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Molecular Aggregation of Poly[(1,3-phenyleneethynylene)-*alt*-oligo(2,5-dialkoxy-1,4-phenyleneethynylene)]: Effects of Solvent, Temperature, and Polymer Conformation

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ABSTRACT: By altering solvent/nonsolvent ratio and temperature, a comprehensive study is carried out to understand the molecular aggregation of poly[(1,3-phenyleneethynylene)-*alt*-oligo(2,5-dialkoxy-1,4-phenyleneethynylene)]s **1** and **2** in solution, which possess different lengths of linear phenylene-ethynylene (PE) fragments. Although both polymers exhibit random-coil conformation in THF solution, PPE **2** of longer rigid-rod fragment exhibits a higher tendency to form aggregate than **1**. In a good solvent, optical spectra of PPEs reveal a gradual spectral shift in responding to the temperature change, which is attributed to molecular conformational change (planarity of chromophore). With addition of methanol to polymer solutions in THF, UV−vis absorption spectroscopy detects the aggregation band from **2** but not from **1**. The combination of solvent/nonsolvent and low temperature provides improved sensitivity to probe molecular aggregation. Although chromophore planarity is anticipated to play an important role, current results favor the $\pi-\pi$ interaction in the aggregate formation of **1** and **2**.

Introduction

Molecular aggregation represents an important phenomenon in molecular biology and material science. In the case of π-conjugated materials, facile interaction between polarizable π-electron clouds of large planar chromophores makes aggregate formation even more common, which affect the optical properties of the materials. Recent studies show that aggregation of π-conjugated molecules leads to formation of weakly emissive interchain species in thin films that significantly reduce the luminescence quantum efficiency of light-emitting diode (LED) devices.[1,2] Understanding the formation and structure of aggregation, which represents an early stage in forming the solid-state films, will provide valuable guidance to develop materials of improved luminescence efficiency. Poly(*p*-phenyleneethynylene) derivatives (PPEs)[3] represent a unique example of π-conjugated polymers with rodlike backbone and high luminescence, which have exhibited many useful physical properties.

Molecular aggregation in solution can be conveniently detected by various electronic spectroscopic methods, including UV−vis absorption,[4,5] fluorescence,[6] and circular dichroism (CD)[7−9] if the molecule in question possesses chiral properties. Formation of aggregation is commonly induced by changing the nonsolvent/solvent ratio, as observed from poly(*p*-phenyleneethynylene) derivatives (PPE)[5] and well-characterized oligo(*m*-phenyleneethynylene)s.[9] Clearly, significant nonsolvent in solution makes solute−solvent interaction energetically less favorable, thereby forcing polymer chain segments to approach each other for aggregate formation. Temperature-induced aggregation has also been observed from polythienylene (from 22 to −23 °C)[4,10] and poly(2,5-dialkyl-1,4-phenyleneethynylene) (from 110 to 20 °C).[7] The molecular aggregation bands appear at longer wavelength than those nonaggregate bands in both optical absorption and emission spectra. As suggested in Bunz's recent report,[11] two possible explanations can be used to account for the aggregation band in PPEs. The spectroscopically observed aggregation band might be originated from the molecular planarization of PPE backbone, which emphasizes a single molecular effect. The second explanation attributes the aggregation band to the electronic orbital interaction between different PPE backbones ($\pi-\pi$ stacking), which operates through intimate intermolecular or interchain contact. It remains a challenge in the field to determine the origin of aggregate band formation. The possible existence of twisted and planar PPE backbone in its ground and excited states[12] may further complicate the study.

Our recent studies[13,14] have shown that poly(phenyleneethynylene) (PPE) **1** and **2** are highly emissive materials with potential applications for light-emitting diodes. The presence of the *m*-phenylene unit, which introduces a bent angle along the polymer backbone, significantly reduces the polymer chain stiffness. Resulting from effective π-conjugation interruption at adjacent *m*-phenylene units, the chromophores in polymers **1** and **2** may be represented by molecular fragments **3** and **4**, respectively. The apparent difference in linear rigid-rod length between chromophores **3** and **4** provides an opportunity to examine the effect of the rigid chain length to molecular aggregation, which would be useful information for future material development. In addition, polymers **1** and **2** can be simply viewed as a series of conjugated fragments with equal conjugation length, which are jointed together via sharing an *m*-phenylene unit. In this contribution, we have systematically examined aggregation of polymers **1** and **2**, which are induced by both low temperature and solvent/nonsolvent ratio. The proper combination of solvent/nonsolvent ratio with low temperature appears to be more effective in detecting the molecular aggregation. Comparison of polymer chain stiffness will

