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Design, synthesis and study of a photochromic α,ω-diene: Toward new classes of photoswitchable polymers

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A 4,5-dithienylimidazolium salt outfitted with pendant styrenyl groups was synthesized and studied. The salt was found to undergo reversible electrocyclization upon UV irradiation; subsequent exposure to visible light reversed the reaction. Acyclic diene metathesis (ADMET) polymerization of the salt afforded a novel fluorescent, polyelectrolyte.

Introduction

Photochromism is a term that is used to describe reversible isomerizations induced by light.[1] Prototypical examples include the *trans-cis* interconversions displayed by azobenzene and its derivatives[2–4] as well as the electrocyclizations of spiropyran,[5–7] diarylethene, and others.[8–15] Such features have enabled applications in optoelectronics, memory storage devices, and various types of switches.[16–20] In many of these examples, the isomerizations are accompanied by changes in molecular electronic structure that ultimately affect chemical properties.[21,22] For example, we showed[23] that light may be used to change the spectroscopic characteristics of 4,5-dithienylimidazolium species (Figure 1). In the ring-opened form (**1o**), the thienyl groups are cross-conjugated with the imidazolium which effectively decouples electronic communication between the two species. In contrast, electrocyclization (**1c**) promotes electron withdrawal from the imidazolium C2 nucleus and toward electronegative sulfur atoms, which manifests in discernable chemical shifts.[23] The photochromism was successfully extended to deprotonated derivatives wherein the ring-opened forms were found to exhibit different chemical reactivities (e.g., relatively high nucleophilicities and increased electron donating properties) than their ring-closed isomers.[24–26]

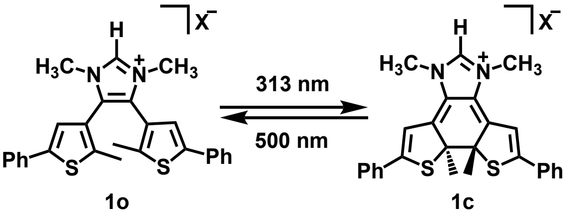

Figure 1. A photoswitchable imidazolium salt. UV light promotes electrocyclization whereas visible light reverse the reaction.

Guided by these results, we hypothesized that the photochromic scaffold described above could outfitted with appropriate functional groups and polymerized. The corresponding polymer was envisioned to feature dithienyl and imidazolium species in an alternating fashion along the backbone and thus should contain a photoswitchable group in every repeat unit. Embedding photoswitches in polymer chains may lead to memory storage devices with increased information densities or enable other applications.[27,28] For example, through appropriate design, polymers that can be switched between non-conjugated and conjugated forms may be realized (Figure 2).[29–32] Such features may be used to alleviate the processing challenges commonly encountered with conjugated polymers,[33,34] particularly if one form exhibits an enhanced solubility, or find utility in photolithography.[35,36]

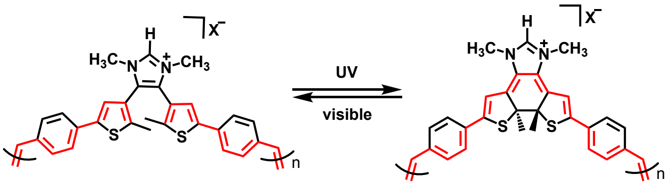

Figure 2. Example of a polymer that displays a photoswitchable conjugated structure.

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Electronic Supplementary Information (ESI) available: Additional X-ray crystallography details, ^1H and ^{13}C NMR spectra, gel permeation chromatography data, UV-vis spectra, fluorescence spectra, and quantum yield measurement details. See DOI: 10.1039/x0xx00000x

