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Synthesis and properties of folded π-stacking polymers having *J*-aggregative, alternative, and staggered assembling structures

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ABSTRACT

Three types of folded polymers showing alternative stacking of two different π-units (A-**3**), *J*-aggregate (J-**3**), and staggered stacking (S-**3**) structures of π-modules were designed and synthesized using 2-substituted 1,3-diaryl tethering units. The UV-absorbing and fluorescent emission properties of these polymers were investigated and compared to those of the corresponding single structural π-molecule component and *H*-type stacking polymer (H-**3**). These three types of polymers exhibited unique optical properties as a result of a distinctive arrangement of π-units.

1. Introduction

Polymeric molecules, particularly those showing ordered assembly of π-moieties, are of interest as optical and/or electronically active polymers because of their low processing costs and desirable mechanical properties. Thus, the two-dimensional orientation of π−molecules (e.g., *J*- and *H*-aggregations) provides these materials with arrange of photophysical, electronic, and photoelectronic properties [1–8].

We recently developed folded π-stacking polymers composed of 2-substituted 1,3-diarylpropane structures and subsequently studied their properties [9–11]. 2-Substituted 1,3-diphenylpropanes predominantly exist in conformation **III** for bulky Z substituents (Equation (1) in Scheme 1), as suggested by MM2 calculations of **I**, **II**, and **III** simplified conformers. These were confirmed by ^{1}H NMR analyses (i.e., chemical shift of aromatic protons by shielding effect) [12,13] and fluorescence (i.e., predominant emission of benzene excimer) measurements [14]. Based on these results, we synthesized polymers composed of 2-substituted 1,3-phenylpropane and π-modules. We found that these polymers spontaneously fold to the π-stacking **V** conformer; this configuration being favored over the linear stretched form **IV** both in solution and film state (Equation (2) in Scheme 1) [9,10]. This stacking of π-units (form **V**), similar to that found unique to *H*-type aggregates of π-molecules, provides the polymers with a large ultra violet (UV) absorption hypochromic shift that is unique to *H*-aggregation materials [15–20]. **V** polymers (H-**3**) were synthesized from π-units (**2**) and tethering units (**1**) by Suzuki-Miyaura coupling polymerization (Equation (3) in Scheme 1).

Herein, in addition to folded *H*-stacking polymers, we designed novel folded π-stacking polymers with *J*-type π-stacking, alternative stacking of two different π-units, and staggered π-stacking structures (Scheme 2).

Folded polymers with *H*-type stacking of π-units (H-**3**) can be synthesized by A_2+B_2 type polymerization of turn-up tethering unit **1** and π-units **2**, as previously reported by our group. Once π-units are selectively connected to two tethering units to yield **4**, polymerization of monomer **4** with different π-units **2′** may produce alternative stacking polymers (A-**3**). π-Unit **6**, bearing two spacer units added to **2**, may react with monomer **4** to afford *J*-type stacking polymers (J-**3**). Polymerization of monomer **5**, bearing a π-unit and a spacer at one end of **1**, will result in staggered stacking polymers (S-**3**).

