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Semiperfluoroalkyl Polyfluorenes for Orthogonal Processing in Fluorous Solvents

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Since the discovery of electroluminescence (EL) in conjugated polymers, polymeric light-emitting diodes (PLEDs) have been extensively studied for display fabrication.[1−4] In order for these devices to be integrated into displays, it is necessary to pattern the light-emitting polymers into small, multilayered elements for full-color visualization.[5,6] In principle, PLEDs can access a wide range of patterning options if suitable processing methods are available.[7,8] Solutions of conjugated polymers can be dispensed onto the desired area by inkjet printing or screen printing,[9,10] or form films on regions where a sacrificial photoresist material defines the target.[5]

Recently, we have identified hydrofluoroethers (HFEs) as chemically benign process solvents for nonfluorinated materials.[11,12] Taking advantage of HFEs and a fluorinated photoresist, we were able to define functional materials photolithographically down to 5 μm-size patterns. This success prompted us to consider an alternative *orthogonal* combination of materials for device patterning, i.e., highly fluorinated functional polymers with conventional photoresists and solvents. Fluorinated polymer films with sufficient F content remain unaffected when exposed to organic solvents even without cross-linking. To prove this concept, we embarked on the synthesis of semiperfluoroalkyl polyfluorenes. Polyfluorene is a well-known blue-emitting polymer and can be conveniently copolymerized with a variety of monomer units to tune its emission.[13,14]

In this communication, we report the challenging synthesis of semiperfluoroalkyl polyfluorenes (Scheme 1) and characterization of their electro-optical properties. Finally, a proof of concept of successful *orthogonal* patterning of the fluorinated polymers under conventional photolithographic conditions is described.

It is known that perfluoroalkyl moieties are strongly electron-withdrawing,[15] which can perturb the electronic characteristics of polyfluorenes.[16,17] In the case of monomer synthesis, the alkyl spacers give the added benefit of enabling S_N2 reactions between semiperfluoroalkyl halides $[X-(CH_2)_y(CF_2)_zF]$ and fluorene anions. It is, therefore, essential to insert alkyl spacers between the polymer backbone and perfluoroalkyl moieties. The initial synthetic targets were set for polyfluorenes which have $(CH_2)_2$ and $(CH_2)_4$ spacers (**PR$_F$F10** and **PR$_F$F12**, respectively). The resulting polymers have *ca.* 60% F content by weight, which is sufficiently high to make the polymers soluble in HFE-7500 for processing.

The Suzuki cross-coupling reaction chosen for the synthesis of target polymers required semiperfluoroalkyl fluorene dibromides **5** and **8** and diboronates **6** and **9** (Scheme 1).[4,18] While the dibromide **8** was obtained conveniently through alkylation reactions of 2,7-dibromofluorene **7** with semifluorinated iodide **3** under phase-transfer catalysis conditions, the same reaction protocol did not work for the dibromide **5**. 2,7-Dibromofluoren-9-one was recovered with a large amount of black viscous impurities. It is postulated that the semifluorinated iodide **2** undergoes an elimination reaction at elevated temperatures to the corresponding vinyl compound, which results in the tarry material. The synthetic pathway was thus modified to permit low temperature synthesis using ^{n}BuLi as a base. Monodeprotonation and alkylation of fluorene **1** produced the monoalkylated intermediate which was again deprotonated and alkylated to give the dialkyl compound **4** in 80% yield over two steps. Subsequent bromination at 60 °C led to the desired dibromide **5**.

A similar situation occurred during the synthesis of diboronate **6**. The dibromide **8** was transformed into the diboronate **9** in good yield through a series of lithiation reactions and substitutions with isopropoxydioxaborolane. However, the same set of reactions did not prove effective in converting the dibromide **5** into the diboronate **6**. Only a large amount of the starting material **5** was recovered after crystallization from acetone. By using the palladium catalyzed borylation method,[19] the fluorene diboronate **6** was isolated in 46% yield after double recrystallizations from acetone.

With all the monomers in hand, Suzuki polycondensation reactions were attempted in toluene, employing parameters optimized for ordinary dialkyl polyfluorenes (Scheme 1).[20] The immediate problem was the early stage precipitation of high F content polymers. Furthermore, the recovered solids were not soluble in common organic solvents. This limited capability of nonfluorinated solvents made it necessary to adopt fluorinated liquids, in particular, fluorinated aromatic solvents. Benzotrifluoride was identified as a suitable alternative to toluene,[21] which finally enabled the successful syntheses of **PR$_F$F10** and **PR$_F$F12**. It is worth noting that the catalyst system based on $Pd(PPh_3)_4$ worked equally well in benzotrifluoride without a fluorinated phosphine ligand.