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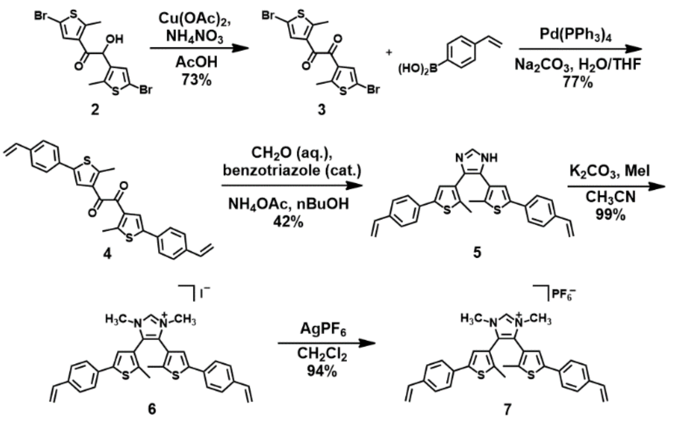
Herein we report the synthesis of a novel 4,5-dithienylimidazolium salt equipped with pendant styrenyl groups and demonstrate that it undergoes reversible photochromism. Acyclic diene olefin metathesis (ADMET)[37–39] was chosen as a methodology to convert the monomer to polymer because unsaturation is conserved during the polymerization reaction,[40] a key feature required to maintain conjugation. The polymers produced from this approach were found to be conjugated, exhibited good fluorescence properties, and establish a path toward realizing the applications described above.

Results and Discussion

The targeted photochromic salt was synthesized by modifying a route reported in the literature (Scheme 1).[23] The synthesis was achieved in five steps from known acyloin **2**.[41] Copper-catalyzed oxidation of the acyloin afforded the diketone **3**, which was subjected to Suzuki coupling with 4-vinylphenylboronic acid to give **4**. Attempts to effect formylative cyclization (to obtain **5**) with aqueous formaldehyde under forcing, acidic conditions (refluxing acetic acid) resulted in polymerization, as evidenced by the observation of broad signals in the ^{1}H NMR spectrum recorded for the crude product. To circumvent this issue, the cyclization was carried out under neutral conditions using a catalytic amount of benzotriazole.[42] Finally, methylation and ion metathesis of the corresponding product (**6**) afforded **7** as determined in part by the appearance of a diagnostic ^{1}H NMR signal at δ 8.87 ppm ($CDCl_3$), which was assigned to the proton at the C2 position of the imidazolium group. The PF_6 anion was introduced to enhance the stability of the imidazolium since it was previously reported that similar imidazolium iodides decomposed under UV irradiation.[23] The structure of **7** was independently confirmed by an X-ray diffraction analysis of crystals that were obtained by slowly diffusing hexane into a saturated CH_2Cl_2 solution (Figure 3).



Scheme 1. Synthesis of the 4,5-dithienylimidazolium salt **7**.

After the targeted imidazolium salt was synthesized, its photophysics were evaluated. Comparison of the UV-vis spectrum recorded for **7** to that of its parent derivative **1** (where X = PF_6^-) revealed that the former exhibited a higher λ_{max} value in acetonitrile (688 nm vs. 666 nm; Figure 4), consistent with a relatively long conjugation length. Exposure of a solution of **7** ($[\mathbf{7}]_0 = 4 \times 10^{-5}$ M) to 313 nm light resulted in the appearance of absorption band at 688 nm (Figure 5a). The band increased in intensity over time and, after approximately 90 seconds of UV irradiation, a photostationary state (PSS) was reached. Subsequent irradiation with visible light (> 500 nm) returned the initial spectrum after several minutes (Figure 5b). The spectral changes described above were accompanied with visual differences. Although initially colorless, the solution of **7** turned pale blue upon exposure to UV light; visible light reversed the process (Figure 5c). Collectively, these distinctive changes were attributed to formation of the ring-closed and ring-opened isomers of the 4,5-dithienylimidazolium salt.

