Efficient Light Harvesting by Sequential Energy Transfer across Aggregates in Polymers of Finite Conjugational Segments with Short Aliphatic Linkages

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Abstract: Interactions between lumophores have a critical influence on the photophysical properties of conjugated polymers. We synthesized a new series of light-harvesting polymers (poly-DSBs, **I**−**IV**) of dialkyloxy- or dialkyl-substituted distyrylbenzene (the substituents being methoxy, 2-ethylhexyloxy, and cyclohexyl) with short aliphatic linkage (methylene or ethylene) and examined the effects of interactions between lumophores and of chemical structures on the absorption, emission, and excitation spectra. The proximity between distyrylbenzene lumophores was shown to be critical to the interactions between lumophores and to the energy-transfer processes. In concentrated solutions and solid films, intermolecular aggregates exist resulting from different extents of interactions between lumophores and are found to involve at least three species: loose, compact, and the most aligned aggregates as observed by photoluminescence and excitation spectroscopies. We also found, for the first time, sequential energy transfer from individual lumophores to the most compact, aligned aggregates via the looser intermolecular aggregates, as observed directly by time-resolved fluorescence spectroscopy. Such a process mimics energy transfer in photosynthesis units and is so efficient such that the fluorescence color can be red-shifted drastically by the presence of comparatively few aggregates and that the light evolved from concentrated solutions and films of poly-DSBs **I**−**IV** is entirely or almost the aggregation emission. Although the sequential energy-transfer process in fully conjugated electro-/photoluminescent polymers due to inhomogenity other than distributed conjugation lengths has never been directly observed at room temperature, we suggest that events similar to those observed in poly-DSBs in conjugated polymers could occur but on a much shorter time scale, i.e., a few picoseconds.

Introduction

Since the first polymer light-emitting diode (PLED) was demonstrated in 1990,[1] conjugated polymers such as poly(phenylene vinylene)s (PPVs), poly(*p*-phenylene)s (PPPs), poly(thiophene)s (PTs), and poly(fluorene)s (PFs) have been widely investigated for their electroluminescent (EL) properties.[2] It was found that both the photophysical properties of the polymers and carrier injection/mobility in the device determine the EL efficiency.

Studies on the photophysics of fully conjugated polymers,[3] main-chain polylumophores,[4] and polymers with pendant lumophores[5] reveal an occurrence of strong interchain or intrachain interactions between the lumophores. The interactions including excimers, exciplexes, and aggregates can lead to a red-shift or generation of a new peak on the longer wavelength side in the fluorescence spectrum and usually to a lowering in quantum efficiency of photoluminescence. An excimer is a dimer of the same lumophores, in which one is originally in the excited state and the other in the ground state. Such a dimer exists only under excitation but is dissociative in the ground state. (A dimer that behaves the same as excimers but consists of different lumophores is specifically termed an excited complex or exciplex.) In contrast, an aggregate involves

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intermolecularly mutual interaction between two or more lumophores in the ground state by extending the delocalization of π-electrons over these conjugated segments. Emission from aggregates can result from direct excitation and/or energy transfer from corresponding excited monomeric species, depending on the wavelength of excitation.

The presence of intrachain or interchain interactions within the aforementioned polymers would inevitably change their emitting colors, which is usually not desirable for most optical and optoelectronic applications. However, intentional change of emitting color is frequently made by doping a small amount of emitting guest material into host polymer matrix by physical blending[6] or by chemical linking as side groups.[7] Both methods involve an energy-transfer process between different emitting species or groups. The light that finally evolves is almost or entirely the emission from the lower-energy species. Such a process is particularly important in PLEDs and OLEDs (small-organic-molecule LEDs) because the device performance can be significantly improved this way.[8,9]

Energy transfer is a process in which excitation energy is released from one species to another. It plays an important role in photosynthesis, by which almost all life activities are sustained directly or indirectly. In a photosynthesis unit, energy is harvested by antenna pigments and then transferred to reaction centers where redox reactions then take place.[10] Morphologically, the antenna molecules are arranged like shells of an onion, in order of excitation energy, around the reaction center. As a result, energy can be harvested and then transferred sequentially, directionally, and efficiently (Figure 1a). Energy transfer in artificial molecules and polymer systems has been extensively investigated, but sometimes its process is not as clearly stated as that in the photosynthesis.

Polymers with a high density of lumophores are known as “light-harvesting” or “antenna” polymers.[11] Common examples involve polyvinylaromatics with pendant lumophores as side chains.[11] Such polymers are capable of efficient light collection and long-range energy transfer. In most instances, energy is transferred intramolecularly between different lumophores in the direction of decreasing band gaps or from a lumophore to an exciplex-forming site (Figure 1b).[12] In conjugated polymers such as PPVs, randomly distributed tetrahedral defects unavoidably form during the Gilch-type polymerization[13] or result from incomplete elimination of the Wessling-type precursor polymer.[14] They act as conjugation interrupters in the polymer chains, and energy is found to transfer from shorter to longer conjugated segments (Figure 1c).[14,15] The other example is poly(*p*-cyclophan-1-ene) and its derivitives,[4b,16] in which “intramolecular” aggregates of lumophores form and energy is transferred from independent lumophores to the aggregates (Figure 1d).[16c,17] Moreover, intermolecular aggregates in conjugated polymers could also act as energy acceptors (Figure 1e).[3f,h] We have reported a series of PPVs with pendant oxadiazole side groups linked to the conjugated main chains

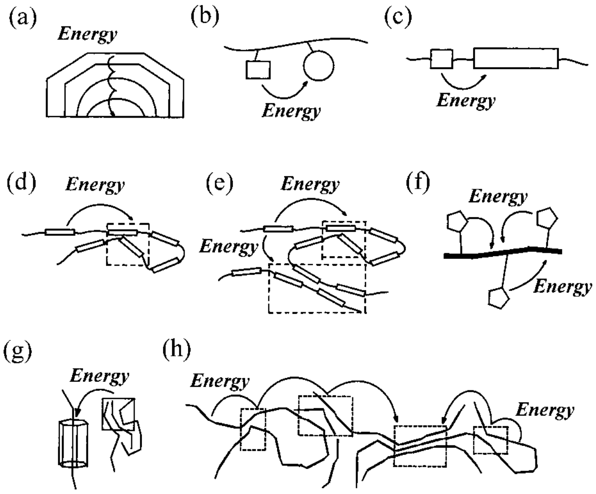

Figure 1. Schematic diagrams of the environments for energy transfer: (a) in a photosynthesis multipigment array; (b) in polymers with different pendent chromphores; (c) in polymers with segments of the same chemical structure but different conjugation lengths; (d) in polymers capable of forming intramolecular associates between conjugated segments; (e) in polymers with intra- and intermolecular interactions between chromphores; (f) in fully conjugated polymers with oxadiazole side groups linked by long aliphatic spacers; (g) in conjugated polymers with oriented segments in mesoporours silica channels; and (h) in the polymer under investigation where aggregates with various extents of interactions between lumophores are formed sequentially and energy is transferred in a cascade from individual conjugated segments to the most aligned, compact intermolecular aggregates via intramolecular associates and less strongly interacted aggregates. (The shell structure in (a) represents the array of antenna pigments. The curved arrow represents the direction of energy transfer. The square and circle in (b) represent chromophores with different chemical structures. The squares with different lengths in (c) indicate of the same chromophores but with different conjugation lengths. The region defined by dashed lines stands for associates or aggregates. The heavy lines in (f) and (h) represent the conjugated segements of polymers, and their conjugation lengths are depicted as the length of lines. The pentacycles and light lines between them and the conjugated main chains in (f) stand for the oxadiazole groups and the aliphatic spacers linked to main chains as pendant side chains. The hexagonal tube in (g) represents the channel in the porous silica.)