2. Experimental

2.1. General

NMR spectra were recorded in $CDCl_3$ at 600 and 500 MHz for ^{1}H

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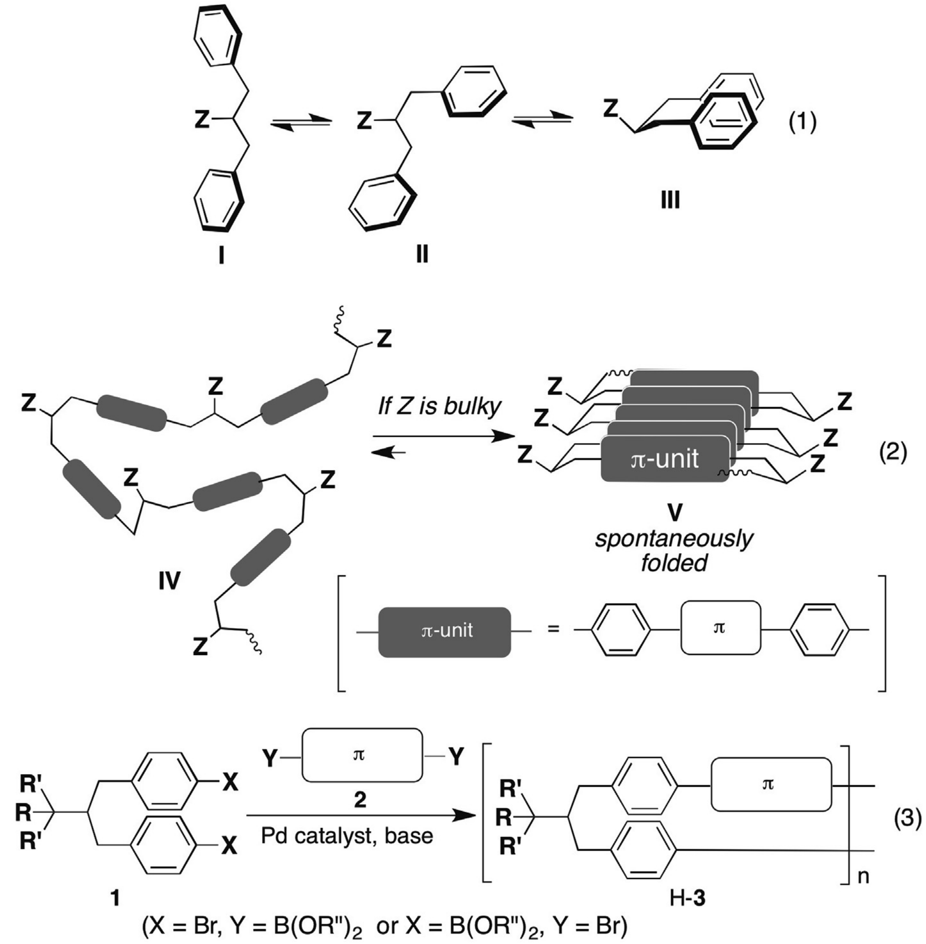
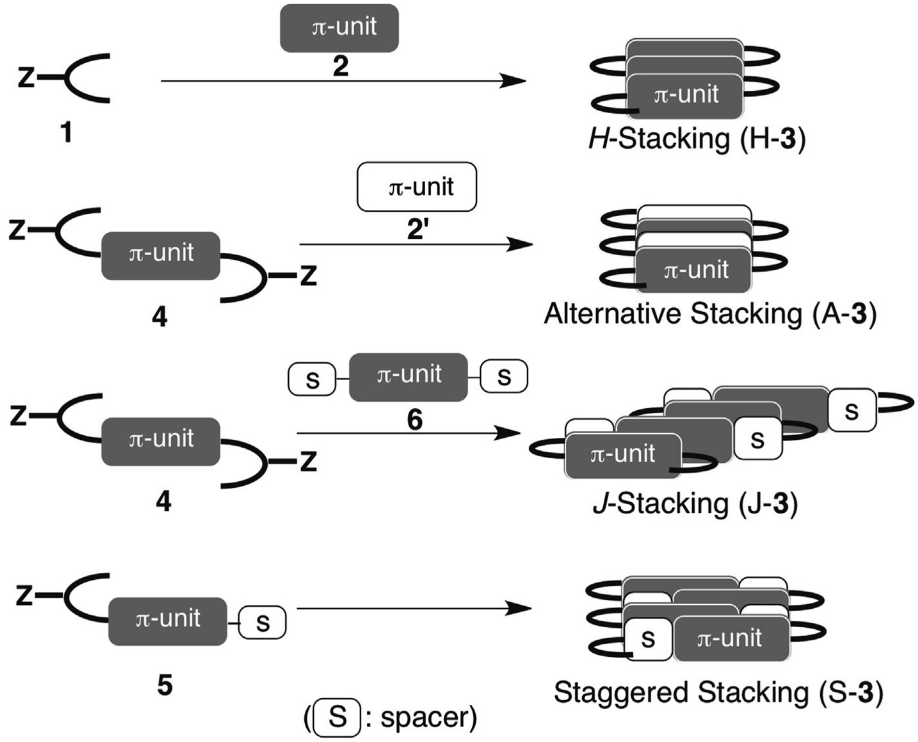
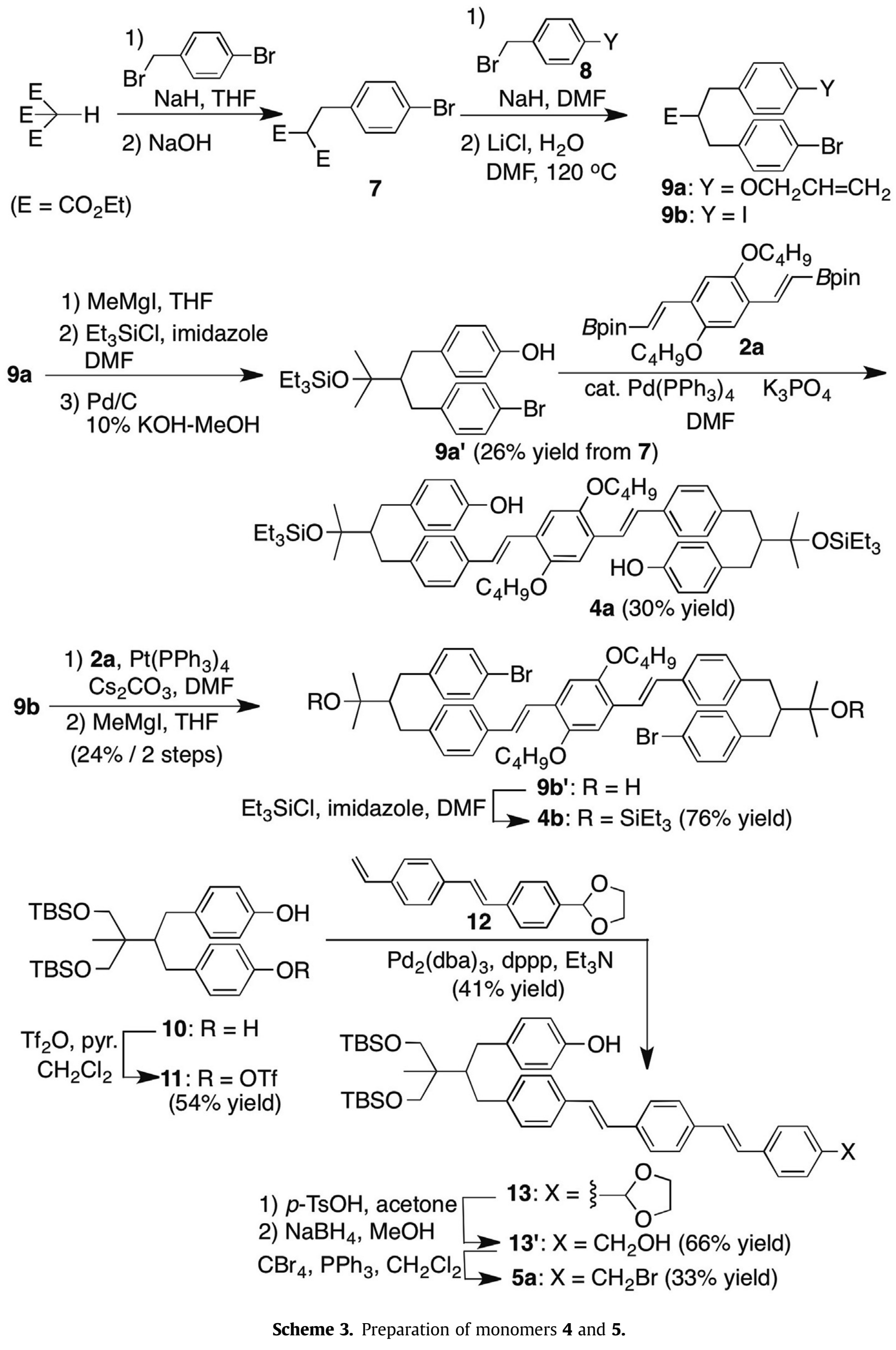


Scheme 1. Basis of folded *H*-stacking polymers.



