

An Air-Stable Low-Bandgap n-Type Organic Polymer Semiconductor Exhibiting Selective Solubility in Perfluorinated 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 (PVCs),^[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 because of the formation of kinetic barriers against the diffusion of O₂ and/or H₂O into the semiconductor films.^[8] Furthermore, CPSs containing highly fluorinated side-chains can have the advantage of orthogonal solubility: they are soluble in perfluorinated 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.^[10] Herein, we report the synthesis of a highly fluorinated conjugated polymer, poly-(2,3-bis(perfluorohexyl)thieno[3,4-*b*]pyrazine) (PPFHTP,

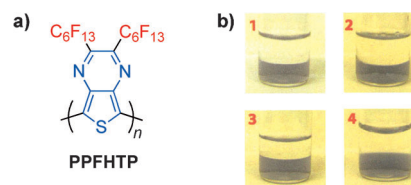


Figure 1. a) Chemical structure of PPFHTP; b) PPFHTP dissolved in FC-77 (*n*-C₈F₁₈) (lower phase, blue) and not dissolved in the upper phase (1) acetone, (2) chloroform, (3) hexane and (4) water.

Figure 1a), on the first fluorinated version of poly(thieno[3,4-*b*]pyrazine)s (pC_nTPs),^[11,12] which are low-bandgap polymers.^[13] The fluorinated polymer exhibited selective solubility in perfluorinated solvents, high air- and thermal stability, high EA, electrochemical n-doping behavior, and a low bandgap. Moreover, OFET devices containing PPFHTP were fabricated and exhibited n-channel FET characteristics.

The synthetic route to PPFHTP is outlined in Scheme 1. The double addition of in situ generated perfluorohexyllithium to imino carbon atoms in the presence of BF₃·OEt₂^[14] was found applicable to thieno[3,4-*b*]pyrazine (**1**),^[15] which gave doubly perfluoroalkylated tetrahydrothienopyrazine **2** in 60% yield. Subsequent oxidative aromatization of **2** with an excess amount of *N*-bromosuccinimide (six 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 ($\lambda_{\text{max}}^{\text{em}} = 562 \text{ nm}$, $\Phi_{\text{f}} = 0.31$ in CHCl₃) and in the solid state (see Figures S1 and S2 in the Supporting Information). Compared to the photophysical properties of thieno[3,4-*b*]pyrazine ($\lambda_{\text{max}}^{\text{em}} = 472 \text{ nm}$, $\Phi_{\text{f}} = 0.0051$ in CH₃CN) and 2,3-dihexylthieno[3,4-*b*]pyrazine ($\lambda_{\text{max}}^{\text{em}} = 465 \text{ nm}$, $\Phi_{\text{f}} = 0.0015$ in CH₃CN),^[16] monomer **3** exhibited a remarkably red-shifted $\lambda_{\text{max}}^{\text{em}}$, and a high emission quantum yield. The red-shifted $\lambda_{\text{max}}^{\text{em}}$ is attributable to an n- π^* transition, and the high quantum yield is most likely due to suppression of intermolecular π - π stacking by the rigid and bulky perfluoroalkyl side-chains.^[17] Recently, it was demonstrated that a fluorinated biphasic solvent system is effective for the synthesis of highly fluorinated conjugated polymers.^[18] Using this strategy, a cross-coupling polycondensation reaction using hexamethylditin^[19] in a fluorinated three-solvent system (THF:NMP:perfluoro(methylcyclohexane) 2:1:2 v/v; THF = tetrahydrofuran and NMP = *N*-methyl-2-pyrrolidone) was found to provide PPFHTP as a dark-blue solid. The resulting polymer showed exclusive solubility in fluorinated solvents, such as perfluorooctane (FC-77), perfluoro(methyl-

