

# Well-Packed Chains and Aggregates in the Emission Mechanism of Conjugated Polymers

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We synthesized dialkoxy-substituted poly[phenylene vinylene]s (dROPPV-1/1, 0.2/1, and 0/1) consisting of two repeating units with different side-chain lengths (methoxy and 3,7-dimethyloctyloxy). These polymers can serve as a model system to clarify roles of aggregates (the sites with ground-state interchain interactions) and the independent chain segments in the well-packed chains (the chain segments that are compactly packed without interaction) in the emission mechanism of conjugated polymers. Due to the packing of polymer chains, films of all of these polymers are accessible to interchain excitations, after which excitons can re-form to result in delayed luminescence. Besides, some chains form aggregates so that the delayed luminescence is no more the ordinary single-chain emission but red-shifted and less structured. Not only the re-formation of these indirect excitons but also the aggregation of chains are facilitated in the polymers with short methoxy side groups, revealing that both packing and aggregation of chain segments require a short spacing between polymer chains. However, the incorporation of other side chains such as the 3,7-dimethyloctyloxy group to dROPPVs is necessary for the formation of aggregates because these long branched side chains can reduce the intrachain order imposed by the short methoxy groups, which accounts for the absence of aggregate emission in the well-studied poly[2,5-dimethoxy-1,4-phenylene vinylene]. This study reveals that the well-packed chains do not necessarily form aggregates. We also show that the photophysical properties and the film morphology of conjugated polymers can be deliberately controlled by fine-tuning of the copolymer compositions, without altering the optical properties of single polymer chains (e.g., as in dilute solutions).

## Introduction

Since the first polymer light-emitting diode (PLED) was demonstrated in 1990,<sup>1</sup> conjugated polymers have been widely investigated on their electroluminescent (EL) properties.<sup>2</sup> The EL efficiency strongly depends on the device structure as well as the photophysical and electrical properties of polymers.

Studies on photophysics of fully conjugated polymers reveal the occurrence of strong interactions between the conjugated segments.<sup>3</sup> Interactions resulting in formations of excimers, exciplexes, and aggregates can lead to a red shift or generation of a new low-energy peak in the fluorescence spectrum and usually result in a lowering in quantum efficiency of photoluminescence. An excimer/exciple is a dimer of same/different lumophores and exists only under excitation but is dissociative in the ground state. On the contrary, aggregates are the new ground-state species formed from conjugated segments that are in close contact with one another by extension of their  $\pi$ -system. Therefore, both the absorption and the emission positions of aggregates are lower in energy than those of the independent chain segments. Note that aggregates are generally acknowl-

edged as the above definition, and we assign "aggregation" specifically to the process for the formation of aggregates. However, there have not been unified criteria for "aggregates" yet, and species described by this term could be intrinsically different from paper to paper.

Upon optical irradiation of energy higher than the band gap of a conjugated polymer, electrons in the valence band of the polymer are excited to the conduction band and in the meantime holes are created in the previously occupied levels. The excited electrons relax to the lowest unoccupied molecular orbital (LUMO) and then recombine with the holes to form "excitons" from which excitation energy can be relaxed nonradiatively (as vibration energy and heat) or radiatively (as light). In most circumstances, the excited electron-hole pairs are created on the same conjugated segment and the process is assigned as "intrachain" excitation. However, interchain excitations are also possible for conjugated polymers and may not be unusual in concentrated solutions and films.<sup>4</sup> ("Interchain" just means that the referred species are located across two adjacent conjugated segments, which can either be on different chains or parts of the same polymer chain, because a conjugated polymer chain could fold back to make its conjugated segments side by side.)