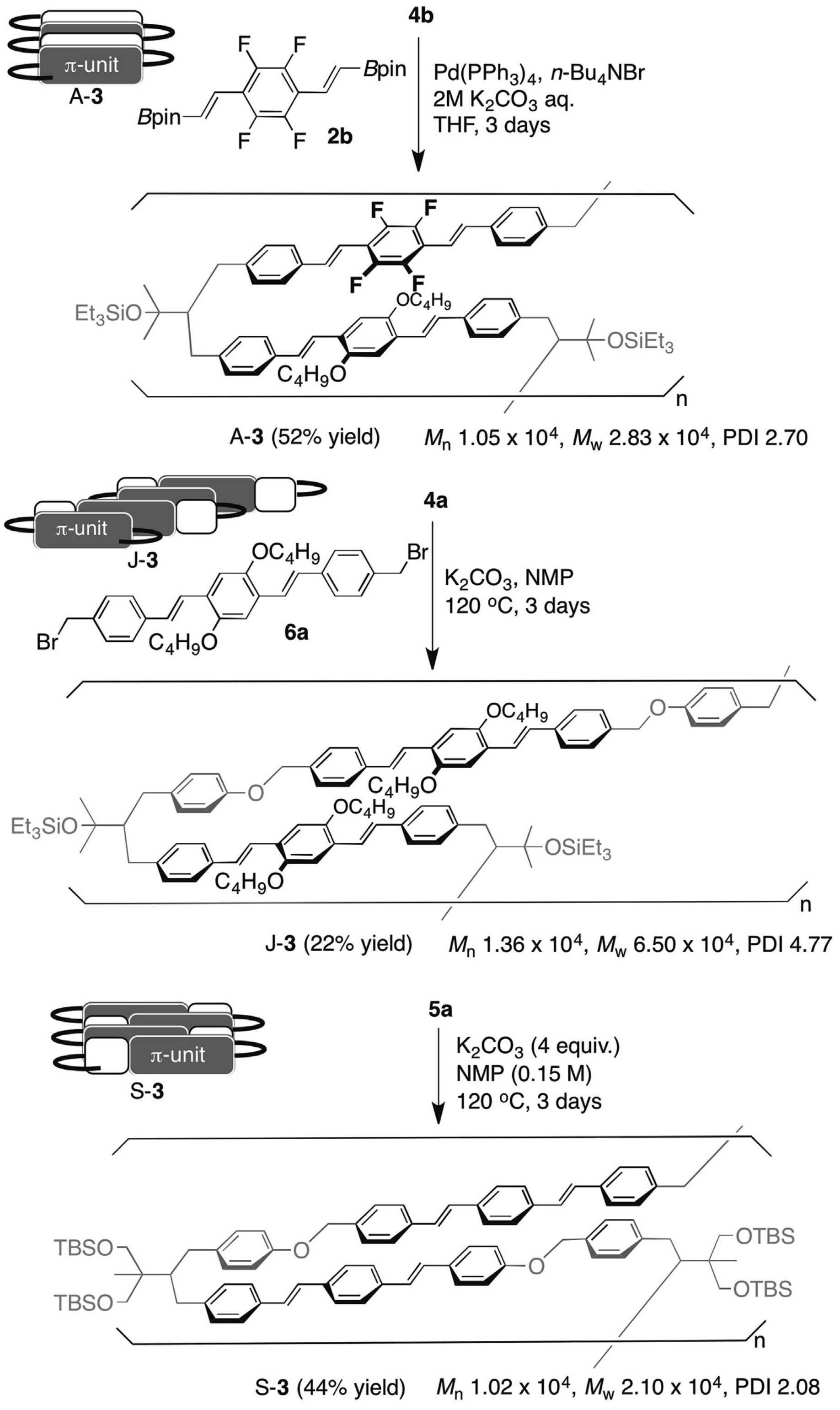
Scheme 2. Synthetic approach for *H*-, *J*-, alternative, and staggered stacking polymers.



Scheme 3. Preparation of monomers **4** and **5**.

and 150 and 125 MHz for ^{13}C, respectively, on JEOL JMN-ECA600 and 500 spectrometers. Chemical shifts are reported in part per million (ppm, δ) relative to Me_4Si (δ 0.00) or residual $CHCl_3$ (δ 7.26 for ^{1}H NMR), or a center peak of $CDCl_3$ (δ 77.0 for ^{13}C NMR). IR spectra were recorded on an FT/IR 4100 (JASCO) and are reported in wave numbers (cm^{-1}). The M_n and M_w of polymers were measured with a TOSOH HLC-8020 gel-permeation chromatography (GPC) unit (eluent: THF; calibration: polystyrene standards) using two TSK-gel columns (2 Multipore H_{XL}-M). MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) mass spectra were recorded by a Shimadzu Biotech Axima CFR plus curved field reflection (CFR) in the reflection ion mode by use of a laser (λ = 337 nm). High-resolution mass spectra (HR-MS) were measured on JEOL Accu TOF T-100 equipped with ESI ionization. The UV-Vis absorption spectra were recorded with a UV-2450 SHIMADZU spectrophotometer. Fluorescence emission spectra (FL) and excitation spectra were recorded with a RF-5300PC SHIMADZU spectrophotometer. All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. Dry solvents (THF, DMF, CH_2Cl_2) were purchased from Kanto Chemical Co., Inc., and used as received without any additional purification and degassing procedure.

Polymers H-**3A**, H-**3B**, and H-**3C** were synthesized according to the similar procedure to that for synthesis of A-**3**. Polymer H-**3D** was prepared by a similar protocol for synthesizing J-**3**. For synthetic procedures for monomers **4** and **5**, see Supplementary

