# Synthesis and Properties of Poly(phenylene ethynylene)s with Pendant Hexafluoro-2-propanol Groups

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ABSTRACT: Several poly(phenylene ethynylene)s with pendant hexafluoro-2-propanol (HFIP) groups have been synthesized and characterized in terms of their solution and thin-film optical properties. The incorporation of strongly hydrogen-bond-donating HFIP groups into conjugated polymers is shown to greatly enhance their fluorescence response upon exposure to the vapors of several hydrogen-bond-accepting analytes such as pyridine and 2,4-dichloropyrimidine. The enhanced sensitivity of these conjugated polymer-based chemosensors is the result of stronger analyte/polymer binding interactions and more facile photoinduced charge-transfer reactions with hydrogen-bonded analytes.

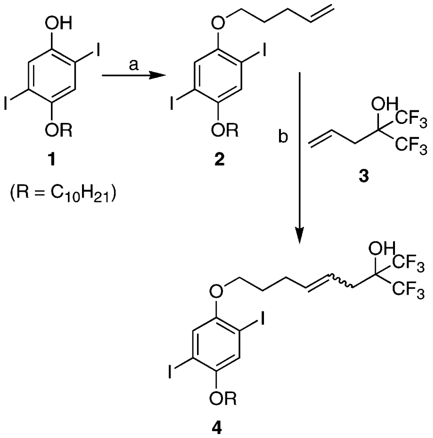
## Introduction

Conjugated polymer-based fluorescent chemosensors have shown great promise in the detection of trace analytes and explosive vapors.[1] Planar, electron-deficient aromatic compounds such as trinitrotoluene (TNT) tend to have very strong electrostatic interactions with electron-rich conjugated polymers such as poly(phenylene ethynylene)s (PPEs). Furthermore, these analytes often possess sufficiently low redox potentials to accept electrons via photoinduced charge transfer (PICT) reactions with PPEs, which results in quenching of the excited state of the conjugated polymer. Analytes such as TNT can be readily detected by specially designed PPE thin films, even though the equilibrium vapor pressure of TNT is only in the ppb range ($8.02 \times 10^{-6}$ mmHg at 25 °C).[2]

We are interested in extending conjugated-polymer-based sensing systems toward the detection of analytes that have weak electrostatic interactions with conjugated polymers such as PPEs. Compounds of interest include those typically incorporated into plastic explosives formulations as well as a number of toxic industrial chemicals (TICs). Various common organic solvents and pesticide residues are also important target analytes for chemical sensing applications. Many of these analytes are poorer electron acceptors (higher redox potentials) than nitro-aromatics and are reluctant to undergo PICT reactions with PPEs.

Strong hydrogen-bond-donating groups, such as hexafluoro-2-propanol (HFIP) groups, have found application in coatings for many chemical microsensor technologies, including surface acoustic wave (SAW) devices.[3] One HFIP-containing coating, polysiloxane fluoroalcohol (SXFA), is commonly used in these applications as a hydrogen-bond-donating sorbant.[4,5] This coating has demonstrated significant affinity for the vapors of weakly hydrogen-bond-accepting analytes such as nitro-aromatics, many organic solvents, and some nerve agent simulants.[6] Similar HFIP-containing coatings have also been used in concert with various dyes in luminescence-based sensors for the detection of organophosphonate vapors.[7] We are interested in determining whether the incorporation of such strong hydrogen-bond-donating capability into a conjugated polymer can lead to stronger polymer/analyte binding interactions and result in improved sensitivity of conjugated-polymer-based chemosensors toward a wide variety of weakly binding analytes.

**Scheme 1. Synthesis of HFIP-Substituted Diiodoarene Monomer 4**[a]



[a] (a) 1-Bromo-4-pentene, $K_2CO_3$, KI, 2-butanone, 80 °C, 76%; (b) Grubbs second-generation ruthenium catalyst, $CH_2Cl_2$, 65 °C, 67%.

