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Phenyleneethynylene- and Thienyleneethynylene-Based π-Conjugated Polymers with Imidazolium Units in the Main Chain

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ABSTRACT: Phenyleneethynylene-based and thienyleneethynylene-based π-conjugated polymers with imidazolium cationic units in the main chain and their model compounds were synthesized and characterized. The imidazolium-containing cationic polymers were transferred to an ionic liquid by the spontaneous anion-exchange from iodide to bis(trifluoromethanesulfonyl)imide (TFSI). The fluorescence quantum yield of phenyleneethynylene-based π-conjugated polymer in the ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (emimTFSI), was higher than that of polymer based on iodide anion in pyridine because of a low degree of aggregation of the main chain and/or the absence of an external heavy-atom effect of the iodide counteranion. UV−vis and fluorescence spectra of N-methylated polymer and model compound with TFSI counteranion exhibited a significant blue shift with respect to the parent neutral molecules. Density functional theory (DFT) calculations for the model compounds showed a decrease in π-conjugation by quaternization of the N-position at the imidazole unit, supporting the blue shift observed for UV−vis and fluorescence spectra. The quaternization of the N-position at the imidazole unit in the thienyleneethynylene-based π-conjugated polymers and model compounds resulted in a red shift of the UV−vis absorption and fluorescence spectra compared with those of neutral polymers and model compounds. The DFT results suggest that the red shift comes from the contribution of coplanarization in the quaternized π-conjugated compounds.

Introduction

In the past two decades, π-conjugated oligomers and polymers have been widely studied for functional and practical applications such as light source,[1] electronic devices,[2] and sensors.[3] Considerable effort has been made for the design and synthesis of functional π-conjugated oligomers and polymers whose electronic properties can be modulated with external stimuli. Because their electrical and optical properties are largely determined dominantly with the expansion of π-conjugation systems on the main chains, modulation of the coplanarity in the π-conjugated main chain and bond alternation by means of photoirradiation and chemicals has been studied.[4,5] In this regard, π-conjugated polymers with heteroaromatic units containing imine nitrogen, for example, thiazole,[6] pyridine,[7] and benzimidazole,[8] in their main chain have been attracting considerable interest because their properties can be modulated by metal binding, protonation, or quaternization at the N-position. For example, Curtis et al. demonstrated that optical and electrical properties of π-conjugated polymers with thiazolium units obtained by *N*-alkylation of the thiazole ring in the main chain are considerably different from those of the corresponding neutral thiazole-based polymers.[9] Swager et al. investigated conducting polymers containing pyridinium units in the main chain.[10] The quaternization of the pyridine to pyridinium provided polymers with longer effective π-conjugation lengths by stretching their conformation and subsequently with high electrical conductivity. From this point of view, quaternization of the N-position would afford a new route toward charged π-conjugated backbones that have specific electrical and optical properties.

Imidazole is an aromatic heterocycle containing imine nitrogen, which acts as an important building unit for biomolecules and has attractive chemical properties such as formation of coordination compounds and effective nitrogen bonding.[11] Therefore, it is considered to be a building unit for π-conjugated molecular and polymer systems in recent studies.[12,13] Imidazole is easily converted into imidazolium cation, which has a cationic charge by protonation or quaternization of the N-position similar to thiazole and pyridine. The imidazolium ring, a cationic N-heteroaromatic ring containing quaternized nitrogen atom, has thus been interested as a building block for self-assembled, supramolecular systems and specific ion/photomodulation units.[14] It is also recognized as the most popular structure for the cationic moiety of ionic liquids. In the field of conjugated polymers, Leclerc et al. demonstrated that polythiophene derivatives with imidazolium units in the side chain could be used to detect iodide anions[15] and nucleic acids by fluorescence signal amplification.[16] Yamamoto et al. reported π-conjugated polymers with imidazole units in the main chain.[13] The optical properties of poly(imidazole)s could be modulated by the addition of acid, indicating modulation of the conjugation length upon quaternization by protonation. In their report, however, the degree of the protonation was not high enough because of Coulombic repulsive interaction between the neighboring imidazolium positive charges. Quaternization at the N-position, especially N-alkylation, in imidazole-based polymer is also expected to modulate its optical properties. However, π-conjugated polymers, particularly those with *N*,*N*′-dialkylated imidazolium units in the main chain, have never been studied to the best of our knowledge.

Here we report the preparation and optical properties of phenyleneethynylene-based and thienyleneethynylene-based

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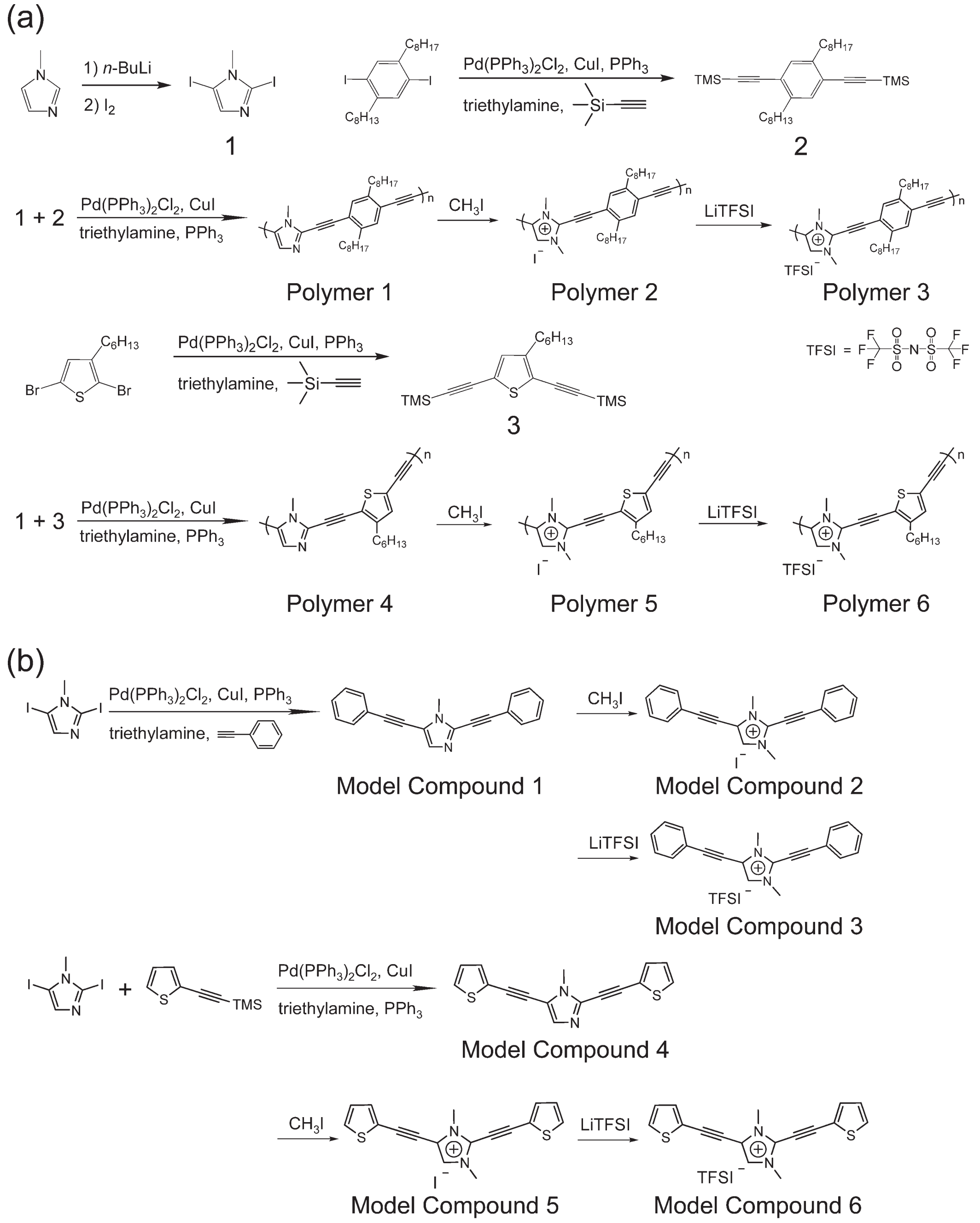
Scheme 1. (a) Syntheses of Monomers and Polymers and (b) Syntheses of Model Compounds



