Fluorescent conjugated polymer films as TNT chemosensors

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Abstract

Three prototypical light emitting conjugated polymers, two poly(*p*-phenylene vinylenes) (MEH-PPV and DP10-PPV) and a poly(diphenylacetylene), were examined for chemosensor applications to detect explosive compounds such as 2,4,6-trinitrotoluene (TNT) and 2,4- and 2,6-dinitrotoluene (DNTs). All polymer thin films showed high fluorescence quenching sensitivity towards TNT and DNTs, indicating that a wide range of emissive conjugated polymers are potentially useful chemosensor materials for detecting landmines. The relative sensitivity of fluorescence quenching of the polymers by the analytes has been rationalized in terms of the vapor pressure of the analytes, the solubility parameters of the polymers and the analytes, and the relative energy levels of the polymers.
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With unique semiconducting and photoelectrical properties, conjugated polymers have been explored for a wide range of novel applications, such as organic light emitting diodes [1], thin film transistors [2], solar cells [3], as well as chemosensors [4]. The electronic properties of conjugated polymer films provide unique opportunities as chemosensory materials. The development of fluorescent sensors for organic molecules is of great practical importance in chemical, biological, and pharmaceutical sciences [5,6]. Several poly(*p*-phenylene acetylenes) (PPA) have been demonstrated as highly sensitive chemosensor materials for 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT) [4], the principle constituents of about 120 million unexploded landmines worldwide. It was shown that PPA containing pentiptycene groups were particularly effective due to their rigid three-dimensional structure that give rise to cavities to accommodate TNT molecules [4]. Using the polymers, a sensor prototype has been developed at Nomadics Inc. [7]. However, pentiptycene type polymers are not readily accessible because the corresponding monomers require multi-step syntheses. There is a need to develop less expensive materials for TNT sensing application.

In order to explore other easily accessible conjugated polymers for TNT sensor application, we examine herein three prototypical light emitting conjugate polymers, namely poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) [8], poly(2,3-diphenyl-5-*n*-decyl-*p*-phenylenevinylene) (DP10-PPV) [9], and poly[1-(*p*-*n*-butylphenyl)-2-phenylacetylene] (BuPA) [10] (shown below).
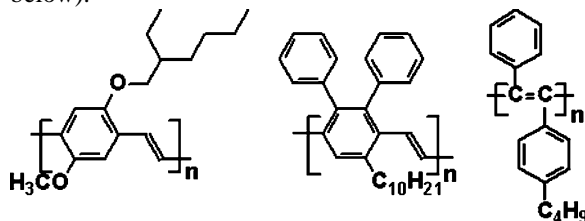
MEH-PPV   **DP10-PPV**   **BuPA**

All these polymers can be easily prepared from commercial starting materials in two to five steps in more than 100 g scale. In addition, all three polymers showed good TNT sensing capability, suggesting that many other conjugated light emitting polymers are potential candidates for TNT sensor application. This implies that most light-emitting polymer thin films should have adequate porosity or free volume to accommodate TNT-like small molecules.

The molecular weight, optical properties, and redox potentials of the fluorescent polymers are shown in Table 1.

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Table 1
Relevant physical properties of polymers and analytes

Polymers and analytes	GPC Mn (PDI)	Abs/PL, λ_{max} (nm)	Φ_F	E_g (eV)	E_A (eV)	IP (eV)	Vapor pressure[a] (mmHg at 25 °C)
MEH-PPV	400000 (2.50)	488/556 (in CHCl$_3$), 504/574 (film)	0.12	2.1	2.8	4.9	–
DP10-PPV	123000 (3.32)	357/485 (in CHCl$_3$), 368/488 (film)	0.69	2.3	2.4	4.7	–
BuPA	42810 (1.97)	426/490 (in CHCl$_3$), 424/517 (film)	0.49	2.7	2.6	5.3	–
TNT	–	–	–	–	3.74	9.84	8.02×10^{-6}
2,4-DNT	–	–	–	–	3.54	9.00	1.74×10^{-4}
2,6-DNT	–	–	–	–	3.40	8.34	5.7×10^{-4}
4-NT	–	–	–	–	3.23	–	1.64×10^{-1}
p-BQ	–	–	–	–	3.89	–	9.0×10^{-2}

[a] See Ref. [11].

