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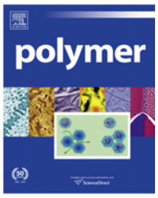

Synthesis and optical studies of conjugated polyfluorenyl cations

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ABSTRACT

Polyfluorene based precursor polymers were synthesized either by Yamamoto type or Suzuki polycondensation. These polymers were then converted to the corresponding conjugated polycations by treatment with trifluoroacetic acid. The formation of the conjugated polycations were followed by UV–vis and characterized by ^{1}H NMR. The absorption maxima of the polycations fall in the range of 580–690 nm. The formation of the polycations is evidenced by a red shift in absorption maxima compared to the parent polymers due to the generation of stable cations with more extended conjugation and planarity. The cationic polymers show low solubility in common organic solvents, however the solubility of the cationic salt can be greatly enhanced by controlling the cation density along the polymer chain by copolymerization.

1. Introduction

During the past two decades, the design and synthesis of new classes of conjugated polymers have attracted attention due to their interesting optical, electrochemical and electrical properties [1–4]. Fluorene-containing molecules represent an important class of aromatic systems that have received considerable attention due to their unique photophysical properties and potential for chemical modification [5–7]. Easy dialkylation at the 9-position and selective bromination at the 2,7-positions of fluorene allow versatile molecular manipulation to enhance solubility and extend conjugation easily by means of transition-metal catalyzed cross-coupling reactions [8–10]. Due to their high fluorescence quantum yield, excellent hole-transporting properties, good film-forming properties, and exceptional chemical stability, polyfluorene-based (PF) conjugated polymers have been extensively studied and utilized specifically in the field of light-emitting diodes [11–13]. Well-defined, fluorene based oligomers and copolymers also find application in organic thin film transistors [14,15]. However, the large optical band gap of poly(9,9-dialkylfluorene) limits its application in photovoltaic devices. For use in efficient solar cells, the absorption spectrum of the conjugated polymer needs to cover both the red and near infrared regions to harvest the maximum photon flux. The optical band gap of poly(9,9-dialkylfluorenes) is above 3 eV, which is too high for efficient sunlight harvesting where the maximum photon flux is around 1.7 eV (700 nm) [16]. Copolymerization of fluorene with acceptor type materials to form a donor–acceptor alternating arrangement in the polymer backbone is a strategy reported in literature for narrowing the band gap for optimal sunlight collection [17–19]. Carbinols, which contain oligo(1,4-phenylenevinyline) (OPV) chains and triaryl carbinol based polymers on treatment with strong acid lead to the formation of corresponding carbocations which exhibit strong bathochromic shift of the absorption maxima [20,21]. It is also reported that electron impact ionization and vacuum ultraviolet photoionization of fluorenes and photoheterolysis of 9-fluorenols with alkali metal zeolites generate corresponding fluorenyl cations having absorption maxima at higher wavelength region [22,23]. Fluorenyl cations can also be easily generated from their alcoholic or neutral methoxy precursors under acidic conditions [24,25]. Polycations derived from polyfluorenes with cationic functionalities incorporated into the polymer side chains has been widely investigated because of their unique characteristics that are different from those of neutral polymers [26–30]. Apart from a few limited reports in literature, there has been no systematic study into the synthesis and characterization of conjugated polycations in which cations are in conjugation with the polymer backbone [31,32]. The objective of our present study is to synthesize, and characterize conjugated polycations bearing cations in conjugation with the polymer backbone and investigate their effect on optical properties of the resulting materials. In our efforts to understand the effects of introducing conjugated cations along a polymeric network on conjugation and optical properties, we have explored the possibility of generating fluorenyl cations in the polymer chain. A

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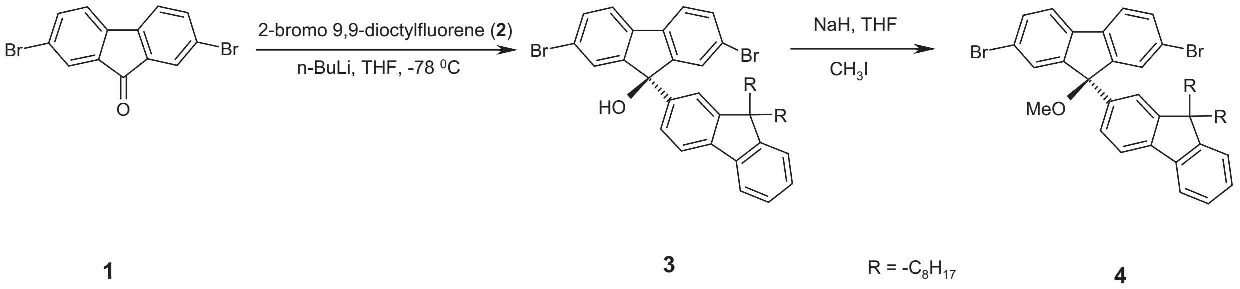


Scheme 1. Synthetic route for monomer **4**.

carbocation centered at the 9-position of fluorene in a conjugated material can be stabilized by extensive delocalization of the charge along the polymer backbone. Here, we report on the synthesis and characterization of conjugated polycations based on fluorene bearing alkylfluorene sidechains. Also, we report on copolymerization studies whereby the cation density along the polymer chain has been systematically varied.

2. Experimental

2.1. Materials

Dry solvents stored in a glove box were used for specified reactions. 2,7-dibromofluorenone (**1**), 2-bromo 9,9-dioctylfluorene (**2**), 2,7-dibromo-9,9-dioctylfluorene (**5**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2 dioxaboralan-2-yl)-9,9-dioctylfluorene (**6**) were synthesized in accordance with literature procedure [33–35].