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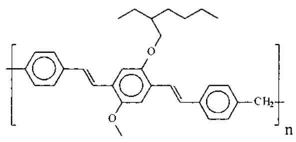
[17] Lumophores may interact with one another within a single polymer chain or between different polymer chains. We will define the former “intramolecular associates” and the latter “intermolecular aggregates” to make statements in the following text clear. The processes for such interactions are termed “association” and “aggregation”, respectively. However, interactions and the resulting species will be generlly described as association and as associates for simplicity in the cases where doing so does not cause misunderstanding.

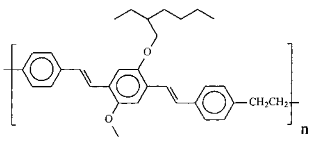
by long aliphatic spacers,[18] by which the efficiency of electroluminescence can be greatly improved. In these polymers, energy can also transfer from oxadiazole groups to conjugated main chains to some extent (Figure 1f). Recently, energy transfer under control was found to occur from aggregated, randomly oriented poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) segments to the isolated, aligned single chains in the channels of mesoporous silica (Figure 1g),[19] which are of lower energy to allow a reception of energy transfer. It is worth noting that, despite the various energy-transfer processes that have been recognized, the process itself in conjugated polymers has never been directly observed by time-resolved fluorescence spectroscopy, except for that between segments of different conjugation lengths.[20] The novel process for energy transfer proposed in this study is shown in Figure 1h.

PPV copolymers with well-defined conjugation length were first synthesized by Karasz and co-workers in 1993.[21] In these copolymers, saturated spacers such as aliphatic linkages[8b,21,22] and silicon,[23] nitrogen,[24,25] and oxygen[25] atoms confine the main-chain conjugation in finite regions and provide additional solubility. For very short spacer length (less than three atoms), local concentrations of lumophores are very high. Accordingly, distinct photophysical properties are supposed to take place due to the proximity of lumophores. However, little attention was paid to their photophysics, especially in relation to interactions between the lumophores.

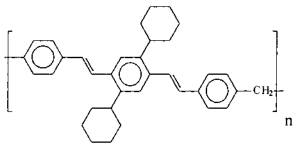
Being complicated by a disordered environment and the aforementioned various photophysical processes, the identification of energy migration mechanisms in fully conjugated polymers is usually difficult or ambiguous. Accordingly, it is necessary to design polymers with appropriate structures to simplify the situation. Therefore, we synthesized polymers of substituted distyrylbenzene (DSB) with well-defined conjugation length as repeating units linked by methylene and ethylene linkages (polymers **I**−**IV** as shown below) in this study. With such architectures, confusion caused by the variation of conjugation lengths due to conformational distortion and tetrahedron defects is excluded. Therefore, the effects of interactions between individual lumophores (DSB units) on the photophysical properties and the effects of chemical structure on such interactions can be isolated and then investigated by UV−vis absorption and excitation, steady-state, and time-resolved photoluminescence spectroscopy. We report the first direct observation of energy-transfer process from individual DSB units to their aggregates and then between aggregates of different extents of intermolecular interactions. The results of this study provide some fundamental understanding about energy-transfer processes among segmental lumophores and their aggregates in fully conjugated polymers in which the light emission mechanism is complicated and not well understood and may provide useful information about the influence of chemical structures on luminescence properties.



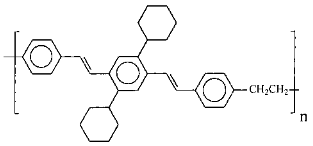
Polymer **I**



Polymer **II**



Polymer **III**



Polymer **IV**

Experimental Section

Syntheses of Monomers and Polymers. Syntheses of the monomers and polymers are outlined in Scheme 1 and are described in detail in the Supporting Information. Conditions (solvent/monomer/base ratio, reaction timing and temperature, etc.) for all the polymerizations were kept the same as much as possible to minimize possible influences of process variations on polymers structures.

Instrumentation. Gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and spectroscopies of ultraviolet−visible absorption (UV−vis), excitation (PLE), and time-resolved as well as steady-state continuous wave photoluminescence (CW-PL) are also described in detail in the Supporting Information. All optical spectra of polymer solutions presented in this work were measured using a 1-cm-path length cuvette. CW-PL, PLE spectra, and luminescence decay curves of polymer solutions with concentrations higher than 0.01 mg/mL were recorded from the front surface of a quartz cuvette to minimize the self-absorption effect.

Results and Discussion

All the polymers **I**−**IV** so synthesized are soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and *N*,*N*-dimethylformamide. Results of polymer characterizations are listed in Table 1. Due to the larger steric hindrance imparted by cyclohexyl groups than 2-ethylhexyloxy and methoxy groups, polymers **III** and **IV** are more rigid than polymers **I** and **II**. Therefore, the glass transition temperatures (T_g) of polymers **III** and **IV** are higher than those of polymers **I** and **II**, even if the weight-average molecular weights of polymers **III** and **IV** are smaller. All polymers emit deep blue light in dilute solutions and emit yellow (**I**), yellowish green (**II**), and sky blue (**III** and **IV**) lights in the film state, respectively.

1. Absorption and Steady-State Fluorescence (Emission) Spectroscopies.

Figure 2a shows UV−vis spectra of the polymers in dilute solutions (3×10^{-3} mg/mL), in which polymers **I** and **II** exhibit a perfect correspondence to their small molecular model compound, 2-methoxy-5-(2′-ethylhexyloxy)-1,4-distyryl-benzene,[26] except for a red shift of 10 nm due to the incorporation of methylene linkages. An elevated tail

