

# The Effects of Structural and Micro-Environmental Disorder on the Electronic Properties of MEH-PPV and Related Oligomers

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## Abstract

In this study, electroabsorption (Stark) spectroscopy is used to determine the trace of the change in polarizability ( $Tr\overleftrightarrow{\Delta\alpha}$ ) and the absolute value of the change in dipole moment ( $|\overrightarrow{\Delta\mu}|$ ) of the electroluminescent polymer MEH-PPV and several model oligomers in solvent glass matrices. We find a value of  $Tr\overleftrightarrow{\Delta\alpha}$  of  $\sim 2000 \text{ \AA}^3$  for the polymer and for a 9-ring substituted oligomer in both toluene and 2-methyl tetrahydrofuran matrices at 77K with smaller values being obtained for 3 and 5 ring unsubstituted oligomers. Although gas-phase calculations of  $Tr\overleftrightarrow{\Delta\alpha}$  using INDO/SCI yield values that are about a factor of 8 smaller than the experiment, excellent agreement is obtained when the effects of solid-state dielectric screening are included. Screening increases  $Tr\overleftrightarrow{\Delta\alpha}$  by bringing the energy gap between the  $1B_u$  and  $mA_g$  states into agreement with solid-state measurements. Substantial values of  $|\overrightarrow{\Delta\mu}|$  are observed experimentally both for the polymer and the oligomers (6-11 D). Because in a symmetric

planar ( $C_{2h}$ ) geometry the oligomer and polymer are centro-symmetric, the observed  $|\vec{\Delta\mu}|$  is an indication of disorder-induced symmetry breaking in the material. Calculations indicate that disorder in the ground state geometry of the polymer (inner-sphere disorder) can account for roughly one third of the observed  $|\vec{\Delta\mu}|$ . Disorder in the glassy environment (outer-sphere disorder) leads to a non-uniform electrostatic environment, and calculations show that this is a substantial contributor, accounting for about two thirds of the observed  $|\vec{\Delta\mu}|$ .

## Introduction

Due to their favorable fluorescence properties, poly(*p*-phenylene vinylene) (PPV) and its derivatives such as poly[2-methoxy, 5-(2'-ethyl-hexaoxy)-1, 4 phenylene vinylene] (MEH-PPV) (Scheme 1) and others are well suited for photo-physical applications such as light-emitting diodes,<sup>1, 2</sup> lasers,<sup>3-6</sup> and analyte detectors.<sup>7</sup> In order to optimize these material for applications, a number of important photo-physical issues must be addressed. These include determining how chain length, conformation, and the properties of the matrix containing the polymer affect the de-localization length of the excitation on the polymer (size of the exciton). Likewise, the complex interplay between film morphology, molecular conformation, and photo-physics is of substantial current interest.<sup>8-16</sup> One specific goal of understanding this relationship is the ability to use the optical and electronic properties of these materials as a qualitative and perhaps quantitative gauge of the extent of disorder and/or aggregation in the sample. Disorder and aggregation are important because of their profound effect on the luminescence yield

and charge transport efficiencies of MEH-PPV and related molecules and therefore on the overall efficiency of LED devices fabricated from them.

Electroabsorption is a technique that permits the measurement of two fundamental electronic properties of a molecule, namely the trace of the change in polarizability,  $\text{Tr}\overrightarrow{\Delta\alpha}$ , and the absolute change in dipole moment,  $|\vec{\Delta\mu}|$ , on excitation by analysis of the shift in the absorption band of a frozen isotropic sample in an applied electric field. The value of  $\text{Tr}\overrightarrow{\Delta\alpha}$  is frequently associated with the size of the exciton in a given material, a quantity that is frequently related to charge mobility through the molecular skeleton.<sup>17, 18</sup> The quantity  $|\vec{\Delta\mu}|$  is associated with the charge-transfer character of the optical transition. For symmetric molecules,  $|\vec{\Delta\mu}|$  is expected to be zero, though disorder can break the symmetry of the molecule and allow a substantial  $|\vec{\Delta\mu}|$  to be observed.

Previously, we have applied this technique to films of emeraldine base (EB) and of a 5-ring model oligomer dispersed in a poly(methyl methacrylate) (PMMA) matrix.<sup>19</sup> These measurements revealed a surprisingly large  $|\vec{\Delta\mu}|$  in this nominally symmetric molecule. Using electronic structure calculations to probe the source of the symmetry breaking, we found that small torsions of the rings of the molecule were sufficient to induce net charge-transfer character to the optical absorption band. In this system, the experimentally measured  $|\vec{\Delta\mu}|$  could be rationalized solely on the basis of this intramolecular structural disorder, without the need to invoke additional disorder arising from the glassy matrix. As the value of  $\text{Tr}\overrightarrow{\Delta\alpha}$  of EB is relatively small ( $200 \pm 20 \text{ \AA}^3$ ), one would *not* expect a significant contribution from induced moments due to local fields.

Here, we apply the same technique to measure the electronic properties of MEH-PPV and several model oligomers (Scheme 1) dispersed in solvent glass matrices, focusing on the transition between the ground ( $1A_g$ ) and lowest excited ( $1B_u$ ) electronic states. Once again, the observed  $|\Delta\vec{\mu}|$ 's are found to be fairly large ( $|\Delta\vec{\mu}| > 6$  D) though the molecules are nominally symmetric. However, unlike EB, these molecules all exhibit significant  $\text{Tr}\overleftrightarrow{\Delta\alpha}$ 's, making them potentially more sensitive probes of local fields in their environment. The observed values of  $\text{Tr}\overleftrightarrow{\Delta\alpha}$  are, in fact, a factor of 8 larger than what would be predicted based on INDO/SCI finite field calculations of the *gas-phase* polarizabilities of a planar oligomer. However, when the electronic states of this molecule are solvated, using the methodology of Moore, *et al.*,<sup>20</sup> good agreement between experimental and calculated polarizabilities are obtained. Cast in the language of continuum solvation theory, the method accounts for the enhancement of  $\text{Tr}\overleftrightarrow{\Delta\alpha}$  due to the reaction field arising from the high-frequency dielectric response of a non-polar environment. The high-frequency dielectric response screens the electron-hole interaction in the excited states, lowering the energy gaps between the excited states and increasing their polarizability. Of particular importance is the energy gap between the  $1B_u$  and  $mA_g$  state. The  $mA_g$  state carries most of the optical intensity out of the  $1B_u$  state,<sup>21</sup> and electron-hole screening must be included to obtain calculated values for the  $1B_u$ - $mA_g$  energy gap that are in agreement with experiment. Properly accounting for this electron-hole screening effect also proved critical to successfully modeling the origin of the experimental  $|\Delta\vec{\mu}|$ , as will be shown below.

The observation of a non-zero  $|\Delta\vec{\mu}|$  in nominally symmetric ( $C_{2h}$ ) polyenes has ample precedent in the literature. Values of  $|\Delta\vec{\mu}|$  of up to 20 D have been measured for carotenoids entrained in protein matrices, which have been attributed to substantial organized fields in these environments.<sup>22, 23</sup> Typically, polyenes and smaller carotenoids have exhibited  $|\Delta\vec{\mu}|$ 's of 1-5 D even in polymer and solvent glass matrices.<sup>24-27</sup> Likewise, a  $|\Delta\vec{\mu}|$  of 50 D was reported for the highly polarizable polymer, polydiacetylene.<sup>28</sup>

One of the most detailed studies of this phenomenon in polyenes was performed by Kohler and coworkers, who observed splittings in the narrow holes burned in the  $2A_g$ - $1A_g$  transition of octatetraene entrained in a polycrystalline *n*-alkane matrix at 1.7 K.<sup>29, 30</sup> The lineshape of this high-resolution Stark spectrum was successfully modeled by taking into account the orientations of the alkane molecules surrounding the octatetraene probe as well as their detailed charge distributions. From this it was concluded that the local fields due to the C-H bonds of the alkanes create substantial internal fields that add vectorially with the externally applied field acting on the octatetraene and lead to splitting of the hole.

These studies all suggest that internal fields in the environment can induce dipoles in a polarizable molecule that are manifested as a bulk  $|\Delta\vec{\mu}|$  in an electroabsorption experiment. Here, to mimic this disorder due to the local environment (outer sphere disorder), we surround a planar symmetric model oligomer of PPV either with explicit solvent molecules or with a matrix consisting of random dipoles. We find that a

substantial  $|\vec{\Delta\mu}|$  can be induced in this fashion, but *only* if the electron-hole screening arising from the fast dielectric response of the environment is also included.

Motivated by the success of our earlier studies on EB,<sup>19</sup> we also examined the effect of twisting about the single bonds of a model oligomer of PPV (inner-sphere or geometric disorder) on both  $\text{Tr}\vec{\Delta\alpha}$  and  $|\vec{\Delta\mu}|$  of the molecule. Unlike what was found for EB, calculations on distorted isolated oligomers produced only a minimal  $|\vec{\Delta\mu}|$ . When the electron-hole screening arising from the fast dielectric response of the environment is included, geometric disorder leads to an average  $|\vec{\Delta\mu}|$  of 1-4 D.

These results indicate that the origin of the  $|\vec{\Delta\mu}|$  measured experimentally for MEH-PPV and the oligomers may be traced to a combination of inner-sphere disorder, arising from geometric distortion, and outer-sphere disorder, arising internal fields applied by dipoles in the disordered glassy environment. Since  $|\vec{\Delta\mu}|$  is predicted to be zero in the absence of symmetry breaking, electroabsorption measurements provide a facile and sensitive probe of the degree of disorder in these samples that may find applications, for instance, in screening materials.

## Experimental Methods

**Sample preparation.** Toluene and 2-methyltetrahydrofuran (MeTHF) were used to form organic glasses. Because fully dispersing the polymer in solvent is a slow process, we stirred the sample for two weeks before using. The sample was than placed between two ITO-coated glass slides separated by a Kapton tape spacer such that the thickness of the

sample was  $110 \pm 4$   $\mu\text{m}$ . The optical density (OD) of the polymer glass samples was 0.01-0.19 (monomer unit concentration  $10^{-4} - 2 \times 10^{-3}$  M), and 0.01-0.55 for the oligomer (monomer unit concentration  $10^{-4} - 5.5 \times 10^{-3}$  M).

**Instrumentation.** The electroabsorption apparatus is home built and has been previously described in detail.<sup>31</sup> Briefly, it consists of a 0.3m single monochromator (Spex) that disperses the light coming from a 150W xenon arc lamp (Oriel) and gives a spectral resolution of 3-5 nm. The spectrally narrow light is then horizontally polarized with a Glan-Thomson polarizer in order to define the angle between the direction of polarization of the electric field of the incident light and the direction of the electric field vector of the applied ac voltage. A  $10^5$ - $10^6$  V/cm AC electric field on the sample was generated by a high-voltage power supply at 470 Hz. The transmitted light after passing through the sample was detected by a photodiode (UDT). Small changes in the OD of the sample due to the applied electric field were monitored with a lock-in amplifier. Low-temperature measurements were made using a liquid nitrogen dewar (H. S. Martin). Steady-state fluorescence spectra were obtained using a Fluorolog-2 instrument (Spex) with 1 nm resolution in front-face geometry.

