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Two-Dimensional Conjugated Polymer Assemblies: Interchain Spacing for Control of Photophysics

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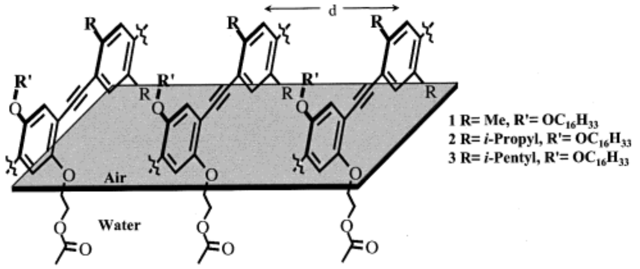
The viability of conjugated polymer thin film electrooptical devices and sensors depends strongly on high quantum efficiency thin films with excellent charge and exciton mobilities.[1,2] The brightness of electroluminescent devices depends on the charge transport and emission efficiency, and energy migration to low energy sites can provide the necessary wavelength shifts for lasing.[3] A highly sensitive and specific sensory device requires that a recognition event be coupled to an amplification mechanism. We are particularly interested in exploiting the collective transport properties of electrons, electron holes, or excitons traveling along a conjugated polymer backbone to amplify analyte binding events.[1] Movement of these excited states strongly depends on the interaction and orientation of an individual polymer relative to its neighbors.[4] Interchain distance has strong impact on the performance of electrooptical devices based on conjugated polymers[5] and only very recently has a theoretical model describing the interaction between neighboring chains become available.[6] Despite the accepted fact that interchain interactions alter photoluminescent properties of conjugated polymers, no reports of a general method for controlling the interchain spacing have appeared. In both small molecules[7] and polymers,[4d,e] close association of π-systems often causes a substantial decrease in the PL quantum yield relative to isolated chromophores. The diminished PL quantum yields make conjugated polymer thin films containing close cofacial π-stacking unattractive for use as transducing elements in chemosensors.[8] However, minimizing interpolymer distance is necessary for optimal energy transfer of excitons between polymer chains.[4d,e]

Interrogation of the influence that interchain distance has on thin film photophysics requires precise control over the packing and order of the individual polymer chains with respect to one another.[9] By restricting the polymer chains to a 2-dimensional liquid interface, a Langmuir monolayer provides the requisite polymer ordering and dynamics necessary to probe interchain effects. Scheme 1 depicts poly(*p*-phenylene ethynylenes) (PPEs)[10] containing a substitution pattern (regiorandom) where the hydrophilic and hydrophobic groups are para to each other producing an "edge-on" organization at the air−water interface.[12] Our previous studies indicated that the edge-on orientation forces the phenyl rings (barring any steric repulsion) on the polymer chains to pack in a close cofacial manner causing fluorescence quenching. Despite the low quantum yields, the edge-on polymers are attractive because Langmuir−Blodgett or Langmuir−Schaefer[13] films of these polymers provide high surface density and orient polar recognition elements toward the air−film interface.

Scheme 1



Herein, we report a systematic study of the relationship between cofacial interpolymer distance and solid-state photophysics. We predict that increasing the interpolymer distance will provide improved photophysical properties. To investigate our hypothesis, polymers (**1**−**3**) with differing degrees of side chain bulk were synthesized.[14] As expected, the side chain bulk influences the packing of the polymers at the air−water interface. Table 1 includes the area per repeating unit for polymers **1**−**3**, derived from extrapolated onset of the pressure−area isotherm. The area per repeating unit increases as the bulk of the side chain increases from dimethyl (**1**) to diisopentyl (**3**) and the area per repeat unit suggests that both subunits in each polymer orient edge-on. We calculate interchain distances of 4.0, 4.4, and 4.9 Å for polymers **1**, **2**, and **3** respectively.[12] X-ray diffraction data obtained from drop cast films of polymers **1**−**3** on aluminum corroborate the interchain distance trend observed on the Langmuir trough. From the X-ray data, interchain spacings of 3.6, 3.9, and 4.3 Å were observed for polymers **1**−**3** respectively, providing further indication that increased side chain bulk provides greater polymer−polymer spacing.[15]

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Table 1. Summary of the Photophysical and Geometrical Properties of Polymer **1**−**3**

	abs (Em)[a]		
	polymer 1	polymer 2	polymer 3
solution	435 (453)	435 (454)	435 (450)
LS film[b]	466 (560)	447 (550)	441 (453)
SC film[c]	464 (556)	449 (463)	448 (457)
DC film[d]	462 (566)	448 (463)	448 (461)
area/repeat	55 Å^2	60 Å^2	67 Å^2
LB dis[e]	4.0 Å	4.4 Å	4.9 Å
XRD dis	3.6 Å	3.9 Å	4.3 Å
Φ_f[f]	7%	12%	16%

[a] All wavelengths are the $\lambda_{\max}$ values and are reported in nm. [b] Langmuir−Schaefer film. [c] Spin cast film. [d] Drop cast film. [e] Chain distance calculated from the pressure−area isotherm. [f] The photoluminescent quantum yield of the Langmuir−Schafer films.[13]

