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Evidence of Aggregate Formation for 2,5-Dialkylpoly(*p*-phenyleneethynylenes) in Solution and Thin Films

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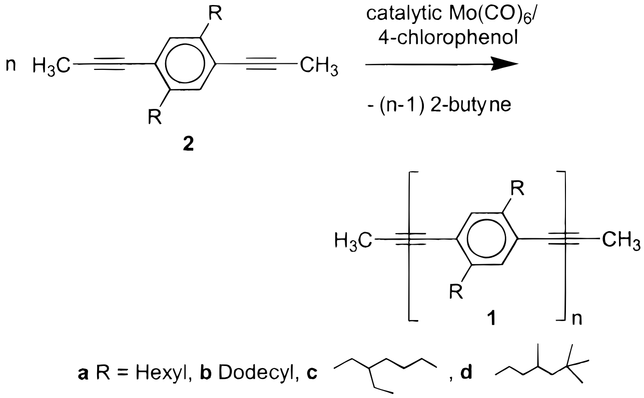
ABSTRACT: The absorptive and emissive behavior of four highly fluorescent bisalkyl-substituted poly(*p*-phenyleneethynylenes) (R = hexyl, dodecyl, 2-(ethyl)hexyl, and 3,5,5-trimethylhexyl) was examined. Aggregate and excimer formation was seen in solution and in the solid state by a combination of absorption and fluorescence spectroscopy in solvent/nonsolvent (chloroform/methanol) mixtures and in thin films. The aggregates were identified by the occurrence of a sharp absorption centered at 440 nm, undetectable in dilute chloroform solution, and a broad emission at 504 nm. The average size of the aggregate formed in chloroform/methanol solvent mixtures must exceed 1.5 μm, as was evidenced in filtering-experiments utilizing a set of membranes with different pore sizes to successively remove smaller aggregates.

Introduction

In this contribution we report the first example of aggregate and excimer formation in poly(*p*-phenyleneethynylenes) (**1**) based on the results of emission and absorption spectra taken from **1a**−**d** in solution and as thin films.



Conjugated organic polymers play an increasingly important role as organic semiconductors, due to their superb optical and emissive properties. In the past decade, they have found applications as emitting layers in LED's,[1] "plastic" lasers,[2] light-emitting electrochemical cells,[3] and polarizers for LC displays, just to name a few. Conjugated polymers have uniquely useful characteristics such as ease of processability and the ability to form large, flexible films. Additionally, facile manipulation of substituents and backbones enables tuning of their (molecular) band gap. These properties make them competitive with their inorganic counterparts.[1,4] However, in contrast to the strictly crystalline inorganic semiconductors with their well-defined long-range order, conjugated polymers (as organic semiconductors) can display a wide variety of different morphologies and solid-state structures with concomitant changes in optical properties and band gaps, even if the same backbone is employed. The emissive characteristics of these materials are strongly dependent upon their substituents, sample preparation, and history. A classic example is Scherf's[5,6] ladder polymer (LPPP), which displays blue fluorescence in solution but can emit either yellow or blue in the solid state. Scherf's extremely rigid LPPP is instructive insofar as it cannot change its *molecular* conformation upon formation of thin films.

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The observed optical effects must arise from the occurrence of aggregates and/or excimers. Similar differences in the optical and emissive spectra can be seen in poly(*p*-phenylenevinylene)s (PPV) as it has been pointed out by Conwell.[7] However, by suitable choice of the substitution pattern and topology in oligomeric phenylenevinylenes, Bazan[8] and Yu[9] have both been able to obtain completely amorphous and nonaggregating PV's.

While excimer and aggregate formation in the PPV case is under intense scrutiny,[7b] the related poly(*p*-phenyleneethynylenes) have found less interest in the past[10] but are becoming increasingly popular.[11−13] From the beginning, the high fluorescence quantum yields of PPEs in solution recommended them as attractive candidates for optical applications in emitting organic devices. It has been noted that thin films of alkoxy-substituted PPEs can display some bathochromic shift in their absorption spectra when compared to those for dilute solutions, but the phenomenon has not been studied systematically and no data for the electronically unperturbed (but thermally more stable) dialkyl-substituted derivatives of **1** are available.

