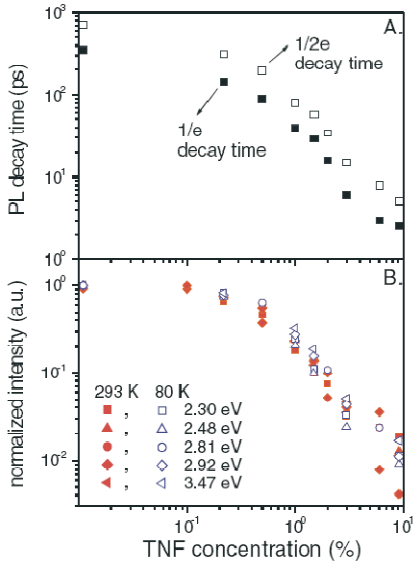



**Fig. 8** (online colour at: www.interscience.wiley.com) A) TNF concentration dependences of PL decay time in a PhPPV film as **1**/*e* (full rectangle) and 1/2*e* (open rectangle). (**B**) TNF concentration dependences of cw-**PL** intensity at 295 K and 80 K with various excitation energies.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)





## Photoluminescence quenching in doped polymers

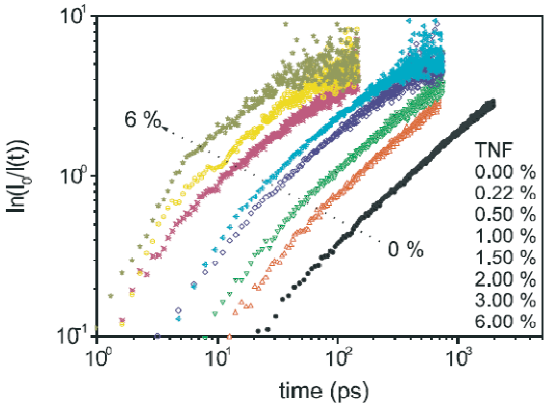



**Fig. 9** (online colour at: www.interscience.wiley.com) KWW plots for PhPPV films with various TNF concentrations.

Kohlrausch–Williams–Watts' (KWW) stretched exponential law

$$I(t) = I_0 e^{-(\frac{t}{t_0})^{\beta}}$$

The fact that the KWW plots of the fluorescence intensity from both doped and neat PhPPV films approach a straight line with $\beta = 0.65 \pm 0.05$ asymptotically while the kinetics of fluorescence from an isolated PhPPV chain in solution is exponential indicates that it is due to intra- as well as interchain exciton transport, which ultimately leads to the formation of a $(TNF)^-$ and $(PhPPV)^+$ geminate pairs via short range electron transfer.

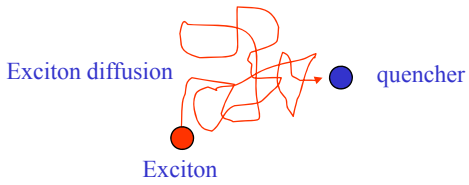
V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

## A model of dopant-assisted exciton dissociation

• The concentration of impurities in a device-quality organic material is normally below 0.1% unless it is doped intentionally. At such small densities of CT centers the quenching rate has to be limited by exciton diffusion towards the quenchers.

• The underlying microscopic mechanism is the Förster energy transfer among the polymer chains followed by short range charge transfer to the electron acceptor.

• Exciton diffusion is time-dependent due to spectral relaxation because the jump rate decreases with time due to energy relaxation. In the course of energy relaxation an exciton of an energy $E$ will, most probably, jump to a molecule in which its energy will be smaller than $E$. The density of accessible molecules will decrease after every exciton jump and, therefore, the distance to a next accessible acceptor molecule will, on average, increase with time.




V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)





## A model of dopant-assisted exciton dissociation

Probability density of having an acceptor over the distance $r$ is given by the Poisson distribution as

$$w(\mathrm{r}) = 4\pi r^2 N(E) e^{-\frac{4\pi}{3} r^3 N(E)}$$

where $N(E)$ is the density of acceptor molecules, accessible for an exciton of an energy $E$.

