First Hydrogen-Bonding-Induced Self-Assembled Aggregates of a Polyfluorene Derivative

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ABSTRACT: A convenient approach to a novel polyfluorene derivative (**P1**) with hydrogen-bonding interactions and another derivative **P2** without hydrogen-bonding interactions has been developed. The structure of polymers **P1** and **P2** is verified by FT-IR, ¹H and ¹³C NMR, and elemental analysis. The investigation demonstrates that the intramolecular and intermolecular H-bonding interactions play an important role in the optical properties of **P1** in the dilute solution and in films. **P1** emits different light in dilute solutions (blue color) and in solid states (yellowish-orange) under the irradiation of UV light. The time-resolved PL decay dynamics also demonstrate the existence of such interactions in **P1**. However, this phenomenon is not observed in another polymer (**P2**) without hydrogen-bonding interactions. The scanning electron microscopic (SEM) results of **P1** at solid states reveal the formation of entangled nanostructures induced though the hydrogen and the hydroxy group at the 9-position effectively affects the optical properties of **P1**, which might provide a new approach to control over molecular ordering through interactions, especially the hydrogen bonding.

Introduction

One of the expectations in material science is to discover surprising properties or functionality of novel materials. In the past two decades, since conjugated (semiconducting) polymers serve as highly responsive optical and electrical platforms for the new generation of the display technologies, extensive experimental and theoretical attention has been devoted to studies of $\pi\text{-}\mathrm{conjugated}$ polymers in science and emerging industry technologies.¹ Control of nano- and mesoscopic order in conjugated systems is a subject of great importance because it enables the tuning of macroscopic properties of electrooptical devices such as organic light-emitting diodes (OLEDs),² field effect transistors (FET),³ and chemosensors and biosensors.⁴ As electrical and optical functionalities rely on extended conjugated systems, a lot of work has been devoted to π stacking as the major driving force for one-dimensional columnar superstructures.⁵ However, the concomitant electronic interactions are not always desired because of substantial and hardly predictable changes of the molecular properties of the chromophores. Recently, control over molecular ordering to nanoscale dimension through hydrogen bonding, π -stacking, solvatochromic, and other intramolecular and/or intermolecular interactions is a challenging field of material research. The optical response of chromophores aggregates provides an important tool in studies of intermolecular and intramolecular interactions and bonding. Mesoscopic order can be achieved by applying the self-assembly technique in molecules with well-defined structures. Superstructures including cylindrical strands have also been achieved and formed resulting from hydrogen-bonding complexation and interactions.⁶ Especially, a series of biomaterials based on polyacetelyene with chiral amino acid and glucose as substituents exhibited excellent mesoscopic order and superstructures through interchain interactions.⁷

Herein, to understand the effect of the hydrogen-bondinduced intramolecular and intermolecular interactions on the optical and electronic properties of conjugated polymers, which may also be the main driving force in the mesoscopic order, we designed and synthesized two polyfluorene compounds. Polyfluorene and derivatives (PFs), as blue light-emitting polymers, are one class of the most promising materials, and their chemical and physical properties have been actively investigated.⁸ Although they exhibit the high efficiency and good thermal stability, chain aggregation and excimer formation tend to degrade the performance of optical and electrooptical devices.⁸ Excimers are known to provide nonradiative relaxation pathways in polyfluorenes, which lead to reduced emission efficiency relative to exciton luminescence. In this contribution, within polymer **P1**, hydroxide and 5'-methyl-2,2'-bipyridyl-5-methyl groups were introduced at the 9-position of fluorene rings. The intramolecular and/or the intermolecular hydrogen bond between the hydrogen atom of the hydroxide group and the nitrogen atom of the pyridine ring may form in the dilute solution and/or in the solid states, which may affect the molecular structure and the properties of polymer P1. Therefore, to further demonstrate this effect, we also synthesized another derivative, polymer P2, in which the hydrogen bond was interrupted because of the replacement of hydroxy group by a benzyloxy group at the methylene bridge of the fluorene ring.

