**Abstract**

A summary of the significant scientific accomplishments that resulted from research supported under AFOSR F49620-99-1-0031 is included in this Final Technical Report with emphasis on the following specific areas: (i) Time Resolved Forster Energy Transfer in Polymer Blends (ii) Ultrafast Detection of Charged Photocarriers in Conjugated Polymers (iii) Photophysics of poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene) (iv) Single Exciton Binding Energy in Poly(phenylene vinylene) (v) Excitation Spectrum for Ultrafast Photogeneration of Charged Solitons in Polycarbonate (vi) Optical Investigation of intra- and interchain charge dynamics in metallic polymers (vii) High Efficiency Polymer-based Electrospoushorent Devices
Air Force Office of Scientific Research

Final Technical Report

"Charge Transfer Polymers as Ultrafast Holographic Materials"

F49620-99-0031

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Abstract

A summary of the significant scientific accomplishments that resulted from research supported under AFOSR F49620-99-0031 is included in this Final Technical Report with emphasis on the following specific areas:

(i) Time Resolved Förster Energy Transfer in Polymer Blends
(ii) Ultrafast Detection of Charged Photocarriers in Conjugated Polymers
(iii) Photophysics of poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene
(iv) Singlet Exciton Binding Energy in Poly(phenylene vinylene)
(v) Excitation Spectrum for Ultrafast Photogeneration of Charged Solitons in Polyacetylene
(vi) Optical Investigation of intra- and interchain charge dynamics in metallic polymers
(vii) High Efficiency Polymer-based Electrophosphorescent Devices
Research Accomplishments during the three year funding period:

Time Resolved Förster Energy Transfer in Polymer Blends

As shown by Förster, the dipole-dipole interaction leads to efficient long range energy transfer from an absorbing host chromophore to an emitting guest chromophore. As a result, complete, rapid energy transfer can result even at dilute concentrations of the guest. Although the Förster Resonant Energy Transfer (FRET) mechanism has been known for over fifty years, we succeeded, for the first time, in time resolving the energy transfer process through ultrafast pump-probe measurements. Since the emission and the absorption from the guest and host excited states are different, the time evolution was monitored by carefully choosing the probe wavelength. The dynamics of the stimulated emission and photoinduced absorption of blends of semiconducting (conjugated) polymers indicate that 10-2- ps are required for complete energy transfer. Quantitative measurements of energy transfer rates give a Förster interaction range of 3-4 nm, 1.5 times longer than the theoretical values as calculated from the spectral overlap. This difference was attributed to delocalization of the excited state in the semiconducting polymer. In related experiments, FRET was used to lower the threshold for amplified spontaneous emission (“mirrorless lasing”) in blends of conjugated polymers.


For details see the following publication:
“Time Resolved Förster Energy Transfer in Polymer Blends”
A. Dogariu, R. Gupta, A.J. Heeger and H. Wang
Synth. Met. 100, 95 (1999)

