



# Chemically robust conjugated polymer platform for thin-film sensors

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## ABSTRACT

To examine chemically robust thin conjugated polymer films for use as optical and conductometric sensors, we graft polythiophene and two alkyl-based derivatives to optically transparent substrates. Though structurally contrasting to other film deposition techniques, grafted polythiophene films preserve their documented absorption, luminescence and electrical properties. Photoluminescence intensities are sensitive to trace amounts of iron and iodine in solution with reasonable Stern–Volmer constants and downward sloping Stern–Volmer plots characteristic to thin-film sensors. Rising conductivities indicate chemical doping is responsible for photoluminescence quenching. We vary reaction times and solvents to optimize desired properties and produce robust polythiophene films, verified by X-ray photoemission spectroscopy, that are uniform across the substrate with thicknesses ranging from 20 to 200 nm and controllable levels of surface roughness. Due to steric effects, polythiophene and poly(3-methylthiophene) films exhibit the highest conductivities while poly(3-hexylthiophene) films exhibit greater photoluminescence efficiencies. These platforms show promise as thin films for in-solution sensing.

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## 1. Introduction

The unique optical and electrical properties of semiconducting polymers encourage extensive research in organic polymer photovoltaics [1], polymer light emissive displays [2–4] and polymer actuators [5]. Conjugated polymers are also sensitive to their surrounding environment, rendering them useful materials for chemical and biological sensing. Most studies on solid-state conducting polymer sensors focus on the advancement of conductometric or amperometric sensors in which polypyrrole, polythiophene or polyaniline films are spun-cast [6], electrochemically grown [7,8] or deposited by electrostatic means [9,10]. However, these materials are also promising in optically based sensing techniques. For example, nano-molar quantities of biotinylated methyl viologen quench the photoluminescence of water-soluble poly(phenylene vinylene)s (PPV) and polythiophenes (PT) in solution because single methyl viologen molecules affect the fluorescence of entire polymer chains [11,12]. Other researchers report the optical sensitivity of spun-cast polymer films to nitro-aromatic compounds in air [13]. Prospects of reusability, portability and lower waste generation justify the pursuit of developing a robust thin-film conducting polymer transducer that can optically quantify small amounts of analytes in solution. We

report a survey of physical, optical and electrical characterizations on chemically grafted polythiophene films and draw conclusions on improving the design and functionality for high-sensitivity optical transduction based on photoluminescence quenching.

Polythiophene (PT) is an environmentally stable conducting polymer that is polymerized using well known oxidative techniques [14]. Previously, polythiophenes have been chemically grafted to non-metallic surfaces such as polyethylene [15] and silicon [16]. We have developed a method using silane-based surface chemistry in which thiophene monomers are covalently attached to silicon, glass, and quartz, and then directly polymerized to the surface. Furthermore, this method is extended to graft poly(3-methylthiophene) (P3MT) and poly(3-hexylthiophene) (P3HT) as side chains enhance polymer solubility and would thus allow better analyte infiltration from the solution. The grafted conjugated polythiophenes we report show improved photoluminescence intensities and conductivities over spun-cast or electrochemically deposited films. Photoluminescence quenching by three electron acceptors, methyl viologen, iodine and ferric chloride in solution, exhibits nonlinear Stern–Volmer relationships with reasonable Stern–Volmer constants.

## 2. Experimental

Fisher microscope slides, polished silicon, and quartz were used as substrates for grafting. Anhydrous methanol, acetonitrile, chloroform, thiophene, 2-thiophene ethyl amine, 3-methyl thiophene, 3-hexyl thiophene and reagents for the piranha etching were

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purchased from Fisher. The 3-isocyanatopropyl trimethoxysilane was purchased from Gelest. The substrates were prepared with the following cleaning procedures: first, sonication in successions of milli-Q water and isopropanol. Second, wet piranha etching with 7:3 sulfuric acid to 30% hydrogen peroxide was performed at 80 °C for 1 h.