Experimental Section

Instrumentation. ¹H and ¹³C NMR spectra were obtained as solutions in deuterated chloroform and recorded on a Bruker

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Polymer 1: R = H; Polymer 2: R = Bn

Figure 1. Synthetic route to polymers P1 and P2.

ACF 300 and AMX 400 spectrometer. TMS was used as internal reference for all compounds. FT-IR spectra were obtained as KBr pellets on a Bio-Rad FTS 165 spectrometer. Elemental analyses were obtained on a Perkin-Elmer 2400 elemental analyzer in the Microanalysis Lab at the National University of Singapore. Molecular weights of the polymer were determined by gel permeation chromatography (GPC) against the standard of polystyrene on a Perkin-Elmer model 200 HPLC system and THF as the eluting solvent. The UVvis absorption spectra of the polymer were recorded on a Shimadzu UV-3101 scanning spectrophotometer. The fluorescence spectra were collected on a Perkin-Elmer LS50B luminescence spectrometer. The scanning electron microscope results were carried out on a JEDL JSM 6700F field emission gun scanning electron microscope with 1.0 nm (1.5 kV) resolution.

Poly[(9,9-di-n-hexyl-9H-fluoren-2,7-ylene)-co-alt-(9-hydroxy-9-((5'-methyl-2,2'-bipyridyl)-5-yl)methyl)-9H-fluoren-2,7-ylene] (P1). Under an argon atmosphere, monomers 1 (0.502 g, 1 mmol) and 2 (0.506 g, 1 mmol) were added together with 1.5 mol % of Pd(PPh₃)₄, 3 mL of toluene, and 2.5 mL of 2 M aqueous sodium carbonate solution. The mixture was stirred under vigorous at 80-90 °C for 48 h. The mixture was poured into stirred 100 mL of methanol to precipitate plenty of light-yellow solids. The solids were collected by filtration and washed with methanol and water. The polymer was washed with refluxing acetone in Soxhlet for 2 days. The light-yellow solids were dried under vacuum at room temperature. Yield: 80%. ¹H NMR (CDCl₃, 400 MHz, ppm): 8.06-7.50 (10H, b), 7.28-7.01 (8H, m), 5.55 (1H, s, OH), 3.77 (2H, s, Py-CH₂), 2.30 (3H, s, Py-CH₃), 2.15-0.81 (26H, b). Anal. Calcd for C₅₀H₅₀N₂O: C, 86.42; H, 7.25; N, 4.03. Found: C, 86.29; H, 7.52; N 4.39. FT-IR (λ, cm⁻¹): 3639, 2956, 2859, 1603, 1459, 1435, 1401, 1248, 1231, 886, 860, 814, 770, 698,

Poly[(9,9-di-*n***-hexyl-9***H***-fluoren-2,7-ylene)-***co***-alt-(9-benzyloxyl-9-((5'-methyl-2,2'-bipyridyl)-5-yl)methyl)-9***H***-fluoren-2,7-ylene] (P2). The polymer were also obtained through the same procedure to produce P1 utilizing monomers 1 and 3. ¹H NMR (CDCl₃, 400 MHz, ppm): 8.58 (1H, s, Py–H), 8.41 (1H, s, Py–H), 8.36–8.29 (2H, q, Py–H), 7.77–7.20 (19H, m, aromatic–H), 4.17 (2H, s, OCH₂), 3.60 (2H, s, Py–CH₂), 2.46 (3H, s, Py–CH₃), 2.05 (4H, s, CH₂), 1.54–0.67 (22H, m). ¹³C NMR (CDCl₃, 100 MHz, ppm): 154.99, 154.16, 152.28, 151.71,** 150.02, 146.20, 141.51, 140.66, 140.16, 139.73, 139.54, 139.35, 137.76, 133.58, 132.48, 128.89, 128.67, 127.83, 126.60, 123.63, 121.66, 121.06, 120.92, 120.48, 120.01, 88.48, 66.86, 55.84, 43.51, 40.76, 31.87, 30.04, 24.20, 22.98, 18.81, 14.42. Anal. Calcd for $C_{57}H_{56}N_2O$: C, 87.20; H, 7.19; N, 3.57. Found: C, 86.65; H, 7.36; N, 3.51. FT-IR (λ , cm⁻¹): 3028, 2925, 2853, 1597, 1551, 1459, 1405, 1248, 889, 814, 779, 743, 696.