2.2. Characterization

^{1}H and ^{13}C NMR spectra were taken on a Bruker 300 MHz spectrometer operating respectively at 300 MHz for ^{1}H and 75 MHz for ^{13}C using deuterated solvents with tetramethylsilane (TMS) as a reference for chemical shifts. Elemental analyses were measured on Elementar Vario EL III elemental analyzer. UV–vis absorption spectra were recorded in chloroform solution on a Perkin–Elmer Lambda 25 Spectrophotometer. Photoluminescence measurements were carried out with a Fluorolog HORIBAJOBIN YVON spectrophotometer using a xenon-arc lamp as a source, in chloroform solution. Thermal degradation was studied by TGA on a Perkin–Elmer Pyris 7 thermal analysis system in a dynamic atmosphere of nitrogen at a heating rate of 20 °C/min. The molecular weights of the polymers were determined by Gel Permeation Chromatography against polystyrene standard in THF at 30 °C.

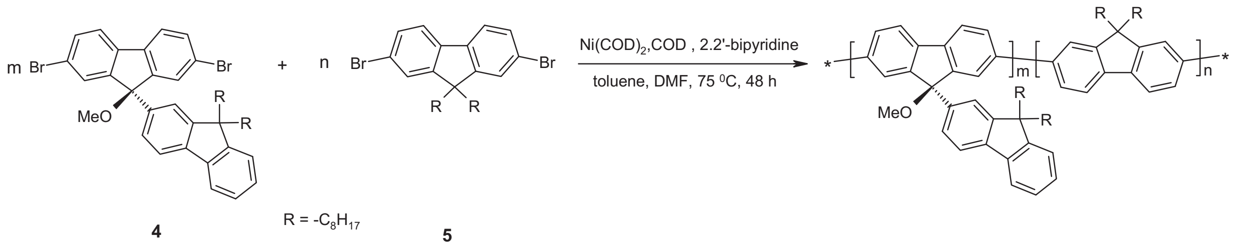
2.3. Synthesis

2.3.1. Synthesis of 2,7-dibromo-9-(9,9-dioctylfluorene-2-yl)-9-hydroxyfluorene (*3*)

To a solution of **2** (1.084 g, 2.308 mmol) in dry THF (5 mL) kept at −78 °C, *n*-BuLi in hexane (1.4 mL, 1.6 M, 2.260 mmol) was added dropwise and the mixture was stirred for 2 h at the same temperature. 2,7-dibromofluorenone (0.600 g, 1.775 mmol) was added to the reaction mixture and the temperature was gradually increased to room temperature. After stirring for 20 h the reaction was quenched by the addition of water. The product was extracted with diethyl ether, washed with saturated brine and dried over Na_2SO_4. The crude so obtained was purified by column chromatography with 0–1% ethylacetate in hexane as eluent to obtain **3** as a colorless oil (0.600 g, 46%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60$–7.17 (m, 12H), 6.88 (d, $J = 7.5$ Hz, 1H), 2.43 (s, 1H), 1.84 (t, $J = 8.1$ Hz, 4H), 1.34–0.54 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.13$, 151.16, 150.89, 140.82, 140.50, 140.38, 137.39, 132.29, 128.33, 127.05, 126.69, 123.84, 123.29, 122.76, 122.47, 121.49, 119.73, 119.62, 119.53, 83.57, 55.11, 40.20, 31.74, 30.02, 29.21, 23.87, 22.57, 14.09. Elem. Anal. Calc. For $C_{42}H_{48}Br_2O$: C, 69.23, H, 6.64; Found: C, 68.87, H, 7.04.

2.3.2. Synthesis of 2,7-dibromo-9-(9,9-dioctylfluorene-2-yl)-9-methoxyfluorene (*4*)

Compound **3** (0.550 g, 0.755 mmol) was dissolved in dry THF (4 mL) and NaH (0.072 g, 3.020 mmol) was added to this solution. The reaction mixture was stirred for 30 min at room temperature. Methyl iodide (0.470 mL, 7.550 mmol) was added to this solution and after stirring at room temperature for 18 h the product was extracted with diethyl ether and dried over Na_2SO_4. The crude so obtained was purified by column chromatography with 0–1% ethylacetate in hexane as eluent to obtain **4** as a white solid (0.480 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60$–7.39 (m, 12H), 6.89 (d, $J = 7.8$ Hz, 1H), 3.02 (s, 3H), 1.92 (t, $J = 9$ Hz, 4H), 1.20–0.59



P1-OMe ; m = 1, n = 0

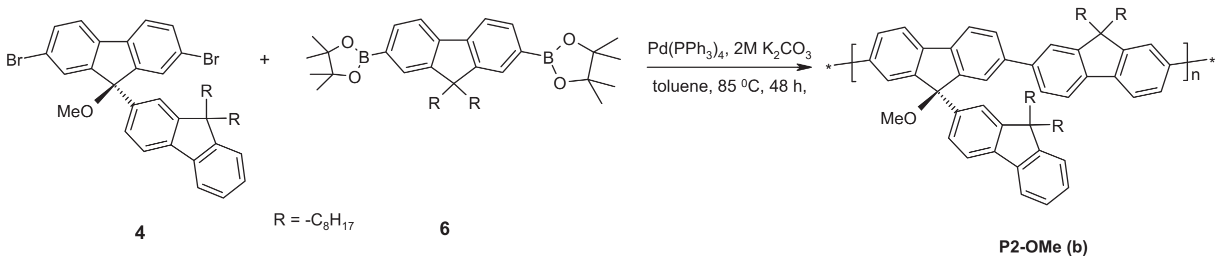
P2-OMe (a) ; m = 1, n = 1

P3-OMe ; m = 1, n = 2

P4-OMe ; m = 1, n = 6

P5-OMe ; m = 1, n = 10

Scheme 2. Synthesis of polymers via Yamamoto polycondensation.



Scheme 3. Synthesis of **P2-OMe** (**b**) via Suzuki polycondensation.

(m, 30H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 151.03, 150.93, 149.03, 140.70, 140.62, 138.74, 132.33, 128.68, 126.98, 126.68, 124.04, 122.77, 122.45, 121.39, 120.07, 119.60, 119.38, 55.11, 51.73, 40.25, 31.78, 30.05, 29.23, 23.86, 22.60, 14.10. Elem. Anal. Calc. For $C_{43}H_{50}Br_2O$: C, 69.54, H, 6.79; Found: C, 69.400, H, 6.91.

