Synthesis and Properties of Through-Space Conjugated Polymers Based on π–π Stacked 1,3-Biarylpropane Tethering Units

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ABSTRACT:: Novel skipped-π polymers in which the π-components are connected with 2-substituted trimethylene tethering units exhibit bathochromically shifted, broadened ultraviolet absorption with a unique lower-energy absorption band and a largely red-shifted fluorescent emission. These results suggest that through-space π–π interactions owing to a stair-like stacking substructure in these polymers extend the π-conjugation of the components in the ground and excited states. As the photophysical properties of the polymers observed both in a solution and in a dried film are similar to those of the *J*-aggregates of π-molecules, these polymers may be considered as pseudo *J*-stacking (or *J*-like-stacking) polymers. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

KEYWORDS: conformational analysis; conjugated polymers; fluorescence; stacking; UV–vis spectroscopy

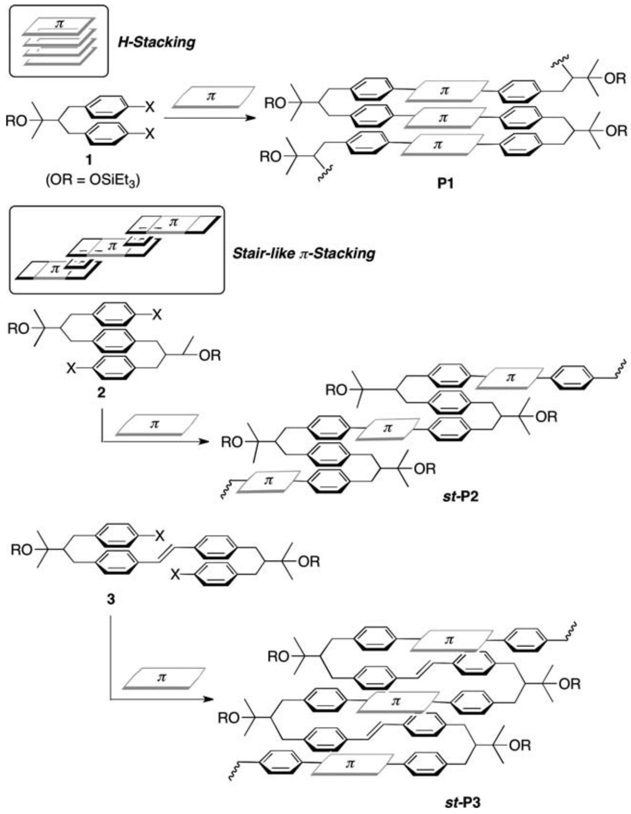
INTRODUCTION The construction of conjugated polymers that usually consist of an extended π-conjugated system(s) of newly formed bonds between sp- and/or sp^2-hybridized carbons generated in a polymerization reaction is of great importance because of their unique properties such as their electrical conductivity, photoconductivity, electroluminescence, liquid crystallinity, and nonlinear optical properties and chemical sensing properties.[1] Meanwhile, through-space and through-bond interactions between π systems that are tethered by one or more saturated carbon atoms in organic molecules, such as artificial aliphatic–aromatic systems or systems involving biomolecules such as proteins and DNA, are significant for understanding the electronic interactions that affect the spectroscopic properties, reactivities, and electric conductivities of these systems.[2–11] Efforts have recently been devoted to the development of through-space π-interacting polymers with nonbonding π–π interactions, such as those in cyclophane-containing polymers[12] or between pendant aryl moieties.[13]

Recently, we developed a new class of folded stacking polymers that are prepared via the A_2+B_2 type polymerization of π-units and 1,3-diphenylpropane tethering groups **1** bearing a bulky substituent at the 2-position.[14] The tethering unit **1** promotes a predominant stacking-conformation of π-units (a closed form) in the polymers as shown in Scheme 1. As a result, polymers of type **P1,** derived from **1** and π modules, exhibit a folded *H*-type stacking form in the solution and in the solid form. Herein, we report the design and synthesis of new stair-like folded polymers ***st*-P2** and ***st*-P3** (Scheme 1). Polymers ***st*-P2** and ***st*-P3** have triphenyl stacking units **2** and stilbene-type stacking units **3** as tethering units, respectively, which are expected to have a stair-like (zigzag) π-stacking structure. It was found that these polymers exhibit unique optical properties that are probably the result of through-space π–π interactions.

EXPERIMENTAL

General Data

NMR spectra using $CDCl_3$ solutions were recorded at 500 and 600 MHz for ^{1}H and at 125 and 150 MHz for ^{13}C, respectively, on JEOL JMN-ECA500 and 600 spectrometers. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si ($\delta = 0.00$) or residual $CHCl_3$ ($\delta = 7.26$ for ^{1}H and $\delta = 77.0$ for ^{13}C NMR). IR spectra were recorded on an FT/IR 4100 (JASCO) and are reported in wave numbers (cm^{-1}). Ultraviolet (UV) absorption spectra were recorded with a SHIMADZU UV-2450 spectrophotometer. Fluorescence (FL) emission and excitation spectra were recorded with a SHIMADZU RF-5300PC or JASCO FP-6500 spectrophotometer. The M_n and M_w of polymers were measured with a TOSOH HLC-8020 GPC unit (eluent: tetrahydrofuran [THF]; calibration: polystyrene standards) using two TSK-gel columns (2× Multipore HXL-M). All reactions sensitive to oxygen and/or



SCHEME 1 Structure of folded *H*-stacking polymers (**P1**) and stair-like stacking polymers (***st*-P2** and ***st*-P3**).

moisture were performed under an argon atmosphere. Dry solvents were purchased from Kanto Chemicals.