The polymers were purified through repeated precipitations from MeOH, after which they appeared to have M_n's as high as 25 000 g mol^{-1} with polydispersity *ca.* 2 (Table 1). For comparison, nonfluorinated poly(9,9-didodecylfluorene) (**PF12**) was synthesized in toluene, which showed a similar molecular weight to the fluorinated polymers. In thermogravimetric analysis (TGA), the semiperfluoroalkyl polyfluorenes exhibited higher decomposition temperatures (> 400 °C) than the nonfluorinated reference (Table 1 and Supporting Information). Differential scanning calorimetry (DSC) did not provide information on glass transition temperatures of the polymers. Only transitions possibly associated with their liquid crystalline phase behavior could be observed (Supporting Information).[25,26] Solubility tests confirmed that all the semiperfluoroalkyl polyfluorenes are only soluble in fluorinated solvents, including HFE-7500, at least to the extent that spin-coating from solution is suitable for EL device fabrication.

Optical properties of the polyfluorenes, including absorption maxima of the UV−vis spectra and photoluminescence are also summarized in Table 1. It is evident that semifluorination of the

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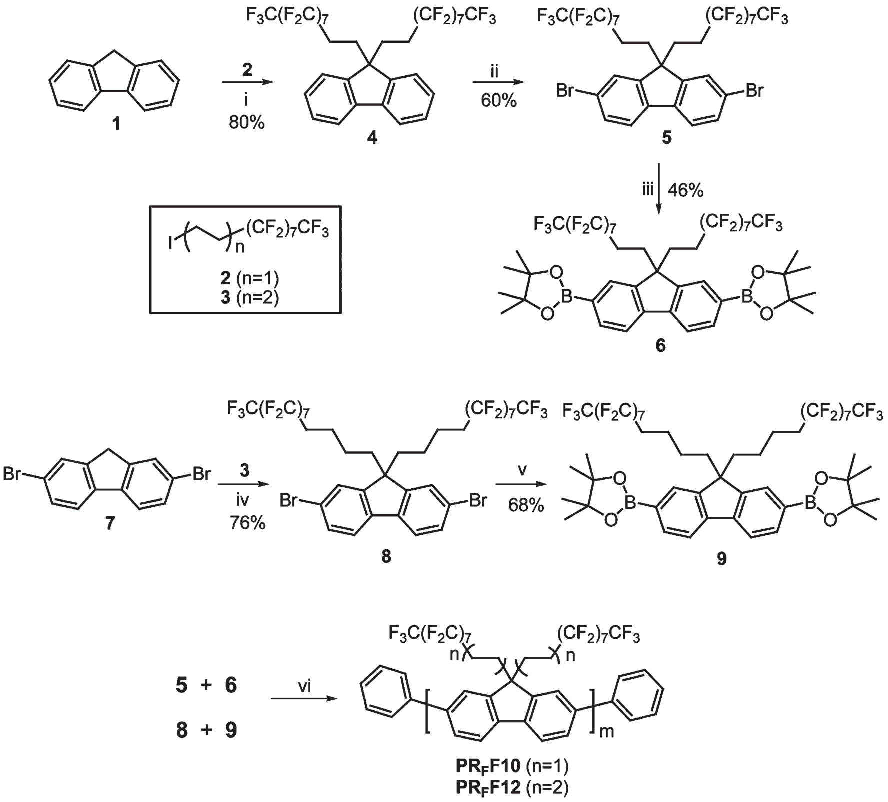
Scheme 1. Synthesis of Monomers and Polymers PR_FF10 and PR_FF12[a]



[a] **Reagents and conditions: (i) ^{n}BuLi, 2 (1 equiv), THF, −78 °C → room temperature, 1 h, followed by ^{n}BuLi, 2 (1.2 equiv), THF, −78 °C → room temperature, 1 h; (ii) Br_2 with catalytic I_2, $CHCl_3$, 60 °C, overnight; (iii) bis(pinacolato)diboron, Pd(dppf)Cl_2, KOAc, DMF, 80 °C, 2 h; (iv) NaOH, Bu_4NBr, toluene + water, 80 °C, overnight; (v) ^{t}BuLi, 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane, THF, −78 °C → room temperature, 1.5 h; (vi) Pd(PPh_3)$_4$, Et_4NOH, benzotrifluoride + water, 90 °C, 2 h, end-capping with PhB(OH)$_2$ and PhBr.**