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In such kind of excitation, charges are created on adjacent conjugated chain segments and bound as a pair of polarons due to the Coulombic force. Polaron pairs are nonemissive, and the quantum yield for the formation of these pairs can be very high (50–90%).<sup>4b,d</sup> Therefore, the fluorescence quantum efficiency of conjugated polymers is usually significantly lowered in the solid state.<sup>5</sup>

Although bound polarons pairs do not directly contribute to the emission of conjugated polymers, emissive excitons can be re-formed from them indirectly (also described as energy transfer from interchain excitations back to conjugated segments).<sup>4d,6</sup> This process is characterized by a “long tail” led by the ordinary fast decaying component in the time-resolved luminescence decay curves and an emission profile the same as the prompt fluorescence. The emission caused by such process is always deferred after the prompt fluorescence and thus can be regarded as a special kind of “delayed luminescence”.<sup>7</sup>

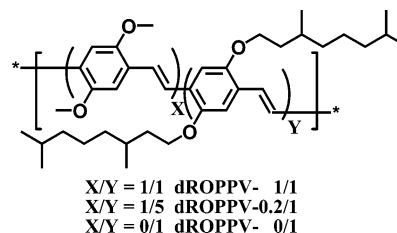
For the model conjugated polymer, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), the addition of methanol (nonsolvent) into its toluene solutions can introduce assemblies of well-packed chains in the solutions.<sup>6b</sup> Chain segments in such assemblies have longer effective conjugation lengths, and the absorption of these solutions extends to longer wavelengths as if the polymer chains were in films. The methanol-containing toluene solutions and films of MEH-PPV all show delayed emission, due to the re-formation of excitons from bound polaron pairs on the segments in these assemblies. Also, the emission profile of the well-packed chain segments is well-structured and characteristic of single-chain luminescence, indicating the independence of these segments in the assemblies. (In that paper, well-packed chains were described as “aggregated species”. However, those chains have nothing to do with what have been defined in the second paragraph of this Introduction, because the chain independence still retains after the addition of nonsolvent.<sup>6b</sup>)

Because polymer chains are close to one another in the solid state, aggregation of chains usually occurs in films of conjugated polymers. The presence of aggregates complicates the photo-physics of the solid-state conjugated polymers and is featured by an emission profile containing a featureless, direct excitation accessible and red-shifted band.<sup>8</sup> The influence of side-chain structure on the aggregation of polymer chains and emission properties of conjugated polymers has already been well-studied.<sup>9</sup> For example, interactions between conjugated segments can be effectively suppressed by the attachment of bulky side groups to the main chain, as in poly[2,5-bis(cholestanoxyl)-1,4-phenylene vinylene](BCHA-PPV).<sup>9a</sup> However, for polymers without side chains or with very short side groups such as poly[1,4-phenylene vinylene](PPV)<sup>10</sup> and poly[2,5-dimethoxy-1,4-phenylene vinylene](PdMeOPV),<sup>11</sup> the absence of emission from aggregates has been evidenced. Obviously, besides a short chain-to-chain spacing, it requires more in the supramolecular structure for conjugated polymers to form aggregates.<sup>10d,12</sup>

Although the film-like chain packing can be induced and simulated in solutions by the addition of nonsolvent,<sup>6b</sup> yet no aggregate forms. Therefore, this method reveals very little about the influence of aggregates on the properties of solid-state conjugated polymers. Moreover, the correlation between packing and aggregation of chain segments remains unclear. Obviously, other strategies are required for further understanding on the photophysics of solid-state conjugated polymers, where aggregates are usually involved.

Therefore, in this study, we synthesized copolymers consisting of two repeating units with different side-chain lengths as a

model system to clarify the roles of well-packed chains (where chains are independent species) and aggregates (where the  $\pi$ -system extends over adjacent segments) in the emission mechanism of conjugated polymers, and to investigate the requirements for the formation of conjugated polymer aggregates. For the copolymerization, one monomer bears two short methoxy side groups, and the other has two long 3,7-dimethyloctyloxy side chains. Random copolymerization of these two monomers in molecular ratios of 1/1, 1/5, and 0/1 afforded dROPPV-1/1, 0.2/1, and 0/1. The homopolymer dROPPV-0/1 (poly[2,5-di(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene]) is also known as OC<sub>10</sub>C<sub>10</sub>-PPV.<sup>13</sup> The photophysical properties of the synthesized conjugated polymers were then investigated by UV-vis absorption, emission, excitation, and time-resolved photoluminescence spectroscopies. We also propose a general emission mechanism for conjugated polymers.