**Data fitting.** The analysis of the electroabsorption data follows that in the literature.<sup>32, 33</sup> The equations shown here are appropriate for the experimental conditions used, *i.e.* the sample is embedded isotropically in a rigid glass. Essentially, the change in absorption due to the application of an external electric field is fit to the weighted sum of zeroth, first and second derivatives of the zero-field absorption spectrum. The overall change in

absorbance caused by the application of an electric field can be described by the following equation:

$$\Delta A(\tilde{\nu}) = \vec{F}_{eff}^2 \left[ \mathbf{a}_\chi A(\tilde{\nu}) + \mathbf{b}_\chi \frac{\tilde{\nu}}{15\hbar} \left\{ \frac{\partial}{\partial \tilde{\nu}} \left( \frac{A(\tilde{\nu})}{\tilde{\nu}} \right) \right\} + \mathbf{c}_\chi \frac{\tilde{\nu}}{30\hbar^2} \left\{ \frac{\partial^2}{\partial \tilde{\nu}^2} \left( \frac{A(\tilde{\nu})}{\tilde{\nu}} \right) \right\} \right] \quad (1)$$

The term  $A(\tilde{\nu})$  represents the unperturbed absorption as a function of frequency ( $\tilde{\nu}$ ) and  $\vec{F}_{eff}$  represents the field at the sample in V/cm. This effective field includes the enhancement of the applied field due to the cavity field of the matrix. The subscript  $\chi$  represents the angle between the direction of the applied electric field and the electric field vector of the linearly polarized light. The experiments reported here are performed at  $\chi = 54.7^\circ$  (magic angle). Note that magic angle is determined in the cell by taking into account the relevant indices of refraction as in Ref. 34. At  $\chi = 54.7^\circ$ , the expressions of  $a_\chi$ ,  $b_\chi$ , and  $c_\chi$  are related to the change in the transition moment polarizability ( $A_{ij}$ ) and hyperpolarizability ( $B_{ijj}$ ), the average change in the electronic polarizability ( $\langle \underline{\Delta a} \rangle$ ), and the change in the dipole moments ( $|\overrightarrow{\Delta \mu}|$ ) respectively, as given in Eqns. 2-4 below.

$$\mathbf{a}_{54.7} = \frac{1}{3|\vec{m}|^2} \sum_{i,j} A_{ij}^2 + \frac{2}{3|\vec{m}|^2} \sum_{i,j} m_i B_{ijj} \quad (2)$$

$$\mathbf{b}_{54.7} = \frac{10}{|\vec{m}|^2} \sum_{i,j} m_i A_{ij} \Delta \mu_j + \frac{15}{2} \langle \underline{\Delta a} \rangle \quad (3)$$

$$\mathbf{c}_{54.7} = 5 |\overrightarrow{\Delta \mu}|^2 \quad (4)$$

In this work we quote  $Tr \overrightarrow{\Delta \alpha}$  which represents the trace of the change in electronic polarizability between the ground and excited state (i.e.  $\langle \underline{\Delta a} \rangle = 1/3 Tr \overrightarrow{\Delta \alpha}$ ) in order to be consistent with the bulk of published work in the area of Stark spectroscopy

on polymers. Information regarding  $|\overrightarrow{\Delta\mu}|$  for the molecule is contained in the  $c_{54.7}$  term (Eqn. 4). It is important to emphasize that, for an isotropic sample such as those studied in this work, only the magnitude and not the sign of  $\overrightarrow{\Delta\mu}$  is measured. In the above equations, the tensors  $\underline{A}$  and  $\underline{\underline{B}}$  represent the transition polarizability and hyperpolarizability respectively. These describe the effect of  $\vec{F}_{eff}$  on the molecular transition moment:  $\bar{m}(\vec{F}_{eff}) = \bar{m} + \underline{A} \cdot \vec{F}_{eff} + \vec{F}_{eff} \cdot \underline{\underline{B}} \cdot \vec{F}_{eff}$ . These terms are generally small for allowed transitions and can therefore be neglected relative to other terms in the expression for  $\langle \underline{\Delta\alpha} \rangle$  (Eqn 3).

The coefficients,  $a_\chi$ ,  $b_\chi$  and  $c_\chi$ , are extracted by means of a linear least-squares (LLSQ) fit of the electroabsorption signal to the sum of the derivatives of  $A(\tilde{\nu})$ . If the resultant fit to the absorption line-shape (a single set of  $a_\chi$ ,  $b_\chi$  and  $c_\chi$ ) is *not* of high quality, this is an indication that there is more than one transition (electronic or vibronic) underlying the absorption band, each having different electro-optical properties. Our fitting strategies are described in Ref. 35.

## Computational Methods

**Geometry optimization and introduction of inner-sphere disorder.** The two types of oligomers studied computationally are shown in Scheme 2. The first (Scheme 2a) is the unsubstituted PPV while the second (Scheme 2b) has hydroxyl groups attached to every other ring so as to resemble the substituted oligomer studied experimentally, OPPV-9 (Scheme 1b). Planar oligomers of PPV with 2 to 16 rings were constructed to study the chain-length dependence of the electro-optical properties. To determine the effect of

chain conformation on the electronic properties of these species, non-planar geometries of an 8-ring PPV oligomer (PPV-8), were obtained by constraining the dihedral angles ( $\phi$  in Scheme 2a) between adjacent phenylene rings while optimizing all other coordinates. Ten non-planar structures were created having dihedral angles between  $-45^\circ$  to  $+45^\circ$  generated by a uniform random number generator. This geometry distortion is defined as the inner-sphere disorder in this paper.

All of the geometry optimizations were performed using MOPAC 7 with the AM1 Hamiltonian.<sup>36</sup> Following optimization, the inertial axes for each structure were used to define a coordinate system for the calculation of the polarizabilities. These were defined such that the moments of inertia along the X-, Y-, and Z-axes increase in magnitude and the origin lies at the center of mass. In the linear and planar structure, this corresponds to the X-axis lying along the long dimension of the molecule and the Y-axis being in the molecular plane.

**Electronic structure calculations.** All calculations reported in this paper were performed at the INDO/SCI level. A recently developed direct CI method was applied that permits inclusion of single excitations between all molecular orbitals (full-SCI).<sup>37</sup> Full SCI was used for all calculations except for those in which a PPV oligomer was surrounded by a random dipole lattice (see below). In this case, because of the need to construct hundreds of different lattices to obtain a statistical distribution of the electro-optical properties, the associated INDO/SCI calculations included only  $\pi$  and  $\pi^*$  orbitals of the planar PPV-8 oligomer. For planar PPV, the primary effect of restricting the SCI

calculation to  $\pi$  orbitals is to increase the  $1B_u$ - $mA_g$  energy separation by  $\sim$ 0.2 eV. This is corrected by changing the dielectric screening parameter (see below).

**Finite-field method for electro-optical property calculations.** The finite field method, described by Kurtz *et al.*,<sup>38</sup> was used to calculate the dipole moments and polarizabilities of the ground and excited states. The magnitude of the applied electric field used was  $5 \times 10^5$  V·cm<sup>-1</sup>, or  $9.7 \times 10^{-5}$  a.u. Use of a field strength that is too large or too small causes numerical errors that make the calculated results unstable (see Supplemental Materials). The value chosen here leads to stable numerical results, and is also of the same magnitude as the external field used in the experiments reported here.

Both the energy derivative method, which obtains the dipole and polarizability from derivatives of the energy, and the dipole moment derivative method, which obtains the polarizability from derivatives of the induced dipole moment, were tested. Although, in most cases, the results obtained with these two methods were very similar, we found that the dipole moment derivative method was more stable both with regard to the magnitude of the finite field used to evaluate the derivatives and with regard to truncation of the molecular orbitals included in the SCI calculation (see Supplemental Materials). Therefore, in this paper, only the dipole moment derivative results are reported.

**Dielectric screening model for inclusion of solvation effects.** Dielectric screening effects are included in the calculation in order to obtain reasonable results for the higher energy excited states, especially the  $mA_g$  state that plays an important role, as we will demonstrate, in establishing the magnitude of the excited-state polarizability. Moore *et*

*al.*<sup>20</sup> compared a dynamic dielectric model, that explicitly includes the timescales of both the electron-hole motion and the dielectric response, with a simpler fast dielectric model, that assumes the dielectric polarization can follow the electron-hole motion and screen their interaction. This comparison indicated that the fast dielectric model provides a reasonable description of the effects of dielectric screening on the excited states, and it is this model that is used throughout this paper.

The fast dielectric model is implemented by first transforming from the delocalized, canonical Hartree-Fock orbitals to local orbitals that are centered on particular molecular segments. This is done by using the local orbital method of Pasquinelli,<sup>39</sup> with the segments of the PPV oligomer chosen as the individual phenylene and vinylene groups. In these localized orbitals, the singly-excited configurations of SCI theory contain an electron and hole, each of which is centered on a particular phenylene or vinylene group of the oligomer. The diagonal elements of the SCI Hamiltonian matrix represent the energy of each particular arrangement of the electron and hole, and dielectric screening is included by adding a dielectric stabilization energy to each of these diagonal elements.

The dielectric stabilization (or solvation) energy is obtained as follows. Within a linear dielectric approximation, the solvation energy of an arbitrary charge distribution may be written as,

$$E_{solv} = \sum_{i,j}^N \rho_i \rho_j G(\mathbf{r}_i, \mathbf{r}_j) \quad (5)$$

where  $\rho_i$  is the charge density at site  $i$ , and the Green's function,  $G(\mathbf{r}_i, \mathbf{r}_j)$ , describes the energy of interaction between a unit charge at  $\mathbf{r}_i$  and the polarization induced by a unit

charge at  $\mathbf{r}_j$ . Here, we assume the Green's function depends only on the distance between the two points,  $|\mathbf{r}_i - \mathbf{r}_j|$ . For large  $|\mathbf{r}_i - \mathbf{r}_j|$ , a continuum dielectric model gives,

$$G(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \left[ \frac{1-\varepsilon}{\varepsilon} \right] \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (6)$$

where  $\varepsilon$  is the dielectric constant of the material. As organic systems typically have low optical dielectric constants,  $\varepsilon = 2.0$  was used in the calculations presented here. The short-range behavior of  $G(\mathbf{r}_i, \mathbf{r}_j)$  is evaluated explicitly for point charges surrounded by polyacetylene chains, each of which is modeled at the Hückel level,<sup>20</sup> and this function is spliced with that of Eqn. 6 to obtain a smooth function of  $|\mathbf{r}_i - \mathbf{r}_j|$  (see Supplementary Materials). This approach provides a function that interpolates in a reasonable manner between  $G(0)$ , the solvation energy of a point charge (-1.1 eV for the function used here), and the form of Eqn. 6 for distances greater than about 6 Å. While this is a reasonable function for  $G(\mathbf{r}_i, \mathbf{r}_j)$ , it may not be quantitative and so we introduced a semi-empirical scaling parameter,  $S_{\text{diel}}$ , that is multiplied by  $G(\mathbf{r}_i, \mathbf{r}_j)$  and sets the strength of the dielectric screening. Below,  $S_{\text{diel}}$ , is adjusted based on the experimentally observed energy of the  $mA_g$  state which is ~0.6 eV above the  $1B_u$  state.<sup>40, 41</sup> Inclusion of sigma orbitals alters the gap between the  $1B_u$  and  $mA_g$  states, such that a 0.6 eV gap between the  $1B_u$  and  $mA_g$  states is obtained for  $S_{\text{diel}} = 1.4$  in full SCI and for  $S_{\text{diel}}=1.0$  when only  $\pi$  orbitals are included in the S-CI basis. These values for  $S_{\text{diel}}$  are used in the remainder of the paper.