2.3.3. *Synthesis of poly[2,7-9-(9,9-dioctylfluorene-2-yl)-9-methoxyfluorene],* ***P1-OMe***

Ni(COD)$_2$ (0.338 g, 1.228 mmol), COD (0.150 mL, 1.228 mmol) and 2,2′-bipyridine (0.192 g, 1.228 mmol) were added to a Schlenk tube containing a mixture of DMF (1.4 mL) and toluene (1 mL) in a glove box. The resulting solution was heated under nitrogen at 60 °C for 30 min and then a solution of **4** (0.380 g, 0.520 mmol) in toluene (4.6 mL) was added. The reaction mixture was heated for 48 h at 75 °C. After cooling to room temperature, the viscous solution was poured into 250 mL of methanol and the precipitated polymer was isolated by filtration. It was further purified by extraction with acetone in a Soxhlet apparatus. The polymer was redissolved in chloroform and washed with saturated aqueous EDTA solution and distilled water. The organic layer was extracted, concentrated to minimum volume and poured into 250 mL of methanol causing the precipitation of the polymer to yield **PI-OMe** as a pale yellow powder (0.166 g, 54% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.57–6.98 (m, 13H, br), 2.95 (s, 3H, br), 1.83 (t, 4H, br), 0.89–0.56 (m, 30H, br). UV–vis (CHCl$_3$) λ_{max}: 372 nm. GPC: M_w = 4.2 kDa, M_n = 2.9 kDa, PDI = 1.45.

2.3.4. *Synthesis of poly[2,7-(9,9-dioctylfluorene)-co-2′,7′-9-(9,9-dioctylfluorene-2-yl)-9-methoxyfluorene],* ***P2-OMe(a)***

P2-OMe(**a**) was prepared according to the procedure reported for **P1-OMe** using **4** (0.150 g, 0.202 mmol), **5** (0.110 g, 0.202 mmol), Ni(COD)$_2$ (0.256 g, 0.929 mmol), COD (0.114 mL, 0.929 mmol), 2,2′-bipyridine (0.64 g, 0.929 mmol), toluene (4.3 mL) and DMF (1.1 mL). The polymer was obtained as a yellow solid (0.150 g, 76%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.58–6.95 (m, 19H, br), 3.02 (s, 3H, br), 1.88 (t, 8H, br), 1.01–0.56 (m, 60H, br). UV–vis (CHCl$_3$) λ_{max}: 375 nm. GPC: M_w = 8.3 kDa, M_n = 3.8 kDa, PDI = 2.1.

2.3.5. *Synthesis of poly[2,7-(9,9-dioctylfluorene)-co-2′,7′-9-(9,9-dioctylfluorene-2-yl)-9-methoxyfluorene],* ***P2-OMe(b)***

The monomers **4** (0.338 g, 0.404 mmol) and **6** (0.274 g, 0.424 mmol), Pd (PPh$_3$)$_4$ (14 mg, 2 mol %), toluene (4 mL), Aliquat 336 (3 drops) and 1.2 mL of 2 M Na$_2$CO$_3$ solution were added to a Schlenk tube. The solution was purged under nitrogen for 30 min, and then stirred for 48 h at 85 °C. Bromobenzene (45 μL, 0.42 mmol) was added as end capping agent to the mixture and stirred for 12 h under the same conditions. After cooling to room temperature, the viscous solution was poured into 300 mL of methanol. The precipitated polymer was isolated by filtration. It was further purified by Soxhlet extraction with acetone followed by reprecipitation from methanol. The polymer was dried under reduced pressure to yield **P2-OMe** as a pale yellow solid (0.382 g, 97%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.80–7.13 (m, 19H, br), 3.18 (s, 3H, br), 1.98 (t, 8H, br), 1.06–0.78 (m, 60H, br). UV–vis (CHCl$_3$) λ_{max}: 383 nm. GPC: M_w = 151.1 kDa, M_n = 23.9 kDa, PDI = 6.38.

2.3.6. *Synthesis of* ***P3-OMe***

P3-OMe was prepared according to the procedure reported for **P1-OMe** using **4** (0.160 g, 0.215 mmol), **5** (0.235 g, 0.423 mmol), Ni (COD)$_2$ (0.392 g, 1.423 mmol), COD (0.175 mL, 1.423 mmol), 2,2′-bipyridine (0.223 g, 1.423 mmol), toluene (6.8 mL) and DMF (1.7 mL). The polymer was obtained as a pale yellow solid (0.25 g, 84%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.67–7.26 (m, 25H, br), 3.16 (s, 3H, br), 1.99 (t, 12H, br), 1.24–0.80 (m, 90H, br). UV–vis (CHCl$_3$) λ_{max}: 381 nm. GPC: M_w = 34.1 kDa, M_n = 14.1 kDa, PDI = 2.62.

2.3.7. *Synthesis of* ***P4-OMe***

P4-OMe was prepared according to the procedure reported for **P1-OMe** using **4** (0.100 g, 0.135 mmol), **5** (0.440 g, 0.808 mmol), Ni (COD)$_2$ (0.597 g, 2.167 mmol), COD (0.265 mL, 2.167 mmol), 2,2′-bipyridine (0.339 g, 2.167 mmol), toluene (9.6 mL) and DMF (2.4 ml). The polymer was obtained as a yellow solid (0.290 g, 74%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.82–6.97 (m, 49H, br), 3.20 (s, 3H,

Table 1
The initial feed ratio and ratio as determined by ^{1}H NMR for the two comonomers.

