Self-Amplifying Semiconducting Polymers for Chemical Sensors

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Abstract

The ability of excited states (excitons) to migrate rapidly and efficiently through conjugated polymers makes these materials ideal for use in sensors based on fluorescence quenching or amplification of fluorescence signals. The structural features we are able to introduce into these polymers have allowed us both to design highly sensitive fluorescent sensors for specific analytes, such as the explosive trinitrotoluene (TNT), and to create assemblies that control energy transfer along a predetermined path. The principles involved have broad utility in the design of sensory materials as well as of electronic devices and display components based on electronic polymers.

Keywords: *electroactive organic materials, energy migration, fluorescence, polymers.*

Carrier mobility is a critical performance determinant in most electronic materials applications—for example, the mobility of electrons and holes in semiconductor devices controls the amplification afforded by field-effect transistors. Similarly, carrier transport has been used in conducting polymers to create highly sensitive sensors in which molecular interactions are used to trap charge carriers or inject new ones. Gain (amplification) in these systems is optimized by enhancing carrier mobility. By introducing receptor units capable of interrupting charge-carrier transport on binding a target species (analyte), we have demonstrated several polymeric, reversible, and chemoresistive sensors.[1,2] However, the amplifying ability of electronic polymers extends beyond the use of conventional charge carriers, and we have further introduced the concept of energy migration (exciton transport) as a mechanism for amplifying a sensory signal.[3]

Exciton transport has of late been studied in the context of electroluminescence, but it has long been important in the study of molecular crystals.[4] When considering exciton migration in organic polymeric semiconductors, one must consider that the disorder inherent in these materials creates energy gradients that the excitons follow to give a reduction in their energy.[5] The deliberate introduction of low-energy trapping sites into electroluminescent displays has been used to provide specific colors. As a result of exciton transport, these sites need only be very dilute for their effects to dominate the emission of the material. The same phenomenon can be used in conjugated polymers to amplify a chemical signal if the analyte produces trapping sites.

In this article, we discuss how exciton transport can be used to create self-amplifying, ultrasensitive sensory polymers and how exciton mobility can be optimized through molecular design. This technology has broad applicability and can be extended to many different types of processes commonly used in fluorescent sensing. There have been a number of innovative extensions of our amplification methods by other groups, and the interested reader is directed to a recent comprehensive review.[6]

To establish and quantify the amplification afforded by exciton transport in conducting polymers, we first synthesized polymers containing well-defined receptors with known binding constants and analyzed their response to analyte binding as a function of molecular weight. The receptors were selective for binding paraquat (*N,N'*-dimethyl-4,4'-bipyridine), a power-ful electron-accepting molecule that is an excellent fluorescence quencher. As shown in Figure 1, occupation of a single receptor site on a polymer by a paraquat molecule can effectively quench the fluorescence of the entire polymer. By analyzing the effective binding constant, we found that this high sensitivity reflects an additivity of the relatively small binding constants of the individual receptors. As a result, this system has the advantage of both rapid reversibility, due to modest individual binding constants, as well as a high overall sensitivity, due to their additive effect.

These initial studies in dilute solution provide the most direct measurement of the one-dimensional (1D) diffusion of excitons on an individual polymer chain. By analyzing the quenching as a function of molecular weight, we determined that the excitons diffuse approximately 140 phenylene ethynylene units during their lifetimes. As a result, extending the length of the polymers beyond the 140-unit diffusion length produces no additional amplification, indicating that the exciton is incapable of sampling the entire length of the polymer. However, the 140-unit limit to the amplification possible with this method is not absolute. Extension of the 1D random walks of excitons on a dissolved (isolated) polymer to two dimensions using Langmuir–Blodgett techniques (a means of coating a substrate evenly with a monolayer of a desired substance) makes receptor-site sampling much more efficient, as the chances of an exciton landing on an already-sampled receptor site are greatly reduced. Extension to a 3D multilayer system increases the efficiency of energy migration still further.[7]

Given that 3D structures are superior for facilitating exciton transport, it is worthwhile to design sensors that function in thin films or solid particles. It is also possible, and indeed likely, that in these structures the amplification will exceed predictions based on simple dimensionality arguments. This prospect for added amplification stems from the potential in thin films for greater electronic coupling both within a chain—due to improved conjugation that generally accompanies a transformation from solution to thin films*—and between chains, due to their close proximity to one another.