π-conjugated polymers with imidazolium units in their main chain. Model compounds that have monomeric unit structures of corresponding polymers were also synthesized to discuss the effect of cationic charge on their electronic structures by means of theoretical calculations. Chemical structures of polymers and their model compounds studied here are shown in Scheme 1. For the phenyleneethynylene-based π-conjugated polymers and model compounds, a characteristic blue shift in the optical band upon the quaternization of imidazole-1,5-yl units to imidazolium is observed, and the effects of the quaternization on the bond alternation in the imidazole/imidazolium units are discussed. Thienyleneethynylene-based π-conjugated polymers and their model compounds show a characteristic red shift by introducing cationic imidazolium units into the main chain. Furthermore, DFT calculations in the B3LYP/DGDZVP level for some model compounds are performed, and the origins of spectral shifts upon quaternization are discussed.

Experimental Section

General. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a JEOL JNM-AL300 instrument. High-resolution mass spectroscopy (HRMS) data were recorded by JEOL JMS-700 MStation. Elemental analyses were performed for C, H, and N by a Perkin-Elmer 2400 II CHNS/O instrument. UV−vis spectra were obtained on JASCO V-550 and V-650 spectrophotometers. X-ray crystal structure was given by the use of a Rigaku R-AXIS RAPID/S apparatus. Fluorescence spectra were recorded on a JASCO FP-6500 fluorescence spectrophotometer. Absolute fluorescence quantum yields of polymers and model compounds were measured using a Hamamatsu C9920-02 apparatus. All spectroscopic measurements were performed at the 10^{-6} M level at room temperature. Gel permeation chromatography (GPC) was carried out (COSMO SIL 5GPC-60 Waters column, particle size: 5 μm, pore size: 60 Å) using tetrahydrofuran (THF) as an eluent with a flow rate of

3.0 mL/min at room temperature using polystylene standard as a calibrant (detector: JASCO UV-2086). FT-IR spectra were recorded on a JASCO FT/IR-4200 instrument using the KBr matrix.

Materials. The compounds 1-methylimidazole (Wako, >98%), iodine (Wako, >99.8%), iodomethane (Wako, >95%), trimethylsilylacetylene (TCI, >98%), ethynylbenzene (TCI, >97%), 2-trimethylsilylethynylthiophene (Aldrich, >97%), 2,5-dibromo-3-hexylthiophene (Aldrich, >97%), 1,4-diiodo-2,5-dioctylbenzene (Aldrich, >99%), lithium bis(trifluoromethanesulfonyl)imide (Kanto Chemical, >99.7%), *N*,*N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide (Kanto Chemical, >99.7%), and polystylene standard (Chemco Scientific) were used as received without further purification. Anhydrous THF and ether were obtained by distillation with the standard Na−benzophenone system.

Synthesis. *1-Methyl-2,5-diiodoimidazole* (***1***). 1-Methylimidazole (8.6 g, 0.11 mol) was added over 20 min to a well-stirred solution of tetramethylethylenediamine, TMEDA (30.0 g, 0.26 mmol), and *n*-BuLi (160 mL, 1.6 M in hexane, 0.25 mol) under nitrogen at −20 °C. The stirred mixture was warmed to 20 °C for 1 h and diluted with 300 mL of anhydrous THF and cooled to −65 °C. A solution of iodine (70 g, 0.28 mol) in 300 mL of anhydrous THF was added over 90 min. The stirred mixture was warmed to 20 °C over 10 h. The reaction was quenched by the addition of ethyl acetate (50 mL), water (50 mL), dichloromethane (250 mL), and saturated Na_2SO_3 solution (180 mL). The organic layer was separated and dried over $MgSO_4$, and the solvent was removed to provide a crude product as a brown solid. The product was crystallized from acetonitrile to yield 9.5 g (yield: 25%) of a white crystal. ^1H NMR ($CDCl_3$, δ): 3.67 (3H, s, CH_3-N), 7.18 (1H, s, imidazole-*H*). ^{13}C NMR ($CDCl_3$, δ): 37.7 (CH_3-N), 71.8, 89.9, 139.9 (imidazole).

1,4-Bis-octyl-2,5-bis-trimethylsilylethynylbenzene (***2***). A mixture of 1,4-diiodo-2,5-dioctylbenzene (1.0 g, 1.8 mmol), trimethylsilylacetylene (0.70 g, 7.1 mmol), CuI (35 mg, 0.18 mmol), PPh_3 (0.12 g, 0.44 mmol), and triethylamine (15 mL) was stirred in 5 mL of anhydrous THF. After N_2 bubbled for 20 min, $Pd(PPh_3)_2Cl_2$ (0.13 g, 0.18 mmol) was added, and the solution was heated overnight at 70 °C. The reaction mixture was poured into brine and extracted with chloroform. The organic layer was washed with brine several times and dried over $MgSO_4$. After the removal of the solvent, the crude product was purified with the alumina column chromatography using hexane as an eluent to yield 0.56 g (yield: 63%) of yellow oil. ^1H NMR ($CDCl_3$, δ): 0.25 (18H, s, CH_3-Si), 0.88 (6H, m, CH_3-). 1.30 (20H, m, $-CH_2-$) 1.59 (4H, m, $-CH_2-$), 2.67 (4H, t, $-CH_2$-phenyl), 7.24 (2H, s, phenyl-*H*). ^{13}C NMR ($CDCl_3$, δ): 0.0 (CH_3-Si), 14.1, 22.7, 29.3, 29.5, 29.6, 30.6, 31.9, 34.2 (alkyl), 98.9, 104.0 (alkyne), 122.6, 132.5, 142.7 (phenyl). EI-HRMS (*m*/*z*) Calcd for $C_{32}H_{54}Si_2$ [M^+]: 494.3800. Found: 494.3760.