Herein we report the synthesis and properties of several PPEs with pendant HFIP groups. We demonstrate that these HFIP groups can significantly enhance the response of conjugated-polymer-based chemosensors toward certain hydrogen-bond-accepting analyte vapors through strengthened analyte/polymer binding and more facile charge-transfer reactions between the PPE and the hydrogen-bonded analytes.

## Results and Discussion

**Monomer Synthesis.** The synthesis of PPEs with pendant HFIP groups begins with the synthesis of HFIP-substituted diiodo-arene monomers. Monomer **4** contains a single HFIP functionalized side chain as well as an unfunctionalized alkoxy side chain and is prepared as illustrated in Scheme 1. Compound **1** can be prepared in four steps by previously reported proce-

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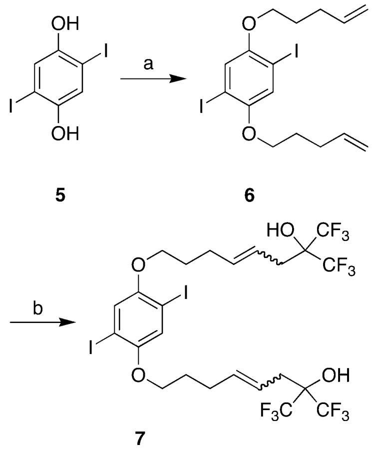
**Scheme 2. Synthesis of Bis-HFIP-Substituted Diiodoarene Monomer 7**[a]



[a] (a) 1-Bromo-4-pentene, $K_2CO_3$, KI, 2-butanone, 80 °C, 85%; (b) **3**, Grubbs second-generation ruthenium catalyst, $CH_2Cl_2$, 65 °C, 12%.

**Table 1. Summary of Photophysical Data for Polymers P1, P2, and P3**[a]

| | CHCl3 (film) | | | |
|---|---|---|---|---|
| polymer | abs $\lambda_{max}$ (nm) | em $\lambda_{max}$ (nm) | $\Phi_F$[b] | $\tau$ (ns)[c] |
| **P1** | 413 (454) | 452 (463) | 0.51 | 0.6 |
| **P2** | 413 (445) | 452 (462) | 0.63 | 0.5 |
| **P3** | 401 (405) | 449 (457) | 0.67 | 0.6 |

[a] See Supporting Information for details of experimental conditions. Quantum yields and fluorescence lifetimes of polymers **P1**, **P2**, and **P3** were measured as solutions in $CHCl_3$. [b] Solution-state fluorescence quantum yields are relative to an equiabsorbing solution of quinine sulfate ($\Phi_F$ = 0.53 in 0.1 N $H_2SO_4$).[12] [c] Reported fluorescence lifetimes are fit to a single-exponential function.

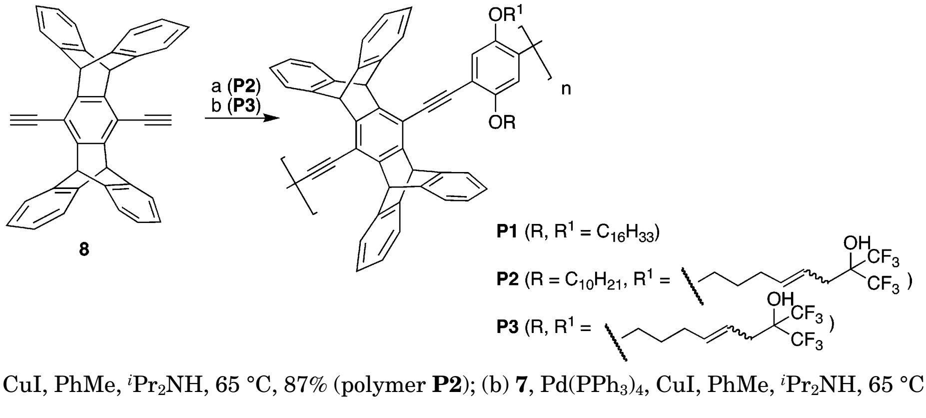
dures.[8] Williamson etherification of **1** with 1-bromo-4-pentene affords **2** in good yield (76%). Olefin cross-metathesis between **2** and a commercially available HFIP-substituted terminal olefin, **3**, with Grubbs second-generation ruthenium catalyst[9] proceeds in good yield (67%) to the HFIP-substituted monomer **4**.

