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A Poly(*p*-phenyleneethynylene) with a Highly Emissive Aggregated Phase

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Conjugated organic polymer-based materials are finding broad applicability in light-emitting diodes (LEDs),[1] light-emitting electrochemical cells (LECs),[2] plastic lasers,[3] solar cells,[4] batteries,[5] field-effect transistors[6] and sensors.[7] Due to their desirable optical, electronic, and mechanical properties, poly(*p*-phenylenevinylenes) (PPVs),[8] poly(*p*-phenyleneethynylenes) (PPEs)[9] and poly(*p*-phenylenes) (PPPs)[10] have been the materials of choice for semiconductor applications. Interchain interactions are an important determinant of the emissive properties of conjugated organic polymers in the solid-state. It has often been the rule that aggregation of polymer chains results in the undesirable side effect of self-quenching, to the detriment of fluorescence efficiencies. Therefore, a measure of control must be exerted over the structures adopted by these polymers in the solid-state, if one desires to exploit their emissive properties. We have previously demonstrated amplification in fluorescence-based polyreceptor chemosensors using the energy transport properties of conjugated polymers.[11] To enhance the versatility of these systems and allow the introduction of specific analyte binding functionalities, the cyclophane-based polymer **1** (incorporating amines) was prepared (Scheme 1).[12] During the course of our investigations, it was discovered that spin-cast films of polymer **1** exhibited an aggregated phase with an extraordinarily high fluorescent quantum yield. This unprecedented result has broad implications for the design of luminescent polymers and therefore warranted the further studies reported herein.

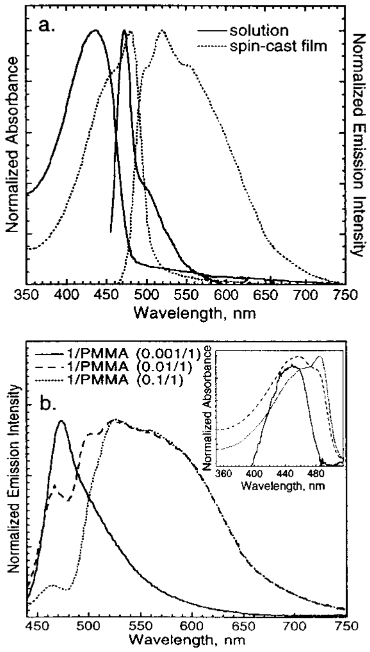

Figure 1. (a) Normalized absorption and emission spectra of polymer **1** in solution (CHCl3, OD @ $\lambda_{max} = 0.340$) and solid-state (spin-cast film, OD @ $\lambda_{max} = 0.186$); (b) Normalized absorption and emission spectra of spin-cast films of varying polymer **1**/PMMA composition (OD @ $\lambda_{max} = 0.017$ (0.001/1); 0.119 (0.01/1); and 0.554 (0.1/1).

Cyclophane **5** was readily synthesized, starting from ditosylate **2**. Reaction of ditosylate **2** with 2-nitrobenzenesulfonamide followed by di-iodo-ditosylate **3** yielded the cyclized compound **4**, which was then converted to cyclophane **5** after treatment with thiophenol. A palladium-catalyzed cross-coupling reaction of monomers **5** and **6** yielded the desired polymer **1**.