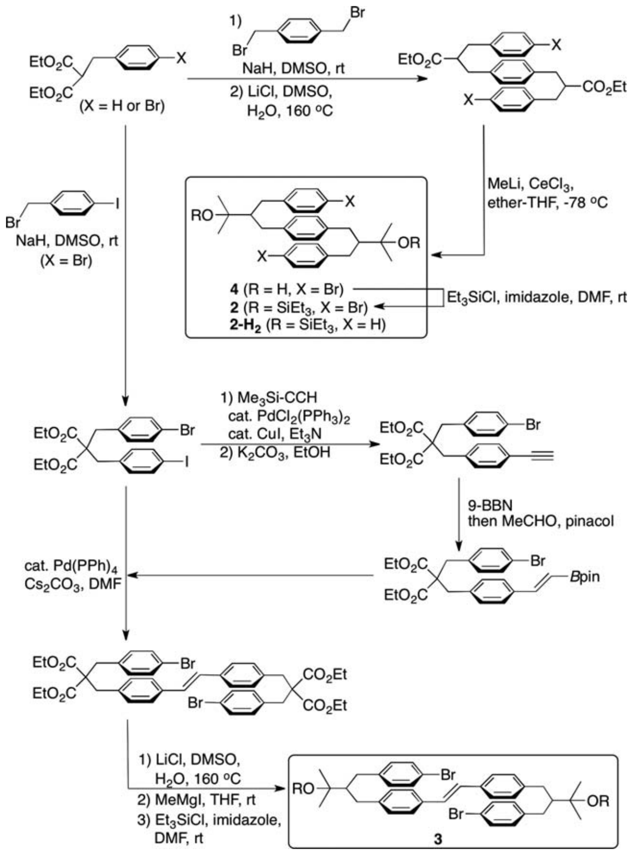
1,4-Bis(2-(4-bromobenzyl)-3-methyl-3-((triethylsilyl)oxy)butyl)benzene (2)

To a mixture of NaH (55 wt % in oil, 1.92 g, 44.0 mmol) and dimethyl sulfoxide (DMSO, 50 mL), a solution of diethyl 2-(4-bromobenzyl)malonate (15.1 g, 46.0 mmol) was added in DMSO (10 mL) at 0 °C. After stirring for 30 min, a solution of 1,4-*bis*(bromomethyl)benzene (5.28 g, 20.0 mmol) in DMSO (40 mL) was added and the mixture was stirred for 12 h at room temperature. After addition of saturated aqueous NH_4Cl, the mixture was extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated in vacuo, and chromatographed on silica gel to yield tetraethyl 2,2′-(1,4-phenylenebis(methylene))*bis*(2-(4-bromobenzyl)malonate) (11.4 g) in 75% yield. A mixture of the resulting tetraethyl 2,2′-(1,4-phenylenebis(methylene))*bis*(2-(4-bromobenzyl)malonate) (11.4 g, 15.0 mmol), LiCl (2.55 g, 60.0 mmol), H_2O (0.68 mL), and DMSO (25 mL) was heated to 160 °C for 7 h. After cooling to ambient temperature and addition of water, the mixture was extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated, and chromatographed on silica gel to give diethyl 3,3′-(1,4-phenylene)*bis*(2-(4-bromobenzyl)propanoate) (7.14 g) in 78% yield. To a solution of anhydrous $CeCl_3$ (14.3 g, 58.0 mmol) in THF (200 mL), a diethyl ether solution of MeLi (51.8 mL, 1.12 M, 58.0 mmol) was added at −78 °C. After stirring for 30 min at this temperature, a solution of diethyl 3,3′-(1,4-phenylene)*bis*(2-(4-bromobenzyl)propanoate) (7.14 g, 11.6 mmol) was added in THF (24 mL) and the mixture was stirred for 2 h at −78 °C. After addition of 10% aqueous acetic acid, the mixture was extracted with ethyl acetate. The organic layers were dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated, and chromatographed on silica gel to afford 4,4′-(1,4-phenylene)*bis*(3-(4-bromobenzyl)-2-methylbutan-2-ol) (**4,** 6.14 g) in 90% yield. To a mixture of the resulting **4** (2.94 g, 5.00 mmol), imidazole (1.36 g, 20.0 mmol), and *N,N*-dimethylformamide (DMF, 25 mL), triethylchlorosilane (2.51 mL, 15.0 mmol) was added at 0 °C and the mixture was stirred for 12 h at room temperature. After addition of saturated aqueous $NaHCO_3$, the mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated, and chromatographed on silica gel to provide the title compound **2** (3.19 g) as a mixture of *dl*- and *meso*-isomers in 78% yield.

^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 7.19$ (dd, 4H, $J = 2.4$, 8.4 Hz, Ar), 6.80 (d, 4H, $J = 8.4$ Hz, Ar), 6.80 (s, 4H, CH_2ArCH_2) 2.91–2.83 (m, 4H, CH_2Ar), 2.38–2.26 (m, 4H, CH_2Ar), 2.01–1.95 (m, 2H, $CHCH_2Ar$), 1.18 (s, 12H, $(CH_3)_2C$), 0.97 (t, 18H, $J = 7.8$ Hz, $(CH_3CH_2)_3Si$), 0.60 (q, 12H, $J = 7.8$ Hz, $(CH_3CH_2)_3Si$); ^{13}C NMR (150 MHz, $CDCl_3$) $\delta = 142.0$ (2C), 130.9, 130.7, 128.7, 118.9, 76.2, 54.9, 36.4, 35.9, 28.6, 28.2, 28.0, 7.3, 6.9; IR (neat) 2955, 2873, 1488, 1456, 1383, 1237, 1142, 1011, 773.4, 720.3 cm^{-1}; HR-MS: m/z = calcd For $C_{42}H_{64}Br_2NaO_2Si_2$ $[M+Na]^+$: 837.2709, found 837.2710.