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*By creating organized assemblies of polymers at the air–water interface, we have been able to assign the spectroscopic signatures of different polymer conformations [see J. Kim and T.M. Swager, *Nature* **411** (2001) p. 1030]. Based upon this knowledge, we find that poly(phenylene ethynylene)s exhibit low degrees of conjugation in solution and that the conjugation is generally increased in thin films.

Monomeric chemosensor: sensitivity determined by the equilibrium constant
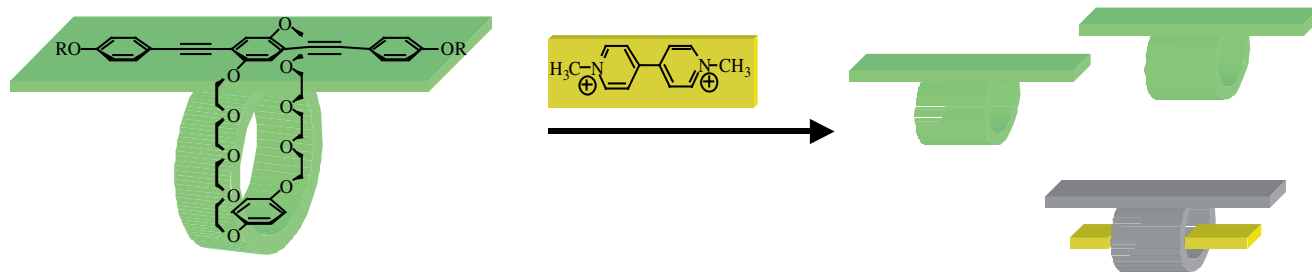
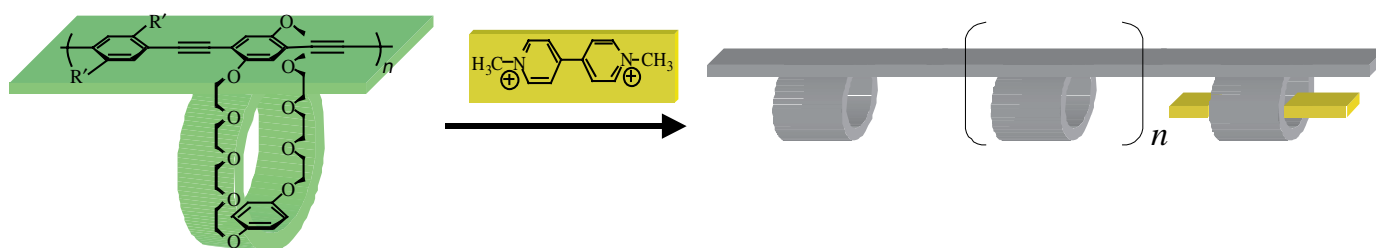Receptor wired in series: amplification due to a collective system response

Figure 1. Initial demonstration of amplified fluorescence quenching of a conjugated polymer. Fluorescent monomers containing receptors (cyclophane) for paraquat (N,N′-dimethyl-4,4′-bipyridine) are quenched on binding. However, in a polymer, only one of many receptors need be occupied to elicit a complete response. In this way, the polymer exhibits an effective binding constant that is additive of all of the receptors in the polymer.

To generate optimal exciton-transporting media, we have considered a number of factors. We have focused principally on self-amplifying polymers of the poly(arylene ethynylene) (PAE) class. These materials are nominally rigid rods with persistence lengths (a measure of the rigidity of a polymer) of 90 Å,[8] and this structural element may be used to create organized materials.[9] As shown in Scheme I, the cylindrical nature of the π orbitals of the ethynylene groups in PAEs allows for electronic delocalization (conjugation), even in
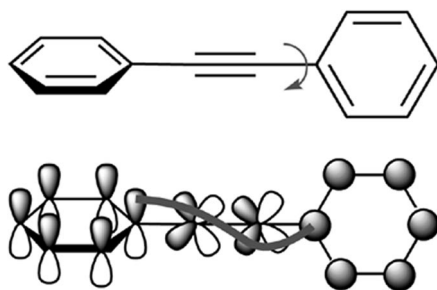

Scheme 1. Rehybridization of triple bond allows conjugation.

highly twisted structures. This is manifested in a smaller degree of solvatochromism (the dependence of the color of a substance on the solvent it is dissolved in) relative to the closely related poly(arylene vinylene)s (PAVs), in which the π orbitals are not free to rehybridize to maintain conjugation through twisted segments in the polymer backbone. The inherent disorder that accompanies polymers thus generally results in smaller π-orbital energy differences in PAEs, causing less dispersion of the energy levels of the polymer. The result is a relatively flat excited-state-energy surface, which prevents excitons from being rapidly trapped at local minima and allows for more flexibility in exciton diffusion. A complementary approach, discussed later, involves the introduction of deliberate energy gradients between relatively flat energy surfaces to direct excitons to specific sites.