Ultrafast Detection of Charged Photocarriers in Conjugated Polymers

Ultrafast measurements of transient excited-state absorption in the spectral region spanning the infrared active vibrational active (IRAV) modes in the prototypical luminescent polymers PPV and MEH-PPV reveal charge carrier generation within 100 fs after photoexcitation. The photocarrier quantum efficiency in MEH-PPV is \( \phi_0 = 0.1 \) in zero applied electric field. There is no correlation between the temporal behavior of the photoinduced IRAV signals and the exciton lifetime. Comparison of the recombination dynamics in MEH-PPV and PPV demonstrates the importance of the strength of inter-chain interaction on the carrier recombination dynamics. The quantum efficiency is the same (\( \phi_0 = 0.1 \)) when the system is pumped either at photon energies well above the first \( \pi-\pi^* \) transition (at 267 nm, 4.7 eV) or when pumped into the first \( \pi-\pi^* \) transition (at 400 nm, 3.1 eV). The carrier lifetime, however, increases at the higher photon energy, providing a natural explanation for the increase in the photoconductivity at photon pump energies above 3 eV. These findings indicate that charged carriers (positive and negative polaron) are primary photoexcitations; the carriers are photoexcited directly and not generated via a secondary process from exciton annihilation. The observation of photoinduced IRAV modes at 100 fs after photoexcitation confirms the ultrafast formation of polarons predicted over twenty years ago by Su and Schrieffer [Proc. Nat. Acad. Sci. U.S.A. 77, 5626 (1980)]
Subsequently, the quantum yield for charge generation ($\phi_{eh}$) was measured as a function of pump photon energy by exciting the samples with ultrashort pulses in the spectral range from 2.2 to 6.2 eV ($\sim 100$ fs pulsewidth) and probing the photoinduced absorption of the IRAV modes. The ultrafast nature of charge generation, the significant quantum yield observed ($\phi_{eh} \sim 0.1$) and its weak photon energy dependence imply that polaron are directly generated by optical excitation within $\sim 100$ fs and rule out indirect charge generation mechanisms.

For details see the following publications:

“Ultrafast Photoinduced Charge Generation in Conjugated Polymers”
D. Moses, A. Dogariu and A.J. Heeger

“Ultrafast Detection of Charged Photocarriers in Conjugated Polymers”
D. Moses, A. Dogariu and A.J. Heeger

“Electric Field Induced Ionization of the Exciton in Poly(phenylene vinylene)”
P. Miranda, D. Moses and A.J. Heeger
Synthetic Metals, 119 503 (2001)

“Ultrafast Charge Photogeneration in Conjugated Polymers”
P. Miranda, D. Moses and A.J. Heeger
Synthetic Metals, 119 619 (2001)

Photophysics of poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene)

Time resolved photoinduced absorption and stimulated emission measurements, with temporal resolution of approximately 100 fs, demonstrate that the emissive properties of the blue-green emitting conjugated polymer, poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene (DP6-PPV), are fully consistent with a simple “four-level” model. The stimulated emission spectrum is the same as the photoluminescence spectrum, and the stimulated emission decay time is the same as the photoluminescence decay time. The absence of spectral overlap between the emission and the photoinduced absorption is an important result; it is in fact a requirement for low threshold polymer lasers. However, this absence is not surprising. The photoinduced absorption spectrum depends on the energy distribution of the higher lying states (both intra-chain and inter-chain) whereas the emission spectrum depends only on the energy of the (relaxed) first excited state. Thus, there is no general (or intrinsic) reason why these two spectral features should overlap. Nevertheless, until a deeper understanding of the higher lying excited states is developed, the identification of semiconducting polymers with high optical gain will depend on the synthesis and characterization of the photophysics of new polymers.

For details see the following publication:

“Photophysics of poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene”
A. Dogariu, A.J. Heeger and H. Wang
Singlet Exciton Binding Energy in Poly(phenylene vinylene)

A central issue in the field of conjugated polymers is the strength of the electron-electron (el-el) interaction relative to the bandwidth: Is the attraction of a geminate electron-hole pair so strong that the photoexcitations are localized and strongly correlated Frenkel excitons? Or rather, are the charge carriers sufficiently well screened that a band picture supplemented by the electron-phonon interaction (polaron formation) and the el-el interaction (weakly bound excitons) is justified? Determination of the exciton binding energy \(E_b\) is critically important to answering these questions and thereby to understanding the electronic structure of semiconducting polymers.

Because this issue has not been resolved, the extensive literature on the optical properties of semiconducting (conjugated) polymers contains two conflicting assignments for the lowest energy \(\pi-\pi^*\) absorption.\(^1\)

(1) The lowest energy \(\pi-\pi^*\) absorption results from the creation of tightly bound neutral singlet excitons with the onset of the interband transition at a significantly higher energy, as for example, in molecular crystals such as anthracene.\(^2\)

(2) The lowest energy \(\pi-\pi^*\) absorption results from a direct band-to-band transition, as for example, in direct gap semiconductors such as GaAs.