1,4-Bis(2-(4-ethynylbenzyl)-3-methyl-3-((triethylsilyl)oxy)butyl)benzene (5)

To a mixture of **4** (2.94 g, 5.00 mmol), $PdCl_2(PPh_3)_2$ (280 mg, 0.400 mmol), CuI (76.2 mg, 0.400 mmol), PPh_3 (210 mg, 0.800 mmol), and THF (16.7 mL), triethylamine (7.14 mL) and ethynyltrimethylsilane (2.83 mL, 20.0 mmol) were added at room temperature. After stirring for 12 h at 80 °C and confirmation of completion of the reaction by thin-layer chromatography (TLC) analysis, saturated aqueous NH_4Cl was added to the mixture. The mixture was extracted with ethyl acetate and the organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of silica gel, and concentrated under reduced pressure. A mixture of the resulting residue, K_2CO_3 (∼0.1 g), MeOH (10 mL), and THF (5.0 mL) was stirred at room temperature. After confirming the completion of the reaction by TLC analysis (∼3 h), saturated aqueous NH_4Cl was added. The mixture was extracted with ethyl acetate and the organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated in vacuo, and chromatographed on silica gel to give 4,4′-(1,4-phenylene)*bis*(3-(4-ethynylbenzyl)-2-methylbutan-2-ol). To a mixture of the resulting 4,4′-(1,4-phenylene)*bis*(3-(4-ethynylbenzyl)-2-methylbutan-2-ol), imidazole (1.36 g, 20.0 mmol), and DMF (25 mL), chlorotriethylsilane (2.51 mL, 15.0 mmol) was added at 0 °C. After stirring for 12 h at room temperature, saturated



SCHEME 2 Synthesis of tethering units **2** and **3**.

aqueous $NaHCO_3$ was added. The mixture was extracted with diethyl ether and the organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated in vacuo, and chromatographed on silica gel to produce the title compound **5** (2.16 g) as a mixture of *dl*- and *meso*-isomers in 61% yield through three steps.

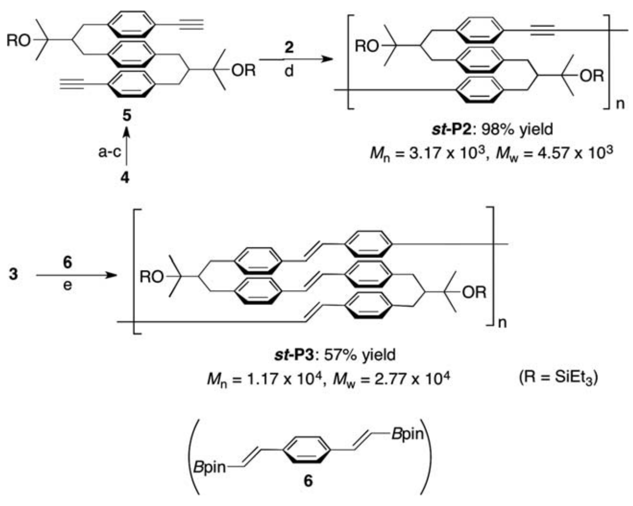
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.24 and 7.23 (2d, J = 7.8 Hz, 4H, Ar), 6.91 (br d, J = 7.8 Hz, 4H, Ar), 6.81 and 6.80 (2s, 4H, Ar), 2.99 (s, 2H, acetylenic H), 2.94–2.84 (m, 4H, CH_2), 2.43–2.37 (m, 2H, CH_2), 2.34–2.28 (m, 2H, CH_2), 2.04–1.99 (m, 2H, CH), 1.17 (s, 12H, CCH_3), 0.96 (t, J = 7.8 Hz, 18H, $SiCH_2CH_3$), 0.59 (q, J = 7.8 Hz, 12H, $SiCH_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.2, 139.5, 131.8, 128.9, 128.8, 118.8, 84.0, 76.2, 54.8, 36.6, 36.5, 36.3, 28.6, 28.5, 28.2, 7.2, 6.9; IR (neat) 3080, 2956, 2874, 1507, 1456, 1415, 1237, 1142, 1017, 719.3, 670.1 cm^{-1}; HR-MS: m/z = calcd For $C_{46}H_{66}KO_2Si_2$ $[M+K]^+$: 745.4238, found 745.4231.

(E)-1,2-Bis(4-(2-(4-bromobenzyl)-3-methyl-3-((triethylsilyl)oxy)butyl)phenyl)ethane (3)

To a mixture of diethyl 2-(4-bromobenzyl)-2-(4-iodobenzyl)-malonate (6.57 g, 11.5 mmol), (*E*)-diethyl 2-(4-bromobenzyl)-2-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl) benzyl)ma6lonate (5.45 g, 10.0 mmol), Cs_2CO_3 (6.52 g, 20.0 mmol), and DMF (44 mL), a solution of $Pt(PPh_3)_4$ (622 mg, 0.50 mmol) was added in DMF (22 mL) at room temperature. After stirring for 12 h at 120 °C and cooling to ambient temperature, saturated aqueous NH_4Cl was added and the mixture was extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated in vacuo, and chromatographed on silica gel to give (*E*)-tetraethyl 2,2′-((ethene-1,2-diylbis(4,1-phenylene))*bis*(methylene))*bis*(2-(4-bromobenzyl)malonate) (5.00 g) in 58% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.41 (d, J = 8.4 Hz, 1H, Ar), 7.39 (d, J = 8.4 Hz, 4H, Ar), 7.13 (d, J = 7.8 Hz, 4H, Ar), 7.05 (d, J = 7.8 Hz, 4H, Ar), 7.04 (s, 2H, alkene), 4.12 (br q, J = 7.2 Hz, 8H, CH_2O), 3.22 and 3.16 (2s, each 4H, CH_2), 1.17 (t, J = 7.2 Hz, 12H, CH_3).