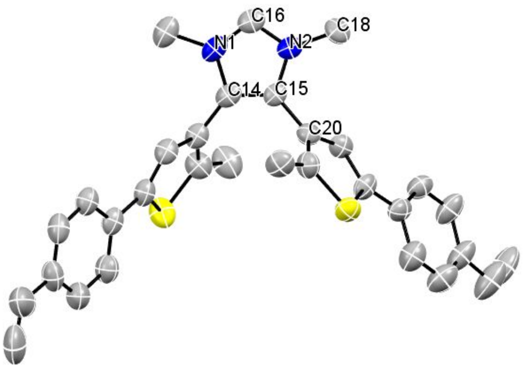


Figure 3. A representation of the solid-state structure of **7**. The ellipsoids shown are at the 50% probability level. Solvent molecules, counter anion and H atoms were omitted for clarity. Selected distances (Å) and angles (°): C14-C15 1.336(10), C15-N2 1.404(10), C15-C20 1.477(10), C16-N2 1.338(10), C18-N2 1.439(10); N1-C16-N2 108.4(7), C16-N2-C15 107.3(7), C14-C15-N2 108.2(7), C15-N2-C18 127.0(7), N2-C15-C20 122.2(7).

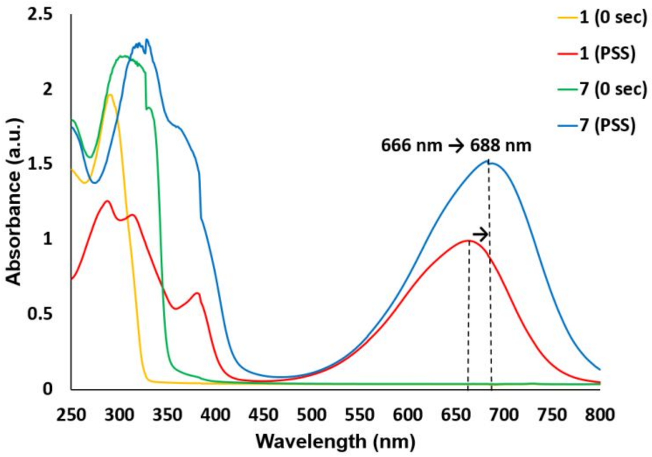


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Figure 4. A comparison of UV-vis spectra recorded for **7** to its parent analogue (**1**). The spectra were recorded prior to irradiation at 313 nm and after reaching the respective PSS states. Conditions: [**7** or **1**]$_0$ = 4 x 10^{-5} M; acetonitrile.

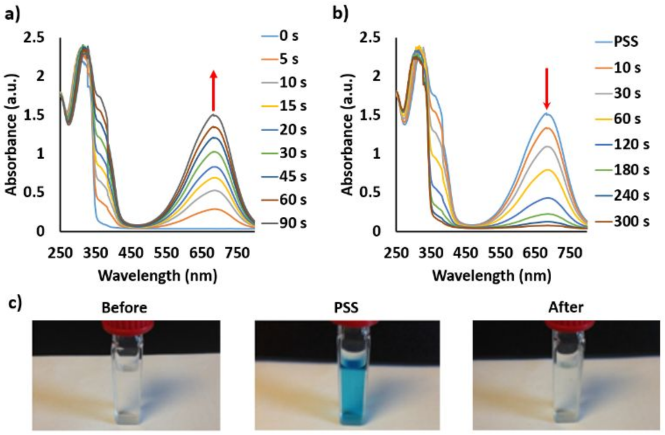
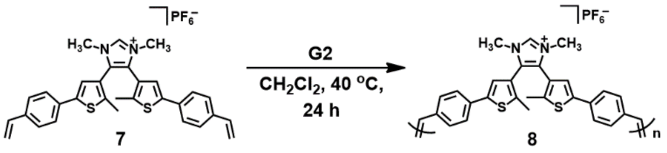


Figure 5. (a) UV-vis spectra recorded over time as a solution of **7** was irradiated with UV light (313 nm) and (b) subsequent exposure to visible light (500 nm). The red arrows represent the evolution of spectral changes. (c) Photographs of vials containing solutions of **7** before irradiation with UV light, at the PSS, and after irradiation with visible light (indicated). Conditions: [**7**]$_0$ = 4 x 10^{-5} M; acetonitrile.