Polymer thin films were deposited on a cover glass (25 mm × 25 mm) with a Synrex SSP-01A spin coater at a spin rate of 2500 rpm using polymer–chloroform solutions (10 mg of polymer in 20 ml of chloroform for 25 Å films), and placed under vacuum overnight before use. The thickness of selected films was determined by ellipsometry and correlated with the optical density [4a]. A series of exposure vials, each contained a specific solid analyte and cotton gauze, were prepared. The cotton gauze was used to prevent direct polymer–analyte contact and to maintain a constant vapor pressure. Exposure of a polymer film to the vapor of an analyte was performed by placing a polymer film into a sealed vial (20 mL size) at room temperature. The fluorescence spectra were recorded immediately after exposing the polymer film to the analyte for a specific period of time at excitation wavelengths of 504, 368, and 424 nm for MEH-PPV, DP10-PPV, and BuPA, respectively. The data reported were based on an average of two readings. The equilibrium vapor pressures of the analytes are assumed to be similar to the documented values given in Table 1 [11].

Rapid photoluminescence quenching was observed for all three polymer thin films upon exposing to TNT vapor. Fig. 1 shows decreasing fluorescence intensity of MEH-PPV film (25 Å) upon exposure to TNT vapor over several different time periods. Fig. 2 (top) shows the time-dependent
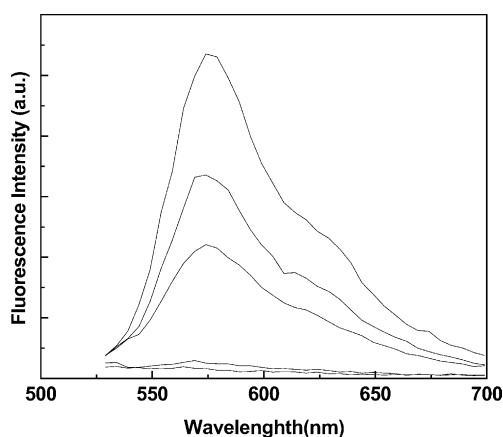
fluorescence intensity of MEH-PPV, DP10-PPV, and BuPA (~25 Å) upon exposure to TNT vapor. MEH-PPV shows the highest quenching efficiency, close to 90% after 1000 s of exposure, followed by DP10-PPV and then BuPA. It appears that the quenching percent of MEH-PPV film is better than pentiptycene type PPA. For instance, MEH-PPV shows 38% quenching by TNT in 10 s, which is higher than the 30% quenching reported for the pentiptycene PPA [4a]. Smaller TNT quenching can be seen for DP10-PPV and BuPA (19 and 10% respectively in 10 s). The stronger fluorescence quenching in MEH-PPV may be related to a stronger polar–polar interaction between the electron donating MEH-PPV and the electron accepting TNT molecules. Such polar–polar interaction should be absent in the

Fig. 1. Fluorescence intensity of MEH-PPV in a 25 Å film upon exposure to TNT at 0, 10, 60, 600, and 3600 s (top to bottom).
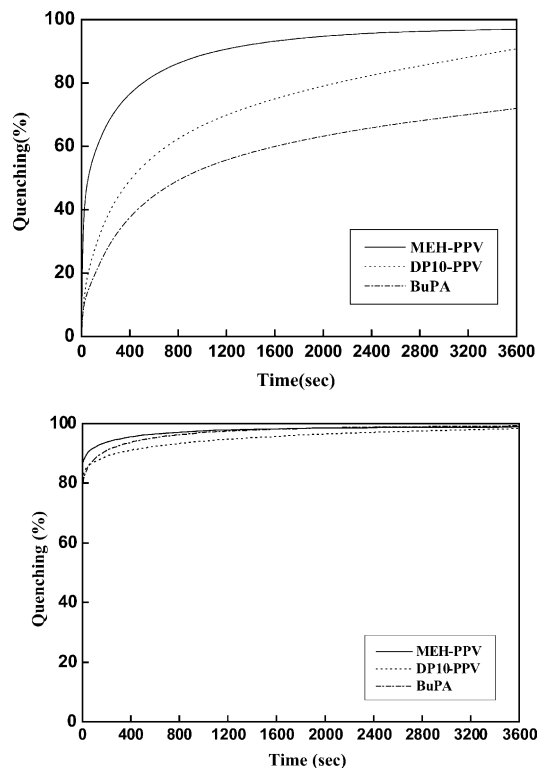

