

# Probing Phase Segregation in Porphyrin-Polymer Blends with Multidimensional IR Spectroscopy

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**Abstract**—Multidimensional IR spectroscopy is used to study blends of the regioregular semiconducting polymer, poly(3-hexylthiophene) with ruthenium porphyrins in solid state thin films. A ruthenium-bound carbon monoxide ligand is a sensitive reporter of the local electrostatic environment and indicates that the porphyrins localize into phase-segregated domains upon annealing in solvent vapor. The FTIR spectrum of this ligand reports on the state of aggregation, which we then correlate with transmission electron microscopy images of these films before and after annealing. We then use 2D-IR spectroscopy, an ultrafast IR technique, to measure the fast structural dynamics that are present in the vicinity of the CO ligand when it is homogeneously blended in the polymer film and phase segregated into purely porphyrinic domains.

## I. INTRODUCTION

THE control of morphology and phase segregation in blended organic materials is crucial for achieving optimal performance. This control has led to a wealth of self-assembled nano- and microscopic structures in multifunctional block copolymers [1-4]. Bulk heterojunction solar cells rely heavily on phase segregation to achieve electron and hole carrying domains with appropriate size dimensions and connectivities [5]. The induced aggregation of perylene derivatives during thermal annealing in fluorene copolymers and polystyrene blends was recently shown to produce higher charge mobilities and photovoltaic device efficiencies [6]. This behavior was previously exploited in blends of perylenes that generated relatively high photocurrents [7,8]. In contrast, thermal annealing of fullerene derivatives in polystyrene was reported to degrade electron mobility through the fullerene phase [9]. One of the most common polymers used in these organic blends is the regioregular form of poly(3-hexylthiophene-2,5-diyl) (P3HT) due to its ability to form highly ordered, semicrystalline regions that enhance charge mobility [5]. In organic photovoltaic cells, P3HT is often blended with the fullerene derivative [6,6]-phenyl-C61-butyric-acid-methyl-ester (PCBM), and then thermally annealed to increase the crystallinity in the P3HT regions and drive phase segregation of the P3HT and PCBM molecules [5]. It has been shown that this phase segregation initially enhances the efficiency of photovoltaic devices, but ultimately becomes

detrimental, perhaps due to a decrease in the electron mobility in the fullerene domains [9] or because the domain size has exceeded the exciton diffusion length [5,10]. Clearly, the thermodynamic segregation of dissimilar chemical species can alternately enhance or ruin the performance of blended organic materials, and understanding and controlling this phenomenon is necessary for material optimization.

Owing to their strong light absorbing properties, porphyrins are a general class of organic molecules that have a long history in organic photovoltaic systems [11,12]. The visible absorption spectrum of porphyrins is a natural complement to that of P3HT, which has led to their inclusion in blended photoanodes with extended spectral responses [13]. Since porphyrins are hole transporting semiconductors, their blends with P3HT often constitute a hybrid p-type domain, although in some cases the porphyrin has been reported to serve as a charge transfer mediator between the P3HT and an n-type material [14]. While aggregation of porphyrins in solution is a well-documented phenomenon [15], little is reported about their phase segregation in blended organic thin films.

In this work, we demonstrate that the degree of phase segregation between an octaethyl-ruthenium-porphyrin carbonyl (RuOEP) and P3HT can be achieved in a controllable manner by carefully annealing the blended films in solvent vapor. In the mid-IR, the ruthenium-bound carbonyl (CO) symmetric stretching mode serves as a sensitive probe of the phase segregation progress and provides insight into the aggregation process at the molecular level. The segregated phases are directly observed using transmission electron microscopy (TEM), and a model is described that explains the collective experimental results. We apply two-dimensional IR (2D-IR) [16,17] spectroscopy to the different phase segregated states to measure differences in structure freedom of motion on the fast timescales that are relevant for device charge mobilities.

## II. PROCEDURES

### A. Materials

Electronic grade regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) was used as received from Rieke Metals Inc. and 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine ruthenium(II)carbonyl (RuOEP) was used as received from Sigma Aldrich. All solvents were reagent grade and were used as received without further purification.

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### B. Sample preparation and characterization

Thin films of P3HT and RuOEP blends were prepared by mixing various ratios (m/m) of the two components in chloroform and spincoating onto clean  $\text{CaF}_2$  wafers at 400 rpm for 2 minutes.