If an exciton has the nearest accessible molecule over the distance $r$, the probability $p(r, t)$ that it has not yet jumped to this molecule until the time $t$ is also described by the Poisson formula

$$p(r,t) = e^{-\nu(r)t} = e^{-\frac{t}{\tau}(\frac{r_F}{r})^6} \qquad \text{Forster energy tra nsfer rate : } \nu(\mathrm{r}) = \frac{1}{\tau}(\frac{r_F}{r})^6$$

$$\therefore \quad w(E,r,t) = 4\pi r^2 N(E) e^{-\frac{4\pi}{3} r^3 N(E) - \frac{t}{\tau}(\frac{r_F}{r})^6}$$

The energy distribution of such states is given by the product of $W(E, t, r)$ and the excitonic DOS distribution $g(E)$ as

$$f(E,r,t) = A(t) r^2 g(E) N(E) e^{-\frac{4\pi}{3} r^3 N(E) - \frac{t}{\tau}(\frac{r_F}{r})^6}$$

where $A(t)$ is the normalization constant.

$$A(t) = e^{-\frac{t}{\tau}} \left[ \int_0^\infty dr r^2 \int_0^\infty dE g(E) N(E) e^{-\frac{4\pi}{3} r^3 N(E) - \frac{t}{\tau}(\frac{r_F}{r})^6} \right]^{-1}$$

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

## A model of dopant-assisted exciton dissociation

Average number of jumps, $n$, to be made by an exciton during its entire lifetime as

$$n = \frac{r_F^6}{\tau}\int_0^\infty dt' \exp\left(-\frac{t'}{\tau}\right) \times\left\{\int_0^\infty \frac{dr}{r^4}\left[1-\exp\left(-\frac{4\pi N_t}{3}r^3\right)-\frac{4\pi N_t}{3}r^3\exp\left(-\frac{4\pi N_t}{3}r^3\right)\right]\exp\left[-\frac{t'}{\tau}\left(\frac{r_F}{r}\right)^6\right]\right\}^{-1} \times\int_0^\infty \frac{dr}{r^{10}}\left[1-\exp\left(-\frac{4\pi N_t}{3}r^3\right)-\frac{4\pi N_t}{3}r^3\exp\left(-\frac{4\pi N_t}{3}r^3\right)\right]\exp\left[-\frac{t'}{\tau}\left(\frac{r_F}{r}\right)^6\right].$$

In conjugated polymers, excitons are delocalized within conjugated molecular segments $l$. If deep traps are distributed homogeneously, the probability $w_q$ that a given segment is an exciton quencher is determined by the Poisson distribution

$$w_q = 1 - e^{-\pi r_q^2 l N_d}$$

The probability to be quenched at a quencher, $W_q$, is given by $W_q = \frac{\tau_j}{\tau_q + \tau_j}$

Estimating the exciton jump time as $\tau_j = \tau/n$ and using the Poisson distribution of probabilities yields the following expression for the probability η that an exciton has not been quenched and eventually decayed radiatively

$$\eta = \left[\frac{n\tau_q + \tau e^{-\pi r_q^2 l N_d}}{n\tau_q + \tau}\right]^{n+1}$$

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)





## A model of dopant-assisted exciton dissociation

$$\eta = \left[\frac{n\tau_q + \tau e^{-\pi r_q^2 l N_d}}{n\tau_q + \tau}\right]^{n+1}$$

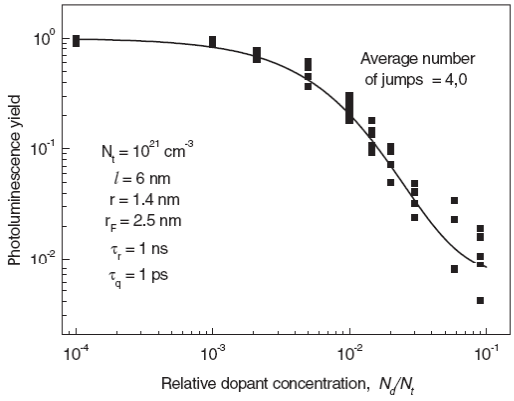



**Fig. 10** Dopant concentration dependence of the PL intensity in PhPPV films. Experimental data are taken from Fig. 8 B, the solid line was calculated from Eq. (24).

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

# A model of dopant-assisted exciton dissociation

The average exciton jump rate at a time $t$

$$\nu_t(t) = \frac{r_F^6}{\tau}\exp\left(-\frac{t}{\tau}\right) \times\left\{\int_0^\infty \frac{\mathrm{d}r}{r^4}\left[1-\exp\left(-\frac{4\pi N_t}{3}r^3\right)-\frac{4\pi N_t}{3}r^3\exp\left(-\frac{4\pi N_t}{3}r^3\right)\right]\exp\left[-\frac{t}{\tau}\left(\frac{r_F}{r}\right)^6\right]\right\}^{-1} \times\int_0^\infty \frac{\mathrm{d}r}{r^{10}}\left[1-\exp\left(-\frac{4\pi N_t}{3}r^3\right)-\frac{4\pi N_t}{3}r^3\exp\left(-\frac{4\pi N_t}{3}r^3\right)\right]\exp\left[-\frac{t}{\tau}\left(\frac{r_F}{r}\right)^6\right].$$