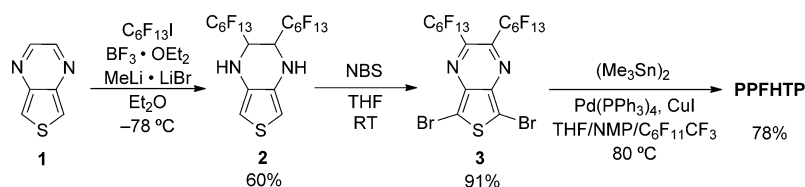
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Scheme 1. Synthesis of PPFHTP.

cyclohexane), 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 PPFHTP in 78% yield. The fluorine content of the polymer was found to be 65.5 wt%, in good agreement with the calculated value, so this polymer can be considered “heavily” fluorinated.^[9]

Thermogravimetric analysis (TGA) of PPFHTP in air showed a high starting decomposition temperature (T_d , 5 wt % loss) of 337 °C (see 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 fluorinated 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 peak in the 2θ region ranging from 27 to 30° 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 $\lambda_{\max}$ is observed at 1100 nm in both cases, thin films of PPFHTP show a broad and structureless peak compared to solution samples. The optical bandgap (E_g^{opt}) estimated from the absorption onset (λ_{onset}) of the thin film was found to be 0.87 eV. This is even lower than that of the corresponding nonfluorinated counterpart of PPFHTP, poly(2,3-dihexylthieno[3,4-*b*]pyrazine) (pC₆TP, E_g^{opt} 0.93 eV), which is prepared by Grignard metathesis (GRIM) polymerization.^[11a]

The comparatively lower bandgap of PPFHTP versus pC₆TP can be ascribed to the contribution of a stabilized quinoid resonance structure to the highest occupied molecular orbital (HOMO) of the fluorinated polymer.^[20] This was confirmed through calculations (DFT, B3LYP/6-31G(d)) performed

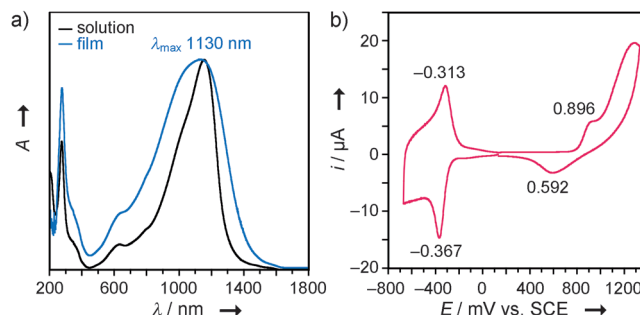


Figure 2. a) UV/Vis-NIR absorption spectra of PPFHTP in dilute FC-77 solution (black line) and as a thin film deposited on a glass substrate (blue line). b) Cyclic voltammogram of a thin film of PPFHTP deposited on ITO-coated glass ($7 \times 50 \times 0.9 \text{ mm}^3$, $8\text{--}12 \Omega \text{ cm}^{-1}$) in a CH₃CN solution of Bu₄NPF₆ (0.1 M) measured at a scanning rate of 10 mV s^{-1} .

on oligomeric thieno[3,4-*b*]pyrazines containing CF₃ substituents (CF₃TP_{*n*}, *n* = 1–4). The optimized ground-state structure of the tetramer CF₃TP₄ was found to be nearly planar (Figure 3a and b; the inter-ring torsional angles varies from