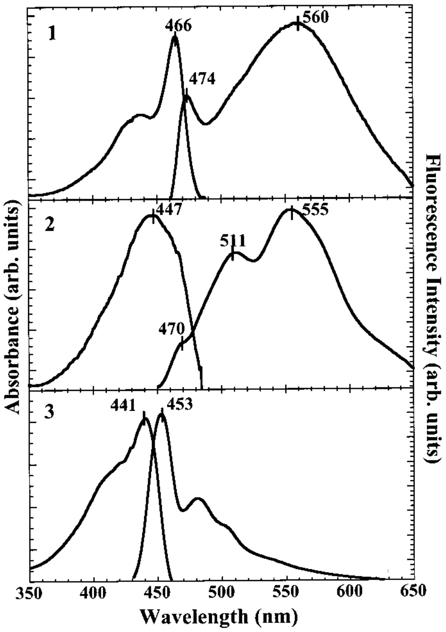

Figure 1. Normalized UV−vis and PL spectra of the monolayer LS films of polymers **1**−**3** cast onto hydrophobic glass slides.

Thin films were prepared on glass substrates by drop casting, by spin casting, and by using the Langmuir−Schaefer (LS) method.[13] Comparison of the spectral properties of solution, LS films, spin cast films, and drop cast films of polymers **1**−**3** reveals the influence chain distance imposes on polymer−polymer interactions. PPE films composed of polymers that do not strongly π-stack typically display a broad absorbance spectrum with a $\lambda_{\max}$ between 440 and 450 nm and a narrowed emission spectrum with a $\lambda_{\max}$ between 450 and 470 nm (see Figure 1, polymer **3**, as a representative example).[2c] In contrast, the UV−vis spectrum of polymer **1** shows a sharp band at 466 nm in the LS film, which does not appear in the solution spectra (Figure 1). We attribute this band to strong interchain π-stacking.[11,12] The PL from the LS film (Figure 1), the spin cast film, and the drop cast film of polymer **1** are identical and show a broad featureless band with maxima of 560, 556, and 566 nm, respectively. The broad red-shifted PL band indicates that the emission arises from the π-stacked aggregates. Despite the strong π-stacking, the LS film of polymer **1** is emissive, having a PL quantum yield of 7%.[16]

The LS thin film absorption spectrum of polymer **2** does not contain a new band but has a red-shifted $\lambda_{\max}$ (12 nm) relative to the solution data. The lack of a new band indicates that the isopropyl groups diminish π-stacking. The PL emission from the LS film shows three bands at 470, 511, and 555 nm ($\lambda_{\max}$). The 511 and 555 nm peaks are sharper than the broad emission observed for the PL of polymer **1** (Figure 1). The multiple peaks indicate more than one aggregated emitting species; currently, we are probing the excited-state lifetimes of these films to help clarify the origin of the observed differences. The increase in interpolymer distance increases the PL quantum yield of polymer **2** to 12%, further illustrating the impact a decrease in π-stacking has on the PL properties.

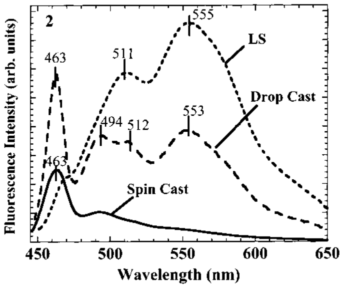

Figure 2. Normalized UV−vis and PL spectra of the spin cast, drop cast, and LS films of polymer **2**.

Conversely, the spin cast spectrum (Figure 2) and the solution spectrum of polymer **2** are very similar, illustrating the lack of order in the spin cast film relative to the LS film. However, the drop cast film has a PL maximum at 463 nm arising from nonaggregated polymer chains, along with three other red-shifted peaks at 494, 512, and 553 nm which may arise from multiple aggregated states (Figure 2), indicating that the drop cast film is intermediate between the LS (fully aggregated case) and the spin cast (least aggregated state). Spin casting kinetically traps the polymer chains in a highly disordered state, which is in contrast to the drop cast method that allows for organization to occur as the solvent evaporates more slowly. These data indicate that the diisopropyl groups maintain the interchain distance on the cusp between forming an aggregated state or not, depending on the deposition conditions.[17] Such a delicate balance is an ideal situation for the design of chemical sensors. We are currently investigating methods of exploiting the fact that small changes in the polymer−polymer distance can strongly influence the photophysical response.

The films of polymer **3** have the largest interchain distance and show only a small shift in the absorbance $\lambda_{\max}$ and almost no shift in the PL spectrum when compared to solution (Table 1). The solid-state PL spectrum of polymer **3** shows much sharper peaks than the PL spectra of polymers **1** and **2**, indicating that the interchain spacing of **3** is larger than the distance required for the chains to form emissive aggregates (Figure 1) and as expected polymer **3** has the highest PL quantum yield of 16%.

These data demonstrate that interchain distance has a strong influence on the spectral properties of PPEs and provides a strategy for controlling polymer spacing and thus film characteristics. Utilizing this approach, we are currently developing sensors which take advantage of the orientation and the higher density that the edge-on structure provides. On the basis of our results, we are also investigating sensors that respond to an analyte by forcing the polymer chains closer together, causing a change in the polymer photophysics similar to the change observed moving from the LS film to the spin cast film of polymer **2** (Figure 2).

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Supporting Information Available: Experimental details, characterization of polymers **1**−**3**, and X-ray scattering data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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