2,5-Bis-trimethylsilylethynyl-3-hexylthiophene (***3***). A mixture of 2,5-dibromo-3-hexylthiophene (1.0 g, 3.1 mmol), trimethylsilylacetylene (0.69 g, 7.0 mmol), CuI (35 mg, 0.18 mmol), PPh_3 (0.10 g, 0.37 mmol), and triethylamine (10 mL) was stirred in 5 mL of anhydrous THF. After N_2 bubbled for 20 min, $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol) was added and heated overnight at 50 °C. The reaction mixture was poured into brine and extracted with chloroform. The organic layer was washed with brine several times and dried over $MgSO_4$. After the removal of the solvent, the crude product was purified with the alumina column chromatography using hexane as an eluent to yield 1.7 g (yield: 75%) of colorless oil. ^1H NMR ($CDCl_3$, δ): 0.20 (18H, s, CH_3-Si), 0.88 (3H, t, CH_3-). 1.29 (6H, m, $-CH_2-$) 1.55 (2H, m, $-CH_2-$), 2.63 (2H, t, $-CH_2-$thiopene), 6.95 (1H, s, thiophene-*H*). ^{13}C NMR ($CDCl_3$, δ): −0.13 (CH_3-Si), 22.6, 28.8, 29.4, 29.9, 31.6 (alkyl), 97.0, 97.5, 99.4, 101.9 (alkyne), 120.0, 123.0, 133.4, 148.4 (thiophene).

Polymer 1 (***P1***). A mixture of 1-methyl-2,5-diiodoimidazole **1** (0.19 g, 0.56 mmol), 1,4-bis-octyl-2,5-bis-trimethylsilylethynylbenzene **2** (0.28 g, 0.56 mmol), CuI (5.8 mg, 0.030 mmol), tetrabutylammonium fluoride (1.5 mL), PPh_3 (71 mg, 0.26 mmol), and triethylamine (2 mL) was stirred in 5 mL of anhydrous THF. After N_2 bubbling for 20 min, $Pd(PPh_3)_2Cl_2$ (80 mg, 0.11 mmol) was added and heated at 70 °C under a N_2 atmosphere for 24 h. The reaction mixture was then cooled and poured into a large amount of methanol to precipitate the polymer. The resulting precipitate was filtered, washed with methanol and dried in vacuo to give 0.15 g (yield: 58%) as a yellow powder. ^1H NMR ($CDCl_3$, δ): 0.88 (6H, br, $-CH_3$), 1.27 (20H, br, $-CH_2-$). 1.69 (4H, br, $-CH_2-$) 2.80 (4H, br, $-CH_2$-phenyl), 3.86 (3H, br, CH_3-N), 7.26−7.42 (2H, br, phenyl-*H*), 7.85 (1H, br, imidazole-*H*). FT-IR (KBr, cm^{-1}): 2201 (s, ν (C≡C)), 2851 (s, ν (CH_2)), 2924 (s, ν (CH_2)), 2960 (s, ν (CH_2)). $M_n = 1.1 \times 10^4$, PDI = 2.6.

Polymer 2 (***P2***). A mixture of **P1** (50 mg, 0.11 mmol/monomer unit) and iodomethane (10 g, 70 mmol) was stirred and refluxed at 40 °C for 15 h. After the removal of the solvent, the crude product was washed with chloroform and methanol many times and dried in vacuo to yield 60 mg (yield: 93%) of a dark-reddish solid. ^1H NMR (DMSO-d_6, δ): 0.85 (6H, br, $-CH_3$), 1.24 (20H, br, $-CH_2-$), 1.65 (4H, br, $-CH_2-$), 2.84 (4H, br, $-CH_2$-phenyl), 4.02 (6H, br, CH_3-N), 7.77 (2H, br, phenyl-*H*), 8.44 (1H, br, imidazole-*H*). FT-IR (KBr, cm^{-1}): 2211 (s, ν (C≡C)), 2852 (s, ν (CH_2)), 2925 (s, ν (CH_2)), 2951 (s, ν (CH_2)).

Polymer 3 (***P3***). **P2** (20 mg, 0.034 mmol) was dissolved in 10 mL of pyridine. Distilled water (10 mL) dissolved LiTFSI (1.0 g, 3.5 mmol) was added and stirred for 20 h at room temperature. An ionic liquid (5 mL), emimTFSI, was added, and pyridine was removed by evaporation and dried in vacuo. The ionic-liquid-dissolving polymer was washed with distilled water many times until a yellowish-white turbidity of the residual water disappeared through dropping silver nitrite aqueous solution to confirm the complete anion-exchange and dried in vacuo after the removal of water.

Polymer 4 (***P4***). A mixture of 1-methyl-2,5-diiodoimidazole **1** (0.46 g, 1.4 mmol), 2,5-bis-trimethylsilylethynyl-3-hexylthiophene **3** (0.50 mg, 1.4 mmol), CuI (40 mg, 0.22 mmol), tetrabutylammonium fluoride (1.0 mL), PPh_3 (0.10 g, 0.38 mmol), and triethylamine (4 mL) was stirred in 4 mL of anhydrous THF. After N_2 bubbling for 20 min, $Pd(PPh_3)_2Cl_2$ (0.30 g, 0.44 mmol) was added and refluxed at 70 °C under a N_2 atmosphere for 4 days. The reaction mixture was then cooled and poured into a large amount of methanol to precipitate the polymer. The resulting precipitate was filtered, washed with methanol. and washed with acetone on a Soxhlet extraction apparatus to give 0.27 g (yield: 63%) as a red powder. ^1H NMR (DMSO-d_6, δ): 0.72 (3H, br, $-CH_3$), 1.03 (8H, br, $-CH_2-$), 1.61 (2H, br, $-CH_2$-thiopene), 4.01 (3H, br, CH_3-N), 7.41 (2H, br, thiophene-*H*, imidazole-*H*). FT-IR (KBr, cm^{-1}): 2200 (s, ν (C≡C)). $M_n = 4.9 \times 10^3$, PDI = 3.5.

