# Aggregation and Self-Assembly of Oligo(2,5-dialkoxy-1,4-phenyleneethynylene)]s: An Improved Probe To Study Inter- and Intramolecular Interaction

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ABSTRACT: Molecular aggregation of an oligo(2,5-dialkoxy-1,4-phenyleneethynylene) **4** was successfully detected by simply using a combination of a proper solvent/nonsolvent system with low temperature. The study evaluated aggregation solely originating from intermolecular chromophore–chromophore interaction under high dilution. Spectroscopic investigation showed that the aggregate absorption band of **4** in solution was red-shifted by ~29 nm from its 0–0 absorption band ( $\lambda_{max} \approx 431$  nm). In the aggregate state, the chromophore molecules appeared to be arranged in a parallel fashion for a maximum level of interaction. Absorption and fluorescence spectra of film **4** showed that the aggregate structures formed in its solution were largely retained in the film state. The study provided useful information to aid the understanding of aggregation of polymer **1**, which possessed the effective chromophore of the same conjugation length, and allowed both inter- and intramolecular chromophore–chromophore interactions.

### Introduction

 $\pi$ -Conjugated polymers play an increasingly important role in emerging display technologies.<sup>1</sup> Facile interaction between polarizable  $\pi$ -electron clouds of large planar chromophores makes aggregate formation a common phenomenon, which affects the optical properties of the materials. Recent studies show that aggregation of  $\pi$ -conjugated molecules leads to the formation of weakly emissive interchain species in thin films that significantly reduce the luminescence quantum efficiency of light-emitting diode (LED) devices.<sup>2,3</sup> Understanding the formation and structure of aggregation, which represents an early stage in forming the solidstate films, will provide valuable information to guide future development of highly luminescent materials and superior device performance.

A typical characteristic of conjugated polymers is that the conjugation length of chromophore is not welldefined. For example, poly(p-phenyleneethynylene) of high molecular weight exhibits a coillike conformation<sup>4</sup> in solution, which is very different from an ideal rigidrod conformation expected from the molecular structure. Because of the presence of inevitable structural defects and thermodynamic equilibrium in polymer conformation, conjugation of the  $\pi$ -conjugated polymer is randomly interrupted, resulting in chromophores with a statistical distribution of various conjugation length. The presence of many chromophores along a single polymer chain opens the possibility for intramolecular interaction, which is expected to play an active role in the molecular aggregation. Although both intra- and intermolecular chromophore-chromophore interactions are available pathways for aggregate formation in a polymer solution, study from poly(3-hexylthiophene) at different concentrations and temperatures<sup>5</sup> leads to the assumption that the aggregate is fundamentally a single-chain phenomenon. To gain further understanding about the origin of aggregate formation, it is desirable to study the aggregation of a small molecular model compound, which isolates intermolecular from intramolecular chromophore—chromophore interaction. The conjugation length of an ideal model compound should be the same as that of the polymer. Such study has not been reported, partly due to one's inability to determine the actual conjugation length in a  $\pi$ -conjugated polymer.

By changing the ratio of solvent/nonsolvent composition, formation of aggregation has been observed from poly(phenylene ethynylene) derivatives (PPE),<sup>6</sup> a highly luminescent material with many useful properties.<sup>7</sup> Molecular aggregation has also been reported from wellcharacterized  $oligo(m-phenylene ethynylene)s^8$  and oligo(p-phenyleneethynylene)-containing block copolymer.<sup>9</sup> Our recent study<sup>10</sup> shows that proper combination of solvent/nonsolvent ratio with low temperature provides a more sensitive method in promoting the molecular aggregation of PPE 1. Aggregation induced by lowering the temperature, in contrast to addition of nonsolvent into a polymer solution, has an advantage of not altering the polymer concentration and solvent composition during the aggregate formation process. The true chromophores in 1 can be represented by molecular fragment **2** as a result of effective  $\pi$ -conjugation interruption at adjacent *m*-phenylene units. Comparison between the aggregation of 1 and its model compound 4 would reveal some useful information about the nature of aggregate formation, as intermolecular interaction is the only option available in the solution of 4.

## **Results and Discussion**

**Synthesis of Model Compound.** The penta(phenyleneethynylene) **4** was synthesized from the coupling of **3** with 1,4-dibutoxy-2,5-diiodobenzene by using a palladium-catalyzed reaction (Sonogashira coupling).<sup>11</sup>



(a:  $R_1 = H, R_2 = H; b: R_1 = CH_3, R_2 = OC_4H_9$ )

After purification on a silica gel column, the product was confirmed by elemental and NMR analysis.