As shown in Scheme 2, efforts were directed toward polymerizing **7** using ADMET polymerization in conjunction with the Grubbs 2nd generation catalyst (G2). Such reactions are typically performed under concentrated conditions and under a vacuum to promote the condensation of ethylene as well as to drive polymer formation.[38] With these considerations in mind, a set of preliminary experiments were conducted (not shown) and optimization conditions were determined to be as follows: [**7**]$_0$ = 0.50 M, [**7**]$_0$/[G2]$_0$ = 20, CH_2Cl_2, and 40 °C. The polymers formed under these conditions precipitated from the reaction mixtures over time, which facilitated isolation. The number average molecular weight (M_n) of the polymer obtained was calculated to be 4800 Da using ^{1}H NMR spectroscopy in conjunction with an end-group analysis. In this method, the intensity of a signal attributed to the protons at the C2 positions of the imidazolium species in the polymer repeat units (δ 9.40 ppm; DMSO-d_6) was compared to the intensity of a signal assigned to the terminal benzylidene groups (6.73 ppm). Gel permeation chromatography (GPC) revealed that the M_n of polymer was 8.4 kDa and exhibited a multimodal distribution (Đ = 1.45), as expected from a step-growth polymerization. The discrepancies between the NMR and GPC derived molecular weights may due to the technique employed as the former provides an absolute value whereas the latter is reported as a calibration standard (polystyrene) equivalent.



Scheme 2. ADMET polymerization of **7**.

The λ_{max} recorded for the polymer **8** was measured at 378 nm (Figure 6a), a significantly red-shifted value when compared to its respective monomer (**7**) (301 nm) and consistent with a relatively extended, conjugated structure. To probe for any fluorescence characteristic, a solution of the polymer in *N,N*-dimethylformamide (DMF) ([**8**]$_0$ = 5 x 10^{-6} mg/mL) was photoexcited at 365 nm; two strong emission bands centered at 422 nm and at 444 nm were subsequently observed (Figure 6b). Emission was exclusive to the polymer (Φ = 0.65)[43] as the monomer did not appear to fluoresce under similar conditions (Figure 6c). Irradiation of polymer solutions with lower wavelengths of light did not afford any significant spectral changes which may be due to either a suppressed electrocyclization enforced by the physical constraints of the polymer backbone or dissipation of the absorbed light due to the extended π-conjugation.[44–46] Photochromic enhancement may be achieved by tuning the conjugation length or through the strategic integration of donor and acceptor substituents on the main chain of the polymer in a manner that increases the excitation density of the chromophore.[22,44]

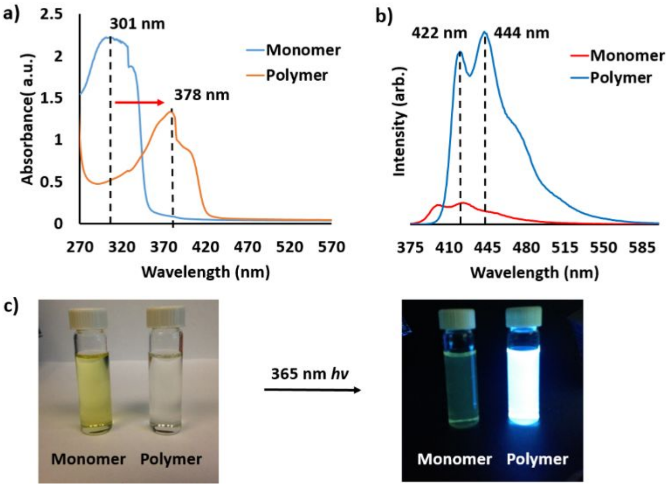


Figure 6. (a) A comparison of UV-vis spectra recorded for monomer **7** and its respective polymer **8**. (b) Emission spectra recorded for monomer **7** and polymer **8** after excitation at 365 nm. (c) Photographs of vials containing solutions of monomer **7** or polymer **8** (indicated) before and after excitation at 365 nm. Conditions: [monomer or polymer repeat unit]$_0$ = 1 x 10^{-6} M; DMF.