Polymer 5 (***P5***). A mixture of **P4** (50 mg, 0.15 mmol/monomer unit) and iodomethane (10 g, 70 mmol) was stirred and refluxed at 40 °C for 20 h. After the removal of the solvent, the crude product was washed with chloroform and methanol many times and dried in vacuo to yield 62 mg (yield: 92%) of a red powder. ^1H NMR (DMSO-d_6, δ): 0.75 (3H, br, $-CH_3$), 1.08−1.21 (8H, br, $-CH_2-$), 1.76 (2H, br, $-CH_2$-thiophene), 4.15 (6H, br, CH_3-N), 7.77 (2H, br, thiophene-*H*, imidazolium-*H*). FT-IR (KBr, cm^{-1}): 2232 (s, ν (C≡C)).

Polymer 6 (***P6***). **P2** (30 mg, 0.050 mmol/monomer unit) was dissolved in 50 mL of pyridine, and 80 mL of dichloromethane was added. Distilled water (10 mL) dissolved LiTFSI (1.0 g, 3.5 mmol) was added, and the solution was stirred for 15 h at room temperature. The organic layer was washed with distilled water several times and dried with $MgSO_4$. After the removal of the solvent, red powder was washed with acetone to yield 28 mg (yield: 93%) of a red powder. ^1H NMR (DMSO-d_6, δ): 0.75 (3H, br, $-CH_3$), 1.08−1.21 (8H, br, $-CH_2-$), 1.77 (2H, br, $-CH_2$-thiopene), 4.15 (6H, br, CH_3-N), 7.78 (2H, br, thiophene-*H*, imidazolium-*H*). FT-IR (KBr, cm^{-1}): 2200 (s, ν (C≡C)).

1-Methyl-2,5-bis(phenylethynyl)imidazole (***Model Compound 1, M1***). A mixture of 1-methyl-2,5-diiodoimidazole **1** (0.50 g, 1.5 mmol), ethynylbenzene (0.31 g, 3.0 mmol), CuI (48 mg, 0.26 mmol), PPh_3 (0.36 g, 1.3 mmol), and triethylamine (30 mL) was stirred in 15 mL of anhydrous THF. After N_2 bubbled for 20 min, $Pd(PPh_3)_2Cl_2$ (80 mg, 0.11 mol) was added and refluxed at 70 °C for 13 h. The reaction mixture was poured into brine and extracted with ethyl acetate. The organic layer was washed with brine several times, separated, and then dried over $MgSO_4$. After the removal of the solvent, the crude product was purified with the alumina column chromatography using 1:4 (v/v) ethyl acetate/hexane solution to yield 0.31 g (yield: 72%) of a yellow solid. ^1H NMR ($CDCl_3$, δ): 3.83 (3H, s, CH_3−N), 7.36−7.40 (7H, m, aryl-*H*), 7.51−7.60 (4H, m, aryl-*H*). ^{13}C NMR ($CDCl_3$, δ): 32.1 (CH_3−N), 78.5, 96.7 (alkyne), 117.1, 121.6, 122.2, 128.5, 128.8, 129.3, 131.4, 131.8, 134.6 (aryl). FT-IR (KBr, cm^{-1}): 2214 (s, ν ($C\equiv C$)). EI-HRMS (*m*/*z*) Calcd for $C_{20}H_{14}N_2$ [M^+]: 282.1200. Found: 282.1160. Anal. Calcd for $C_{20}H_{14}N_2 \cdot 0.3H_2O$: C, 83.48; H, 5.11; N, 9.74. Found: C, 83.59; H, 4.81; N, 9.74.

1,3-Dimethyl-2,5-bis(phenylethynyl)imidazolium Iodide (***Model Compound 2, M2***). A mixture of **M1** (22 mg, 0.078 mmol) and iodomethane (0.12 mg, 0.84 mmol) was stirred and refluxed at 40 °C for 5 h. After the removal of solvent, the crude product was washed with hexane several times to yield 28 mg (yield: 87%) of a yellow powder. ^1H NMR ($CDCl_3$, δ): 4.03 (3H, s, CH_3−N), 4.27 (3H, s, CH_3−N). 7.42−7.72 (10H, m, aryl-*H*), 8.40 (1H, s, aryl-*H*). ^{13}C NMR ($CDCl_3$, δ): 34.9 (CH_3−N), 38.0 (CH_3−N), 69.7, 72.5, 100.8 (alkyne), 117.9, 118.8, 119.9, 127.4, 128.7, 129.0, 130.5, 131.1, 132.1, 132.7 (aryl). FT-IR (KBr, cm^{-1}): 2221 (s, ν ($C\equiv C$)). Anal. Calcd for $C_{21}H_{17}N_2I \cdot 0.5H_2O$: C, 58.21; H, 4.19; N, 6.47. Found: C, 57.92; H, 3.87; N, 6.39.

1,3-Dimethyl-2,5-bis(phenylethynyl)imidazolium TFSI (***Model Compound 3, M3***). **M2** (41 mg, 0.10 mmol) dissolved in chloroform (5 mL) was added to an aqueous solution of LiTFSI (2.0 g, 7.0 mmol) and stirred for 32 h at room temperature. The organic layer was washed with distilled water several times and dried with $MgSO_4$. After the removal of the solvent, yellow powder was washed with hexane to yield 56 mg (yield: 97%) of a yellow solid. ^1H NMR ($CDCl_3$, δ): 4.01 (3H, s, CH_3−N), 4.06 (3H, s, CH_3−N), 7.40−7.72 (11H, m, aryl-*H*). ^{13}C NMR ($CDCl_3$, δ): 34.6, 36.8 (CH_3−N), 69.2, 72.0, 100.8, 108.0 (alkyne), 117.9, 119.3, 119.9, 122.0, 126.3, 128.8, 130.6, 131.1, 132.2, 132.8 (aryl). Anal. Calcd for $C_{23}H_{17}N_3F_6O_4S_2$: C, 47.83; H, 2.97; N, 7.28. Found: C, 47.53; H, 2.81; N, 7.14.

1-Methyl-2,5-bis(thienylethynyl)imidazole (***Model Compound 4, M4***). A mixture of 1-methyl-2,5-diiodoimidazole **1** (1.2 g, 3.6 mmol), 2-trimethylsylilethynylthiophene (1.2 g, 7.6 mmol), CuI (0.13 g, 0.72 mmol), PPh_3 (1.0 g, 3.8 mmol), and diisopropylamine (90 mL) was stirred in 45 mL of anhydrous THF. After N_2 bubbled for 20 min, $Pd(PPh_3)_2Cl_2$ (0.38 g, 0.52 mol) was added and refluxed at 70 °C for 16 h. The reaction mixture was poured into brine and extracted with ethyl acetate. The organic layer was washed with brine several times and separated and then dried over $MgSO_4$. After the removal of the solvent, the crude product was purified with silica column chromatography using 7:1 (v/v) chloroform/ethyl acetate solution to yield 890 mg (yield: 84%) of a yellow solid. ^1H NMR ($CDCl_3$, δ): 3.79 (3H, s, CH_3−N), 7.04 (2H, t, aryl-*H*), 7.32−7.39 (5H, m, aryl-*H*). ^{13}C NMR ($CDCl_3$, δ): 32.2 (CH_3−N), 80.49, 86.8 (alkyne), 127.3, 128.2, 128.8, 132.7, 133.6, 135.1 (aryl). EI^+-HRMS (*m*/*z*) Calcd for $C_{16}H_{10}N_2S_2$ [$M+H^+$]: 295.0319. Found: 295.0315.

