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Synthesis, Layer Assembly, and Fluorescence Dynamics of Poly(phenylenevinylene) Oligomer Phosphonates

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Abstract: We report the synthesis and spectroscopic study of a new molecularly engineered multilayer structure. The chromophore, which is an oligomer of poly(*p*-phenylenevinylene), is analogous to polymeric PPV which has been used in the fabrication of LEDs. This study was initiated specifically to explore if a multilayer geometry would aid the transport properties of the material leading to better semiconductor performance. We describe the synthesis and film formation of these novel materials. Detailed dynamic photophysical measurements on several new multilayer materials have shown that spectroscopically these thin films behave similarly to the polymers. The quantum yields of the films are of the same order of magnitude indicating that the emissive properties in both materials are due to localized molecular interactions. The relevance of the material properties to device applications is discussed.

Electroluminescent materials with properties compatible with current VLSI processing are of growing interest for data displays and optical interconnects. For the former, increased resolution, a wider range of tolerable ambient light levels, and the avoidance of power-intensive switching electronics and backlighting are the main attractions of these materials. For interconnects, a greater dynamic range may be achievable with electroluminescence strategies than with proposed optical refractive index modulation approaches. In general, all applications require fast and efficient conversion of electrical energy to light, preferably of a controllable wavelength, which can be shifted throughout the visible region of the spectrum. Miniaturization and facile integration compatible with silicon VLSI processing technologies of the emitting devices are also necessary for a wide variety of applications. These requirements are not fully met by existing luminescent devices.

The poly(phenylenevinylene)s (PPVs) are among the most extensively studied organic electroluminescent materials.[1] Processable PPV derivatives and PPV itself have been used to form the active layers in thin film light-emitting diodes (LEDs) with promising efficiencies. By tuning the morphologies, bandgaps, and charge transport properties of the polymers, device stabilities have been increased, and emitters at a wide variety of wavelengths have been fabricated. Modification of the optical and electrical properties have been noted in devices containing layers of different types of PPV in particular sequences.[2]

Despite the rapidity with which PPV has been developed for electroluminescence applications, many questions and difficulties remain. The factors governing luminescence efficiency are controversial, with the relative importance of photophysical responses and charge carrier mobility not yet established. The effects of impurities, unconjugated sequences, and ordered domains on device performance are inconsistent with simple, general models.[3] The reasons for device breakdown over time are poorly understood. More importantly, it is not clear that the polymeric character of PPV is essential to its electroluminescence; extensive data have been reported on electroluminescent devices consisting of small molecules evaporated onto substrates[4] or dispersed in inert matrices.[5]

Oligomeric PPV fragments should be useful in addressing some of these issues. The three-phenyl ring oligomers (*p*-distyrylbenzenes), for example, fluoresce with high quantum yields[6,7] and have been employed as scintillators[8] and as the active materials in vacuum-deposited electroluminescent films[9] and electroluminescent copolymers.[10] Interestingly only minor substituent effects on absorbance and fluorescence are observed in end-substituted distyrylbenzenes,[11] so that attachment of these compounds to matrices should only cause minor perturbations. More importantly, the wavelengths of absorbance, emission, and photoconductivity maxima as a function of PPV oligomer length begin converging at the four-ring (distyrylstilbene) level.[12] Longer oligomers could therefore be assumed to mimic PPV itself, with any photophysical differences attributable to intermolecular association and morphology. The electronic mobility in these oligomers, on the other hand, is completely unknown and would have to be investigated from first principles.

Transition metal phosphonate self-assembly[13] provides a convenient way to study these oligomers in the solid state. This protocol involves the alternating chemisorption of transition metal ions and organophosphonates or phosphates on phosphorylated substrates, resulting in dense, transparent, solvolytically, and thermally stable films of controlled thickness. We have employed Zr^{4+} as the metal ion and various rigid chromophores, including