Polymer	Initial feed ratio (m:n)	Ratio in the polymer (m:n)
P1-OMe	1:0	1:0
P2-OMe (**a**)	1:1	1:1
P3-OMe	1:2	1:1.96
P4-OMe	1:6	1:6.06
P5-OMe	1:10	1:10.03

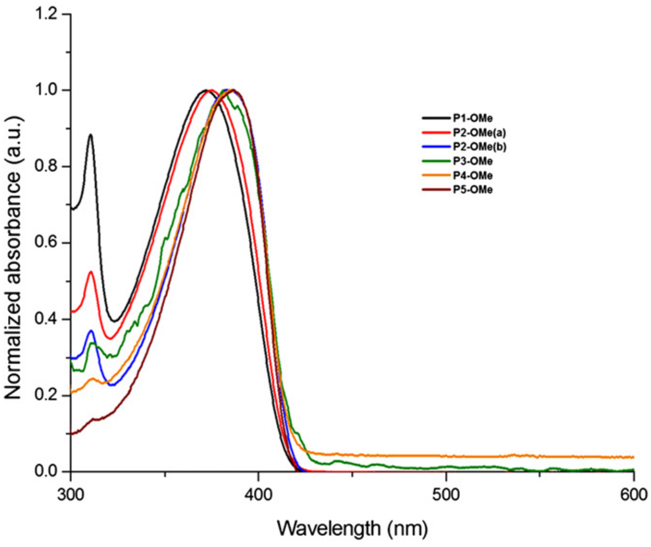


Fig. 1. UV–vis spectra of polymers in chloroform solution.

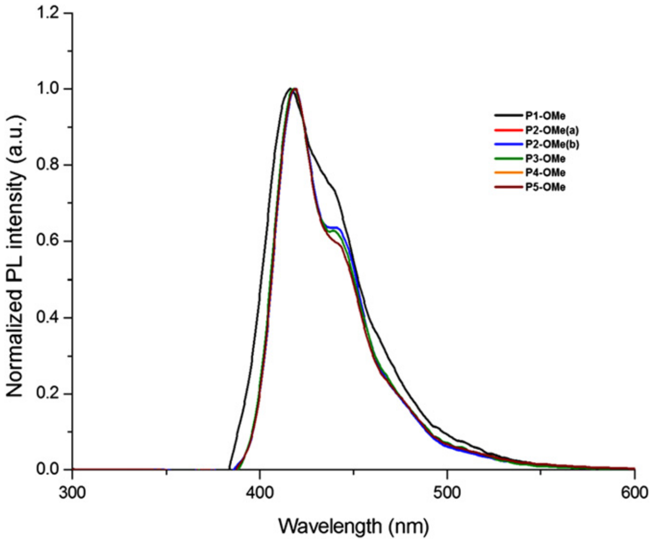


Fig. 2. PL spectra of precursor polymers in chloroform solution.

br), 2.10 (t, 28H, br), 1.13–0.81 (m, 210H, br). UV–vis ($CHCl_3$) λ_{max}: 385 nm. GPC: M_w = 179.1 kDa, M_n = 32.2 kDa, PDI = 5.59.

2.3.8. Synthesis of ***P5-OMe***

P5-OMe was prepared according to the procedure reported for **P1-OMe** using **4** (0.050 g, 0.067 mmol), **5** (0.367 g, 0.673 mmol), Ni$(COD)_2$ (0.469 g, 1.703 mmol), COD (0.209 mL, 1.703 mmol), 2,2′-bipyridine (0.226 g, 1.703 mmol), toluene (8 mL) and DMF (2 mL). The polymer was obtained as a yellow solid (0.245 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76–6.99 (m, 73H, br), 3.13 (s, 3H, br), 2.04 (t, 44H, br), 1.06–0.74 (m, 330H, br). UV–vis ($CHCl_3$) λ_{max}: 386 nm. GPC: M_w = 119.8 kDa, M_n = 30.2 kDa, PDI = 3.93.

2.4. General procedure for the synthesis of conjugated polycations

The polymer/model compound (20 mg) was dissolved in chloroform (3 mL) and trifluoroacetic acid (0.1–0.2 mL) was added to the chloroform solution. Within 2–3 min, the solution turned dark green. ^{1}H NMR spectra of the conjugated polycations were taken in deuterated chloroform after generating the cations with deuterated TFA. The UV–vis spectra were taken from this solution after diluting it to very low concentration (10^{-6} M).

2.4.1. ***P1***

^{1}H NMR (300 MHz, $CDCl_3/CF_3COOD$): δ = 7.67–7.24 (m, 13H, br), 1.95 (t, 4H, br), 1.02–0.74 (m, 30H, br). UV–vis ($CDCl_3/CF_3COOD$). λ_{max}: 690 nm, 478 nm, 357 nm.

Table 2
Molecular weights and optical properties of precursor polymers.

Polymers	Yield (%)	M_n (kDa)	PDI	T_d (°C)[a]	λ_{abs} (nm)[b]	λ_{em} (nm)[c]
P1-OMe	54	2.9	1.45	346	372	417
P2-OMe (**a**)	76	3.8	2.1	357	375	418
P2-OMe (**b**)	97	23.7	6.37	339	383	419
P3-OMe	84	14.1	2.41	382	381	418
P4-OMe	74	32.2	5.56	380	385	419
P5-OMe	82	30.2	3.96	393	386	419

[a] The temperature at 5% weight loss measured by TGA with a heating rate of 20 °C/min under nitrogen atmosphere.

[b] UV–vis absorption maxima recorded in chloroform solution.

[c] Photoluminescence emission maxima recorded in chloroform solution at λ_{exc} = 370 nm.

2.4.2. ***P2 (a)***

^{1}H NMR (300 MHz, $CDCl_3/CF_3COOD$): δ = 7.69–7.26 (m, 19 H, br), 2.03 (t, 8H, br), 1.27–0.79 (m, 60H, br). UV–vis ($CDCl_3/CF_3COOD$). λ_{max}: 682 nm, 481 nm, 323 nm.

2.4.3. ***P2 (b)***

^{1}H NMR (300 MHz, $CDCl_3/CF_3COOD$): δ = 7.74–7.26 (m, 19H, br), 2.02 (t, 8H, br), 1.10–0.79 (m, 60H, br). UV–vis ($CDCl_3/CF_3COOD$). λ_{max}: 682 nm, 481 nm, 349 nm.