Fig. 2. Time-dependent TNT fluorescence quenching (top) and 2,6-DNT fluorescence quenching (bottom) for MEH-PPV, DP10-PPV, and BuPA (25 Å).

non-polar DP10-PPV and BuPA. This argument is in agreement with the calculated solubility parameters to be discussed below. The other possible reason is related to the stronger amplification effect in MEH-PPV due to its relatively planar backbone that enables a more facile propagation of an exciton [4,7]. According to the results of molecular modeling, MEH-PPV has an almost planar polymer backbone; DP10-PPV has a slightly twisted one; while BuPA is highly twisted. The rotational angles between two repeat units were found to decease from 180° for MEH-PPV to 175° for DP10-PPV and to 51° for BuPA [12]. MEH-PPV may have longer conjugation and persistence lengths than the other two polymers. On these bases, one may assume that exciton migration along a polymer backbone is less effective in DP10-PPV and least so in BuPA.

Fig. 2 (bottom) shows fluorescence quenching percent of the polymers with 2,6-DNT. It can be seen that all three polymers have very high quenching efficiencies (more than 80% in 10 s) with 2,6-DNT, higher than the 75% quenching found for pentiptycene type PPA [4a]. This high sensitivity toward 2,6-DNT can be attributed to the significantly higher vapor pressure of 2,6-DNT relative to TNT, more than 100× greater as shown in Table 1 [11].

The fluorescence quenching of MEH-PPV, DP10-PPV, and BuPA films (25 Å) were investigated for additional analytes, namely 2,4-DNT, 4-nitrotoluene (4-NT) and benzoquinone (p-BQ). Fig. 3 shows fluorescence quenching percent of the polymers with the five analytes after 10 and

60 s of exposure. Overall, the polymer thin films show relatively strong fluorescent quenching upon exposure to all the nitro compounds; but they show relatively weak response to 1,4-benzoquinone (BQ) even after prolonged exposure. Although BQ has the highest vapor pressure and is most readily to be reduced, it shows the weakest fluorescence quenching ability toward the light emitting polymers. For example, fluorescence quenching percent with BQ at 1 and 10 min respectively is 8.2 and 10% for MEH-PPV, 9.3 and 18% for DP10-PPV, and 5 and 14% for BuPA.

Several factors contribute to the observed fluorescence quenching. We consider kinetic effects from analyte permeation first. Since molecular sizes of the present analytes are similar, the values of the diffusion coefficient D should be similar. Hence, permeability P ($=SD$, where S is the solubility) is determined mainly by analyte solubility in the polymer, which is determined by the free energy of mixing ΔG_M defined as

$$\Delta G_M = \Delta H_M - T\Delta S_M$$

where ΔH_M is the enthalpy of mixing and ΔS_M the entropy of mixing. According to Hildebrand, the enthalpy of mixing can be calculated by

$$\Delta H_M = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2$$

where Φ_1 and Φ_2 are the volume fractions of components 1 and 2 and δ_1 and δ_2 the solubility parameters of the two components [13]. Since negative ΔG_M is required for solubility, ΔH_M and $(\delta_1 - \delta_2)^2$ (or $\Delta\delta$) should be as small as possible. Values of the three-dimensional solubility parameter [13] for all analytes and polymers used, as estimated from the group-contribution method of Hoftyzer and Van Krevelen are given in Table 2. From these data, the $\Delta\delta$s for all analyte/polymer pairs were calculated and are given in Table 3. It can be seen that for any given analyte, $\Delta\delta$ follows the order of MEH−PPV < DP10−PPV ∼ BuPA, in a qualitative agreement with the quenching results given in Fig. 3. One the other hand, for any given polymer, $\Delta\delta$ follows the order of BQ < 4NT < 2,4−DNT < TNT. This is not in accord with the quenching results given in Fig. 3, suggesting that solubility parameters may not be the dominant factors. Similar discrepancy has also been observed for the pentiptycene containing PPA and has been attributed
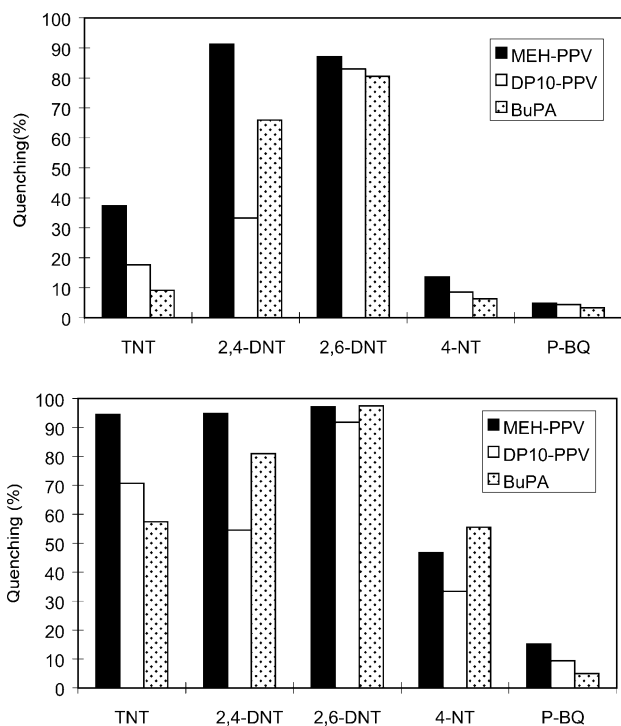