**Models for outer-sphere disorder.** The dielectric screening discussed in the previous section models the effects of optical polarization on the electron-hole interaction in the excited states. This effect results from the dynamic polarization induced in the solvent molecules by the electron and hole. In this section, we consider a quite different effect, that of symmetry breaking due to the permanent charges on the solvent molecules and the amorphous arrangement of these solvent molecules. Such environmental effect is defined as the outer-sphere disorder in the paper. Results are presented for the following two models.

**A. Explicit small molecules as the environment.** In this model, molecular mechanics is used to surround a PPV-8 oligomer that is constrained to remain in an ideal planar geometry, with an amorphous sample of MeTHF molecules. The charges on the MeTHF were Mulliken charges obtained from an AM1 calculation on an isolated MeTHF molecule. The amorphous structure was obtained by running a molecular dynamics trajectory and quenching the sample at four different times (see Supplementary Materials for details). The resulting charge distribution was then used to calculate the potential applied to the PPV-8 structure using Coulomb's law,

$$V_a = \frac{1}{4\pi\epsilon_0} \sum_i^N \frac{q_i}{|\mathbf{r}_a - \mathbf{r}_i|} \quad (7)$$

where  $V_a$  is the potential for atom  $a$  at  $\mathbf{r}_a$ , and  $q_i$  is a charge at  $\mathbf{r}_i$  in this random charge distribution with a total of  $N$  charges. While these calculations do give some insight into the effects of an amorphous environment, visual examination of the lattices shows unphysically large density fluctuations (*i.e.* voids). This is due to the fact that the calculations were not performed at constant pressure. To avoid this complication and to

permit the examination of a large number of lattices in a computationally efficient manner, the dipole lattice model, described below, was developed.

**B. Dipole lattice model of random environment.** A lattice was constructed containing a cavity for planar PPV-8 in which each lattice site was occupied by a randomly-oriented dipole moment. The orientations of the dipoles were obtained from a random number generator to generate the polar angles  $\theta$  (using a  $\sin\theta$  distribution) and  $\phi$  (using a uniform distribution). The cavity size, the number of dipoles in the lattice, the magnitude of the dipoles, and the spacing between the lattice sites were parameters that were varied in building and testing the dipole lattice model. The dependence of the electro-optical properties on these lattice parameters is discussed in detail in the Supplemental Materials.

In the main text, we report calculations performed using two types of lattices. The first lattice models the overall dipole moment of the solvent molecules. This lattice has a spacing of 6 Å, which is similar to the size of MeTHF, and dipoles with magnitude 1.5 D, which is that calculated for a MeTHF molecule using AM1. The cavity is such that the spacings between the outmost hydrogen atoms in the PPV-8 and the closest lattice sites are 4.5 Å, 3.5 Å, and 6 Å in the X-, Y-, and Z- directions, respectively. Results were generated for 500 randomly generated lattices.

The second lattice reported in the main text models CH bond dipoles. In Kohler's studies of octatetraene entrained in *n*-alkane matrices, in which the alkane molecules of the matrix have no net dipole, significant internal fields were found to arise from the CH bond dipoles.<sup>29, 30</sup> To model the CH dipoles of the glass within the random lattice approach, we used a lattice with the same cavity size as used above, but with a lattice

spacing of 3 Å and dipoles of 0.65 D, the dipole moment of a CH<sub>2</sub> group. These lattice parameters give results that are similar to those of the above lattice.

## Results and Discussion

**Fluorescence spectra in organic glasses.** In order to examine the effect of the frozen glass matrix on the properties of the oligomers and of MEH-PPV, their fluorescence excitation and dispersed fluorescence spectra in toluene at room temperature and at 77K were obtained (Figs. 1 and 2). The spectra of MEH-PPV and OPPV-9, in addition, were obtained in MeTHF glass (Fig. 1). In all cases, the excitation spectra at 77K are substantially narrower than at room temperature and the Stokes shift is significantly smaller. Moreover, reasonable mirror image symmetry is observed in the glass for all systems, though, for MEH-PPV in MeTHF, it is apparently obscured by the presence of multiple conformers within the glass matrix (see below). Both the narrowing of the spectra and the decrease in the observed Stokes shift upon formation of the glass are likely to be the result of decreased excitation of low-frequency torsional modes at low temperature.<sup>42-45</sup>

As noted above, the emission spectrum of MEH-PPV in MeTHF is complicated by the presence of at least two spectrally distinct species. Unlike what is seen in toluene, the spacings between the three most prominent bands in the emission spectrum (solid line, Fig. 1c) of MEH-PPV in MeTHF are irregular, suggesting that they do *not* constitute a vibronic progression. Moreover, two excitation spectra having different vibronic spacings from one another (dashed line spectra labeled 1 and 2 respectively in Fig. 1c) are obtained upon excitation of each of the two bands at lowest energy (labeled 1 and 2 in the solid line spectrum, Fig. 1c). From this we conclude that the two most intense bands

in the MEH-PPV spectrum in MeTHF glass represent the respective origins of two distinct conformers of the polymer. It is interesting to note that Barbara and coworkers have identified two distinct conformers of MEH-PPV dispersed in inert polymer matrices such as polystyrene using single molecule fluorescence spectroscopy.<sup>46</sup>

**Electroabsorption spectra in organic glasses.** Fig. 3 contains the absorption and the electroabsorption spectra of the lowest energy band of OPPV-9 and MEH-PPV dispersed in toluene and in MeTHF at 77K. The middle row shows the electroabsorption spectra (solid line) and fit (dashed line) while the bottom row contains the decomposition of the fits into the zeroth, first, and second derivatives of the corresponding absorption spectrum (see Experimental Section). These measurements were made in the low concentration limit, (OD of ~0.01 in a path length of ~ 110  $\mu\text{m}$ ), which corresponds to monomer unit concentration of about  $10^{-4}$  M. We therefore expect that these results at low concentrations can be meaningfully compared to the time-resolved microwave conductivity (TRMC) results of Warman *et al.* that were obtained in dilute room temperature solution ( $10^{-4}$  M in monomer units).<sup>18, 47</sup>

High-quality fits to the electroabsorption spectrum are observed for both the oligomer and for the polymer in both solvent glasses. These fits yield similar values of  $\overrightarrow{\text{Tr}\Delta\alpha}$  for OPPV-9 as for the polymer, though the change in dipole moment is somewhat smaller for the oligomer (6.3 D) than for the polymer (11 D).

As noted earlier for the fluorescence spectra, the identity of the solvent has a dramatic effect on the appearance of the polymer absorption spectrum, though not on that of OPPV-9. In toluene glass, both the oligomer and the polymer exhibit a vibronic

progression with a spacing of  $\sim 1350 \text{ cm}^{-1}$  with that in the oligomer being more highly resolved (compare Fig. 3d to Fig. 3j). In MeTHF glass, the oligomer exhibits a similar progression to that seen in the toluene glass (Fig. 3a) while the absorption spectrum of the polymer is significantly altered (Fig. 3g). Specifically, the spacing between the first two peaks in the polymer spectrum (seen most readily in the electroabsorption spectrum, Fig. 3h) is  $\sim 1000 \text{ cm}^{-1}$  while that between the second and third peaks is  $\sim 1350 \text{ cm}^{-1}$ . The irregularity in these spacings suggests that more than one species of MEH-PPV is present in the MeTHF glass though similar heterogeneity is not evident in the toluene glass. This confirms the interpretation of the fluorescence spectrum of this sample given above.

Despite this apparent heterogeneity in the MEH-PPV sample in MeTHF, the overall fit to the electroabsorption spectrum is of reasonably high quality, at least in the low concentration limit. However, as the concentration of MEH-PPV is increased, the experimental data and the fit deviate substantially in MeTHF (data not shown), suggesting that these different species may have different values of  $Tr\overrightarrow{\Delta\alpha}$  and/or  $|\overrightarrow{\Delta\mu}|$ . Another possible explanation is that aggregates are formed at higher concentration and these have different values of  $Tr\overrightarrow{\Delta\alpha}$  and/or  $|\overrightarrow{\Delta\mu}|$  than the isolated species.

Turning now to the electroabsorption results for the PPV oligomers (Scheme 1c and d), shown in Fig. 4, we find that the fits to the data are of exceptionally high quality, suggesting that all possible conformers present and all of the vibronic levels have similar electro-optical parameters. As expected, the values obtained for  $Tr\overrightarrow{\Delta\alpha}$  of these shorter oligomers (780 Å for PPV-5 and 140 Å for PPV-3) are smaller than those obtained for the 9-ring substituted oligomer. The values of  $|\overrightarrow{\Delta\mu}|$  are also somewhat smaller than those

obtained for the longer chain length species, consistent with a mechanism in which the dipole moment is induced by interaction of the molecular polarizability with a disordered local field (see below).

**Comparison to other literature results.** The results obtained here for  $Tr\overrightarrow{\Delta\alpha}$  of MEH-PPV lie within the range of values that have been reported earlier ( $\sim$ 400–20 000 Å<sup>3</sup>) for both MEH-PPV and PPV also using electroabsorption.<sup>41, 48, 49</sup> This variation may in part reflect differences in sample conditions, *i.e.* solvent glass versus neat film. It is particularly interesting to compare our findings with the microwave conductivity measurements of Warman, *et al.*<sup>18, 47</sup> obtained for the oligomer and the polymer in dilute room temperature toluene because the two techniques used probe different regions of the excited-state surface. As electroabsorption probes the Franck-Condon region, it is sensitive to the presence of a distribution of ground-state conformations having different effective conjugation lengths. Normally, solid state or frozen glass samples are used as well. Microwave conductivity, on the other hand, measures the properties of the *relaxed* excited state in a liquid-phase sample.

Microwave conductivity gives somewhat larger values of  $Tr\overrightarrow{\Delta\alpha}$  ( $\sim$ 3000 Å<sup>3</sup> for the oligomer and  $\sim$ 4800 Å<sup>3</sup> for the polymer) than those reported here (Table 1). A somewhat larger discrepancy is seen when we compare our results for PPV-3 and PPV-5 (Table 1) to those obtained from microwave conductivity which are  $\sim$ 1100 and  $\sim$ 2800 Å<sup>3</sup>, respectively.<sup>18</sup> One may expect a discrepancy to arise in the case of the polymer because microwave conductivity measures the properties of the system presumably after rapid intra-molecular energy transfer to the longest segment has occurred. However, to explain

differences between the results obtained on the oligomer using the two methods, it may be necessary to consider the effects of the environment (glass versus solution) and/or the characteristics of the region of the excited state surface being probed. The latter possibility is currently being investigated *via* electrofluorescence measurements in organic glasses.