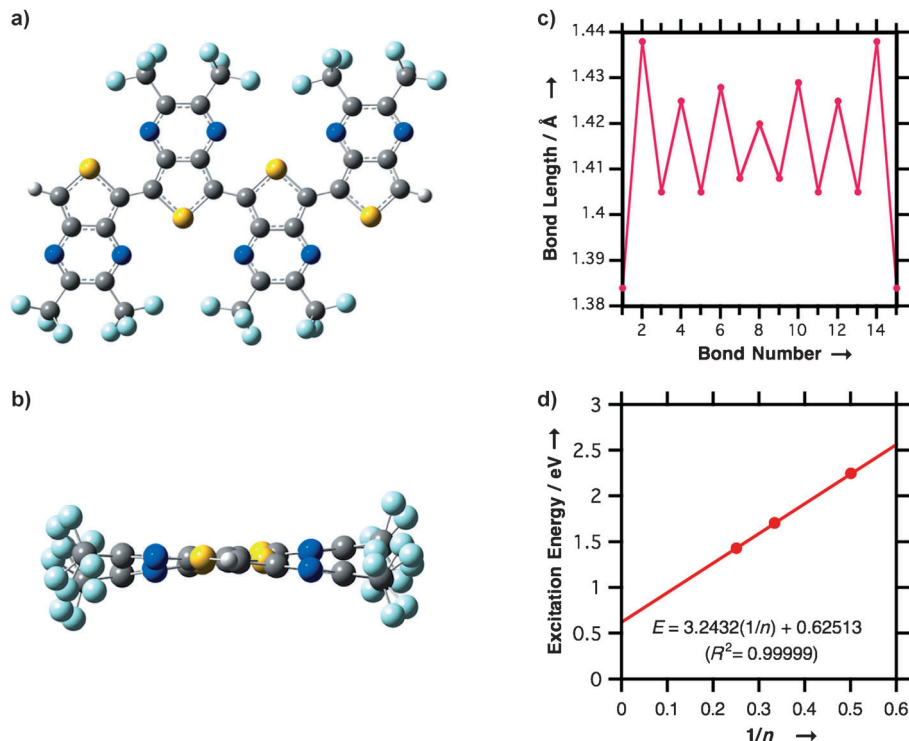


Figure 3. a) Top view and b) side view of the optimized geometry of CF₃TP₄. c) Bond length plots of the optimized CF₃TP₄. d) Excitation energy plots against the reciprocal numbers of monomer unit for CF₃TP_{*n*}.

2.86° to 6.96°),^[21] and little bond length alternation (between 0.012 to 0.054 Å)^[22] was observed along the tetramer backbone (Figure 3c). Furthermore, the CF₃C=N bond lengths of the tetramer were 1.30–1.31 Å, which are closer in value to those of localized C=N bonds (1.28 Å)^[23] than the C=N bond lengths typically observed in thieno[3,4-*b*]pyrazines (1.35–1.36 Å). These results indicate that the maximized conjugation of CF₃TP₄ is due to the quinoid valence tautomeric form.

Estimating that PPFHTP is equivalent to CF₃TP_{*n*} (*n* = ∞), the theoretical bandgap (E_g^{cal}) of the polymer is found to be 0.63 eV by extrapolating linear plots of the excitation energy (calculated by TD-DFT)^[12a] versus reciprocal number of monomer units (Figure 4d). The 0.24 eV discrepancy between E_g^{cal} and the observed optical bandgap (E_g^{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 behavior of PPFHTP was investigated by cyclic voltammetry, using a dip-coated thin-film of PPFHTP on indium–tin oxide (ITO) glass as the working electrode (Figure 2b). Notably, a sharp, reversible reduction peak was observed at –0.34 V (versus saturated calomel electrode, SCE). The EA estimated from the reduction onset potential^[24] is calculated to be 4.12 eV, which is much higher