A mixture of the resulting dibromide (4.31 g, 5.00 mmol), LiCl (1.70 g, 40.0 mmol), H_2O (0.36 mL), and DMSO (16.7 mL) was stirred for 12 h at 160 °C. After cooling to ambient temperature and addition of water, the mixture was extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated in vacuo, and chromatographed on silica gel to give (*E*)-diethyl 3,3′-(ethene-1,2-diylbis (4,1-phenylene))*bis*(2-(4-bromobenzyl)propanoate) (2.44 g) in 68% yield. To a solution of the resulting diester (3.59 g, 5.00 mmol) in THF (16.7 mL), MeMgI (1.46 M in diethyl ether, 41.1 mL, 60.0 mmol) was added at 0 °C and the mixture was stirred for 12 h at room temperature. After addition of aqueous 1 M of HCl, the mixture was extracted with ethyl acetate. The organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated in vacuo, and chromatographed on silica gel to give (*E*)-4,4′-(ethene-1,2-diylbis(4,1-phenylene))*bis*(3-(4-bromobenzyl)-2-methylbutan-2-ol) (2.25 g) in 73% yield. To a mixture of the resulting diol (3.45 g, 5.00 mmol), imidazole (1.36 g, 20.0 mmol), and DMF (25 mL), chlorotrimethylsilane (2.51 mL, 15.0 mmol) was added at 0 °C and the mixture



SCHEME 3 Synthesis of polymers ***st*-P2** and ***st*-P3**: *Reagents*: (a) Me_3SiCCH, $Cl_2Pd(PPh_3)_2$, CuI, Et_3N, THF; (b) K_2CO_3, MeOH, THF; (c) Et_3SiCl, imidazole, DMF; (d) $Pd(PPh_3)_4$, CuI, Et_3N, THF; and (e) $Pd(PPh_3)_4$, K_2CO_3, $(n\text{-}Bu)_4NBr$, THF.

was stirred for 12 h at room temperature. After addition of saturate aqueous $NaHCO_3$, the mixture was extracted with diethyl ether. The organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, concentrated in vacuo, and chromatographed on silica gel to give the title compound **3** (2.94 g) as a mixture of *dl*- and *meso*-isomers in 64% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28 (d, 4H, J = 7.8 Hz, Ar), 7.23 (d, 4H, J = 7.2 Hz, Ar), 6.97 (s, 2H, alkene), 6.94 (d, 4H, J = 8.4 Hz, Ar), 6.83 (d, 4H, J = 7.2 Hz, Ar), 2.99–2.89 (m, 4H, CH_2Ar), 2.40–2.33 (m, 4H, CH_2Ar), 2.08–2.03 (m, 2H, $CHCH_2Ar$), 1.22 (s, 12H, CCH_3), 0.98 (t, 18H, J = 8.1 Hz, $SiCH_2CH_3$), 0.61 (q, 12H, J = 7.4 Hz, $SiCH_2CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 141.79, 141.75, 134.9, 131.0, 130.7, 129.2, 127.7, 126.2, 119.0, 76.2, 54.9, 36.6, 28.2, 7.2, 6.8; IR (neat) 2953, 2873, 1488, 1456, 1237, 1178, 1143, 1011, 963.3, 720.3 cm^{-1}; HR-MS: m/z = calcd For $C_{50}H_{70}Br_2NaO_2Si_2$ $[M+Na]^+$: 939.3179, found 939.3150.

Synthesis of Polymer st-P2 from 2 and 5

To a mixture of **2** (245 mg, 0.300 mmol), $Pd(PPh_3)_4$ (34.7mg,0.0300 mmol), and CuI (5.71 mg, 0.0300 mmol), a solution of **5** (212 mg, 0.300 mmol) was added in THF (3.00 mL) and then Et_3N (1.50 mL) at room temperature and the mixture was stirred for 3 days at 80 °C. After cooling to ambient temperature and addition of saturated aqueous $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and then dried over Na_2SO_4. After filtration and evaporation, the residues were dissolved in CH_2Cl_2 and poured into a large amount of MeOH. The solvents were decanted and the precipitated polymer was washed several times with diethyl ether and dried under reduced pressure. Polymer ***st*-P2** (401 mg) was obtained in 98 % yield as a light yellow viscosity solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28–7.16 (br m, overlap with $CHCl_3$ peak, Ar), 7.00–6.88 (br m, Ar), 6.88–6.76 (br m, Ar), 3.00–2.87 (br m, 4H, CH_2Ar), 2.50–2.26 (br m, 4H, CH_2Ar), 2.08–1.96 (br, 2H, $CHCH_2Ar$), 1.17 (br s, 12H, CCH_3), 0.97–0.91 (br m, 18H, $(CH_3CH_2)_3Si$), 0.59–0.52 (br m, 12H, $(CH_3CH_2)_3Si$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.7, 143.34, 143.3, 142.0, 139.6, 139.5, 139.4, 139.3, 132.1, 131.2, 130.9, 130.7, 129.0, 128.8, 120.3, 118.9, 88.9, 76.3, 76.2, 54.9, 36.6, 36.4, 36.3, 36.0, 28.6, 28.5, 28.4, 28.3, 28.2, 28.1, 7.2, 6.9; IR (neat) 3046, 2958, 2875, 1606, 1513, 1458, 1414, 1383, 1365, 1260, 1143, 1107, 1017, 801.3, 742.5, 723.2 cm^{-1}; M_n = 3.17×10^3, M_w = 4.57×10^3, polydispersity index (PDI) = 1.44 based on Gel permeation chromatography (GPC) analysis (polystyrene standard).

