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Selective Detection of TNT and Picric Acid by Conjugated Polymer Film Sensors with Donor−Acceptor Architecture

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S Supporting Information

Selective and sensitive sensors for detection of nitroaromatic explosives, in particular 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (picric acid, PA), are of great current interest in both national security and environmental protection because they are not only explosives but also recognized as toxic pollutants.[1] Because of their strong electron accepting capability, TNT and PA have often been detected by fluorescence film sensors through a photoinduced electron transfer (PET) quenching process (Scheme 1).[2] Among fluorescent sensory materials, conjugated polymers (CPs), as good electron donors, are one of the most promising candidates for explosive detection even in both vapor phases and aqueous solutions.[3] A variety of conjugated polymers, such as polyacetylenes,[4] poly(*p*-phenyleneethynylenes),[5] polysilanes,[6] poly(*p*-phenylenevinylenes),[7] and polymetalloles,[8] have been widely investigated as thin film sensing materials for their extremely high sensitivity, which can be explained on the basis of the molecular wire effect.[9] For CP sensors, introduction of electron-donating groups are believed to enhance the interaction between the electron-rich polymers and the electron-deficient explosives, which will lead to higher sensitivities,[2,5] so most of them are based on donor-only structures.

Owing to the PET fluorescence quenching process, these CP sensors will suffer from an intrinsic selectivity problem in a complex environment containing different electron acceptors. For example, the discrimination of TNT and PA is still a challenge because both of them are extremely strong electron acceptors. In practical applications, selectivity is critical to a successful detection, so a lot of efforts have been put on this area. Recently, Knapp et al. and Anslyn et al. reported the application of fluorescence arrays in organic or aqueous solutions to identify nitrated explosives with complicated linear discriminant analysis statistics, respectively.[10] Goldman et al., Singh et al., Cerruti et al., and others also have utilized special designed antibodies or peptides as biosensors for selective detection of TNT in aqueous solutions.[11] Molecularly imprinted polymers were also applied for selectively sensing TNT.[12] In most cases, PA exhibited somewhat higher quenching efficiencies than TNT because its lowest unoccupied molecular orbital (LUMO) energy level is lower.[1c,6a,8a,13] However, the clear discrimination of TNT and PA and especially detection of TNT in the presence of PA in aqueous solution by simple fluorescence CP film sensors are still unexplored.

In this paper, we designed a donor−acceptor (D−A) conjugated polymer (Scheme 1, **P1**). First, the strong D−A structure will lead to a substantial intrachain charge transfer from donor groups (diethylamine phenyl) to acceptor groups (2,1,3-benzothiadiazole, BT) groups and a dipole moment (negative poles at the BT. units).[14] Second, the LUMO will also mainly localize on the BT units as for many D−A polymers.[15] Because PA can easily form a negative charged anion in aqueous solution, an electrostatic repulsion interaction between the BT unit and PA will block the efficient electron transfer from the LUMO of **P1** to PA as shown in Scheme 1, which will not happen in the cases of TNT. Therefore, **P1** can selectively detect TNT instead of PA in aqueous solution. On the other hand, the reference polymers **P2** and **P3** with only donor groups should behave as most CP sensors with higher selectivity toward PA.[1c,6a,8a]

P1−**P3** were prepared by Suzuki polymerization (Scheme S1 in Supporting Information), and their structures are confirmed by standard spectroscopic analyses. Their number-average molecular weights (M_n) and the polydispersity indexes (PDI) appear to be in the range of 16 000−55 000 g/mol and 1.7−3.3, respectively, with reference to polystyrene standards. They are highly soluble in common organic solvents such as chloroform, toluene, and tetrahydrofuran (THF), and their thin films (estimated to be 10 nm thick) were prepared by spin-coating their THF solution on freshly cleaned and dried quartz substrates.[4,5]

The photophysical properties of **P1**−**P3** were characterized by UV−vis absorption and photoluminescence (PL) spectroscopy in THF solutions and in thin films (Table S1 in Supporting Information). The lowest energy absorption was observed at 465 nm for **P1** in THF, which was gradually blue-shifted to 392 nm for **P2**, due to the disappearance of the D−A structure. When the strong electron donor group (amine) was replaced by a weaker one (alkoxyl), the absorption band was further blue-shifted to 360 nm for **P3**. As for most 2,2-diphenyl-1,1-diphenylethylene (TPE)-based materials, the emissions of all these polymers in THF solutions are very poor (Φ_{PL} <1%), while their emissions in films are much stronger, indicating that they are aggregation-induced emission polymers.[16] In particular, thin film of **P3** emits bright green emission with a Φ_{PL} of 43.9%, which is comparable to CP film sensors reported by Swager et al.[5] The Φ_{PL} decreased gradually to 13.0% and 6.9% for the yellow and deep-red emissive polymers **P2** and **P1** (Figure S1 in Supporting