0.08 M of 3-isocyanatopropyl trimethoxysilane was reacted with passivated oxide surface layers in methanol for 1 h allowing silanol groups to bond to the substrate. 2-Thiophene ethyl amine was then reacted with the isocyanato functional group in methanol leaving thiophene monomers covalently attached to the surface (see Fig. 1). Polymerization of thiophene to the modified substrate was performed oxidatively by immersing the slides in ferric chloride solution with acetonitrile or chloroform solvents. After an allotted time, the polymerization reaction was stopped by removing the substrate and washing with methanol. Polythiophene films were further cleaned by successive sonications in methanol and milli-Q water for 30 min at 35 °C. Experimental variations included monomer type, polymerization solvent type, ferric chloride to monomer concentration ratios and polymerization time. Surface modifications were analyzed using a Physical Electronics Quantum 2000 scanning X-ray photoemission spectrometer. Calculated atomic percentages for major peaks are ~90%.

Optical analysis of the films consisted of transmission measurements with n&k Varion 300 spectrophotometer and photoluminescence measurements with a PerkinElmer LS45 luminescence spectrometer. Aqueous iodine solutions are made by first making a solution of 1 g potassium iodide in 10 mL of water, then adding 0.5 g iodine. Adding 1 mL of that solution into 5 mL of water makes the next lower concentration. And the rest follow similarly. In our measurements, we consider the concentration of iodine as the molar concentration of iodine ions though several ionic forms exist. For photoluminescence quenching experiments, the quenching solution was injected into a small fillable volume approaching 0.1 mL that was built around the films using glass slides and epoxy. For most quenchers, photoluminescence was measured immediately after injection of the solution. Some however, exhibited slower reactions and were left in place for allotted amounts of time before taking measurements.

Film thickness and morphological quantities were determined using a Park Scientific Instruments Autoprobe atomic force micro-

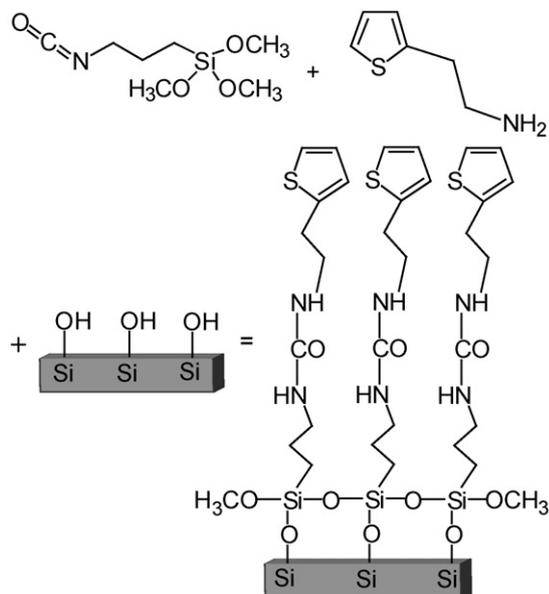


Fig. 1. Pictorial representation of thiophene monomer grafting procedure before polymerization.

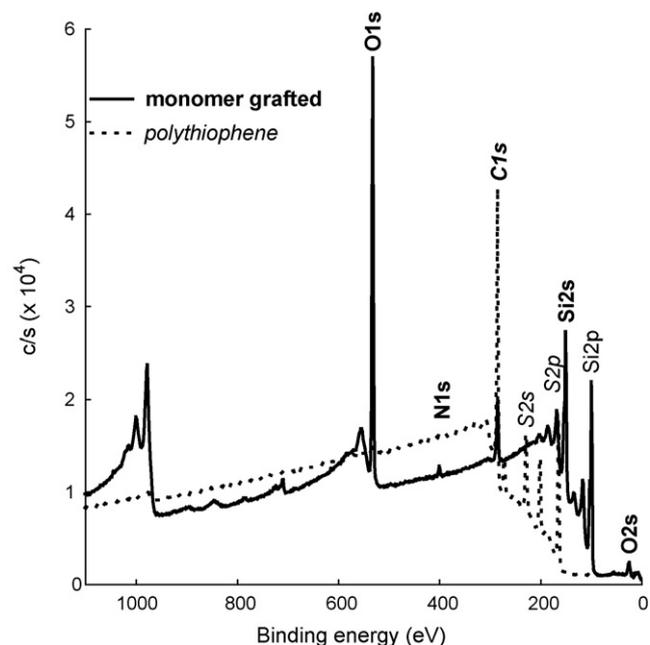


Fig. 2. XPS survey spectra of substrate before and after polymerization.

scope with Veeco phosphorous doped silicon non-contact AFM tips with tip radius < 12 nm. The films were analyzed using Image SXM 179 software. RMS roughness is the root mean squared value of all vertical deviations from the mean surface level. Current/voltage measurements for doped and undoped films were taken across a 100  $\mu\text{m}$  gap in an evaporated layer of chromium and silver using a two probe setup with 5  $\mu\text{m}$  tungsten probes from Signatone. The films were doped by a 0.2 M solution of ferric chloride in acetonitrile. They were dried before metal contacts were evaporated and the conductivity was tested 2 h later. The values obtained for thickness, surface roughness and conductivities are averages of several samples.

