

STABLE SUPERHYDROPHOBIC FLUORINE CONTAINING POLYFLUORENES*

Mei-fang Liu, Yu-lan Chen, Chi Zhang and Zhi-shan Bo**
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract Fluorene-based polymers containing perfluorooctyl moieties were designed and synthesized. The high electronegativity and $F\cdots H-C$ interactions are present in the fluorinated polymers, which slightly induce blue-shift of UV-Vis absorption in film. The fluoropolymer films prepared from fluorinated solvents show larger contact angles than those prepared in non-fluorinated solvents.

Keywords: Conjugated polymers; Contact angle; Fluorinated; Fluoropolymers; Superhydrophobic.

INTRODUCTION

Polymers containing fluorine groups have been known to possess certain much improved properties, such as rigidity, thermal stability, chemical and oxidative resistance, hydrophobicity and a high tendency for phase separation with hydrocarbon segments^[1, 2]. In consideration of the electronegativity of fluorine atoms, fluorine substitution could lower the LUMO and HOMO energy states, so that the electroluminescence (EL) efficiency would be enhanced. Lower HOMO energies would also result in increased oxidation potential and enhanced stability against photo-oxidation^[3, 4]. In the past two decades, a broad variety of organic materials containing fluorine characterized by semiconducting properties have been developed for applications in electronic devices^[5–11]. These conducting materials and the efficiency of the devices are markedly influenced by the environmental exposure, particularly moisture^[12, 13]. Thus, it appears that it is of great interest to obtain stable liquid repellent conducting polymers.

The wettability of a solid surface by a liquid is a characteristic property of materials and is determined by two factors: the chemical composition and the geometrical microstructure of the surface^[14–16]. An efficient approach for the chemical factor is the introduction of perfluorocarbon chain in the polymer backbone. Polymers containing fluorine have been extensively used for the modification of surface to confer upon them repellency toward both polar and nonpolar liquids. Some conjugated polyfluorenes containing fluorine have been studied for their thermal stability, photoluminescence and electronic devices^[17–20]. However, few works were devoted to the surface properties of the polymers containing fluorine.

We report a facile approach to get hydrophobic films by dropping cast a solution of fluorinated polymer in THF or 1,2,4-trifluorobenzene onto a glass wafer by naturally evaporating the solution. It is noting that the number of the fluorinated chains of the polymer really influences the contact angle of films. Compared with the films prepared from THF, the contact angles of the films from 1,2,4-trifluorobenzene were improved.

* This work was financially supported by the NSF of China (Nos. 20834006 and 50821062) and the National Basic Research Program of China (973 Program: 2009CB623601).

** Corresponding author: Zhi-shan Bo (薄志山), E-mail: zsbo@iccas.ac.cn

Received May 31, 2011; Revised July 16, 2011; Accepted July 19, 2011

doi: 10.1007/s10118-012-1127-1

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich or Acros and used without further purification. 2,7-Dibromo-9,9-dioctylfluorene^[21] and 4,4,5,5-tetramethyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-9H-fluorene-7-yl)-1,3,2-dioxaborolane (**6**)^[22] were prepared according to literature procedures. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature^[23] and stored in a Schlenk tube under nitrogen. All solvents were purified and dried by standard methods.

Characterization

All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh). ¹H- and ¹⁹F-NMR spectra were recorded on a Bruker AV400 spectrometer in CDCl₃. The electrochemical behavior of compounds was investigated by using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF₆) solution in CH₃CN at room temperature at nitrogen atmosphere with a scanning rate of 20 mV s⁻¹. A glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgNO₃ (0.01 mol/L in CH₃CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum. Electronic absorption spectra were obtained on a SHIMADZU UV-visible spectrometer model UV-1601PC. Fluorescence spectra were recorded on a Varian FLR025. Elemental analyses were performed on a Flash EA 1112 analyzer. TGA (Pyris 1 TGA) and DSC (TA 2910) measurements were carried out under nitrogen atmosphere at a heating rate of 10 K/min. Contact angle measurements were performed using the sessile drop method on an OCA20 contact angle goniometer. Samples for measurement were prepared by dropping a solution onto a glass substrate followed by air drying.