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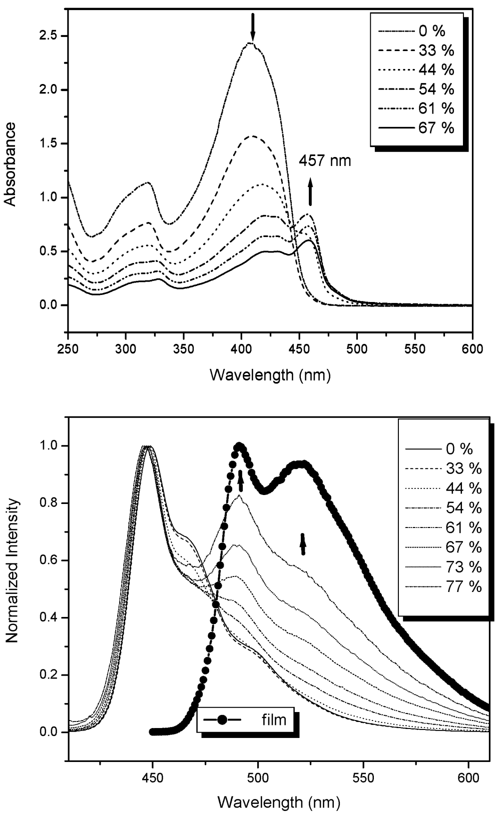
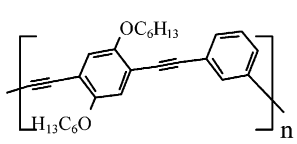


Figure 1. UV–vis (top) and fluorescence (bottom) spectra of **2b** at room temperature in THF/methanol mixtures. The inset shows the volume percentage of methanol in the solvent mixture.

also provide some useful information to understand the aggregation formation.



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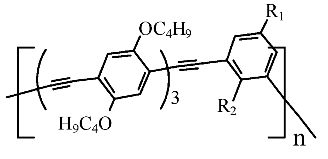
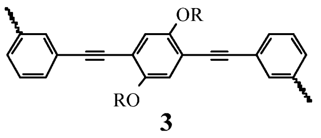


2a (R_1 = H, R_2 =H)
2b (R_1 = CH_3, R_2 = OC_4H_9)



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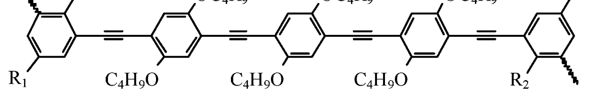

4a (R_1 = H, R_2 =H)
4b (R_1 = CH_3, R_2 = OC_4H_9)

Results and Discussion

Solvent-Induced Aggregation. As shown in Figure 1, polymer **2b** (M_w = 55 100) in THF exhibits a strong absorption band at about 406 nm. As the nonsolvent (methanol) component increases to about 44 vol %, a new absorption band at 457 nm is developed along with decrease of the absorption band at 406 nm. The wavelength of this new absorption band is comparable to that of thin film **2b** (~450 nm),[14] indicating formation of molecular aggregation. Fluorescence of **2b** in the solven/nonsolvent mixture reveals a similar trend. As the methanol concentration increases to about 44 vol %, new emission bands start to emerge at 491 and 519 nm, whose relative intensity increases with the nonsolvent concentration. The new emissive bands, which are superimposed to that of the thin film **2b**, further confirm the formation of molecular aggregation in solution. It is also noted that the intensity of aggregation band from **2** is comparable to that from poly(*p*-phenyleneethynylene) derivatives,[7] although the latter possesses a rigid-rod PE fragment of much longer length.