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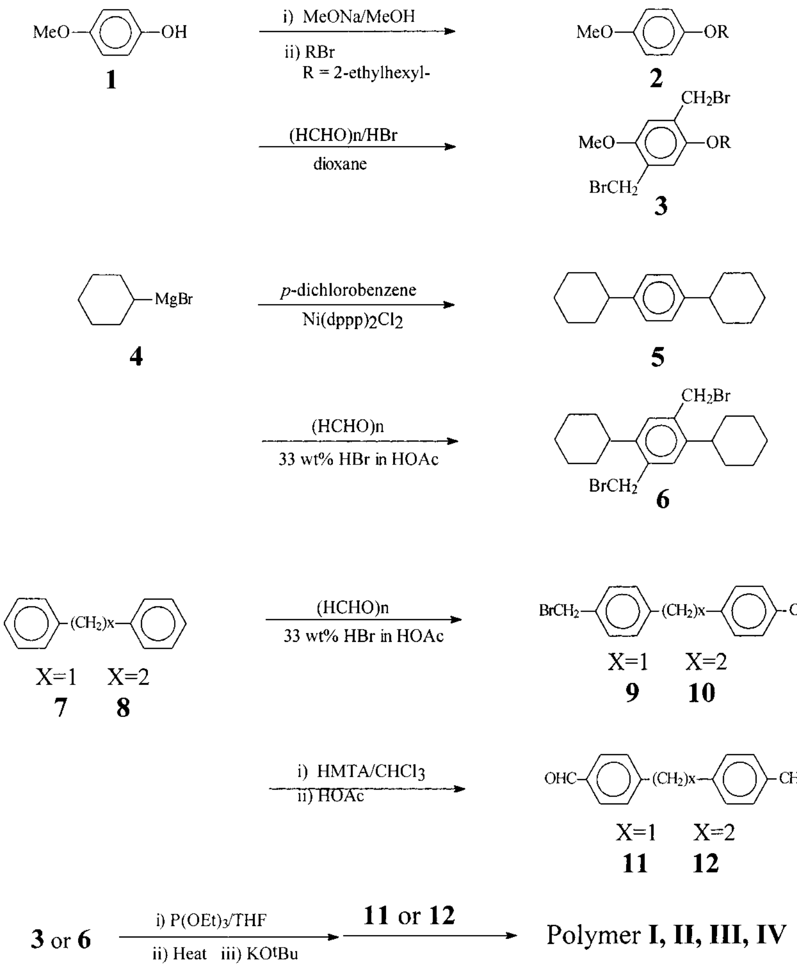
Scheme 1. Synthesis Route of Monomers and Polymers



Polymer	I	II	III	IV
dibromide	3	3	6	6
dialdehyde	11	12	11	12

Table 1. Characterization of Polymers **I**−**IV**

			T_g	T_{wlp}[b]	UV λ_{max} (nm)		PL λ_{max} (nm)	
polymer	M_w	PDI[a]	(°C)	(°C)	soln[c]	film	soln[d]	film
I	12 000	1.6	93	382	332	330	449	
					396	392	475	529
II	35 000	2.4	92	385	331	331	448	497
					394	390	472	531
III	12 000	1.7	209	425	345	344	413	
							438	470
IV	6 300	1.5	176	412	342	334	413	
							437	479

[a] PDI: polydispersity index = M_w/M_n. [b] Temperature at maximum derivative of percentage weight loss with respect to temperature. [c] Taken from 3×10^{-3} mg/mL chloroform solutions. [d] Taken from 10^{-4} mg/mL chloroform solutions.

between 450 and 490 nm appears in polymer **I**, while such a situation is not obvious in polymer **II**. Similarly, polymer **III** has a slightly longer and elevated tail than polymer **IV**. The UV−vis spectra do not change as the concentration increases. These weak tails would suggest the presence of a very low content of associates, which are evidenced by their photoluminescence excitation spectra, as to be revealed in section 2. The λ_{max} of the methylene-spaced poly-DSBs, **I** and **III**, are slightly longer than those of their ethylene-spaced counterparts, **II** and **IV**, by about 1 and 3 nm, respectively. The molar absorptivities at λ_{max} (ϵ_{max}) of the methylene-spaced poly-DSBs are also larger than those of the ethylene-spaced poly-DSBs (29 400 versus 27 600 based on the concentration of repeating units for polymers **I** and **II**, respectively). The same phenomenon also occurs in small molecules such as toluene versus diphenylmethane derivatives[27] (λ_{max} red-shifted by 1−10 nm and ϵ_{max} increased by 1 order), which was recognized as the effect of homoconjugation between phenyl rings through a methylene linkage. Since saturated C−C bond in ethylene linkage will prevent the occurrence of such an interaction, additional electron delocalization between adjacent conjugated segments across benzylic carbons exists only in polymers **I** and **III**. The differences in ϵ_{max} between polymers **I** and **II** or between **III** and **IV** are much smaller in comparison with those between toluene and diphenylmethane derivatives. Hence, the contribu-

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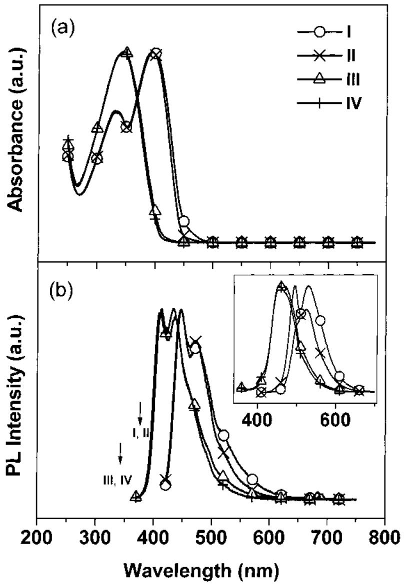

Figure 2. (a) Normalized UV−vis absorption spectra of polymers in chloroform: 3 × 10^{-3} mg/mL (note: the absorption spectra of the films are nearly identical to these spectra) and (b) normalized PL spectra of the polymer solutions, 10^{-4} mg/mL (excited at $\lambda_{\max}$ in (a) as indicated by the arrows). Normalized PL spectra of the polymer films are shown in the inset in (b) with the same excitation wavelengths as for the solutions.

tion of homoconjugation to the whole electron delocalization is less significant in the present poly-DSBs.

Figure 2b shows the PL spectra of the polymers in chloroform (10^{-4} mg/mL). All polymers emit blue light. As in the absorption spectra, the emission $\lambda_{\max}$ of polymers **I** and **II** red-shift relative to those of polymers **III** and **IV**, which result from a stronger electron-donating effect by the alkoxy groups than the alkyl groups. The long-wavelength tail appears in the PL spectra of all polymers and is more elevated in polymers **I** and **III** (methylene-linked) than in polymers **II** and **IV** (ethylene-linked), respectively. The long-wavelength tail is the luminescence from lumophore associates, as to be revealed in the following sections. Compared with the UV spectra, the PL spectra have a significantly enhanced long-wavelength tail, which implies that an unusually large portion of the luminescence comes from those few lumophore associates. Accordingly, energy transfer from individual excited DSBs to their associates must occur. Evidence for the energy-transfer processes will be provided in the section concerning time-resolved photoluminescence measurement.

The PL spectra of polymer **I** change drastically with concentration, as shown in Figure 3a. The spectra from the solutions show structured peaks near 450 nm (**i**) and 470 nm (**ii**) and a low-energy shoulder at about 525 nm (**iii**). The intensities of peak **ii** and shoulder **iii** relative to that of peak **i** grow with concentration. For the solid film, peak **i** disappears, peak **ii** becomes a weak shoulder, and peak **iii** is the main peak. Since the relative absorbances at 450−480 nm are very low (Figure 2a) and the spectra were taken from the front surface of the cuvette, the changes of the PL spectra should not be attributed to the self-absorption effect. By comparing the PL spectrum of the model compound,[26] emission of peaks **i** and **ii** should originate from individual DSB units and is termed the monomeric luminescence. As the concentration increases, peak **iii** grows up. Therefore, it must result from an emission of lumophore associates (the association luminescence) in polymer **I**, as will be further confirmed in the later sections on excitation spectra and photoluminescence decay. The growth of peak **ii** reveals that the monomeric and association luminescence overlap significantly.