### 3. Film growth

Chemical processes were verified in the grafting procedure by hydrophobicity tests and X-ray photoemission spectroscopy (XPS). Passivated oxide layers on the surface of the substrate are characteristically hydrophilic and thus demonstrate a visual increase in the wettability of the surface after cleaning. The surface then proceeds from hydrophilic to successively more hydrophobic after reactions with the silane, 2-thiophene ethyl amine and finally polymerization. In Fig. 2, more quantitative XPS survey scans comparing monomer functionalized surfaces with those post-polymerization are shown. Concomitant decreases in the oxygen content of the surface with increases in carbon and sulfur, consistent with a binding energy of a thiophene environment, indicate polymerization of polythiophene. Table 1 lists the atomic percentages of a series of high-resolution XPS scans from the silanized substrate to the polymerized polythiophene and P3MT. Decreases in oxygen content, increases in carbon content and the presence of nitrogen indicate

Table 1  
Atomic percentages from XPS high-resolution scans.

Atomic percentages	C1s	N1s	O1s	S2p	Cl2p	Fe2p
Just isocyanato silane	26.08	0.63	71.04	0.00	1.23	1.01
Thiophene monomer	39.01	2.17	56.39	0.00	1.17	1.21
Polythiophene	74.10	0.00	6.57	13.74	1.33	0.13
Poly(3-methylthiophene)	77.83	0.00	6.57	13.74	1.33	0.13

**Table 2**  
PT, P3HT and P3MT film characteristics for different polymerization reactions.

Film # PT	Monomer:FeCl <sub>3</sub> ratio	Solvent type	Reaction time	Film thickness (nm)	RMS roughness (nm)
1	1:5	CHCl <sub>3</sub>	3 h	280	52
2	1:5	ACN	3 h	46	13
3	1:6	ACN	3 h	44	10
4	1:8	ACN	3 h	52	21
5	1:6	ACN	30 min	40	20
6	1:8	ACN	30 min	41	18
7	1:4	ACN	30 min	51	11
8	1:4	CHCl <sub>3</sub>	30 min	90	43
9	3:8	ACN	30 min	90	34
P3HT					
1	1:5	ACN	3 h	34	18
2	1:5	CHCl <sub>3</sub>	3 h	121	45
3	1:4	ACN	30 min	35	19
1 spun		CB		17–33	
2 spun		di CB		13–25	
P3MT					
1	1:4	ACN	30 min	89	32
2	1:4	CHCl <sub>3</sub>	30 min	92	39
3	1:4	ACN	3 h	91	17
4	1:4	CHCl <sub>3</sub>	3 h	115	69

successful grafting of the thiophene monomer while increasing chlorine levels indicate contamination from the polymerization in ferric chloride. We consider the films chemically robust as they sufficiently pass sonication and tape tests while unmodified substrates do not.

Table 2 shows how polymerization solvent, oxidant to monomer ratio and polymerization time affect the thickness and morphology of the resulting film. Choice of polymerization solvent has the most impact because weak solvation interactions between chloroform and ferric chloride leave more active oxidant than in acetonitrile [15]. Thus polymer films are thicker and rougher compared to those grown in acetonitrile. Film characteristics follow more subtle trends with time and monomer to oxidant ratios. It is expected that increasing the oxidant relative to the monomer concentration in acetonitrile would result in more available solvent for polymerization. For longer reaction times, this is reflected in the increasing film thickness. However, we see the opposite trend in films reacted for 30 min and the highest monomer concentrations in acetonitrile produced similar films (~90 nm) to those in chloroform. This could be due to the amount of monomer that reaches the surface before being polymerized. Steric hindrances due to the long side chains also affect grafted derivatives of PT. P3HT films were thinner, exhibited higher roughness factors and lower surface coverage. Surface roughness of the support substrate is only apparent in PT films thinner than 20 nm.