More relevant from the point of view of this study is that the substantial values of  $|\overline{\Delta\mu}|$  that we measure for MEH-PPV and for both the substituted and unsubstituted oligomers have no precedent in the literature, either in electroabsorption or microwave conductivity studies. However, using electroabsorption, Hovárh *et al.* have reported a  $|\overline{\Delta\mu}|$  of 50 D for a disordered polydiacetylene film having an estimated average polarizability of  $\sim 7000 \text{ \AA}^3$  ( $Tr \overrightarrow{\Delta\alpha}$  of  $\sim 21\,000 \text{ \AA}^3$ ).<sup>28</sup> Whether or not a value for  $|\overline{\Delta\mu}|$  is reported for MEH-PPV in any given study may be attributed to differences in data interpretation that are summarized below. In this contribution, *we will argue that it is valid to associate this second-derivative contribution to the field response in the organic glass matrices with a non-zero effective  $|\overline{\Delta\mu}|$  that is induced by disordered matrix fields.*

**Models for the origin of a non-zero  $|\overline{\Delta\mu}|$ .** Similar to what is found here for MEH-PPV and the oligomers, numerous other studies in the literature have also reported substantial values of  $|\overline{\Delta\mu}|$  for all-*trans* polyenes as well as for longer (up to polymeric) conjugated species.<sup>23-26, 28, 29</sup> In all cases, the molecules studied are *nominally* symmetric ( $C_{2h}$ -derived) and would therefore be predicted to have a  $|\overline{\Delta\mu}|$  that is close to zero.

Two frequently invoked mechanisms for the required symmetry breaking are the following. One is that structural disorder (torsions, *etc.*), possibly induced by the surrounding matrix, can lead to a reduction in the effective point group of the molecule. Weiser and coworkers observed a  $\sim 50$  D dipole moment in disordered samples of polydiacetylene but not in ordered crystalline samples.<sup>28</sup> They attributed the large dipole to defects in the disordered sample, and suggested that these defects break the centrosymmetry of the exciton state by imposing asymmetric boundary conditions on the exciton wavefunction. The second symmetry breaking mechanism is the presence of asymmetric fields in the local condensed-phase environment, which will induce a substantial  $|\overrightarrow{\Delta\mu}|$  in molecules having a significant  $\overrightarrow{\Delta\alpha}$ .<sup>22, 50</sup>

A third model, recently outlined by Vardeny *et al.*, is that a second-derivative contribution to the fit to the electroabsorption spectrum can arise from having a variety of effective conjugation lengths in a given sample of a long-chain polyene all of which have different values of  $Tr \overrightarrow{\Delta\alpha}$ .<sup>41</sup> Fitting such a heterogeneous sample using the formalism commonly used to model electroabsorption data (see Experimental section) can lead to the observation of higher (second) derivatives that are then *incorrectly* ascribed to a characteristic molecular  $|\overrightarrow{\Delta\mu}|$ . An upper limit of this contribution to the second derivative of the EA spectrum can be obtained by assuming that regions with short conjugation length, on the blue side of the absorption line, have zero  $Tr \overrightarrow{\Delta\alpha}$ . If this were the case, only the red side of the absorption line would shift in the applied field, and the observed broadening of the line would be roughly twice the observed red shift. A useful benchmark is to consider the value of  $|\overrightarrow{\Delta\mu}|$  that would arise from interpreting a

broadening that is twice the observed red shift in terms of a  $|\overrightarrow{\Delta\mu}|$ . This can be obtained by dividing the observed  $Tr\overrightarrow{\Delta\alpha}$  by the applied external field of about  $3 \times 10^5$  V/cm., which gives a value of 2 D. This is a small fraction of the broadening that we observe, which corresponds to 6-10 D. This indicates that this third mechanism, by which the dependence of the polarizability on conjugation length leads to a broadening of the spectral line in an applied field, can only account for a small portion of the observed broadening.

In another model, Martin *et al.* have suggested that the electroabsorption signal of nominally symmetric polyenes deviates from the pure first-derivative lineshape expected for a field response dominated by  $Tr\overrightarrow{\Delta\alpha}$  because of the contribution of a bleach signal in the higher-energy region.<sup>51</sup> This bleach is attributed to intensity borrowing from the  $1B_u$  state by an even-parity state that becomes allowed in the presence of the applied field. This model does not appear to match our results, particularly for the oligomers, as all of our electroabsorption lineshapes deviate from the first derivative of the absorption spectra more or less equally across the entire frequency range probed (Figs 3 and 4, bottom panels). We will therefore not consider it further here.

The computational results presented below address the first two models described above. Specifically, two mechanisms for inclusion of symmetry breaking are examined here: (1) inner-sphere disorder or geometric distortion of the molecule in a dielectric medium and (2) outer-sphere disorder or inclusion of a random dipole field surrounding a symmetric molecule that mimics the solvent glass. Our results suggest that both types of disorder, in conjunction with dielectric screening, may contribute significantly to the observed  $|\overrightarrow{\Delta\mu}|$ , with the contribution due to the random dipole field being somewhat

larger. We note that *neither* mechanism will lead to a significant  $|\overrightarrow{\Delta\mu}|$  if the effects due to dielectric screening are not also accounted for.

## Computational Results

**Predictions for  $\overrightarrow{Tr\Delta\alpha}$ .** Fig. 5 shows the chain length dependence of  $Tr\overrightarrow{\Delta\alpha}$  for planar oligomer structures of PPV-n obtained with and without inclusion of dielectric screening.  $Tr\overrightarrow{\Delta\alpha}$  saturates by n~8, in accordance with other studies.<sup>18, 52-55</sup> However, the gas-phase  $Tr\overrightarrow{\Delta\alpha}$  value is only  $\sim 300 \text{ \AA}^3$  for long-chain oligomers, which is *considerably smaller* than the experimentally observed values of Table 1. However, inclusion of dielectric screening (shown in Fig. 5 by the triangles) *via* the fast dielectric model (see Experimental Section) increases the predicted  $Tr\overrightarrow{\Delta\alpha}$  to be roughly ten times the value from the gas phase calculation, leveling off at around  $3000 \text{ \AA}^3$  for long chains. This produces a significantly better match to experiment (Table 1). A similar situation arises in density functional theory calculations of excited state polarizabilities, where addition of dielectric screening of electron-hole interactions leads to a good match between theory and experiment.<sup>56</sup> The inset of the figure shows that  $Tr\overrightarrow{\Delta\alpha}$  approaches the long chain limit more quickly in the gas-phase calculations than in those including dielectric screening, but in either case,  $Tr\overrightarrow{\Delta\alpha}$  is near the long chain limit by 8 rings.

The PPV-8 oligomer was studied in greater detail, and Fig. 6 shows the calculated  $Tr\overrightarrow{\Delta\alpha}$  as the scaling factor for the dielectric interaction is increased from  $S_{\text{die}}=0$  (gas phase) to  $S_{\text{die}}=1.4$ . The top axis of the graph shows  $S_{\text{die}}$  while the lower axis represents the calculated energy difference between the  $1B_u$  and  $mA_g$  states. Fig. 6 indicates that the

experimental energy difference (0.55-0.65 eV) is obtained with a value of  $S_{\text{diel}}$  lying between 1.32-1.44. This value of  $S_{\text{diel}}$  in turn places  $\overrightarrow{\text{Tr}\Delta\alpha}$  between 2100 and 3000 Å<sup>3</sup>. A similar result is obtained for the OPPV-9 oligomer (Supplemental Materials), which is in excellent agreement with the experimentally observed value (Table 1).

The dependence of  $\overrightarrow{\text{Tr}\Delta\alpha}$  on the  $1B_u-mA_g$  energy gap can be understood as follows. The  $\overrightarrow{\text{Tr}\Delta\alpha}$  is dominated by the component along the long axis of the oligomer,  $\Delta\alpha_{xx}$ . In this direction, assuming the excited state polarizability is dominated by the transition moment between the  $1B_u$  and the  $mA_g$  state, the polarizability change  $\Delta\alpha_{xx}$  can be written as,

$$\Delta\alpha_{xx} \approx \frac{\left| \langle 1B_u | \mu_x | mA_g \rangle \right|^2}{\Delta E} \quad (8)$$

If we further assume that the oscillator strength between the  $1B_u$  and  $mA_g$  states is a constant, the transition moment has the following dependence on the energy gap:

$$\left| \langle 1B_u | \mu_x | mA_g \rangle \right|^2 \propto \frac{1}{\Delta E} \quad (9)$$

The dependence of Eqn. 9 results from the definition of the oscillator strength as the product of  $\Delta E$  and the square of the transition moment. With these assumptions,  $\overrightarrow{\text{Tr}\Delta\alpha}$  should be inversely related to the square of  $\Delta E$ . The inset of Fig. 6 shows that this is indeed the case for the calculations performed here.

**Effect of inner-sphere disorder (chain conformation) on electronic properties.** Table 2 contains the values of  $\overrightarrow{\text{Tr}\Delta\alpha}$  obtained for ten oligomers of PPV-8 with dihedral angles between adjacent phenylene rings assigned randomly within the range  $-45^\circ$  to  $+45^\circ$ . The

$\overleftrightarrow{Tr\Delta\alpha}$  values for all structures are slightly smaller than that of a planar PPV-8 oligomer. Specifically, the values of  $\overleftrightarrow{Tr\Delta\alpha}$  are ~90% of that of the planar structure without inclusion of dielectric screening and ~80% with screening. In contrast, the predicted excitation energy of the lowest energy electronic transition is quite sensitive to chain conformation, with the average 0-0 energy in the ten random PPV-8 structures being ~0.14 eV ( $1100 \text{ cm}^{-1}$ ) to higher energy than that of the planar geometry.

More interesting is the fact that the average  $|\overline{\Delta\mu}|$  of the ten structures is nearly zero without the inclusion of dielectric screening, but increases to  $4 \pm 1 \text{ D}$  with screening. The larger  $|\overline{\Delta\mu}|$  obtained with the inclusion of screening can be understood as follows. For a symmetric structure, the electron and hole are symmetrically distributed in the excited state. The calculated  $|\overline{\Delta\mu}|$ 's are a measure of how geometric distortions break this electronic symmetry. Screening weakens the attraction between the electron and hole, increasing the degree of electronic symmetry breaking. The above results suggest that loss of  $C_{2h}$  symmetry in the oligomer structure itself (inner-sphere disorder) can account for a portion of the observed  $|\overline{\Delta\mu}|$ , but that other symmetry breaking mechanisms, such as the outer-sphere disorder considered below, are needed to account for the remainder of the values observed experimentally.

**Effect of outer-sphere disorder (disordered solvent environment) on electronic properties.** The effects of outer-sphere disorder were investigated in two ways, first by surrounding a planar PPV-8 with explicit MeTHF molecules in a disordered arrangement

in order to simulate the glassy environment and second by simulating the presence of a disordered solvent with a random dipole field (see Experimental Section).

In the explicit MeTHF environments, the gas-phase  $|\overline{\Delta\mu}|$ 's obtained are similar to those obtained without the random environment (less than 1 D). However, when dielectric solvation is included, values of  $|\overline{\Delta\mu}|$  anywhere between 0 and 9 D are observed, depending on the specific MeTHF matrix used.

Although the large  $|\overline{\Delta\mu}|$  values obtained for certain MeTHF matrices are suggestive of the substantial values that can be induced by environmental asymmetry, it is more informative to obtain a statistical distribution of  $\overline{\Delta\mu}$  over many random environments. To construct a more controlled and reproducible ensemble of environments, the lattice model of random dipoles described earlier was used. Because the Stark experiments measure the square of the dipole moment averaged over randomly-oriented molecules within a solid sample, we will compare the experimental value to the root mean square of  $\overline{\Delta\mu}$ ,  $rms\text{-}\overline{\Delta\mu}$ , obtained from 500 randomly generated lattices.