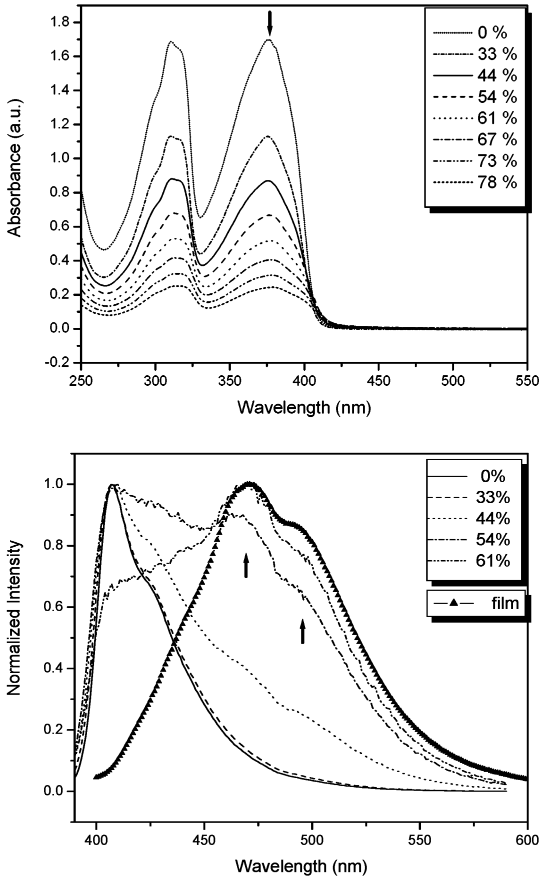

Figure 2. UV–vis (top) and fluorescence (bottom) spectra of **1** at room temperature in THF/methanol mixtures. The inset shows the volume percentage of methanol in the solvent mixture.

In sharp contrast to **2**, no aggregate band is observed from the absorption spectra of **1** (M_w = 176 900) in various ratios of THF/methanol (Figure 2). The results suggest that the chromophore–chromophore interaction in **1** is much weaker than that in **2**, attributing to the higher *m*-phenylene content and shorter linear rod length[15] in the former. The assumption that the presence of *m*-phenylene in PPEs reduces the chromophore–chromophore interaction appears to be in agreement with PPE,[7] in which aggregation band starts to occur at much lower methanol concentration (~20%). The emission spectra of **1** detect weak aggregation bands at about 469 and 493 nm when the methanol concentration exceeds about 50%. Detection of aggregation only from the emission of **1**, but not from its absorption, indicates that chromophore–chromophore interaction in the excited state is stronger than that in the ground state. In comparison with **1**, observation of aggregation from the

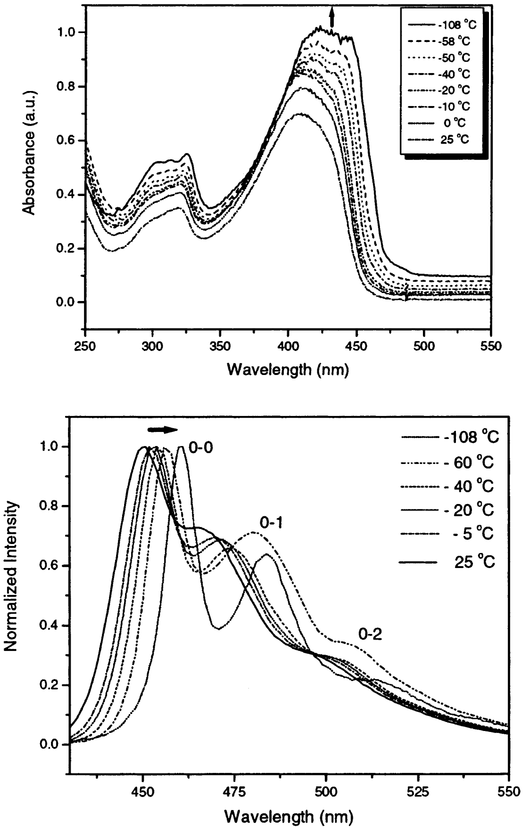

Figure 3. UV−vis (top) and fluorescence (bottom) spectra of **2b** in THF at variable temperatures (see inset). UV−vis spectra are slightly offset for clarity.

absorption spectra of **2** further suggests that the chromophore−chromophore interaction in the solution of **2** is so strong that they even occur in the ground state. The assumption of stronger chromophore−chromophore in **2** is consistent with its longer linear rod dimension (in comparison with that of **1**).