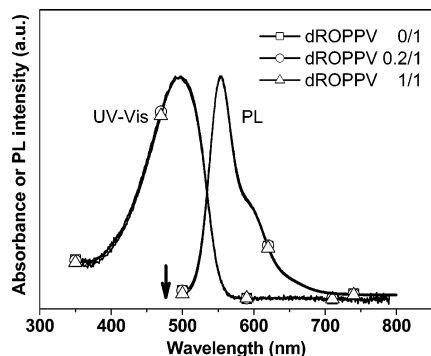
## Experimental Section

**Syntheses of Monomers and Polymers.** Syntheses of the monomers and polymers are described in detail in the Supporting Information (SI).

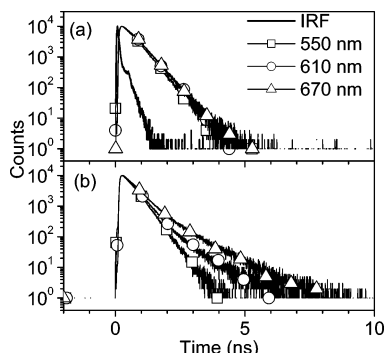
**Instrumentation.** Gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and spectroscopies of ultra-violet–visible absorption (UV-vis), excitation (PLE), and emission (CW-PL) as well as time-resolved photoluminescence (TR-PL) are also described in detail in the SI. CW-PL, PLE spectra, and luminescence decay curves of polymer solutions with concentrations equal to and higher than 0.01 mg/mL were recorded from the front surface of a quartz cuvette to minimize the inner filter (self-absorption) effect.<sup>14</sup> All film samples were made in a glovebox, where the oxygen and moisture contents are less than 1 ppm. All film samples were made from the degassed chloroform solutions. For the measurement of absorption spectra of drop-cast films, dilute (0.1 mg/mL) chloroform solutions were used to cast the films. Spin coating was carried out at the rate of 200 rpm. Annealing was performed at 110 °C for 1 h in a vacuum chamber inside the glovebox, and the annealed films were then left to cool slowly to room temperature. Film samples for the luminescence decay measurements were encapsulated by a slide glass and UV-curing epoxy to prevent photooxidation under the exposure to laser excitation. Also, luminescence decay curves of all of the samples were obtained with low enough excitation fluences to prevent bimolecular process (such as the triplet–triplet annihilation).<sup>15</sup> All other spectroscopic measurements were done in the ambient atmosphere.

## Results and Discussion

**1. Solutions of dROPPV Polymers: Interchain Excitation and Delayed Luminescence due to the Well-Packed Chains.** Figure 1 shows the absorption and emission spectra of the 10<sup>−2</sup> mg/mL solutions of dROPPV polymers in chloroform. As expected, all three polymers show identical profiles ( $\lambda_{\text{max}}$ : 497 nm for UV-vis and 555 nm for PL), because in the dilute solutions individual polymer chains of the well-soluble dROPPV



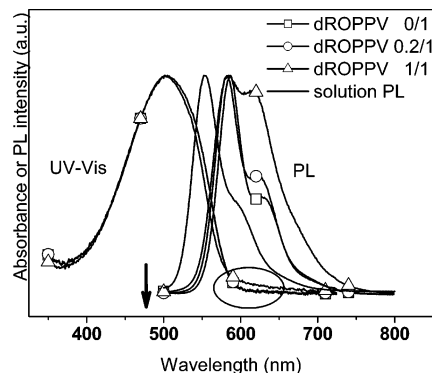
**Figure 1.** Absorption and emission spectra of solutions ( $10^{-2}$  mg/mL) of dROPPV polymers in chloroform (arrow marks the excitation position for PL).