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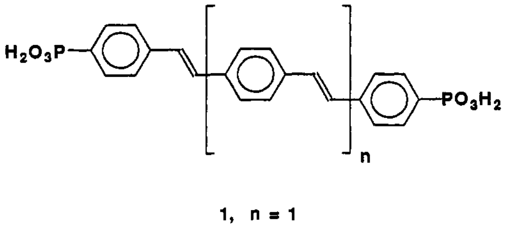
azo dyes,[14] thiophene oligomers,[15] and porphyrins[16] as the organic components in previous studies using this deposition chemistry. The method is especially useful for depositing sparingly soluble compounds without forming opaque aggregates. Possible substrates include highly transmissive silica surfaces and electrode materials. The deposition method allows for control of the spacing and sequence of different molecular units in a single film, so that hole and electron transporting compounds could be positioned among the emitting molecules in a film designed to be electroluminescent. Lithographically patterned deposition is also possible via self-assembly.[17]

Here, we describe the syntheses and layer deposition conditions for compounds **1** and **2**. Fluorescence spectra and decays are reported for the compounds as dilute solutions, deposited monolayers and bilayers, and as powdered sodium salts. These are the first examples of substrate-bound, solid films consisting almost entirely of PPV fragments; in particular, the deposition of the five-ring compound is unprecedented. The fluorescence decays and quantum yields of the solid oligomer films are similar to what is observed in spun films of PPV, despite the different chemical constitution and morphologies of the two types of films. Two distinct behaviors govern all the samples considered, depending on whether the molecules are dispersed (in a liquid or glass) or aggregated (as in a homogeneous solid). In this respect, the Zr phosphonate layers are decidedly solid-like. The role of aggregation in absorbance and energy transfer, important to both the oligomer films and PPV, is discussed in detail. While multilayer deposition is a conceivable deposition method for LEDs, the principal aim of this work is to gain additional information about PPV-like materials so that LEDs based on PPV can be improved.



1, n = 1
2, n = 3

Experimental Section

General Methods. All reactions involving lithium reagents were performed under N_2. NMR spectra were recorded in DMSO-d_6 except for the benzylphosphonate esters, whose spectra were obtained in $CDCl_3$. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ. Ellipsometric thicknesses were measured on a Gaertner ellipsometer as previously described,[13,15] assuming a film refractive index of 1.54. Substrates were cleaned by pirhana etching and primed with 19-acetoxynonadecyltriethoxysilane[18] with the acetate converted to a phosphate at the surface as previously described.[18] Phosphate-terminated substrates were immersed in 5 mmol aqueous $ZrOCl_2$ overnight before deposition of phosphonate layers. Depositions were from saturated DMSO solutions at 100 °C for **1** and 130 °C for **2**. The pH was kept sufficiently acidic so that pH paper indicated pH < 4 by the occasional addition of aqueous HCl. Rinsing with hot DMSO and zirconation with 5 mmol of $ZrOCl_2$ for 10 min preceded deposition of additional layers of **1** or **2**.

Diethyl 4-Bromobenzylphosphonate. A solution of $(EtO)_2PONa$ was prepared from 29 g of $(EtO)_2POH$ and 8.4 g of 60% NaH in mineral oil (0.21 mol of each) in 500 mL of toluene by stirring for 2 h at 0 °C under N_2. The mixture was warmed to reflux, and 40 g (0.16 mol) of 4-bromobenzyl bromide was added when the temperature exceeded 30 °C. After 3 h at reflux, the resulting suspension was cooled, washed with aqueous $NaHCO_3$, dried, and concentrated to an oil that contained 43 g (86%) of product, and a small amount of toluene, $(EtO)_2POH$, and mineral oil: NMR δ 1.2 (t, 6H), 3.08 (d, 2H), 4.0 (m, 4H), 7.13 and 7.42 (ab q, 4H).

Diethyl (((Diethoxyphosphinyl)methyl)phenyl)phosphonate (3). To a solution of the above monophosphonate (10 g, 0.032 mol) in 200 mL of anhydrous THF at −78 °C were added 0.032 mol of *n*-BuLi, 0.064 mol of *t*-BuLi, and 0.032 mol of $(EtO)_2POCl$ at 5 min intervals. Conversion was 90% in <1 h. After 1 h, 150 mL of saturated aqueous $NaHCO_3$ and sufficient diethyl ether to maintain two phases were cautiously added to the cold solution. The organic layer was separated from an emulsion and the aqueous layer to give an oil containing 5 g of product. Chromatography on 75 g silica gel, eluting with CH_2Cl_2 and EtOAc gave 3.9 g (33%) of pure product, NMR δ 1.2 and 1.3 (2 t, 12 H), 3.16 (d, 2H), 4.0 and 4.15 (2 m, 8H), 7.35 and 7.75 (2 m, 4H).