2.4.4. ***P3***

^{1}H NMR (300 MHz, $CDCl_3/CF_3COOD$): δ = 7.64–7.26 (m, 25H, br), 2.12 (t, 12H, br), 1.12–0.84 (m, 90H, br). UV–vis ($CDCl_3/CF_3COOD$). λ_{max}: 687 nm, 480 nm, 384 nm.

2.4.5. ***P4***

^{1}H NMR (300 MHz, $CDCl_3/CF_3COOD$): δ = 7.67–7.00 (m, 49H, br), 2.28 (t, 28H, br), 1.43–0.81 (m, 210H, br). UV–vis ($CDCl_3/CF_3COOD$). λ_{max}: 587 nm, 324 nm.

2.4.6. ***P5***

^{1}H NMR (300 MHz, $CDCl_3/CF_3COOD$): δ = 7.67–7.25 (m, 73H, br), 2.15 (t, 28H, br), 1.17–0.83 (m, 330H, br). UV–vis ($CDCl_3/CF_3COOD$). λ_{max}: 606 nm, 325 nm.

2.4.7. ***M4***

^{1}H NMR (300 MHz, $CDCl_3/CF_3COOD$): δ = 7.59–7.25 (m, 13H br), 1.96 (t, 4H, br), 1.27–0.62 (m, 30H, br). UV–vis ($CDCl_3/CF_3COOD$). λ_{max}: 693 nm, 468 nm, 315 nm.

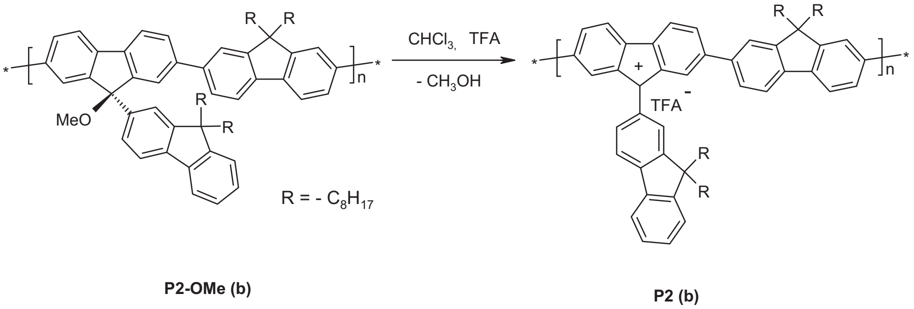
3. Results and discussion

3.1. Synthesis of monomers and precursors for conjugated polycations

The synthetic approach toward the synthesis of monomer **4** is shown in Scheme 1. Fluorenol derivative **3** was obtained in 46% yield by reacting the lithium reagent formed by dropwise addition of *n*-BuLi into a THF solution of 2-bromo 9, 9-dioctylfluorene (**2**) at −78 °C with 2,7-dibromofluorenone (**1**). Alkylation of **3** with methyl iodide under basic condition generated monomer **4** in 85% yield. The monomer 2,7-dibromo-9-(9,9-dioctylfluorene-2-yl)-9-methoxyfluorene **4** bearing substituted fluorenyl group at 9-position was polymerized by Yamamoto type polymerization to yield polymer **P1-OMe** of high solubility.

The synthetic routes toward polymers by Yamamoto and Suzuki polycondensation methods are outlined in Schemes 2 and 3, respectively. The homopolymer **P1-OMe** ($m = 1, n = 0$) and random copolymers **P2-OMe** (**a**) ($m = 1$, $n = 1$), **P3-OMe** ($m = 1$, $n = 2$), **P4-OMe** ($m = 1, n = 6$) and **P5-OMe** ($m = 1, n = 10$) were prepared by nickel(0)-mediated Yamamoto type polycondensation. The alternating copolymer **P2-OMe** (**b**) was prepared by standard Suzuki polycondensation of 2,7-dibromo-9-(9,9-dioctylfluorene-2-yl)-9-methoxyfluorene (**4**) with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-9,9-dioctylfluorene (**6**) in presence of $Pd(PPh_3)_4$. The copolymers having different molar feed ratios of monomer **5** were synthesized as a means to control the density of cations along the polymer chain to understand its effect on solubility and optical properties. After precipitation in methanol, the polymers were further purified by Soxhlet extraction and then by reprecipitation. All the polymers show good solubility in THF, $CHCl_3$ and CH_2Cl_2.

The polymers were characterized by ^{1}H NMR, UV–vis and photoluminescence (PL) spectroscopy, molecular weight determination and TGA. The actual ratio of monomers **4** and **5** in the



Scheme 4. Conversion of precursor polymer **P2-OMe** (**b**) to the conjugated polycation **P2** (**b**).

copolymers (m:n) as determined from ^{1}H NMR analysis are in good agreement with initial feed ratios, and are summarized in Table 1.

The electronic absorption and photoluminescence emission ($\lambda_{exc} = 370$ nm) spectra of the precursor polymers in chloroform solution are depicted in Figs. 1 and 2, respectively.

The observed absorption and emission maxima are comparable to that of poly (9,9-dialkyl fluorene-2,7-diyl) reported in literature [36,37]. This implies that replacing the two flexible alkyl chains on fluorene unit with methoxy and alkylated fluorene groups does not alter the electronic structure of the polyfluorene backbone.