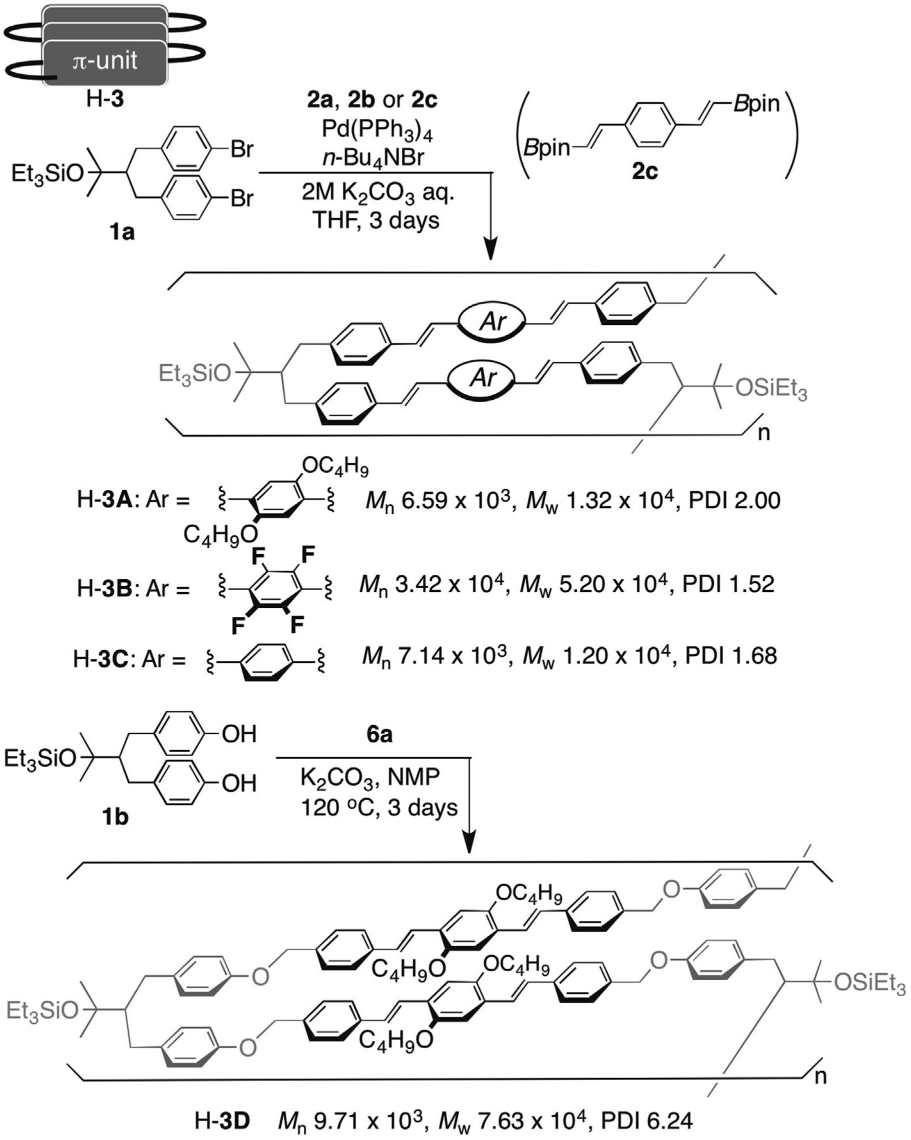


Scheme 4. Synthesis of polymers A-, J-, and S-**3**.

Materials. Model compounds OBu-BStB and F-BStB were prepared by the similar procedure to the reported synthesis of BStB [9].

2.2. Polymer A-*3*

Under Ar atmosphere, to a mixture of **4b** (582 mg, 0.500 mmol), (n-Bu)$_4$NBr (161 mg, 0.500 mmol), **2b** (227 mg, 0.500 mmol), 2 M aqueous K_2CO_3 (1.00 mL), and THF (1.67 mL) was added a solution of $Pd(PPh_3)_4$ (23.1 mg, 0.020 mmol) in THF (1.67 mL) at room temperature. After the mixture was stirred for 3 days at 80 °C, saturated aqueous $NaHCO_3$ (3 mL) was added and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed



Scheme 5. Synthesis of *H*-stacking polymer H-**3**.

with $\mathrm{H_2O}$, dried over $\mathrm{Na_2SO_4}$, and filtered. Residue obtained by concentration of the filtrate was dissolved in $\mathrm{CH_2Cl_2}$ and the solution was poured into MeOH. The obtained polymer precipitate was collected by filtration, washed with $\mathrm{Et_2O}$ and dried under reduced pressure. Polymer A-**3** (313 mg) was obtained in 52% yield as a yellow solid: ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$) δ 7.45–6.77 (br m, overlap with $\mathrm{CHCl_3}$ peak, 26H, Ar and CH=CH), 4.10–3.82 (br, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 3.02–2.85 (br, 4H, $\mathrm{C}\mathit{H}_2\mathrm{Ar}$), 2.52–2.31 (br, 4H, $\mathrm{C}\mathit{H}_2\mathrm{Ar}$), 2.16–2.01 (br, 2H, $\mathrm{C}\mathit{H}\mathrm{CH_2Ar}$), 1.89–1.72 (br, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.60–1.48 (br, 4H, $\mathrm{OCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.27–1.13 (br, 12H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{C}$), 1.04–0.80 (br m, 24H, $(\mathrm{C}\mathit{H}_3\mathrm{CH_2})_3\mathrm{Si}$ and $\mathrm{OCH_2CH_2CH_2C}\mathit{H}_3$), 0.66–0.47 (br, 12H, $(\mathrm{CH_3C}\mathit{H}_2)_3\mathrm{Si}$). IR (film) 2954, 2933, 2873, 1606, 1482, 1417, 1203, 1011, 965.2, 721.2 cm^{-1}. $M_\mathrm{n} = 1.05 \times 10^4$, $M_\mathrm{w} = 2.83 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 2.70$ based on GPC analysis.