Experimental

General Considerations

All procedures were performed under an atmosphere of nitrogen unless otherwise noted. Solvents were dried and degassed by a Vacuum Atmospheres Company solvent purification system and stored over 4 Å molecular sieves in a nitrogen-filled glove box. Unless otherwise specified, reagents were purchased from commercial sources and used without further purification. Melting points were obtained using a Stanford Research Systems MPA100 OptiMelt automated melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts (δ) are given in ppm and are referenced to the residual solvent (^{1}H: $CDCl_3$, 7.26 ppm; DMSO-d_6, 2.50 ppm; ^{13}C: $CDCl_3$, 77.16 ppm; DMSO-d_6, 39.52 ppm). High resolution mass spectra (HRMS) were obtained with a Waters Micromass Autospec-Ultima (CI) or Agilent 6530 QTOF (ESI) mass spectrometer. Gel permeation chromatography (GPC) was performed using DMF as the eluent on a Viscotek system equipped with a VE 1122 pump, a VE 7510 degasser, two fluorinated polystyrene columns (I-MBHW-3078 and I-MBLMW-3078) thermostated to 35 °C (using a ELDEX CH 150 column heater) and arranged in series, a Viscotek 270 Dual Detector (light scattering detector and differential viscometer), and a VE 3580 refractive index detector. UV-vis spectra were acquired using a Perkin-Elmer Lambda 35 UV-vis Spectrometer in 6Q Spectrosil quartz cuvettes with 1.0 cm path lengths and 3.0 mL sample solution volumes. The photochemical reactions were performed in the same quartz cuvettes using 4.0 mL sample solution volumes. The irradiation source for photochemical reactions was a Newport/Oriel 66942 200-500W Hg Arc system equipped with a 350 W Hg lamp, a Newport 6117 liquid filter, a Newport 71445 electronic safety shutter, and a Newport 71260 filter holder. The source was powered by a Newport 669910 power supply and mounted on a Newport XL48 optical rail with a Newport 13950 shielded cuvette holder placed at a distance of 8 cm from the end of the source. The irradiation wavelength for the photocyclization reactions was provided by a 313 nm bandpass filter (Andover Corporation). A long-pass edge filter (> 500 nm) (Andover Corporation) was used to introduce visible light. Fluorescence spectra were recorded on a PTI QuantaMasterTM 40 intensity based spectrofluorometer equipped with 814 photomultiplier detection system. A 75 W Xenon arc lamp was used as the excitation source.

Synthetic Procedures

1-(5-bromo-2-methylthiophen-3-yl)ethan-1-one

An oven-dried Schlenk flask equipped with a magnetic stir bar was charged with 2-bromo-5-methylthiophene (4.7 g, 26.5 mmol), evacuated, and then refilled with nitrogen three times. Dry toluene (88 mL) was added to the flask and cooled to 0 °C in an ice bath. Acetic anhydride (2.75 mL, 29.3 mmol) was added via syringe under an atmosphere of nitrogen. At the same temperature, tin(IV) chloride (3.67 mL, 31.9 mmol) was added dropwise via a nitrogen purged syringe. The reaction mixture was stirred for 2 h in an ice bath, and then poured into a mixture of acidic, cold water. The organic layer was separated and washed with deionized water, dried over sodium sulfate, and then concentrated under reduced pressure. Purification of the resulting residue by column chromatography on silica gel afforded the desired product (3.45 g, 60%). Spectral values were in accord with data reported in the literature.[41]

2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetaldehyde

A mixture of 1-(5-bromo-2-methylthiophen-3-yl)ethan-1-one (500 mg, 2.28 mmol), SeO_2 (658 mg, 5.93 mmol) in dioxane (4.6 mL), and water (0.15 mL) was heated to reflux for 5 h. The mixture was cooled to room temperature and filtered through Celite, and the resulting filtrate was concentrated under reduced pressure. The remaining residue was washed with cold ethyl acetate and subjected to a flash chromatography to obtain the desired product (436 mg, 82%). Spectral values were in accord with data reported in the literature.[41]

1,2-bis(5-bromo-2-methylthiophen-3-yl)-2-hydroxyethan-1-one (2)