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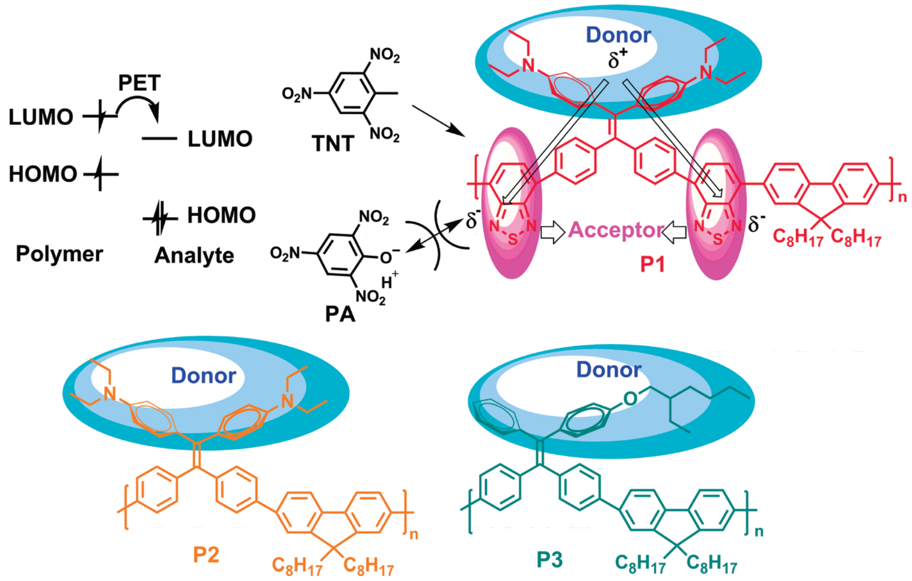
Scheme 1. Electron Transfer Fluorescence Quenching Process and Structures of P1−P3



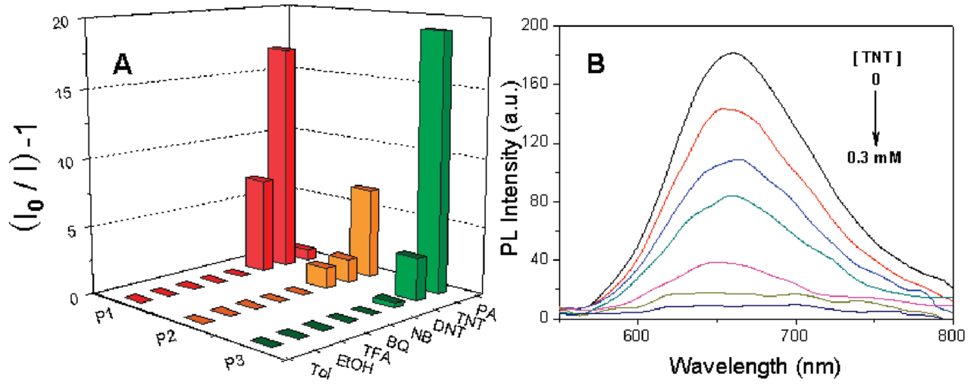


Figure 1. (A) Effects of different analytes (0.2 mM) on the emission of the polymer films in aqueous solutions (I_0 and I are the PL intensity of the film in the absence and presence of the analyte, respectively) and (B) emission spectra of **P1** film in the presence of different concentrations of TNT.

Information) because their smaller energy gaps are typically accompanied by more nonradiative processes.

Cyclic voltammetry (CV) was carried out on these polymers to determine their highest occupied molecular orbital (HOMO) and LUMO energy levels (Figure S2 in Supporting Information). For the D−A polymer **P1**, both the oxidation and reduction processes were observed, while for the donor-only polymers **P2** and **P3**, only oxidation processes can be found, suggesting the LUMO resides primarily around the acceptor BT unit in **P1**. In all cases, their LUMO energy levels (−2.23 to −2.92 eV) are much higher than those of TNT and PA, which will guarantee the electron transfer from the excited polymers to TNT or PA in a PL quenching process.