Although electronic coupling between polymer chains is preferred for exciton transport, it can also give rise to detrimental self-quenching. To maintain the highest quantum yields in 2D and 3D systems, the chains must be prevented from forming nonemissive aggregates. To accomplish this,

we have developed a PAE with a rigid 3D structure (Chart 1) that effectively restricts cofacial interactions between the conjugated polymer backbones.[10]

Polymer **1** (Chart 1) displays high quantum yields in thin films and has been shown to have exquisite sensitivity to trinitrotoluene (TNT), the principal explosive used in land mines.[10] The detection of land mines is made difficult by the fact that they are constructed almost entirely of plastic and cannot be selectively located using metal detectors. As a result, the vapor signatures of TNT and the ubiquitous impurity dinitrotoluene (DNT) represent the most reliable markers of a buried land mine. The equilibrium vapor pressure of TNT is extremely low (5–10 ppb) and, given the small concentrations of explosives in the soil around a land mine, the vapor pressure of TNT in the head space over a land mine is orders of magnitude lower than the saturation vapor pressure.[11] Nevertheless, trained dogs are able to detect land mines based upon these chemical signatures. At present, sensors using self-amplifying semiconducting polymers are the only method (other than the use of canines) capable of detecting buried land
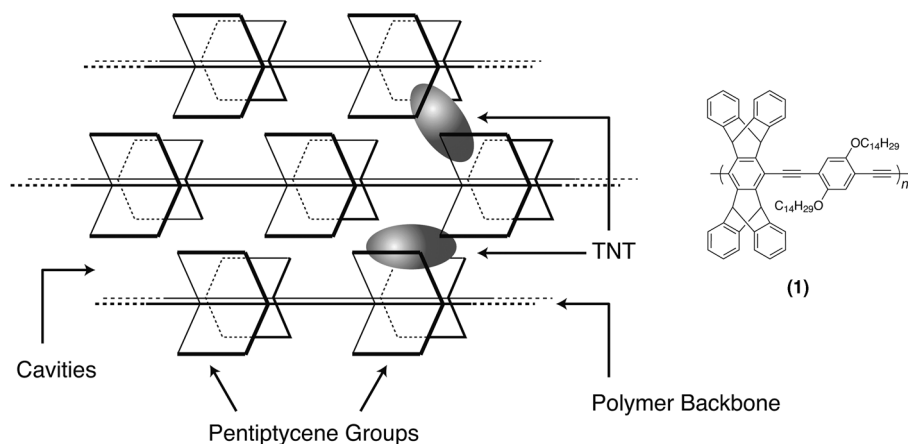
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mines using a chemical vapor signal in real time. Sensors using PAEs have been extensively field-tested (Figure 2) for the detection of land mines by keying on ultra-trace TNT and/or DNT vapor signatures.[12] These devices have femtogram (10^{-15} g) detection limits for TNT, which is orders of magnitude more sensitive than any other explosive-detection system.[12]


Figure 2. Land-mine detector, based on self-amplifying polymers, undergoing field tests. This prototype, the FIDO 4A, is capable of detecting femtograms (10^{-15} g) of TNT and has undergone extensive field testing at Fort Leonard Wood, Mo., and the Yuma Proving Ground, Ariz., as well as in Croatia. (Photograph courtesy of Nomadics Inc.)

Enhancements in energy migration produce materials that have greater amplification in sensors, like the explosives detector just discussed. Understanding the dominant mechanisms of exciton transport and how to optimize them is therefore necessary in order to produce the ultimate sensory materials. The dominant mechanism of energy transport in conjugated polymers depends on the polymer and its physical state. In poly(phenylene vinylene)s (PPVs), which have a larger energy dispersion than PAEs, there is evidence that through-space energy-transfer (Förster) processes are the most important.[13] These processes are favored by the strong transition dipoles and large energy-level dispersion that create the required spectral overlap between donor and acceptor sites in PPVs. In PAEs, we initially considered that the lower dispersion in the energy levels would favor mechanisms based on strong elec-

tronic coupling. In small molecules, this phenomenon is called Dexter energy transfer, and in semiconducting polymers, it is easiest to envision this process as resulting from strong interactions between individual units to form energy bands. The band model for energy transport is illustrated in Figure 3. As shown in the figure, analyte binding can function either to reduce the emission (as in the case of strong electron acceptors such as TNT and paraquat), or to produce a new lower-energy emission that will be amplified due to trapping of excitons at that site (Figure 3b).