Synthesis of Monomers

Compound 1

A mixture of 4-bromobenzaldehyde (370 mg, 2 mmol), Cu bronze (1.02 g, 16 mmol) and dry DMSO (10 mL) was stirred and heated under a nitrogen atmosphere at 120°C for 45 min while the iodoperfluorooctane was added (with materials b.p. < 100°C, the addition was made below the surface of the hot solvent). The reaction mixture was stirred and heated at 120°C for further 18 h. CH₂Cl₂ was added; the cuprous salt was removed by filtration; and the organic layer was washed with water and dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified by chromatography on silica gel eluting with petroleum ether/CH₂Cl₂ (15:1, *V/V*) to afford **1** as a white solid (960 mg, 91%). ¹H-NMR (400 MHz, CDCl₃): δ = 10.12 (1H, s), 8.04 (2H, d), 7.79 (2H, d).

Compound 2

Compound **1** (623 mg, 1.2 mmol) was dissolved in alcohol, NaBH₄ (75 mg, 2 mmol) was added in portion. Then the mixture was stirred at 0°C for 20 min. After removal of the solvent, water was added, the aqueous layer was extracted with CH₂Cl₂ (50 mL × 3), the combined organic layers were dried over MgSO₄. After removal of the solvent, the residue was purified by chromatography on a short pad of silica gel eluting with dichloromethane to afford **2** as white solid. The yield was quantitative. ¹H-NMR (400 MHz, CDCl₃): δ = 7.59 (2H, d), 7.51 (2H, d), 4.80 (2H, s), 1.70 (1H, s). Anal. Calcd for C₁₅H₇F₁₇O: C, 34.24; H, 1.34. Found: C, 34.27; H, 1.48.

Compound 3

To a mixture of **2** (1.51 g, 2.87 mmol) and CBr₄ (1.9 g, 5.74 mmol) in THF was added a solution of PPh₃ (1.5 g, 5.74 mmol) in THF under nitrogen, and the reaction mixture was stirred under nitrogen for 15 min. A large excess of CBr₄ and PPh₃ (2 equiv) were required to force the reaction of completion. Water was added, and the aqueous layer was extracted with CH₂Cl₂ (50 mL × 3). After drying of the organic layer and remove of the solvent under reduced pressure, the crude product was purified by chromatography on silica gel eluting with

hexane/dichloromethane (10:1, *V/V*) to afford **3** as a white solid (1.31 g, 73%). ¹H-NMR (400 MHz, CDCl₃): δ = 7.58 (2H, d), 7.54 (2H, d), 4.51 (2H, s). Anal. Calcd. for C₁₅H₆F₁₇Br: C, 30.58; H, 1.03. Found: C, 30.52; H, 1.26.

Compound 4

A mixture of **3**, TBAB (tetra butyl ammonium bromide) and 2,7-dibromofluorene in DMSO was degassed three times; a 40 wt% aqueous NaOH solution was degassed and stirred for 10 min under N₂. To this solution was added the mixture of **3** under nitrogen; the reaction mixture was stirred under nitrogen at room temperature for 10 h, water was added, and the aqueous layer was extracted with CH₂Cl₂ (50 mL $\times$ 3). The combined organic phases were dried over MgSO₄. After removal of the solvent, the residue was purified by chromatography on a short pad of silica gel eluting with dichloromethane to afford **4** as white solid (0.80 g, 85%). ¹H-NMR (400 MHz, CDCl₃): δ = 7.55 (2H, s), 7.36 (2H, d), 7.16 (6H, d), 6.74 (4H, d), 3.43 (4H, s). ¹⁹F-NMR (100 MHz, CDCl₃): δ = -80.82, -110.93, -121.37, -121.99, -122.47, -122.78, -126.16. Anal. Calcd. for C₄₃H₁₈F₃₄Br₂: C, 38.53; H, 1.35. Found: C, 38.61; H, 1.60.