The response of the fluorescence films to nitroaromatic compounds such as PA, TNT, 2,4-dinitrotoluene (DNT), nitrobenzene (NB), and common interferents such as benzoquinone (BQ), trifluoroacetic acid (TFA), ethanol (EtOH), and toluene (Tol) in aqueous solutions were studied first. As illustrated in Figure 2A, the addition of nitrobenzene and common interferents has almost no effect on the emission of thin films of these polymers. On the other hand, clear fluorescence quenching can be observed upon the addition of PA, TNT (Figure 1B), and DNT, indicating the highly selectivity toward explosives. It is also very obvious that the quenching effect of TNT is much higher than PA for **P1** as expected. When 0.2 mM TNT was added into the aqueous solution, PL intensity of **P1** film decreased

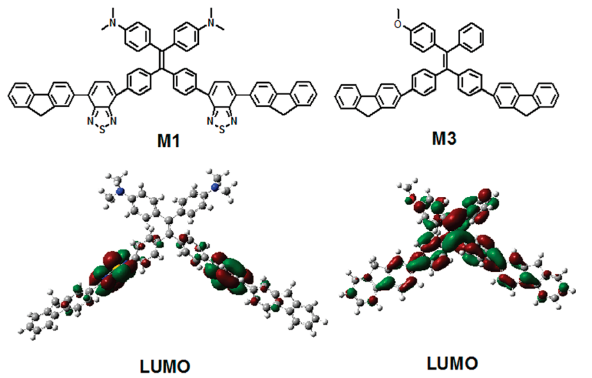


Figure 2. Structures of model compounds **M1**, **M3**, and their LUMO.

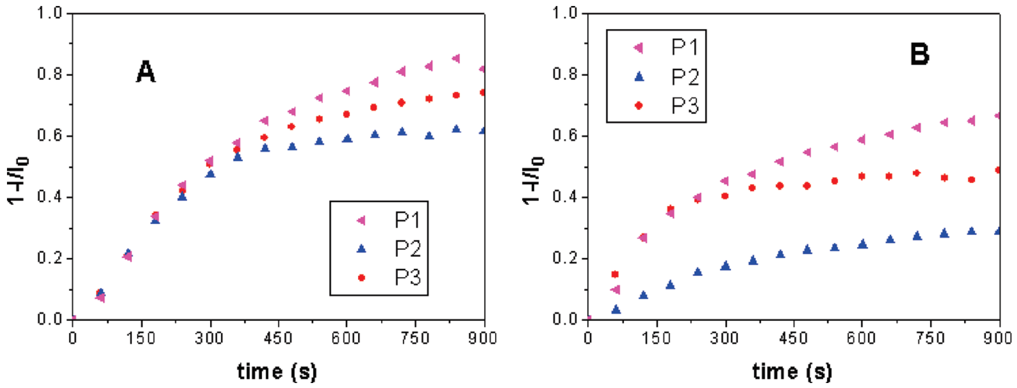


Figure 3. Time-dependent fluorescence quenching of polymer films on exposure to saturated (A) DNT and (B) TNT vapors.

dramatically with 17-fold PL quenching, while the presence of PA only induced about 0.77-fold PL quenching. The fluorescence quenching results can also be evaluated with the Stern−Volmer equation, $I_0/I - 1 = K_{sv}[\text{analyte}]$, where K_{sv} is the Stern−Volmer quenching constant (Figures S3 and S4 in Supporting Information). On the basis of the fluorescence titration of **P1** thin film with TNT and PA, a linear relationship was observed. The K_{sv} constant of TNT (1.2×10^5 M^{-1}) is almost 2 orders higher than that of PA (1.8×10^3 M^{-1}), and the limit of detection (LOD) of TNT is about 23 ppb. As we expected, **P1** can selectively detect TNT in the presence of PA in aqueous solution (Figure S7 in Supporting Information). On the contrary, the donor-only polymers **P2** and **P3** exhibit higher selectivity toward PA as most CP sensors. The sensitivity of **P3** film (a 19-fold emission quenching) for PA is higher than that of **P2** (a 6.6-fold emission quenching), perhaps due to its higher Φ_{PL} (43.9% for **P3** and 13.0% for **P2**). In the case of **P3**, a linear relationship was also observed for PA and TNT with K_{sv} constants of 2.8×10^4 and 7.5×10^3 M^{-1}. PA is a more efficient quencher than TNT for the **P3** film, and its LOD can reach 2 ppb. Thus, the **P1** and **P3** films can be used as highly selective and sensitive fluorescent film sensors in aqueous solution toward TNT and PA, respectively.