#### 4. Photoluminescence quenching

Fig. 3 displays normalized absorption spectra for PT, P3MT and P3HT and normalized photoluminescence spectra for only PT and P3HT. Absorbance spectra are similar to those of previous studies with solution processed films [17]. Peak absorptions of P3MT and P3HT are slightly red-shifted from PT because side chains induce a stiffer polymer structure [18]. However, stoke shifts remain the same between all polymers. P3HT films exhibit higher levels (up to 50%) of photoluminescence intensities because sterically hindered surface coverage [19] prompts lower levels of self-absorption and interchain interactions. In general, thin films of polythiophenes exhibit low photoluminescence efficiencies and intensities however, we significantly improved photoluminescence intensities with proper purification of thicker films. Polythiophene derivatives are known to exhibit good environmental stability [20,14]. We found the grafted polythiophene films were optically active

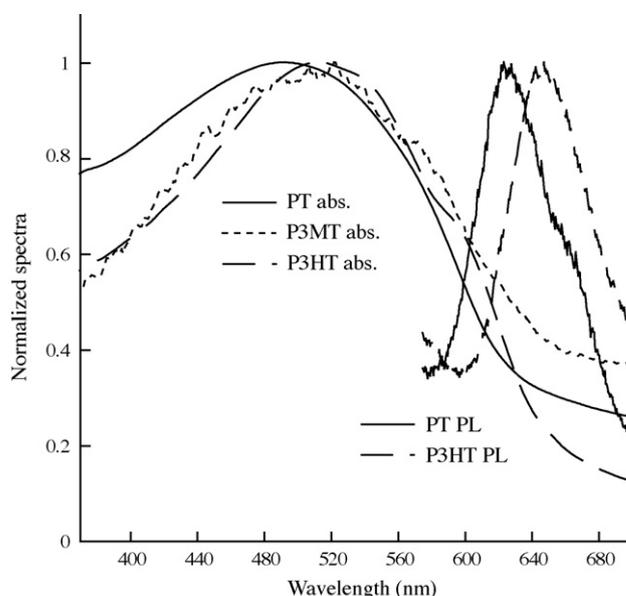
and responsive after months of storage in a vacuum desiccator.

We tested electron acceptors methyl viologen, ferric chloride and iodine, commonly used in conjugated polymer quenching or doping studies [21,22], as quenchers for the grafted polythiophene films. Both ferric chloride in acetonitrile (see Fig. 4) and aqueous iodine solution significantly quench the photoluminescence of polythiophene.

Static and dynamic quenching are typically quantified by the Stern–Volmer constant  $K_{SV}$  in the equation:

$$\frac{PL_0}{PL} - 1 = K_{SV}[Q]$$

where  $PL_0$  is the photoluminescence of the unquenched material,  $PL$  is the quenched photoluminescence and  $[Q]$  is the quencher concentration. For sensing applications, high  $K_{SV}$  constants are preferred for greater sensitivities to particular analytes. Linearity is expected, however in thin films, nonlinear diffusion of quencher molecules into films containing heterogeneous populations of flu-



**Fig. 3.** Absorbance and photoluminescence spectra for PT, P3MT and P3HT

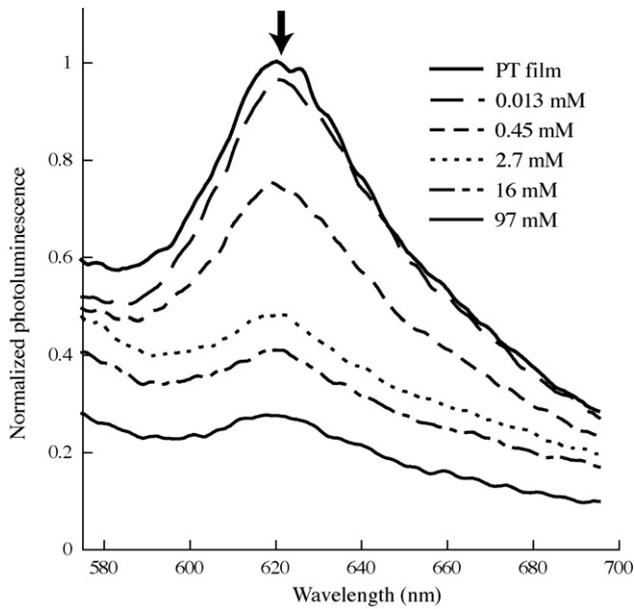


Fig. 4. Florescence quenching of PT films with ferric chloride in acetonitrile.