Polymer **1** exhibited relatively featureless absorption ($\lambda^{a}_{max} = 437$ nm) and emission ($\lambda^{e}_{max} = 473$ nm) bands in solution (typical for alkoxy-PPEs). While **1** is noticeably emissive, it exhibits a reduced solution quantum yield ($\Phi_F = 0.06$) when compared to closely related cyclophanes, previously synthesized in our group ($\Phi_F = 0.70$).[11] Hence in solution, the amine residues produce a reduction in fluorescence, most likely by an electron transfer quenching mechanism. In contrast, samples prepared via spin-casting displayed a visibly brilliant, yellow emission. Spectroscopic studies revealed a large, red-shifted absorption ($\lambda^{a}_{max} = 480$ nm, shoulder at ~450 nm) and a large, broad, red-shifted emission profile (Figure 1a). Previous studies of poly(*p*-phenyleneethynylenes) in thin films[13] and in monolayers[14] have shown similar spectral shifts, which originate from aggregated main chains. *However, in all of these previous examples the emission is highly quenched and is at most a few percent of the solution values*. In contrast, the aggregated phase of polymer **1** has a quantum yield 350% ($\Phi_F = 0.21$) of its solution value. To verify that the observed spectral features were indeed due to aggregation, a solid-state dilution experiment in poly(methyl methacrylate) (PMMA) was undertaken. This involved the preparation of spin-cast films of varying polymer **1**/PMMA concentrations and observation of the resultant absorption/emission profiles (Figure 1b). At dilute concentrations ($10^{-4}-10^{-3}$M), the spectra obtained were essentially solution-like in nature ($\lambda^{a}_{max} = 445$ nm; $\lambda^{e}_{max} = 474$ nm) whereas at higher concentrations ($10^{-2}-10^{-1}$M), red-shifted aggregate bands appeared and steadily intensified in both the absorption ($\lambda^{a}_{max} = 485$ nm, shoulder at ~460 nm) and

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(12) Experimental details are included in the Supporting Information. We encountered problems obtaining molecular weight information for polymer **1** by GPC, due to irreversible binding of the polymer to the cross-linked-PS support. GPC analysis was conducted on an acetamide derivative (M_n = 21, 200; PDI = 1.5) of **1** prepared via reaction with excess 1-acetylimidazole in CH$_2$Cl$_2$.

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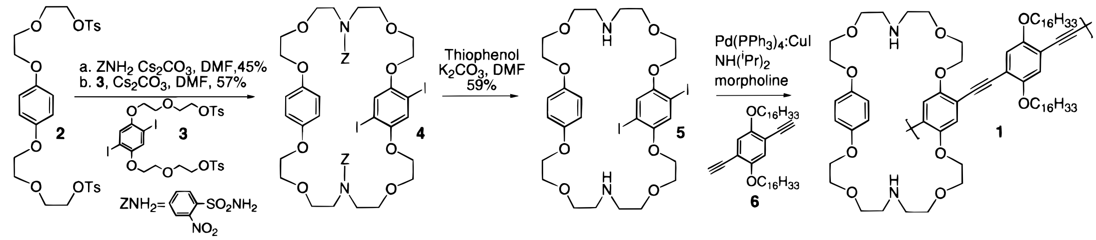
10.1021/ja0007298 CCC: $19.00

Scheme 1



emission (maxima at 499, 526, and 557 nm) spectra. These observations were entirely consistent with the formation of solid-state aggregates.

Aggregate films of polymer **1** become less emissive over long periods (weeks) in ambient atmosphere and after months display spectral properties similar to those obtained in $CHCl_3$ and dilute PMMA solutions. We initially thought that perhaps the amine residues were slowly reacting with atmospheric CO_2 to affect this change. Indeed, when a freshly prepared spin-cast film was treated with CO_2, a steady decrease in the absorption aggregate band at 478 nm was observed, coupled with an apparent blue-shift (after 22 h, $\lambda^{a}_{max} = 457$ nm) (Figure 2a). This effect was mirrored in the emission spectra, with a gradual decrease in the aggregate bands at 499, 519, and 550 nm and their eventual replacement by a weak, blue-shifted band ($\lambda^{e}_{max} = 481$ nm, shoulder at ~510 nm). Similar de-aggregation also occurred after a 1 min exposure to headspace vapor over a concentrated aqueous solution of HCl (Figure 2b). However, in the case of CO_2 we failed to see evidence for a buildup of carbamic acid moieties and neutralization of the protonated amines failed to reestablish the aggregate. These results suggest a kinetically controlled aggregate, which upon chemical modification (presumably via a carbamic acid–amine equilibrium and protonation of the cyclophane amine functionalities), rearranges polymer **1** to the more thermodynamically favored de-aggregated state. This process is very unusual since aggregation is generally thermodynamically preferred. Identical de-aggregation behavior could likewise be induced thermally by annealing the spin-cast films at 140 °C for 30 min (Figure 3a). Once again, aggregation would be expected to be thermally induced in most systems.