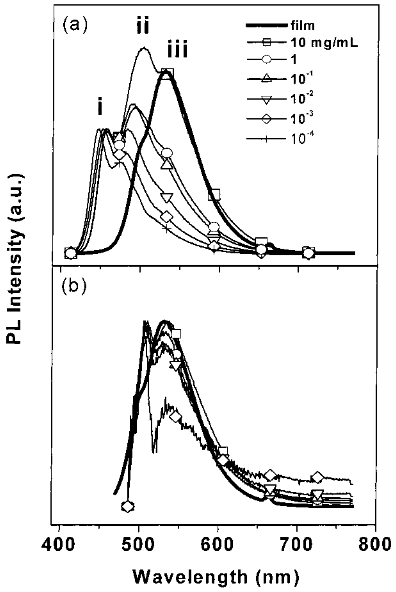

Figure 3. (a) PL spectra of polymer **I** in chloroform for different concentrations (excited at 399 nm as indicated by the arrow; normalized at peak **i** except for the case of the film) and (b) normalized spectra of the intermolecular aggregation emission of polymer **I** in chloroform solutions (the total PL spectrum of the film is shown for comparison).[28]

It is observed that long-wavelength emissions (>500 nm) are always present in the PL spectra of polymer **I** solutions, even at a low concentration down to 3 × 10^{-7} mg/mL (~7 × 10^{-10} M DSB, the detection limit of our instrument), and a dilution of the solution 10^{-4} mg/mL gives only a little change on the PL spectrum. Note that the decay rate of photoluminescence of this emission tail is different from that of the short-wavelength (<500 nm) emission in the time-resolved photoluminescence measurement, as to be revealed in section 3. (The dilute solution of lowest concentration used for the time-resolved measurement is of 10^{-3} mg/mL, where both intra- and intermolecular associates are expected to present.) In addition, the presence of ground-state associates in the polymer **I** solution (10^{-4} mg/mL), which can be directly excited and emits at longer wavelengths (>500 nm), will be revealed in Figure 4a. Thus, these observations would indicate that the DSB lumophores interact to form "intramolecular" associates[17] in the solutions. Similar behavior has also been reported in poly(paracyclophan-1-ene) and its derivatives.[4b,16] Species formed by the interaction of lumophores within a single polymer chain or between different polymer chains are termed as "intramolecular associates" and "intermolecular aggregates", respectively. However, both will be regarded as associates for simplicity in the cases when the use of "associates" does not cause any misunderstanding.[17]

The drastic spectrum shifts and changes and the decreased contribution of the monomeric emission with concentration in Figure 3a imply an occurrence of efficient energy transfer from individual DSB units to their associates and an increased extent of associations of lumophores with concentration. Since intramolecular associates have already formed in the dilute solutions, the presence of such interactions in the concentrated solutions and solid films is expected also. To investigate the contribution of energy transfer to the emission spectra, the total PL spectrum of the dilute (10^{-4} mg/mL) solution is subtracted from those of the more concentrated solutions by normalizing at 486 nm.[28] In this way, the contribution from the emission of the monomeric lumophores and intramolecular associates (in-

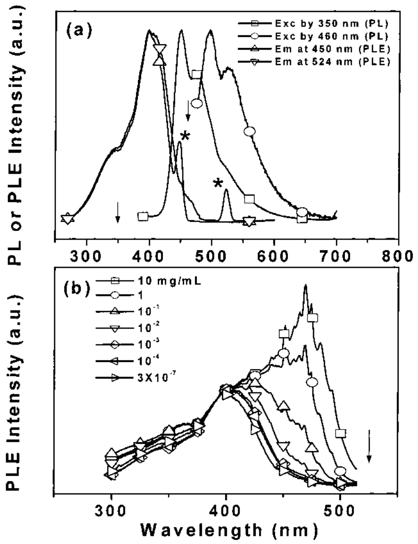

Figure 4. (a) PL and PLE spectra of polymer **I** solution (10^{-4} mg/mL in $CHCl_3$). (Normalized; arrows and asterisks represent the excitation and monitored wavelengths, respectively.) (b) PLE spectra of polymer **I** solutions monitored at 525 nm for different concentrations (normalized at 390 nm; arrow represents the wavelength monitored).

tegratedly described as single-chain emission) can be separated from that of "intermolecular" DSB aggregates.[28] Note that because normalization was made at 486 nm, the contribution of the single-polymer-chain emission has been overestimated to ensure a complete removal of it from the total PL spectra, which results in negative intensities at wavelengths shorter than 486 nm after subtraction. Therefore, the relative intensity of emission bands could inevitably be lower than what actually should be at the region close to single-polymer-chain emission.

Figure 3b shows the results of such subtraction after normalization with reference to the peak at about 505 nm. The treated spectra are similar: each has two characteristic peaks (500 and 530 nm) and a tail at the long-wavelength side. Note that the relative intensities of emission bands change with concentration, which implies the involvement of more than one emitting species in the aggregation emission. The PL spectrum of the solid film of polymer **I** is shown as well in Figure 3b for comparison, and the same characteristics are also retained, except that the peak at 500 nm now becomes a shoulder, indicating that the emission originates mainly from the "intermolecular" aggregates of DSB units. To the best of our knowledge, this could be the first report showing the imperceptible contribution of single-chain emission to the fluorescence of a polylumophore as a solid film. Further discussion on the intermolecular aggregates will be given in section 5.

The emission spectra of polymers **I**−**IV** in the film state are shown in the inset in Figure 2b. The monomeric emission at shorter wavelengths, which appears for the solutions of each polymer, almost disappears now, and the emission colors of the films are quite different from those of the solutions. From the preceding discussion for polymer **I**, emissions of the films for polymers **II**, **III**, and **IV** should be mainly due to intermolecular aggregates of lumophores as well.

2. Photoluminescence Excitation Spectroscopy. The dependence of the PL of the dilute solution (10^{-4} mg/mL) of polymer **I** on excitation wavelength is shown in Figure 4a. A typical spectrum for the monomeric emission with the peaks at 450 and 476 nm appears after exciting at the wavelength corresponding to the absorption of individual DSB units (350 nm). Changing the excitation wavelength to 460 nm produces a PL spectrum with the peaks at 496 and 524 nm, very similar to that of the solid film. Since emission spectra of one-emitting-species systems are insensitive to excitation wavelength, such behavior would suggest an occurrence of interactions between lumophores. Since excimers cannot be directly excited, DSB lumophores must associate in the ground state to form "intramolecular associates" in the polymer **I** solutions to emit light at longer wavelength, as revealed in the above section.

Figure 4a also shows the normalized photoluminescence excitation (PLE) spectra of polymer **I** in the same solution monitored at the monomeric (450 nm) and association (524 nm) emissions (the two sharp peaks close to the asterisk result from the excitation light and should not be considered as parts of the spectra). The PLE spectrum monitored at 524 nm shows a relatively elevated luminescence intensity over that monitored at 450 nm in the longer wavelength region (>450 nm), indicating the existence of lumophore associates, which absorb light at longer wavelengths than the monomeric lumophores do. Thus, this result further supports the inference that absorption at wavelengths longer than 450 nm in Figure 2a can be attributed to absorption by such associates.