(*E,E*)-Tetraethyl-1,4-phenylenebis(1,2-ethenyl-4-phenylphosphonate) (6). A solution of diisopropylamine (300 mg, 3 mmol) in 30 mL of THF was cooled in a dry ice–acetone bath under N_2. To this was added *n*-BuLi (2.5 mmol), and the solution was warmed to 0 °C and recooled to −70 °C. A solution of **3** (0.90 g, 2.5 mmol) in 20 mL of THF was added, and the solution was again allowed to warm to 0 °C. A solution of terephthalaldehyde (480 mg, 0.6 mmol) in 20 mL of THF was added, and the mixture clarified and became yellow. After stirring overnight at room temperature, Et_2O and saturated aqueous $NaHCO_3$ were added. The organic layer was dried, filtered, and concentrated to a yellow oil. This was dissolved in hexane, EtOH, and MeOH in turn, reconcentrating each time. Yellow needles grew in the final concentrate and were washed with 1:1 toluene–hexane followed by pure hexane: yield 205 mg (62%); NMR δ 1.28 (t, 12 H, CH_3), 4.1 (m, 8H, CH_2), 7.18 (AB q, 4H, J = 16 Hz, ViH), 7.57 (s, 4H, central ArH), 7.6 (d of d, 4H, J = 8 Hz and 3 Hz, ArH), 7.8 (d of d, 4H, J = 8 Hz and 13 Hz, ArH). Anal. Calcd for $C_{30}H_{36}P_2O_6$: C, 65.0; H, 6.5; P, 11.2. Found: C, 64.7; H, 6.6; P, 10.7.

(*E,E*)-1,4-Phenylenebis(1,2-ethenyl-4-phenylphosphonic acid) (1). A 55-mg portion of the above ester was dissolved in 10 mL of anhydrous CH_2Cl_2 and 370 mg of Me_3SiBr was added. After 18 h, 4 mL of deionized water was added. After 5 min a pale yellow solid formed, which was collected, washed with H_2O, EtOH, and CH_2Cl_2, and dried. The yield was quantitative: NMR δ 7.34 (AB q, 4H, J = 18 Hz, ViH), 7.63–7.69 (m, 12H, ArH). Anal. Calcd for $C_{22}H_{20}P_2O_6 + H_2O$: C, 57.4; H, 4.8; P, 14.0. Found: C, 57.9; H, 4.8; P, 13.5. Deprotonation with NaSMe in DMSO followed by precipitation with EtOH gave the sodium salt.

(*E,E*)-1,4-Phenylenebis(1,2-ethenyl-4-benzaldehyde) (5). A suspension of 2.5 g (5.7 mmol) of bis(4-bromostyryl)benzene[11] (prepared from diethyl 4-bromobenzylphosphonate and **4** as described for **6**, with solid product precipitating directly from the reaction mixture) in 275 mL of THF was cooled to −78 °C. BuLi (12.5 mmol) was added, and the resulting mixture stirred for 1 h at −78 °C, 0.5 h at 0 °C, and then at −78 °C again. *N*-Formylmorpholine (1.44 g, 12.5 mmol) was added, and the mixture was stirred at room temperature overnight. Dilute aqueous HCl was added, followed by sufficient CH_2Cl_2 to separate an aqueous layer from the organic suspension. The suspension was isolated, concentrated, and triturated with EtOH, and the solids were collected. These were contaminated with 10–15% of distyrylbenzene. Fractionation by crystallization from 150 mL of hot PhCl gave a material in the *mother liquor* that was >90% pure **5**: NMR δ 7.48 (AB q, 4H, J = 15Hz, ViH, 7.71 (s, 4H, central ArH), 7.83 and 7.91 (AB q, 8H, J = 9 Hz, end ArH), 10.0 (s, 2H, CHO).