Results and Discussion

The structure of polymers P1 and P2 is outlined in Figure 1. The monomers and polymers were prepared by the multistep synthetic approach. The monomer M1, 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), was prepared using 2,7-dibromofluorene following the literature procedures.⁹ The lithiation of 5,5'-dimethyl-2,2'bipyridine reacted with 2.7-dibromo-9-fluorenone afforded 2,7-dibromo-9-hydroxy-9-(5'-methyl-2,2'-bipyridyl-5-methyl)fluorene (monomer M2). The benzylation of the hydroxide group of monomer M2 afforded compound **3**. According to our previous contributions, 9c,10 the Suzuki coupling polymerization with $Pd(PPh_3)_4$ as catalyst was employed to produce the desired polymers (**P1** and **P2**). After careful purification to remove ionic impurities and catalyst residues, brown fibrous polymers were obtained with a yield of over 85%. The chemical structure and the purity of the polymers were verified by FT-IR, ¹H and ¹³C NMR, and elemental analysis. The number molecular weight $(M_{\rm n})$ measurement by GPC against the standard of polystyrene and THF as eluent was about 7000 with a PD of 1.8 for P1 and 13 500 with a PD of 1.8 for P2. The polymers were readily dissolved in toluene, THF, p-dioxane, chloroform, NMP, DMF, and pyridine.

The UV-vis absorption and photoluminescence (PL) spectra of polymers **P1** and **P2** in solution were investigated. Both polymers exhibited almost the same absorption spectra in THF solution and peaked at about 382 nm as poly(9,9-dialkylfluorene)s. The fluorescence spectrum of **P1** in THF solution peaked at about 410



Figure 2. Steady-state fluorescence spectra of **P1** in different solvents: toluene (cycle), THF (square), *p*-dioxane (diamond), DMF (cross), NMP (line), and pyridine (triangle).

and 436 nm and exhibited a shoulder at about 468 nm; however, it also showed a broad band that peaked at 538 nm (spread from 500 to 650 nm) with low intensity, which was not observed in the emission spectra of P2 and poly(9,9-dialkylfluorene). In comparison with P2, the new emitted peak of P1 in THF solution may be due to the possibility of self-assembled structures through the intra- and/or intermolecular hydrogenbonding interactions or π -aggregation or both. From its structure, we can find that the hydroxy group at the same position of fluorene ring of P1 can interact with the nitrogen atom of bipyridine group at the 9-position of the fluorene ring to form intra- or interunit hydrogen bonding in the dilute solution. To investigate this possibility, we also measured the absorption and fluorescent spectra of P1 in different solvents, which possess different hydrogen-bonding ability. Figure 2 exhibits the PL spectra of P1 in different organic solvents. It was observed that a similar broad peak at about 520 nm emerged in toluene and *p*-dioxane solutions, which was also observed in THF solution, although the fluorescent intensity decreased with increase of the polarity of the solvents from toluene to THF and *p*-dioxane. However, this new fluorescent peak fully disappeared in the PL spectra in strong hydrogen-bonding solvents such as DMF and NMP. These observations implied that P1 formed self-assembled aggregates through hydrogenbonding interactions in toluene, p-dioxane, and THF at room temperature whereas such self-assembly was totally disrupted by the addition of strong hydrogenbonding solvents. Further measurement of the PL spectrum of **P1** in pyridine solution exhibited that the broad band was observed with an additional about 20 nm red-shifted in comparison to ones in toluene, pdioxane, and THF. We guess that new aggregation might form between the hydroxide group of **P1** and the solvent, pyridine, and induce the energy level of their excited states shifted. As shown in Figure 2, the solution of P1 still emitted blue light under the irradiation of UV light in the different solvents.