These two different assignments imply very different results for the photogeneration of charged excitations. When the lowest energy \(\pi-\pi^*\) absorption results from a direct band-to-band transition, one expects to observe a threshold for photogeneration of charge carriers \(h\nu_{ch}\) close in energy to the onset of absorption \(E_{\pi-\pi^*}\); i.e. at

\[
h\nu_{ch} = E_{\pi-\pi^*}
\]

(1a)

If, however, \(E_b\) is large, one expects to observe the threshold for photogeneration of charge carriers via the lowest band-to-band transition at energy greater than the onset of optical absorption by \(E_b\); i.e. at

\[
h\nu_{ch} = E_{\pi-\pi^*} + E_b
\]

(1b)

For poly(phenylene vinylene), PPV, and several of its soluble derivatives, the quantum efficiency for photogeneration of charged excitations (polarons) was measured (by the Heeger group), in zero external field, using ultrafast photo-induced absorption by infra-red active vibrational (IRAV) modes. The results demonstrated charge carrier photogeneration with a single threshold that is close in energy to the onset of absorption, in agreement with Eqn.(1a). Although photoconductivity data have been reported by others with a second threshold well above the onset of absorption, we have detected and characterized a contribution to the transient and steady-state photocurrent that originates from electron photoemission. After quenching the photoemission contribution, the true bulk photoconductivity data in PPV and all the PPV derivatives show a threshold close to the onset of optical absorption, above which the photocurrent is nearly independent of excitation energy (up to 6.2 eV), again in agreement with Eqn.(1a).\(^8\) These data demonstrate that the oscillator strength in the lowest energy optical absorption band of PPV (and its soluble derivatives) arises from the lowest energy band-to-band transition.

Theoretical models have yielded estimates for the exciton binding energy in PPV that range from values of order 0.1 eV to 1 eV. Moreover, the photoluminescence is proportional to the light intensity (I) rather than \(I^2\), indicative of emission from a bound electron-hole pair. Thus, finding the exciton with spectroscopic accuracy and measuring
the exciton binding energy remain as important goals for experimental studies of the photophysics of semiconducting polymers.

During the past year, we have measured the exciton binding energy in chain-oriented PPV through high resolution excitation profile spectroscopy of the steady state photocurrent ($I_{\text{photo}}$) at various external fields ($F$) and temperatures ($T$), and in samples with different defect concentrations. The spectral signature of the exciton is observed in the excitation profile as a narrow peak that emerges just below the band edge upon increasing the external electric field or the defect density. Since the exciton absorption and emission are polarized parallel to the chain axis, measuring the excitation profile of $I_{\text{photo}}$ with light polarized parallel and perpendicular to the PPV chain axis enables the identification (and separation) of carrier generation via exciton dissociation from carrier generation via the $\pi-\pi^*$ inter-band transition. From these studies, we have determined $E_g$ (2.42 eV) and $E_b$ ($\approx 60$ meV), and we have clarified the role of the external field and of defects in the carrier photogeneration process.

As a result of this series of experiments, we have resolved the long-standing controversy regarding the electronic structure of PPVs. For details see the following publication:

"Singlet exciton binding energy in poly(phenylene vinylene)"
D. Moses, J. Wang, A.J. Heeger, N. Kirova, and S. Brazovski

Excitation Spectrum for Ultrafast Photogeneration of Charged Solitons in Polyacetylene

The discovery of electrical conductivity in doped polyacetylene\(^1\) initiated the field of semiconducting and metallic polymers. Motivated in part by their potential for use in applications, this novel class of materials, which combine the optical and electronic properties of semiconductors and metals with the mechanical properties and processability of polymers, continues to be the focus of an active field of research.