The molecular weights of the polymers were determined by Gel Permeation Chromatography. The weight-average molecular weights (M_w) were found to be 4.2, 8.3, 151.1, 34.1, 179.1 and 119.8 kDa with PDI of 1.45, 2.1, 6.37, 2.41, 5.56 and 3.96 respectively for the precursor polymers **P1-OMe** to **P5-OMe**. The homopolymer **P1-OMe** has low yield (54%) and low molecular weight ($M_n = 2.9$ kDa) compared to the copolymers which is due to the formation of insoluble gel during polymerization. In the case of copolymers no such gel formation is observed. **P3-OMe** also has significantly low M_w compared to **P4-OMe** and **P5-OMe**. Since the latter two have higher amount of alkyl solubilizing groups, it appears that the 9,9-dioctyl flourene content has a direct bearing on the molecular weight and solubility of the resulting copolymers. The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA). The decomposition temperature (T_d) of the polymers based on 5% weight loss is given in Table 2. The onset decomposition temperature of the polymers are in the range of 346–393 °C which is less than that of poly(9,9-dioctyl fluorene 2,7-yl) [37]. This could be attributed to the presence of varying ratios of methoxy group and flexible alkyl chain in the polymer. The physical and optical properties of the various polymers are summarized in Table 2.

3.2. Synthesis and characterization of conjugated polycations

The absorption maxima of all precursor polymers reported in this study is in the range of 370–385 nm. Generation of cations can be used as a means to red shift the absorption and extend the spectral window. In order to study the effect of cation formation on absorption spectra of conjugated polymers, polycations were generated from the precursor polymers by treatment with trifluoroacetic acid (TFA). The general route for the conversion of precursor polymers to their cationic form is shown in Scheme 4.

To convert the methoxy precursors to the cationic form, the polymer was dissolved in chloroform and treated with TFA. Within 2–3 min, the formerly colourless solution turned dark green. The polycation generated from precursor polymer **P1-OMe** is named as **P1**, **P2-OMe** as **P2** and so on and the one from the monomer **4** is named as **M4** (the model compound). The cations were characterized by ^{1}H NMR and UV–vis spectroscopy. For example, the ^{1}H NMR spectra of **P1-OMe** and **P1** in chloroform solution are shown in Figs. 3 and 4 respectively.

Compared to the ^{1}H NMR spectrum of **P1-OMe**, there is significant displacement of signals in **P1**, upon conversion to the polycationic form. The signal **a** corresponding to –OMe at 2.95 ppm completely disappears and an additional signal at 3.59 ppm corresponding to the $-CH_3$ resonance of methanol, released on cation formation, appears in ^{1}H NMR of **P1**. This indicates that the conversion of methoxy form to the cationic form is complete. Similar observations were made in the NMR spectra for all the other cationic polymers as well. The structures of all polycations were investigated by generating cations in NMR experiments, however, it is possible to remove the generated methanol by evaporation under vacuum and obtain spectra of the polycation alone (See Supporting information Fig.S1 and Fig.S2). This confirmed quantitative conversion of the methoxy precursors to the polycationic form. The molecular structure of the polycations can be confirmed by 2D NMR analysis. But in this case the solubility of none of the polycations is

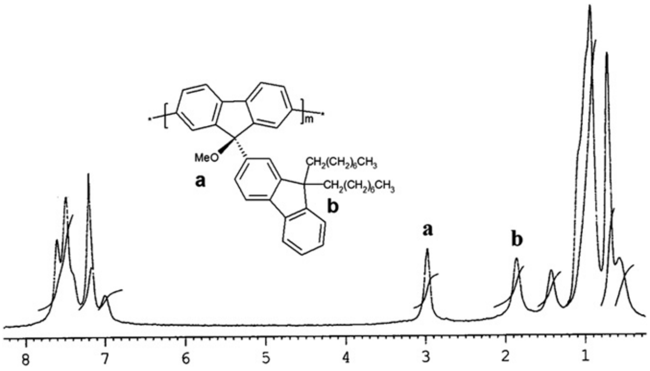


Fig. 3. ^{1}H NMR spectrum of **P1-OMe** (300 MHz; $CDCl_3$).

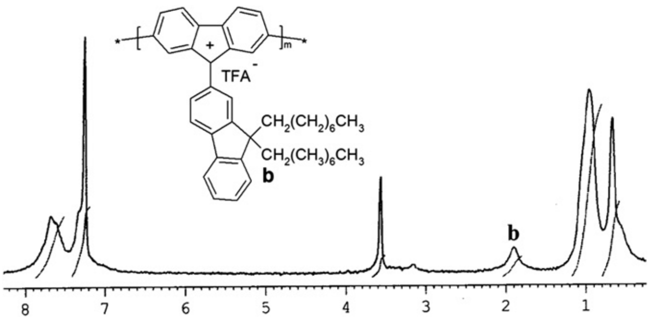


Fig. 4. ^{1}H NMR spectrum of **P1** (300 MHz; $CDCl_3/CF_3COOD$).

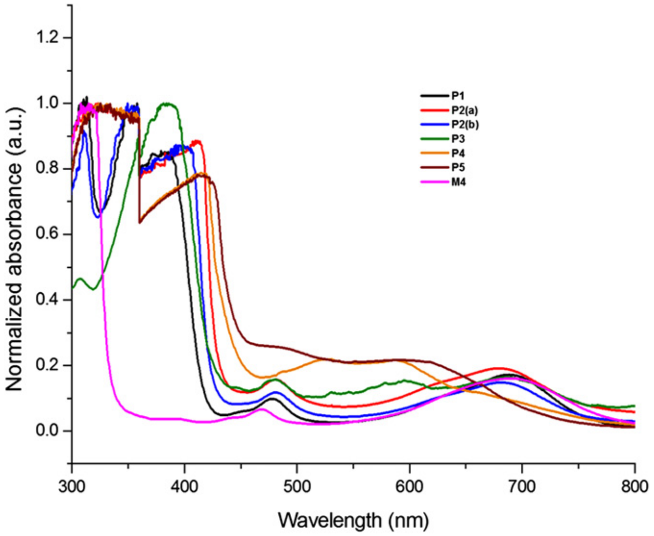


Fig. 5. UV–vis spectra of polycations in chloroform/TFA solution.

high enough to get satisfactory data by ^{13}C and ^{1}H–^{13}C HSQC NMR spectra to obtain ^{1}H–^{13}C connectivity in the polycations. The 300 MHz ^{1}H–^{1}H 2D COSY spectra of **P2-OMe** (b) and **P2**(**b**) is given in Supporting information (Fig.S3 and Fig.S4)

The acid catalyzed removal of methoxy group at the C-9 position fluorene units is facilitated by the increase in stability of cations through extensive conjugation along the backbone of the polymer and also along the alkylfluorene sidechain. This is also accompanied by a red shift in absorption maximum for the polycations compared to their methoxy form. For comparison of the photophysical properties of the polymers UV–vis spectrum of monomer **4** as a model compound was taken on treatment with trifluoroacetic acid (TFA) which is depicted as **M4** in Fig. 5 along with UV–vis spectra of polycations (**P1**–**P5**). The photophysical properties of conjugated cations are summarized in Table 3.