We now have access to high molecular weight PPEs **1a**−**d** by the ADIMET (acyclic diyne metathesis) of dipropynylated benzenes **2** utilizing an active in situ catalyst formed from $Mo(CO)_6$ and *p*-(trifluoromethyl)phenol or *p*-chlorophenol.[14,15] Four representative PPEs, **1a**−**d,** were examined with respect to (1) their absorption in chloroform/methanol mixtures, (2) the concentration dependence of their emission, (3) their emission in chloroform/methanol mixtures, (4) their absorption and emission in thin films, and (5) the size of the emitting species.

Results

1. Absorption Spectra. The absorption spectra[16] of **1a**−**d** in chloroform are unremarkable and show the features reported for alkyl substituted PPEs.[11a] Even in relatively concentrated solutions (1.14 g/L, measured in a 1 mm cuvette) only the broad unresolved feature at 384 nm, typical for PPEs, is observed. However, in all cases, the absorption spectra change dramatically if methanol is added. Even though PPEs are insoluble in pure methanol, up to 70% can be added to a dilute chloroform solution of polymers **1** without visible precipitation. The extremely fine suspensions formed are stable for hours. Upon addition of methanol to **1b** (identical behavior is observed for **1a**) the wavelength of the main transition changes from 384 to 400 nm. A second sharp transition centered at 435 nm grows (see Figure 1a) with increasing methanol concentration. At 70% methanol content, the intensity of the primary transition and that of the sharp, red-shifted band are equal. Qualitatively similar behavior is found for **1d** in solution (see Figure 1b; **1c** closely resembles **1d**). The absorption spectra of thin films (see Figure 2a; **1a**, emission and absorption) are similar to the ones obtained from methanol/chloroform mixtures in solution. However, annealing a thin film of **1a** or **1d** for 16 h at 150 °C leads to a considerable gain in intensity of the narrow red-shifted band at 435 nm. In **1b,c** the effect of annealing is not as distinct as in **1a**.

2. Emission Spectra. In very dilute chloroform solution ($<10^{-2}$ mg/L), the emission spectra[17] of **1a,b,d** show a sharp feature at 425 nm and a second one of lower intensity at 450 nm, in perfect accord with literature observations.[11−13] In the case of **1c** the shoulder is observed at 440 nm. The fluorescence quantum yield of all examined polymers **1a**−**d** in solution is unity. When the concentration of the PPE solutions is increased from 10^{-2} mg/L to 1 g/L, the emission at 425 nm disappears completely. *The feature observed at 450 nm however, remains, and is shifted to 463 nm in the case of* ***1a,b***. This indicates the formation of excimers, because the *absorption* spectra are independent of concentration. In **1c,d** the same behavior is observed, but the growing transition at 450 nm is not red-shifted (Figure 3). If ca. 20% methanol (a nonsolvent for **1**) is added to the dilute solutions of **1a,b**, the spectra change and the shoulder at 450 nm starts to grow. Upon further addition of methanol (Figure 4a), two additional features at 480 and 500 nm emerge, and the primary emission line at 425 nm almost completely disappears. The emission of both **1a** and **1b** in the thin film is centered at 500 nm with a shoulder at 480 nm (Figure 2a). The fluorescence spectrum taken in methanol overlaid with the solid-state spectrum (Figure 2b) shows the similarity of both. Upon annealing a thin film for 16 h to 150 °C, the intensity of the emission line increases, but stays unstructured in **1a,b**.