Polyacetylene, $(\text{CH})_x$, is the simplest semiconducting (conjugated) polymer. The theoretical description of the degenerate ground state, the electronic structure and the soliton excitations of trans-$(\text{CH})_x$ has been generalized to the broader class of semiconducting polymers in which the ground state degeneracy has been lifted. The successful model of Su, Schrieffer and Heeger (SSH) treats the polymer chain as a tight-binding one-dimensional semiconductor in the one-electron approximation and explicitly includes the electron-phonon interaction, but neglects electron-electron (el-el) interactions, assuming they are relatively weak due to screening. The SSH model predicts that the lowest energy fundamental excitations in polyacetylene are solitons, self-localized by the electron-phonon interaction. The solitons in trans-$(\text{CH})_x$ have a reversed spin-charge relationship; neutral solitons ($S^0$) have spin $\frac{1}{2}$, and charged solitons ($S^+$, $S^-$) have spin 0. The minimum energy required for creation of a soliton pair was calculated to be $2E_g/\pi$ within the SSH model, where $E_g$ is the $\pi-\pi^*$ energy gap. Solitons in polyacetylene have been studied experimentally by a number of techniques.

Calculations by Su and Schrieffer\(^1\) described the process of charged soliton pair formation subsequent to photoexcitation via the $\pi-\pi^*$ interband transition in trans-$(\text{CH})_x$ with a photon energy ($h\nu$) equal to $E_g$. They showed that within $\sim 100$ fs, the lattice around a
photoexcited electron-hole pair relaxes to form a well separated $S^+ - S^-$ pair. Other calculations have shown that this picture remains correct when weak electron-electron interactions are included in the model. Early ultrafast experiments used photoexcitation energies above the energy gap ($h\nu \geq E_g$). However, direct photogeneration of soliton pairs can occur even for $2E_g/\pi < h\nu < E_g$, enabled by nonlinear zero-point motion of the lattice. The absorption coefficient for direct soliton photoexcitation was predicted to be small near the threshold $2E_g/\pi$, and to increase exponentially as the photon energy approaches $E_g$. If this is the dominant absorption process in the trans-(CH)$_x$ samples below the energy gap, one would expect that the quantum efficiency for charged soliton pair photogeneration ($\phi_{ch}$) to be unity for $2E_g/\pi < h\nu < E_g$ and, if the charged soliton pair is the lowest energy photoexcitation, well above $E_g$.

Under the AFOSR funding, we have developed the experimental technique of ultrafast photoinduced absorption by infrared-active vibrational (IRAV) modes, an all-optical technique with subpicosecond time resolution carried out in zero applied electric field. The IRAV absorption results from Raman-active vibrational modes that become infrared-active when the local symmetry is broken by self-localization of charges with associated changes in the bond lengths (e.g. soliton formation). The IRAV modes have a one-to-one correspondence with the strongest modes observed in resonant Raman scattering and have an unusually high infrared absorption cross-section ($\sigma_{IRAV} \sim 10^{16}$ cm$^2$, comparable to electronic transitions). The intensities of the IRAV modes are a well-known probe of photo- or doping-induced charged excitations (solitons, polarons and bipolarons) in conjugated polymers. Thus, ultrafast photoinduced IRAV absorption can probe the early time photogeneration and dynamics of charged solitons in polyacetylene, but without being sensitive to neutral solitons.

In recent studies, we have used photoinduced IRAV modes to study the photogeneration and recombination dynamics of charged solitons in polyacetylene with ~250 fs time resolution. We observe that solitons are generated within our time resolution and have a very fast recombination dynamics (initial decay < 1 ps), which is moderately sensitive to the excitation photon energy. The quantum efficiency for charged soliton pair formation ($\phi_{ch}$) is inferred from our measurements to be close to unity. The excitation spectrum for $\phi_{ch}$ has an onset at ~1.0 eV and a relatively weak photon energy dependence out to 4.7 eV. These results imply that photoexcitation of polyacetylene above the SSH threshold of $2E_g/\pi$ leads to ultrafast charged soliton pair formation with nearly unity quantum efficiency, followed by very fast and almost complete recombination.