Absorption and Emission Spectra in Good Solvent. While altering the solvent/nonsolvent ratio forces the polymer molecules to approach each other and facilitate the aggregate formation, the single polymer chain folding may also play an important role in the detected molecular aggregation formation. It is known that temperature change can also induce the aggregation,[4] as the polymer solubility in a given solvent decreases with temperature. The UV−vis spectra of **2b** in THF, however, did not give any new absorption band when the temperature was lowered from 25 to −108 °C (Figure 3). Both absorption and fluorescence spectra were notably red-shifted (~20 nm for UV−vis and 10 nm for fluorescence) as the temperature lowered, indicating that the chromophore adopted a more planar conformation at low temperature. In addition, the vibronic structure in the fluorescence spectrum became more pronounced as a result of reduced molecular motion and increased solvent viscosity at the low temperature. In accordance with the increased environmental rigidity at the low temperature, the fluorescence intensity of the solution increased as temperature was lowered. The lack of an aggregation band in the absorption suggests that the spectroscopic shift observed from THF solution of **2** is primarily (if not entirely) due to the single chain movement. The fact that the spectroscopic bathochromic shift gradually occurs with decreasing temperature further indicates that aggregation in THF solution is negligible even at the low temperature. The emission band near 510 nm can be attributed to the vibrational 0−2 band (not aggregation), since its relative emission intensity decreases with temperature. In other words, both absorption and emission spectra reveal no sign of aggregation even at low temperature, as the polymer **2b** remains in a good solvent (THF) under high dilution.

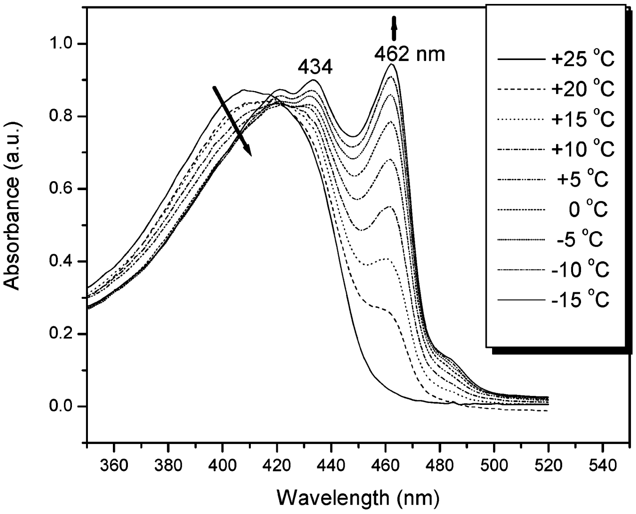

Figure 4. UV−vis spectra of **2b** in solvent mixture THF/methanol (methanol volume 33%) at various temperatures. The polymer concentration is about 10^{-5} M on the basis of its repeating unit.

Aggregation Induced in a Mixture of Solvent/Nonsolvent at Low Temperature. It appears that the temperature-induced aggregation depends highly on the solvent system used. In a good solvent such as THF, the polymer molecule adopts an extended conformation as a result of favorable interaction between polymer chain and solvent. Highly diluted solution (~1×10^{-5} M) further prevents the intermolecular interaction, leaving intramolecular chain interaction (or single chain effect) as the predominate contribution to molecular aggregation. To investigate whether a combination of solvent/nonsolvent and low temperature would lead to additional information about the molecular aggregation, absorption and emission spectra were acquired from the solution of **2b** in a solvent mixture (THF/methanol = 77:33) (Figure 4). As temperature is lowered by gradual addition of liquid nitrogen to the solution, an aggregation band is developed at about 462 nm. In accordance with aggregate formation, the relative intensity of the aggregation band is notably increased as the temperature is lowered. The nonaggregate band at about 410 nm is gradually red-shifted with temperature decrease, attributing to adoption of a more planar molecular conformation. The aggregation band at 462 nm, however, is not affected, as its optical properties should resemble the solid-state behaviors of the polymer, where little chain movement is expected. In addition, the low-temperature condition partially resolved the vibronic structure of the nonaggregation band, which is not observed when only the solvent/nonsolvent ratio is changed (Figure 1). The detected vibrational bands at −15 °C are positioned at 420 and 430 nm (corresponding to 23 753 and 23 059 cm^{-1}, respectively) with an energy gap of about 658 cm^{-1}. Further decrease of temperature to below −15 °C leads to partial polymer precipitation from its solution.