**Figure 2.** Luminescence decay curves of the 5 mg/mL solutions in chloroform for dROPPV-0/1 (a) and 1/1 (b) (excitation position: 395 nm).

are supposed to behave similarly. Also, the independence of absorption and emission spectra on concentration (up to 10 mg/mL) has indeed been observed. However, the time-resolved PL does not support such a simple assumption. Figure 2 shows the decay curves of luminescence at 550, 610, and 670 nm for the 5 mg/mL solutions of dROPPV-0/1 (a) and 1/1 (b) in chloroform. Unlike dROPPV-0/1, which shows monoexponential decays ( $\tau \approx 0.46$  ns) for all of the monitored wavelengths, dROPPV-1/1 shows complicated decay curves for long-wavelength luminescence (610 and 670 nm).

Because the CW-PL values of dROPPV-0/1 and 1/1 (Figure 1) are the same, such results suggest the occurrence of some emission mechanism other than what ordinarily happens (i.e., intrachain excitation followed directly by formation of intrachain excitons). The most obvious feature of Figure 2b is the dragged tail of luminescence decay curves for long-wavelength emission. Similar behavior has also been observed in the toluene solutions of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with the addition of nonsolvent (methanol).<sup>6b</sup> In such solutions, well-packed chains as in the film are induced to form due to the addition of nonsolvent. The dragged luminescence decay tail has been characterized as the delayed luminescence from indirect excitons, which are re-formed from bound polaron pairs. As for the investigated dROPPVs, Figure 2 clearly reveals that the formation of indirect excitons (and delayed luminescence) from bound polaron pairs is controlled by the length of the side group. This can be attributed to that segments with short methoxy side groups are more likely to get close to other chain segments. Because the occurrence of interchain excitations and delayed luminescence indicate the presence of film-state well-packed chains, the investigated dROPPV-1/1 solution in chloroform should inherently possess well-packed structures as in its corresponding film to some extent.



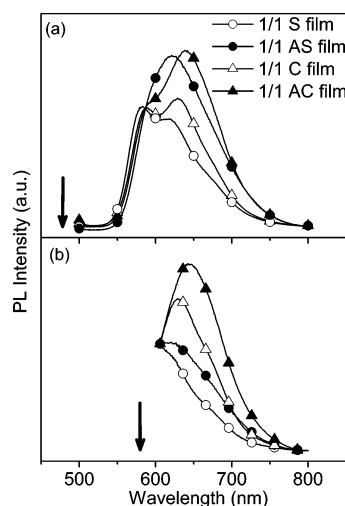
**Figure 3.** Absorption and emission spectra of the as spin-coated films of dROPPV polymers (spin rate = 200 rpm, from thoroughly stirred 10 mg/mL chloroform solutions, and arrow marks the excitation position for PL). PL of solutions in Figure 1 was also shown for comparison.

It is worth noting that a strong absorption shoulder suggestive of stable film-like chain packing always appears in nonsolvent-containing solutions of a conjugated polymer.<sup>6b,16</sup> However, solutions of all of the dROPPV polymers in chloroform show an exactly identical absorption profile. Therefore, the well-packed chains in solutions of dROPPV-1/1 should not be as persistent as those in the MeOH-containing toluene solutions of MEH-PPV,<sup>6b</sup> probably due to the good solubility of the polymer in the adopted solvent (chloroform).

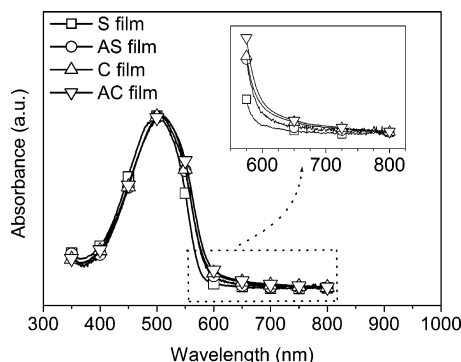
From the above results, the solution-state photophysical behaviors exhibited by dROPPV polymers are similar to those of MEH-PPV.<sup>6b</sup> Solutions of dROPPV polymers in chloroform (a good solvent) have emission characteristics of "independent" conjugated segments. However, in addition to the ordinary intrachain excitations, interchain excitations can also be involved in the solutions of dROPPV-1/1, due to the formation of well-packed chain assemblies.