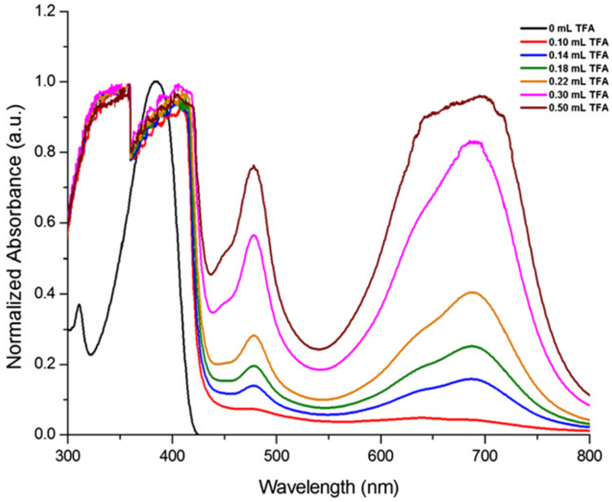


Fig. 6. UV–vis spectrum of **P2-OMe** (b) in $CHCl_3$ with addition of TFA.

The absorption spectra of polycations (**P1**–**P3**) reveal two new long wavelength absorption bands around 480 nm and 680 nm along with strong peaks around 320–380 nm, while the spectra of **P4** and **P5** exhibit long wavelength absorption bands between 580 and 610 nm along with strong peaks around 325 nm. These values are in good agreement with the electronic absorption spectrum of fluorenyl cation generated from the monomer **4** which is having long wavelength absorption bands at 468 and 693 nm and another strong absorption band at 315 nm. Formation of cation at C-9 position enhances the π conjugation compared to the methoxy form, resulting in a red shift in absorption maxima for the cationic polymers. As a result of cation formation the electronic structure of the conjugated polymer is modified which resulted in new electronic transitions within the band structure of the conjugated polycation to give additional bands in the absorption spectra of the polycations. The UV–vis spectra of polymers were taken at different intervals of time after addition of trifluoroacetic acid. Once the cation is generated as indicated by the dark green color change, the observed absorption maxima of the conjugated polycations did not show any variation with time or amount of added trifluoroacetic acid. As an example variation in absorption spectra of **P2-OMe**(**b**) in chloroform solution (5 mg/mL) upon addition of varying amount of trifluoroacetic acid is shown in Fig. 6. It can be seen that the intensity of long wavelength absorption band of polycations increases with addition of TFA, but the absorption maxima (λ_{max}) remains almost same. Similar results have been reported in literature [38,39]. The observed time independent absorption maxima of polycations suggest complete conversion of precursor polymers to the cationic form instantaneously with extended conjugation and planarity. Also, the polycations **P2** (**a**) and **P2** (**b**) generated from precursor copolymers made respectively by Yamamoto and Suzuki polycondensation did not show any significant difference in optical properties.

Table 3
Absorption data for conjugated polycations.

Polymer/Model	λ_1 (nm)	λ_2 (nm)	λ_{max} (nm)
M4	315	468	693
P1	357	478	690
P2(**a**)	323	481	679
P2(**b**)	349	481	682
P3	384	480	687
P4	324		587
P5	325		606

3.3. Stability studies

Applications of polycations are possible only if they are stable enough in the working condition of device. We have conducted preliminary studies on the stability of the polyconjugated cations in solution by monitoring the intensity of absorption in UV–vis spectra. The polycations are stable in air at room temperature for a time period of 24 h as indicated by their color stability and intensity of absorption. After two weeks, the color of the polymer solutions kept in air faded, along with a slight decrease in intensity of the long wavelength absorption band. But polycation solutions kept under nitrogen atmosphere did not show any such variation in color and intensity of absorption. Thus, the polycations show enhanced stability in solution under nitrogen as evidenced by the reproducibility of absorption spectra over a two week period. It is also observed that the phenomenon of cation formation is reversible and upon addition of methanol, the polycations recover their initial color.

3.4. Effect of cation density on solubility and optical properties of conjugated polycations

The trifluoroacetate salt **P1** shows low solubility in common organic solvents. Copolymers with varying cation density along the polymer chain were synthesized to study its effect on the solubility of the conjugated cationic salt. The polymers with relatively low cation density (**P4** and **P5**) have good solubility in chloroform and dichloromethane compared to those with high cation density (**P1**, **P2** and **P3**). The absorption maxima of conjugated polycations **P1**–**P5** are 690 nm, 682 nm, 687 nm, 587 nm and 606 nm respectively. The relatively low red shift in absorption maxima of **P4** and **P5** compared to the other polycations (~75 nm) may be attributed to the lower cation density along the polymer chain. The polymer solutions with higher comonomer ratio have lower cation density and exhibit lower absorption maxima.

4. Conclusions

In conclusion, conjugated polycations based on fluorene bearing alkyfluorene side chains have been synthesized and characterized. The observed absorption maxima suggest that the generation of stable conjugated cations along the polymer chain can be used as a strategy to synthesize polyfluorenes with extended absorption maxima. From the copolymerization studies it is found that the cation density along the polymer has remarkable influence on the solubility of the conjugated polycationic salt. Polymers with lower cation density show good solubility in chloroform and dichloromethane compared to those having higher cation density. The absorption maxima of polyconjugated cations exhibit a large red shift compared to the parent precursor polymers due to the formation of planar cations with extended conjugation along the polymer chain. Also, a decrease in cation density causes blue shift in absorption maxima among the conjugated cations. The stability of conjugated polyfluorenyl cations along with their extended absorption maxima to longer wavelength region holds promise for use in photovoltaic devices. Also these materials can be used as p- type electrically conducting materials in various optoelectronic devices. Our future work will focus on the testing of these polycations in devices. This strategy can be extended to new oligomers and polymers, which will allow for the preparation of libraries of low band gap materials.