For details see the following publications:

"Excitation Spectrum for Ultrafast Photogeneration of Charged Solitons in Polyacetylene"
P. B. Miranda, D. Moses, A. J. Heefer
Phys. Rev. B (accepted and In Press)

**Optical Investigation of intra- and interchain charge dynamics in metallic polymers**

Understanding the "metallic" state of conducting polymers continues to be a subject of both interest and controversy. In particular, although finite interchain coupling is essential for the metallic state in these systems, the strength of the interchain transfer
integral ($t_L$) and the anisotropy of the transport properties continue to be of interest. While a weak $t_L$ is expected in these quasi one-dimensional (1D) systems, there are relatively few measurements of the anisotropy in the metallic properties. Some studies have been interpreted in terms of metallic islands separated by amorphous regions. In this picture, orientation by tensile drawing would be expected to affect primarily the amorphous regions. Other studies have suggested a single metallic strand picture with negligible $t_L$.

We carried out the first measurements of polarized optical reflectance, $R(\omega)$, obtained from high-quality, stretch-oriented (tensile-drawn) films of metallic polypyrrole (PPy) doped with PF$_6$. Since tensile drawing induces anisotropy in the physical properties of the films by chain extension and chain alignment, high-precision reflectance studies on such materials enable a separation of the parallel and perpendicular contributions to the optical constants. The $R(\omega)$ results were analyzed in terms of intrachain and interchain contributions to the optical conductivity $\sigma(\omega)$. The intrachain $\sigma(\omega)$ was found to be typical of a disordered Drude metal with $\sigma(\omega \to 0) = 2 \times 10^2$ S/cm, while the interchain $\sigma(\omega)$ is dominated by spectral features of strongly localized conductors, implying the interchain charge dynamics is incoherent.

For Details, see the following publication:

"Optical investigation of intra- and interchain dynamics in conducting polymers"
K. Lee and A.J. Heeger

**High Efficiency Polymer-based Electrophosphorescent Devices**

Organic light emitting diodes (OLEDs) are under active investigation because of their potential for application in flat panel displays. Research on OLEDs has focused on the improvement of the emission efficiency by developing high efficiency fluorescent materials and on the use of novel device architectures.

The existence of an upper limit for the electroluminescence (EL) internal quantum efficiency (QE) has been widely discussed. Since charge carrier recombination in $\pi$-conjugated systems can produce both emissive singlet and non-emissive triplet excited states, the simple statistical argument leads to an upper limit for the internal QE of 25% [3]. The 25% upper limit assumes similar cross sections for the formation of singlets and triplets. Experiments have recently shown, however, that in luminescent semiconducting polymers, the singlet cross section is considerably larger than the triplet cross section (by a factor of 3-4). As a result, electroluminescent quantum efficiencies as high as 50% have been reported. Nevertheless, by utilizing a phosphorescent dye which captures both singlet and triplet excited states, the OLED internal efficiency can, in principle, be increased to 100%.

Utilization of the triplet excitations in OLEDs was proposed several years ago. These devices incorporate a heavy metal atom with strong spin-orbit coupling that enhances intersystem crossing and mixes the singlet and triplet states. In this way, the lowest triplet state is efficiently populated and can produce light emission via phosphorescence. Recently, electrophosphorescent OLEDs based on small molecules as the transport materials have achieved considerable success.
In our labs at UCSB, we have achieved high efficiency green electrophosphorescent OLEDs, fabricated by doping [Ir(HPPF)_3] into a host polymer matrix of poly(vinylcarbazole) (PVK) blended with the electron transport molecule, 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD). Depending on the [Ir(HPPF)_3] concentration, the devices showed external quantum efficiencies as high as 10 % and luminous efficiencies as high as approximately 60 cd/A at a current density of 12 mA/cm². Even at the relatively high current density of 75 mA/cm², an external quantum efficiency of 3.5% and a luminous efficiency of 17.2 cd/A were obtained. The operating voltage of the electrophosphorescence increased with increased concentration of [Ir(HPPF)_3]. Brightness in excess of 8000 cd/m² was achieved at high bias (55 volts).