Compound 5

A mixture of **4** (0.51 g, 0.38 mmol), bis(pinacolato)diboron (390 mg, 1.52 mmol), KOAc (447 mg, 4.58 mmol) and DMF (15 mL) was carefully degassed before Pd(dppf)₂Cl₂ (8 mg, 0.01 mmol) was added. The mixture was stirred for 24 h at 80°C. Water and CH₂Cl₂ (100 mL) were added, the organic layer was separated, the aqueous layer was extracted with CH₂Cl₂ (50 mL $\times$ 2), and the combined organic layers were dried over MgSO₄. After the removal of the solvent, the crude product was chromatographically purified on silica gel eluting with CH₂Cl₂/hexane (1:2) to afford **5** as a white solid (280 mg, 51%). ¹H-NMR (400 MHz, CDCl₃): δ = 7.88 (s, 2H), 7.70 (d, 2H), 7.39 (d, 2H), 7.08 (d, 4H), 6.72 (d, 4H), 3.48 (s, 4H), 1.42 (s, 24H); ¹⁹F-NMR (100 MHz, CDCl₃): δ = -80.86, -110.83, -121.44, -122.01, -122.34, -122.81, -126.19. Anal. Calcd. for C₅₅H₄₂F₃₄Br₂O₄: C, 46.05; H, 2.95. Found: C, 45.86; H, 3.03.

Procedure for the Polycondensation

P1. A mixture of monomer 9,9-dioctylfluorene diboronic ester (63.2 mg, 0.1 mmol), monomer **5** (134 mg, 0.1 mmol), THF (16 mL), water (4 mL) and NaHCO₃ (0.34 g) was carefully degassed and charged with nitrogen, and then Pd(PPh₃)₄ (3 mg) was added. The reaction mixture was stirred and refluxed for 3 days. THF was then added, and the organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the residue was dissolved in a minimum amount of THF and precipitated into methanol. The formed yellow-green precipitate was collected by filtration and freeze-dried to afford **P1** as a yellow solid in a yield of 69%. ¹H-NMR (400 MHz, CDCl₃): δ = 0.78 (t, 6H), 1.15 (broad, 24H), 2.15 (broad, 4H), 3.61 (broad, 4H), 6.97 (d, 4H), 7.24 (s, 2H), 7.56–7.66 (broad, 12H), 7.86 (d, 2H). δ = ¹⁹F-NMR (100 MHz, CDCl₃): δ = -80.86, -110.77, -121.37, -121.99, -122.21, 122.79, 126.18.