FTIR spectra were collected on a ThermoElectron 6700 spectrometer with  $2\text{ cm}^{-1}$  resolution, automatic atmospheric suppression, and 100 scans averaged. Baselined spectra were obtained by auto-baseline corrections in the Omnic software.

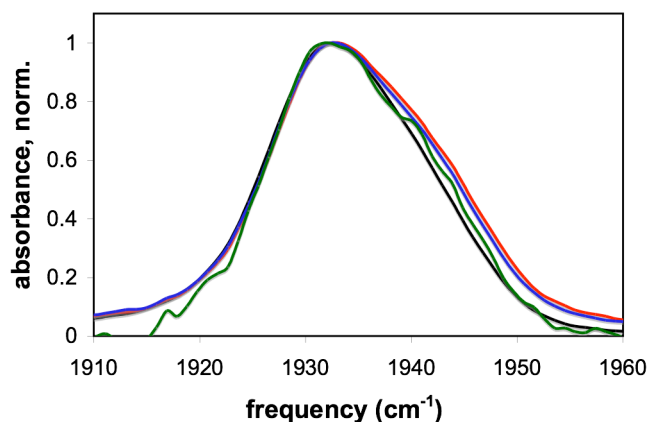
Solvent vapor annealing was performed in a 32 oz jar with  $\text{CaF}_2$  windows as its endcaps. This enabled the FTIR spectra to be collected during the annealing process. A small reservoir of chloroform was placed in the jar with the sample and the lid was quickly secured. Spectra were collected at regular increments.

TEM was performed at the University of Minnesota Characterization Facility on a JEOL 1210 at 120V. Samples were prepared as above and spun onto glass microscope slides. Prepared slides were then scored and placed in a dish with millipure water. Small sections of the films were allowed to float away from the surface of the glass and were carefully caught on top of copper 400 mesh TEM grids (Ted Pella). The loaded grids were allowed to dry for at least an hour before use.

2D-IR spectroscopy was performed using a setup similar to others described in the literature [16]. Briefly, an amplified Ti:Sapphire laser system (Spectra-Physics) was used to pump an optical parametric amplifier to convert the 800 nm light to near IR signal and idler beams, which were then frequency mixed (DFG) in a type II  $\text{AgGaS}_2$  crystal. This generated tunable mid-IR pulses with approximate durations of 90 fs and bandwidth of  $200\text{ cm}^{-1}$ . The mid-IR pulses were split into 3 roughly equal intensity beams and were timed to arrive at the sample in a “boxcars” geometry. The timings between pulses 1 and 2 (called “tau”) and 2 and 3 (called  $T_w$ ) were controlled by computer controlled delay stages (Newport Corp.). The vibrational echo signal was generated in the phase-matched direction and was spectrally resolved in a 0.3 meter monochromator. The signal was measured at the intensity level with a liquid nitrogen cooled InSb detector.

### III. RESULTS AND DISCUSSION

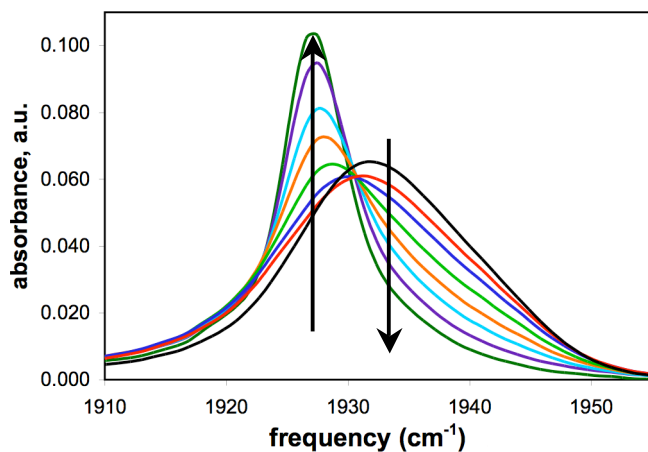
The ruthenium-bound CO symmetric stretching vibration is centered at  $1932\text{ cm}^{-1}$  for the porphyrin blended with P3HT films. In order to demonstrate the absence of aggregates in the blended RuOEP and P3HT films, we performed a concentration study of the FTIR spectra for this stretching region. Figure 1 shows the FTIR spectra of the CO region for 1:10, 1:25, and 1:50 m/m ratios for RuOEP:P3HT. The spectral shapes are the same and the center frequency does not change within the resolution of our instrument. The slight broadening of the lower concentrations is likely the result of the baselining procedure, which affects the low concentrations more