(**a**:  $R_1$ =H,  $R_2$ =H; **b**:  $R_1$ =OC<sub>4</sub>H<sub>9</sub>,  $R_2$ =CH<sub>3</sub>)

Absorption and Emission Spectra in a Good Solvent (THF). The UV–vis spectrum of 4 in THF (Figure 1) exhibited a major absorption band ( $\lambda_{max} = 407 \text{ nm}$ ), which was very similar to that of polymer 1 ( $\lambda_{max} = 406 \text{ nm}$ ).<sup>10</sup> Nearly identical absorption profile and  $\lambda_{max}$  values confirmed the comparable chromophore conjugation length present in both 1 and 4. As the solution temperature was gradually decreased, the absorption of 4 was slightly red-shifted to longer wavelength, attributing to the adoption of a more planar conformation. As the temperature was decreased to -40 °C, vibronic structures became visible in the electronic absorption spectrum as a result of increased environmental rigidity, which reduces the molecular vibration and rotation.<sup>12</sup>

Fluorescence spectrum of **4** (Figure 2) exhibited a major band ( $\lambda_{max} = 448 \text{ nm}$ ) at 24 °C. The emission  $\lambda_{max}$  was gradually red-shifted with decreasing temperature, indicating that the molecular conformation was respond-



Figure 1. UV–vis spectra of 4b in THF solution with the concentration of  $2.16\times 10^{-5}$  M at various temperatures. The vibronic bands at –60 °C have  $\lambda_{max}$  values at 419 and 436 nm.



Figure 2. PL spectra of 4b in THF with the concentration of  $2.16 \times 10^{-5}$  M at various temperatures.

ing to the environmental change in a continuous fashion. In a good solvent such as THF, it was reasonable to assume that the molecules were uniformly distributed in the solution. The observed spectral shift, therefore, corresponded to a unimolecular behavior. It was noted that the spectrum at -60 °C became relatively well resolved, showing emission bands at 454 nm (22 026 cm<sup>-1</sup>), 479 nm (20 877 cm<sup>-1</sup>), and 504 nm (19 841 cm<sup>-1</sup>). The wavenumber separation between the vibronic bands was estimated to be about 1036-1149 cm<sup>-1</sup>.

Aggregation Induced in a Mixture of Good/Poor Solvent at Low Temperature. The absorption spectrum of 4 in a mixture of solvents (Figure 3) was basically the same as that in THF at room temperature, showing the absorption  $\lambda_{max}$  at 406 nm. Attempts to induce aggregation of 4 were not successful by using

Table 1. Spectroscopic Data of Model Compou
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	$\mathrm{UV} ext{-vis}\lambda_{\mathrm{max}}(\mathrm{nm})^a$		fluorescence $\lambda_{max}(nm)$		
compd	THF	film	THF	film	$\phi_{\mathrm{fl}}{}^b$
4a	318, <b>404</b>	296, 326, <b>421</b> , <b>454</b>	<b>445</b> , 472, 494	472, <b>499</b>	0.61
<b>4b</b>	319, <b>407</b>	296, 330, <b>433</b> , <b>456</b>	<b>448</b> , 473, 498	484 (sh), <b>501</b>	0.62
1b	318, <b>410</b>	327, 417, <b>450</b>	<b>449</b> , 468(sh)	<b>491</b> , 520	

<sup>*a*</sup> The bold number indicates the most intense peak. <sup>*b*</sup> The  $\phi_{fl}$  values were taken in THF solution and averaged over three independent measurements.



**Figure 3.** UV–vis spectra of **4b** in a mixture solvent (2.16 ×  $10^{-5}$  M) of methanol and THF (methanol/THF = 20:1 by volume) at various temperatures.

the pure methanol (a poor solvent) at room temperature. When the solution of **4** in the mixed solvent (methanol: THF = 20:1) was cooled below -10 °C, however, a new absorption band was observed at  $\lambda_{max} \approx 460$  nm. This new absorption band was associated with chromophorechromophore interaction as it was not observed in THF solution and was attributed to the aggregate formation. As discussed in the previous section, the chromophores had a tendency to adopt a more planar conformation at the lower temperature, which would improve the chromophore-chromophore interaction and facilitate the aggregate formation. The intensity of the aggregate band increased with decreasing temperature, as decreased solubility at the lower temperature forced the molecules to approach each other for the aggregate formation. The aggregate band in solution occurred at nearly the same wavelength as that in the spin-cast film of 4, clearly showing that the aggregate structure retained in the film state once formed in solution.

A similar trend was also observed from the fluorescence spectra of 4 in the same solvent mixture (Figure 4). At room temperature, the solution in methanol/THF (20:1 in volume) revealed the similar profile as that in pure THF. As the temperature was decreased to -60 °C, new bands at 478 nm (20 920 cm<sup>-1</sup>), 503 nm (19 881 cm<sup>-1</sup>), and 533 nm (18 762 cm<sup>-1</sup>) emerged clearly at the expense of the unimolecular emission band (at  $\lambda_{max} = 444$  nm). These new emissive bands conformed well with the broad emission peak of spin-cast film 4, further showing that the aggregate structures remained in the solid films. The wavenumber separation between the emissive bands at -60 °C was estimated to be about  $1039-1119 \text{ cm}^{-1}$ , quite comparable with that observed in pure THF at the same temperature. Observation of vibronic structures from aggregate, but not from film, showed that study of aggregate could reveal some useful information about the electronic band structure of the chromophore, which may not be observed from the film study.