1,3-Dimethyl-2,5-bis(thienylethynyl)imidazolium Iodide (***Model Compound 5, M5***). A mixture of **M4** (43 mg, 0.14 mmol) and iodomethane (0.30 g, 1.8 mmol) was stirred and refluxed at 40 °C for 12 h. After the removal of solvent, the crude product was washed with hexane several times to yield 56 mg (yield: 91%) of a yellow powder. ^1H NMR ($CDCl_3$, δ): 3.98 (3H, s, CH_3−N), 4.25 (3H, s, CH_3−N), 7.08 (1H, t, aryl-*H*), 7.17 (1H, t, aryl-*H*), 7.47 (2H, d, aryl-*H*), 7.64 (1H, d, aryl-*H*), 7.70 (1H, d, aryl-*H*), 8.38 (1H, s, aryl-*H*). ^{13}C NMR ($CDCl_3$, δ): 32.1, 38.0 (CH_3−N), 101.7, 112.9 (alkyne), 127.6, 128.2, 130.4, 132.6 132.9, 135.2, 137.7 (aryl). ESI^+-HRMS (*m*/*z*) Calcd for $C_{17}H_{13}N_2S_2$ [M-$TFSI^+$]: 309.0540. Found: 309.0547.

1,3-Dimethyl-2,5-bis(thienylethynyl)imidazolium TFSI (***Model Compound 6, M6***). **M5** (30 mg, 0.069 mmol) dissolved in chloroform (5 mL) was added to an aqueous solution of LiTFSI (3.4 g, 11 mmol) and stirred for 4 h at room temperature. The organic layer was washed with distilled water several times and dried with $MgSO_4$. After the removal of the solvent, yellow powder was washed with hexane to yield 39 mg (yield: 95%) of a yellow solid. ^1H NMR ($CDCl_3$, δ): 3.97 (3H, s, CH_3−N), 4.04 (3H, s, CH_3−N), 7.10 (1H, t, aryl-*H*), 7.17 (1H, m, aryl-*H*), 7.48 (1H, s, aryl-*H*), 7.49 (1H, s, aryl-*H*), 7.63−7.69 (3H, m, aryl-*H*). ^{13}C NMR ($CDCl_3$, δ): 35.8, 38.5 (CH_3−N), 105.3, 114.1 (alkyne), 120.4, 126.6, 127.2, 127.7, 128.2, 133.0, 134.8, 135.3, 136.8, 137.7 (aryl). ESI^-−HRMS (*m*/*z*) Calcd for $C_2F_6NO_4S_2$ [$TFSI^-$]: 279.9166. Found: 279.9173. ESI^+−HRMS (*m*/*z*) Calcd for $C_{17}H_{13}N_2S_2$ [M-$TFSI^+$]: 309.0510. Found: 309.0517.

Density Functional Theory Calculations. DFT geometry optimizations and time-dependent DFT (TD-DFT) excitation energy calculations for model compounds were carried out with the Gaussian 03 package[17] employing the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang, and Parr (B3LYP).[18] The DGDZVP basis sets were used for all atoms.

Results and Discussion

Polymerization. Neutral polymers **P1** and **P4** were prepared via the Sonogashira−Hagihara coupling reaction.[19] Coupling reactions utilizing Pd and Cu catalysts between monomers gave the corresponding polymers, as illustrated in Scheme 1a. The number-average molecular weights of **P1** and **P4** were evaluated with the polystylene standard to be 1.1×10^4 with 2.6 of polydispersity index and 4.9×10^3 with 3.5 of polydispersity index, respectively, by GPC measurement. The neutral polymers **P1** and **P4** were readily converted to cationic **P2** and **P5**, respectively, by the methylation with methyliodide. The conversion ratio of quaternization of **P2** and **P5** were more than 90%, which were estimated by integrating the ^1H NMR signals of CH_3 protons linked to the N^+ atoms around 4.4 and 4.1 ppm, respectively. (See the Supporting Information.) The *N*-methyl region and also the signals of aromatic regions were shifted to a lower magnetic field compared with those of the neutral polymers **P1** and **P4** because of the introduction of cationic charges into the main chain. **P3** was obtained by extraction of **P2** dissolved in pyridine into an ionic liquid accompanied by the anion exchange from I^- to $TFSI^-$. **P6** was obtained by anion exchange from I^- to $TFSI^-$ using LiTFSI in dichloromethane.

Syntheses of Model Compounds. We also applied the Sonogashira−Hagihara coupling reaction to give **M1** and **M4**. **M2** and **M5** were obtained by the methylation of **M1** and **M2**, respectively. **M3** and **M6** were obtained by anion-exchange, as illustrated in Scheme 1b. The molecular structures of model compounds were confirmed by ^1H NMR, ^{13}C NMR, HRMS, FT-IR spectroscopy, and elemental analysis. Because of the decreased electronic density of the N-heteroaromatic ring by quaternization, the chemical shifts of the *N*-methyl groups on **M2**, **M3**, **M5**, and **M6** shifted to a lower magnetic field to be above 4.0 ppm from 3.8 ppm for neutral compounds **M1** and **M4**.

Optical Properties of P1−P3 and M1−M3. The optical properties of phenyleneethynylene-based polymers **P1−P3** and model compounds **M1−M3** were studied by UV−vis absorption and fluorescence spectroscopies, and the results are summarized in Table 1. Absorption and normalized

Table 1. Optical Properties of Phenyleneethynylene-Based Polymers and Their Model Compounds

compounds	UV−vis (λ_{max}, nm)	emission (λ_{em}, nm)	quantum yield (Φ_f, %)
Polymer 1	393[a]	474[a]	31[a]
Polymer 2	387[a]	483[a]	9.5[a]
Polymer 3	375[b]	425[b]	20[b]
Model 1	331[a]	399[a]	7.6[b], 5.7[c]
Model 2	327[a]	407[a]	40[c]
Model 3	323[b]	389[b]	1.8[b], 86[c], 32[d]

[a] In pyridine. [b] In 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. [c] In chloroform. [d] In *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide.