rophores results in downward curving Stern–Volmer plots. Fig. 5 shows Stern–Volmer relationships for grafted polythiophene films quenched with ferric chloride in acetonitrile and iodine in water. The insert displays a close-up of the low concentration region. The data was corrected for the molar absorptivities of ferric chloride and iodine at excitation wavelengths of 500 nm and emission wavelengths at 620 nm [23]. The shape of the Stern–Volmer curves are comparable to solution-based studies involving mixtures of water-soluble PTs and PPVs in ionic solutions [12,24] as well as to thin-film studies on oxygen sensors in which the fluorophore is embedded in a polymer matrix [25]. We more accurately fit our data to the equation:

$$1 - \frac{PL}{PL_0} = \frac{f_a K_{SV}^a [Q]}{1 + K_{SV}^a [Q]}$$

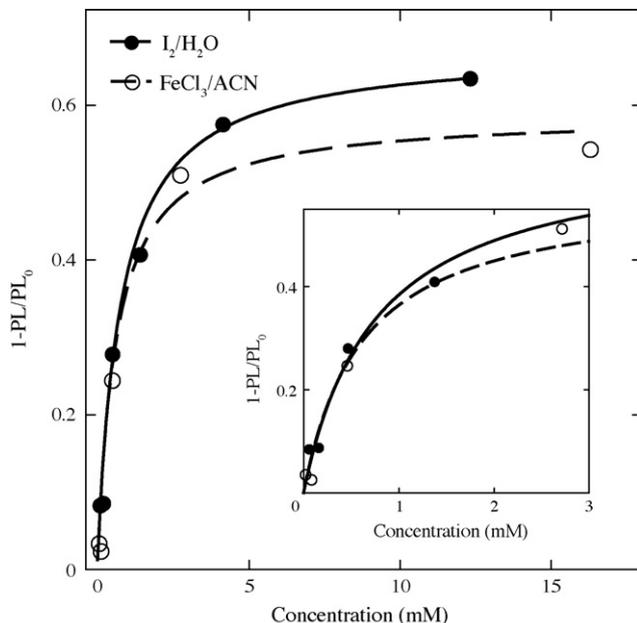


Fig. 5. Plot for determining the Stern–Volmer constant.

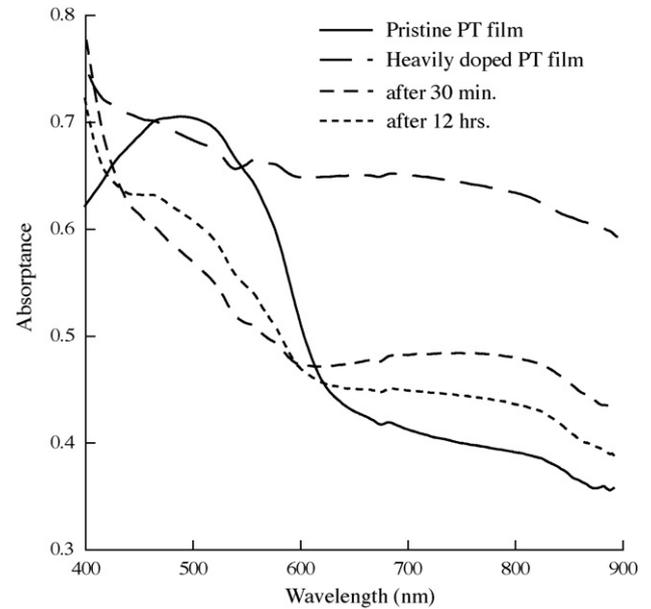


Fig. 6. Absorbance spectra over time for PT and P3HT films doped with FeCl<sub>3</sub>.

derived from considering that only a fraction,  $f_a$ , of fluorophores are available for quenching. The model is similar in form to the Langmuir equation which illustrates equilibrium conditions between adsorbates and adsorbents on surfaces immersed in solutions or gases and can be expanded to include multiple fluorophore species [26]. In Fig. 5, Stern–Volmer plots for ferric chloride in acetonitrile and iodine in water are fit with the single fractional species model described above. In grafted polythiophene films, for ferric chloride,  $f_a = 0.59$  and  $K_{SV}^a = 1621 \text{ M}^{-1}$  and for iodine,  $f_a = 0.67$  and  $K_{SV}^a = 1321 \text{ M}^{-1}$ . Both quenchers are similarly efficient. P3HT films exhibit similar Stern–Volmer relationships with slightly higher Stern–Volmer constants because of lower surface densities.