**2. Films of dROPPV Polymers: Formation of Aggregates in the Presence of Well-Packed Chains.** For films of dROPPVs, the situation is more complicated. Figure 3 shows UV-vis and PL spectra of films spun from 10 mg/mL chloroform solutions. The absorption profiles are almost identical, except that the absorbance of the long-wavelength tail (marked in an ellipse for clarity) increases in the order of  $0/1 < 0.2/1 \ll 1/1$ . The influence of this tiny difference in absorption behavior on PL is, however, very significant. These three polymers all show PL  $\lambda_{\text{max}}$  at about 585 nm, but the PL shoulder ( $\sim 630$  nm) is elevated for dROPPV-0.2/1 and is very strong for dROPPV-1/1. Contrarily, the dROPPV-0/1 as film bears the same spectral characteristics as in solutions, indicating that the emitting species in these two cases have similar geometries (i.e., only differ in effective conjugation length). Obviously, additional emitting species other than independent conjugated segments (e.g., present in all of the solutions and the dROPPV-0/1 film) must exist in dROPPV-1/1 and 0.2/1 films.

Figure 4a shows the PL spectra of dROPPV-1/1 films with the excitation at 480 nm having different solidification and thermal histories (spin coating at 200 rpm and drop casting, both with and without 1 h annealing at 110 °C). The  $\lambda_{\text{max}}$  of PL spectra red-shifts in the increased sequence: the as-spin-coated film (S film, 583 nm), the annealed spin-coated film (AS film, 621 nm), the as-cast film (C film, 628 nm), and then the annealed cast film (AC film, 639 nm). Figure 4b shows PL spectra with the excitation at 590 nm (onset of the absorption tail in Figure 3). The intensity of the peak around 630 nm increases in the same sequence: S film < AS film < C film < AC film. Figure 5 shows the corresponding absorption spectra



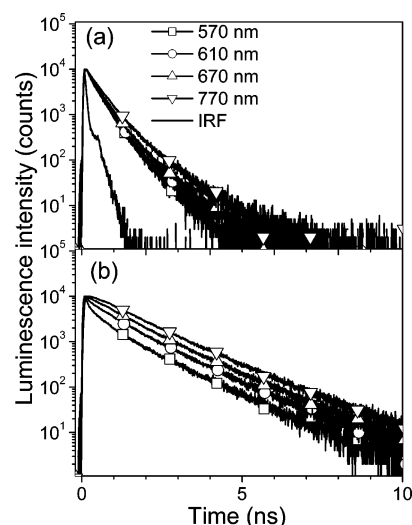
**Figure 4.** (a) PL spectra of dROPPV-1/1 films from different solidification processes. (b) PL spectra of the same set of films with the excitation at 590 nm. (Curves for films are normalized at 587 and 606 nm in (a) and (b), respectively. Abbreviations: S film for as-spin-coated film, AS film for annealed spin-coated film, C film for as-cast film, and AC film for annealed cast film; arrows indicate the excitation wavelengths.)