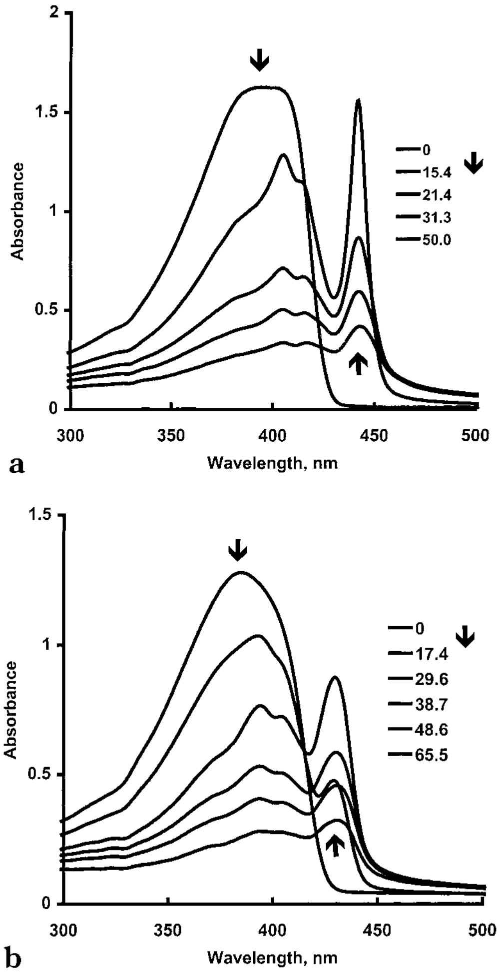

Figure 1. (a) Absorption spectrum of **1b** in chloroform/methanol mixtures. Inset: % methanol; arrows indicate the growth or decline of bands with increasing methanol concentration. (b) Absorption spectrum of **1d** in chloroform/methanol mixtures. Inset: % methanol; arrows indicate the growth or decline of bands with increasing methanol concentration.

The bulky side chains in polymers **1c,d** should attenuate their propensity toward aggregation. And indeed, changes in emissions are observed only after addition of approximately 30% methanol. Again, the

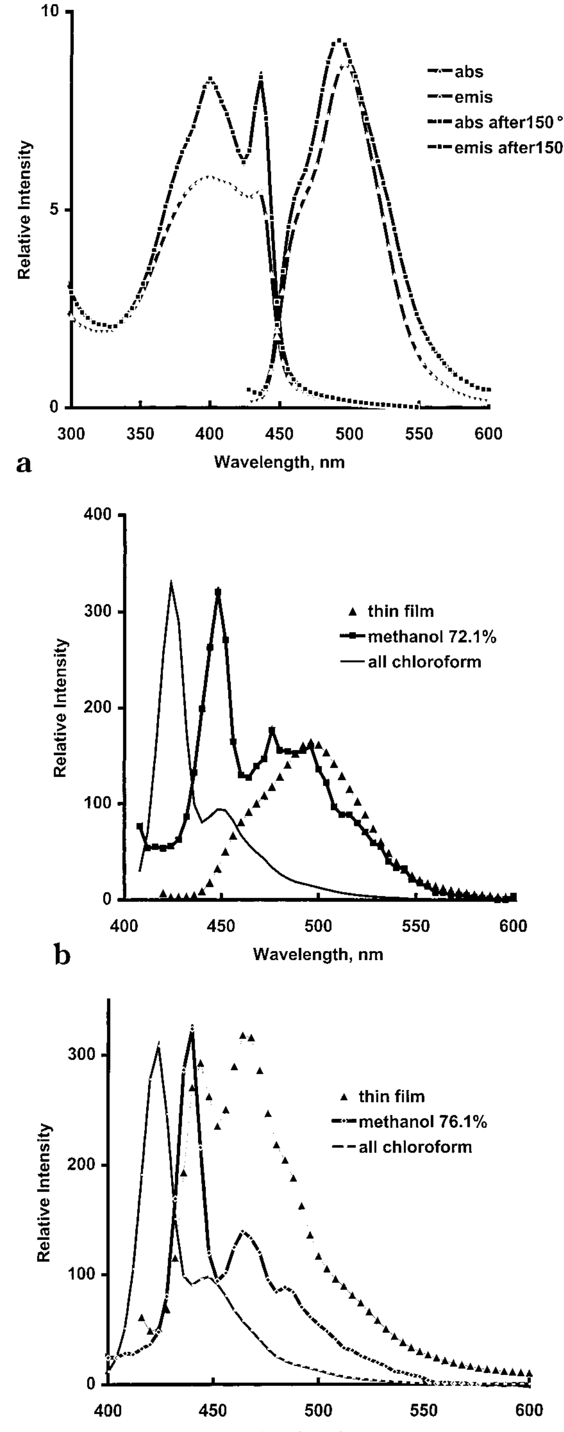

Figure 2. (a) Absorption and emission spectrum of **1a** as thin film before and after annealing at 150 °C for 16 h. (b) Partial emission spectrum of **1b** as thin film and as solution in methanol/chloroform. For comparison, the emission spectrum of **1b** in pure chloroform is shown. (c) Emission spectrum of **1d** as thin film and as solution in methanol/chloroform. For comparison, the emission spectrum of **1d** in pure chloroform is shown as well.