Synthesis of Polymer st-P3 from 3 and 1,4-Bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl) benzene (6)

To a mixture of **3** (408 mg, 0.500 mmol), tetra-*n*-buthylammonium bromide (161 mg, 0.500 mmol), **6** (191 mg, 0.500 mmol), THF (1.67 mL), and aqueous 2 M K_2CO_3 (1.0 mL), a solution of $Pd(PPh_3)_4$ (23.1 mg, 0.0200 mmol) was added in THF (1.67 mL) at room temperature. The mixture was stirred for 3 days at 80 °C. After cooling to ambient temperature and addition of saturated aqueous $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, dried over Na_2SO_4, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and then dried over Na_2SO_4. After filtration and evaporation, the residue was dissolved in CH_2Cl_2 and poured into a large amount of MeOH. The solvents were decanted and the precipitated polymer was washed several times with diethyl ether and dried under reduced pressure. Polymer ***st*-P3** (0.275 g) was obtained in 70 % yield as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.45–7.17 (br m, overlap with $CDCl_3$ peak, 10H, Ar), 7.09–6.78 (br, 12H, Ar and CH=CH), 2.95–2.81 (br, 4H, CH_2Ar), 2.48–2.30 (br, 4H, CH_2Ar), 2.07–2.01 (br, 2H, $CHCH_2Ar$), 1.23–1.05 (br, 12H, $(CH_3)_2C$), 1.03–0.86 (br m, 18H, $(CH_3CH_2)_3Si$), 0.65–0.50 (br, 12H, $(CH_3CH_2)_3Si$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 136.7, 131.8, 129.3, 128.9, 128.4, 127.1, 126.6, 126.2, 76.3, 55.0, 36.3, 28.3, 7.2, 6.9; IR (neat) 3022, 2953, 2874, 1514, 1458, 1383, 1365, 1143, 1040, 1016, 818.6, 741.5, 723.2 cm^{-1}; M_n = 1.61×10^4, M_w = 3.50×10^4, PDI = 2.16 based on GPC analysis (polystyrene standard).

RESULTS AND DISCUSSION

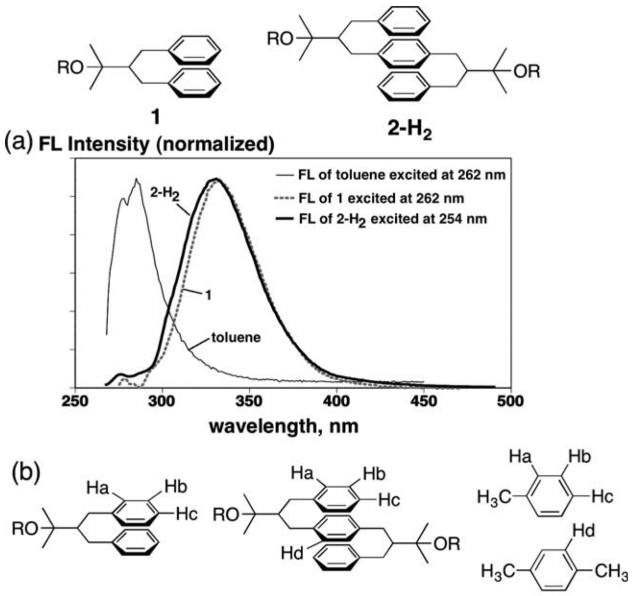
Synthesis

The requisite tethering units **2** and **3** were readily synthesized starting from diethyl α-(4-bromophenylmethyl)-malonate[14] via the α-alkylation of the malonate and selective Sonogashira and Suzuki–Miyaura coupling reactions (Scheme 2). As a model compound, **2-H$_2$** (X = H) was also prepared similarly.

With the tethering units **2** and **3** in hand, polymers ***st*-P2** and ***st*-P3** (Scheme 3) were synthesized. The dibromotriphenyl unit **2** was polymerized with diethynyl-triphenyl unit **5**, which was derived from **4**, via a Sonogashira coupling reaction to furnish ***st*-P2** (M_n = 3.17×10^3, M_w = 4.57×10^3: determined by GPC, eluent: THF, calibration: polystyrene standards) in 98% yield after reprecipitation from THF using methanol. Polymer ***st*-P3** (M_n = 1.17×10^4, M_w = 2.77×10^4: determined by GPC, THF/polystyrene standards) was obtained in 57% yield via the Suzuki coupling polymerization of unit **3** and bis-boryl compound **6**.

Conformational Analysis of Triphenyl Compound 2

Our previous study on conformational analyses of 2-substituetd 1,3-diphenylpropane **1** using FL, ^{1}H NMR measurement, and MM2 calculation clarified that **1** superiorly exists in a closed (stacked) conformation in solution.[14] We carried out a similar investigation for elucidating the conformation of compound **2-H$_2$**, a model compound for a tethering unit of polymer ***st*-P2**. Figure 1(a) compares the FL properties of toluene, diphenyl stacking compound **1** (X = H), and triphenyl unit **2-H$_2$**. Both **1** and **2-H$_2$** exhibited only a benzene-excimer emission ($\lambda_{em\ max}$ =332 nm for **1** and 331 nm for **2-H$_2$**) without FL from a single benzene ring ($\lambda_{em\ max}$ =285 nm