(*E,E,E,E*)-Tetraethyl 1,4-Phenylenebis(1,2-ethenyl-4-phenyl-1,2-ethenyl-4-phenylphosphonate) (7). A solution of diisopropylamine (150 mg, 1.5 mmol) in 20 mL of THF was cooled to −78 °C, and 1.25 mmol of n-BuLi was added. After warming to +10 °C and recooling to −78 °C, a solution of **3** (0.46 g, 1.26 mmol) in 10 mL of THF was added. After allowing the mixture to warm to 0 °C, the phosphonate anion solution was added to 106 mg (0.31 mmol) of **5** fully dissolved in 100 mL of THF. A yellow precipitate formed. After 3 days, the solid was collected and washed with MeOH, Et_2O, and deionized water: yield 165 mg (69%); NMR δ 1.25 (12H, Me), 4.0 (8H, CH_2), 7.2-7.4 (8H, ViH), 7.6–7.75 (20H, ArH). Anal. Calcd for $C_{46}H_{48}P_2O_6 + 0.5H_2O$: C, 71.9; H, 6.4; P, 8.1. Found: C, 71.9; H, 6.4; P, 7.6.

(*E,E,E,E*)-1,4-Phenylenebis(1,2-ethenyl-4-phenyl-1,2-ethenyl-4-phenylphosphonic acid tetrasodium salt) ($Na_4$2). A sample of **7** (21 mg) was dissolved in 30 mL of DMSO at 130 °C. An equal weight of NaSMe was added. A precipitate formed in <1 min. After 5 min, solids were collected and washed with hot DMSO and MeOH. The yield was 27 mg. The material was too insoluble to record the NMR spectrum. Anal.

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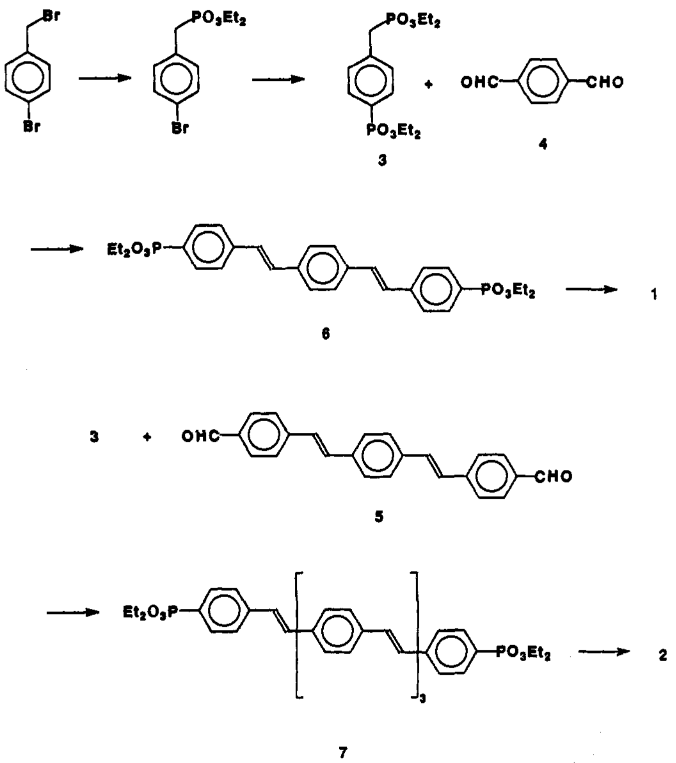
Scheme 1



Calcd for $C_{38}H_{28}P_2O_6Na_4 + 4H_2O$): C, 56.6; H, 4.5; P, 7.7. Found: C, 56.8; H, 4.2; P, 7.3.

Spectroscopic Experiments. Thin film absorption spectra were obtained on a Hewlett-Packard Model 8452A diode array absorbance spectrometer. Fluorescence excitation and emission spectra were collected using a SPEX Fluorolog fluorimeter. Unpolarized light from a tungsten lamp was used to excite the sample, and the dispersed fluorescence was measured with a standard S20 photomultiplier tube (note: both the excitation and the emission radiation were imaged through 0.25 M spectrometers). Spectra were corrected for lamp and detector responses.