Figure 4b shows the PLE spectra normalized at 390 nm of the polymer **I** solutions of various concentrations monitored at 525 nm (association emission). The band growing with concentration at long wavelengths (>450 nm) originates from the direct absorption of excitation energy by associates (and aggregates) of DSB units and hence is related to the number of associates formed. However, energy transfer from monomeric DSB units to associates would suppress the appearance of this band in the PLE spectrum, which will be discussed later in this section. The Stokes shift is approximately 2270 cm^{-1} (0.28 eV) (taken by a comparison of 525 nm with the peak 469 nm of the 10 mg/mL solution), which is much smaller than those for excimers and exciplexes (∼0.5 eV).[3a,f,29] This result further supports that the presence and growth of peak **iii** in Figure 3a are not contributed by excimers. An enhanced emission at 525 nm by excitation at wavelengths longer than 450 nm is observed in the solutions with concentrations higher than 10^{-2} mg/mL. In contrast, there is no correspondently increased absorption at the low-energy side with concentrations in the UV−vis spectra, indicating that the number of associates does not increase too much as concentration increases. It should be emphasized that a reproduction of the concentration-dependent PLE spectra of polymer **I** like Figure 4b is possible only for a cuvette with a long enough path length, such as 1 cm, but not for a 0.1-cm one. Because the absorption of polymer **I** at wavelengths shorter than 450 nm (absorbed mainly by the major component, monomeric DSB units) is much higher than those at longer wavelengths (absorbed mainly by the trace component, associates), the penetration depth of the short-wavelength excitation light is smaller than that of the long-wavelength one in the concentrated solutions. Only in the 1-cm-path length cuvette can the short-wavelength excitation light be completely absorbed in the concentrated solutions during transmitting of the cuvette. In such a situation, only the portion of DSB units close to the

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(28) Since the PL spectra of solutions with concentration lower than 10^{-4} mg/mL are almost the same, the PL spectrum of a 10^{-4} mg/mL polymer **I** solution is assumed to result from single-polymer-chain photoluminescence and to contain only emission from individual distyrylbenzene units and strictly "intramolecular" associates of them. The PL spectra of polymer **I** solutions and the film exclusive of single-polymer-chain emission were obtained as follows. All the original PL spectra were normalized at 486 nm, and then the emission from the 10^{-4} mg/mL solution was subtracted from all other PL spectra of the solutions with higher concentrations.

(29) Aguiar, M.; Karasz, F. E.; Akcelrud, L. *Macromolecules* **1995**, *28*, 4598.

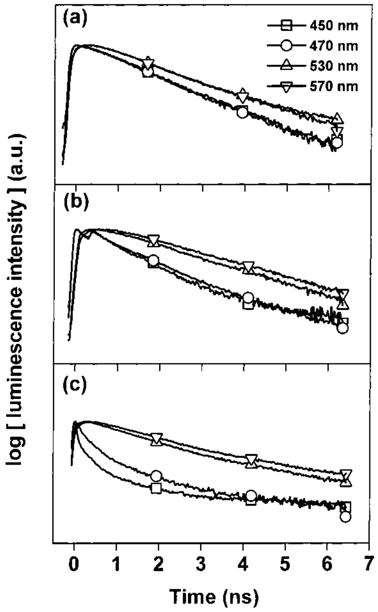

Figure 5. Luminescence decay curves of polymer **I** in chloroform of concentrations 10^{-3} (a) and 10 mg/mL (b) and as a film (c) monitored at different wavelengths (excitation at 375 nm).

surface can be excited, and only the associates located in this region can be indirectly excited by the energy released from directly excited monomeric DSB units. It follows that a relatively weak association emission, and therefore relatively weak PLE signals, are obtained by short-wavelength excitation.

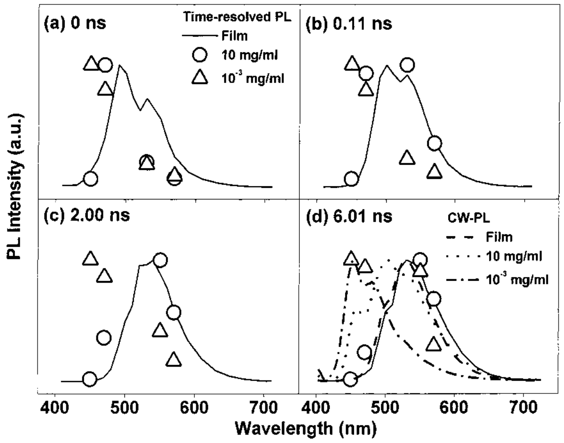

Figure 6. Normalized PL spectral dynamics of polymer **I** as a film and in chloroform with concentration of 10 or 10^{-3} mg/mL. (The emission from solutions was taken at 450, 470, 530, and 570 nm.) The normalized continuous-wave PL spectra are also shown for comparison.

3. Time-Resolved Photoluminescence Spectroscopy. Direct evidence for energy transfer is provided by time-resolved photoluminescence measurements. Figure 5 shows the decay of emission at different wavelengths of polymer **I** solutions and film excited by a laser pulse at 375 nm with a FWMH 200 fs and a CW power of 0.7 mW. The decay dynamics of monomeric and association emission (450, 470 and 530, 570 nm, respectively) are quite different. The monomeric emissions decay faster than the association emission, and the dynamics become very complicated for the concentrated solution and film. Besides, the association emissions always decay behind the monomeric emissions in the initial stage right after the excitation. A similar smooth grow-up phenomenon also occurs in amorphous inorganic semiconductors and two-dimensional σ-conjugated silicon polymers and has been attributed to the hopping of optical excitations in a "bandtail-like" inhomogeneous distribution of electronic states.[30] The delay should be the time needed for sufficient energy transfer from individual excited lumophores to the associates, because changing the excitation wavelength to 460 nm, where energy is solely absorbed by the associates, afforded a much simpler exponential decay curve without a growing-up region. Because the overlap between the emission of individual DSB units (Figure 2b, PL of 10^{-4} mg/mL) and the absorption of associates (Figure 4b, PLE of 10 mg/mL, which can be taken as the corresponding absorption spectrum) is very large, we believe that a long-range nonradiative (or Forster-type) energy-transfer mechanism[31] is involved in the emission process of polymer **I**. (The reabsorption energy transfer might exist, but its contribution is relatively low because the fractions of the absorbing species, associates and aggregates, are very limited.)

In Figure 5a, the monomeric emissions (at 450 and 470 nm) in the dilute solution (10^{-3} mg/mL) of polymer **I** decay monoexponentially (decay constant $\tau = 1.17$ ns), and the association emissions (at 530 and 570 nm) show a smooth growth followed by a simple decay ($\tau = 1.30$ ns). In the more concentrated solution (10 mg/mL, Figure 5b), the monomeric emission decays faster in a more complicated way. In the film, an extremely fast decay of monomeric emission is observed, as shown in Figure 5c. The increased decay rate of emissions at 450 and 470 nm would indicate the increased extent of nonradiative processes and a more efficient energy transfer from individual to associated lumophores. Since neighboring associated lumophores are getting closer as concentration increases, the energy-transfer process in solid films would be the most efficient. Therefore, the speeding decay of monomeric emission would be partially due to a faster energy transfer. We conclude that the drastic change of emission color in concentrated solutions and solid films of polymers **I**−**IV** results from both the formation of more associates and a more efficient energy transfer from individual lumophores to these sites.