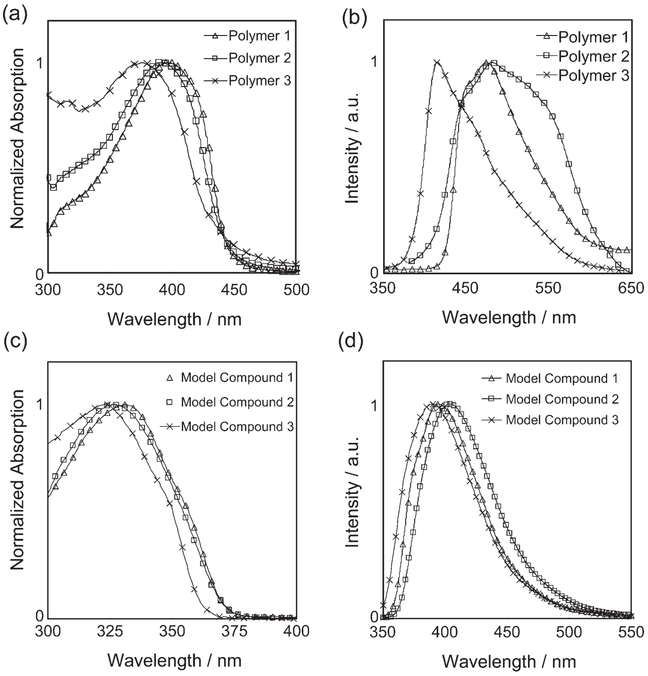
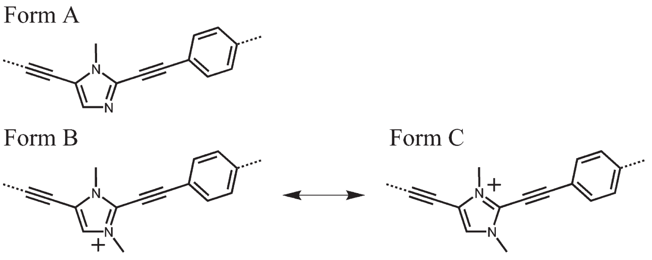


Figure 1. (a) Absorption spectra of **Polymer 1**, **Polymer 2** in pyridine, and **Polymer 3** in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (emimTFSI). (b) Normalized fluorescence spectra of **Polymer 1**, **Polymer 2** in pyridine, and **Polymer 3** in emimTFSI. (c) Absorption spectra of **Model Compound 1**, **Model Compound 2** in pyridine, and **Model Compound 3** in emimTFSI. (d) Normalized fluorescence spectra of **Model Compound 1**, **Model Compound 2** in pyridine, and **Model Compound 3** in emimTFSI.

Scheme 2. Structure of Imidazole Unit and Resonance Structures of Imidazolium Unit



fluorescence spectra of **P1**, **P2**, and **P3** are shown in Figure 1a,b, respectively. The neutral polymer **P1** showed absorption bands at $\sim$400 nm, which is responsible for the $\pi-\pi^*$ transition in their π-conjugated mainchain. The imidazolium polymers with iodide anion **P2** showed a significant blue shift in λ_{max} compared with that of neutral polymer. This blue shift can be attributed to the restricted expansion of the π-conjugated system on the imidazolium units in the cationic polymers. The emission peak position, λ_{em}, of **P1** was at 474 nm, whereas that of **P2** was significantly broadened and shifted to 483 nm. Because the concentrations of the samples of the test solutions were about 10^{-6} M, the effect of reabsorption is not significant in the emission spectra. These broadening and bathochromic shifts could be explained by the aggregation of the polymer caused by enhanced intermolecular and intramolecular electrostatic interactions between the cationic charge of imidazolium and counteranion.[20] Because this aggregation behavior is difficult to observe in the absorption spectra, the ratio of aggregated parts might be small, and aggregation behavior can be observed in only the emission spectrum. That is, excitons can be easily migrated into aggregated parts, so we could easily observe the effects of aggregated parts in the emission spectrum. To rule out the possibility of the specific effects of the pyridine unit such as the coordination effect of the pyridine ring with **P2** or **M2**, we tried to measure the absorption and fluorescence spectra of **P2** in solvents other than pyridine. However, unfortunately, the solubility of **P2** was low in ordinary solvents such as $CHCl_3$ and THF. In the case of **M2**, meanwhile, the shapes of absorption and fluorescence spectra in $CHCl_3$ were quite similar to those in pyridine (Supporting Information), and then we could eliminate the possibility of a specific effect of pyridine in these spectra. Both UV−vis absorption and fluorescence spectra of imidazolium polymer with TFSI anion **P3** in an ionic liquid (emimTFSI) showed significant blue shift in comparison with those of polymer **P2** with iodide anion. The emission profile of the $TFSI^-$-type polymer **P3** was considerably narrower than that of **P2** and exhibited clear vibrational structure. Additionally, fluorescence quantum yields of **P1** and **P2** were 31 and 9.5%, respectively, and that of **P3** was 20%. (See Table 1.) The markedly low emission quantum yield of **P2** can be attributed to the enhanced energy migration to the nonradiative recombination sites by the interchain electrostatic interaction in the aggregated structure or by the external heavy-atom effect with the iodide anion for **P2**. These results suggest that the effect of solvent to polymer could be mainly related to the change of aggregation state of the polymer. The spectral feature of **P3** suggests that the ionic polymer tends to aggregate in organic media but not in the ionic liquid where the ionic interaction between the main chains should be heavily suppressed because of the extremely high salt concentration.[21] It should be also mentioned that both the absorption and the emission bands of **P3** shifted to the blue-side in comparison with the neutral polymer **P1**. In particular, in the case of **P3**, the emission profile exhibits rather clear vibrational structure, and the effect of the aggregation might be excluded. Therefore, the blue-shifted optical properties of **P3** can be attributed to the intrinsic expansion of the energy gap between the HOMO and the LUMO levels in the cationic polymer. For the neutral polymer **P1**, the imidazole units are introduced into the π-conjugated main chain and the π-conjugated electron system expands over the whole main chain through the alternating structure of single and double or triple bonds as shown in Scheme 2 (Form A). For the imidazolium-based polymer **P3**, the positive charge should be delocalized over two nitrogen atoms, and their electronic structure might be described as a hybrid of the two canonical structures, as illustrated in Scheme 2 (Forms B and C). That is, the π-conjugation expansion might be at least partially limited by the contribution of the metha-linkage Form C. A similar structure can also be supposed for the neutral polymer **P1**. However, the contribution of the metha-linkage