	Chemical Shifts (ppm)			
	Ha	Hb	Hc	Hd
1	6.98	7.14	7.07	—
Toluene	7.18	7.26	7.16	—
2-H$_2$	6.98	7.12	7.05	6.80
p-Xylene	—	—	—	7.04

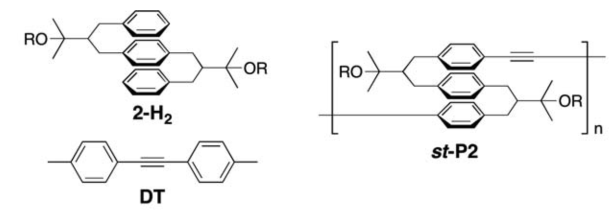
FIGURE 1 (a) Normalized FL spectra of **1, 2-H$_2$,** and toluene. Excited at 254 nm (**2-H$_2$,** 10^{-4} M), 262 nm (**1,** 10^{-4} M), and 262 nm (toluene, 2 × 10^{-5} M) in CH_2Cl_2. (b) Comparison of the chemical shifts of the aromatic protons of **1, 2-H$_2$,** toluene, and *p*-xylene ($CDCl_3$, 500 MHz).

for toluene). This result indicates that compounds **1** and **2-H$_2$** preferentially exist in a π–π stacked conformation in the excited state. As evident from the results of ^{1}H-NMR analyses of **1** and **2-H$_2$** [Fig. 1(b)], the aromatic protons are shifted up-field compared to those of toluene and *p*-xylene owing to the shielding effect in the stacked form in the ground state.[14] Therefore, these data suggest that triphenyl compound **2-H$_2$** exists predominantly in a folded (stacked) conformation in the ground and excited states.

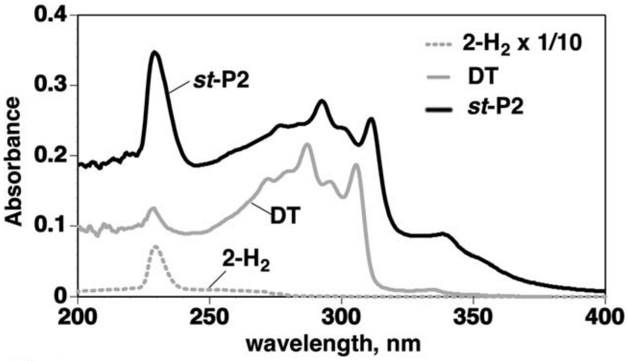
Properties of Polymer *st*-P2

Next, we investigated the optical properties of polymer ***st*-P2**. Figure 2 shows the UV absorption and FL spectra of ***st*-P2** along with those of **2-H$_2$** and di(4-tolyl)acetylene (**DT**) in CH_2Cl_2. **2-H$_2$** and **DT** are model compounds for the structure components of ***st*-P2**. The UV and FL spectra of **DT** and ***st*-P2** were each measured using a 10^{-5} M solution, whereas those of **2-H$_2$** were obtained using a 10^{-4} M solution. The concentration (M) of ***st*-P2** was adjusted such that the concentration of the repeated unit was 10^{-5} M. To compare their properties, the resulting absorbance and FL intensity values were adjusted to be 10^{-5} M of tolan or triphenyl unit concentration. In these solutions, intermolecular interaction (an aggregation effect) can be ruled out, because the UV absorbance linearly increased as the concentration increased in the range of 10^{-6}–10^{-4} M. The FL quantum yields of **DT** and ***st*-P2** were determined by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi_F = 0.442$).[15] The results are summarized in Table 1.

UV spectra of ***st*-P2** consisted of absorptions based on benzene ring and dialkyltolan units, and the absorbance was enhanced compared with those of **2-H$_2$** and **DT**. Absorption spectra by tolan units of ***st*-P2** (λ_{max} = 293 nm (log ε = 4.44), 311 nm (log ε = 4.40)) had a similar shape but red-shifted about 5 nm compared with that of **DT**. In addition, it is noteworthy that an additional broadened absorption band appeared at lower energy (320–400 nm) in the spectrum of ***st*-P2**. As mentioned above, as intermolecular interaction was ruled out at the concentration used for the analysis, this result suggests that extended conjugation via through-space interactions with the triphenyl stacking units might exist.



(a) UV Absorption



(b) Fluorescence

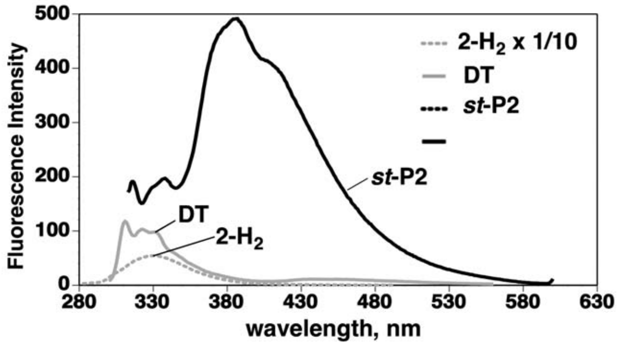


FIGURE 2 UV absorption and FL spectra of **2-H$_2$, DT,** and ***st*-P2.** UV absorption: **2-H$_2$** (10^{-4} M), **DT** (10^{-5} M), and ***st*-P2** (10^{-5} M) in CH_2Cl_2. FL: excited at 254 nm (**2-H$_2$,** 10^{-4} M), 287 nm (**DT,** 10^{-5} M), and 305 nm (***st*-P2,** 10^{-5} M) in CH_2Cl_2.