We also investigated the behavior of the emission spectra of **P1** in THF solution with successive addition of methanol. As shown in Figure 3, although the bandwidth and fluorescent intensity of two emission peaks at about 410 and 436 nm and the shoulder peak at 485 nm were identical, the broad peak at about 500–650 nm obviously decreased upon the addition of methanol to the solution (each 0.5 μ L of methanol to 3 mL solution in THF) and completely disappeared when



Figure 3. Steady-state fluorescence spectra of polymer **1** in THF–methanol: from up to down, methanol–THF, v/v = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 12.0, 17.0, and 27.0 μ L/3 mL.

the concentration of methanol reached 1% (v/v). The results further indicated that addition of methanol did not affect the backbone structure of polymer in the solution but caused an obvious effect on the interaction of the hydrogen bonding. Therefore, addition of small amounts of strong H-bonding solvents such as methanol to THF solution of **P1** induces a considerable effect on the forming of the intra- and/or intermolecular H-bonding.

The absorption and PL spectra in films of polymers P1 and P2 were also measured (as shown in Figure 4). From both absorption and PL spectra of **P2** in films, we observed that they were identical with those in dilute solutions. For P1, an interesting change occurred in its fluorescent spectra in the transparent film spin-cast from toluene solution (2% w/v) although the absorption spectrum in the film exhibited only a slight red shift in comparison with that in the solution in THF. We found that the broad peak at 572 nm appeared more apparent. Two fluorescent peaks at 415 and 425 nm, which were slightly red-shifted in comparison with those in the dilute solution, were also found in very low intensity (1/10 as that of the main peak at 572 nm). In the dilute toluene solution, the emission spectrum showed wellresolved vibronic structure. The thin-film emission spectrum was generally broad, structureless, and redshifted in comparison with solution ones. It implies that the emission from the singlet excited state of the chromophores ¹A* observed in the dilute solution emission spectrum did not play a main role in the thin-film emission. On the contrary, the emission from P1 might originate from another chromophores, mainly singlet excimers ¹(AA)*, formed by the intra- and/or interchain interactions due to the hydrogen bonding and aggregation, which was not observed in P2 and other polyfluorene derivatives with disubstituted alkyl groups at the methylene bridge of the fluorine rings. This physical degradation usually leads to a red-shifted fluorescence and reduced intensity by exciton migration and relaxation through lower energy excimer traps. The films of **P1** emitted yellowish-orange light under the irradiation of UV light. We did not think that this low-energy emission bands (red-shift of the emission spectra) in our polymer were due to the formation of keto defect sites at the methylene bridge as the key role in the fluorescence spectra of polyfluorenes,¹¹ since the obvious difference between the absorption spectra of P1 in the



Figure 4. Absorption (circle) and steady-state fluorescence spectra (diamond) of **P2** and the fluorescence spectrum (square) of **P1** and in film states spin-casting from xylene solution.



Figure 5. Time-resolved photoluminescence decays for solution of polymer **1** at detection wavelengths of $\lambda_{em} = 538$ nm in THF solution and THF/methanol (100/1) solution.

solutions and the solid films was not observed, and we suggested that it might be impossible to generate any defects including keto sites in our polymers (P1 and P2) through forming the fluorenyl anions.¹¹ Actually, the dominated peak in the emission spectra of P1 in the solid states was also red-shifted in comparison with the polyfluorene derivatives with keto defects sites. Some results indicated that the introduction of bulky side chains could effectively prevent the formation of the aggregation in the solid states, causing the emission spectra red shift (the low-energy bands), which we usually observed among the polyfluorene derivatives bearing slightly less bulky side chains.¹² However, these low-energy bands did not dominate the fluorescence spectra like P1 in the solid states. Meanwhile, the emission spectra of P1 in the solutions also exhibited such low-energy bands, which were not observed from any polyfluorene derivatives including P2. Therefore, our novel results strongly indicated the key role of the intermolecular and intramolecular hydrogen bonding as the formation of low-energy bands in P1, which was due to the hydroxy substituents at the methylene bridged.