**Figure 1.** Baselined and normalized FTIR spectra of the CO stretching region for 1:10, 1:25, 1:50, and 1:100 blends of RuOEP:P3HT (m/m) demonstrating no significant spectral shape changes with dilution in the film.

severely because the CO-absorbances are very small compared to the background. We therefore believe that the IR spectra of this vibrational mode, which is very sensitive to its local environment, to be the same. This indicates no significant aggregation in these as-prepared films.

Upon exposure to solvent vapors, the CO absorbance in the mid-IR undergoes a dramatic change in shape and frequency. Figure 2 shows that the absorption band red-shifts to  $1927\text{ cm}^{-1}$  and becomes noticeably thinner. The lineshape for a condensed phase sample is likely the reflection of the range of chemical environments (inhomogeneously broadened), rather than a change in dynamics. We will test this notion with the 2D-IR spectroscopic results described below. Thus we can say that



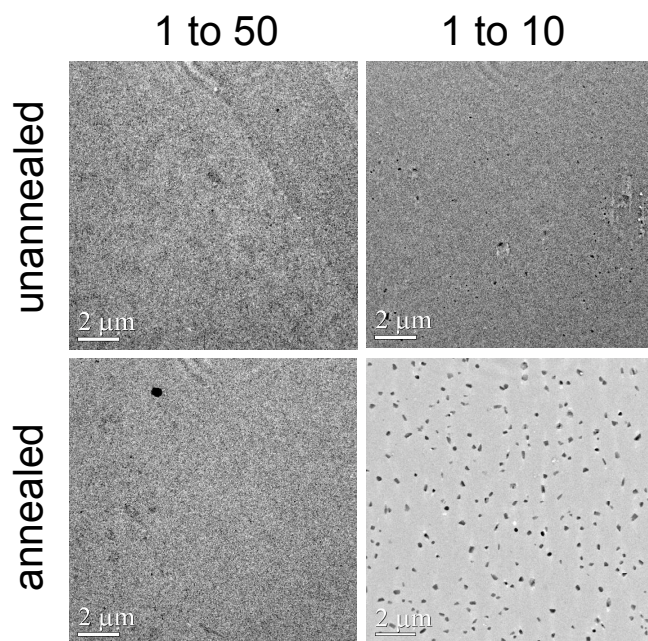
**Figure 2.** Baselined and normalized FTIR spectra of a 1:10 RuOEP:P3HT film with progressive annealing in chloroform vapor. The arrows indicate the direction of change for the spectra with annealing times of 0, 1, 3, 5, 10, 20, 30, and 40 minutes, respectively.

the homogeneity of the chemical environments around the CO oscillator is greater after annealing than before. During the early annealing times, there is an isosbestic point at  $1930\text{ cm}^{-1}$ , indicating that during this process there are two states that are interconverting. However, during longer times this coincident point is lost as the red-shifted state narrows. This narrowing demonstrates a decrease in the inhomogeneity of

the chemical environments around the CO ligand.

The red-shifting of the CO absorption band can be explained by dipole-dipole coupling effects in which two or more transition dipoles interact to modify each other's transition energies [18]. In this context, since the transition dipole of the CO ligand lies along the bond axis, we can attribute the shift to lower energy to an alignment of the CO dipoles in a head-to-tail orientation. It would appear that the annealing process results in aggregation of porphyrins that otherwise were not proximal to each other. This phase behavior has been documented for PCBM and P3HT blends upon thermal annealing, and occurs because the P3HT molecules crystallize faster than the PCBM species, thereby separating the two materials on a microscopic level [5].