Monomer **7** presents two HFIP groups and is prepared as illustrated in Scheme 2. Compound **5** can be prepared in two steps by previously reported procedures.[1a,10] Williamson etherification of **5** with 1-bromo-4-pentene affords **6** in good yield (85%). Olefin cross-metathesis between **2** and **3** with Grubbs second-generation ruthenium catalyst proceeds to yield the bis-HFIP-substituted monomer **7**. The material is isolated by recrystallization (hexanes) in poor yield (12%, first crop) since chromatography was unsuccessful for the separation of **7** from the homo-metathesis product of **3**.

**Polymer Synthesis.** The incorporation of rigid iptycene groups into conjugated polymers has been shown to increase polymer solubility, reduce solid-state aggregation, and increase solid-state fluorescence quantum yields.[1b,11] Additionally, these groups provide some amount of porosity in the solid state to facilitate increased analyte diffusion and binding within the polymer films. PPEs that contain iptycene frameworks along their chains are known to have excellent performance in solid-state fluorescence chemosensing applications.[1] A palladium-catalyzed Sonogashira−Hagihara cross-coupling polymerization (Scheme 3) of monomer **4** with a dialkynyl-substituted pentiptycene moiety **8** yields polymer **P2** in 87% yield with a number-average molecular weight ($M_n$) of 17 000 (DP 20). The pendant olefins and HFIP groups appear to have no significant effect on the polymerization as acceptable polymer molecular weights were obtained. Polymer **P3** was prepared in a similar manner from monomers **7** and **8** (75% yield, $M_n$ 26 000, DP 20). All polymers were characterized by $^1H$ and $^{19}F$ NMR spectroscopy, gel permeation chrmoatography (GPC), and UV−vis as well as fluorescence spectroscopy. For comparison, a similar PPE of comparable molecular weight, polymer **P1**, which presents only simple unfunctionalized alkoxy-substituted side chains, was employed.

The photophysical properties of polymers **P1**, **P2**, and **P3** are listed in Table 1. The pendant HFIP groups do not appear to significantly affect the photophysical properties of polymers **P2** and **P3**, as they are both similar to polymer **P1** in terms of solution and solid-state absorption and emission spectra as well as solution-state fluorescence quantum yields and fluorescence lifetimes. To determine the effect of the pendant HFIP groups on the performance of PPE-based fluorescent chemosensors, we employed a Fido 4TD, a commercial fluorescence-based vapor sensor designed and manufactured by Nomadics Inc. (Stillwater, OK).[13] The Fido sensor measures the real-time fluorescence intensity of a conjugated polymer film as it is exposed to various analyte vapors. For implementation in a Fido sensor **P1**, **P2**, or **P3** are spin-cast on the inside of a heavy-walled glass capillary and the emission of this film is monitored, while analyte vapors are passed through the capillary. Using this device, the responses of **P1**, **P2**, and **P3** to the vapors of a number of different analytes were evaluated by monitoring the change in fluorescence intensity upon drawing analyte vapor through the capillary at a flow rate of 35 mL/min. For these experiments, equilibrium vapor pressures of the analytes were delivered to the sensor (see Supporting

**Scheme 3. Synthesis of PPEs with Pendant HFIP Groups**[a]



[a] (a) **4,** $Pd(PPh_3)_4$, CuI, PhMe, $^iPr_2NH$, 65 °C, 87% (polymer **P2**); (b) **7**, $Pd(PPh_3)_4$, CuI, PhMe, $^iPr_2NH$, 65 °C, 75% (polymer **P3**).