An oven-dried Schlenk flask equipped with a stir bar was charged with 2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetaldehyde (3.6 g, 15.4 mmol), 2-bromo-5-methylthiophene (2.7 g, 15.4 mmol), and dry toluene (50 mL) under an atmosphere of nitrogen. The reaction mixture was cooled to 0 °C in an ice bath, and tin (IV) chloride (1.8 ml, 15.4 mmol) was added dropwise. The reaction mixture was stirred in the ice bath for 6 h, and then poured into ice water. The mixture was extracted with ethyl acetate and the combined organic layers were washed with deionized water as well as brine. After removing the residual solvent under reduced pressure, the resulting residue was subjected to a column chromatography to afford the desired product (3.1 g, 49%). Spectral values were in accord with literature reports.[41]

1,2-bis(5-bromo-2-methylthiophen-3-yl)ethane-1,2-dione (3)

A round bottom flask equipped with a stir bar was charged with the requisite α-hydroxy ketone (2.4 g, 5.85 mmol) in glacial acetic acid (20 mL), copper (II) acetate (234 mg, 1.17 mmol), and NH_4NO_3 (1.17 g, 14.6 mmol). The mixture was heated to reflux for 24 h, cooled to room temperature, and then poured into ice water. To the mixture was added concentrated ammonium hydroxide until a pH of 7 was measured. The mixture was extracted with ethyl acetate and the combined organic layers were washed with deionized water as well as brine. The solvent was removed under reduced pressure and the resulting residue was passed through a short column of silica gel aided with dichloromethane as eluent. The residual solvent was removed under reduced pressure to yield the desired product as a yellow solid (1.74 g, 73%). m.p. = 160 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.82, 155.01, 132.09, 131.47, 108.65, 16.16. HRMS (ESI): $[M]^+$ calcd. for $C_{12}H_8Br_2O_2S_2$: 405.8332; Found: 405.8332.

1,2-bis(2-methyl-5-(4-vinylphenyl)thiophen-3-yl)ethane-1,2-dione (4)

Tetrakis(triphenylphosphine)palladium(0) (470 mg, 0.41 mmol) and 4-vinylphenyl boronic acid (1.26 g, 8.54 mmol) was added to a stirred solution of 2-bis(5-bromo-2-methylthiophen-3-yl)ethane-1,2-dione (1.66 g, 4.07 mmol) in THF (13.5 mL). A

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solution of aqueous Na_2CO_3 (2 N; 13.5 mL) was added to the reaction mixture, which was then heated at 80 °C under an atmosphere of nitrogen. After 24 h, the solution was cooled to room temperature and poured onto water. The organic layer was extracted with dichloromethane, dried over anhydrous $MgSO_4$, and concentrated. Purification using column chromatography afforded the desired product as a yellow powder (1.43 g, 77%). m.p. = 240 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.44 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.27 (dd, *J* = 10.9, 0.7 Hz, 1H), 2.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.77, 152.76, 140.44, 137.28, 136.05, 132.81, 132.34, 126.77, 125.83, 124.38, 114.36, 16.35. HRMS (ESI): $[M]^+$ calcd. for $C_{28}H_{22}O_2S_2$: 454.1061; Found: 454.1066.

4,5-bis(2-methyl-5-(4-vinylphenyl)thiophen-3-yl)-1H-imidazole (5)

In a round bottom flask, benzotriazole (18 mg, 0.16 mmol) and formaldehyde (37 wt% in H_2O, 505 mg, 6.20 mmol) were taken in n-butanol (15.5 mL). Then, the requisite 1,2-dione (1.41 g, 3.10 mmol) and ammonium acetate (1.2 g, 15.5 mmol) were added. After heating at 80 °C for 12 h, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude residue was recrystallized from hexane to afford the desired product as a beige powder (600 mg, 42%). m.p. = 250 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.47 – 7.40 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 3H), 7.17 (s, 1H), 6.68 (dd, *J* = 17.5, 10.9 Hz, 2H), 5.72 (d, *J* = 17.5 Hz, 2H), 5.23 (d, *J* = 10.9 Hz, 2H), 2.13 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.14, 136.48, 136.29, 136.21, 134.49, 133.51, 126.66, 125.32, 124.11, 113.74, 14.21. HRMS (ESI): $[M+H]^+$ calcd. for $C_{29}H_{24}N_2S_2$: 465.1454; Found: 465.1458.

