Substitution position effect on photoluminescence emission and chain conformation of poly(diphenylacetylene) derivatives†


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The significant variation in photoluminescence emission of poly(diphenylacetylene) derivatives according to the substitution position is due to the differences in the intramolecular π-stack structure and chain conformation.

Many types of conjugated polymers have been extensively studied for various applications such as polymer light-emitting devices (PLED) and organic thin film transistors (OTFT). These polymers have been precisely designed in order to satisfy the requirements of specific functions and applications. From the viewpoint of the molecular design, the electronic action, bulkyness of substituents attached to the main chain, whether to attach a smaller or a bulkier group, whether to attach the substituent symmetrically or unsymmetrically have been largely considered in order to optimize their HOMO/LUMO energy levels and the band gap energy in the desired direction. Thus, such molecular designs are very important in relation to fluorescence-color tuning, efficient exciton confinement, and charge-carrier transport performance.

Recently, some polymers having stable and regulated π-stacked structures in the side chains have been reported by many research groups. Such chain conformation significantly influenced their properties and functions. Tsuchihara et al. have synthesized poly[1-phenyl-2-(p-trimethylsilyl)phenylacetylene] [p-PTMSDPA in Fig. 1a] in 1991. The corresponding meta-substituted polymer [m-PTMSDPA in Fig. 1a], having a trimethylsilyl group on the meta-position of the side phenyl ring, was also synthesized in the same year. Surprisingly, these two polymers show completely different photoluminescence (PL) emission properties merely due to the subtle difference in substitution position, despite their structural similarity. As shown in Fig. 1b and c, the m-PTMSDPA shows much weaker emission at a longer wavelength relative to the p-PTMSDPA (see Fig. S1 and the description in ESI† for the detailed absorption/emission spectrum analysis). It is a remarkable event that only the slight difference in the chemical structure, i.e., whether the trimethylsilyl group is attached to the para- or meta-position on the side phenyl rings, results in a significant difference in the PL emission property. However, the reason has not been clarified yet and has remained unknown.

The PL emission of diphenylacetylene polymer derivatives originates from the intramolecular excimer emission due to the cofacial phenyl–phenyl stack in the side chains. Thus, the emission origin of the present polymers is completely different from the intramolecular excimer emission of the coplanar aromatic π-conjugated polymers with the cofacial chain packing structure in a solid state. Such an intramolecular excimer emission should be shown in dilute solution as well as in bulk solids. In comparison of both the polymers, the emission of m-PTMSDPA in solution is very weak (quantum emission yield, $\Phi_{PL}$: 2.9 in toluene), while the p-PTMSDPA in solution shows about 11 times more intense emission ($\Phi_{PL}$: 32.0). The dominant fluorescence lifetime (t$_{PL}$: 0.611 ns in toluene) of p-PTMSDPA is much longer than that (t$_{PL}$: 0.114 ns in toluene) of m-PTMSDPA (Table S1, ESI†). In general, the greater the degree of aromatic stack in a fluorophore molecule, the less intense the emission, and shifts into the longer wavelength of the emission band. This suggests that the electronic clouds of m-PTMSDPA are highly dense in the phenyl–phenyl stack structure and that the molecular torsional and scissoring motions of the side phenyl rings are highly restricted; thus, the cross-sectional phenyl–phenyl stack area becomes greater, resulting in a chain conformation...
mainly with a nonradiative electronic structure even at the isolated chain state in a dilute solution. On the other hand, \( p \)-PTMSDPA should have a less dense phenyl–phenyl stack structure and thus the side phenyl rings have a smaller cross-sectional phenyl–phenyl stack area to undergo a radiative electronic transition process.

The intramolecular excimer, due to the cofacial aromatic stack structure, will be more easily generated in a solid film rather than in an ideal solution, because the molecular torsional and scissoring motions of the side phenyl rings should be further restricted in the denser space of the solid film than in the solution-state isolated chains. The \( \Phi_{\text{PL}} \) of \( p \)-PTMSDPA in film is 1.2 (\( \tau_{\text{PL}}: 0.167 \) ns in film). Especially, the \( \Phi_{\text{PL}} \) value of \( m \)-PTMSDPA in film is as small as <0.2 (\( \tau_{\text{PL}}: 0.094 \) ns in film). It should be also noted that the unsubstituted poly(diphenylacetylene) with no trimethylsilyl groups showed the weaker PL emission (\( \Phi_{\text{PL}}: 0.09 \) in film) at a little longer wavelength (emission maximum wavelength, \( \lambda_{\text{max,em}}: 547 \) nm in film) relative to both \( p \)- and \( m \)-PTMSDPA (Fig. S2, ESI).1 In a previous study, it was found that the PL emission of diphenylethylene polymer derivatives in bulk films significantly depended on the lamellar layer distance (LLD).9,12 The longer the LLD, the smaller the cross-sectional area of the cofacial phenyl–phenyl stack, and the more intense the emission. Thus, when a polymer derivative film with a shorter LLD is swollen by an appropriate non-solvent, the PL emission is significantly enhanced to be able to stand a comparison with that of a longer LLD polymer derivative.9,13 However, both \( p \)- and \( m \)-PTMSDPA showed almost the same LLD of 13.0 Å in the X-ray diffraction (XRD) patterns (Fig. S3, ESI). When both the polymer films were swollen by a hydrocarbon liquid such as hexane, the PL intensity dramatically increased, probably due to the enhanced chain mobility accompanied with the stack structure relaxation. Actually, the \( \Phi_{\text{PL}} \) values of \( p \)- and \( m \)-PTMSDPA, after fully swelling with hexane, increased about 10 times relative to those before swelling, to reach up to 11.0 and 2.0, respectively. However, the difference in emission intensity between the \( p \)- and \( m \)-PTMSDPA is still remarkable. These results suggest that the difference in emission between both polymers should be ascribed to the intramolecular chain conformation, but not to LLD.

