An Air-stable Low Bandgap n-Type Organic Polymer Semiconductor Exhibiting Selective Solubility in Fluorous Solvents**

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Over the past few decades, intense research efforts have been dedicated to developing solution-processable conjugated polymer semiconductors (CPSs).\(^1\) CPSs have the potential to realize the low-cost and solution-based fabrication of large-area optoelectronic devices,\(^2\) such as photovoltaic cells (PVs),\(^3\) organic light-emitting diodes (OLEDs),\(^4\) and organic field effect transistors (OFETs).\(^5\) Although numerous examples of p-type (hole-transporting) CPSs have been reported, air-stable and soluble n-type (electron-transporting) CPSs are still very limited in scope.\(^6\) In this regard, the incorporation of fluorine substituents into p-type semiconductors has emerged as a promising strategy to gain access to n-type polymer semiconductors.\(^7\) The highly electron-withdrawing nature of fluorine increases the electron affinity (EA), which is essential for smooth electron injection and stabilization of the resulting radical anions. In addition, the incorporation of highly fluorinated alkyl chains is effective for enhancing the air- and thermal stability due to the formation of kinetic barriers against the diffusion of \(O_2\) and/or \(H_2O\) into the semiconductor films.\(^8\)

Furthermore, CPSs containing highly fluorinated side-chains can have the advantage of orthogonal solubility: they are soluble in fluorous solvents\(^9\) but insoluble in common organic solvents. This feature would allow for orthogonal processing of optoelectronic devices with multi-layered configurations, in which successive layer deposition is required, while keeping the underlying polymer layers intact.\(^9\) Herein we report the synthesis of a highly fluorinated conjugated polymer, poly(2,3-bis(perfluorohexyl)thieno[3,4-b]pyrazine) (PFHFHTP, Figure 1a), on the first fluorinated version of poly(thieno[3,4-h]pyrazine) (pCTPs),\(^11,12\) which are low bandgap polymers.\(^13\) The fluorinated polymer exhibited selective solubility in fluorous solvents, high air- and thermal stability, high EA, electrochemical n-doping behavior, and a low bandgap. Moreover, OFET devices containing PFHFHTP were fabricated and exhibited n-channel FET characteristics.

Figure 1. a) Chemical Structure of PFHFHTP; b) PFHFHTP dissolved in FC-77 (\(n\)-C\(_2\)F\(_4\)) (lower phase, blue) and not dissolved in the upper phase (1) acetone, (2) chloroform, (3) hexane and (4) water.

The synthetic route to PFHFHTP is outlined in Scheme 1. The double addition of \textit{in situ} generated perfluorohexyllithium to iminocarbons in the presence of BF\(_3\)-OEt\(_2\)\(^{14}\) was found applicable to thieno[3,4-b]pyrazine (1),\(^{15}\) which gave doubly perfluoralkylated tetrahydrothienopyrazine 2 in 60% yield. Subsequent oxidative aromatization of 2 with an excess amount of N-bromosuccinimide (6 equiv) gave dibromothienopyrazine 3 in excellent yield (91%). Since monomer 3 is highly soluble in common solvents, it could be purified by column chromatography on neutral alumina with hexane as an eluent. Thienopyrazine 3 emits orange fluorescence both in solution (\(\lambda_{\text{em}}\max = 562\) nm, \(\Phi = 0.31\)) in CHCl\(_3\)) and in the solid state (Figures S1 and S2). Compared to the photophysical properties of thieno[3,4-b]pyrazine (\(\lambda_{\text{em}}\max = 472\) nm, \(\Phi = 0.0051\)) in CH\(_2\)Cl\(_2\)) and 2,3-dihexylthieno[3,4-b]pyrazine (\(\lambda_{\text{em}}\max = 465\) nm, \(\Phi = 0.0015\)) in CH\(_2\)CN\(^{16}\)), monomer 3 exhibited a remarkably red-shifted \(\lambda_{\text{em}}\max\), and a high emission quantum yield. The red-shifted \(\lambda_{\text{em}}\max\) is attributable to an n-\(\pi^*\) transition, and the high quantum yield is most likely due to suppression of intermolecular \(\pi-\pi\) stacking by the rigid and bulky perfluoroalkyl side chains.\(^{17}\) Recently, it was demonstrated that a fluorobiphephosphate solvent system is effective for the synthesis of highly fluorinated conjugated polymers.\(^{18}\) Using this strategy, a cross-coupling polycondensation reaction using hexamethyliditin\(^{19}\) in a fluoruous three-solvent system (THF : NMP : perfluoro(methylcyclohexane) 2 : 1 : 2 v/v) was found to provide PFHFHTP as a dark-blue solid. The resulting polymer showed exclusive solubility in fluorous solvents, such as perfluorooctane (FC-77), perfluorooctyl(methylcyclohexane), and perfluorodecalin, whereas it was insoluble in water and common organic solvents, like acetone, chloroform, and hexane (Figure 1b). Taking advantage of its orthogonal solubility, the crude product was easily purified by liquid-to-liquid extraction with FC-77, followed by Soxhlet washing with hexane, acetone, and chloroform to give pure PFHFHTP in 78% yield. The fluorine content of the polymer was found to be 65.5 wt%.