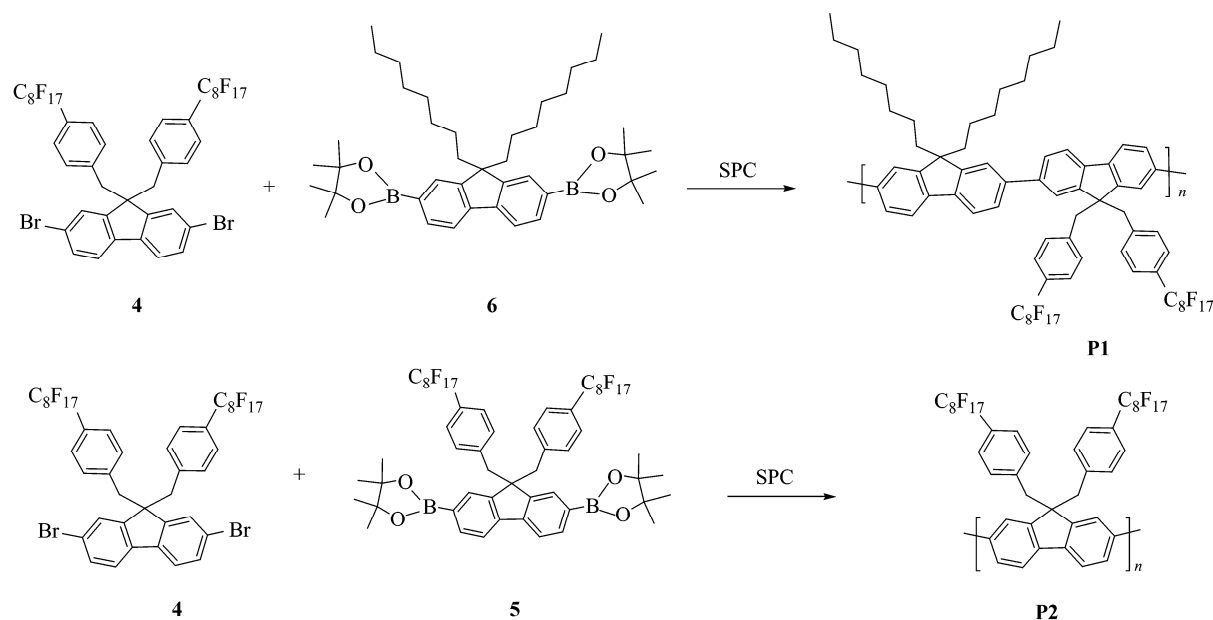
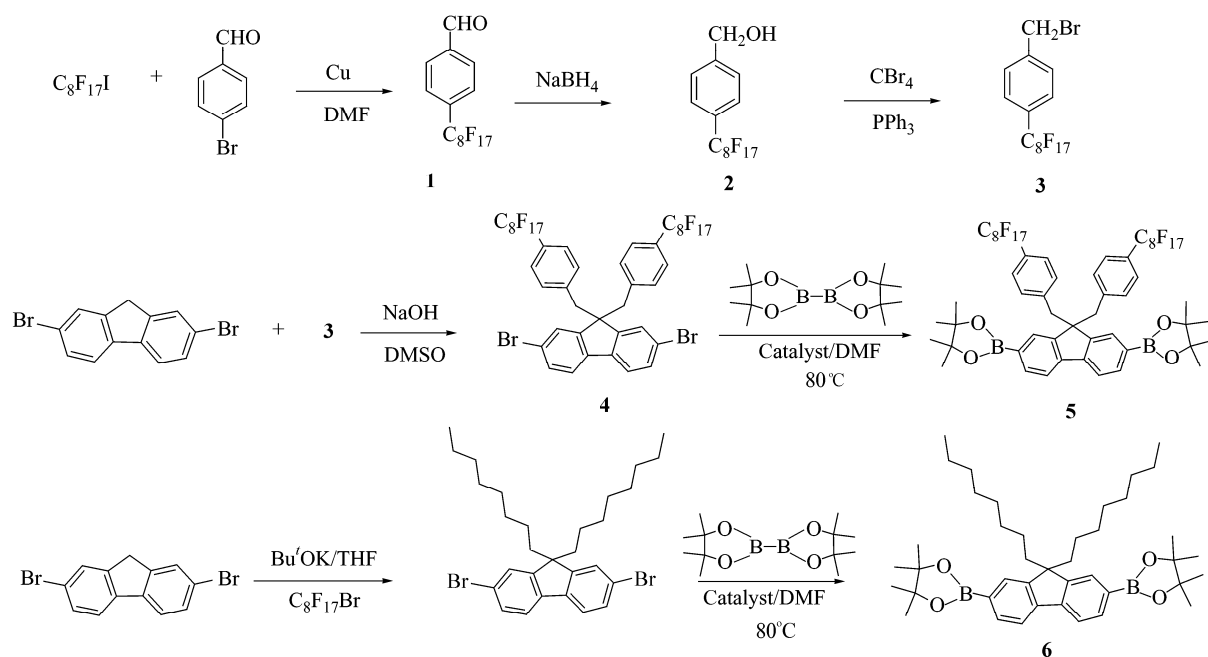
P2. A mixture of monomer **4** (133.7 mg, 0.1 mmol), monomer **5** (143.4 mg, 0.1 mmol), THF (16 mL), water (4 mL) and NaHCO₃ (0.34 g) was carefully degassed and charged with nitrogen, and then Pd(PPh₃)₄ (3 mg) was added. The reaction mixture was stirred and refluxed for 3 days. THF was added, and the organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the residue was dissolved in a minimum amount of THF and precipitated into methanol. The product was collected by filtration to afford **P2** as a yellow-green solid in a yield of 92%. ¹H-NMR (400 MHz, CDCl₃): δ = 3.62 (broad, 4H), 6.98 (d, 4H), 7.24 (s, 2H), 7.56–7.67 (broad, 6H), 7.86 (d, 2H). ¹⁹F-NMR (100 MHz, CDCl₃): δ = -80.96, -81.03, -110.94, -121.53, -122.16, -122.35, 122.94, 126.33.

RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers

The chemical structures and the synthetic routes of monomers **4** and **5** are shown in Scheme 1. Compound **1** was prepared in a yield of 91% by the reaction of 4-bromobenzaldehyde and perfluoro-8-iodooctane in DMF with Cu

as catalyst at 120°C for 24 h. Treatment of **1** with NaBH₄ in a solvent mixture of THF and methanol afforded the corresponding compound **2** in a quantitative yield. The reaction of **2** with CBr₄ and PPh₃ in THF afforded the compound **3** in a yield of 73%. Monomer **4** was obtained in a yield of 85% by the reaction of 2,7-dibromofluorene and compound **3** in DMSO with aqueous NaOH as a base and tetrabutylammonium bromide as a phase transfer catalyst. Compound **5** was achieved in a yield of 51% by reaction of **4** with bis(pinacolato)diboron in DMF with Pd(dppf)₂Cl₂ as a catalyst precursor and KOAc as a base.