In the Förster energy-transfer regime, the rate of energy transfer k_{et} is inversely related to the lifetime (the amount of time a molecule remains in an excited state), giving lower rates of energy transfer with longer lifetimes. Conversely, for Dexter processes, the longer lifetime enhances energy transfer, and the energy-transfer rate in one dimension scales as the square root of the lifetime. In higher-dimension systems, the dependence of energy-transfer rate on lifetime will be greater and is related to the relative rates of energy transfer in different directions. The presence of different energy-transfer rate/lifetime relationships in the Förster and Dexter mechanisms means that modifying polymer lifetimes and observing the resulting changes in the energy-transfer rate can be used to unambiguously determine which mechanism is dominant—extending the intrinsic excited-state lifetimes will either enhance or diminish k_{et}. However, to carry out this experiment, we first needed to design polymers having high quantum yields and extended intrinsic-fluorescence lifetimes. Our approach takes advantage of the fact that although the extended electronic structure of the material dominates its properties, some of the local character
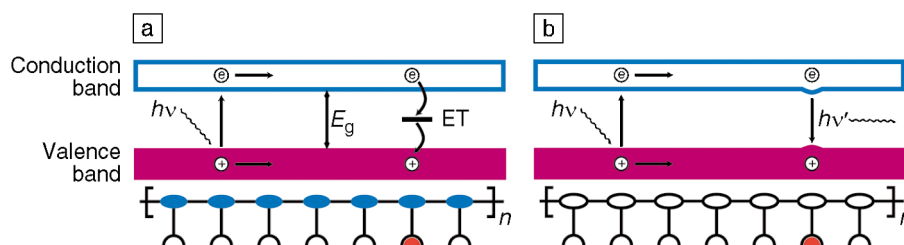
Figure 3. Schematic representation of energy migration in a conjugated polymer and how it produces amplification. The horizontal axis represents the distance along the polymer backbone, and the semicircles and red balls represent receptors and ligands, respectively. (a) Excitons migrate along the polymer backbone and are quenched when they encounter a receptor that has bound an acceptor ligand. (b) When a receptor is occupied with a nonquenching ligand, a local bandgap minimum is created that leads to the selective recombination of excitons at that site. E_g is the bandgap energy, $h\nu$ is a photon, and ET stands for electron transfer.

of the aromatic residues that are "wired" into the backbone are retained. For example, the aromatic groups in the polymers still have ring currents that move the nuclear magnetic resonance chemical shift of their protons downfield. Indeed, Brédas' model for predicting bandgaps involved consideration of the relative aromatic character of the respective units.[14] To obtain longer intrinsic lifetimes in our PAEs, we have integrated aromatic units (such as triphenylene[15] and dibenzo[g,p]chrysene[16]) with extended lifetimes (Chart 2). The representative examples shown have approximately the same fluorescence quantum yields, and so the lifetime difference reflects a true difference in radiative rate. In the polymers containing diacetylene linkages, every phenyl ring is replaced by a triphenylene unit. The larger lifetime increase in this system is consistent with our model, as a larger effect is expected when all the phenyl groups of a PAE are replaced by triphenylenes.

Within a structurally related class of polymers, relative rates of energy migration can be determined by fluorescence-depolarization measurements. This technique takes advantage of the fact that large polymers cannot undergo significant geometrical reorientations within the lifetimes of excited states. By irradiating a polymer with polarized light, regions that have their transition dipoles aligned with the polarization will be selectively excited. As the resulting exciton moves through the polymer, it will effectively lose memory of the initial polarization—the farther it migrates, the greater the loss of the polarization. The loss of polarization also depends on the excitation wavelength: excitation at the band edge populates only low-energy chromophores that are restricted in their ability to migrate, while excitation at shorter wavelengths populates segments of the polymer that experience a larger energy gradient and can more easily lower their energy. For these reasons, fluorescence depolarization is higher when the polymer is excited to the blue of the bandgap. We have further established that increases in the lifetimes of PAEs result in greater degrees of fluorescence depolarization.[15] These studies are direct evidence that Dexter energy transport (the band model) is the dominant mechanism for exciton transport in PAEs. This is also consistent with the fact that organic semiconductors, with their extended electronic structures, are excellent energy-transfer conduits.