Also notable in quenching observations is the choice of solvent. In water, both ferric chloride and methyl viologen quench up to 20% of the film's photoluminescence, but only after hours of exposure. Reasons for delayed diffusion of quencher molecules into the film may involve solvent/quencher interactions and charge neutral polymer side chains. Overall, Stern–Volmer constants vary depending on choice of quencher molecules and solvent but would show improvement in more purified films with higher molecular weights [12] and side chains that allow solvation in the surrounding liquid and thus greater penetration of the quencher molecules.

Photoluminescence quenching caused by iodine and ferric chloride molecules relate to chemical doping of the conjugated polymer chain by oxidizing species:  $\text{Fe}^{3+}$  and  $\text{I}_2$ . Fig. 6 shows the absorption of PT doped in a 0.1 M ferric chloride solution. The primary absorption band of the polythiophene decreases in intensity and in correlation with previous studies [27], a broad absorption band appears between 700 and 800 nm. Chemical doping introduces polaron and bipolaron defects along the polymer chain causing a change in absorption spectra because of new allowed energy transitions [28]. After 30 min, the primary PT absorption band returns slightly, however overnight, lack of significant change indicates the film remains at that particular doping level.

## 5. Conductivity of grafted films

High doping levels can lead to large conductivities in conjugated polymers. We investigated the conductivity of doped and undoped polythiophene films with a two-point probe method. This method is sufficient for most of the films considering the resis-

**Table 3**  
Conductivities of doped and undoped polythiophene films.

Film #	$\sigma$ (S/cm) undoped	$\sigma$ (S/cm) doped
4	$5.5 \times 10^{-8}$	0.0024
6	$1.2 \times 10^{-5}$	0.0044
7	$5.1 \times 10^{-6}$	1.47
8	$1.0 \times 10^{-5}$	0.43
9	$4.0 \times 10^{-6}$	1.79
2 (P3HT)	$1.1 \times 10^{-7}$	$1.2 \times 10^{-5}$
3 (P3HT)		$2.7 \times 10^{-5}$
1 P3HT (CB) spun	$3.2 \times 10^{-5}$	$3.9 \times 10^{-5}$
2 P3HT (diCB) spun	$3.5 \times 10^{-5}$	$4.2 \times 10^{-5}$
1 (P3MT)		1.91
2 (P3MT)	$1.7 \times 10^{-5}$	1.92
3 (P3MT)	$1.7 \times 10^{-5}$	0.23
4 (P3MT)	$7.2 \times 10^{-7}$	1.61

tivity of the films is orders of magnitude larger than the probes themselves. Table 3 shows calculated conductivities for some of the films described above. Polythiophene and P3MT films exhibit the highest conductivities while grafted and spun-cast P3HT films are significantly less conductive due to steric effects that decrease the planarity of the polymer chain [29]. Lower surface coverage in grafted P3HT films also prevents conduction.

## 6. Conclusion

In an effort to harness the optical and electrical sensitivity of conjugated polymers in a functionally versatile and chemically robust design, we have succeeded in grafting polythiophene (PT), poly(3-methyl thiophene) (P3MT) and poly(3-hexylthiophene) (P3HT) to various transparent substrates using patternable organosilane surface chemistry and oxidative polymerization. Polymerization solvent and polymer side-chain length were the two experimental variations that most drastically affected polymer growth—and thus, greatly influenced the optical and electrical properties of the film. While reactions performed in chloroform produced thick films with high photoluminescent intensities and variable surface coverage, films produced in acetonitrile exhibited reliable substrate coverage and reproducible photoluminescence spectra. Because of low sterically induced surface densities, P3HT films showed the highest photoluminescence efficiencies and both PT and P3HT films were sensitive to iron and iodine in acetonitrile and water solutions with Stern–Volmer constants between 1300 and 1600 M<sup>-1</sup>. This work was a first attempts effort at designing an optically efficient, thin-film-based sensing platform for transduction in solution. These materials show promise in sensor design as further chemical modification, for example using water-soluble polythiophenes or highly luminescent poly phenylene vinylenes, will make them more selective and soluble—allowing specific analytes to infiltrate the film.

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