An initial decay followed by a transient rise of the emission at 450 and 470 nm in the 10 mg/mL chloroform solution of polymer **I** appears, as can been seen from Figure 5b. Furthermore, the association emissions (530 and 570 nm) start to decay right after the time that 450 and 470 nm emissions reach their temporal maximal values. The decay constants for the association emissions are 1.6−1.7 ns, and that for the 450 or 470 nm emission before its transient rise is 0.5−0.6 ns, respectively. We found that the decay of emissions at 450 or 470 nm after 1 ns can fit quite well with a biexponential equation with time constants 0.55 and 1.65 ns. Therefore, the decay-then-rise curves observed probably result from a slight overlap of the association emission with the monomeric emission at 450 and 470 nm.

The spectral dynamics of polymer **I** in solutions and as solid film excited by a 375 nm laser shown in Figure 6 illustrates how the energy-transfer process is working. A continuously red-shifted luminescence was observed in solutions and in the film of polymer **I** due to the faster decay of monomeric luminescence and the efficient energy transfer to the associates whose emission is at longer wavelengths. In the first instance, the emission spectrum shows the characteristic of monomeric luminescence and association emission for solutions and the film, respectively. The dominance of association emission over monomeric lumi-

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[30] (a) Fischer, R.; Göbel, E. O.; Noll, G.; Thomas, P.; Weller, A. In *Hopping and Related Phenomena*; Fritzsche, H., Pollak, M., Eds.; World Scientific Publishing Co.: Singapore, 1990; Vol. 2, p 403. (b) Wilson, W. L.; Weidman, T. W. *J. Phys. Chem.* **1991**, *95*, 4568.

[31] Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH Publishers: New York, 1995; p 287.

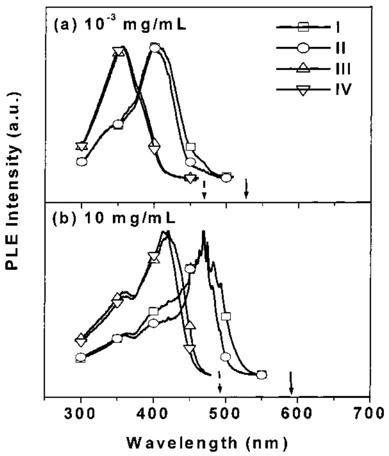

Figure 7. Excitation spectra of polymers **I**−**IV** in chloroform: 10^{-3} and 10 mg/mL. (Solid and dashed arrows: the monitored wavelengths for polymers **I**, **II** and **III**, **IV**, respectively.)

nescence right after the excitation illustrates the decay dynamics of monomeric emissions, and the energy-transfer process is much faster in the film than in the solutions. In the 10^{-3} mg/mL solution, it takes a long time, e.g., 6 ns, for the aggregation emission (530 and 570 nm) to match the strength of monomeric emission. In contrast, the dynamics is so fast in the 10 mg/mL solution that the monomeric luminescence (450 and 470 nm) loses its dominance in the emission spectrum within 2 ns. Moreover, the luminescence at 6 ns after the excitation in all cases is even more red-shifted from the initial spectrum than the continuous-wave (CW) PL.[32] These results confirm the energy-transfer processes from individual DSB units to associates of DSB units.[33]

4. Effects of Steric Hindrance and Spacer Length on Extents of Aggregation and Fluorescence. The effect of chemical structures on emission behaviors of the associates can be deduced from the emission and excitation spectra. In the dilute polymer solutions (10^{-3} mg/mL), where the intramolecular association of DSB units plays an important role, the UV−vis, PL, and PLE spectra of polymer **I** (Figures 2 and 7a) all show an elevated low-energy tail over those of polymer **II**. This results from the higher local DSB density in polymer **I** than in polymer **II** due to the shorter saturated linkages (methylene versus ethylene) between lumophores, so that DSB units would interact more strongly in polymer **I**. From Figure 7b, the association interaction in the concentrated solution of polymer **I** is so strong that aggregates so formed can even absorb light of wavelength longer than 500 nm, where the dilute solution almost has no absorption. The long-wavelength absorption tail of polymer **I** being more elevated than that of polymer **II** in Figure 2a also discloses that aggregates formed in the former outnumber those in the latter. Since aggregates can survive through the spin-coating process,[3b,34] a relatively less-structured PL spectrum of the film due to strong reabsorption at wavelengths around 500 nm by associates, and more associates emitting at wavelengths longer than 500 nm, are observed for polymer **I** than for polymer **II** (inset in Figure 2b). For polymers **III** and **IV**, the cyclohexyl side groups are more bulky than 2-ethylhexyloxy side groups in polymers **I** and **II**, so that stacking between DSBs is more difficult, causing a lower extent of association. Therefore, increasing the spacer length by one methylene is not expected to change the extent of intramolecular association too much, as reflected in the superposed PLE spectra of polymers **III** and **IV** in the dilute solutions (Figure 7a). A similar steric effect on the interaction between lumophores also operates in other systems.[4a] In contrast to the case for polymers **I** and **II**, the UV (and the PLE) spectra of polymers **III** and **IV** (Figures 2a and 7a, respectively) are almost identical. Therefore, the difference between PL spectra of polymers **III** and **IV** in the dilute solutions (Figure 2b) results mainly from a decreased extent of energy transfers in polymer **IV**. In concentrated solutions, the intermolecular aggregation of DSB units takes place to a larger extent in polymer **III** than in polymer **IV**, as reflected in Figure 7b. Therefore, the PL spectrum of the polymer **III** film is slightly red-shifted compared to that of the polymer **IV** film (inset in Figure 2b). All the results above unambiguously reveal that the proximity between lumophores of the same chain and of neighboring chains is critical to the occurrence of intramolecular association, intermolecular aggregation, and energy-transfer processes.

5. Emitting Species from Intermolecular Aggregates. Aggregates can strongly affect the photoluminescence properties of conjugated polymers by red-shifting their fluorescence spectra and lowering photoluminescence quantum efficiency. [3b,c,e−h,34,35] On the other hand, aggregates are found to improve the performance of photovoltaic devices and polymer light-emitting diodes,[3i,34,36] probably by improvement of interchain charge transport (at the expense of lowering PL efficiency). However, little is known about the nature of the aggregates in polylumophores and conjugated polymers. We have found that the electroluminescence (EL) spectrum of poly-DSBs is the same as the PL spectrum of the solid film, indicating the equivalent importance of the aggregates to EL and PL.

Figure 8 shows that the treated PL spectra in Figure 3b, which represent the intermolecular aggregation emissions in polymer **I**, can be fitted very well by the three Gaussian curves A, B, and C that peak at 505, 530, and 565 nm, respectively. It is worth noting that the relative intensities of these peaks vary with concentration and that fitting by only two Gaussian curves gives very poor results. This strongly indicates the presence of at least three emitting species in the aggregates. The different aggregates could result from various extents of interaction between neighboring lumophores, which leads to formation of loose, compact, and the most aligned aggregates characterized by the three different emission $\lambda_{\max}$ in the solutions. Note that the PL spectrum dynamics of the film for polymer **I** shown in Figure 6 has provided the relative intensities of emission at different wavelengths at different times after the excitation. The time-resolved PL spectrum of the polymer **I** film, which red-shifts slightly with time, is characterized by two emission peaks as well as a long-wavelength tail whose positions are quite similar to those in the PL spectra from intermolecular aggregates, as shown in Figure 8. From the above deconvolution analysis, a clear assignment of the emission from loose, compact, and the most aligned aggregates can now be made for the PL of film in Figure 6.