*2.3. Polymer J-**3***

The mixture of **4a** (520 mg, 0.500 mmol), **6a** (306 mg, 0.500 mmol) and NMP (5.00 mL) were added $\mathrm{K_2CO_3}$ (276 mg, 2.00 mmol) at room temperature. The mixture was stirred for 3 days at 120 °C. The reaction was quenched by addition of saturated aqueous $\mathrm{NaHCO_3}$ and the aqueous layer was extracted with $\mathrm{CH_2Cl_2}$. The combined organic layers were washed with $\mathrm{H_2O}$, dried over $\mathrm{Na_2SO_4}$. After filtration and evaporation, the residues was dissolved in $\mathrm{CH_2Cl_2}$ and poured into MeOH. The obtained polymer precipitate was washed $\mathrm{Et_2O}$ several times and dried under reduced pressure. Polymer J-**3** (164 mg) was obtained in 22% yield as a yellow solid: ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$) δ 7.57–6.57 (br m, overlap with $\mathrm{CHCl_3}$ peak, 36H, Ar and C*H*=C*H*), 4.11–3.84 (br, 12H, $\mathrm{ArC}\mathit{H}_2\mathrm{OAr}$ and $\mathrm{OC_4}\mathit{H}_9$), 3.02–2.77 (br, 4H, $\mathrm{C}\mathit{H}_2\mathrm{Ar}$), 2.48–2.24 (br, 4H, $\mathrm{C}\mathit{H}_2\mathrm{Ar}$), 2.10–1.97 (br, 2H,$\mathrm{C}\mathit{H}\mathrm{CH_2Ar}$), 1.91–1.65 (br, 8H, $\mathrm{OC_4}\mathit{H}_9$), 1.65–1.38 (br, 8H, $\mathrm{OC_4}\mathit{H}_9$), 1.65–1.11 (br, 12H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{C}$), 1.11–0.72 (br m, 30H, $(\mathrm{C}\mathit{H}_3\mathrm{CH_2})_3\mathrm{Si}$ and $\mathrm{OC_4}\mathit{H}_9$), 0.72–0.49 (br, 12H, $(\mathrm{CH_3C}\mathit{H}_2)_3\mathrm{Si}$). IR (film) 3421, 2954, 2871, 1668, 1510, 1417, 1200, 1012, 963.3, 802.2, 720.3 cm^{-1}. $M_\mathrm{n} = 1.36 \times 10^4$, $M_\mathrm{w} = 6.50 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 4.77$ based on GPC analysis.

*2.4. Polymer S-**3***

To a mixture of **5a** (109.6 mg, 0.133 mmol) and NMP (0.90 mL) was added $\mathrm{K_2CO_3}$ (73.4 mg, 0.532 mmol), and the mixture was

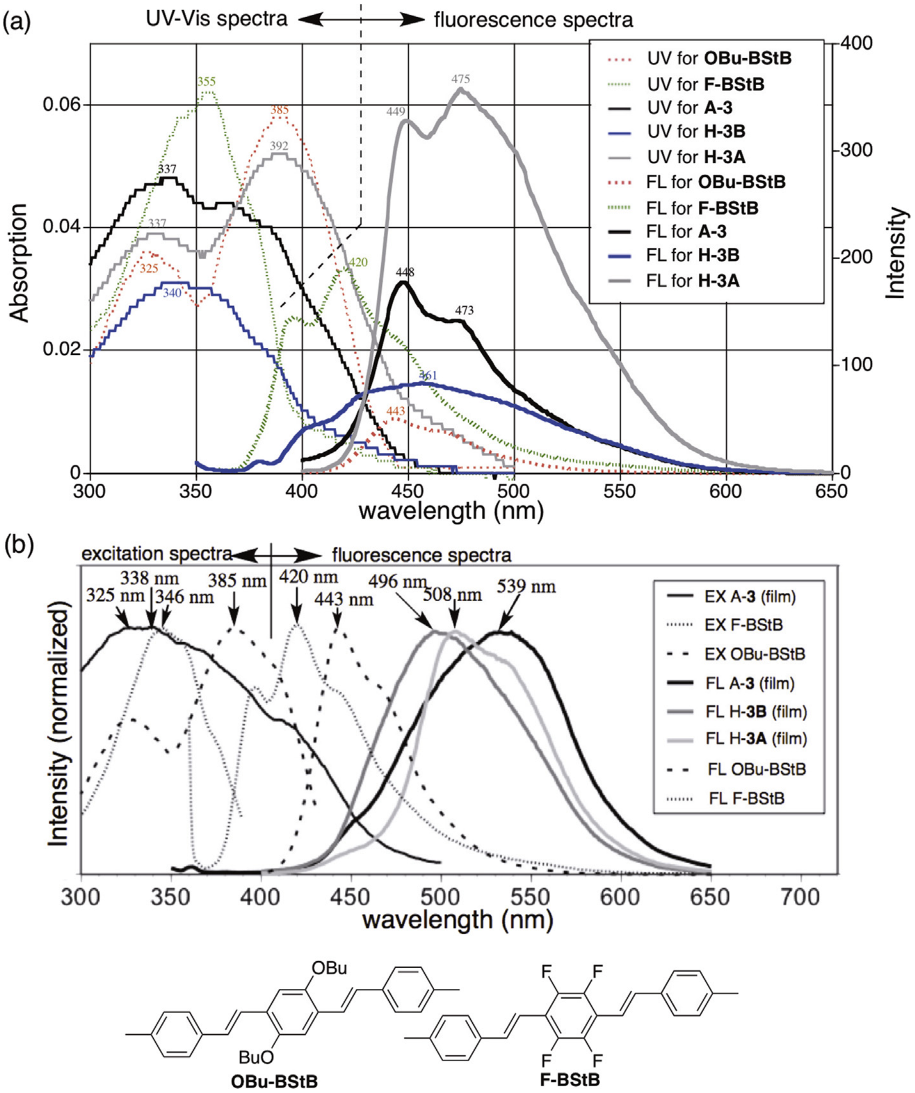


Fig. 1. (a) UV-Vis Absorption (UV) and Fluorescence (FL) Spectra of **OBu-BStB**, **F-BStB**, **A-3**, **H-3A** (x 10), and **H**–**3B** in CH_2Cl_2 (10^{-6} M). FL: Excited at 337 nm for **OBu-BStB**, 355 nm for **F-BStB**, 336 nm for **A-3**, 341 nm for **H-3A** (measured using a 10^{-7} M solution and spectra are indicated using tenfold intensity), and 343 nm for **H**–**3B**. (b) Fluorescence (FL) and excitation (EX) spectra of A-**3** (film), H-**3A** (film), H–**3B** (film), F-BStB (10^{-7} M in CH_2Cl_2), and OBu-BStB (10^{-7} M in CH_2Cl_2). FL (normalized): excited at 340 nm for A-**3**, 390 nm for H-**3A**, 443 nm for H–**3B**, 355 nm for F-BStB, and 388 nm for OBu-BStB. EX (normalized): monitored at 530 nm for A-**3**, 443 nm for H-**3A**, and 420 nm for H–**3B**.

