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An Air-Stable Low-Bandgap n-Type Organic Polymer Semiconductor Exhibiting Selective Solubility in Perfluorinated Solvents

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

*Youhei Takeda, Trisha L. Andrew, Jose M. Lobez, A. Jolene Mork, and Timothy M. Swager**

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 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.[10] Herein we report the synthesis of a highly fluorinated conjugated polymer, poly(2,3-bis(perfluorohexyl)thieno[3,4-b]pyrazine) (**PPFHTP**, Figure 1a), on the first fluorinated version of

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poly(thieno[3,4-b]pyrazine)s (pC_nTPs),[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 **PPFHTP** were fabricated and exhibited n-channel FET characteristics.
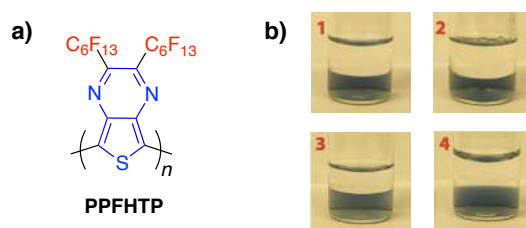

Figure 1. a) Chemical Structure of **PPFHTP**; b) **PPFHTP** dissolved in FC-77 (n-C_8F_{18}) (lower phase, blue) and not dissolved in the upper phase (1) acetone, (2) chloroform, (3) hexane and (4) water.

The synthetic route to **PPFHTP** is outlined in Scheme 1. The double addition of *in situ* generated perfluorohexyllithium to imino-carbons in the presence of $BF_3·OEt_2$[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 (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 (λ^{em}_{max} 562 nm, Φ_f 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 (λ^{em}_{max} 472 nm, Φ_f 0.0051 in CH_3CN) and 2,3-dihexylthieno[3,4-b]pyrazine (λ^{em}_{max} 465 nm, Φ_f 0.0015 in CH_3CN),[16] monomer **3** exhibited a remarkably red-shifted λ^{em}_{max}, and a high emission quantum yield. The red-shifted λ^{em}_{max} 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 fluorous biphase 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 fluorous three-solvent system (THF : NMP : perfluoro(methylcyclohexane) 2 : 1 : 2 v/v) was found to provide **PPFHTP** as a dark-blue solid. The resulting polymer showed exclusive solubility in fluorous solvents, such as perfluorooctane (FC-77), perfluoro(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 **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" fluorous.[9]

Scheme 1. Synthesis of **PPFHTP**

Thermogravimetric analysis (TGA) of **PPFHTP** under air showed a high starting decomposition temperature (T_d, 5 wt% loss) of 337 °C (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° 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_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 non-fluorinated counterpart of **PPFHTP,** poly(2,3-dihexylthieno[3,4-b]pyrazine) (pC$_6$TP, E_g^{opt} 0.93 eV), which is prepared by Grignard metathesis (GRIM) polymerization.[11a]
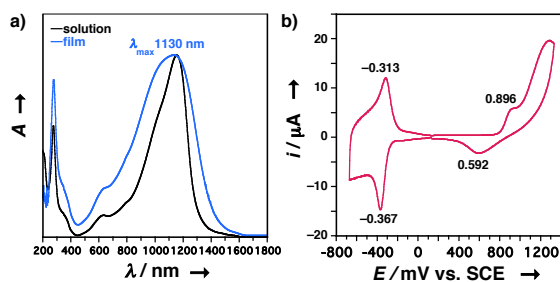

Figure 2. a) UV-vis-NIR absorption spectra of **PPFHTP** in dilute FC-77 solution (black line) and as a thin film deposited on a glass substrate (blue line). b) Cyclic voltammogram of a thin film of **PPFHTP** deposited on ITO-coated glass (7 × 50 × 0.9 mm, 8–12 Ω cm^{-1}) in a CH$_3$CN solution of Bu$_4$NPF$_6$ (0.1 M) measured at a scanning rate of 10 mV/s.