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Appendix. Supporting information

Supporting information associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.09.062.

References

[1] Li X-G, Huang M-R, Duan W, Yang Y-L. Chem Rev (Washington DC U.S.) 2002;102(9):2925–3030.

[2] Li X-G, Hou Z-Z, Huang M-R, Moloney MG. J Phys Chem C 2009;113 (52):21586–95.

[3] MacDiarmid AG. Angew Chem Int Ed 2001;40(14):2581–90.

[4] Li X-G, Liu Y-W, Huang M-R, Peng S, Gong L-Z, Moloney MG. Chem Eur J 2010;16(16):4803–13.

[5] Yu W-L, Cao Y, Pei J, Huang W, Heeger AJ. Appl Phys Lett 1999;75(21):3270–2.

[6] Grell M, Bradley DDC, Ungar G, Hill J, Whitehead KS. Macromolecules 1999;32 (18):5810–7.

[7] Ding J, Day M, Robertson G, Roovers J. Macromolecules 2002;35(9):3474–83.

[8] Wong K-T, Chien Y-Y, Chen R-T, Wang C-F, Lin Y-T, Chiang H-H, et al. J Am Chem Soc 2002;124(39):11576–7.

[9] Yamamoto T, Morita A, Miyazaki Y, Maruyama T, Wakayama H, Zhou ZH, et al. Macromolecules 1992;25(4):1214–23.

[10] Miyaura N, Suzuki A. Chem Rev (Washington D.C.) 1995;95(7):2457–83.

[11] Bernius MT, Inbasekaran M, O'Brien J, Wu W. Adv Mater (Weinheim Ger.) 2000;12(23):1737–50.

[12] Neher D. Macromol Rapid Commun 2001;22(17):1365–85.

[13] Scherf U, List EJW. Adv Mater (Weinheim Ger.) 2002;14(7):477–87.

[14] Kim YM, Lim E, Kang I-N, Jung B-J, Lee J, Koo BW, et al. Macromolecules 2006;39(12):4081–5.

[15] Meng H, Bao Z, Lovinger AJ, Wang B-C, Mujsce AM. J Am Chem Soc 2001;123 (37):9214–5.

[16] Gunes S, Neugebauer H, Sariciftci Niyazi S. Chem Rev 2007;107(4):1324–38.

[17] Yang R, Tian R, Yan J, Zhang Y, Yang J, Hou Q, et al. Macromolecules 2005;38 (2):244–53.

[18] Lee W-Y, Cheng K-F, Wang T-F, Chen W-C, Tsai F-Y. Thin Solid Films 2010;518 (8):2119–23.

[19] Shi C, Yao Y, Yang Y, Pei Q. J Am Chem Soc 2006;128(27):8980–6.

[20] Meier H, Kim S. Eur J Org Chem 2001;(6):1163–7.

[21] Bartholome D, Klemm E. Macromolecules 2006;39(17):5646–51.

[22] O'Neill MA, Cozens FL, Schepp NP. Tetrahedron 2000;56(36):6969–77.

[23] Szczepanski J, Banisaukas J, Vala M, Hirata S, Bartlett RJ, Head-Gordon M. J Phys Chem A 2002;106(1):63–73.

[24] Dahl BJ, Mills NS. Org Lett 2008;10(24):5605–8.

[25] Mladenova G, Chen L, Rodriquez CF, Siu KWM, Johnston LJ, Hopkinson AC, et al. J Org Chem 2001;66(4):1109–14.

[26] Yang R, Wu H, Cao Y, Bazan GC. J Am Chem Soc 2006;128(45):14422–3.

[27] Huang F, Wu H, Wang D, Yang W, Cao Y. Chem Mater 2004;16(4):708–16.

[28] Liu B, Lai Y-H, Yu W-L, Huang W. Chem Commun (Cambridge) 2000;(7):551–2.

[29] Ma W, Iyer PK, Gong X, Liu B, Moses D, Bazan GC, et al. Adv Mater (Weinheim Ger.) 2005;17(3):274–7.

[30] Hoven CV, Garcia A, Bazan GC, Nguyen T-Q. Adv Mater (Weinheim Ger.) 2008;20(20):3793–810.

[31] Shim N, Moon B, Lee H. React Funct Polym 2006;66(12):1506–14.

[32] Wang F, Lai Y-H, Kocherginsky NM, Kosteski YY. Org Lett 2003;5(7):995–8.

[33] Sugio Y, Kitamura N, Mori H, Hachiya T. Process for the preparation of 2,7-dibromofluorenone. US Patent 6,977,313;2004.

[34] Khan MS, Al-Mandhary MRA, Al-Suti MK, Ahrens B, Mahon MF, Male L, et al. Dalton Trans 2003;(1):74–84.

[35] Ranger M, Rondeau D, Leclerc M. Macromolecules 1997;30(25):7686–91.

[36] Liu S-P, Ng S-C, Chan HSO. Synth Met 2005;149(1):1–11.

[37] Cheon CH, Joo S-H, Kim K, Jin J-I, Shin H-W, Kim Y-R. Macromolecules 2005;38 (15):6336–45.

[38] Bangcuyo CG, Rampey-Vaughn ME, Quan LT, Angel SM, Smith MD, Bunz UHF. Macromolecules 2002;35(5):1563–8.

[39] Kappaun S, Horner S, Kelterer A-M, Waich K, Grasse F, Graf M, et al. Macromol Chem Phys 2008;209(20):2122–34.