Suzuki polycondensation (SPC) of monomers **5** and **6** with monomer **4** was carried out in a biphasic system (THF/aqueous NaHCO_3) with freshly prepared $\text{Pd}(\text{PPh}_3)_4$ as a catalyst precursor (Scheme 2). Reactions were kept stirring at reflux for 96 h. Standard workup afforded **P1** and **P2** as amorphous, slightly yellow solids in yields of 69% and 92%, respectively. The structures of the polymers were fully characterized by ^1H - and ^{19}F -NMR.

Optical Properties

P1 was only partially soluble in common organic solvents such as methylene chloride and THF, but readily soluble in fluorinated organic solvents such as 1,2,4-trifluorobenzene; whereas **P2** was almost insoluble in any organic solvents, and only partially soluble in fluorinated organic solvents. In solution, both **P1** and **P2** exhibited bright blue fluorescence. The absorption and FL spectra of **P1** in dilute THF solution and films on quartz plates prepared by spin-coating are shown in Fig. 1. In solution, **P1** exhibited a narrow absorption band with the absorption maximum at about 390 nm and an emission band in the blue region with two peaks at 417 and 440 nm, respectively. In contrast to its solution spectrum, the absorption band of **P1** in films was slightly broader and blue-shifted for about 12 nm due to the high electronegativity and $\text{F}\cdots\text{H}-\text{C}$ interactions of fluorinated polymers. The film emission spectrum of **P1** was red-shifted for about 2 nm with two peaks located at 419 nm and 442 nm, respectively. Similar situations occurred for **P2**, as shown in Fig. 2. In dilute THF solution, **P2** exhibited an absorption maximum at 371 nm and an emission band with two peaks at 413 and 436 nm, respectively. In its thin film, the absorption maximum was red shifted to 378 nm, and the two emission peaks were red-shifted to 424 nm and 447 nm. The broadening and red-shifting in solid state indicated that there existed some aggregations or interactions of polymeric backbones. The quantum yields (Φ_{F}) of polymers **P1** and **P2** in dilute THF solutions were measured with 9,10-diphenylanthracene as a reference standard ($\Phi_{\text{F}} = 0.9$ in THF solution) to be 0.97 and 1.0, respectively, and both showed high photoluminescent quantum yields in THF solutions respectively.