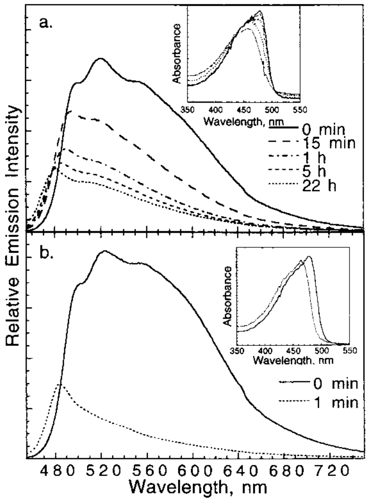


Figure 2. (a) Absorption and emission spectra of a spin-cast film of polymer **1** before and after exposure to CO_2. (b) Absorption and emission spectra of a spin-cast film of polymer **1** before and after a one minute exposure to HCl vapor.

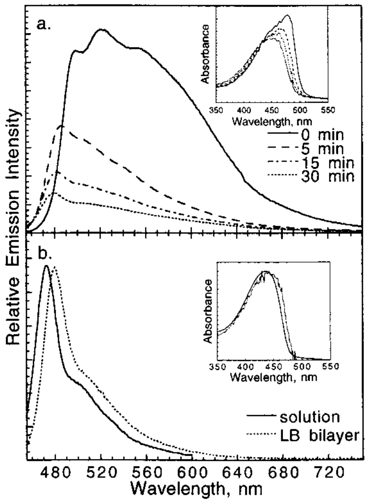


Figure 3. (a) Absorption and emission spectra of a spin-cast film of polymer **1** before and after annealing at 140 °C; (b) Normalized absorption and emission spectra of polymer **1** in solution ($CHCl_3$, OD @ $\lambda_{max} = 0.340$) and solid-state (LB bilayer, OD @ $\lambda_{max} = 0.016$).

To further investigate this unusual aggregation behavior, we have studied polymer **1** in a more ordered phase. Specifically, we have used the Langmuir–Blodgett (LB) technique, which is a powerful method for the introduction of chain alignment.[15] Thin-films of polymer **1** prepared via LB deposition showed absorption (443 nm) and emission (480 nm) bands, similar to solution or chemically/thermally treated spin-cast films (Figure 3b). In accord the quantum yield of films prepared by the LB technique were 0.046% or about 77% of the solution values. All of our results are consistent with the following explanation: Chain alignment and the buttressing effect of the cyclophanes (i.e. blocking of cofacial π-stacking of the polymer mainchains), prevents aggregation. The rapid evaporation of solvent in spin-casting leaves the polymer chains in a metastable skewed alignment that allows interchain interactions. However, after chemical or thermal modification, these chains rearrange into chain aligned, thermodynamically preferred, microdomains (similar to LB) with substantially diminished fluorescence. Our results are particularly interesting in light of recent theoretical studies on phenylenevinylene oligomers that propose that deviations from chain aligned (high symmetry) aggregates should produce a more efficient emission.[16]

In summary, we have created a new cyclophane-based PPE, which has been shown to undergo unusual solid-state aggregation to give highly emissive materials. This aggregation has been demonstrated to be controllable via the method of film preparation (LB versus spin-casting) with facile de-aggregation possible by the introduction of specific analytes or annealing. The subsequent decrease in the fluorescence intensities of spin-cast films after chemical/thermal modifications (due to chain alignment) has potential applications in sensor technologies.

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Supporting Information Available: Experimental details and spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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