Figs. 7 and 8, respectively, contain the distributions of  $Tr\overrightarrow{\Delta\alpha}$  and  $\Delta\mu_x$  obtained from the dipole lattice model with lattice parameters chosen to mimic the overall dipole of the MeTHF solvent molecules (see Experimental Section). Only  $\Delta\mu_x$  is reported because, in all cases, the dipole moments are very small in both the Y- and Z- directions. These dipole lattices produce an  $rms\text{-}\overline{\Delta\mu}$  of 7.5 D in a nominally symmetric oligomer, illustrating the large effects that the properties of the matrix can have on the electro-optical parameters. Consistent with what was seen earlier in the uniform dielectric model, the average values and the standard deviations of the  $1B_u\text{-}mA_g$  energy gap and

$\overrightarrow{Tr\Delta\alpha}$  are respectively  $0.65 \pm 0.07$  eV, and  $2300 \pm 500$  Å<sup>3</sup> (the median is  $\sim 2200$  Å<sup>3</sup> and the mode is  $\sim 2000$  Å<sup>3</sup>). To summarize, the  $Tr\overrightarrow{\Delta\alpha}$  and the  $rms\text{-}\overline{\Delta\mu}$  values are all in very good agreement with the Stark measurements reported here, and the  $1B_u\text{-}mA_g$  energy difference is also within the range of 0.55-0.65 eV reported previously in the literature.<sup>40</sup>

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Similar values to these are obtained for lattice parameters that are chosen to model CH bond dipoles (see Experimental Section). This lattice leads to a  $rms\text{-}\overline{\Delta\mu}$  of 8.4 D, a  $1B_u\text{-}mA_g$  energy gap of  $0.64 \pm 0.08$  eV, and a  $Tr\overrightarrow{\Delta\alpha}$  of  $2400 \pm 500$  Å<sup>3</sup> (with median of  $\sim 2200$  Å<sup>3</sup> and mode of  $\sim 2000$  Å<sup>3</sup>).

The above results were obtained with the inclusion of dielectric screening. Without screening, the  $rms\text{-}\overline{\Delta\mu}$  is only 1.7 D. This is similar to what was seen earlier for calculations using explicit MeTHF matrices. The  $rms\text{-}\overline{\Delta\mu}$  reflects the ability of the charges on the solvent to induce a dipole moment, and is therefore related to the polarizability of the  $1B_u$  state. Since inclusion of dielectric screening is required to reproduce the observed  $Tr\overrightarrow{\Delta\alpha}$ , it is not surprising that dielectric screening must be included to obtain reasonable results for  $\overline{\Delta\mu}$ . In other words, *it is only when both solvation and the random charge environment are included that the experimental electro-optical properties can be reproduced.*

We note, however, that  $\overline{\Delta\mu}$  is not simply related to  $Tr\overrightarrow{\Delta\alpha}$ . That is, if the solvent could be viewed simply as applying a uniform static electric field to the oligomer, one would expect that the ratio  $\mu_x(1B_u)/\mu_x(gs)$  would be given simply by the ratio of the polarizabilities of these two states, since the polarizabilities are not strongly dependent on

the strength of the local fields in the environment (*i.e.* the hyper-polarizabilities are small). Fig. 8 shows that this is *not* the case, indicating that the electrostatic environment arising from permanent charges in the surroundings cannot be modeled by a simple uniform electric field. This is consistent with Kohler's finding that the electric field arising from the CH bond dipoles in an *n*-alkane matrix is very non-uniform.<sup>29, 30</sup>

## Summary and Conclusions

This paper presents experimental measurements of the change in polarizability ( $\overrightarrow{Tr\Delta\alpha}$ ) and permanent dipole moment ( $|\vec{\Delta\mu}|$ ) accompanying photo-excitation from the ground electronic state to the  $1B_u$  excited state of MEH-PPV polymer and several model oligomers in solvent glass matrices. Computational studies of these properties, *via* INDO with single-configuration interaction (SCI) theory, reveal two roles played by the glassy environment.

The first role of the environment arises from the fast (optical) dielectric response of the medium, which screens the Coulomb interaction between the electron and hole present in the excited electronic states. This screening lowers the energy gap between the  $1B_u$  and  $mA_g$  electronic states and increases the polarizability of the  $1B_u$  state. A simple three-state model ( $1A_g$ ,  $1B_u$  and  $mA_g$  state) in which the oscillator strength between the  $1B_u$  and  $mA_g$  is assumed to be independent of screening reproduces the results of the INDO/SCI calculations. Within this three-state model, the  $Tr\overrightarrow{\Delta\alpha}$  is a sensitive function of the energy gap between the  $1B_u$  and  $mA_g$  electronic states, and the observed  $Tr\overrightarrow{\Delta\alpha}$ , coupled with INDO/SCI's value for the oscillator strength between the  $1B_u$  and  $mA_g$  states, places this gap at  $0.6 \pm 0.05$  eV. This is the most precise estimate of this energy

gap available, although the accuracy of this estimate depends on the validity of INDO/SCI oscillator strength.

The second role played by the glassy environment is to break the symmetry of the nominally  $C_{2h}$  structure of the oligomer and polymer. This symmetry breaking gives rise to rather substantial experimentally observed  $|\Delta\vec{\mu}|$ 's of 6 D to 11 D.

The INDO/SCI calculations indicate that disorder in the ground state geometry of the polymer (inner-sphere disorder) can account for roughly half of the observed  $|\Delta\vec{\mu}|$ .

Disorder in the glassy environment (outer-sphere disorder) leads to a non-uniform electrostatic environment, and calculations indicate that this is also a substantial contributor to the observed  $|\Delta\vec{\mu}|$ . Note that substantial  $|\Delta\vec{\mu}|$ 's are observed only when the electron-hole screening effects arising from the fast dielectric response of the environment are taken into account. This screening weakens the attraction between the electron and hole such that disorder leads to more asymmetric distributions of the electron and hole and thereby larger observed dipole moments. Since  $|\Delta\vec{\mu}|$  is zero in the absence of symmetry breaking, electroabsorption measurements provide a sensitive probe of the degree of disorder in these samples that may find applications, for instance, in screening materials. We are currently working on more detailed models of the interplay between inner-sphere and outer-sphere disorder that can serve as structure-property relations for interpreting the observed  $|\Delta\vec{\mu}|$ 's.

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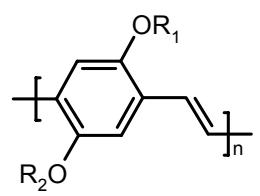
## **Scheme Captions**

**Scheme 1** (a) The repeat unit of MEH-PPV. R<sub>1</sub>=methyl; R<sub>2</sub>=2-ethylhexyl, n>>100

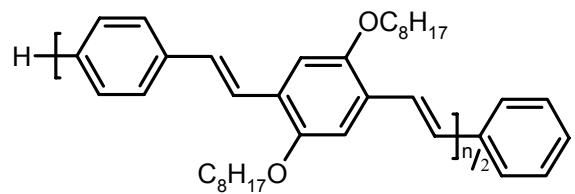
(b) The oligomer OPPV-9 (c) PPV-3 (d) PPV-5.

**Scheme 2** (a) The repeat unit of PPV showing the definition of the dihedral angle

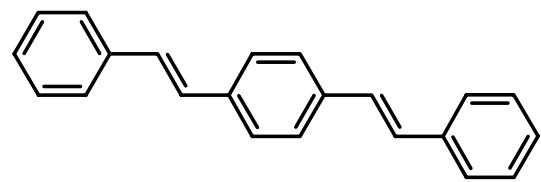
between the phenylene rings ( $\phi$ ). (b) The model OPPV-9 oligomer with hydroxy substitution.



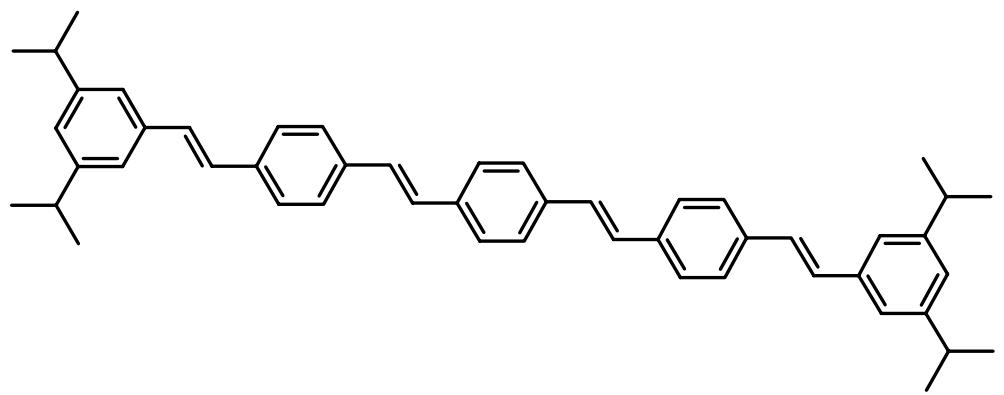
(a)



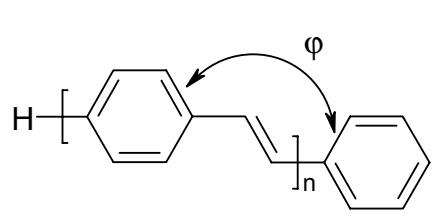
(b)



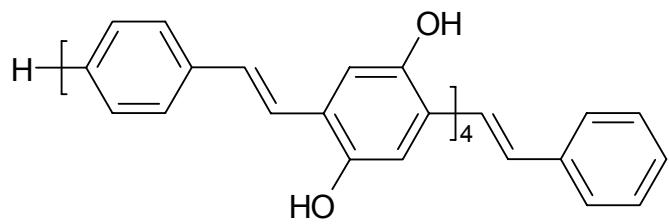
(c)



(d)



(a)



(b)

## Figure Captions

**Fig. 1:** Fluorescence and fluorescence excitation spectra of MEH-PPV and OPPV-9 dispersed in toluene and MeTHF measured at 77 K and room temperature, as indicated in the insets. Intensities have been normalized for better comparison. MEH-PPV in MeTHF at 77 K shows an unequal spacing between the fluorescence peaks. Excitation spectra (1) and (2) correspond to collection wavelengths of 573 nm and 608 nm, respectively, which are designated on the emission spectrum.

**Fig. 2:** Fluorescence and fluorescence excitation spectra of PPV-3 and PPV-5 dispersed in toluene, measured at 77 K. Intensities have been normalized for better comparison.

**Fig. 3:** Absorption (top panels) and electroabsorption spectra (middle panels, solid line) of OPPV-9 and MEH-PPV dispersed in glassy MeTHF and toluene. The fits to the electroabsorption spectra are also shown in the middle panels (dashed lines) along with the parameters derived from the fit. In the lower panels, the zeroth (circles), first (stars), and second (squares) derivatives of the absorption spectra are shown together with the electroabsorption spectra (solid lines).

**Fig. 4:** Absorption (a, d) and electroabsorption spectra (b, e) of PPV-3 and PPV-5, respectively, dispersed in glassy toluene. The fits to the electroabsorption spectra are shown with dashed lines in panels b and e and the parameters derived from each fit are given in the inset of the panel. The zeroth (circles), first (stars), and second (squares)

derivatives of the absorption spectra are shown together with the electroabsorption spectra (solid lines) in the lower panels.