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(32) The CW-PL spectrum represents an averaged emission weighted by luminescence intensity over time. For polymer **I**, the extent of red shift of the spectrum increases with time, but the emission intensity becomes weaker. Therefore, a more red-shifted PL spectrum than the CW-PL one long after excitation is reasonable.

(33) It is worth noting that the emission positions of the intramolecular associates and the intermolecular aggregates overlap, so that to distinguish one from the other is difficult in the total emission spectra. We believe they function similarly in the energy-transfer processes.

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(36) (a) Nguyen, T.-Q.; Kwong, R. C.; Thompson, M. E.; Schwartz, B. J. *Appl. Phys. Lett.* **2000**, *76*, 2454. (b) Shi, Y.; Liu, J.; Yang, Y. *J. Appl. Phys.* **2000**, *87*, 4254. (c) Liu, J.; Shi, Y.; Ma, L.; Yang, Y. *J. Appl. Phys.* **2000**, *88*, 605.

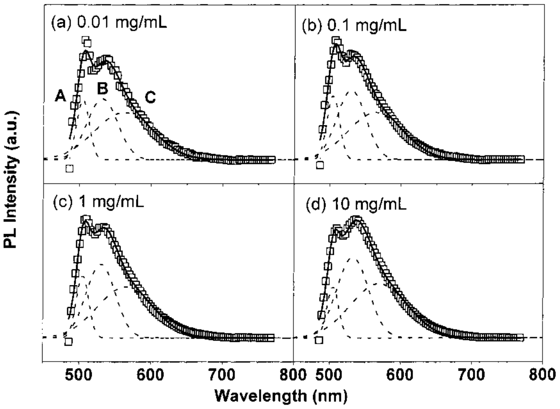

Figure 8. Deconvolution of the PL spectra in Figure 3b for intermolecular aggregation emission of polymer **I** in chloroform solutions with concentrations (a) 0.01, (b) 0.1, (c) 1, (d) 10 mg/mL by the three Gaussian curves that peak around 505, 530, and 565 nm. Squares: experimental results as shown in Figure 3b. Dashed lines: component Gaussian curves (**A**, **B**, and **C**). Heavy lines: fitting curves. R^2 for curve fitting in (a), (b), (c), and (d) is 0.993, 0.996, 0.996, and 0.997, respectively.

In principle, the absorption and excitation spectra of an emitting species should possess the same features. Therefore, one can image the absorption spectrum of one species with the aid of the more procurable excitation profile if ordinary UV−vis absorption measurement is difficult or if the absorption spectrum is heavily contaminated as a result of involving the absorption profiles of other species. As shown in Figure 4b, the excitation spectra of the association emission (525 nm) in polymer **I** solution comprise two portions which originate from the absorption of aggregates (and associates) themselves and the excitation of monomeric DSB units followed by efficient energy transfer to the emitting aggregates, respectively. The contributions of the directly excited aggregates to the PLE signals should be higher in more concentrated solutions. The PLE spectrum of the 10^{-4} mg/mL solution should comprise mainly the contribution from energy transfer and the absorption of intramolecular associates to a lesser extent. On the other hand, the PLE spectra of solutions with higher concentrations consist mainly of directly excited intermolecular aggregates. Therefore, the excitation profile and so the absorption spectra of intermolecular aggregates themselves can be isolated from the original PLE spectra by subtracting the PLE spectrum of the 10^{-4} mg/mL solution from spectra of solutions with higher concentrations.[37] The resulting spectra are shown in Figure 9; each has a characteristic peak at about 440 nm (A), a shoulder at about 470 nm (B), and a tail at the long-wavelength side (C). Unfortunately, further analysis of the aggregation excitation spectra in Figure 9 by deconvolution is not reliable due to the poor quality of the original PLE spectra.

The three components A, B, and C in Figure 9 could suggest actual absorption profiles of the three different intermolecular aggregates, which is the main cause for the elevated tail in the original absorption spectrum of polymer **I** (Figure 2a) at longer wavelengths. The red shift of the PLE spectra in Figure 9 clearly reveals the gradual growth of aggregates from the looser to the more compact and aligned ones in the order ABC as the concentration increases. However, the relative intensities of the three components of spectra A, B, and C in Figure 8 (aggregation PL spectra) do not vary with concentration as much as those in Figure 9 (aggregation PLE spectra). Such a result could suggest a quick drop in the photoluminescence efficiency of aggregates as they form and grow gradually.

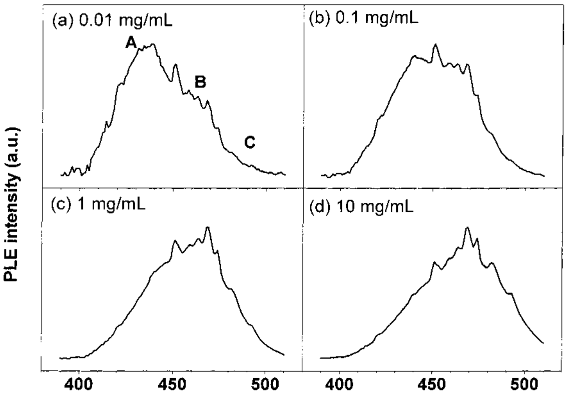

Figure 9. Normalized excitation spectra of polymer **I** in chloroform solutions monitored at the intermolecular aggregation emission (525 nm) after removal of the contribution of excitation energy transfer from the excitation spectra in Figure 4b:[39] (a) 0.01, (b) 0.1, (c) 1, and (d) 10 mg/mL. **A**, **B**, and **C** represent the three possible components of these spectra.

6. Sequential Energy-Transfer Processes across Intermolecular Aggregates. Figure 3a manifests that most DSB units act independently in the dilute solutions (below 10^{-4} mg/mL), and intermolecular loose aggregates of DSB units form first as the concentration increases to 10^{-3}−1 mg/mL, some of which become more compact as the solution concentration increases further (10 mg/mL). As the solvent is completely evaporated during the film preparation using the spin-coating method, some of the DSB units of neighboring chains can align to yield intermolecular aggregates. The more tightly aggregated sites would be expected to absorb the light of lower energy and to emit light with longer wavelengths. Accordingly, the morphology of the film can be pictured as a rather few aligned aggregates surrounded by a few compact and loose aggregates distributed randomly in the DSB units matrix. Therefore, energy transfer from individual lumophores to the most aligned aggregates via loose and compact aggregates is expected. Figure 1h describes such cascading energy transfer. This model predicts sequentially delayed growth of the intermolecular aggregation luminescence after the monomeric luminescence in the time-resolved photoluminescence measurement. Figure 10 supports this consideration in the solid film of polymer **I**. Energy is clearly transferred from individual DSB units (emit at 450 nm and decay immediately after the excitation) to the most aligned aggregates (emit at 570 nm and reach maximum intensity 0.38 ns after the excitation) via the loose aggregates (emit at 500 nm, maximum intensity at 0.09 ns) and the compact aggregates (emit at 530 nm, maximum intensity at 0.27 ns). [33]