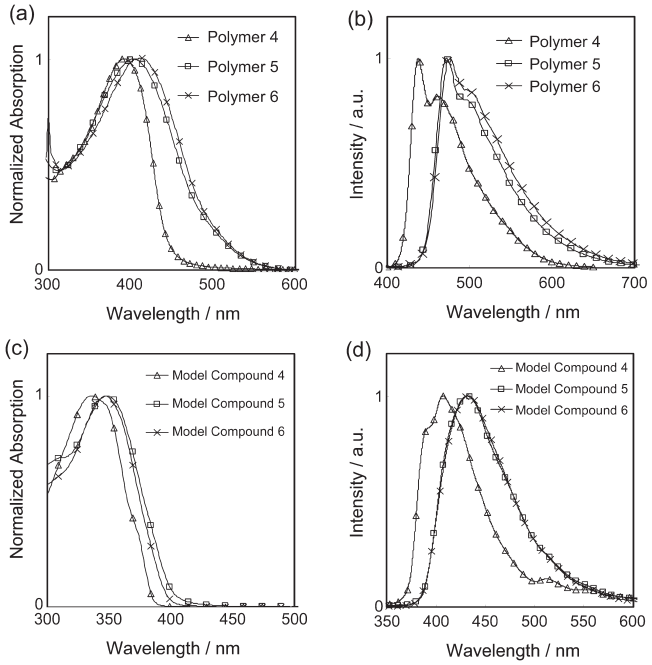


Figure 2. (a) Absorption spectra of **Polymer 4**, **Polymer 5**, and **Polymer 6** in pyridine. (b) Normalized fluorescence spectra of **Polymer 4**, **Polymer 5**, and **Polymer 6** in pyridine. (c) Absorption spectra of **Model Compound 4**, **Model Compound 5**, and **Model Compound 6** in pyridine. (d) Normalized fluorescence spectra of **Model Compound 4**, **Model Compound 5**, and **Model Compound 6** in pyridine.

form should be rather minor because charge separation should be assumed. The absorption and fluorescence spectra of model compounds **M1**−**M3** are also shown in Figure 1c,d, respectively. The $\lambda_{\max}$ and λ_{em} of **M3** in the ionic liquid were 323 and 389 nm, respectively, and were shifted to shorter wavelengths in comparison with those of **M1** ($\lambda_{\max}$: 331 nm, $_{\text{em}}$: 399 nm) as well as polymers. The fluorescence quantum yields of **M1**, **M2**, and **M3** in $CHCl_3$ were 5.7, 40, and 86%, respectively. The fluorescence quantum yields of **M1** and **M3** in emimTFSI were 7.6 and 1.8%, respectively. Although the reason of the lower quantum yields of **M3** in the ionic liquid is not clear in this stage, it might be attributed to photoinduced charge transfer from **M3** to the ionic liquid. This is supported by the fact that the fluorescence quantum yield of **M3** in the ionic-liquid-based aliphatic ammonium, *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide, was 32%. Because both ionic liquid and **M3** have similar molecular structures, their HOMO and LUMO levels might be of similar potential, and photoinduced electron transfer would thus be possible.

Optical Properties of P4−P6 and M4−M6. The optical properties of thienyleneethynylene-based polymers **P4**−**P6** and model compounds **M4**−**M6** were also studied by UV−vis absorption and fluorescence spectroscopies in pyridine, and the results are summarized in Table 2. Absorption and normalized fluorescence spectra of **P4**, **P5**, and **P6** are shown in Figure 2a,b, respectively. Absorption spectra showed $\lambda_{\max}$ of neutral polymer **P4** at 392 nm because of the $\pi-\pi^*$ transition in the π-conjugated main chain. $\lambda_{\max}$ of cationic polymers **P5** and **P6** were 403 and 415 nm, respectively, which were shifted to longer wavelengths compared with neutral polymer **P4**. Furthermore, in the case of the fluorescence spectra, λ_{em} of **P5** and **P6** were 473 and 477 nm, respectively, which also showed a red shift in comparison with λ_{em} of **P4**, 438 nm, as shown in Figure 2b. Each fluorescence spectra had vibronic fine structures (461 nm for **P4**, 500 nm for **P5**, and 505 nm for **P6**), indicating that the effect of aggregation could be suppressed in pyridine. **P5** and **P6** were soluble in pyridine but not in common organic solvents such as $CHCl_3$, THF, DMF, DMSO, and dioxane. The absorption and fluorescence spectra of **P5** and **P6** exhibited a marked red shift compared with those of neutral P4 in pyridine, and this trend was also observed in the ionic liquid emimTFSI. The red shift might be due to their intramolecular donor−acceptor (D−A) structures. Namely, thiophene units are the electron-rich donors, and the imidazolium units are the electron-deficient acceptors. Another possible origin is the imported coplanarization in their main chains associated with the location of counteranion. The absolute fluorescence quantum yields (Φ_f) of **P4**−**P6** are summarized in Table 2. The lower Φ_f values of **P5** and **P6** suggest that the emission efficiency in these donor−acceptor type polymers, that is, polymers having intramolecular charge transfer, could significantly suppress fluorescence quantum yield.[22] The absorption and fluorescence spectra of model compounds **M4**−**M6** are also shown in Figure 2c,d, respectively. The $\lambda_{\max}$ and λ_{em} of a cationic model compound with iodide anion **M5** in pyridine were 349 and 432 nm, respectively, and those of a model compound with TFSI anion **M6** were 348 and 432 nm, respectively, were shifted to longer wavelength in comparison with those of neutral model compound **M4** ($\lambda_{\max}$: 336 nm, λ_{em}: 407 nm).

Table 2. Optical Properties of Thyenyleneethynylene-Based Polymers and Their Model Compounds

compounds	UV−vis ($\lambda_{\max}$, nm)[a]	emission (λ_{em}, nm)[a]	quantum yield (Φ_f, %)[a]
Polymer 4	392	438	3.6
Polymer 5	403	473	0.66
Polymer 6	415	477	0.81
Model 4	336	407	5.1
Model 5	349	432	7.7
Model 6	348	432	11

[a] All measurements were performed in pyridine.