The ability to transfer energy effectively to low-energy emissive traps (Figure 3b) creates many opportunities for the use of self-amplifying fluorescent polymers in fluorescence resonance energy-transfer
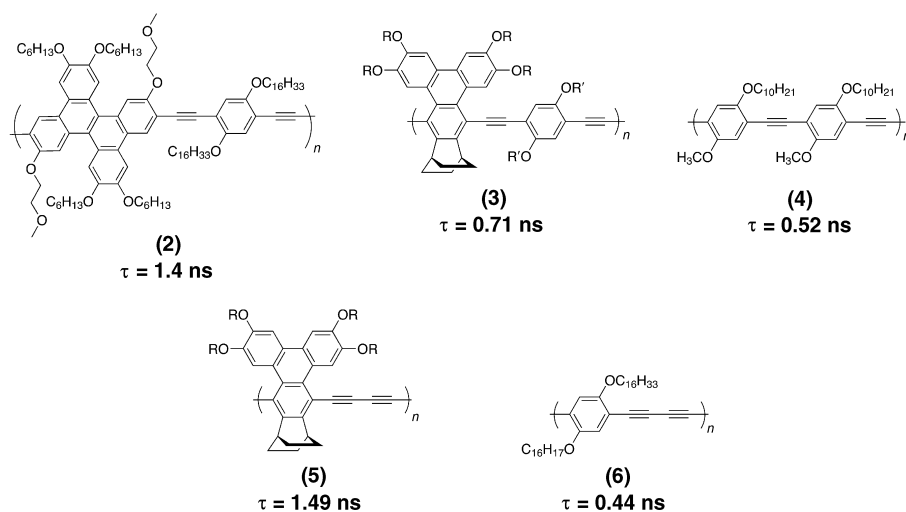

Chart 2. Poly(phenylene ethynylene)s (PPEs) containing dibenzo[g,p]chrysene (2) or triphenylene (3, 5) units in the polymer backbone exhibit long lifetimes (τ), relative to more conventional PPEs (4, 6).

(FRET) schemes of the kind often used in biological assays and biosensors. We initially studied these processes to characterize the intermolecular energy transport between PAEs in well-defined Langmuir–Blodgett films. We have subsequently demonstrated the use of electrostatic assembly processes[17] to assemble pH-sensitive films on glass substrates. In these studies (Figure 4), we showed that the fluorescence signal from a fluorescein-containing layer underlaid with a PAE is amplified when the polymer rather than the dye itself is excited.[18] These studies pave the way for the use of self-amplifying polymer schemes in numerous biological assays utilizing FRET processes.

The random diffusion of excitons in conjugated polymers can be used to provide amplified responses in a diverse array of
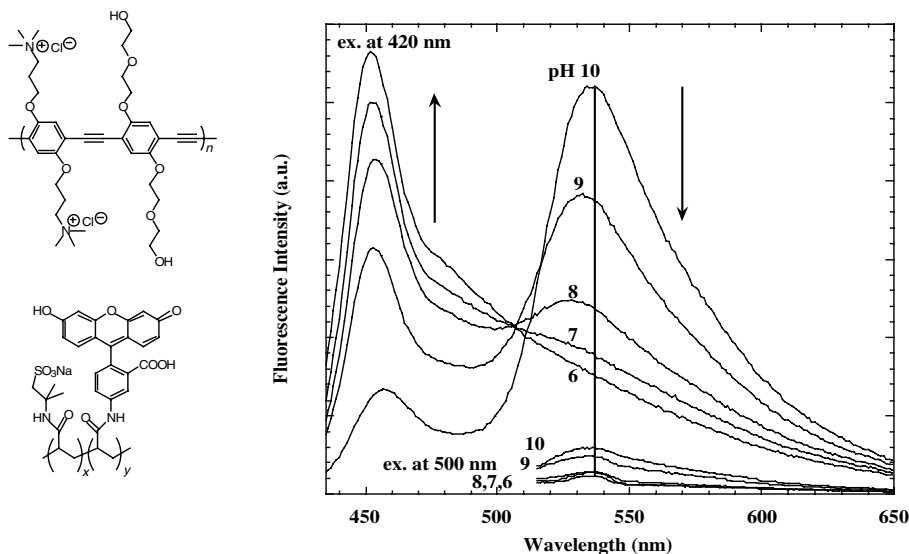