stirred at 120 °C for 3 days. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over Na_2SO_4. After filtration and evaporation, the residues was dissolved in $CHCl_3$ and poured into a large amount of MeOH. The obtained polymer was washed with hexane several times and dried under reduced pressure to give polymer S-**3** (43 mg) in 44% yield as a brown solid: ^1H NMR (600 MHz, $CDCl_3$) δ 7.87–6.39 (br, overlap with $CHCl_3$ peak, 20H in one unit, Ar), 5.17–4.64 (br, 2H in one unit, OCH_2), 3.84–3.15 (br, 4H in one unit, $SiOCH_2$), 3.15–2.61 (br, 2H in one unit, $CHCH_2Ar$), 2.61–2.06 (br, 3H in one unit, $CCHCH_2$), 1.19–0.59 (br, 21H in one unit, $SiCCH_3$, CCH_3), 0.24–0.29 (br, overlap with TMS peak, 12H in one unit, $SiCH_3$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 142.8, 136.9, 136.6, 136.3, 129.8, 129.2, 128.6, 128.6, 128.4, 127.9, 127.7, 127.0, 126.8, 126.7, 126.6, 126. 114.5, 69.8, 65.3, 44.1, 26.0, 18.3, 16.0, -5.5, -5.6. IR (film) 3023, 2952, 2926, 2854, 1509, 1250, 1086, 960.4, 773.3, 664.4 cm^{-1}. $M_n = 1.02 \times 10^4$, $M_w = 2.10 \times 10^4$, $M_w/M_n = 2.06$ based on GPC analysis.

3. Results and discussion

3.1. Synthesis

3.1.1. Synthesis of monomers

As required by the synthetic approach herein designed, monomers **4** and **5** were prepared following the procedure shown in Scheme 3. Triethyl methanetricarboxylate was alkylated with *p*-$BrC_6H_4CH_2Br$ followed by mono-decarboxylation to afford **7** that was further alkylated with benzyl bromide derivatives **8a** or **8b** and subsequently decarboxylated to afford 1,3-diarylpropanes **9a** and **9b**, respectively. **9a** ($Y = OCH_2CH{=}CH_2$) was reacted with MeMgI and subsequenly silylated with Et_3SiCl. Deallylation of the resulting silyl ether gave phenol derivative **9a'** (26% yield from **7**). Suzuki-Miyaura coupling of **9a'** and diboronate **2a** furnished monomer **4a** (30% yield). Similarly, iodobromo compound **9b** was coupled with **2a** to provide dibromo compound **9'** (24% yield) after reaction with excess MeMgI. Diol **9b'** was silylated to give monomer **4b** (76% yield). Moreover, AB-monomer **5a** was prepared from diphenol

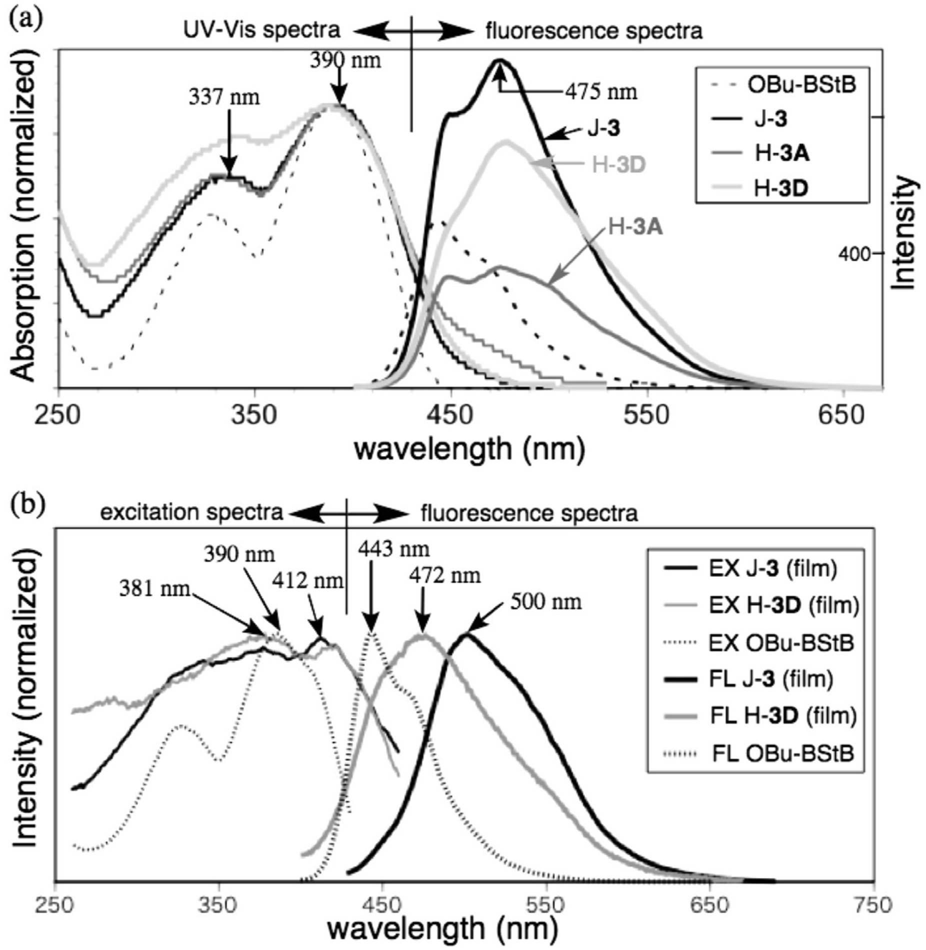


Fig. 2. (a) UV-Vis absorption and FL spectra of J-**3** (10^{-6} M in CH_2Cl_2), H-**3A** (2×10^{-6} M in CH_2Cl_2), H-**3D** (2×10^{-6} M in CH_2Cl_2), and OBu-BStB (10^{-7} M in CH_2Cl_2). FL: excited at 390 nm for J-**3**, 390 nm for H-**3A**, 387 nm for H-**3D**, and 388 nm for OBu-BStB. (b) FL and EX spectra of J-**3** and H-**3D** films. FL: excited at 412 nm for J-**3**, 340 nm for H-**3D**, and 388 nm for OBu-BStB. EX: monitored at 503 nm for J-**3**, 472 nm for H-**3D**, and 443 nm for OBu-BStB.

compound **10** [11] by conversion into the mono trifluoromethnane sulfonate **11** (54%) followed by Heck coupling (41%) with **12**, acetal cleavage under acidic conditions, reduction of the resulting aldehyde, and finally conversion of the alcohol to the corresponding bromide (see Scheme 3).