Density Functional Theory Calculations of Model Compounds. To evaluate the origin of spectra shifts upon the introduction of cationic charge on the π-conjugated chain, we calculated the frontier orbitals and geometrical structures of **M1** and **M4** and their N-methylated compounds, **M1-Me**$^+$ and **M4-Me**$^+$, respectively, by quantum chemical calculation based on the DFT method at the B3LYP/DGDZVP level. Absorption maxima together with oscillator strength for these compounds were also estimated by the TD-DFT method. As seen Figure 3a, **M1** was calculated to have a complete coplanar structure as the most stable conformation. Reflecting this structure and the π-conjugation connection, molecular orbitals (HOMO and LUMO) expand from one phenyl ring to the other through the central imidazole ring. The first electronic transition from HOMO to LUMO for **M1** was calculated to be 370 nm with the oscillator strength of 1.5770, which is longer than the observed value by 40 nm, probably because calculation is based on only the most stable coplanar structure under vacuum condition. Two dominant transitions with substantial oscillator strengths were calculated for **M1-Me**$^+$ at 393 and 319 nm on the basis of the coplanar conformation, whereas the absorption maxima were observed at 327 nm for **M2** and 323 nm for **M3** as a single peak. These transitions are based on the electronic transitions from fully expanded HOMO and HOMO-2 to LUMO and LUMO+1 with localized molecular orbitals (Figure 3b, Table 3). Hybridization of these two transitions accompanied by the rotation about the ethynyl bonds might result in the blue shift of absorption

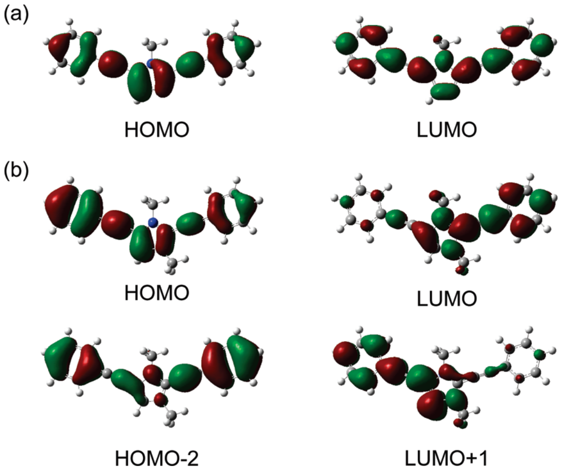


Figure 3. Frontire orbitals of (a) **Model Compound 1** (**M1**) and (b) methylated **Model Compound 1** (**M1-Me**$^+$) without counteranion.

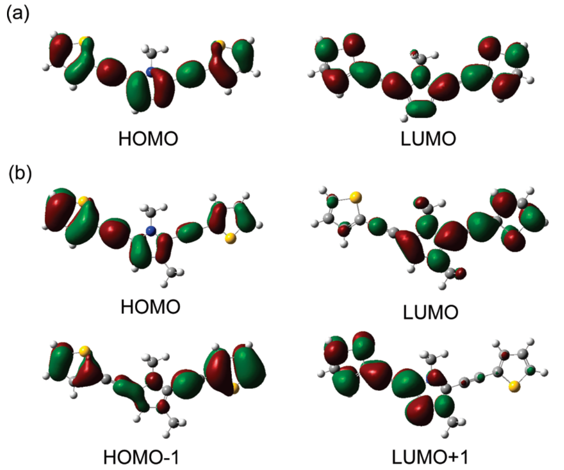


Figure 4. Frontire orbitals of (a) **Model Compound 4** (**M4**) and (b) methylated **Model Compound 4** (**M4-Me**$^+$) without counteranion.

maxima for N-methylated imidazolium π-conjugated molecules with respect to **M1**. Another mechanism might be attributed to the effect of counteranion. Electrostatic interaction between counteranion such as I^- and imidazolium cation hinders the free rotation about the ethynyl bond to stabilize the twisted conformation as the optimized structure (Supporting Information), leading to the suppression of effective π-conjugation legth.[12]

Unlike phenyleneethynylene-based compound **M1**, thienyleneethynylene-based π-conjugated molecule **M4** was calculated to show the twisted conformation as the optimized structure, in which one thienyl ring linked to the two-position of the imidazole unit twists at 54° from the imidazole unit, and the other one also rotates by 48° about the ethynyl bond. The molecular orbitals for HOMO and LUMO of **M4** expand the entire molecule, as shown in Figure 4a. The HOMO−LUMO transition for **M4** was estimated to appear at 361 nm on the basis of the TD-DFT method. Again, the calculated value is longer than the observed one (336 nm). Meanwhile, N-methylated **M4-Me**$^+$ showed two transitions based on HOMO to LUMO and the combination of HOMO-1 to LUMO and HOMO to LUMO+1 at 396 and 332 nm, respectively, whereas only a single transition peak was observed for **M5** and **M6**. These observations might be attributed to the hybridization of these two peaks caused by rotation around two thienyl bonds between thiophene and imidazolium rings, and the apparent absorption maximum should depend on the favorable conformation. Given the effect of counteranion, the coplanar conformation, which expands the effective π-conjugation length, is favored for **M5** (Supporting Information), unlike phenyleneethynylene-based **M2**, for which the preferential structure is the twisted conformation. Although DFT calculations thus indicated the certain relationship between transition energy and conformation, the complex conditions, for example, solvent, ionic interactions should be taken into account for better understanding.

Table 3. Calculated UV−vis Absorption Wavelength and Oscillator Strength of Model Compounds and Methylated Model Compounds without Counter Anion

compounds	UV−vis calcd ($\lambda_{\text{calcd.}}$, nm)	oscillator strength
Model 1	370^a	1.5770^a
Model 1-Methyl$^+$	393^a, 319^b	0.8707^a, 0.7217^b
Model 4	361^a	0.9131^a
Model 4-Methyl$^+$	396^a, 332^c	0.5966^a, 0.6517^c

^{a} HOMO > LUMO. ^{b} HOMO-2 > LUMO, HOMO > LUMO+1. ^{c} HOMO-1 > LUMO, HOMO > LUMO+1.

Conclusions

The synthesis, characterization, and optical properties of the phenyleneethynylene- and thienyleneethynylene-based π-conjugated polymers with imidazolium units in the main chain were demonstrated. Phenyleneethynylene-based imidazolium polymers were easily aggregated in pyridine, whereas they stably dispersed in an ionic liquid, emimTFSI. The fluorescence quantum yield of imidazolium polymer in emimTFSI was higher than that of the iodide-based polymer in pyridine because of disaggregation and exclusion of the external heavy-atom effect with the iodide anion. For thienyleneethynylene-based cationic imidazolium polymers, UV−vis absorption and fluorescence spectra were shifted to longer wavelengths compared with the neutral polymer, which indicates coplanarization of aromatic rings in the main chains, formation of donor−acceptor (D−A) structures, or both. DFT calculations at the B3LYP/DGDZVP level were demonstrated and suggested that the spectral shift upon the introduction of cationic charge on the π-conjugated chain might be attributed to the change of molecular orbitals coupled to molecular rotation about ethynyl bonds. Main-chain-type imidazolium polymers are expected to be the starting material for new ionic polymers exhibiting the possibility of tunable color that depends on the polymer structure in the main chain.

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Supporting Information Available: ^{1}H NMR spectra of polymers and model compounds, X-ray crystal structure of **M1**, absorption and fluorescence spectra of **M2** in $CHCl_3$ and pyridine, and DFT calculation data of model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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