TABLE 1 Optical Properties of 2-H_2, DT, and Polymer *st*-P2

	UV λ_{max}[a] (nm)		FL λ_{max}[a] (nm)	
Compound	In Solution (log ε)	Film	In Solution (Φ_F[c])	Film
2-H_2	230 (3.85)	–	331	–
DT	229 (4.10), 287 (4.33), 306 (4.27)	–	311 (0.001)[d]	–
Polymer ***st*-P2**	229 (4.54), 293 (4.44), 311 (4.40)	293, 312	386 (0.016)[e]	450

[a] Absorption and emission spectra were recorded in dilute CH_2Cl_2 solutions at room temperature.

[b] The sample solutions were excited at 254, 287, and 305 nm for **2-H_2**, **DT**, and ***st*-P2**, respectively. Film of ***st*-P2** was excited at 313 nm.

[c] The quantum yield (Φ_F) was calculated based on the measurements of 10^{-5} M CH_2Cl_2 solutions by using 9-anthracenecarboxylic acid as a standard.

[d] Excited at 287 nm.

[e] Excited at 293 nm.

Figure 2(b) shows the FL spectra of these compounds. **2-H_2** exhibited benzene-excimer emission at approximately 330 nm. Polymer ***st*-P2** exhibited a smaller benzene-excimer emission and a smaller emission from a single tolan moiety, and the spectra was largely red-shifted ($\lambda_{max} = 386$ nm) and its intensity ($\Phi_F = 0.016$) remarkably increased compared with that of **DT** ($\Phi_F = 0.001$). These results can be attributed to the overlapping of the benzene-excimer emission region (nearly, 330 nm) with that of the lower-energy absorption band of ***st*-P2**. The bathochromic shift of the emission of ***st*-P2** may originate from the extended conjugation via through-space interaction owing to a stacking structure in the stair-like folded polymer.

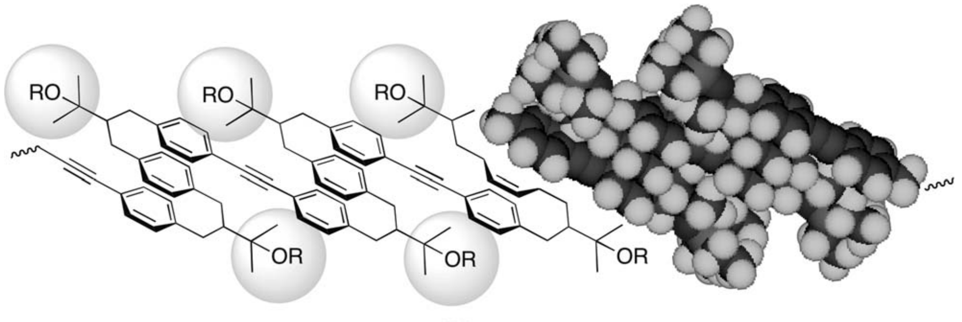
The space-filling model shown in Figure 3 is the result of molecular mechanics calculation (MM2) (nonsolvent conditions) for a part of ***st*-P2**. It indicates the folded stair-like structure as a superior conformation.

The FL of ***st*-P2** was further red-shifted in the film form [Fig. 4(a)], and the absorption and excitation spectra of the film showed an additional broad absorption band nearly 400 nm that is not present in the UV spectrum of the polymer in the solution. This increase in the absorption at lower energy may be attributed to intramolecular through-space interactions as well as intermolecular interactions via aggregation. X-ray diffraction (XRD) analysis of polymer powder peeled from the dried film, prepared by spin-coating on a glass substrate and removing the solvent, was carried out for the samples of ***st*-P2** [Fig. 4(b)]. It showed broad spectra without any sharp peak, and therefore a solid of ***st*-P2** had no crystalline form.

In summary, skipped-π polymer ***st*-P2,** comprising phenylene and phenylene–ethynylene–phenylene units connected by trimethylene tethers, exhibited largely red-shifted, broadened UV absorption and red-shifted FL emission compared with those of dimethyltolan (**DT**). It can be concluded that these properties are attributed to the extended conjugation via through-space interactions owing to a stair-like stacking structure.

Properties of Polymer st-P3

Next, the optical properties of stilbene-type polymer ***st*-P3** were investigated. Figure 5 compares the UV absorption and FL spectra of ***st*-P3** with those of model compounds 4, 4′-dimethylstilbene (**DMeSt**) and 1,4-*bis*((*E*)-4-methylstyryl)-benzene (**BSt**) in CH_2Cl_2. The UV spectra were each measured using a 10^{-6} M solution, whereas FL spectra were measured using a 10^{-7} M solution. The concentration (M) of ***st*-P3** was adjusted such that the concentration of the repeated unit was 10^{-6} or 10^{-7} M. In these solutions, intermolecular interaction (an aggregation effect) can be ruled out, because the UV absorbance linearly increased as the concentration increased in the range of 10^{-7}–10^{-5} M. The results are summarized in Table 2.



***st*-P2**

FIGURE 3 The space-filling model based on the result of molecular mechanics calculation (MM2) (nonsolvent conditions) for a part of ***st*-P2**.