Photoluminescence decays were collected with a novel multichannel time-correlated single-photon counting apparatus described elsewhere.[19] The excitation source was a cavity-dumped Coherent 7200 dye laser synchronously pumped by the frequency-doubled output of an Coherent Antares cw-mode-locked Nd:YAG laser. The tunable dye laser output ranging from 580 to 610 nm (Rhodamine 6G) was frequency doubled in a BBO crystal to produce pulses of ≈7 ps duration in the UV. The samples were excited with linearly-polarized light at a repetition rate < 4 MHz, with the emission dispersed in a ISA 640 grating monochromator. The collected photons were imaged onto a resistive anode array detector[19] without polarization discrimination. The samples were studied in a N_2-purged cell to reduce the presence of oxygen. The total instrument resolution was better than 100 ps.

Synthesis

The key intermediate in the synthesis of the two oligomers is compound **3**. It was originally prepared from 4-bromobenzaldehyde by sequential ketalization, halogen–metal exchange/diethylphosphorylation, deprotection, and reduction to give diethylphosphorylbenzyl alcohol, conversion to the benzyl bromide, and substitution with sodium diethylphosphonite. A much more efficient synthesis, described in the Experimental Section, was subsequently discovered requiring just two steps from 4-bromobenzyl bromide. Essential to this preparation was the passivation of the benzylphosphonate moiety by deprotonation before halogen–metal exchange, and the selective reaction of the aryllithium with diethylphosphoryl chloride in the presence of the benzyllithium. The Wittig–Horner condensation of **3** with dialdehydes **4** and **5** was routine,[20] as was the dealkylation of **6** to give **1**. However, **7** was too insoluble for the Me_3SiBr reaction, so an alternative nucleophilic dealkylation was carried out.

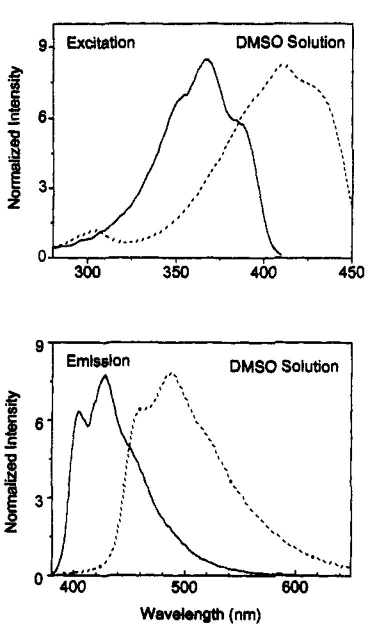


Figure 1. Fluorescence excitation and emission spectra for the three-ring oligomer **1** (solid curves) and the five-ring oligomer **2** (dashed curves) in dilute DMSO solution. The emission spectra were obtained with an excitation wavelength of 350 nm; excitation spectra were collected for peak emission wavelengths of 450 and 490 nm for **1** and **2**, respectively.

Ellipsometric thicknesses of individual layers of **1** and **2** deposited on zirconated phosphonate or phosphate surfaces are 24 and 38 Å, respectively, in good agreement with the theoretical expectations of 24 and 36 Å based on CPK molecular models. The compounds form multilayers in the same manner as other rigid diphosphonate chromophores,[15] with linear plots of absorbance and ellipsometric thickness vs layer number. Studies on a large number of compounds indicate that these multilayers consist of approximately monolayer quantities of organophosphonate separated by monolayers of $Zr,^{4+}$ especially as observed by XPS and FTIR.[18] However, long-range order leading to X-ray diffraction patterns is generally not observed in these materials.

Results

Effect of Chain Length. Fluorescence excitation and emission spectra for **1** and **2** in dilute DMSO solution are shown in Figure 1. The observed spectra are in agreement with previous oligomer data.[6,12] The maximum absorbance of these dilute samples was on the order of 0.1 AU. The excitation spectra coincide with the absorption spectra, indicating that they are dominated by the wavelength-dependent absorption probability. Note that only excitation spectra obtained on optically thick samples will directly reveal the relative quantum efficiency for emission as a function of wavelength.