**Fig. 5:** Chain length dependence of the polarizability change  $\overrightarrow{Tr\Delta\alpha}$  calculated for planar PPV-n oligomers in the gas phase (circles) and with the inclusion of dielectric screening (triangles). The dielectric screening parameter  $S_{\text{diel}}=1.4$  such that for longer chains, the  $1B_u-mA_g$  energy separation is  $\sim 0.6$  eV. The inset shows the ratio of  $Tr\overrightarrow{\Delta\alpha}$ (PPV-n) to  $Tr\overrightarrow{\Delta\alpha}$ (PPV-16) to illustrate the rate at which  $Tr\overrightarrow{\Delta\alpha}$  approaches the long chain limit.

**Fig. 6:** The value of  $Tr\overrightarrow{\Delta\alpha}$  for a planar and linear PPV-8 oligomer as function of the strength of the dielectric medium. The upper axis shows the solvation scaling factor,  $S_{\text{diel}}$ , and the lower axis shows the  $1B_u-mA_g$  energy separation ( $\Delta E$ ). The inset illustrates the linear relationship between  $Tr\overrightarrow{\Delta\alpha}$  and  $1/\Delta E^2$ .

**Fig. 7:** The distribution of  $Tr\overrightarrow{\Delta\alpha}$  for a planar PPV-8 surrounded by 500 different random dipole lattices. The lattice parameters are given in the Experimental Section.

**Fig. 8:** The distribution of  $\Delta\mu_x$  for a planar PPV-8 surrounded by 500 different random dipole lattices. The lattice parameters are given in the Experimental Section.

**Fig. 9:** The distribution of  $\mu_x(1B_u)/\mu_x(gs)$  for a planar PPV-8 surrounded by 500 random dipole lattices. The lattice parameters are given in the Experimental Section.



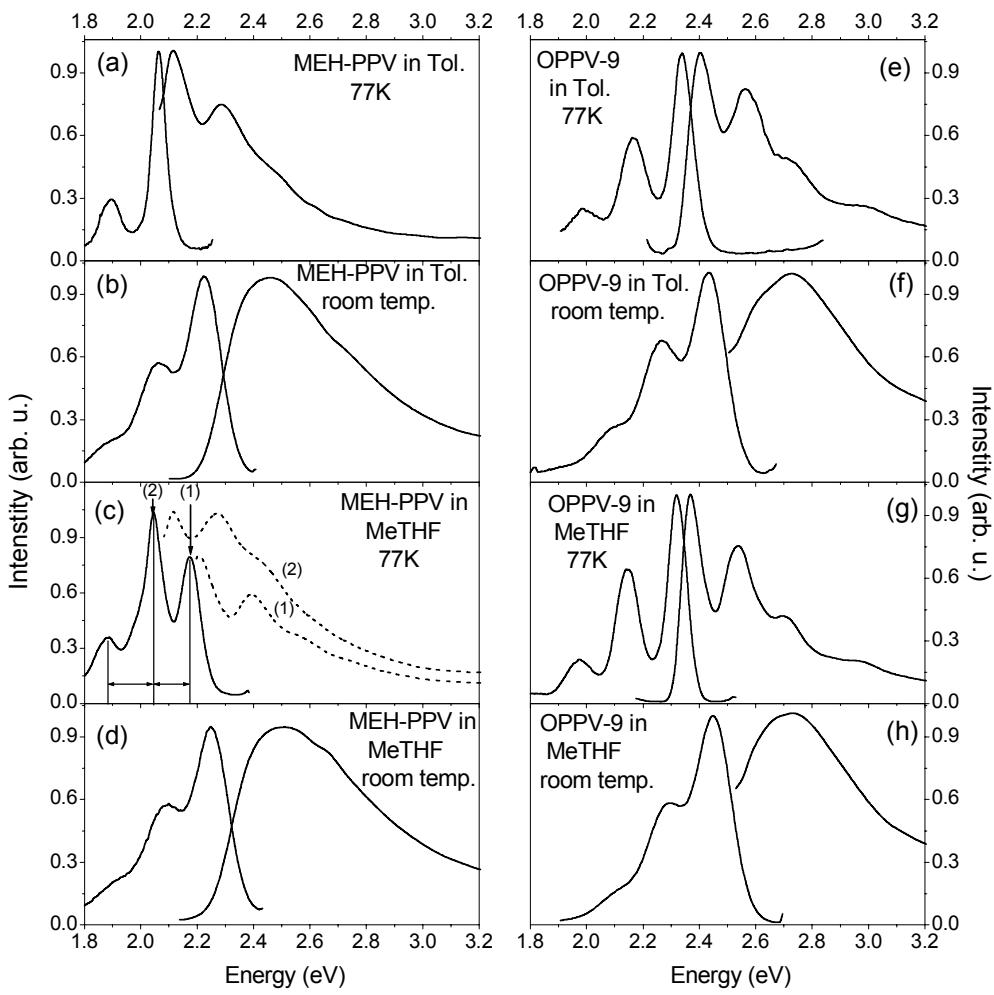


Fig.