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in good agreement with the calculated value, so this polymer can be considered “heavily fluorous.”[9]

Scheme 1. Synthesis of PPFHTP

Thermogravimetric analysis (TGA) of PPFHTP under air showed a high starting decomposition temperature (T onset, 5 wt% loss) of 337 ºC (Figure S3), indicating the high air- and thermal stability of the fluorinated polymer. Differential scanning calorimetry (DSC) analysis indicated no drastic thermal transitions, implying the absence of mesophase formation (Figure S4). To understand the microstructure of the polymer, the X-ray diffraction spectrum of the polymer film was measured. Although various samples grown from various fluorous solutions such as FC-77 and perfluorobenzene were used for the measurements, distinctive reflection patterns were not detected at all except for a broad halo peaks in the 2θ region ranging from 27 to 30 º which was the strongest for the samples cast from perfluorobenzene solutions, indicating that the fluorinated polymer samples had amorphous structures.

Figure 2a shows the UV-vis-NIR absorption spectra of a dilute solution of PPFHTP in FC-77 (black line) and of a thin film deposited on a glass substrate (blue line). Although the λ max is observed at 1100 nm in both cases, thin films of PPFHTP show a broad and structureless peak compared to solution samples. The optical band-gap (E opt) estimated from the absorption onset (λ max) of the thin film was found to be 0.87 eV. This is even lower than that of the corresponding non-fluorinated counterpart of PPFHTP, poly(2,3-dihexythieno[3,4-b]pyrazine) (pC6TP, E opt = 0.93 eV), which is prepared by Grignard metathesis (GRIM) polymerization.[11a]

Figure 2. a) UV-vis-NIR absorption spectra of PPFHTP in dilute FC-77 solution (black line) and as a thin film deposited on a glass substrate (blue line). b) Cyclic voltammogram of a thin film of PPFHTP deposited on ITO-coated glass (7 × 50 × 0.9 mm, 8–12 Ω cm–1) in a CH3CN solution of Bu4NPF6 (0.1 M) measured at a scanning rate of 10 mV/s.

The comparatively lower bandgap of PPFHTP versus pC6TP can be ascribed to the contribution of a stabilized quinoid resonance structure to the HOMO of the fluorinated polymer.[20] This was confirmed through calculations (DFT, B3LYP/6-31G(d)) performed on oligomeric thieno[3,4-b]pyrazines containing CF3 substituents (CF3TPn, n = 1–4). The optimized ground-state structure of tetramer CF3TP4 was found to be nearly planar (Figure 3a and b; the inter-

Figure 3. a) Top view and b) side view of the optimized geometry of CF3TP4. c) Bond length plots of the optimized CF3TP4. d) Excitation energy plots against the reciprocal number of monomer unit for CF3TP4.

Estimating that PPFHTP is equivalent to CF3TPn (n = ∞), the theoretical bandgap (E opt) of the polymer is found to be 0.63 eV by extrapolating linear plots of the excitation energy (calculated by TD–DFT) [21] versus reciprocal number of monomer units (Figure 4d). The 0.24 eV discrepancy between E opt and the observed optical bandgap (E opt) of PPFHTP films could be due to the difference in fluoroalkyl chain length (CF3 vs. C6F13), or the result of effective conjugation length saturation.