Both the absorption (excitation) and emission spectra red shift by nearly 3000 cm^{-1} in going from the three-ring to the five-ring oligomer. The shift is consistent with a decrease in transition energy as the conjugation length (extent of delocalization) is increased. This is as would be expected from a simple particle in a box model for the electronic states. Similar spectral shifts between **1** and **2** are found for all forms of media studied. Excitation and emission spectra for self-assembled monolayer films of **1** and **2** (also optically thin) on quartz are shown in Figure 2, along with the emission spectrum for a typical polymeric PPV sample. Again, red shifts of 2500–3000 cm^{-1} are observed between the peak maxima of **1** and **2**. The polymer emission spectra is clearly redder than that for either oligomer studied, although the smaller shift between peak maxima (1600 cm^{-1}) and the overlap of the tails between the five-ring system and the

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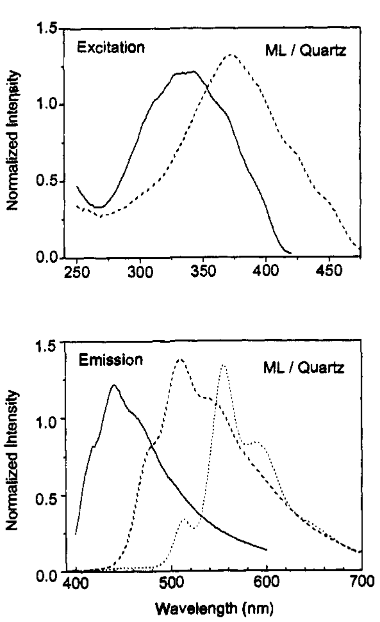

Figure 2. Fluorescence excitation and emission spectra for self-assembled monolayer films of **1** (solid curves, $\lambda_{ex} = 345$ nm) and **2** (dashed curves, $\lambda_{em} = 510$ nm; $\lambda_{ex} = 350$ nm). Also shown is the emission for the polymer (dotted curve, $\lambda_{ex} = 350$ nm).

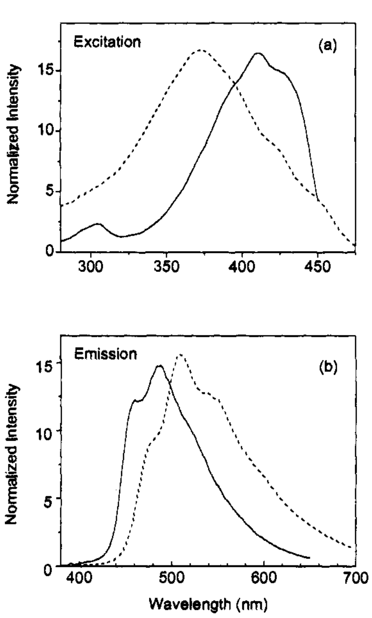

Figure 3. Fluorescence excitation and emission spectra for the five-ring oligomer (**2**) in a dilute DMSO solution (solid curves) and in a self-assembled monolayer film (dashed curves). $\lambda_{ex} = 350$ and $\lambda_{em} = 490$ and 510 nm for the solution and film, respectively.

polymer does indicate that the oligomer spectral behavior is beginning to converge to that of the polymer.[21]

Condensed Matter Effects. The enhanced solubility of the oligomers compared to the phenylenevinylene polymer allows the study of the oligomer in various physical forms, and facilitates a comparison of photoluminescence behavior between the dispersed and aggregated states of the material. The data reveal differences in both spectral and temporal behavior between the two forms, implying a clear distinction between the two classes of matter.

Steady-state fluorescence spectra for **2** in both dilute and condensed states are shown in Figure 3. In particular, excitation and emission spectra for a dilute DMSO solution and a self-assembled monolayer film on a quartz substrate are compared. The general trend observed with increased concentration (going from a dilute solution to a packed monolayer film) on the excitation spectrum is a blue shift of approximately 2350 cm^{-1} (Figure 3a). As stated above, this shift is indicative of the change of the UV/visible absorption behavior. In contrast, the emission spectrum shifts in the opposite sense, i.e., to lower energy, upon increased concentration, as evident in Figure 3b. Importantly, we note that the features of these spectra are not specific to the particular materials shown. Any dilute form such as the oligomer in liquid DMSO, solid PMMA solutions, as well as a dilute monolayer film (1:3 ratio of chromophore to ~1,16-hexadecanediyldiphosphonic acid, prepared by the usual Arbuzov route from the dibromide[18]) is shifted in the same direction and by approximately the same magnitude compared to any condensed form (such as the neat monolayer film, multilayer films, or bulk solid sodium salts). These observations, coupled with the result that the spectra of dilute solutions of **1** in either liquid (DMSO) or solid (PMMA) forms are nearly identical, indicate that the spectral characteristics are not completely dominated by conformational differences[22] but rather are strongly influenced by intermolecular interactions that are a consequence of the condensed state of the material.