3.1.2. Synthesis of polymers A-, J-, S-, and H-3

Once monomers **4** and **5** were obtained, polymers A-**3**, J-**3**, and S-**3** were synthesized (Scheme 4). Polymer A-**3** (M_n: 1.05×10^4, M_w: 2.83×10^4, M_w/M_n: 2.70, determined by GPC analysis with polystyrene standard), composed of an alternative stacking structure of two different π-units, was obtained in 52% yield (after re-precipitation from MeOH) by Suzuki-Miyaura coupling polymerization of **4b** and fluoro diboronate compound **2b**. *J*-Stacking polymer J-**3** (M_n: 1.36×10^4, M_w: 6.50×10^4, M_w/M_n: 4.77) was prepared in 22% yield (after re-precipitation from MeOH) by Williamson etheration polymerization of diphenol derivative **4a** with dibromide **6a** under basic conditions. Polymer S-**3** (M_n: 1.02×10^4, M_w: 2.10×10^4, M_w/M_n: 2.08) with staggered-stacking structure of π-units (44% yield after re-precipitation from MeOH) was readily synthesized by Williamson etheration polymerization of bromo phenol monomer **5a**.

With the aim to compare the properties of A-**3**, J-**3**, and S-**3** polymers with their corresponding *H*-stacking counterparts, homo polymers H-**3A**, H-**3B**, and H-**3C** were prepared by reacting **1a** [10] with the corresponding diboronate **2a**, **2b**, or **2c**, respectively (Scheme 5). Ether tethered polymer H-**3D** was also prepared from **1b** [11] and **6a** by Williamson etheration.

3.2. Optical properties

3.2.1. Polymer A-3

UV-Vis absorption (UV) and fluorescence (FL) spectra of CH_2Cl_2 solutions of A-**3**, H-**3A**, H-**3B**, and model compounds OBu-BStB and F-BStB are shown in Fig. 1(a). The concentration (M) of the polymer solutions refers to the molar amount of the repeat unit per volume of solution (L). For A-**3**, the concentration refers to the total molar amount of two π-units. Although UV of H-**3A** ($\lambda_{abs\ max}$: 392 nm) was similar to its single π-model OBu-BStB ($\lambda_{abs\ max}$: 385 nm), UV absorption of A-**3** ($\lambda_{abs\ max}$: 337 nm) and H-**3B** ($\lambda_{abs\ max}$: 340 nm) showed hypochromic shifts, compared to model compounds, which suggested their *H*-type aggregating orientation of π-units. Compared to F-BStB ($\lambda_{em\ max}$: 420 nm) and OBu-BStB ($\lambda_{em\ max}$: 443 nm), emission spectra for polymers A-**3** ($\lambda_{em\ max}$: 448 nm), H-**3A** ($\lambda_{em\ max}$: 475 nm), and H-**3B** ($\lambda_{em\ max}$: 4461 nm) bathochromically shifted. Emission from A-**3** was mainly ascribed to emission from OBu-BStB units in the polymer but not to that of F-BStB, probably due to intramolecular energy transfer from F-BStB units to OBu-BStB units.

Fig. 1(b) shows the FL and excitation (EX) spectra of A-**3**, H-**3A**, and H-**3B** films. These films were simply prepared by applying a