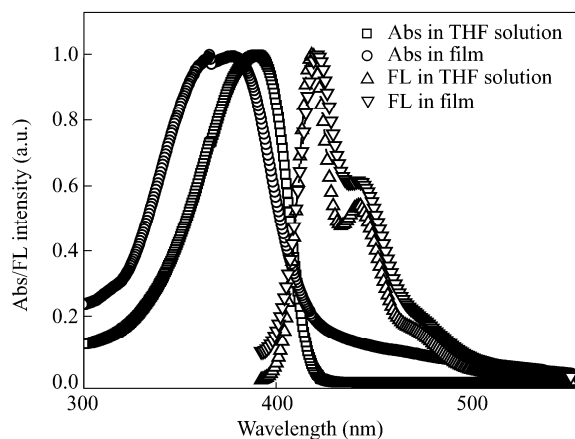


Fig. 1 UV-Vis absorption and FL spectra of **P1** in THF solutions and in films

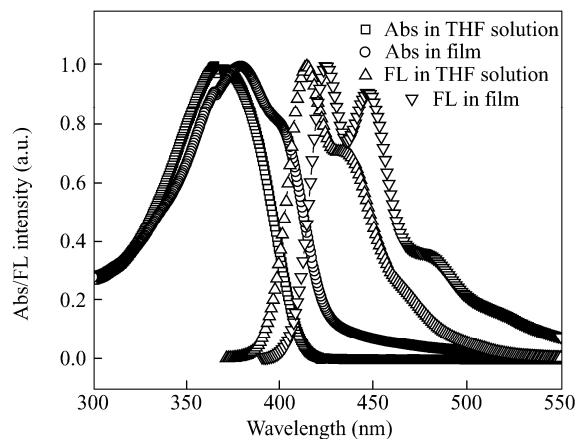


Fig. 2 UV-Vis absorption and FL spectra of **P2** in THF solutions and in films

Thermal Properties

Thermal properties of the fluorine-containing conjugated polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both **P1** and **P2** exhibited good thermal stability. The 5% weight loss temperatures in a nitrogen atmosphere were about 350°C for **P1** and 365°C for **P2** at a heating rate of 10 K/min, respectively, as shown in Fig. 3. To eliminate the influence of the thermal history, samples used for DSC measurements were first heated from room temperature to 250°C at a heating rate of 10 K/min, kept at 250°C for 1 min, and then cooled to room temperature at a cooling rate of 10 K/min in a nitrogen atmosphere. The DSC curves of the second heating were recorded by heating samples from 25°C to

250°C in a nitrogen atmosphere at a heating rate of 10 K/min. For the two polymers, no distinct glass transitions were detected in the range of 25°C to 250°C.

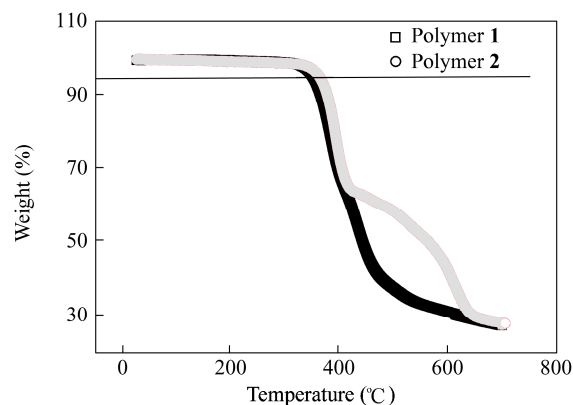


Fig. 3 TGA curves of P1 and P2

Electrochemical Properties

The electrochemical properties of the polymers were investigated by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF₆) solution in acetonitrile at room temperature with a scanning rate of 20 mV s⁻¹. A glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgNO₃ (0.01 mol/L in acetonitrile) reference electrode were used. The oxidation potentials were measured versus Ag/Ag⁺ as a reference electrode with a standard ferrocene/ferrocenium (Fc/Fc⁺) redox system as the internal standard for estimating the HOMO energy levels of the polymer films; we assumed the energy level of Fc/Fc⁺ was 4.8 eV below the vacuum level and that the formal potential of Fc/Fc⁺ was 0.09 V against Ag/Ag⁺. The polymer films on the working electrodes were cast from THF solutions. The CV curves of the polymers are shown in Fig. 4. In the range of 0–1.6 V, all the polymers showed electrochemistry instability. The cathodic waves were not observed from the polymers beyond the solvent limit. The HOMO energy levels and the band gaps were estimated from the first oxidation potentials of the cyclic voltammograms and the onset of the absorption spectra, respectively. The LUMO energy levels were calculated according to the following equation: LUMO energy level = HOMO energy level + Band gap energy. The electrochemical potentials and energy levels of P1 and P2 are summarized in Table 1. Due to the influence of the fluorine atoms, polymer P2 showed lower HOMO and LUMO energy levels in comparison with polymer P1.

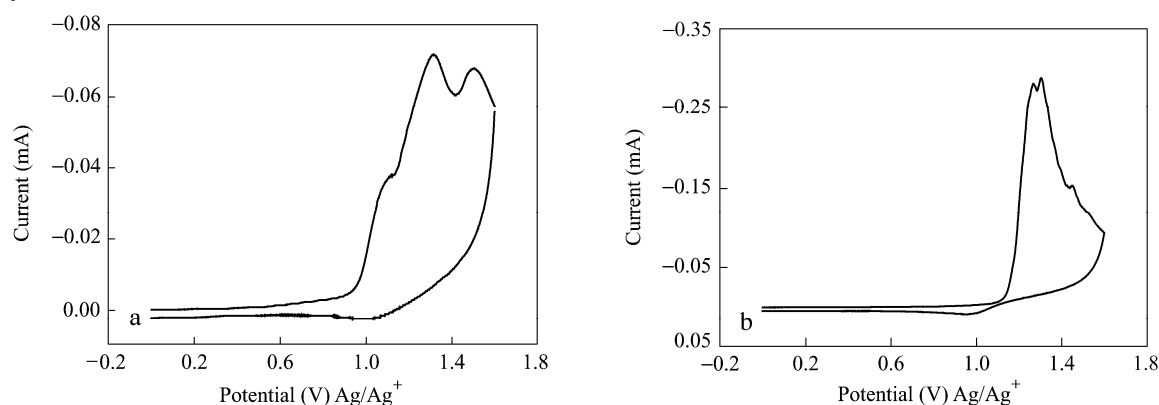


Fig. 4 Cyclic voltammograms of P1 (a) and P2 (b) films recorded at a sweep rate of 50 mV s⁻¹ versus Ag/Ag⁺ in acetonitrile with TBAPF₆ as the supporting electrolyte