Integrating over time from $t$ to infinity yields the average number of jumps between different conjugated segments, $n(t)$, to be made by an exciton after the time $t$.

$$n(t) = \beta\int_{t/\tau}^\infty \mathrm{d}z\exp(-z)\left\{\int_0^\infty \frac{\mathrm{d}x}{x^2}\left[1-\exp(-x)-x\exp(-x)\right]\exp\left(-\frac{\beta z}{x^2}\right)\right\}^{-1} \times\int_0^\infty \frac{\mathrm{d}x}{x^4}\left[1-\exp(-x)-x\exp(-x)\right]\exp\left(-\frac{\beta z}{x^2}\right),$$

$$\beta = \left(\frac{4\pi}{3}N_t r_F^3\right)^2.$$

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)





# A model of dopant-assisted exciton dissociation

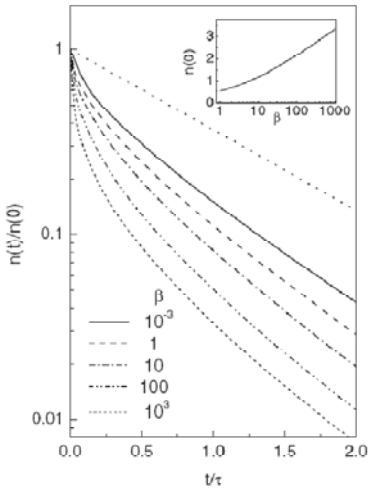



Fig. 11 Time dependence of the average number of jumps of an exciton with intrinsic lifetime $\tau$ to be made after the time $t$. The dotted line shows an exponential decay of the exciton density, i.e. the PF intensity in the absence of spectral relaxation.

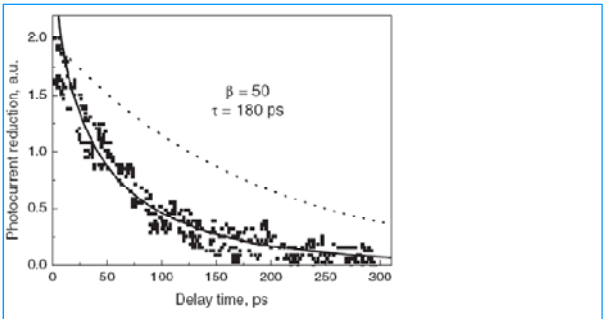



Fig. 12 The decrease of the photocurrent in a MeLPPP film due to the second depleting laser pulse in the two-pulse experiment of Ref. [14]. The solid line is calculated from Eq. (25) with the exciton lifetime $\tau$ = 180 ps, as determined in Ref. [14] from the PF decay, and $\beta$ = 50 that corresponds to e.g. $N_t = 10^{21}$ cm$^{-3}$ and $r_F$ = 1.2 nm. The dotted line shows for comparison an exponential decay of the exciton density with the intrinsic lifetime of 180 ps.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

Photoconductivity in pristine and weakly doped polymers





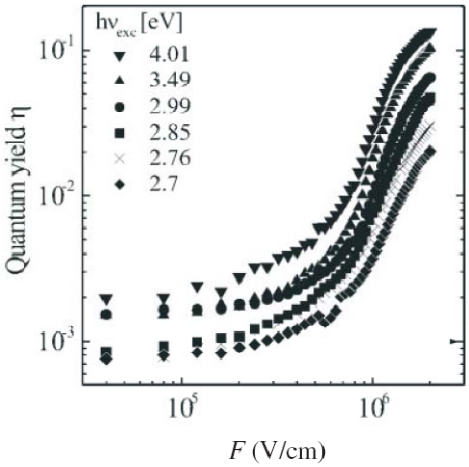



**Fig. 13** Field dependence of the charge carrier photogeneration yield in MeLPPP for different photon energies of photoexcitation.

V. I. Arkhipov and H. Bässler, phys. stat. sol. (a) 201, 1152–1187 (2004)

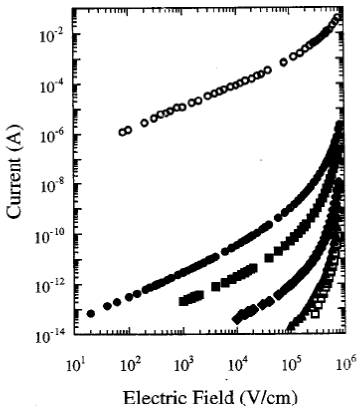



FIG. 2. The dependence of the peak transient photocurrent ($I_p$) and dark current ($I_d$) on external field at various temperatures in tensile drawn, oriented PPV, $l/l_0=10$. The top curve (○) shows that $I_p$ is temperature independent. The lower curves represent $I_d$: 300 K (●), 250 K (■), 200 K (♦), 150 K (▲), 100 K (□).