In addition to features observed under steady-state excitation, time-resolved photoluminescence measurements reveal intriguing differences between the condensed and isolated oligomer samples. In the dilute limit, the emission decays as a single exponential with a lifetime of approximately 1 ns. This lifetime is characteristic of all dilute samples we have studied, including compounds **1** and **2** in DMSO solution and compound **1** in a PMMA matrix. In contrast, the decay of the condensed, concentrated oligomer samples are highly nonexponential. Figure 4 illustrates the decay for the five-ring compound in both dilute DMSO solution and is deposited as a monolayer film on quartz. Almost the same photoluminescence decay curve as that for the monolayer of **2** is observed for monolayer and multilayer films of both **1** and **2**.

The photoluminescence decay curve, which can be fit to a stretched exponential, is indicative (to some extent) of the complex diffusive transport behavior of the excited state consistent with the condensed nature of the material mentioned above and is driven by the intermolecular interactions which are active in the densely packed regions of this material. Particularly notable is the presence of a long tail (significantly longer than the 1 ns lifetime measured for the dilute oligomer) which characterizes the photoluminescence decay of every condensed phase sample studied. (note: We do not expect interaction with the quartz substrate to affect the decay, as electronic energy transfer with quartz is expected to be extremely inefficient due to a large energy mismatch.) The form of the decay will be addressed in more detail in a future publication.[23]

Discussion

In order to understand the spectral behavior, we consider the effect of molecular aggregation on the absorption and emission spectra. In a sample of sufficiently high concentration, radiative transitions may occur between complexes involving more than one molecule, such as dimers or larger aggregates. Either the ground state, the excited state, or in some cases both may be characterized by a molecular complex. Excimer emission is one well-known example of this phenomenon. In an ordered system, one can predict to some extent the spectral shifts between these new states. This has been done qualitatively for j and h aggregates.[24] In a homomolecular aggregate, the previously isoenergetic molecular electronic states split into states which are both lower and higher in energy. This would occur even if the aggregates were simply dimers. In general, however, it can be difficult to predict the position and/or optical response of

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these cooperative transitions a priori and nearly impossible in a disordered array. Important here is that it will not be clear which of the new electronic states will be probed by absorption (or emission) because of the existence of selection rules that are dependent upon the symmery and/or relative orientations of the species which define the complex. The spectroscopic signature of aggregation is generally a shift and a broadening in the absorption and/or emission bands.[25] Ideally, this interaction will result in an increase in the radiative rate of the aggregate relative to the monomer due to the collective nature of the states. Yet the presence of phonons and disorder induced dephasing as well as averages over orientation will make some of the interband transitions forbidden, with the nature of nonradiative processes unclear.

Clearly, in densely packed samples such as the self-assembled monolayer films, *some, if not extensive aggregation of the oligomers must take place.* Aggregation in these types of aromatic compounds is quite common.[26] The effective concentration of the film is quite high (2–3 M, estimated from the absorption). In light of this, it is reasonable to postulate that aggregation effects do play an important role in the blue-shift of the condensed-phase excitation spectra compared to dispersed forms.

The shift in the emission spectrum, on the other hand, can be explained in terms of migration of mobile excitons in condensed phases of **1** or **2**. Recall in Figure 3, a red-shift for the monolayer film of **2** compared to the dilute solution. Red shifts of emission upon increased concentration are often attributed to exciton diffusion. In a simple model, an excitation initially produced on one molecule might hop to another molecule, generally by dipole–dipole (Forster/Dexter) type interactions. In particular, the exciton diffusion will occur from a molecule of higher energy to a species of lower energy. The ability of the exciton to diffuse easily throughout a condensed sample until it becomes trapped on the lowest energy molecule locally available results in a red shift in the emission spectrum. Similar absorption and emission shifts have been previously observed in Langmuir–Blodgett films of stilbene and distyrylbenzene derivatives.[26]

For the polyphenylenevinylene system, exciton diffusion has been previously demonstrated by several groups.[27] Here the observed emission red-shift for the concentrated oligomer materials compared to the isolated oligomers, while not in itself proof of exciton diffusion, is consistent with such a model. Notably, however, a time-dependent shift of the emission spectrum to the red, which is another signature of exciton diffusion, is not observed in the present system with our current time resolution. The time scale and extent of this process is highly dependent on the geometry of the system involved. In some polymer samples the distribution of conjugation lengths may mask the diffusion in emission.