Table 1. Band gaps and energy levels of polymers

Polymer	HOMO (eV)	LUMO (eV)	Band gap (eV) ^a
P1	−5.64	−1.92	3.92
P2	−5.84	−1.65	3.99

^a The band gap was obtained with the following equation: Band gap = $1240/\lambda_{\text{edge}}$, where λ_{edge} is the onset value of the absorption spectrum in the long-wavelength direction.

Surface Properties

Contact angle measurements were performed using the sessile drop method on OCA20 contact angle goniometer. The angles reported here were the averages of at least five measurements. Reproducibility was within 3°. They were recorded at $(25 \pm 1)^\circ\text{C}$ using distilled water as wetting liquids. Samples for contact angle measurements were prepared by dropping an amount of solution in THF or 1,2,4-trifluorobenzene onto a glass wafer followed by naturally evaporating the solvent. The surface properties of polymers were investigated in air at the room temperature. When comparing contact angle values for the polymers prepared from THF and 1,2,4-trifluorobenzene (Table 2), it clearly appears that the introduction of fluorocarbon chain on the 9 position of monomer leads to an increase of contact angle. It is noting that the number of the fluorinated chain of the polymer really interferes with the contact angle (Fig. 5). The use of fluorinated solvent such as 1,2,4-trifluorobenzene was dictated by a better solubility of fluorinated compound in fluorinated solvent and also by a better organization and orientation of the fluorinated chains in the polymer, induced by the interaction with the solvent molecules during evaporation. Contact angles of both polymers were improved by the use of 1,2,4-trifluorobenzene instead of THF.

Table 2. Contact angle data of **P1** and **P2**

Polymer	THF	1,2,4-Trifluorobenzene
P1	113°	126°
P2	145°	154°

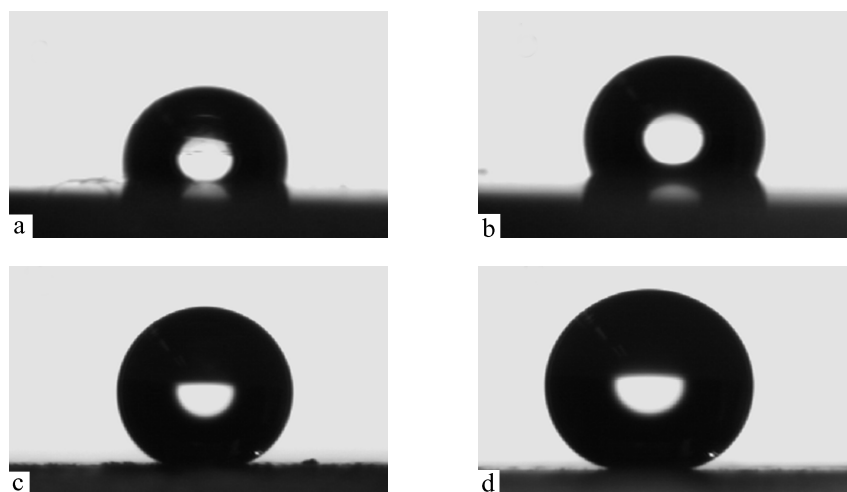


Fig. 5 (a) **P1** drop cast from THF solution, (b) **P1** drop cast from THF solution from fluorobenzene, (c) **P2** drop cast from THF solution and (d) **P2** drop cast from THF solution from fluorobenzene

CONCLUSIONS

Two fluorinated conjugated polymers containing perfluoroalkyl moieties were prepared by Suzuki polycondensation. Incorporation of perfluoroalkyl moieties into the polyfluorene backbone increased the contact angle. The number of the fluorocarbon chain had a significant influence on the contact angle. The fluoropolymer films prepared from a fluorinated organic solvent show a larger contact angle than those prepared in a non-fluorinated solvent.

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