Fig. 3. Fluorescence quenching percent at an exposure time of 60 s (top) and 10 s (bottom) for MEH-PPV, DP10-PPV, and BuPA (25 Å films) with different analytes.

Table 2
Solubility parameters for the polymers and analytes[a]

	δ_d (J/mL)$^{1/2}$	δ_p (J/mL)$^{1/2}$	δ_h (J/mL)$^{1/2}$
MEH-PPV	16.1	0.6	4.7
DP10-PPV	17.8	0.5	0
BuPA	18.8	0.7	0
TNT	19.5	11.3	5.8
2,4-DNT and 2,6-DNT	17.2	9.7	4.4
4-NT	18.6	9.1	3.6
p-BQ	15.1	0	6.6

[a] δ_d, δ_p, and δ_h are the solubility parameters associated with dispersion forces, polar forces and hydrogen bonding, respectively.

Table 3
Solubility parameters for the polymers and analytes[a]

	$\Delta\delta_d$ $(J/mL)^{1/2}$	$\Delta\delta_p$ $(J/mL)^{1/2}$	$\Delta\delta_h$ $(J/mL)^{1/2}$	$\Delta\delta$ $(J/mL)^{1/2}$
TNT/MEH-PPV	3.4	10.7	1.1	11.3
2,4-DNT/MEH-PPV	1.1	9.1	−0.3	9.2
4NT/MEH-PPV	2.5	8.5	−1.1	8.9
BQ/MEH-PPV	−1.0	0.6	1.9	2.2
TNT/DP10-PPV	1.7	10.8	5.8	12.4
2,4-DNT/DP10-PPV	−0.6	9.2	4.4	10.2
4NT/DP10-PPV	0.8	8.6	3.6	9.4
BQ/DP10-PPV	−2.7	0.5	6.6	7.2
TNT/BuPA	0.7	10.6	5.8	12.1
2,4-DNT/BuPA	−2.3	9.0	4.4	10.3
4NT/BuPA	−0.2	8.4	3.6	9.1
BQ/BuPA	−3.7	0.7	6.6	7.6

[a] $\Delta\delta_d$, $\Delta\delta_p$, and $\Delta\delta_h$ are solubility parameters differences between a polymer and an analyte associated with dispersion forces, polar forces and hydrogen bonding, respectively: $\Delta\delta = [(\Delta\delta_d)^2 + (\Delta\delta_p)^2 + (\Delta\delta_h)^2]^{1/2}$.

to low polymer–BQ interaction [4]. Since the mechanism of fluorescence attenuation is electron-transfer from the excited polymer to the analytes, the overall free energy change (ΔG°) for an electron-transfer reaction must be considered [14]. In the case of oxidative quenching, this is approximated by

$$\Delta G^\circ = E(P/P^{+\circ}) - \Delta E_{0-0} - E(Q/Q^{-\circ})$$

where $E(P/P^{+\circ})$, ΔE_{0-0} and $E(Q/Q^{-\circ})$ are the redox potential of polymer $P \rightarrow P^{+\circ}$, the lowest singlet 0–0 excitation energy of the polymer, and the redox potential of quencher $Q \rightarrow Q^{-\circ}$, respectively. The fluorescence quenching (FQ) per unit time is affected by the vapor pressure (VP) of analytes, the exergonicity ($-\Delta G^\circ$) of electron transfer, and the binding strength (K_b): FQ $\propto$ (VP)[exp($-\Delta G^\circ)^2$](K_b). The low fluorescence quenching for BQ, which is an excellent electron acceptor with high vapor pressure, may be the result of low polymer–BQ interactions (small K_b), as suggested by Swager and coworkers [4].