Figure 4. A bilayer film is assembled electrostatically from the two polymers shown at left. The cationic PPE is first bound to a base-treated (negatively charged) glass slide to generate a cationic surface on which the anionic fluorescein-containing polymer is deposited. The emission is pH-dependent: excitation of the PPE at 420 nm shows a decrease in the PPE emission at 460 nm and a large increase in the fluorescein emission at high pH. Direct excitation of the fluorescein fluorophore at its absorption maximum (500 nm) produces a much weaker response, indicating that emission at high pH is amplified by the polymer.

sensory schemes. However, the most effective devices will likely involve photonic circuitry that directs the excitons to particular sites, causes them to traverse particular functional groups, or creates higher logic elements.[†] Toward this end, we have developed multilayer polymer assemblies that direct energy transport to surface sites.[19] As shown in Figure 5, three different polymers were developed such that a progression of bandgaps is present in a striated three-layer film. Energy transfer between the layers is efficient enough that an excitation generated in the blue-emitting poly-

mer will cascade through the layers to give a dominant emission from the red-emitting polymer. This process was shown to dramatically improve the interpolymer diffusion of excitons relative to that measured for single-polymer films.[7]

In summary, the principle of self-amplification in fluorescent sensing using conjugated polymers has been shown to have broad ramifications and has been used to create sensors capable of detecting the ultratrace concentrations of specific chemicals, such as TNT, that are associated with buried land mines. In the case of land-mine detection using a chemical vapor, the required detection limits were previously only attainable in real-time using trained dogs. Emissive electronic polymers can be tailored to function in a variety of sensory schemes, and the full potential of this approach remains largely

untapped. The continued optimization of transport properties is a common goal of many researchers concerned with emissive displays, transistors, and sensors based on electronic polymers. Exciting advances from this collective research may result in ever-greater amplification in sensory devices. Additionally, the development of new photonic techniques that direct energy, control emission wavelengths (photonic crystals), or generate new logic elements presents opportunities that have yet to be fully imagined.

[†]Logic elements in small-molecule sensor schemes have been developed. For example, see A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, and T.E. Rice, *Chem. Rev.* **97** (1997) p. 1515.

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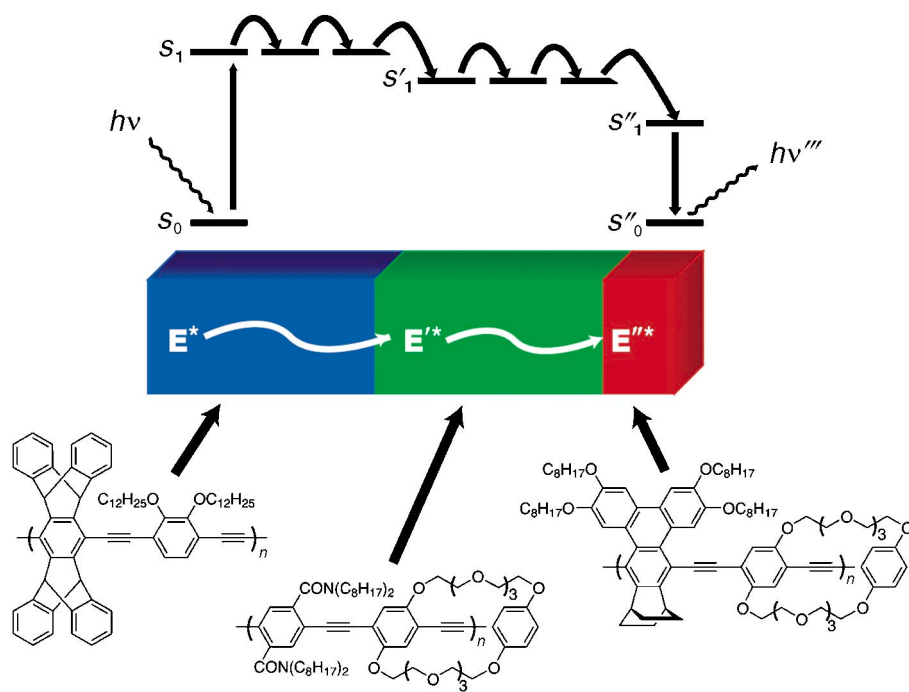
Figure 5. Three-layer striated film of poly(arylene ethynylene)s, designed to transport energy from the highest-energy blue emitter to the lowest-energy red emitter. S_0 represents the ground state of the blue polymer, S_1 is the first excited state of the blue polymer, S'_1 is the first excited state of the green polymer, S''_1 is the first excited state of the red polymer, and S''_0 is the ground state of the red polymer.