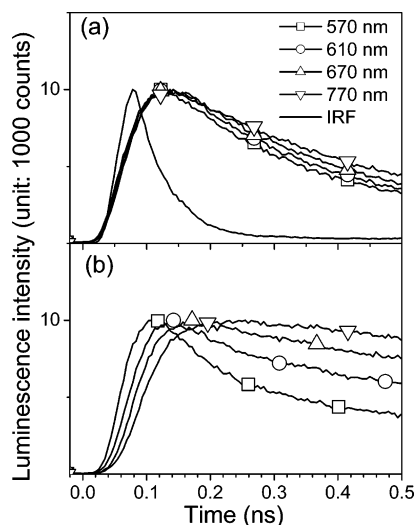
**Figure 5.** Normalized absorption spectra of dROPPV-1/1 films from different solidification processes. The insert shows the absorption edge region. (The films were cast from the 0.1 mg/mL solution in chloroform.<sup>17</sup> Abbreviations are the same as those in Figure 4.)

of the films.<sup>17</sup> All have a common  $\lambda_{\text{max}}$  at 505 nm, but the relative intensities of the low-energy absorption tail ( $>600$  nm) also increase in the same order. These results undoubtedly account for the increased long-wavelength luminescence in the PL of the films (Figure 4). Excimers (and exciplexes) should not be responsible for this result because they do not contribute to the UV-vis spectra and cannot be directly excited. The low-energy emitting species in the films should not be the independent segments either, because the emission profiles are featureless at the low-energy excitation (Figure 4b). Undoubtedly, the species responsible for the enhanced low-energy emission ( $\sim 625$  nm) in films of dROPPV-1/1 and 0.2/1 (Figure 3) must be aggregates. Interestingly, thermal treatment of dROPPV-0/1 film (1 h annealing at 110 °C, the same as for Figure 4) does not induce any apparent formation of aggregates (UV-vis and PL are unaffected after the annealing). The resistance of dROPPV-0/1 chains to aggregating is undoubtedly due to the hindrance effect exerted by its long 3,7-dimethyloctyloxy side chains.

Figure 6 compares the luminescence decay curves of dROPPV-0/1 (a) and 1/1 (b) films. Both have dragged tails, indicating the occurrence of delayed luminescence (due to good packing of chains). Again, dROPPV-1/1 shows a much more obvious dragged tail than dROPPV-0/1. Obviously, as compared to the dROPPV-0/1 film, interchain excitations and the successive re-



**Figure 6.** Luminescence decay curves of the spin-coated dROPPV-0/1 (a) and 1/1 (b) films (excitation position, 395 nm; IRF, the instrument response function).

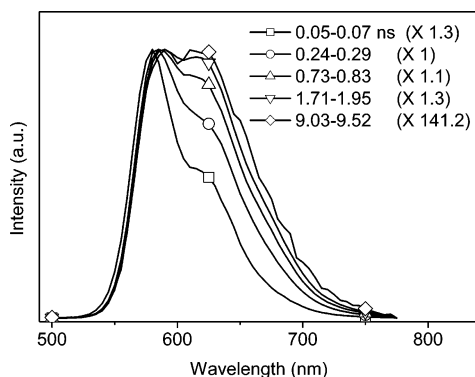


**Figure 7.** Luminescence decay curves within 0.5 ns after the excitation (a close look of Figure 6) for the spin-coated dROPPV-0/1 (a) and 1/1 (b) films.

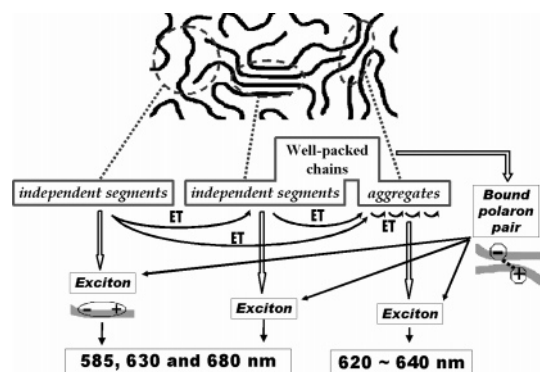
formation of excitons are much more facilitated in dROPPV-1/1. It is worth recalling that dROPPV-0/1 shows emission only from independent chain segments (Figure 3). This reveals that, in the dROPPV-0/1 film, excitons that are indirectly transformed from bound polarons pairs are also located on the independent chain segments, exactly the same as what happens in the add-on-solvent method.<sup>6b</sup>