Fluorescent quenching was also observed for thicker conjugated polymer films (ca. 200 Å), although sensitivity was significantly lower than that of the thinner films described above. This trend can 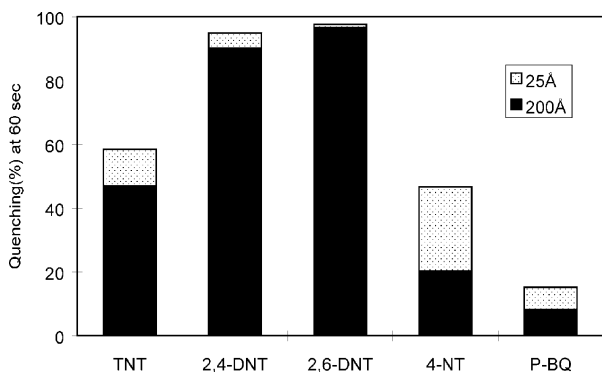be seen in Fig. 4 where quenching percent for several analytes for 25 and 200 Å films of MEH-PPV for 60 s is shown. For instance, the quenching percent for TNT is reduced from 59 to 47% as film thickness increased from 25 to 200 Å. In thicker films, the combination of slow diffusion of the analytes into the interior of thicker films and the limited distance of energy migration produces lower fluorescence quenching values.

The fluorescence quenching of the emissive polymers can be qualitatively accounted for by quenching of excitons of the polymers by the electron accepting molecules. This mechanism is depicted schematically in Fig. 5, where the HOMO–LUMO levels of the conjugated polymers were deduced from electrochemical and optical measurements [15,16] and the reduction and ionization potentials of the acceptor molecules are given in Table 1 [17,18]. This type of fluorescence quenching mechanism due to acceptor doping is well documented and accepted for emissive conjugated polymers [18–20]. For example, fluorescence quenching was observed for PPV and MEH-PPV upon doping with a dicyanomethane compound and C_{60}, respectively [19,20].

In summary, fluorescence-based chemosensing method merits attention because of its sensitivity, selectivity and

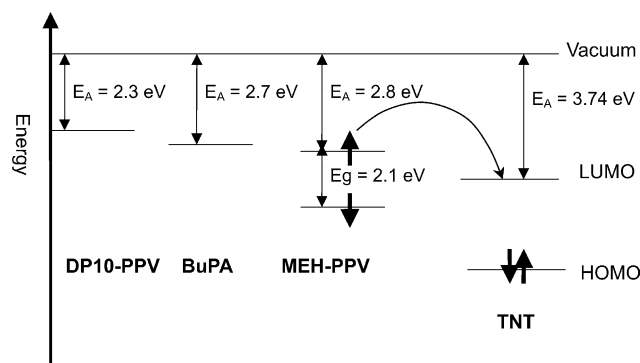Fig. 4. Fluorescence quenching percent of MEH-PPV in 25 and 200 Å films at an exposure time of 60 s.

Fig. 5. Energy level diagram depicting the charge transfer mechanism involving TNT quenching of emissive excitons in MEH-PPV, DP10-PPV and BuPA.

simplicity. The fact that MEH-PPV, DP10-PPV, and BuPA all showed high fluorescence quenching sensitivity towards TNT, 2,4-DNT, and 2,6-DNT indicated that they are potential candidates chemosensor materials for detecting landmines. The sensitivity of fluorescence quenching by analytes depends on factors, such as the solubility parameters, the interchain charge transfer quenching the exciton and the binding strength (polymer–analyte interactions). These relationships can be used to create more efficient and sensitive conjugated polymers for TNT chemosensors. We can give a suggestion that as long as there exists an adequate energy level matching, emissive conjugated polymers other than those reported here may also be suitable for TNT chemosensors.

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