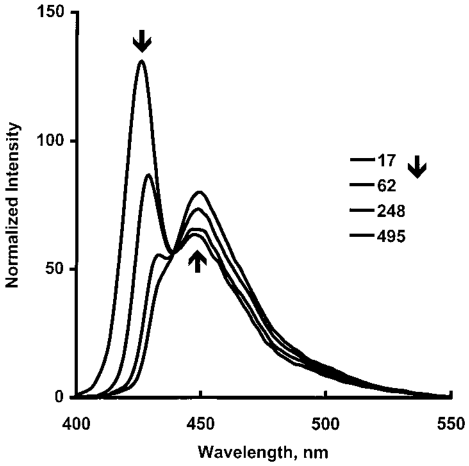

Figure 3. Emission spectrum of **1c** as function of concentration in chloroform. Numbers are concentration of **1c** in mg/L; the arrows indicate the growth or decline of bands with increasing concentration of **1c**.

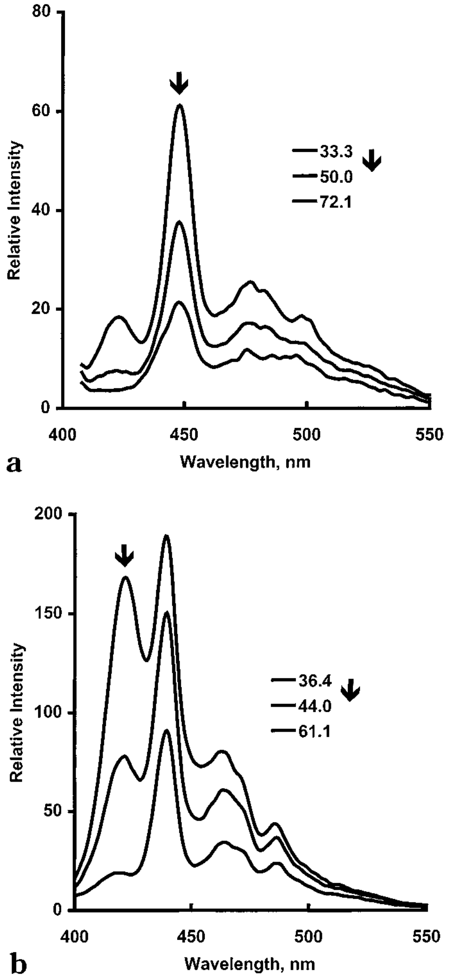

Figure 4. (a) Emission spectrum of **1b** in chloroform as function of added methanol (inset, content of methanol in %). The arrows indicate the growth or decline of bands with increasing methanol concentration. (b) Emission spectrum of **1c** in chloroform as function of added methanol (inset, content of methanol in %). The arrows indicate the growth or decline of bands with increasing methanol concentration.

primary emission at 425 nm disappears after 65% methanol has been added and the shoulder at 445 nm has developed *via* an isosbestic point into three distinct emissions at 438, 465, and 480 nm. An emissive tail reaches to 580 nm. In films of **1c,d** the emission is centered at 480 nm and develops more structure after annealing for 16 h at 150 °C. The thin film emission spectra can almost be superimposed with the spectra taken in methanol as seen in the overlay (Figure 2c).