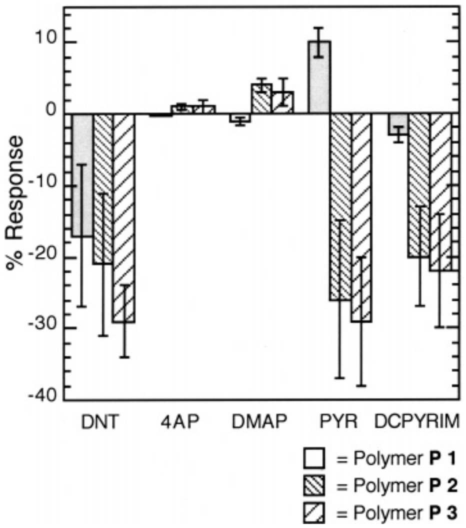


**Figure 1.** Average changes in fluorescence emission intensity upon repeated exposures of polymers **P1** (gray bars), **P2**, and **P3** (crosshatched bars) to equilibrium vapor pressures of various analytes (1 s exposures for DNT, 3 s exposures for all other analytes). A negative response indicates a quench in polymer fluorescence intensity upon exposure to the analyte vapor. A positive response indicates an increase in polymer fluorescence intensity upon exposure to the analyte vapor. The error bars represent one standard deviation. Equilibrium vapor pressures of selected analytes: [DNT: 2,4-dinitrotoluene, VP = 1.47 × $10^{-4}$ mmHg at 22 °C (0.2 ppm)] [4AP: 4-aminopyridine, VP = 3.70 × $10^{-4}$ mmHg at 25 °C (0.5 ppm)] [DMAP: *N,N′*-(dimethylamino)pyridine, VP = 1.00 mmHg at 25 °C (1300 ppm)] [PYR: pyridine, VP = 20.8 mmHg at 25 °C (27 000 ppm)] [DCPYRIM: 2,4-dichloropyrimidine, VP = 2.98 × $10^{-1}$ mmHg at 25 °C (390 ppm)].[2a,14]

Information for experimental details). Upon removal of analyte vapor source, ambient air is pulled through the capillary. The results for selected analytes chosen to survey the scope of responses possible are presented in Figure 1.

The presence of HFIP groups has the general effect of increasing the sensitivity of **P2** and **P3** relative to **P1**. The differences are most profound in analytes that will display the strongest hydrogen-bonding behavior. For example, all three polymers demonstrate similar quenching responses to the weak hydrogen-bonding, but strongly electron-deficient, aromatic analyte, dinitrotoluene (DNT). The very strong electrostatic interaction between this analyte and the electron-rich PPEs appears to overwhelm any effect of HFIP substitution in polymers **P2** and **P3**. Pyridine, on the other hand, possesses much weaker electrostatic interactions with the PPEs, and we observe that polymer **P1** shows 10−12% increases in fluorescence intensity upon exposure to pyridine vapor, as shown in Figure 2a (five separate 3 s exposures). The increased fluorescence emission intensity is immediately lost upon removal of the pyridine vapor source and is likely due to swelling that will reduce interchain interactions and increase the thin film quantum yield of the polymer.[15] The rapid reversion of the initial fluorescence intensity indicates a fairly weak interaction between polymer **P1** and the pyridine vapor. The response of **P1** is in stark contrast to that of **P2** (Figure 2b) and **P3** (Figure 2c), which both display strong decreases in fluorescence intensity upon exposure to pyridine vapor. We suggest that a hydrogen-bonded pyridinium species is sufficiently electron deficient to undergo PICT reactions or form charge transfer complexes with the PPE that result in a quenched fluorescence upon exposure to this analyte. Similar fluorescence quenching phenomena with hydrogen-bonded pyridines have been previously reported in small molecule systems.[16] This interesting result suggests that incorporation of HFIP groups, in addition to enabling more favorable polymer/analyte interactions, can also serve to modulate the electronic properties of some targeted analytes.