1,3-dimethyl-4,5-bis(2-methyl-5-(4-vinylphenyl)thiophen-3-yl)-1H-imidazol-3-ium iodide (6)

A flask equipped with a stir bar was charged with the requisite imidazole (590 mg, 1.27 mmol), K_2CO_3 (440 mg, 3.17 mmol), CH_3CN (12 mL), and iodomethane (0.4 ml, 6.35 mmol), and then heated to 80 °C. After 24 h, the reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was concentrated under reduced pressure to afford the desired product as a beige powder (900 mg, 99%). m.p. = 270 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.17 (s, 1H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 3.95 (s, 2H), 2.16 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.72, 138.18, 137.44, 135.98, 132.27, 128.18, 126.85, 125.66, 121.94, 114.48, 35.15, 14.47. HRMS (ESI): $[M]^+$ calcd. for $C_{31}H_{29}N_2S_2$: 493.1767; Found: 493.1769.

1,3-dimethyl-4,5-bis(2-methyl-5-(4-vinylphenyl)thiophen-3-yl)-1H-imidazol-3-ium hexafluorophosphate (7)

A flask equipped with a stir bar was charged with the requisite imidazolium iodide (800 mg, 1.29 mmol) and dichloromethane (13 mL). Silver hexafluorophosphate (326 mg, 1.29 mmol) was then added and the reaction mixture stirred. Although a white precipitate formed immediately, the mixture was stirred at room temperature for an additional 15 min and then filtered through a 0.2 µm PTFE filter. The filtrate was concentrated and dried under reduced pressure to afford the desired product as a pale-yellow solid (774 mg, 94%). m.p. = 199 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.16 (s, 1H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (dd, *J* = 17.6, 0.5 Hz, 1H), 5.33 – 5.20 (m, 1H), 3.81 (s, 2H), 2.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.48, 137.69, 137.32, 136.03, 132.41, 128.19, 126.83, 125.62, 122.14, 114.37, 34.46, 13.92. HRMS (ESI): $[M]^+$ calcd. for $C_{31}H_{29}N_2S_2$: 493.1767; Found: 493.1767.

Poly(1,3-dimethyl-4,5-bis(2-methyl-5-(4-vinylphenyl)thiophen-3-yl)-1H-imidazol-3-ium hexafluorophosphate (8)

In a Schlenk flask, a solution of monomer **7** (100 mg, 0.157 mmol) in dichloromethane (0.3 mL) was degassed by bubbling with nitrogen for 10 min. Catalyst (6.6 mg, 7.83 µmol) was added under a positive pressure of nitrogen. The vessel was placed under a dynamic vacuum (70 torr absolute pressure) and the mixture was stirred at 40 °C for 24 h. Solvent (0.3 mL) was periodically added. Over the course of the polymerization, precipitation was observed. After 24 h, the reaction was quenched through the addition of excess ethyl vinyl ether. The precipitated solids were collected, washed with dichloromethane, and dried to obtain the corresponding polymer (30 mg). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.40 (s, 1H), 7.94 – 7.41 (m, 4H), 7.31 (s, 1H), 6.80 – 6.44 (m, 1H), 5.86 (d, *J* = 17.5 Hz, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 3.81 (d, *J* = 5.7 Hz, 3H), 2.03 (s, 3H). M_n: 8.4 kDa, M_w: 12.2 kDa, Đ: 1.45.

Conclusions

In conclusion, a new 4,5-dithienylimidazolium salt (**7**) outfitted with styrenyl groups was designed and synthesized. Compared to previously reported dithienylimidazolium salts, **7** exhibited a relatively long conjugation length. Alternately irradiating solutions of the salt with UV and visible light facilitated the ring-opening and ring-closing isomerizations, respectively. The photochromic diene was successfully polymerized using acyclic diene olefin metathesis to afford a new class of fluorescent polyelectrolytes.[47–51] These results and their underlying data provide a framework for building new classes of photoswitchable polymers from their photochromic monomers. Further structural modifications, including adjustment of the conjugation length and/or the installation of donor-acceptor groups, may facilitate the realization of the applications described above among others.

Conflicts of interest

There are no conflicts to declare.

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