The electrochemical behaviour of PPFHTP was investigated by cyclic voltammetry, using a dip-coated thin-film of PPFHTP on ITO glass as the working electrode (Figure 2b). Notably, a sharp, reversible reduction peak was observed at ~0.34 V (vs. SCE). The EA estimated from the reduction onset potential[22] is calculated to be 4.12 eV, which is much higher than that of pC6TP (3.2 eV)[11a] and comparable to those of well-known electron transporting compounds, such as PCBM (4.2 eV)[23] and BBL (4.0 eV).[24] The royal blue PPFHTP film is observed to reversibly change color to deep purple upon n-doping (Figure S5), thus suggesting that the electron-injected state is stabilized (presumably due to the strong electron-withdrawing effect of the perfluoroalkyl side chains). Conventional low-bandgap conjugated polymers have reportedly suffered from over-oxidation due to the low ionization potential (IP) of the valence bands ranging from 0.1 to 0.5 V while that for PPFHTP being larger than 0.79 V, leading to chemical degradation of the polymers. For example, Rasmussen et al. reported that over-oxidation of alkyl-substituted pC6TP begins at 0.9 V.[11a] Contrary to pC6TPs, PPFHTP did not show oxidative degradations in the p-doping cycles (Figure 2b), although the p-doping/dedoping process was electrochemically irreversible,[26] demonstrating the validity of incorporating fluoroalkyl chains into low bandgap polymers to enhance their electrochemical stability. Due to the
electrochemical irreversibility of oxidative doping, an accurate IP for PPFHTP cannot be determined by cyclic voltammetry. Thus, an upper and lower range for the electrochemical bandgap ($E_{g}^{\text{ox}}$) was estimated: the value of $E_{g}^{\text{ox}}$ has to be higher than the difference between the reduction potential of the oxidized polymer (0.592 V) and the onset reduction potential of the neutral polymer (0.278 V); additionally the value of $E_{g}^{\text{ox}}$ has to be lower than the difference between the onset oxidation potential of the neutral polymer (0.792 V) and the onset reduction potential of the neutral polymer (0.278 V). These upper and lower limits reveal that $E_{g}^{\text{ox}}$ lies between 0.87 and 1.07 eV. The slightly higher value of $E_{g}^{\text{ox}}$ than $E_{g}^{\text{opt}}$ can be explained by the fact that $E_{g}^{\text{ox}}$ corresponds to the energy required to form a strongly bound exciton, whereas $E_{g}^{\text{ox}}$ corresponds to the energy required to form free charge carriers ($E_{g}^{\text{opt}}$ plus the exciton binding energy).[27] It should be noted that the electrochemical behaviour was strongly dependent on film preparation methods. Whereas films prepared by dip-coating from FC-77 clearly demonstrated reversible reduction peaks, films prepared by other methods, such as spin-coating or drop-casting from hexafluorobenzene, did not give reproducible results. These observations imply that the morphology and, as a result, the band structure of the fluorinated polymer drastically changes with film preparation conditions.

To characterize the performance of PPFHTP as a n-type polymer semiconductor, top-gated OFETs with a poly(methyl methacrylate) (PMMA) gate dielectric, aluminum gate electrode, and gold source/drain bottom contacts were fabricated (Figure 4a). PPFHTP clearly exhibited n-channel conduction and negligible source-drain current under p-channel operation (Figure 4b). The saturation-regime electron mobility ($\mu_e$) was measured to be 2.15×10$^{-6}$ cm$^2$/Vs. Notably, the OFET device that had been stored under ambient conditions for one month showed no significant changes in n-channel transfer characteristics (Figure S6), demonstrating the high air-stability of PPFHTP as a n-type material. However, “electron-only” devices containing PPFHTP (Figure S7) revealed $\mu_e$ of 4.1×10$^{-3}$ cm$^2$/Vs in the space-charge limited current (SCLC) regime. These results, combined with the aforementioned X-ray diffraction studies, suggest that the relatively low $\mu_e$ measured in top-gated OFETs can be ascribed to unfavourable polymer morphology within the lateral source-drain conduction channel. Further investigations into optimizing electron transport in PPFHTP by changing film morphology are currently underway.

![Figure 4](image_url)

**Figure 4.** a) OFET architecture; b) Output curves, and c) Transfer curves of the OFET device.

In conclusion, we have successfully synthesized perfluoroalkyl-substituted p$_2$CTPs (PPFHTP), which showed exclusive solubility in fluorous solvents. This n-type polymer semiconductor can be used for the multi-layered processing of organic based electronic devices. Further elaboration aimed at applying the unique polymer to orthogonal processes of organic photovoltaic devices is ongoing in our laboratory.

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A new class of air-stable n-type polymer semiconductor, poly (2,3-bis(perfluorohexyl)thieno[3,4-b]pyrazine) (PPFHTP), is synthesized through a Pd-catalyzed polycondensation employing a fluorous multi-phase solvent system. This is the first example of an n-type polymer semiconductor with exclusive solubility in fluorous solvents. Moreover, PPFHTP possesses a high electron affinity and low band gap. The fabrication of OFETs containing this new n-type polymer semiconductor is demonstrated.