The difference between the photoluminescence decays for dispersed and condensed forms of the oligomer was presented above. It is clear that the particular form of the decay, with its strongly nonexponential shape, is characteristic of the oligomers in a condensed state. Even more striking is the observation that the luminescence time behavior of a film of the polymer itself is nearly the same as that of the oligomer films, as evident in Figure 4. For both the polymer and oligomer films, the photoluminescence decays rapidly at short times (1/e occurs at <200 ps), followed by a much slower decay observable for more than 50 ns. The similarities between decays indicate the existence of some decay mechanism(s) common to both the oligomeric and polymeric films.

Other comparisons can be made between the oligomeric systems and the polymer. The fluorescence spectra are similar (except for the bluer emission of the oligomers compared to the polymer), and vibronic structure is evident in both oligomer and polymer systems (see Figure 2). However, the vibronic structure appears weaker in the monolayer film of **2** than in the polymer. This is most likely due to inhomogeneous broadening as a result of disorder in the self-assembled monolayer film. The multilayer films resemble PPV electronically as well as optically; a preliminary characterization of a Au-**1**-Si diode showed rectification behavior that was similar to that observed in PPV diodes.[28]

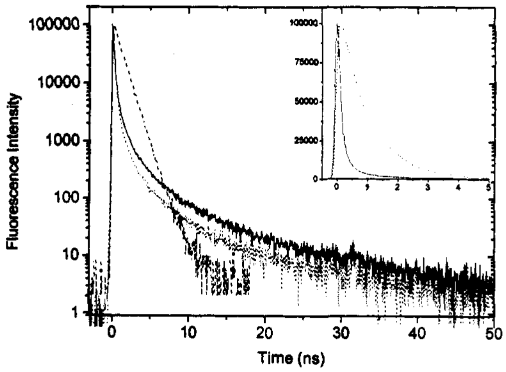

Figure 4. Normalized photoluminescence decays for compound **2** in dilute DMSO solution (dashed curves), compound **2** in a self-assembled monolayer film on a quartz substrate (solid curves), and the polymer film (dotted curves). The luminescence decay data are collected at the peak of the spectrum.

We have compared the relative photoluminescent quantum efficiencies for films of both the polymer and oligomers (as self-assembled mono- or multilayers) and find them to be the same within a factor of 2. These efficiencies are very difficult to measure but are in the range of 1–5%.[29] Quantum efficiencies on the order of 50% have been measured for the oligomers in dilute solution using the apparatus described above. The initially rapid photoluminescence decay observed in the self-assembled monolayer films (Figure 4) suggests significant depopulation at short time, consistent with the yield for the condensed form of the oligomers being significantly lower than that measured for the dispersed oligomers. One would expect quenchers to have a more pronounced effect in a solid than in a dilute solution.

Finally, we note that some photodegradation was observed both in the self-assembled films of **1** and **2** and in the polymer. Upon even weak irradiation, a decrease in luminescence was evident even in the absence of ambient O_2. This effect, which has been noted previously for the polymer, can be minimized by flowing N_2 over the material.[30]

Conclusions

The similarities between condensed forms of the oligomers (particularly self-assembled monolayers) and the polymer are many. We conclude that the polymer can be best described as an aggregation of oligomeric units. Based on the oligomer studies, we attribute much of the reported behavior of the polymer (and oligomer films) to properties of condensed phase, including aggregation and exciton diffusion. Isolation of the polymer, like that of the oligomer, should change the photoluminescent properties and result in higher quantum yield, slower decay, and bluer emission. Increasing the conjugation length, except for the concomitant removal of electronic traps, should not change the fluorescence dynamics dramatically. The spectroscopic similarities suggest that the oligomeric species should perform comparably to polymeric materials; however, the challenge remains to design device geometries that efficiently channel electrons and holes to the emissive molecules.

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