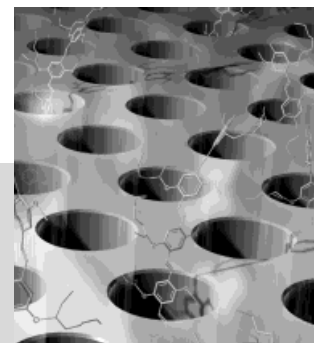


# Control of Energy Transport in Conjugated Polymers Using an Ordered Mesoporous Silica Matrix\*\*

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*How fast does energy transfer along a conjugated polymer chain, and how fast between chains? A semiconducting polymer/mesoporous silica composite, which provides just enough space for one polymer chain per pore (see Figure), provides the answer through investigations of the polymer's luminescence anisotropy, with remarkable results.*



## 1. Understanding and Controlling Energy Transfer in Conjugated Polymers

Conjugated polymers have gained much attention as promising optoelectronics materials, based in large part on their facile wet chemical processing and the ability to simply tune emission energy through synthetic variation.<sup>[1–3]</sup> While significant advances have been made in device fabrication in recent years, many fundamental properties of these materials remain poorly understood. One of the important questions is understanding how energy is transported: does energy migrate along the backbone of the chain between adjacent segments (intrachain transport), or does energy hop between segments that are in close physical proximity, whether or not the segments are physically part of the same polymer chain (interchain transport)? Understanding and controlling the flow of energy in conjugated polymers is extremely important for the optimization of devices. For example, if excitations can flow rapidly between or along polymer chains, then they can easily migrate to defects, leading to quenching of the emission.

In the photosynthetic reaction center, nature has designed a structure, in which light energy harvested at multiple sites spontaneously flows to the appropriate location so that elec-

tron transfer can take place with minimal quenching.<sup>[4,5]</sup> It is complexity and positional control on the nanometer length scale, designed by nature through evolution, that produces this type of efficient, directional energy migration. Mimicking this type of efficient energy transport is one of the outstanding challenges in the design of new nanostructured materials. In this report, we show how control over energy flow can be achieved in an artificial system consisting of a composite of conjugated polymer chains that have been aligned on the nanometer scale and encapsulated into the channels of a periodic mesoporous silica glass. The design of the composite takes advantage of the variation of the energy of a polymer segment with conjugation length to force excitations to flow unidirectionally into the interior of the composite with minimal energy loss.<sup>[6]</sup> Moreover, the architecture of the material forces the energy transport to be along the polymer backbone, allowing us to quantify the roles of interchain and intrachain energy transfer in conjugated polymers.<sup>[7]</sup> Thus, the new material not only allows harvested energy to be directed to desired locations, but also provides valuable information for the optimization of polymer-based optoelectronic devices.<sup>[6,7]</sup>

## 2. Materials Design and Synthesis

The conjugated polymer we use in this work is poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV),<sup>[8]</sup> whose chemical structure is shown in the inset in Figure 3. An oriented mesoporous silica host is synthesized by combining silica/surfactant self-assembly with magnetic field alignment.<sup>[9]</sup> Surfactant removal results in a nanoporous silica with long, straight pores arranged in a hexagonal array; pore surface treatment with organic groups promotes compatibility

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of the channel interiors with the semiconducting polymer.<sup>[10]</sup> MEH-PPV chains are incorporated from solution and the resulting composite is index matched in a glycerol/propanol mixture to suppress scattering from the polycrystalline domain structure of the silica framework.<sup>[10]</sup> The system is designed so that each of the hexagonally arrayed 22 Å-diameter channels is capable of physically accommodating only a single MEH-PPV chain (Fig. 1). Polarized luminescence spectroscopy indicates that in the final composite material, the

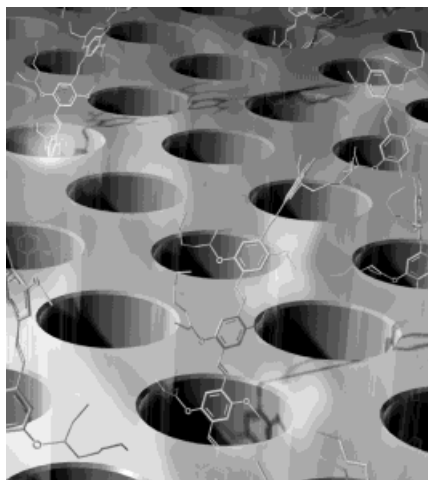


Fig. 1. Schematic representation of single polymer chains embedded in the channels of an ordered mesoporous silica glass. The MEH-PPV chains within the channels are oriented and isolated from each other; the chain tails that extend out of the pores are randomly oriented and can be in contact with each other. Graphic courtesy of Daniel Schwartz, D.I.S.C. Corporation.