Theoretical calculations were carried out on the 10-mer model compounds of both polymers to see their energy-minimized structures (Spartan 04, V1.0.1, AM1 semiempirical). Fig. 2 shows the side and top views of 10-mer model compounds of both \( p \)- and \( m \)-PTMSDPA polymers. Both model compounds show repeating conformational patterns, especially for spatial arrangements of trimethylsilyl groups. The difference in chain conformation between the \( para \)- and \( meta \)-polymers is clearly seen: The trimethylsilyl groups of \( p \)-PTMSDPA are discontinuously arranged in a zigzag pattern, while the \( m \)-PTMSDPA is continuously coiled in a helical manner. As for \( p \)-PTMSDPA, the dihedral angles between two planes of molecular backbone with neighboring \( ipso \)-carbon of the \( p \)-trimethylsilylphenyl group are sequentially twisted with angles of \( +63 \pm 1^\circ, -109 \pm 2^\circ \) and \( +54 \pm 1^\circ \) in a repetitively zigzag pattern (Fig. S4, ESI). However, in the case of \( m \)-PTMSDPA, the corresponding dihedral angles are fixed at \(-55 \pm 0.5^\circ \) in a helical manner (Fig. S5†). Thus, the molecular backbone of \( m \)-PTMSDPA is also helically coiled, and consequently, one turn of the helix exactly involves six monomer units. In \( m \)-PTMSDPA, both the stack of phenyl rings and the stack of phenyl rings with a trimethylsilyl group on the \( meta \)-position are coiled in a helical manner in a direction parallel to each other. The side phenyl groups are stacked one on top of the other, with an average distance of ca. 2.4 Å between two phenyl rings. Because six phenyl rings are involved in one complete turn of the helix, the pitch of the helix is calculated to approximately 12.0 Å. Accordingly, there is a considerable difference in the stack degree of the aromatic pendant groups between the \( para \)- and \( meta \)-polymers.

The difference in chain conformation is also reflected in the main chain rigidity. The \( m \)-PTMSDPA shows the stiff nature of the main chain, as determined by the high viscosity index of \( \alpha = 1.07 \) (in THF at 40 °C). On the other hand, \( p \)-PTMSDPA has a lower value of 0.80. The higher main chain rigidity of the \( meta \)-polymer should be ascribed to the helix-like, continuous phenyl–phenyl stack structure, while the lower rigidity of the \( para \)-polymer is due to the discontinuous stack structure in a zigzag pattern. On direct observation of single chains in solution using a high-speed atomic force microscope (AFM), the \( meta \)-polymer chain behaves as a rigid rod while the \( para \)-polymer does exist as a shrunk coil (Fig. S6, Movies S1 and S2, ESI†).

In summary, we clearly verified the substitution position effect on PL emission of poly(diphenylacetylene) derivatives. The steady-state/dynamic PL spectroscopy and XRD studies revealed that the PL emission properties were significantly dependent on the substitution position of a trimethylsilyl group on the side phenyl ring. The theoretical calculations on both model compounds revealed that the remarkable difference in the PL emission property is because the intramolecular cofacial phenyl–phenyl stack structure significantly varies according to the substitution position of the trimethylsilyl group. These results help us to comprehensively understand the origin of the PL emission of poly(diphenylacetylene) derivatives. It would be also a new guideline for synthetic
strategies of the intramolecularly z-stacking polymers towards various (opto)electronic device applications.\textsuperscript{14}

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Notes and references


11 The unsubstituted poly(diphenylacetylene) is not soluble in any organic solvent. Teraguchi and Masuda have developed this polymer film via the in situ desilylation reaction of p-PTMSDPA and its analogues in an acidic organic solvent mixture of trifluoroacetic acid and hexane (M. Teraguchi and T. Masuda, Macromolecules, 2002, 35, 1149). We also used the same synthetic method to prepare the polymer film for PL emission spectroscopy measurement.


13 In a previous paper (ref. 9f), the authors already explained this issue in Fig. 2 and 3 of the paper by using fluorescence emission spectra and XRD patterns. This type of polymers of poly-(diphenylacetylene) derivatives show intramolecular excimer emission due to intramolecular phenyl-phenyl stack structure. Thus, the emission properties (wavelength and intensity) are significantly dependent on the phenyl-phenyl stack degree. The steric crowding of the side phenyl groups should be greater in the polymer with shorter LLD than in the polymer with longer LLD. Thus, the cross-sectional phenyl-phenyl stack area in the polymer with shorter LLD decreases with an increase in LLD along with the degree of swelling in order to restrain the formation of excimers of energy trapping sites, leading to emission enhancement and blue shift. When the same method was applied to the polymers with longer LLD, the PL emission hardly increased probably because the steric crowding of side phenyl groups has already been relaxed enough.