Table 1. Physical and Optical Properties of Semiperfluoroalkyl Polyfluorenes

polymer	M_n (M_w/M_n) (g mol^{-1})[b]	$T_{decomp.}$ (°C)[c]	Abs$_{max}$ (nm)[d]	E_{gap} (eV)[e]	E_{HOMO} (eV)[f]	PL/EL$_{max}$ (nm)[g]
PR_FF10	25 000 (2.0);	452	380	2.90	−5.83	418[h]
PR_FF12	29 000 (1.8);	433	391	2.88	−5.83	422
PF12[a]	19 000 (1.7);	418	395	2.80	−5.66	435

[a] Poly(9,9-didodecylfluorene) (**PF12**) was prepared as a reference. [b] GPC using fluorinated solvent (Supporting Information).[22] [c] Onset temperature on TGA thermogram. [d] UV absorption was measured using polymer thin films. [e] Energy bandgap was extracted from the onset of absorption spectrum employing a polymer thin film. [f] Energy level was obtained by photoelectron spectroscopy in air.[23,24] [g] Photoluminescence in thin film state. [h] PL only.

alkyl side chains influences the energy band gap by lowering the both the HOMO and LUMO levels of the polymer. In addition, reducing the length of alkyl spacers from $(CH_2)_4$ to $(CH_2)_2$ results in enlargement of the band gap. A detailed study into the structure−property relationships of a more diverse range of semiperfluoroalkyl polyfluorenes is in progress.

The EL characteristics were then investigated in a device structure of ITO/PEDOT:PSS/light-emitting polymer/CsF/Al. Films of the fluorinated polymers were deposited from HFE-7500 solution onto a hole injection layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). We observed different EL behavior in the fluorinated polymers compared to their corresponding nonfluorinated polymer **PF12**. In the case of **PR_FF10**, the emission brightness from the device was below 50 cd m^{-2}. With **PR_FF12**, the device exhibited a similar emission spectrum to its PL characteristics (Figure 1a), but the device operated at a higher voltage (> 10 V) than that of **PF12** and its lifetime was of the order of seconds. This difference in device performance was attributed to the electron-withdrawing nature of semiperfluoroalkyl chains.[15] It is probable that the introduction of semiperfluoroalkyl groups leads to charge traps in the polymer film adversely affecting charge transport.

During our effort to improve the EL performances of the semifluorinated polymers, we found that a small portion of electron-accepting comonomers, including pyridine or benzotriazole,[27] enhanced device performance. An EL device made of the statistical copolymer **P(R_FF12-R_FBTz)** (Figure 1b, M_n = 26 000, Supporting Information) turned on at 5 V, reached 1000 cd m^{-2} at 10 V (Figure 1c), and exhibited a sky-blue emission spectrum (EL$_{max}$ = 490 nm, Figure 1d). The copolymer showed a current efficiency of 1 cd A^{-1} at 0.1 mA cm^{-2}. The device lifetime was also highly improved compared to semiperfluoroalkyl homopolymers. Currently, we are tuning polymer structures for full color configuration.

Finally, we attempted to prove that the highly fluorinated polymers are patternable under conventional photolithographic conditions (Figure 2a). A commercial photoresist film was patterned lithographically on a prepatterned ITO substrate, onto which an aqueous dispersion of PEDOT:PSS and a solution of **P(R_FF12-R_FBTz)** in HFE-7500 (3 parts by volume)/benzotrifluoride (1 part by volume) mixed solvent were spin-coated (Supporting Information). After vacuum deposition of CsF/Al cathode on top of **P(R_FF12-R_FBTz)** film, lift-off of the photoresist layer in 1-methyl-2-pyrrolidinone produced a patterned EL