For all of the investigated polymer films, the packing of chains results in interchain excitations and delayed luminescence. For films of dROPPV-1/1, the occurrence of chain aggregation complicates the emission mechanism further. Figure 7 is a close look of Figure 6 in the very initial region right after the excitation ( $<0.5$  ns). Sequential grow-up of the rising component appears in the luminescence decay curves of dROPPV-1/1, whereas dROPPV-0/1 has a common rising component for luminescence at all of the monitored wavelengths. For dROPPV-1/1, the deferred grow-up should result from optical excitation migration between localized density-of-states in the bandtail.<sup>18</sup> It is of no doubt that the inhomogeneity in dROPPV-1/1 films is the result of chain aggregation. Also, the sequential rising components of the long-wavelength luminescence just reveal a downward migration of excitations





**Figure 8.** Emission spectrum dynamics of the spin-coated dROPPV-1/1 film (excitation position: 395 nm).



**Figure 9.** A proposed emission mechanism for the investigated dROPPV polymers at the excitation of energy higher than the band gap. ET stands for energy transfer. Schematic representations are shown for excitons and bound polaron pairs. Note that bound polaron pairs are allowed to form on the well-packed chains and energy can migrate or transfer downward between sites of different extents of aggregation.

between sites of different extent of aggregation.<sup>19</sup> The apparent influence of the inhomogeneity in films of dROPPV-1/1 is a growing emission shoulder at ca. 625 nm in the TR-PL spectrum, as shown in Figure 8.

The above findings can shed light on the emission mechanism of the investigated dROPPVs, as proposed in Figure 9. This diagram could also apply to other conjugated polymers if no other photophysical species (e.g., emissive defects<sup>20</sup>) exist. In dROPPV polymers, most chains are independent species without any interchain interaction. Morphologically, assemblies of well-packed chains can form due to compact contact between chain segments, and the segments in the well-packed regions could possess longer conjugated lengths due to the packing. Within these assemblies, chain segments may retain as independent species or aggregate (i.e., extend their delocalization system over one another). Upon optical irradiation, excitons can form directly and the excitation energy is released via nonradiative/radiative relaxations or by energy transfer processes to other species of lower energies. Such excitations are the intrachain-type. Besides, in the assemblies of well-packed chains, interchain excitations are also allowed because chain segments are in close contact with one another. Also, excitons can be re-formed indirectly by such an excitation via the bound-polaron-pairs state. After that, energy flows downward as usual. Depending on the final emitting species, the emission spectrum can be either structured (contributed by independent chains, higher energy) or featureless (contributed by aggregates, lower energy). For the investigated dROPPV polymers, the former has characteristic luminescence at ca. 585, 630, and 680 nm, and the latter has a broad emission band at ca. 620–640 nm.

**3. Comparison of dROPPV-1/1 and PdMeOPV: Hints for Aggregates and Well-Packed Chains in Conjugated Polymers.** Poly[2,5-dimethoxy-1,4-phenylene vinylene] (PdMeOPV)<sup>11</sup> is a well-studied homopolymer analogous to the investigated dROPPV-0/1. Due to the short side chains, PdMeOPV is insoluble in any solvent and must be synthesized via the Wessling precursor route.<sup>11a–c</sup>

Because the copolymer dROPPV-1/1 consists of both repeating units of dROPPV-0/1 and PdMeOPV, it is expected to have properties between dROPPV-0/1 and PdMeOPV. From the above analysis, it is also reasonable to assume that PdMeOPV polymer chain can also form aggregates as dROPPV-1/1 and in a more pronounced extent. However, PdMeOPV films do not show aggregate emission but an unexpectedly structured, single-chain like PL that features the independence of chain segments.<sup>11b</sup> The reason for this contradiction lies in the prototype conjugated polymer, PPV. Like PdMeOPV, PPV is also crystalline and has considerably good intrachain order.<sup>10a,b</sup> At normal atmosphere pressure, adjacent PPV chains are slipped relative to each other so that overlap of  $\pi$ -orbitals between chains is not possible, even though the nearest distance between them is short enough ( $\sim 0.3$  nm).<sup>10c</sup> Hence, PPV film only shows single-chain emission in the normal condition. However, the relative position of adjacent PPV chains in the film can be altered by applying high pressure, so that intermolecular interactions are allowed, together with a red-shifted, broadened, and less structured emission profile.<sup>10d</sup>