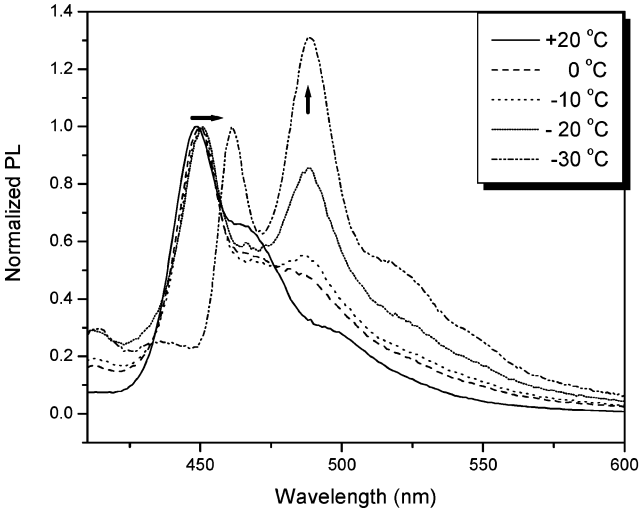

Figure 5. PL spectra of **2b** in solvent mixture THF/methanol (methanol volume 33%) at various temperatures.

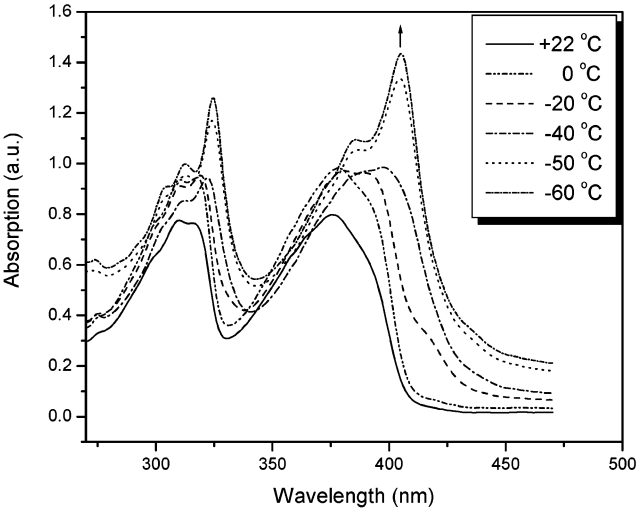

Figure 6. UV−vis of polymer **1** in a solvent mixture of THF/methanol (methanol volume 33%) at variable temperature.

Fluorescence spectra of **2b** in the solvent mixture (THF/methanol = 77:33) at 20 °C (Figure 5) exhibit a major band at 449 nm (22 272 cm^{-1}) and a shoulder at ~465 nm (21 503 cm^{-1}). The vibrational energy gap of **2b** in the ground state, therefore, is estimated to be about 769 cm^{-1}, which is slightly larger than 658 cm^{-1} in the excited state (observed from its absorption spectrum). As the temperature is lowered, the emission spectra from the solvent mixture appear to be slightly less red-shifted than that from pure THF solvent (in comparison with Figure 2). This observation can be rationalized by considering the temperature-induced solvent effect[16] from the more polar methanol, which causes a slight blue shift in emission and partially offsets the bathochromic shift induced at the low temperature. In agreement with UV−vis absorption spectra, the aggregation band at ~488 nm quickly grows as temperature decreases. The observed stronger aggregation might be attributed to the more planar chromophore conformation achieved at low temperature, which facilitates $\pi-\pi$ stacking interaction.

The effectiveness to probe aggregate formation via using the combination of a solvent/nonsolvent mixture and low temperature was further illustrated by dissolving PPE **1** into a mixture of THF/methanol (2:1 by volume). As shown in Figure 6, a shoulder at longer wavelength is developed when the solution temperature is lowered to −20 °C. Absorbance of the shoulder gradually rises with decreasing temperature. At −50 °C or lower, a well-resolved new aggregate band is observed at ~405 nm. Much lower temperature required for aggregation of **1** than that for **2** in the same solvent system further supports the assumption that the former has less tendency to form aggregate than the latter. It should be pointed out that aggregation from **1** is not observed by changing either solvent/nonsolvent ratio or temperature. Observation of aggregation from **1** shows that combination of solvent/nonsolvent mixture with low temperature provides a more sensitive probe for molecular aggregation study.