1

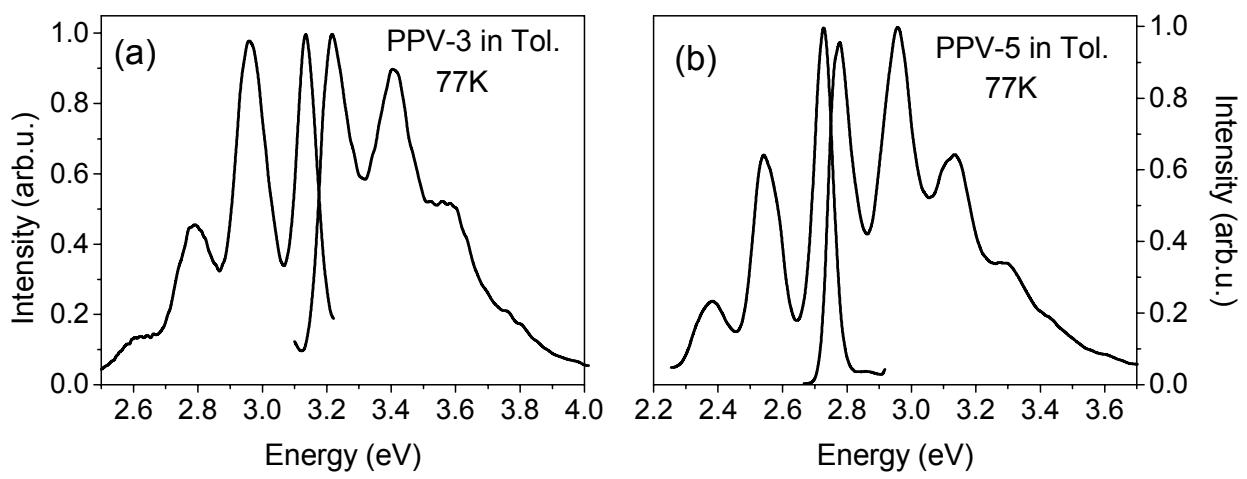


Fig. 2

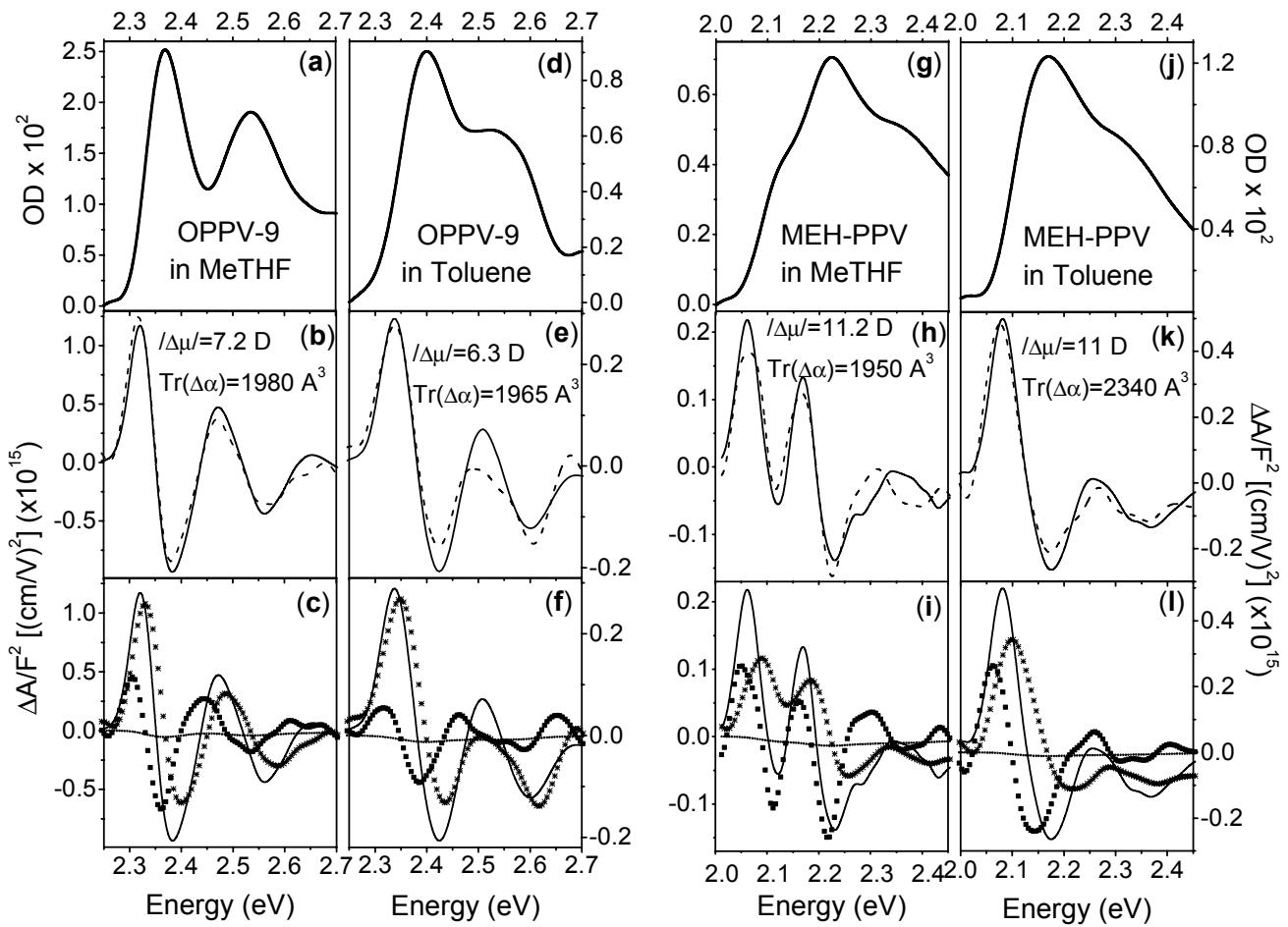


Fig. 3

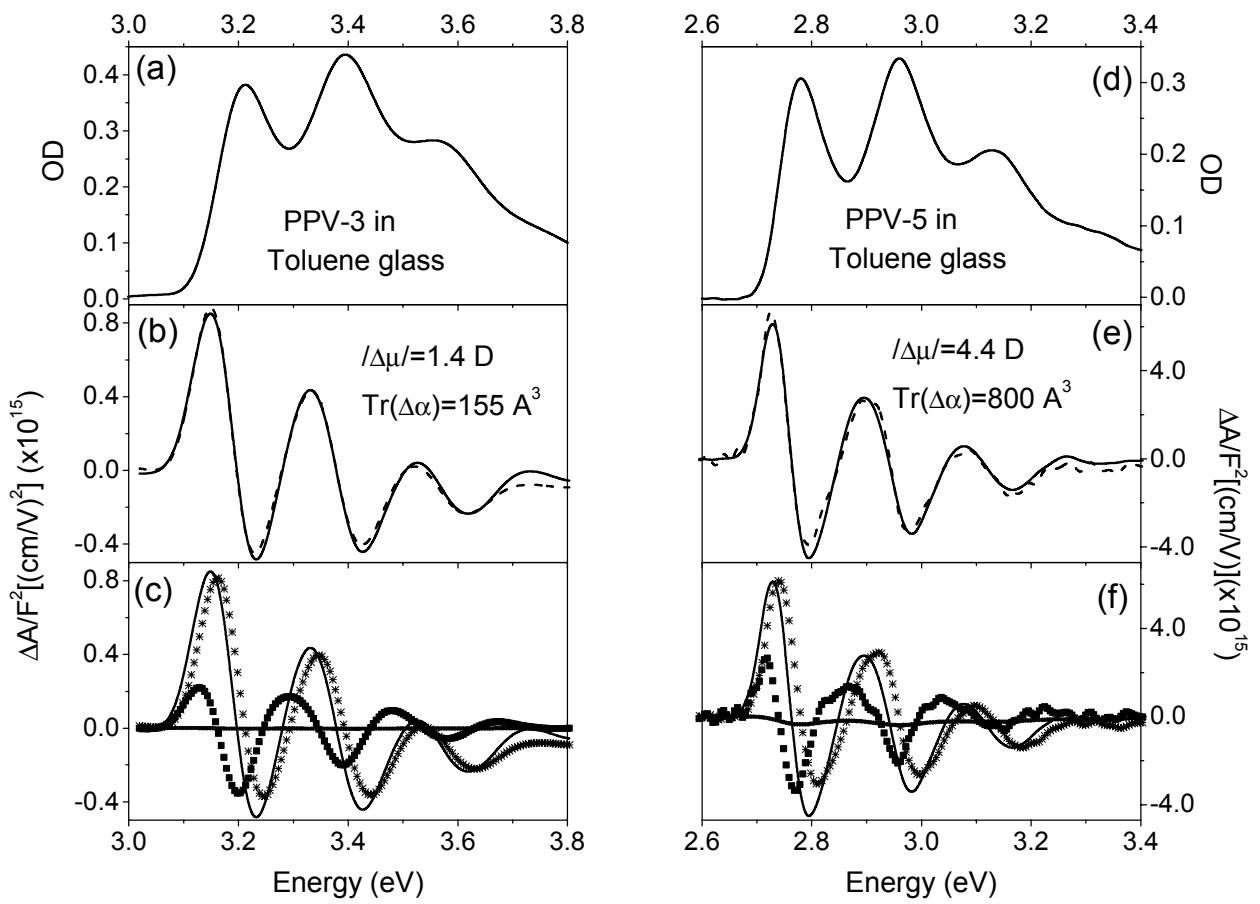


Fig. 4

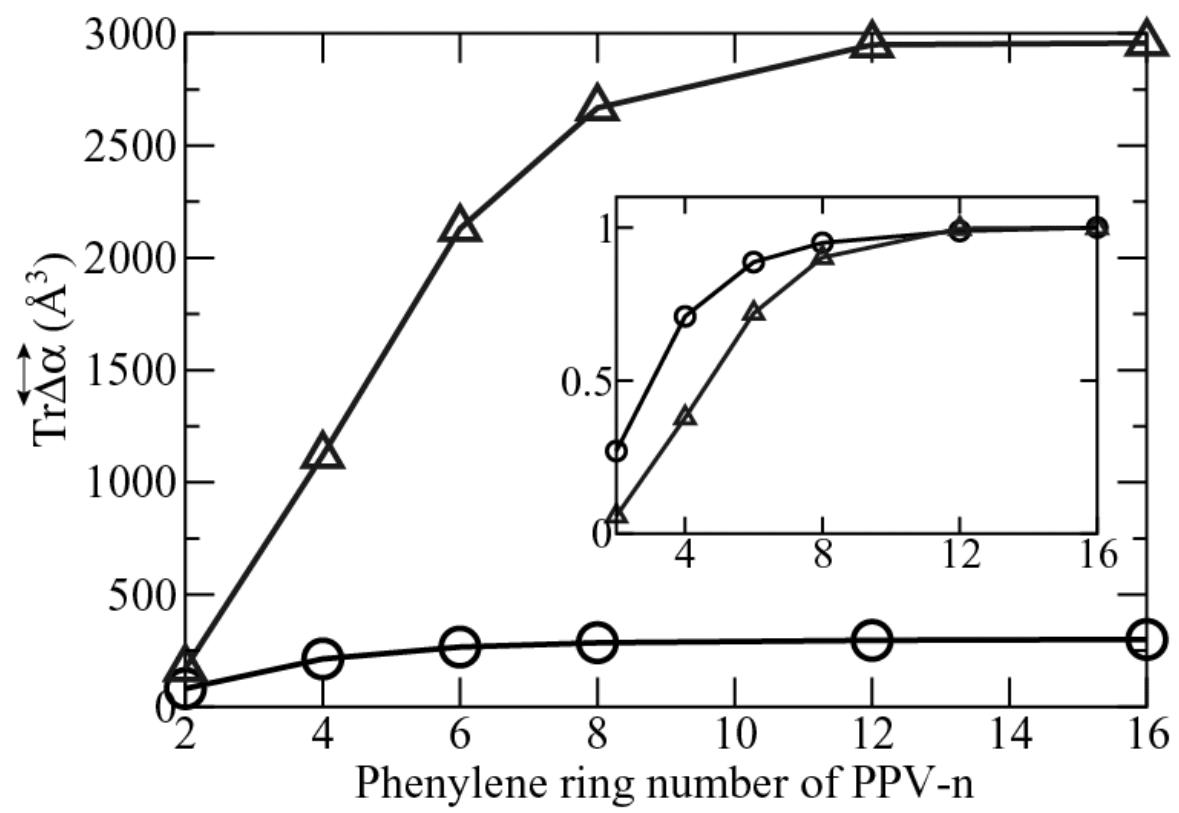


Fig. 5



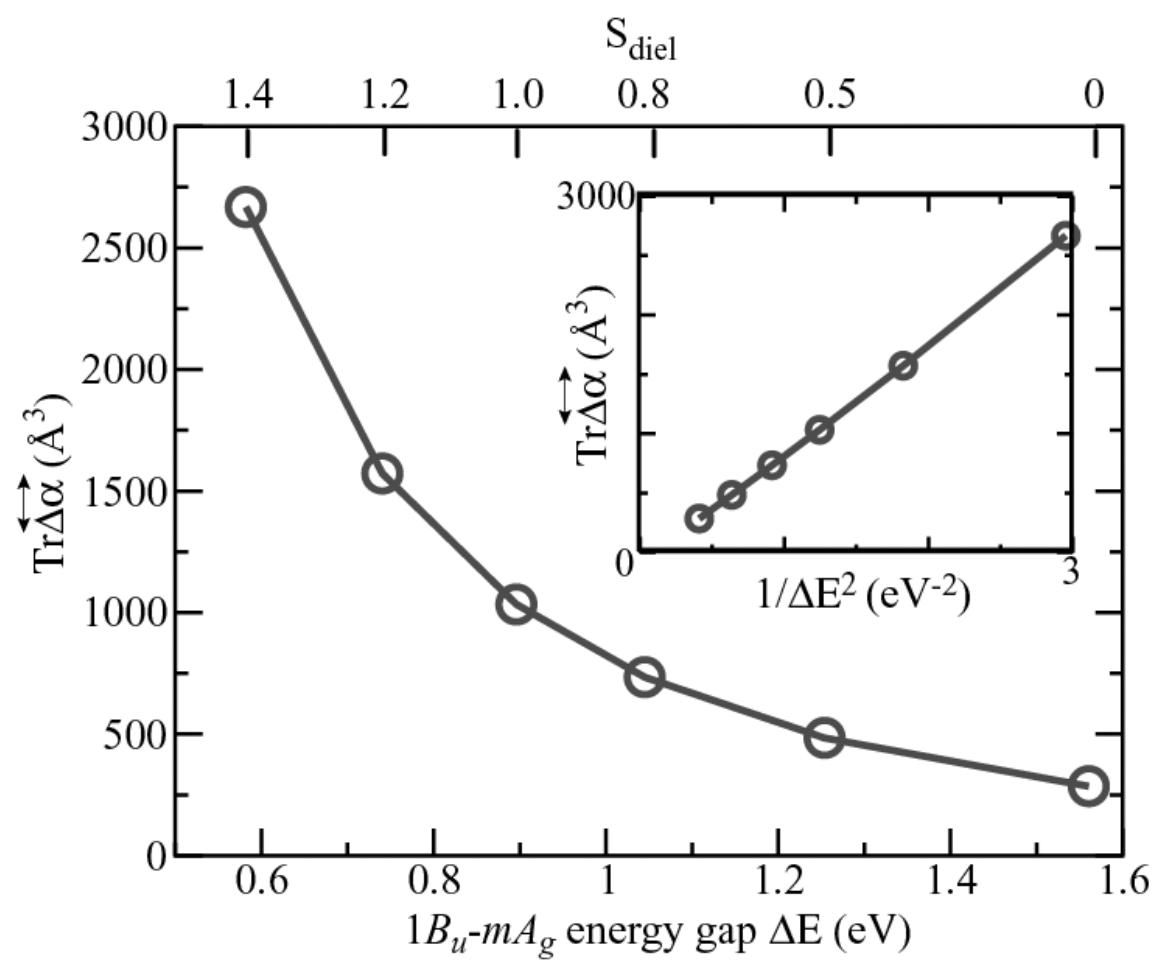


Fig. 6

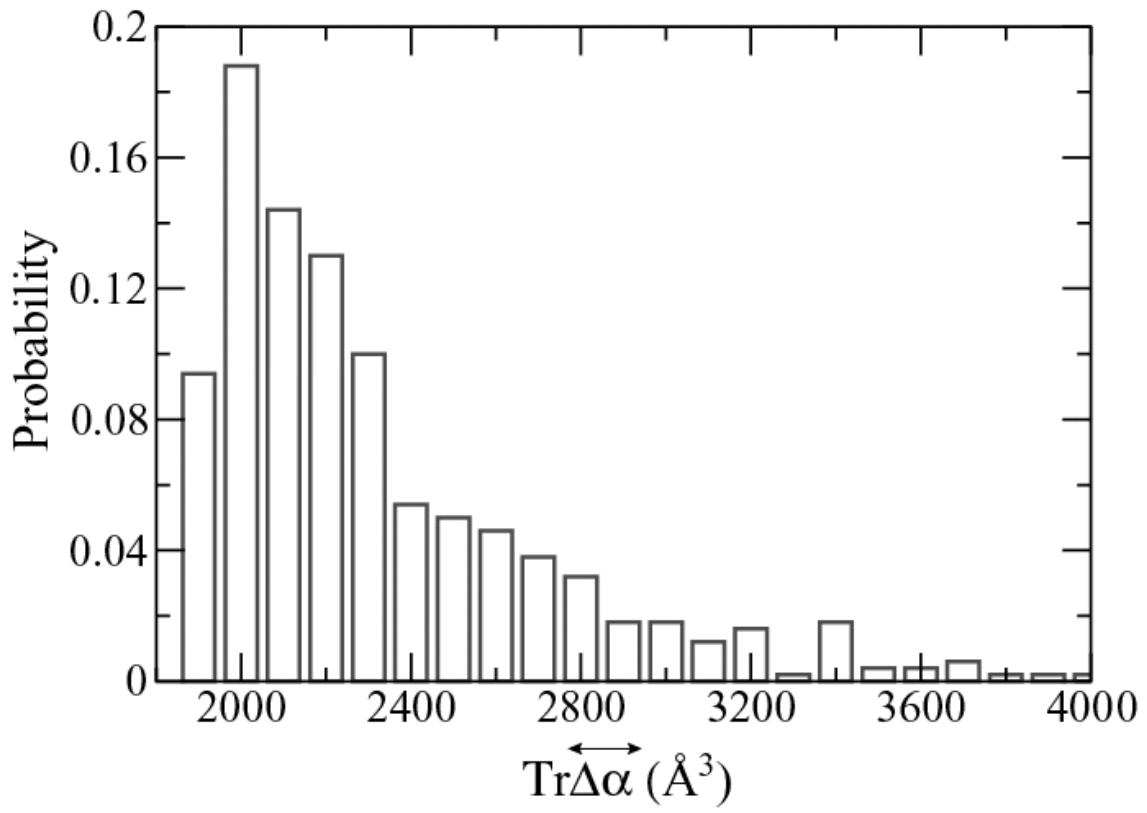


Fig. 7



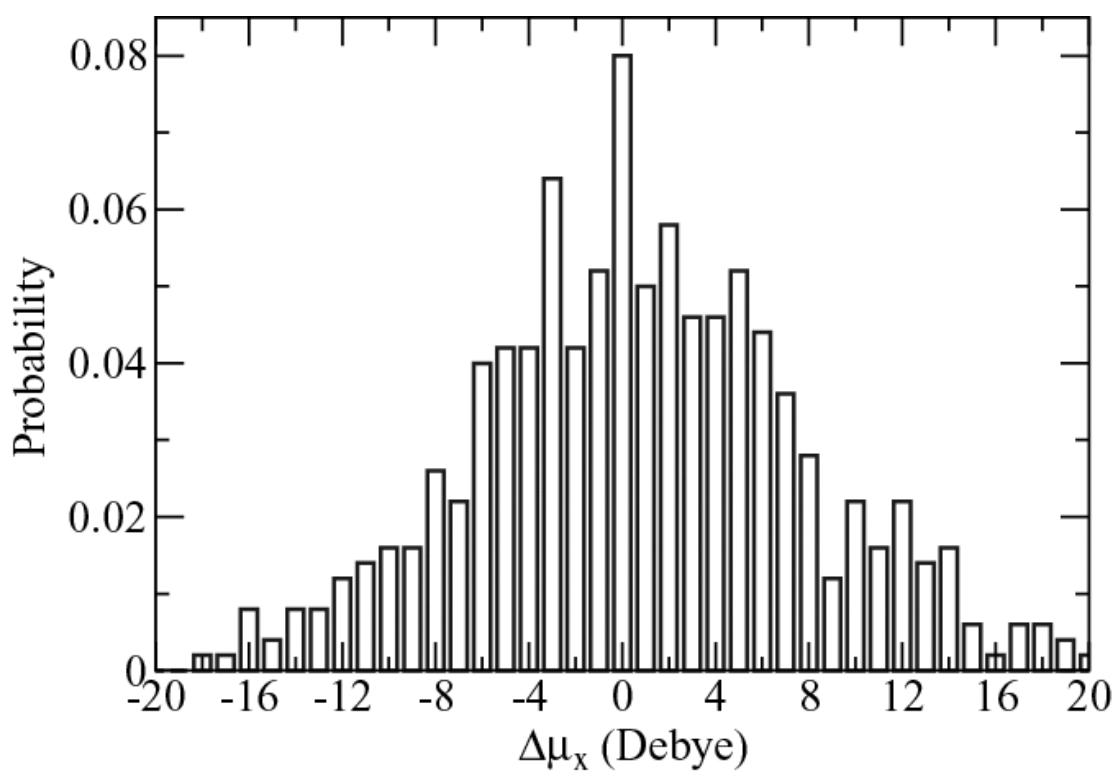


Fig. 8

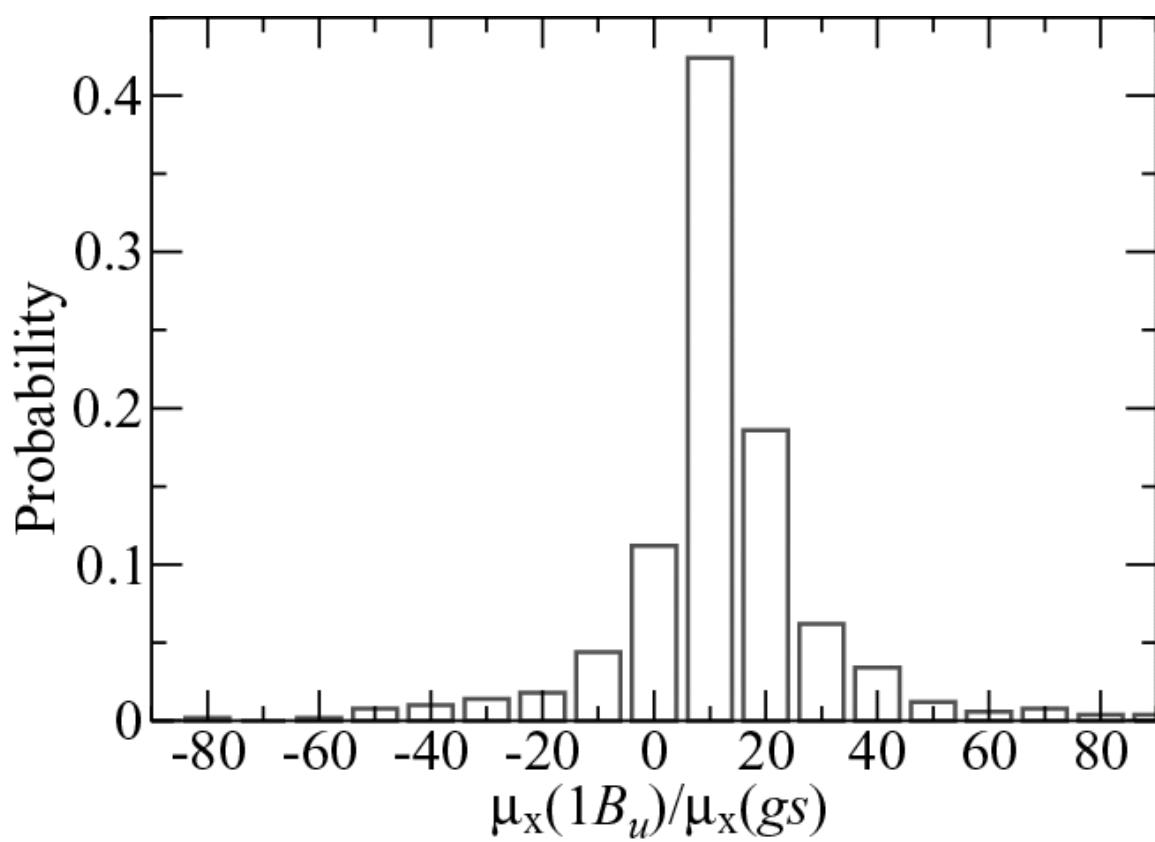


Fig. 9

## Tables

**Table 1.** Parameters Obtained from Absorption, Emission and Electroabsorption Spectra.

| Molecule | Solvent/<br>Temp. | Abs. Max.<br>0-0,0-1 bands <sup>a</sup> | Emission max.<br>0-1, 0-1 bands <sup>a</sup> | $Tr\overleftrightarrow{\Delta\alpha}$ <sup>c</sup> | $ \overrightarrow{\Delta\mu} ^d$ |
|----------|-------------------|---|--|--|----------------------------------|
| MEH-PPV  | MeTHF / 298 K     | 2.490                                   | 2.250, 2.087                                 |  |                                  |
|          | MeTHF / 77 K      | ~ <sup>b</sup>                          | ~ <sup>b</sup>                               | 2000 ± 200   | 11 ± 1                           |
|          | Toluene / 298 K   | 2.450                                   | 2.226, 2.066                                 |  |                                  |
| OPPV-9   | Toluene / 77 K    | 2.119, 2.291                            | 2.066, 1.895                                 | 2300 ± 200   | 11 ± 2                           |
|          | MeTHF / 298 K     | 2.710                                   | 2.450, 2.283                                 |  |                                  |
|          | MeTHF / 77 K      | 2.371, 2.539                            | 2.318, 2.146                                 | 2000 ± 200   | 7.2 ± 1.0                        |
| PPV-5    | Toluene / 298 K   | 2.720                                   | 2.432, 2.266                                 |  |                                  |