Influences of the sequential energy transfer across intermolecular aggregates on the PL spectrum dynamics are clearly revealed in Figure 6. As mentioned in section 3, the neighboring lumophores in the film state are so close that the decay of monomeric emission is extremely fast. Therefore, the PL spectrum of the film for polymer **I** at the instant right after the excitation is dominated by the aggregation emission. However, the relative intensities of the emission peak at 530 nm and the

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(37) A procedure similar to what had been done for obtaining the aggregation emission spectra[28] was adopted. The excitation spectra of the emission at 525 nm (emission from intramolecular associates and intermolecular aggregates) in a 10^{-4} mg/mL solution and in solutions with higher concentration ($\geq 10^{-3}$ mg/mL) (Figure 4b) were normalized at 390 nm. Subtraction of the former from the latter is expected to afford the emission spectra of intermolecular aggregates themselves without being contaminated by other species. The final results were obtained after normalization of the treated spectra at their maximum intensity.

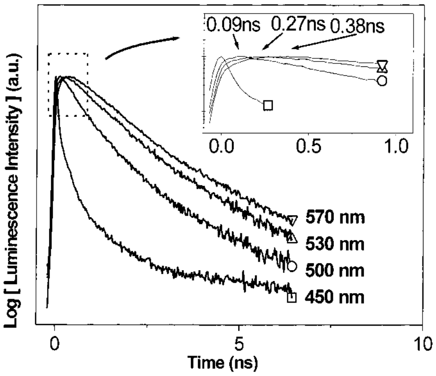

Figure 10. Luminescence decay curves of polymer **I** film monitored at monomeric (450 nm) and aggregation (500, 530, and 570 nm) emissions. The inset shows the initial region after the excitation and the time at which the aggregation emissions reach the maximal intensity. The excitation light was at 375 nm.

tail at 570 nm increase continuously with time, at the cost of decreasing the intensity of the peak at about 490 nm, indicating that energy is sequentially transferred from the loose aggregates to the most aligned aggregates. As a result, the PL spectrum continuously red-shifts with time. For the concentrated solution (10 mg/mL), although the PL spectrum is rather monomeric-like at the instant of excitation, the emission finally comes to closely match the CW-PL of the film, whose emission originates mostly from aggregates. Consequently, the proposed sequential energy transfer across aggregates is evidenced once again. The same situation also takes place in the dilute solution (10^{-3} mg/mL), but it takes a relatively longer time for the aggregation emission to grow due to the slow decay of monomeric emission and the slow sequential energy-transfer process. However, the monomeric emissions always dominate, even though the aggregation emission can match the monomeric emissions in intensity at a time long after the excitation (6 ns).

It is worth noting that the energy-transfer processes in poly-DSBs and in the array of antenna pigments in photosynthesis units are quite similar, as shown in Figure 1a. For instance, in the photosynthetic algae named *Porphyridium cruentum*, energy is transferred sequentially from the outermost shell of the array, B-phycoerythrin (PL $\lambda_{\max}$ at 578 nm), to the innermost core, chlorophyll a (685 nm), via R-rhycocyanin (640 nm) and then allophycocyanin (660 nm).[10,38] The same characteristic of the time-resolved fluorescence reveals that the same strategy for efficient light harvesting is adopted by this algae and poly-DSBs.

It is reasonable to expect an occurrence of the same efficient light-harvesting processes in π-conjugated polymers, such as PPVs, in which the presence of tetrahedral defects has been evidenced.[13] However, the proposed light-harvesting process could be masked by other energy relaxation events or is too fast to be detected easily.[39] For example, the segmental environment with a variation of conjugation lengths in PPV also causes a sequential rise of luminescence intensity with wavelength in the time-resolved fluorescence, though in a much shorter subpicosecond regime.[20] The sequential energy-transfer events can easily be observed in the poly-DSBs, probably due to the chemical structures, for which the conjugation length and the extent of aggregation are just appropriate to result in a comparatively slow dynamics (hundreds of picoseconds) to be detected. We recently reported that the spectral dynamics of poly(2,5-dioctyloxyphenylene vinylene) (PdOPV) can be observed only at 20 K but not at room temperature, and a spectrum more red-shifted than the CW-PL is also observed long after the excitation.[3c] Moreover, the PL spectrum of MEH-PPV in tetrahydrofuran was found to have a strong red-shift with concentration, but the excitation spectrum has only a little change and is independent of the monitored wavelengths of emission.[3j] The fact that poly-DSBs behave in exactly the same way implies a possible presence of the proposed light-harvesting process in the tetrahydrofuran solutions and in the spin-coated film of MEH-PPV. Additionally, aggregation could be more serious in PPVs than in poly-DSBs, so that such a light-harvesting process in PPVs is probably 1 or 2 orders faster in the solid film at room temperature.

Conclusions and Summary

We have demonstrated the occurrence of intramolecular association as well as intermolecular aggregation of lumophores in the novel light-harvesting poly-DSBs **I**−**IV** and proposed an energy-transfer process between the same kinds of lumophores but with different extents of mutual interaction in the ground state. Intramolecular association of lumophores is an intrinsic property in these polymers, while intermolecular aggregation occurs to a very small extent in concentrated solutions and in films. Various extents of intermolecular interactions between DSB lumophores result in loose, compact, and the most aligned aggregates of lumophores. Sequential energy transfers, mimicking the light-harvesting process in photosynthesis units from individual lumophores to the most aligned intermolecular aggregates via loose and compact intermolecular loose aggregates, are directly observed by time-resolved fluorescence spectroscopy. Therefore, the fluorescence color of poly-DSBs changes drastically as a result of the presence of intermolecular aggregates and the efficient energy transfer in concentrated solutions and films. The bulky cyclohexyl side groups of **III** and **IV** prevent neighboring DSB units from strongly interacting (intra- and inter molecualrly) with one another. The extent of intra- and intermolecular interactions between lumophores and the energy-transfer process are controlled by the proximity between the lumophores. Although the energy-transfer process in fully conjugated electro-/photoluminescent polymers due to inhomogenity other than distributed conjugation lengths has never been directly observed, our results suggest that a similar sequential energy-transfer process due to various extents of aggregation, such as that in poly-DSBs, could take place in fully conjugated polymers with ultrafast dynamics, which is probably masked behind other photophysical processes.

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Supporting Information Available: Instrumentation details, detailed experimental procedures, and characterizations for all of the monomers and polymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Porter, G.; Tredwell, C. J.; Searle, G. F. W.; Barber, J. *Biochim. Biophys. Acta* **1978**, *501*, 232.

(39) We found that polymer **II**, in which the linkages between lumophores are the longer ethylene spacers, shows more deferred growth of aggregation luminescence behind the excitation than polymer **I** does. Since the tetrahedral defects are much fewer in common PPVs than in poly-DSB,[13] a much lower deferred growth of the aggregation luminescence and thus a much faster energy transfer from individual chromophores to aggregates is expected.