The time-resolved PL decay dynamics further investigated the PL mechanism of **P1** in dilute solution. **P1** in dilute THF solution all exhibited a single-exponential decay at three various detection wavelengths, 410, 436, and 468 nm, which corresponded to three peaks of the fluorescent spectrum. This indicated that only a single fluorescent species ${}^{1}A^{*}$ was involved in the fluorescence process at the three various wavelengths. The measured lifetime of ${}^{1}A^{*}$ varied from 420 ps at 410 nm to 439 ps



Figure 6. Scanning electron micrographs (SEM) of the thin film of **P1** dropping from toluene solution.

at 436 nm, to 472 ps at 468 nm, respectively. The corresponding PL decay dynamics of **P1** in dilute THF solution at 538 nm detection wavelength was fit to be nonexponential and could be best described by a biexponential with measured lifetimes of 0.3 and 3.1 ns, indicating different fluorescent species like excimers and aggregated complexes. While adding 1% of methanol to the THF solution of **P1**, the corresponding PL decay dynamics at the same detection wavelength appeared as a single exponential with a measured lifetime of 0.3 ns as shown in Figure 5, which further demonstrated that the intra- and/or intermolecular hydrogen-bonding interactions in the dilute THF solution was interrupted with the addition of methanol, a strong hydrogen-bonding solvent. Actually, although much theoretical

and experimental work has been done on the photophysics of conjugated polymers, including the nature of the excited states, the origin of luminescence, and the nature of charge photogeneration, these photophysical processes in conjugated polymers remain poorly understood and controversial.¹³ More experiments about the mechanism are in progress in our laboratory.

We also employed scanning electron microscopic (SEM) to observe the mesoscopic superstructure at dried films of **P1**. After slow evaporation of toluene solution of **P1**, SEM results revealed the formation of entangled nanostructures, which was induced through the hydrogen bonding and aggregation as Figure 6 shows. The diameters of the cylindrical strands are in the range of about 10–100 nm, with certain diameters occurring more frequently, which meant the existence of further hierarchical organizations. After being exposed to air, the solid films of **P1** did not exhibit any obvious change. The folding process of **P1** induced by intra- and/or intermolecular interactions (hydrogen-bonding and aggregation) can be compared to the superstructure formation in proteins.¹⁴

Conclusion

In conclusion, a convenient approach to homopolyfluorenes with different substituents at the fluorene ring, which might have special intramolecular and/or intermolecular interactions through the hydrogen bonding, had been developed in this contribution. It is possible to prepare a series of polyfluorene derivatives containing H-bonding or other noncovalent interactions through a similar approach. The studies on the optical properties of P1 demonstrated that it exhibited intramolecular and intermolecular H-bonding in the dilute solution and in the film. The fluorescent spectra of P1 showed that the new emission peak at about 525 nm appeared in the dilute toluene solution, and its intensity was decreased with increase of the polarity of solvents and fully disappeared in high hydrogen-bonding solvents or with addition of methanol. In solid films, this new emission peak red-shifted to 572 nm and became the maximum although other two peaks at about 410 and 436 nm were also observed with quite low intensity. It implied that the interactions were strengthened through the hydrogen bonding. P1 emitted different light in dilute solutions (blue color) and in films (yellowish-orange color) under the irradiation of UV light. The time-resolved PL decay dynamics were also demonstrated the existence of such interactions in P1. However, this phenomenon was not observed in another polymer (P2) without hydrogen-bonding interactions. The scanning electron microscopic (SEM) results of P1 at dried films revealed the formation of entangled nanostructures induced through the hydrogen-bonding interactions. Therefore, the investigation showed that the interaction between the nitrogen and the hydroxy group at the 9-position occupied an important role in the optical properties, which might provide a new approach to control over molecular ordering through interchain interactions, especially the hydrogen bonding.

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