To test this idea, we examined thin films of P3HT/RuOEP blends before and after annealing, and at different concentrations using TEM measurements. The ruthenium in the RuOEP provides a strongly scattering core that leads to contrast in the TEM images in domains where there are concentrations of RuOEP (i.e. RuOEP clusters appear dark). The TEM images of these films are shown in Figure 3. What is immediately apparent is that the higher concentration of RuOEP in P3HT (1:10 m/m) develops into a film with clusters of dark aggregates upon annealing. This is consistent with the spectroscopic evidence of aggregation,

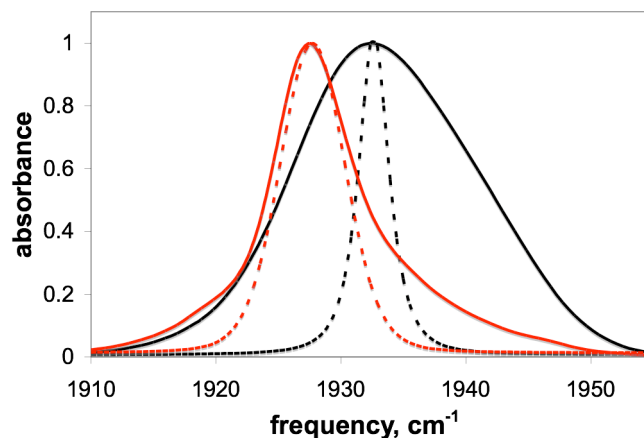


**Figure 3.** TEM images of 1:50 (left column) and 1:10 (right column) RuOEP:P3HT (m/m) films in the unannealed state (top row) and annealed in chloroform vapor for 40 minutes (bottom row).

though it lacks the molecular orientational information that we obtain through the dipole coupling shifts. It is also worth noting that the 1:50 concentration film exhibits no cluster formation after annealing, and its FTIR spectra also show no shape changes with annealing (not shown here). Together, these data support the conclusion that the IR spectrum of the ruthenium-bound CO in the unannealed samples (Fig. 1) is

the spectrum of the “free” porphyrin that is only surrounded by P3HT macromolecules, not by other porphyrins. In the more concentrated samples, however, the annealing process drives phase segregation and enables the porphyrins to find other porphyrins. Initially, while there is an isosbestic point in Figure 3, the aggregation is disordered, but at longer times we believe that the narrowing in the CO absorption band reflects an ordering, and perhaps partial crystallization, of the RuOEP molecules.

The 2D-IR spectroscopy of the annealed and unannealed ruthenium-bound CO demonstrates some unique dynamical environments that evolve around the ligand. One of the most powerful features of 2D-IR spectroscopy is that after fitting the 2D-IR lineshapes using nonlinear response theoretical treatments, one can “turn off” the inhomogeneity in the linear spectrum to observe the true homogeneous lineshape. In Figure 4, the homogeneous lineshapes for these two states are shown overlaid with the inhomogeneous FTIR lineshapes. What is apparent is that the structural environment around the CO is notably more inhomogeneous in the unannealed films, while at the same time it is structurally less dynamic. The narrow homogeneous lineshape shows that the electronic environment around the CO in the unannealed films results in less frequency



**Figure 4.** 2D-IR dynamic lineshapes with inhomogeneous components removed (dashed lines) overlaid on FTIR spectra of the unannealed and annealed 1:10 RuOEP:P3HT blends (solid lines).

fluctuations on the ultrafast timescale (fs and ps). On the other hand, the FTIR of the annealed films is significantly less inhomogeneously broadened, and apparently more dynamically broadened. The increased dynamics in the annealed film could be interpreted as an increase in perturbations due to proximity to neighboring RuOEP molecules within the aggregates that have formed. The CO ligand itself, being that it is fairly polar, would likely contribute strongly to the local electric field near an aggregated RuOEP, thereby increasing its dynamic lineshape. An alternate explanation is that the structural dynamics within the porphyrin aggregates are simply larger in amplitude or occur at a frequency that couples more efficiently to the CO vibration.

#### IV. CONCLUSION

In closing, we have demonstrated that the annealing process drives phase segregation of porphyrins from P3HT. The progress of this action can be followed by monitoring the IR absorption spectrum of the CO ligand bound to the porphyrin. TEM images provide direct evidence of this segregation process, though the microscopic picture is obtained through the spectroscopic changes. The 2D-IR data provide another facet to the change in environments, showing that the dynamical environments around the CO are fundamentally different in the annealed and unannealed films. While this is perhaps not surprising, it underscores the disconnect that may occur between the static and dynamic interpretation of this phenomenon, and may have important implications for optoelectronic applications of these organic blends.

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