For details, see the following publication:
“High-efficiency polymer-based electrophosphorescent devices”
Xiong Gong, Matthew R. Robinson, Jacek C. Ostrowski, Daniel Moses, Guillermo C. Bazan and Alan J. Heeger

Publications which acknowledged support from this AFOSR support:

1. “Ultrafast nonlinear optical properties of Charge-Transfer Polymers: Transient Holography and Transient Absorption Studies”
   D.W. McBranch, E.S. Maniloff, D. Vacar and A.J. Heeger

2. “Index of refraction and waveguiding in thin films of a conjugated polymer which exhibits stimulated emission”
   E.K. Miller, M.D. McGehee, M. Diaz-Garcia, V. Srikant and A.J. Heeger
   Synth. Met. 102, 1091 (1999)

3. “Excited State Spectral and Dynamic Studies of MEH-PPV”
   A. Dogariu, D. Vacar and A.J. Heeger
   Synth. Met. 102, 202 (1999)

4. “Ultrafast Photoinduced Charge Generation in Conjugated Polymers”
   D. Moses, A. Dogariu and A.J. Heeger

4. “Ultrafast Detection of Charged Photocarriers in Conjugated Polymers”
   D. Moses, A. Dogariu and A.J. Heeger

6. “Carrier Density and Quantum Efficiency Measurements in Conjugated Polymers:
   Ultrafast Photoinduced IRAV Absorption”
   D. Moses, A. Dogariu and A.J. Heeger
7. “Photophysics of poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene)
   A. Dogariu, A.J. Heeger and H. Wang

8. “Narrow Bandwidth Luminescence from Blends with Energy Transfer from
   Semiconducting PolymerstoEuropium Complexes”
   M.D. McGehee, T. Bergstedt, C. Zhang, A.P. Saab, M.B. O'Regan, V.I. Srdanov
   and A.J. Heeger

   A. Dogariu, D. Moses and A.J. Heeger

10. “Time Resolved Förster Energy Transfer in Polymer Blends”
    A. Dogariu, R. Gupta, A.J. Heeger and H. Wang
    Synth. Met. 100, 95 (1999)

11. “Semiconducting (Conjugated) Polymers as Materials for Solid State Lasers”
    M.D. McGehee and A.J. Heeger,

12. “Mechanism of carrier generation and recombination in conjugated polymers”
    A. Dogariu, D. Moses and A.J. Heeger

13. “Electric Field Induced Ionization of the Exciton in Poly(phenylene vinylene)”
    P. Miranda, D. Moses and A.J. Heeger
    Synthetic Metals, 119 503 (2001)

14. “Ultrafast Charge Photogeneration in Conjugated Polymers”
    P. Miranda, D. Moses and A.J. Heeger
    Synthetic Metals, 119 619 (2001)

15. “Singlet exciton binding energy in poly(phenylene vinylene)”
    D. Moses, J. Wang, A.J. Heeger, N. Kirova, and S. Brazovski

    Xiong Gong, Matthew R. Robinson, Jacek C. Ostrowski, Daniel Moses,
    Guillermo C. Bazan and Alan J. Heeger
17. "Optical investigation of intra- and interchain dynamics in conducting polymers"
   K. Lee and A.J. Heeger

18. "Excitation Spectrum for Ultrafast Photogeneration of Charged Solitons in
    Polyacetylene"
    P. B. Miranda, D. Moses, A. J. Heeger
    Phys. Rev. B (accepted and In Press)

19. "Optical investigation of intra- and interchain dynamics in conducting polymers"
    K. Lee and A.J. Heeger