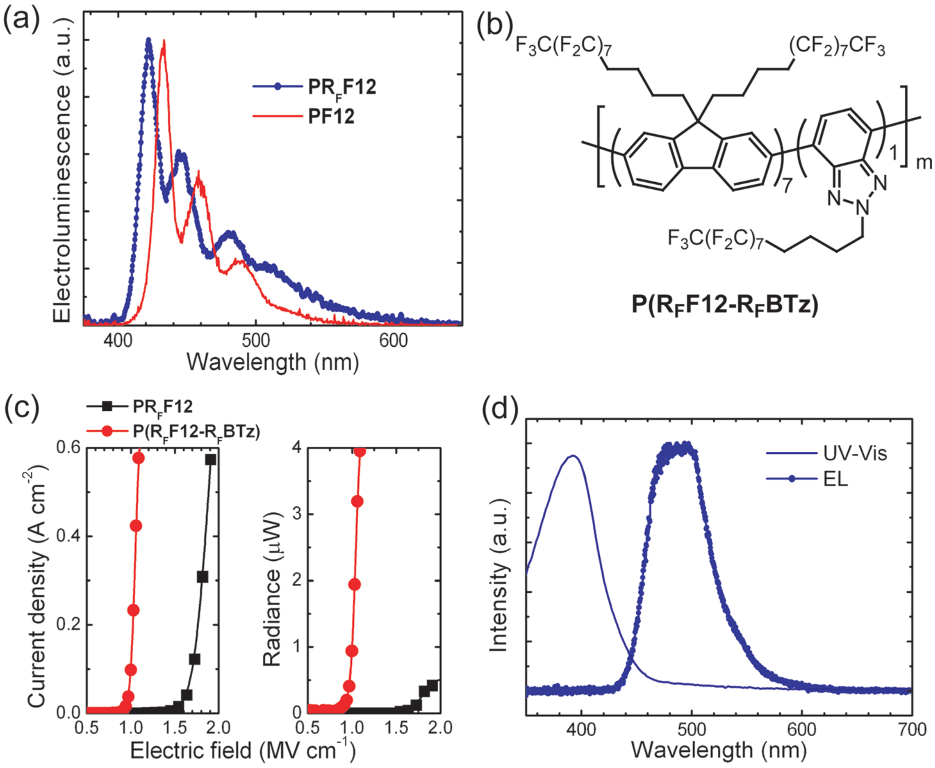


Figure 1. (a) EL spectra of **PR$_F$F12** and the reference polymer **PF12**. (b) Statistical copolymer **P(R$_F$F12-R$_F$BTz)** composed of semiperfluoroalkyl fluorene and semiperfluoroalkyl benzotriazole units. (c) Current−voltage−luminance plot of **PR$_F$F12** and **P(R$_F$F12-R$_F$BTz)**. (d) UV−vis absorption and EL spectra of **P(R$_F$F12-R$_F$BTz)**.

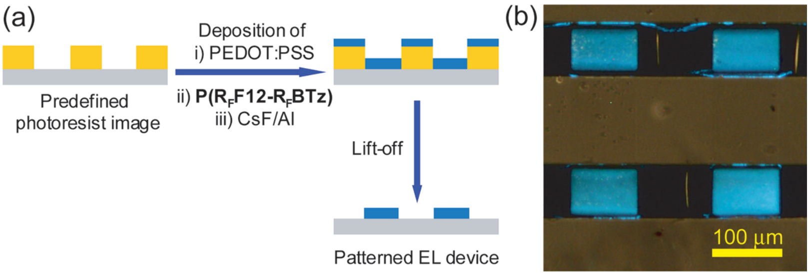


Figure 2. (a) Fabrication of a patterned EL device using **P(R$_F$F12-R$_F$BTz)** and a conventional photoresist. (b) Operating pixels of the EL device described in (a).

device. The resulting pixel array operated to give light emission in a 100 μm scale (Figure 2b).

In summary, semiperfluoroalkyl polyfluorenes with ca. 60 wt % F content were synthesized by Suzuki polycondensation reactions in benzotrifluoride. Their optical and EL properties were evaluated, exhibiting distinctive characteristics from their nonfluorinated analogues. Good performance and processability of **P(R$_F$F12-R$_F$BTz)** in fluorinated solvents enabled the fabrication of a patterned EL device by conventional photolithographic methods. This concept of *orthogonality* between highly fluorinated electronic polymers and nonfluorinated imaging materials is proposed as a promising strategy to construct patterned organic electronic devices in a more efficient way.

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Supporting Information Available: Text giving the synthetic procedure (with structures), thermal analysis data, and photolithographic patterning conditions. A scheme showing the reactions used, and figures showing size exclusion chromatograms, ^{1}H NMR spectra, TGA and DSC plots, and UV−vis and PL spectra. This material is available free of charge via the Internet at http://pubs.acs.org

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