majority of the MEH-PPV chain segments are oriented and isolated from each other by incorporation into the aligned channels of the mesoporous silica glass.<sup>[10]</sup> A small amount of unincorporated polymer remains in the composite; these polymer chromophores reside outside the channels where they are both randomly oriented and in contact with conjugated segments on neighboring polymer chains.<sup>[6,10]</sup> It is this complexity, the presence of two distinct types of polymer environments in a single material, which allows for the control and understanding of energy transfer.<sup>[6,7]</sup>

### 3. Intrachain versus Interchain Energy Transfer in Conjugated Polymers

The dynamics of energy transfer in the MEH-PPV/mesoporous silica composites can be studied using both steady-state<sup>[10]</sup> and time-resolved polarized luminescence spectroscopies.<sup>[6,11]</sup> A wide variety of work has established that the correct “zeroth order” picture of a conjugated polymer chain is that of a series of linked chromophores, each with a different conjugation length.<sup>[12–17]</sup> In polymer films, excitations rapidly move from the shortest conjugated segments, which are higher in energy, to the longest conjugated segments, which are lower in energy. This energy transfer normally results in scrambling of the emission polarization. Figure 2 shows the results of steady-state luminescence experiments performed with the pores

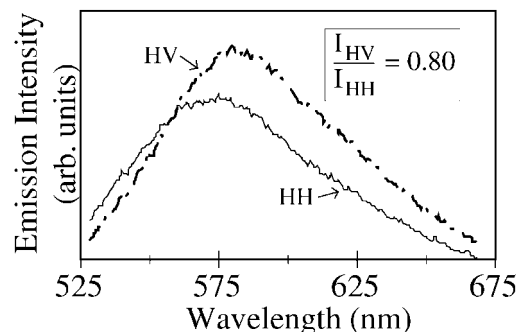


Fig. 2. Steady-state fluorescence spectra of MEH-PPV/mesoporous silica composites. The channels of the composite are oriented vertically in the lab frame. The solid curve shows the results when exciting with horizontally polarized light and collecting the horizontally polarized emission (HH). The dashed curve shows the results when exciting with horizontally polarized light and collecting the vertically polarized emission (HV). The relative intensities of the two spectra are as measured and have not been scaled.

oriented vertically in the lab frame and the excitation light polarized perpendicular to the pores. Instead of the normal depolarization, in the composite, more light is emitted polarized in the direction along the pores (HV) than along the direction of excitation (HH). This suggests that excitations on the short, randomly-oriented conjugated polymer segments outside the pores, which are preferentially excited by the light polarized against the pore direction, migrate to the segments, which are held rigidly in the pores. The driving force for this energy migration can be seen in the red-shift of the emission polarized parallel to the pores relative to that along the excitation direction: there is a clear gradient for moving energy from the polymer segments outside the channels to the rigid and straight segments that reside inside the pores.

Figure 3 shows the results of time-resolved polarized luminescence experiments; the anisotropy,  $r(t)$ , which depends only on the degree of polarization of the luminescence.<sup>[18]</sup> At early times, all of the emission from the sample comes from the chromophores that were originally excited; thus, the emission is highly polarized along the same direction as the excitation laser. As energy migrates from one segment to the next, memory of this initial polarization is lost, leading to a decay of the anisotropy. Indeed, Figure 3 shows an initial loss of anisotropy in the first few ps following excitation. On the basis of previous studies in conjugated polymers, we can assign this initial loss of anisotropy to interchain energy transfer between the conjugated polymer segments that are in contact on the outside of the pores. This energy transfer likely proceeds by the Förster mechanism (i.e., dipole–dipole coupling between adjacent chromophores).<sup>[19]</sup>