For both TNT and PA, the quenching effect is found to be reversible by simple washing of the **P1** and **P3** films with excess methanol followed by drying in air, the fluorescence intensity can be entirely recovered, and the film sensing ability is very stable (Figures S5 and S6 in Supporting Information). This off−on cycle can be repeated more than 10 times without significant deviations. These results indicate that **P1** and **P3** films can be reversible film sensors for TNT and PA.

To further confirm our explanation for the unusual selectivity of **P1**, the geometry of its model compound **M1** was optimized by density functional theory calculations at the B3LYP/6-31G-(d) level.[8b,c] As shown in Figure 2, the LUMO are localized on the BT unit, just as our analysis. At the same time, the electrostatic potential (Mullikan charges) of **M1** also shows net negative charge on the BT unit (−0.130) and net positive charge on the dimethylamine phenyl group (+0.152). Since PA may form negative charged anion in aqueous solution, the electrostatic repulsion between PA and the BT unit will keep them apart, which can block the PET process from the LUMO of **P1** (the BT unit) to PA. On the other hand, compared to the twisted TPE unit, the planar conformation of the BT unit will facilitate its $\pi-\pi$ interaction with TNT[2b,f] and therefore lead to the higher sensitivity of **P1** toward TNT than **P2** and **P3**. For the model compound of **P3** (**M3**), its LUMO orbital is delocalized through the whole polymer, and it has no special different interaction with TNT or PA, so it is reasonable that the quenching effect of PA is higher than TNT due to the lower LUMO energy level of PA.

The response properties of these fluorescent polymer films toward TNT, DNT, and PA vapors were also studied. The films were inserted into sealed vials containing solid analytes and cotton gauze as Swager et al. described.[5] The fluorescence spectra were recorded immediately after exposing the polymer films to the analyte for every certain time, as shown in Figure 3. **P1** and **P3** films showed higher sensitivity toward DNT and TNT vapors than **P2** films again. The **P1** and **P3** film lost nearly 85% and 75% of fluorescent intensity after 15 min of exposure to DNT vapor, respectively. The quenching effects of TNT are not as high as DNT; however, more than 60% fluorescence quenching can still be observed for the **P1** film. On the other hand, unlike its strong quenching effect in aqueous solution, PA vapor have almost no effect on the emission spectra of the polymer films. Clearly, the fluorescence quenching response follows the order of DNT > TNT ≫ PA, which can be explained by their different vapor pressures. The vapor pressures of DNT, TNT, and PA are 1.74×10^{-4}, 8.02×10^{-6}, and 5.80×10^{-9} mmHg at 25 °C, respectively. Thus, the considerable faster and greater quenching effect of DNT can be attributed to its high vapor pressure, while the poor performance of PA is also due to its extremely low vapor pressure. In other words, **P1** and **P3** films have been proved to be sensitive fluorescence film sensors for DNT and TNT vapors. As is well-known, the vapor pressure and water solubility of TNT are usually very low, so we perform a surface sensing method for imaging trace TNT solid particles. The fluorescence quenching of polymer films could be visually detected toward TNT particles using filter papers. **P1** exhibits the best sensitivity for TNT with a detection limit of 3 ng/cm^2, while the detection limits of **P2** and **P3** are around 30 ng/cm^2 (Figures S8, S9, and S10 in Supporting Information). For all the three polymers, the quenching effects of both DNT and PA are not as good as TNT.

In this work, on the basis of the rational analysis of the electrostatic potential and the LUMO distribution, we have designed and synthesized a strong donor−acceptor polymer **P1** and two donor-only polymers **P2** and **P3** for highly selective and sensitive detection of TNT and PA in aqueous solutions, respectively. Although their emission in solution states is very poor, spin-coating films of these AIE-active polymers exhibit bright emission. For the **P1** film, the K_{sv} constant of TNT (1.2×10^5 M^{-1}) is almost 2 orders higher than that of PA (1.8×10^3 M^{-1}), and the detection limit of TNT is about 23 ppb, while the emission of the **P3** film can be selectively quenched by

PA with the K_{sv} constant 2.8×10^4 M^{-1} and the detection limit 2 ppb. These quenching effects of both TNT and PA on the **P1** and **P3** films are found to be reversible. In addition, it was also demonstrated that the emission of **P1** and **P3** films could be efficiently quenched by TNT and DNT vapors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis, experimental details, and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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