3. Filter Experiments. The change in emission and absorption upon addition of methanol to solutions of **1** in chloroform raises the question whether aggregate

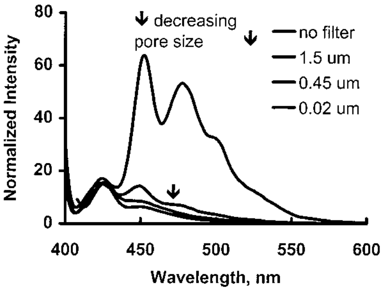

Figure 5. Filter experiment of **1b** as function of different pore sizes. The arrow indicates decreasing pore sizes.

formation is responsible for the changes. Alternatively, a charge-transfer interaction induced by the polar solvent or a locked molecular conformation in the PPEs could be operative. To test the aggregate hypothesis, a simple method was developed by Yamamoto's group, utilizing membranes of different pore size to determine presence and size of aggregates formed by the addition of methanol to polythiophenes.[18]

The emission of a dilute solution of **1b** in chloroform/methanol (85/15) is similar to that observed in the thin films (vide supra). Filtering of this solution through a 1.5 μm membrane leads to a fluorescence spectrum which is close (see Figure 5) to that of a dilute solution of **1b** in chloroform. Use of membrane filters with 0.45 μm and 0.2 μm pore sizes leads to spectra superimposable to that of **1b** in pure chloroform. Filtered samples of **1c** or **1d** (chloroform/methanol: 50/50; 1.5 μm pore size) likewise show emissive features observed in dilute chloroform solutions, while further filtration does not change the fluorescence spectra.

We approximate the polymer chain of **1d** to have a molecular cross-section of roughly 1.2 nm × 0.5 nm. The cross-section of the aggregates, according to the filtering experiments, is $>2.25\ \mu\text{m}^2$, leading to a rough estimate for the number of molecules involved in a single aggregate (approximately 10^6), assuming a lamellar geometry. For a spherical aggregate of 1.5 μm in diameter, an estimated volume of $3.4\ \mu\text{m}^3$ is obtained. A P_n value of 100 in **1d** renders an approximated molecular volume of 42 nm^3 per polymer chain. From these data, one aggregate particle would contain approximately 10^5 molecules as a lower estimate.

Discussion

Aggregate formation and concomitant change of structure is not well understood in alkoxy-substituted PPEs.[11b] According to a recent study by Fiesel and Scherf,[13] alkoxy-substituted PPEs do not display solvatochromism in chloroform/methanol mixtures, as was evidenced by the unchanged UV–vis spectra. The examination of the absorptive and emissive behavior of **1a**–**d** in chloroform, chloroform/methanol solutions, and in the solid state, however, corroborates the presence of aggregates in the mixed chloroform/methanol solvent and in thin films. The alkyl-substituted PPEs **1** are obviously different from their alkoxy-substituted counterparts, and we infer aggregate formation of PPEs **1** from the following observations: (a) The absorption changes and red-shifted transitions are observed, once methanol is added to a solution of **1**. (b) A very similar spectral feature is observed in the absorption spectra of solid films; it narrows and gains intensity upon annealing at 150 °C for 16 h. (c) Concomitantly, the emission spectra of **1a**–**d** experience a red-shift upon addition of methanol. The two emission bands observed in chloroform disappear almost completely, and instead a broad emission appears at 520 nm. (d) Upon passing through membranes of different sizes, (Whatman PTFE membranes: 1.5 and 0.45 μm) the transitions at 472 nm disappear and a weak but significant fluorescence, superimposable to that of **1** in diluted solution is recorded. Most of the red-shifted emission has disappeared after passing through the 1.5 μm membrane, and the 0.45 μm filter only leaves nonaggregated polymer chains. (e) At increasing concentrations in chloroform, the absorption spectra of **1** do not change appreciably, but the emission spectra do (example see Figure 3). The feature at 415 nm disappears via an isosbestic point at 440 nm. At the same time, growth of the transition centered at 455 nm is observed. After membrane filtration these spectra stay unchanged. We tentatively assign the emission at 455 nm to the formation of an excimer complex of unknown constitution. West[11c] has observed a similar behavior for alkoxy-substituted PPEs, but in his case the red-shifted feature never superseded the primary emission, suggesting only partial formation of excimers.