The comparatively lower bandgap of **PPFHTP** versus pC$_6$TP 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 CF$_3$ substituents (**CF$_3$TP$_n$**, $n = 1$–4). The optimized ground-state structure of tetramer **CF$_3$TP$_4$** was found to be nearly planar (Figure 3a and b; the inter-

ring torsional angles varies from 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 CF$_3$C=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 **CF$_3$TP$_4$** is due to the quinoid valence tautomeric form.
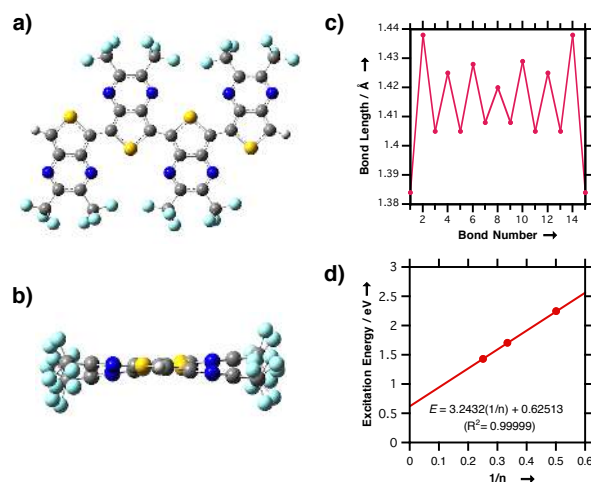

Figure 3. a) Top view and b) side view of the optimized geometry of **CF$_3$TP$_4$**; c) Bond length plots of the optimized **CF$_3$TP$_4$**; d) Excitation energy plots against the reciprocal numbers of monomer unit for **CF$_3$TP$_n$**.

Estimating that **PPFHTP** is equivalent to **CF$_3$TP$_n$** ($n = \infty$), 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 (CF$_3$ vs. C$_6$F$_{13}$), 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[24] is calculated to be 4.12 eV, which is much higher than that of pC$_6$TP (ca. 3.2 eV)[11c] and comparable to those of well-known electron transporting compounds, such as PCBM (4.2 eV)[3d] and BBL (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 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 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 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^{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} than 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] It should be noted that the electrochemical behaviour 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, 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 (μ_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 μ_e of 4.1×10^{-5} 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 μ_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.
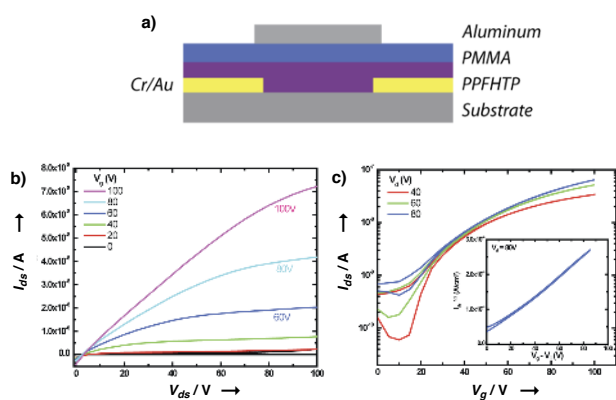

Figure 4. a) OFET architecture; b) Output curves, and c) Transfer curves of the OFET device.

In conclusion, we have successfully synthesized perfluoroalkyl-substituted pC$_n$TPs (**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 orthogonally processed organic photovoltaic devices is ongoing in our laboratory.

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[26] We classify the p-doping of **PPFHTP** to be electrochemically irreversible since a 300 mV overpotential is required to dedope the oxidized polymer film. Concurrently, we note that the integrated current values for the p-doping and dedoping processes are equivalent, thus confirming that p-doping does not chemically degrade the film.

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Conjugated Polymers

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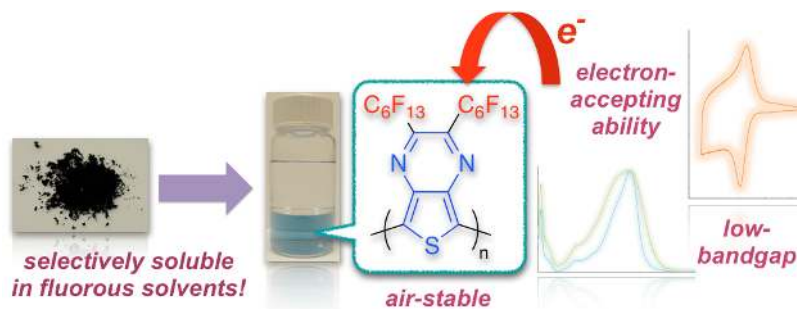
A new class of air-stable n-type polymer semiconductor, poly (2,3-bis(perfluorohexyl)thieno[3,4-*b*]pyrazine) (**PPFHTP**), is synthesized through a Pd-catalyzed polycondensation employing a fluorous multi-phase solvent system. This is the first example of an n-type polymer semiconductor with exclusive 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.