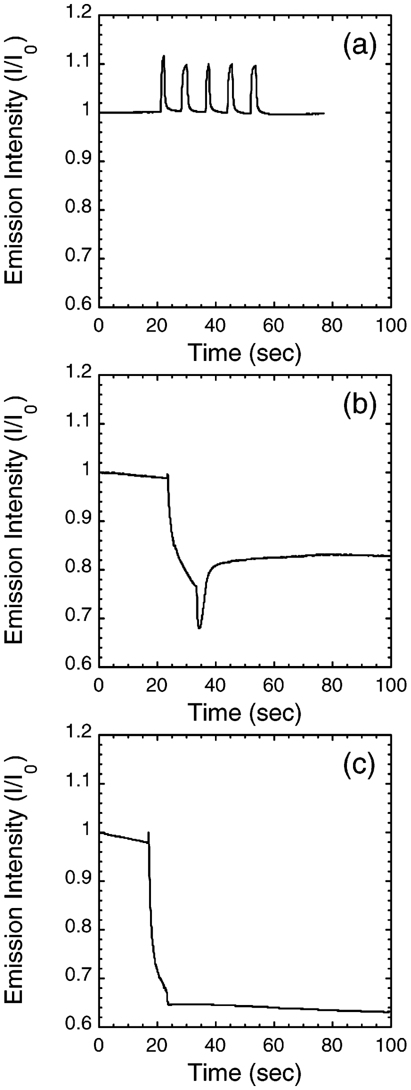


**Figure 2.** (a) Real-time fluorescence response of polymer **P1** to five separate 3 s exposures to pyridine vapor. (b) Real-time fluorescence response of polymer **P2** to a single 3 s exposure to pyridine vapor. (c) Real-time fluorescence response of polymer **P3** to a single 3 s exposure to pyridine vapor.

The very slow recovery of the initial fluorescence intensity for **P2** (Figure 2b) is indicative of strong analyte/polymer interactions. In other words, the pyridine vapor appears to adsorb much more strongly to the HFIP substituted polymer **P2** and remains there for a significant period of time after the initial exposure. The Fido data for polymer **P3** (Figure 2c) reveals even stronger interactions with pyridine and the fluorescence does not appear to recover after removal of the vapor source.

Other analytes such as 4-aminopyridine (4AP) vapor and *N,N′*-(dimethylamino)pyridine (DMAP) vapor appear to be too electron rich to undergo PICT reactions with any of the PPEs. From the Fido data, we find that polymers **P1**, **P2**, and **P3** demonstrate minimal responses to both of these analytes. Similar to the responses observed for pyridine, a more electron-deficient analyte, 2,4-dichloropyrimidine (DCPYRIM), also results in a significant 20% quenching of fluorescence from the HFIP-substituted polymers **P2** and **P3**, while polymer **P1** only demonstrates a minimal quench in fluorescence.

Polymer **P2**, which demonstrates at least some amount of reversibility in pyridine binding, appears to be the superior material for sensing applications involving these types of analytes, since sensors that can survive repeated analyte exposures are attractive for practical purposes. However, polymer **P3**, which demonstrates irreversible binding with some analytes (pyridine, 2,4-dichloropyridine, and DNT to some extent), may be an attractive sensory material for the detection of trace compounds or those with extremely low vapor pressures. For such analytes, a long analyte exposure time could be employed to increase the amount of the adsorbed analyte to higher levels, since the greater HFIP content of **P3** makes the analyte desorption process less favorable.

## Conclusion

We have synthesized two new PPEs that contain side chains substituted with pendant hexafluoro-2-propanol (HFIP) groups. The incorporation of strong hydrogen-bond-donating groups as a pendant functionality into a conjugated polymer-based fluorescent chemosensor can lead to greatly strengthened interactions between the polymer and some weakly binding analyte vapors. We have found that the strengthened analyte/polymer binding interactions, as well as the increased electron deficiency of some hydrogen-bonded analytes, can lead to very strong fluorescence quenching responses from HFIP-substituted conjugated polymers. We are currently investigating the role of HFIP substituents in conjugated polymer-based chemosensors for the detection of a wide variety of explosive vapors and other compounds of interest.

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**Supporting Information Available:** Experimental details for monomer and polymer synthesis, absorbance and fluorescence spectra for polymers **P1**, **P2**, and **P3**, and additional Fido experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The vapor intake of the Fido 4TD is heated to 135 °C in order to facilitate transport of the analyte to the conjugated polymer coating. The temperature of the polymer was maintained at 20 °C.

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