The red-shifted absorption at 440 nm is narrow for an aggregate band, which is usually broadened and unstructured. An alternative explanation (to that of aggregation) for the appearance of the solid-state spectral behavior would invoke the conformational locking of the phenyleneethynylene units of **1** with enhanced intrachain interaction between the chromophores. That has been observed in the polythiophenes[19] and polyphenylenes[19] but is unrealistic for **1**. In the aforementioned polymers, twisting the aryl–aryl single bond in solution leads to decreased conjugation and blue-shifted transitions in their solution phase UV–vis spectra. In the solid phase, the chains are planar and the observed bathochromic shift is a consequence of the improved *intrachain* interaction of the chromophores. PPEs show rotation of the phenylene units around the C–C≡C–C axis with a barrier of less than 0.5 kcal/mol,[20] proving that conjugation of PPEs is *not* particularly twist-dependent. That is reasonable, because the rotational symmetry of the alkyne linkage serves as an electronic coupler between the phenylenes, leading to a productive orbital overlap insensitive to the twist angle. As a result, the absorption should be independent of conformation. Supportive to our view, Moore[21] studied the *intrachain* folding of *meta*-linked PPEs and found that in acetonitrile a hyperchromic effect (i.e. an intensity shift in two adjacent transitions) was observed for the helix formations of larger oligomers. However, no bathochromically shifted absorption bands appeared during these folding experiments, suggesting that the UV–vis spectra of PPEs are highly independent of the conformation of the PE-units. *Thus, according to our experiments, the red-shifted optical features in absorption/emission spectra of **1a**–**d** must be due to aggregate formation in PPEs **1**.*

Conclusion

We have demonstrated that the highly fluorescent PPEs **1a**–**d** form aggregates in methanol/chloroform solution and in thin films. The increased bulkiness of the side chains in **1c,d** as compared to **1a,b**, does not prevent the formation of solid-state aggregates, but delays its onset. The fundamental examination of PPEs' optical properties will help to make polymers **1**, in which aggregate formation can be influenced at will, attractive for applications in light emitting devices and solid-state lasers. In the future, we plan to examine the time-resolved spectroscopy of unperturbed, excimer, and aggregate forms of **1a**−**d**.

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(15) Synthesis of **1b** and **1d**. **2b** (500 mg, 1.02 mmol), $Mo(CO)_6$ (13 mg, 0.051 mmol), and *p*-chlorophenol (131 mg, 1.02 mmol) in 1,2-dichlorobenzene (5 mL) are placed in a 25 mL Schlenk flask equipped with a reflux condenser. The reaction mixture was heated for 16 h to 150 °C under N_2-purge. Addition of dichloromethane, removal of the phenol by basic extraction, precipitation into methanol, and drying at 0.1 mmHg for 12 h gave 410 mg (92%) of polymer **1b** as yellow flakes. ^1H NMR ($CDCl_3$): δ 7.36 (s, 2H), 2.82 (s, 4H), 1.71 (bs), 1.54 (bs), 1.39−1.24 (bs), 0.88−0.85 (bs). ^{13}C NMR ($C_2Cl_4D_2$, 120 °C): δ 141.8, 132.2, 122.9, 93.3, 34.0, 31.6, 30.3, 29.4, 29.3, 29.0, 22.3, 13.6. UV ($CHCl_3$), λ_{max} 401.0 nm. SEC: M_w 4.36×10^6, M_n 8.14×10^5. In the same way we obtained **1d** (>99%, 4.51 g; from **2d**, 5.00 g, 12.1 mmol; $Mo(CO)_6$, 162 mg, 0.615 mmol; *p*-chlorophenol 1.58 g, 12.1 mmol; and 1,2-dichlorobenzene, 50 mL). ^1H NMR ($CDCl_3$): δ 7.36 (s, 2H), 2.80 (bs, 4H), 2.09 (s), 1.60−1.32 (bs), 1.24 (bs), 1.13−0.96 (bs), 0.91−0.83 (bs); UV ($CHCl_3$), λ_{max} 376.5 nm. SEC: M_n 3.80×10^4; M_w 6.09×10^4. Further characterization: see ref 14.

(16) Absorption spectra were taken on a Perkin-Elmer Lambda 6 spectrophotometer.

(17) Emission spectra were recorded on a Perkin-Elmer LS50 fluorometer. Fluorescence quantum yields were calculated using quinine sulfate as the reference. In the concentration dependent study, a pinhole was used along with slits of 10 mm.

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