than that of pC₆TP (about 3.2 eV)^[11c] and comparable to those of well-known electron-transporting compounds, such as PCBM ([6,6]-phenyl-C₆₁-butyric acid methyl ester, 4.2 eV)^[3d] and BBL (poly(benzobisimidazobenzophenanthroline), 4.0 eV).^[25] 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 because of the strong electron-withdrawing effect of the perfluoroalkyl side-chains). Conventional low-bandgap conjugated polymers have reportedly suffered from over-oxidation because of 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, Kenning and Rasmussen reported that over-oxidation of alkyl-substituted pC_{*n*}TPs begins at 0.9 V.^[11c] Contrary to pC_{*n*}TPs, PPFHTP did not show oxidative degradations in the p-doping cycles (Figure 2b), although the process of p-doping and removing the dopant was electrochemically irreversible,^[26] demonstrating the validity of incorporating fluoroalkyl chains into low-bandgap polymers to enhance their electrochemical stability. Because of 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^{ech}) was estimated: the value of E_g^{ech} 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^{ech} 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^{ech} lies between 0.87 and 1.07 eV. The slightly higher value of E_g^{ech} relative to E_g^{opt} can be explained by the fact that E_g^{opt} corresponds to the energy required to form a tightly bound exciton, whereas E_g^{ech} corresponds to the energy required to form free charge carriers (E_g^{opt} plus the exciton binding energy).^[27] The electrochemical behavior was also 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 an n-type polymer semiconductor, top-gated OFETs with a poly(methyl methacrylate) (PMMA) gate dielectric, aluminium 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 (μ_e) was measured to be $2.15 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. 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 an n-type material. However, “electron-only” devices containing

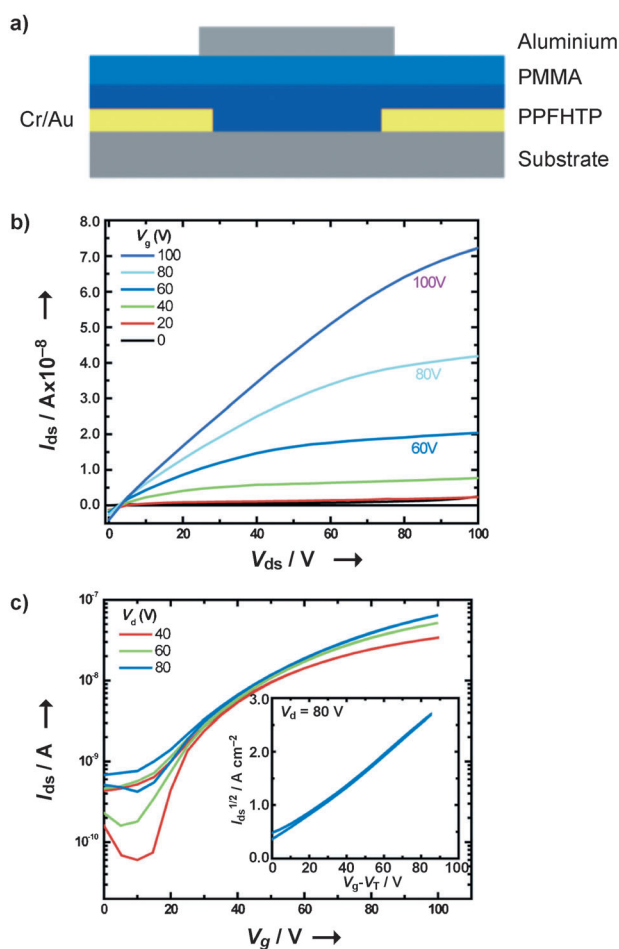


Figure 4. a) OFET architecture. b) Output curves, and c) transfer curves of the OFET device.

PPFHTP (Figure S7) revealed an electron mobility (μ_e) of $4.1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the space-charge limited current (SCLC) regime. These results, combined with the aforementioned X-ray diffraction studies, suggest that the relatively low μ_e measured in top-gated OFETs can be ascribed to an unfavorable polymer morphology within the lateral source-drain conduction channel. Further investigations into optimizing electron transport in PPFHTP by changing the film morphology are currently underway.

In conclusion, we have successfully synthesized perfluoroalkyl-substituted pC_nTPs (PPFHTP), which showed exclusive solubility in perfluorinated solvents. This n-type polymer semiconductor can be used for multilayered processing of organic based electronic devices. Further elaboration aimed at applying the unique polymer to orthogonally processed organic photovoltaic devices is ongoing in our laboratory.

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