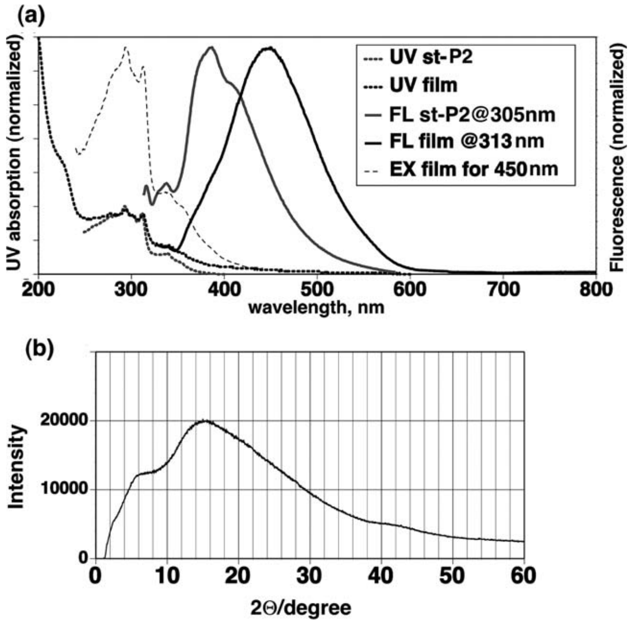
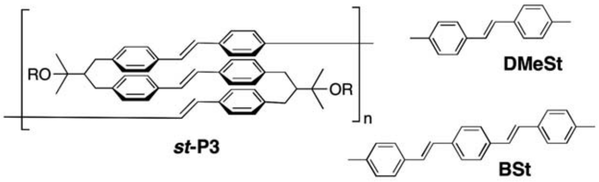
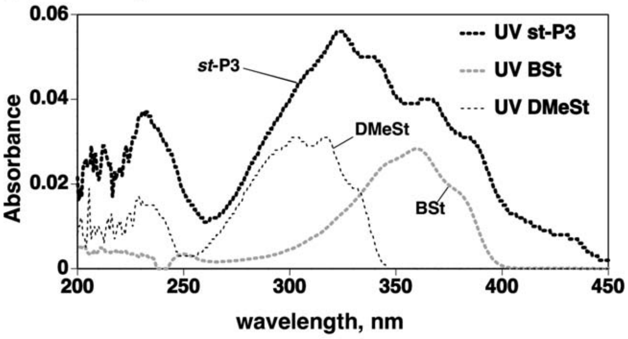


FIGURE 4 (a) Normalized UV absorption, FL, and excitation spectra of a CH_2Cl_2 solution (10^{-5} M) and a film of ***st*-P2**. (b) XRD analysis of polymer powder peeled from the film of ***st*-P2**.



(a) UV absorption



(b) Fluorescence (normalized)

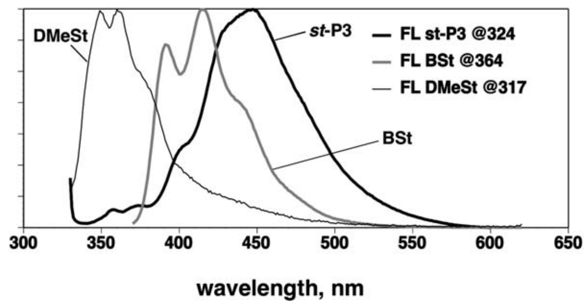


FIGURE 5 UV absorption and normalized FL spectra of **BSt, DMeSt,** and ***st*-P3**. (a) UV absorption: **BSt** (10^{-6} M), **DMeS** (10^{-6} M), and ***st*-P3** (10^{-6} M) in CH_2Cl_2. (b) FL: excited at 364 nm (**BSt,** 10^{-7} M), 324 nm (**DMeS,** 10^{-7} M), and 317 nm (***st*-P3,** 10^{-7} M) in CH_2Cl_2.

TABLE 2 Optical Properties of DMeSt, BSt, and Polymer *st*-P3

Run	Compound	UV λ_{max}[a] (nm) In Solution (log ε)	FL λ_{max}[a] (nm) In Solution (Φ_F[c])
1	**DMeSt**	303 (4.49), 317 (4.47)	360 (0.104)[d]
2	**BSt**	360 (4.45)	414 (0.884)[e]
3	Polymer ***st*-P3**	324 (4.75), 364 (4.60),	447 (0.207)[f]

[a] Absorption and emission spectra were recorded in dilute CH_2Cl_2 solutions at room temperature.
[b] The sample solutions were excited at 324, 364, and 317 nm for **DMeSt**, **BSt**, and ***st*-P3**, respectively.
[c] The quantum yield (Φ_F) was calculated based on the measurements of 10^{-7} M CH_2Cl_2 solutions by using 9-anthracenecarboxylic acid as a standard.
[d] Excited at 303 nm.
[e] Excited at 360 nm.
[f] Excited at 324 nm.

Similar to ***st*-P2,** polymer ***st*-P3** exhibited a unique absorption band in the lower energy region (>400 nm) which cannot be explained by superimposing the spectra of **DMeSt** and **BSt** [Fig. 5(a)]. A largely red-shifted emission of ***st*-P2** was also observed compared with those of the structural π-components (**DMeSt** and **BSt**) [Fig. 5(b)]. Therefore, it can be concluded again that these properties may be attributed to a through-space π–π interaction that arises from the folded conformation of the polymer.

CONCLUSIONS

We synthesized novel skipped-π polymers in which π-components are connected with 2-substituted trimethylene tethering units and demonstrated that their stair-like stacking structure resulted in unique photophysical properties. The stair-like stacking polymers ***st*-P2** and ***st*-P3** exhibited bathochromically shifted, broadened UV absorption behavior involving unique lower-energy absorption bands and largely red-shifted FL emission. These results suggest that through-space π–π interactions owing to the stacking substructure in these polymers extend the π-conjugation of the components in the ground and excited states. As the photophysical properties of the polymers observed both in the solution and in the dried films are similar to those of *J*-aggregates of π-molecules, these polymers may be considered as pseudo *J*-stacking (or *J*-like-stacking) polymers. UV-absorbing and fluorescent polymers are important as functional macromolecules with various prospective applications.[16–20] Further investigations to determine a more detailed mechanism of the optical properties and the potential applications of this type of polymer, such as hole transporting or nonlinear optical materials, are underway in our laboratories.

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