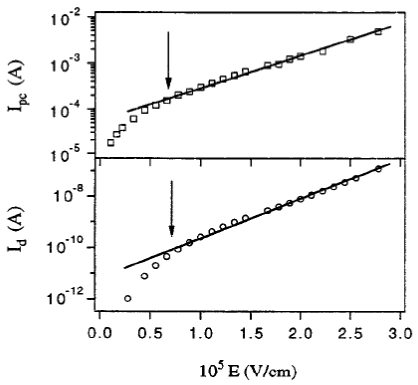



FIG. 4. The dependence of the transient photocurrent at 77 K on external field is compared to that of the dark current at the same temperature on a semilogarithmic graph. The arrows show the onset of the nonlinearity.

D. Moses, H. Okumoto, C. H. Lee, A. J. Heeger, T. Ohnishi and T. Noguchi, Phys. Rev. B 54, 4748 (1996).





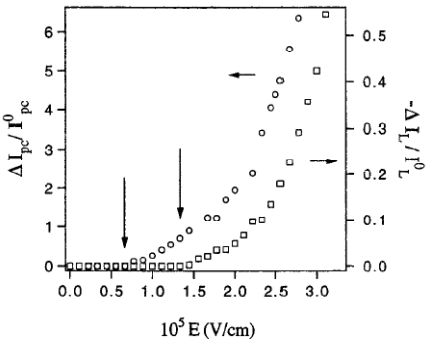



FIG. 5. The dependence of the normalized change in the transient photocurrent $\Delta I_{pc}/I^0_{pc}$ and the photoluminescence luminescence quenching $-\Delta I_L(E)/I^0_L$ on external field in oriented PPV ($l/l_0=2$) at 77 K. The arrows denote the onset of the nonlinearity in the photoconductivity (open circles) and the onset of the photoluminescence quenching (open squares).

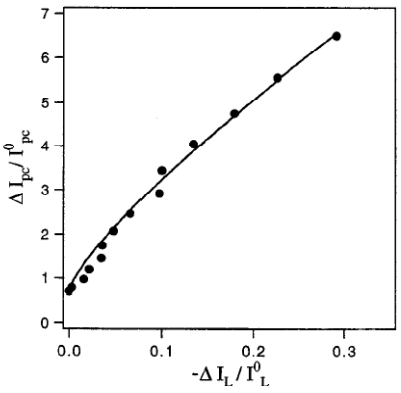



FIG. 6. The normalized change in the transient photocurrent ($\Delta I_{pc}/I^0_{pc}$) is plotted vs the photoluminescence luminescence quenching [$-\Delta_L(E)/I^0_L$]. The solid curve is a fit to a power-law functional form of $y=A+Bx^\beta$, where $y=\Delta I_{pc}/I^0_{pc}$, and $x=-\Delta I_I(E)/I^0_I$; the best fit to the power law yields $\beta=0.78$.

D. Moses, H. Okumoto, C. H. Lee, A. J. Heeger, T. Ohnishi and T. Noguchi, Phys. Rev. B 54, 4748 (1996).

## Mechanism of carrier generation in polyphenylene vinylene

• The fast transient photocurrent is independent of temperature (T);
• The fast transient photocurrent is linearly proportional to the light intensity;
• The fast transient photocurrent is linearly proportional to the external field (E) in the low-field regime, at fields orders of magnitude below the onset of nonlinear transport.

→ *a carrier generation mechanism independent of external field.*

At high fields, the transient and steady-state photoconductivity both increase exponentially with *E*. The better the polymer chain alignment, the lower the threshold field for the onset of nonlinear transport. The dependence of the nonlinearity on sample orientation and order, and the appearance of a similar exponential component in the dark current imply that the nonlinearity must arise from nonlinear carrier transport rather than nonlinear carrier generation; the nonlinear increase in transient photocurrent with field results from a field-induced increase in the transport mobility.

• The absence of correlation between $\Delta\sigma(E)/\sigma_{pc}(0)$ and $\Delta I_L(E)/I_L(0)$ implies that field-induced dissociation of strongly bound excitons is not the mechanism responsible for the luminescence quenching.
• The relatively low field required for the onset of luminescence quenching implies a weak exciton binding energy.

D. Moses, H. Okumoto, C. H. Lee, A. J. Heeger, T. Ohnishi and T. Noguchi, Phys. Rev. B 54, 4748 (1996).