Aggregation of polymer chains in solution begins at the molecular level, as a result of close interaction between π-conjugated chromophores. It is conceivable that molecular aggregation is, at least partially, dependent on the polymer conformation, which keeps the chromophores within favorable interaction distance. The Mark−Houwink exponents ($\alpha \approx 0.65$ for **1** and 0.78 for **2**),[14] which describe the polymer conformation in solution, indicate that both polymers adopt a random-coil conformation in THF solution. The high molecular weight (M_w = 180 000) of **1**, in addition to the low rotational barrier along acetylenic bond,[17] provides ample opportunity for chain folding−unfolding[9] and intramolecular interaction. Addition of nonsolvent to the polymer solution in THF compresses the polymer random coil conformation for increased chromophore−chromophore interaction, thereby leading to the aggregate formation. The degree of the chromophore−chromophore interaction also depends on the polymer chain stiffness, as the longer dimension of chromophore in **2** permits stronger interaction than the chromophore in **1**. The trend appears to be also true when considering poly(*p*-phenyleneethynylene) derivatives, which exhibit both higher chain stiffness ($\alpha \approx 1.92$)[18] and higher tendency[19] to form aggregate in solution than **2**.

A fundamental issue in the field is to understand the origin of the observed aggregation band of the π-conjugated polymer. Among two possible explanations to account for the aggregation band in PPEs are molecular planarization of PPE backbone[11] and $\pi-\pi$ orbital interaction between different PPE chromophores. As seen in Figure 4, the single-chain absorption band at ~434 nm is developed along with a gradual red shift, as a result of low-temperature effect to chromophore conformation (or planarization). The aggregation band of **2** at 462 nm, however, is insensitive to temperature perturbation, showing that the chromophore is in a relatively confined environment. An appreciable but limited bathochromic shift observed from the chromophore in the freely mobile **2** in THF (Figure 3) suggests that the natural conformational change may not be sufficient to lead to the new absorption band at 462 nm. Although aggregate formation can provide additional driving force to further induce the conformation-related bathochromic shift, there is no compelling reason (such as distance) to prohibit their orbital interaction when the chromophores approach each other. In addition, molecular planarization should induce the bathochromatic shift in a continuous way along with constant temperature decrease. The sudden appearance of the aggregation band at the 462 nm, which is significantly red-shifted from the absorption λ_{max} of the single molecular chromophore and is not temperature-dependent, therefore appears to favor the explanation involving $\pi-\pi$ interaction in the aggregate formation of **2**.

Experimental Section

Materials and Measurements. Polymers **1** ($M_w \approx$ 176 900)[13] and **2** ($M_w \approx$ 55 100)[14] were prepared as reported previously. UV−vis spectra were acquired on a Hewlett-Packard 8453 diode array spectrophotometer. Fluorescence spectra were obtained on a PTI steady-state fluorometer. Temperature from 25 to −60 °C was directly measured by using a low-temperature thermometer before and after the spectral measurement (±1.0 °C). The temperature of −108 °C was conveniently determined by keeping the sample in the equilibrium of THF solid−solution. In the solvent-induced experiment, the spectra were taken were acquired at each ratio of THF/methanol by stepwise addition of a certain volume methanol to the polymer solution in THF.

Conclusion

In summary, molecular aggregation of PPEs **1** and **2** has been systematically examined under solvent-induced and temperature-induced conditions. Both polymers exhibit random-coil conformation in THF solution, though polymer **2** of longer rigid-rod length is slightly more rigid than that of **1**. With increasing content of nonsolvent methanol in solution, polymer conformation is compressed to form aggregates, which can be detected by aggregation bands present in both absorption and emission spectra. Aggregate formation appears to be related to its molecular stiffness in solution, as the more rigid polymer **2** shows a higher tendency to form aggregate than **1**. The study also clarifies the temperature effect to molecular chromophores in solution. In a good solvent, the temperature effect will be reflected primarily in the molecular conformation. As the temperature lowers, the chromophore tends to adopt an energetically more stable planar conformation (i.e., chromophore planarity), causing a continuous red shift in both absorption and emission spectra. In a relatively poor solvent system, which can be conveniently achieved by adjusting the ratio of a suitable pair of solvent/nonsolvent, the molecular aggregation can also be induced as the solubility of chromophore decreases with temperature. The detected electronic spectrum usually is a combination of both molecular aggregation and chromophore coplanarity. The aggregation band of **2**, which is distinctively different from the absorption band of the single molecular chromophore, shows no sign of a continuous bathochromatic shift with decreasing temperature. The current evidence suggests that the $\pi-\pi$ stacking interaction might be a major contribution to the observed aggregation of **2**. Although aggregation can be induced individually by either solvent/nonsolvent ratio or low temperature, their coupling proves to be a superior method for detecting and characterizing molecular aggregation.

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