It should be noted that the absorption spectrum of the film 4 exhibited two major absorption bands at  $\sim$ 430 and 460 nm (Figure 3). While the absorption band at  $\sim$ 460 nm was attributed to aggregate formation, the strong absorption band at 430 nm from film 4 indicated that a significant amount of the molecules packed in



**Figure 4.** PL spectra of **4b** in a mixture solvent (2.16  $\times$  10<sup>-5</sup> M) of methanol and THF (methanol/THF = 20:1 by volume) at various temperatures. The spectrum of the film ( $\blacktriangle$ ) is also shown for direct comparison.



**Figure 5.** UV-vis absorption of polymer **1b** in a mixed solvent (THF/methanol = 67:33 by volume) at 25 and -15 °C. The spectrum of the spin-cast film is also shown for comparison.

the film state retained their unimolecular characteristics. Fluorescence of film **4**, however, appeared to arise only from the aggregate, as a result of the energy transfer from a high (unimolecular chromophore) to low (aggregate) band-gap chromophore.

To closely mimic the chromophore-chromophore interaction in 4, aggregation of 1 was recorded by using the same solvent pair and under a similar concentration  $(\sim 10^{-5} \text{ M})$ . Aggregate formation from 1 required to use a higher content of THF (methanol:THF  $\stackrel{-}{\approx}$  1:2)<sup>10</sup> than that from 4 (methanol:THF = 20:1), attributing to the lower solubility of the former. The aggregate absorption band of 1 occurred at  $\sim$ 462 nm (Figure 5), which was bathochromically shifted from the 0-0 absorption band  $(at 434 \text{ nm})^{10}$  by ~28 nm. This bathochromical shift could be related to the degree of chromophore-chromophore interaction in the aggregate. Interestingly, the aggregate absorption band of 4 occurred at nearly the same wavelength (at 460 nm) as that of 1, which was red-shifted from the 0–0 absorption band (at 431 nm) by  $\sim 29$  nm. Comparable aggregate band position in wavelength and its bathochromic shift from the 0-0

absorption band indicated that the chromophore-chromophore interactions in both 1 and 4 were very similar.

Spin-cast film 4 exhibited two absorption bands at about 433 and 456 nm (Figure 3), corresponding to the single chromophore and its aggregate in the solid state. Clearly, the ordered structure formed in the aggregate remained intact in the film state. The aggregate absorption band of the spin-cast polymer film 1, however, occurred at 450 nm (Figure 5), which was about 12 nm blue-shifted from that of its solution. It appeared that the chromophores in the film state had slightly looser contact than that in the solution, since the chromophores along the polymer chain did not have sufficient time to orient themselves for optimum interaction during the spin-casting process.

Aggregate formation from 4 under the similar concentration as 1 indicated that intermolecular interaction remained to be a major factor for aggregation under high dilution. Difference in the solvent compositions for 4 and 1 could be largely offset by their solubility, as the polymer required a significantly higher content of good solvent to reach the same solubility level as the model compound. A similar level of chromophore—chromophore interaction observed from both 1 and 4 suggested that intermolecular interaction remained to be predominant in the aggregate formation. The assumption was supported by the optical spectra of 4 in film state, which closely resembled that of its solution aggregate.

#### Conclusion

Molecular aggregation of an oligo(2,5-dialkoxy-1,4phenyleneethynylene) 4 was induced by using a combination of solvent/nonsolvent with low temperature. The current technique was shown to be superior than by changing the solvent composition (or polarity) alone, thereby providing an effective method to study molecular aggregation. The improved detection of aggregate could be partially attributed to the more planar conformation that chromophore achieved at the low temperature, which facilitates the chromophore-chromophore interaction. Spectroscopic comparison of 4 in both solution and film states (UV-vis and fluorescence) showed that the aggregate structure developed in the solution largely retained in the film. Although the chromophore were present in both aggregate and nonaggregate forms, the former appeared to predominate the emissive properties of the film, as the energy transfer from a high to low band-gap chromophore became more convenient in the solid state.

Comparison of aggregation behavior between the model compound 4 and polymer 1 revealed useful

information about the aggregate structure. Since the molecules of 4 were freely mobile, the rodlike molecules are preferably to assemble in a parallel fashion<sup>13,14</sup> to achieve a maximum degree of interaction. A similar degree of chromophore-chromophore interaction was observed from 1 and 4, as characterized by nearly the same bathochromic shift from their respective 0-0absorption bands (Figures 3 and 5). The observed similarity in the chromophore-chromophore interaction suggested that the chromophores in the aggregate of polymer 1 were also assembled in a parallel (or nearly parallel) fashion. Although intramolecular interaction was still a permitted pathway, the chromophores along the single chain are required to be relatively apart from each other in order for them to comfortably fold toward each other and to reach the preferable parallel alignment.

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**Supporting Information Available:** Synthesis and characterization of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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