Following the initial rapid decay of the anisotropy, Figure 3 shows the remarkable result that the emission polarization actually increases with time. As with the steady-state data in Figure 2, the only way to explain this increase in anisotropy is by migration of excitations from the coiled and non-aligned high-energy segments outside the pores to the straight and oriented low-energy segments encapsulated in the pores.<sup>[6]</sup> Thus, energy initially deposited on polymer segments on the exterior of the pores is driven to segments in the interior,

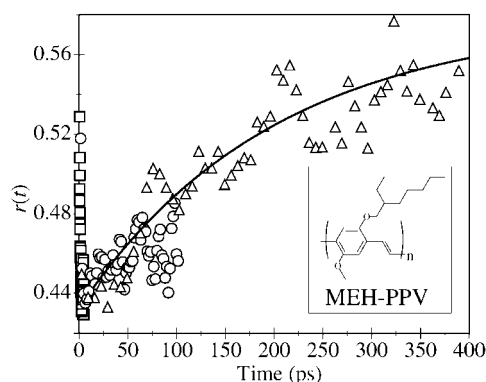


Fig. 3. Femtosecond stimulated emission anisotropy of MEH-PPV/mesoporous silica composites. The sample is excited with 480 nm light polarized along the pore direction, stimulated emission is monitored near the emission maximum at 590 nm. The different symbols represent scans taken with different time spacings between points. The inset shows the chemical structure of MEH-PPV.

while energy deposited in the interior remains in the interior. The ultimate result is that the polarization of the luminescence from the sample is greater after energy transfer is complete than before any energy transfer has occurred, as seen in Figure 3 by the fact that the long time anisotropy is larger than that at time zero.

The anisotropy rise in Figure 3 also allows us to make arguments concerning the nature of interchain and intrachain energy transport in conjugated polymers. Since there is physically enough room for only one polymer chain per pore, energy migration from chromophores outside the pores to chromophores inside the pores must take place along the polymer backbone. The anisotropy rise in Figure 3, which results from intrachain energy migration, is orders of magnitude slower than the rapid anisotropy loss due to interchain energy transport via Förster transfer. Why is intrachain energy transport so much slower than interchain energy transport? We suspect that energy migration along the backbone requires “healing” of the broken conjugation between adjacent polymer segments.<sup>[7]</sup> This means that the chain segments must physically reorient to allow excitations to migrate from one conjugated region to the next, a process that is likely to be thermally activated. The Förster transfer mechanism, while efficient for interchain transfer, is ineffective for intrachain transport because the dipoles on adjacent chain segments lie head-to-tail.

#### 4. Implications for Nanostructured Materials and Conjugated Polymer Devices

Overall, the data in Figure 2 and Figure 3 show that energy transport in the MEH-PPV/mesoporous silica composite is analogous to that in the photosynthetic reaction center: the aligned polymer chains within the pores behave as guides for energy harvested from the polymer segments outside the pores, the antenna chromophores. Moreover, energy in the composite material is transported with very little loss. The polymer segments in the interior of the composite are no

further downhill energetically than the longest segments present in a typical conjugated polymer film. Thus, the nanoscale design of the composite provides for control and direction of the flow of energy in the polymer with virtually no additional energy loss. We emphasize that the ability to carry out this type of directed energy transfer without significant loss requires the nanoscale complexity and positional control necessary to define two different conjugated polymer environments.

The use of the aligned composite also allows us to distinguish the roles of intrachain and interchain energy transfer in conjugated polymers. The fact that intrachain energy transfer is much slower than interchain energy transfer has important consequences: with proper isolation of polymer chains, we could greatly increase the efficiency of devices based on these materials. A device based on electrical contact to single polymer chains encapsulated in mesoporous glass should have efficient charge transport since the current would not be limited by the hopping of carriers between chains, as in an amorphous polymer film.<sup>[20]</sup> After the injected electrons and holes recombine on a single chain, the newly formed excitation would not be able to migrate a significant distance along the backbone during its lifetime, reducing the probability of quenching at defect sites. Moreover, such a device would provide polarized emission because of the net alignment of the chains. Clearly, with sufficient control over the conformation<sup>[21]</sup> and interactions between chains,<sup>[11]</sup> there is an enormous potential waiting to be tapped for the use of conjugated polymers in a variety of optoelectronic applications.

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