|          | Toluene / 77 K    | 2.404, 2.571                            | 2.339, 2.168                                 | 2000 ± 200   | 6.3 ± 0.8                        |
|          | Toluene / 77 K    | 2.780, 2.959                            | 2.725, 2.546                                 | 780 ± 80   | 4.4 ± 0.5                        |
| PPV-3    | Toluene / 77 K    | 3.207, 3.391                            | 3.133, 2.952                                 | 140 ± 20   | 1.8 ± 0.4                        |

<sup>a</sup> In eV. Errors are ±0.003 eV. <sup>b</sup> Indicates the presence of overlapping transitions (see text). <sup>c</sup> In Å<sup>3</sup>. <sup>d</sup> in Debye.

**Table 2.** Calculated Electro-optical Properties for 10 Randomly-Distorted PPV-8 Structures.

|   | Disordered PPV-8 Structures <sup>a</sup> |                       | Linear and Planar PPV-8 |                       |
|---|--|-----------------------|-------------------------|-----------------------|
|   | Gas Phase                                | Solvated <sup>b</sup> | Gas Phase               | Solvated <sup>b</sup> |
| $\Delta E^c (mA_g^{-1}B_u)$             | $1.552 \pm 0.004$                        | $0.62 \pm 0.01$       | 1.561                   | 0.58                  |
| $Tr\overleftrightarrow{\Delta\alpha}^d$ | $264 \pm 5$                              | $2000 \pm 100$        | 285                     | 2668                  |
| $ \vec{\Delta\mu} ^e$                   | $0.04 \pm 0.02$                          | $4 \pm 1$             | 0.00                    | 0.02                  |
| $E_{1B_u}^c$                            | $2.98 \pm 0.02$                          | $2.38 \pm 0.03$       | 2.873                   | 2.237                 |

<sup>a</sup> The numbers in this column represent the average values and standard deviations for a set of 10 randomly generated geometrically disordered structures of PPV-8 (see text).

<sup>b</sup> For solvated calculations, the dielectric scaling factor is 1.4 (see text).

<sup>c</sup> in eV, <sup>d</sup> in Å<sup>3</sup>, <sup>e</sup> in Debye