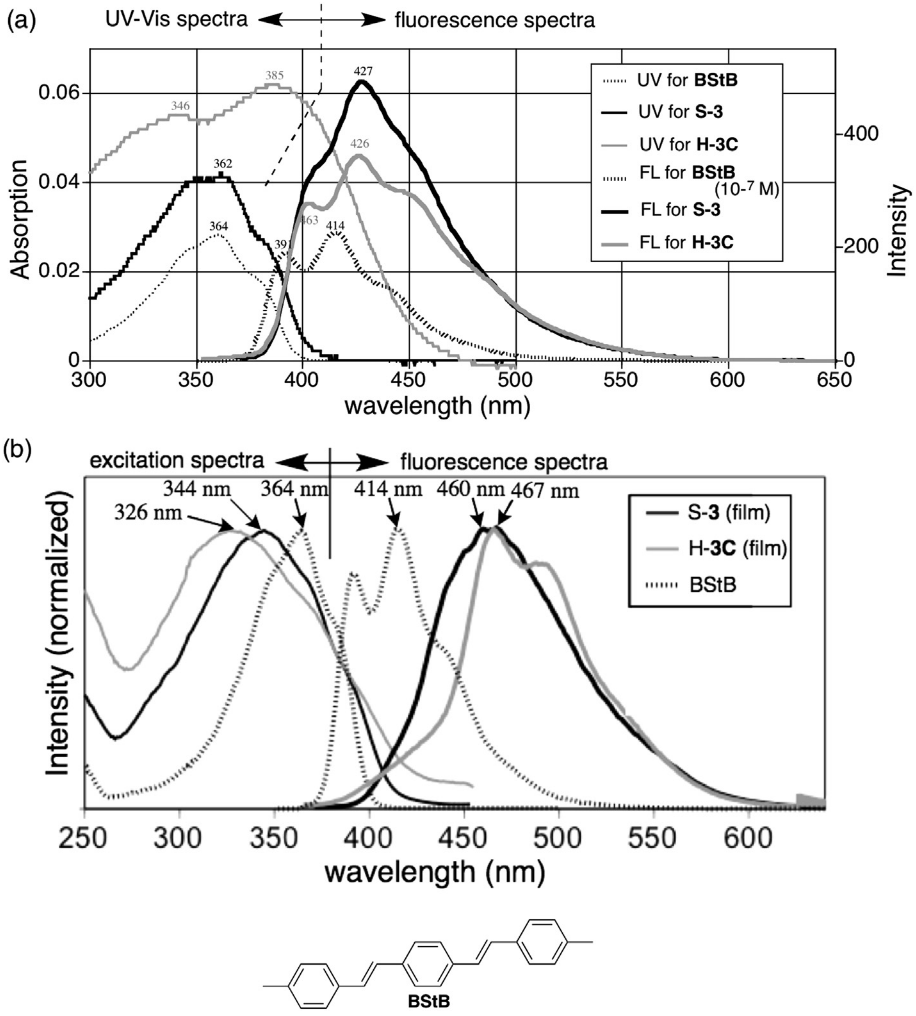


Fig. 3. (a) UV-Vis Absorption (UV) and Fluorescence (FL) Spectra of **BStB**, **S-3**, **H**–**3C**, and **H**–**3B** in CH_2Cl_2 (10^{-6} M). FL: Excited at 364 nm for **BStB** (measured using a 10^{-7} M solution), 362 nm for **S-3**, and 383 nm for **H**–**3C**. (b) FL and EX spectra of S-**3** (film), H–**3C** (film), and BStB (10^{-7} M in CH_2Cl_2). FL (normalized): excited at 347 nm for S-**3**, 342 nm for H–**3C**, and 326 nm for BStB. EX (normalized): monitored at 467 nm for S-**3**, 426 nm for H–**3C** and 466 nm for BStB.

CH_2Cl_2 solution containing the polymers to a quartz glass and subsequently removing the solvent. The spectra of F-BStB and OBu-BStB (CH_2Cl_2 solutions) are also shown for comparison. Compared to F-BStB and OBu-BStB, the *H*-stacking H-**3A** ($\lambda_{em\ max}$: 508 nm) and H-**3B** ($\lambda_{em\ max}$: 496 nm) polymers showed FL emission spectra with a large red-shifting, this being mainly ascribed to the excimer-like emission by *H*-type aggregation of π-units. Interestingly, a larger bathochromic shift ($\lambda_{em\ max}$: 539 nm), potentially attributed to exciplex-like emitting of the two different π-units, was observed for A-**3**. This large shift of emission for A-**3** was unique to the film form and quite different from its behavior in a CH_2Cl_2 solution. A-**3** possesses an alternative stacking structure of two different π-units with the same π-length as those of *H*-type aggregation materials, thereby leading to similar stacking arrangement for both types of polymers. Thus, compared to F-BStB and OBu-BStB, A-**3** showed EX spectra with a large hypochromic shift. Hypochromic shift of UV absorption and excitation (EX) spectra are an unique phenomenon to *H*-type aggregation polymers. The difference of FL behavior between a solution and film can be rationalized by assuming that polymer folded stacking structure may be tighter in film than in a solution.

3.2.2. *Polymer J-3*

The UV-Vis absorption and FL spectra of CH_2Cl_2 solutions of *J*-type (J-**3**) and *H*-stacking (H-**3A** and H-**3D**) polymers are summarized in Fig. 2(a). The spectra of a single π-unit model OBu-BStB are also given for comparison. The concentration (M) of the polymer solutions refers to the molar amount of the repeat unit per volume of solution (L). Therefore, the concentration of H-**3A** and H-**3D** polymers was adjusted to be twice than that of J-**3**. In terms of shape and $\lambda_{max\ abs}$ (ca 390 nm), these polymers showed nearly similar normalized UV spectra. J-**3**, H-**3A**, and H-**3D** polymers exhibited red-shifted FL emission compared to a single π-unit OBu-BStB. It can be noted that the emission spectra of the *J*-like stacking polymer J-**3** were more intense as compared to H-**3A** and H-**3D**. The fluorescence quantum efficiencies (Φ_F) of J-**3** (Φ_F 0.23), H-**3A** (Φ_F 0.10), and H-**3D** (Φ_F 0.14) polymers were relatively determined by comparing with that of 9,10-diphenylanthracene (Φ_F 0.81). Fig. 2(b) shows the FL and EX spectra of J-**3** and H-**3D** films. Unlike FL spectra in solution (Fig. 2(a)), emission spectra of films bathochromically shifted to a large extent compared to the single π-unit model OBu-BStB (CH_2Cl_2 solution). *J*-like stacking polymer J-**3** showed larger bathochromic shifts as compared to its analogous *H*-stacking H-**3D**.

3.2.3. Polymer S-**3**

The UV-absorption and emission properties of the staggered π-stacking polymer S-**3** in a CH_2Cl_2 solution are shown in Fig. 3(a). The spectra of H-**3C** and BStB were also investigated for the sake of comparison. The UV-spectra of S-**3** ($\lambda_{abs\ max}$: 362 nm) was similar to those of BStB ($\lambda_{abs\ max}$: 364 nm) in terms of shape and $\lambda_{abs\ max}$. However, S-**3** ($\lambda_{em\ max}$: 427 nm) exhibited red-shifted emission than BStB ($\lambda_{em\ max}$: 414 nm). Interestingly, emission of S-**3** indicated a similar shape and $\lambda_{abs\ max}$ to those of H-**3C** ($\lambda_{em\ max}$: 426 nm) but showed higher intensity. Fig. 3(b) summarizes the FL and EX spectra of S-**3** in film. As we reported previously, the *H*-stacking polymer H-**3C** exhibits large hypochromic UV (and EX) and bathochromic FL shifts compared to the single π-unit model compound BStB. This hypochromic shift is a characteristic of the *H*-aggregate of π-modules, whereas the bathochromic phenomenon may be attributed to excimer-type emission by the stacked structure of π-moieties within the polymer. In contrast, the *J*-stacking structure resulted in broadened bathochromic shifted absorption (Fig. 2). Similar to *H*-staking H-**3C**, the staggered π-stacking polymer S-**3** showed blue-shifted absorption and red-shifted emission (Fig. 3(b)). However, when compared to H-**3C**, S-**3** showed a lower hypochromic shift that may be attributed to a partial *H*-stacking structure of stilbene moieties in π-conjugate units (distyrylbenzene) of S-**3**. Accordingly, S-**3** resembles *H*-stacking polymers with moderate EX hypochromic shift characteristics.

4. Conclusions

We synthesized three types of spontaneously folded polymers involving alternative arrangement of two different π-units (A-**3**), *J*-aggregate (J-**3**), and staggered stacking (S-**3**) structures of π-modules. The UV-absorbing and fluorescent emission properties of these three polymers were compared with those of the corresponding single structural π-molecule component and *H*-type stacking polymer (H-**3**). As a result of the distinctive arrangement of π-units, each polymer exhibited unique optical properties. These characteristics were observed more prominently in film than in a solution.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.05.075.

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