Because PdMeOPV is also considerably crystalline and possesses good intrachain order,<sup>10c,d</sup> it is reasonable to expect that a situation similar to that in PPV also occurs in this polymer. On the other hand, dROPPV-1/1 is much less crystalline than PdMeOPV because it is intrinsically a random copolymer. The short methoxy groups of PdMeOPV can promote the intrachain order by interlocking chain segments,<sup>10a,b</sup> but this effect would be much less pronounced in dROPPV-1/1 due to the disturbance of the other side chains (3,7-dimethyloctyloxy groups). Therefore, the appearance of strong aggregate emission in dROPPV-1/1 instead of in the as-predicted PdMeOPV should be simply because the arrangement of polymer chains is less restricted in the former and hence orientations between adjacent segments appropriate for aggregation can be more readily adopted in dROPPV-1/1.

The above analysis reveals that aggregate emission of conjugated polymers should be contributed only by the domains, if any, that are amorphous or of low crystallinity. This drawing is consistent with recent observations on MEH-PPV and poly[9,9-di-*n*-octyl-2,7-fluorene] (PFO).<sup>21</sup> For MEH-PPV, the aggregate emission of annealed films is related to the formation of nematic mesophase,<sup>21a,b</sup> and the “nanocrystals” of MEH-PPV in aged solutions can retard aggregate emission in the subsequently cast films.<sup>21c</sup> For PFO, it should be the liquid-crystalline matrix rather than crystalline domains that dominate the emission.<sup>21d</sup> Our results, together with these findings, may imply a universal insignificance of “crystalline domains” in the aggregate emission of conjugated polymers.

In this study, the supramolecular effect of “chemical structure” and “chain arrangement” on the aggregation of conjugated polymer chains is clearly revealed. Further investigation for the effect of chain packing on the formation of aggregates is on the way.

## Conclusions

In summary, we illustrate that photophysics and the supramolecular structure of conjugated polymers can be controlled by

fine-tuning of the copolymer composition, without altering the intrinsic properties of single polymer chains. The investigated copolymers (dROPPV-0/1, 0.2/1, and 1/1, in an increasing order of the content of short methoxy side groups) can be a model system from which roles of aggregates (i.e., ground-state species consisting of conjugated segments with an extension of  $\pi$ -system over one another) and the well-packed independent chain segments in the emission mechanism of conjugated polymers can be revealed unambiguously. In assemblies of the well-packed chains, chain segments are accessible to interchain excitations by which delayed luminescence is resulted. Both the delayed luminescence and the aggregation of chains are facilitated by the presence of short methoxy groups and the extent is both in the increasing order,  $0/1 < 0.2/1 \ll 1/1$ . This result suggests that the formation of well-packed chains and the aggregation of chains are closely related and the requirements in "chemical structure" for the two processes are similar: both are favored by a reduction in the bulkiness of side chains. Besides that, differences in the emission behaviors of the investigated dROPPV-1/1 and the well-studied polymer PdMeOPV reveal an additional requirement in "chain arrangement" for the occurrence of aggregate emission: the intrachain order must be spoilt. This implies that aggregate emission of conjugated polymers should not originate from the domains of high crystallinity. As long as aggregates form, the continuous-wave fluorescence spectrum (and also the delayed luminescence) will red shift and become less structured, because the excitation energy can migrate or transfer from the independent conjugated segments to these aggregated sites.

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

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